

Group 14 Lewis Acids in Catalysis and Coordination Chemistry

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Submitted by NILS ANSMANN, M. Sc.
born in Heidelberg.

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Major parts of this dissertation have been published in peer-reviewed journals and presented at national and international conferences.

Meinen Eltern.

“Wer nichts beweist, der beweist schon verdammt viel”.

H. GRÖNEMEYER

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ABSTRACT

Effective Lewis acidity denotes the perturbative influence of a Lewis acid on the electronic structure of a coordinated Lewis base, thereby addressing the extent of induced activation. This dissertation investigates the deliberate application of *effective* Lewis acidity through group-14-based Lewis acids in catalysis and coordination chemistry.

The catalytic potential of the Lewis superacid $\text{Si}(\text{cat}^{\text{Cl}})_2$ in the C–O bond metathesis of oligo- and polyethers was systematically examined. Its high activity, even in the presence of strongly chelating substrates, enabled the chemoselective upcycling of polyethers. Mechanism-guided catalyst design led to a second-generation system with enhanced activity, capable of mediating the challenging cross-metathesis of alkyl ethers. Subsequent in-depth analysis of deactivation pathways provided the basis for an optimized protocol that enabled *in-situ* catalyst generation under ambient atmosphere, even tolerating protic functionalities. The broad substrate scope presents the opportunity for a more sustainable circular economy for this polymer class.

The impact of *effective* Lewis acidity on transition metal chemistry was further explored with two ambiphilic group-14-based Z-type ligands, addressing a field previously dominated by group 13 and 15 Lewis acids. The palladium chemistry of the respective silane ligand was investigated in depth, yielding the first isolated anionic square-planar Pd(0) complex; a proposed key intermediate in cross-coupling catalysis. Redox studies revealed Z-type-triggered reversible Pd(0)/Pd(II) electromerism, representing the first example for this redox-pair and a unique opportunity to further use Z-type interactions for spin-state switching. A systematic study on the bonding characteristics in a series of the first Rh(I)-silane Z-type complexes fundamentally eased the understanding of the influence of the metal's coordination environment on the Z-type interaction. Finally, the limits of Z-type chemistry were pushed by achieving the synthesis and characterization of the first group 8 Z-type complex and exploring the oxidation chemistry of this molybdenum complex.

KURZZUSAMMENFASSUNG

Effektive Lewis Acidität beschreibt den Einfluss einer Lewis Säure auf die elektronische Struktur einer koordinierten Lewis Base und damit das Ausmaß der induzierten Aktivierung. Diese Dissertation dediziert die gezielten Anwendung des Konzepts *effektiver* Lewis-Acidität in der Katalyse und Koordinationschemie mit der Hilfe von Gruppe 14 Lewis Säuren.

Das katalytische Potenzial der Lewis-Supersäure $\text{Si}(\text{cat}^{\text{Cl}})_2$ in der C-O-Bindungsmetathese von Oligo- und Polyethern wurde systematisch untersucht. Hohe katalytische Aktivität, selbst in Gegenwart stark chelatisierender Substrate, ermöglichte das chemoselektive Upcycling von Polyethern. Mechanismus-basiertes Katalysatordesign ergab eine zweite Katalysator-Generation, die in der Lage ist, die anspruchsvolle Kreuzmetathese von Alkylethern zu vermitteln. Eine anschließende Analyse verschiedener Deaktivierungswege lieferte die Grundlage für ein optimiertes Reaktions-Protokoll, das die *In-situ*-Erzeugung des Katalysators unter Umgebungsatmosphäre ermöglichte. Die breite Anwendbarkeit dieser Methode bietet die Möglichkeit für eine nachhaltigere Kreislaufwirtschaft dieser Polymerklasse.

Die Auswirkung *effektiver* Lewis Acidität auf die Chemie der Übergangsmetalle wurde mit zwei Gruppe 14 basierenden ambiphilen Z-Typ Liganden untersucht. Die Palladiumchemie des entsprechenden Silanliganden ermöglichte die Charakterisierung des ersten anionischen quadratisch-planaren Pd(0)-Komplexes, einem möglichen Intermediat in Kreuzkupplungsreaktionen. Redox-Studien zeigten eine Z-Typ gesteuerte reversible Pd(0)/Pd(II)-Elektromer; das erste Beispiel für dieses Redox-Paar und eine Möglichkeit, Z-Typ-Wechselwirkungen für das Schalten von Spinzuständen zu nutzen. Systematische Bindungsanalyse in einer Reihe von Rh(I)-Silan-Z-Typ-Komplexen förderte grundlegendes Verständnis des Einflusses der Koordinationsumgebung des Metalls auf die Z-Typ-Wechselwirkung. Letztlich wurden die Grenzen der Z-Typ-Chemie durch die Synthese des ersten Z-Typ-Komplexes der Gruppe 8 und die Erforschung der Oxidationschemie dieses Molybdänkomplexes erweitert.

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1.1. PREFACE

Chemical reactions proceed through the breaking and formation of chemical bonds, necessitating bonds that are sufficiently activated to undergo transformation. Because naturally activated bonds occupy a limited chemical space, a central area of chemical research focuses on methods to deliberately activate otherwise inert bonds. Ideally, this activation occurs catalytically, as is the case for approximately 90% of all industrially produced chemicals.^[1] The majority of employed catalysts are transition metal based, due to their unique ability to mediate a wide range of transformations thanks to their partially filled d-orbitals.^[2] Despite their predominance, several efforts focus on the replacement of these often toxic, scarce and precious metals with more abundant main group elements.^[3,4] A key strategy in this pursuit lies in the design and application of main group Lewis acids.^[5] However, this approach entails several limitations, as the Lewis acid must exceed a certain strength, while at the same time it should be robust enough to be handled without special equipment.^[6]

Transition metals and main group Lewis acids do not have to be two separate alternatives when it comes to catalysis. Some of the most prominent heterogeneous processes in chemical industry (HABER-BOSCH, ZIEGLER-NATTA or FISCHER-TROPSCH) rely on the interplay of transition metals and main group Lewis acids, often found as promoters that either structurally or electronically enhance the inherent reactivity of the metal.^[7] In homogeneous catalysis however, reactivity of the transition metal can be steered by the design of the ligand.^[8] While the most common approaches vary steric and electron-donating capabilities of the employed ligand, an emerging field focusses on the implementation of Lewis acidic features into the ligand framework.^[9] Thereby, electron density is transferred from filled d-orbitals of a late transition metal to the Lewis acid in a σ -accepting interaction - a Z-type interaction.^[10] This allows for a precise adjustment of electron density at the transition metal and opens pathways to diverse reactivity of the metal center.^[11]

In this dissertation, Lewis acidity is discussed in the context of catalysis and Z-type ligands. Therefore, a theoretical background and the state of knowledge regarding Lewis acidity in general, group 14 Lewis acids and their catalytic potential as well as Z-type ligands and their coordination chemistry is laid in this chapter. Furthermore, this chapter discusses literature on bond metathesis, palladium-catalyzed cross-coupling, and the concept of electromerism, as these topics are of particular relevance to the present dissertation.

1.2. LEWIS ACIDITY - CONCEPT AND SCALING

Acidity is a concept that had multiple definitions throughout the commencements of modern chemistry in the late 19th and early 20th century. Two of the most fundamental paradigms were ultimately formulated by JOHANNES N. BRØNSTED and GILBERT N. LEWIS.^[12–14] While Brønsted acidity is solely defined by the tendency of a compound to donate a proton, Lewis acidity draws a more general picture. Every molecular entity that accepts an electron pair is a Lewis acid, whereas every compound that donates these electrons is considered a Lewis base. Although this principle can be applied to a broad range of different chemical reactions, its universality inevitably raises questions regarding possible methods for qualitative and quantitative classification of Lewis acids. According to the IUPAC recommendation, Lewis acidity can be defined as “*the thermodynamic tendency of a substrate to act as a Lewis acid*”,^[15] ultimately calling for a reference Lewis base in order to quantify a series of acids. This dependency on the Lewis base is the fundamental scaling problem for Lewis acidity and renders a one-dimensional scale, like the pK_A scale for Brønsted acids, impractical.

Before different scaling approaches can be discussed in detail, a closer look into the actual process of the formation of a Lewis pair must be taken. In principle, this process can be split into two sections and follows a potential energy surface, as depicted for the reaction of a tetrel chloride and diethyl ether in Fig. 1.1.

Since neither Lewis acid, nor Lewis base adopt the same geometry in the final Lewis pair, as they would independently from each other, in the first step of the pair formation both entities have to undergo a structural change.^[16] This deformation is inevitably accompanied by an energy penalty - the deformation energy E_{Def} , which is usually significantly higher for the Lewis acid.^[17-19] After this pre-organization, the deformed partners can form the Lewis pair in the second step - the association - alongside with the liberation of the association energy E_A . The difference of deformation energy and association energy therefore determines the reaction enthalpy ΔH and in combination with entropic factors whether Lewis pair formation can occur.^[20] Hence, the formation of a Lewis adduct is dependent on both, Lewis acid and base and relies on the respective strength as well as geometrical parameters.

A special case takes place, when steric factors inhibit the formation and a *Frustrated Lewis Pair* (FLP) forms.^[21] Nowadays this definition rather refers to a kinetic event,^[22] since FLP reactivity can also occur in Lewis pairs with a dative bond.^[23,24] While FLP systems display a broad spectrum of reactivity and provide a powerful means of mimicking transition-metal-like behavior with main-group elements, their detailed coverage lies beyond the scope of this dissertation.^[25-29]

With this general model in hand, we can now separate different scaling methods regarding the type of Lewis acidity that they are gauging.^[6,31] In principle, one can differentiate between three aspects of Lewis acidity:

- *Intrinsic* Lewis acidity describes inherent features of the Lewis acid in the absence of a Lewis base. It is probably the most general description of the Lewis acidity of a molecule and can, for example, be classified by the energy of its lowest unoccupied molecular orbital (LUMO).^[32]
- *Global/general* Lewis acidity is the most common aspect of Lewis acidity and describes the thermodynamic tendency of a Lewis acid to bind a Lewis base (ΔH), hence resembling IUPAC's definition. Through its universality it serves as a comprehensive model for the assessment of Lewis acidity. This

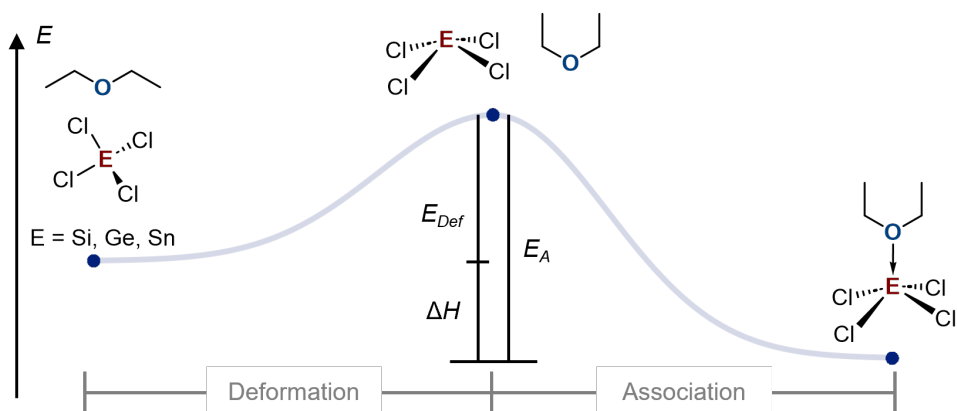


FIG. 1.1.: Potential energy surface for an exothermic Lewis pair formation reaction of diethyl ether and a Lewis acidic tetrel-chloride ($E = \text{Si, Ge, Sn}$). The reaction is schematically drawn and separated in two steps (deformation and association). Parts of this figure were created using *EveRPlot*.^[30]

model takes both, deformation and association energy in account and usually requires computational-assisted methods for a meaningful evaluation, since experimental thermodynamic values are not trivially obtained.^[33–35]

- *Effective* Lewis acidity focusses on the perturbative effect that a Lewis base experiences after coordination to a Lewis acid. Unlike global Lewis acidity, *effective* acidity only considers what happens after the Lewis acid is already pre-organized. The alteration in the electronic structure of the Lewis base can be assessed through spectroscopic experiments (IR, UV-Vis or NMR).^[36–46] *Effective* Lewis acidity is the key factor when it comes to substrate activation.^[6]

As already mentioned, methods to scale *intrinsic* Lewis acidity forgo an external Lewis base. Popular methods include the calculated global electrophilicity index (GEI) as well as the measurement of electrochemical potentials.^[47,48] While these methods may offer comparability of similar Lewis acids, their complete neglect

of interactions with Lewis bases limits their actual expressiveness when it comes to comparing larger sets of Lewis acids.

The prevalent method to scale Lewis acidity is given by the *Fluoride Ion Affinity* (FIA), which evaluates the global Lewis acidity of a compound with regard to the fluoride ion as the reference base.^[49,50] Defined by the negative binding enthalpy of a fluoride, its widespread use can be traced back to the unique Lewis basicity of the fluoride, which readily coordinates even to weak Lewis acids. Additionally, the establishment of accurate *in silico* determination of thermodynamic values eradicates the need for tedious experimental determination of these values in the gas-phase. A modern approach even enables the estimation of FIAs with machine-learning based approaches through a graphical neural network (GNN) within seconds.^[51] Despite its widespread use, the FIA only describes one dimension of Lewis acidity and is more generally seen as a scale for the fluoridophilicity of a Lewis acid.^[6] It is not without reason that PEARSON introduced the concept of *hard and soft Lewis acids and bases* (HSAB) in the 1960s, describing different binding-preferences for Lewis acids dependent on the polarizability of both reaction partners.^[52,53] While the generality of this mostly empirically based theory is debatable, it underlines that the FIA alone is an incomplete description of the Lewis acidity of a compound. Hence, GREB suggested the additional classification through the *Hydride Ion Affinity* (HIA), which in contrast to the hard fluoride ion serves as a gauge for soft Lewis acidity.^[6] Further approaches were made to compare FIA and HIA to a variety of affinity scales towards several Lewis bases, including the chloride ion, methid ion as well as water and ammonia, highlighting the dependency of different aspects of global Lewis acidity on the used reference base.^[50]

KROSSING used the FIA to define a benchmark for Lewis acidity in the constantly growing field of strong Lewis acids.^[54] Every Lewis acids that exceeds the FIA of SbF_5 in the gas phase can be classified as “Lewis superacid”. Similarly, every Lewis acid exceeding the HIA of $\text{B}(\text{C}_6\text{F}_5)_3$ may be termed a “soft Lewis superacid”.^[55]

When assessing applications of Lewis acidity, the *general* Lewis acidity may provide an initial indication of suitability; however, the *effective* Lewis acidity ultimately determines the true potential of a Lewis acid in a given application. Since it describes the perturbative effect on the electronic structure of a coordinated Lewis base, several spectroscopic protocols have been established to scale this aspect of Lewis acidity. They all rely on the change of spectroscopic characteristics of a probe Lewis base, usually a shift of the NMR resonance, the IR- or the UV-Vis absorption. The difference in the spectroscopic characteristics of the “free” Lewis base and the respective Lewis pair then serves as a criteria for the strength of the Lewis acid. Since the deformation of the Lewis acid is not encoded in these spectroscopic approaches, an unbiased statement on the *effect* of a Lewis acid on a given Lewis base can be made.

The two most commonly used spectroscopic methods both rely on NMR spectroscopy, namely the GUTMANN-BECKETT- (GB) and CHILDS method.^[36–39] In the GB method, the resonance of the phosphorous nucleus in triethylphosphine oxide (OPEt₃) serves as the probe, whereas the Childs method detects the change in the chemical shift of the H³ proton of *trans*-crotonaldehyde. In-depth computational analysis further underlined the weak correlation between *global*- and *effective* Lewis acidity in these experimental methods.^[56,57] While the Childs method mainly suffers from secondary interactions that influence the chemical shift of the investigated proton, the GB method serves as a more reliable probe. A correlation of $r = 0.81$ between the association energy E_A and the difference in chemical shift $\Delta\delta(^{31}\text{P})$ underscores the importance of distinguishing deformation-biased thermodynamic values from the actual *effect* of a Lewis acid.

1.3. GROUP 14 LEWIS ACIDS

1.3.1. LEWIS ACIDITY OF TETRELS

Unlike their hypovalent neighbours in group 13, tetravalent tetrelsⁱ (Si, Ge, Sn) naturally occur in a tetrahedral geometry at the central element in their energetically preferred +IV oxidation state. This can most prominently be seen in the earth's crust, where silicon in the form of SiO₂ or silicates is the second most abundant element and therefore reasons the majority of its structural motives.^[58] Due to the lack of an empty p_z -orbital, tetrels are less prone to act as a Lewis acid. Hence, structural or electronic changes in the ligand sphere must be induced to render tetrels Lewis acidic. This can readily be achieved by introducing electron-withdrawing groups, in the simplest case just by considering the tetrel halides. Silicon tetrachloride for example is a relatively easy-to-handle chemical and can be used in a variety of chemical transformations.^[59–62] With naturally occurring trivalent group 13 Lewis acids with inherent acceptor orbital, one might ask why SiCl₄ nevertheless is often used as a Lewis acid. The reason lies within the high *effective* Lewis acidity of tetrels, as evident by the GB shift of SiCl₄ ($\Delta\delta(^{31}\text{P}) = 25.1 \text{ ppm}$),^[56] which is larger compared to the strong *global* Lewis acid AlMe₃ ($\Delta\delta(^{31}\text{P}) = 20.5 \text{ ppm}$).^[63] Again, this can be traced back to the deformation energy of tetrels, showcasing that *global* Lewis acidity scaling methods are underestimating this class of Lewis acids.

An alternative way to harness the Lewis acidity of tetrels through ligand control lies in structural constraint.^[64] Multi-dentate ligand can force the tetrel element in a pre-organized geometry, which increases its *global* Lewis acidity by lowering the required deformation energy for Lewis pair formation. This was prominently demonstrated by the spiro-silane and -germane by MARTIN and DENMARK.^[65,66] In these cases, a strain-release was observed after Lewis base coordination, reasoning their high FIAs.^[67] Forcing tetrels out of their natural tetrahedral VAN'T HOFF-LE-

ⁱThroughout this work, whenever the word tetrel is used it refers to tetravalent compounds of the elements Si, Ge and Sn in the oxidation state +IV. The other group 14 elements C and Pb are not discussed in this work, due to their significantly altered chemistry.

BEL geometry results in an energetic stabilization of their LUMO, accompanied by increased Lewis acidity.^[68] This was demonstrated for a series of macrocyclic group 14 Lewis acids that exhibited remarkable bond activation reactions once forced into a planar coordination environment.^[69–72]

1.3.2. BIS(CATECHOLATO)-TETRELS

A predestine ligand class for the chemistry of silicon and germanium are catechols (cat^{X} ; $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}$).^[73] Following the concept of structurally strained Lewis acids, bidentate catecholates readily form a variety of neutral tetrel complexes as well as hypercoordinated silicates and germanates. This chemistry dates back to the early 19th century, when ROSENHEIM demonstrated the depolymerization of SiO_2 with catechol under basic conditions, ultimately furnishing tris(catecholato)silicates - a concept which was used a century later to synthesize silanes directly from silica.^[74,75] The neutral bis(catecholato)silane $\text{Si}(\text{cat}^{\text{H}})_2$ already hints the drastic potential of this compound class, since its FIA significantly exceeds the value of electronically comparable $\text{Si}(\text{OPh})_4$ due to the strained coordination geometry at Si (391 kJ mol^{-1} vs. 302 kJ mol^{-1} , respectively).^[76] This also explains the numerous reports of catecholate based hyper-coordinated silicates.^[77–82]

While its chemistry has been studied extensively, the structure of bis(catecholato)silanes was topic of debates throughout the century, due to its low solubility in the absence of Lewis bases and missing solid-state structures.^[83] Extensive studies by GREB unravelled the mystery by a combination of gas phase electron diffraction, NMR- and IR- spectroscopy in conjunction with crystallographic methods and theoretic calculations.^[84] In the gas phase, monomeric $\text{Si}(\text{cat}^{\text{H}})_2$ indeed adopts a tetrahedral geometry (FIG. 1.2 A), but in condensed phases formation of cyclic oligomers is observed through rapid Si-O bond metathesis reactions, due to low barriers. The degree of oligomerization is dependent on the substitution pattern at the catechol, as exemplary observed for the perfluorinated *14mer* (FIG. 1.2 B).^[85] For the perchlorinated derivative, a polymeric structure is assumed ($[\text{Si}(\text{cat}^{\text{Cl}})_2]_n$, FIG.

1.2 C), as judged by its chemical shift in the solid-state $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum.^[82] Steric shielding of the Si-O bonds by *tert*-butyl groups at 3,6-substituted catechols even allows for the isolation of monomeric species in the solid state.^[86]

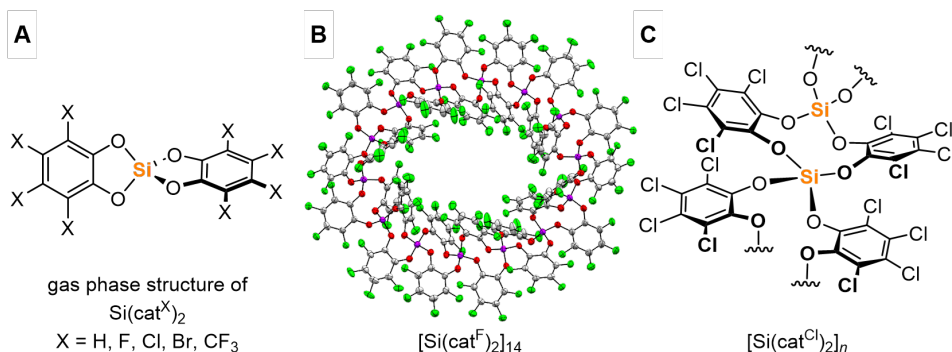


FIG. 1.2.: Structural motives of bis(catecholato)silanes: A) Monomeric form in the gas phase, B) oligomeric macrocyclic structure for perfluorinated derivatives (CCDC 2016065, dcm omitted for clarity, vibrational ellipsoids at 30% probability)^[85] and C) the polymeric structure of $[\text{Si}(\text{cat}^{\text{Cl}})_2]_n$.

Similar to the chemistry of its lighter homologue, germanium's catechol chemistry has been known for decades. Unlike respective silanes, bis(catecholato)germanes are stable towards hydrolysis as effectively demonstrated by the synthesis of the bis-(H_2O) adduct of bis(catecholato)germane in 1954 by reaction of germanium dioxide and catechol in water.^[87,88] This remarkable water stability was reasoned by a reduced ring strain in the Ge-O-C-C-O-unit, compared to its lighter and smaller homologue Si.^[89] Bis(catecholato)germanes have long been overlooked as potential Lewis acids, although penta-coordinated germanes and germanates have been studied in the past.^[90–92]

Tin's catechol chemistry is younger compared to its lighter homologues, but still well explored. Early studies used tin's affinity towards this ligand class to detect this element spectroscopically after the formation of catechol violet complexes.^[93,94] In 1975, the reaction of catechol and tetraphenyl stannane was reported to yield bis(catecholato)stannane.^[95] Varying the stoichiometry of the reaction led to the

isolation of alcohol adducts of this complex, already hinting its Lewis acidity. Nowadays, multiple derivatives of bis(catecholato)stannanes have been isolated and characterized.^[96–98]

A unique feature of catechol ligands is their redox non-innocence and their ability to act as an electron reservoir.^[99–101] While this is further discussed in section 1.7, this phenomenon can also be observed for aminophenols (amp).^[102] Aminophenols further prevent oligomerization of silane based Lewis acids, due to their increased steric demand.^[46,103] However, their comparably electron-rich character limited their application in Lewis acid chemistry, with most reports focussing on the Sn(II) and Sn(IV) chemistry.^[104–106] This work focuses on both, catecholate and amidophenolate based group 14 Lewis acids, exploiting the strengths of each ligand class.

1.3.3. BOND ACTIVATION BY NEUTRAL GROUP 14 LEWIS SUPERACIDS

As mentioned above, bis(catecholato)silanes and germanes are predestined *effective* Lewis acids due to their structural strain at the central element. In combination with electron-withdrawing groups at the catecholate ($X = F, Cl, Br, CF_3$), these Lewis acids can be used for bond activation in terms of catalysis.

This was first demonstrated by TILLEY in 2018, who introduced the bis-MeCN adduct of $Si(cat^F)_2$ as a catalyst for the hydrosilylation of benzylic aldehydes (FIG. 1.3 A), proposing a strong *effective* activation of the $C=O$ bond in the initially formed $Si(cat^F)_2-(OCHAR)$ Lewis pair.^[107] Exchange of the fluorine atoms at the catecholates by less electronegative chlorides counter-intuitively gave rise to the neutral Lewis acid $Si(cat^{Cl})_2$ that surpassed the threshold of Lewis superacidity.^[108] This boost in Lewis acidity was reasoned by a weaker π -overlap of the lone pairs at the halides with the aromatic system, an effect which was even more expressed for $Si(cat^{Br})_2$.^[76] The high fluoridophilicity of this compound class was showcased by catalytic hydrodefluorination of fluoro-alkanes. Stoichiometric FLP-type fixation and activation of CO_2 was further demonstrated for $Si(cat^{Cl})_2$ (FIG. 1.3 B).^[109,110]

By installing highly electron-withdrawing CF_3 -groups in all four available positions of the catechol backbone, the Lewis acidity of bis(catecholato)silanes was pushed to its maximum, expanding its catalytic portfolio to deoxygenation reactions as well as the carbonyl olefin metathesis.^[111]

It is emphasized that all catalytic applications of $\text{Si}(\text{cat}^X)_2$ relied on the use of donor (MeCN, sulfolane) stabilized Lewis pairs of the respective Lewis acid, since donor-free versions were challenging to access before a synthetic route was discovered in 2022.^[82] This limited the application of these silanes to chemical transformations with strongly donating substrates that replace the initially coordinating Lewis base.

INOUE reported an approach related to the catecholate chemistry, using strongly electron-withdrawing, but also highly toxic perfluoropinacolates as ligands for silicon.^[112] The acetonitrile adduct displayed remarkable activities in several catalytic applications, even demonstrating heterolytic cleavage of the C-O bond in diethyl ether.^[113]

Isolation of a donor-free, highly-soluble and monomeric silane with high *effective* Lewis acidity was only achieved by using a perfluorinated *N*-phenylamidophenolate ligand for Si(IV), yielding $\text{Si}(\text{amp}^F)_2$ (FIG. 1.3 C).^[103] Without the need for highly Lewis basic substrates, the heterolytic FLP-type splitting of dihydrogen was accomplished, a rare example for this type of chemistry with a tetrahedral Lewis acid. This reactivity was further stretched by the demonstration of a catalytic C-H activation of electron-rich aromates and a reversible C-H silylation *via* a FLP approach.^[114]

Germanium catecholate complexes are also *effective* catalysts and due to their resistance regarding hydrolysis promising candidates for Lewis acid catalyzed reactions. Bis(perchloro-catecholato)germane outperformed its Si derivative in hydrosilylation reactions, hydrodefluorinations, Friedel-Crafts reactions and carbonyl olefin metatheses, when employed catalytically in form of its bis-(MeCN) adduct.^[89] Other catalytic applications of perhalogenated bis(catecholato)germanes

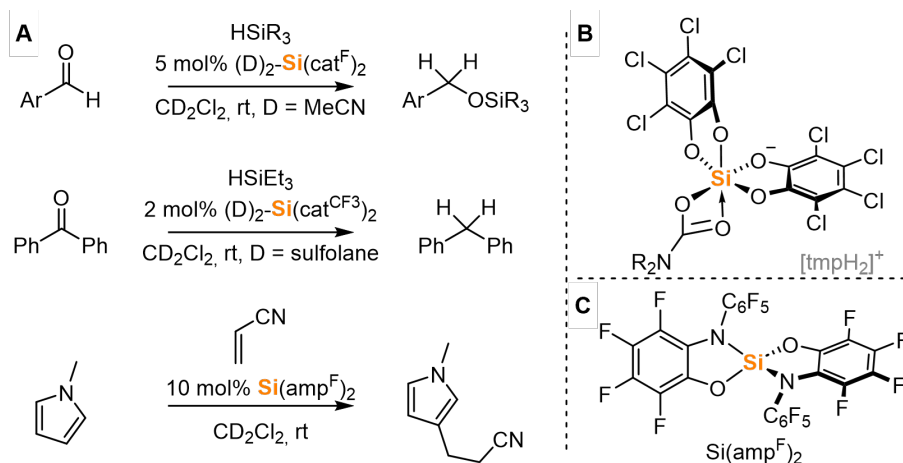


FIG. 1.3.: Bond activation by strong *effective* Lewis acids: A) Silanes as catalysts in a variety of transformations. B) FLP type CO₂-capture by Si(cat^{Cl})₂. C) Lewis structure of Si(amp^F)₂.

were reported by BAINES, including hydroboration reactions and the oligomerization of styrene derivatives.^[115] However, the overall low abundance of germanium puts these results in context and emphasizes sustainable solutions with its lighter homologue silicon.^[116]

1.4. Z-TYPE LIGANDS

1.4.1. GENERAL CONSIDERATIONS

The remarkable ability of transition metals to catalyze a wide range of chemical transformations has long motivated the development of tailor-made ligands to fine-tune the reactivity of the coordinated metal and thereby expand its applications in chemistry.^[2,8] While most ligands are electron-donating, contributing either two or one electrons (L-type or X-type) to the metal center and thus increasing its local electron density, comparatively less attention was initially devoted to σ -accepting ligands (Z-type) that formally receive an electron-pair from the metal.^[9]

Generally speaking, a Z-type ligand is a Lewis acid that accepts electron density from a filled d-orbital of the metal, thereby increasing its valency by two.^[10] This interaction results additionally in the energetic stabilization of the vacant p-orbitals of the metal fragment, as sketched in the qualitative MO diagram in FIG. 1.4.

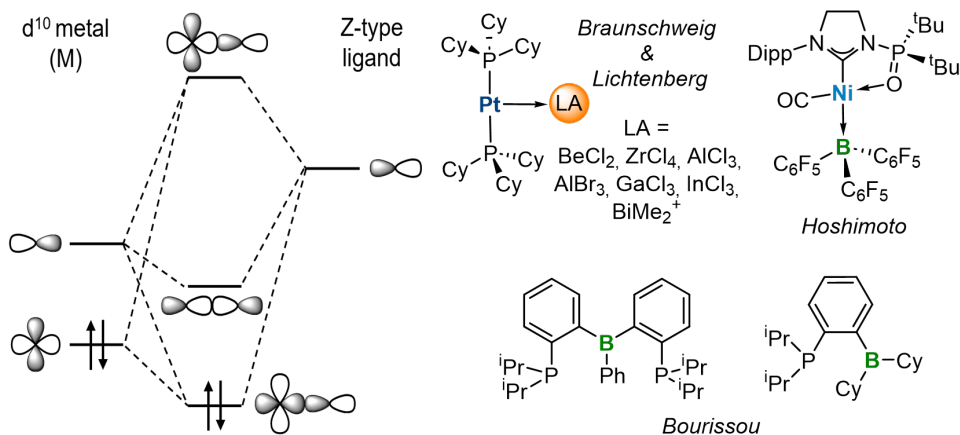


FIG. 1.4.: Left: Qualitative molecular orbital diagram for a Z-type interaction between a d^{10} -metal and a Lewis acid. Right: Examples of unsupported Z-type interactions and pioneering ambiphilic phosphino boranes.

Recognizing the potential of precisely modulating the electron density at a reactive metal center *via* a σ -accepting Z-type interaction, this research area has gained considerable significance over the past two decades. Although in principal every molecular Lewis acid can act as a Z-type ligand when a Lewis basic metal is coordinating it, reports on such unsupported interactions are scarce, and their inherent lability and susceptibility for side reactions (e.g., ligand abstraction from the metal fragment) limits their applicability in catalytic transformations.^[117] Usually reports of unsupported Z-type interactions rely on very Lewis basic metal fragments, as shown by pioneering work by BRAUNSCHWEIG, who reported a series of Lewis pairs of the strongly donating $\text{Pt}(\text{PCy}_3)_2$ (FIG. 1.4).^[118–123] One disadvantage of this modular approach was however quickly observed when this Pt(0) fragment oxidatively cleaved weak E-X bonds in the Lewis acids, which later was deliberately

used to generate the first Pt-stabilized boron-oxygen triple bond.^[124] Although unsupported Z-type complexes included a broad range of group 13 Lewis acids (Al, Ga, In),^[125,126] it was only recently that the first unsupported Z-type borane interaction was reported (FIG. 1.4), highlighting the challenges of these Lewis pair formations.^[127]

The problems of unsupported Z-type interactions were largely overcome by the introduction of ambiphilic ligands that integrate both donor (L-type) and σ -accepting (Z-type) functionalities within the same framework, benefiting from the chelate effect.^[11,128–130] To date, most reported Z-type systems incorporate group 13 Lewis acids, whose vacant p_z orbitals confer inherent Lewis acidity.^[131,132] Hence, it is not surprising that boranes laid the conceptual foundation for this field of research through pioneering work by HILL in 1999, who isolated a ruthenium(0) Z-type complex - or in other words a ruthenaboratrane - by reduction of a Ru(II) precursor by a poly(azolyl)borate.^[133] This ligand concept was soon derivatized by PARKIN and used for Fe(0), Rh(I), Ir(I) and Pd(0) Z-type complexes.^[134–136] BOURISSOU extended the field of ambiphilic borane ligands to mono-, bis-, and tris-phosphine boranes (FIG. 1.4),^[132,137–143] followed by the invention of alanes, gallanes, and indanes as Z-type ligands by other groups.^[144–149] Heavier group 15 elements (Sb, Bi) have also been explored as Z-type ligands.^[150–158] In contrast, group 14 elements remain underexplored in this context, partly because exploiting their Lewis acidity demands more sophisticated ligand designs.^[159–166] Given the fact that group 14-based Lewis acids can exert a pronounced perturbative influence on coordinated Lewis basic probes, indicative of strong *effective* Lewis acidity, they should present promising candidates for strong Z-type interactions and lead to significant alterations of the electronic structure of transition metals, hence drastically modifying their reactivity.

1.4.2. GROUP 10 CHEMISTRY OF Z-TYPE LIGANDS

A crucial aspect of the Z-type interaction relies on energetically accessible filled d-orbitals at the transition metal, which form the dative bond with the Lewis acidic ligand. Therefore, the usage of late transition metals in low oxidation states dominates this field of research, with the majority of reported systems relying on noble 4d and 5d metals. Besides the Z-type chemistry of gold, the majority of reported systems investigated group 10 and 9 metals. In the following, selected examples of group 10 Z-type complexes with relevance for this dissertation are discussed.

PETERS pioneered in the nickel(0) chemistry of Z-type ligands by reporting a Ni(0) complex of an ambiphilic diphosphine-borane ligand in 2011 (FIG. 1.5).^[167] Upon exposure to H₂, reversible activation of dihydrogen was observed, forming a Ni(II)-hydride hydrido-borate complex, whereas in the additional presence of olefines, catalytic hydration was observed. In a similar manner, this PBPNi complex reacted with silanes and catalyzed hydrosilylation reactions.^[168] Exchanging the phenyl groups at the phosphines to *iso*-propyl residues - like originally envisioned by BOURISSOU - allowed for the investigation of respective η^1 -N₂ and Ni(0)-H₂ complexes.^[169]

By changing to a tripodal system, LU isolated a series of group 13 Ni(0)-Z-type complexes (FIG. 1.5), disclosing stronger Z-type interactions with heavier main group elements.^[170,171] In line with the observations made, a respective borane system did not display a Z-type interaction in its neutral state. However base-assisted splitting of dihydrogen furnished an anionic Ni(0)-hydride complex, stabilized by a Z-type interactions, thereby showcasing a rare example of a Lewis base triggered Z-type interaction.^[172] Interestingly, only the respective gallane system displayed high catalytic activity in the hydrogenation of olefins.^[171]

Palladium's Z-type chemistry is longer known than the one of its lighter homologue, dating back to 2006 when PARKIN reported a palladaboratrane, similar to HILL's ruthenaboratrane.^[136] Two years later, Pd(II) and Pt(II) complexes of

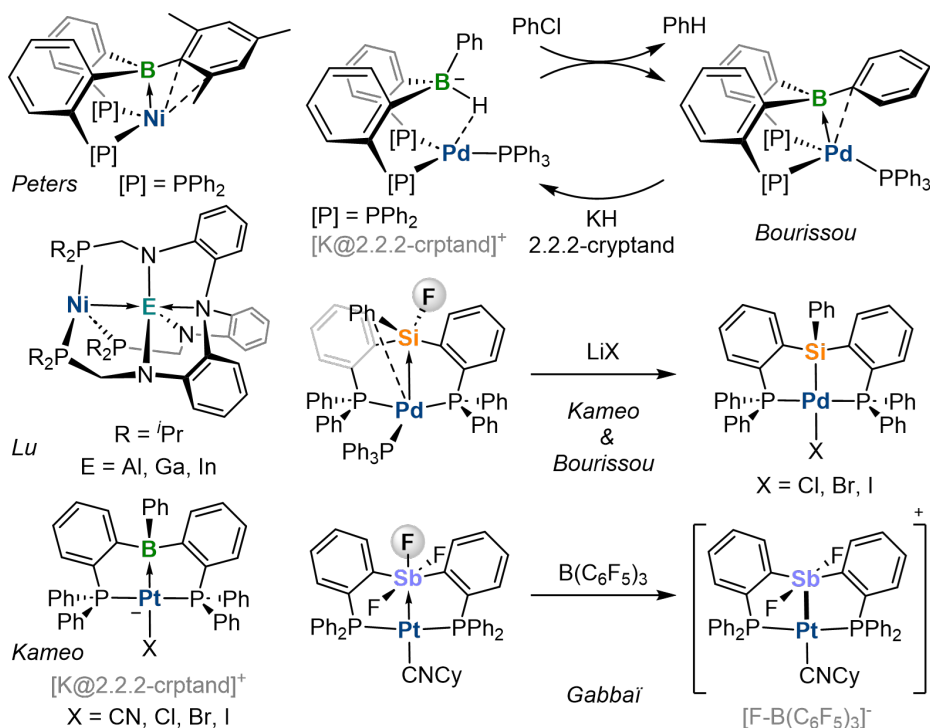


FIG. 1.5.: Examples of Z-type complexes of group 10 metals and their typical reactivity.

BOURISSOU's bis(phosphino)-borane were reported, however a Z-type interaction was rather weakly expressed due to the d⁸ configuration of the metal center.^[173] The related Pd(0) complex, stabilized by an additional phosphine ligand and π -coordination by the phenyl group, displayed intriguing reactivity when exposed to hydride sources (FIG. 1.5). Formation of an anionic Pd(0) hydrido-borate complex with a weak Pd-H interaction was observed - a rare example of an anionic d¹⁰ complex (compare section 1.6).^[174] Further reactivity of this complex included the catalytic hydro-dechlorination of aryl chlorides. TAUCHERT further investigated the behavior of related complexes in the oxidative addition of iodobenzene, ultimately discovering a spontaneous follow-up reaction with the B-Ph bond, resulting in C-C coupling of biphenyl accompanied by formation of a boryl Pd(II) complex.^[175]

Chemoselective oxidative addition of acyl chlorides over aryl halides was later reported for a structurally related bis-phosphine borane complex; a reaction that was only accomplished due to the Z-type induced stabilization of Pd's d-orbitals and therefore its inertness towards C(sp²)-X bond.^[176]

Besides borane-based Pd complexes, an interesting example of a silane Pd(0) complex was reported by KAMEO and BOURISSOU (FIG. 1.5).^[177] Only a weak Z-type interaction was observed in this complex, judged by its long Pd-Si bond length ($d = 2.9770(8)$ Å), the tetrahedral coordination environment at Pd and the small Wiberg bond index (WBI). Interestingly, addition of lithium halides induced an oxidative addition, followed by transmetallation, yielding respective silyl-Pd(II) halides, which were identified as intermediates in a sila-Negishi coupling of fluorosilanes.

While a platinaboratrane was already discovered in 2004 by using similar approaches as for the respective Ru(0) and Pd(0) complexes,^[178] two specific examples of Pt(0) Z-type complexes relevant for this work shall be discussed in the following. Recently, KAMEO and BOURISSOU reported the isolation of a T-shaped bis-phosphine borane L₂Z-Pt(0) complex.^[140] Due to its electrophilic character, which is well-reflected in the localization of the LUMO at the Pt center, this complex formed a series of anionic Pt(0) complexes through reaction with (pseudo-) halide salts in the presence of cryptands or crown-ethers (FIG. 1.5). While these complexes represented a rare example of anionic Pt(0) complexes, their unusual square planar (*sqp*) geometry was raising questions regarding platinum's oxidation state. X-ray photoelectron spectroscopy (XPS) however clearly confirmed the d¹⁰-configuration at Pt. The resemblance of *sqp*-Pt(II) complexes therefore can be traced back to their identical valency. An interesting fact however was revealed when the T-shaped complex reacted with CO, forming a tetrahedral Pt(0) complex, highlighting the different bonding characteristics of this π -accepting ligand when used in the presence of a Z-type borane.

GABBAÏ and co-workers reported a trifluorostiborane Pt(0) complex (FIG. 1.5) with a strong Pt→Sb(V) Z-type interaction.^[179] Abstraction of the fluoride by a strong Lewis acid modulated the σ -accepting character of the Sb center, furnishing a strong covalent Sb-Pt bond, accompanied by a pronounced electrophilic character of the Pt center - closely related to the observations made by KAMEO in his fluoro-silane Pd complex.^[177] As a consequence, this complex exhibited high catalytic activity in the cyclization of 1,6-enynes. GABBAÏ therefore successfully demonstrated an example of 2nd-sphere manipulation of the bonding characteristics of a Z-type ligand.

1.4.3. RHODIUM CHEMISTRY OF Z-TYPE LIGANDS

After his initial success with d⁸-metallaboratranes (Ru(0) and Os(0)),^[133,180] in 2006 HILL expanded the chemistry of his tris(methimazolyl)borane Z-type ligand to the isoelectronic Ir(I) and Rh(I) (FIG. 1.6).^[181–184] In the respective rhodaboratrane, the d⁸-Rh(I)L₄XZ fragment adopted a pseudo-octahedral geometry, as also observed for a related Rh(I)L₅Z complex with pyrazolyl arms.^[185]

Rhodium was also the first metal used by BOURISSOU for his ambiphilic PBP system (FIG. 1.6).^[139] By using a strong Lewis base like 4-(dimethylamino)pyridine (DMAP), the initially formed dimeric structure was split into monomeric d⁸-Rh(I)L₃XZ fragments, in which the donating ligands formed a *sqp*-coordination environment at Rh(I), as expected for a d⁸-metal complex. A Z-type interaction from the filled d_z-orbital into the p_z-orbital was already indicated by a tetrahedral structure at boron and was ultimately disclosed by DFT-based orbital analysis.

OZEROV further investigated the chemistry of this system, discovering a previously overlooked partial oxidative addition of the B-Ph bond over the Rh(I) center in the absence of DMAP,^[186] or in the presence of alkali carbonates at elevated temperature, mimicking the Pd(0) chemistry of this ligand.^[187]

Further investigations into the Z-type chemistry of Rh(I) gave rise to bis-phosphine alane complexes (FIG. 1.6).^[188,189] Similarly to related bis-phosphine borane sys-

tems, migration of anionic ligands (H^- , Cl^- and Me^-) between Al and Rh was observed, most likely *via* aluminyl supported Rh complexes.^[190] These results highlight the problems arising from bis-phosphine group 13 complexes, namely the reactivity of the remaining E-X bond in the coordination sphere of a late transition metal, rendering this ligand design unsuitable for several applications.

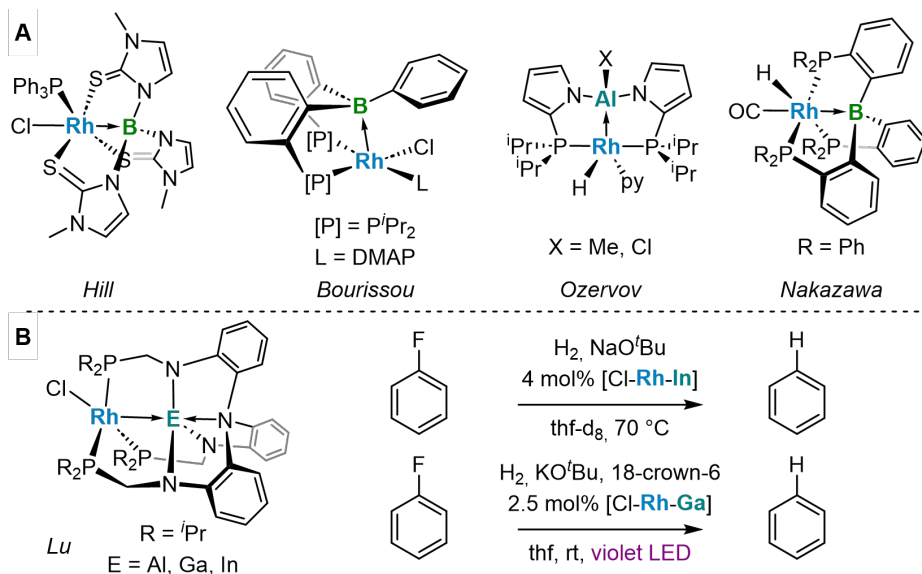


FIG. 1.6.: A) Examples of group 13 Z-type complexes of Rh(I). B) Hydrodefluorination of aromatic substrates catalyzed by tripodal Rh Z-type complexes.

Inspired by the versatility of tris(imazoly)boranes as Z-type ligands, NAKAZAWA isolated tripodal Rh complexes with a tris-phosphine borane ligand and demonstrated a Z-type induced rich redox-chemistry of the system.^[191] The respective carbonyl Rh(I) hydride complex adopted a pseudo-octahedral geometry (FIG. 1.6), as already observed for the other $\text{d}^8\text{-Rh(I)L}_4\text{XZ}$ complexes. Ambivalent reactivity of the hydride was observed as protonation by $[\text{HOEt}_2][\text{BF}_4]$ furnished the cationic $\text{d}^8\text{-Rh(I)L}_4\text{Z}$ complex with a square pyramidal structure, whereas deprotonation with KH yielded an trigonal bipyramidal (*tbp*) anionic $\text{d}^{10}\text{-Rh(-I)L}_4\text{Z}$ complex.

This strategy of generating anionic Rh(-I) complexes *via* a Z-type stabilized hydride presents a powerful toolbox, which was also applied to other related tripodal Rh complexes by the Lu-group. Using the same ligands that gave rise to the interesting Ni(0) chemistry in section 1.4.2, a series of group 13 Rh(I)-X (X = Cl, H, Me, Ph) complexes was isolated and characterized (FIG. 1.6).^[146,149] Deprotonation of the hydrides furnished the respective anionic Rh(-I) complexes with structural similarities to their related Ni(0) complexes. In the presence of a strong base and under 4 bar of H₂, the Rh-In complex catalyzed the hydrodefluorination of aryl fluorides (FIG. 1.6), proposing oxidative addition of the C-F bond at the reduced Rh(-I) center as the key step of the reaction.

Interestingly, the respective alane and gallane did not exhibit significant catalytic activity. However, in the presence of violet light ($\lambda = 395$ nm) all systems showed catalytic conversion in the hydrodefluorination reaction (FIG. 1.6), with the gallane system outperforming the other two, which was reasoned by “*a careful balance between SET reactivity and stability of the active species*”.^[147] Again, the anionic Rh(-I) species was proposed as a key intermediate in the catalytic cycle, undergoing a single electron transfer (SET) in the excited state to the aryl fluoride, effectively generating a Rh(0) complex. The latter was isolated through a comproportionation reaction and in the case of the allane system even studied crystallographically. Exchanging the phosphines for pyridines resulted in a Rh-Ga Z-type complex, which, when incorporated in a metal organic framework (MOF), selectively catalyzed the semi-hydrogenation of alkynes to respective *E*-olefines.^[192] Studies on the mechanism showed that the Lewis acidic Ga promotes the reaction and gives rise to the selectivity.^[193]

While these results emphasize the catalytic potential of Rh(I) Z-type complexes, the missing understanding of the correlation between the Z-type interaction and the desired catalytic activity hitherto raised the need for empirical iteration. Fundamental investigations into the Rh-Lewis acid interaction could provide valuable insights for future catalyst development.

1.4.4. LIMITATIONS OF Z-TYPE INTERACTIONS

One of the most famous examples that scrutinized the potential of Z-type ligands for applications in catalysis was certainly given by PETERS' anionic Fe(-I) tris(phosphino)borane complex, which is depicted in FIG. 1.7.^[194] Using BOURIS-sou's tripodal borane ligand, a Fe(I)-Br complex with a Fe→B Z-type interaction was isolated, which upon reduction by one electron formed a neutral terminal Fe(0)-N₂ complex. A second reduction with sodium amalgam in the presence of N₂ furnished the anionic Fe(-I)-complex. This complex was later reported to homogeneously catalyze the reduction of N₂ with KC₈ in the presence of a proton source to form NH₃, proposebly *via* several Z-type stabilized Fe-N_xH_y intermediates.^[195,196] While the turn over number (TON) of this complex is relatively low (7 ± 1) compared to heterogenous systems, this model compound proved the catalytic capability of Fe, which is the only transition metal found in every nitrogenase.^[197]

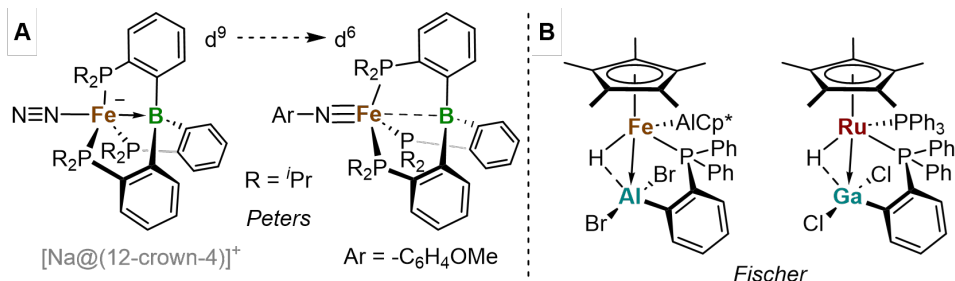


FIG. 1.7.: Limitations to Z-type interactions: A) Oxidation of the d⁹-ferroboratrane results in drastic weakening of Z-type interaction. B) Two rare examples of d⁶-complexes with Z-type interactions.

Despite its ground-breaking activity in N₂-reduction, this model compound further draws the borders of Z-type interactions. Reaction of the neutral Fe(0)-N₂ complex with an aryl azide formed a diamagnetic imido-Fe(II) complex (FIG. 1.7).^[194] Its solid state structure already hinted the weakening of the Fe-B interaction, since the Fe-center was found tetrahedrally coordinated by the three phosphines and the imido-N with an elongated Fe-B bond length of 2.608 Å, com-

pared to a Fe-B bond length of 2.293 Å in the Fe(-I) complex.^[194] Still, Kohn-Sham orbital analysis revealed a HOMO with small contributions by the p_z-orbital from boron.

In fact, only a few reports on d⁶-metal centers engaging in Z-type interactions can be found in the literature, consistent with the principle that such interactions require a high electron density at the metal. Most of these examples were found rather accidentally, as by FISCHER, who investigated the reactivity of bis-phosphine Fe(II) halide complexes with two equivalents of low valent AlCp*, discovering an unpredicted formation of the complex depicted in Fig. 1.7.^[198] Cp* transmetallation to Fe, as well as electrophilic substitution of one *ortho*-H at PPh₃ with a AlBr₂ fragment gave rise to a rare Fe(II)→Al complex with a bridging hydride. In a similar way, tris(triphenylphosphine)Ru(II) dichloride reacted with GaCp*, forming a respective Ru(II)→Ga(III) Z-type complex.

Although the results above underline the feasibility of d⁶-Z-type interactions, to date no reports on the Z-type chemistry of group 8 (Cr, Mo, W) exist. Closing that gap in Z-type chemistry should be from high interest, given the unprecedented potential of group 6 complexes in the fixation and activation of dinitrogen.^[199–202]

1.5. LEWIS ACID CATALYZED C-O BOND METATHESIS

It is not without reason that the *Royal Swedish Academy of Sciences* awarded the 2005 Nobel prize in chemistry to CHAUVIN, GRUBBS and SCHROCK “for the development of the metathesis method in organic synthesis”,^[203] since it is undoubtedly a core technologies in modern chemistry, whether in total synthesis, or in chemical industry.^[204–209] Despite the widespread use of metathesis reactions, even of polarized double bonds,^[210–212] much less is reported on the metathesis reactions of single C-X bonds, due to their overall diminished reactivity.^[213–217] Many of these reports involve the transition metal mediated reversible oxidative addition of C(sp²)-X bonds as an entry point for bond diversification.^[218–220] This strategy

however can not be easily applied to $C(sp^3)$ -X bonds, due to increased reaction barriers and possible side-reactions, like β -hydride elimination, in the immediately formed alkyl-metal complexes.^[221,222] Hence, Lewis acid catalysis provides a suitable alternative for this type of reaction.^[223] In the following, key-findings on the metathesis of $C(sp^3)$ -O bonds with relevance to this dissertation are discussed.

C-O bond metathesis provides a powerful tool for polymer degradation, as demonstrated by ENTHALER, who depolymerized several polyethylene oxides (pEO) in the presence of stoichiometric amounts of reactive intercepting reagents, like acid chlorides or anhydrides, in combination with catalytic amounts of a transition metal Lewis acid (FIG. 1.8 A).^[224–226] Later, this approach was modified by CANTAT, employing a main group Lewis acid ($B(C_6F_5)_3$) as a catalyst, although in the presence of an excess of hydrosilanes.^[227]

Eliminating the need for stoichiometric corrosive reagents, ENTHALER reported an example of the Lewis acid catalyzed ring closing metathesis (RCM) in polytetrahydrofuran (FIG. 1.8 B).^[228,229] While this transformation can also be catalyzed by a Brønsted acid,^[230] this approach is solely limited to the less prevailing poly-thf and requires high reaction temperatures as well as continuous removal of formed thf.

In 2011 JUTZI observed the formation of a Lewis pair of his electrophilic $[Cp^*Si(II)]^+$ cation and dimethoxyethane.^[231] While its structure was confirmed crystallographically, prolonged storage at room temperature resulted in the formation of 1,4-dioxane, dimethyl ether and the half-sandwich cation. This observation was reasoned by a RCM, which was further applied to a variety of methyl-capped oligo-ethers and even to the cyclic 12-crown-4, ultimately showcasing that $[Cp^*Si]^+$ acted as a catalyst, although with very low turn over frequencies (TOF) at room temperature (FIG. 1.8 C). Interestingly, based on the isolated intermediate, the group proposed a catalytic cycle in which the ether coordinates the Lewis acid in a bidentate fashion before the nucleophilic attack of a second ether functionality can occur.

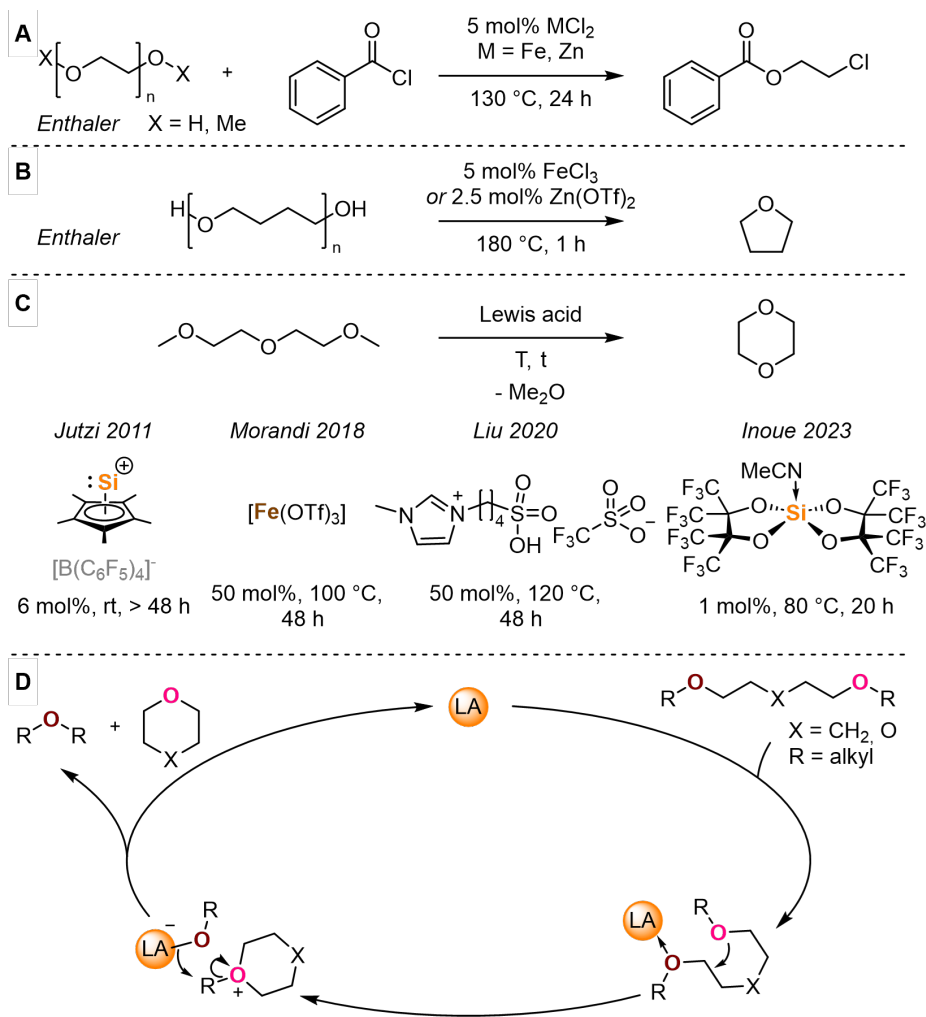


FIG. 1.8.: Examples of Lewis acid catalyzed bond metathesis reactions in oligo- and polyethers. A) Lewis acid catalyzed depolymerization of polyethers with stoichiometric amounts of acid chlorides. B) Lewis acid catalyzed RCM of polytetrahydrofuran under harsh conditions. C) Reports on the C-O bond metathesis of diglyme, catalyzed by a variety of Lewis acidic systems. D) General mechanism of the Lewis acid catalyzed C-O bond metathesis as proposed by previous works.

MORANDI *et al.* followed up on the Lewis acid catalyzed C-O bond RCM in a series of oligo-ethers, using the commercially available $\text{Fe}(\text{OTf})_3$ as the catalyst.^[232] Although their catalyst displayed high activities in the RCM of several di-ether substrates, oligo-ethers that are prone to multi-dentate coordination like di(2-methoxyethyl) ether (also known as diglyme) required increased catalyst loadings, elongated reaction times and elevated temperatures for quantitative conversions, ultimately showcasing the limitations of this systems. A related approach by LIU, using ionic liquids as a catalytically active medium could also not overcome these challenges.^[233] First insights into the reaction mechanism by NMR spectroscopy and NBO calculations suggested hydrogen bond catalysis as a reasonable explanation for the observed reactivity.

After the initial publication of the work presented in section 3.2.1,^[234] the INOUE group reported a high activity of their bis(perfluoropinacolato)silane in the RCM of oligo-ethers, expanding the field of group 14 Lewis superacids as catalysts for this transformation.^[113]

While it is assumed that all of the mentioned reactions follow the same catalytic cycle (FIG. 1.8 D), which is based on few experimental observations, its verification and a profound understanding is still pending. It is assumed that the oligo-ether coordinates to the Lewis acid, which induces a polarization of the adjacent C-O bond. Nucleophilic attack of a second ether functionality at the polarized carbon atom results in the formation of a zwitterionic pair, which upon a second intermolecular $\text{S}_{\text{N}}2$ reaction liberates the products.

1.6. ANIONIC PALLADIUM COMPLEXES IN CROSS-COUPLING REACTIONS

A reaction type, which had an even more pronounced impact on synthetic strategies than the olefin metathesis is the palladium-catalyzed cross coupling reaction, a powerful tool for the creation C-C and C-X bonds.^[235] The well-studied catalytic cycle of a generic Pd-catalyzed cross coupling is depicted in FIG. 1.9 A and includes the oxidative addition of a R-X bond at a Pd(0)-fragment (usually L_2Pd), followed by transmetalation with $R'-M$ and subsequent reductive elimination of the cross-coupling product $R-R'$, refurnishing the active catalyst.

Less is known about the role of anionic Pd(0) and Pd(II) intermediates in these reaction types, despite numerous reports on beneficial effects of ionic additives on crucial factors like reaction rates and yields.^[236–239] Although accepted as intermediates, the explanation of the beneficial effects on a molecular level still remains debated.^[240–244] HARTWIG for example studied the rates of the oxidative addition of aryl triflates at $Pd(P(o\text{-tolyl})_3)_2$ and discovered significantly increased rates in the presence of halide salts, reasoned by the formation of an anionic Pd(0) complex.^[245]

One of the most prominent explanations of these phenomena was given by AMATORE and JUTAND, who based on electrochemic experiments in conjunction with NMR spectroscopy proposed the mechanism depicted in FIG. 1.9 A.^[246–253] According to their studies, the neutral Pd(0) fragment can be coordinated by an anion, forming a penta-coordinated anionic Pd(0) complex, which undergoes oxidative addition significantly faster than its neutral counterpart. Upon loss of one anion (either X^- or Y^-), the catalytic cycle is closed again and follows its well-known path. By using electron-poor aryl phosphine palladium complexes, KOSZINOWSKI *et al.* were able to detect the speculated anionic Pd(0) and Pd(II) species by ESI mass spectrometry.^[254,255] Further efforts to scrutinize the proposed mechanism relied on the use of DFT calculations.^[256–261]

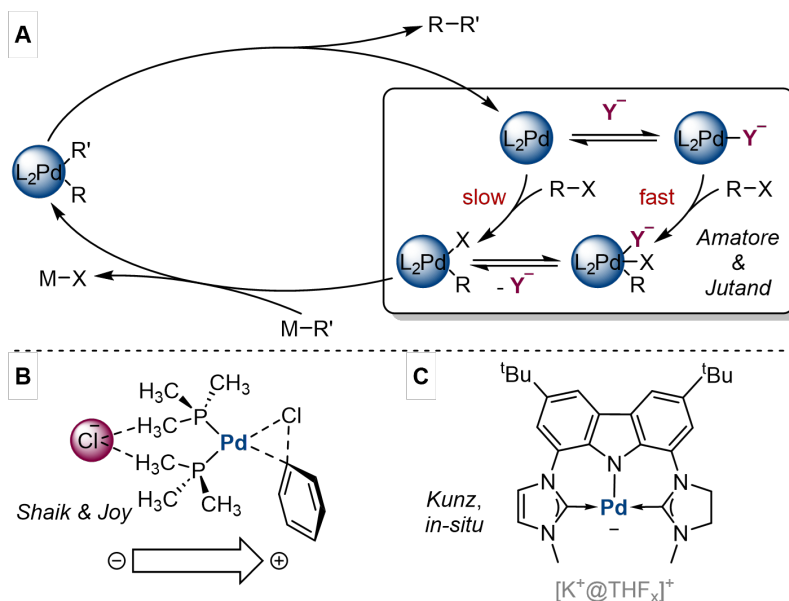


FIG. 1.9.: Anionic Pd(0) complexes in cross-coupling reactions: A) General catalysis cycle for Pd-catalyzed cross-coupling reactions with the side-cycle proposed by AMATORE and JUTAND. B) Transition state of the oxidative addition of chlorobenzene in the presence of a chloride, causing an electric field, as represented by the OEEF vector. C) Example of an anionic Pd(0) complex observed in solution.

A different perspective on rate enhancing effects was given by JOY and SHAIK after careful evaluation of DFT calculations.^[262] Instead of binding directly to Pd, their theoretical work disclosed the possibility of anion coordination in the second coordination sphere of the Pd(0) catalyst. Thereby, a oriented external electric field (OEEF) is created, which effectively lowers the transition state of the oxidative addition in energy (ca. 10 kcal mol⁻¹), as schematically drawn in FIG. 1.9 B.

Debates concerning the true origin of the rate-enhancing effects of anionic additives can, in part, be attributed to the scarcity of reported, isolated anionic group 10 complexes (M(0) = Ni, Pd, Pt).^[263] While some studies have reported on the chemistry of anionic Ni(0) complexes,^[172,264] the second example of an anionic Pt(0) complex was only disclosed in 2023 by the BOURISSOU group (see

section 1.4.2 for details).^[140] Reports of anionic Pd(0) complexes are even rarer and consist of the *in-situ* characterization of an anionic bis(NHC)-carbazole Pd(0) complex by KUNZ (FIG. 1.9 C),^[265] in which the cation (K^+) is likely coordinated by the deprotonated carbazole, and of the isolated hydrido-borate Pd(0) complex presented in section 1.4.2.^[174] In both cases, the anionic charge is largely stabilized within the ligand backbone, and no direct $[X-Pd(0)]^-$ species has been observed.ⁱⁱ

1.7. REDOX NON-INNOCENCE AND ELECTROMERISM

A ligand that is susceptible for ligand-centered oxidation or reduction events - therefore showcasing redox activity - is termed a redox non-innocent ligand, since it actively interferes with the redox chemistry at the coordinated element.^[267] This class of ligands received a significant amount of interest due to their versatile diversification of the central elements reactivity.^[268,269] The reduced form of a non-innocent ligand can act as an electron reservoir to induce reactivity at an electron-poor central element (e.g., oxidative addition at Zr(IV)),^[270] but it can also generate reactive ligand-centered radicals for bond activation or initiate a ligand-to-substrate single electron transfer.^[102] Lastly, oxidation of the ligand can enhance the Lewis acidity of the complex, as recently demonstrated by GREB and coworkers.^[86]

Prevalent ligand motives in the field of redox non-innocent are catechols and aminophenols, two ligand classes that are used throughout this dissertation. In FIG. 1.10, the three accessible oxidation states of these two related ligand classes are depicted. In its fully reduced form, the catecholate or amidophenolate is a bidentate dianionic ligand. Stepwise one-electron oxidation steps yield the monoanionic open-shell semiquinonate ($E = O$) or iminosemiquinonate ($E = NR$) and finally the fully oxidized neutral (imino)quinone. Regardless of the oxidation state, for

ⁱⁱ After the initial publication of the anionic Pd(0) complex in section 3.3.1,^[266] BOURISSOU reported the isolation and characterization of a series of anionic trigonal bipyramidal Pd(0) and Pt(0) complexes.^[143]

$E = O$ all these redox isomers are termed dioxolenes. Since in the presence of a redox-active metal, an unambiguous assignment of the respective oxidation state of these ligands is not always trivial, BROWN developed an empiric model based on structural data of over 100 reported complexes and introduced the “metrical oxidation state” (MOS).^[271] With increasing oxidation state of the ligands, a bond length contraction for the C-E bonds as well as the C-C bonds can be observed in the solid-state structures, which allows for least square fitting against the empiric correlation model and therefore continuous measure of the MOS of the ligands.

One important example of the use of the redox non-innocence of amidophenolates in bond activation is given by PISKUNOV’s bis(amidophenolato)tin(IV) complex, which thf adduct splits the C-X bond of allyl halides homolytically, ultimately forming a new C-C bond in the ligand backbone through element-ligand cooperativity.^[105] VAN DER VLUGT’s diphenylphosphanyl aminophenol (PNO- H_2), a ligand with special relevance for this work, was also used as a redox non-innocent ligand for the one-electron homolytic S-S bond splitting at a Pd(II) complex,^[272] or the fine-tuning of Ni-Au interactions in heterobimetallic complexes.^[273]

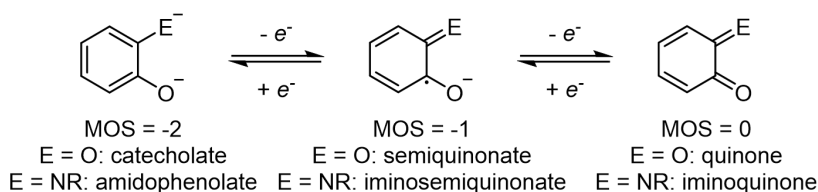


FIG. 1.10.: Schematic representation of possible oxidation states of catecholates and amidophenolates with the respective MOS values. Only one mesomeric structure is depicted.

Redox non-innocent ligands in combination with redox active coordinated elements ultimately gives rise to the phenomenon of electromerism (also known as valence tautomerism), a concept that intrigued chemists for a long time.^[274–277] Electromers differ only in the arrangement of electron density within the complex, ergo the respective partial oxidation states of ligands and elements, while the constitution of the complex remains unchanged. This concept owes much

of its popularity to the opportunity of harnessing these electronic changes for applications such as catalysis or spin-state switching in materials.^[102,272,278–281]

A key factor for electromerism are similar energetically accessible oxidation states at both, the central element and ligand. One of the earliest and most illustrative examples relies on dioxolene ligands in interplay with cobalt and is presented in FIG. 1.11.^[282] This system can either consist of a low-spin Co(III) center with one fully reduced catecholate ligand and one semiquinolate or its electromer, a high-spin Co(II) complex with two partially oxidized semiquinolates. Both electromers are close in energy, therefore minor changes in environmental effects like polarity of the reaction medium,^[283] pressure,^[284] or temperature can favor one isomer over the other.^[285] Further fine-tuning of the relative energies can be achieved by an appropriate choice of the co-ligand (2,2-bipyridine in the example above).^[286] Lately, even pulsed laser photolysis was able to induce the intramolecular electron transfer, thereby switching between the respective electromers.^[287,288]

Since electromerism requires energetically close oxidation states at the central atom, as they are for example found in 3d metals, much less is reported on electromerism in main-group elements.^[277] A computational study by STARIKOVA investigated potential electromerism in a series of amidophenolato group 14 complexes.^[289] While for Si only the +IV state seemed energetically feasible, electromerism in Ge complexes would be prohibited by large energy barriers. However for Sn, they suggested possible electromerism based on a narrow energy gap and a low barrier, which PISKUNOV later proved experimentally by the spectroscopic observation of electromerism in a tin complex with iminoquinone ligands (FIG. 1.11).^[106] While this complex can be accurately described as a diamagnetic Sn(IV) species in the solid-state, UV-Vis, EPR- and ¹¹⁹Sn Mössbauer spectroscopy at low temperatures concluded the existence of the respective electromer, an open-shell triplet diradical. Through a coordination of a Lewis base, however, the Sn(IV) state is stabilized drastically, effectively quenching any electromerism.

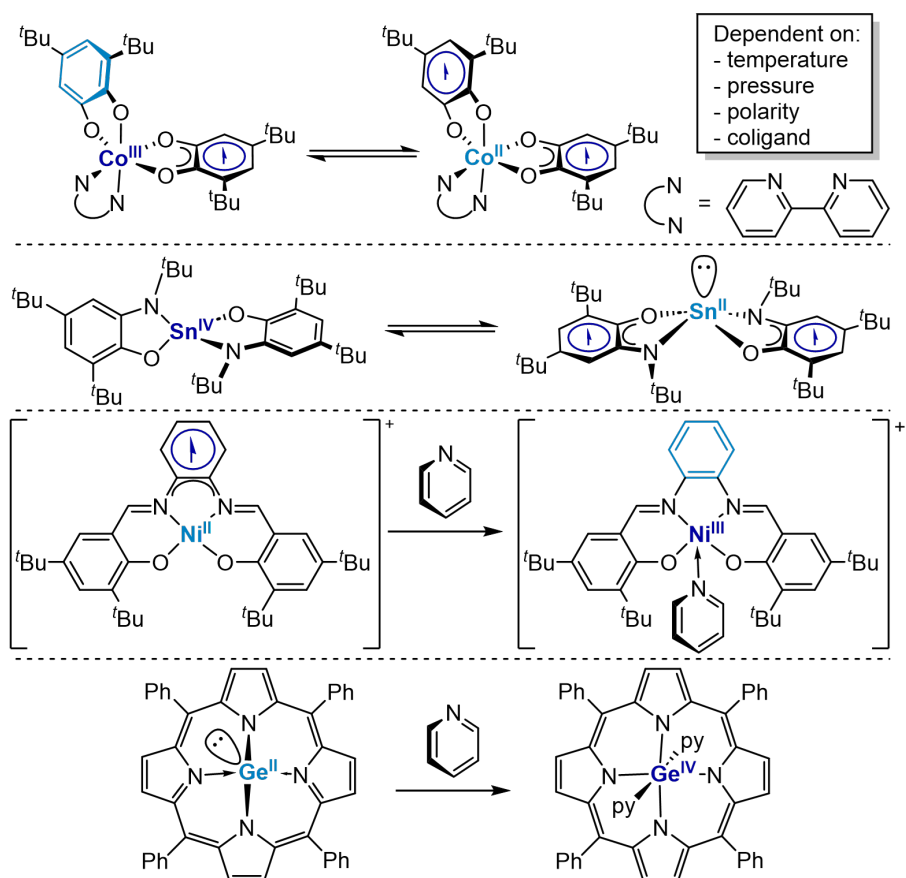


Fig. 1.11.: Examples of electromerism, from top to bottom: Prototypical valence tautomerism in cobalt bis(dioxolene) complexes and factors that influence the equilibrium; Electromerism in a tin complex with *o*-iminoquinone ligands; Lewis base triggered pseudo-electromerism in a cationic salen nickel complex; and in a germanium porphyrin complex.

When electromerism is accompanied by a change of constitution, it is referred to as “pseudo-electromerism”.^[290] A common approach is the coordination of a Lewis base to the redox-active central element, stabilizing the higher oxidation state due to its increased Lewis acidic character. This was for example shown in a cationic Ni(II) salen complex, which upon pyridine coordination experienced

reduction of the ligand and formation of the respective Ni(III) electromer (FIG. 1.11).^[291] Recently, ALCARAZO used the same ligand framework to isolate an arsenium (III) cation, which upon coordination of a strong Lewis base (Cl^- , NHC, or DMAP) exhibited reversible $\text{As(III)} \leftrightarrow \text{As(V)}$ pseudo-electromerism.^[292] Base induced pseudo-electromerism was also reported for an aromatic porphyrin Ge(II) complex (FIG. 1.11), which after coordination of two pyridine ligands formed an anti-aromatic Ge(IV) complex through transfer of the two vacant electrons from Ge(II) to the e_g -acceptor orbitals of the macrocycle.^[293] In the related calix[4]-pyrrol ligand framework, pseudo-electromerism can also be observed when antimony is chosen as the central element.^[294] Oxidation of the respective monoanionic Sb(III) complex with two equivalents of ferrocenium salts gave rise to a cationic Sb(III) complex with an oxidized ligand backbone including two dearomatized pyrrolato-moieties. Upon exposure to a Lewis base however, the respective highly reactive Sb(V) complex is putatively forms, before it undergoes side reactivity.

Reports on electromerism of 4d metals are scarce, mostly because of the large energetic difference of the involved oxidation states.^[295–297] Hence, Pd(0)/Pd(II) electromerism has hitherto not been experimentally realized, although this couple has been suggested in a theoretical study and potential applications of this ubiquitous redox couple in catalysis render its realization highly desirable.^[298,299]

2 | MOTIVATION AND OBJECTIVES

The concept of *effective* Lewis acidity is relatively new, yet holds significant potential to impact several key areas of chemistry. This work explores the application of group 14-based Lewis acids in two major contexts: as catalysts for C-O bond metathesis in oligo- and polyethers, and as Z-type ligands in coordination chemistry. In both domains, the aim is to deepen our understanding of how *effective* Lewis acidity influences reactivity - whether at the level of the substrate or the transition metal center.

Objective A deals with the application of catecholate-based group 14 Lewis superacids in the C-O bond ring-closing metathesis (RCM) reaction. While this reaction was reported to be catalyzed by simple commercially available Lewis acids like $\text{Fe}(\text{OTf})_3$, this work shall investigate the changes in reactivity when Lewis superacids with a high *effective* Lewis acidity are employed as catalysts for this chemical transformation. Moreover, deeper insights into the mechanism of this reaction could be obtained with assistance of theoretical methods. These insights could then be used to design highly efficient catalytic systems that push the reactivity beyond existing borders, even enabling the cross-metathesis of C-O bonds.

In the second part of this work, the overall reaction scheme of Lewis superacid-catalyzed ring-closing metathesis (RCM) is applied to polyethylene oxide (pEO) derivatives, offering a promising upcycling strategy for this class of polymers. The boundaries of reactivity are investigated by expanding the substrate scope and optimizing the tolerance of functional groups, particularly protic hydroxy

groups. By evaluating various pEO substrates, a more refined mechanistic model can be developed. Given the sensitivity of most Lewis superacids, improvements to the reaction protocol are also presented, paving the way for potential industrial applications and contributing to a circular economy for these widely used polymers.

Objective B focuses on the implementation of group 14-based, *effective* Lewis acids as ambiphilic Z-type ligands for the coordination chemistry of electron-rich transition metals. While the field of Z-type ligands has traditionally relied on the inherent Lewis acidity of group 13 elements, this work aims to exploit the strong *effective* Lewis acidity of tetrels, envisioning pronounced interactions between the metal center and the Lewis acid. This requires the design of a tailored ligand framework that enables the effective engagement of the Lewis acidic features of these elements.

Following the successful synthesis of such ambiphilic ligands, their coordination chemistry with late transition metals in low oxidation states - specifically Pd(0) and Rh(I) - will be investigated. It is hypothesized that *effective* Lewis acidity will significantly influence the reactivity and electronic structure of the coordinated metal centers. Furthermore, quantum chemical bonding analyses will be employed to systematically study the nature of the interaction between the Lewis acid and the transition metal.

The redox non-innocence of the Lewis acid - both at the central element and the ligand backbone, may pave the way for Z-type-induced electromerism, when combined with energetically accessible d-orbitals of the coordinated metal fragment.

Finally, this work will explore the boundaries of Z-type ligand chemistry by examining the coordination of molybdenum complexes, thereby expanding the scope of transition metals in Z-type systems.

3 | RESULTS AND DISCUSSION

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3.1. PREFACE

In the first half of this chapter, silane-based Lewis superacids are employed in the **ring-closing metathesis** (RCM) of **oligo- and polyethers**. While **section 3.2.1** explores the reactivity of strong, effective Lewis acids in this transformation and elucidates the underlying reaction mechanism, **section 3.2.2** focuses on the systematic catalytic up-cycling of polyethylene glycol derivatives. Emphasis is placed on improving the process's practicability and mechanistic understanding with a view toward potential industrial application.

Effective Lewis acidity has, until now, not been deliberately applied to **Z-type** interactions. In **section 3.3**, effective group 14 Lewis acids are investigated as σ -accepting ligands for late transition metals, with particular attention to the electronic and structural changes they induce at the metal center.

The first case study, presented in **section 3.3.1**, examines a series of Pd(0) complexes bearing an **ambiphilic silane** ligand. These complexes adopt unusual geometries, and due to the **strong Pd–Si interaction**, even anionic Pd(0) species can be isolated. Their role as **intermediates in cross-coupling reactions** is subsequently explored.

Building on this, **section 3.3.2** presents a unique example of Z-type-controlled **Pd(0)/Pd(II) electromerism** in a dicationic Pd-silane complex. Enabled by the electron-rich silane ligand, which facilitates ligand-centered oxidation, this system highlights the stabilizing influence of the effective silane Lewis acid on a highly electrophilic Pd complex through a strong Z-type interaction.

The coordination chemistry of the investigated silane ligand experiences drastic changes, when d^8 -metal centers are investigated. In **section 3.3.3**, a series of **Rh(I) complexes** bearing the same silane ligand are discussed. Through structural analysis paired with quantum chemical bond analyses, the **influence of co-ligands**

at the Rh center and the nature of the **Rh-Si interaction** are systematically evaluated.

Z-type complexes naturally rely on late transition metals with filled d-orbitals. In **section 3.3.4**, this unwritten rule is bent by the investigation of several molybdenum complexes of a silane Z-type ligand. The first example of a **Mo(0)-Z-type complex** is reported, its behaviour in oxidation reactions is discussed and the Mo-Si interaction is further elucidated.

Lastly, the Lewis acidic central element of the employed ambiphilic Z-type complex is exchanged for the heavier homologue tin. Synthesis and properties of this **ambiphilic stannane** are explored in **section 3.3.5**, which also showcases first examples of potential applications of this ligand in the coordination chemistry of late transition metals.

The publications in **section 3.2.1** to **section 3.3.3** were either distributed under the terms of the Creative Commons CC BY licence, or the rights to adapt the respective content were obtained through RightsLink®.

3.2. RING CLOSING METATHESIS IN POLYETHERS

3.2.1. SILICON CATALYZED C-O BOND RING CLOSING METATHESIS OF POLYETHERS

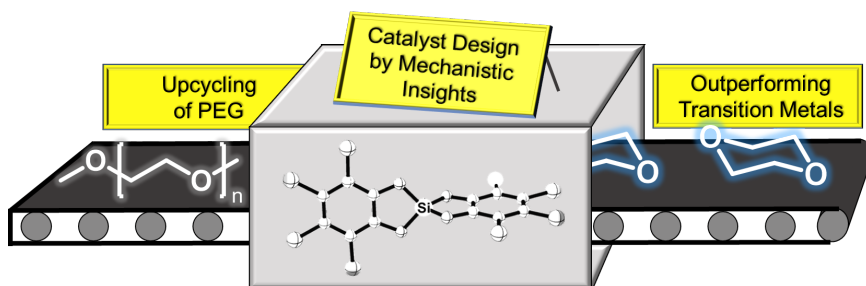


FIG. 3.1.: “Silicon Catalyzed C-O Bond Metathesis of Polyethers” - table of contents figure for the publication discussed in the following section.

The full article including its electronic supplementary information (ESI) presented in this section was published earlier and can be accessed under:

N. Ansmann, T. Thorwart, L. Greb, *Angew. Chem. Int. Ed.* **2022**, 61, e202210132, <https://doi.org/10.1002/anie.202210132>.

Contributions of the three leading authors are rationalized and listed according to the CRediT scheme^[300] on page 41, using the “Formblatt Kumulative Dissertation” (cumulative dissertation form), provided by the faculty of Geo- Sciences and Chemistry at the Ruprecht-Karls Universität Heidelberg. The original article is embedded at page 42 *ff.* The ESI is subsequently attached, starting at page 47.

Formblatt Kumulative Dissertation

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Vollständige bibliographische Referenz/*Complete bibliographic reference*:

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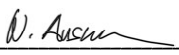
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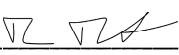
Contributor Role	Doktorand/in/ <i>Doctoral Student</i>	Co-Autor/in 1/ <i>Co-author 1</i>	Co-Autor/in 2/ <i>Co-author 2</i>
Name, first name	Ansmann, Nils	Thorwart, Thaddaeus	Greb, Lutz
Methodology	lead	-	supporting
Software	-	-	-
Validation	lead	-	supporting
Formal analysis	lead	-	-
Investigation	lead	supporting	-
Resources	-	-	lead
Data Curation	lead	-	-
Writing-Original Draft	equal	-	equal
Writing-Review&Editing	equal	-	equal
Visualization	lead	-	-
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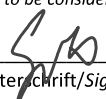

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Metathesis Reactions

Silicon Catalyzed C–O Bond Ring Closing Metathesis of Polyethers

Nils Ansmann, Thaddäus Thorwart, and Lutz Greb*

Abstract: The Lewis superacid bis(perchlorocatecholato)silane catalyzes C–O bond metathesis of alkyl ethers with an efficiency outperforming all earlier reported systems. Chemoselective ring contractions of macrocyclic crown ethers enable substrate-specific transformations, and an unprecedented ring-closing metathesis of polyethylene glycols allows polymer-selective degradation. Quantum chemical computations scrutinize a high Lewis acidity paired with a simultaneous low propensity for polydentate substrate binding as critical for successful catalysis. Based on these mechanistic insights, a second-generation class of silicon Lewis superacid with enhanced efficacy is identified and demonstrated.

Metathesis reactions of molecules with double or triple bonds represent core technologies in organic synthesis and the chemical industry.^[1] Ring-closing metatheses (RCM) of alkenes or alkynes are particularly prominent examples.^[2] In contrast, catalytic metathesis reactions of singly-bonded functionalities are less explored.^[3] Several examples of C–X bond metatheses relying on reversible oxidative addition of C(sp³)–X bonds have been reported.^[4] However, the metathesis of C(sp³)–X bonds by oxidative addition is hampered by high barriers and possible side reactions of the alkyl intermediates (e.g., β -hydride elimination).^[5] Instead, Lewis acid catalysis transpired as a suitable alternative for this type of transformation.^[3a,b,6] The group of Enthaler pioneered the depolymerization of polyethers by using transition metal-based Lewis acids (Figure 1a).^[7] However, stoichiometric amounts of corrosive intercepting reagents such as acyl chlorides were required for sufficient conversions. Similar strategies were reported by Cantat with B(C₆F₅)₃ as the catalyst, requiring excess hydrosilane to propel the

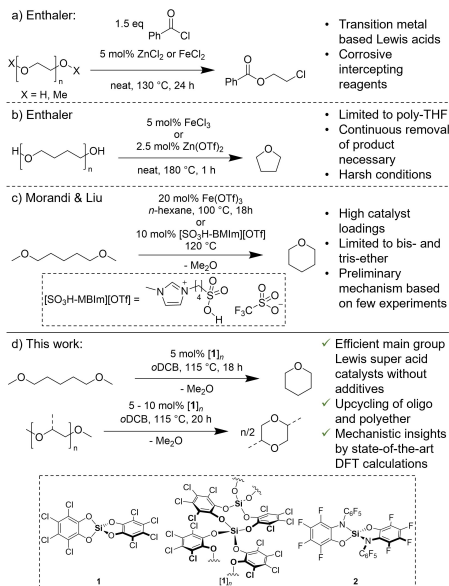


Figure 1. Previously reported Lewis acid catalyzed degradations of ethers. a) Lewis acid catalyzed degradation of polyethers with stoichiometric acyl chloride, b) Lewis acid catalyzed ring-closing metathesis (RCM) of polytetrahydrofuran, c) C–O bond metathesis of bi-ethers, d) RCM in bis- and polyethers catalyzed by main group Lewis superacids **1** and **2** demonstrated in this work.

reaction.^[8] It was also the group of Enthaler that observed a ring-closing C–O bond metathesis from polytetrahydrofuran (Figure 1b).^[9] Harsh reaction conditions and the continuous removal of THF through distillation limited this process to the less prevalent polytetrahydrofuran.^[10] In 2018, Morandi et al. extended the ring-closing C–O bond metathesis to bis- and tris-ethers.^[11] Using 20 mol% of Fe(OTf)₃, a variety of tetrahydropyrans, tetrahydrofurans, 1,4-dioxane and morpholine derivatives were formed from the respective linear dimethoxy alkanes at elevated temperatures (Figure 1c). A comparison with other Lewis acids revealed Fe(OTf)₃ as the most active catalyst. Two years later, Liu et al. implemented a biphasic system consisting of the neat ether substrates and 10 mol% of the ionic liquid 1-butylsulfonate-3-methylimidazolium trifluoromethane sulfonate ([SO₂H-BMI][OTf]) (Figure 1c).^[12] Jutzi's unique silicon(II) cation Cp*Si⁺

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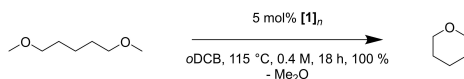
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has also catalyzed related processes.^[13] All these transformations were proposed to follow a mechanism supported by some experimental observations, but a deeper understanding is pending.^[11,12] Beyond, the extension of C–O bond metathesis towards polyethers, including polyethylene glycol (PEG), remains an open challenge.

The present study describes the implementation of the donor-free $[1]_n$ -polymer of Lewis superacid bis(perchlorocatecholato)silane **1** as a catalyst for C–O bond metathesis (Figure 1d).^[14] Mechanistic insights by quantum chemical calculations rationalize the outstanding efficacy of **1**. Most critical is the immunity towards chelation-deactivation by polyethers that unlocks potential recycling strategies of the pervasive PEG. Based on these findings, the design of a second-generation class of silicon(IV) based Lewis superacid catalyst is guided.

We launched our study by testing the catalytic potential of **1** in the previously reported benchmark reaction by Morandi et al., namely the C–O bond metathesis in 1,5-dimethoxypentane.^[11] While a maximum of 85 % yield of the reaction product tetrahydropyran was reported with 20 mol% of $\text{Fe}(\text{OTf})_3$ at 100 °C, only 5 mol% of $[1]_n$ were sufficient to achieve complete conversion (Scheme 1).^[11]

Diglyme (bis(2-methoxyethyl) ether) was chosen as the following model for C–O bond metathesis of substrates amenable for potential chelating-deactivation of the catalyst (Table 1). For this more challenging substrate, 50 mol% of $\text{Fe}(\text{OTf})_3$ had been required to observe a 75 % yield of the product by GC analysis.^[11] Remarkably, only 10 mol% of



Scheme 1. Reaction scheme of the Lewis acid catalyzed selective degradation of 1,5-dimethoxypentane to THP.

Table 1: Reaction optimization of the Lewis acid catalyzed C–O bond metathesis in diglyme.

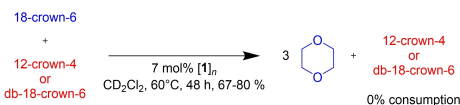
Entry		Deviations from the standard conditions	Yield [%] ^[a]
1	none		> 95
2	5 mol% instead of 10 mol%		43
3	5 mol%, oDFB instead of oDCB		75
4	5 mol%, DCM, Br–Ph or hexanes instead of oDCB, 60–115 °C ^[b]		5–29
5	5 mol%, 1-(sulfolane) ₂ instead of $[1]_n$, 3 d		58
6	5 mol%, $\text{Ge}(\text{cat}^-)_2$ -(sulfolane) ₂ instead of $[1]_n$, 3 d		40
7	5 mol%, AlCl_3 instead of $[1]_n$		3
8	5 mol%, $\text{B}(\text{C}_6\text{F}_5)_3$ instead of $[1]_n$		36
9	5 mol% $\text{Fe}(\text{OTf})_3$		33

[a] Yields were determined by ^1H - and ^{13}C NMR spectroscopy using cyclooctane as an internal standard. [b] See Supporting Information for details.

$[1]_n$ afforded 1,4-dioxane in almost quantitative yield as the reaction product. Dimethyl ether as the stoichiometric side product was observed by ^1H and ^{13}C NMR spectroscopy using J. Young NMR tubes as reaction vessels. To edge the reactivity of **1**, several changes to the reaction parameters were evaluated (Table 1). Lowering the catalyst loading to 5 mol% still yielded a reasonable conversion of 43 % (Table 1, entry 2). Non-coordinating solvents of different polarities were investigated, indicating that higher yields are obtained in more polar solvents (Table entries 3–4). Significantly improved yields were observed with oDFB as a solvent (entry 3), but oDCB was preferred due to a boiling point stronger distinguished from the product 1,4-dioxane. The bis(sulfolane)adduct of **1** was exhibiting a lower TOF (slower reaction rate) while showing a higher TON (higher conversion, 58 %) in comparison to $[1]_n$ (Table 1, entry 5).^[15] Notably, for $[1]_n$ as the catalyst, the activity ceases after >15 hours at elevated temperatures in the investigated reactions. We reasoned that sulfolane stabilizes the catalyst against alternative decomposition channels but lowers the TOF by competing with substrate coordination. The germanium-based analog to **1** showed a diminished TOF compared to the 1-(sulfolane)₂ (Table 1, entry 6).^[16] AlCl_3 as a catalyst showed only poor performance, while with $\text{B}(\text{C}_6\text{F}_5)_3$, a yield of 36 % was achieved (entries 7/8). Interestingly, with 5 mol% of $\text{Fe}(\text{OTf})_3$, 33 % yield was obtained under our conditions (Table 1, entry 9). Still, silicon-based catalyst **1** stood out as the most active for reasons that will be explained later.

Excitingly, cyclization of a nitrogen-containing starting material into a tosyl-protected morpholine derivative also occurred quantitatively with 5 mol% of $[1]_n$ at 60 °C, indicating an extendable substrate scope (see Supporting Information, section 1.6). Next, we investigated whether highly coordinating polyethers can be converted. Indeed, cyclic crown-ethers like 18-crown-6, 15-crown-5 and 12-crown-4 were selectively degraded to 1,4-dioxane or 2,3-dihydrobenzo[b][1,4]dioxine in the case of mono-benzo-18-crown-6. Catalyst loadings of 7 mol% were sufficient for quantitative conversions (for details, see Supporting Information). The bis-benzannulated derivative dibenzo(db)-18-crown-6 was not consumed in the reaction for reasons discussed in the Supporting Information (S3.3). Strikingly, the varying reaction rates allowed the selective degradation of 18-crown-6 in the presence of 12-crown-4 or db-18-crown-6 (Scheme 2). This chemoselectivity represents an attractive new way to influence the distribution and recognition patterns of these prevalent supramolecular sensors.

Finally, polyethylene glycol (PEG) and polypropylene glycol (PPG) were probed as substrates omnipresent in



Scheme 2. Competition experiment of 18-crown-6 and equimolar amounts of other crown ethers.

The nucleophilic attack by a catecholato oxygen atom of **1** on a carbon atom adjacent to the coordinated oxygen atom, as observed for group 15 catecholato-based Lewis acids,^[19] would be a first putative option to launch the reaction cascade. However, an activation energy of 50 kcal mol⁻¹ renders such element ligand cooperative mode unlikely (see Supporting Information section 3.1). Instead, with an activation barrier of 26.7 kcal mol⁻¹, the intramolecular nucleophilic attack of an oxygen atom inside the crown ether is much more plausible (**TS1**), resulting in the zwitterionic intermediate **Int3**. Despite extensive searches, a transition state with a *cis*-coordinated silicon atom was not found. From the zwitterionic intermediate **Int3**, an oxonium ion, the reaction proceeds by a cascade of intramolecular S_N2 attacks on the highly polarized carbon atom with 1,4-dioxane as the leaving group. The activation energies of these steps are lower compared to the first nucleophilic attack and propelled by the release of dioxane. In the last step of the reaction, the mono-dioxane adduct of **1** is formed. This can further react with an additional molecule of 1,4-dioxane to form the respective *trans*-adduct (see ESI for scXRD), or with a molecule of 18-crown-6 to close the catalytic cycle. The exergonic binding of 1,4-dioxane explains the experimentally observed product inhibition and the required elevated processing temperature. The reaction path for the degradation of diglyme relies on the same key steps and displays similar energy barriers (see Supporting Information for details). Hence, the Lewis acid induces the reaction by polarizing the attacked carbon atom and stabilizing the resulting zwitterionic oxonium/silicate intermediate. Most important is the finding that the dicoordinated **Int2** represents a stable intermediate that would slow the overall reaction rate. Thus, mono-, bi- and tridentate binding of diglyme were analyzed for the catalysts that turned out less efficient by experiment (Figure 3, Ge(cat^{Cl})₂, Fe(OTf)₃, AlCl₃). Indeed, the most active silicon Lewis acid **1** shows the slightest tendency for bidentate substrate binding.

For Fe(OTf)₃ and AlCl₃, even the tridentate coordination is favorable and should represent an unproductive thermodynamic sink. Multidentate binding cannot be realized for B(C₆F₅)₃, explaining its second-highest activity in this catalysis.

To support these computational insights by experiment, the ²⁹Si NMR spectroscopic data of a mixture of **1** with 18-crown-6 in CD₂Cl₂ before heating was reevaluated. Indeed, a major peak at -133.9 ppm showed the presence of hexacoordinated silicon, whereas a minor signal at -106.1 ppm revealed the partial formation of the pentacoordinate form.

This mechanistic knowledge allowed us to improve the catalytic system further. Bis(perfluoro-*N*-phenylamido phenolato)silane **2** (Figure 1d), a Lewis acid developed recently in our lab for the FLP type dihydrogen activation, was employed.^[20] This Lewis acid is similarly Lewis acidic as **1**, but even less biased for bidentate substrate binding (Figure 3). Indeed, **2** exhibits a remarkably improved performance in the degradation of diglyme (3 mol%, 81 %), outperforming all previous results (cf. 5 mol% of **1**, 43 %).

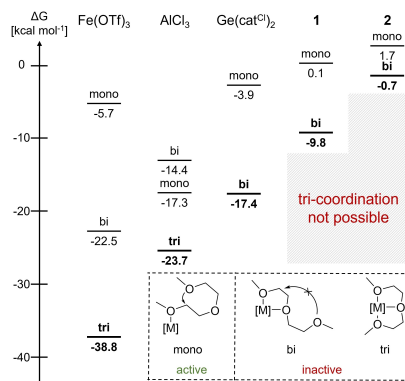


Figure 3. a) Free formation enthalpies of the diglyme complexes of the herein investigated Lewis acids depending on the hapticity of the ether, calculated at the DSD-BLYP(D3B)/def2-QZVPP + SMD(DCM)//PBEBH-3c level. The thermodynamically favored binding mode for each Lewis acid is marked in bold.

In conclusion, bis(perchlorocatecholato)silane **1** catalyzes the C–O bond metathesis reaction of polyfunctional ethers and the selective ring-closing depolymerization of polyethers (PEG and PPG). To the best of our knowledge, these transformations constitute novelties in polymer upcycling and encourage studies on process optimization for a sustainable impact on materials manufacturing and separation. The outperforming activity of **1** pinpoints the vast potential of Lewis superacids for maximum substrate activation,^[21] while the low propensity for multidentate substrate-binding prevents catalyst deactivation. Based on these insights, bis(perfluoro-*N*-phenylamidophenolato)silane, a Lewis superacid immune to chelation-deactivation, is identified as an even more active catalyst.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Lewis Superacid · Organosilanes · Polyethylene Glycol · Reaction Mechanism · Ring Closing Metathesis

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Supporting Information

Silicon Catalyzed C—O Bond Ring Closing Metathesis of Polyethers

*N. Ansmann, T. Thorwart, L. Greb**

SUPPORTING INFORMATION

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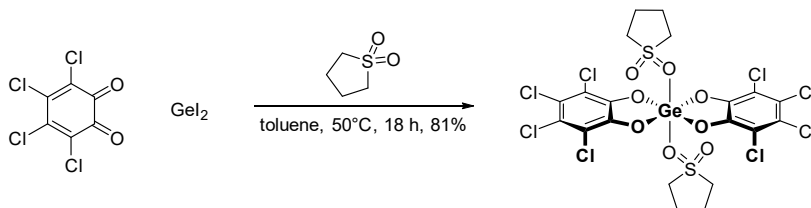
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1. Experimental Procedures

1.1 Materials and General Methods

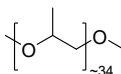
All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame dried glassware or by working in a glovebox (MBraun Labmaster dp, MB-20-G or a Syltech Glovebox) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å). The argon was dried by passing over two columns of phosphorus pentoxide. Inorganic salts were dried at elevated temperatures (50 – 150 °C) in vacuo (10⁻² mbar) overnight prior to use. 18-crown-6 was dried over anhydrous phosphorous pentoxide for several days in vacuo and subsequently a solution of the crown-ether in DCM was stored over molecular sieves (4 Å) for three days before the crown ether was recrystallized. All liquid polyethers were degassed and stored over molecular sieves (4 Å) prior to use. Other commercially available chemicals were used as received. Bis(perchlorocatecholato)silane [1]_n, bis(sulfolane)-bis(perchlorocatecholato)silane 1-(sulfolane)₂ and *N,N*-bis(2-methoxyethyl)-4-methylbenzenesulfonamide were synthesized according to literature known procedures.^[1] All solution phase NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All hetero-nuclei spectra (with the exception of ¹⁹F) were obtained with ¹H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ¹H and ¹³C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants *J* in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublet of doublets, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. NMR spectra were processed and plotted with TopSpin 4.0.8.^[2] ESI-MS spectra were measured on a Bruker ApexQe FT-ICR instrument. IR spectra were recorded on an Agilent Cary 630 spectrometer equipped with diamond ATR units inside a glovebox and processed using OriginPro 2020b. GC-MS were measured on a Thermo Fischer Scientific Ultra Trace GC equipped with an ISQ Single Quadrupole MS.

1.2 Synthesis of Bis(sulfolane)-bis(perchlorocatecholato)germane Ge(cat^{Cl})₂-(sulfolane)₂

In a dry Schlenk flask, germaniumdiiodide (480 mg, 1.47 mmol, 1.00 eq), and *ortho*-chloranil (720 mg, 2.93 mmol, 2.00 eq) were suspended at room temperature in 20 ml of dry toluene. Sulfolane (4.00 ml, 41.9 mmol, 28.5 eq) was added through a syringe and the flask was closed. The red mixture was stirred at 50 °C for 18 h. The product precipitated from the dark red reaction mixture and was filtered off. Washing of this beige solid with respectively 10 ml of benzene, dichloromethane and pentane and drying *in vacuo* yielded the product as a beige powdery solid (953 mg, 1.18 mmol, 81 %).

The poor solubility prevents characterization by NMR spectroscopy in non-donor solvents. By dissolving a specific amount of the product with a specified amount of 1,2-diphenylethane in (CD₃)₂SO, the amount of coordinated sulfolane was determined to be two. ¹H NMR (600 MHz, (CD₃)₂SO, 295 K): δ = 3.00 – 2.98 (m, 8H), 2.08 – 2.05 (m, 8H); **Anal.** Calcd. for C₂₈H₁₆Cl₈GeO₈S₂: C, 29.85; H, 2.00; found: C, 29.46; H, 2.23.

1.3 Synthesis of Polypropylene Glycol Dimethyl Ether (PPG DME)



A solution of polypropylene glycol (*M_w* = ~2000 g/mol, 2.00 ml, 1.00 mmol, 1.00 eq) in 4 ml dry THF was cooled to 0 °C and sodium hydride (96.3 mg, 4.00 mmol, 4.00 eq) was added portion wise. After stirring for 90 min at 0 °C, methyl iodide (187 μ l, 3.00 mmol, 3.00 eq) was added neat and the reaction was stirred at room temperature for 16 h. The reaction was then carefully quenched by the addition of 10 ml water, diluted with 25 ml diethyl ether and the aqueous phase was extracted with diethyl ether (3 x 25 ml). The combined organic layers were washed with brine, dried over Na₂SO₄ and all volatiles were removed *in vacuo* to yield the product as a yellow oil (1.65 g, 817 μ mol, 81 %).

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¹H NMR (600 MHz, CDCl₃, 295 K): δ [ppm] = 3.59-3.50 (m, 2H), 3.41-3.38 (m, 1H), 3.38 (s, 3H), 1.13 (t, J = 5.4 Hz, 3H); **¹³C{¹H} NMR** (151 MHz, CDCl₃, 295 K): δ [ppm] = 76.3 (s, CH), 75.7-75.5 (s, CH), 73.5-73.0 (s, CH₂), 56.9 (s, CH₃), 17.6-16.8 (s, CH₃); **HR-MS (ESI⁺)**: $[M+2Na]^{2+}$ = C₁₀₃H₂₁₀O₃₅Na₂²⁺, calc. 1033.2236, found 1033.2241, Δ = 0.5 ppm.

1.4 General Procedures for the RCMS

General Procedure for the Ring Closing Metathesis of Diglyme (G1)

In a J. Young NMR tube, the respective Lewis acid was suspended with diglyme (28.6 μ l, 200 μ mol, 1.00 eq) and cyclooctane (13.4 μ l, 100 μ mol, 0.50 eq) as an internal standard in oDCB:C₈D₆ (50:1) (0.4 M) at room temperature. The beige suspension was heated at 115 °C over night. The resulting black suspension were then investigated by NMR spectroscopy. If other solvents with lower boiling points were implemented, the reaction temperature was adjusted accordingly.

General Procedure for the Degradation of Crown Ethers (G2)

In a J. Young NMR tube, [1]_n was suspended with the corresponding crown ether (100 μ mol) and cyclooctane (6.68 μ l, 50.0 μ mol, 0.50 eq) as an internal standard in CD₂Cl₂ or oDCB:C₈D₆ (50:1) (0.2 M) at room temperature. The resulting beige suspension was heated at 60 °C or 115 °C over night. The resulting black suspensions were then investigated by NMR spectroscopy.

General Procedure for the Ring Closing Metathesis of Polyethers (G3)

In a J. Young NMR tube, [1]_n was suspended with the respective polyether and cyclooctane as an internal standard in 0.5 ml oDCB:C₈D₆ (50:1) or CD₂Cl₂ at room temperature. The resulting beige solution was heated at 115 °C (or 60 °C respectively) over night. The resulting black suspension was then investigated by NMR spectroscopy. In order to calculate catalyst loadings for these reactions, full conversion of the polymer to the respective product was assumed. The theoretical substance quantity of the product was then used as reference to calculate the amount of catalyst.

1.5 Reaction Optimization

All experiments were carried out according to G1. The standard conditions refer to a catalyst loading of 5 mol%. The altered conditions are summarized with the observed yields in Table S1.

Table S 1: Reaction optimization of the Lewis acid catalyzed C-O bond metathesis in diglyme. The standard conditions refer to G1

Entry	Deviations from the standard conditions (G1)	Yield [%]
1	None	43
2	DCM instead of oDCB, 60 °C	5
3	Hexanes instead of oDCB, 100 °C	15
4	Br-Ph instead of oDCB	29
5	oDCB instead of oDCB	75
6	1-(sulfolane) ₂ instead of [1] _n , 3 d	58
7	Ge(cat ^C) ₂ -(sulfolane) ₂ instead of [1] _n , 3 d	40
8	BCF instead of [1] _n	36
9	AlCl ₃ instead of [1] _n	3

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10	Fe(OTf) ₃ instead of [1] _n	33
11	10 mol% instead of 5 mol%	>95

1.6 Investigated Substrates

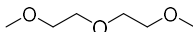
In the following, optimized reaction conditions for several investigated substrates are reported. The respectively characterized products are summarized in section 1.8 whereas the corresponding NMR spectra for each RCM are displayed in section 5.

1,5-Dimethoxypentane

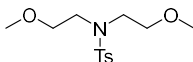


According to a modified procedure G1, 1,5-dimethoxypentane (31.4 μ l, 200 μ mol, 1.00 eq) was treated with [1]_n (5.20 mg, 10.0 μ mol, 5 mol%) in 0.5 ml of a mixture of oDCB and C₆D₆ (50:1) at 115 °C for 18 h. Instead of cyclooctane, 1,2-diphenylethane (17.3 mg, 95.0 μ mol, 0.48 eq) was used as the internal standard. Tetrahydropyran was formed quantitatively as determined by ¹H NMR spectroscopy.

Diglyme



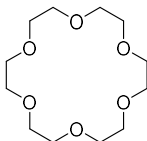
- Using [1]_n as the catalyst: The reaction was carried out following GP1, using [1]_n (10.4 mg, 20.0 μ mol, 10 mol%) in 0.7 ml oDCB and C₆D₆ (50:1). A conversion of 97 % was observed by ¹H NMR spectroscopy.
- Using Si(amp^F)₂ as the catalyst: The reaction was carried out following GP1, with Si(amp^F)₂ (4.32 mg, 6.00 μ mol, 3 mol%) [to achieve a precise catalyst amount, 300 μ l of a stock solution of 7.20 mg of Si(amp^F)₂ in 500 μ l of oDCB and C₆D₆ (50:1) was used]. The resulting colorless solution was treated as in GP1. 1,4-Dioxane was observed as the product of the reaction in 81 % yield by ¹H NMR spectroscopy with dimethyl ether as the co-product. The yield can be increased to 95 % by using 5 mol% of the Lewis acid.

N,N-bis(2-methoxyethyl)-4-methylbenzenesulfonamide

According to a modified procedure G1, *N,N*-bis(2-methoxyethyl)-4-methylbenzenesulfonamide (57.5 mg, 200 μ mol, 1.00 eq) was treated with [1]_n (5.20 mg, 10.0 μ mol, 5 mol%) in 0.5 ml of a mixture of oDCB and C₆D₆ (50:1) at 115 °C for 20 h, using 50 μ mol of cyclooctane as the internal standard. 4-Tosylmorpholine was formed quantitatively (98 %) as determined by ¹H and ¹³C NMR spectroscopy.

When using DCM as the solvent (reaction at 60 °C for 20 h), slightly lower yields can be achieved (87 %).

18-crown-6

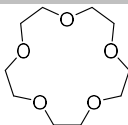


The reaction was carried out according to procedure G2 using [1]_n (10.4 mg, 20.0 μ mol, 7 mol%*) in 0.5 ml of CD₂Cl₂ at 60 °C for 48 h. 1,4-Dioxane formed quantitatively as the product as determined by ¹H NMR spectroscopy.

*in reference to the product

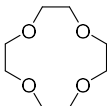
15-crown-5

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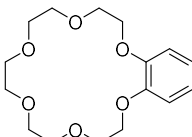
The reaction was carried out according to a modified version of procedure G2 using 15-crown-5 (15.3 μ l, 77.0 μ mol, 2.50 eq) and $[1]_n$ (20.0 mg, 38.5 μ mol, 20 mol%*) in 0.4 ml of oDCB and C_6D_6 (50:1) at 120 °C for 72 h but without internal standard. 1,4-Dioxane formed quantitatively as the product as determined by 1H NMR spectroscopy by the absence of starting material signals.

*in reference to the product

12-crown-4

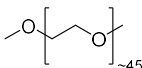
The reaction was carried out according to a modified version of procedure G2 using 12-crown-4 (12.4 μ l, 77.0 μ mol, 2.00 eq) and $[1]_n$ (20.0 mg, 38.5 μ mol, 25 mol%*) in 0.4 ml of oDCB and C_6D_6 (50:1) at 120 °C for 72 h but without internal standard. 1,4-Dioxane formed as the product with a yield of 55 % as determined by 1H NMR spectroscopy in reference to the signals of unconsumed starting material.

*in reference to the product

Monobenzo-18-crown-6

The reaction was carried out according to procedure G2 using $[1]_n$ (26.0 mg, 50.0 μ mol, 17 mol%*) in 0.5 ml of oDCB and C_6D_6 (50:1) at 115 °C for 24 h, but no internal standard was used. 1,4-Dioxane and 2,3-dihydrobenzo[b][1,4]dioxine formed quantitatively as products of the reaction as indicated by 1H NMR spectroscopy by the absence of signals that can be assigned to unconsumed starting material.

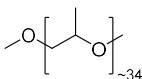
*in reference to the product

Polyethylen Glycol Dimethyl Ether (PEG DME)

Following procedure G3, PEG DME (10.2 mg, 5.00 μ mol, 0.04 eq) was treated with $[1]_n$ (5.85 mg, 11.3 μ mol, 10 mol%*) in 0.5 ml of CD_2Cl_2 at 60 °C for 19 h with cyclooctane (6.68 μ l, 50.0 μ mol, 0.44 eq). 1,4-Dioxane was formed quantitatively as determined by 1H NMR spectroscopy.

This reaction can also be carried out at higher concentrations (up to 80 mg/ml) and also in oDCB at 115 °C with comparable yields. High conversion rates (72 - 82 %) are already observed after shorter reaction times (4 - 6 h). Lowering the catalyst amount to 5 mol%* still yields the product with a yield of 84 %.

*in reference to the product (5 μ mol * 45/2 = 113 μ mol)

Polypropylen Glycol Dimethyl Ether (PPG DME)

Following a modified procedure G3, PPG DME (20.2 mg, 10.0 μ mol, 0.06 eq) was treated with $[1]_n$ (22.1 mg, 42.5 μ mol, 25 mol%*) in 0.5 ml of CD_2Cl_2 at 60 °C for 18 h without internal standard. 2,5-Dimethyl-1,4-dioxane was characterized as the reaction product by 1H , ^{13}C NMR spectroscopy, GC-MS and scXRD, but the mixture of diastereomers and unconsumed PPG DME with variable molecular weight rendered the determination of a yield impossible, but it is estimated to be ~25 %.

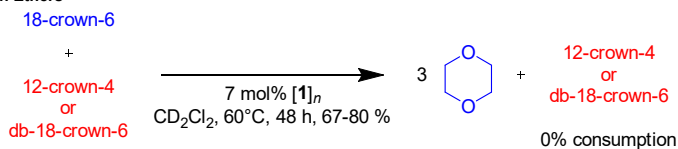
This reaction can also be carried out in oDCB or oDFB at 115 °C with comparable yields.

*in reference to the product (10 μ mol * 34/2 = 170 μ mol)

SUPPORTING INFORMATION

1.7 Competition Experiments

Competing Crown Ethers



The competition experiments concerning crown ethers were conducted according to procedure G2, using $[1]_n$ (10.4 mg, 20.0 μmol , 7 mol%*) in 0.5 ml of CD_2Cl_2 at 60 $^\circ\text{C}$ for 48 h, but a second crown-ether [a] 12-crown-4 (16.2 μl , 100 μmol , 1.00 eq) or b) dibenzo-18-crown-6 (36.0 mg, 100 μmol , 1.00 eq) was added at the start of the reaction. ^1H and ^{13}C NMR spectroscopy confirmed a selective degradation of 18-crown-6 to 1,4-dioxane [a] 80 % yield, b) 67 % yield] while the respective other crown-ethers were not consumed.

*in reference to the product (100 μmol *3 = 300 μmol)

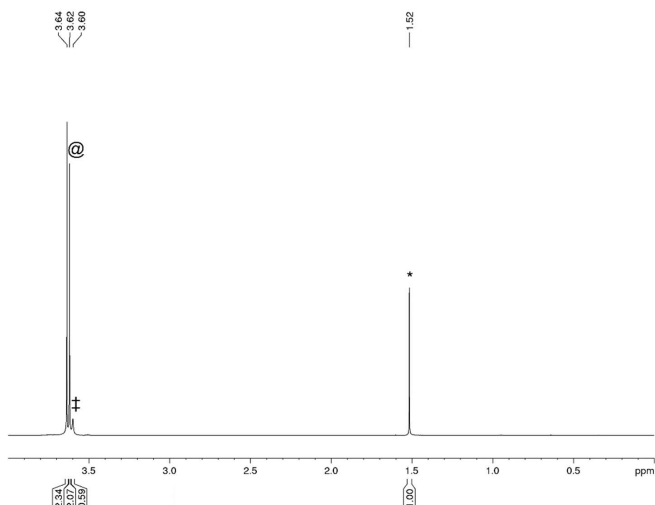
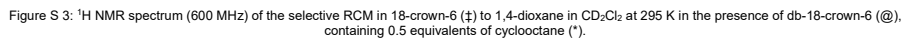
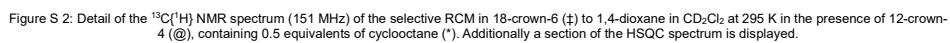
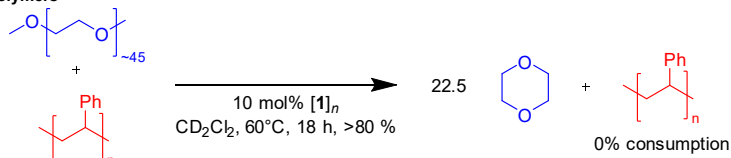


Figure S 1: Detail of the ^1H NMR spectrum (600 MHz) of the selective RCM in 18-crown-6 (‡) to 1,4-dioxane in CD_2Cl_2 at 295 K in the presence of 12-crown-4 (@), containing 0.5 equivalents of cyclooctane (*).



SUPPORTING INFORMATION

Competing Polymers



This competition experiment was conducted according to a modified procedure G3, using $[1]_n$ (11.7 mg, 22.5 μmol , 10 mol%*) and PEG-DME (20.4 mg, 10.0 μmol , 1.00 eq) in 0.5 ml of CD_2Cl_2 at $60^\circ C$ for 18 h, but polystyrene** (20.0 mg) was added at the start of the reaction. Cyclooctane was not used since a signal overlap was estimated with the aliphatic signals of polystyrene. 1H and ^{13}C NMR spectroscopy confirmed a selective degradation of PEG-DME to 1,4-dioxane while polystyrene was not consumed. Addition of 1,2-diphenylethane (18.2 mg, 100 μmol) as an internal standard after completion of the reaction determined a yield of 83 % by 1H NMR spectroscopy.

*in reference to the product (10 μmol *22.5 = 225 μmol)

**Polyfoam packaging material (from Sigma Aldrich) was dissolved in DCM and the solvent was removed *in vacuo* to yield polystyrene as colorless flakes that were redissolved in dry DCM and stored as a solution over 4 Å molecular sieves to eliminate moisture. After removal of the solvent under reduced pressure, the obtained polymer was used in this experiment.

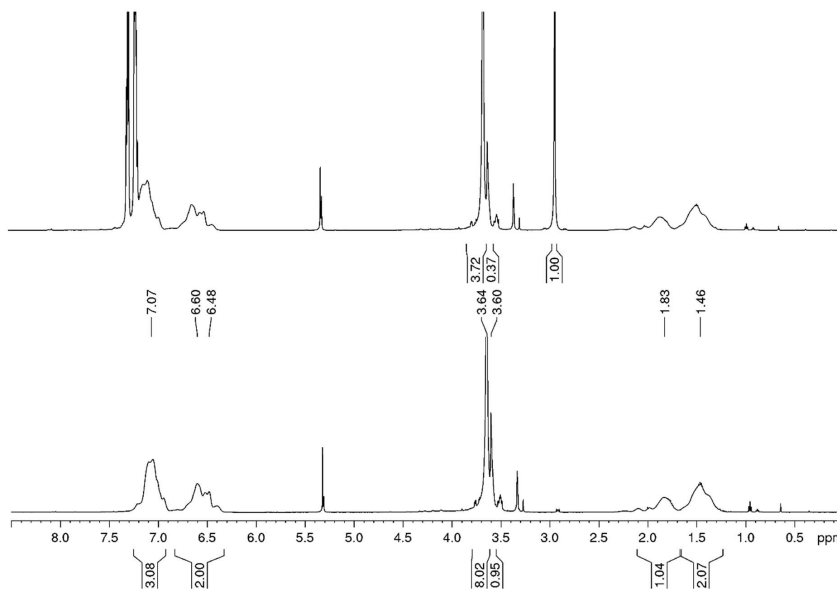


Figure S 4: 1H NMR spectra (600 MHz) of the selective RCM in PEG-DME to 1,4-dioxane in CD_2Cl_2 at 295 K in the presence of polystyrene. The upper spectrum contains 100 μmol 1,2-diphenylethane as internal standard for yield quantification.

SUPPORTING INFORMATION

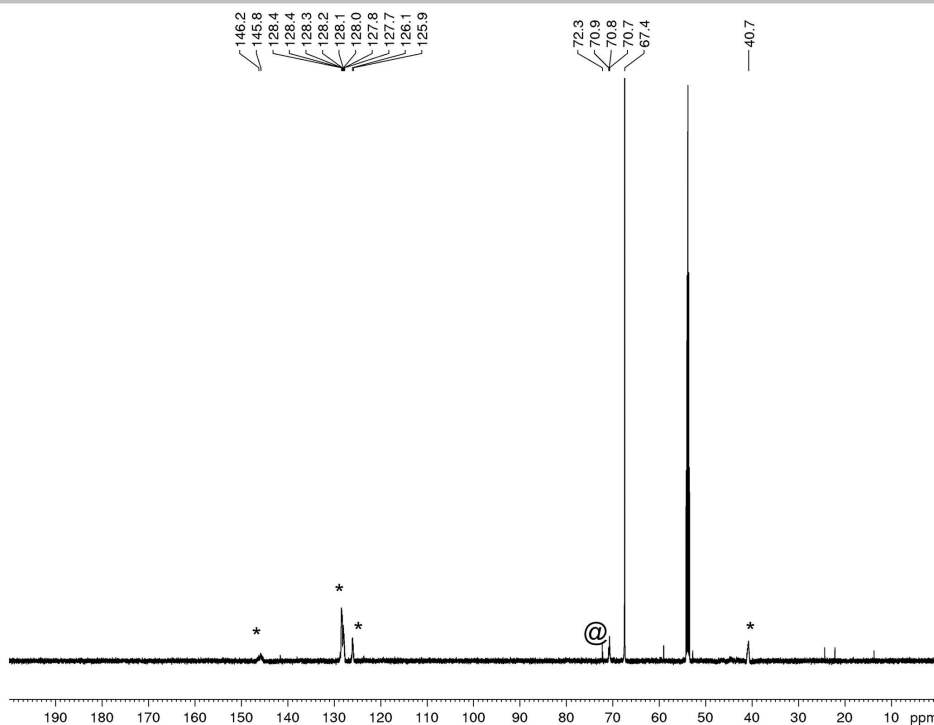
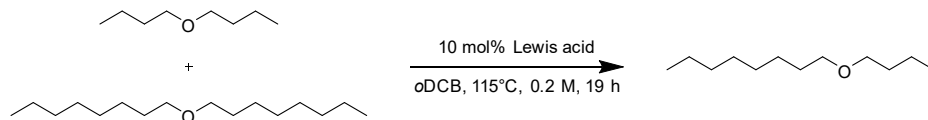


Figure S 5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the selective RCM in PEG-DME (@) to 1,4-dioxane in CD_2Cl_2 at 295 K in the presence of polystyrene (*). Residual signals can be assigned to dibutyl sulfone, which occurs as trace impurities in the used catalyst.

1.8 Cross Metathesis Experiments

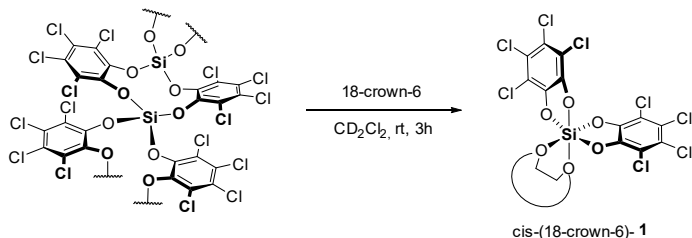


In a screw top vial, the Lewis superacid catalyst **[1]_n** (10.4 mg, 20.0 μmol , 10 mol%) or **2** (14.4 mg, 20.0 μmol , 10 mol%) was mixed with dibutyl ether (16.9 μl , 100 μmol , 0.50 eq), dioctyl ether (33.6 μl , 100 μmol , 0.50 eq) and 1 ml of *o*-DCB. To quantify the yield of the reactions, *n*-dodecane (22.7 μmol , 100 μmol) was added to the reaction vessel, which was subsequently sealed and heated at 115°C under stirring for 19 h.

GC analysis of the resulting reaction mixtures versus *n*-dodecane as the internal standard and samples of butyl octyl ether confirmed the formation of the cross metathesis product in yields of 6 % (**[1]_n**) and 13 % (**2**).

SUPPORTING INFORMATION

1.9 Characterization of the Catalytic Active Species



In a J. Young NMR tube, bis(perchlorocatecholato)silane [**1**]_n (30.0 mg, 57.7 μmol, 1.00 eq) was suspended with 18-crown-6 (25.0 mg, 94.6 μmol, 1.64 eq) in 0.5 ml of CD₂Cl₂. After shaking the tube for 3 h, the resulting suspension was investigated by NMR spectroscopy.

¹H NMR (600 MHz, CD₂Cl₂, 295 K): δ [ppm] = 3.60 (s, 24H); **¹³C{¹H} NMR** (151 MHz, CD₂Cl₂, 295 K): δ [ppm] = 144.9 (s, C_q), 122.3 (s, C_q), 115.7 (s, C_q), 70.7 (s, CH₂); **²⁹Si NMR** (119 MHz, CD₂Cl₂, 295 K): δ [ppm] = −106.1 (s, mono-(18-crown-6)-**1**, minor), −133.9 (s, cis-(18-crown-6)-**1**, major).

The obtained NMR spectra indicate the formation of a soluble hexa-coordinated silicon species (δ (²⁹Si) = −133.9 ppm), which is in line with the predicted cis-18-crown-6 adduct of the Lewis acid **1**. Also the ¹³C NMR shifts of the catecholato ligand indicate a hexagonal species.^[1a] The signal at −106.1 ppm hints the existence of a penta-valent silicon(IV) species, which is presumably the mono-coordinated 18-crown-6 Lewis acid complex.

The fact that only one signal was obtained for the protons and carbon atoms of the crown-ether can be explained by a fast intramolecular exchange between coordinating ether functionalities ("chain walk").

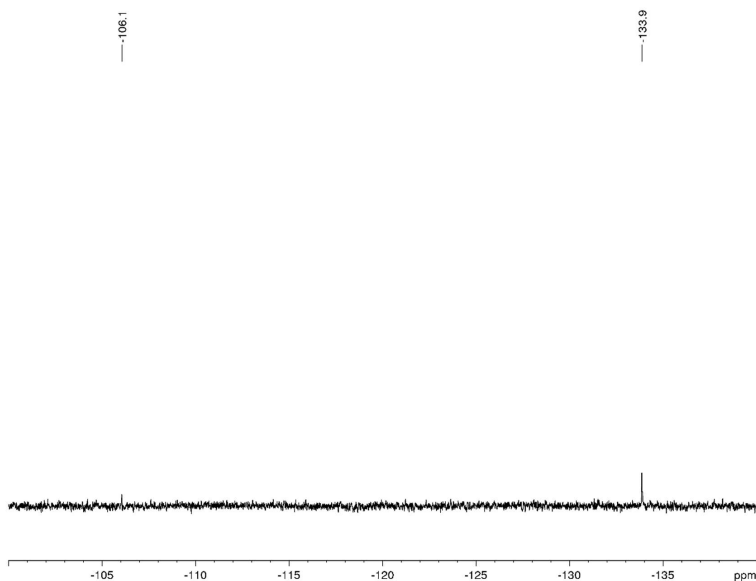


Figure S 6: Detail of the ²⁹Si NMR spectrum (119 MHz) of *in-situ* monitored resting states of the RCM in 18-crown-6 to 1,4-dioxane in CD₂Cl₂ at 295 K. Corresponding ¹H and ¹³C NMR spectra are displayed in section 5.

SUPPORTING INFORMATION

1.10. Characterization of Products

1,4-dioxane^[3]

¹H NMR (600 MHz, CD₂Cl₂, 295 K): δ [ppm] = 3.64 (s, 8H); ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 295 K): δ [ppm] = 67.4 (s, CH₂).

¹H NMR (600 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 3.50 (s, 8H); ¹³C{¹H} NMR (151 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 67.2 (s, CH₂).

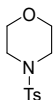
Dimethyl ether



¹H NMR (600 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 3.14 (s, 6H); ¹³C{¹H} NMR (151 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 60.3 (s, CH₃).

Tetrahydropyran^[4]

¹H NMR (600 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 3.51 (br s, 4H), 1.41-1.37 (m, 6H); ¹³C{¹H} NMR (151 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 68.8 (s, CH₂), 27.0 (s, CH₂), 23.8 (s, CH₂).

4-Tosyl-morpholine^[5]

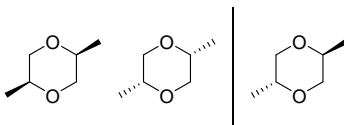
¹H NMR (600 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 7.69 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 3.67 (t, *J* = 4.7 Hz, 4H), 2.96 (m, 4H), 2.37 (s, 3H); ¹³C{¹H} NMR (151 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 143.9 (s, C_q), 129.9 (s, CH), 128.2 (s, CH), 66.1 (s, CH₂), 46.4 (s, CH₂), 21.5 (s, CH₃).*

*The signal for one quaternary carbon atom of the molecule is hidden underneath the solvent signal.

2,3-Dihydrobenzo[*b*][1,4]dioxine^[6]

¹H NMR (600 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 3.96 (s, 4H) (aromatic signals are hidden under the solvent peaks); ¹³C{¹H} NMR (151 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 144.1 (s, C_q), 121.6 (s, CH), 117.7 (s, CH), 64.4 (s, CH₂).

2,5-dimethyl-1,4-dioxane



Diastereomer 1: ¹H NMR (600 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 3.62 (dd, *J* = 11.4 Hz, *J* = 2.4 Hz, 1H), 3.47 (m, 1H), 3.13 (dd, *J* = 11.3 Hz, *J* = 10.3 Hz, 1H), 0.96 (d, *J* = 6.4 Hz, 3H); ¹³C{¹H} NMR (151 MHz, oDCB:C₆D₆ (50:1), 295 K): δ [ppm] = 72.6 (s, CH₂), 71.6 (s, CH), 16.9 (s, CH₃).

SUPPORTING INFORMATION

Diastereomer 2: ^1H NMR (600 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.62 (m, 1H), 3.52 (dd, J = 11.6 Hz, J = 2.8 Hz, 1H), 3.43 (dd, J = 11.6 Hz, J = 5.8 Hz, 1H), 1.11 (d, J = 6.6 Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 68.9 (s, CH), 67.7 (s, CH_2), 16.2 (s, CH_3).

SUPPORTING INFORMATION

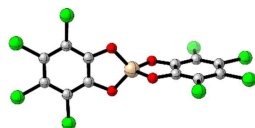
2. Computational Section

All calculations were performed using the Orca 5.0.1 program package and newer versions of it.^[7] Geometry optimizations for structures in the presented reaction pathways were carried out using the r^2 SCAN-3c method including the def2-mTZVPP basis set, geometrical counter-poise correction scheme (gCP) and the atom-pairwise dispersion correction (D4).^[8] For the binding thermodynamic calculations, geometry optimizations of the different Lewis acids ($\text{Fe}(\text{OTf})_3$, AlCl_3 , $\text{Ge}(\text{cat}^{\text{C}})_2$, **1** and **2**) and their respective diglyme adducts in different binding modes were carried out using Grimme's PBEh-3c method.^[9] Calculated geometries were confirmed as energetic minima by frequency calculations at the same level of theory as the optimization calculation. Enthalpies at 298 K were computed at the same level of theory using the rigid-rotor harmonic oscillator (RRHO) approximation.^[10] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[11] Transition states were found by first performing relaxed surface scans along a potential reaction coordinate (starting from the geometric structure of the starting material) and by then optimizing a reasonable input geometry close to the actual transition state with the exact hessian. The surface scans and optimizations were carried out at the same level of theory as the optimization of the local minima. Transition states were confirmed as saddle points of the potential surface by frequency calculations at the same level of theory. For all computational approaches, more precise single point energies were calculated at a DSD-BLYP/def2-QZVPP level of theory after successful geometry optimization.^[12] Hereby, the Becke-Johnson damping scheme (D3BJ) was used.^[13] Solvation corrected energies were calculated using the SMD solvation module with the conductor-like polarizable continuum model, CPCM.^[14] Graphics of calculated geometries were created by the program CYLview20.^[15]

2.1 Cartesian Coordinates for Stationary Points in the Reaction Path of the Degradation of 18-crown-6

Cartesian coordinates (reported in Å) and energies (in hartree) of all stationary points discussed in the reaction profile in the main text. Reported at the r^2 SCAN-3c level of theory.

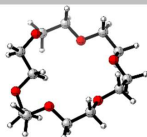
Bis(perchlorocatecholato)silane 1 E = -4729.11302525621



Si	-3.95759007850789	1.95442485088803	0.04528201730316
O	-5.05027541413635	2.78070334381379	-0.88687991299323
O	-5.05184510354252	1.10645034268738	0.95559010962297
O	-2.84580751883813	1.04522932942384	-0.78086085562486
O	-2.88247711533497	2.88737526857372	0.89334154264538
C	-1.61202416434654	2.49770315888332	0.53583619944366
C	-1.59144988453974	1.46549873256139	-0.40160679555043
C	-0.44280511652299	3.04591079908676	1.02957756367318
C	0.77754318180728	2.53044402547888	0.55832386702933
C	0.79817316742711	1.49179767766964	-0.38471723729683
C	-0.40115218839437	0.94645573737863	-0.87596089142211
Cl	-0.43388562177674	-0.33096841229364	-2.03384577893052
Cl	2.25810050143195	3.19167672543662	1.15488392271065
Cl	2.30421665781559	0.86749513775215	-0.95682255823529
Cl	-0.52625765481437	4.32187201495969	2.18659874537489
C	-6.31304024471804	2.40180224732848	-0.49253497536794
C	-6.31397281139159	1.46432284536993	0.53984721147388
C	-7.49242428999570	2.87641301560723	-1.03582371682528
C	-8.70276290095963	2.38539786693060	-0.51522155480520
C	-8.70365628047708	1.44237076178173	0.52364378723704
C	-7.49423407773057	0.97085415857421	1.06402062787705
Cl	-7.43722957159111	-0.18589367614362	2.34165758041094
Cl	-10.19557496630139	2.95797451707752	-1.17008257149143
Cl	-10.19760239844320	0.84640744896544	1.15467244550465
Cl	-7.43316610611900	4.03443208220826	-2.31220877176366

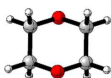
18-crown-6 E = -922.779777009685

SUPPORTING INFORMATION



C	-1.87325574901445	2.76111385748134	0.08190710055838
C	-0.56722110067192	3.15667458897342	0.75864931915452
O	0.20732081881705	2.01116473794926	1.08791787429565
H	-0.78129485933943	3.68035847179953	1.69720454027840
H	-0.00775578658711	3.84982214352731	0.10993489055826
C	1.07054891576752	1.57931952436354	0.04444743461205
C	1.26267573867020	0.08745017954242	0.16001022223332
H	2.04678925201857	2.08860296785284	0.12521100905067
H	0.64825097618122	1.80487553948035	-0.94694981799542
O	0.09545783530821	-0.54872591832440	-0.33350224845048
H	2.14981212900045	-0.22422673011760	-0.42138401217388
H	1.43601513886029	-0.17443786400499	1.21739918152352
C	0.03965864110443	-1.92532519184467	-0.01178631838844
C	-1.22188377086531	-2.51088202546481	-0.59370711742070
H	0.04658241135132	-2.06866871359575	1.08232219403906
O	0.90844116893787	-2.46396027718647	-0.43405405965810
H	-2.33947497032384	-1.99438136739705	0.10581092702970
H	-1.18057104241134	-3.61254103626669	-0.50400847057740
H	-1.28466169746226	-2.25794230483819	-1.66633065550569
C	-3.56484570636513	-2.46871357995844	-0.41928085094124
C	-4.70968791217221	-1.792330761658940	0.29127526214359
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H	-3.63396905554123	-2.26057407990103	-1.50114589774616
O	-4.80400594509843	-0.44624870533914	-0.14383302006407
H	-4.55226542299420	-1.84073246656959	1.38229452521666
H	-5.64244355058317	-2.33738193112642	0.05532271528595
C	-5.93616797285313	0.21009845072134	0.40054317793006
C	-5.95629245216584	1.64079188038856	-0.07583500164889
H	-5.91254461440245	0.19081290695897	1.50359826827002
H	-6.86386600416351	-0.29248397150779	0.06953351239275
O	-5.02688065544099	2.40225629556691	0.68023161684708
H	-6.97311773866984	2.05309042982821	0.05558855643572
H	-5.71756530569006	1.66058548842663	-1.15212725307169
C	-4.86323482856226	3.72725901454702	0.17811957199946
C	-3.77944429916136	3.85593981363180	-0.88823312364426
H	-4.58405244831440	4.35624987338228	1.03227254598179
H	-5.82217777112546	4.10137664034328	-0.22144713759733
O	-2.47200849574052	3.98447969672893	-0.35136326934377
H	-3.95470459018486	4.78008845134074	-1.45452098097176
H	-3.83084603221470	3.00853085684250	-1.59342750642362
H	-2.51733443560675	2.21608141106351	0.78379802343957
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1,4-dioxane E = -307,592491803851

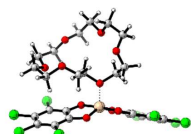


O	-3.63031496495074	2.70802985164728	-1.79691947167906
C	-2.93209105139321	2.45424933269655	-3.01658492949547
C	-3.70137659378807	4.11417611239041	-1.55778280796587
C	-4.37802877581620	4.82068069957002	-2.71875804280971
H	-2.68572348231009	4.52246591848666	-1.41404499272573
H	-4.27281994413045	4.24742546962291	-0.63263164732404
C	-3.60874346554816	3.16075375947121	-4.17756004717665
H	-2.93793200003298	1.36847634967509	-3.16242747248936
H	-1.88686137260485	2.79897476814652	-2.92962453254238
O	-3.67980500159987	4.56690008042797	-3.93842346958704

SUPPORTING INFORMATION

H	-4.62439665934773	2.75246398691151	-4.32129738395172
H	-3.03730054625559	3.02750440207871	-5.10271148360566
H	-4.37218755901788	5.90645367235635	-2.57291536039354
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1-mono(18c6) / (Int1) E = -5651.84970545481

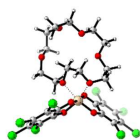


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SUPPORTING INFORMATION

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H	-5.43244032730878	-2.84331808562183	1.25049827259648
H	-3.40711179329838	-3.23887639400015	2.11566822452500
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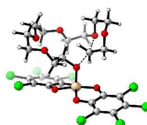


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C	-1.81249742709699	1.04521300333197	2.04361951897603
C	-1.80876178210990	1.73911270996833	0.82529280296608
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C	-0.09695184345063	2.50304303400873	2.88690652059547
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C	-8.15454120859515	0.04213789455382	-1.18406093771586
C	-8.40260547076086	0.70383991300223	0.02391499366414
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H	-4.99189562254336	-6.63051398895092	3.99051705781037
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SUPPORTING INFORMATION

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H	-6.12808597168010	-2.57340265480697	4.17528669279644
H	-6.56839345588235	-2.75502861747713	2.46250079108152
O	-4.37869786187716	-1.79138489173254	1.39486597489124
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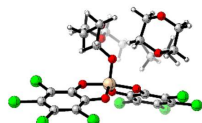


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C	-0.68514660267652	-1.10485141158789	4.68651201401804
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O	-0.63691608131231	-3.03090008630439	3.25380003873638
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H	-0.85193476064905	-3.15973488116181	5.32371816539810
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C	-0.59504230249503	-4.67664002803242	1.54867611155652
H	-0.83255323215531	-5.06986803496538	3.65824897012676
H	0.79612056024086	-4.53207083441116	3.16038433331025
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SUPPORTING INFORMATION

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C	-6.34839299134076	-5.10975026394669	2.32400781647881
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H	-5.13041477276801	-6.69036693182342	1.50751427195889
O	-6.28961508315336	-3.73429599031216	2.67244167450167
H	-6.54746325216808	-5.65740940843710	3.25111055482710
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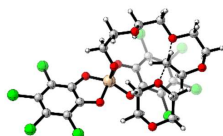


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SUPPORTING INFORMATION

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C	-2.49267283133865	-5.68950870744760	3.63580793163684
H	-1.33036814417055	-4.12331032075234	4.50931937328489
H	-0.50955373379439	-5.70991563254523	4.47284895880208
O	-3.3976488627700	-4.72401090896665	3.03708191423913
H	-2.91245328815476	-6.05260079482164	4.59037795062130
H	-2.35987785983701	-6.55867753677533	2.96833419272388
C	-4.65021658944417	-5.21234244699168	2.76114286262701
C	-5.37355023949961	-4.21165535383069	1.89393655926959
H	-5.20944226102716	-5.35235557935840	3.70121177966229
H	-4.59253490921065	-6.18251194463472	2.24005790368644
O	-4.74442037550735	-4.20317883090858	0.61358972893792
H	-5.34281624027346	-3.21468751263051	2.35970315471031
H	-6.42899835380819	-4.52014944289975	1.80588828430906
C	-5.48708223872789	-3.54459290663516	-0.41133030348069
C	-5.85891693755171	-2.10862620630742	-0.09786604815620
H	-6.41506302805992	-4.10226510787838	-0.62994572487261
H	-4.84508758529524	-3.58308834080145	-1.30024371071510
O	-4.68879220387989	-1.35223680562995	0.18591088889190
H	-6.56747684198795	-2.07405992493246	0.73886383580799
H	-6.36767241198029	-1.69279400077051	-0.98153073748356
C	-2.03009615659483	-3.24605053827431	0.49349257477908
C	-1.83729969050579	-4.33658274756092	-0.52193131171128
H	-2.22107049367180	-3.61330722377835	1.49950874208616
H	-2.77597034690767	-2.50276415551898	0.19878478951723
O	-1.54748805666038	-3.80006765083000	-1.81564279418780
H	-2.77681290211284	-4.88905478761677	-0.59653885709345
H	-1.04687175054815	-5.03840031138626	-0.20840222177535
H	0.51813345878257	-3.68495454693041	-1.58618851804809
H	-0.21956262963812	-2.60706232824992	-2.79038027725951

TS2 E = -5651,91439760135

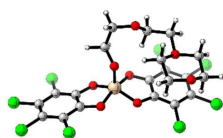


Si	-4.49423122307273	-0.14984025005721	1.69251534472696
O	-4.69045852372903	0.53672268375102	0.08317400099547
O	-5.91984027811685	0.67072702436834	2.20628144442080
O	-2.78472870965385	0.05043145467611	1.42414144356752
O	-4.12781982832365	-0.39699138655573	3.42919181290889
C	-2.82777313782307	-0.56171643522024	3.62952298610273
C	-2.04926344898924	-0.25914320065396	2.49800200054145
C	-2.21598431564542	-1.02544089059427	4.78645262518297
C	-0.81282689860423	-1.11547657555092	4.83349201020283
C	-0.04005185163520	-0.72535330618474	3.73572511355567
C	-0.66729309893521	-0.28269237975602	2.55375589518579
Cl	0.24149798760682	0.15140065822248	1.13900467914797
Cl	-0.04565353303325	-1.75334568587331	6.25562156831397
Cl	1.69207513837261	-0.83994405514240	3.79163115634599
Cl	-3.21021856004268	-1.49489978847260	6.13074372293107
C	-5.90019103655629	1.08829889177006	-0.05022785606753
C	-6.60454874379700	1.17452346535952	1.15894077782453
C	-6.46547847584474	1.55699321504705	-1.22551431013224
C	-7.75018231592991	2.12617618671216	-1.18572363258881
C	-8.44951976140575	2.21083524225905	0.02320239030469
C	-7.87129538754287	1.72710073821040	1.21121045266063
Cl	-8.70045615663322	1.79602157773469	2.73240696879596
Cl	-8.46638757591225	2.71649667472034	-2.65175603121993
Cl	-10.03885821782664	2.90469279506528	0.06881362791470
Cl	-5.56518456776337	1.42204919243552	-2.70443996934347
C	-2.65856506386734	-1.43476048092976	-1.82990399409373
C	-3.34971316949719	-2.68438345408248	-1.33848617522264

SUPPORTING INFORMATION

O	-2.37913925098275	-3.63915081131082	-0.81536519306236
H	-3.87825563730373	-3.18374126890282	-2.16350516231314
H	-4.04522289489902	-2.46488211518780	-0.52539466508862
C	-2.00909047684652	-3.86056195535230	1.26934779711486
C	-0.61058737152832	-3.37294198868242	1.35003486580069
H	-2.22423580732901	-4.89865257357237	1.05820227900779
H	-2.84973753735126	-3.18910939639714	1.41887454967586
O	0.32317135760795	-4.41181913400324	1.59539106805420
H	-0.33846076453287	-2.87854234986095	0.41375807782778
H	-0.55669899234077	-2.60134230405695	2.12949262979557
C	0.39926246067867	-4.70297981064187	2.98729167153312
C	-0.88379344568619	-5.30437040463104	3.51083324236530
H	0.65436830541304	-3.79336509969573	3.55358502828768
H	1.20708587350591	-5.43103228505819	3.11356287387483
O	-1.97263427538410	-4.37438974628788	3.30090009152406
H	-0.79472065474899	-5.49376853032873	4.59001612292479
H	-1.11416628835969	-6.25019956226552	2.99726965491026
C	-3.17837144518374	-4.86070020928106	3.95230345364739
C	-4.37752572351701	-4.04723364725455	3.56046875508610
H	-3.00652106414417	-4.77329167432918	5.03343102790090
H	-3.33255299302070	-5.91560627841939	3.68431091308686
O	-4.74544335349256	-4.41728430527763	2.24062366024623
H	-4.15114247433756	-2.97384406532961	3.64062838327270
H	-5.18629121667890	-4.27306464119899	4.27734140374819
C	-5.97229928197149	-3.83437446326056	1.79700734932593
C	-6.02993128023058	-2.32852801381481	1.95739829471606
H	-6.82476567802721	-4.27888410082831	2.33932233714838
H	-6.04988437806016	-4.11017283634091	0.73998151081711
O	-4.88447631656535	-1.74485982233050	1.34468171538015
H	-6.08874933610121	-2.04627834064907	3.01859200500848
H	-6.95527280794619	-1.97060173151599	1.47957053688029
C	-1.33942212666981	-3.91368438588723	-1.77839850920540
C	-0.71630179022842	-2.63147045345564	-2.31133770106865
H	-0.59597002848549	-4.54372026622783	-1.27612539561836
H	-1.79235320557105	-4.48389895004241	-2.60302179328610
O	-1.70352884089544	-1.76768844161128	-2.84616993398110
H	-0.02100853615929	-2.87587053408503	-3.12231749568187
H	-0.15159073973077	-2.11016981231267	-1.51763515058891
H	-2.16822830547335	-0.90647474341320	-0.99580382527847
H	-3.39073092322021	-0.75593685815666	-2.27594652675092

Int4 E = -5344.3259616572

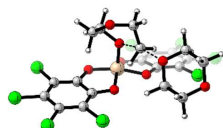


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O	-4.12929571986935	0.60600977497073	0.60658368968943
O	-5.92103646225939	0.29658137668409	2.25594220869917
O	-2.63691304420515	-0.00711190387272	2.36654410380776
O	-4.45321987894414	-0.83467614019872	3.79171956812228
C	-3.26210689292100	-0.94291196374771	4.35799774263737
C	-2.22153022445523	-0.42723761694649	3.56381077538020
C	-2.97619384817299	-1.55013015203911	5.57341304896605
C	-1.64547148906600	-1.58076927071086	6.03025929093200
C	-0.63050990271777	-0.97287344898284	5.28618864323514
C	-0.92401642091678	-0.37287607998267	4.04503298697192
Cl	0.30091794142317	0.41400661517540	3.09666411362995
Cl	-1.26914405414773	-2.40794934512320	7.51291785083160
Cl	1.00575366909479	-0.97187736565986	5.87479727537927
Cl	-4.27066626235847	-2.28455366433764	6.47082411404815
C	-5.30191179434614	1.10542972063696	0.20083434914094
C	-6.32843620351331	0.93604155353416	1.13971884129101
C	-5.54898321033515	1.75059902174910	-1.00088305915236
C	-6.84569122951198	2.22750547485804	-1.26211838019399
C	-7.86922374364399	2.05191491680886	-0.32410523383037

SUPPORTING INFORMATION

C	-7.60891235725653	1.39601672445329	0.89256641337886
Cl	-8.84237569374196	1.14378062841671	2.0858928809043
Cl	-7.17000497854116	3.03172356555541	-2.76520628019361
Cl	-9.47056948235373	2.63249103226626	-0.65484390676410
Cl	-4.25220687357740	1.94078390040275	-2.13606962852059
C	-1.65352446174867	-3.60405402214574	1.63733333869715
C	-0.50115966339089	-2.76676484071298	1.15956501061934
H	-1.63425087019088	-4.62554863397330	1.24376251663035
H	-2.61769999434610	-3.12019768228180	1.46522941937498
O	0.74874066155352	-3.34889468600596	1.51899131563142
H	-0.55427587446777	-2.73712252358993	0.06603059726509
H	-0.58114635013702	-1.73690331450059	1.53478992220302
C	0.86624130919140	-3.33424532013002	2.93110235070644
C	-0.19100738118010	-4.19949096195893	3.57568302740121
H	0.82241564687779	-2.30848754997648	3.31844643236400
H	1.84152787092129	-3.75937250798722	3.19287670231475
O	-1.55201439183192	-3.74169415356022	3.14780987616339
H	-0.19135614912093	-4.10093445380613	4.66510771800272
H	-0.10442226174630	-5.24741803055420	3.26383393334189
C	-2.60367284223685	-4.63025883068877	3.76924905564136
C	-3.99836975074124	-4.22634794410019	3.39232796975689
H	-2.43842445962139	-4.50055644126416	4.84192573151498
H	-2.37223469961626	-5.65128870215207	3.44401047183358
O	-4.24404409034659	-4.64889114029521	2.06690155708054
H	-4.12533868788578	-3.14620814282667	3.52608807197429
H	-4.66562275047493	-4.72597144969701	4.11871749727740
C	-5.41995677756618	-4.10529107080602	1.44550221174627
C	-5.64715768474599	-2.62528791229513	1.69057733011596
H	-6.31551821457202	-4.65287188017111	1.78243456080857
H	-5.27368286549175	-4.29977922012454	0.37828219370308
O	-4.46248429359361	-1.88228878041597	1.40521240024452
H	-5.98271448618080	-2.44650938485383	2.72225553026963
H	-6.47168786343758	-2.30775975404742	1.03397194137283

TS3 E = -5344.3060253116



Si	-4.21692036652797	-0.56956438340192	3.51971962668334
O	-3.68886783485906	0.02252597316664	1.96290331314220
O	-5.72455691241005	0.27821667055200	3.29895606435925
O	-2.53159471225641	-0.99436104750001	3.78010553690855
O	-4.38695134188287	-0.28431228177304	5.20834327921530
C	-3.32464324726563	-0.72613441700590	5.90626355204491
C	-2.26786789809538	-1.13971527339007	5.08793711437572
C	-3.22177239540540	-0.78743431495060	7.28516352446821
C	-2.03270704728299	-1.28233223056878	7.85290909326213
C	-0.97832180020928	-1.70552354619487	7.03489732848114
C	-1.09952074051428	-1.63698741250736	5.63678379164860
Cl	0.17621380665731	-2.15902958616028	4.57242036594297
Cl	-1.88535038882241	-1.37035365720121	9.57717484260610
Cl	0.48149838350384	-2.32593398477659	7.73471670173021
Cl	-4.55518379447216	-0.26406701213317	8.25539890531845
C	-4.70736764146453	0.57046245015995	1.27271934687589
C	-5.87149159958906	0.70847367888884	2.03772996441263
C	-4.68346929496060	0.94258082973289	-0.05915383581418
C	-5.84764357761101	1.47960722338728	-0.63676928537482
C	-7.01276931304285	1.61637150110295	0.12740631474078
C	-7.03034513960941	1.22024736494735	1.47714881551289
Cl	-8.45604369735827	1.33344118390149	2.45345934406771
Cl	-5.83118973192104	1.95863181005978	-2.30195553655722
Cl	-8.45127394144732	2.26578436854771	-0.58649545357593
Cl	-3.22222052715313	0.72277185541360	-0.97413882987624
C	-0.91604266843108	-4.52250399091586	1.46597707873100
C	0.34149851444730	-4.72399243331033	0.64273456082177

SUPPORTING INFORMATION

H	-0.66411738567283	-4.15823736798204	2.47261727066512
O	-1.49685705509882	-5.44812157115761	1.53402279041992
H	1.04819308935074	-3.50024999107627	0.50078451584521
H	1.00779940313857	-5.42503278348315	1.15590505007137
H	0.08102948405401	-5.13695392487812	-0.34670549858510
C	0.22224851945787	-2.53088375768487	-0.13913839702963
C	-1.0387315312793	-2.28144260916746	0.65886545187344
H	-0.03354212467596	-2.86256401012867	-1.15939133150829
H	0.80240637467636	-1.60504870398418	-0.20222953409118
O	-1.76544184424473	-3.54472099670147	0.80675442590052
H	-1.71362569997869	-1.59741353752842	0.13664720454635
H	-0.81516039134923	-1.88577468053711	1.65903249019679
C	-3.35841065772017	-3.10738700872701	1.94354929991825
C	-4.26211958786919	-4.26759372919158	1.68640971015148
H	-3.44504776823173	-2.21196143162472	1.34493133825641
H	-2.69667134956712	-3.09204693555014	2.79771409688844
O	-5.41002226864919	-3.94098627219107	0.92826605836639
H	-4.51879222724649	-4.73424916140109	2.65071264222006
H	-3.72727838811484	-5.02240962253197	1.09809766957119
C	-6.19148086708671	-2.83320613541790	1.41275925747109
C	-6.07085074351091	-2.59288891060788	2.90107756072955
H	-7.23258559489099	-3.06306027157839	1.16058464941720
H	-5.90555755821571	-1.91835302431463	0.87049996779045
O	-4.72399432954455	-2.19055866061941	3.22634220277276
H	-6.29348487047570	-3.50112753677701	3.47363946703493
H	-6.77612772192228	-1.81255270322827	3.20552811695588

Prod / 1-(1,4-dioxane) E = -5036.66063867339



Si	-3.01029568778586	-0.11296935099798	0.14268013025314
O	-4.13500306702148	-0.23726618395644	-1.15808081202333
O	-4.14361382546908	0.83774839371800	1.02498955872559
O	-1.76581507012106	-0.52055067710776	-0.96878371797130
O	-1.81738731218250	0.40456174392004	1.28197514949695
C	-0.56172551018927	0.20173000474717	0.83471447016526
C	-0.53055519922482	-0.32703461038328	-0.45647734504379
C	0.60663325956892	0.44790258985004	1.53558126142743
C	1.83352883491317	0.17025678763562	0.90731306178092
C	1.86445807469045	-0.35440705369374	-0.39236637666532
C	0.66878726250164	-0.61028656761051	-1.08727730039138
Cl	0.65040560791184	-1.26938870275149	-2.68589235541212
Cl	3.30964386406808	0.47389139278426	1.75955312104509
Cl	3.37918092172134	-0.69860363536628	-1.15684743491220
Cl	0.51052385421819	1.07537934968752	3.14509580180734
C	-5.30908058917705	0.36681359215649	-0.88243840454026
C	-5.31536119511653	0.98367989351399	0.36947797409060
C	-6.42570593812772	0.39830103895667	-1.70104195299325
C	-7.57162739388404	1.07127334298511	-1.24107774707387
C	-7.57808522107108	1.68795076319388	0.01795956089018
C	-6.43839278282620	1.64140496958796	0.84041154398611
Cl	-6.39804651797934	2.36730758193708	2.41008054150403
Cl	-8.98180921491594	1.12545113791487	-2.24407615163716
Cl	-8.99586609352620	2.50728035720066	0.58012528945705
Cl	-6.37041465451486	-0.39189365732896	-3.23845574216487
O	-3.33151182883289	-1.77890309175017	0.84743250275029
C	-2.26145106560833	-2.48391066124939	1.59216326007650
C	-2.56467297475296	-3.96302244660225	1.55774373254456
H	-2.24714892093928	-2.07675345070796	2.60861102549436
H	-1.32775607405685	-2.25421170674099	1.07417652466910
O	-3.83831864264778	-4.24108245835252	2.12624967053418
H	-1.81787055431317	-4.49211863508641	2.15829765556843
H	-2.51468540646470	-4.33325866038099	0.52062862205670
C	-4.85557104611462	-3.58483474349946	1.37980447550559

SUPPORTING INFORMATION

C	-4.67038974259195	-2.08640635597675	1.40430773905153
H	-4.86503927757792	-3.94506243481758	0.33801924822941
H	-5.81370470227473	-3.83209833343431	1.84795698589454
H	-4.70474736245487	-1.67181454832935	2.41750099882808
H	-5.39249880783045	-1.58252497366476	0.75831543499588

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Si	-3.61926017508830	1.54059543759480	-0.58976418868556
O	-4.78939802409807	1.11126092029664	-1.80351038068957
O	-4.86508254113031	2.21249281812068	0.42359443961415
O	-2.37432706289047	0.86880450310160	-1.60176036657376
O	-2.44971688067791	1.96938033371637	0.62561908805131
C	-1.20772436523680	1.64924064526398	0.22083981792617
C	-1.1650907025250	1.02901347499518	-1.03451244555113
C	-0.04686854416328	1.85505470724824	0.94848214276346
C	1.18166130266709	1.44180041024866	0.40429975496012
C	1.22436036900016	0.82173238503814	-0.85037565783269
C	0.03900648731135	0.60874846389170	-1.57576493704388
Cl	0.03110009236356	-0.17869164001820	-3.12004447729565
Cl	2.64079023218023	1.70262092747604	1.30053439612759
Cl	2.73666673292980	0.30614665732076	-1.51933030335404
Cl	-0.16132504836691	2.60021037013555	2.50957774404922
C	-6.03201641024631	1.42718534408265	-1.39660493001225
C	-6.07448005996475	2.04755347763505	-0.14131845575866
C	-7.19323317267865	1.21685771899209	-2.12221296549433
C	-8.42241692914494	1.62524807665384	-1.57570885197038
C	-8.46518173271164	2.24494597462864	-0.32086389029806
C	-7.27938331648819	2.46258625562756	0.40226728540624
Cl	-7.27163883134462	3.24941442738120	1.94696281186450
Cl	-9.88221594358466	1.35863154871673	-2.46913078733964
Cl	-9.97840875471667	2.75375339169053	0.35128959158871
Cl	-7.07897667911611	0.47158751586061	-3.68320288293877
O	-3.93168324363210	-0.20411267442167	0.26508882384360
O	-3.30570564815961	3.28551646803646	-1.44204805277669
C	-3.36360649834586	3.47528939437915	-2.89096214998788
C	-3.43412152192938	4.55302241551044	-0.72415705469405
C	-4.70506485924498	5.24981420598648	-1.15710060303181
H	-2.54801180714807	5.14816325692563	-0.97746611042480
H	-3.43348895386072	4.30694454335807	0.33876808707371
H	-4.63847898210991	4.20520368181301	-3.25008735706955
H	-3.31308624700906	2.48003396758810	-3.33516517162297
H	-2.47750453118244	4.06012842742193	-3.16717740102260
C	-3.88126104250579	-0.39420714870082	1.71387998491409
C	-3.80637489638760	-1.47191318020020	-0.45287066002970
C	-2.54005700125386	-2.17395976289740	-0.01494336198824
H	-3.80156891991710	-1.22542323757568	-1.51570085562163
H	-4.69610890889357	-2.06329885899581	-0.20348692489970
C	-2.61117426577158	-1.12986987350325	2.07829488313317
H	-4.77128826389379	-0.97470079564275	1.98673017635954
H	-3.92872243062326	0.60130259541341	2.15782809096575
O	-4.71619203988879	5.45502566902309	-2.56801341168512
H	-5.51393961537324	3.57956425623966	-3.00908889152540
H	-4.64734985762440	4.42453341545721	-4.32267563932475
H	-4.75867581050336	6.23840195894257	-0.68967203041582
H	-5.58540035935132	4.66363182579887	-0.84533569734828
O	-2.53556315779178	-2.37963521718694	1.39590344280192
H	-2.60773852431194	-1.34988424900116	3.15073666691736
H	-1.73215569008466	-0.50760812258512	1.84148270518544
H	-1.65604999558270	-1.59121185890884	-0.32280447374489
H	-2.48857860216961	-3.16264524797380	-0.48247856549367

SUPPORTING INFORMATION

2.2 Free Enthalpies of Diglyme-Complexes for Different Lewis Acids

Free formation enthalpies of the diglyme complexes of the herein investigated Lewis acids depending on the hapticity of the ether were calculated at the DSD-BLYP(D3BJJ)/def2-QZVPP+SMD(DCM)//PBEh-3c level of theory and are summarized in Table S2.

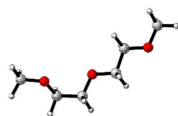
Table S 2: Free formation enthalpies of the diglyme complexes of various Lewis acids depending on the hapticity of Diglyme, calculated at the DSD-BLYP(D3BJJ)/def2-QZVPP+SMD(DCM)//PBEh-3c level of theory. All values in kcal/mol.

	hs-Fe(OTf) ₃	AlCl ₃	Ge(cat ^C) ₂	Si(cat ^C) ₂ (1)	Si(amp ^F) ₂ (2)
mono-adduct	-5.7	-17.3	-3.9	0.1	1.7
bi-adduct	-22.5	-14.4	-17.4	-9.8	-0.7
tri-adduct	-38.8	-23.7	Not possible	Not possible	Not possible

For the mono-diglyme-adduct, only coordination of the O1 atom of the ether was considered, since the O2-binding mode would result in a catalytic inactive system. In hexa-coordinated systems, (η^3 -diglyme-AlCl₃ or η^3 -diglyme-Fe(OTf)₃) both isomers (*fac* and *mer*) were investigated, but the *mer*-isomer was found to be thermodynamically favored and is therefore listed throughout this work. For the open-shell iron-complexes, mono-, bi- and tri-adducts were computed as hexa- and hepta-coordinated complexes (one triflate in each structure is respectively mono- or bi-dentate) but the hexa-coordinated structures were found to be thermodynamically favored and are therefore discussed in this work. Since Fe(III) is an open-shell system and occurs either as a high spin ($S = 6$) or low spin ($S = 2$) system, thermodynamics were calculated for both spin states and the high spin systems were found to be favored for each binding mode by 40-49 kcal/mol and are therefore discussed herein. This result is in line with similar reported calculations.^[16] Despite several attempts, two minor imaginary frequencies occurred in the frequency calculations for the octahedral-coordinated bi- and tri-adduct of Fe(OTf)₃ after successful convergence of the respective geometry optimization runs. We addressed this problem by subtracting 11.2 kJ/mol per imaginary frequency from the final total energy of these compounds to compensate the missing energy contribution by the imaginary frequencies computation of the entropy. The values hereby obtained should be sufficient to discuss thermodynamic trends.

Cartesian coordinates (reported in Å) and energies (in hartree) of all structures used for the computation of these thermodynamics, reported at the PBEh-3c level of theory.

diglyme E = -461,676132041739

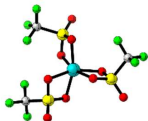


C	-4.67510526343358	0.94241735490286	0.25729216622411
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H	-5.03493633347196	1.50026916371975	-0.61753648385632
H	-4.96797771728235	1.48910677299202	1.15282096206854
H	-5.18942950673815	-0.02861726802021	0.26609632815079
C	-2.79324897741659	0.13796695094495	-0.85204246983386
H	-3.11741872760288	0.62054252978779	-1.78685107205950
H	-3.16139805808135	-0.89975717322738	-0.88736092768157
C	-1.28626882503951	0.10161805806472	-0.80474974794268
O	-0.77761232313952	1.38899066349565	-0.99678381248924
H	-0.93456655358415	-0.58551347285290	-1.58995961394620
H	-0.95760045454444	-0.32083962757033	0.15646544318460
C	0.61991812670208	1.44611790992116	-0.95272531491307
H	1.07241597618348	0.81987779350980	-1.73641543810208
H	1.00664249779048	1.08336627220069	0.01084203804329
C	1.03063050841788	2.89084019322542	-1.15522079890100
H	0.62770321746186	3.25955290481465	-2.11049925092783
O	2.42943186479540	2.94713139671706	-1.13439247084154

SUPPORTING INFORMATION

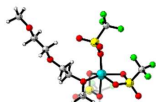
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C	2.92591264527318	4.24353755838266	-1.28405241971976
H	2.63310203023791	4.69440864191827	-2.24147145387003
H	4.01360802961529	4.19352756797745	-1.24949718211958
H	2.58723616824628	4.91465380976025	-0.48378054661510

Fe(OTf)₃ S = 6 E = -4142,68974363214



Fe	0.51682969834167	0.00644945121436	-0.38248033507594
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O	1.61551067368608	-0.89878690983177	-1.82394051981791
O	-0.06381895242793	-1.60769293808341	0.70539751411015
O	1.80691893657844	-0.30007487968602	1.16831030941311
O	-0.74809608777958	1.38895878225344	0.40949727040301
O	1.15564128338979	1.88229561410717	-0.84285992422729
S	0.51934273325454	-0.86616104593103	-2.86782065951746
S	1.09606500559910	-1.53379354974176	1.67499149909716
S	-0.02555953197895	2.57221834570791	-0.19904472337101
O	-0.78227396281375	3.49897338236763	-0.97726269239695
O	0.81200160845648	-0.30501673093652	-4.14759709768249
C	0.05227259779258	-2.62923835132263	-3.13934527259314
C	0.68401533692370	3.49870615399387	1.23519363510514
C	0.35152141050470	-1.02456937442416	3.28445560464002
O	1.85887477063108	-2.71600693291520	1.91647611734897
F	-1.02660204664748	-2.65349952820098	-3.89591876144537
F	1.04724267868631	-3.23895071700997	-3.75107606541242
F	-0.19207132867756	-3.21298641627291	-1.98531206576695
F	-0.38650479025952	-2.01700646528251	3.73625349730281
F	1.33027260778712	-0.76993214449575	4.12901311210557
F	-0.38992521969179	0.05109864558819	3.11762574577048
F	1.56781136053501	4.36241863747526	0.77813607851020
F	-0.29470507608850	4.13443475546090	1.84723183989269
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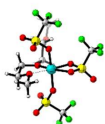


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O	2.11356463202312	1.00867564870699	-1.90877756292251
O	-1.36212649812888	0.25965110758463	-0.15645820628873
O	0.63242952872844	-0.90914657730354	0.16649490280078
O	-0.33538504446261	3.29008521929481	1.96444199591497
O	1.23633967977340	1.87856804450517	0.70395110739616
S	1.52238816980319	0.30131454323780	-3.11603310477074
S	-0.85542665302820	-1.07320374583319	0.34724749532173
S	1.03660792129438	3.16615019984004	1.53748433480784
O	1.72032038488427	4.27926936587629	0.92551241996790
O	1.58581124510908	0.99217338021744	-4.36952013276440
C	2.54724238641910	-1.22342261320398	-3.28310958818204

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C	2.03162426946109	2.71670071721803	3.02226256299179
C	-1.14128865585581	-1.00772732159799	2.16924670293637
O	-1.47764690200576	-2.26481548744046	-0.13657507829966
F	2.11377712056972	-1.90631701339599	-4.32483895448315
F	3.80314956979717	-0.86868917868523	-3.47426453008019
F	2.44742985252506	-1.95317411695308	-2.19207984438683
F	-0.49413946292757	-2.00585273985595	2.73841465571597
F	-0.7153588688160	0.14060407933486	2.64802249902606
F	-2.43595124445553	-1.13221523446983	2.38655331393611
F	3.30241090072263	2.57108751571125	2.69384530034450
F	1.91346336434232	3.69993865041232	3.89928997816977
F	1.58956088737818	1.59501269502333	3.56300339876636
O	-0.43847351738191	2.52127758649860	-1.67780998340232
C	-1.72400239898074	2.41685060275311	-2.30793755161260
H	-1.64436592309930	2.74490483233106	-3.34494392367000
H	-2.45206729532485	3.02802243069348	-1.77697039368176
H	-2.04853110703002	1.38205770405576	-2.28927023191409
C	0.26064816727576	3.74875866128895	-1.98196715984516
C	-0.44542327326725	4.95859170580671	-1.38916593437117
H	0.36129210277708	3.82554262767564	-3.06810220669451
H	1.25930459389064	3.67451948235872	-1.55600476092939
O	0.43685808501399	6.02557134915564	-1.53886572988648
H	-0.67926283429515	4.76221482650667	-0.33551152181707
H	-1.39976334640206	5.15989795166094	-1.89886498150370
C	0.15205142419895	7.12693164680852	-0.71160314359880
C	1.34129859812333	8.06423699808582	-0.76696408815539
H	-0.01063590769545	6.80429111386925	0.32436914584220
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O	1.04027059606643	9.17420517162993	0.02980904670846
H	1.53870798916456	8.35920796289243	-1.80861949897885
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H	3.00100956841388	9.68087761158542	0.49628907269112
H	1.75972823583514	10.92297870242645	0.73491639927453
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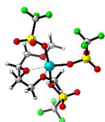


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O	0.72591628866957	1.13256984125866	-2.05509932837676
O	0.07512765291684	0.56314995049465	0.53906549345885
O	1.96762313520532	1.94273397577940	0.43880691991953
O	-3.09612321741436	3.26382355555393	0.65266495932369
O	-0.62685327831273	3.27873255420615	0.79098681289051
S	1.27135957587366	1.22973737981426	-3.48607246857588
S	1.50197569814017	0.61890914380299	1.00747813047068
S	-1.93160658942464	4.08546365147607	0.87939546201838
O	-1.80996785173539	5.36143297254008	0.20717635842319
O	2.05938332976474	2.42445845911848	-3.69924623617846
C	2.45705344518982	-0.17207370620076	-3.43263095861420
C	-1.89755134477268	4.46963846831650	2.67838684957661
C	1.43365193382968	0.90581857405807	2.83079834003708
O	2.32625965415854	-0.53217502757429	0.80924866603792
F	3.09546403973284	-0.23204017478998	-4.59011802706904

SUPPORTING INFORMATION

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F	1.80375807521669	-1.30114163599132	-3.22987605506589
F	0.84832054225705	-0.12990406765103	3.39977400006658
F	2.67333751726924	1.01977815620887	3.27145729048892
F	0.76312619756494	2.00315131761988	3.11063195119622
F	-0.79654511815303	5.14165557635271	2.98037697530411
F	-2.95341800961932	5.21187447037445	2.96944590900580
F	-1.93850323531103	3.35587089687910	3.38882169793033
O	-1.38348841828082	2.91533958327231	-1.83286207232754
C	-2.39372490490546	1.97889161709792	-2.23105359291175
H	-2.04901863043490	1.38807183900633	-3.07949098266637
H	-3.30371751415377	2.52159009083165	-2.48481573908983
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C	-1.00992958257625	3.83730392866898	-2.85352061880511
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H	-0.66148348076025	3.29472575827412	-3.73526181283542
O	0.98441645618548	3.96201646967293	-1.54698690661768
H	-0.37778542693135	5.51670633662418	-1.65067576348536
H	0.58007533536575	5.22970593492846	-3.12541781541625
C	2.26988530628525	4.55724553481798	-1.30612342227179
C	2.22105819250815	5.49942194174815	-0.11510105709724
H	2.57863205716709	5.08265565994702	-2.21223649421445
H	2.97526588140221	3.74526150166027	-1.14116851762919
O	3.47496840344585	6.10723889903131	-0.05560415389353
H	1.99409805598501	4.93575908109721	0.80108471117008
H	1.41720824956021	6.24202504814573	-0.23666417175718
C	3.63239953899375	6.93978963395718	1.05971084156249
H	2.89969805275324	7.75627156919972	1.07348919585912
H	4.62931687455203	7.37420153986974	1.01139555719059
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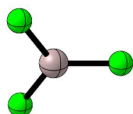


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O	1.67578339425696	2.23775710251886	-2.09064461663681
O	0.76148953845052	1.44294317832085	0.43762040468133
O	2.71931122819341	0.96304902538066	1.83917939516835
O	-2.53491430860407	4.54257049690260	0.84143145563487
O	-0.11997227641988	4.04318176815248	0.83387566720890
S	1.92994899498123	0.80491619181716	-2.58294949760111
S	1.39338174640055	0.51102272313249	1.49341668423400
S	-1.21071926763121	5.11024920815994	0.89655692621045
O	-0.90366058493976	6.26186068153732	0.06527806946543
O	2.74379476707269	0.04034036067330	-1.67596480142734
C	3.00663539987108	1.22087424667679	-4.01715878396655
C	-0.93216275896377	5.69754277288706	2.62126222624189
C	0.32816725654603	0.94779792699901	2.93257909857891
O	1.10840134705699	-0.86164386094625	1.19191447725855
F	2.37490846109190	2.05401781253081	-4.83950230344666
F	4.12585328501454	1.79760333483296	-3.60581989073546
F	3.30583132610697	0.11492271762128	-4.67745912990772
F	-0.95246800381407	0.78058247055298	2.63209165923474
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SUPPORTING INFORMATION

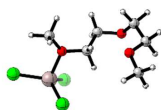
F	0.52847974822225	2.20850826456167	3.28692522351495
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F	-1.20958903963721	4.74922150487852	3.49583504316362
O	-1.18355642747486	2.64282050629168	-1.45784492749634
C	-1.94126855845054	1.45511580771894	-1.18358160834538
H	-1.53813828155843	0.60858721075166	-1.73820023465020
H	-2.98292752933694	1.63028091969177	-1.45243744104022
H	-1.88111169493318	1.26712865827544	-0.11665658462918
C	-1.28621158923678	3.13022109630847	-2.79265912724132
C	-0.77196740493074	4.55720389855876	-2.77854477078468
H	-2.33388475150825	3.12590460029662	-3.10506066627745
H	-0.71837571552052	2.48774435899078	-3.46974403256418
O	0.36501246660868	4.57236429336831	-1.92878908635785
H	-1.51308684741671	5.25441917391455	-2.38218809870981
H	-0.50313510961323	4.85635868473425	-3.79470270994201
C	1.38541872723360	5.53581692432318	-2.10879250541443
C	2.15920021138104	5.59879932952990	-0.80929269129325
H	0.95572769320231	6.51928623128587	-2.31287158965551
H	2.01952260465205	5.23663545076497	-2.94845027810301
O	2.40434168192002	4.26598972690845	-0.36510422970543
H	1.59732972311615	6.14913114776246	-0.05184617480572
H	3.11330152883298	6.10608816955951	-0.97841443365313
C	3.14597408454880	4.20631735631779	0.85888418515927
H	4.10425057785547	4.70935596512009	0.72337964468678
H	3.32386436087574	3.16093923994037	1.09515345846330
H	2.58926728232150	4.67941134152576	1.66904705946710

AlCl₃ E = -1621,43915747357



Al	0.60880664306198	1.29057766354259	-0.00000001379662
Cl	2.67754133350720	1.29057961057021	-0.00000091600396
Cl	-0.43723014406459	2.58427130921008	1.22794004899382
Cl	-0.43722783250460	-0.00311858332289	-1.22793911919324

mono-diglyme-AlCl₃ E = -2083,17663763614



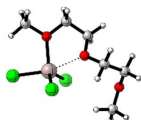
Al	1.45545738066151	1.78428971740062	-0.69209991604318
Cl	1.89859305942444	-0.16349024545430	0.00248351957339
Cl	-0.26896350352875	2.67001337972586	0.14284974889678
Cl	1.76111385639327	2.07914771195473	-2.75708177927669
O	2.90005391695460	2.78725240136226	0.05669695974410
C	4.24179972410274	2.31249660170969	-0.23888785398014
C	5.01818047815927	3.36973899291393	-1.01316187595685
H	4.15055478733763	1.40994292270711	-0.84111756607690
H	4.71803538264162	2.03178249893511	0.69922633799465
C	2.79555947790665	3.51104561223801	1.29157299683188
H	1.81207853854120	3.96797663877065	1.32904583744289

SUPPORTING INFORMATION

H	3.55802539592346	4.28765995901158	1.32445356510618
H	2.92159534798537	2.83123525762997	2.13447972101223
H	4.43734652161580	3.65686652000428	-1.89240149888855
O	6.23473975330005	2.86296090978769	-1.47768650796638
H	5.16418035934446	4.27587430210657	-0.40793890889431
C	7.31480726497647	2.80999127152287	-0.57619471224028
C	7.69117778337234	1.39256403296362	-0.19955195541544
H	7.11862828323588	3.39561430527000	0.33154192877681
H	8.18133054208530	3.26534495909386	-1.06621273668177
O	6.73867497868540	0.85850014334276	0.67467803035326
H	8.68775647013390	1.41059346700189	0.26750048489052
H	7.77749171022805	0.78919740768554	-1.11447394368543
C	6.90385042221453	-0.50966848117222	0.92508605328038
H	7.86224976886325	-0.72824164623965	1.41176900178832
H	6.84582345655095	-1.10663664727901	0.00723409299889
H	6.10111884289010	-0.82596199299361	1.58942097641563

bi-diglyme- AlCl_3

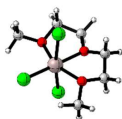
E = -2083,17281078223



Al	3.20082569792921	1.43529598206609	0.44909621836759
Cl	3.91347906837522	0.86995167896968	2.38568385419444
Cl	1.06231132420069	1.25161728618836	0.69364247104975
Cl	3.56201007672020	0.37722113810637	-1.36548015625125
O	3.12122082235665	3.37734500499733	0.01935726017539
C	4.20554263635223	4.09150101083198	-0.58243224527658
C	5.31888011644824	3.11883741800091	-0.89873799383995
H	3.85108074895315	4.59654434629668	-1.48488522030525
H	4.54809233730490	4.84881666775338	0.12905670685875
C	2.06438846482428	4.26725095903623	0.41181956209939
H	1.32614229674148	3.69811433903172	0.96291499517259
H	1.60375360887343	4.69758398957384	-0.47738301703823
H	2.47699427969111	5.05842581875567	1.03928480767491
H	5.14771900196881	2.57440863853434	-1.82990113874823
O	5.34465506879374	2.22959273652183	0.18919747053883
H	6.25309840046705	3.68136074859588	-0.99536963793181
C	6.61540956091713	1.82905401374380	0.68525903562516
C	7.48726725170574	1.10449240829228	-0.32821535585643
H	6.39660225086891	1.21054924354632	1.55289849039640
H	7.16150691215870	2.71154988081363	1.04312557865734
O	6.89220719313591	0.01965995905976	-0.95423768941937
H	8.40899273862699	0.82426719255766	0.21011714812600
H	7.79628577707973	1.78757737438500	-1.12542538268283
C	6.62335929891864	-1.07292844555336	-0.11463884972887
H	5.85653325947738	-0.86232416351508	0.63779489189902
H	7.52863357409422	-1.41938852179090	0.40185422008301
H	6.25426821501587	-1.88029670479952	-0.74313602383978

tri-diglyme- AlCl_3

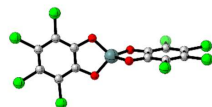
E = -2083,18834951728



SUPPORTING INFORMATION

Al	4.30223524834397	1.42041631422600	0.26038342851817
Cl	4.58391197324029	2.37246707363595	2.28739290572280
Cl	2.74590526788778	0.05027818193724	0.91132441844364
Cl	4.35386003698139	0.73648691642150	-1.86028124709672
O	3.23666535580533	3.08324814794611	-0.28485276102742
C	3.97500913537597	4.28949129706004	-0.15242819341450
C	5.36796798969168	4.03695493335018	-0.70486209550114
H	3.49291956874377	5.08092678363832	-0.73382003441068
H	4.01133409310948	4.58674519056648	0.89775490747009
C	1.88306301490031	3.19948905540271	0.15899651979477
H	1.38906570305098	2.25910986979125	-0.06084050137816
H	1.39507304644891	4.01001252095353	-0.38423438626499
H	1.85108312066353	3.38560368733666	1.23347829421065
H	5.38109665812221	4.09617072156028	-1.79522604389247
O	5.75236129116503	2.72869668079626	-0.33274136575413
H	6.05821616669203	4.78114453585797	-0.30045555853220
C	7.04777578713073	2.43572611242724	0.15004912175847
C	7.17346070455809	0.93167150496350	0.03405054955284
H	7.14893406524368	2.77845228455109	1.18313441633398
H	7.81066939677541	2.91078896218800	-0.47255392779409
O	6.01595757388015	0.34878274939237	0.61424143519338
H	8.06783747666076	0.59047991121712	0.56369817003203
H	7.24526293766521	0.63512427818680	-1.01735385697758
C	5.98437970585665	-1.07528167526158	0.49830163043081
H	6.85760998717939	-1.49584879336669	0.99929684008307
H	5.96380856312463	-1.37207049193743	-0.55119718686092
H	5.07777135870254	-1.41583132884096	0.98782079936029

Ge(cat^{Cl})₂ E = -6510,23858715724

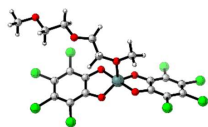


Ge	-3.95776572668169	1.97177240243626	0.03625677471002
O	-5.16241134994132	2.81402558070539	-0.93021076589938
O	-5.15395649880723	1.08864506334177	0.97853623473653
O	-2.73742219031803	1.03405134615221	-0.81750822954080
O	-2.77619716826421	2.94003766304993	0.91117647226740
C	-1.54382734380228	2.50889875349671	0.53322010275000
C	-1.52335271475934	1.47862951230446	-0.40152746050517
C	-0.36995235015943	3.03801969129773	1.02988707347698
C	0.84363959160669	2.51854168066338	0.57527175259791
C	0.86365696083687	1.48869744448219	-0.36418455128896
C	-0.32955615422245	0.95923000766044	-0.85878186281121
Cl	-0.35232096814238	-0.30206692016698	-2.00511705066215
Cl	2.30734958062954	3.15492149031197	1.18152591137778
Cl	2.35153809179517	0.86342886331377	-0.91999774571654
Cl	-0.43977859286284	4.29767351351471	2.17613745431895
C	-6.38398686334751	2.40056173786970	-0.50163707622402
C	-6.37950544999357	1.46775636691314	0.53018562428609
C	-7.56913884262534	2.86206930715459	-1.03699504508679
C	-8.77076242889827	2.37342739927914	-0.52131179010855
C	-8.76716338539699	1.43781340112267	0.51220465118642
C	-7.56196916099796	0.97974466889271	1.04818740150964
Cl	-7.51249213909456	-0.16101969036365	2.31362899110394
Cl	-10.24857765831580	2.93395085760870	-1.16637504088296
Cl	-10.24111926101946	0.84096279077537	1.13345146228125
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SUPPORTING INFORMATION

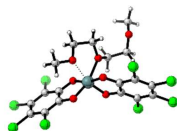
mono-diglyme-Ge(cat^{co})₂

E = -6971,93958489689



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O	-5.70525164423882	2.60799045652507	-1.33415182951819
O	-6.27453523240558	1.29570249904301	0.74298730908071
O	-3.31923749737138	1.56531438894422	-1.36813488438175
O	-3.71431005081934	1.30909015582241	1.11249373114161
C	-2.42452945761115	1.31494129890234	0.73868644126269
C	-2.21085571829850	1.45087902489984	-0.63201165245076
C	-1.36335860001495	1.18885973753727	1.61202060527449
C	-0.06326538609056	1.19708308089848	1.09948055889839
C	0.15240692835743	1.32613590952548	-0.27032171105283
C	-0.92889606841726	1.45017862006057	-1.14630297410036
Cl	-0.71344059126625	1.59797667536903	-2.83569208761643
Cl	1.26242326533279	1.04324190112965	2.16896100472249
Cl	1.74442072361377	1.32957009766182	-0.89361489301128
Cl	-1.67144684206116	1.02160737979897	3.28338542379936
C	-6.97455018980452	2.73248961516689	-0.91203934712804
C	-7.28792124071437	1.99206192768163	0.22709906680287
C	-7.93561830756406	3.49331232220467	-1.54638455092285
C	-9.23787049571563	3.50083632161624	-1.03741559222501
C	-9.55705907660912	2.74251534004127	0.08541603006171
C	-8.57636307737203	1.98078117563237	0.72357639899711
Cl	-8.92865870364282	1.02088014671232	2.09432763838174
Cl	-10.43854589342403	4.44140830664514	-1.81092239297188
Cl	-11.15959361007975	2.72507510169370	0.68608379394564
Cl	-7.51150869249598	4.38459671374706	-2.93951032216037
O	-5.14744302053878	-0.38471502195394	-1.03115429647076
C	-4.07793846882523	-1.26552274607812	-1.42880493623309
H	-4.44831711478727	-2.28866028874176	-1.40592733523285
H	-3.26683736481047	-1.17527597276045	-0.71104150874032
H	-3.72447268634518	-1.00811103572105	-2.42532897586320
C	-6.45867149137656	-0.72208329210560	-1.55596174175975
C	-7.25931006980670	-1.53734244553093	-0.55447151296445
H	-6.31462486961455	-1.25096072523522	-2.50006218800102
H	-6.98693578576035	0.20182125750970	-1.78743812684533
O	-8.56176415657849	-1.53355280960940	-1.05025102774691
H	-7.20100752723948	-1.07036700820405	0.43522556712981
H	-6.85139353638721	-2.55545762221649	-0.46128551470373
C	-9.53916969426334	-2.03100288527947	-0.16210345956950
C	-10.84974229373461	-1.34365601599319	-0.49112376245970
H	-9.27168201171797	-1.81511480751875	0.87924851374905
H	-9.63967226817672	-3.11889892888976	-0.26018727313473
O	-11.83517750658542	-1.88889128976604	0.33710955610009
H	-11.09319693758990	-1.48514351506861	-1.55500863888988
H	-10.73923337717689	-0.26175912353128	-0.32789074124160
C	-13.06639267085683	-1.23576091640487	0.22124527825339
H	-12.99514493042694	-0.17277574280549	0.48385251880001
H	-13.76437893270679	-1.71396800183136	0.90714172307780
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SUPPORTING INFORMATION

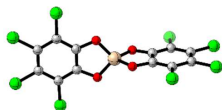
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Ge	-5.79771793881989	0.91726845605609	-0.05837661324948
O	-6.70552851405972	2.27407574676542	-0.85070354079715
O	-6.81120709374603	1.12265338260142	1.43408248892383
O	-4.93101168745792	0.27769548151693	-1.52900078417595
O	-4.23224414486592	1.60074069354755	0.54317556041023
C	-3.24973168351530	1.30127663735621	-0.31093119608599
C	-3.63126577721227	0.57352849124813	-1.44167019666180
C	-1.92356535504803	1.62473468896379	-0.10368903132370
C	-0.96723176905281	1.23492608224740	-1.04554529188808
C	-1.34739285046769	0.51387001517416	-2.17238044910099
C	-2.68886429311803	0.17445408519375	-2.36818063870699
Cl	-3.19894409244339	-0.73736264251546	-3.72514834019788
Cl	0.67552239704700	1.64340361429805	-0.79596880505850
Cl	-0.17778619092198	0.02933071692452	-3.32314473747263
Cl	-1.49656918530898	2.48168805965740	1.31284286991046
C	-7.72594406014814	2.63306546993120	-0.06707419827674
C	-7.78909233469317	1.99573125063092	1.17682356981542
C	-8.70919664990176	3.52489113246331	-0.44753228759560
C	-9.76247777724387	3.80135925947763	0.42823434667869
C	-9.82452622772070	3.17053361787111	1.66621135504621
C	-8.83964560628667	2.25062951786763	2.03711890523616
Cl	-8.90306854645460	1.42483014521665	3.53428790955971
Cl	-10.97807592354893	4.91174999332345	-0.03783897984051
Cl	-11.11268993009704	3.50745580227595	2.74123943799917
Cl	-8.62010118446098	4.23715843148441	-2.00086666836252
O	-5.33557679536497	-0.98904060878519	0.91664672678500
C	-4.05554407252701	-1.28049561344406	1.47767195987207
H	-4.15232538995307	-2.11667880154724	2.17229468963419
H	-3.72225559489085	-0.40387742514664	2.02382306377095
H	-3.33125064304132	-1.53125819840538	0.70005335050955
C	-5.96151804026707	-2.09420217214757	0.28692809995108
C	-7.37718803354951	-1.68168430279036	-0.03273972273783
H	-5.97830659959333	-2.94939043646196	0.96972691191555
H	-5.40991969514646	-2.37784287862557	-0.61591054771799
O	-7.31333898476259	-0.44036273979778	-0.72655644084837
H	-7.97726239391953	-1.56559908186571	0.87100149564645
H	-7.84141461851799	-2.44513658520460	-0.65889118607974
C	-8.13520604590943	-0.26492191849663	-1.89077290414218
C	-9.58489142681814	-0.02130091149170	-1.52481375629034
H	-7.73891656050041	0.59670461640367	-2.42562670785953
H	-8.00739143601393	-1.13952857079750	-2.53631676789847
O	-10.20760089111892	-1.12196269467233	-0.92031351602804
H	-10.11213641463566	0.29161266878326	-2.43788794670635
H	-9.64991779083144	0.81161917987919	-0.82161977839449
C	-10.66896399549261	-2.09288920067329	-1.81958584765249
H	-9.86288291020913	-2.59636379749792	-2.36930993961979
H	-11.36034182655963	-1.67019954304600	-2.55803372384574
H	-11.20356342082897	-2.84736911374635	-1.24467219704881

SUPPORTING INFORMATION

Si(cat^{Cl})₂ (1)

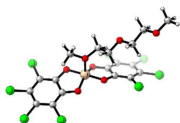
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Si	-3.95762806076695	1.95987899830706	0.04639817601225
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O	-5.05939197134807	1.11798113212875	0.95585965643034
O	-2.83852455352605	1.05240403222310	-0.77378071275455
O	-2.87235350871960	2.89200518283628	0.88586722312232
C	-1.61962906491969	2.49960571517509	0.53301662264901
C	-1.60090787756753	1.46972126574965	-0.39852082343467
C	-0.45243193709027	3.04098929810440	1.02371278241718
C	0.76007795411650	2.52404310301858	0.55623982485371
C	0.77830837807370	1.49315250582016	-0.38261899940933
C	-0.41539045576197	0.95195765806244	-0.87000706839266
Cl	-0.44027503915165	-0.30938843317484	-2.01463394938626
C	2.22550729167310	3.16847912766185	1.14922659829431
Cl	2.26587274416404	0.87799382355633	-0.95040556322988
Cl	-0.51991562701848	4.30057762666800	2.16854790326229
C	-6.30516589057479	2.40054649820367	-0.49060757437274
C	-6.30486021799270	1.46952100856263	0.53991628152565
C	-7.48154780390233	2.86952325107178	-1.03118103934328
C	-8.68456923457401	2.38019632974867	-0.51276216211784
C	-8.68439653053948	1.44210240338860	0.51899215486742
C	-7.48122230112521	0.97723760511769	1.05946859977864
Cl	-7.43512642587881	-0.16599775494206	2.32148233226479
Cl	-10.16108454699139	2.94536259870793	-1.15662450296543
Cl	-10.16082939463808	0.84759257190746	1.13606226371201
Cl	-7.43548966762849	4.01378003596878	-2.29226572736223

mono-diglyme-Si(cat^{Cl})₂

E = -5185,16078832811



Si	-3.75498653177894	1.51057884214299	-0.26161100972445
O	-4.64517227842974	2.07029142258222	-1.59957178195472
O	-5.12145495800124	1.80257963274914	0.75917883368871
O	-2.37309448740207	1.27150620654625	-1.27573144076076
O	-2.73185686029489	1.9836168337759	1.01058808964291
C	-1.43332101125753	1.91866381629161	0.68418264213643
C	-1.23247286528229	1.50501640323966	-0.62699373047451
C	-0.37517431669559	2.19980778043354	1.51877848636160
C	0.92270617170210	2.05975577859741	1.01348788355534
C	1.12746511894008	1.64293733869319	-0.29949338147160
C	0.04108320679488	1.35527063459599	-1.13263413879647
Cl	0.24593081166980	0.81968289445760	-2.74209800041573
Cl	2.25747086253590	2.40032058676818	2.02670167519074
Cl	2.71628884982043	1.47452010644329	-0.90834594424735
Cl	-0.67763858395020	2.69779563669626	3.12431653594963
C	-5.89838961107193	2.42780813920395	-1.27519734947337
C	-6.16834194840720	2.26176834216046	0.07823651237496
C	-6.85968598769737	2.89528943495761	-2.14244152602966
C	-8.12699480708357	3.19643877859530	-1.62841075149320

SUPPORTING INFORMATION

C	-8.40226854161783	3.01938700687858	-0.27495828524036
C	-7.41662424704167	2.53944961137393	0.59230237939989
Cl	-7.71664906783389	2.27502566406249	2.25461387037922
Cl	-9.34109503063423	3.77767755368976	-2.68246583714633
Cl	-9.95475460174178	3.38454582914204	0.34190601461804
Cl	-6.48468682990339	3.08594471755977	-3.79708980394415
O	-4.02181731694092	-0.33080179516039	-0.12688074167449
C	-5.33551343175888	-0.94210074162219	-0.25994062871232
H	-5.21728932505293	-1.83320160149424	-0.88075291406535
H	-5.98257687380086	-0.25384152346390	-0.80240795700068
C	-5.90911019879412	-1.29074701944996	1.10135051956389
C	-2.91861494732515	-1.26617328417088	-0.14075534508618
H	-2.09439415353540	-0.85071191931484	0.43257490284923
H	-2.60868504694507	-1.46025765039128	-1.16507390192340
H	-3.24654401003945	-2.18413180726173	0.34279264497191
H	-5.18494746223975	-1.87891722100881	1.68712310360750
O	-7.06835547618378	-2.01915711671321	0.83911834666500
H	-6.11646190784695	-0.37710210812361	1.66914853247147
C	-7.86821449202257	-2.22456961072933	1.98045334312464
H	-7.31379996714969	-2.76916698288130	2.75679806300420
C	-9.08091591523678	-3.02954670580901	1.55833750228742
H	-8.18324627474570	-1.26535797251609	2.41266416713929
H	-8.75542270775358	-3.97176765553920	1.09212196834234
H	-9.64770017288340	-2.47443475995672	0.79647687810532
O	-9.84824571886809	-3.26192068626766	2.70236954154255
C	-11.01548129297050	-3.98695797445041	2.44322532990425
H	-10.80296286924570	-4.97975491633881	2.02751359724330
H	-11.68212005162108	-3.46608592635394	1.74351023615511
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bi-diglyme-Si(cat^{Cl})₂

E = -5185,18284283712

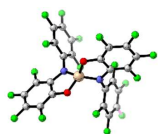


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O	-5.21302968811564	0.39155239145630	-0.95572463433471
O	-5.41920758793672	2.27100829768472	0.61984457626102
O	-3.00097102372065	1.68048502248542	-0.48301107928909
O	-3.43929340964690	1.16838052476820	1.88027500257745
C	-2.18413061740564	1.54452436778586	1.64257161569666
C	-1.93631088446695	1.84178455179787	0.30282805901882
C	-1.17317076397841	1.59461792038443	2.57669329176884
C	0.11449925665634	1.95154596949085	2.16060156705786
C	0.36443589128183	2.23774816175836	0.82248838349137
C	-0.66837716866203	2.17827694429563	-0.12064929358605
Cl	-0.38870142862093	2.44991225410016	-1.78496230821000
Cl	1.38172602436108	2.01504925091532	3.30884728107056
Cl	1.94830294360490	2.63641929482469	0.30874984585175
Cl	-1.52293323853873	1.19319814814178	4.20425249524038
C	-6.33799501311476	1.09172290705983	-1.10745740469902
C	-6.45175170431603	2.16001462049246	-0.22002186632584
C	-7.33792393628451	0.81692236342629	-2.01398598358059
C	-8.47332213764884	1.63458496923599	-2.03548068926263
C	-8.58877649590568	2.69973667922241	-1.14825148107960
C	-7.57067267513664	2.96386943342546	-0.22466310036290
Cl	-7.68264662692107	4.23925891071135	0.90945524855133
Cl	-9.72436582246133	1.30458608379472	-3.15638755049507

SUPPORTING INFORMATION

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Cl	-7.16375395347258	-0.51849149825296	-3.07104008385659
O	-3.40342875884522	-0.85647255640489	0.21174785031079
C	-4.21909898055914	-1.93370323122128	0.65387063870593
H	-3.60167318827293	-2.80797744903976	0.87453092472228
H	-4.94307053554481	-2.19229919719255	-0.12367313089417
C	-4.90148462746051	-1.46368775093451	1.90813557205151
C	-2.54101072677738	-1.18287766394306	-0.90424434448705
C	-1.14634959774807	-1.48138219562416	-0.38232896187405
H	-2.52188778010458	-0.33210931351715	-1.57964187216532
H	-2.96535879936630	-2.03225632029350	-1.44445823591388
H	-5.66860916143216	-2.18185705361036	2.21032513527199
O	-5.50601014536257	-0.21241889012305	1.60443156869699
H	-4.18688248154569	-1.34096685321411	2.72798627072192
C	-6.15574644183538	0.36288041740816	2.74962947095378
H	-6.92230473620194	-0.33037136453685	3.09724762175839
H	-5.43180684313837	0.55408607108184	3.54196432054634
H	-6.61980107605759	1.29530953493763	2.45008135664027
O	-0.35442664185361	-1.73439122537486	-1.50195728972435
H	-1.15418197924426	-2.33862635903200	0.30969312245381
H	-0.78320692206787	-0.61694332236550	0.18778679211090
C	1.01538032807577	-1.52607928280567	-1.28011292370433
H	1.22907351749177	-0.49165126562180	-0.98492753314209
H	1.53432640480519	-1.73139512813839	-2.21464131898248
H	1.41876927421931	-2.19193647910770	-0.50790675806048

Si(amp)² E = -3254.84887280253



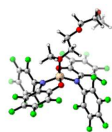
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C	0.35176183693133	-0.51636473106346	1.38130743109099
C	-1.72644321908833	-1.76102840854497	2.77006707848131
C	-1.98333294944095	-1.00779126537151	1.64569479756127
C	-0.94872178897822	-0.39069242911506	0.94004757290408
F	1.86467090340377	-1.40002680298796	2.94121704247515
F	1.35578178634662	0.08176790916644	0.74320375831547
F	-0.13932875969674	-2.61415875398365	4.28154979229119
F	-2.71006877803573	-2.35420594301817	3.42829848861023
O	-3.22320946038070	-0.80185616167284	1.13601536783675
N	-1.44037244488058	0.32003525524909	-0.16090440325697
C	-0.61395853058146	0.77724049175823	-1.19727650395017
C	-0.30544287650859	2.12230003262431	-1.32238361359829
C	-0.09533326051002	-0.11796670853656	-2.12329800573830
C	0.49761384859797	2.57184274164456	-2.35442720148831
F	-0.77567270194517	2.98535697374337	-0.43361895066338
C	1.01447843022423	1.66218891451689	-3.26216507552944
F	0.78405347037907	3.85817807062905	-2.47524791246212
C	0.72013115476500	0.31247916096212	-3.15205008500374
F	1.79848474542933	2.08672607696999	-4.23617223285044
F	1.21302041543079	-0.54788505604753	-4.02866944810678
F	-0.38332832780957	-1.40419950701424	-2.00284482170247
F	-7.18927793366834	0.51115792934290	-4.77549979750132
F	-7.67391695694189	2.80310391019868	-3.42317000727810
C	-6.48397468614396	0.80040784847258	-3.69031932077902
C	-6.73634812324182	1.96910765353861	-2.99572931561433

SUPPORTING INFORMATION

F	-5.24983226167002	-1.18643970622478	-3.92547726252604
C	-5.49458602136257	-0.07178715737940	-3.25415365754563
C	-6.01337757045146	2.28316074463984	-1.85318167234568
F	-6.30528237917344	3.40032523703589	-1.19085313630333
C	-4.77196069236333	0.24905305653547	-2.12601592122530
C	-5.01091927686579	1.43510663350464	-1.42705567316924
F	-4.68884856234888	1.56086242911129	2.35920309949900
O	-3.79563787667434	-0.53433797050843	-1.60283674251397
N	-4.14845216052606	1.55888299781657	-0.32992657079171
Si	-3.15665445550291	0.14324309646506	-0.22858243653310
C	-4.32728035409403	2.70315552933538	1.79441247155601
C	-4.04623032658715	2.72823100560460	0.43662822720541
F	-4.49105455001968	3.80393798868651	3.86437045181334
C	-4.22801354177706	3.84615588384455	2.56781997726946
C	-3.65701860305403	3.93291024769444	-0.13535582043209
C	-3.86800349148131	5.04159611285503	1.97183126319128
F	-3.37488763583141	3.97155279783218	-1.42949476678186
C	-3.58091854276998	5.08817250666705	0.61678757845798
F	-3.79317498174841	6.14458869373909	2.69584970706366
F	-3.22904110283268	6.23689373404778	0.06143165755521

mono-diglyme- Si(amp)^F₂

E = -3716,54983595682



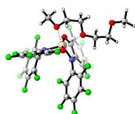
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C	-0.02626727941061	-0.40632020293072	0.29176349295606
F	3.22785081509382	-0.90690112008063	1.75416763649590
F	2.12747875146823	-0.52035756442148	-0.67640776472951
F	1.67458962038378	-1.05312855325821	3.96325689650082
F	-1.01669848748765	-0.77120746841387	3.76523718661787
O	-2.13249288479271	-0.35320286986428	1.20391777759125
N	-0.81894780632521	-0.26673716913513	-0.84126206455021
C	-0.27068653149180	0.15594252331897	-2.06104086868729
C	0.06510162209590	1.48884320585812	-2.23743634279974
C	-0.09814426500757	-0.71580352873170	-3.12298410313912
C	0.55581293277549	1.95458096749645	-3.44220238229467
F	-0.11006381933705	2.32896737428846	-1.22655180473577
C	0.71134249006262	1.06935307526290	-4.49485341548097
F	0.86025906755230	3.23413939812677	-3.60032792945228
C	0.38183327472816	-0.26707292298026	-4.33924970030945
F	1.17075219484096	1.50146552761042	-5.65756978881857
F	0.53047501948368	-1.10007636581299	-5.35939174107720
F	-0.41044647138977	-1.99716884802674	-2.97518948920539
F	-6.13534649772679	1.61687374413218	-5.13911697662425
F	-7.29572505023257	2.84826649633989	-3.02884867323439
C	-5.62980311669117	1.46032558487491	-3.92119037955116
C	-6.21930583782712	2.09249685073734	-2.84178283709411
F	-3.94630530252166	0.04055302993370	-4.76420908951039
C	-4.51587757986370	0.65384655730955	-3.73199357247243
C	-5.70557433437789	1.93332332538928	-1.56001797196610
F	-6.31203784254268	2.54790987910632	-0.54384902766355
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SUPPORTING INFORMATION

C	-4.59270138525035	1.13776749295574	-1.36570094914143
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N	-3.91171106046855	0.80719678886931	-0.19413145877417
Si	-2.55031008863221	-0.28315869616647	-0.47506683643550
C	-4.84824341009494	0.86980024814179	2.04374345204927
C	-4.18087772635976	1.48969689806829	1.00028795534286
F	-5.75970346878514	0.93831906971834	4.21121322754747
C	-5.12287042535517	1.54474359977800	3.21847074572965
C	-3.78520481113012	2.80935735767838	1.16092376414905
C	-4.73744274380653	2.86840554266896	3.35067727511129
F	-3.14024856573412	3.41395336774658	0.17306561846531
C	-4.06316521152574	3.50488286392358	2.32191710969078
F	-5.01385464183834	3.52904347152639	4.46307768919921
F	-3.68926481123654	4.76890819467601	2.45732753328805
O	-3.15550136692425	-2.06102233653683	-0.35844683104329
C	-4.41577510219118	-2.45534176389850	-0.93063280491105
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H	-4.79203521483619	-3.31453251273270	-0.37930591951980
H	-4.29001488052272	-2.70032701090016	-1.98361006116266
C	-2.22588851515404	-3.14498986757644	-0.10145232767514
C	-2.36905612663905	-3.67339314944438	1.31506423452435
H	-1.21975915870212	-2.76656779156905	-0.27064435969908
H	-2.40875208227772	-3.92359494211680	-0.84443001097861
O	-1.39885186761117	-4.67120039929476	1.42442132776130
H	-3.37905797280977	-4.06696162670287	1.49665041504398
H	-2.20982135138785	-2.86047200658503	2.03123827672016
C	-0.81386038035289	-4.81088285898389	2.69882229937432
C	0.40182622678766	-5.71537813672421	2.53986881392565
H	-1.51620605375613	-5.24842177987595	3.41925997363117
H	-0.51620065531728	-3.82864637305211	3.09102385049785
O	1.08795811139309	-5.89076930646859	3.74459541692765
H	1.05284006739457	-5.30560573192546	1.75420648543401
H	0.07570111862890	-6.70305867754863	2.20574877236994
C	1.97532151999157	-4.85386542891301	4.06550988521977
H	2.73555605879324	-4.70867473119140	3.28767662004797
H	2.48228297952232	-5.13142490591420	4.98823985815186
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bi-diglyme- Si(amp)^F₂

E = -3716,55825091709



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C	-1.39923444797233	-0.48251641439031	2.52478401688306
C	-0.45832546445101	0.02892302225276	1.62462313224010
F	1.95532766570314	1.34518176388096	3.96053364526046
F	1.64157347770920	1.07679123382921	1.30794518580513
F	0.10978839876739	0.37011785802580	5.68219300151096
F	-2.11352175865531	-0.87649664163202	4.73174322165185
O	-2.45692900176099	-1.07712378918320	1.96032776482575
N	-0.83550590530149	-0.22717440303799	0.31252700391124
C	-0.21416812426367	0.41005252332802	-0.76592630304746
C	-0.11825127700449	1.79629090534867	-0.82363106478420

SUPPORTING INFORMATION

C	0.3329464449404	-0.30719295466409	-1.82408708991326
C	0.47401379777590	2.45108487683890	-1.88347993790665
F	-0.59091827660498	2.51764961195795	0.18671665492352
C	0.98084785845101	1.71454501901573	-2.93834597928393
F	0.55258839672277	3.77350393653479	-1.89677692298732
C	0.90260920629773	0.3389562159532	-2.91069998084337
F	1.55091682809015	2.32781363513193	-3.96422610395350
F	1.40463741153098	-0.36913525755591	-3.91731456767832
F	0.34561016519243	-1.63378288136219	-1.79705166054032
F	-5.42343986657731	-1.27050920630861	-5.08465365910184
F	-6.73926107904212	0.73522868256333	-3.83188788185594
C	-5.01884677755278	-0.85934417692791	-3.88730618782269
C	-5.69873439958718	0.15648904332903	-3.24147380182879
F	-3.28090166449749	-2.44612390428224	-3.90545024236521
C	-3.92044802974532	-1.45800884218418	-3.28352330813686
C	-5.30752426399265	0.56321399969742	-1.97387111540633
F	-5.99730212045807	1.51945747265178	-1.35091129471285
C	-3.50246368620469	-1.01570167249843	-2.04628720334908
C	-4.20587832142710	-0.01250587068148	-1.37379201224607
F	-4.53790412739970	0.78342008703855	2.52898420775817
O	-2.43993979162358	-1.51237317276925	-1.39205689571944
N	-3.68719629473697	0.22593638358258	-0.10419106810540
Si	-2.44298046725091	-1.03845655821776	0.25125172118473
C	-4.12650180908483	1.76993317531773	1.74028919842319
C	-3.72814444211468	1.51671728234262	0.43179366251415
F	-4.50364862084363	3.24361646777844	3.52643606725034
C	-4.13367601639703	3.04934578289875	2.26756416887469
C	-3.37169378786278	2.62548965954416	-0.33352371467014
C	-3.78885015786891	4.12740123472774	1.47545192277523
F	-2.95787245581290	2.44803661230902	-1.58552081518963
C	-3.41437825507583	3.91204554059740	0.16153305581393
F	-3.81637470673964	5.35458190515584	1.97134213556721
F	-3.07094042537324	4.93304709182761	-0.60959630785193
O	-3.93941387697991	-2.40958661639432	0.41535813520020
C	-4.96282231275583	-2.31046203543683	1.41195545381845
H	-4.64022267866196	-2.74729906763614	2.35701908239510
H	-5.85374069733504	-2.81934326568826	1.04375135358927
H	-5.18539887738743	-1.26111923007923	1.55499032060442
C	-3.58277900869506	-3.74752450821551	0.05501947458027
C	-2.30980143645068	-4.11885044594024	0.76409855698571
H	-3.45742527575133	-3.77965311464200	-1.02692174780740
H	-4.39207255936403	-4.42734069289053	0.32684470264166
O	-1.38179605668921	-3.09204626062976	0.46371494979003
H	-1.96066078801975	-5.08922668132542	0.40919896844783
H	-2.45948209338026	-4.19151234625302	1.84857652145815
C	-0.10865231583498	-3.23006578282100	1.09132982540291
C	0.75241645123761	-4.32304047905291	0.50142146625590
H	-0.23422645598966	-3.37927396947782	2.16979570626043
H	0.40433235399013	-2.28517196107587	0.93702199544400
O	0.31953235305398	-5.58493222175064	0.92846628933412
H	1.78548865518545	-4.13442375463660	0.83187902659297
H	0.75103755258062	-4.24065334551945	-0.59465204951800
C	1.10865606947738	-6.63159048181606	0.43259865736736
H	1.09839514399660	-6.67652131736537	-0.66339641995934
H	0.70528867640981	-7.56600594878545	0.81937514314130
H	2.15321170302881	-6.54740868796998	0.75644080825407

SUPPORTING INFORMATION

3. Detailed Reaction Profiles of Other Substrates

3.1 Possible ELC for the Degradation of 18-crown-6

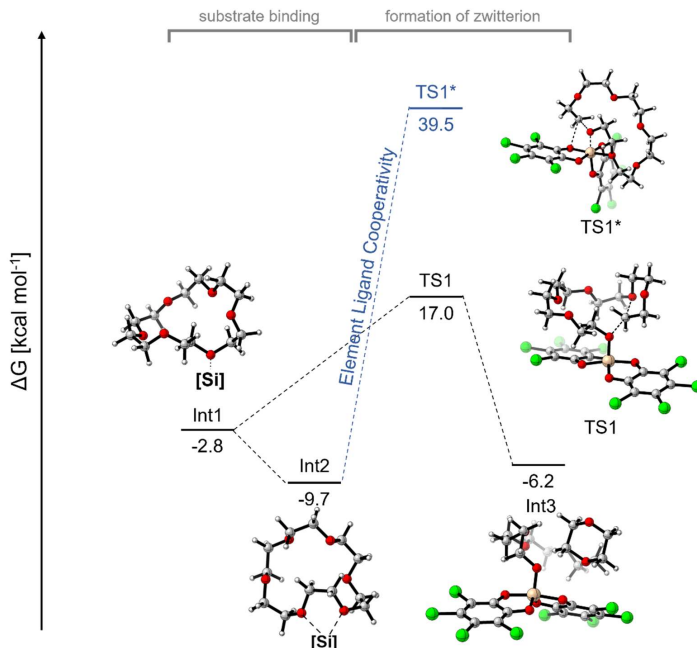


Figure S 7: Detailed section of the first nucleophilic attack in the reaction profile of the degradation of 18-crown-6 by 1 calculated at the DSDBLYP(D3BJ)/def2-QZVPP+SMD(DCM)/r²SCAN-3c level with possible intermediates and transition states. The transition state which incorporates ELC (TS1*) is marked blue

3.2 RCM in Diglyme

Analog to the reaction of 18-crown-6, the first step of this RCM reaction is the coordination of the ether to 1. However, in this case the formation of the mono-adduct is slightly endergonic, while the formation of the *cis*-adduct is again significantly energetically favoured ($\Delta G^\circ = -9.9$ kcal/mol). An intramolecular nucleophilic attack is possible for both adducts, but first configuration isomers with increased thermodynamic stability (Int2_{mono/cis}) form via rotation of a C-C bond in the bound ether. The intramolecular nucleophilic attack in the *cis*-adduct has an energy barrier of 29.4 kcal/mol, which is comparable to the activation energy in the reaction of 18-crown-6. As for the crown-ether, the activation energy for the nucleophilic attack in the mono-adduct is significantly lower (21.6 kcal/mol). This can again be explained by an increased Lewis acidity of the silicon center and a diminished energy penalty for distortion of the ether. Unlike in the reaction of a cyclic polyether, the nucleophilic attack does not result in one zwitterion, but in the negatively charged adduct [1-OMe]⁻ and an oxonium ion (Int3). The missing preorganization of the two molecules results in an increased activation energy for the final S_N2 reaction (28.1 kcal/mol) via TS3 that liberates 1,4-dioxane. Interestingly, the formation of a Lewis adduct of 1 with a product of this reaction (dimethyl ether or dioxane) is not the driving force of the reaction, since it is energetically comparable to the *cis*-adduct Int2_{cis}. However, the fact that dimethyl ether constantly transitions into the gaseous phase probably drives the reaction towards completion.

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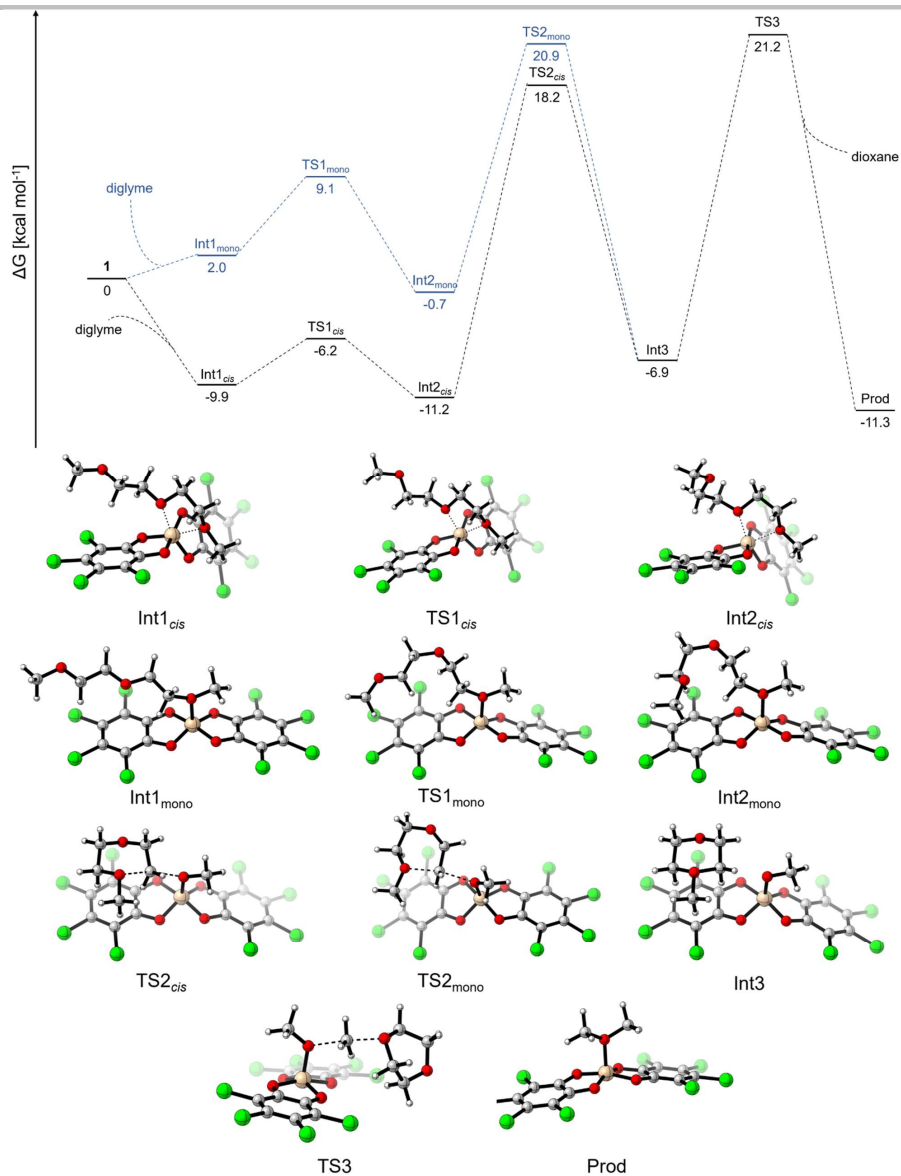


Figure S 8: Reaction profile of the degradation of diglyme by 1 calculated at the DSDBLYP(D3BJ)/def2-QZVPP+SMD(DCM)/r²SCAN-3c level with possible intermediates and transition states.

SUPPORTING INFORMATION

3.3 RCM in Dibenzo-18-crown-6

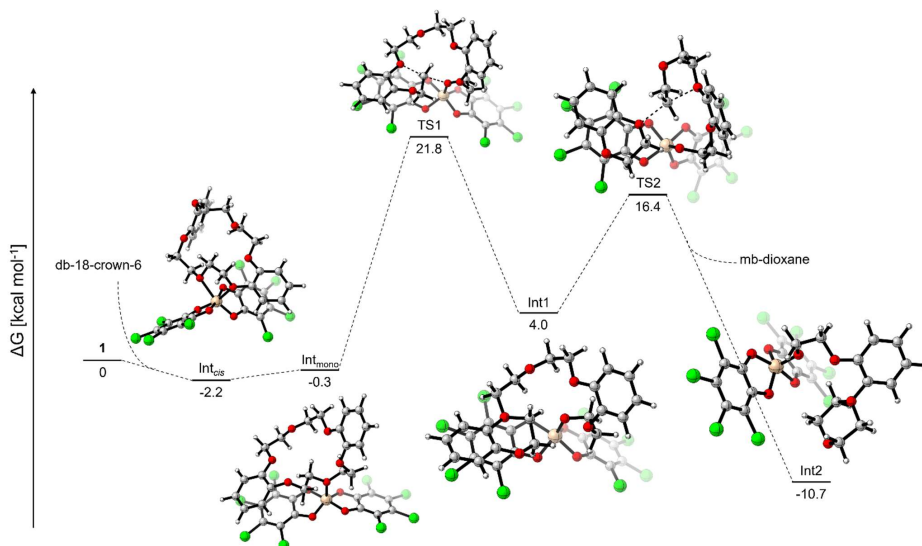


Figure S 9: Reaction profile of the degradation of dibenzo-18-crown-6 by 1 calculated at the DSDBLYP(D3BJ)/def2-QZVPP+SMD(DCM)/ r^2 SCAN-3c level with possible intermediates and transition states.

To shed light on the experimentally observed distinguished reactivity of different crown ethers, the degradation pathway of db-18-crown-6 was computed. Two factors were found decisive here: 1) The formation of the *cis*-adduct 1-(db-18-crown-6) is only favored by $\Delta G_{\text{sol}} = -2.2 \text{ kcal/mol}$, therefore lacking a significant thermodynamic driving force for the initial depolymerization of [1]_n. 2) After two nucleophilic attacks and the liberation of 2,3-dihydrobenzo[b][1,4]dioxine, the resulting zwitterionic intermediate Int2 (see Figure X) cannot undergo further reaction due to the impossibility of an $\text{S}_{\text{N}}2$ reaction at the aromatic position, and therefore presents a dead end to the reaction (pronounced product inhibition).

SUPPORTING INFORMATION

4. X-Ray Diffraction

Suitable crystals for single-crystal structure determination were obtained by gas phase diffusion of pentane in a saturated solution of 1-(dioxane)₂ in 1,4-dioxane at -40°C and by gas phase diffusion of pentane into a reaction mixture of the RCM (catalyzed by [1]_n) of 18-crown-6 in CD₂Cl₂ at -40°C. Suitable crystals of (2*R*,5*S*)-2,5-dimethyl-1,4-dioxane*cat^{CH}H)₂ were grown by gas phase diffusion of pentane into the reaction mixture of the RCM in PPG DME at -40°C (catalyzed by [1]_n in DCM).

The crystals for SCXRD were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperatures with a Nonius-Kappa charge-coupled device diffractometer (graphite-monochromated Mo-K_α radiation, temperature 120 K) for 1-(dioxane)₂ or a dual source Bruker D8 Venture diffractometer (Mo-K_α radiation, microfocus X-ray tube, Photon III detector, temperature 100 K) for (2*R*,5*S*)-2,5-dimethyl-1,4-dioxane*cat^{CH}H). Data were processed with the standard Nonius software^[17] or Bruker (SAINT, APEX3) software package.^[18] Multiscan absorption correction was applied using the SADABS program.^[19] The structures were solved by intrinsic phasing^[20] and refined using the SHELXTL software package (Version 2014/6 and 2018/3).^[21] Graphical handling of the structural data during solution and refinement was performed with Olex2^[22] and the CIF file was generated using FinalCif.^[23] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model.

For data visualization, Mercury 2020.3.0 was used.^[24] The thermal displacement ellipsoids are shown at the probability level of 50 %. CCDC numbers 2143420 and 2183835 contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>.

SUPPORTING INFORMATION

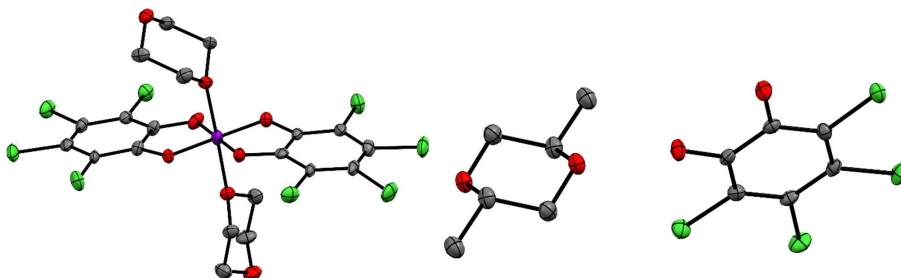


Table S 2: Collected data for the crystal structures of 1-(1,4-dioxane)₂ x 2 1,4-dioxane and (2*R*,5*S*)-2,5-dimethyl-1,4-dioxane*(cat²H)₂. Solvent molecules, hydrogen atoms and s second unit of cat²H were omitted for clarity.

CCDC number	2143420	2183835
Empirical formula	C ₂₈ H ₃₂ Cl ₆ O ₁₂ Si	C ₁₈ H ₁₈ Cl ₆ O ₆
Formula weight	872.22	611.91
Temperature [K]	120(2)	100.00
Crystal system	monoclinic	triclinic
Space group (number)	<i>Pn</i> (7)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	13.7633(16)	7.4105(10)
<i>b</i> [Å]	9.3063(11)	8.1562(10)
<i>c</i> [Å]	13.7809(16)	10.0111(13)
α [°]	90	93.331(5)
β [°]	91.516(5)	91.089(6)
γ [°]	90	104.176(5)
Volume [Å ³]	1764.5(4)	585.32(13)
<i>Z</i>	2	1
ρ_{calc} [gcm ⁻³]	1.642	1.736
μ [mm ⁻¹]	0.733	0.997
<i>F</i> (000)	892	308
Crystal size [mm ³]	0.15×0.12×0.10	0.206×0.184×0.097
Crystal color	colorless	colorless
Crystal shape	block	block
Radiation	Mo- <i>K</i> α (λ =0.71073 Å)	Mo- <i>K</i> α (λ =0.71073 Å)
2 θ range [°]	4.24 to 61.05 (0.70 Å)	5.16 to 53.66 (0.79 Å)
Index ranges	-19 ≤ <i>h</i> ≤ 19 -13 ≤ <i>k</i> ≤ 13 -19 ≤ <i>l</i> ≤ 19	-9 ≤ <i>h</i> ≤ 9 -10 ≤ <i>k</i> ≤ 10 -12 ≤ <i>l</i> ≤ 12
Reflections collected	64567	24853
Independent reflections	10766 <i>R</i> _{int} = 0.0554 <i>R</i> _{sigma} = 0.0400	2414 <i>R</i> _{int} = 0.0443 <i>R</i> _{sigma} = 0.0228
Completeness to θ = 25.242°	99.9 %	96.7 %
Data / Restraints / Parameters	10766/2/443	2414/0/148
Goodness-of-fit on <i>F</i> ²	1.079	1.103
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0526 <i>wR</i> ₂ = 0.1296	<i>R</i> ₁ = 0.0390 <i>wR</i> ₂ = 0.0956
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0621 <i>wR</i> ₂ = 0.1399	<i>R</i> ₁ = 0.0455 <i>wR</i> ₂ = 0.0990
Largest peak/hole [eÅ ⁻³]	0.98/-0.65	0.50/-0.36

SUPPORTING INFORMATION

5. NMR Spectra

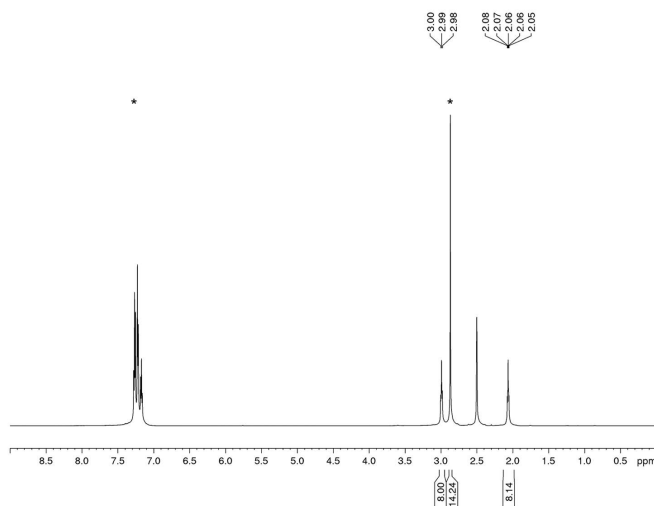


Figure S 10: ¹H NMR spectrum (600 MHz) of Ge(cat^C)₂-(sulfolane)₂ in (CD₃)₂SO at 295 K, containing 3.78 equivalents of 1,2-diphenylethane (marked *).

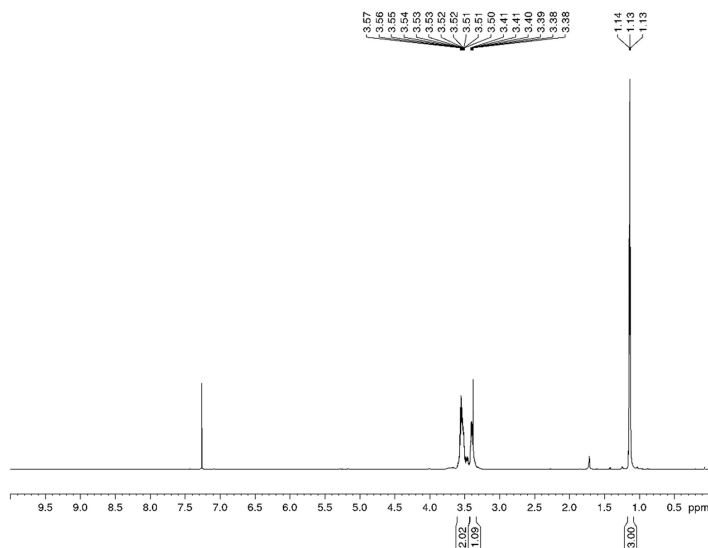
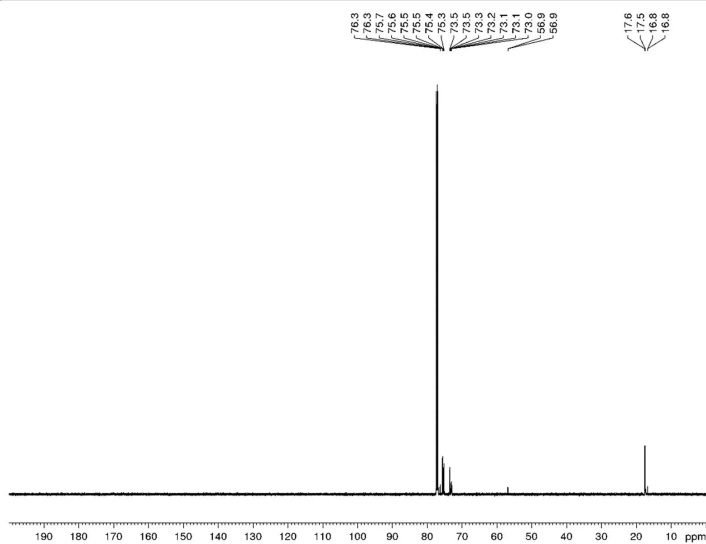
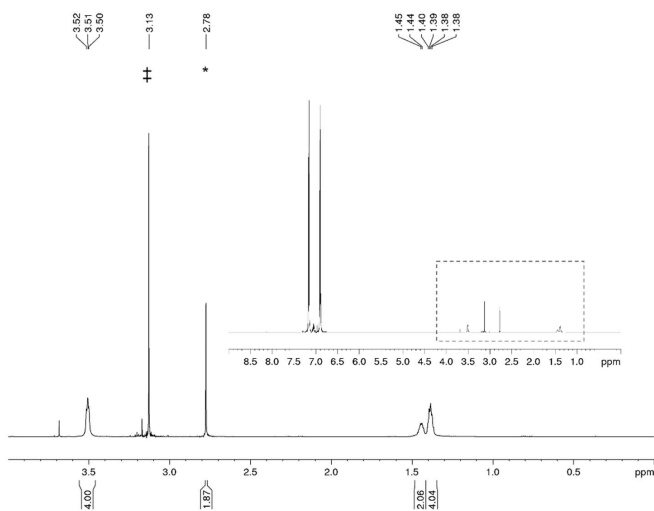


Figure S 11: ¹H NMR spectrum (600 MHz) of PPG-DME (*M_w* ~ 2021 g/mol) in CDCl₃ at 295 K.

SUPPORTING INFORMATION

Figure S 12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of PPG-DME in CDCl_3 at 295 K.Figure S 13: ^1H NMR spectrum (600 MHz) of the RCM of 1,5-dimethoxypentane to tetrahydropyran and dimethyl ether (‡) in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K, containing 0.48 equivalents of 1,2-diphenylethane (marked *).

SUPPORTING INFORMATION

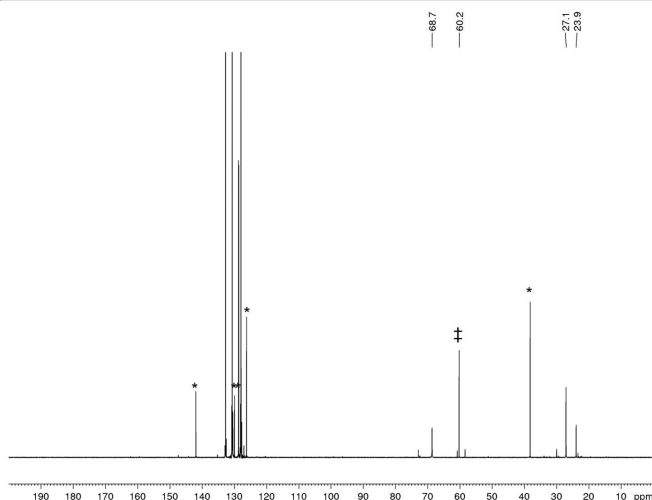


Figure S 14: ^{13}C NMR spectrum (151 MHz) of the RCM in 1,5-dimethoxypentane to tetrahydropyran and dimethyl ether (†) in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K, containing 0.48 equivalents of 1,2-diphenylethane (marked *). Minor signals can be assigned to traces of unconsumed starting material.

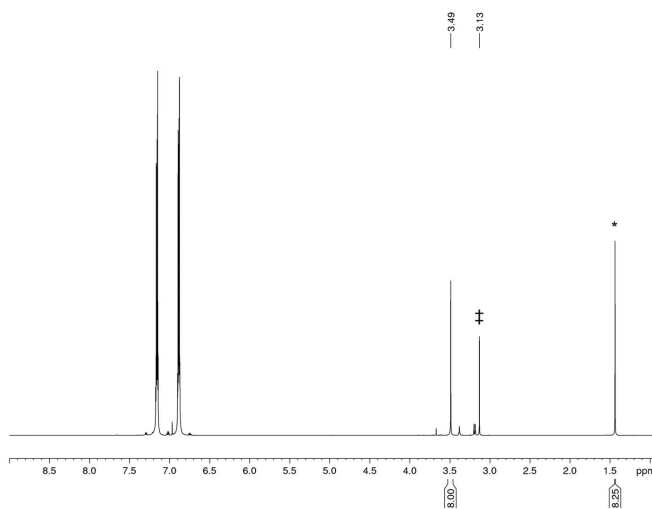


Figure S 15: ^1H NMR spectrum (600 MHz) of the RCM in diglyme to 1,4-dioxane and dimethyl ether (†), catalyzed by [1]₀ in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K, containing 0.5 equivalents of cyclooctane (marked *). Minor signals in the aliphatic region can be assigned to residual diglyme and dimethoxyethane (side-product).

SUPPORTING INFORMATION

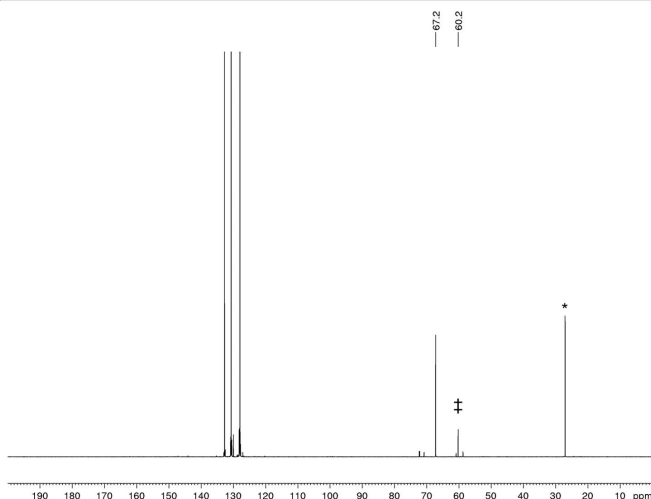


Figure S 16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in diglyme to 1,4-dioxane and dimethyl ether (‡) in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K, containing 0.5 equivalents of cyclooctane (marked *). Minor signals in the aliphatic region can be assigned to residual diglyme and dimethoxyethane (side-product).

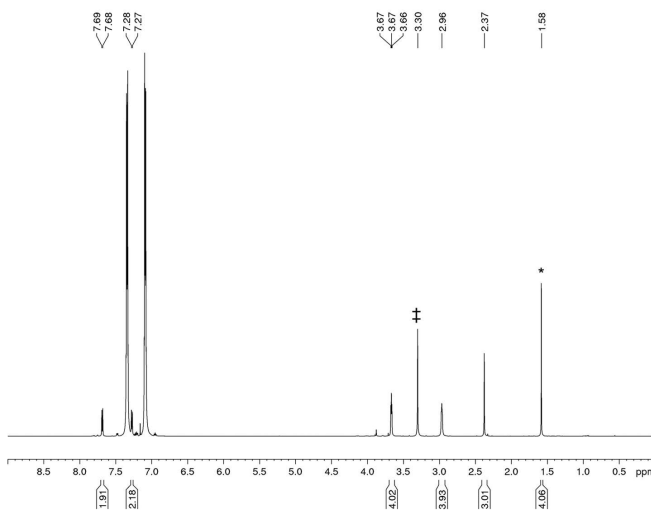


Figure S 17: ^1H NMR spectrum (600 MHz) of the RCM in N,N -bis(2-methoxyethyl)-4-methylbenzenesulfonamide to 4-tosyl-morpholine and dimethyl ether (‡), catalyzed by $[1]_o$ in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K, containing 0.25 equivalents of cyclooctane (marked *).

SUPPORTING INFORMATION

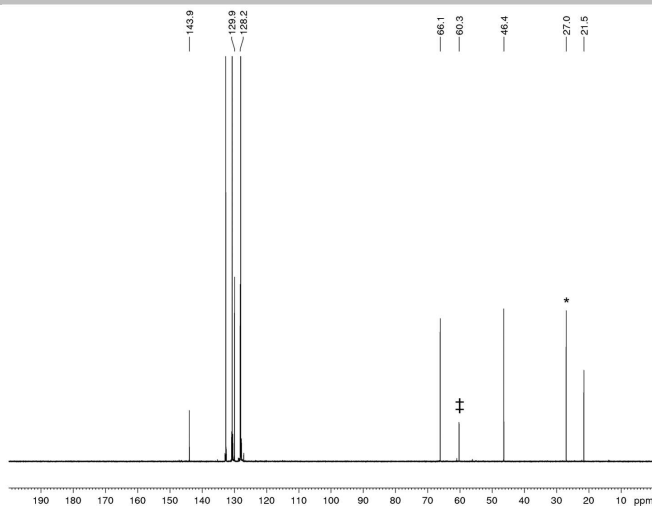


Figure S 18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in *N,N*-bis(2-methoxyethyl)-4-methylbenzenesulfonamide to 4-tosyl-morpholine and dimethyl ether (‡), catalyzed by [1]_o in oDCB:CD₆ (50:1) at 295 K, containing 0.25 equivalents of cyclooctane (marked *).

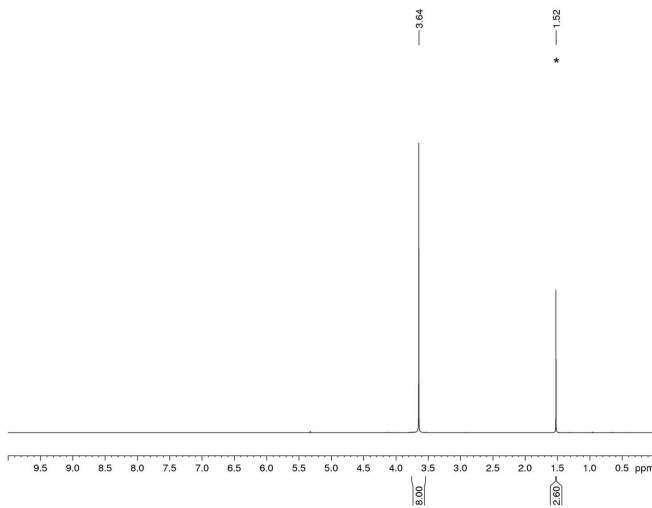


Figure S 19: ^1H NMR spectrum (600 MHz) of the RCM in 18-crown-6 to 1,4-dioxane in CD₂Cl₂ at 295 K, containing 0.5 equivalents of cyclooctane (marked *).

SUPPORTING INFORMATION

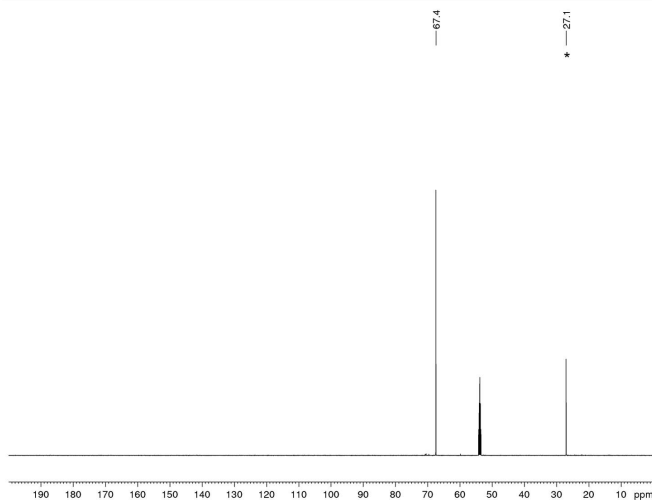


Figure S 20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in 18-crown-6 to 1,4-dioxane in CD_2Cl_2 at 295 K, containing 0.5 equivalents of cyclooctane (marked *).

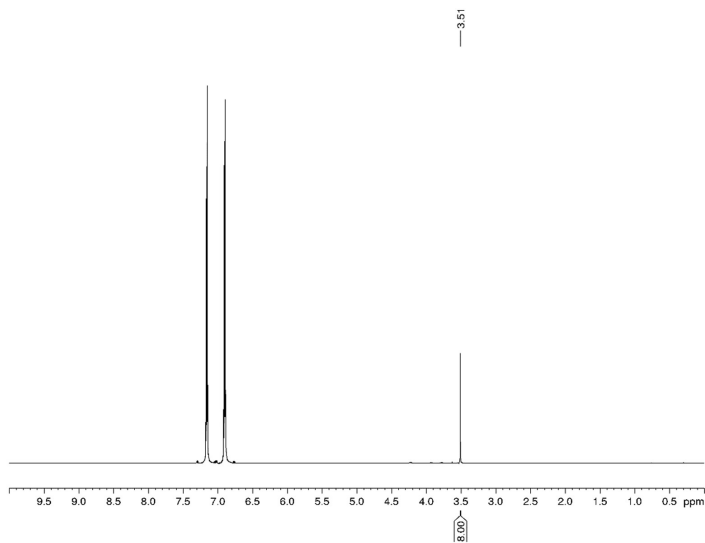


Figure S 21: ^1H NMR spectrum (600 MHz) of the RCM in 15-crown-5 to 1,4-dioxane in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

SUPPORTING INFORMATION

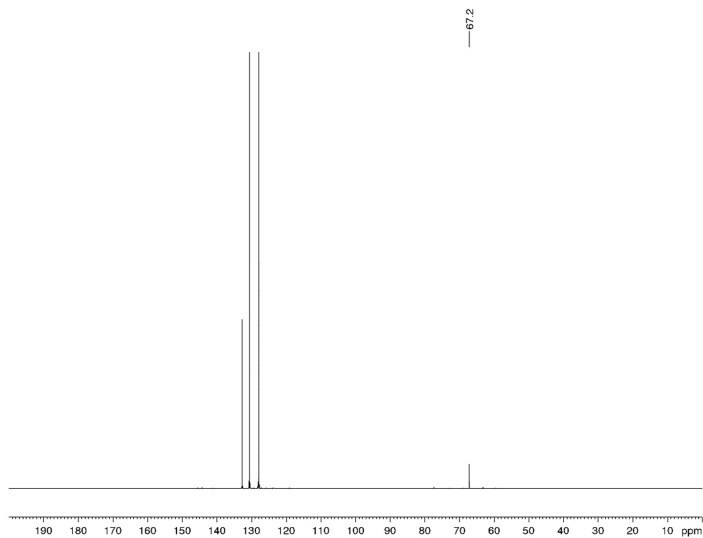


Figure S 22: ^{13}C NMR spectrum (151 MHz) of the RCM in 15-crown-5 to 1,4-dioxane in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

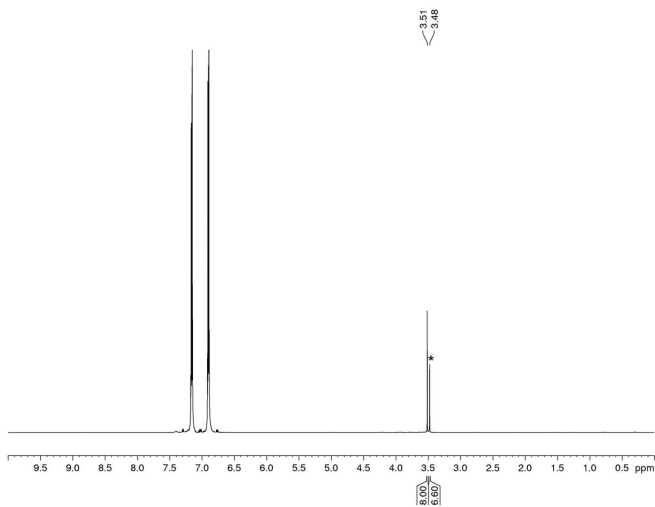


Figure S 23: ^1H NMR spectrum (600 MHz) of the RCM in 12-crown-4 (marked *) to 1,4-dioxane in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

SUPPORTING INFORMATION

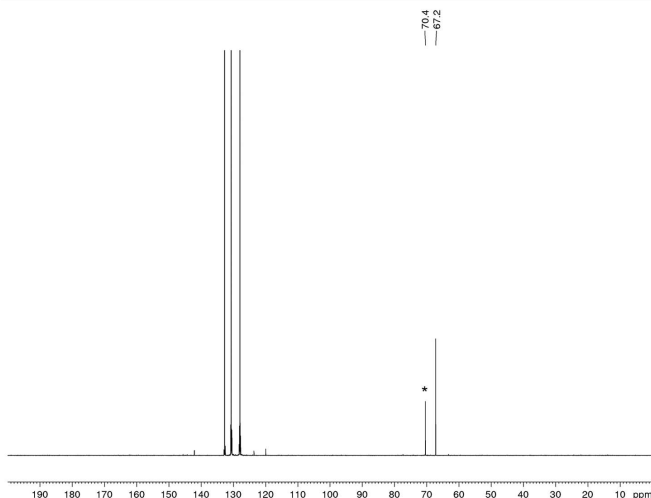


Figure S 24: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in 12-crown-4 (marked *) to 1,4-dioxane in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

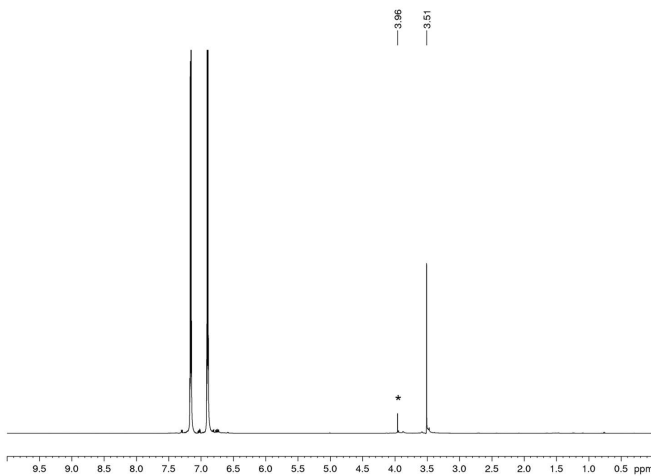


Figure S 25: ^1H NMR spectrum (600 MHz) of the RCM in monobenzo-18-crown-6 to 1,4-dioxane and 2,3-dihydrobenzo[*b*][1,4]dioxine (marked *) in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

SUPPORTING INFORMATION

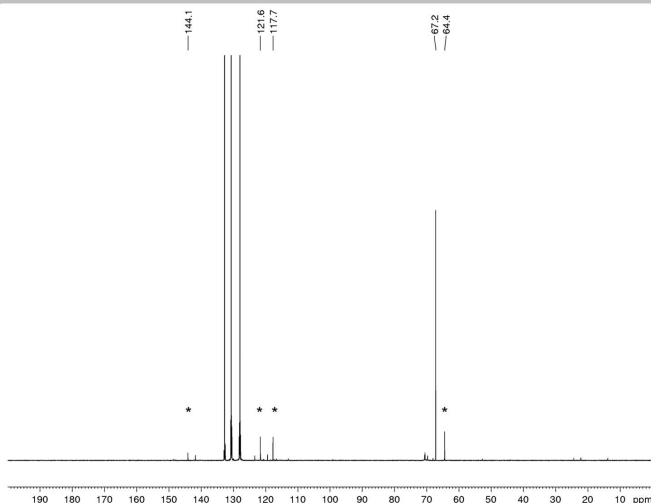


Figure S 26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in monobenzo-18-crown-6 to 1,4-dioxane and 2,3-dihydrobenzo[b][1,4]dioxine (marked *) in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K. Minor signals can be assigned to traces of unconsumed starting material.

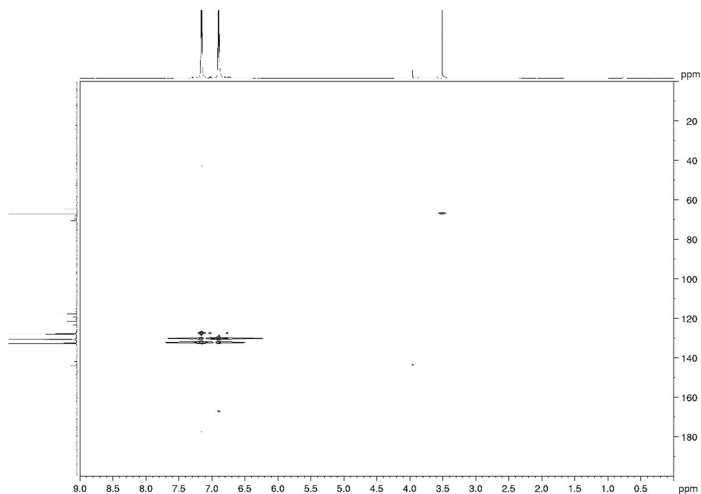


Figure S 27: $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ HMBC NMR spectrum (600 / 151 MHz) of the RCM in monobenzo-18-crown-6 to 1,4-dioxane and 2,3-dihydrobenzo[b][1,4]dioxine in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

SUPPORTING INFORMATION

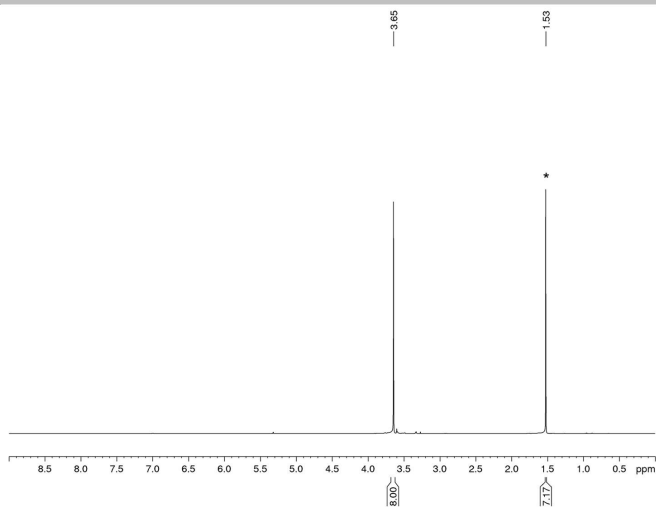


Figure S 28: ^1H NMR spectrum (600 MHz) of the RCM in PEG-DME to 1,4-dioxane in CD_2Cl_2 at 295 K, containing 0.44 equivalents of cyclooctane (marked *).

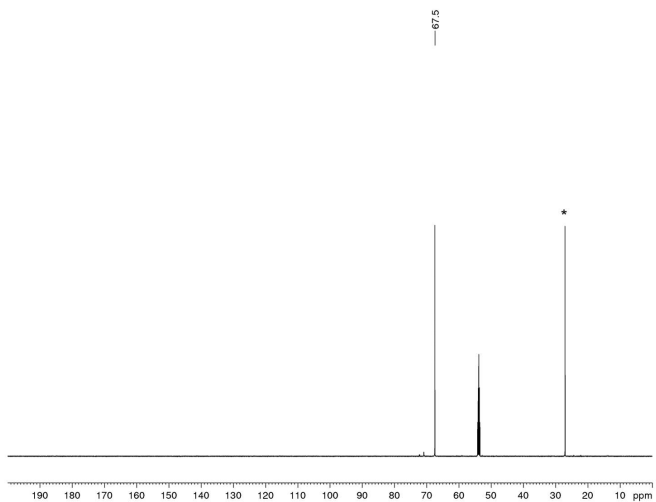


Figure S 29: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in PEG DME to 1,4-dioxane in CD_2Cl_2 at 295 K, containing 0.44 equivalents of cyclooctane (marked *).

SUPPORTING INFORMATION

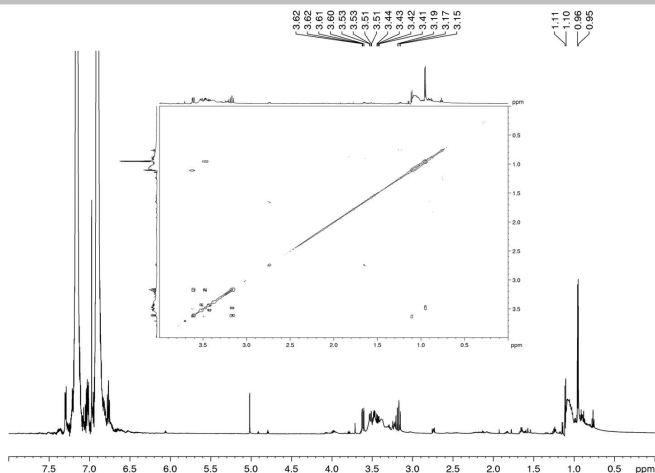


Figure S 30: ^1H NMR spectrum (600 MHz) of the RCM in PPG DME to 2,5-dimethyl-1,4-dioxane (mixture of diastereomers) in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K and the aliphatic section from the respective COSY spectrum. Broad signals in the spectrum are caused by unconsumed starting material and limit the integration of the NMR data.

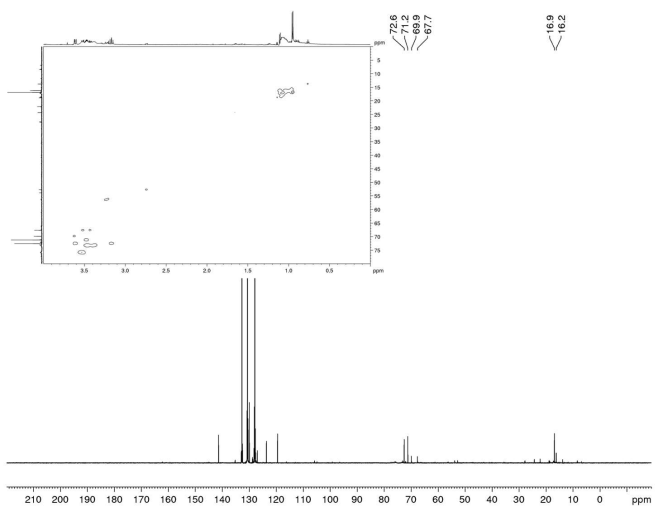


Figure S 31: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the RCM in PPG DME to 2,5-dimethyl-1,4-dioxane (mixture of diastereomers) in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K and the aliphatic section from the respective $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ HSQC spectrum. Additional peaks in the aliphatic section can be assigned to unconsumed starting material while the peaks in the aromatic section are caused by the perchlorocatecholato ligands in $\mathbf{1}$ -(2,5-dimethyl-1,4-dioxane) $_2$.

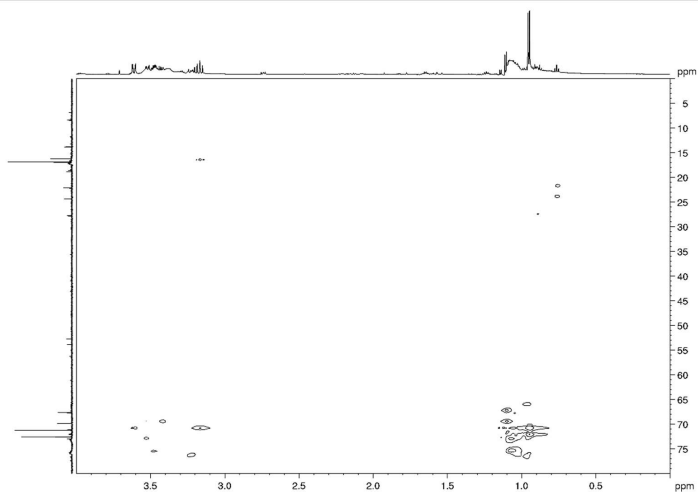


Figure S 32: Aliphatic region of the $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ HMBC NMR spectrum (600 / 151 MHz) of the RCM in PPG DME to 2,5-dimethyl-1,4-dioxane (mixture of diastereomers) in *o*DCB:CaD₆ (50:1) at 295 K.

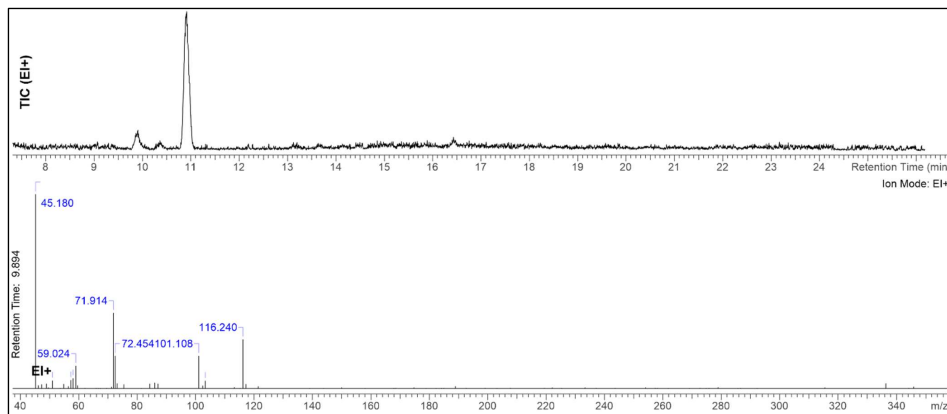


Figure S 33: GC MS diagram of the RCM in PPG DME to 2,5-dimethyl-1,4-dioxane (mixture of diastereomers) in CD_2Cl_2 . The peak with a retention time of 11 min can be assigned to cyclooctane, the internal standard.

SUPPORTING INFORMATION

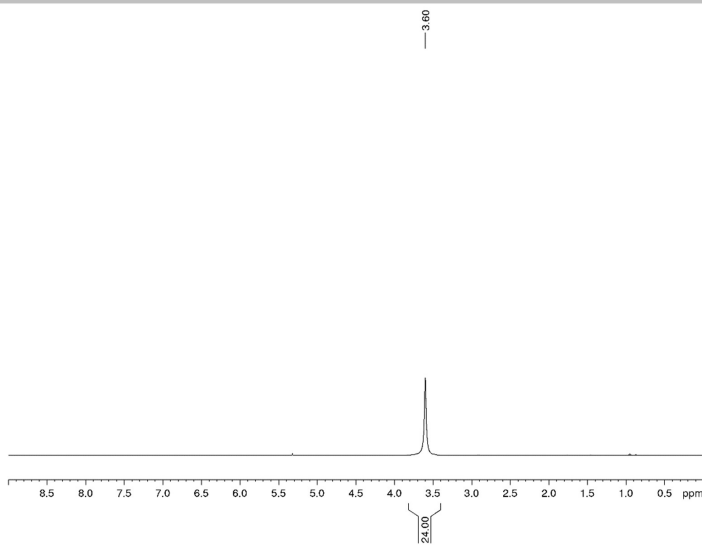


Figure S 34: ^1H NMR spectrum (600 MHz) of the *in-situ* monitored resting state of the RCM of 18-crown-6 (discussed in section 1.8) in CD_2Cl_2 at 295 K.

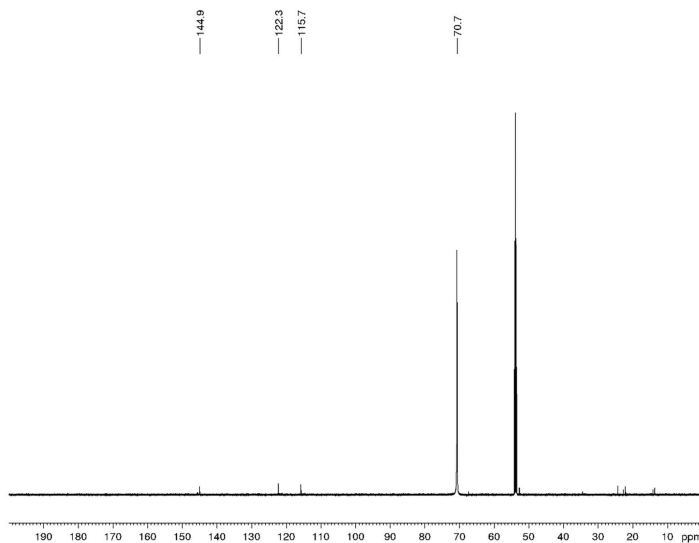


Figure S 35: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the *in-situ* monitored resting state of the RCM of 18-crown-6 (discussed in section 1.8) in CD_2Cl_2 at 295 K. Minor signals in the aliphatic section of the spectrum can be explained by traces of dibutyl sulfone, an impurity in the starting material

SUPPORTING INFORMATION

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3.2.2. SILICON CATALYZED DEPOLYMERIZATION OF POLYETHERS: PUSHING SCOPE, PRACTICABILITY AND MECHANISTIC UNDERSTANDING

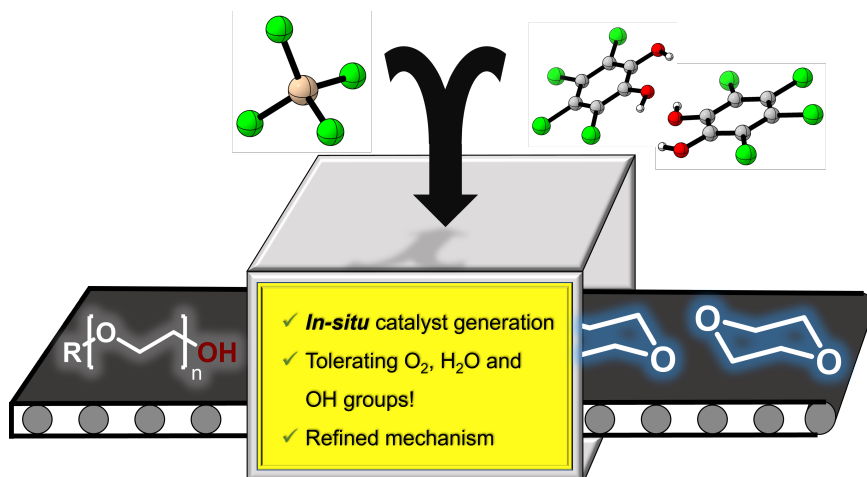


FIG. 3.2.: “Silicon Catalyzed Depolymerization of Polyethers: Pushing Scope, Practicability and Mechanistic Understanding” - table of contents figure for the publication discussed in the following section.

The full article including its electronic supplementary information (ESI) presented in this section was published earlier and can be accessed under:

N. Ansmann, K. Johann, P. Favresse, T. Johann, M. Fiedel, L. Greb, *ChemCatChem* **2024**, *16*, e202301615, <https://doi.org/10.1002/cctc.202301615>.

Contributions of the three leading authors are rationalized and listed according to the CRediT scheme^[300] on page 107, using the “Formblatt Kumulative Dissertation” (cumulative dissertation form), provided by the faculty of Geo- Sciences and Chemistry at the Ruprecht-Karls Universität Heidelberg. The original article is embedded at page 108 *ff*. The ESI is subsequently attached, starting at page 114.

Formblatt Kumulative Dissertation

1. Publikation/*Publication*:

Vollständige bibliographische Referenz/*Complete bibliographic reference*:

N. Ansmann, K. Johann, P. Favresse, T. Johann, M. Fiedel, L. Greb. Silicon-Catalyzed Depolymerization of Polyethers: Pushing Scope, Practicability and Mechanistic Understanding. ChemCatChem 2024, 16, e202301615. doi.org/10.1002/cctc.202301615

2. Erst- oder gleichberechtigte Autorenschaft/*First or equal authorship*: Ja/Yes ☒ Nein/No ☐

Veröffentlicht/*Published*

Zur Veröffentlichung angenommen/*Accepted*

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☐
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4. Beteiligungen/*Contributions***

Contributor Role	Doktorand/in/ <i>Doctoral Student</i>	Co-Autor/in 1/ <i>Co-author 1</i>	Co-Autor/in 2/ <i>Co-author 2</i>
Name, first name	Ansmann, Nils	Johann, Kerstin	Favresse, Philippe
Methodology	lead	-	-
Software	-	-	-
Validation	lead	-	-
Formal analysis	lead	-	-
Investigation	lead	supporting	supporting
Resources	-	supporting	equal
Data Curation	lead	-	-
Writing-Original Draft	equal	-	-
Writing-Review&Editing	equal	-	supporting
Visualization	lead	-	-
Supervision	equal	-	-
Project administration	equal	-	supporting
Funding acquisition	-	-	-

***Kategorien des CRediT (Contributor Roles Taxonomy, <https://credit.niso.org/>)*

Hiermit bestätige ich, dass alle obigen Angaben korrekt sind/*I confirm that all declarations made above are correct.*

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Prof. Dr. Lutz Greb

Name/*Name*


Unterschrift/*Signature*

04.07.25
Datum/*date*

Silicon-Catalyzed Depolymerization of Polyethers: Pushing Scope, Practicability and Mechanistic Understanding

Nils Ansmann,^[a] Kerstin Johann,^[b] Philippe Favresse,^[b] Tobias Johann,^[b] Michael Fiedel,^[b] and Lutz Greb*^[a]

The depolymerization of polyethers is a sustainable yet challenging opportunity for a circular economy in materials processing. While we recently identified silicon Lewis superacids as promising catalysts for this transformation, limited scope (e.g., terminal OH groups not tolerated) and strict requirements for anhydrous conditions hampered wider applicability. In the present work, the impact of different polyether structures and

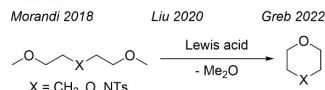
reaction conditions were evaluated. By doing so, the generality for structural variations was confirmed and substantial improvements made the depolymerization feasible for large-scale applications under ambient conditions. Based on systematic experimental screenings, a refined mechanistic model of the depolymerization process is developed.

Introduction

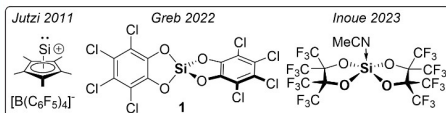
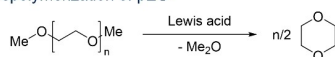
Metathesis of C(sp³)–X bonds gained increasing attention in past decades but is still much underdeveloped compared to metathesis reactions of other bonds.^[1] As commonly employed C–X bond activations by oxidative addition encounter obstacles from high reaction barriers and side reactions like β-hydride elimination, Lewis acid catalysis emerged as a powerful alternative for this type of transformation.^[2] Pioneering work by Enthaler *et al.* established transition metal based Lewis acids in the depolymerization of poly-THF, performing ring-closing metathesis (RCM) to yield the monomer THF under harsh conditions.^[3] The Morandi group broadened the substrate scope by using iron(III) triflate in the RCM of bis- and tris-ethers, which the Liu group extended by using ionic liquids as reaction media (Scheme 1a).^[4] However, these reports did not face the RCM of polyethylene oxide (pEO), a commodity polymer for which selective degradation would present a convenient entry into circular economy.^[5] Enthaler und Cantat presented original approaches for pEO depolymerization, but using stoichiometric amounts of interception agents, while Jutzi was able to catalyze the C–O bond metathesis of short, methyl end-capped oligoethers with the low-valent Lewis acidic Cp⁺Si(III)⁺ cation (Scheme 1b).^[6]

The Lewis acidity of bis(catecholato)silanes has gained importance in the field of catalysis during the past years, which lead us to probe bis(perchlorocatecholato)silane **1** in its oligomeric form [1]_n as a C–O bond metathesis catalyst

a) RCM of Ethers

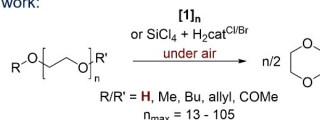


b) Depolymerization of pEO



- Limited scope
- Requires inert atmosphere
- Requires end-capped pEO

c) This work:



- ✓ Extended scope, tolerating air and OH
- ✓ *In-situ* catalyst formation
- ✓ Refined mechanism

Scheme 1. Previously reported Lewis acid catalyzed ring closing C–O metathesis reactions in a) bis- and tris-ethers and b) in methyl end-capped pEO under the exclusion of moisture and air. c) In various pEO with different chain lengths and end-capping groups under air, including an *in-situ* catalyst generation, as demonstrated in this work.

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(Scheme 1a).^[7] This system exhibited high yields in the depolymerization of pEO (Scheme 1b), and computational studies on model substrates allowed the postulation of a mechanism which confirmed preliminary experimental observations made by other groups. A low tendency of polydentate binding of substrates with >1 donor groups and a high Lewis acidity were identified as key signatures for successful catalysis. Based on this knowledge, we employed the latest example of a silicon-based Lewis superacid, bis(nonafluoro-*N*-phenylamidophenolato)silane in this reaction, which even catalyzed the cross-metathesis of ethers.^[8] More recently, the Inoue group successfully demonstrated bis(perfluoropinacolato)silane in the RCM of pEO, confirming our mechanistic model (Scheme 1b).^[9] However, all reported RCM reactions of pEO exhibited major problems that would render further applications, in particular on an industrial scale, as difficult.

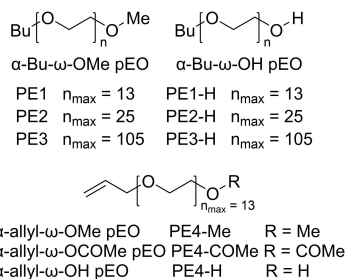
All hitherto employed catalysts are sensitive to moisture and air, which necessarily required handling under inert conditions. In addition, terminal OH groups were found incompatible with the presented systems, which limited the application to protected ethers without protic functionalities. Further, the current scope of polyethers was minimal and focused on polymers with low molecular weight, lacking proof that the protocol can be extended to other polyether derivatives.

The present work aims to broaden this catalytic portfolio while investigating the influences of several structural features of the polyether on the reaction outcome (Scheme 1c). Based on the gathered information, reaction conditions are optimized to make this process feasible for wider applications, including a convenient *in-situ* generation of the catalyst from SiCl₄ and perchloro- and perbromocatechol (H₂cat^{Cl/Br}). Unprotected polyethers, not applicable under previous conditions, are shown to easily undergo RCM, even if handled under ambient atmosphere. Based on the experimental insights, a refined version of our previously reported mechanism is given.

Results and Discussion

We launched our studies by proving the generality of the previously described protocol for depolymerizing a range of polyether derivatives. Therefore, nine polyethylene glycols with different features were investigated regarding the influence of end-capping groups and chain length (Scheme 2).

First, the effect of different end-capping groups was evaluated. While previously, only a single α,ω -methyl end-capped telechelic polyether was investigated, we extended the scope to allyl-, acetyl- and butyl-end-capped pEOs, and compared the results with the uncapped OH functionality (Table 1). Apolar end-capping groups are generally tolerated (entries 1 & 4), yielding comparable results under the established (*ortho*-dichlorobenzene, 115 °C), and milder conditions (dichloromethane, 60 °C). Even the strongly coordinating ester functionality is tolerated, although with decreased yields. The possibility of cleavage of the ester, resulting in stoichiometric amounts of acetate, which has a high affinity towards **1**, could



Scheme 2. Overview about the heterotelechelic polyethers investigated in this study (n_{max} = average length as determined by MS spectrometry).

Table 1. Evaluation of the effect of different end-capping groups of α -allyl telechelic pEO, with $n_{\text{max}} = 13$ on the yield of 1,4-dioxane.^[a]

Entry	Polyether	ω -Capping	Yield [%] ^[b]
1	PE4-Me	R=Me	42 (40)
2	PE4-COMe	R=COMe	34 (32)
3	PE4-H	R=H	24 (12)
4	PE1	R ω =Me, R α =Bu	43 (40)

[a] Standard conditions: 20.0 mg polyether with 5 mol% **1**, in 500 μ l oDCB, 20 h, 115 °C. [b] Determined by ¹H- and ¹³C-NMR spectroscopy and/or GC analysis using cyclooctane as an internal standard. Yields in parentheses refer to reactions in DCM at 60 °C.

explain these findings.^[10] To our surprise, even the unprotected ω -OH terminal polyether (PE4-H) was degraded, but only with a TON of 5, which underlines the severe catalyst deactivation.

Probing the behavior of varying molecular weights in α -Bu- ω -OMe polyethers in the C–O bond metathesis, indicated beneficial effects of longer polyether chains (Table 2).

We reasoned that the higher local concentration of ether functionalities in close proximity to the catalytically active center of the Lewis acid-substrate complex, that occurs in the case of longer polyethers, has beneficial effects for the reaction outcome.^[11] This can be explained by an overall increase in polarity around the catalyst, which stabilizes ionic intermediates in the mechanism and by close proximity of nucleophilic groups which are necessary to close the catalytic cycle via a subsequent

Table 2. Evaluation of the effect of different chain lengths of α -Bu- ω -OMe heterotelechelic pEO on the yield of 1,4-dioxane.^[a]

Entry	Polyether	Chain length	Yield [%] ^[b]
1	PE1	$n_{\text{max}} = 13$	43 (40)
2	PE2	$n_{\text{max}} = 25$	75 (57)
3	PE3	$n_{\text{max}} = 105$	65 (68)

[a] Standard conditions: 20.0 mg polyether with 5 mol% **1**, in 500 μ l oDCB, 20 h, 115 °C. [b] Determined by ¹H- and ¹³C-NMR spectroscopy and/or GC analysis using cyclooctane as an internal standard. Yields in parentheses refer to reactions in DCM at 60 °C.

intermolecular S_N2 reaction (see *Mechanism*, below). To corroborate this hypothesis, reactions at different polyether concentrations but identical chain lengths were conducted (Table 3). Indeed, increased concentrations had a beneficial influence on the yield. Noteworthy, the reaction worked even solvent-free in bulk polyether on a 300 mg scale in 50% yield.

This information underlined the hypothesis that side reactions between the key intermediate oxonium ion and a nucleophile other than the alkoxy-silicate lead to the inhibition of the catalyst, another crucial piece for the mechanistic proposal (see below).

With the knowledge that an increased molecular weight and concentration improves the catalyst lifetime, we returned to the central problem, namely the limited compatibility with unprotected, (α), ω -OH polyethers, as observed in entry 3 of Table 1. To our delight, an increased molecular weight also shows beneficial effects for the catalyst activity in the degradation of polyethers with OH functionalities (Table 4), although

the yields were still reduced compared to the results obtained with protected ethers (Table 2).

We were speculating, if the deactivation occurred from the cleavage of catechol from the silicon-based catalyst **1** by reaction with the terminal OH groups, which also renders this catalyst sensitive towards moisture. To evaluate this problem, we tested the reaction with catalytic amounts of the bis-sulfonate (sulf) adduct of the heavier germanium analogue **2-sulf₂**, which is known for its stability under protic conditions and its potential as catalyst for the RCM of diglyme (Scheme 3).^[7d,12]

To our surprise, the obtained yields were only slightly improved, indicating that OH functionalities cause similar catalyst deactivation for **2** (Table 4). For instance, when **2-sulf₂** was implemented as a catalyst for the degradation of the ω -methyl-protected polyether PE3, significantly higher yields were achieved (73%) compared to the unprotected derivative (entry 3 & 4, Table 4). This observation led to the crucial conclusion that not alcoholysis of the catalyst seemed the major problem, but rather catalyst inhibition through formation of a catalytically inactive alkoxy-silicate/germanate *via* acidification of a coordinated alcohol, which requires subsequent reaction with an electrophile (oxonium-ion, H^+ , etc.) to revert to its active form. Before approaching the thus still remaining "OH-problem", another improvement was attempted. It was known that donor-adducts of **1** rapidly form by the reaction of $HSiCl_3$ or $SiCl_4$ with perchlorocatechol. Hence, we tried an *in-situ* generation of catalysts from these commercial precursors without isolating the moisture-sensitive Lewis acid. In a first attempt, we achieved promising results for the *in-situ* preparation of **1** in the presence of liquid α -allyl- ω -OMe pEO, PE4-Me (Table 5).

Table 3. Evaluation of the effect of concentration on the degradation of α -Bu- ω -OMe heterochelelic pEO PE1 ($n_{max} = 13$).^[a]

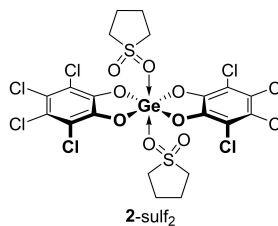
Entry	Polyether concentration	Yield [%] ^[b]
1	10 mg/ml	40
2	20 mg/ml	43
3	40 mg/ml	51
4	80 mg/ml	57

[a] Standard conditions: 20.0 mg PE1 with 5 mol% [**1**]₀ in oDCB, 20 h, 115 °C. [b] Referring to 1,4-dioxane as the reaction product, determined by 1H - and ^{13}C -NMR spectroscopy and GC analysis using cyclooctane as an internal standard.

Table 4. Degradation of α -Bu- ω -OH heterochelelic pEOs with different chain lengths by [**1**]₀ compared to the water-stable Lewis acid **2** as a catalyst.^[a]

Entry	Polyether	Chain length	Yield ([1] ₀) [%] ^[a]	Yield (2-sulf₂) [%] ^[b]
1	PE1-H	$n_{max} = 13$	17	18
2	PE2-H	$n_{max} = 25$	43	58
3	PE3-H	$n_{max} = 105$	57	59
4 ^[c]	PE3	$n_{max} = 105$	65	73

[a] Standard conditions: 20.0 mg polyether with 5 mol% Lewis acid in 500 μ l oDCB, 15–21 h, 115 °C. [b] Referring to 1,4-dioxane as the reaction product, determined by GC analysis using cyclooctane as an internal standard. [c] Degradation of α -Bu- ω -OMe heterochelelic pEO PE3 as comparison to the ω -hydroxy terminated derivative.



Scheme 3. Lewis structure of the bis(sulfonate) adduct of bis(perchlorocatechol)germane **2**.

Table 5. Degradation of different pEOs by *in-situ* generation of **1** out of $SiCl_4$ and perchlorocatechol.^[a]

Entry	Polyether	End-Capper	Chain length	Yield [%] ^[b]
1	PE4-Me	α -allyl/ ω -OMe	$n_{max} = 13$	67 ^[c]
2	PE3	α -Bu/ ω -OMe	$n_{max} = 105$	73
3	PE1-H	α -Bu/ ω -OH	$n_{max} = 13$	62

[a] Standard conditions: 100 mg polyether with 10 mol% perchlorocatechol and an excess of $SiCl_4$ in 2.5 mL oDCB, 18–21 h, 115 °C. [b] Referring to 1,4-dioxane as the reaction product, determined by GC analysis using cyclooctane as an internal standard. [c] 20 mol% perchlorocatechol was used.

Control experiments with only SiCl_4 or perchlorocatechol resulted in no depolymerization, corroborating the role of **1** as the active species. The activity was not exclusive to allyl-end-capped polyether, but also $\alpha\text{-Bu}/\omega\text{-OMe}$ pEO PE3 was degraded in higher yields compared to the use of oligomeric $[1]_n$ as catalyst (compare Table 2, entry 3). With this new approach, we returned to the "OH-problem". Much to our delight, unprotected polyether, $\alpha\text{-Bu}/\omega\text{-OH}$ pEO PE1-H, which during our study proved to be the most challenging substrate, efficiently depolymerized when using the *in-situ* catalyst formation. The observed yield (62%) is significantly higher than the results with $[1]_n$ (17%, Table 4, entry 1). The *in-situ* formation is even feasible in neat PE1-H, although with diminished yields (300 mg scale, 31%). While we are aware, that the *in-situ* generation of **1** requires an excess of the volatile SiCl_4 , which readily reacts with moisture, the thereby formed catalytic system turned out as the most effective and robust one, substantially improving and facilitating the process and making isolation and handling of the sensitive oligomer $[1]_n$ obsolete.

With the possibility of an *in-situ* generation of the catalyst in hand, we aimed to evaluate remaining factors. Since previous findings in our group revealed the increased Lewis acidity in the heavier bis(perbromocatecholato)silane,^[7b] we tried to replace the more expensive and more toxic perchlorocatechol with the cheaper and non-toxic perbromocatechol. Indeed, a similar yield in the degradation of the unprotected PE1-H ($\alpha\text{-Bu}/\omega\text{-OH}$ pEO) was achieved (60%). We also investigated other silane precursors but found that SiCl_4 already performed superior (see ESI section 1.4 for details).

The fact that an *in-situ* catalyst generation, which liberates HCl, increases the catalyst lifetime and, therefore, the yields

significantly, lead to the question whether chloride ions or acidic conditions have a beneficial influence on the catalytic activity of **1**. While reactivity was quenched after the addition of 10 mol% PPh_4Cl (see SI for details), the effect of acidic conditions was further investigated by adding bis(trifluoromethane)sulfonimide (HNTf_2) as an additive to the depolymerization catalyzed by $[1]_n$.

As suspected, the addition of HNTf_2 increased the yields substantially (Table 6). Notably, control experiment with 5 mol% HNTf_2 in the absence of the Lewis acid also catalyzed the reaction in a moderate yield (entry 4, Table 6). This is in line with the findings of Morandi *et al.*,^[4a] but the Lewis superacid $[1]_n$ alone still shows superior reactivity in comparison to Brønsted catalysis (51%, entry 3, Table 3). While the increased yields in the presence of the Brønsted acid could be explained by two independent catalytic cycles, the fact that the addition of an electrophile (H^+ in the case of HNTf_2) is beneficial for the lifetime of the catalyst is further supported by the finding that stoichiometric amounts of iodomethane increase the yield in the degradation of $\alpha\text{-Bu}/\omega\text{-OMe}$ pEO PE3 by 11%, while other additives like Et_3SiH negatively affected the observed yields (see SI for details). This observation again underlines the hypothesis that the anionic silicate plays a major role in catalyst inhibition. By reaction with an external electrophile, a regeneration of the catalyst seems plausible.

To gain further insight into the processes during the depolymerization, we conducted a series of reactions in neat polyether ($\alpha\text{-Bu}/\omega\text{-OMe}$ pEO PE2, $n_{\text{max}}=25$) and stopped the reaction after several timepoints, as seen in Table 7. Already after 30 minutes of reaction time, much less than the usually employed time margins for this reaction (18 h), substantial yields were observed (Entry 2). MALDI-MS analysis of the residual polyether indicated a statistical distribution of chain lengths with its maximum (n_{max}) shifting from 25 to 12 with increased reaction time.

Remarkably, a broadening of the chain length distribution can be observed for increased reaction time, which is indicating cross-metathesis occurring along with depolymerization. This observation introduces novel opportunities that could be achieved by chain redistribution to affect the properties of polyethers – a hitherto not considered aspect.

Finally, to establish large-scale applicability of our approach, we combined the gained insights to elaborate a system that can be handled without inert atmospheres. By using an excess of SiCl_4 , which acts as a drying- as well as capping reagent (H_2O

Table 6. Influence of HNTf_2 as an additive in the silicon-catalyzed depolymerization of $\alpha\text{-Bu}/\omega\text{-OMe}$ pEO PE1 ($n_{\text{max}}=13$).^[a]

Entry	Amount of HNTf_2	Yield [%] ^[b]
1	5 mol%	63
2	10 mol%	73
3	50 mol%	95
4	5 mol%	36 ^[c]

[a] Standard conditions: 20.0 mg PE1 with 5 mol% $[1]_n$ in 500 μl oDCB, 15 h, 115 °C. [b] Referring to 1,4-dioxane as the reaction product, determined by GC analysis using cyclooctane as an internal standard. [c] Without $[1]_n$.

Table 7. Restructuration of the molecular weight and chain length during the ring-closing depolymerization of $\alpha\text{-Bu}/\omega\text{-OMe}$ pEO PE2, $n_{\text{max}}=25$.^[a]

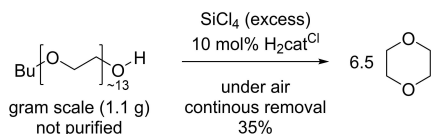
Entry	Time [min]	n_{max} ^[b]	$D^{[c]}$	M_n [g/mol] ^[c]	Yield [%] ^[d]
1	0	25	1.06	1449	–
2	30	14	10.18	3593	45
3	60	12	13.87	4638	53
4	240	12	13.81	4766	47

[a] Standard conditions: 200 mg PE2 with 5 mol% $[1]_n$, 115 °C. Reactions were stopped by cooling to –28 °C [b] Determined via MALDI-MS. [c] Determined via GPC against polystyrene. [d] Referring to 1,4-dioxane as the reaction product, determined by GC analysis using cyclooctane as an internal standard.

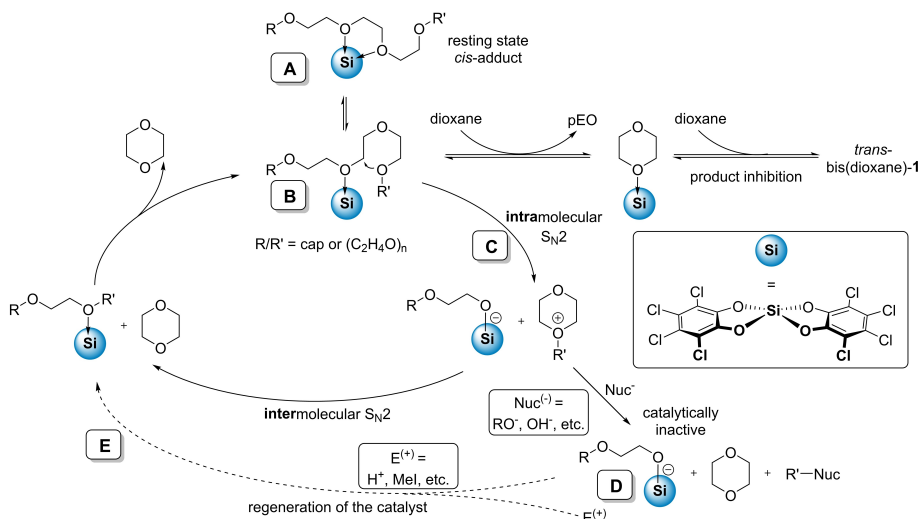
and terminal OH groups in unprotected polymers) and reacts with other impurities within the polyether, and 10 mol% perchlorocatechol, the gram scale degradation of α -Bu/ ω -OH pEO (PE1-H, $n_{\max} = 13$) was achieved without purification of the used ingredients and in the presence of air and moisture (Scheme 4). Continuous removal of the product by trap-to-trap condensation was successfully managed. The conversion of 35% after four hours of reaction time is similar to the yields obtained when using neat PE1-H (α -Bu/ ω -OH pEO, $n_{\max} = 13$) under entirely inert conditions, which underlines the feasibility of this process on practical scale. Nevertheless, adding a high-boiling solvent should be considered to facilitate stirring and increasing the yield, as already mentioned above.

Mechanistic Considerations

Based on all the above-mentioned experimental observations and our calculations on the degradation of diglyme,^[7d] a refined catalytic cycle for the depolymerization was developed



Scheme 4. Gram scale degradation of α -Bu/ ω -OH pEO (PE1-H, $n_{\max} = 13$) under air through *in-situ* generation of the catalyst, using SiCl_4 and H_2catCl .



Scheme 5. Refined proposed mechanism with deactivation pathways of the catalyst, through reaction with nucleophiles in solutions or through competitive binding of 1,4-dioxane to the Lewis acid.

(Scheme 5). The bidentate *cis*-coordination of the polyether is identified as the resting state A. Only in the mono-adduct B, the intramolecular $\text{S}_{\text{N}}2$ type attack of the oxygen atom at the polarized α -carbon of the polyether can take place to form an oxonium ion and an alkoxy-silicate C. The subsequent $\text{S}_{\text{N}}2$ attack of the alkoxyate bound to silicon to liberate dioxane is an *intermolecular* step, explaining increased yields at higher concentrations. At lower concentrations, an *intermolecular* reaction attack of other nucleophiles, such as other polyethers, can compete, which gives rise to catalytically inactive silicate D. The anionic silicate D can react with a different electrophile to regenerate the neutral, catalytically active silane E. Therefore, acidic conditions favor the reaction, decrease the number of nucleophiles in solution, and simultaneously enable catalyst regeneration. Competitive binding of the product 1,4-dioxane to the Lewis acid poses another major challenge to the reaction and adversely affects the reaction rate (product inhibition). The higher affinity towards the strongly donating and sterically less demanding dioxane leads to the inactive *trans*-dioxane adduct of 1. Constant removal of 1,4-dioxane through distillation accelerates the reaction by affecting this equilibrium.

Conclusions

The applicability of the depolymerization process for various pEO derivatives with different end-capping groups and chain lengths is demonstrated within this work. Problematic side reactivities were identified and the catalyst lifetime was increased by adjusting the reaction conditions. By combining

SiCl_4 and perchloro- or perbromocatechol, we developed an easy-to-apply *in-situ* generation of the catalyst. We thereby did not only circumvent the problematics of working under an inert atmosphere but did also improve the reaction yields. On top, this approach also presents a way to efficiently depolymerize unprotected polyethers, thereby broadening the substrate scope of this process, giving rise to large-scale depolymerization without sample preparation and without the need of air-free manipulations. With the obtained experimental signatures, the previously proposed mechanism^[7d,9] was refined and supported by experiment, corroborating intermolecular reactions of the immediately formed oxonium ion with other nucleophiles as the major pathway for catalyst inhibition that can be circumvented by the presence of external electrophiles. We thereby pave the way for further improvements and applications of this reaction.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: depolymerization · Lewis acids · silicon · polyether · ambient conditions

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Supporting Information

Silicon-Catalyzed Depolymerization of Polyethers: Pushing Scope, Practicability and Mechanistic Understanding

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Supplementary Information for:

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1. Experimental Procedures

1.1. Materials and General Methods

Unless otherwise stated, all experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame dried glassware or by working in a glovebox (Sylatech Glovebox) under a nitrogen atmosphere. Solvents and substrates, including cyclooctane were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å). The argon was dried by passing over two columns of phosphorus pentoxide. Polyethers were received from Evonik, degassed via exposure to vacuum ($< 10^{-2}$ mbar) for hours and if in the liquid state, stored over molecular sieves (4 Å) prior to use. Other commercially available chemicals were used as received. Perchlorocatechol, bis(perchlorocatecholato)silane [1], and bis(sulfolane)-bis(perchlorocatecholato)germane 1-(sulfolane) were synthesized according to literature known procedures.^[1] All solution phase NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All hetero-nuclei spectra (with the exception of ^{19}F) were obtained with ^1H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ^1H and ^{13}C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants J in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublet of doublets, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. NMR spectra were processed and plotted with TopSpin 4.0.8.^[2] ESI-MS spectra were measured on a Bruker ApexQe FT-ICR instrument while MALDI-MS spectra were recorded on a Bruker Autoflex Speed MALDI-TOF or a Bruker tims TOFEx instrument. GC-MS were measured on a Thermo Scientific Ultra Trace GC equipped with an ISQ Single Quadrupole MS using EI ionization. GC for quantification purposes was measured on a Shimadzu GC-2010 Pro instrument equipped with a BID-2010 Plus detector.

1.2. General Procedures for the Degradation of Polyethers

Calibration Curve for GC-Analysis

In the glovebox, four samples, each containing cyclooctane (13.5 μL , 101 μmol) and 500 μL of a mixture of *o*-dichlorobenzene (oDCB) and C_6D_6 (50:1), were treated with varying amounts of 1,4-dioxane (a) 25.6 μL , 300 μmol ; b) 17.1 μL , 199 μmol ; c) 8.5 μL , 99.4 μmol ; d) 4.5 μL , 52.6 μmol). Of these samples, a few drops were diluted with DCM for GC analysis. The peaks of 1,4-dioxane (retention time 4.1 min) and cyclooctane (retention time 8.1 min) were automatically integrated and the ratio was fitted against the amount of dioxane using linear regression, as implemented in the Origin 2020b Pro program package. The results are shown in table S1 and figure S1.

Table S 1: Results for the GC calibration curve.

	area 1,4-dioxane	area cyclooctane	A (dioxane)/ A(cyclooctane)	n (dioxane)/ n(cyclooctane)
A	72344	96263	0.7515	2.9703
B	38069	76233	0.4994	1.96733
C	25394	91883	0.2764	0.98416
D	10410	87806	0.1186	0.52079

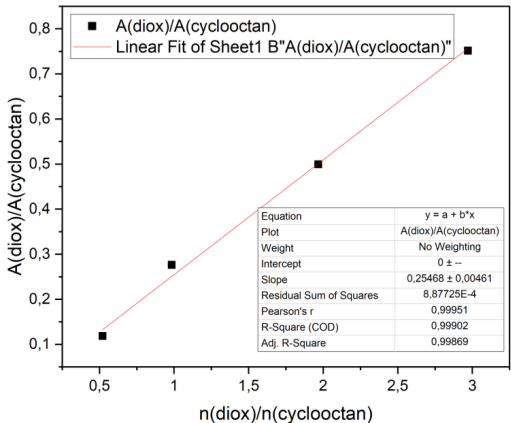


Figure S 1: Linear regression (calibration curve) for the determination of dioxane contents for the experiments in this work.

Standard Conditions on 20 mg Scale in Screw Cap Vial (G1)

In the glovebox, a DWK screw cap vial (41x20 mm, 5 mL, DIN 18) equipped with a stir bar was charged with the respective polyether (20.0 mg, 1.00 eq) and 5 mol%* of **[1]_n**, followed by the internal standard cyclooctane (13.4 μ L, 100 μ mol) and either 500 μ L of CD₂Cl₂ or a mixture of *o*-dichlorobenzene (oDCB) and C₆D₆ (50:1), resulting in a colorless suspension. If an additive was going to be added, it would be at this point. Afterwards the vial was tightly screwed and placed in a heated metal block (60 °C for CD₂Cl₂ or 115 °C for oDCB) with fitting cavities. While stirring, the reactions were heated overnight (15 – 21 h), yielding a grey-black suspension. In order to stop the reaction, the vials were subsequently cooled to –28 °C in a freezer. The contents of the vials were transferred to NMR tubes using glass pipettes at room temperature. The vials were rinsed with 2 mL of DCM, which was filtered through syringe filters prior to GC(-MS) analysis. Yields were determined using NMR spectroscopy and/or GC analysis independently, whereby the obtained results were similar.

Standard Conditions on 20 mg Scale in a J Young NMR tube (G2)

This procedure is similar to G1, with the difference that instead of screw cap vial a J. Young NMR tube was used as reaction vessel. This method also does not rely on stirring.

In-Situ Generation on 20 mg Scale in Screw Cap Vial (G3)

Caution: Tetrachlorosilane is volatile, corrosive and reacts heavily with moisture. Experiments should therefore only be carried out in well-ventilated fume hoods and with proper personal protective equipment.

This procedure is similar to G1, but instead of 5 mol%* of **[1]_n**, 10 mol%* of perchlorocatechol are added in the glovebox. The vial is then fitted with a septum (NS 14.5), transferred to a Schlenk line, and charged with an excess of SiCl₄ or a different silane (ca. 50-100 μ L) via syringe. Subsequently, the septum is exchanged for a screw cap using an argon counter stream. Then the procedure follows G1 again.

300 mg Scale, neat in Screw Cap Vial (G4)

This procedure is similar to G1/G3 with the difference that 300 mg polyether are employed and no solvent or cyclooctane are added. After completion of the reaction, a solution of cyclooctane (134 μ L, 1.00 mmol) in 2 mL toluene was added. Afterwards, aliquots for NMR and GC analysis were taken

* mol% are referring to a conversion of 100 %. Example: Experiment with 10 μ mol polyether with *n* = 20, maximum yield of dioxane is therefore 10*20/2 = 100 μ mol. 5 mol% of catalyst would therefore be 0.05*100 μ mol = 5 μ mol.

1.3. Results of Experiments Performed by G1-G4

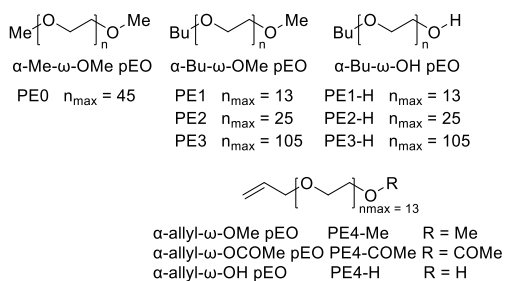


Figure S 2: Overview about the investigated polyethers. PE0, which is not discussed in the main text, was previously commercially purchased at sigma Aldrich.

Polyether	GP	Polyether Structure	catalyst	solvent	T [°C]	c [mg/ml]	t	mol%	yield%	Additives/comments
PE0	G1	α -Me-p(EO)45- ω -OCH3	[1]n	oDCB	115	40	23h	10	88	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n + HNTf2	oDCB	115	40	15h	5	95	50 mol% HNTf2,
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	oDCB	115	40	23h	10	69	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n + HNTf2	oDCB	115	40	15h	5	73	10 mol% HNTf2,
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n + HNTf2	oDCB	115	40	15h	5	63	5 mol% HNTf2,
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	oDCB	115	80	18h	5	57	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	oDCB	115	40	18h	5	51	
PE1	G4	α -Bu-p(EO)13- ω -OCH3	neat	neat	115		18h	5	50	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	oDCB	115	40	20h	5	43	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	oDCB	115	20	18h	5	43	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	DCM	60	40	24h	5	40	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n	oDCB	115	10	18h	5	40	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	HNTf2	oDCB	115	40	18h	5	36	
PE1	G1	α -Bu-p(EO)13- ω -OCH3	[1]n + PPh ₃ Cl	oDCB	115	40	19h	5	0	10 mol% PPh ₃ Cl
PE2	G1	α -Bu-p(EO)25- ω -OCH3	[1]n	oDCB	115	40	23h	10	88	
PE2	G2	α -Bu-p(EO)25- ω -OCH3	HNTf2	oDCB	200	40	18h	10	83	
PE2	G1	α -Bu-p(EO)25- ω -OCH3	[1]n	oDCB	115	40	20h	5	75	
PE2	G1	α -Bu-p(EO)25- ω -OCH3	[1]n	DCM	60	40	24h	5	57	
PE3	G1	α -Bu-p(EO)105- ω -OCH3	[1]n	oDCB	115	40	23h	10	97	
PE3	G3	α -Bu-p(EO)105- ω -OCH3	SiCl ₄ /CatClH	oDCB	115	40	18h	5	83	
PE3	G3	α -Bu-p(EO)105- ω -OCH3	HSiCl ₃ /CatClH	oDCB	115	40	18h	5	82	
PE3	G2*	α -Bu-p(EO)105- ω -OCH3	[1]n	DCM	60	40	17h	5	79	100 mol% MeI
PE3	G1	α -Bu-p(EO)105- ω -OCH3	Ge(sulf)	oDCB	115	40	21h	5	73	
PE3	G3	α -Bu-p(EO)105- ω -OCH3	SiCl ₄ /CatClH	oDCB	115	40	15h	5	73	
PE3	G1	α -Bu-p(EO)105- ω -OCH3	[1]n	DCM	60	40	24h	5	68	
PE3	G1	α -Bu-p(EO)105- ω -OCH3	[1]n	oDCB	115	40	20h	5	65	
PE3	G2	α -Bu-p(EO)105- ω -OCH3	[1]n	DCM	60	40	17h	5	60	100 mol% TMS-OTf
PE3	G2	α -Bu-p(EO)105- ω -OCH3	[1]n	DCM	60	40	17h	5	57	100 mol% Et ₃ SiH
PE3	G2*	α -Bu-p(EO)105- ω -OCH3	[1]n	DCM	60	40	17h	5	32	100 mol% TMS-Cl
PE3	G3	α -Bu-p(EO)105- ω -OCH3	SiH ₄ /CatClH	oDCB	115	40	18h	5	14	
PE3	G3	α -Bu-p(EO)105- ω -OCH3	TiCl ₄ /CatClH	oDCB	115	40	18h	5	0	
PE1-H	G3	α -Bu-p(EO)13- ω -OH	SiCl ₄ /CatClH	oDCB	115	40	18h	5	62	

PE1-H	G3	α -Bu-p(EO)13- ω -OH	SiCl4/CatBrH	oDCB	115	40	14h	5	60
PE1-H	G3	α -Bu-p(EO)13- ω -OH	HSiCl3/CatClH	oDCB	115	40	14h	5	56
PE1-H	G4	α -Bu-p(EO)13- ω -OH	SiCl4/CatClH	neat	115		18h	5	31
PE1-H	G1	α -Bu-p(EO)13- ω -OH	Ge(sulf)	oDCB	115	40	15h	5	18
PE1-H	G1	α -Bu-p(EO)13- ω -OH	[1]n	oDCB	115	40	21h	5	17
PE1-H	G1	α -Bu-p(EO)13- ω -OH	GeO2+catClH	oDCB	115	40	15h	5	3
PE2-H	G1	α -Bu-p(EO)25- ω -OH	Ge(sulf)	oDCB	115	40	15h	5	58
PE2-H	G1	α -Bu-p(EO)25- ω -OH	[1]n	oDCB	115	40	21h	5	43
PE3-H	G1	α -Bu-p(EO)105- ω -OH	Ge(sulf)	oDCB	115	40	21h	5	59
PE3-H	G1	α -Bu-p(EO)105- ω -OH	[1]n	oDCB	115	40	21h	5	57
PE4-Me	G3	α -allyl-p(EO)13- ω -OMe	SiCl4/CatClH	oDCB	115	40	21h	10	67
PE4-Me	G3	α -allyl-p(EO)13- ω -OMe	SiCl4	oDCB	115	40	14h	10	0
PE4-Me	G3	α -allyl-p(EO)13- ω -OMe	CatClH	oDCB	115	40	14h	10	0
PE4-Me	G1	α -allyl-p(EO)13- ω -OMe	[1]n	oDCB	115	40	20h	5	42
PE4-Me	G1	α -allyl-p(EO)13- ω -OMe	[1]n	DCM	60	40	24h	5	29
PE4-COMe	G1	α -allyl-p(EO)13- ω -OCOMe	[1]n	oDCB	115	40	20h	5	34
PE4-COMe	G1	α -allyl-p(EO)13- ω -OCOMe	[1]n	DCM	60	40	24h	5	32
PE4-H	G1	α -allyl-p(EO)13- ω -OH	[1]n	oDCB	115	40	20h	5	24
PE4-H	G1	α -allyl-p(EO)13- ω -OH	[1]n	DCM	60	40	24h	5	12

Table S.2: Overview of performed degradation reactions of different polyethers with different catalysts and conditions.

Entries, marked with a * after the general procedure, were set up under ambient atmosphere.

1.4 Evaluation of *in-situ* Silane Sources

We employed several silicon precursors in the depolymerization of PE3 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 105$), using the procedure G3. While trichloro- and tetrachlorosilane performed successfully, only 14 % yield were achieved for SiI_4 , indicating a beneficial effect of HCl in the reaction mechanism. This also underlines that the economically affordable SiCl_4 already performs superior in this reaction, leaving no need for further optimization in this regard. A substitution of silicon by titanium was unsuccessful, again underscoring the unique feature of the silicon-based Lewis acid **1**.

Table S 3: Influence of different precursor in the *in-situ* approach on the depolymerization of PE3 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 105$).^[a]

Entry	Silicon/Titanium Source	Yield [%] ^[b]
1	SiCl_4	83
2	HSiCl_3	82
3	SiI_4	14 ^[c]
4	TiCl_4	0

[a] Standard conditions: 100 mg polyether with 10 mol% perchlorocatechol and an excess (50-100 mol%) of respective reagents in 2.5 mL oDCB, 18 h, 115 °C. [b] Referring to 1,4-dioxane as the product, determined by GC analysis using cyclooctane as an internal standard. [c] 5 mol% tetraiodosilane was used.

1.5 Alteration of the Polyether Structure of PE2

This series of reactions is set up similar to G1, with the difference that 200 mg of PE2 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 25$, 168 μmol) were employed and no solvent or cyclooctane was added. The black reaction mixtures were quenched by cooling to -28 °C after 30 min, 60 min or 240 min. Afterwards, 500 μL of a solution of cyclooctane (134 μL , 1.00 mmol) in 2.4 mL C_6D_6 was added, equaling 200 μmol internal standard. Afterwards, NMR and GC analysis was performed like previously described. To gain insights into the polymer structure, all volatiles were removed and the samples were analyzed using MALDI-MS and GPC against polystyrene.

Table S 4: Restructuration of the molecular weight and chain length during the ring-closing depolymerization of PE2 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 25$).^[a]

Entry	Time [min]	$n_{\text{max}}^{[b]}$	$M_n^{[c]}$ [g/mol]	$M_w^{[c]}$ [g/mol]	$M_z^{[c]}$ [g/mol]	D	Yield [%] ^[d]
1	0	25	1362	1449	1523	1.06	
2	30	14	352.8	3593	32460	10.18	45
3	60	12	334.3	4638	48390	13.87	53
4	240	12	345.1	4766	56690	13.81	47

[a] Standard conditions: 200 mg PE2 with 5 mol% **1**, 115 °C. Reactions were stopped by cooling to -28 °C [b] Determined via MALDI-MS. [c] Determined via GPC against polystyrene. [d] Referring to 1,4-dioxane as the product, determined by GC analysis using cyclooctane as an internal standard

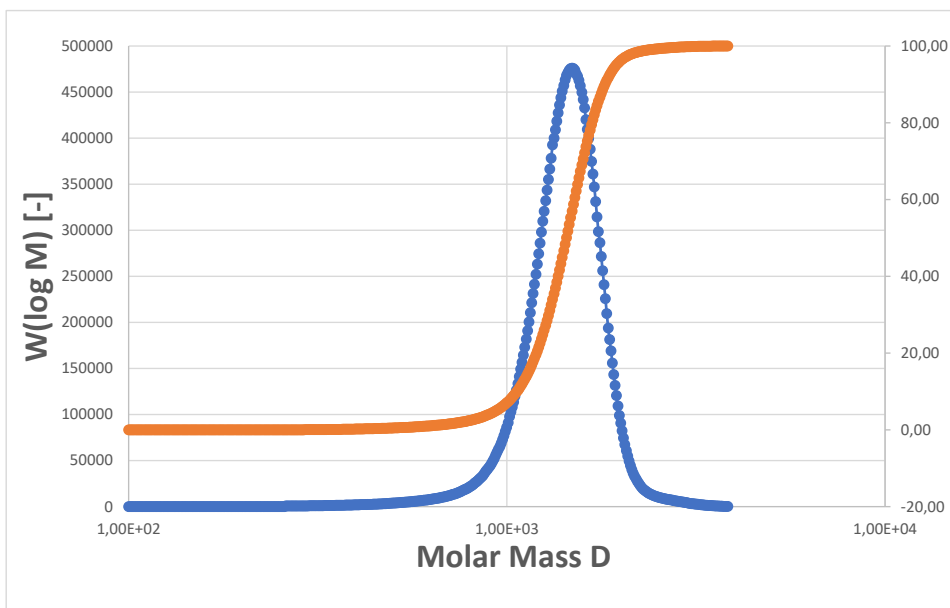


Figure S 3: Results of the GPC analysis of polyether PE2.

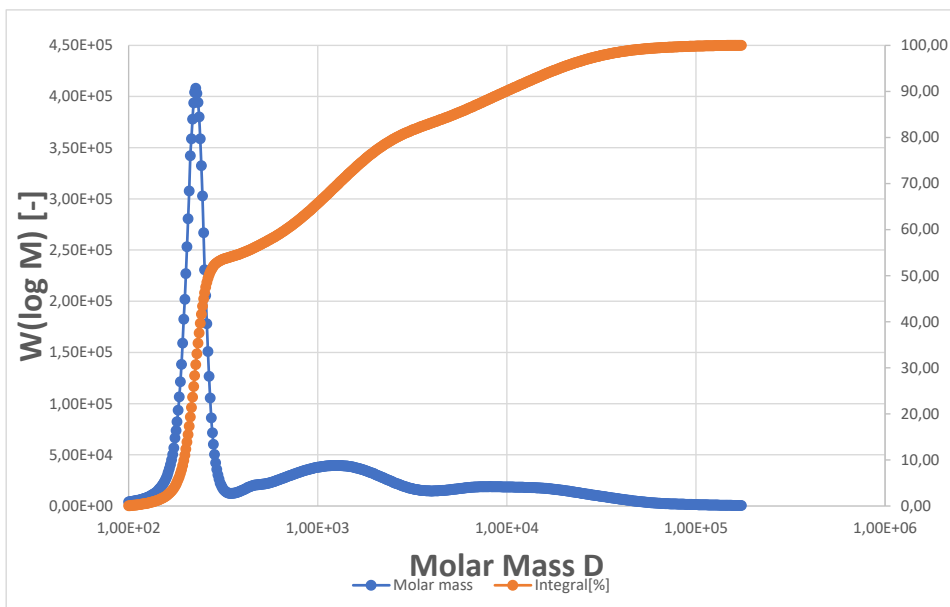


Figure S 4: Results of the GPC analysis of the polyether obtained after 30 minutes of degradation (entry 2 in table S4).

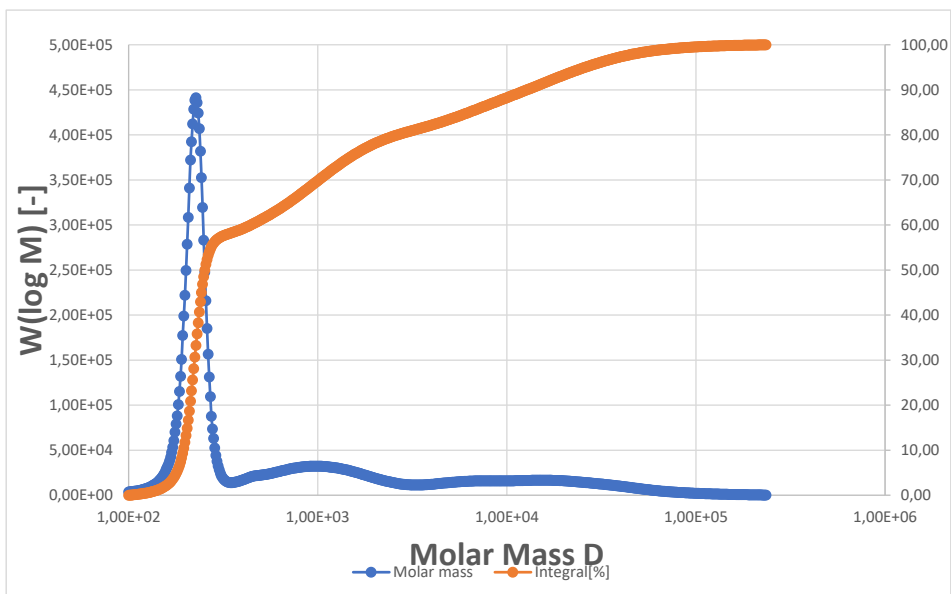


Figure S 5: Results of the GPC analysis of the polyether obtained after 60 minutes of degradation (entry 3 in table S4).

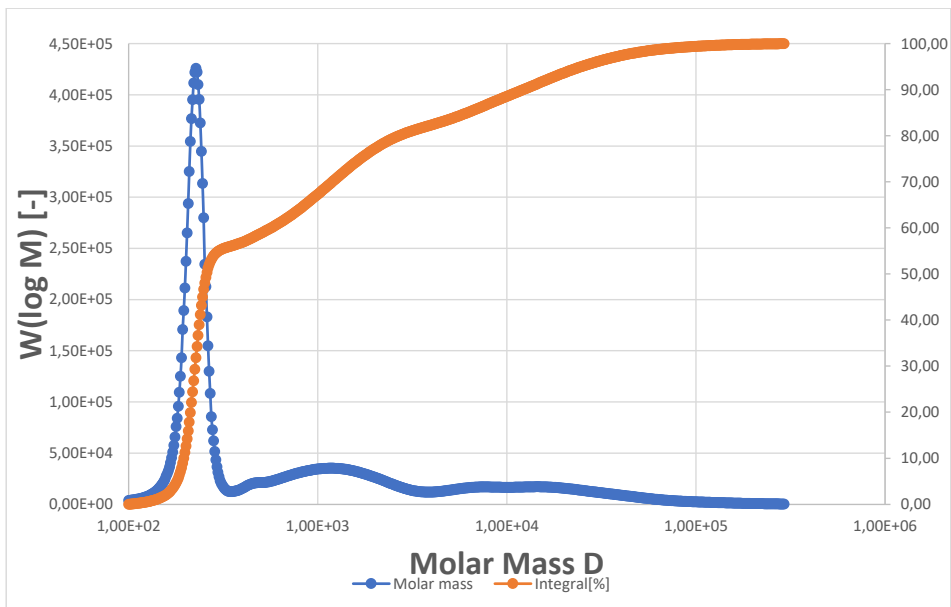


Figure S 6: Results of the GPC analysis of the polyether obtained after 240 minutes of degradation (entry 4 in table S4).

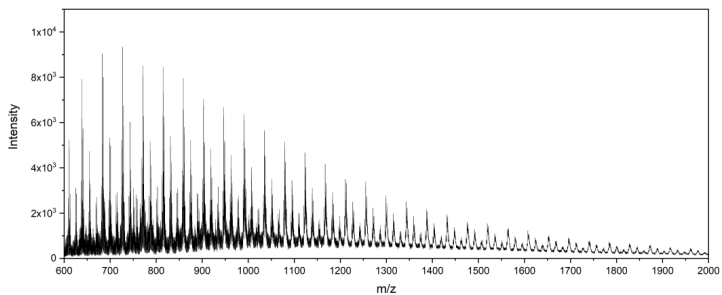


Figure S 7: MALDI-MS diagram of the polyether obtained polyether obtained after 30 minutes of degradation (entry 2 in table S4).

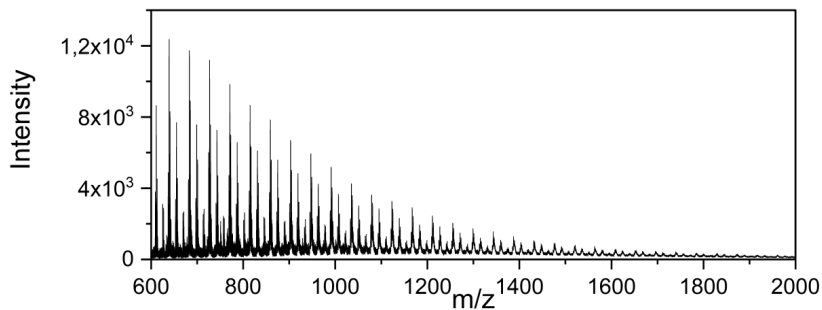


Figure S 8: MALDI-MS diagram of the polyether obtained polyether obtained after 60 minutes of degradation (entry 3 in table S4).

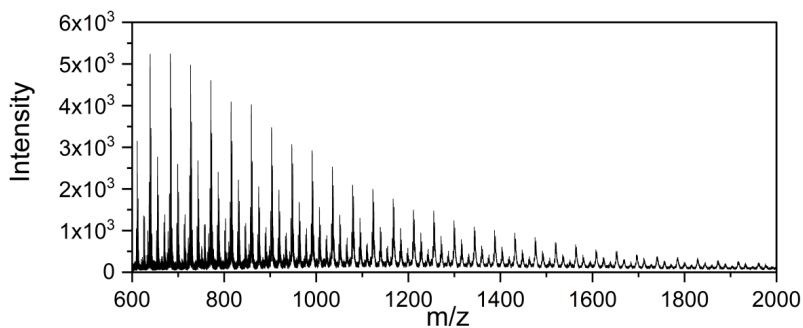


Figure S 9: MALDI-MS diagram of the polyether obtained polyether obtained after 240 minutes of degradation (entry 4 in table S4).

1.6 Gram Scale Reaction Under Atmospheric Conditions

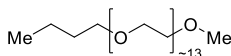
In a two-neck flask, equipped with a stir bar, a septum and a stopper, unpurified α -Bu- ω -OH pEO, $n_{\text{max}} = 13$, PE1-H (1.11 g, 1.72 mmol, 1.00 eq) was mixed with unpurified perchlorocatechol (252 mg, 1.02 mmol, 9 mol%) under ambient atmospheric. All joints were secured with Glindeman PTFE rings. Through the septum, an excess of tetrachlorosilane (400 μL , 3.51 mmol, 2.04 eq) was added, resulting in the formation of gases. The resulting suspension was heated at 60 $^{\circ}\text{C}$ for 3 h to initiate catalyst formation. Afterwards, the septum was exchanged for a distillation setup (see fig. S7) and the reaction was heated to 115 $^{\circ}\text{C}$, while regularly equalizing the pressure. After 4 h, the black solidified reaction mixture was brought back to room temperature and all volatiles were removed *in vacuo*. The yield of 1,4-dioxane (35 %) was determined by weighing the leftover solid.



Figure S 10: Setup for the gram-scale depolymerization of pEO with continuous removal of dioxane.

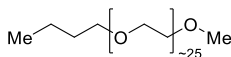
1.7. Characterization of Polyethers

PE1 - α -Bu- ω -OMe pEO, $n_{\max} = 13$



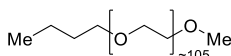
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.45 (broad s, 46H, O-CH₂), 3.33 (m, 2H, O-CH₂), 3.26 (t, J = 6.5 Hz, 2H, O-^{*Bu*}CH₂), 3.14 (s, 3H, O-CH₃), 1.42 (p-quint, J = 7.0 Hz, 2H, ^{*Bu*}CH₂), 1.25 (m, 2H, ^{*Bu*}CH₂), 0.79 (t, J = 7.5 Hz, 3H, ^{*Bu*}CH₃) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 72.1 (s, O-CH₂), 70.9 (s, O-^{*Bu*}CH₂), 70.7 (s, O-CH₂), 70.5 (s, O-CH₂), 70.3 (s, O-CH₂), 58.5 (s, O-CH₃), 32.0 (s, ^{*Bu*}CH₂), 19.5 (s, ^{*Bu*}CH₂), 14.0 (s, ^{*Bu*}CH₃). **HR-MS (ESI⁺)**: $[\text{M}+\text{K}]^+ = \text{C}_{31}\text{H}_{64}\text{O}_{14}\text{K}^+$, calc. 699.3928, found 699.3931.

PE2 - α -Bu- ω -OMe pEO, $n_{\max} = 25$



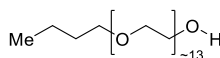
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.47 (broad s, 132H, O-CH₂), 3.36 (m, 2H, O-CH₂), 3.29 (t, J = 6.5 Hz, 2H, O-^{*Bu*}CH₂), 3.17 (s, 3H, O-CH₃), 1.45 (p-quint, J = 6.5 Hz, 2H, ^{*Bu*}CH₂), 1.29 (m, 2H, ^{*Bu*}CH₂), 0.82 (t, J = 7.2 Hz, 3H, ^{*Bu*}CH₃) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 72.2 (s, O-CH₂), 71.1 (s, O-^{*Bu*}CH₂), 70.9 (s, O-CH₂), 70.7 (s, O-CH₂), 70.5 (s, O-CH₂), 58.7 (s, O-CH₃), 32.3 (s, ^{*Bu*}CH₂), 19.7 (s, ^{*Bu*}CH₂), 14.2 (s, ^{*Bu*}CH₃). **HR-MS (ESI⁺)**: $[\text{M}+\text{K}]^+ = \text{C}_{55}\text{H}_{112}\text{O}_{26}\text{K}^+$, calc. 1227.7073, found 1227.7072.

PE3 - α -Bu- ω -OMe pEO, $n_{\max} = 105$



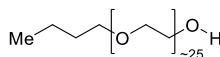
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.47 (broad s, 398H, O-CH₂), 3.17 (s, 3H, O-CH₃), 1.43 (p-quint, J = 6.5 Hz, 2H, ^{*Bu*}CH₂), 1.26 (m, 2H, ^{*Bu*}CH₂), 0.80 (t, J = 7.3 Hz, 3H, ^{*Bu*}CH₃) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 72.3 (s, O-^{*Bu*}CH₂), 70.9 (s, O-CH₂), 58.7 (s, O-CH₃), 32.3 (s, ^{*Bu*}CH₂), 19.8 (s, ^{*Bu*}CH₂), 14.3 (s, ^{*Bu*}CH₃). **MS (MALDI⁺ DCTB)**: $[\text{M}+\text{Na}]^+ = \text{C}_{107}\text{H}_{436}\text{O}_{107}\text{Na}^+$, calc. 4733.83, found 4736.15.

PE1-H - α -Bu- ω -OH pEO, $n_{\max} = 13$



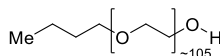
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.58 (t, J = 4.7 Hz, 2 H, O-CH₂), 3.42 (broad s, 46H, O-CH₂), 3.25 (broad s, 1H, O-H), 3.22 (t, J = 6.4 Hz, 2H, O-^{*Bu*}CH₂), 1.37 (p-quint, J = 7.0 Hz, 2H, ^{*Bu*}CH₂), 1.20 (p-hex, 2H, J = 7.5 Hz, ^{*Bu*}CH₂), 0.74 (t, J = 7.5 Hz, 3H, ^{*Bu*}CH₃) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 73.1 (s, O-CH₂), 71.1 (s, O-^{*Bu*}CH₂), 70.9 (s, O-CH₂), 70.6 (s, O-CH₂), 70.5 (s, O-CH₂), 61.8 (s, O-CH₂), 32.3 (s, ^{*Bu*}CH₂), 19.7 (s, ^{*Bu*}CH₂), 14.2 (s, ^{*Bu*}CH₃).

PE2-H - α -Bu- ω -OH pEO, $n_{\max} = 25$



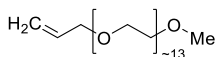
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.61 (s, 2 H, O-CH₂), 3.45 (broad s, 134H, O-CH₂), 3.26 (t, J = 6.6 Hz, 2H, O-^{*Bu*}CH₂), 2.83 (broad s, 1H, O-H), 1.40 (p-quint, J = 6.5 Hz, 2H, ^{*Bu*}CH₂), 1.23 (p-hex, 2H, J = 7.6 Hz, ^{*Bu*}CH₂), 0.77 (t, J = 7.3 Hz, 3H, ^{*Bu*}CH₃) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 73.1 (s, O-CH₂), 71.2 (s, O-^{*Bu*}CH₂), 70.9 (s, O-CH₂), 70.6 (s, O-CH₂), 70.6 (s, O-CH₂), 61.8 (s, O-CH₂), 32.3 (s, ^{*Bu*}CH₂), 19.8 (s, ^{*Bu*}CH₂), 14.3 (s, ^{*Bu*}CH₃).

PE3-H - α -Bu- ω -OMe pEO, $n_{\max} = 105$



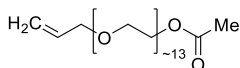
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.47 (broad s, 464H, O-CH₂), 2.62 (broad s, 1H, O-H), 1.42 (p-quint, J = 6.7 Hz, 2H, ^{*Bu*}CH₂), 1.26 (m, 2H, ^{*Bu*}CH₂), 0.79 (t, J = 7.5 Hz, 3H, ^{*Bu*}CH₃) ; $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 73.1 (s, O-^{*Bu*}CH₂), 70.9 (s, O-CH₂), 61.8 (s, O-CH₂), 32.3 (s, ^{*Bu*}CH₂), 19.8 (s, ^{*Bu*}CH₂), 14.3 (s, ^{*Bu*}CH₃).

PE4-Me - α -allyl- ω -OMe pEO, $n_{\max} = 13$



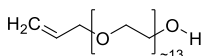
^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 5.74-5.65 (m, 1H, allyl/CH), 5.08 (dd, $J = 17.2$ Hz, $J = 1.7$ Hz, 1H, $\text{allyl/CH}_2\text{a}$), 4.93 (dd, $J = 10.4$ Hz, $J = 1.4$ Hz, 1H, $\text{allyl/CH}_2\text{b}$), 3.76 (d, $J = 5.4$ Hz, 2H, O-allyl/CH_2), 3.38 (broad s, 48H, O-CH_2), 3.27 (m, 2H, O-CH_2), 3.09 (s, 3H, O-CH_3); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 135.4 (s, allyl/CH), 116.1 (s, allyl/CH_2), 72.1 (s, O-CH_2), 72.0 (s, O-allyl/CH_2), 70.7 (s, O-CH_2), 70.6 (s, O-CH_2), 69.8 (s, O-CH_2), 58.6 (s, O-CH_3). **HR-MS (ESI $^+$)**: $[\text{M}+\text{Na}]^+ = \text{C}_{30}\text{H}_{60}\text{O}_{14}\text{Na}^+$, calc. 667.3875, found 667.3877.

PE4-COME - α -allyl- ω -OCOMe pEO, $n_{\text{max}} = 13$



^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 5.73-5.64 (m, 1H, allyl/CH), 5.08 (dd, $J = 17.2$ Hz, $J = 1.7$ Hz, 1H, $\text{allyl/CH}_2\text{a}$), 4.93 (dd, $J = 10.4$ Hz, $J = 1.4$ Hz, 1H, $\text{allyl/CH}_2\text{b}$), 4.01 (t, $J = 4.9$ Hz, 2H, $\text{CH}_2\text{-O-C(=O)}$), 3.76 (d, $J = 5.3$ Hz, 2H, O-allyl/CH_2), 3.38 (broad s, 48H, O-CH_2), 1.78 (s, 3H, C(=O)-CH_3); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 170.2 (s, C(=O)), 135.6 (s, allyl/CH), 116.2 (s, allyl/CH_2), 72.1 (s, O-allyl/CH_2), 70.9 (s, O-CH_2), 69.9 (s, O-CH_2), 69.2 (s, O-CH_2), 63.7 (s, C(=O)-O-CH_2), 20.7 (s, CH_3). **HR-MS (ESI $^+$)**: $[\text{M}+\text{Na}]^+ = \text{C}_{31}\text{H}_{60}\text{O}_{15}\text{Na}^+$, calc. 695.3824, found 695.3827.

PE4-H - α -allyl- ω -OH pEO, $n_{\text{max}} = 13$



^1H NMR (400 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 5.75-5.65 (m, 1H, allyl/CH), 5.09 (dd, $J = 17.2$ Hz, $J = 1.7$ Hz, 1H, $\text{allyl/CH}_2\text{a}$), 4.94 (dd, $J = 10.4$ Hz, $J = 1.4$ Hz, 1H, $\text{allyl/CH}_2\text{b}$), 3.77 (d, $J = 5.6$ Hz, 2H, O-allyl/CH_2), 3.55 (t, 2H, $J = 4.9$ Hz, HO-CH_2), 3.39 (broad s, 48H, O-CH_2); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 135.5 (s, allyl/CH), 116.3 (s, allyl/CH_2), 73.2 (s, O-CH_2), 72.1 (s, O-allyl/CH_2), 70.9 (s, O-CH_2), 70.6 (s, O-CH_2), 69.9 (s, O-CH_2), 61.7 (s, HO-CH_2). $[\text{M}+\text{Na}]^+ = \text{C}_{29}\text{H}_{58}\text{O}_{14}\text{Na}^+$, calc. 653.3719, found 653.3721.

1.8. Characterization of Product

1,4-dioxane^[3]



^1H NMR (600 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 3.50 (s, 8H); **$^{13}\text{C}\{^1\text{H}\}$ NMR** (151 MHz, $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), 295 K): δ [ppm] = 67.2 (s, CH_2).

The obtained spectroscopic data is in accordance with the literature.^[3]

2. NMR spectra

2.1 NMR spectra of Polyethers

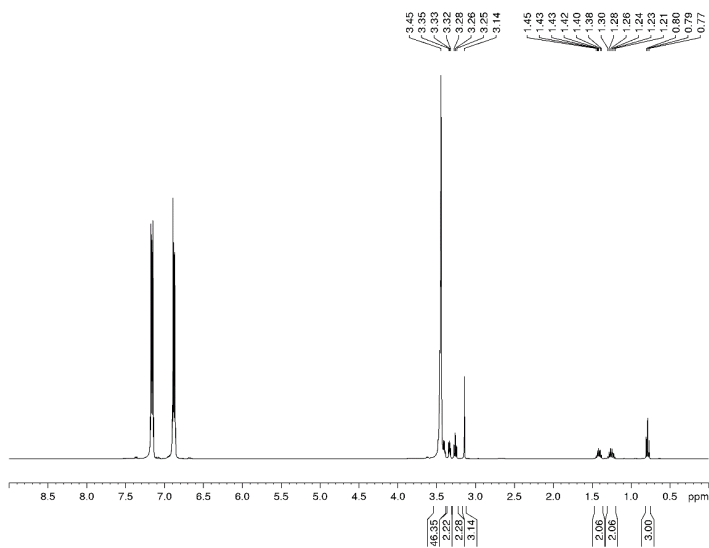


Figure S 11: ^1H NMR spectrum (400 MHz) of PE1 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

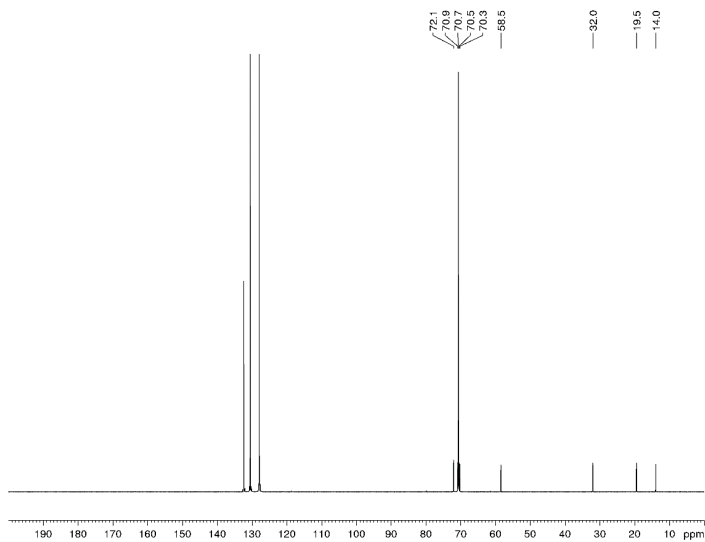


Figure S 12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE1 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

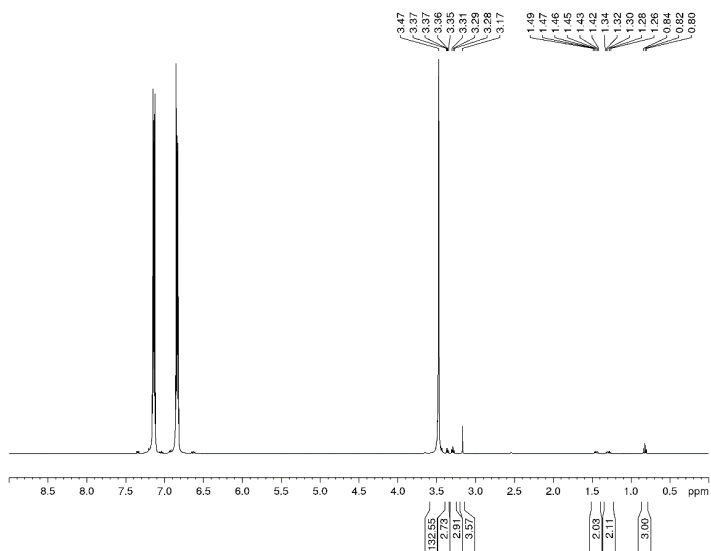


Figure S 13: ^1H NMR spectrum (400 MHz) of PE2 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 25$) in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

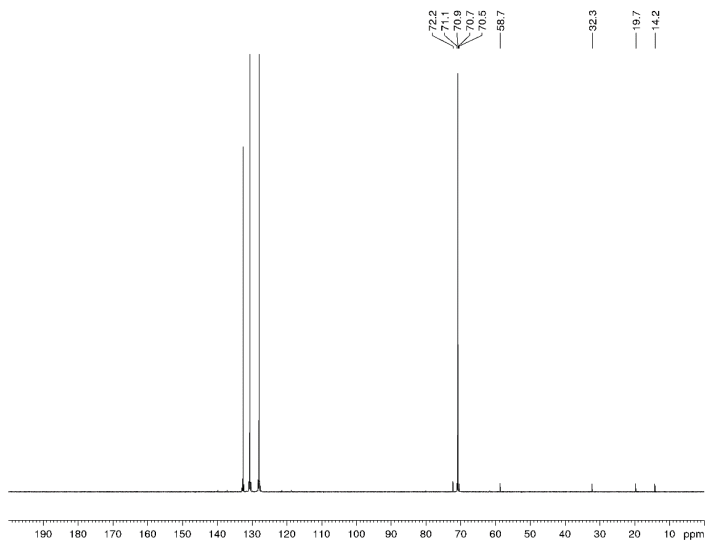


Figure S 14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE2 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 25$) in $o\text{DCB}:\text{C}_6\text{D}_6$ (50:1) at 295 K.

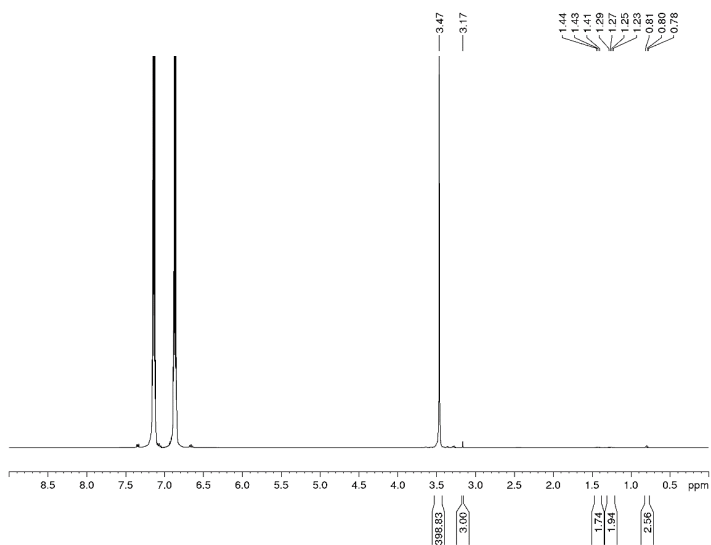


Figure S 15: ^1H NMR spectrum (400 MHz) of PE3 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 105$) in oDCB: C_6D_6 (50:1) at 295 K.

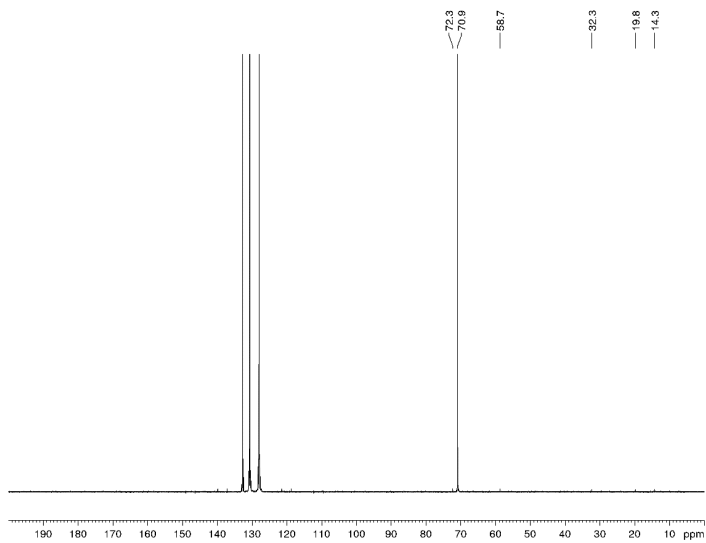


Figure S 16: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE3 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 105$) in oDCB: C_6D_6 (50:1) at 295 K.

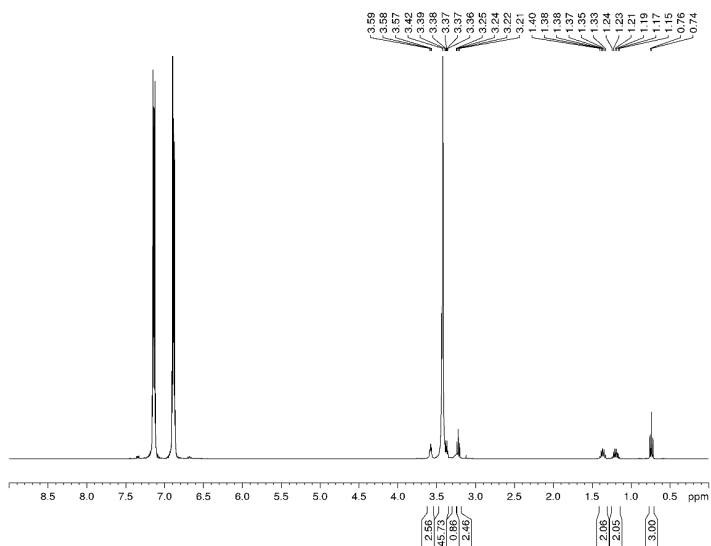


Figure S 17: ^1H NMR spectrum (400 MHz) of PE1-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

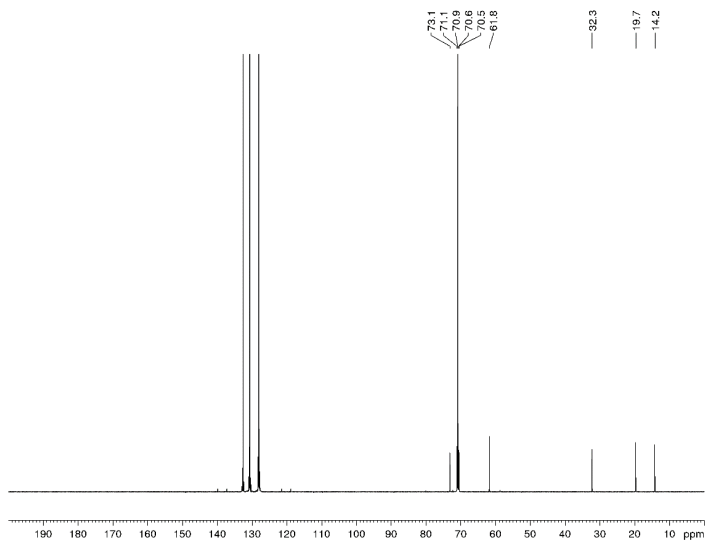


Figure S 18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE1-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

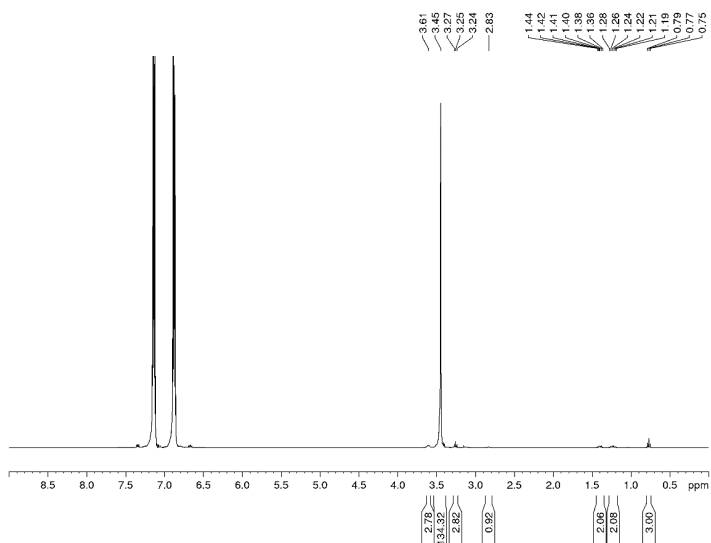


Figure S 19: ^1H NMR spectrum (400 MHz) of PE2-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 25$) in oDCB: C_6D_6 (50:1) at 295 K.

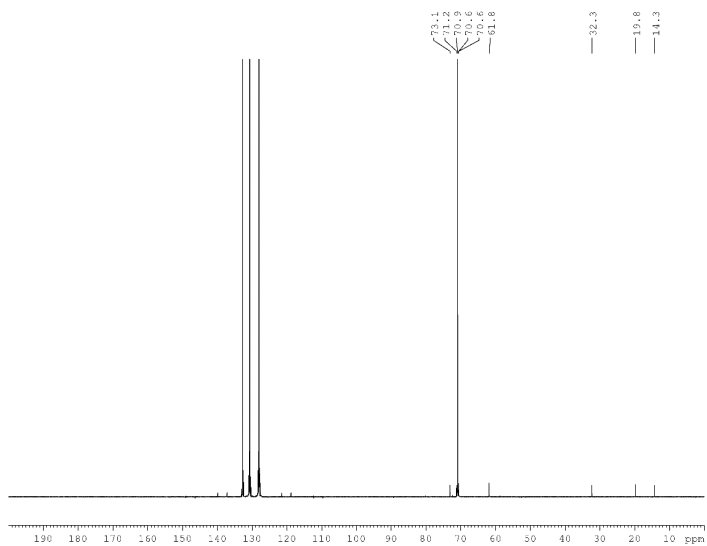


Figure S 20: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE2-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 25$) in oDCB: C_6D_6 (50:1) at 295 K.

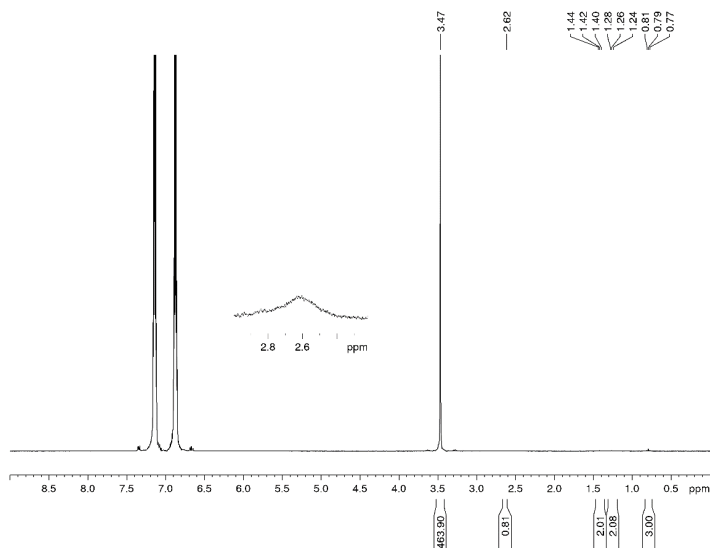


Figure S 21: ^1H NMR spectrum (400 MHz) of PE3-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 105$) in oDCB: C_6D_6 (50:1) at 295 K.

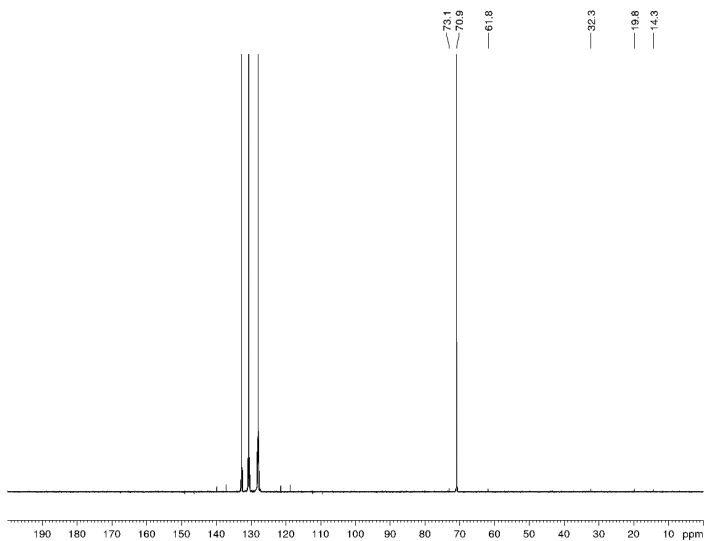


Figure S 22: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE3-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 105$) in oDCB: C_6D_6 (50:1) at 295 K.

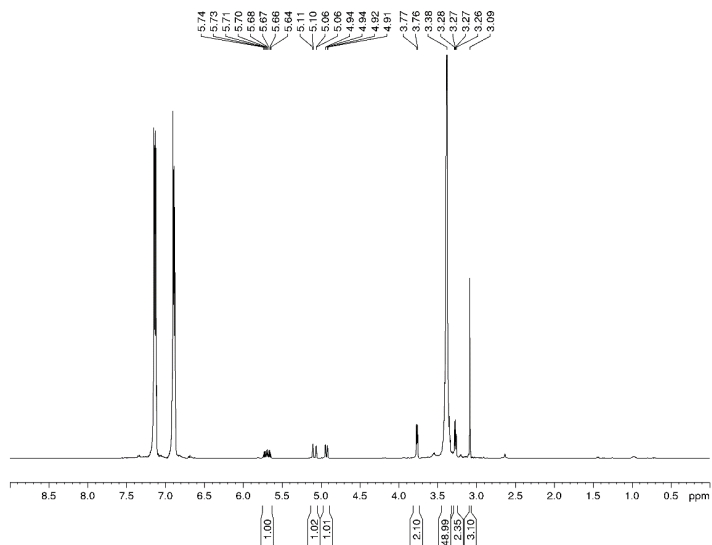


Figure S 23: ¹H NMR spectrum (400 MHz) of PE4-Me (α-allyl-ω-OMe pEO, $n_{\max} = 13$) in oDCB:C₆D₆ (50:1) at 295 K.

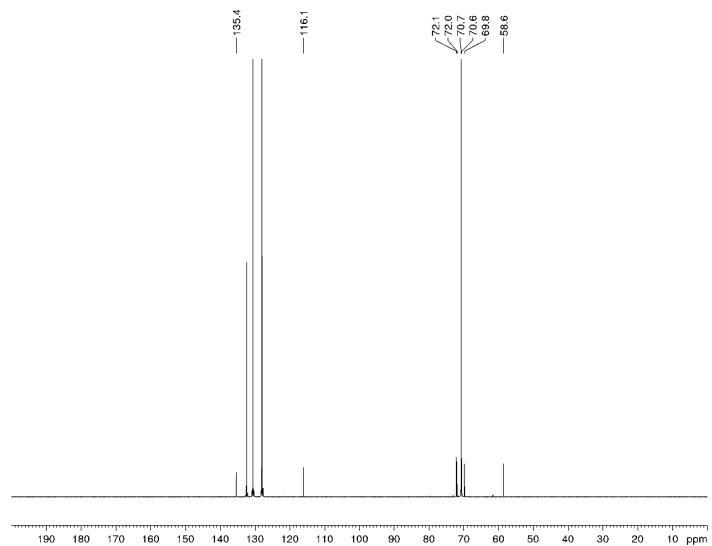


Figure S 24: ¹³C NMR spectrum (101 MHz) of PE4-Me (α-allyl-ω-OMe pEO, $n_{\max} = 13$) in oDCB:C₆D₆ (50:1) at 295 K.

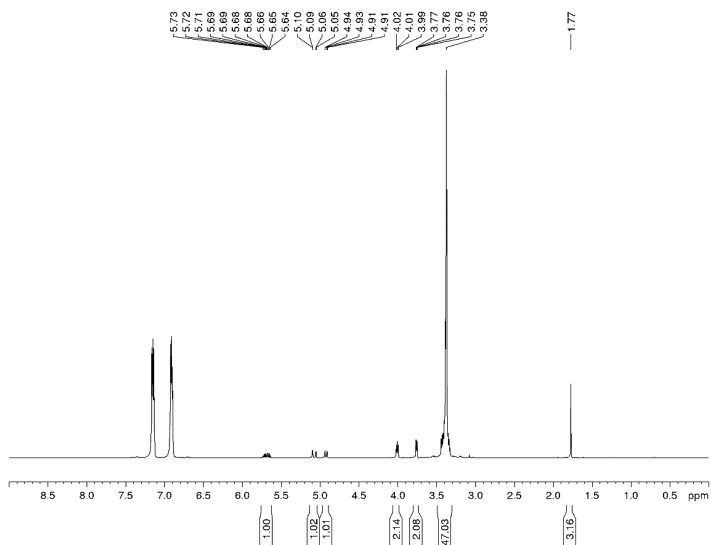


Figure S 25: ^1H NMR spectrum (400 MHz) of PE4-COMe (α -allyl- ω -OCOMe pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

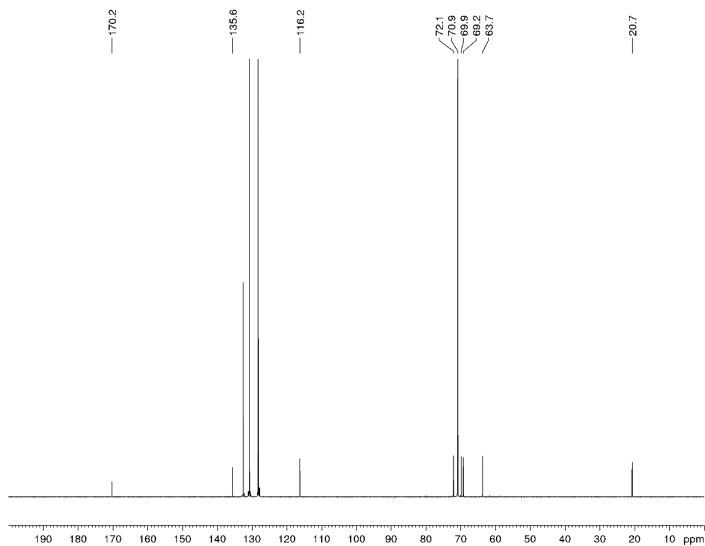


Figure S 26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE4-COMe (α -allyl- ω -OCOMe pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

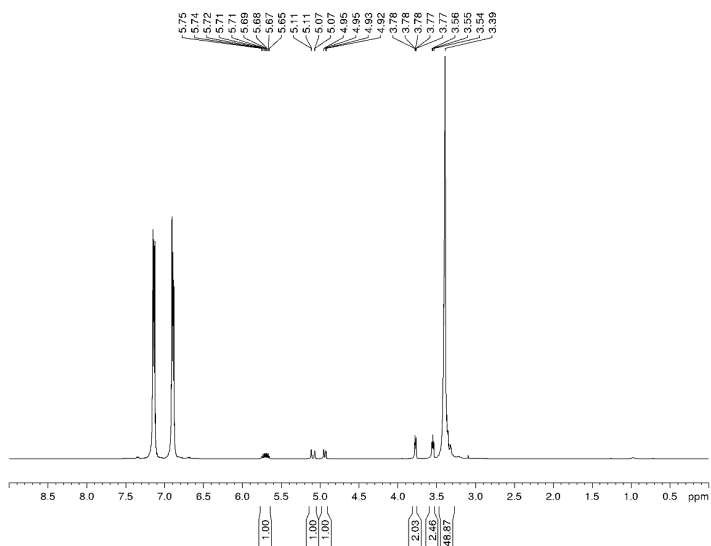


Figure S 27: ^1H NMR spectrum (400 MHz) of PE4-H (α -allyl- ω -OH pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

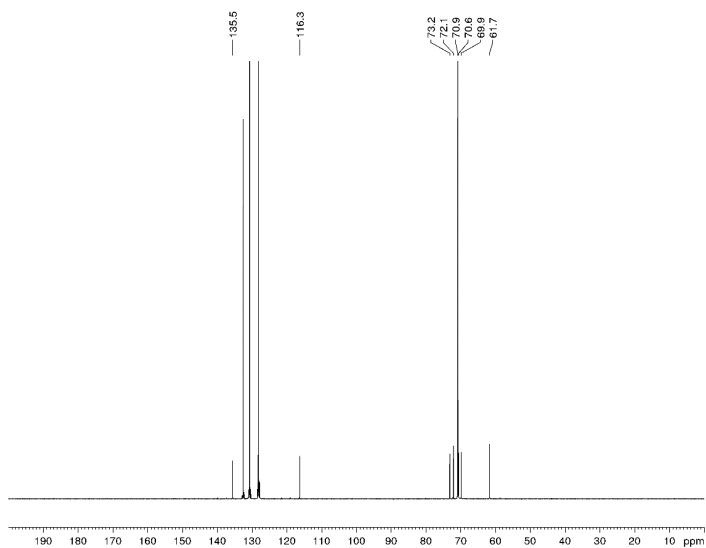


Figure S 28: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of PE4-H (α -allyl- ω -OH pEO, $n_{\text{max}} = 13$) in oDCB: C_6D_6 (50:1) at 295 K.

2.2 Exemplary NMR spectra of Degradation Reactions

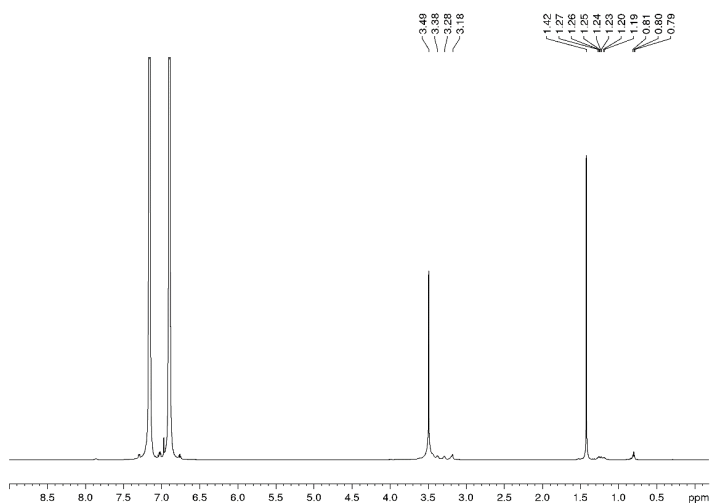


Figure S 29: ^1H NMR spectrum (600 MHz) of the degradation reaction of PE1 ($\alpha\text{-Bu-}\omega\text{-OMe pEO}$, $n_{\text{max}} = 13$), catalyzed by 5 mol% of $[1]_0$ in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), containing cyclooctane as an internal standard, measured at 295 K. The product peaks overlap with the starting material.

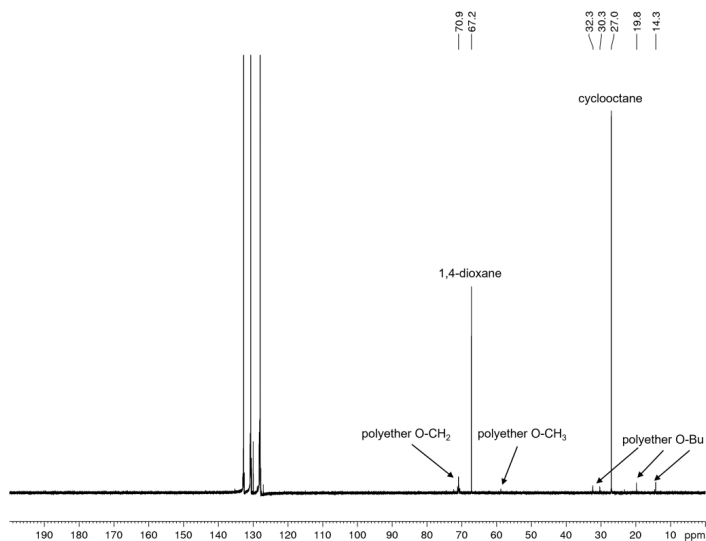


Figure S 30: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the degradation reaction of PE1 ($\alpha\text{-Bu-}\omega\text{-OMe pEO}$, $n_{\text{max}} = 13$), catalyzed by 5 mol% of $[1]_0$ in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), containing cyclooctane as an internal standard, measured at 295 K.

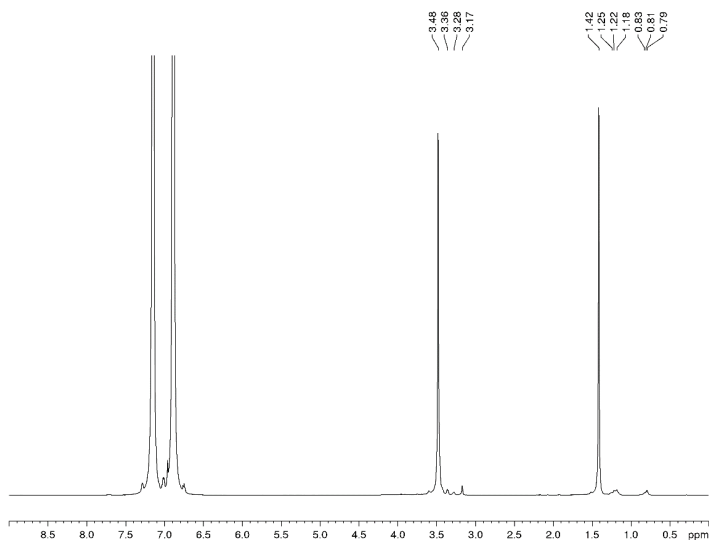


Figure S 31: ^1H NMR spectrum (600 MHz) of the degradation reaction of PE2 ($\alpha\text{-Bu-}\omega\text{-OMe pEO}$, $n_{\text{max}} = 25$), catalyzed by 5 mol% of **[1]**, in $\text{oDCB:C}_6\text{D}_6$ (50:1), containing cyclooctane as an internal standard, measured at 295 K. The product peaks overlap with the starting material.

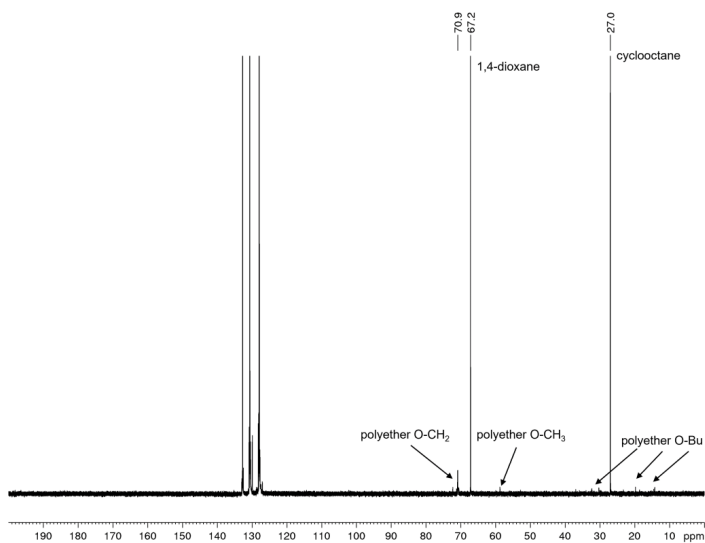


Figure S 32: $^{13}\text{C}(^1\text{H})$ NMR spectrum (151 MHz) of the degradation reaction of PE2 ($\alpha\text{-Bu-}\omega\text{-OMe pEO}$, $n_{\text{max}} = 25$), catalyzed by 5 mol% of **[1]**, in $\text{oDCB:C}_6\text{D}_6$ (50:1), containing cyclooctane as an internal standard, measured at 295 K.

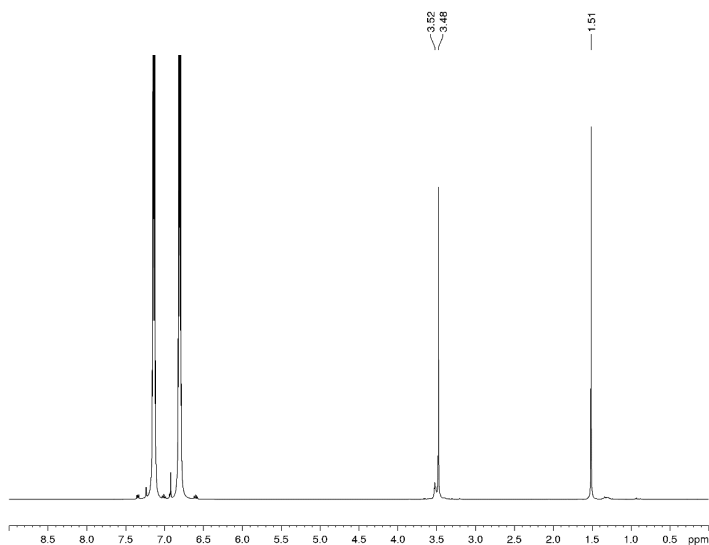


Figure S 33: ^1H NMR spectrum (600 MHz) of the degradation reaction of PE3 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 105$), catalyzed by 5 mol% of **[1]**, in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), containing cyclooctane as an internal standard, measured at 295 K. The product peaks partially overlap with the starting material.

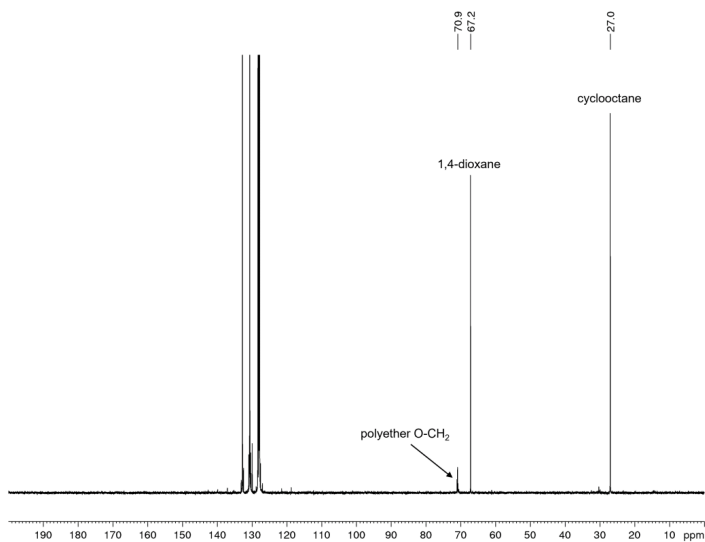


Figure S 34: $^{13}\text{C}(^1\text{H})$ NMR spectrum (151 MHz) of the degradation reaction of PE3 (α -Bu- ω -OMe pEO, $n_{\text{max}} = 105$), catalyzed by 5 mol% of **[1]**, in $\text{oDCB}:\text{C}_6\text{D}_6$ (50:1), containing cyclooctane as an internal standard, measured at 295 K.

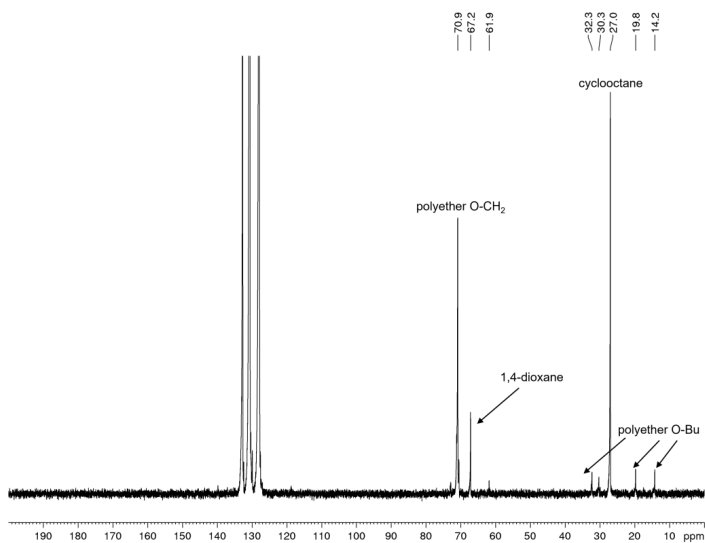


Figure S 35: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of the degradation reaction of PE1-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 13$), catalyzed by 5 mol% of [1]_n in oDCB:C₆D₆ (50:1), containing cyclooctane as an internal standard, measured at 295 K.

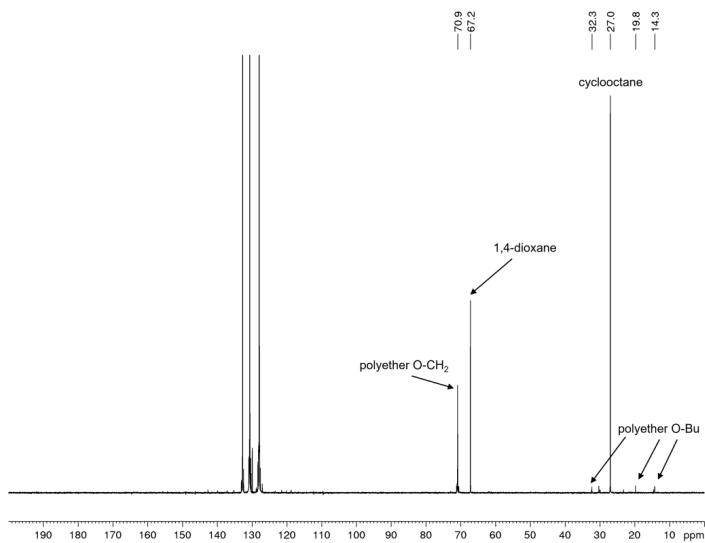


Figure S 36: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of the degradation reaction of PE2-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 25$), catalyzed by 5 mol% of [1]_n in oDCB:C₆D₆ (50:1), containing cyclooctane as an internal standard, measured at 295 K.

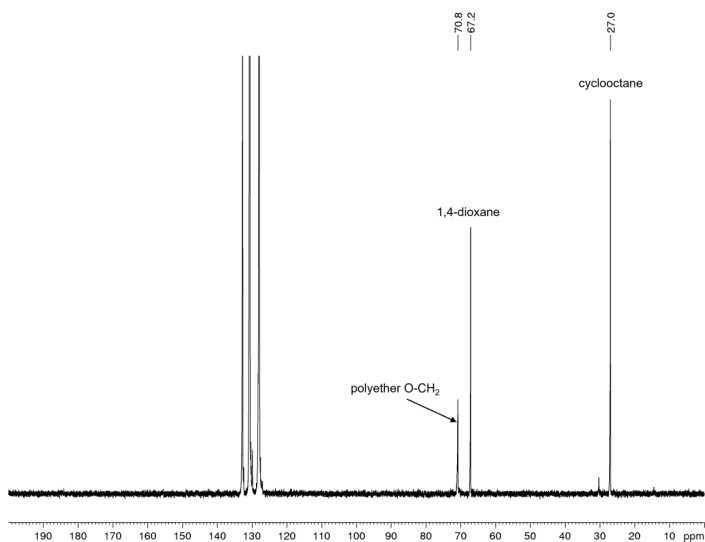


Figure S 37: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of the degradation reaction of PE3-H (α -Bu- ω -OH pEO, $n_{\text{max}} = 105$), catalyzed by 5 mol% of [1], in oDCB: C_8D_8 (50:1), containing cyclooctane as an internal standard, measured at 295 K.

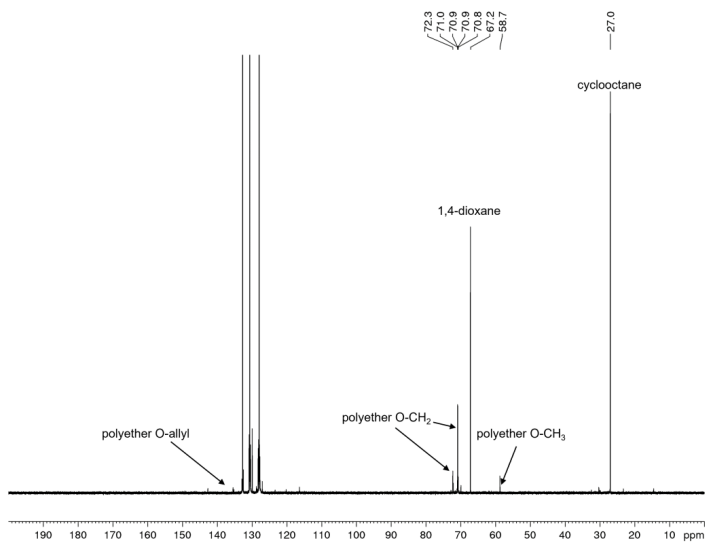


Figure S 38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the degradation reaction of PE4-Me (α -allyl- ω -OMe pEO, $n_{\text{max}} = 13$), catalyzed by 5 mol% of [1], in oDCB: C_8D_8 (50:1), containing cyclooctane as an internal standard, measured at 295 K.

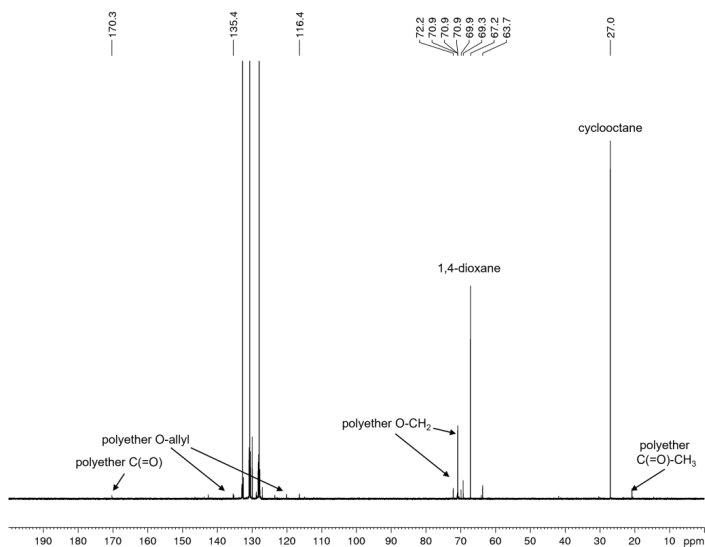


Figure S 39: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the degradation reaction of PE4-COMe (α -allyl- ω -OCOMe pEO, $n_{\text{max}} = 13$), catalyzed by 5 mol% of [1]_n in oDCB: C_8D_8 (50:1), containing cyclooctane as an internal standard, measured at 295 K.

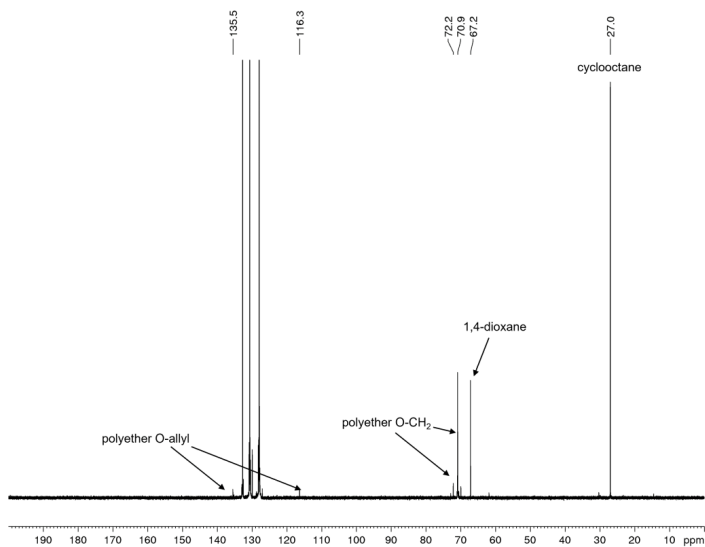


Figure S 40: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of the degradation reaction of PE4-H (α -allyl- ω -OH pEO, $n_{\text{max}} = 13$), catalyzed by 5 mol% of [1]_n in oDCB: C_8D_8 (50:1), containing cyclooctane as an internal standard, measured at 295 K.

References

- [1] a) R. Maskey, M. Schädler, C. Legler, L. Greb, *Angew. Chem. Int. Ed.* **2018**, 57, 1717–1720; b) N. Ansmann, D. Hartmann, S. Sailer, P. Erdmann, R. Maskey, M. Schorpp, L. Greb, *Angew. Chem. Int. Ed.* **2022**, n/a, e202203947; c) N. Ansmann, T. Thorwart, L. Greb, *Angew. Chem. Int. Ed.* **2022**, 61, e202210132.
- [2] Bruker TopSpin 4.0.8, 2019, <https://www.bruker.com/products/mr/hmr/software/topspin.html>
- [3] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176-2179.

3.3. BIS(AMIDOPHENOLATO)TETRELS AS Z-TYPE LIGANDS

3.3.1. NEUTRAL AND ANIONIC SQUARE PLANAR PALLADIUM(0) COMPLEXES STABILIZED BY A SILICON Z-TYPE LIGAND

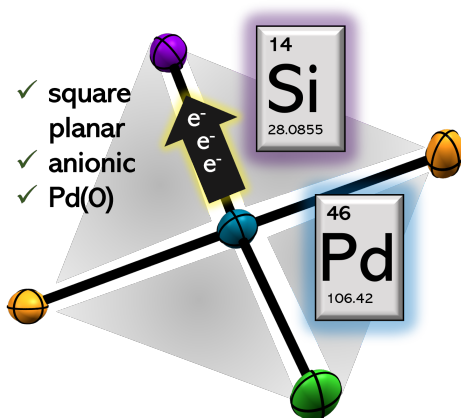


FIG. 3.3.: “Neutral and Anionic Square Planar Palladium(0) Complexes Stabilized by a Silicon Z-Type Ligand” - table of contents figure for the publication discussed in the following section.

The full article including its electronic supplementary information (ESI) presented in this section was published earlier and can be accessed under:

N. Ansmann, J. Münch, M. Schorpp, L. Greb, *Angew. Chem. Int. Ed.* **2023**, 62, e202313636, <https://doi.org/10.1002/anie.202313636>.

Contributions of the three leading authors are rationalized and listed according to the CRediT scheme^[300] on page 144, using the “Formblatt Kumulative Dissertation” (cumulative dissertation form), provided by the faculty of Geo- Sciences and Chemistry at the Ruprecht-Karls Universität Heidelberg. The original article is embedded at page 145 ff. The ESI is subsequently attached, starting at page 151.

Formblatt Kumulative Dissertation

1. Publikation/*Publication*:

Vollständige bibliographische Referenz/*Complete bibliographic reference*:

N. Ansmann, J. Muench, M. Schorpp, L. Greb. Neutral and Anionic Square Planar Palladium(0) Complexes Stabilized by a Silicon Z-Type Ligand. Angew. Chem. Int. Ed. 2023, 62, e202313636. doi.org/10.1002/anie.202313636

2. Erst- oder gleichberechtigte Autorenschaft/*First or equal authorship*: Ja/Yes ☒ Nein/No ☐

Veröffentlicht/*Published*

Zur Veröffentlichung angenommen/*Accepted*

Eingereicht/*Submitted*

Noch nicht eingereicht/*Not yet submitted*

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4. Beteiligungen/*Contributions***

Contributor Role	Doktorand/in/ <i>Doctoral Student</i>	Co-Autor/in 1/ <i>Co-author 1</i>	Co-Autor/in 2/ <i>Co-author 2</i>
<i>Name, first name</i>	Ansmann, Nils	Muench, Joshua	Schorpp, Marcel
Methodology	lead	-	-
Software	-	-	-
Validation	lead	-	supporting
Formal analysis	lead	supporting	-
Investigation	lead	supporting	supporting
Resources	-	-	-
Data Curation	lead	-	-
Writing-Original Draft	equal	-	supporting
Writing-Review&Editing	equal	-	-
Visualization	lead	-	-
Supervision	equal	-	-
Project administration	equal	-	-
Funding acquisition	-	-	-

****Kategorien des CRediT (Contributor Roles Taxonomy, <https://credit.niso.org/>)**

Hiermit bestätige ich, dass alle obigen Angaben korrekt sind/*I confirm that all declarations made above are correct.*

Unterschrift/*Signature*


Doktorand/in/*Doctoral student*


Co-Autor/in 1/*Co-author 1*

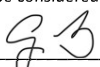

Co-Autor/in 2/*Co-author 2*

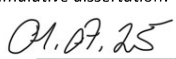
Betreuungsperson/*Supervisor*:

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Prof. Dr. Lutz Greb

Name/*Name*


Unterschrift/*Signature*


Datum/*date*

Silicon Ligands

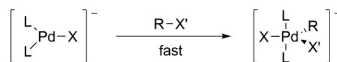
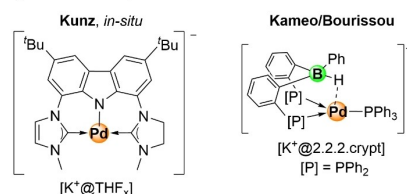
Neutral and Anionic Square Planar Palladium(0) Complexes Stabilized by a Silicon Z-Type Ligand

Nils Ansmann, Joshua Münch, Marcel Schorpp, and Lutz Greb*

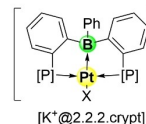
Abstract: Anionic $[\text{Pd}(0)\text{-X}]^-$ ate complex were proposed as key intermediates in Pd-catalyzed cross-coupling for decades, but their isolation remained elusive. Herein, a chelating Lewis acidic bis(amidophenolato)silane is introduced as a strong Z-type ligand which enables the characterization of the first anionic $[\text{Pd}(0)\text{-X}]^-$ ate complex. Intriguingly, these compounds and the neutral $\text{L-Pd}(0)$ analogs exhibit a square planar coordination that is highly unusual for a d^{10} metal. Theoretical methods scrutinize the interaction between the Lewis acidic Si(IV) center and the late transition metal, while reactivity studies shed light on the potential role of anionic additives in oxidative addition reactions.

The involvement of anionic Pd(0) intermediates in cross-coupling reactions like the Heck, Suzuki, Stille or Buchwald-Hartwig reactions is widely accepted in organometallic catalysis.^[1] While increased yields were often noticed upon the addition of halide salts, corresponding intermediates were never isolated, and the molecular explanation of the effect remained debated.^[2] In pioneering work, Amatore and Jutand used electrochemistry and ³¹P NMR spectroscopy to justify the rate acceleration in the oxidative addition by the formation of $[\text{Pd}(0)\text{-X}]^-$ ate complexes (Scheme 1a).^[3] Theoretical studies corroborated the involvement of such and various other anionic species in the catalytic cycle.^[4] As an alternative, Joy and Shaik suggested that the beneficial role of anionic additives could be attributed to oriented external electric fields (OEEFs) from anions that are not directly bound, but hold in proximity to the Pd(0) center by non-covalent interactions.^[5] Karaghiosoff and Koszinowski extended the experimental character-

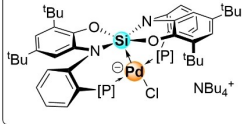
a) Amatore Jutand Mechanism


 proposed Pd(0) ate
complex
b) Anionic M⁰ complexes

c) Bourissou



d) This work



Scheme 1. a) Pd(0) ate complexes as proposed as possible intermediates in the Amatore Jutand catalytic cycle of cross-coupling reactions. b) Examples of anionic d¹⁰ complexes. c) The first isolated anionic sq-Pt(0) ate-complex with a boron Z-type ligand. d) Isolated anionic sp-Pd(0) ate complex with a Si(IV) Z-type ligand presented in this work.

ization by using electron-poor phosphines as co-ligands and could prove the existence of Pd(II) ate complexes by mass spectrometry and NMR analysis.^[6] In general, isolated examples of anionic group 10 M⁰ (M⁰=Ni, Pd, Pt) complexes are scarce in the literature (Scheme 1b), and the full characterization of a $[\text{Pd}(0)\text{-X}]^-$ ate complex remained elusive.^[7]

Ambiphilic ligands incorporating Lewis acidic sites to function as σ-accepting Z-type ligands have risen in popularity in the past 20 years.^[8] A substantial alteration of the reactivity at the metal center was achieved by adjusting the electron density at the transition metal through the Z-type interaction.^[9] Only recently, the Bourissou group used this concept to isolate the first square-planar (sp) anionic d¹⁰ Pt complex by employing a diphosphine-borane as an ambiphilic L₂Z-ligand (Scheme 1c).^[7] While group 13 elements are well established as Z-type ligands due to the inherent Lewis acidic features caused by their empty p_z-orbital, much

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less is reported in such context on using neutral group 14 based Lewis acids.^[10] In recent years, we developed several examples of Lewis superacidic neutral silanes with application potential in catalysis and in the stabilization of intermediates of interest in organic synthesis.^[11]

Although common neutral silanes possess comparably low fluoride ion affinities (FIA, *general* Lewis acidity), they cause strong ³¹P NMR shifts of coordinated phosphine oxide in the Gutmann Beckett test, meaning they inherit a highly *effective* Lewis acidity.^[12] Hence, we were encouraged to probe the putatively strong *effect* of Si(IV) Lewis acids on d-block metals. Aiming for a strong interaction between the transition metal and the Lewis acid in Z-type, we here report the synthesis of an ambiphilic bisphosphine-Si(IV) ligand. The corresponding Pd(0) complex exhibits strong push-pull binding and enables the isolation of the first neutral and anionic sp Pd(0) complexes (Scheme 1d).

Our study was launched by designing a ligand that combines a Si(IV)-centered acceptor with P-donor functionalities. We were inspired by van der Vlugt's redox active diphenylphosphanyl aminophenol (PNO-H2) **1**, which had been successfully employed as a ligand for hetero-bimetallic Ni–Au complexes (Figure 1).^[13] Reacting **1** with silicon tetrachloride cleanly furnished the protonated chloridosilicate [H][2-Cl] with a characteristic ²⁹Si NMR shift ($\delta = -96.3$ ppm), implying a penta-coordinated Si species. Its structure was confirmed by scXRD analysis (see ESI for details). Deprotonation with tetramethyl piperidine (TMP) and chloride abstraction with either TMSOTf or NaBARF₂₀

cleanly afforded silane **2**. Alternatively, the latter could be synthesized by reaction of **1** with tris(dimethylamino)silane to yield the dimethyl amine adduct [2-NHMe₂], which, in comparison to [H][2-Cl], exhibits two signals in the ³¹P{¹H} NMR spectrum instead of one. This is caused by hydrogen bonding of one phosphine arm to the coordinated amine, leading to a rigid structure, as confirmed in the solid state structure (see ESI for scXRD). Abstraction of the amine with the oligomeric Lewis superacid [Si(cat¹)₂]_n cleanly furnished **2**.

No coordination of the phosphines to the Lewis acidic center can be observed in **2**, resulting in a tetrahedral geometry at the silicon center, as confirmed by ²⁹Si NMR spectroscopy ($\delta(^{29}\text{Si}) = -44.2$ ppm) and scXRD (Figure 1).^[14] Reacting **2** or [2-NHMe₂] with cyclopentadienyl allyl palladium(II) resulted in the formation of a pristine compound **3** with a single resonance in the ³¹P NMR spectrum, indicating a symmetric coordination of Pd(0) that is formed by reductive elimination (Figure 2a). A first indication of a silicon-palladium interaction in **3** was observed by ²⁹Si NMR spectroscopy, showing a high-field

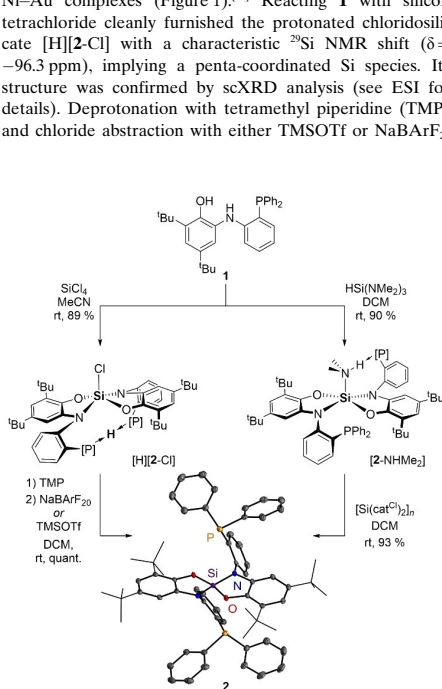


Figure 1. Synthesis of the Z-type ligand **2** from phosphanyl aminophenol **1** and ORTEP plot of the solid state structure of **2** (hydrogen atoms and solvent molecules omitted for clarity; vibrational ellipsoids displayed at 50%).

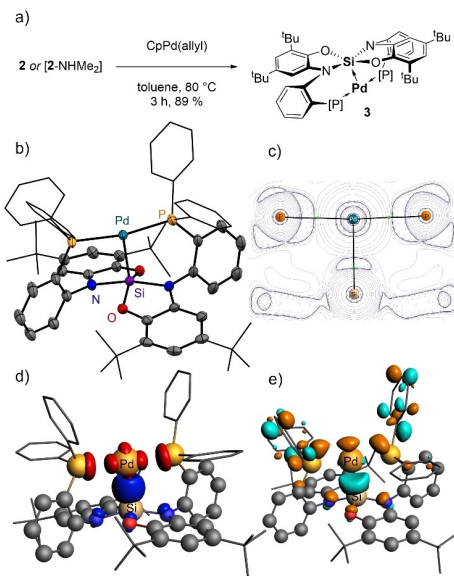


Figure 2. a) Synthesis of **3** through reductive elimination of CpPd(allyl) in the presence of silane **2**. b) ORTEP plot of the solid-state structure of **3**. Hydrogen atoms and disordered PPh₂ units were omitted for clarity; vibrational ellipsoids are displayed at 50%. c) View of the P₂–Pd–Si interaction in complex **3** as obtained by QTAIM analysis, displaying the Laplacian of the electron density, bond paths and bond critical points. d) ETS-NOCV deformation density $\Delta\rho$ of the NOCV corresponding to the Pd–Si interaction (charge flow from red to blue, BP86-D3BJ/TZVP//PBEh-3c, 0.045 e/A³). e) LUMO of **3** (BP86-D3BJ/TZVP//PBEh-3c, 0.045 e/A³).

shifted signal ($\delta(^{29}\text{Si}) = -83.6$ ppm) as a triplet from ^2J coupling (6.3 Hz) of the ^{29}Si nucleus with the two equivalent phosphorus nuclei. Analysis of single-crystals by X-ray diffraction revealed a Si–Pd bond length of 2.3707(6) Å in the T-shaped complex (Figure 2b), which is significantly shorter than the Si–Pd bond lengths for previously observed dative Pd–Si bonds (Grobe et al.: 3.875 Å, Bourissou et al.: 2.9770(0) Å).^[15] The Si–Pd bond length is even comparable to the P–Pd bonds (2.2909(6) and 2.2939(6) Å), indicating equal contributions of Pd by σ -acceptor (P-donors) and σ -donor (Si-acceptor) interaction. The calculated ratio of bond-length and covalent radii ($r = 0.95$) is within the range of a Z-type interaction.^[8b,16]

A series of theoretical analyses was employed to investigate the Pd–Si bond in **3**. The Wiberg bond index of the Si–Pd bond is 0.43, which is even higher than the Pd–P WBIs (0.42). Natural charges obtained by NPA show a diminished positive charge at the Si center (2.038 vs. 2.354 in **2**), underlining a Pd- $\rightarrow$ Si charge flow. Second-order perturbation theory analysis manifests the Pd- $\rightarrow$ Si donation from a filled d-orbital into a non-Lewis type Si-centered NBO (61 % s-, 39 % p-character) with a stabilization energy of 112 kcal/mol. QTAIM analysis of **3** revealed a bond path between Si and Pd. The electron density at the bond critical point ($\rho(\mathbf{r}_{\text{BCP}}(\text{Si–Pd})) = 0.074$) is substantially larger as in the previously reported Z-type interaction of a less Lewis acidic silane with gold ($\rho(\mathbf{r}_{\text{BCP}}(\text{Si–Au})) = 0.021$),^[17] but of similar magnitude to a strong Pt–Sb(V) interaction.^[18] The negative Laplacian of the electron density $\nabla^2\rho(\mathbf{r}_{\text{BCP}})$ and other topological descriptors attribute a pronounced covalent character (shared interaction) to the Si–Pd interaction (Figure 2c and section 2f in the ESI). ETS-NOCV calculations (BP86-D3BJ/TZ2P/PBEh-3c) further explained the bond formation between the neutral Pd(0) and the ligand. The major contribution to the total overall orbital interaction energy is provided by the NOCV orbital with deformation density $\Delta\rho$ shown in Figure 2d ($\Delta E_{\text{orb}} = -65.5$ kcal mol⁻¹). It reflects the push-pull interaction of the ligand through the electron flow of the phosphines to the Pd center with simultaneous electron donation from filled dz^2 and dx^2-y^2 orbitals at Pd in the p_z -type acceptor and antibonding $\sigma^*(\text{Si–N/O})$ orbital of the silane. We note in passing that the pseudo-four-fold symmetry of the acceptor unit might allow interactions of δ -symmetry (dx^2-y^2 orbital as donor), that would be symmetry-forbidden for the three-fold symmetric acceptor sites with the established group 13 based Z-type ligands (see Figure S9). While the results obtained by calculations strongly indicate the formation of a dative Pd- $\rightarrow$ Si bond, we wanted to address the possibility that the potentially redox non-innocent amidophenolate could contribute electrons to the Si center, resulting in a formal Si(II)- $\rightarrow$ Pd interaction in complex **3**. While a bond-length contraction in the OCCN scaffold of **3** can in fact be observed in the solid state structures after coordination of Pd compared to silane **2**, the calculated metric oxidation states (MOS) of -1.92 in the ligands indicate only minor contributions of such bonding mode (see ESI, section 3c). Furthermore, the computed triplet state geometries strongly diverged from the experimental molecular structures, while

no broken symmetry DFT solutions could be found. The Pd–Si interaction can therefore be seen as a push-pull system, with electron withdrawing effects at the Si(IV) center strongly dominating any silylene donating effects. Expected trends in the reactivity of **3** were derived from the frontier molecular orbitals. While the HOMO is located at the ligand backbone (see ESI for details), the LUMO shows strong contributions at Pd, indicating electrophilicity at the formally electron rich d^{10} metal center (Figure 2e).

Indeed, while **3** behaves inert in reactions with electrophiles like aryl halides at room temperature, it readily undergoes reactions with nucleophiles in solution (Figure 3a). These findings are in line with other Z-type Pd complexes that do not undergo oxidative addition with aryl iodides at room temperature.^[19] We first investigated the reactivity towards the weakly σ -donating but π -accepting CO. Pressurizing a solution of **3** with 5 bar of CO results in an increase of the observed ^2J coupling in the ^{29}Si NMR spectrum (6.3 Hz $\rightarrow$ 13.4 Hz). A resonance at 185.2 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum states the formation of **[3-CO]**, in line with the DFT-computed free energy of this process ($\Delta G^\circ = -24.1$ kJ/mol).^[20] The binding equilibrium depends on the CO pressure and is reversed under reduced pressure. A weak back-donation of the Pd center to the CO ligand was confirmed by ETS-NOCV analysis (for more details, see ESI). While isolation of **[3-CO]** rendered impractical, the reaction of **3** with cyclohexyl isocyanide (CNCy) cleanly furnished complex **[3-CNCy]**, which could be fully characterized. The $^2\text{J}_{\text{Si-P}}$ coupling in the ^{29}Si NMR spectrum ($\delta(^{29}\text{Si}) = -78.4$ ppm) increased to 37.3 Hz, indicating a strong coordination of CNCy to **3**. As already suggested for **[3-CO]**, no significant π -backbonding takes place in **[3-CNCy]**, as noted from the blue-shifted $\nu(\text{CN})$ band in the IR spectrum (2178 cm⁻¹ vs. 2136 cm⁻¹ in free CNCy). Interestingly, this behavior contrasts a previously reported isocyanide Z-type Pd(0) complex, which showed a red-shifted IR band for the respective stretching modes due to remaining π -back binding.^[21] The molecular structure of **[3-CNCy]** in the solid state revealed the coordination of the Lewis basic isocyanide to occur at the Pd, as already supposed by the LUMO in **3**. Remarkably, although being a d^{10} Pd(0) species, the coordination geometry at the Pd is square planar ($\Sigma(\text{Pd–X}) = 360.05(7)^\circ$). To our knowledge, this structure represents the first report of a sp Pd(0) complex.

When dissolved in THF, strongly shifted resonances of **3** in the ^1H NMR spectrum indicate coordination of the σ -donating solvent to the complex. These findings are supported by an increase in the observed $^2\text{J}_{\text{Si-P}}$ coupling (9.3 Hz) and were proven by scXRD analysis of the donor-adduct **[3-THF]** (Figure 3b). As for the π -accepting CNCy complexes, the coordination geometry at the Pd(0) center is sp ($\Sigma(\text{Pd–X}) = 360.13(5)^\circ$). The weakly bound THF (computed $\Delta G^\circ = -7.2$ kJ/mol)^[22] is easily replaced with a chloride anion, resulting in the formation of the anionic Pd(0) complex **[NBu₄][3-Cl]**, which was isolated and fully characterized (Figure 3c). Again, the increased σ -donation of the Pd towards the Si center is reflected in an increased $^2\text{J}_{\text{Si-P}}$ coupling (27.3 Hz), as well as in a shortened Pd–Si

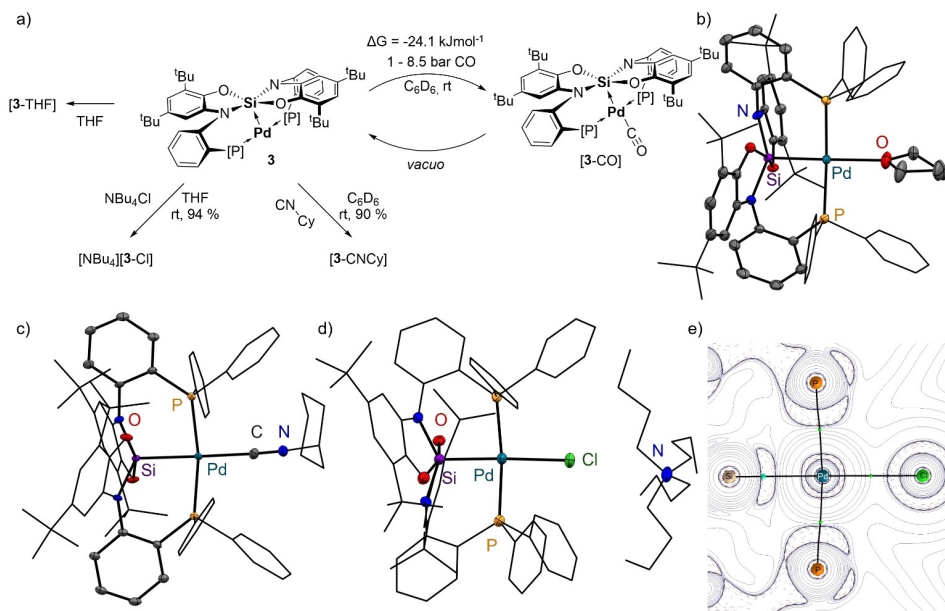


Figure 3. a) Reactivity of **3** with different nucleophiles. ORTEP plots of the solid state structure of b) **[3-(THF)]**, c) **[3-CNCy]** and d) **[NBu₄][3-Cl]** (hydrogen atoms, non-coordinating solvent molecules and disordered positions are omitted for clarity, vibrational ellipsoids displayed at 50 %). e) View of the P₂-Pd-Si interaction in complex **[3-Cl]** as obtained by QAIM analysis, displaying the Laplacian of the electron density, bond paths and bond critical points.

bond (2.3185(14) Å, cf. 2.3707(6) Å in **3**). As its neutral counterparts, the coordination environment at Pd is almost ideally sp ($\Sigma(\text{Pd-X}) = 361.46(5)$). The compound **[NBu₄][3-Cl]** thus not only represents a unique example of an isolated anionic Pd(0) ate complex but also features the unusual sp geometry. A relaxed surface scan along the Si-Pd-Cl angle underlines the energetically favored sp-coordination geometry (ESI section 2a). ETS-NOCV analysis illustrates the dominant σ -donation of the chloride fragment into the Pd-Si bond (see ESI for details). NPA of **[3-Cl]⁻** supports the d¹⁰ configuration of the Pd atom (0.0537 in **[3-Cl]⁻** vs. -0.1388 in **3**), and a significant charge transfer to the Lewis acidic Si center (1.868 vs 2.038 in **3**). In line with all experimental and spectroscopic findings, the WBI for the Si-Pd increased to 0.69 (cf. 0.43 for **3**). An increased electron density at the bond critical point ($\rho(\text{r}_{\text{BCP}}(\text{Si-Pd})) = 0.093$) with an even stronger covalent character compared to **3** was found by the QAIM analysis (Figure 3e and Section 2f in the ESI).

To probe the effect of coordination or charge states on the rates of oxidative addition with arylhalides, the reactivity of **3** (in C₆D₆), **[3-(THF)]** and **[3-Cl]⁻** towards PhX (X=Cl, Br, I) was compared. For all three complexes, no reaction

with phenyl chloride or bromide took place, even at elevated temperatures (80 °C).

However, the oxidative addition of phenyl iodide took place at 60 °C, with a slightly increasing rate from **3** (in C₆D₆) < **[3-(THF)]** < **[3-Cl]⁻** (Table S1). Interestingly, scXRD analysis of the final product of oxidative addition revealed a phenyl group migrated to the Lewis acidic silicon center, yielding **[Ph-2-Pd(II)-I]** (see ESI, Figure S6 for details). Although a significant boost in reactivity for the anionic ate-complex, as would be expected according to the Amatore-Jutand cycle, was not observed, the trend generally agrees with the beneficial effect of directly bound nucleophile additives to the Pd-center, most pronounced for anions. Evidently, the particular type of ligand **2**, primarily aiming for the stabilization of electron rich Pd centers, or potential cooperative and solvent effects must not be ignored while speculating on any generality of this statement.^[23]

In conclusion, we successfully employed a Si(IV) based Z-type ligand with highly effective Lewis acidity for the complexation of Pd(0). A pronounced Pd-Si interaction, confirmed by spectroscopic and theoretical methods, causes significant changes in the reactivity of this late transition metal. The isolation and characterization of the

first (anionic) sp Pd(0) complex is achieved, providing a missing piece of the Amatore/Jutand catalytic cycle in cross coupling reactions. A slightly increased rate of the anionic d¹⁰ complexes in the oxidative addition of phenyl iodide was observed, leaving room for speculation whether this trend is general, exclusive to this specific system, outbalanced from other effects, or instead promoted according to Shaik's oriented external electric field hypothesis.

Supporting Information

The authors have cited additional references within the Supporting Information.

Author Contributions

L. G. and N. A. devised the project and designed the experiments. N. A. carried out calculations, did the experimental work together with J. M. and analyzed the obtained data. M. S. solved and refined the scXRD data. L. G. and N. A. wrote the manuscript.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Cross Coupling · Lewis Acid · Palladium · Silicon · Z-Type Ligand

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Supporting Information

**Neutral and Anionic Square Planar Palladium(0) Complexes
Stabilized by a Silicon Z-Type Ligand**

*N. Ansmann, J. Münch, M. Schorpp, L. Greb**

SUPPORTING INFORMATION

Supporting Information

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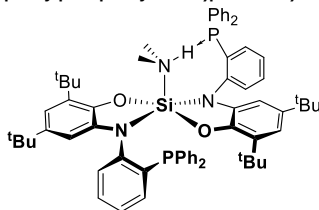
SUPPORTING INFORMATION

1. Experimental Procedures

a. Materials and General Methods

All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame dried glassware or by working in a glovebox (MBraun Labmaster dp, MB-20-G or a Sylatech Glovebox) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å). Argon was dried by passing over two columns of phosphorus pentoxide. Commercially available chemicals were used as received. 2,4-Di-*tert*-butyl-(2-diphenylphosphanylaniolino)phenol (PNO^H), bis(perchlorocatecholato)silane and cyclopentadienyle allyl palladium(II) were synthesized according to literature known procedures.^[1] All NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All hetero-nuclei spectra (with the exception of ¹⁹F) were obtained with ¹H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ¹H and ¹³C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants J in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublets of doublets, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. All NMR-spectra were processed with Bruker TopSpin 4.0.1. LIFDI-MS spectra were measured on a JEOL AccuTOF GCx instrument. IR spectra were recorded on an Agilent Cary 630 spectrometer equipped with diamond ATR units inside a glovebox and processed using OriginPro 2020b.

b. Syntheses

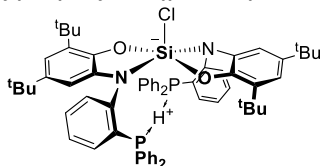
Dimethylamin-bis(2,4-di-*tert*-butyl-(2-diphenylphosphanylamido)phenolato)silane - [2-NHMe₂]

To a solution of 1 PNO^H (2.00 g, 4.15 mmol, 2.00 eq) in 10 ml dry DCM, tris(dimethylamino)silane (480 μ l, 2.94 mmol, 1.20 eq) was added neat at room temperature, whereupon gas evolution was observed. The resulting yellow solution was stirred at room temperature for 18 h, while connected to a overpressure bubbler. After reaction control by ³¹P NMR spectroscopy showed full conversion, the reaction mixture was condensed to dryness to remove excess silane. The residue was re-suspended in 20 ml *n*-pentane, filtered through a G4 frit and washed with additional 20 ml of *n*-pentane. After drying *in vacuo*, the crude compound was isolated as a colorless solid (1.93 g, 1.87 mmol, 90 %). Further purification of the product was achieved through recrystallization by layering a concentrated solution in DCM with equal amounts of *n*-pentane at -40 °C. Decanting the mother liquor, washing with *n*-pentane and drying *in vacuo* yielded colorless crystals (1.34 g, 1.30 mmol, 63 %). Crystals suitable for scXRD were obtained by gaseous diffusion of *n*-pentane into a saturated solution of [PNO₂Si-NHMe₂] in DCM at -40 °C.

¹H NMR (600 MHz, CD₂Cl₂, 295 K): δ [ppm] = 7.77 (m, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.37 (m, 10H), 7.31 (m, 4H), 7.19-7.14 (m, 6H), 7.07-7.03 (m, 2H), 6.89 (t, J = 7.3 Hz, 2H), 6.52 (s, 1H), 6.42 (t, J = 7.5 Hz, 2H), 6.36 (s, 1H), 5.83 (bs, 1H), 5.68 (s, 1H), 5.62 (s, 1H), 2.71 (d, J = 5.8 Hz, 3H), 2.66 (d, J = 5.3 Hz, 3H), 1.04 (s, 9H), 1.03 (s, 9H), 0.93 (s, 9H), 0.79 (s, 9H); ¹³C{¹H} NMR (151MHz, CD₂Cl₂, 295 K): δ [ppm] = 151.7 (d, J = 24.5 Hz, C_q), 151.3 (d, J = 24.5 Hz, C_q), 144.5 (s, C_q), 144.5 (s, C_q), 142.7 (s, C_q), 141.7 (s, C_q), 139.7 (s, C_q), 139.6 (s, C_q), 139.5 (s, C_q), 139.5 (s, C_q), 138.4 (d, J = 6.6 Hz, C_q), 138.1 (d, J = 13.0 Hz, C_q), 137.8 (d, J = 24.5 Hz, C_q), 137.2 (d, J = 6.7 Hz, C_q), 136.9 (d, J = 2.8 Hz, CH), 135.4 (t, J = 1.6 Hz, CH), 134.5 (s, CH), 134.4 (s, CH), 134.3 (s, 2CH), 134.2 (s, CH), 134.2 (s, CH), 134.1 (s, CH), 134.0 (s, CH), 132.8 (dd, J = 10.1 Hz, J = 3.8 Hz, CH), 131.7 (s, CH), 131.0 (d, J = 2.8 Hz, CH), 130.6 (s, C_q), 130.6 (s, C_q), 130.5 (s, CH), 129.2 (s, CH), 129.1 (s, CH), 129.0 (q, J = 6.9 Hz, CH), 128.9 (s, CH), 128.7 (d, J = 6.6 Hz, CH), 128.4 (d, J = 6.6 Hz, CH), 128.2 (d, J = 2.8 Hz, CH), 128.2 (s, CH), 127.8 (s, CH), 126.2 (s, CH), 126.0 (s, CH), 112.5 (s, CH), 111.8 (s, CH), 106.9 (s, CH), 106.3 (s, CH), 40.7 (d, J = 6.6 Hz, CH₃), 38.1 8s, CH₃), 34.5 (s, C_q), 34.3 (s, C_q), 34.3 (s, C_q), 34.2 (s, C_q), 32.0 (s, CH₃), 31.8 (s, CH₃), 30.2 (s, CH₃), 30.0 (s, CH₃); ³¹P{¹H} NMR (243 MHz, CD₂Cl₂, 295 K): δ [ppm] = -17.9 (s, 1P), -24.9 (s, 1P); ²⁹Si (IG) NMR (119 MHz, CD₂Cl₂, 295 K): δ [ppm] = -101.2 (s); MS (EI(+)): [M-NHMe₂]⁺, calcd.: 986.45, found: 986.46; Anal. Calcd. for C₆₆H₇₃N₃O₂P₂Si: C, 76.79; H, 7.32; N, 4.07 found: C, 75.54; H, 7.33; N, 4.03.

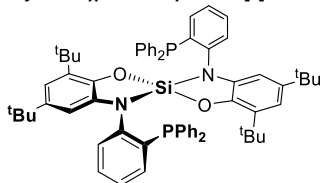
SUPPORTING INFORMATION

Deviations in the elemental analysis can be explained by co-crystallizing molecules of DCM and NHMe_2 , which can also be observed by NMR spectroscopy.

Chlorido-bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl-amido)phenolato)silicate – [H][2-Cl]

To a colorless suspension of **1** $\text{PNO}^{\text{H}2}$ (2.00 g, 4.15 mmol, 2.00 eq) in 30 ml dry acetonitrile, silicon tetrachloride (286 μl , 2.49 mmol, 1.20 eq) was added neat at room temperature, which lead to a complete dissolution of the starting material. The resulting colorless solution rapidly turned yellow and solid started to precipitate. The Schlenk flask was then closed and the reaction mixture was stirred at room temperature for 6 h. After completion of the reaction, the mixture was condensed to dryness to remove excess silane. The residue was re-suspended in 20 ml acetonitrile, filtered through a G4 frit and washed with 20 ml of *n*-pentane. After drying *in vacuo*, the crude compound was isolated as a bright-yellow powder (1.90 g, 1.86 mmol, 89 %). Further purification of the product was achieved through recrystallization by layering a concentrated solution in DCM with equal amounts of *n*-pentane at -40°C . Decanting the mother liquor and drying *in vacuo* yielded analytical pure yellow brick-formed crystals that were suited for scXRD (1.45 g, 1.42 mmol, 68 %).

^1H NMR (600 MHz, CD_2Cl_2 , 295 K): δ [ppm] = 10.16 (bs, 1H), 7.75-7.74 (m, 2H), 7.70 (t, J = 7.5 Hz, 2H), 7.33-7.29 (m, 6H), 7.18-7.13 (m, 10H), 6.89-6.85 (m, 8H), 6.57 (s, 2H), 5.86 (s, 2H), 1.07 (s, 18H), 0.80 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 295 K): δ [ppm] = 153.4 (t, J = 8.2 Hz, C_q), 144.0 (s, C_q), 141.2 (s, C_q), 139.8 (s, C_q), 134.7 (s, CH), 134.2-134.0 (m, CH), 132.6 (s, CH), 131.9 (s, C_q), 131.6 (s, CH), 131.1 (s, CH), 129.2 (q, J = 3.6 Hz, CH), 128.5 (bs, C_q), 126.9 (bs, C_q), 126.4 (t, J = 3.3 Hz, CH), 112.5 (s, CH), 105.4 (s, CH), 34.6 (s, C_q), 34.1 (s, C_q), 32.0 (s, CH_3), 29.6 (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -14.9 (s); ^{29}Si (IG) NMR (119 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -96.3 (s); MS (ESI(-)): $[\text{M}-\text{H}]^-$, calcd.: 1021.42, found: 1021.40; Anal. Calcd. for $\text{C}_{64}\text{H}_{69}\text{ClN}_2\text{O}_2\text{P}_2\text{Si}$ x CH_2Cl_2 : C, 70.42; H, 6.46; N, 2.53 found: C, 70.47; H, 6.90; N, 2.65.

Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl-amido)phenolato)silane - [2]A) Via Abstraction of Dimethylamine from [2-NHMe₂]

To a solution of [2-NHMe₂] (1.10 g, 1.07 mmol, 1.00 eq) in 10 ml dry DCM, bis(perchlorocatecholato)silane (665 mg, 1.28 mmol, 1.20 eq) was added in one portion at room temperature. The resulting colorless suspension was stirred at room temperature for three days, before filtering it through a pad of Celite®. The pad was rinsed with additional 20 ml of DCM and the combined filtrates were condensed to dryness, yielding the title compound as a colorless powder (980 mg, 993 μmol , 93 %). Crystals suitable for scXRD were obtained by gaseous diffusion of *n*-pentane into a saturated solution of $[\text{PNO}_2\text{Si}]$ in toluene at -40°C .

B) Via Abstraction of Chloride and Subsequent Deprotonation from [H][2-Cl] using NaBAR^F

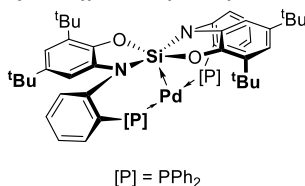
To a solution of [H][2-Cl] x CH_2Cl_2 (50.0 mg, 45.1 μmol , 1.00 eq) in 2 ml dry DCM, sodium tetrakis(pentafluorophenyl)borate (31.7 mg, 45.1 μmol , 1.00 eq) and 2,2,6,6-tetramethylpiperidine (7.68 μl , 45.1 μmol , 1.00 eq) were added and the resulting colorless suspension was stirred at room temperature for 18 h, before filtering it through a syringe filter. The filtrate was condensed to dryness and extracted with *n*-pentane (3 x 5 ml). The combined extracts were filtered through a syringe filter and subsequent removal of the solvent under reduced pressure yielded the title compound as an off-white solid (20.0 mg, 20.3 μmol , 45 %).

SUPPORTING INFORMATION

C) Via Abstraction of Chloride and Subsequent Deprotonation from [H][2-Cl] using TMS-OTf

To a solution of [H][2-Cl] (20.0 mg, 19.5 μ mol, 1.00 eq) in 0.5 ml dry CD_2Cl_2 , 2,2,6,6-tetramethylpiperidine (3.30 μ l, 19.5 μ mol, 1.00 eq) was added and the resulting colorless suspension was stirred at room temperature for 10 minutes, before trimethylsilyl triflate (3.53 μ l, 19.5 μ mol, 1.00 eq) was added. The resulting suspension was stirred for two hours at room temperature, before analysis via NMR spectroscopy indicated quantitative conversion to the target species. To the mixture, *n*-pentane (0.5 ml) was added and the suspension was filtered through a syringe filter, before the solvent was removed *in vacuo*, yielding **2** as a colorless solid (14.8 mg, 15.0 μ mol, 77 %). The silane obtained by this route could be further purified by sublimation (30 $^\circ\text{C}$, 10^{-2} mbar).

^1H NMR (600 MHz, CD_2Cl_2 , 295 K): δ [ppm] = 7.30-7.27 (m, 2H), 7.21-7.18 (m, 10H), 7.16-7.14 (m, 4H), 6.93 (t, J = 7.6 Hz, 2H), 6.88 (d, J = 1.6 Hz, 2H), 6.83 (pt, J = 7.3 Hz, 6H), 6.77 (t, J = 7.3 Hz, 2H), 6.51 (d, J = 1.7 Hz, 2H), 6.42 (dd, J = 7.7 Hz, J = 4.9 Hz, 2H), 1.49 (s, 18H), 1.23 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 295 K): δ [ppm] = 145.6 (d, J = 24.9 Hz, C_q), 143.4 (s, C_q), 142.6 (s, C_q), 139.1 (s, C_q), 137.9 (d, J = 14.7 Hz, C_q), 137.5 (d, J = 13.5 Hz, C_q), 135.0 (d, J = 22.8 Hz, CH), 134.8 (s, C_q), 134.4 (d, J = 9.1 Hz, C_q), 134.3 (s, CH), 133.1 (d, J = 18.3 Hz, CH), 130.3 (s, CH), 129.0 (s, CH), 128.8 (d, J = 7.5 Hz, CH), 128.6 (d, J = 6.2 Hz, CH), 128.5 (s, CH), 127.5 (s, CH), 126.0 (s, CH), 114.8 (s, CH), 107.1 (s, CH), 35.0 (s, C_q), 34.9 (s, C_q), 31.9 (s, CH_3), 30.0 (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -20.7 (s); ^{29}Si (IG) NMR (119 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -44.2 (s); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057 (w), 2957 (m), 2904 (w), 2867 (w), 1583 (m), 1482 (m), 1470 (s), 1418 (s), 1293 (s), 1220 (s), 1028 (s), 1014 (vs), 742 (vs); MS (EI(+)): $[\text{M}]^+$, calcd.: 986.45, found: 986.46; Anal. Calcd. for $\text{C}_{68}\text{H}_{68}\text{N}_2\text{O}_2\text{P}_2\text{Si} \times \text{CH}_2\text{Cl}_2$: C, 72.81; H, 6.58; N, 2.61 found: C, 72.37; H, 6.10; N, 2.80.

Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane palladium (0) – [3]

A) Using [2] as the precursor

A red solution of **2** (400 mg, 405 μ mol, 1.05 eq) and cyclopentadienyl allyl palladium (II) (82.0 mg, 386 μ mol, 1.00 eq) in 10 ml dry toluene was stirred at 80 $^\circ\text{C}$ in a PTFE sealed ampoule for 3 h. The resulting brown suspension was condensed to dryness and the residue was re-suspended in 3 ml toluene and filtered through a syringe filter. The resulting deep red solution was layered with 9 ml of *n*-pentane and placed in a -40 $^\circ\text{C}$ freezer for 3 days. The resulting red crystals were isolated by decanting the mother liquor and drying *in vacuo* yielded analytical pure red brick-formed crystals that were suited for scXRD. Recrystallization of the mother liquor yielded a second batch of crystals (combined yields: 375 mg, 343 μ mol, 89 %).

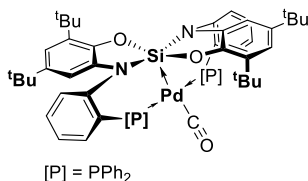
B) Using [2-NHMe₂] as the precursor

A red suspension of 2-NHMe₂ (100 mg, 96.9 μ mol, 1.00 eq) and cyclopentadienyl allyl palladium (II) (20.6 mg, 96.9 μ mol, 1.00 eq) in 5 ml dry toluene was stirred at 80 $^\circ\text{C}$ in a Schlenk tube for 3 h. The resulting red solution was condensed to dryness and the residue was re-suspended in 1 ml toluene and filtered through a syringe filter. The resulting deep red solution was layered with 7 ml of *n*-pentane and placed in a -40 $^\circ\text{C}$ freezer for 6 days. The resulting red crystals were isolated by decanting the mother liquor, washed with 4 ml of a mixture of *n*-pentane and toluene (4:1) and dried *in vacuo* yielding red brick-formed crystals of **3**, co-crystallized with 0.5 units of toluene and 0.25 units of *n*-pentane per molecule as observed by NMR spectroscopy. Yield: 75.0 mg, 68.6 μ mol, 71 %.

^1H NMR (600 MHz, C_6D_6 , 295 K): δ [ppm] = 7.60-7.59 (m, 2H), 7.50-7.46 (m, 4H), 7.43 (q, J = 6.2 Hz, 4H), 7.30-7.28 (m, 2H), 7.19 (td, J = 7.6 Hz, J = 1.1 Hz, 2H), 6.95 (d, J = 2.0 Hz, 2H), 6.92-6.90 (m, 8H), 6.87 (t, J = 7.8 Hz, 2H), 6.85 (d, J = 1.9 Hz, 2H), 6.78 (t, J = 7.6 Hz, 4H), 1.34 (s, 18H), 1.14 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 295 K): δ [ppm] = 151.6 (t, J = 8.0 Hz, C_q), 144.3 (s, C_q), 141.8 (s, C_q), 140.2 (s, C_q), 135.3 (t, J = 8.7 Hz, CH), 135.2 (s, C_q), 135.0 (s, C_q), 134.0 (s, CH), 133.9 (t, J = 7.8 Hz, CH), 133.9 (s, C_q), 133.8 (s, C_q), 132.1 (s, CH), 130.0 (s, CH), 129.6 (s, CH), 128.7 (q, J = 5.1 Hz, CH), 124.0 (t, J = 3.1 Hz, CH), 112.6 (s, CH), 105.9 (s, CH), 34.9 (s, C_q), 34.3 (s, C_q), 32.2 (s, CH_3), 30.0 (s, CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6 , 295 K): δ [ppm] = 4.5 (s); ^{29}Si (IG) NMR (119 MHz, C_6D_6 , 295 K): δ [ppm] = -83.6 (t, J = 6.1 Hz); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057 (w), 2951 (m), 1579 (m), 1469 (s), 1434 (s), 1308 (m), 1237 (s), 1004 (s), 842 (s), 744 (vs), 690 (vs); HR-MS (EI(+)): $[\text{M}]^+$, calcd.: 1092.3560, found: 1092.3573; Anal. Calcd. for $\text{C}_{64}\text{H}_{68}\text{N}_2\text{O}_2\text{P}_2\text{SiPd}$: C, 70.28; H, 6.27; N, 2.56 found: C, 70.02; H, 6.39; N, 2.60.

SUPPORTING INFORMATION

CO-PPSi-palladium (0) – [3-CO]



In a *New era* pressure NMR tube, **3** (17.5 mg, 16.0 μ mol, 1.00 eq) was dissolved in 0.3 mL of C₆D₆. The red solution was pressurized with 5 bar of dry carbon monoxide, which led to a darkening of the solution. The solution was subsequently analyzed via NMR spectroscopy.

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 7.68-7.67 (m, 2H), 7.52 (q, J = 5.9 Hz, 4H), 7.36 (q, J = 6.2 Hz, 4H), 7.29-7.26 (m, 2H), 7.17 (t, J = 8.0 Hz, 2H), 7.07 (d, J = 2.1 Hz, 2H), 6.95-6.92 (m, 6H), 6.90-6.86 (m, 4H), 6.83 (t, J = 7.5 Hz, 2H), 6.70 (t, J = 7.5 Hz, 4H), 1.37 (s, 18H), 1.09 (s, 18H); **¹³C{¹H} NMR** (101 MHz, C₆D₆, 295 K): δ [ppm] = 185.2 (broad, C=O), 152.4, (t, J = 8.4 Hz, C_q), 144.6 (s, C_q), 142.0 (s, C_q), 140.6 (s, C_q), 136.7 (t, J = 18.3 Hz, C_q), 135.1 (t, J = 8.9 Hz, CH), 134.5 (t, J = 18.4 Hz, C_q), 134.2 (s, CH), 134.1 (s, CH), 133.3 (t, J = 7.5 Hz, CH), 131.9 (s, CH), 129.8 (s, CH), 129.4 (s, CH), 128.6 (q, J = 5.7 Hz, CH), 127.2 (t, J = 25.3 Hz, C_q), 126.4 (s, CH), 123.8 (s, CH), 113.1 (s, CH), 106.3 (s, CH), 34.9 (s, C_q), 34.3 (s, C_q), 32.2 (s, CH₃), 29.9 (s, CH₃); **³¹P{¹H} NMR** (162 MHz, C₆D₆, 295 K): δ [ppm] = 3.7 (s); **²⁹Si {¹G} NMR** (79 MHz, C₆D₆, 295 K): δ [ppm] = -80.4 (t, J = 12.8 Hz).

This experiment was repeated several times, using different pressures of CO atmosphere (1 bar, 2.5 bar, & 8.5 bar), indicating a pressure dependent dynamic equilibrium of the CO binding. Isolation of the target compound was not possible, since exchange of the CO atmosphere resulted in the formation of **3**, which rendered the recording of an IR spectrum impossible.

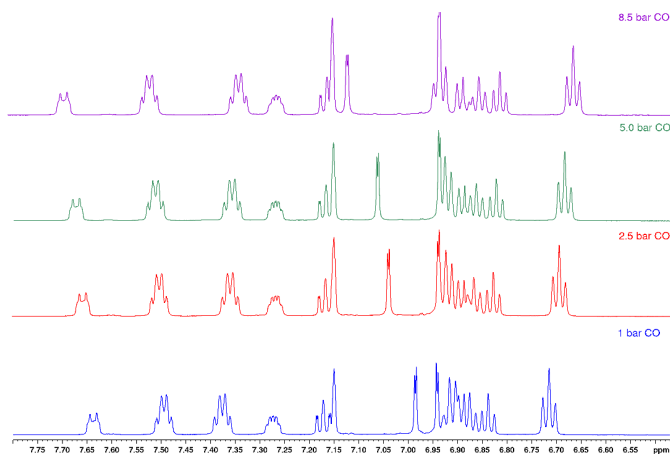


Figure S 1: Aromatic regions of ¹H NMR spectra (600 MHz) of [3-CO] at different pressures of CO gas in C₆D₆ at 295 K.

SUPPORTING INFORMATION

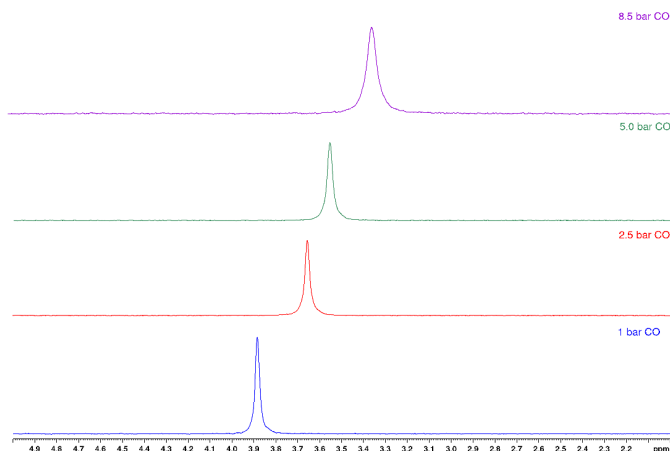
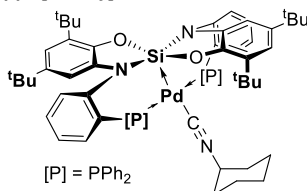


Figure S 2: Details of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (243 MHz) of $[\mathbf{3}\text{-CO}]$ at different pressures of CO gas in C_6D_6 at 295 K.

Cyclohexyl isocyanide-PPSi-palladium (0) – $[\mathbf{3}\text{-CNCy}]$



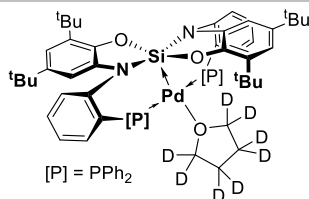
In a J. Young NMR tube, **3** (15.0 mg, 13.7 μmol , 1.00 eq) was dissolved in 0.5 mL of C_6D_6 . To the red solution, cyclohexyl isocyanide (1.88 μL , 15.1 μmol , 1.10 eq) was added, resulting in an immediate change of color (yellow). After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting yellow powder was washed with 1 mL of *n*-pentane to remove the excess isocyanide. Drying the yellow powder *in vacuo* yielded the target complex (14.8 mg, 12.3 μmol , 90 %). Crystals suitable for scXRD were grown from a saturated solution in benzene at 20 $^\circ\text{C}$.

^1H NMR (600 MHz, C_6D_6 , 295 K): δ [ppm] = 7.69–7.63 (m, 10H), 7.35–7.32 (m, 2H), 7.21 (td, $J = 7.7$ Hz, $J = 1.4$ Hz, 2H), 6.96 (pq, $J = 7.7$ Hz, 6H), 6.91 (pt, $J = 7.3$ Hz, 6H), 6.86 (t, $J = 7.5$ Hz, 2H), 6.78 (d, $J = 2.1$ Hz, 2H), 6.76 (d, $J = 2.1$ Hz, 2H), 2.26 (bs, 2H), 1.35 (s, 18H), 1.25 (s, 18H), 0.76 (bs, 4H), 0.66 (bs, 2H), 0.54 (bs, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 295 K): δ [ppm] = 155.0, (t, $J = 7.1$ Hz, C_q), 146.8 (s, C_q), 140.0 (s, C_q), 139.4 (s, C_q), 137.3 (t, $J = 18.6$ Hz, C_q), 136.7 (t, $J = 19.9$ Hz, C_q), 134.7 (t, $J = 8.1$ Hz, CH), 134.3 (t, $J = 7.7$ Hz, CH), 133.9 (s, CH), 132.1 (s, C_q), 131.7 (s, CH), 129.3 (s, CH), 129.1 (s, CH), 128.2 (m, CH)*, 127.4 (s, CH), 127.3 (t, $J = 27.0$ Hz, C_q), 122.7 (t, $J = 2.9$ Hz, CH), 111.6 (s, CH), 104.8 (s, CH), 51.8 (b, CH), 34.7 (s, C_q), 34.2 (s, C_q), 32.4 (s, CH_3), 31.8 (b, CH_2), 30.2 (s, CH_3), 24.8 (s, CH_2), 22.4 (b, CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6 , 295 K): δ [ppm] = 3.4 (s); ^{29}Si (IG) NMR (119 MHz, C_6D_6 , 295 K): δ [ppm] = –78.4 (t, $J = 37.3$ Hz); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054 (w), 2941 (m), 2859 (m), 2178 (m, ν C=N), 1574 (m), 1477 (s), 1464 (s), 1425 (s), 1305 (s), 1244 (vs), 1096 (m), 1003 (s), 909 (s), 839 (vs), 745 (vs); **Anal.** Calcd. for $\text{C}_{71}\text{H}_{70}\text{N}_3\text{O}_2\text{P}_2\text{SiPd}$: C, 70.89; H, 6.62; N, 3.49 found: C, 69.89; H, 6.48; N, 3.67.

*Hidden beneath solvent signal, observed by DEPT135. The quaternary carbon atom of the coordinating isocyanide was not detected.

Tetrahydrofuran-d8-PPSi-palladium (0) – $[\mathbf{3}\text{-THF}]$

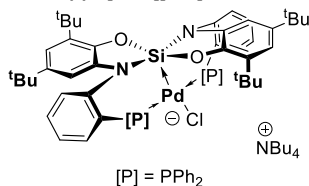
SUPPORTING INFORMATION



In a J. Young NMR tube, **3** (15.0 mg, 13.7 μ mol, 1.00 eq) was dissolved in 0.5 mL of THF-d₈. Analysis of the solution by NMR spectroscopy showed full conversion to the solvent adduct. Crystals suitable for scXRD were obtained by gas phase diffusion of pentane into a saturated solution in THF-d₈ at -40°C .

^1H NMR (600 MHz, THF-d₈, 295 K): δ [ppm] = 7.50-7.46 (m, 6H), 7.44-7.40 (m, 6H), 7.29 (t, $J = 7.3$ Hz, 2H), 7.25-7.22 (m, 2H), 7.20-7.17 (m, 6H), 7.14-7.11 (m, 6H), 6.37 (d, $J = 2.1$ Hz, 2H), 6.05 (d, $J = 2.1$ Hz, 2H), 1.06 (s, 18H), 0.92 (s, 18H); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, THF-d₈, 295 K): δ [ppm] = 152.6 (t, $J = 7.3$ Hz, C_q), 144.8 (s, C_q), 140.2 (s, C_q), 139.7 (s, C_q), 135.3 (t, $J = 8.5$ Hz, CH), 134.8 (t, $J = 8.5$ Hz, CH), 134.6 (t, $J = 18.4$ Hz, C_q), 134.4 (t, $J = 19.5$ Hz, C_q), 134.0 (s, CH), 132.2 (s, C_q), 132.0 (s, CH), 130.5 (s, CH), 130.1 (s, CH), 129.7 (t, $J = 27.4$ Hz, C_q), 128.9 (q, $J = 5.7$ Hz, CH), 128.8 (t, $J = 5.2$ Hz, CH), 124.3 (t, $J = 3.3$ Hz, CH), 111.6 (s, CH), 104.7 (s, CH), 34.7 (s, C_q), 34.2 (s, C_q), 32.1 (s, CH₃), 30.1 (s, CH₃); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF-d₈, 295 K): δ [ppm] = 6.0 (s); ^{29}Si (IG) NMR (119 MHz, THF-d₈, 295 K): δ [ppm] = -87.0 (t, $J = 9.3$ Hz).

The reaction is driven by the excess of tetrahydrofuran. Experiments with stoichiometric amounts of THF in non-donor solvents did not result in formation of the adduct.

Tetrabutylammonium Chlorido-PPSi-palladium (0) – [NBu₄][3-Cl]

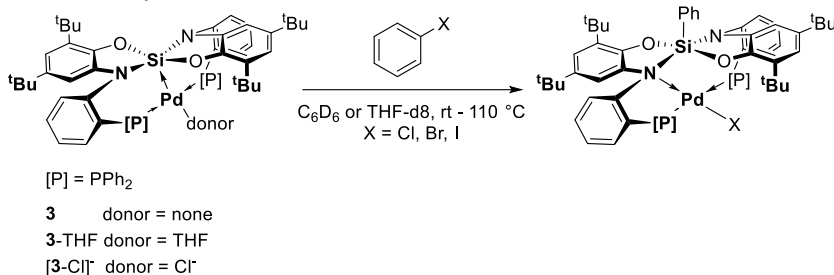
In a J. Young NMR tube, [(PNO₂Si)Pd](x 0.5 toluene) (30.0 mg, 25.9 μ mol, 1.00 eq) and tetrabutylammonium chloride (7.20 mg, 25.9 μ mol, 1.00 eq) were suspended in 0.5 mL of THF-d₈ for 30 minutes. After analysis by NMR spectroscopy showed full conversion to the target complex. The resulting red solution was condensed to dryness resulting in a yellow solid, which was dried *in vacuo* (33.4 mg, 24.4 μ mol, 94 %). Crystals suitable for scXRD were obtained by gas phase diffusion of pentane into a saturated solution in toluene at room temperature.

^1H NMR (400 MHz, THF-d₈, 295 K): δ [ppm] = 7.76-7.71 (m, 4H), 7.58-7.53 (m, 4H), 7.34-7.27 (m, 4H), 7.24-7.20 (m, 2H), 7.17-7.13 (m, 5H), 7.05-6.89 (m, 9H), 6.14 (d, $J = 2.0$ Hz, 2H), 6.03 (d, $J = 2.2$ Hz, 2H), 3.10-3.06 (m, 8H), 1.47-1.39 (m, 8H), 1.18 (ps-sext, $J = 7.3$ Hz, 8H), 1.06 (s, 18H), 0.89 (s, 18H), 0.85 (t, $J = 7.4$ Hz, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF-d₈, 295 K): δ [ppm] = 155.0 (broad, C_q), 146.4 (s, C_q), 140.2 (s, C_q), 137.7 (s, C_q), 136.4 (t, $J = 7.9$ Hz, CH), 135.8 (t, $J = 7.5$ Hz, CH), 135.5 (t, $J = 19.1$ Hz, C_q), 134.4 (s, CH), 130.8 (s, CH), 130.4 (s, C_q), 129.2 (s, CH), 129.0 (s, CH), 128.9 (s, CH), 127.7 (t, $J = 4.7$ Hz, CH), 122.8 (s, CH), 109.7 (s, CH), 102.6 (s, CH), 59.0 (s, CH₂), 34.6 (s, C_q), 33.9 (s, C_q), 32.3 (s, CH₃), 30.4 (s, CH₃), 24.5 (s, CH₂), 20.4 (s, CH₂), 13.9 (s, CH₃); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, THF-d₈, 295 K): δ [ppm] = 6.9 (s); ^{29}Si (IG) NMR (119 MHz, THF-d₈, 295 K): δ [ppm] = -86.9 (t, $J = 26.2$ Hz); HR-MS (ESI(-)): [M-NBu₄]⁻, calcd.: 1172.3254, found: 1172.3242. Anal. Calcd. for C₈₀H₁₀₄ClN₃O₂P₂SiPd: C, 70.05; H, 7.64; N, 3.02 found: C, 69.29; H, 7.57; N, 3.02.

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c. Reactivity Studies

Oxidative Addition of Aryl Halides



In a J. Young NMR tube, [NBu₄][**3-Cl**] (15.0 mg, 10.9 μmol, 1.00 eq) was dissolved in 0.5 mL of THF-d₈. Afterwards, the aryl halide was added (2.0 eq for X = Cl, Br; 1.10 eq for X = I). The reaction mixture was observed by NMR spectroscopy. Observing no change in the respective NMR spectra, the temperature was increased for X = Cl, Br stepwise (21 h 50 °C, 20 h, 80 °C) until a final temperature of 110 °C was reached. Even after two days at 110 °C, no oxidative addition was observed for X = Cl, Br.

For X = I, a change in the ³¹P{¹H} spectrum was observed after 3 h at 60 °C (21 % conversion). The reaction was further heated at 60 °C for additional 3 days, showing slow conversion of **[3-Cl]⁻** to two species, which, after comparison of the results obtained with **3** in C₆D₆ (see below and figure S6), are believed to consist of [Ph-2-Pd-Cl] and [Cl-2-Pd-Ph]. (Conversion after 1 day: 39%, conversion after 2 days: 61 % conversion after 3 days: 79 %).

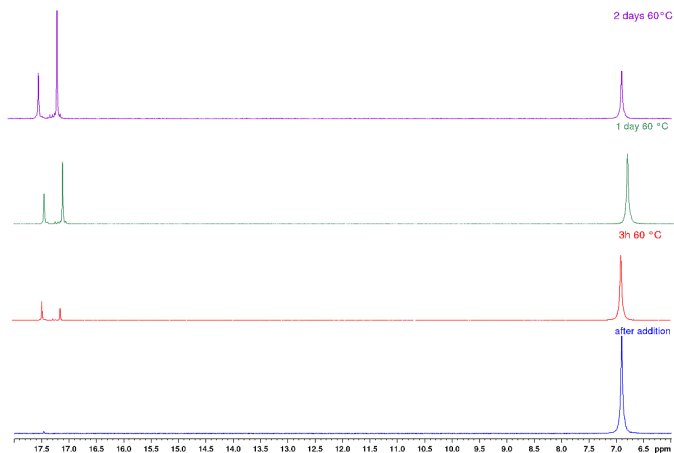


Figure S 3: Details of ³¹P{¹H} NMR spectra (243 MHz) of the reaction of [NBu₄][**3-Cl**] with PhI after specific times, measured in THF-d₈ at 298 K.

For X = I, a comparison experiment with complex **3** (11.9 mg, 10.9 μmol, 1.00 eq) was carried out under identical conditions, and conversion of **3** was measured using NMR spectroscopy, unravelling slightly slower reactivity (conversion after 3 h: 7 %, conversion after 1 day: 32%,

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conversion after 2 days: 57 %). Unlike in the case above, only one species was observed as the product ($\delta(^{31}\text{P}) = 17.4$ ppm, $\delta(^{29}\text{Si}) = -102.5$ (s) ppm), which – in comparison with the results obtained in C_6D_6 (see below) – is likely $[\text{Ph-2-Pd-I}]$. The formation of a sole product can be explained by the absence of chloride ions, and therefore no competition between the phenyl- and chloride- ligand at the Lewis acidic Si centre.

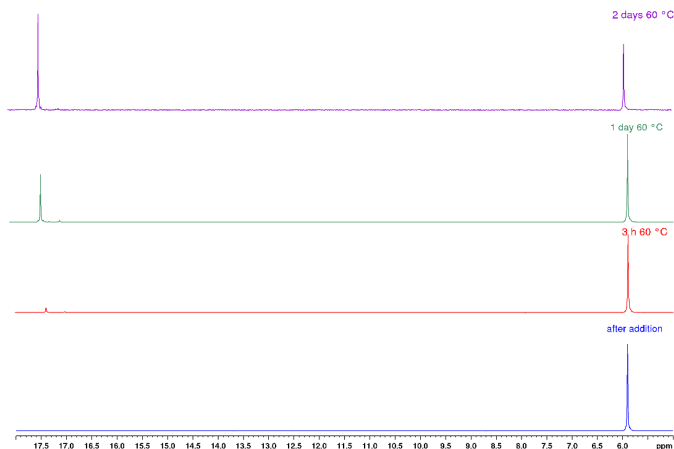


Figure S 4: Details of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (243 MHz) of the reaction of **3**-THF with PhI after specific times, measured in THF-d_8 at 298 K.

To see whether the coordination of THF has an effect on the kinetics of this oxidative addition, the reaction was repeated with **3** in C_6D_6 . Leaving all other reaction parameters constant, an overall slower reaction was observed (conversion after 3 h: 3 %, conversion after 1 day: 30%, conversion after 2 days: 48 %, conversion after 3 days: 57 %). Unlike in the cases above, the reaction was less selective and visible degradation of the complex was observed as $\text{Pd}(0)$ and minor impurities in the ^{31}P NMR spectrum. Major product species: $\delta(^{31}\text{P}) = 20.5$ ppm, $\delta(^{29}\text{Si}) = -83.4$ (s) ppm. Filtration of the reaction and gas-phase diffusion of *n*-pentane into the solution lead to the growth of crystals of the product $[\text{Ph-2-Pd-I}]$, suitable for scXRD. The obtained structure (shown in figure S6) is also concise with the obtained ^{29}Si -NMR spectra, which indicate the formation of a penta-valent silicon centre without Pd interaction (no coupling to the phosphorous atoms).

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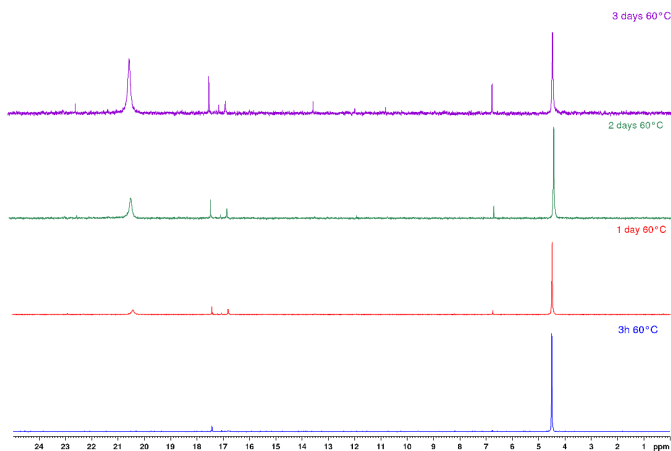


Figure S 5: Details of $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (243 MHz) of the reaction of **3** with PhI in C_6D_6 after specific times, measured at 298 K.

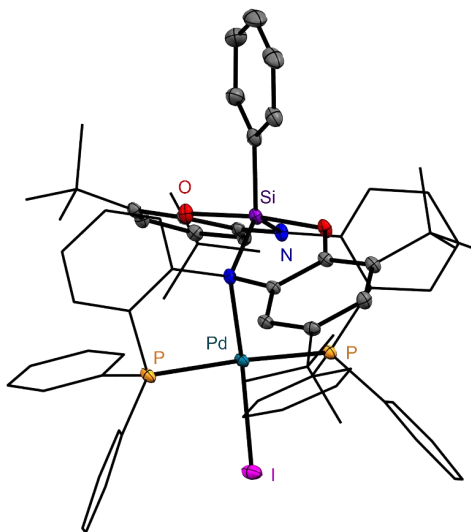


Figure S 6: ORTEP plot of the solid state structure of the product of oxidative addition of PhI at **3**, [Ph-2-Pd-I], as obtained by scXRD. Hydrogen atoms and co-crystallized molecules of C_6D_6 were omitted for clarity; vibrational ellipsoids are displayed at 50 %.

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Table S 1: Overview of conversions of respective Pd complexes in the oxidative addition of PhI at 60 °C, after respective times.

Time	[3] in C ₆ D ₆	[3-THF] in THF-d ₈	[NBu ₄][3-Cl] in THF-d ₈
3 h	3	7	21
1 day	30	32	39
2 days	48	57	61
3 days	57		79

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2. Computational Details

a. Structure Optimization

All computations have been performed using the Orca 5.0.3 program package.^[2] Geometry optimizations were carried out with Grimme's PBEh-3c/def2-mSVP, including the geometrical counter-poise correction scheme (gCP), atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ), using *VeryTightSCF* settings.^[3] As in all following calculations (except the QTAIM analysis), ECP was used for Pd (def2-ECP).^[4] All obtained structures have been approved to be energetic minima on the potential energy surface by analytical calculation of harmonic frequencies at the PBEh-3c level. Structures with imaginary frequencies $>10\text{ cm}^{-1}$ have been reoptimized with *TightOPT* settings. Unscaled ZPEs and thermal corrections at 298 K from the rigid-rotor harmonic oscillator (RRHO) approximation^[5] were later used for the calculation of thermodynamic values. For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[3e, 3f, 6] As starting geometries, VSEPR structures preoptimized with UFF were used.^[7]

To explore the influence of the Si-Pd-Cl angle on the energy of anionic complex $[\mathbf{3}\text{-Cl}]^-$, a relaxed surface scan of this angle, reaching from the initial value (179.3°) till 90° , was carried out in 20 steps, using the computational approach described above. The resulting electronic energies are displayed as a function of the angle in fig. S6:

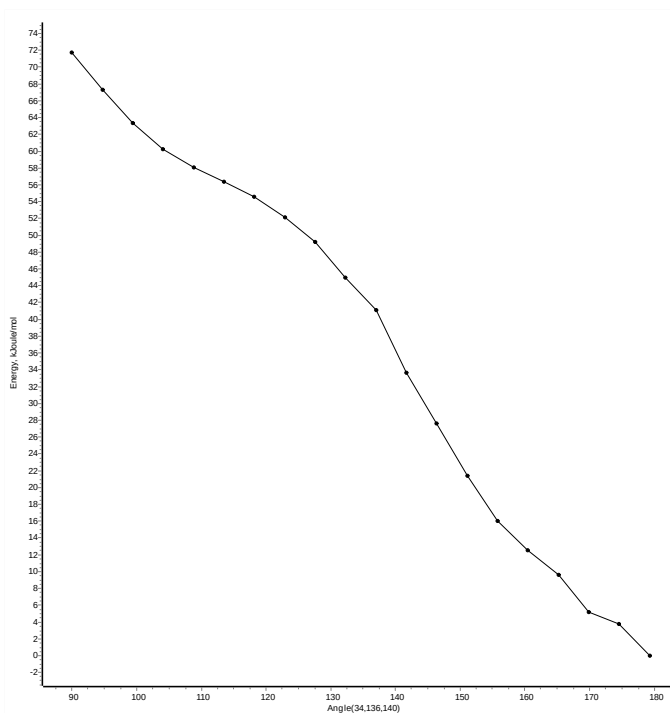


Figure S 7: Dependency of the relative electronic energy of compound $[\mathbf{3}\text{-Cl}]^-$ on the Si-Pd-Cl angle, as observed in the relaxed surface scan of this parameter.

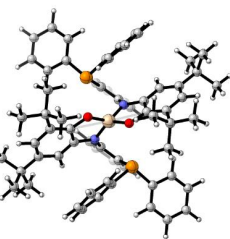
b. Cartesian Coordinates

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Cartesian coordinates (reported in Å) and energies (in hartree) of all stationary points discussed in the reaction profile in the main text. Reported at the PBEh-3c level of theory.

2

E = -3705.02673658286



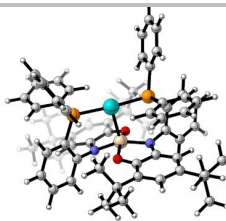
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C	0.09721132488895	-2.5993613867599	-4.32148974165279
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E = -3832.99160823088

SUPPORTING INFORMATION



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C	2.06476760963422	1.06065209685324	1.89662263217767
C	2.45977533930959	-0.27762803782085	1.84960556220434
C	6.14631093947877	-0.02217219627844	2.76906698390052
H	4.05238365653507	-1.68973405392391	2.01529819576903
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N	1.38472063235834	-1.09917563153763	1.54309012241804
C	5.19852858982032	-2.45050721889430	1.23061068927715
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C	1.21509820468867	-5.48735649644925	-0.42688760075279
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C	1.95353099207512	3.98651327537895	0.92181705950969
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H	2.66976684585137	3.84891839372866	0.1077886756350
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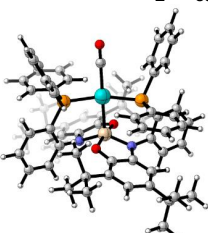
SUPPORTING INFORMATION



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3-CO

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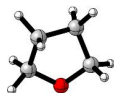
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C 2.07978884071210	1.10629618494266	1.62566695839868	H 6.15677272606957	-1.94510738765723	2.20621570883602
C 2.14187109314277	-0.24434870077355	1.76271681663825	H 5.438996866405971	-2.08590043265927	3.81535140080880
C 5.92409274673239	-0.03336633718565	2.33192011461870	C 1.512525171492038	3.93669822045221	2.80011711924630
H 3.87645575707009	-1.69160896657245	2.31496830895554	C 2.23898168912918	3.92851956028845	0.40888417052833
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SUPPORTING INFORMATION

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O	-0.23715815493672	0.13709644333188	-4.83224767242104

THF

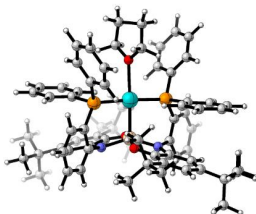
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H	-0.43360851894619	-5.72280333935572	2.43067575875588
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H	-1.15621918304500	-3.46060183692223	2.90814204101542
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3-THF

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C	5.99473249454719	-0.06243745500513	1.86777332067727
C	3.93426684531621	-1.708010769403636	2.19913076097568
C	1.9526846077780	3.55264642706140	2.04019096440156
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C	1.55012017299554	-2.45271742665932	1.21100621734075
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C	-2.90620136185903	-0.41850955300970	0.79995249232769
C	-3.30353467124777	-2.59547803093710	1.18162273328336
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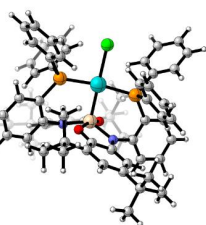
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N	-1.66537812259513	0.59984727045525	1.51193391449350
Si	-0.13803765555099	-0.18683610101972	0.95785481377777
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C	-1.87404222338495	2.67581545612589	0.28859508238861
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P	-1.69661247531577	1.66636239755685	-1.21897724591180
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SUPPORTING INFORMATION

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			H -2.16287309869755	-4.72201993003704	2.54502326304275
			H -0.87188973899674	-3.98249142399150	1.59754391392874
			H -3.64751602663070	-5.97635604675436	0.20694261916303
			H -4.7797892467436	-4.68842722382853	-1.5227991596077
			H -4.4312456356557	-5.14760517512455	0.1444899982700
			H -1.32165522119265	-3.36839198128447	-0.86805224782075
			H -2.95526318259098	-5.5016883415707	-1.52187743005219
			H -1.99776195411629	-4.95776024921605	-1.20542988573258
			H -7.66878076854248	-1.57578560097242	3.95750552923687
			H -5.96865152924691	-1.40330848883304	4.41200097401244
			H -6.48007954370389	-2.76958356811352	3.43128745041057
			C -3.1163662612672	1.28791202867346	-1.79475737672014
			C -1.15680262014210	3.27750402395234	-2.44128160810993
			C -2.19661212043845	4.00026569413475	0.1086746088013
			C 0.158233996621284	3.64288107865623	-2.7108271729926
			C 0.42775136748264	4.73656156887429	-3.51778304186835
			C -0.61247542652898	5.46115957017621	-0.08117045005361
			C -1.92544115276748	5.08817757328182	-3.83497072747237
			H -3.22375734894184	3.71250649826295	-2.83109212392964
			H 0.97337471242437	3.06353031929802	-2.29851085712049
			H 1.45477933213576	5.01017126804984	-3.72087773371300
			H -0.3996877927910	6.30927469809161	-4.7197473286164
			H -2.7420033275487	5.64216003243401	-2.9024917129132
			C -3.2141801524117	0.52093782880514	-2.82959712563126
			H -4.44837722804824	0.05194187950489	-3.37801261909757
			C -5.59275864094987	0.33023427596614	-2.64210277208487
			C -5.49780248990369	1.09018049494728	-1.48589620890993
			C -4.26558369643112	1.57149520454967	-1.069279529201435
			H -4.20768925118888	2.15970286016349	-0.16340503721376

[3-Cl]

E = -4292.825355918641



SUPPORTING INFORMATION

H -2.32284060359892	0.29838805596456	-3.53700773047958	C 4.32372717457410	-1.58538804615659	-0.85109790156528
H -4.51381055630905	-0.54092179979390	-4.28131944403064	C 3.56349391310376	0.09899999519727	-2.38856730773092
H -6.55390463045402	-0.04916519649962	-2.96554321056660	C 4.85349327865093	0.59785651030618	-2.47058413745658
H -6.38230407742133	1.30586645738403	-0.90266796143096	C 5.88088310681551	0.01339860928166	-1.74268838312866
P 1.56562468554767	-1.61278743864979	-1.50439266196747	C 5.61305048419600	-1.08032311819135	-0.93598265572500
C 1.43561727201298	-2.67328230051525	-2.98514785933832	H 6.40634210434612	-1.54108337852475	-0.36077251001350
C 3.28923644866495	-0.99815269374390	-1.57179172095177	H 4.12881439600304	-2.43401270539330	-0.20949125197254
C 0.16787923001381	-2.93478689960773	-3.49621288692338	H 5.05380140865220	1.45241671066478	-3.10384925198744
C 0.01413975002426	-3.76833407234672	-4.59163344369174	H 6.88548994331657	0.41306069973355	-1.80084005066835
C 1.12618908659901	-4.32903059186248	-5.20305986722006	H 2.76678752933451	0.55248882888175	-2.96808298636338
C 2.39377661065969	-4.05379404599201	-4.71283083832029	Pd 0.07771949809773	0.16020182450488	-1.55010991008745
C 2.54799108859606	-3.23120523259057	-3.60605028636714	H 1.59529299030381	3.84217447862674	3.82665890272457
H 3.54153750661793	-3.01702040008236	-3.23247529703200	H 0.46668488217226	3.41039694875363	2.54160494057338
H -0.70012712043119	-2.47347668318004	-3.04387130722827	H 1.07530078887696	5.05664399589673	2.65258320984540
H -0.97703261059891	-3.96312679969531	-4.97963131343457	Cl 0.30816909385861	0.47868163634055	-3.99688222459000
H 1.00565116382655	-4.96947389080665	-6.06764987938607			
H 3.26709757221000	-4.47624167071213	-5.19322201016852			

c. Thermodynamic Values

In order to calculate solvent corrected, more precise energies of the optimized structures for free reaction enthalpies, single point calculations, using Head-Gordon's ω b97x-V method with the def2-TZVPP basis set (including DFT-NL dispersion correction, and ECP for Pd) were calculated.^[4, 8] Solvent effects were accounted for by the SMD solvation module, using toluene and tetrahydrofuran as solvents.^[9] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[3e, 3, 6] All calculations were carried out using *VeryTightSCF* settings.

d. ETS-NOCV Calculations and Frontier Orbitals

For energy decomposition analysis (EDA), using the Extended Transition State (ETS) method^[10] combined with the natural orbitals for chemical valence (NOCV) concept,^[11] calculations were performed at the BP86-D3BJ/TZ2P level^[9c, 12] as implemented in the AMS2022.103 software package.^[13] The obtained frontier molecular orbitals were used for interpretation of the reactivity of complex **3**.

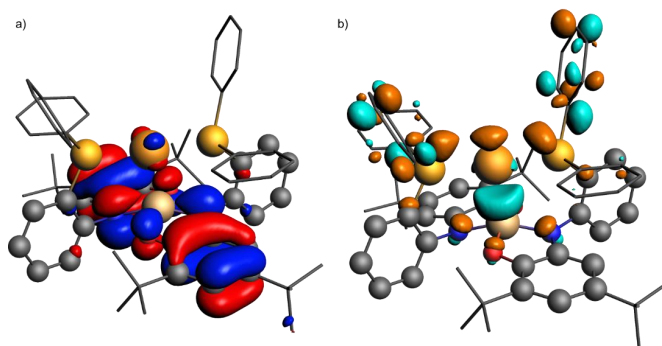


Figure S 8: Frontier molecular orbitals of **3**, as calculated at the BP86-D3BJ/TZ2P level of theory (a: highest occupied molecular orbital - 0.03 eV, b: lowest unoccupied molecular orbital - 0.045 eV). Hydrogen atoms are hidden for clarity.

SUPPORTING INFORMATION

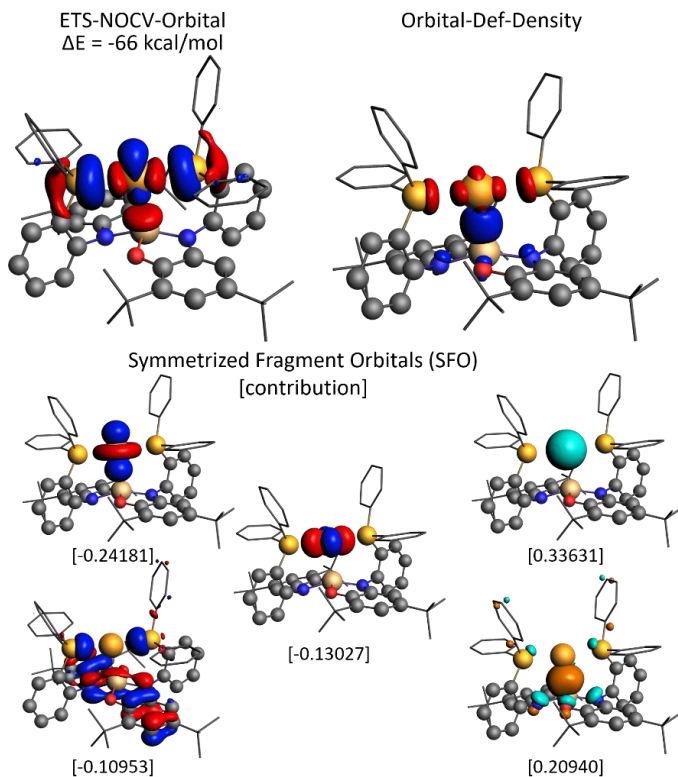


Figure S 9: ETS-NOCV orbital with the major contribution to the orbital interaction energy of **3**, as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Additionally shown is the corresponding deformation density $\Delta\rho$ and the symmetrized fragment orbitals (SFOs) with the highest eigenvalues v (symbolizing charge flow). Hydrogen atoms are hidden for clarity.

SUPPORTING INFORMATION

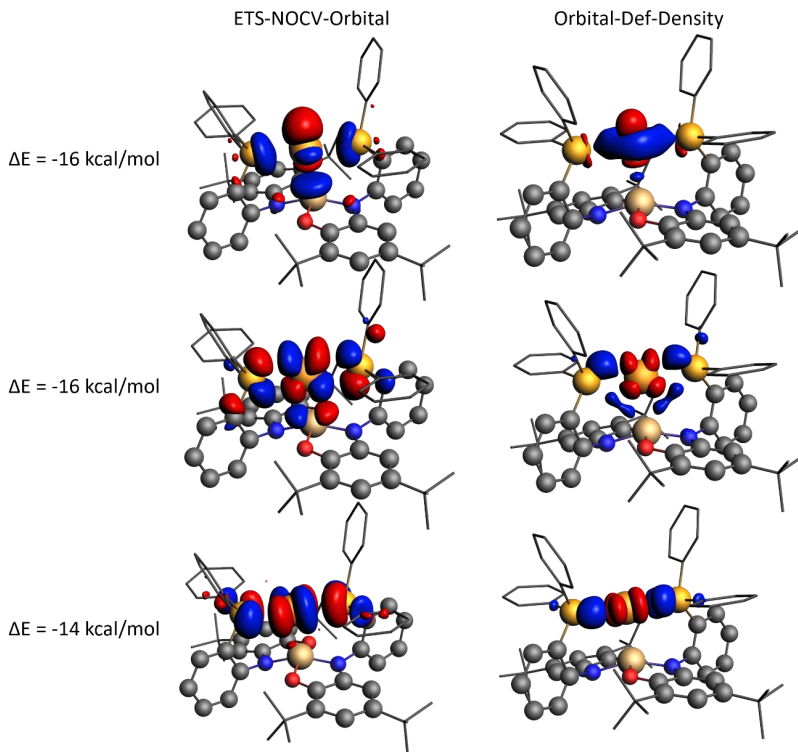


Figure S 10: ETS-NOCV orbitals with $\Delta E_{\text{orb}} < -10$ kcal/mol of **3**, as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Additionally shown is the corresponding deformation density $\Delta\rho$. Hydrogen atoms are hidden for clarity.

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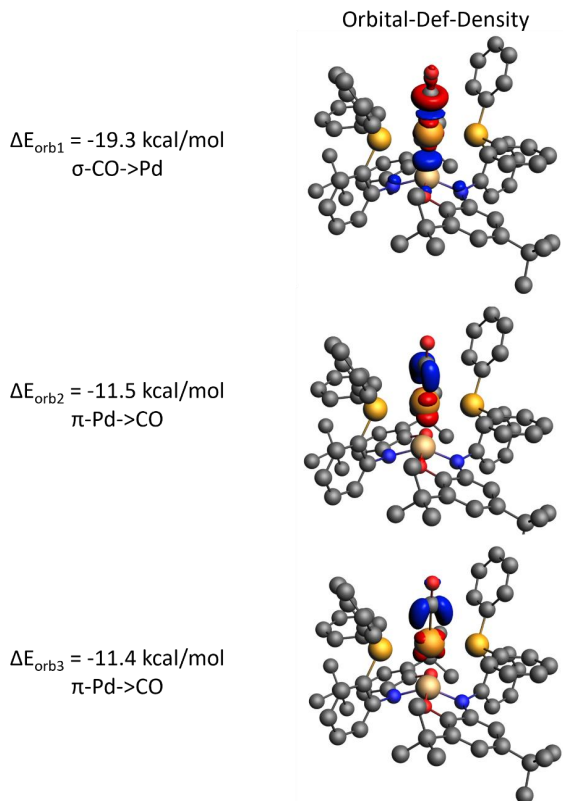


Figure S 11: Results of the ETS-NOCV analysis of [3-CO], as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Shown are the deformation densities $\Delta\rho$ of the NOCV orbitals that represent the major interactions between the CO fragment and the Pd complex ($\Delta E_{\text{orb}} < -10 \text{ kcal/mol}$). The σ -donation of the CO ligand is the most energetic interaction, while the two π -back-donations to the CO ligand are underrepresented energetically. Charge flow from red to blue, hydrogen atoms are hidden for clarity.

SUPPORTING INFORMATION

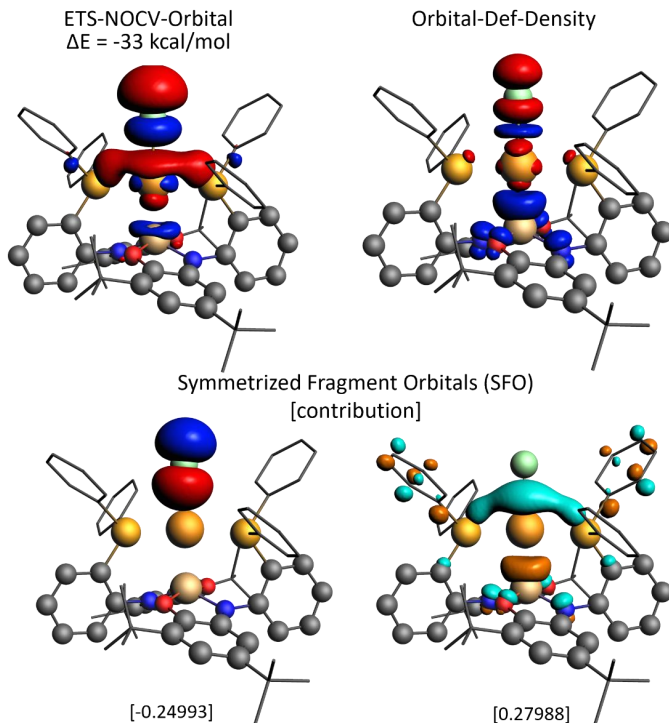


Figure S 12: ETS-NOCV orbital with the major contribution to the orbital interaction energy of [3-C], as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Additionally shown is the corresponding deformation density $\Delta\rho$ and the SFOs with the highest eigenvalues v (symbolizing charge flow). Hydrogen atoms are hidden for clarity.

e. NBO Calculations

Natural Bond Orbital (NBO) calculations were conducted on PBE0/def2-TZVPP level of theory,^[3e, 8b, 14] using NBO 6.0.18a as included in Orca 5.0.3.^[15] ECP for Pd was employed.^[4] Wiberg bond indices were calculated using the BNDIDX keyword. NBOs were rendered and plotted using Chemcraft.^[16]

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NBO analysis for complex **3**:

Important NBOs of **3** that take major roles in the Pd-Si interaction are listed below and displayed in figure S2.

Table S2: List of selected NBOs in complex **3** with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
100	1.99	LP (Pd)	4d (100 %)
102	1.94	LP (Pd)	4d (100 %)
104	1.73	LP (Pd)	4d (98 %), 5s (2 %)
273	0.72	LV (Si)	3s (61 %), 3p (39 %)
274	0.44	LV (Si)	3s (39 %), 3p (60 %)
275	0.40	LV (Si)	3p (100 %)
276	0.34	LV (Si)	3p (100 %)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] for selected bonding interactions between the listed NBOs:

- $\Delta E^{(2)}$ 104 (LP_{Pd}) $\rightarrow$ 273 (LV_{Si}) 111.81
- $\Delta E^{(2)}$ 100 (LP_{Pd}) $\rightarrow$ 276 (LV_{Si}) 3.65
- $\Delta E^{(2)}$ 102 (LP_{Pd}) $\rightarrow$ 275 (LV_{Si}) 2.56
- $\Delta E^{(2)}$ 104 (LP_{Pd}) $\rightarrow$ 274 (LV_{Si}) 2.65

SUPPORTING INFORMATION

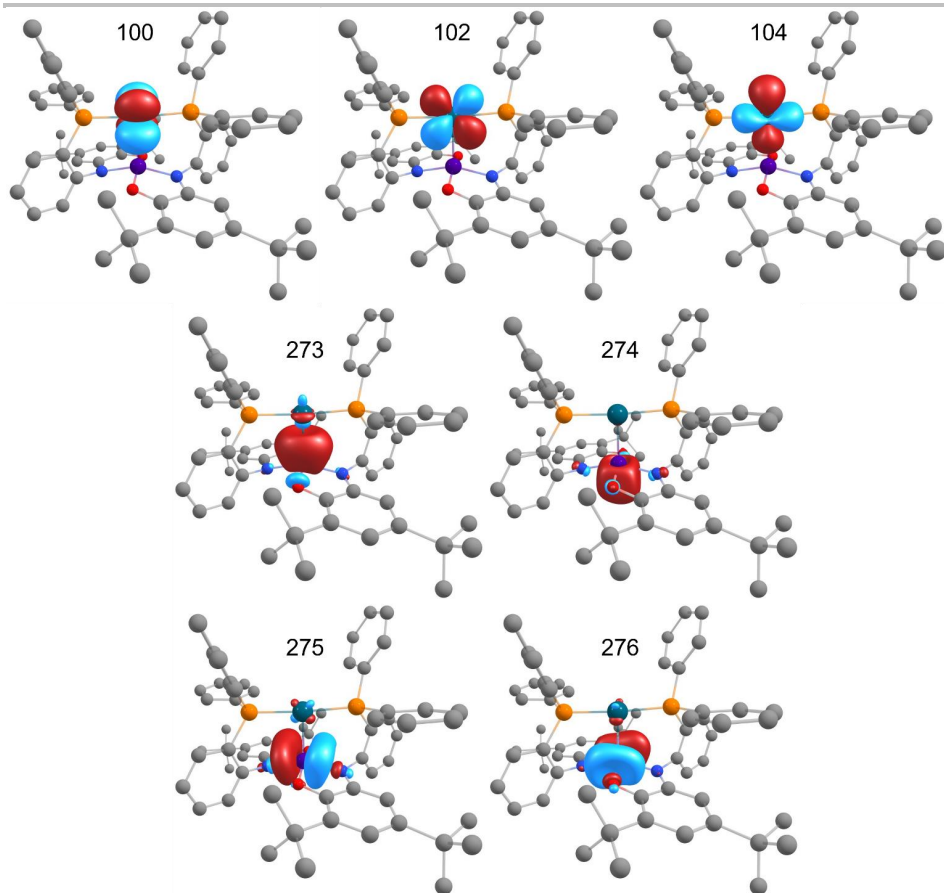


Figure S 13: Selected NBOs (PBE0/def2-TZVPP//PBEh-3c) of **3**, displayed at 0.07 e/Å³. Hydrogen atoms are hidden for clarity.

f. QTAIM Analysis

QTAIM analyses were performed on the PBE0/DKH-def2-TZVP (Pd: SARC-DKH-TZVP) electron densities,^[8b, 14, 17] using the AIMAll software with default integration.^[18] A variety of descriptors have been used in the context of Bader's theory of AIM, to describe and compare the nature of chemical bonds.^[19] The main components considered are the electron density, $\rho(r_{\text{BCP}})$, and the Laplacian of the density, $\nabla^2\rho(r_{\text{BCP}})$ at the bond critical points (bcp's). Positive Laplacians, as found at the bcp's the Si-O/N bonds suggest closed shell (ionic) interactions, whereas the opposite is found for Si-Pd bonds, meaning shared (covalent) interactions. The total electronic energy density $H(r_{\text{BCP}})$ serves as a criterion for the bond classification, with negative values for shared-type (covalent) atomic interactions (typical covalent single bonds ≈ -0.35) and positive values in closed-shell bonds.^[20] In addition, the ratio of $G(r_{\text{BCP}})/\rho(r_{\text{BCP}})$ (Lagrangian kinetic energy per electron) indicates the kind of interatomic interactions, with a value <1 for shared interaction and >1 for closed-shell (ionic) bonding.^[21] The ellipticity ($\epsilon=\lambda_1/\lambda_2-1$) of a bond quantifies the

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anisotropy of the electron density, with deviations from a cylindrical distribution leading to values larger than zero. The delocalization index is yet another indicator for covalent bonding.

Table S3: Result for the QTAIM analysis of **3** and **[3-Cl]**.

QTAIM								Bader charge analysis	
3	$\rho(r_{\text{BCP}})$	$\nabla^2\rho(r_{\text{BCP}})$	$H(r_{\text{BCP}})$	$G(r_{\text{BCP}})$	$G(r_{\text{BCP}})/\rho(r_{\text{BCP}})$	$\varepsilon=\lambda_1/\lambda_2-1$	DI		Q
Si-Pd	0.0737	-0.042	-0.046	0.036	0.488	0.058	0.355	Si	3.00
Si-N	0.1154	0.432	-0.052	0.160	1.386	0.226	0.349	N	-1.52
Si-O	0.1146	0.575	-0.042	0.186	1.623	0.123	0.322	O	-1.37
Pd-P	0.0986	0.155	-0.037	0.076	0.771	0.022	0.849	Pd	-0.37
								P	1.84
[3-Cl]									
Si-Pd	0.0928	-0.096	-0.066	0.042	0.453	0.064	0.476	Si	2.94
Si-N	0.1100	0.390	-0.050	0.147	1.336	0.160	0.330	N	-1.51
Si-O	0.1031	0.480	-0.038	0.158	1.532	0.091	0.291	O	-1.37
Pd-P	0.0963	0.155	-0.036	0.074	0.768	0.057	0.840	Pd	-0.34
Pd-Cl	0.0602	0.189	-0.012	0.059	0.980	0.059	NA	P	1.83

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3. X-Ray Diffraction

a. General

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperatures with a Bruker D8 Venture diffractometer, dual source (Mo- K_{α} radiation, microfocus X-ray tube, Photon III detector, temperature 100 K). Data were processed with the standard Bruker (SAINT, APEX3) software package.^[22] Multiscan absorption correction was applied using the SADABS program.^[23] The structures were solved by intrinsic phasing^[24] and refined by full-matrix least-squares methods against F^2 using the SHELXTL software package (Version 2018/3).^[25] Graphical handling of the structural data during solution and refinement was performed with shelXle.^[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.^[27] For the structure of **3**, three distorted molecules of co-crystallized toluene were treated with the SQUEEZE procedure, as implemented in PLATON.^[28] Finalisation of gathered data was done using final cif tool.^[29]

For data visualization, Mercury 2020.2.0 was used.^[30] The thermal displacement ellipsoids are shown at the probability level of 50%. CCDC numbers 2294415-2294420 and 2303185 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>.

The data obtained from the scXRD analysis from crystals of **[2-NHMe₂]** could not be refined to a degree that an entry in the CCDC seems appropriate, due to significant electron density which only can poorly be modelled with solvent models. However, the data is sufficient to underline the geometry, already speculated by interpretation of NMR spectroscopic data. A picture is shown in figure S12.

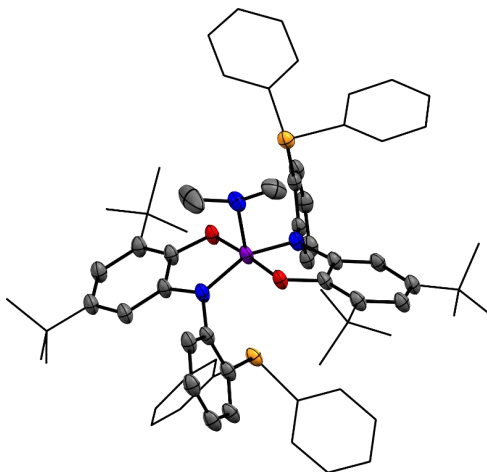
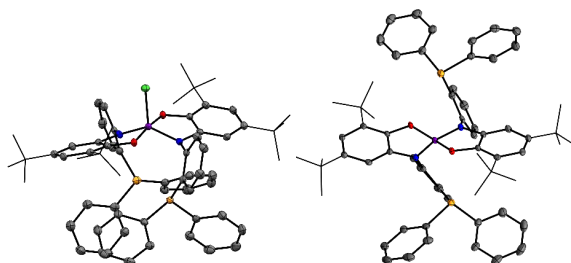


Figure S 14: Solid state structure of **[2-NHMe₂]**, as obtained by scXRD analysis. Vibrational ellipsoids displayed at 50 % probability, hydrogen atoms and solvent molecules omitted for clarity. This structure is not fully refined due to heavily distorted co-crystallized solvent molecules.

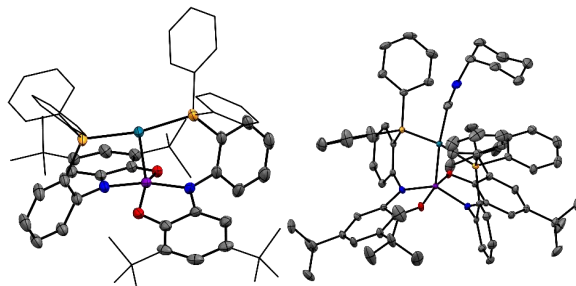
SUPPORTING INFORMATION

b. Summarized Data



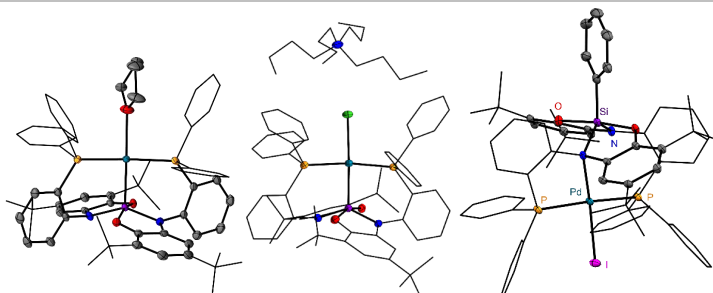
Compound CCDC number	[H][2-Cl] 2294420	2 2294419
Identification code	mo_najm05b_2_0m_a	mo_na_jm26_2_0ma_a
Empirical formula	C ₆₅ H ₇₁ Cl ₃ N ₂ O ₂ P ₂ Si	C ₆₇ H ₇₁ N ₂ O ₂ P ₂ Si
Formula weight	1108.61	1026.28
Temperature [K]	100(2)	100(2)
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i> (14)
<i>a</i> [Å]	18.5080(16)	16.1281(10)
<i>b</i> [Å]	24.432(2)	21.7164(15)
<i>c</i> [Å]	26.258(3)	17.1773(11)
α [°]	90	90
β [°]	90	106.168(2)
γ [°]	90	90
Volume [Å ³]	11873.5(19)	5778.3(7)
<i>Z</i>	8	4
ρ_{calc} [g cm ⁻³]	1.240	1.180
μ [mm ⁻¹]	0.274	0.142
<i>F</i> (000)	4688	2188
Crystal size [mm ³]	0.147×0.139×0.093	0.20×0.12×0.01
Radiation	Mo-K α (λ = 0.71073 Å)	Mo-K α (λ = 0.71073 Å)
2 θ range [°]	4.15 to 57.57 (0.74 Å)	3.75 to 54.23 (0.78 Å)
Index ranges	-25 ≤ <i>h</i> ≤ 25 -33 ≤ <i>k</i> ≤ 33 -35 ≤ <i>l</i> ≤ 35	-20 ≤ <i>h</i> ≤ 20 -27 ≤ <i>k</i> ≤ 27 -22 ≤ <i>l</i> ≤ 22
Reflections collected	759797	323123
Independent reflections	15425 [<i>R</i> _{int} = 0.1272, <i>R</i> _{sigma} = 0.0290]	12744 [<i>R</i> _{int} = 0.1123, <i>R</i> _{sigma} = 0.0326]
Data/Restraints/Parameters	15425/65/719	12744/0/679
Goodness-of-fit on <i>F</i> ²	1.062	1.090
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0410, <i>wR</i> ₂ = 0.0901	<i>R</i> ₁ = 0.0468, <i>wR</i> ₂ = 0.1127
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0560, <i>wR</i> ₂ = 0.1007	<i>R</i> ₁ = 0.0571, <i>wR</i> ₂ = 0.1202
Largest peak/hole [e Å ⁻³]	0.37/-0.34	0.48/-0.45

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Compound CCDC number	3 2294418	[3-CNCy] 2294415
Identification code	mo_na261w_0ma_a_sq	mo_na436_0m_tw
Empirical formula	C ₆₄ H ₆₈ N ₂ O ₂ P ₂ PdSi[+3C ₇ H ₈]	C ₈₆ H ₉₄ N ₃ O ₂ P ₂ PdSi
Formula weight	1093.63	1398.07
Temperature [K]	100(2)	120(2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	14.8818(12)	11.2603(8)
<i>b</i> [Å]	15.5903(12)	14.6614(10)
<i>c</i> [Å]	18.1794(14)	23.3821(14)
α [°]	84.371(3)	84.242(3)
β [°]	72.185(3)	82.728(3)
γ [°]	67.494(2)	79.733(3)
Volume [Å ³]	3708.9(5)	3755.9(4)
<i>Z</i>	2	2
ρ_{calc} [g cm ⁻³]	0.979	1.236
μ [mm ⁻¹]	0.344	0.355
<i>F</i> (000)	1144	1474
Crystal size [mm ³]	0.202×0.134×0.112	0.340×0.273×0.256
Radiation	Mo-K α (λ = 0.71073 Å)	Mo-K α (λ = 0.71073 Å)
2 θ range [°]	4.40 to 57.68 (0.74 Å)	3.92 to 55.88 (0.76 Å)
Index ranges	-20 $\leq$ <i>h</i> $\leq$ 20 -21 $\leq$ <i>k</i> $\leq$ 21 -24 $\leq$ <i>l</i> $\leq$ 24	-14 $\leq$ <i>h</i> $\leq$ 14 -19 $\leq$ <i>k</i> $\leq$ 19 -30 $\leq$ <i>l</i> $\leq$ 30
Reflections collected	163663	17903
Independent reflections	19312 [<i>R</i> _{int} = 0.0580, <i>R</i> _{sigma} = 0.0311]	17903
Data/Restraints/Parameters	19312/1275/814	17903/1830/1060
Goodness-of-fit on <i>F</i> ²	1.018	1.053
Final <i>R</i> indexes [<i>I</i> $\geq$ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0487, <i>wR</i> ₂ = 0.1245	<i>R</i> ₁ = 0.0464, <i>wR</i> ₂ = 0.1215
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0604, <i>wR</i> ₂ = 0.1322	<i>R</i> ₁ = 0.0487, <i>wR</i> ₂ = 0.1233
Largest peak/hole [e Å ⁻³]	2.96/-2.27	2.80/-0.74

SUPPORTING INFORMATION



Compound CCDC number	3-THF 22994417	[NBu ₄][3-Cl] 2294416	[Ph-2-Pd-I] 2303185
Identification code	mo_na355_0m_a	mo_na286_4_0m_a	mo_na443_0m
Empirical formula	C ₇₆ H ₈₂ N ₂ O ₅ P ₂ PdSi	C ₈₀ H ₁₀₄ ClN ₃ O ₂ P ₂ PdSi	C ₆₂ H ₆₅ IN ₂ O ₂ P ₂ PdSi
Formula weight	1309.94	1371.54	1453.84
Temperature [K]	100(2)	100(2)	120(2)
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (2)	<i>P</i> 1 (1)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	11.487(3)	12.337(2)	13.2772(9)
<i>b</i> [Å]	13.900(3)	13.582(3)	15.7252(12)
<i>c</i> [Å]	22.330(5)	13.683(2)	17.3707(13)
α [°]	86.077(9)	100.739(7)	83.790(3)
β [°]	83.814(9)	113.130(7)	75.935(3)
γ [°]	72.973(9)	111.464(7)	84.612(3)
Volume [Å ³]	3386.7(14)	1810.3(6)	3488.8(4)
<i>Z</i>	2	1	2
ρ_{calc} [g cm ⁻³]	1.285	1.258	1.384
μ [mm ⁻¹]	0.391	0.402	0.821
<i>F</i> (000)	1384	728	1500
Crystal size [mm ³]	0.243×0.167×0.133	0.172×0.077×0.026	0.342×0.323×0.279
Radiation	Mo- <i>K</i> α (λ = 0.71073 Å)	Mo- <i>K</i> α (λ = 0.71073 Å)	Mo- <i>K</i> α (λ = 0.71073 Å)
2 θ range [°]	4.00 to 61.33 (0.70 Å)	4.11 to 61.51 (0.69 Å)	3.96 to 57.67 (0.74 Å)
Index ranges	-16 ≤ <i>h</i> ≤ 16 -19 ≤ <i>k</i> ≤ 19 -32 ≤ <i>l</i> ≤ 32	-17 ≤ <i>h</i> ≤ 17 -19 ≤ <i>k</i> ≤ 19 -19 ≤ <i>l</i> ≤ 19	-17 ≤ <i>h</i> ≤ 17 -21 ≤ <i>k</i> ≤ 21 -23 ≤ <i>l</i> ≤ 23
Reflections collected	214351	79199	232814
Independent reflections	20882	22233 [<i>R</i> _{int} = 0.0751, <i>R</i> _{sigma} = 0.0750]	18164 [<i>R</i> _{int} = 0.0663, <i>R</i> _{sigma} = 0.0334]
Data/Restraints/Parameters	20882/1044/979	22233/358/897	18164/585/887
Goodness-of-fit on <i>F</i> ²	1.073	1.073	1.064
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0445, <i>wR</i> ₂ = 0.1003	<i>R</i> ₁ = 0.0524, <i>wR</i> ₂ = 0.1232	<i>R</i> ₁ = 0.0374, <i>wR</i> ₂ = 0.0924
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0521, <i>wR</i> ₂ = 0.1054	<i>R</i> ₁ = 0.0681, <i>wR</i> ₂ = 0.1362	<i>R</i> ₁ = 0.0393, <i>wR</i> ₂ = 0.0938
Largest peak/hole [e Å ⁻³]	0.72/-1.26	1.69/-1.54	1.56/-1.06

SUPPORTING INFORMATION

c. Metric Oxidation States

Since amidophenolates are known for their redox non-innocence, we further want to address the oxidation situation at the silicon center, to explain how much of the Si-Pd interaction consists of dative Pd→Si(IV) bonding and if the amidophenolate could contribute electrons to the Si center, resulting in a Si(II)→Pd interaction. Therefore, metric oxidation states (MOS) of the ligand fragments based on the model of Brown are calculated using the bond lengths that were obtained from scXRD analysis of compounds **2** and **3**.^[31]

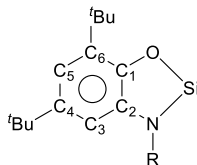


Figure S 15: Numbering scheme for the carbon atoms in compounds **2** and **3**, as suggested by Brown.^[31]

Table S 3: Average bond lengths (Å) and resulting MOS for silane **2** and complex **3**.

	silane 2	Pd complex 3
$d_{\text{averaged}}(\text{C1-O})$	1.3920(18)	1.368(3)
$d_{\text{averaged}}(\text{C2-N})$	1.418(2)	1.389(3)
$d_{\text{averaged}}(\text{C1-C2})$	1.397(2)	1.403(3)
$d_{\text{averaged}}(\text{C2-C3})$	1.380(2)	1.390(3)
$d_{\text{averaged}}(\text{C3-C4})$	1.398(2)	1.396(3)
$d_{\text{averaged}}(\text{C4-C5})$	1.391(2)	1.404(3)
$d_{\text{averaged}}(\text{C5-C6})$	1.410(2)	1.401(3)
$d_{\text{averaged}}(\text{C6-C1})$	1.388(2)	1.392(3)
MOS	-2.29	-1.92

Although a bond elongation in the aromatic backbone can be observed when coordination of the Pd takes place, the metric oxidation state of -1.92 indicates major contributions of Si(IV) and only minor contributions from an open-shell Si(II) system in compound **3**.

Furthermore, an intense coloration of compound **3** would have been expected to occur, when the amidophenolates are oxidized. Although complex **3** exhibits a red coloration, it is far from an intensity that would indicate oxidation of the ligand scaffold.

Furthermore, we calculated the geometries of complex **3** in the singlet state, the triplet spin state and additionally using broken-symmetry DFT in order to look for open-shell singlet states. While the geometry of compound **3** in a triplet state significantly differs from the experimentally observed structure (see figure S16), the broken-symmetry calculation consistently converged to a closed-shell singlet geometry with spin expectation value of close to zero. These theoretic findings further support the Pd→Si(IV) binding situation, as already stated by MOS, EDA-NOCV and NBO calculations.

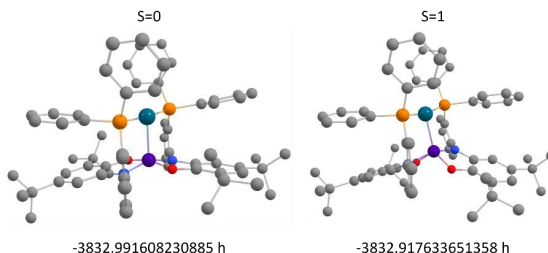
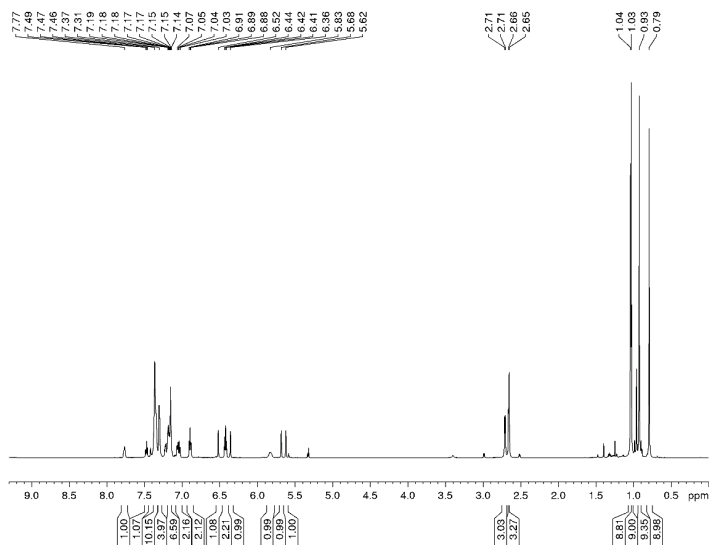
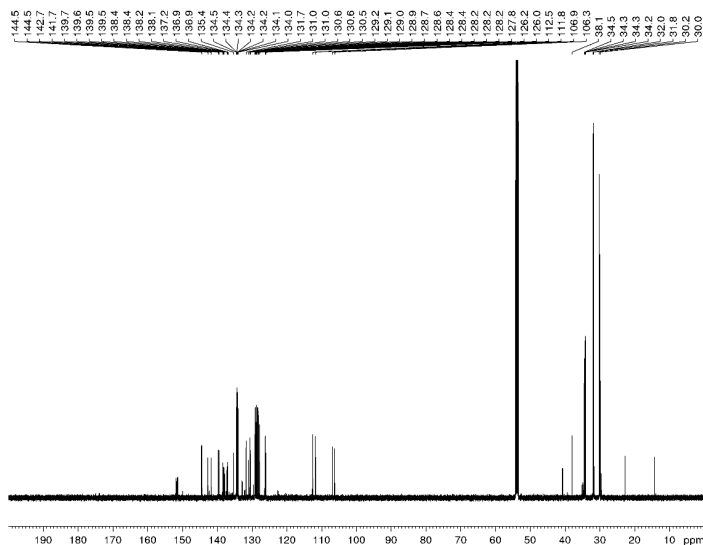


Figure S 16: Geometries of complex **3**, calculated at the PBEh-3c level of theory in different spin-states and their single point energies (hydrogens were omitted for clarity). The strong deformation of one amidophenolate unit in the case of a triplet system can clearly be seen.

SUPPORTING INFORMATION

4. NMR Spectra

Figure S 17: ^1H NMR spectrum (600 MHz) of $[2\text{-NHMe}_2]$ in CD_2Cl_2 at 295 K.Figure S 18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of $[2\text{-NHMe}_2]$ in CD_2Cl_2 at 295 K.

SUPPORTING INFORMATION

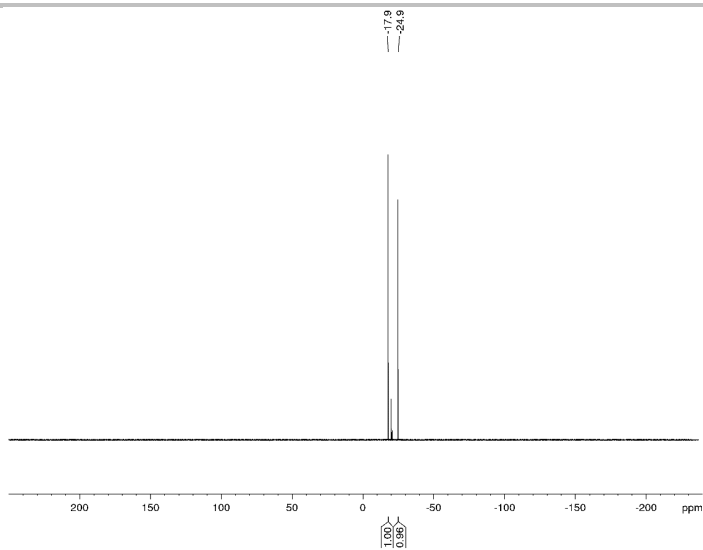


Figure S 19: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of $[\mathbf{2}\text{-NHMe}_2]$ in CD_2Cl_2 at 295 K, contains impurities of $\mathbf{2}$.

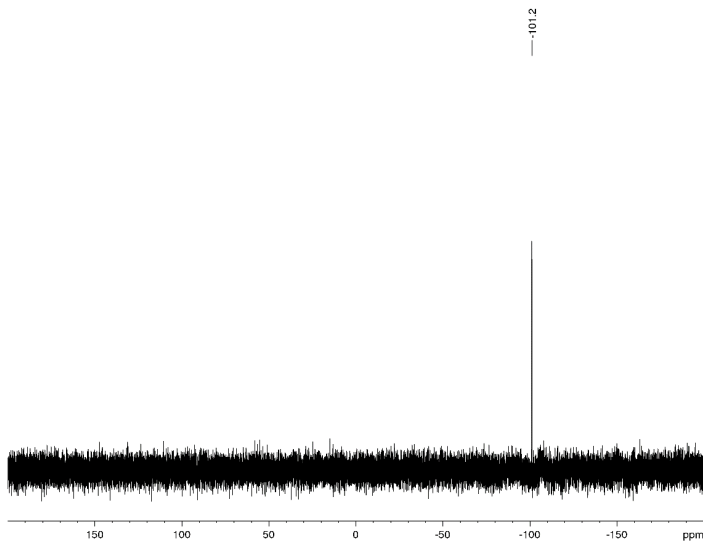
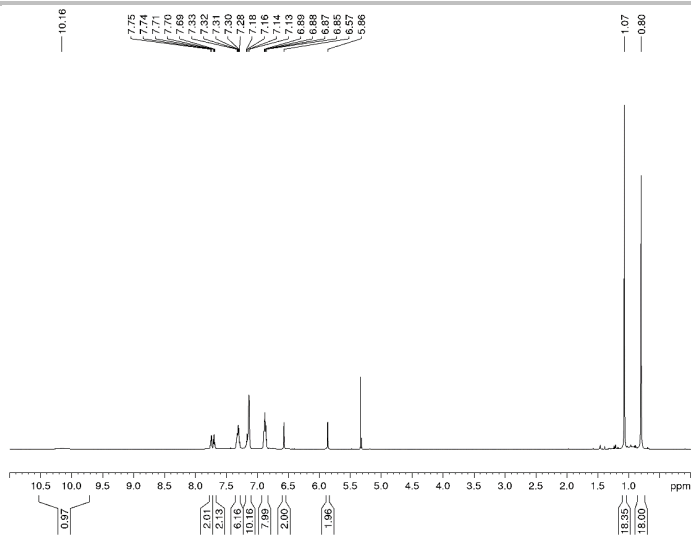
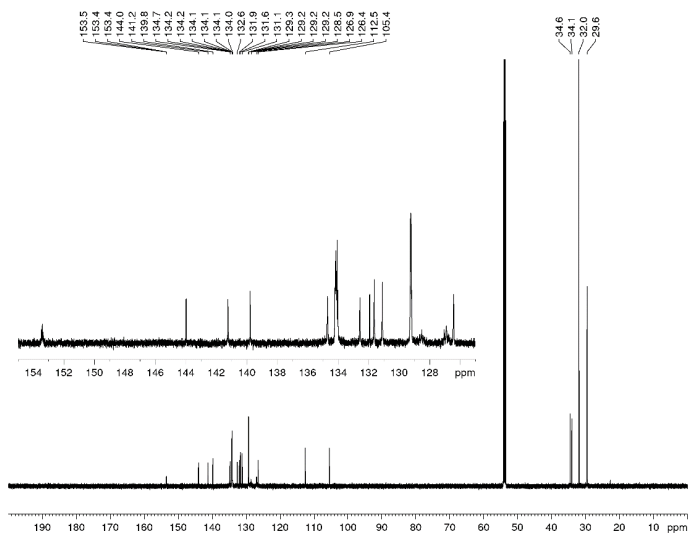


Figure S 20: ^{29}Si (1G) NMR spectrum (119 MHz) of $[\mathbf{2}\text{-NHMe}_2]$ in CD_2Cl_2 at 295 K.

SUPPORTING INFORMATION

Figure S 21: ^1H NMR spectrum (600 MHz) of $[\text{H}][2\text{-Cl}]$ in CD_2Cl_2 at 295 K.Figure S 22: $^{13}\text{C}(^1\text{H})$ NMR spectrum (151 MHz) of $[\text{H}][2\text{-Cl}]$ in CD_2Cl_2 at 295 K.

SUPPORTING INFORMATION

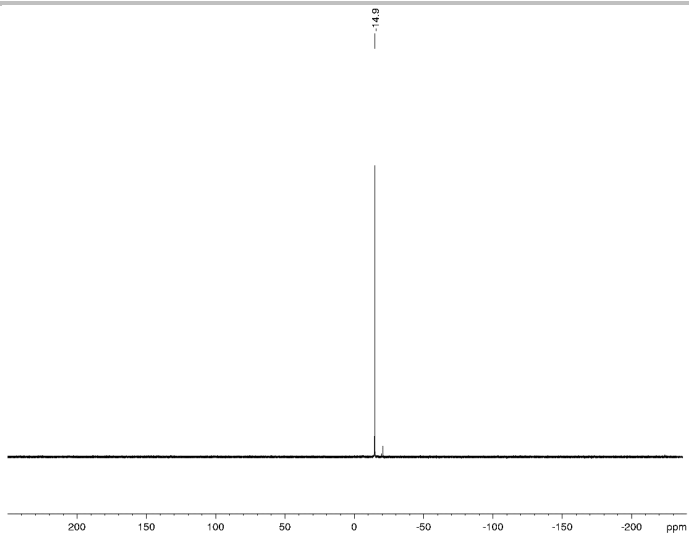


Figure S 23: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of $[\text{H}][2\text{-Cl}]$ in CD_2Cl_2 at 295 K.

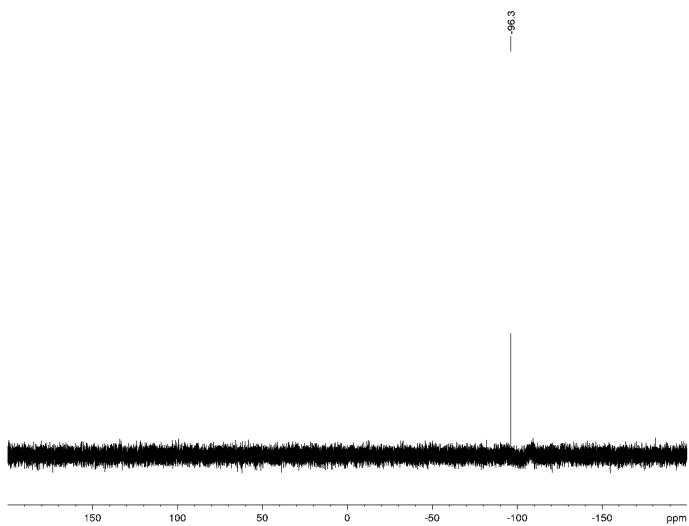
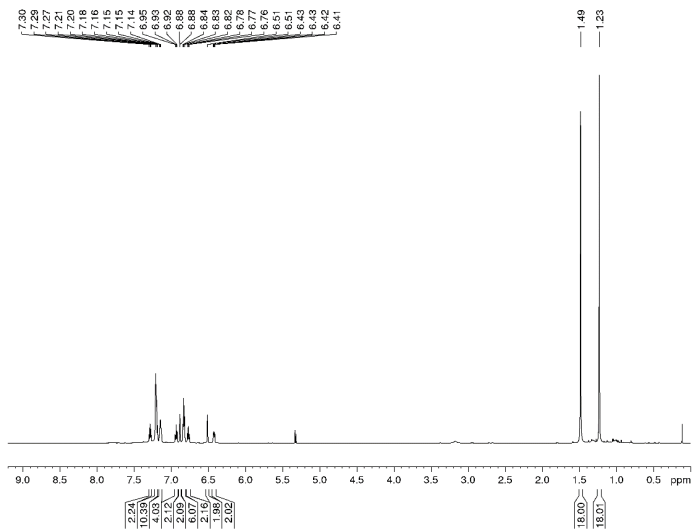
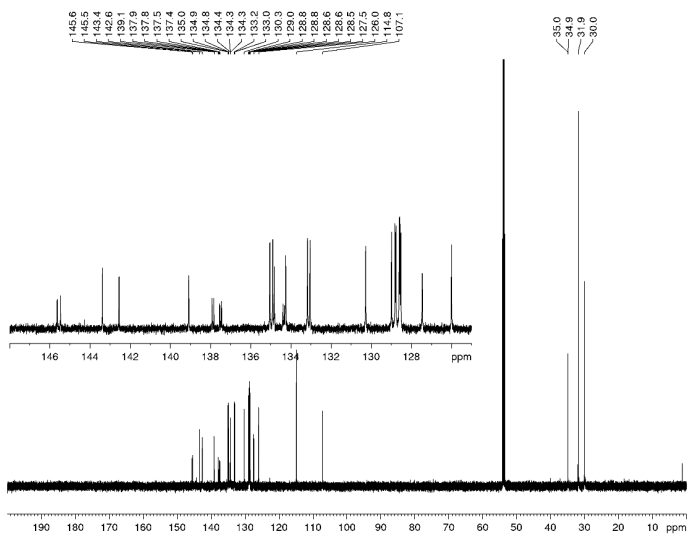


Figure S 24: ^{29}Si (1G) NMR spectrum (119 MHz) of $[\text{H}][2\text{-Cl}]$ in CD_2Cl_2 at 295 K.

SUPPORTING INFORMATION

Figure S 25: ¹H NMR spectrum (600 MHz) of **2** in CD₂Cl₂ at 295 K.Figure S 26: ¹³C{¹H} NMR spectrum (151 MHz) of **2** in CD₂Cl₂ at 295 K.

SUPPORTING INFORMATION

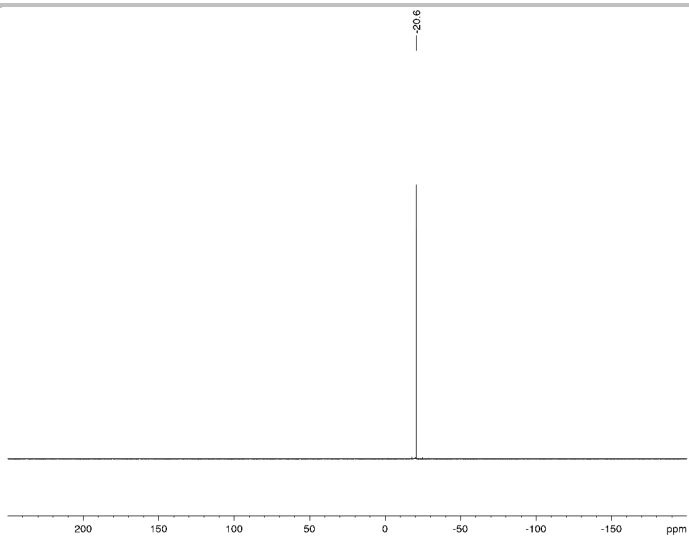


Figure S 27: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of **2** in CD_2Cl_2 at 295 K.

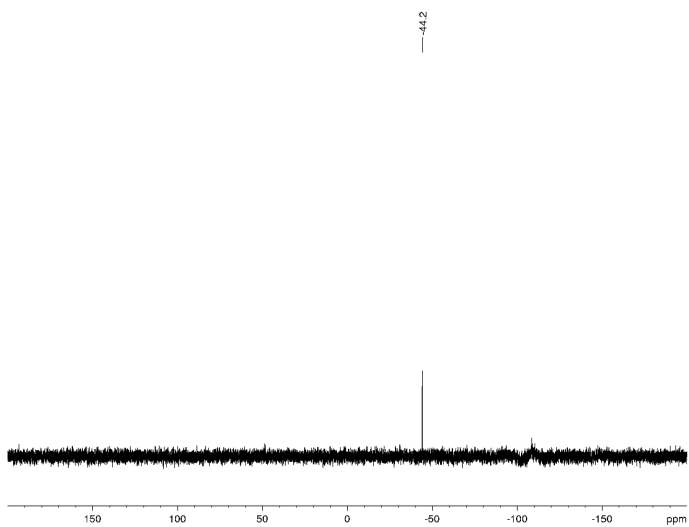
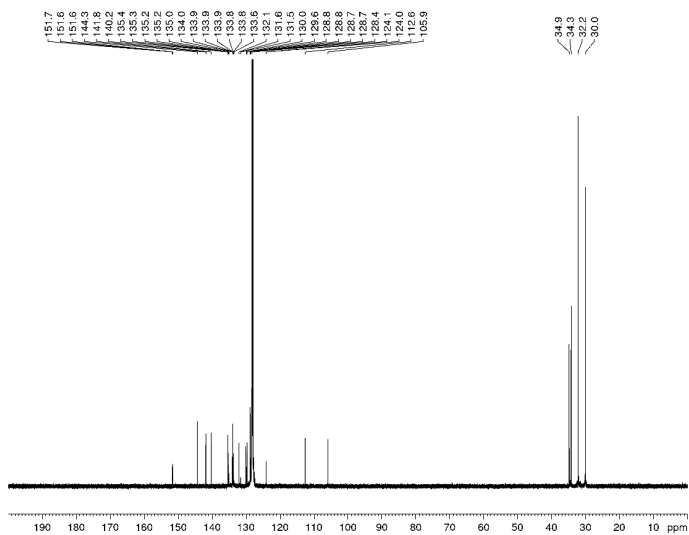
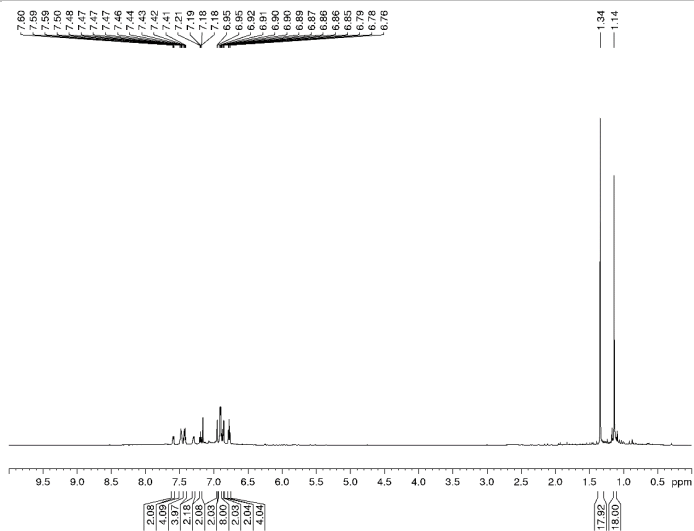
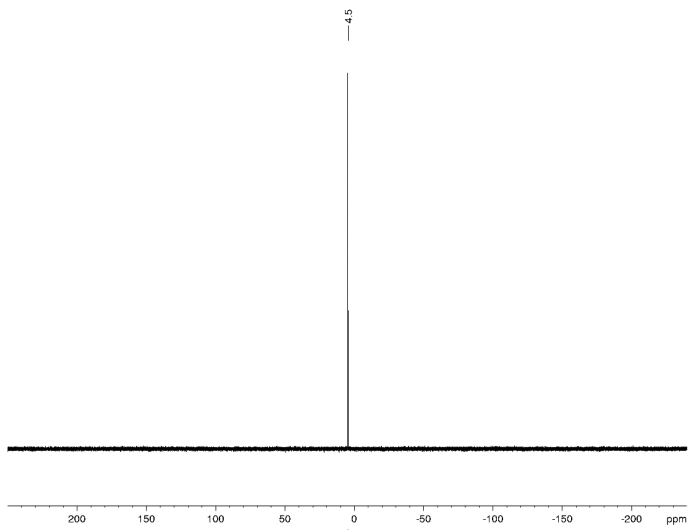
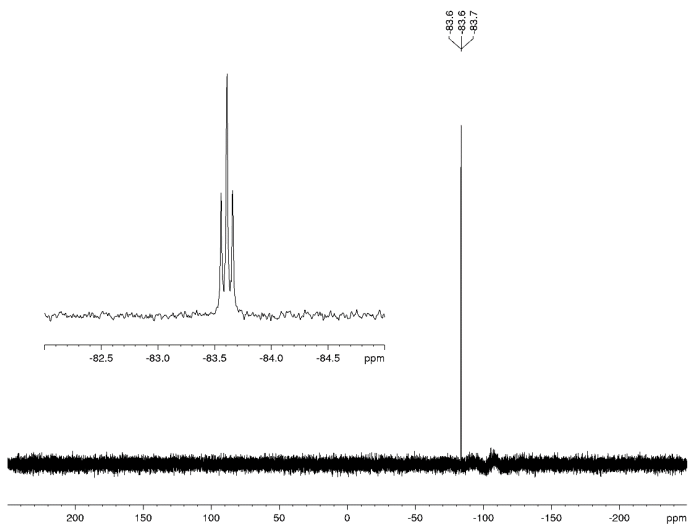


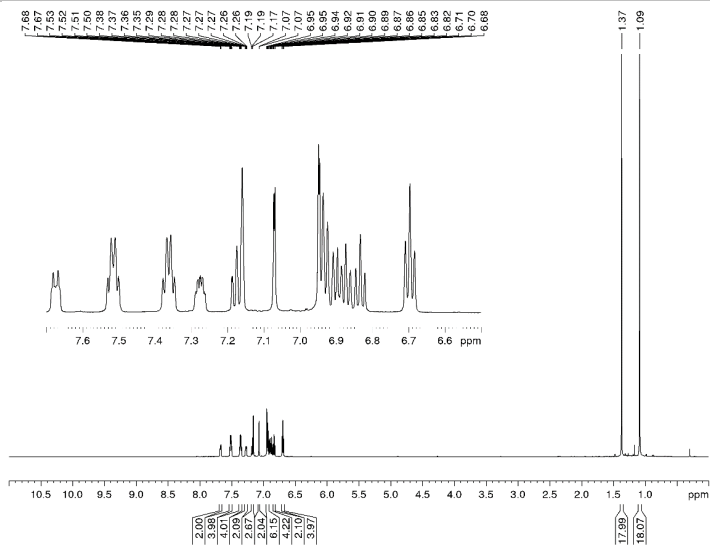
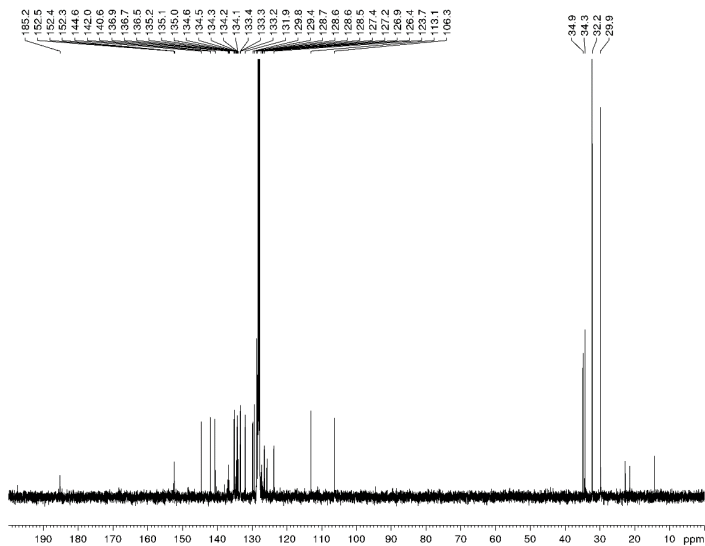
Figure S 28: ^{29}Si (1G) NMR spectrum (119 MHz) of **2** in CD_2Cl_2 at 295 K.



SUPPORTING INFORMATION

Figure S 31: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of **3** in C_6D_6 at 295 K.Figure S 32: ^{29}Si (1G) NMR spectrum (119 MHz) of **3** in C_6D_6 at 295 K.

SUPPORTING INFORMATION

Figure S 33: ^1H NMR spectrum (400 MHz) of [3-CO] at 5 bar in C_6D_6 at 295 K.Figure S 34: $^{13}\text{C}(^1\text{H})$ NMR spectrum (101 MHz) of [3-CO] under 5 bar in C_6D_6 at 295 K with traces of toluene and *n*-pentane.

SUPPORTING INFORMATION

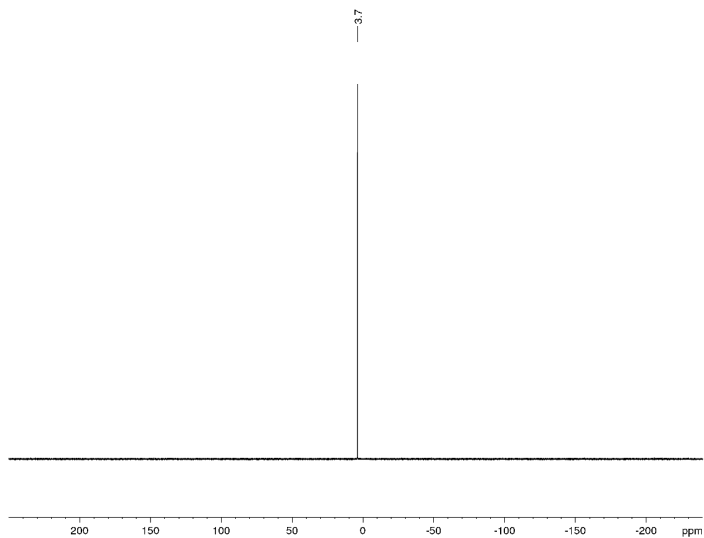


Figure S 35: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of [3-CO] under 5 bar in C_6D_6 at 295 K.

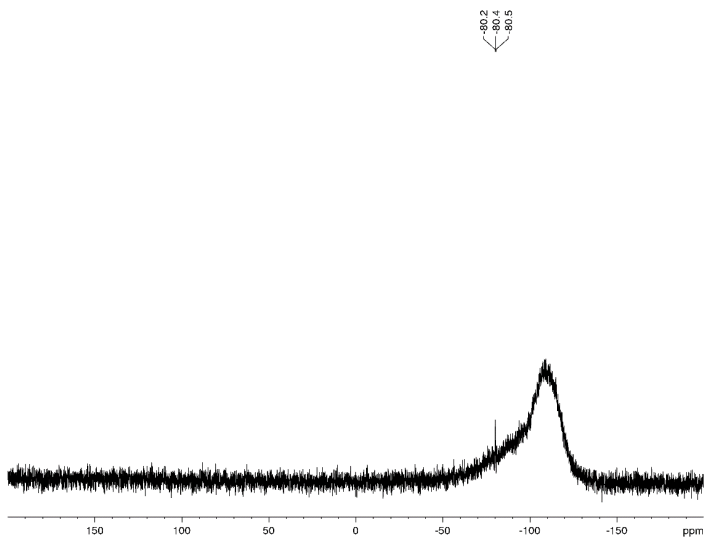
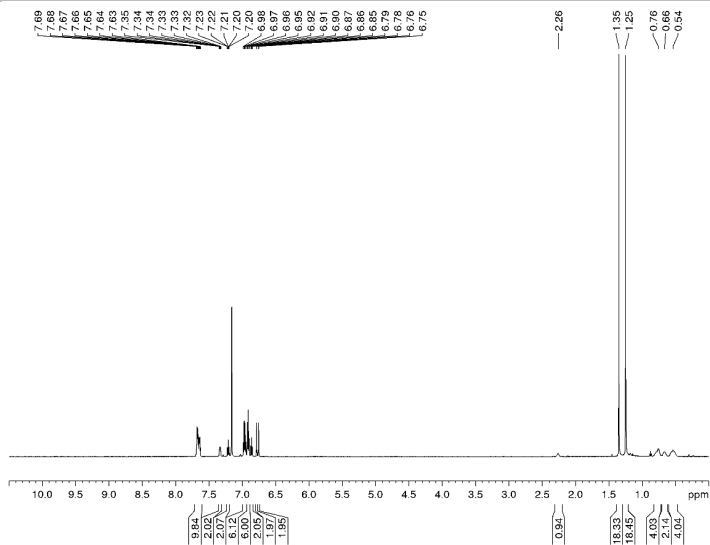
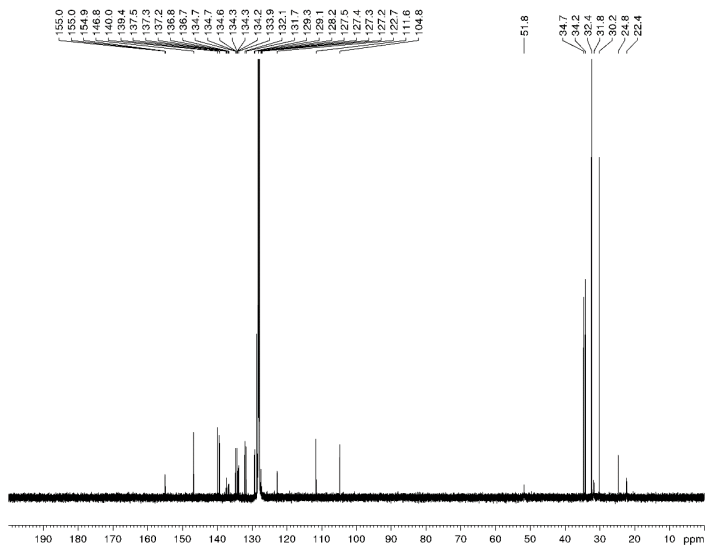


Figure S 36: ^{29}Si (IG) NMR spectrum (79 MHz) of [3-CO] under 5 bar in C_6D_6 at 295 K.

SUPPORTING INFORMATION

Figure S 37: ¹H NMR spectrum (600 MHz) of [3-CNCy] in C₆D₆ at 295 K.Figure S 38: ¹³C{¹H} NMR spectrum (151 MHz) of [3-CNCy] in C₆D₆ at 295 K with traces of benzene.

SUPPORTING INFORMATION

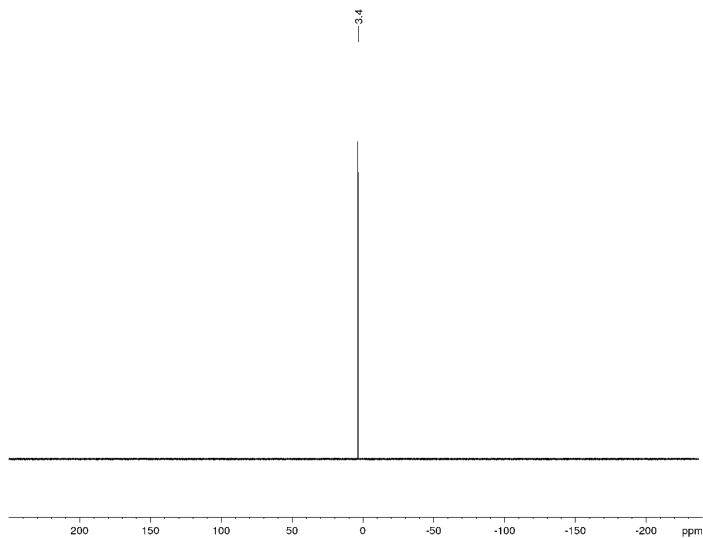


Figure S 39: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (252 MHz) of [3-CNCy] in C_6D_6 at 295 K.

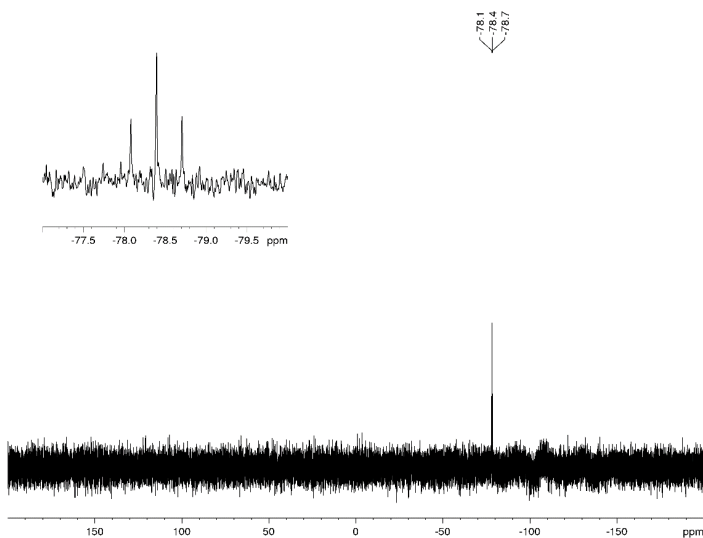
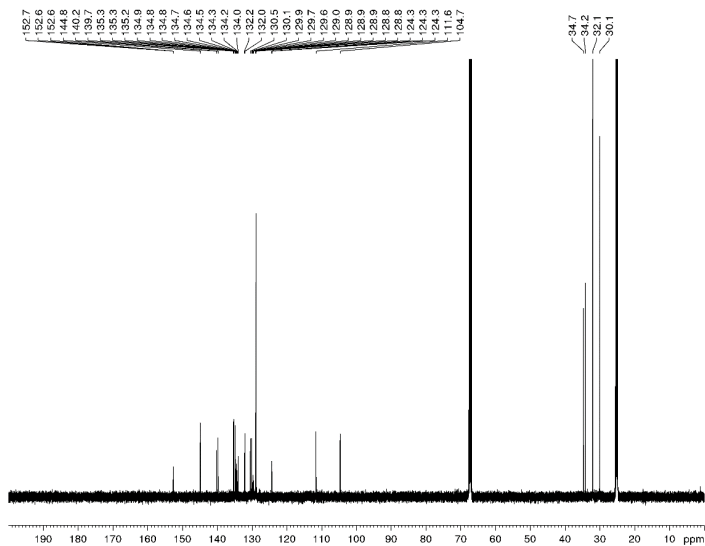
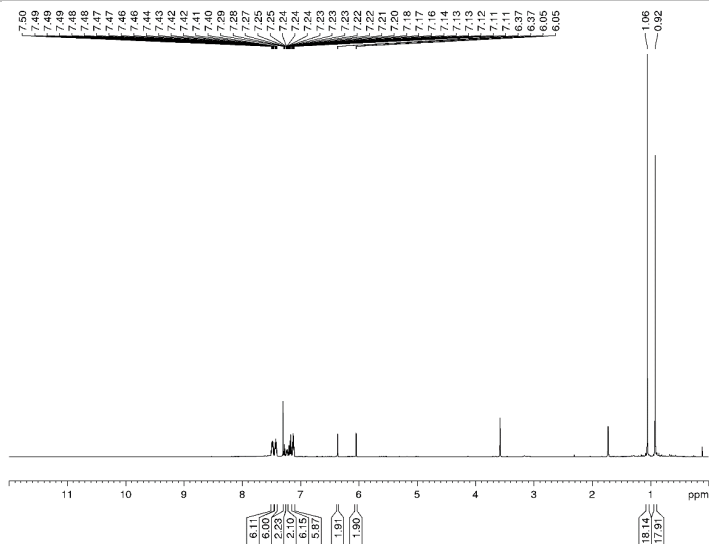
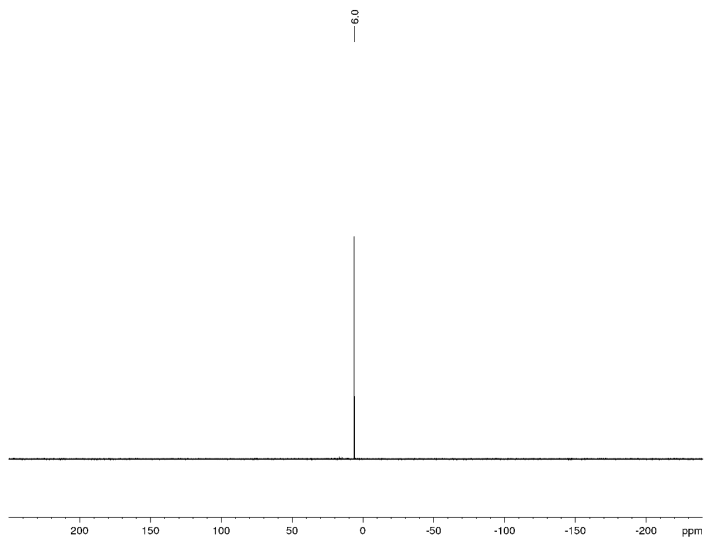
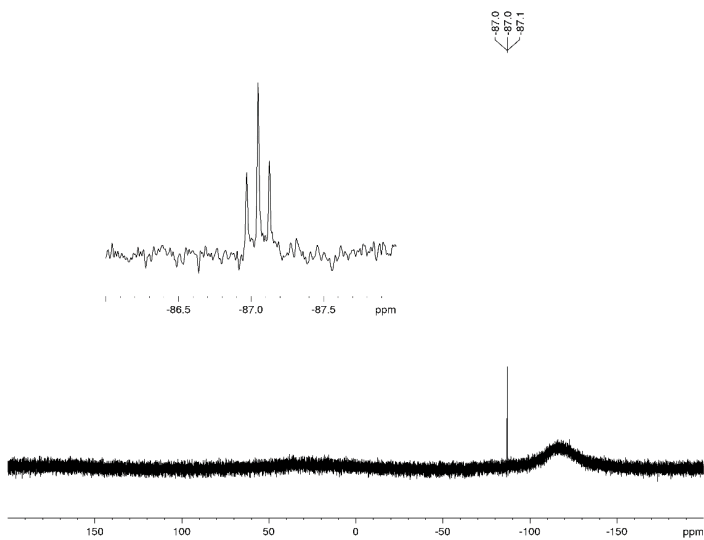
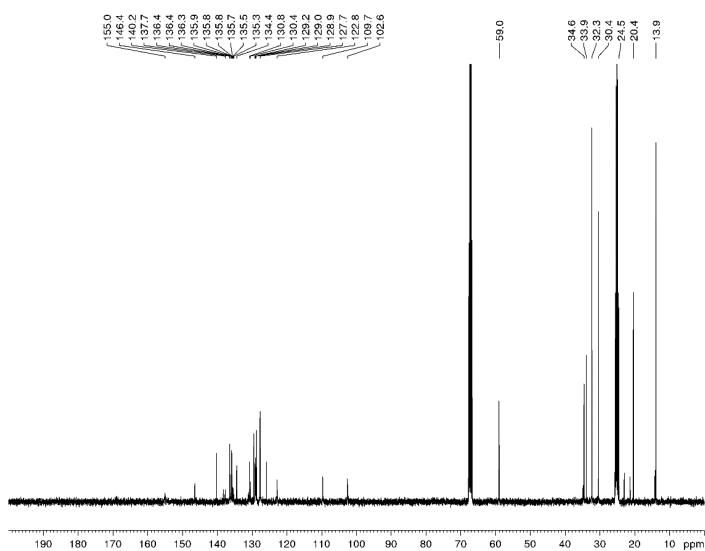
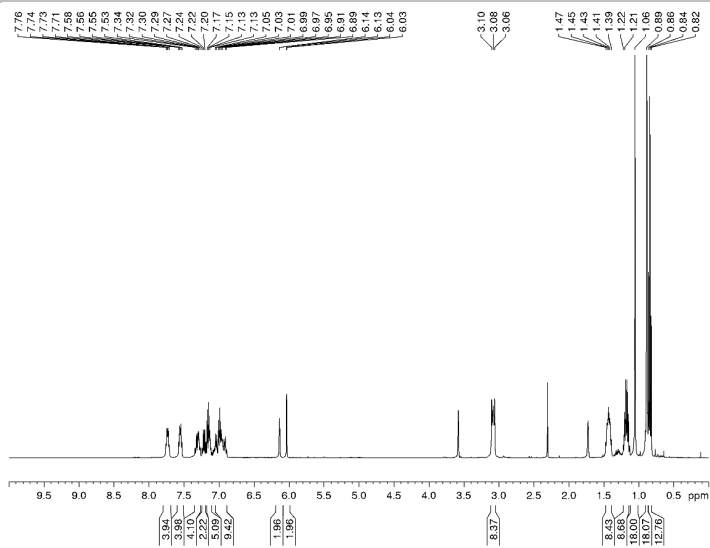


Figure S 40: ^{29}Si (1G) NMR spectrum (119 MHz) of [3-CNCy] in C_6D_6 at 295 K.

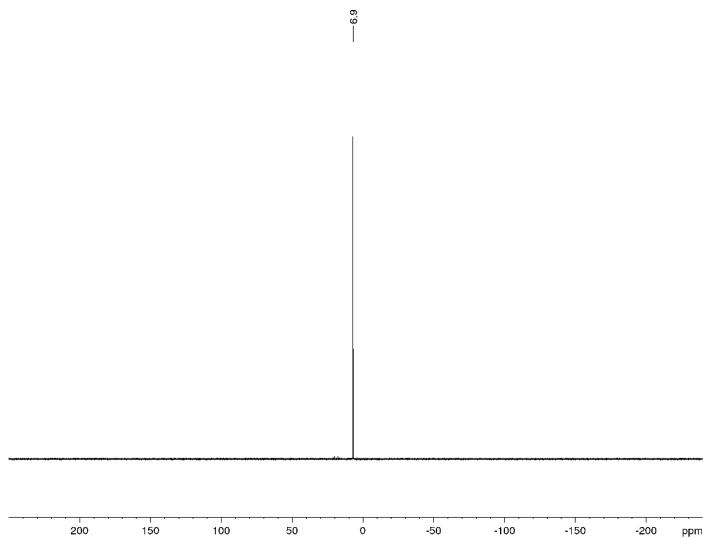
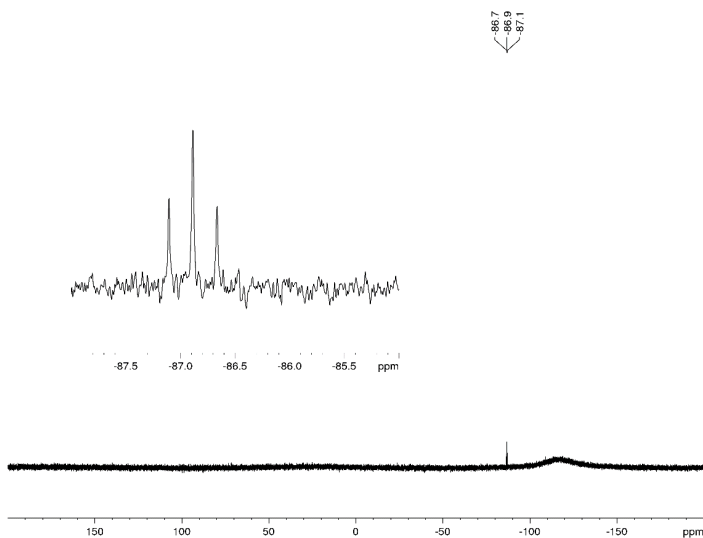


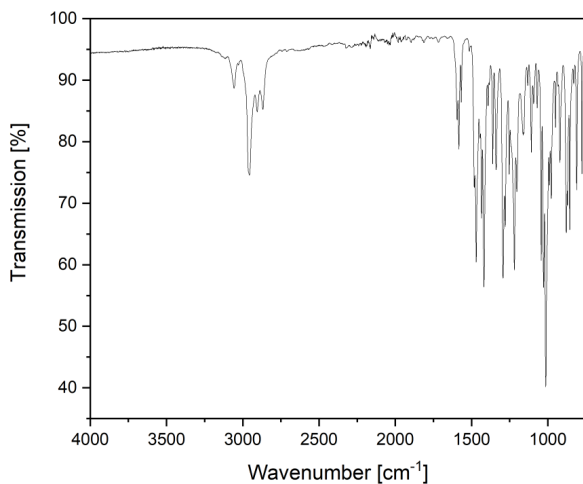
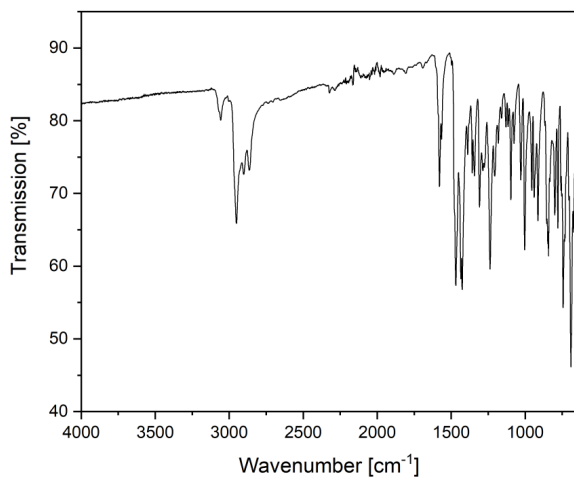
SUPPORTING INFORMATION

Figure S 43: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (151 MHz) of [3-THF] in THF- d_8 at 295 K.Figure S 44: ^{29}Si (IG) NMR spectrum (119 MHz) of [3-THF] in THF- d_8 at 295 K.



SUPPORTING INFORMATION

Figure S 47: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (151 MHz) of $[\text{NBu}_4][3\text{-Cl}]$ in THF- d_8 at 295 K.Figure S 48: ^{29}Si (IG) NMR spectrum (119 MHz) of $[\text{NBu}_4][3\text{-Cl}]$ in THF- d_8 at 295 K.

Figure S49: IR (ATR) spectrum of **2** under nitrogen atmosphere at 298 K.Figure S50: IR (ATR) spectrum of **3** under nitrogen atmosphere at 298 K.

SUPPORTING INFORMATION

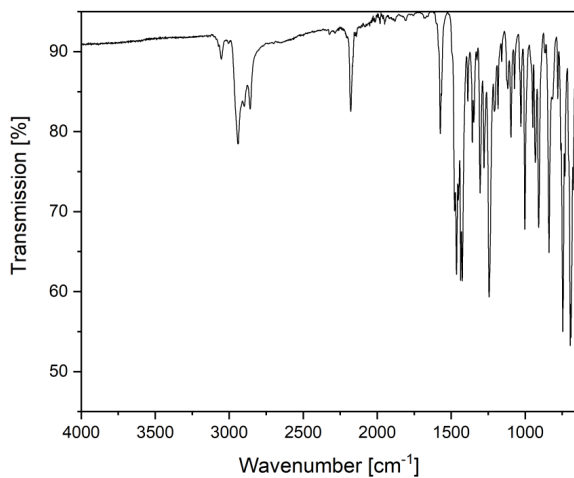


Figure S51: IR (ATR) spectrum of [3-CNCy] under nitrogen atmosphere at 298 K.

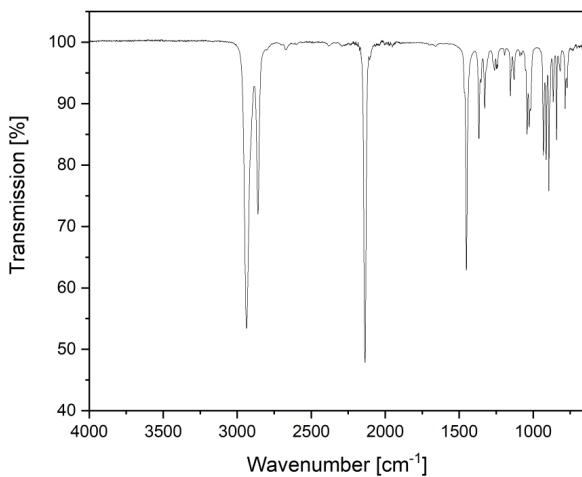


Figure S52: IR (ATR) spectrum of CNCy under nitrogen atmosphere at 298 K.

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3.3.2. Pd(0)/Pd(II) ELECTROMERISM TRIGGERED BY LEWIS BASE COORDINATION TO A REDOX-ACTIVE SILICON Z-TYPE LIGAND

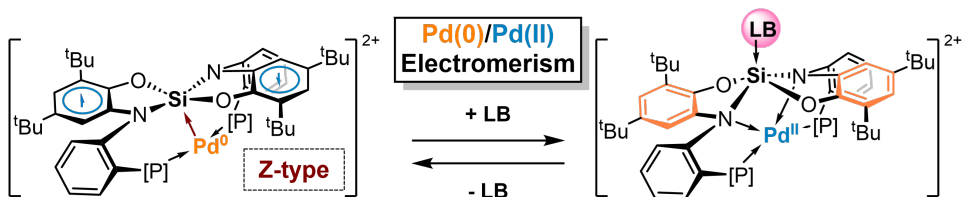


FIG. 3.4.: “Pd(0)/Pd(II) Electromerism Triggered by Lewis Base Coordination to a Redox-Active Silicon Z-Type Ligand” - table of contents figure for the publication discussed in the following section.

The full article including its electronic supplementary information (ESI) presented in this section was published earlier and can be accessed under:

N. Ansmann, M. Kerscher, L. Greb, *Angew. Chem. Int. Ed.* **2025**, 64, e202417581, <https://doi.org/10.1002/anie.202417581>.

Contributions of the three leading authors are rationalized and listed according to the CRediT scheme^[300] on page 202, using the “Formblatt Kumulative Dissertation” (cumulative dissertation form), provided by the faculty of Geo- Sciences and Chemistry at the Ruprecht-Karls Universität Heidelberg. The original article is embedded at page 203 *ff.* The ESI is subsequently attached, starting at page 210.

Formblatt Kumulative Dissertation

1. Publikation/*Publication*:

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☐

4. Beteiligungen/*Contributions***

Contributor Role	Doktorand/in/ <i>Doctoral Student</i>	Co-Autor/in 1/ <i>Co-author 1</i>	Co-Autor/in 2/ <i>Co-author 2</i>
Name, first name	Ansmann, Nils	Kerscher, Marion	Greb, Lutz
Methodology	lead	-	supporting
Software	-	-	-
Validation	lead	-	supporting
Formal analysis	lead	supporting	-
Investigation	lead	supporting	-
Resources	-	-	lead
Data Curation	lead	supporting	-
Writing-Original Draft	equal	-	equal
Writing-Review&Editing	equal	supporting	equal
Visualization	lead	-	-
Supervision	equal	-	equal
Project administration	equal	-	equal
Funding acquisition	-	-	lead

****Kategorien des CRediT (Contributor Roles Taxonomy, <https://credit.niso.org/>)**

Hiermit bestätige ich, dass alle obigen Angaben korrekt sind/*I confirm that all declarations made above are correct.*

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Prof. Dr. Lutz Greb

Name/*Name*

Unterschrift/*Signature*

Datum/*date*

Redox Chemistry

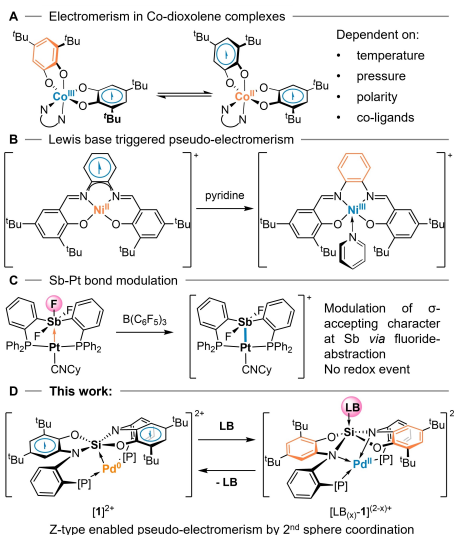
Pd(0)/Pd(II) Electromerism Triggered by Lewis Base Coordination to a Redox-Active Silicon Z-Type Ligand

Nils Ansmann, Marion Kerscher, and Lutz Greb*

Abstract: Electromerism (aka. valence tautomerism) corresponds to the switching of electronic distributions between redox-active ligands and central elements. While this phenomenon is well established for several transition metals, the Pd(0)/Pd(II) couple could not yet be involved due to the high energy of the Pd(0) state. In this study, we present Pd(0)/Pd(II) electromerism by using a redox-active bis(phosphanyl-aminodiphenolato)silane. Strong silicon-based Z-type interaction stabilizes the Pd(0) state with an oxidized dicationic open-shell singlet ligand while binding of a Lewis base at the Lewis acidic silicon results in the loss of Z-type interaction and the intramolecular rearrangement to the Pd(II)/reduced ligand electromer. It introduces a novel concept for spin state switching by combining ligand ambiphilicity and redox activity.

Introduction

The interplay of redox-active ligands and central element oxidation states by electromerism, also known as valence tautomerism, has fascinated chemists for several decades.^[1] This interest is vastly motivated by the potential of using electronic structure changes, e.g., for spin state switching or novel catalytic pathways.^[2] One of the first and most prominent examples are dioxolene cobalt complexes, such as [(3,5-*t*Bu-cat)(3,5-*t*Bu-sq)(bpy)Co(III)] (Scheme 1 A, cat = catechol, sq = semiquinone, bpy = 2,2-bipyridine).^[3] Low-spin (LS) Co(III) can receive one electron from the catechol ligand to form the high-spin (HS) [(3,5-*t*Bu-sq)₂(bpy)Co(II)] complex. Since both electronic states are energetically close, environmental parameters such as temperature, pressure,^[4] polarity^[5] or co-ligands^[6] can determine the stability of one state over the other,^[7] but also pulsed laser photolysis can switch between both states.^[8] An



Scheme 1. Previous works on electromerism and Lewis base triggered changes in electronics. (A) Prototypical electromerism in cobalt bis(dioxolene) complexes. (B) Pseudo-electromerism triggered by coordination of pyridine to a Ni salen complex. (C) Fluoride abstraction in a Z-type Sb(V)–Pt complex results in a Pt–Sb bond with increased covalent character. (D) This work: 2nd sphere coordination of a Lewis base triggers pseudo-electromerism in a dicationic Pd(0) complex [1]²⁺.

alternative to induce electromerism involves the coordination of a Lewis base to the metal center, as reported for an oxidized Ni(II) salen complex (Scheme 1B).^[9] Since the change in electronics is accompanied by the alteration of the sum formula, this rearrangement has been termed pseudo-electromerism.^[10] A closely related example for a p-block element was reported for an aromatic tetraphenylporphyrin Ge(II) complex, which exhibits pseudo-electromerism to its antiaromatic Ge(IV) form upon pyridine coordination.^[11] While electromerism is well established for 3d metal complexes and currently emerging for p-block elements, examples of 4d metals are scarce.^[1c,d,12] Indeed, although research on palladium complexes with redox-active ligands has been actively pursued,^[13] and an electromeric Pd(0)/

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Pd(II) couple has been predicted theoretically,^[14] experimental realization has not been achieved.

Another mode to control the electronic structure in transition metal complexes is the variation of the accepting ability of Z-type ligands. For example, the removal of fluoride from antimony to modify the σ -accepting character of stiboranyl-Z-type Pt complexes was described by the Gabbaï group (Scheme 1 C).^[15] The same group reported an alternative strategy for changing the Z-type ability by Sb(III)-to-Sb(IV) oxidation of the central Lewis acidic element in a chlorostibine gold complex.^[16] However, no oxidation state change at the transition metal or the ligand was involved in all of these latter cases.

Lately, we reported a Pd(0) complex **1** with a redox-active bis(amidophenolato)silane Z-type ligand.^[17] We hypothesized whether this Z-type interaction might stabilize the high energy Pd(0) state to such an extent that elusive Pd(0)/Pd(II) electrophilicity might come into reach. In this work, we present the ligand-centered oxidation of **1** to form the dicationic $[1]^{2+}$, in which the Pd(0) state is preferred by the strong Z-type interaction with silicon (Scheme 1D). Upon Lewis base binding, this stabilization is released, leading to formal oxidation of palladium and reduction of the ligand and resulting in the Pd(II) complex $[LB_{(x)}-1]^{(2-x)+}$. It represents the first example of Pd(0)/Pd(II) electrophilicity and introduces the concept of 2nd sphere coordination triggering.

Results and Discussion

Reactions with Non-Innocent Oxidation Agents

To gain insights into the redox chemistry of **1**, we conducted cyclic voltammetry (CV) in *ortho*-difluorobenzene (*o*DFB) with $[NBu_4][Al(pftb)_4]$ (pftb = perfluoro-*tert*-butoxide) as supporting electrolyte (Figure S37). The compound exhibits three oxidation waves at $E_{ox} = -0.13$ V, -0.04 V and $+1.02$ V vs. Fc. While the first two oxidations appear to be quasi-reversible ($E_{1/2} = -0.085$ V), the last oxidation is irreversible. The first two oxidations are accounted for by two ligand-centered one-electron oxidations, forming a dicationic complex $[1]^{2+}$. Further oxidation at higher potentials results in additional metal-centered oxidation, which leads to decomposition of the complex. The results of the cyclic voltammogram suggested ferrocenium salts as suitable oxidants. Accordingly, reacting **1** with 2 equiv. of ferrocenium tetrachloridoferate $[Fc][FeCl_4]$ in *o*DFB led to an immediate intense coloration of the solution. A single resonance in the ^{31}P NMR spectrum ($\delta_{31P} = 45.6$ ppm) suggested the formation of a distinct species down-field shifted compared to the neutral Pd(0) complex **1** ($\delta_{31P} = 4.5$ ppm). Liquid injection field desorption/ionization mass spectrometry (LIFDI-MS) analysis of the reaction mixture showed the presence of a chlorido adduct of $[1]^{2+}$, which was confirmed by single crystal X-ray diffraction (scXRD) as $[Cl-1][FeCl_4]$ (Figure 1, structural discussion below).^[18] The formation mechanism can be understood by chloride abstraction from $[FeCl_4]^-$ through the putative Lewis acidic intermediate

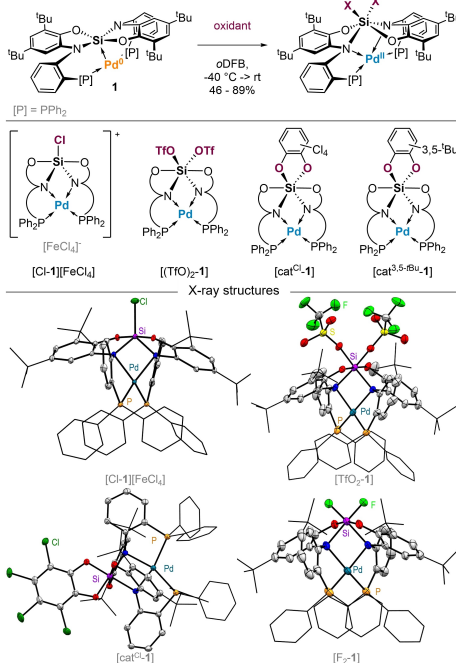


Figure 1. Oxidation of Pd complex **1** with 2 equiv. $[Fc][FeCl_4]$, 2 equiv. AgOTf and 1 equiv. *o*-chloranil or 3,5-di-*t*-butyl-*o*-quinone resulting in penta- and hexa-coordinated silicato-Pd(II) complexes. Thermal ellipsoid plots of the corresponding solid-state structures are displayed at 50% probability, hydrogen atoms, counter anions, disordered ^{*i*}Bu- or Ph-groups and additional formula units within the asymmetric unit are omitted for clarity (for the solid-state structure of $[cat^{3,5-tBu}-1]$ see Figure S52). Selected bond lengths: $[Cl-1][FeCl_4]$: d(Si–Pd1) = 2.6549 (10) Å, d(Pd1–N1) = 2.1850 (19) Å, d(Pd1–N2) = 2.1718 (19) Å; $[(OTf)_2-1]$: d(Si–Pd1) = 2.9399 (11) Å, d(Pd1–N1) = 2.104 (2) Å, d(Pd1–N2) = 2.108 (2) Å; $[cat^{Cl}-1]$: d(Si–Pd1) = 2.9574 (14) Å, d(Pd1–N1) = 2.112 (2) Å, d(Pd1–N2) = 2.104 (2) Å; $[Fc-1]$: d(Si–Pd1) = 3.0177 (8) Å, d(Pd1–N1) = 2.076 (2) Å, d(Pd1–N2) = 2.0840 (19) Å.

$[1]^{2+}$, with the formation of a penta-coordinated silicon ($\delta_{29Si} = -98.4$ ppm). Similarly, reacting **1** with 2 equiv. of AgOTf in *o*DFB, the ^{31}P NMR spectrum indicated the clean formation of a single complex ($\delta_{31P} = 39.9$ ppm), while the ^{29}Si NMR spectra suggested a dynamic equilibrium between a penta- and a hexa-coordinated silicon with a broad resonance at $\delta_{29Si} = -152.7$ ppm. In the solid-state structure of $[(TfO)_2-1]$, both triflates coordinate to silicon (Figure 1). Similar results were obtained when quinones were used as 2-electron oxidants instead of Fc^+ or Ag^+ . Reaction of **1** with *o*-chloranil or 3,5-di-*t*-butyl-*o*-quinone furnished the hexa-coordinated silicon complexes $[cat^{Cl}-1]$ and $[cat^{3,5-tBu}-1]$ (Figure 1, and Figure S52). Interestingly, $[cat^{Cl}-1]$ was also

obtained by reacting **1** with the strongly oxidizing diradical silicon tris(perchloro)dioxolene $[\text{Si}(\text{O}_2\text{C}_6\text{Cl}_4)_3]^{109}$. The abstraction of a perchloro-catecholate from the herby formed tris-catecholato-silicate $[\text{Si}(\text{cat}^{\text{Cl}})_3]^{2-}$, the catecholato adduct of the Lewis superacid $[\text{Si}(\text{cat}^{\text{Cl}})_2]^{200}$ confirmed the high acceptor strengths of putative $[\text{I}]^{2+}$. Upon reacting the ambiphilic Z-type ligand PNO_2Si with $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ in a MeCN/toluene solution, a similar dark-red coloration of the solution was observed. NMR spectra indicated fluoride abstraction from the tetrafluoroborate counter anion, further confirmed by scXRD analysis, revealing the formation of a hexacoordinated silicato complex $[\text{F}_2\text{-1}]$ (see Figure 1). Again, formation of this complex was reasoned by the *in situ* formation of a dicationic Pd complex $[\text{I}]^{2+}$, which abstracts two fluorides from $[\text{BF}_4]^-$ due to its high Lewis acidity.

Closer examination of the obtained molecular structures provided insights into the oxidation state of palladium. All of the penta- and hexa-coordinated silicato Pd-complexes exhibit a square-planar (sqpl.) coordination at Pd spanned by the NPPN framework of the silicate, indicating a Pd(II) state (avg. summed bond angles $\Sigma \angle (\text{X}'\text{-Pd-X}'') = 368.59^\circ$ (9), see Figure 1 for solid state structures and table S3 for bond angles). The metrical oxidation states (MOS) of the amidophenolates range from -2.16 to -2.01 and the MOS of the catecholates from -2.16 to -1.90 , in agreement with palladium-centered oxidation. The NPPN coordination mode is facilitated by accompanying Lewis base binding to silicon, effectively quenching the Lewis acidity of the silicon center, elongating the Si–Pd distances from 2.3707(6) Å in **1** to 2.6549(10) Å in $[\text{Cl-1}][\text{FeCl}_4]$, and up to 3.0177(8) Å in $[\text{F}_2\text{-1}]$.

All mentioned complexes exhibited an intense red-purple color in solution and the solid state. To understand the origin of this coloration, excitation profiles for $[\text{cat}^{\text{Cl}}\text{-1}]$ and $[\text{cat}^{3,5\text{-tBu}}\text{-1}]$ were calculated by TD-DFT (CAM-B3LYP/def2-TZVPP//PBEh-3c, Figure 2 and section 2d in ESI), well reproducing the experimental spectra. While the band at 456 nm is mainly based on d-d transitions, the intense band at 566 nm (HOMO–LUMO transition) can be assigned to ligand to metal charge transfer (LMCT) from the amidophenolate backbone into the empty d-orbital at Pd(II) (see FMOs, Figure 2b). This LMCT is independent of the silicon-bound Lewis bases and explains the characteristic coloring of this series of penta- and hexa-coordinated silicato/Pd(II) complexes.

Reactions with Innocent Oxidation Agents

Aiming to isolate dicationic $[\text{I}]^{2+}$ without additional substituents at silicon, we switched to oxidation agents with inert and weakly coordinating anions. Oxidation of **1** with *Magic Blue* (tris(4-bromophenyl)ammoniumyl hexachloroantimonate) in oDFB still resulted in chloride abstraction from $[\text{SbCl}_6]^-$ as indicated by ^{31}P and ^{29}Si NMR spectroscopy. Similarly, oxidation with the silver salt of the more robust hexafluoroantimonate resulted in the degradation of the anion and formation of a product mixture, which

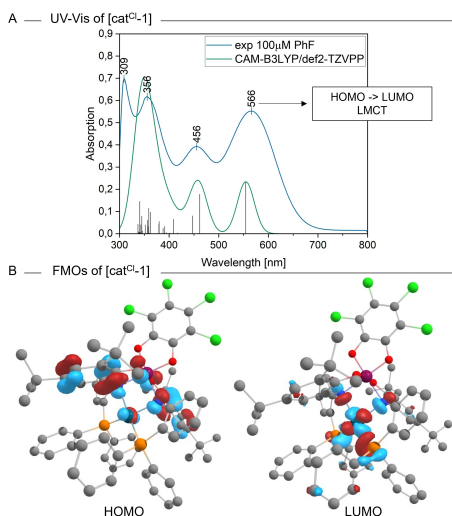


Figure 2. (A) UV-Vis spectrum of compound $[\text{cat}^{\text{Cl}}\text{-1}]$ in PhF (0.1 mM, blue line) compared to the computed excitation profile (TD-DFT CAM-B3LYP/def2-TZVPP (SMD=PhF)//PBEh-3c, green line with vertical excitations (black), red-shifted by 100 nm). (B) Frontier molecular orbitals (FMO) of $[\text{cat}^{\text{Cl}}\text{-1}]$ calculated at the CAM-B3LYP/def2-TZVPP (SMD=PhF)//PBEh-3c level of theory.

included $[\text{F}_2\text{-1}]$. This observation experimentally confirmed Lewis superacidity for the putative $[\text{I}]^{2+}$.^[21]

Reaction of **1** with two equivalents of the silver salt of the weakly coordinating tetrakis(nonafluoro-*t*-butanolato)aluminate $(\text{Ag}[\text{Al}(\text{pftb})_4])^{[22]}$ in oDFB resulted in an immediate color change, but unlike all cases described above, to a dark brown. The absence of the intense purple-red LMCT was indicating an alternative electronic structure. Indeed, the reaction mixture revealed no resonance by ^{29}Si NMR spectroscopy and only a few resonances with very low intensity in the ^{31}P NMR spectrum, suggesting the major product has an open-shell ground state. LIFDI-MS analysis of mixtures from several reaction conditions revealed secondary products of $[\text{I}]^{2+}$, namely $[\text{H-1}]^+$, $[\text{C}_6\text{H}_4\text{F-1}]^+$, $[\text{F-1}]^+$ and $[\text{pftb-1}]^+$. The latter compound was also observed as trace in the ^{19}F NMR spectra and serves as explanations for the impurity resonances in the ^{31}P NMR spectrum (Figure S15). Thermodynamic feasibility for the partial abstraction of the nona-fluoro-*tert*-butoxide from the $[\text{Al}(\text{pftb})_4]^-$ anion is supported by solvation-corrected DFT calculations ($\Delta G^\circ = -36.3$ kJ/mol),^[23] and proven by scXRD analysis of $[\text{pftb-1}][\text{Al}(\text{pftb})_4]$ (see ESI section 3a). However, these side reactions appear to only occur in the early seconds of the oxidation for kinetic reasons, presumably *via* the mono-oxidized $[\text{I}]^+$ with the anion or the solvent. Accordingly, the final product mixture remained unchanged upon storage under inert conditions at room temperature for days, but

decomposes through further abstraction reactions at elevated temperatures (80 °C). The high reactivity of intermediate $[1]^+$ was supported by adding only one equivalent of oxidant to **1**, resulting in incomplete oxidation and multiple unidentified side-products. Lowering the reaction temperature to -40 °C only slightly improved the selectivity. Similar observations were made when using 2 equiv. $[\text{Fc}][\text{B}(\text{C}_6\text{F}_5)_4]$ as the oxidation agent. Elemental analysis of the isolated product supported the bulk product as $[1][\text{Al}(\text{pftb})_4]_2$. Despite several efforts, no crystals of $[1][\text{Al}(\text{pftb})_4]_2$ could be obtained.

To corroborate that the majority product of the reaction between **1** and $\text{Ag}[\text{Al}(\text{pftb})_4]$ consists of $[1]^{2+}$, we probed whether the oxidation can be reversed to the neutral compound **1**. Addition of KC_8 to the reaction mixture led to a loss of the intense coloration of the sample and furnished compound **1** as the major species (> 90 %). This oxidation/

reduction cycle was repeated with the same sample to prove reversibility, with similar results (Figure S26). Oxidation of **1** with $\text{Ag}[\text{Al}(\text{pftb})_4]$ in the presence of one equivalent of PPh_4Cl cleanly furnished complex $[\text{Cl}-1]^+$, as indicated by NMR spectroscopy (Figure S28). Alternatively, oxidation in the presence of two equivalents DMAP (4-dimethylaminopyridine) yielded the hexacoordinated $[(\text{DMAP})_2-1][\text{Al}(\text{pftb})_4]_2$ (for scXRD structure, see Figure 3D). Notably, the addition of respective Lewis bases to samples of $[1]^{2+}$ resulted in identical NMR spectra, ultimately confirming that the NMR silent $[1]^{2+}$ is the major product of the oxidation (Figures S28 and S33).

Due to the characteristic optical absorption spectra, these processes can be tracked by UV/Vis spectroscopy. Figure 3B shows a reaction sequence shown in A. Neutral Pd complex **1** (purple line ①). After oxidation with $\text{Ag}[\text{Al}(\text{pftb})_4]$, an intense band at 409 nm and a broad tailing in the

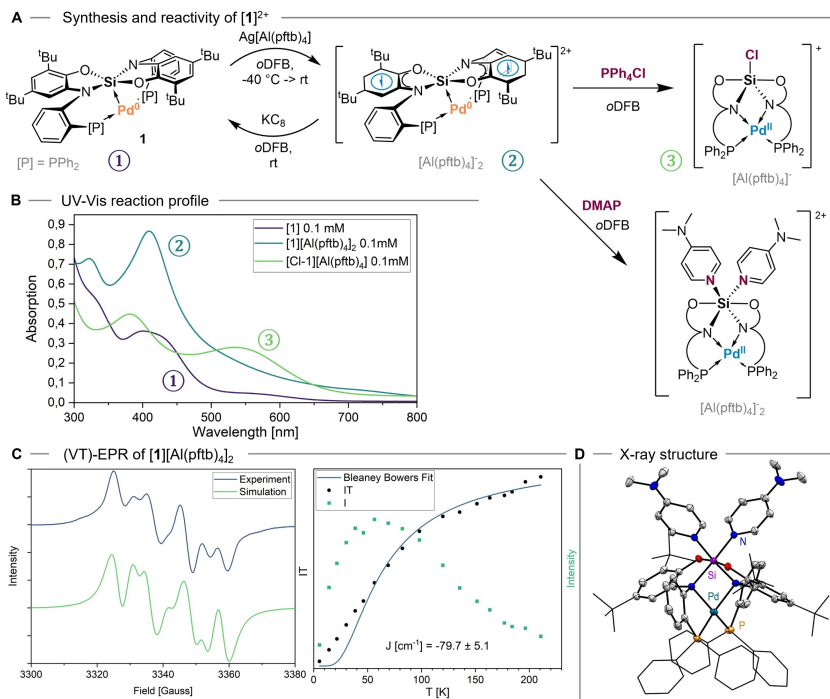


Figure 3. (A) Synthesis of dicationic $[1]^{2+}$ through oxidation with $\text{Ag}[\text{Al}(\text{pftb})_4]$ in oDFB and subsequent reactivity towards reducing agents and Lewis bases. (B) UV/Vis spectra (0.1 mM in oDFB) of the reaction sequence shown in A. Neutral Pd complex **1** (①), after oxidation with $\text{Ag}[\text{Al}(\text{pftb})_4]$, forming the dicationic complex $[1][\text{Al}(\text{pftb})_4]_2$ (②) and after subsequent addition of one equivalent of PPh_4Cl (③), forming $[\text{Cl}-1][\text{Al}(\text{pftb})_4]$. (C) EPR spectrum of $[1][\text{Al}(\text{pftb})_4]_2$ in oDFB solution at room temperature (blue line, $\nu = 9.376024$ GHz) stacked with the simulated spectrum (green) and IT vs. T plots including a Bleaney Bowers fit of the experimental data obtained by VT-EPR (5.4 K to 196.4 K, oDFB matrix, 9.631 GHz). (D) Thermal ellipsoid plot of $[(\text{DMAP})_2-1][\text{Al}(\text{pftb})_4]_2$ (displayed at 50% probability, anions, solvent molecules and hydrogens omitted for clarity). Selected bond-lengths: $d(\text{Si1}-\text{Pd1}) = 2.9534(12)$ Å, $d(\text{Pd1}-\text{N1}) = 2.111(2)$ Å, $d(\text{Pd1}-\text{N2}) = 2.116(3)$ Å.

Vis section of the spectrum was observed, accounted by $[1]^{2+}$ (blue line ②). Subsequent addition of a chloride source (PPh₃Cl) resulted in substantial changes in the observed spectrum (green line ③). While the intense band at 409 nm declines in a less intense band at 381 nm, the LMCT charge transfer band at 535 nm, characteristic of the red-violet Pd(II)-state, appears.

Having sufficient evidence for the formation of $[1]^{2+}$, its electronic structure was scrutinized. Given the consumption of two equivalents of oxidation agent and the absence of Pd(II), formation of an amido-phenolato centered diradical was assumed. Hence, an EPR spectrum of $[1][Al(pftb)_4]_2$, *in situ* generated by oxidation of **1** by $Ag[Al(pftb)_4]$, was recorded in *o*DfB (Figure 3C, blue line). The spectrum confirms organic centered spin density ($g=2.0044$), with hyperfine coupling by delocalization of the unpaired electrons over both nitrogens and hydrogens. It is in good agreement with the simulated EPR spectrum (Figure 3C, green line), which exhibits major hyperfine-coupling contributions from the named nuclei. No half-field signal could be observed. To explore the electronic ground state of $[1]^{2+}$, variable temperature EPR (VT-EPR) spectra were recorded in a frozen *o*DfB matrix (Figure S39). Stepwise warming the probe from 5.4 K to 210.7 K resulted in a non-uniform intensity change. The signal integral intensities up to 56.4 K, indicating an open-shell singlet (OSS) ground state with increasing population of the triplet state at higher temperatures. Subsequent warming results in a Curie behavior of the signal intensity. The OSS ground state is further supported by the IT/T plot, which displays the expected asymptotic course (Figure 3C).^[24] Fitting the data according to the Bleaney–Bowers equation allowed to approximate the magnetic coupling constant of $J = -79.7 \pm 5.1 \text{ cm}^{-1}$.^[25]

Broken symmetry (BS) calculations at the PBE0-D4/def2-TZVPP/PBEh-3c align with the experimental data, resulting in antiferromagnetic coupling of $J = -88.6 \text{ cm}^{-1}$ in compound $[1]^{2+}$. In agreement with the small antiferromagnetic coupling, the open-shell $S=1$ state was only slightly higher in energy compared to the broken-symmetry solution

(1.1 kJ/mol). The $S=0$ state (with a Pd(II)) was found to be energetically disfavored (49.5 kJ/mol) compared to the ligand-centered open-shell singlet diradical/Pd(0) complex. The optimized structure of the OSS state displayed a MOS of -1.08 for the amidophenoxide (amp) ligand at Si, supporting localization of the unpaired electrons in the ligand backbone. The singly occupied molecular orbitals (SOMOs) are mainly located on the ligand, but also contribution of Pd can be observed, in line with substantial redox-non-innocence (Figure S48). The calculated spin density (Figure 4A) is mainly located on the redox-non-innocent ligand backbone, which is in good agreement with the experimental and simulated EPR data, but still exhibits a small degree of localization at the Pd atom, in line with the observed g value, which only differs slightly from the expected value for a purely organic radical. The natural charges at Si and Pd in $[1]^{2+}$, obtained by natural population analysis (NPA), indicate minor changes compared to its neutral counterpart **1** (figure 4B). The charge at Pd increased from -0.14 (**1**) to 0.02 ($[1]^{2+}$), accounting for a Pd(0), further supported by the natural electron configuration ($5s$ (0.54), $4d$ (9.44)). The natural charge at Si slightly decreased after oxidation, which could be explained by a stronger Pd->Si interaction due to the increased Lewis acidity of Si. This is supported by the Wiberg Bond Index (WBI) of the Si–Pd bond, which increased to 0.60 (cf. 0.43 in **1**). Due to oxidation of the ligand, the WBI of the P->Pd as well as the Si–O and Si–N bonds in the Si(amp)₂ framework decreased in comparison to **1**. Thus, while all other bonds weaken due to oxidation, the Pd->Si Z-type interaction stabilizes this highly electrophilic and hitherto unreported dicationic Pd(0) complex. The Si–Pd bond is composed of 39% Si (sp-character) and 61% Pd (44% s, 56% d-character) (Figure 4 C). ETS-NOCV analysis further underlines the strong Pd–Si interaction. The major contribution to the total orbital interaction energy consists of the donation of electron density from the electron-rich Pd(0) fragment to the Lewis acidic silicon ($\Delta E_{\text{orb}2} = -59 \text{ kcal/mol}$,

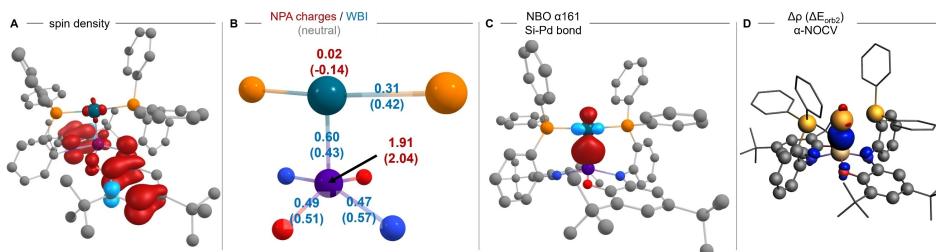


Figure 4. (A) Visualization of the Spin density of $[1]^{2+}$ calculated at the UKS-PBE0-D4/def2-TZVPP//PBEh-3c level of theory, displayed at 0.005 au. Hydrogen atoms are hidden for clarity. (B) Charges obtained by natural population analysis (NPA) and Wiberg bond indices in dicationic $[1]^{2+}$ compared to values for the neutral Pd complex **1**, calculated at the BS-PBE0-D4/def2-TZVPP//PBEh-3c level of theory. (C) Natural Bond Orbital $\alpha 161$ (BS-PBE0-D4/def2-TZVPP//PBEh-3c), representing the Si–Pd bond in $[1]^{2+}$, composed of 39% Si (49% s, 49% p character) and 61% Pd (44% s, 56% d character). (D) ETS-NOCV deformation density $\Delta\rho$ of the α -NOCV corresponding to the Pd–Si interaction (charge flow from red to blue, BP86-D3BJ/TZVPP//PBEh-3c).

α -deformation density $\Delta\rho$ shown in Figure 4D; for more, see ESI section 2d).

Hence, this sequence of investigations confirms the Pd(0) state stabilized by strong Z-type interaction with the twofold-oxidized ligand in $[1]^{2+}$, which switches to the Pd(II) state upon binding of Lewis bases to silicon by effectively quenching the Z-type character (Figure 5).

The remaining piece for a fully operative Pd(0)/Pd(II) electromerism is the reversibility from Pd(II) back to Pd(0). Indeed, this switching is achieved by the abstraction of the Lewis base from a pentacoordinate silicon/Pd(II) species. Reacting $[Cl-1][FeCl_4]$ with two equivalents of silylium ion $[Et_3SiC_7D_8][B(C_6F_5)_4]$, the indicative red color of the Pd(II) complex changed to the brown color of the Pd(0) and the resonance of the Pd(II) complex vanished in the ^{31}P NMR spectrum (Figure S34). The disappearance of the indicative LMCT band in the UV/Vis spectrum (Figure S35) further suggests the re-formation of the open-shell Pd(0) complex $[1]^{2+}$. Furthermore, the EPR spectrum obtained after abstraction (Figure S36) is in line with the one of freshly oxidized $[1][Al(pfb)_4]$, ultimately proving the reversibility of the Lewis base triggered pseudo-electromerism.

Conclusion

To conclude, we report the isolation and characterization of a highly Lewis acidic dicationic diradical Pd(0) complex with an open-shell singlet ground state, as confirmed by VT-EPR spectroscopy and computations. The importance of the Z-type interaction for the overall stabilization of the Pd(0) state is revealed by bonding analysis. Addition of Lewis bases to the oxidized Pd(0) complex $[1]^{2+}$ lifts this Z-type binding, resulting in electromerism (intra-molecular reorganization of electron density) to the diamagnetic Pd(II) state. To the best of our knowledge, it is the first example of Pd(0)/Pd(II) electromerism, which might have further implications on this important redox couple ubiquitous in palladium catalysis.^[26] It also corresponds to the first process wherein electromers can be switched by means of variation of Z-type interaction, and a novel approach for secondary sphere spin state control. Potential applications of this unprecedented electromerism could include stimulated oxidative addition or alteration of reductive elimination

tendencies by 2nd sphere coordination of Lewis bases to the Z-type ligand.

Author Contributions

N.A.: Conceptualization (lead), Investigation (lead), Project Administration (equal), Visualization (lead), Writing, Review and Editing (equal), M.K.: Investigation (supporting), Review and Editing (supporting), L.G.: Project Administration (equal), Resources (lead), Supervision (lead), Writing, Review and Editing (equal).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: valence tautomerism · electromerism · Z-type ligand · silicon · palladium

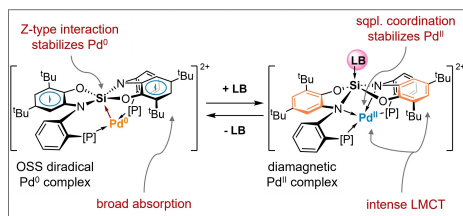


Figure 5. Summary of the observed Pd(0)/Pd(II) electromerism triggered by Lewis base coordination at a dicationic Pd–Z-type complex.

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Supporting Information

Pd(0)/Pd(II) Electromerism Triggered by Lewis Base Coordination to a Redox-Active Silicon Z-Type Ligand

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SUPPORTING INFORMATION

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Nils Ansmann, Marion Kerscher, Lutz Greb*

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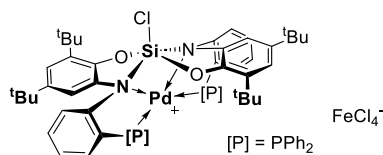
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1. Experimental Procedures

a. Materials and General Methods

All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame dried glassware or by working in a glovebox (Sylatech Glovebox) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å). Argon was dried by passing over two columns of phosphorus pentoxide. Commercially available chemicals were used as received. Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane palladium (0) **1**, $[\text{Si}(\text{O}_2\text{C}_6\text{Cl}_4)_2]$, $[\text{Fc}][\text{FeCl}_4]$, $[\text{Fc}][\text{B}(\text{C}_6\text{F}_5)_4]$, $[\text{NBu}_4][\text{Al}(\text{ptfb})_4]$ and $[\text{Et}_3\text{Si} \times \text{C}_7\text{D}_8][\text{B}(\text{C}_6\text{F}_5)_4]$ were synthesized according to literature known procedures.^[1] $\text{Ag}[\text{Al}(\text{ptfb})_4] \times \text{oDFB}$ was synthesized by using oDFB as the solvent instead of DCM in the literature known-procedure.^[2] All NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All hetero-nuclei spectra (with the exception of ^{19}F) were obtained with ^1H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ^1H and ^{13}C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants J in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublets of doublets, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. All NMR-spectra were processed with Bruker TopSpin 4.3.0. LIFDI-MS spectra were measured on a JEOL AccuTOF GCx instrument. Elemental analysis (C, H, N) was measured on an Elementar vario MICRO Cube machine. Systematically low values for Carbon can be explained by the formation of SiC during the combustion process. UV-Vis-NIR absorption spectra were recorded at room temperature (295 K) on a spectrophotometer (Agilent Cary 5000). The substances were measured as dilute solutions in Normag quartz glass cuvettes. The solutions were prepared under inert conditions in the glovebox. Before each measurement a background spectrum of the solvent was recorded followed by a baseline correction. EPR spectra between 4 – 295 K were recorded with a Bruker Elexsys E500 EPR spectrometer, equipped with a continuous wave dual-mode resonator (Bruker ER 4116DM). The regulation of the temperature for low-temperature measurements was performed with a Bruker ER 4112HV-CF42 In-Cavity Cryogen Free VT system and a temperature controller (ITC 4, Oxford Instruments). The low-temperature measurements were directly measured in quartz tubes. Double integration of the VT-EPR data in order to determine the signal intensity was performed with the Bruker Xepr 2.6b.86 program. Plots were generated using OriginPro 2024.

b. Syntheses

[Cl-1][FeCl₄]

Pd complex **1** (30.0 mg, 27.4 μmol , 1.00 eq) was dissolved in 1 mL cold (-20°C) oDFB before ferrocenium tetrachloridoferrat (21.1 mg, 54.9 μmol , 2.00 eq) was added in one portion. The resulting purple suspension was stirred at room temperature for 18 h. The reaction mixture was then filtered through a syringe filter and concentrated to approximately 300 μL under reduced pressure. The compound was crystallized by gas phase diffusion on *n*-pentane into the concentrated solution at room temperature for 24 h. After formation of crystals (suited for scXRD) was observed, the crystallisation setup was transferred to the fridge (-40°C) for 5 days. The dark purple crystals were isolated by decantation of the yellow mother liquor and washed with 1 mL of *n*-pentane. In order to remove co-crystallized solvent molecules, the crystals were redissolved in a benzene/oDFB mixture (5:1). Removing the solvent *in vacuo* yielded the target compound as a purple powder (29.3 mg, 21.1 μmol , 81 %).

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, $\text{C}_6\text{D}_5\text{Br}$, 295 K): δ [ppm] = 45.6 (broad, s); **^{29}Si (IG) NMR** (119 MHz, oDFB, 295 K): δ [ppm] = -98.4 (broad, s); **MS** (LIDFI(+)): $[\text{M}]^+$, calcd.: 1129.33, found: 1129.38; **Anal.** Calcd. for $\text{C}_{64}\text{H}_{68}\text{F}_6\text{Cl}_5\text{N}_2\text{O}_2\text{P}_2\text{PdFeSi}$: C, 57.94; H, 5.17; N, 2.11 found: C, 55.78; H, 4.72; N, 1.85.

Due to paramagnetic line broadening by the $\text{Fe(III)} \text{hs-d}^5$ counter anion, no resolved ^1H or ^{13}C NMR spectra could be obtained.

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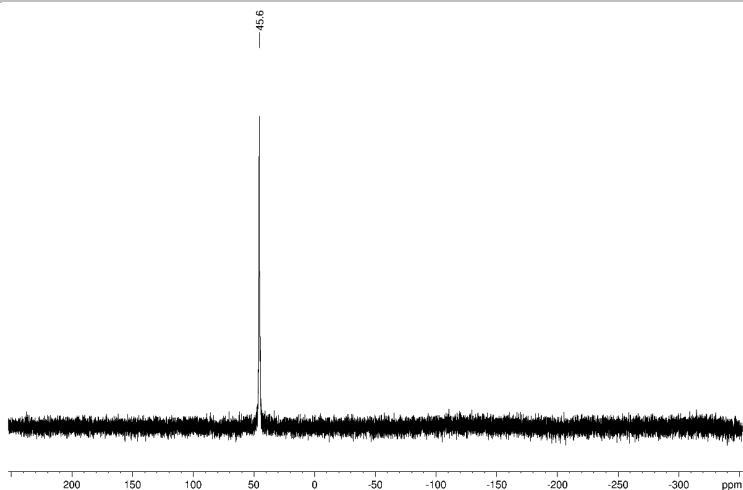


Figure S 1: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (253 MHz) of $[\text{Cl-1}][\text{FeCl}_4]$ in $\text{C}_6\text{D}_6\text{Br}$ at 295 K.

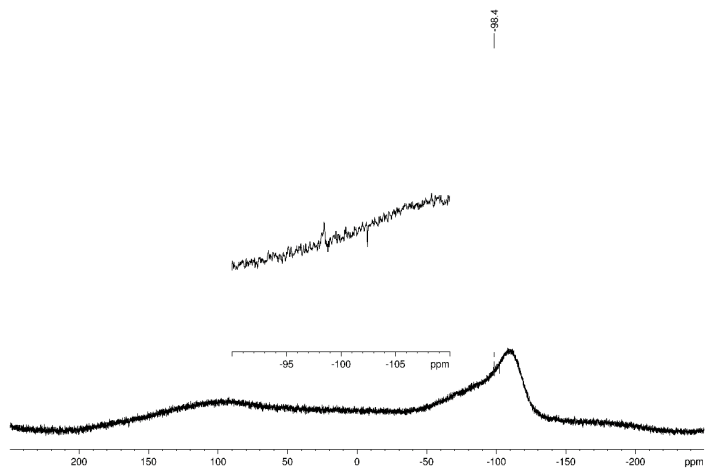
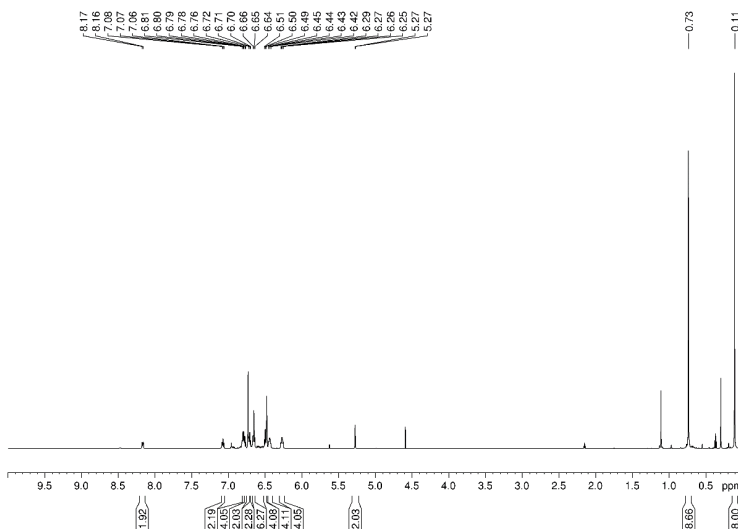
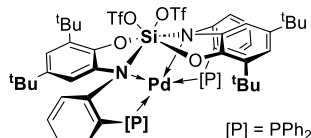


Figure S 2: ^{29}Si (IG) NMR spectrum (119 MHz) of $[\text{Cl-1}][\text{FeCl}_4]$ in oDFB at 295 K. Contains an artefact of the spectrometer (-102.4 ppm). Low resolution is caused by paramagnetic broadening of $[\text{FeCl}_4]$.



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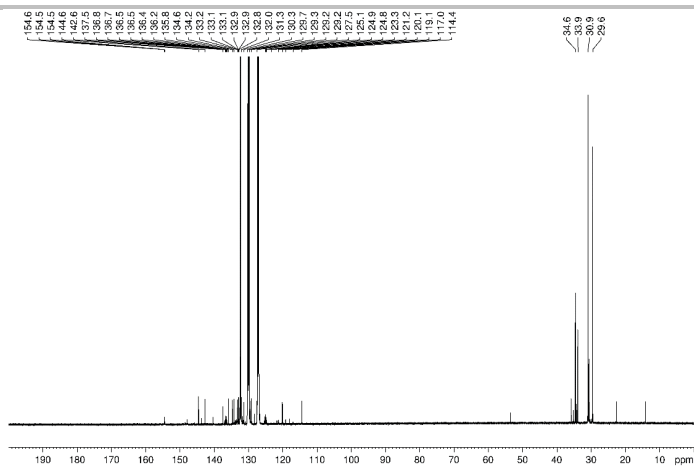


Figure S 4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of $[\text{TiO}_2\text{-1}]$ in $o\text{-DCB-d}_4$ at 295 K. Contains traces of $n\text{-pentane}$ and CH_2Cl_2 .

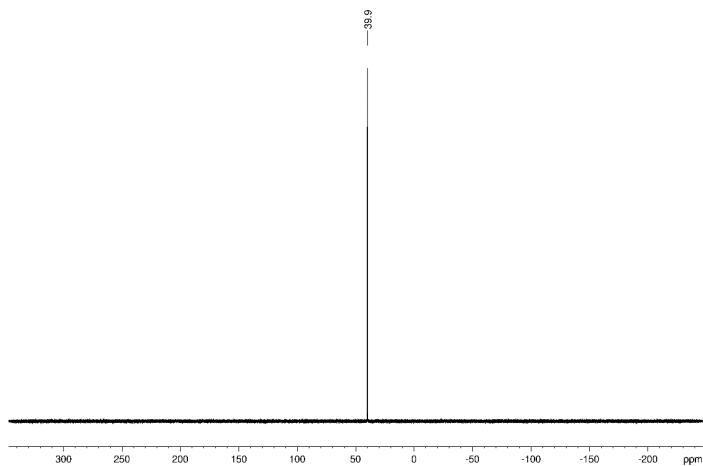


Figure S 5: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of $[\text{TiO}_2\text{-1}]$ in $o\text{DFB}$ at 295 K.

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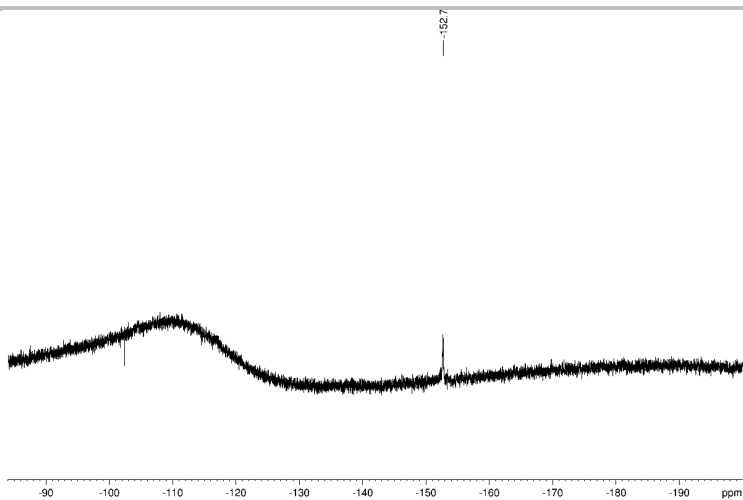
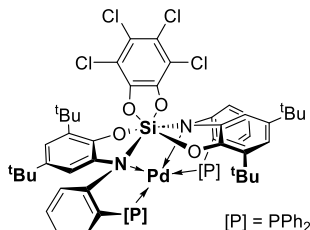


Figure S 6: ^{29}Si (IG) NMR spectrum (119 MHz) of $[\text{TfO}_2\text{-1}]$ in $o\text{-DCB-d}_4$ at 295 K. Contains an artefact of the spectrometer (-102.4 ppm).

SUPPORTING INFORMATION

[cat^{Cl}-1]A) Reaction of 1 with *o*-chloranil

1 [x0.5 toluene x0.25 *n*-pentane] (30.0 mg, 26.0 μ mol, 1.00 eq) and *o*-chloranil (6.38 mg, 26.0 μ mol, 1.00 eq) were suspended in 1 mL toluene for 2.5 hours at room temperature. The dark suspension was layered with 1 mL *n*-pentane at -40°C . After two hours, the purple precipitate was isolated by centrifugation, washed with *n*-pentane and recrystallized from oDFB/*n*-heptane (layered at -40°C). The resulting deep purple crystals were twice washed with *n*-pentane before drying *in vacuo* yielded the target compound in analytical pure form (16.0 mg, 12.0 μ mol, 46 %). Crystals that were suited for scXRD analysis were obtained by layering a concentrated solution in oDFB with *n*-heptane at -40°C .

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 9.83 (dd, J = 8.3 Hz, J = 2.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 2H), 7.06 (d, J = 1.7 Hz, 2H), 7.05-7.02 (m, 2H), 6.93-6.87 (m, 14H), 6.85-6.81 (m, 4H), 6.70 (t, J = 7.1 Hz, 4H), 5.83 (d, J = 2.1 Hz, 2H), 1.15 (s, 18H), 0.63 (s, 18H); **¹³C{¹H}(³¹P) NMR** (151 MHz, C₆D₆Br, 295 K): δ [ppm] = 157.1 (s, C_q), 148.6 (s, C_q), 146.6 (s, C_q), 140.0 (s, C_q), 139.7 (s, C_q), 136.0 (s, C_q), 134.8 (s, C_q), 134.6 (s, CH), 133.3 (s, CH), 133.2 (s, CH), 132.6 (s, C_q), 131.5 (s, CH), 128.9 (s, CH), 129.5 (s, CH)*, 128.3 (s, C_q), 126.9 (s, CH), 120.8 (s, C_q), 119.3 (s, CH), 119.0 (s, C_q), 114.3 (s, CH), 114.1 (s, C_q), 34.4 (s, C_q), 33.7 (s, C_q), 31.0 (s, CH₃), 29.0 (s, CH₃); **²⁹Si{¹H} NMR** (243 MHz, C₆D₆, 295 K): δ [ppm] = 39.2 (s); **²⁹Si (IG) NMR** (119 MHz, C₆D₆Br, 295 K): δ [ppm] = -132.4 (s); **MS** (LIDFI(+)): [M]⁺, calcd.: 1336.22, found: 1336.15; **Anal.** Calcd. for C₇₀H₆₈Cl₄N₂O₄P₂PdSi: C, 62.76; H, 5.12; N, 2.09 found: C, 62.27; H, 5.34; N, 2.20.

* Signal is hidden under the solvent signal, but was observed by DEPT135 experiment.

B) Reaction of 1 with [Si(O₂C₆Cl₄)₃]

1 [x0.5 toluene x0.25 *n*-pentane] (15.0 mg, 13.0 μ mol, 1.00 eq) was dissolved in oDFB (0.5 mL) in a J Young NMR tube and cooled to -40°C . [Si(O₂C₆Cl₄)₃] (10.0 mg, 13.0 μ mol, 1.00 eq) was added in one portion and the reaction mixture was shaken aggressively while reaching room temperature. Subsequent analysis by NMR spectroscopy indicated quantitative consumption of the starting material and formation of [cat^{Cl}-1] as the major product. Crystals that were suited for scXRD analysis were obtained by layering a concentrated solution in oDFB with *n*-heptane at -40°C , further confirming the nature of the product.

SUPPORTING INFORMATION

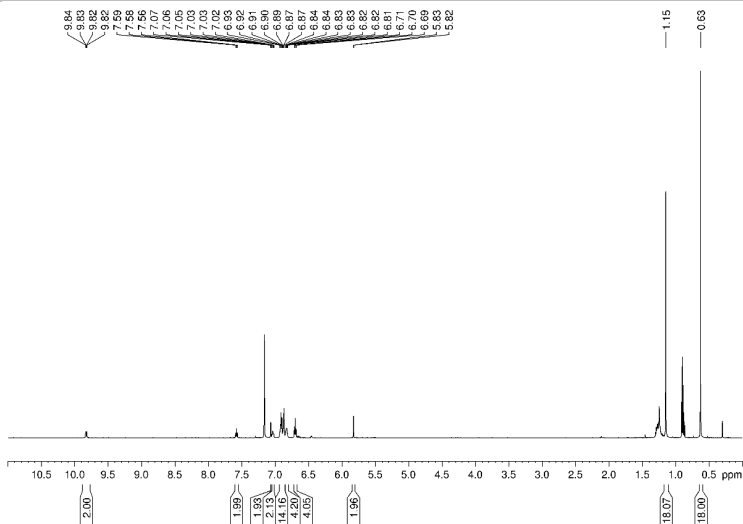


Figure S 7: ¹H NMR spectrum (600 MHz) of [cat^C-1] in C₆D₆ at 295 K. Contains traces of *n*-pentane.

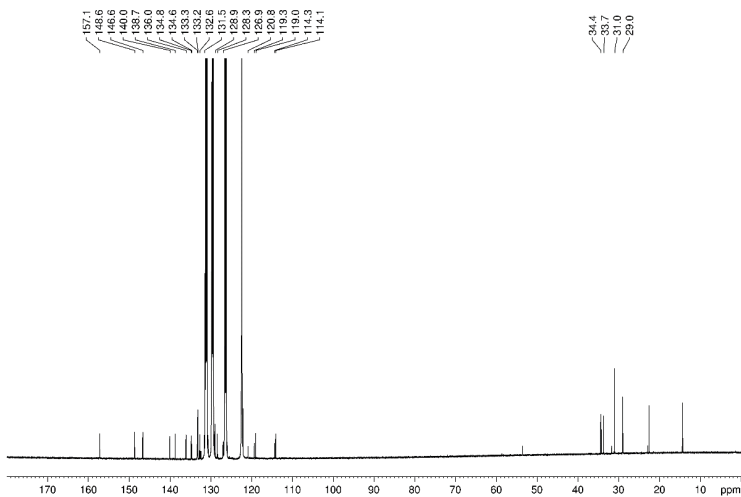


Figure S 8: ¹³C{¹H}(³¹P) NMR spectrum (151 MHz) of [cat^C-1] in C₆D₅Br at 295 K. Contains traces of *n*-pentane and CH₂Cl₂.

SUPPORTING INFORMATION

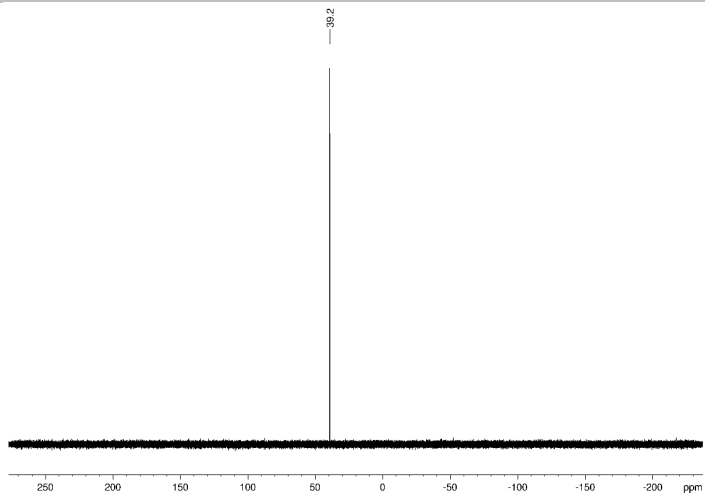


Figure S 9: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) [cat $^{\text{Cl-}}$ -1] in C_6D_6 at 295 K.

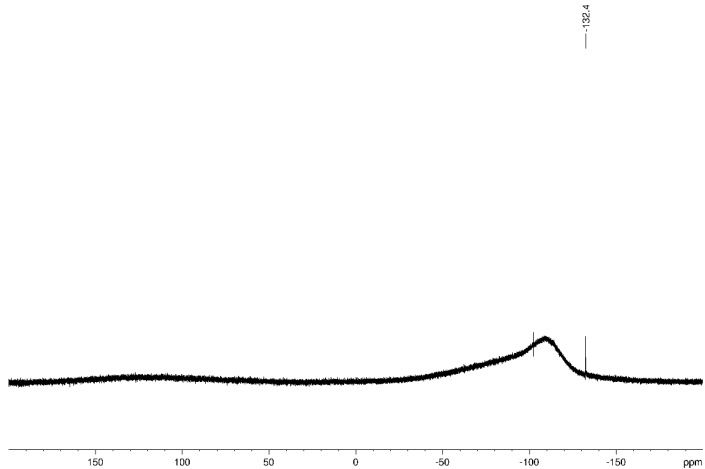
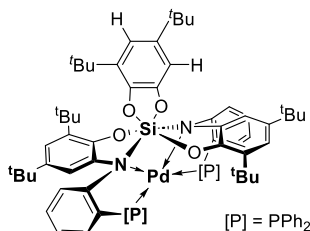


Figure S 10: ^{29}Si (IG) NMR spectrum (119 MHz) of [cat $^{\text{Cl-}}$ -1] in $\text{C}_6\text{D}_5\text{Br}$ at 295 K. Contains an artefact of the spectrometer (-102.4 ppm).

SUPPORTING INFORMATION

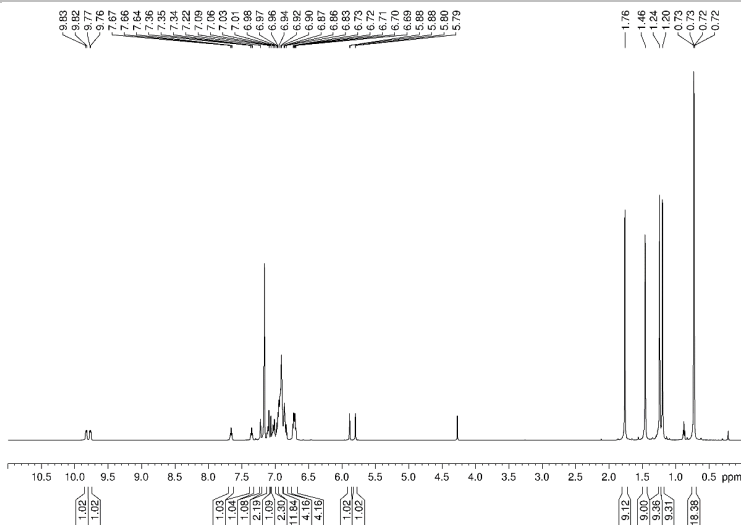
[cat^{3,5-tBu-1}]

1 (49.6 mg, 45.4 μ mol, 1.00 eq) and 3,5-*tert*-butyl-*o*-quinone (10.0 mg, 45.4 μ mol, 1.00 eq) were suspended in 1.5 mL oDFB for three hours at room temperature. The deep purple solution was concentrated to 0.4 mL under reduced pressure and layered with 6 mL *n*-pentane at -40°C . The dark solid was isolated by decantation of the mother liquor, washed with *n*-pentane and lyophilized from benzene (2 mL), yielding the target compound as a dark blue powder (49.8 mg, 37.9 μ mol, 84 %). Crystals that were suited for scXRD analysis were obtained by layering a concentrated solution in oDFB with *n*-pentane at -40°C .

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 9.83 (d, J = 7.9 Hz, 1H), 9.77 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.35 (t, J = 8.2 Hz, 1H), 7.22 (s, 1H), 7.12-7.09 (m, 2H), 7.06 (s, 1H), 7.03-7.01 (m, 2H), 6.98-6.90 (m, 12H), 6.87-6.83 (m, 4H), 6.74-6.69 (m, 4H), 5.88 (d, J = 1.8 Hz, 1H), 5.80 (d, J = 1.8 Hz, 1H), 1.76 (s, 9H), 1.46 (s, 9H), 1.24 (s, 9H), 1.20 (s, 9H), 0.73-0.72 (m, 18H); **¹³C{¹H}[³¹P]** NMR (151 MHz, C₆D₆, 295 K): δ [ppm] = 159.6 (s, C_q), 159.3 (s, C_q), 151.3 (s, C_q), 148.6 (s, C_q), 148.4 (s, C_q), 146.9 (s, C_q), 140.3 (s, C_q), 140.0 (s, C_q), 139.4 (s, C_q), 139.2 (s, C_q), 138.9 (s, C_q), 135.9 (s, C_q), 135.7 (s, C_q), 135.3 (s, C_q), 135.2 (s, C_q), 134.8 (s, CH), 134.4 (s, CH), 133.9 (s, C_q), 133.7 (s, C_q), 133.6 (s, 2 CH), 133.6 (s, 2 CH), 133.6 (s, 2 CH), 133.6 (s, 2 CH), 133.0 (s, CH), 132.9 (s, CH), 132.3 (s, CH), 132.0 (s, CH), 131.2 (s, C_q), 131.2 (s, CH), 130.4 (s, CH), 130.4 (s, CH), 129.5 (s, 2 CH), 129.4 (s, 2 CH), 129.0 (s, 2 CH), 128.9 (s, 2 CH), 128.4 (s, CH)*, 127.6 (s, C_q), 127.6 (s, C_q), 126.6 (s, CH), 126.6 (s, CH), 119.2 (s, CH), 118.9 (s, CH), 114.8 (s, CH), 114.7 (s, CH), 111.2 (s, CH), 107.8 (s, CH), 34.9 (s, C_q), 34.8 (s, C_q), 34.7 (s, C_q), 34.1 (s, C_q), 34.1 (s, C_q), 32.5 (s, CH₃), 31.5 (s, CH₃), 31.5 (s, CH₃), 30.2 (s, CH₃), 29.5 (s, CH₃), 29.4 (s, CH₃); **³¹P{¹H}** NMR (major isomer 243 MHz, C₆D₆, 295 K): δ [ppm] = 38.5 (s, 1P), 38.5 (s, 1P); **²⁹Si (IG) NMR** (119 MHz, C₆D₆, 295 K): δ [ppm] = -128.7 (s); **MS** (LIDFI(+)): [M]⁺, calcd.: 1312.50, found: 1312.57; **Anal.** Calcd. for C₇₈H₈₈N₂O₄P₂SdSi: C, 71.30; H, 6.75; N, 2.13 found: C, 69.93; H, 6.33; N, 2.52.

* Signal is hidden under the solvent signal, but was observed by DEPT135 experiment.

SUPPORTING INFORMATION



SUPPORTING INFORMATION

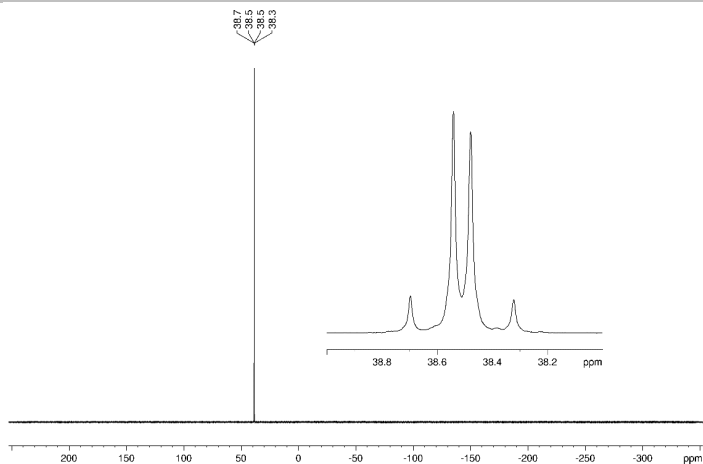


Figure S 13: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of $[\text{cat}^{3,5\text{-tBu}}\mathbf{1}]$ in C_6D_6 at 295 K. The spectrum displays both stereomers.

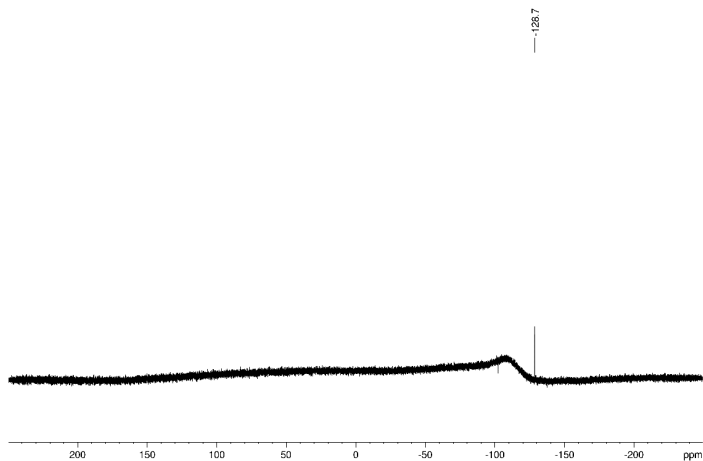
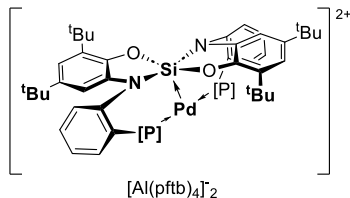


Figure S 14: ^{29}Si (1G) NMR spectrum (119 MHz) of $[\text{cat}^{3,5\text{-tBu}}\mathbf{1}]$ in C_6D_6 at 295 K. Contains an artefact of the spectrometer (-102.4 ppm).

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[1][Al(pftb)₄]₂

1 (10.0 mg, 9.15 μmol , 1.00 eq) and $\text{Ag}[\text{Al}(\text{pftb})_4] \cdot \text{oDFB}$ (21.7 mg, 18.3 μmol , 2.00 eq) were mixed at room temperature. While stirring the solids, 0.4 mL cold (-40°C) oDFB was added, resulting in a brown suspension. After stirring at room temperature for two minutes, the mixture was filtered through a syringe filter and the solvent was subsequently removed *in vacuo*, resulting in a red-brown oil. This was further dispersed in 0.5 mL of toluene, condensed to dryness and then washed with 0.5 mL of *n*-pentane and 2 x 0.5 mL of toluene. The residue was dried *in vacuo* over night to yield the target compound with several impurities as a dark brown solid (19.7 mg, 6.51 μmol , 71 %).

^{19}F NMR (565 MHz, oDFB, 295 K): δ [ppm] = -75.4 (s); **MS** (LIDFI(+)): $[\text{M}-\text{F}]^+$, calcd.: 1111.35, found: 1111.39; **Anal.** Calcd. for $\text{C}_{96}\text{H}_{68}\text{Al}_2\text{F}_{72}\text{N}_2\text{O}_{10}\text{P}_2\text{SiPd}$: C, 38.08; H, 2.26; N, 0.93 found: C, 37.51; H, 2.63; N, 1.14.

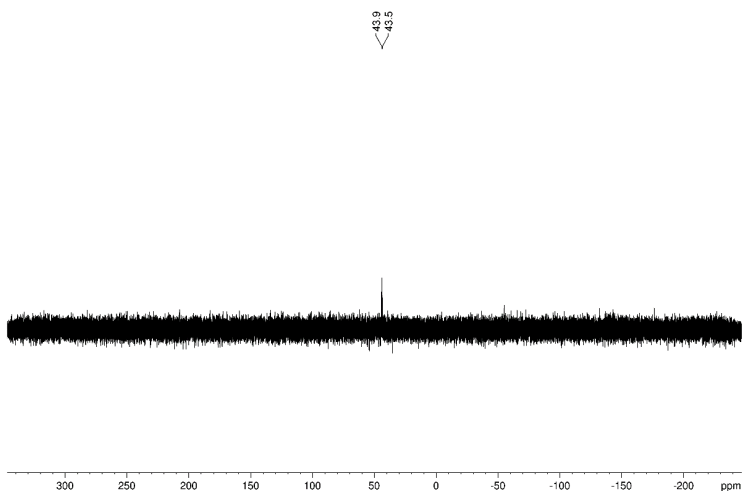


Figure S 15: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (162 MHz) of $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$ in oDFB at 295 K. The spectrum displays only the diamagnetic side products.

SUPPORTING INFORMATION

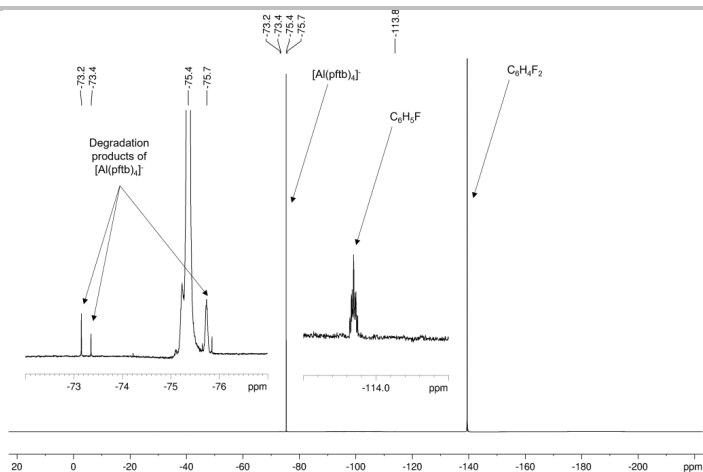


Figure S 16: ^{19}F NMR spectrum (565 MHz) of $[1][\text{Al}(\text{pftb})_4]_2$ in $\text{oDFB}/\text{C}_6\text{D}_6$ (50:1) at 295 K. The spectrum displays the major product, as well as the degradation products through side reactions.

After Oxidation

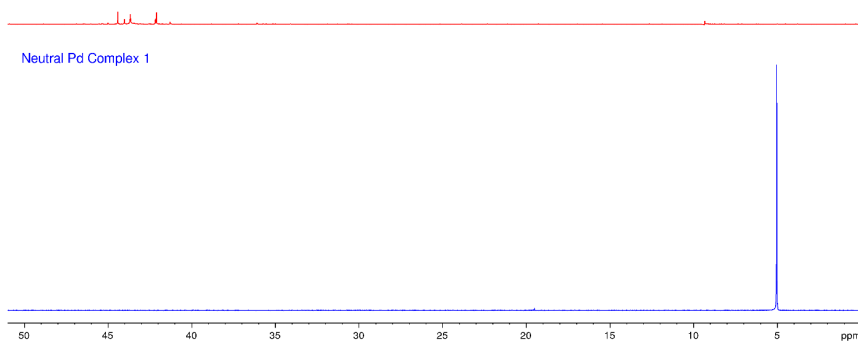
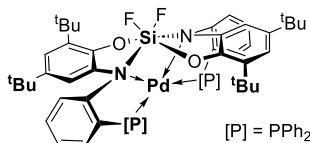
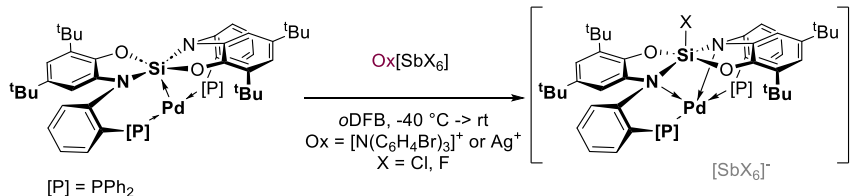


Figure S 17: $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (243 MHz) of **1** and of isolated $[1][\text{Al}(\text{pftb})_4]_2$ in oDFB at 295 K.

Generation of [F₂-1] from the reaction of PNO₂Si and [Pd(MeCN)₄][BF₄]



Oxidation of 1 with Deelectronators Containing Hexahalidoantimonates



1) Oxidation with *Magic Blue* – Formation of [Cl-1][SbCl₆]

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SUPPORTING INFORMATION

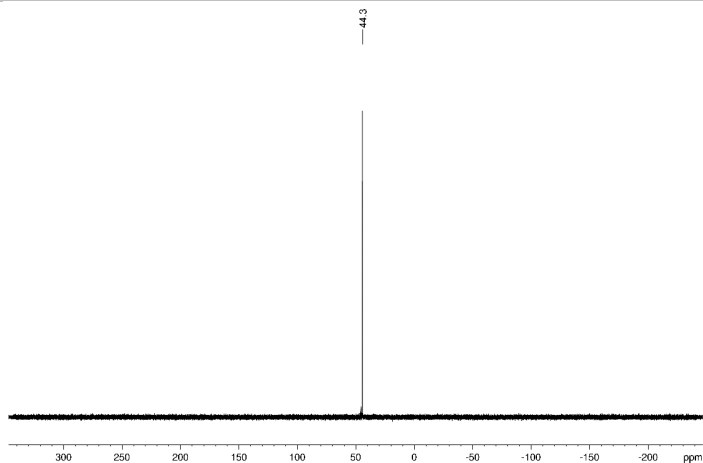


Figure S 18: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of the reaction of **1** and $[\text{N}(\text{C}_6\text{H}_4\text{Br})_3][\text{SbCl}_6]$ in oDFB/ C_6D_6 50:1 at 295 K.

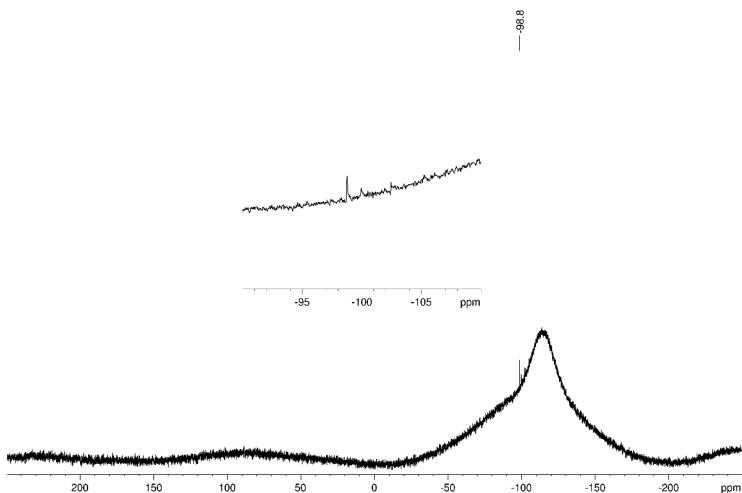


Figure S 19: ^{29}Si (IG) NMR spectrum (119 MHz) of the reaction of **1** and $[\text{N}(\text{C}_6\text{H}_4\text{Br})_3][\text{SbCl}_6]$ in oDFB/ C_6D_6 50:1 at 295 K.

2) Oxidation with $\text{Ag}[\text{SbF}_6]$ – Formation of $[\text{F-1}][\text{SbF}_6]$ and $[\text{F}_2\text{-1}]$

In a J. Young NMR tube, **1** (15.0 mg, 13.7 μmol , 1.00 eq) was dissolved in 0.5 mL of oDFB. Silver hexafluoroantimonate (9.43 mg, 27.4 μmol , 2.00 eq) was added in one portion, the cap was closed and the mixture was mixed vigorously, resulting in the formation of a deeply purple colored solution and the formation of $\text{Ag}(0)$, which was subsequently investigated by NMR spectroscopy. The observed resonances in the ^{31}P ,

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^{19}F and ^{29}Si NMR spectra state full consumption of the starting material, partial degradation of the antimonate and subsequent unselective follow up reactions of the *in-situ* formed SbF_5 . Mass spectrometry further stated the formation of $[\text{F}-\mathbf{1}]^+$, $[\text{F}_2-\mathbf{1}]$ and $[\text{C}_6\text{H}_4\text{F}-\mathbf{1}]^+$.

$^{31}\text{P}\{^1\text{H}\}$ NMR (major product, 243 MHz, oDFB, 295 K): δ [ppm] = 43.2 (s); $^{19}\text{F}\{^1\text{H}\}$ NMR (major product, 376 MHz, oDFB, 295 K): δ [ppm] = -164.9 (s); ^{29}Si (IG) NMR (major product, 119 MHz, oDFB, 295 K): δ [ppm] = -116.9 (broad, s); MS (LIDF(+)): $[\text{F}-\mathbf{1}]^+$, calcd.: 1111.35, found: 1111.40; $[\text{F}_2-\mathbf{1}]^+$, calcd.: 1130.35, found: 1130.40; $[\text{C}_6\text{H}_4\text{F}-\mathbf{1}]^+$, calcd.: 1187.39, found: 1187.32.

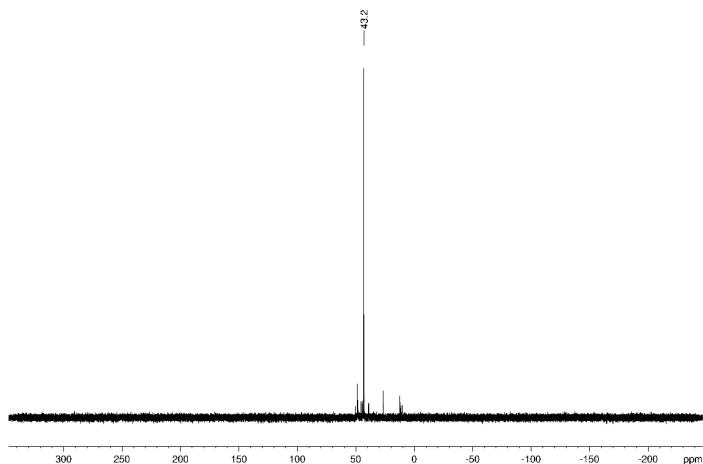


Figure S 20: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of the reaction of **1** and $\text{Ag}[\text{SbF}_6]$ in oDFB at 295 K.

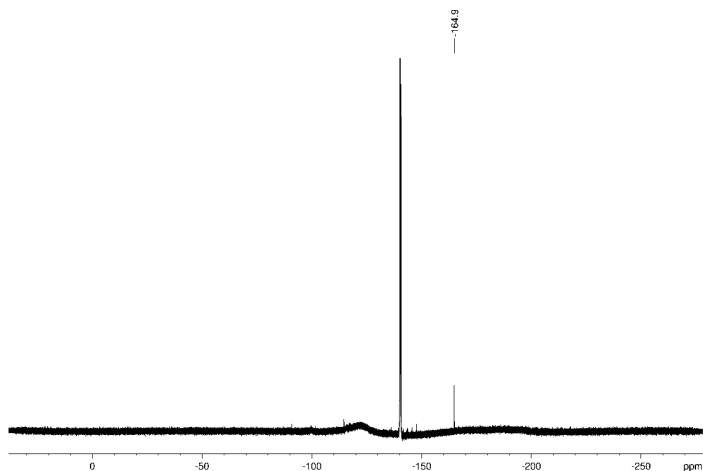


Figure S 21: $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (376 MHz) of the reaction of **1** and $\text{Ag}[\text{SbF}_6]$ in oDFB at 295 K.

SUPPORTING INFORMATION

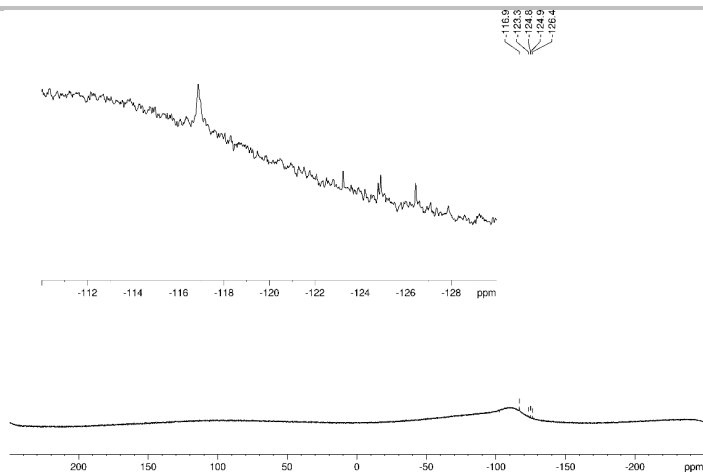
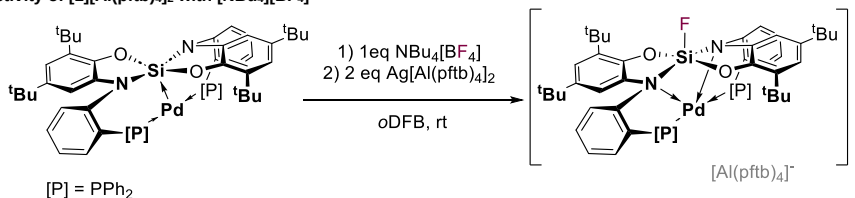


Figure S 22: ^{29}Si (1G) NMR spectrum (119 MHz) of the reaction of **1** and $\text{Ag}[\text{SbF}_6]$ in $\text{oDFB}/\text{C}_6\text{D}_6$ 50:1 at 295 K.

Reactivity of $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$ with $[\text{NBu}_4][\text{BF}_4]$



In a J. Young NMR tube, **1** (15.0 mg, 13.7 μmol , 1.00 eq) and tetrabutylammonium tetrafluoroborate (4.52 mg, 13.7 μmol , 1.00 eq) were dissolved in 0.5 mL of oDFB . The orange solution was investigated via NMR spectroscopy, before $\text{Ag}[\text{Al}(\text{pftb})_4]\text{oDFB}$ (32.6 mg, 27.4 μmol , 2.00 eq) was added in one portion, resulting in a dark purple solution, which was subsequently analysed by NMR spectroscopy and mass spectrometry. The spectra indicate full consumption of the tetrafluoroborate and the formation of $[\text{F-1}]^+$ as the major species. Removal of all volatiles *in vacuo* and recrystallisation from benzene/*n*-pentane resulted in the formation of purple needles, which were characterized by NMR spectroscopy.

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6 , 295 K): δ [ppm] = 43.7 (s); ^{19}F NMR (565 MHz, C_6D_6 , 295 K): δ [ppm] = -74.8 (s, 36F), -97.9 (s, 1F); MS (LIDF(+)): $[\text{F-1}]^+$, calcd.: 1111.35, found: 1111.29.

SUPPORTING INFORMATION

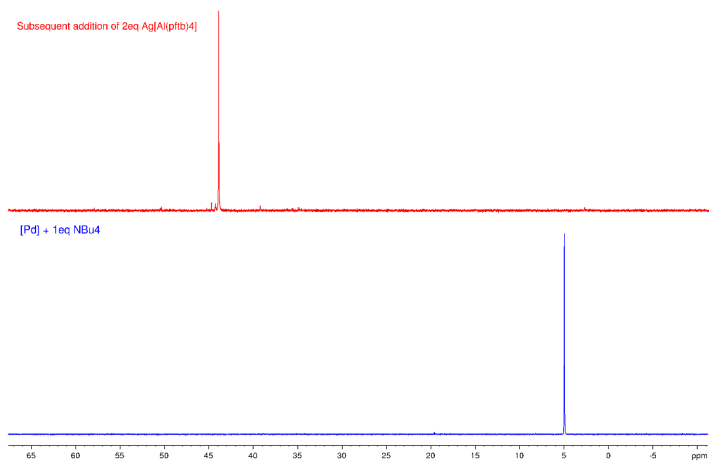


Figure S 23: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz) of the reaction of **1**, NBu₄BF₄ and Ag[Al(pftb)₄] in oDFB at 295 K.

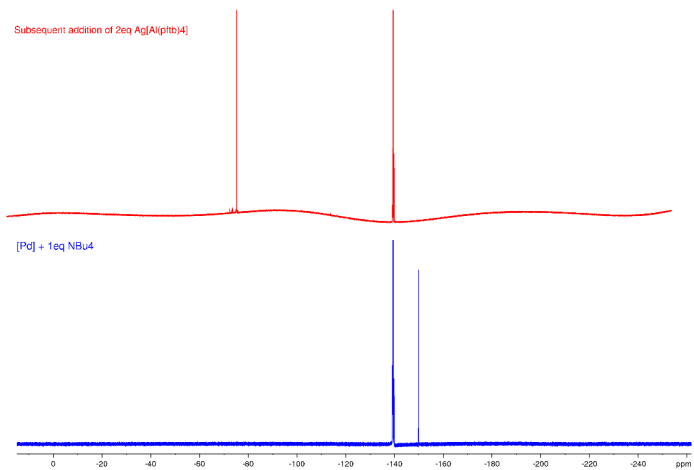


Figure S 24: Stacked ^{19}F NMR spectra (376 MHz) of the reaction of **1**, NBu₄BF₄ and Ag[Al(pftb)₄] in oDFB at 295 K.

SUPPORTING INFORMATION

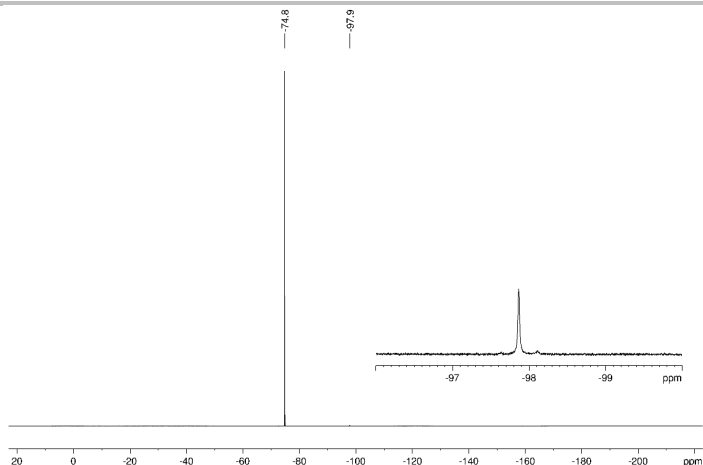
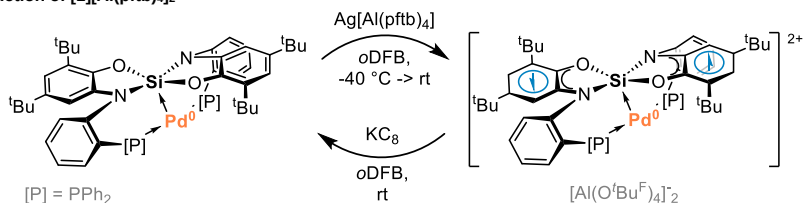


Figure S 25: ^{19}F NMR spectrum (564 MHz) of the crystals isolated from the reaction of **1**, NBu_4BF_4 and $\text{Ag}[\text{Al}(\text{pftb})_4]$ in C_6D_6 at 295 K.

Reduction of $[\text{1}][\text{Al}(\text{pftb})_4]_2$ 

In a vial, **1** (10.0 mg, 9.14 μmol , 1.00 eq) was dissolved in 0.5 mL of oDFB to form a light orange solution and cooled to $-40\text{ }^\circ\text{C}$. $\text{Ag}[\text{Al}(\text{pftb})_4]\text{oDFB}$ (21.7 mg, 18.3 μmol , 2.00 eq) was added in one portion and the vial was shaken for three minutes while reaching room temperature. The deep brown suspension was filtered through a syringe filter into a flame dried J Young NMR tube to remove $\text{Ag}(0)$. After obtaining NMR spectra and ensuring full conversion of the starting material, an excess of KC_8 (6.18 mg, 45.7 μmol , 5.00 eq) was added and the suspension was shaken inside the NMR tube, which led to a color change from deep brown to red to purple and ultimately after several hours to light orange. The mixture was analyzed by NMR spectroscopy to reveal the formation of **1** as the major species ($\delta_{31\text{P}} = 4.8\text{ ppm}$, $\delta_{31\text{P}} = -84.3\text{ ppm}$ (t, $J = 6.9\text{ Hz}$)), alongside several anionic silicato $\text{Pd}(0)$ abstraction products (presumably $[\text{K}][\text{F}-\mathbf{1}]$, $[\text{K}][\text{pftb}-\mathbf{1}]$, etc., formed through reduction of the side products of the oxidation).

After removal of graphite and excess KC_8 by filtration, the above-described process was repeated once more, resulting in similar results.

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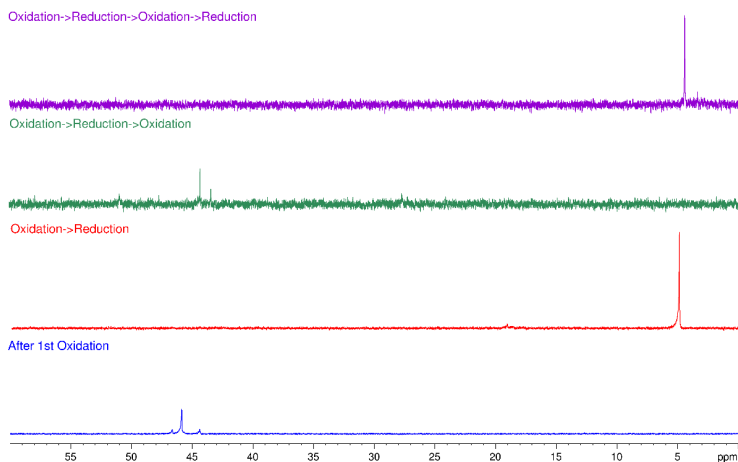


Figure S 26: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz) of the stepwise oxidation and reduction sequence of **1** in oDFB at 295 K.

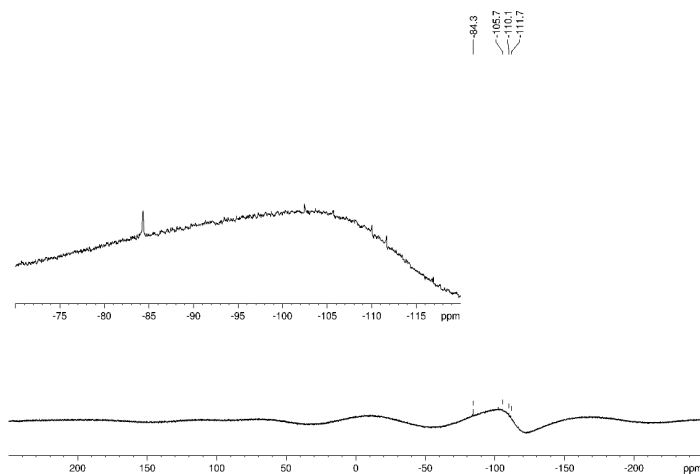
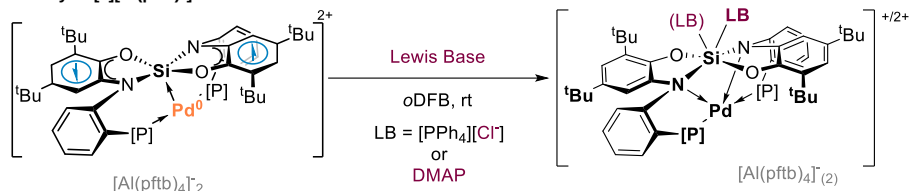


Figure S 27: ^{29}Si (IG) NMR spectrum (119 MHz) after the first oxidation/reduction cycle in oDFB at 295 K. Contains an artefact of the spectrometer (-102.4 ppm).

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Reactivity of $[1][\text{Al}(\text{pftb})_4]_2$ with Lewis Bases1) Reaction with PPh_4Cl – Formation of $[\text{Cl-1}][\text{Al}(\text{pftb})_4]$ a) Oxidation in the presence of PPh_4Cl

In a flame-dried J. Young NMR tube, **1** (15.0 mg, 13.7 μmol , 1.00 eq), tetraphenylphosphonium chloride (5.24 mg, 13.7 μmol , 1.00 eq) and $\text{Ag}[\text{Al}(\text{pftb})_4]\text{oDFB}$ (32.6 mg, 27.4 μmol , 2.00 eq) were cooled to -40°C . 0.5 mL of -40°C cold oDFB was added, the tube was closed and the contents were mixed vigorously resulting in a dark red suspension containing precipitated black $\text{Ag}(0)$. The mixture was analyzed by NMR spectroscopy, concluding the clean formation of $[\text{Cl-1}][\text{Al}(\text{pftb})_4]$ and $[\text{PPh}_4][\text{Al}(\text{pftb})_4]$. LIDFI mass spectrometry of the mixture further underlined this result.

Unfortunately, all attempts to separate $[\text{Cl-1}][\text{Al}(\text{pftb})_4]$ and $[\text{PPh}_4][\text{Al}(\text{pftb})_4]$ were unsuccessful due to the similar polarity of both salts.

b) Addition of PPh_4Cl to $[1][\text{Al}(\text{pftb})_4]_2$

In a vial, **1** (15.0 mg, 13.7 μmol , 1.00 eq) and $\text{Ag}[\text{Al}(\text{pftb})_4]\text{oDFB}$ (32.6 mg, 27.4 μmol , 2.00 eq) were cooled to -40°C . 0.5 mL of -40°C cold oDFB was added and the mixture was mixed vigorously while reaching room temperature. The deep brown suspension was filtered through a syringe filter into a flame dried J Young NMR tube, containing tetraphenylphosphonium chloride (5.24 mg, 13.7 μmol , 1.00 eq), resulting in a deep dark red solution. Analysis of the solution via NMR spectroscopy revealed similar spectra compared to a), although F^- and pftb-abstractions as side reactions from the oxidation were observed by ^{19}F -NMR spectroscopy and mass spectrometry.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, oDFB, 295 K): δ [ppm] = 44.2 (s); ^{19}F NMR (564 MHz, oDFB/ C_6D_6 50:1, 295 K): δ [ppm] = -75.4 (s); ^{29}Si (IG) NMR (119 MHz, oDFB/ C_6D_6 50:1, 295 K): δ [ppm] = -98.8 (s); MS (LIDFI(+)): $[\text{Cl-1}]^+$, calcd.: 1129.33, found: 1129.40, $[\text{Cl}_2-1]^+$, calcd.: 1164.29, found: 1164.36.

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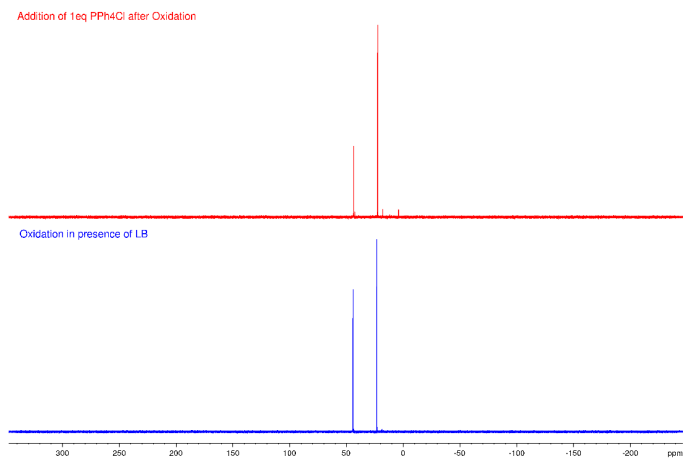


Figure S 28: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz) of the reaction of chloride with $[1][\text{Al}(\text{pftb})_4]_2$ in oDFB at 295 K. The peak at 23.2 ppm corresponds to the PPh_4^+ cation, side product of the reaction.

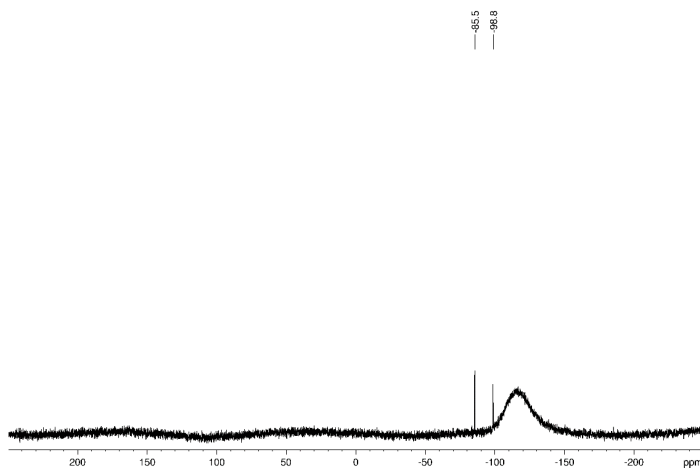


Figure S 29: ^{29}Si (IG) NMR spectrum (119 MHz) of the reaction of chloride with $[1][\text{Al}(\text{pftb})_4]_2$ in oDFB:C₆D₆ 50:1. The peak at -85.5 ppm corresponds to unconsumed **1**.

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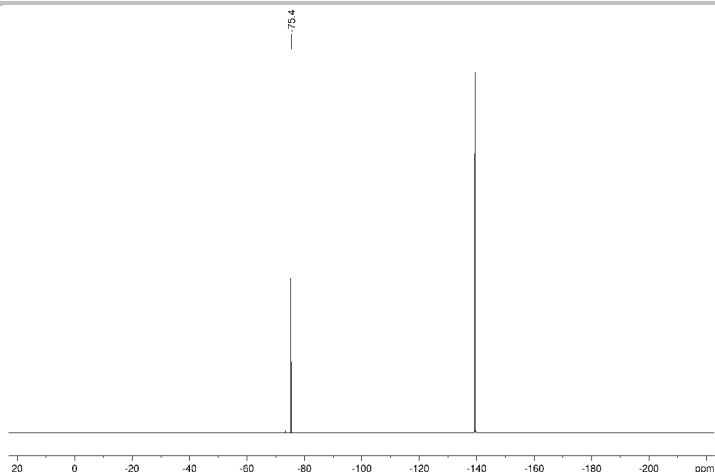


Figure S 30: ^{19}F NMR spectrum (564 MHz) of the reaction of chloride with $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$ in oDFB: C_6D_6 50:1 at 295 K. The small signal at -73.4 ppm is accounted by the formation of $[\text{pftb}-\mathbf{1}][\text{Al}(\text{pftb})_4]$.

2) UV-Vis Monitoring of the reaction with PPh_4Cl – Formation of $[\text{Cl}-\mathbf{1}][\text{Al}(\text{pftb})_4]_2$

In a vial, **1** (5.50 mg, 5.00 μmol , 1.00 eq) was dissolved in 5 mL of oDFB to form a 10^{-3} M solution, from which an UV-Vis spectrum was recorded.

The solution was transferred back to a vial and $\text{Ag}[\text{Al}(\text{pftb})_4]\text{x oDFB}$ (11.9 mg, 10.0 μmol , 2.00 eq) was added. The resulting mixture was stirred for 15 minutes, filtered twice via a syringe filter to remove the formed $\text{Ag}(0)$. From this brown solution, 200 μL were diluted with 1.80 mL of oDFB to a concentration of 10^{-4} M and an UV-Vis spectrum of $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$ was recorded.

2 mL of the 10^{-3} M $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$ solution were transferred to a new vial. Separately, a suspension of PPh_4Cl (3.75 mg, 10.0 μmol , 2.00 eq) in 1000 μL oDFB was prepared. 200 μL of this suspension was transferred to the vial with the $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$ solution, resulting in a red solution. From this solution, containing $[\text{Cl}-\mathbf{1}][\text{Al}(\text{pftb})_4]$ and $[\text{PPh}_4][\text{Al}(\text{pftb})_4]$, 330 μL were taken, diluted with 2650 μL oDFB to form a 10^{-4} M solution, which was analyzed by UV-Vis spectroscopy.

The summarized spectra are displayed in figure 3B in the main text.

3) Reaction with DMAP – Formation of $[\text{DMAP}_2-\mathbf{1}][\text{Al}(\text{pftb})_4]_2$

a) Oxidation in the presence of DMAP

In a flame-dried J. Young NMR tube, **1** (15.0 mg, 13.7 μmol , 1.00 eq), 4-dimethylamino-pyridine (DMAP) (3.35 mg, 27.4 μmol , 2.00 eq) and $\text{Ag}[\text{Al}(\text{pftb})_4]\text{x oDFB}$ (32.6 mg, 27.4 μmol , 2.00 eq) were cooled to -40°C . 0.5 mL of -40°C cold oDFB was added, the tube was closed and the contents were mixed vigorously resulting in a blood-red suspension containing precipitated black $\text{Ag}(0)$. The mixture was analyzed by NMR spectroscopy, concluding the clean formation of $[\text{DMAP}_2-\mathbf{1}][\text{Al}(\text{pftb})_4]_2$.

b) Addition of DMAP to $[\mathbf{1}][\text{Al}(\text{pftb})_4]_2$

In a vial, **1** (15.0 mg, 13.7 μmol , 1.00 eq) and $\text{Ag}[\text{Al}(\text{pftb})_4]\text{x oDFB}$ (32.6 mg, 27.4 μmol , 2.00 eq) were cooled to -40°C . 0.5 mL of -40°C cold oDFB was added and the mixture was mixed vigorously while reaching room temperature. The deep brown suspension was filtered through a

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syringe filter into a flame dried J Young NMR tube, 4-dimethylamino-pyridine (DMAP) (3.35 mg, 27.4 μmol , 2.00 eq), resulting in a deep blood red solution. Analysis of the solution via NMR spectroscopy revealed similar spectra compared to a). LIFDI MS analysis indicated the dissociation of the DMAP molecules and therefore sole detection of $[\text{F-1}]^+$ and $[\text{pftb-1}]^+$, formed inside the spectrometer. Gas phase diffusion of *n*-pentane into the oDFB solution at room temperature resulted in the formation of crystals suitable for scXRD.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, oDFB, 295 K): δ [ppm] = 41.5 (s); ^{19}F NMR (564 MHz, oDFB/ C_6D_6 50:1, 295 K): δ [ppm] = -75.3 (s); ^{29}Si (IG) NMR (119 MHz, oDFB/ C_6D_6 50:1, 295 K): δ [ppm] = -154.4 (s); MS (LIFDI(+)): $[\text{F-1}]^+$, calcd.: 1111.35, found: 1111.44.

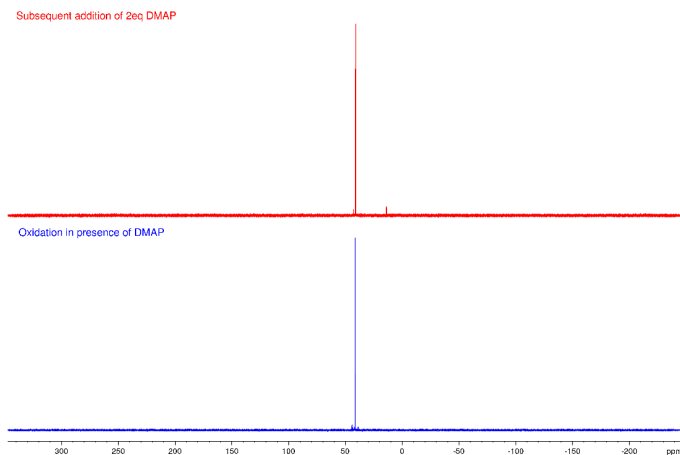


Figure S 31: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (162 MHz) of the reaction DMAP with $[\text{1}]\text{Al}(\text{pftb})_4$ in oDFB at 295 K.

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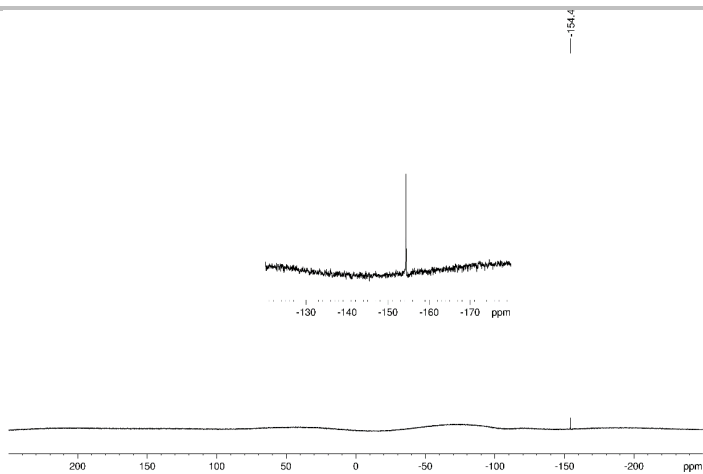


Figure S 32: ^{29}Si (IG) NMR spectrum (119 MHz) of the reaction of DMAP with $[1][\text{Al}(\text{pftb})_4]_2$ in oDFB: C_6D_6 50:1.

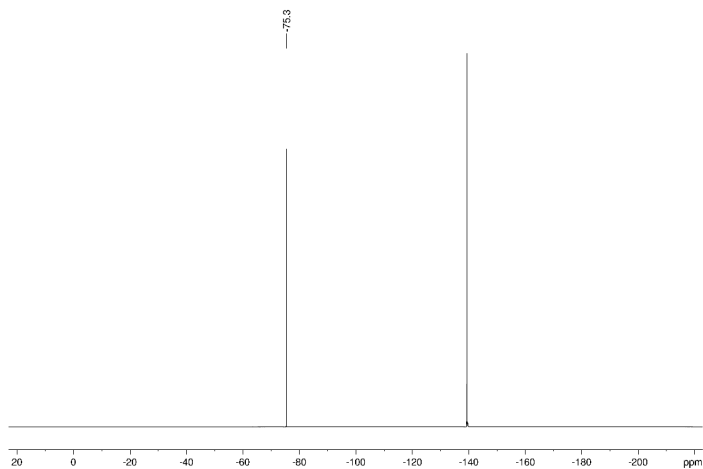
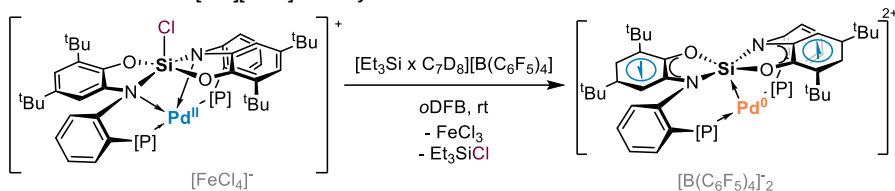


Figure S 33: ^{19}F NMR spectrum (564 MHz) of the reaction of DMAP with $[1][\text{Al}(\text{pftb})_4]_2$ in oDFB: C_6D_6 50:1 at 295 K.

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Chloride Abstraction from [Cl-1][FeCl₄] with Silylium Cations

1) NMR spectroscopic investigation

In a flame-dried J. Young NMR tube, [Cl-1][FeCl₄] (10.0 mg, 7.54 μmol, 1.00 eq) was dissolved in 0.5 mL of oDFB to form a deep purple red solution and NMR spectra were obtained. Afterwards, [Et₃Si x C₇D₈][B(C₆F₅)₄] (13.5 mg, 15.1 μmol, 2.00 eq) was added in one portion at room temperature, leading to an immediate color change from red to brownish. The mixture was analyzed by NMR spectroscopy, concluding the consumption of [Cl-1]⁺.

After addition of 2eq [Et₃Si]⁺

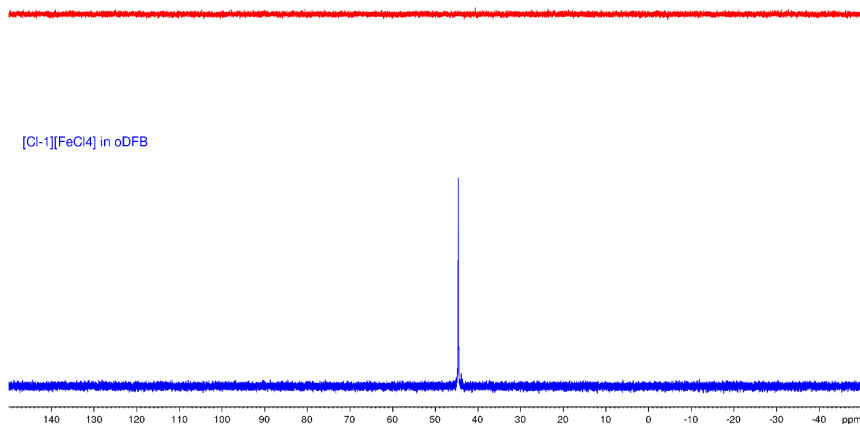


Figure S 34: Stacked ³¹P{¹H} NMR spectra (162 MHz above/ 243 MHz below) of the reaction of [Cl-1][FeCl₄] and [Et₃Si x C₇D₈][B(C₆F₅)₄] in oDFB at 295 K.

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2) Investigation by UV-Vis spectroscopy

[Cl-1][FeCl₄] (11.9 mg, 8.97 μ mol, 1.00 eq) was dissolved in 450 μ L of oDFB to form a 2×10^{-2} M deep purple red solution. 30 μ L of this solution were diluted with 2970 μ L oDFB to form a 2×10^{-4} M solution, which was 1:1 diluted to measure an UV-Vis spectrum of the starting material (final concentration 10^{-4} M, purple line). To the concentrated solution, [Et₃Si x C₇D₈][B(C₆F₅)₄] (16.1 mg, 17.9 μ mol, 2.00 eq) was added in one portion at -40 °C, leading to an immediate color change from red to brownish. The mixture was stirred at room temperature for one minute and filtered through a syringe filter before 15 μ L of this solution were diluted with 2985 μ L oDFB to form a 1×10^{-4} M solution, of which an UV-Vis spectrum was recorded (blue line). Finally, the latter diluted solution was treated with an excess of PPh₄Cl (2.0 mg), filtered and an UV-Vis spectrum was recorded, indicating the reformation of [Cl-1]⁺ (green line).

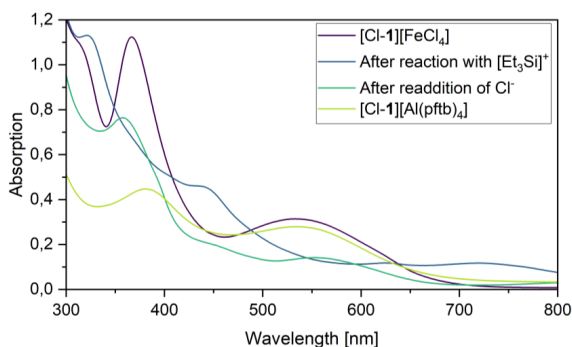


Figure S 35: Stacked UV-Vis spectra (10^{-4} M, oDFB) of the reaction of [Cl-1][FeCl₄] and [Et₃Si x C₇D₈][B(C₆F₅)₄] in oDFB including further reaction with a chloride source at 295 K. In comparison, a spectrum of [Cl-1][Al(pftb)₄] is depicted.

3) Investigation by EPR spectroscopy

The 2×10^{-2} M solution containing proposed [1][B(C₆F₅)₄]₂ was transferred to a capillary, placed inside a J. Young NMR tube, which was sealed afterwards and EPR spectra were measured at a *magnettech MiniScope MS 400* EPR spectrometer at room temperature. The normalized spectrum is compared to the spectrum, which was obtained by direct oxidation of **1** with Ag[Al(pftb)₄] and recorded on a *Bruker Elexsys E500* EPR spectrometer, equipped with a Bruker Super High QE (SHQE) resonator. While minor differences in the spectra can be retraced to different experimental setups, the overall pattern of the obtained signals is identical and concludes the successful formation of [1]²⁺.

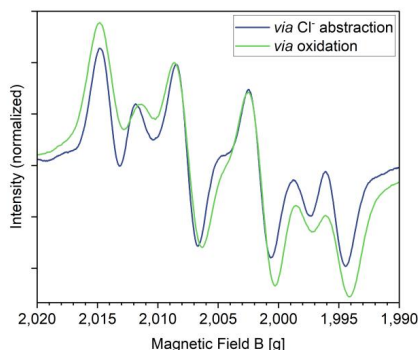


Figure S 36: Normalized EPR spectra of [1]²⁺ in oDFB obtained by different experimental approaches.

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d. Cyclic Voltammetry

Electrochemical investigations via cyclic voltammetry were performed within a nitrogen filled glovebox in a glass cell using the PalmSens Compact EmStat3+ Blue electrochemical interface and the PSTrace 5.10 program. A three electrode configuration consisting of a glassy carbon working electrode (area 0.07 cm²), a silver wire as quasi reference electrode and a platinum wire as counter electrode. For internal referencing, ferrocene was added at the end of each measurement. The concentration of the investigated species was set to 1 mM, while the electrolyte concentration was set to 0.1 M with a total volume of 5 ml. A scanning rate of 100 mV/s was used, unless stated otherwise.

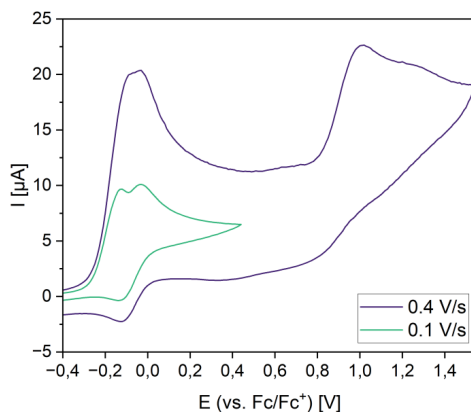


Figure S 37: Cyclic voltammogram of **1**, measured in oDFB (scan-rate: 0.1 V/s (green); 0.4 V/s (purple)), using [NBu₄][Al(pftb)₄] as supporting electrolyte (0.1 M).

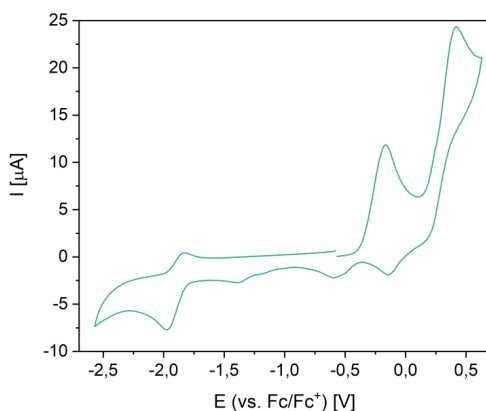


Figure S 38: Cyclic voltammogram of **1**, measured in THF (scan-rate: 0.1 V/s), using [NBu₄][PF₆] as supporting electrolyte (0.1 M). Due to reactivity of oxidized [1]⁺ and [1]²⁺ with the electrolyte (fluoride abstraction) or the solvent (coordination), only limited information can be drawn from this diagram.

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e. EPR Spectroscopy

EPR spectra between 4 – 295 K were recorded with a Bruker Elexsys E500 EPR spectrometer, equipped with a continuous wave dual-mode resonator (Bruker ER 4116DM). The regulation of the temperature for low-temperature measurements was performed with a Bruker ER 4112HV-CF42 In-Cavaty Cryogen Free VT system and a temperature controller (ITC 4, Oxford Instruments). The low-temperature measurements were directly measured in quartz tubes. Baseline correction of the obtained spectra and double integration of the VT-EPR data in order to determine the signal intensity was performed with the Bruker Xepr 2.6b.86 program.

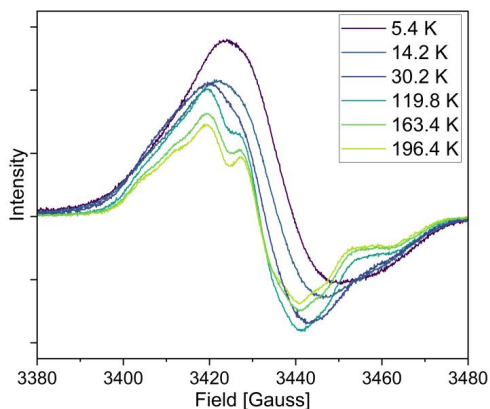


Figure S 39: VT-EPR (5.4 K to 196.4 K) spectra of $[1][\text{Al}(\text{pftb})_2]$ in oDFB matrix at 9.631 GHz.

In order to determine the coupling constant, a Bleaney Bowers fit according to the equation:

$$I \cdot T = \frac{C}{3 + e^{-2J/kT}}$$

was employed in OriginPro 2024, using the “Fitting Function Builder” using the parameters C and E = 2J/k according to

$$y = \frac{C}{3 + e^{-E/x}}$$

as already used several times in the literature.^[3] The results are summarized in table S1.

Table S1: Summary of the fitted parameters for the VT-EPR intensities.

E	E	C	C	Statistics	Statistics
Value	Standard Error	Value	Standard Error	Reduced Chi-Sqr	Adj. R-Square
-114,61363	7,34787	1735,23052	37,30561	75,88766	0,99638

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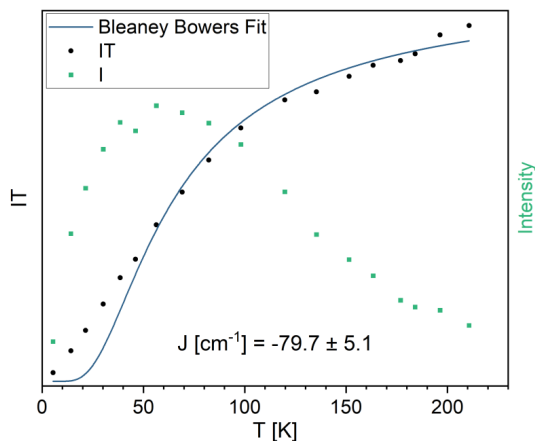


Figure S 40: IT vs T and I vs T plots for the intensities of the EPR signal at $g = 2.0042$ of compound $[1]^{2+}$ with a Bleaney Bowers fit.

For the measurement at room temperature, a capillary was used due to the high dielectric constant of oDFB. For better resolution, this measurement was carried out with a Bruker Super High QE (SHQE) cavity resonator at $\nu = 9.376024$ GHz.

The spectrum was simulated using the matrix diagonalization method implemented within the *XSophe Computer Simulation Software Suite* Version 1.1.4.^[4] Simulation Parameters: two equivalent isotropic magnetic centres with $r = 9.56$ Å and $X = (\angle z, r) = 46.1^\circ$; $g = 2.00431$; $A_N = 5.38$ G; $A_H = 9.05$ G; line width $\sigma = 3.1$ G.

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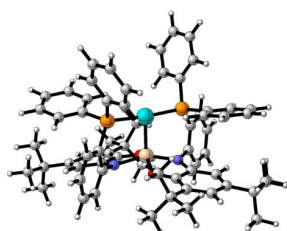
2. Computational Details

a. Structure Optimization

All computations have been performed using the Orca 5.0.3 program package.^[5] Geometry optimizations were carried out with Grimme's PBEh-3c/def2-mSVP, including the geometrical counter-poise correction scheme (gCP), atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ), using *VeryTightSCF* settings.^[6] As in all following calculations, ECP was used for Pd (def2-ECP).^[7] For open-shell structures, the UKS keyword was used. As for all following calculations broken-symmetry solutions were requested by specification in the %scf block using the "BrokenSym 1,1" keyword, setting the maximum number of iterations to 5000 (MaxIter 5000), automatically requesting full convergence in the wavefunctions (SCFConvForced true). All obtained structures have been approved to be energetic minima on the potential energy surface by analytical calculation of harmonic frequencies at the PBEh-3c level. Structures with imaginary frequencies $>10\text{ cm}^{-1}$ have been reoptimized with *TightOPT* settings. Unscaled ZPEs and thermal corrections at 298 K from the rigid-rotor harmonic oscillator (RRHO) approximation^[8] were later used for the calculation of thermodynamic values. For the Coulomb Integral, the RI approximation (RJCOSX) was applied along with the corresponding auxiliary basis sets.^[9e, 6f, 9] As starting geometries, VSEPR structures preoptimized with UFF were used.^[10]

b. Cartesian Coordinates

Cartesian coordinates (reported in Å) and energies (in hartree) of all compounds discussed in the main text. Reported at the PBEh-3c level of theory.

1²⁺ S=1**E = -3832.485757071257**

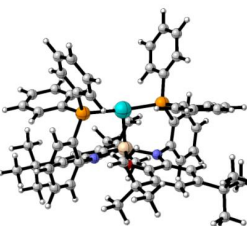
C	4.64245935169146	0.26670145228214	2.52306174124718	H	-2.24219906783687	2.23424043846920	3.50498632829551
C	4.16943021480569	1.61347803570838	2.64480318292451	O	-1.00024917899374	-1.62173926642254	1.26016966923759
C	3.77087779949182	-0.69903690687560	2.10545860916053	N	-1.73146454502089	0.68832842666504	1.39267300552606
C	2.88141339226795	2.04048388233485	2.37391156364283	Si	-0.10954450974162	-0.15448683632378	0.98754203798184
C	1.99548146581141	1.02534844587058	1.99768753539803	C	-2.16963384363012	2.77498596941259	2.57025517029384
C	2.43816506929924	-0.33094719247714	1.84785734628754	C	-1.913154445748900	2.09040013814224	1.39418275178512
C	6.08765311625493	-0.02929605940570	2.89335500818509	H	-2.51777117203060	4.69126477321535	3.45403962394452
H	4.07787468284262	-1.72452459251836	1.96397400308223	C	-2.31719597933187	4.15381962910983	2.53726483262711
C	2.45889020699653	3.50323097054493	2.46464460731523	C	-1.81253746252033	2.77145968363898	0.17987910044364
O	7.0198040134314	1.19044625512273	1.71525533226982	C	-2.19593311404240	4.84351034560696	1.33982194870461
N	1.44868271069210	-1.10731327499283	1.40813838989630	P	-1.59474354447086	1.76409911703524	-1.31018151471402
C	1.64904451363582	-2.47207645192103	1.09685167523380	C	-1.94543594544161	4.15557204093209	0.16198120504901
C	1.74971893336496	-3.42678021872379	2.09462153215467	H	-2.30548113298049	5.91900771071017	1.31977464520889
C	1.73317957215920	-2.83413704745952	-0.24846001122977	H	-1.85925916089622	4.69940850439872	-0.77024462674356
C	1.92587604868459	-4.75809596272668	1.74637306856811	H	4.88758572957179	2.35461352563164	2.96243724259070
H	1.68116157613156	-3.13169583483212	1.33366900364044	C	6.25985712043702	0.20902176806301	4.39149936907723
C	1.99173472688379	-5.13173605103480	0.41197940164236	C	7.02583289092179	0.90248064599535	2.10327475350369
C	2.00359928499446	-5.50678366840304	2.52284233462900	C	6.47169398433662	-1.47281060552799	2.56442500174267
H	1.8783056414102	-4.17306805566682	-0.58568850930861	H	7.29198418342683	0.01084649093905	4.68353241690245
H	1.2518016900612	-6.17126403967852	0.14612263572963	H	5.61670978268794	-0.44980219019409	4.97575071943007
H	1.95761953200740	-4.47129006044775	-1.62484164131985	H	6.03631310637865	1.23690201446332	4.68095328895295
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C	-3.20577611142600	-2.58767585368479	1.39816101349722	H	5.88220687039201	-2.19567229576699	3.13058843954582
C	-4.12054740291637	-0.14820222497255	1.63947529390865	C	1.36188381375268	3.66704126934700	3.52412866142024
C	-4.33119801002225	1.18056546152213	1.69718560502760	C	1.94937400850175	3.97208983658973	1.09265773647381
C	-2.30562800503720	-5.1744744966837	1.38878545633409	C	3.63183412139221	4.40294394166053	2.85808520816995
C	-2.75568452604786	-0.15938758440592	1.49383389819997	H	2.71803728769680	3.84393532428272	0.32725624146516
				H	1.69856449337748	5.03292468246241	1.13328475354755
				H	1.05120497068140	3.44269919304252	0.77739750380460
				H	4.02875118352352	4.1620553969188	3.84557639139326
				H	3.29347913242712	5.43790221156077	2.89940854283201
				H	4.45146995709524	4.36475709244738	2.13791584484392
				C	-7.2767036000278	-1.3761668806108	0.74532319887086
				C	-6.88139710652219	0.80923460510623	1.85804381083305
				C	-6.9197508330090	-1.26919951211603	3.22869441795246
				H	-7.96014263706816	0.91678901577229	1.9673358370871
				H	-6.59957985760699	1.28853186489486	0.91877990366314
				H	-6.42438834609938	1.36210477401487	2.68045996912155
				H	-6.97117294276047	-1.00330126640371	-0.23230958279079
				H	-8.34559882505058	-1.19154023840684	0.85636703792844
				H	-7.14383634007854	-2.45846793154344	0.75000513452658
				H	-1.87000975598977	-4.44131743862502	2.41974891069747
				C	-1.98323860212794	-4.19726110066320	-0.0829283313301
				C	-3.95255661216141	-4.98968059517590	1.1928260439557
				H	-1.55028680946396	-5.47835873322592	2.30585479474300

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H -2.41397422531389	-4.36737264991583	3.362099586251310	C 2.39553755688245	-0.33452978479536	1.79846039615579
H 0.97222026611878	-3.83123683607962	2.49225508891715	C 5.98198116103589	-0.09433889765872	3.03958951780698
H -3.59502658201778	-6.01059866974135	1.06148017184713	H 3.98666340781107	-1.76359149257064	2.04792501872710
H 4.62869487272111	-4.7782617827199	0.36198295410445	C 2.4750331842412	3.51347781774948	2.37293157177894
H -4.52962820611882	-4.78781452878683	2.11886064799456	O 0.73863970175960	1.22682945807453	1.54890044862171
H 1.03774562844200	-3.65737199393682	-0.0890330184806	N 1.40449441684828	-1.09634251234119	1.32520560023543
H -2.5795357280223	-8.56291251505424	-0.29324944273853	C 1.60866454965451	-2.46003966015461	1.00799744405550
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H -7.99004422731347	-1.12883121113538	3.38393949762626	C 1.71339179251656	-2.81094916434390	1.077991672092808
H -6.39719556831282	-0.78361657419301	4.05341833025396	C 1.89931540019129	-4.74766775928638	1.64885328929247
H -6.72442286719319	-2.34046674580062	3.29321314243287	H 1.62830113836268	-3.13041664041127	3.04115172113636
C -3.25654370248051	1.15195288422982	-1.68838794176069	C 1.97920906913858	-5.11241026934357	0.31290982874293
C -1.11626378828973	2.8980361169133	-2.63397887387769	H 1.97335344711987	-5.50010557623853	2.42205345656065
C -1.88490536654923	3.070238444214753	-3.78177613337804	C 1.89043679104158	-4.14791867161864	-0.67987326021759
C 0.10976148462825	3.56007002411423	-2.51374945344885	H 2.12142140158635	-6.14937338169016	0.04151146880682
C 0.54580746721047	4.4005852066121	-3.52240967974020	H 1.96623766462222	-4.44057800056862	-1.71946102687871
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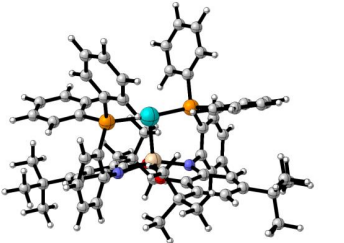


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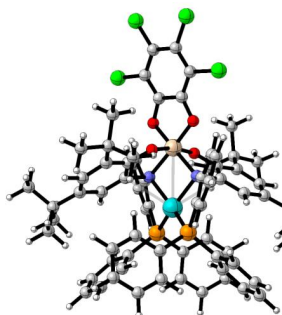


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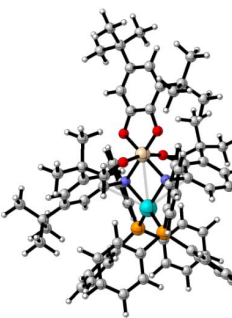
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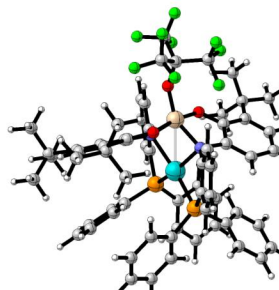
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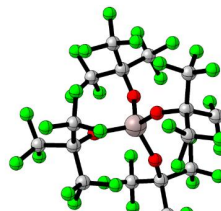
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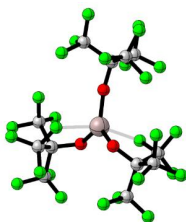
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 F -4.32832800000000 1.28254800000000 -0.94392100000000



Al -2.60611400000000 2.18745400000000 -0.08235600000000
 O -2.07086900000000 1.99467800000000 -1.72244200000000
 O -3.26978900000000 3.68267700000000 0.33369000000000
 O -2.47874800000000 0.89414800000000 1.07206700000000
 C -3.78968200000000 4.72957200000000 1.00969600000000
 C -2.85537300000000 1.60416200000000 -2.76200400000000
 C -1.32218300000000 0.47214800000000 1.64825600000000
 C -2.68915700000000 5.83356100000000 1.10438500000000
 C -4.23560800000000 4.27900500000000 2.43634200000000
 C -5.02692400000000 5.25620000000000 0.20806400000000
 C -1.63796300000000 -0.03403200000000 3.08776200000000
 C -0.32668300000000 1.67557700000000 1.70127200000000
 C -0.70637500000000 -0.67698600000000 0.79019900000000
 F -3.27051500000000 3.57769600000000 3.01988100000000
 F -5.30509900000000 3.48986900000000 2.36632300000000
 F -4.53152600000000 5.30356900000000 3.22624000000000
 F -1.74858100000000 5.48380000000000 1.98025500000000
 F -3.18215200000000 7.00706800000000 1.48124700000000
 F -2.09069400000000 5.98819400000000 -0.06856700000000
 F -4.64671800000000 5.88206400000000 -0.90018800000000
 F -5.76925800000000 6.09501300000000 0.92194700000000
 F -5.80061300000000 4.24099000000000 -0.15703500000000
 F -1.63797700000000 -1.55457800000000 0.45935600000000
 F 0.27468300000000 -1.31463200000000 1.41939400000000
 F -0.21101500000000 -0.16864300000000 -0.34002200000000
 F -0.50246400000000 2.45252200000000 2.74537000000000
 F -0.62354800000000 2.47033700000000 0.59015300000000
 F 0.94470000000000 1.37131900000000 1.60439600000000
 F -2.43850700000000 0.81013800000000 3.71498400000000
 F -0.52233100000000 -0.16564000000000 3.80478500000000
 F -2.24516600000000 -1.21286900000000 3.04526200000000
 C -2.00822200000000 0.73875400000000 -3.74283500000000
 C -3.40593600000000 2.86619500000000 -3.48714100000000
 C -4.03606300000000 0.75189000000000 -2.19754100000000
 F -2.44438500000000 3.75928400000000 -3.64753800000000
 F -4.37490100000000 3.43043600000000 -2.77489600000000
 F -3.90693200000000 2.57387200000000 -4.69304100000000

c. Thermodynamic Values

In order to calculate solvent corrected, more precise energies of the optimized structures for free reaction enthalpies, single point calculations, using Head-Gordon's ω b97x-V method with the def2-TZVPP basis set (including DFT-NL dispersion correction, and ECP for Pd) were calculated.^[7, 11] Solvent effects were accounted for by the SMD solvation module, using fluorobenzene as solvent.^[12] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[6e, 6f, 9] All calculations were carried out using *VeryTightSCF* settings. For the calculation of broken-symmetry solutions, the converged S = 1 geometries were used instead of geometries by optimization with broken symmetry settings, since only little deviations were observed ($\Delta G = 2.6$ kJ/mol) and it simplified the work flow.

SUPPORTING INFORMATION

d. TD-DFT Calculation of Excited States

In order to calculate the excitation profile of the compounds with the intention of comparing it to experimental data, time-dependent DFT calculations with the hybrid exchange-correlation functional CAM-B3LYP and the def2-TZVPP basis set (including ECP for Pd) were performed for the first 30 excited states.^[11b, 13] Solvent effects were accounted for by the SMD solvation module, using fluorobenzene as solvent.^[12] For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[6e, 6f, 9] All calculations were carried out using *VeryTightSCF* settings. The calculated spectra were plotted using ChemCraft, using Gaussian line broadening. In order to account for systematic blue-shifted theoretical spectra, calculated spectra were manually red-shifted by 100 nm. In order to compare other functionals, the absorption spectrum for neutral Pd complex **1** was also calculated using Head-Gordon's ω B97x-D3 method and compared, resulting in accurate description by CAM-B3LYP.

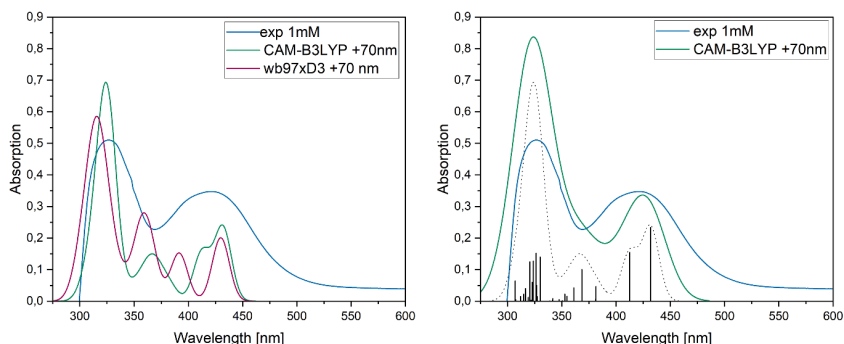


Figure S 41: Experimental (blue, PhF, 1mM) spectrum of **1** compared to results obtained by TD-DFT calculations with different functionals and different line-broadening settings.

In the following, the results for the Pd complexes **1**, [cat^C-**2**] and [cat^{3,5-tBu}-**2**] are summarized and compared to their experimental spectra. The nature of the excitations is also included.

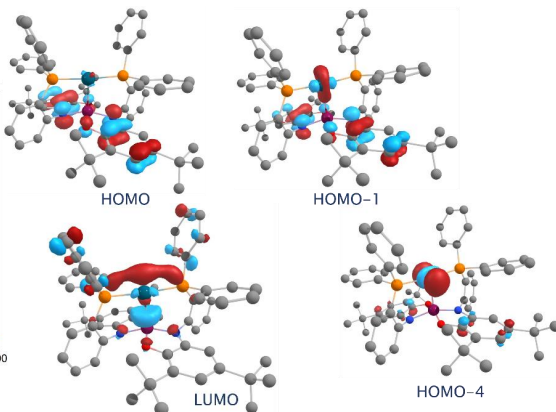
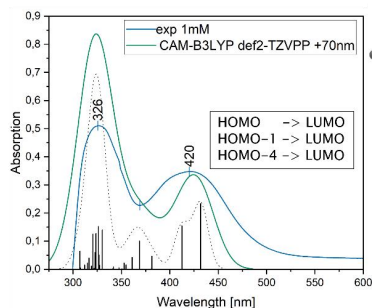
TD-DFT for [PNO₂SiPd]

Figure S 42: Experimental (blue, PhF, 1mM) spectrum of **1** compared to results obtained by TD-DFT (CAM-B3LYP/def2-TZVPP(SMD=PhF))/PBEh-3c). Also listed are the major transitions that contribute to the band together with representations of the involved molecular orbitals.

SUPPORTING INFORMATION

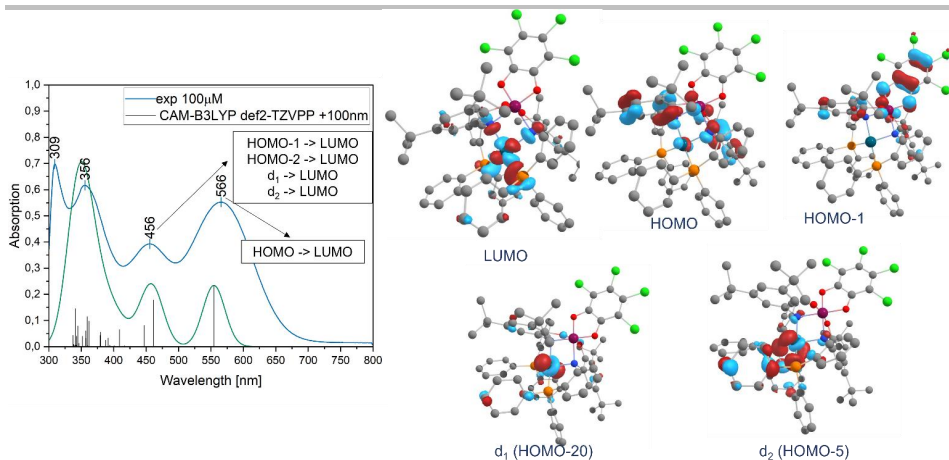


Figure S 43: Experimental (blue, PhF, 0.1 mM) spectrum of [cat^C-1] compared to results obtained by TD-DFT (CAM-B3LYP/def2-TZVPP(SMD=PhF)/PBEh-3c). Also listed are the major transitions that contribute to the band together with representations of the involved molecular orbitals.

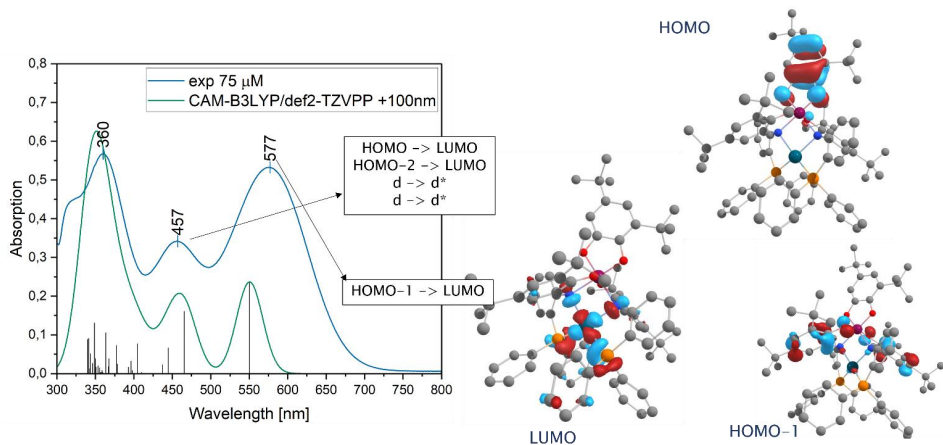


Figure S 44: Experimental (blue, PhF, 75 μM) spectrum of [cat^{3,5-Bu}-1] compared to results obtained by TD-DFT (CAM-B3LYP/def2-TZVPP(SMD=PhF)/PBEh-3c). Also listed are the major transitions that contribute to the band together with representations of the involved molecular orbitals. Note how regardless of the coordinating catecholate, the band at 577 nm still is caused by the amp → Pd(II) LMCT albeit not being the HOMO-LUMO transition.

SUPPORTING INFORMATION

d. ETS-NOCV Calculations

For unrestricted energy decomposition analysis (EDA), using the Extended Transition State (ETS) method^[14] combined with the natural orbitals for chemical valence (NOCV) concept,^[15] calculations were performed at the BP86-D3BJ/TZ2P level^[6c, 16] as implemented in the AMS2022.103 software package.^[17]

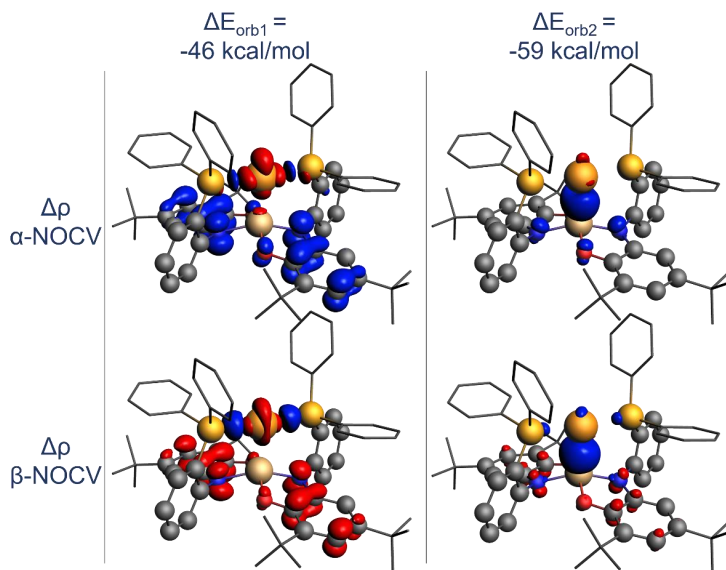


Figure S 45: ETS-NOCV deformation densities $\Delta\rho$ with the major contribution to the orbital interaction energy of $[1]^{2+}$, as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Hydrogen atoms are hidden for clarity. Charge flow from red to blue. The interaction on the left symbolizes donation of electron density from filled d-orbitals at Pd into the oxidized Pd-backbone, partially also from Si. The interaction on the right corresponds to the Pd-Si bond, which is even partially stabilized by electron flow from the ligand backbone.

SUPPORTING INFORMATION

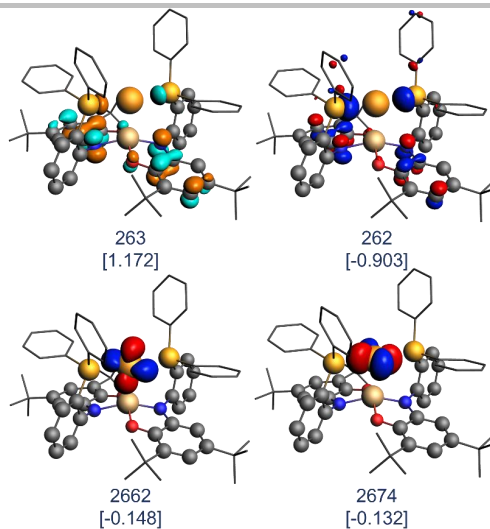


Figure S 46: Visualization of the symmetrized fragment orbitals (SFOs) with the highest eigenvalues ν (symbolizing charge flow) contributing to ΔE_{orb1} , as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Hydrogen atoms are hidden for clarity.

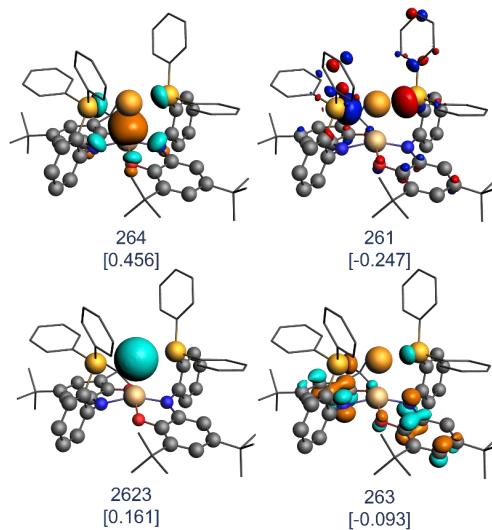


Figure S 47: Visualization of the symmetrized fragment orbitals (SFOs) with the highest eigenvalues ν (symbolizing charge flow) contributing to ΔE_{orb2} , as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory. Hydrogen atoms are hidden for clarity.

SUPPORTING INFORMATION

e. Frontier Molecular Orbitals, Spin Densities and NBO Calculations

Natural Bond Orbital (NBO) calculations were conducted on BS-PBE0-D4/def2-TZVPP level of theory,^[6e, 11b, 18] using NBO 6.0.18a as included in Orca 5.0.3.^[19] ECP for Pd was employed.^[7] Wiberg bond indices were calculated using the BNDIDX keyword. NBOs were rendered and plotted using Chemcraft.^[20] Broken symmetry was invoked as for the calculations described above. The respectively obtained wave-functions were used to visualize the frontier molecular orbitals (BS solution) and the spin-density for the $S = 1$ state.

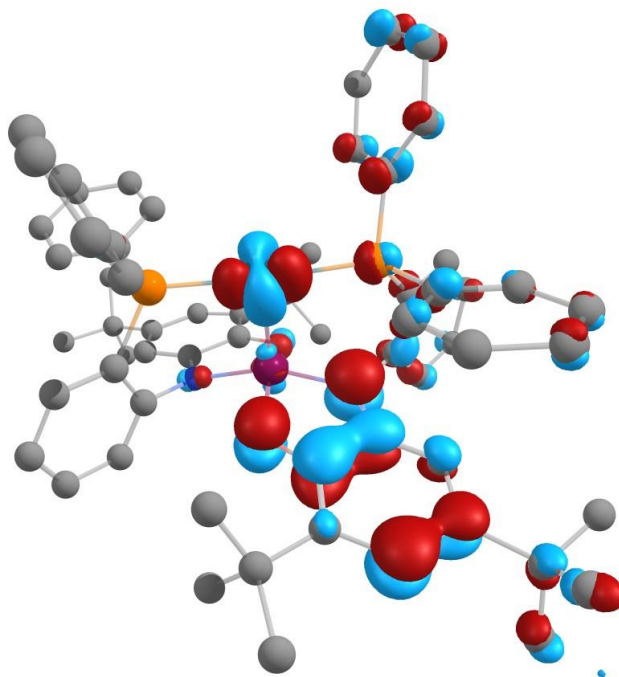


Figure S 48: α -SOMO of $[1]^{2+}$ (BS-PBE0-D4/def2-TZVPP//PBEh-3c, contour value 0.05).

SUPPORTING INFORMATION

NBO analysis for complex $[1]^{2+}$:

Important NBOs of $[1]^{2+}$ that take major roles in the Pd-Si interaction are listed below and displayed in figure S47.

Table S2: List of selected NBOs in complex $[1]^{2+}$ with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
$\alpha 161$	0.89	BD (Si-Pd)	39% Si (3s (49%), 3p (49%), 3d (2%)); 61% Pd (4s (44%), 4d (56%))
$\alpha 272$	0.33	LV (C30)	2p (100 %)
$\alpha 273$	0.21	LV (Si)	3s (51 %), 3p (49 %)
$\alpha 274$	0.20	LV (Si)	3p (100%)
$\alpha 275$	0.16	LV (Si)	3p (100%)
$\beta 161$	0.89	BD (Si-Pd)	39% Si (3s (50%), 3p (49%), 3d (2%)); 61% Pd (4s (43%), 4d (57%))
$\beta 272$	0.33	LV (C30)	2p (100 %)
$\beta 273$	0.22	LV (Si)	3s (51 %), 3p (49 %)
$\beta 274$	0.20	LV (Si)	3p (100%)
$\beta 275$	0.16	LV (Si)	3p (100%)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] for selected interactions between the listed NBOs (only α -interactions are listed, since the β -interactions do not differ significantly ($\Delta \Delta E^{(2)} < 0.05$ kcal/mol):

- $\Delta E^{(2)} 99 (LP_{Pd}) \rightarrow 275 (LV_{Si})$ 2.87
- $\Delta E^{(2)} 101 (LP_{Pd}) \rightarrow 274 (LV_{Si})$ 2.49
- $\Delta E^{(2)} 161 (BD_{Si-Pd}) \rightarrow 417 (BD^*_{P-Si})$ 63.54
- $\Delta E^{(2)} 243 (BD_{P-Pd}) \rightarrow 335 (BD^*_{Si-Pd})$ 23.20
- $\Delta E^{(2)} 95 (LP_O) \rightarrow 272 (LV_{C30})$ 47.21
- $\Delta E^{(2)} 145 (BD_{C24-C28}) \rightarrow 272 (LV_{C30})$ 55.15
- $\Delta E^{(2)} 158 (BD_{C31-N34}) \rightarrow 272 (LV_{C30})$ 14.33

SUPPORTING INFORMATION

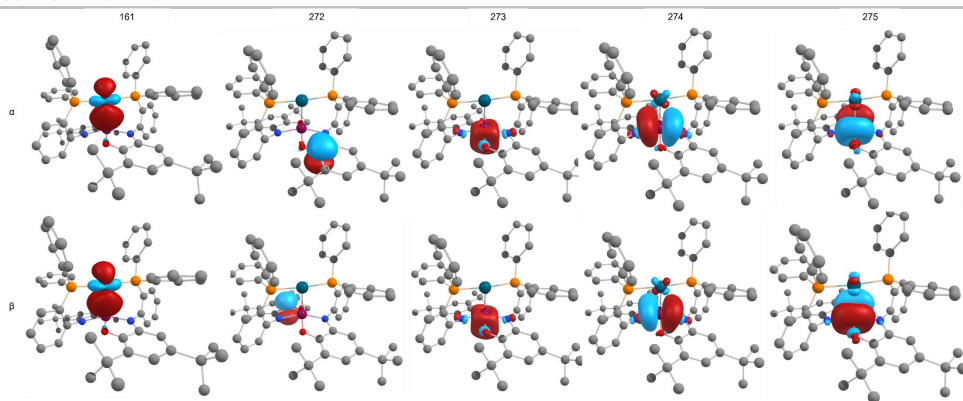


Figure S 49: Selected NBOs (BS-PBE0-D4/def2-TZVPP//PBEh-3c) of $[1]^+$, displayed at 0.05 au. Hydrogen atoms are hidden for clarity. Alpha (above) and beta orbitals are listed separately.

SUPPORTING INFORMATION

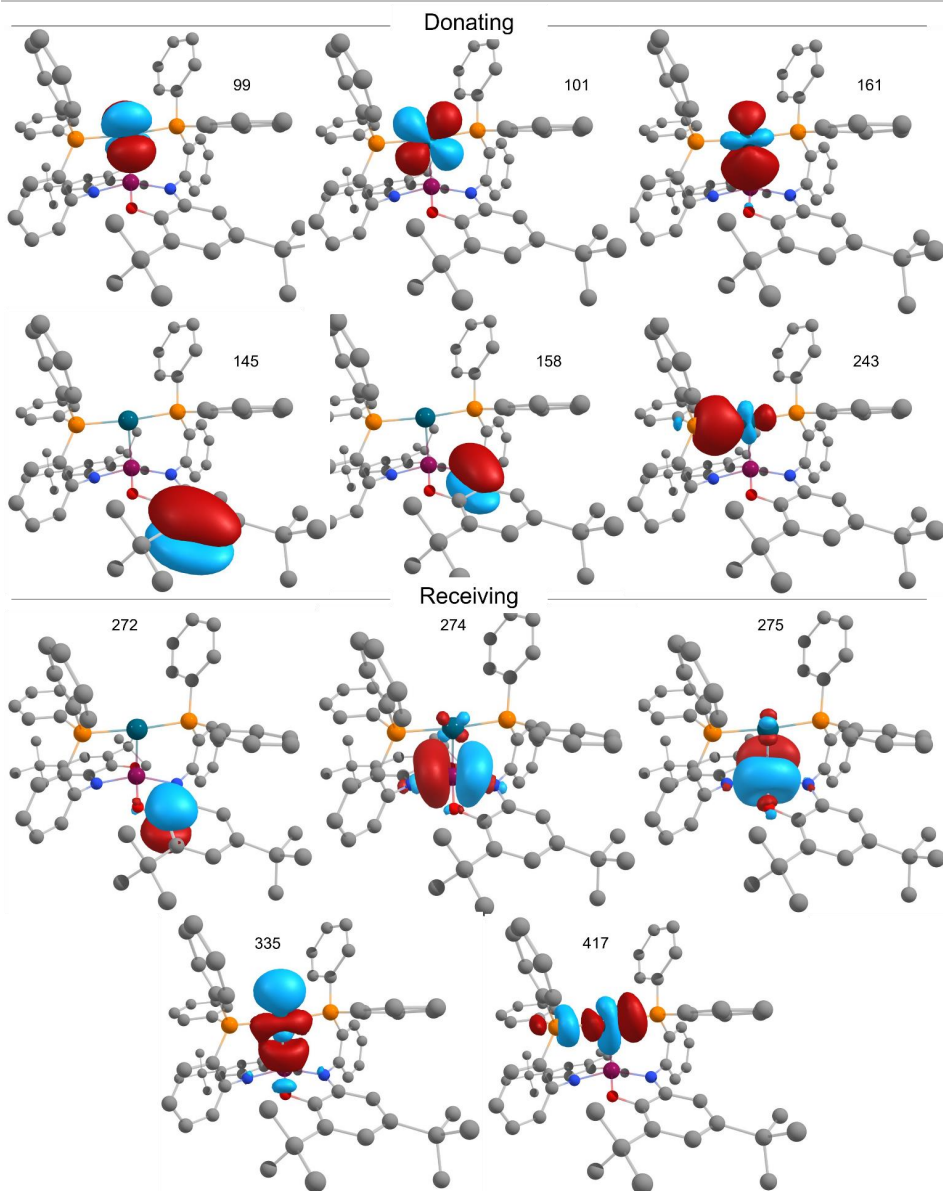


Figure S 50: Selected alpha NBOs (BS-PBE0-D4/def2-TZVPP//PBEh-3c) of $[1]^{2+}$, displayed at 0.05 au. Hydrogen atoms are hidden for clarity.

SUPPORTING INFORMATION

3. X-Ray Diffraction

a. General

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperatures with a Bruker D8 Venture diffractometer, dual source (Mo- K_α radiation, microfocus X-ray tube, Photon III detector, temperature 100 K). Data were processed with the standard Bruker (SAINT, APEX3) software package.^[21] Multiscan absorption correction was applied using the SADABS program.^[22] The structures were solved by intrinsic phasing^[23] and refined by full-matrix least-squares methods against F^2 using the SHELXTL software package (Version 2018/3).^[24] Graphical handling of the structural data during solution and refinement was performed with shelXle.^[25] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.^[26] For the structures of [TfO₂-1] and [cat^{Cl}-1] distorted co-crystallized solvent molecules were treated with the SQUEEZE procedure, as implemented in PLATON (4 *n*-pentane molecules and 1 *n*-heptane molecule respectively).^[27] Finalisation of gathered data was done using final cif tool.^[28]

For data visualization, Mercury 2020.2.0 was used.^[29] The thermal displacement ellipsoids are shown at the probability level of 50%. CCDC numbers 2382810 - 2382815 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>.

The data obtained from the scXRD analysis from crystals of [(pftb)-1][Al(pftb)4] could not be refined to a degree that an entry in the CCDC seems appropriate, due to the fact that multiple domains in the crystal render sufficient refinement of the obtained data impossible. However, the data is sufficient to underline the geometry of the compounds, as already speculated by interpretation of NMR spectroscopic data and mass spectrometry. A picture is shown in figure S49.

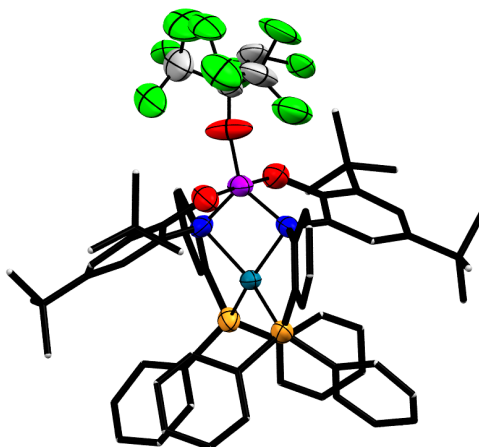


Figure S 51: Solid state structure of [(pftb)-1][Al(pftb)4], as obtained by scXRD analysis. Vibrational ellipsoids displayed at 50 % probability, hydrogen atoms, solvent molecules and the counter anion omitted for clarity. This structure is not fully refined due to the existence of a second domain in combination with poor data quality.

SUPPORTING INFORMATION

b. Structural Comparison of Pd(II) Complexes

An overview of the solid-state structures that were obtained in this work is given in figure S50. A selection of bond lengths, angles and the calculated metrical oxidation states are summarized in table S3 and table S4.

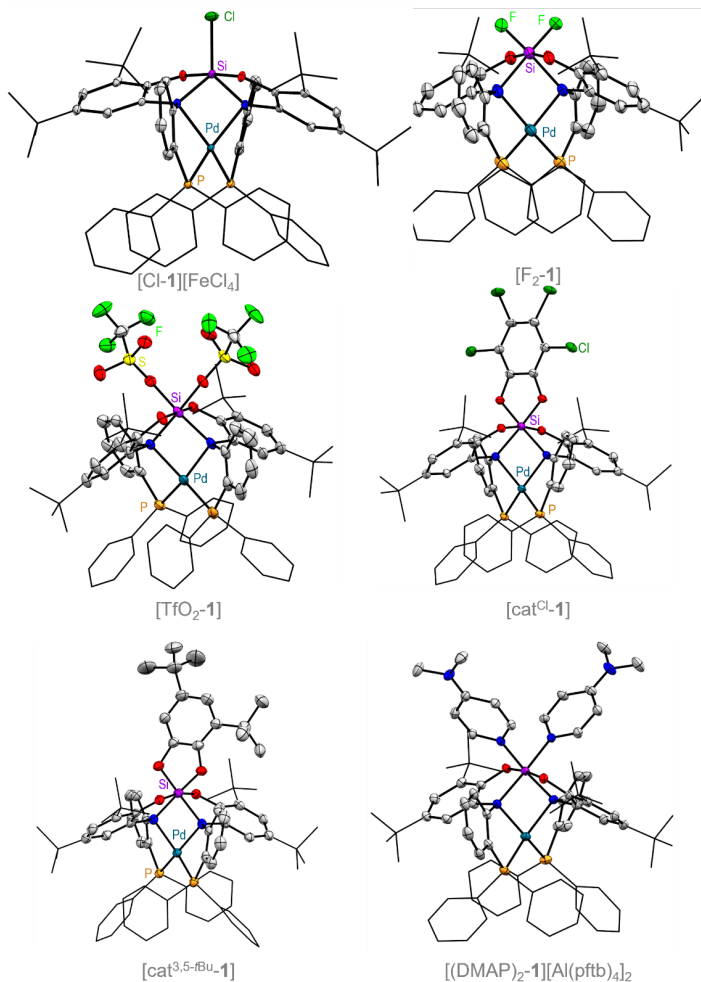


Figure S 52: Thermal ellipsoid plots of the solid-state structures discussed in this work. Ellipsoids are displayed at 50% probability, hydrogen atoms, counter anions, disordered ^tBu or Ph-groups and additional formula units within the unit cell are omitted for clarity.

SUPPORTING INFORMATION

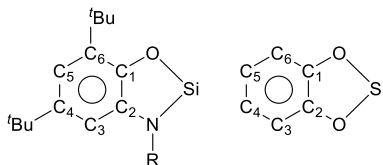
Figure S 53: Numbering scheme for the carbon atoms in amidophenolates and catecholes, as suggested by Brown.^[30]

Table S3: Bond lengths (Å), angles (°) and resulting MOS for the amidophenolato complexes synthesized in this work.

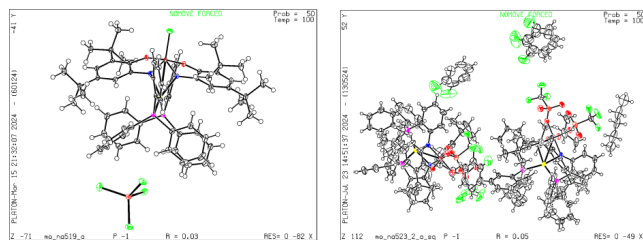
	[Cl-1][FeCl ₄]	[TfO ₂ -1]	[cat ^{Cl} -1]	[cat ^{3,5-tBu} -1]	[F ₂ -1]	[DMPAP ₂ -1][Al(pftb) ₄] ₂	[1] ²⁺ (BS-PBEh-3c)
d (Si-Pd)	2.6549(10)	2.9399(11)	2.9574(14)	2.9782(13)	3.0177(8)	2.9534(12)	2.287
d (Pd-N1)	2.1850(19)	2.104(2)	2.112(2)	2.083(3)	2.076(2)	2.111(2)	3.273
d (Pd-N2)	2.1718(19)	2.108(2)	2.104(2)	2.088(3)	2.0840(19)	2.116(3)	3.262
∠ N1-Pd-N2	87.16(7)	83.25(8)	84.52(7)	83.81(12)	83.81(8)	84.55(9)	-
∠ N1-Pd-P1	86.33(5)	87.00(6)	86.10(6)	86.32(9)	86.74(6)	88.19(7)	-
∠ N2-Pd-P2	85.48(5)	86.87(6)	86.52(6)	86.35(9)	86.09(7)	87.89(7)	-
∠ P1-Pd-P2	109.24(2)	110.49(3)	112.66(3)	113.40(4)	110.79(3)	108.93(4)	174.95
Σ ∠ X'-Pd-X''	368.21(7)	367.61(8)	369.80(7)	369.88(12)	367.43(8)	369.56(7)	-
d _{averaged} (C1-O)	1.362(3)	1.360(3)	1.352(3)	1.351(4)	1.346(3)	1.370(3)	1.316
d _{averaged} (C2-N)	1.450(3)	1.450(3)	1.447(3)	1.442(4)	1.443(3)	1.439(4)	1.332
d _{averaged} (C1-C2)	1.388(3)	1.394(3)	1.402(3)	1.399(5)	1.399(4)	1.399(4)	1.435
d _{averaged} (C2-C3)	1.390(3)	1.391(3)	1.399(3)	1.392(5)	1.391(3)	1.393(4)	1.407
d _{averaged} (C3-C4)	1.398(3)	1.396(4)	1.397(3)	1.394(5)	1.392(4)	1.397(4)	1.366
d _{averaged} (C4-C5)	1.402(3)	1.396(4)	1.407(3)	1.403(6)	1.401(4)	1.398(5)	1.433
d _{averaged} (C5-C6)	1.397(3)	1.397(4)	1.400(3)	1.392(5)	1.397(4)	1.406(4)	1.383
d _{averaged} (C6-C1)	1.400(3)	1.402(4)	1.404(3)	1.404(5)	1.399(4)	1.403(4)	1.399
MOS _{amp}	-2.16	-2.15	-2.03	-2.01	-2.02	-2.16	-1.08

Table S4: Bond lengths (Å), angles (°) and resulting MOS for the catecholato complexes synthesized in this work.

	[cat ^{Cl} -1]	[cat ^{3,5-tBu} -1]
d(C1-O)	1.337(3)	1.378(5)
d(C2-O)	1.343(3)	1.361(5)
d(C1-C2)	1.415(3)	1.381(6)
d(C2-C3)	1.378(3)	1.387(6)
d(C3-C4)	1.413(3)	1.401(6)
d(C4-C5)	1.392(4)	1.388(7)
d(C5-C6)	1.410(3)	1.399(6)
d(C6-C1)	1.383(3)	1.400(6)
MOS _{cat}	-1.90	-2.16

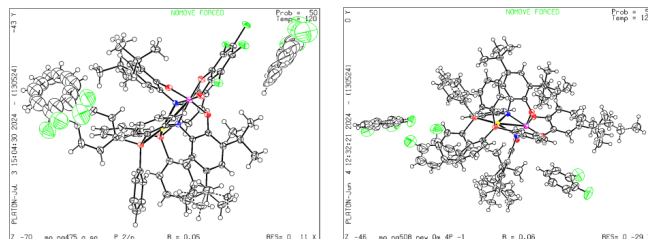
SUPPORTING INFORMATION

c. Summarized Data



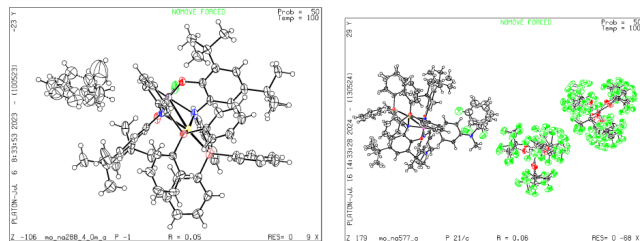
Compound CCDC number	[Cl-1][FeCl ₄] 2382813	[TfO ₂ -1] 2382815
Empirical formula	C ₆₄ H ₆₈ Cl ₅ FeN ₂ O ₂ P ₂ PdSi	C ₇₄ H ₇₆ F ₈ O ₈ N ₂ P ₂ PdS ₂ Si
Formula weight	1326.73	1552.42
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
<i>a</i> [Å]	12.819(6)	14.102(7)
<i>b</i> [Å]	15.652(6)	22.041(9)
<i>c</i> [Å]	15.883(6)	25.658(11)
α [°]	86.012(12)	91.479(13)
β [°]	82.415(19)	91.175(12)
γ [°]	78.368(14)	103.444(13)
Volume [Å ³]	3091(2)	7751(6)
<i>Z</i>	2	4
ρ_{calc} [g cm ⁻³]	1.425	1.330
μ [mm ⁻¹]	0.857	0.423
<i>F</i> (000)	1366	3204
Crystal size [mm ³]	0.87×0.09×0.06	0.21×0.15×0.11
Radiation	MoK α (λ =0.71073 Å)	MoK α (λ =0.71073 Å)
2 θ range [°]	3.63 to 52.95 (0.80 Å)	3.80 to 59.15 (0.72 Å)
Index ranges	-16 ≤ <i>h</i> ≤ 16, -19 ≤ <i>k</i> ≤ 19, -19 ≤ <i>l</i> ≤ 19	-19 ≤ <i>h</i> ≤ 19, -30 ≤ <i>k</i> ≤ 30, -35 ≤ <i>l</i> ≤ 35
Reflections collected	259944	478048
Independent reflections	12718 [<i>R</i> _{int} = 0.1015, <i>R</i> _{sigma} = 0.0337]	43499 [<i>R</i> _{int} = 0.1187, <i>R</i> _{sigma} = 0.0563]
Completeness to θ = 25.242°	99.9%	99.9 %
Data/Restraints/Parameters	12718/0/715	43499/2908/2163
Absorption correction	0.6374/0.7454	0.6765/0.7245
<i>T</i> _{min} / <i>T</i> _{max} (method)	(multi-scan)	(multi-scan)
Goodness-of-fit on <i>F</i> ²	1.1015	1.072
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0323, <i>wR</i> ₂ = 0.0824	<i>R</i> ₁ = 0.0503, <i>wR</i> ₂ = 0.1232
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0364, <i>wR</i> ₂ = 0.0850	<i>R</i> ₁ = 0.0735, <i>wR</i> ₂ = 0.1383
Largest peak/hole [e Å ⁻³]	0.90/-0.47	0.80/-1.17

SUPPORTING INFORMATION



Compound CCDC number	[cat ^C -1] 2382811	[cat ^{3,5-ib} -1] 2382810
Empirical formula	C ₈₂ H ₇₈ Cl ₄ F ₄ N ₂ O ₄ P ₂ PdSi	C _{93.78} H _{101.16} F _{4.75} N ₂ O ₄ P ₂ PdSi
Formula weight	1567.67	1607.07
Temperature [K]	120(2)	120(2)
Crystal system	monoclinic	triclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (13)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	23.414(14)	14.372(5)
<i>b</i> [Å]	14.324(10)	14.425(5)
<i>c</i> [Å]	24.782(15)	21.884(10)
α [°]	90	80.102(14)
β [°]	112.56(2)	86.004(12)
γ [°]	90	68.445(7)
Volume [Å ³]	7675(8)	4157(3)
<i>Z</i>	4	2
ρ_{calc} [g cm ⁻³]	1.357	1.284
μ [mm ⁻¹]	0.499	0.339
<i>F</i> (000)	3232	1685
Crystal size [mm ³]	0.36×0.22×0.11	0.22×0.15×0.08
Radiation	MoK α (λ =0.71073 Å)	MoK α (λ =0.71073 Å)
2 θ range [°]	4.07 to 58.45 (0.73 Å)	3.69 to 50.58 (0.83 Å)
Index ranges	−31 ≤ <i>h</i> ≤ 31, −19 ≤ <i>k</i> ≤ 19, −33 ≤ <i>l</i> ≤ 33	−17 ≤ <i>h</i> ≤ 17, −16 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 26
Reflections collected	363639	14941
Independent reflections	20582 [<i>R</i> _{int} = 0.1399, <i>R</i> _{sigma} = 0.0498]	14941 [<i>R</i> _{int} = 0.1301, <i>R</i> _{sigma} = 0.0607]
Completeness to θ = 25.242°	99.4 %	99.1 %
Data/Restraints/Parameters	20582/1557/1091	14941/1884/1245
Absorption correction	0.6142/0.6961	0.308596/0.745161
<i>T</i> _{min} / <i>T</i> _{max} (method)	(multi-scan)	(multi-scan)
Goodness-of-fit on <i>F</i> ²	1.028	1.090
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.1112	<i>R</i> ₁ = 0.0593, <i>wR</i> ₂ = 0.1265
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0606, <i>wR</i> ₂ = 0.1222	<i>R</i> ₁ = 0.0748, <i>wR</i> ₂ = 0.1316
Largest peak/hole [e Å ⁻³]	1.64/−0.94	0.77/−0.78

SUPPORTING INFORMATION



Compound CCDC number	[F ₂ -1] 2382814	[(DMAP) ₂ -1][Al(pftb) ₄] ₂ 2382812
Empirical formula	C ₇₁ H ₇₆ F ₂ N ₂ O ₂ P ₂ PdSi	C ₁₁₈ H ₉₂ Al ₂ F ₇₄ N ₆ O ₁₀ P ₂ PdSi
Formula weight	1223.76	3386.32
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	monoclinic
Space group (number)	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 ₁ /c (14)
<i>a</i> [Å]	11.6662(13)	19.424(6)
<i>b</i> [Å]	14.4607(16)	38.163(11)
<i>c</i> [Å]	19.497(2)	20.072(7)
α [°]	78.786(4)	90
β [°]	83.055(4)	115.751(11)
γ [°]	75.920(4)	90
Volume [Å ³]	3120.0(6)	13401(7)
<i>Z</i>	2	4
ρ_{calc} [g cm ⁻³]	1.303	1.678
μ [mm ⁻¹]	0.421	0.346
<i>F</i> (000)	1280	6768
Crystal size [mm ³]	0.167×0.152×0.112	0.28×0.24×0.20
Radiation	MoK α (λ =0.71073 Å)	MoK α (λ =0.71073 Å)
2 θ range [°]	3.93 to 61.38 (0.70 Å)	3.91 to 55.98 (0.76 Å)
Index ranges	-16 ≤ <i>h</i> ≤ 16, -20 ≤ <i>k</i> ≤ 20, -27 ≤ <i>l</i> ≤ 27	-25 ≤ <i>h</i> ≤ 25, -50 ≤ <i>k</i> ≤ 50, -26 ≤ <i>l</i> ≤ 26
Reflections collected	191470	697229
Independent reflections	19248 [<i>R</i> _{int} = 0.0783, <i>R</i> _{sigma} = 0.0399]	32169 [<i>R</i> _{int} = 0.0721, <i>R</i> _{sigma} = 0.0259]
Completeness to θ = 25.242°	100.0 %	99.8 %
Data/Restraints/Parameters	19248/345/808	32169/64130/3711
Absorption correction		0.6614/0.7456
<i>T</i> _{min} / <i>T</i> _{max} (method)		(multi-scan)
Goodness-of-fit on <i>F</i> ²	1.035	1.108
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0523, <i>wR</i> ₂ = 0.1245	<i>R</i> ₁ = 0.0617, <i>wR</i> ₂ = 0.1511
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0762, <i>wR</i> ₂ = 0.1410	<i>R</i> ₁ = 0.0769, <i>wR</i> ₂ = 0.1654
Largest peak/hole [e Å ⁻³]	1.39/-1.28	0.89/-0.85

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Software	-	-	-
Validation	lead	-	-
Formal analysis	lead	-	-
Investigation	lead	supporting	supporting
Resources	-	-	-
Data Curation	lead	-	-
Writing-Original Draft	equal	supporting	-
Writing-Review&Editing	equal	-	-
Visualization	lead	-	-
Supervision	equal	-	-
Project administration	equal	-	-
Funding acquisition	-	-	-

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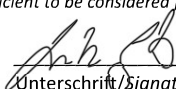

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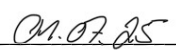
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Co-Ligand-Dependent Rh(I)–Si(IV) Interactions in Silicon Z-Type Complexes

Nils Ansmann, Jakob H. Alberts, Finn Hagen, Immanuel E. Blaum, and Lutz Greb*

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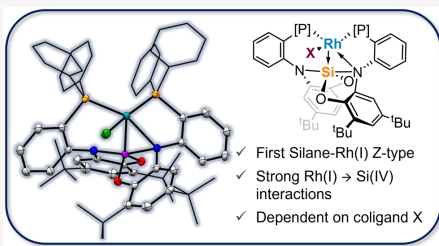
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ABSTRACT: Rh(I) Z-type complexes featuring σ -accepting group 13 Lewis acids have been well established over recent years and proven efficient in catalytic transformations. In this work, we report the isolation and characterization of the first Rh(I) silane Z-type complexes. Distinct properties compared to their group 13 counterparts are exhibited due to the high effective Lewis acidity of Si(IV), which leads to remarkably strong Rh(I)–Si(IV) bonding. The nature of this interaction is found to be highly dependent on the choice of coligands at Rh(I) (e.g., Cl, Me, Cp, H, and CNCy). Through a combination of experimental techniques and quantum chemical analyses (NBO, QTAIM, and ETS–NOCV), we systematically investigate this coligand dependency. These findings provide valuable insights into the design and optimization of catalytically active Rh(I) Z-type complexes.

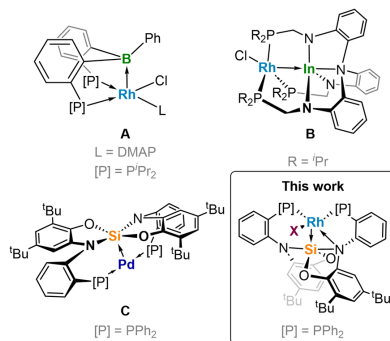


INTRODUCTION

Ambiphilic, σ -accepting Z-type ligands have developed as promising tools for tuning the electron density and reactivity of late transition metals.^{1–6} To date, Z-type chemistry is dominated by group 13 Lewis acids owing to their naturally occurring empty p -orbital.^{7–10} Group 14 based systems are less explored,^{11–15} especially for Rh(I)–Z-type chemistry.^{14–16} Pioneering work by Bourissou employed a diphosphine borane ligand for directed Rh→B interactions (Chart 1, A).^{17–19} Ozerov further studied diphosphine boranes and alanes as ambiphilic ligands for Rh(I).^{20–23} Tripodal trisphosphine group 13 Rh complexes have been reported by Nakazawa (E = B),²⁴ and the Lu group (E = Al, Ga, In).^{25,26} These systems have proven versatile in several catalytic applications, like the selective semi hydrogenation of alkynes, or the hydrodefluorination of aryl-fluorides by Rh–In complex B.^{26–29} While the relationship between Z-type interaction and catalytic activity in these complexes is not fully disclosed, systematic screening of several Rh–E combinations elucidated the most promising systems.

In contrast to group 13 elements, neutral silanes are often overlooked as Lewis acids, due to their comparably low FIAs (fluoride ion affinity); a criteria for general Lewis acidity.^{30,31} While this phenomenon can be traced back to the energy penalty caused by the large deformation energy to form the respective hyper-coordinated complex, the perturbative effect of the Lewis acidic silane on the bound Lewis base is relatively high, as evident in the Gutmann Beckett test (Δ^3P of coordinated OPeEt_3) or in structural alteration of bound substrates.^{32,33} This high effective Lewis acidity renders Si(IV)

Chart 1. Different Structural Motifs of Group 13 Rh(I)–Z-type Complexes Using Borane (A) or Indane (B) Ligands Compared to Silane-Based Z-Type Complexes of Pd (C) and Rh (This Work)



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Lewis acids as efficient catalysts in organic transformations.^{34–42} Recently, we showed that applying the concept of high effective Lewis acidity in an ambiphilic bis-(amidophenolato)silane **1** (Figure 1) for the coordination

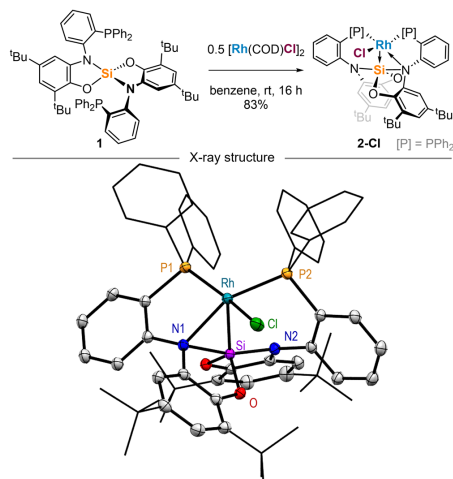


Figure 1. Synthesis of Rh(I) Z-type complex **2-Cl** and its solid-state structure (vibrational ellipsoids displayed at 50%, hydrogens and solvent molecules omitted for clarity).

chemistry of Pd(0) allows for the isolation of a neutral Pd(0) complex **C** with strong Pd→Si bonding.⁴³ This interaction was crucial for the isolation of anionic Pd(0)-ate complexes and could be further used in combination with the redox noninnocence of the amidophenolato to realize Z-type controlled Pd(0)/Pd(II) electromerism.⁴⁴ Herein we apply the concept of effective Lewis acidity to the Z-type chemistry of Rh(I), which has to date not been attempted with silane Z-type ligands. In hindsight of the catalytic application of Rh-silyl

complexes, this neglected area promises interesting advancements.^{45–52}

RESULTS AND DISCUSSION

We launched our studies by reacting two equivalents of silane **1** with the readily available [Rh(COD)Cl]-dimer (COD = 1,5-cyclooctadiene) in C₆D₆ at room temperature. Investigation of the reaction mixture after 16 h by ³¹P NMR spectroscopy revealed the selective formation of a single species with two chemically inequivalent phosphorus nuclei, resonating at 57.5 and 39.6 ppm. Each signal appeared as doublet of doublets, due to ¹J_{103Rh} (172.2/143.6 Hz) and ²J_{31P} coupling (24.6 Hz), indicating the formation of a Rh(I) complex with *cis*-oriented phosphine ligands. ²⁹Si NMR spectroscopy suggested a Rh–Si interaction, with a doublet of doublets of doublets at $\delta_{29\text{Si}} = -68.4$ ppm, reasoned by coupling to the ¹⁰³Rh nucleus as well as the two individual ³¹P nuclei through a Rh–Si bond. Indicative for Z-type complexes, this resonance is high-field shifted compared to the tetrahedral silane ($\delta_{29\text{Si}} = -44.2$ ppm).⁴³ Analysis of single crystals by X-ray diffraction (scXRD) confirmed the formation of complex **2-Cl** with a Rh–Si bond length of 2.2613(6) Å, which is significantly shorter than the Pd–Si bond in the Pd(0) complex of silane **1** (2.3707(6) Å)⁴³ (Figure 1). This Rh–Si bond is also shorter than the shortest reported Rh–Al bond in Nakao's aluminyl Rh(I) complex (2.3183(8) Å).⁵³ Most notably, the Rh→Si(IV) bond length lies in the range for typical Rh(III)-silyl (X-type) bonds (2.21–2.38 Å),⁵⁴ or the tripodal P₃Rh(I)-H-silyl system ($d_{\text{Rh} \rightarrow \text{Si}} = 2.2702(5)$ Å),⁵⁵ underlining the pronounced effect of the Z-type interaction in compound **2-Cl**. Division of the Rh–Si bond length by the sum of the covalent radii⁵⁶ results in a factor $r = 0.89$, which is significantly lower than in the bis-phosphine borane Rh(I) complex **A** (cf. $r = 1.02$)¹⁷ and slightly lower than in Rh–In complex **B**.²⁶ Interestingly, the observed value for r is also smaller than the one for the analogous neutral Pd–Si complex ($r = 0.95$),⁴³ indicating a strong Rh–Si interaction in complex **2-Cl**. The Rh center is, although expected for a d⁸ configuration, not ideally square planar coordinated by the two phosphines $\angle(\text{P} \rightarrow \text{Rh} \rightarrow \text{P}) = 105.60(2)^\circ$, the chloride and by the lone pair of one nitrogen atom of the amidophenolato (amp) ligand. This coordination mode of the amp-N1 forces the central Si atom in a sawhorse

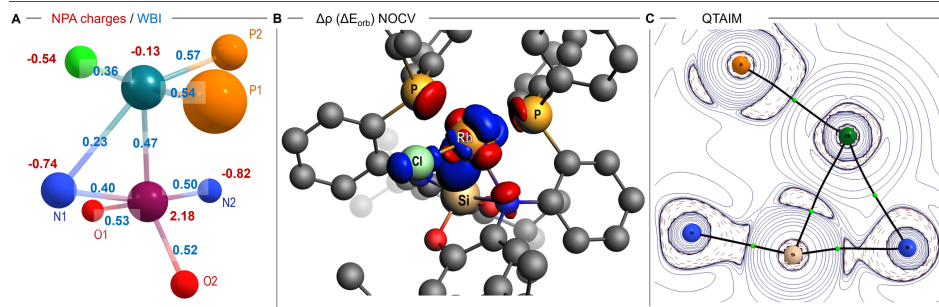


Figure 2. (A) Charges obtained by natural population analysis (NPA) and Wiberg bond indices in complex **2-Cl**, calculated at the PBE0-D4/def2-TZVPP//PBEh-3c level of theory. (B) ETS-NOCV deformation density $\Delta\rho$ ($E_{\text{orb}2}$) of the NOCV orbital corresponding to the Rh–Si interaction (charge flow from red to blue, BP86-D3BJ/TZVP//PBEh-3c). (C) View of the P2–Rh–N1–Si–N2 interaction in complex **2-Cl** as obtained by QTAIM analysis, displaying the Laplacian of the electron density, bond paths and bond critical points.

structure. Due to the N1–Rh interaction (2.1926(17) Å), the respective Si–N1 bond is elongated compared to the Si–N2 bond (1.9547(18) Å vs 1.7819(18) Å). Given the redox noninnocence of the amp backbone of **1** and its possibility for electron donation toward the Si center, we wanted to exclude a possible Si(II)→Rh interaction enabled by electromerism. The metrical oxidation states (MOS) of the amp fragments in **2-Cl** (−2.14 and −2.15) are only slightly increased compared to silane **1** (−2.29),⁴³ corroborating a Rh→Si(IV) situation. This is in contrast to complex **C**, where a minor Si(II)→Pd contribution was speculated, and can be reasoned by the altered coordination sphere at Si.⁴³ Although the synthesis of **2-Cl** and its follow up reactions were carried out under a nitrogen atmosphere, nitrogen fixation was neither observed in solution nor the solid state.

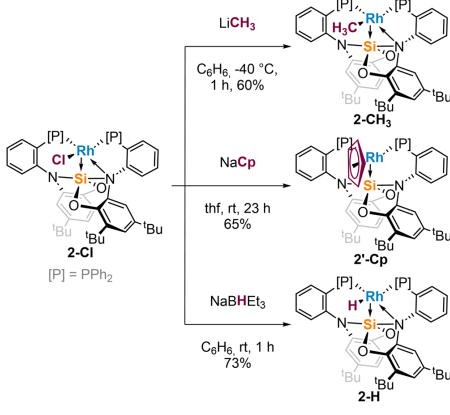
The bonding scenario in compound **2-Cl** was investigated by a series of quantum chemical calculations on the PBEh-3c optimized structures. NBO calculations at the PBE0-D4/def2-TZVPP level of theory result in a natural electron configuration of 5s (0.40), 4d (8.69) at Rh and describe the N1–Rh–Si bonding situation as a 3-center-4-electron hyperbond, with contributions of the σ (Si–N1) bond and the filled d_{z^2} -orbital of Rh. The Wiberg bond index (WBI, Figure 2A) of the Rh–Si bond is 0.47, which is slightly higher than in Pd–Si complex **C** (0.43).⁴³ In agreement with the elongated Si–N1 bond length, a reduced WBI of 0.40 was found (for comparison: WBI_{Si–N2} = 0.50). The WBI for the N1–Rh bond (0.23) is comparably low, which indicates that the ONONSi framework is intact. Natural charges obtained by natural population analysis (NPA) are in line with the expectations for a Z-type complex. Caused by the Rh→Si bonding, a diminished positive charge at Si (2.18) can be observed in **2-Cl** compared to the silane **1** (cf. 2.35),⁴³ which also is in good accordance with a slightly increased valence population of the Si center in **2-Cl** (3s (0.60), 3p (1.13)) compared to **1** (3s (0.52), 3p (1.06)).⁴³ Second-order perturbation theory analysis manifests donations of filled d-orbitals at Rh as well as the σ (Rh–P) bonds into Si-centered acceptor NBOs (see ESI section 2d). The energetically most important interaction can be described as a donation from the d_{z^2} -orbital at Rh into the empty σ^* (Si–N1) bond (86% Si, 14% N).

ETS-NOCV calculations (BP86-D3BJ/TZ2P//PBEh-3c) further shed light into the bonding situation between the Rh–Cl fragment and silane **1** in **2-Cl**. The dominant NOCV orbital (deformation density $\Delta\rho$ in Figure 2B) reflects the push–pull interaction by σ -donating PPN framework to Rh and electron flow from the d_{z^2} -orbital to the empty p_z -type orbital of the silane (see section 2c in ESI for details). QTAIM analysis of **2-Cl** reveals bond-paths between Rh and Si as well as N1 (Figure 2C). The electron density at the bond critical point between Rh and Si ($\rho(r_{\text{BCP}}(\text{Rh–Si})) = 0.0926$) is higher compared to Pd–Si complex **C** and also higher than the Si–N1 interaction $\rho(r_{\text{BCP}}(\text{Si–N1})) = 0.0869$, matching the observed WBIs. In contrast to the covalent Pd–Si interaction in **C**, a positive Laplacian $\nabla^2\rho(r_{\text{BCP}}(\text{Rh–Si}))$ indicates a closed-shell/donor–acceptor interaction instead.

After confirming the strong dative Rh(I)–Si(IV) interaction in **2-Cl** we probed the reactivity of this compound. In contrast to Pd complex **C**, reaction with nucleophiles did not resolve in the formation of silicato-complexes or binding of the nucleophile *trans* to the accepting silane. Instead, the chloride of **2-Cl** was easily replaced by transmetalation reagents

(Scheme 1). Reaction with MeLi yielded complex **2-CH₃**. Compound **2-CH₃** displayed a characteristic resonance of the

Scheme 1. Reactivity of Complex **2-Cl** towards Transmetalation Reagents



methyl group bound to the Rh in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (Figure 3A), which appears as a doublet of doublets of doublets due to $^1J_{\text{Rh-CH}_3}$ (21.8 Hz) and $^3J_{\text{Si-CH}_3}$ (63.1 and 12.0 Hz). The solid-state structure obtained by sXRD (Figure

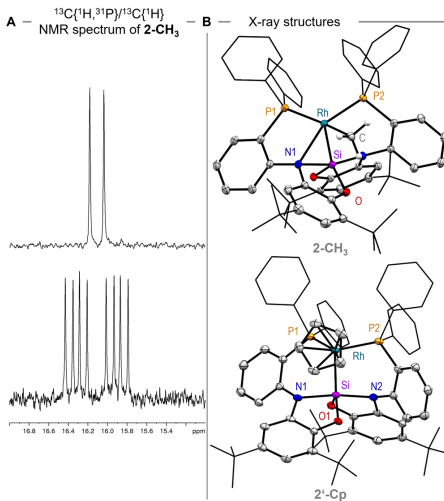


Figure 3. (A) Section of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-CH₃** with and without ^{31}P coupling. (B) Solid-state structure of **2-CH₃** and **2'-Cp** (vibrational ellipsoids displayed at 50%, hydrogens (with exception of the methyl group), disordered ^tBu and solvent molecules omitted for clarity. Only one formula unit of the asymmetric unit is shown.

3B) displays the N1–Rh–Si ring already observed for **2-Cl**, but with an even shorter Rh–Si bond ($d_{\text{Rh–Si}} = 2.2342(4)$ Å, $r = 0.88$) and a slightly elongated Rh–N1 bond ($d_{\text{Rh–N1}} = 2.1997(10)$ Å). The Rh–C1 bond ($d_{\text{Rh–C}} = 2.1299(13)$ Å) is elongated compared to Lu's Al and Ga based Rh–CH₃ Z-type complexes (2.118 Å), which at the same time display significant higher r values for the Rh–E bond (0.97 and 0.94).²⁵ The increased Rh–Si interaction is well reflected in the calculated WBI of this bond (0.50) and could be explained by additional donation of the $\sigma(\text{Rh–C})$ bond into the non-Lewis type orbitals at Si and the $\sigma^*(\text{Si–N1})$ bond, as observed by NBO calculations (see ESI section 2d), weakening the Rh–C bond while strengthening the Rh–Si bond.

2-Cl reacted with sodium cyclopentadienide (NaCp) to form complex **2'-Cp**. The ³¹P NMR resonances (26.6 and 19.0 ppm) of this complex were significantly high-field shifted compared to **2-X** ($X = \text{Cl, Me}$) with an increased ² J_{31P} coupling (36.0 Hz), indicating a different coordination environment at Rh. Similarly, the ²⁹Si NMR resonance ($\delta_{29\text{Si}} = -72.1$ ppm) was detected highfield-shifted compared to **2-X**. The solid-state structure of **2'-Cp** (Figure 3B) confirmed the assumptions. Due to the η^5 coordination of the Cp and the accompanying strong donation of electron density to the Rh-center, additional coordination by the amp-N1 is not required, resulting in a reduced P–Rh–P angle ($\angle(\text{P–Rh–P})_{\text{avg}} = 103.79(3)^\circ$). The loss of N→Rh coordination also results in an elongated Rh–Si bond ($d_{\text{avg}} = 2.4382(9)$ Å, $r = 0.96$). In solution, the Cp ring rotates around its C₅ axis, as indicated by a single resonance in the ¹H and ¹³C{¹H} NMR spectra.

To elucidate the electronic changes that are accompanied by the altered coordination environment at Rh, we further analyzed **2'-Cp** by means of NBO and QTAIM analysis. While no significant change of natural charges or WBIs was observed in the P–Rh–P fragment, the Rh–Si interaction is different. Its WBI is reduced (0.43), which is line with the elongated Rh–Si bond, while the positive natural charge at Si (2.07) is diminished compared to **2-Cl**. At the same time, the electron density at the bond critical point is reduced ($\rho_{\text{RCP}}(\text{Rh–Si}) = 0.0848$), while in contrast to **2-Cl**, its negative Laplacian and the other QTAIM parameters indicate a more covalent character for this interaction. The WBIs of the Si–O and Si–N2 interactions are slightly diminished compared to **2-Cl** (0.41–0.47, see section 2d in ESI), which is in line with the increased Si–N2 bond length ($d_{\text{avg}} = 1.869(2)$ Å). Interestingly the WBI of the Si–N1 bond remains unchanged, although the Si–N1 bond is shortened compared to **2-Cl** ($d_{\text{avg}} = 1.881(3)$ Å), reflecting the symmetrized Si(amp)₂ coordination environment. Still, the S–Nx bond lengths are significantly elongated compared to free silane **1** ($d_{\text{avg}} = 1.7192(14)$ Å),⁴³ underlining the electron donating nature of the Rh(I)→Si(IV) interaction. Second order perturbation analysis underlined the beneficial influence of the altered geometry for covalent interaction, since the $\text{dz}^2 \rightarrow \text{LV}(\text{Si})$ donation is significantly more pronounced compared to **2-Cl**, possibly due to the geometry-caused altered directionality of the interaction. Overall, this comparison underlines the substantial impact of the coligand on the Rh–Si Z-type interaction.

2-Cl reacted with sodium triethylborohydride to form hydride complex **2-H**, as evident by a high-field shifted hydride resonance at $\delta_{\text{1H}} = -6.40$ ppm, which splits into a doublet of doublets of doublets (Figure 5B), the same coupling pattern observed for the ¹³C resonance of **2-CH₃**. The Rh–H

vibration was observed by IR spectroscopy ($\tilde{\nu} = 1914$ cm^{−1}). Although no solid-state structure of **2-H** was obtained, all acquired spectroscopical data suggest a geometry similar to the one of **2-Cl**. This is also in line with the DFT-optimized geometry (PBEh-3c, see ESI section 2b). **2-H** did not undergo reaction with N₂ and CO, and neither with CO₂, a substrate well-known for its reactivity toward metal-hydrides.^{57,58} Against intuition, **2-H** did also not react with the unsaturated C=C bond in styrene, even at elevated temperatures (90 °C). The inertness of **2-H** could be explained by a stabilization of the Rh–H bond due to the electron-accepting Z-type interaction accompanied by its inability to interact with unsaturated substrates by π -back-bonding. This is supported by an increased WBI for the Rh–Si interaction in **2-H** (0.50), a calculated very short Rh–Si bond length ($d_{\text{DFT}} = 2.2136$ Å) and strong interaction of the Rh–H bond and the non-Lewis type accepting orbitals at Si in addition to Rh(4d)→Si donation. This stabilization is further supported by a WBI between the hydride H and Si (0.12). These interactions are even stronger than in complex **2-CH₃**, which could be reasoned by the different characteristics of the Rh–X bonds, allowing better overlapping with Si centered orbitals (see Figures S6 and S10). Comparison of the computational features with a model Rh hydride complex [HRh(PPh₃)(PNOMe₂)] further underlines the stabilizing effect of the Z-type interaction. Natural charges at Rh (−0.41) and the hydride (−0.22) in the model compound are significantly more negative compared to **2-H** (−0.29 and −0.08 respectively). Additionally, the occupation of the NBO characterizing the Rh–H bond is lowered by the Z-type interaction in **2-H** (1.68 vs 1.84), indicating decreased reactivity (see section 2d in ESI).

However, the stability of **2-H** is limited, since the more reactive phenyl-acetylene readily inserted in the Rh–H bond at room temperature, quantitatively forming the respective E-product **2-C₂H₂Ph**, as observed by NMR spectroscopy and scXRD analysis (Figure 4). This difference in reactivity compared to CO or alkenes could eventually be explained by a necessity of significant bond activation through π -interactions with the metal in order to undergo the hydride insertion for these particular substrates.

Since **2-Cl** did not react with substrates that rely on π -interactions for bonding, we probed whether it reacted with strong σ -donors. While most phosphines and NHCs are too bulky to approach the Rh center, isocyanides were regarded as promising candidates (Scheme 2). Indeed, **2-Cl** reacted with cyclohexyl isocyanide at room temperature, but addition of two equivalents was necessary to observe full consumption of the starting material. NMR spectroscopy of the bis-isocyanide complex **3-Cl** revealed the formation of a species with increased symmetry, given the observation of a single ³¹P NMR resonance with ² $J_{\text{103Rh–31P}}$ coupling (119.3 Hz), indicating a C₂ symmetric complex.

Insights into the altered geometry of **3-Cl** was given by its solid-state structure, obtained by scXRD analysis (Figure 5A). Two CNCy coordinate *trans* to each other at the Rh center, resulting in a reorientation of the chemically equivalent phosphines *cis* to CNCy. The chloride is oriented *trans* to Si, as already observed in anionic Pd(0) complexes of this ligand.⁴³ With the coordination environment at the Rh-center being reminiscent of Rh(III) complexes, we calculated the MOs of the amp-ligands to rule out the plausible description of a Si(II)→Rh(III) interaction in **3-Cl**. While indeed slightly

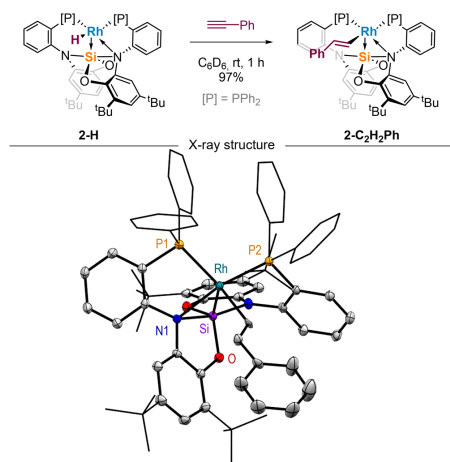
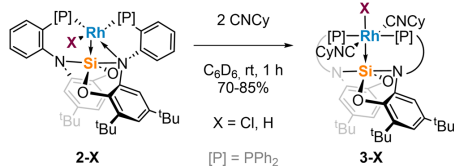


Figure 4. Reactivity of 2-H with alkynes including the solid-state structure of 2-C₂H₂Ph (vibrational ellipsoids displayed at 50%, hydrogens, disordered ^tBu, Ph, and C₂H₂Ph groups omitted for clarity).

Scheme 2. Reactivity of 2-X towards Cyclohexyl Isocyanide



increased MOSs can be observed in comparison to 2-Cl or 2'-Cp, the values of -1.97 and -1.94 still strongly support the formulation as a Rh(I)→Si(IV) complex, similar to Pd complex C (cf. MOS = -1.92).⁴³ The Rh–Si bond is elongated compared to complex 2-Cl ($d = 2.4272(12)$ Å; $r = 0.96$), but is comparable to 2'-Cp, which also does not show coordination of N1 to Rh. Furthermore, the Si–Nx bond lengths in 3-Cl ($d_{\text{Si-Nx}} = 1.871(3)$ Å, $1.853(3)$ Å) are not only similar to each other, but are also reminiscent of the observed bond lengths in 2'-Cp. The similarity of the Rh→Si interactions in complexes 2'-Cp and 3-Cl is further underlined by similar bonding characteristics, as determined by QTAIM analysis (Table S7). The increased covalency of the Rh–Si bond ($\nabla^2\rho(r_{\text{BCP}}(\text{Rh-Si})) = -0.121$) could be a consequence of the parallel orientation of the involved orbitals.

As anticipated for a Z-type complex, no π -back-bonding from Rh to the π^* orbitals at the isocyanides can be observed. The CN stretching band in the IR spectrum of 3-Cl is blue-shifted compared to free CNCy (2184 cm^{-1} vs 2136 cm^{-1}),⁴³ which is an effect already observed for Pd complex C-CNCy. This also reflects in the CN bond distance ($d_{\text{avg}} = 1.150(4)$ Å), which matches the bond distance in C-CNCy in the margins of error.⁴³

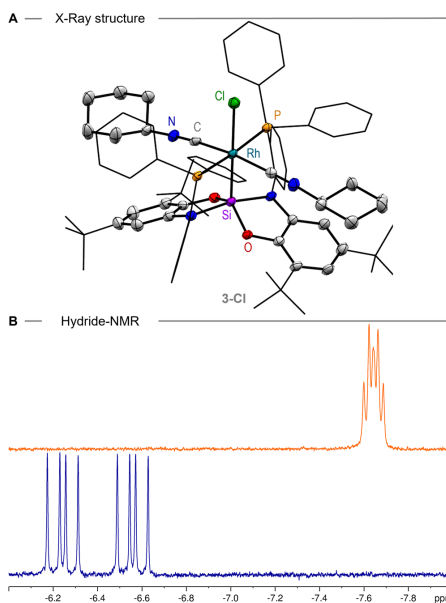


Figure 5. (A) Solid-state structure of 3-Cl (vibrational ellipsoids displayed at 50%, hydrogens, disordered ^tBu or Cy groups and solvent molecules omitted for clarity). (B) Sections of the ¹H NMR spectra (400 MHz, 295 K, C₆D₆) of hydride complexes 3-H (orange) and 2-H (blue).

The observed reactivity of 2-Cl toward isocyanides can also be applied to 2-H. The spectroscopic data of 3-H is in line with an octahedral Rh center and a hydride *trans* to Si, as most prominently seen in the coupling of the hydride resonance in the ¹H NMR spectrum, which in contrast to 2-H splits into a stacked doublet of triplets due to the chemically equivalent phosphines (Figure 5B). Interestingly, the altered geometry results in a destabilization of the hydride, rendering its isolation difficult. This could be explained by the inability to efficiently transfer the increased electron density to the Lewis acidic center and is reflected in the increased negative charges (calculated by NPA) at the hydride and Rh (-0.27 and -0.32), accompanied by a weakened WBI of the Rh–H bond (0.26 , cf. 2-H, $\text{WBI}_{\text{Rh-H}} = 0.48$). The weakened Rh–H bond is presumably also a consequence of the competing d_{z^2} →LV(Si) bonding.

CONCLUSION

In conclusion, we have reported the synthesis and characterization of a series of Rh(I) Z-type complexes, using an ambiphilic silane ligand. These complexes represent, to the best of our knowledge, the first examples of Rh(I) silane Z-type complexes and expand the thriving field of Rh Z-type chemistry, which was predominantly based on group 13 based Lewis acids. The high effective Lewis acidity of silanes, as observed by theoretical and experimental methods, results in strong Rh→Si interactions, which are significantly stronger

than in previously reported systems, even matching Rh–silyl (X-type) interactions. Due to the resulting stabilization of the Rh center, it does not undergo π -back-bonding with substrates, and even reactive Rh hydride species are tamed. Hence, this study sheds light into how Rh–Si Z-type interaction control the reactivity of coligands, and in turn, how the coligands alter the Z-type bonding. Especially, X-type ligands with high s-orbital contributions stabilize the Rh–Si interaction, when located *cis* to the Rh–Si bond. Based on these results, Z-type Rh(I) systems for catalysis should be carefully designed: The Rh–Z-type interaction should not exceed a certain level or otherwise drastic stabilization of intermediates in the catalytic cycle is risked, inhibiting conversion toward the desired products.

EXPERIMENTAL SECTION

General Remarks. All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame-dried glassware or by working in a glovebox (Sylatche Glovebox) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å respectively 4 Å). Argon was dried by passing over two columns of phosphorus pentoxide. Commercially available chemicals were used as received. Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane **1** was synthesized according to literature known procedures.⁴³ All NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All heteronuclear spectra were obtained with ¹H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ¹H and ¹³C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants *J* in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion. Overlapping signals with indistinct shapes are described as *m* = multiplet. All NMR-spectra were processed with Bruker TopSpin 4.3.0. ESI-MS spectra were measured on a Bruker ApexQe FT-ICR instrument, while LIFDI-MS spectra were measured on a JEOL AccuTOF GCx instrument. Elemental analysis (C, H, N) was measured on an Elementar vario MICRO Cube machine. IR spectra were recorded on an Agilent Cary 630 spectrometer equipped with diamond ATR units inside a nitrogen filled glovebox. Plots were generated using OriginPro 2024.

Synthesis of Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-chlorido Rhodium (2-Cl). An orange solution of **1** (500 mg, 506 μ mol, 1.01 equiv) and [Rh(COD)Cl]₂ (124 mg, 751 μ mol, 0.50 equiv) in benzene (50 mL) was stirred at room temperature overnight. The resulting red/orange suspension was condensed to dryness, yielding the target complex as an orange powder, which was further washed with *n*-pentane (3 $\times$ 5 mL) and dried *in vacuo* (470 mg, 444 μ mol, 83%). ¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.14–8.12 (m, 1H), 8.06–8.04 (m, 2H), 7.92–7.86 (m, 3H), 7.39–7.35 (m, 2H), 7.33 (s, 2H), 7.24–7.21 (m, 1H), 7.14–7.09 (m, 3H), 7.05–6.92 (m, 8H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.62 (t, *J* = 7.5 Hz, 1H), 6.51–6.48 (m, 3H), 6.41–6.38 (m, 2H), 6.30–6.27 (m, 2H), 1.54 (s, 9H), 1.47 (s, 9H), 1.27 (s, 9H), 0.95 (s, 9H); ¹³C{¹H}(³¹P) NMR (151 MHz, C₆D₆, 295 K) δ [ppm] = 156.5 (s, C_q), 147.4 (s, C_q), 144.6 (s, C_q), 142.4 (s, C_q), 141.4 (d, *J* = 34.7 Hz, C_q), 138.4 (s, C_q), 138.0 (s, CH), 134.8 (s, C_q), 134.3 (s, C_q), 133.6 (s, C_q), 133.3 (s, CH), 132.8 (s, CH), 132.4 (s, CH), 132.0 (s, CH), 131.5 (d, *J* = 2.1 Hz, C_q), 131.3 (d, *J* = 15.4 Hz, CH), 131.1 (s, C_q), 130.3 (d, *J* = 11.7 Hz, CH), 123.0 (s, CH), 123.0 (s, C_q), 128.7 (s, CH), 128.4 (s, CH), 128.1 (s, CH), 127.6 (s, C_q), 127.4 (s, C_q), 127.3 (s, CH), 127.2 (s, CH), 127.0 (d, *J* = 10.5 Hz, CH), 127.0 (s, CH), 126.2 (s, CH), 125.5 (d, *J* = 3.4 Hz, C_q), 125.1 (s, C_q), 123.7 (s, CH), 121.9 (s, CH), 120.9 (s, CH), 117.9 (s, CH), 115.7 (s, CH), 111.1 (s, CH), 102.6 (s, CH), 77.4 (d, *J* = 14.2 Hz, CH), 34.0 (s, C_q), 33.8 (s, C_q), 33.6 (s, C_q), 33.1 (s, C_q), 31.1 (s,

CH₃), 30.8 (s, CH₃), 28.9 (s, CH₃), 28.8 (s, CH₃); ³¹P{¹H} NMR (243 MHz, C₆D₆, 295 K) δ [ppm] = 57.5 (dd, *J* = 143.6 Hz, 24.6 Hz, 1P), 39.6 (dd, *J* = 172.2 Hz, 24.6 Hz, 1P); ²⁹Si (IG) NMR (119 MHz, C₆D₆, 295 K) δ [ppm] = –68.4 (ddd, *J* = 22.4 Hz, 7.3 Hz, 6.9 Hz); HR-MS (ESI⁺): [M+Na]⁺, calcd.: 1147.3616, found: 1147.3165; Anal. Calcd for C₆₄H₆₈ClN₂O₂P₂SiRh: C, 68.29; H, 6.09; N, 2.49 found: C, 67.16; H, 5.99; N, 2.77.

Synthesis of Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-methyl Rhodium (2-CH₃). An orange solution of **2-Cl** (100 mg, 88.8 μ mol, 1.00 equiv) in 5 mL of toluene was cooled to –40 °C, before MeLi (1.6 M in Et₂O, 56.1 μ L, 89.7 μ mol, 1.01 equiv) was added, followed by 0.5 mL of Et₂O. The red reaction mixture was stirred while warming to room temperature for 1 h, before it was condensed to dryness under reduced pressure. The residue was washed with 2 $\times$ 2 mL of *n*-pentane to remove impurities, before it was extracted with benzene (4 mL). The extract was filtered through a syringe filter, before lyophilization yielded the target compound as a beige solid (59.0 mg, 53.4 μ mol, 60%). ¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.16 (dd, *J* = 7.6 Hz, 5.0 Hz, 1H), 7.90–7.87 (m, 2H), 7.84 (dd, *J* = 8.3 Hz, 4.8 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 2.1 Hz, 1H), 7.31–7.28 (m, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.23 (dd, *J* = 11.4 Hz, 7.4 Hz, 2H), 7.19–7.17 (m, 1H), 7.14–7.11 (m, 1H), 7.06–7.01 (m, 4H), 6.95 (t, *J* = 7.3 Hz, 2H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.82–6.79 (m, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.59–6.56 (m, 2H), 6.50 (t, *J* = 7.4 Hz, 1H), 6.45 (t, *J* = 7.2 Hz, 2H), 6.36 (t, *J* = 7.1 Hz, 2H), 1.50 (s, 9H), 1.47 (s, 9H), 1.28 (s, 9H), 0.99 (s, 9H), 0.54 (pseudo-t, *J* = 3.9 Hz, 3H); ¹³C{¹H}(³¹P) NMR (151 MHz, C₆D₆, 295 K) δ [ppm] = 160.6 (s, C_q), 148.2 (s, C_q), 146.9 (s, C_q), 144.0 (s, C_q), 142.6 (s, C_q), 142.1 (s, C_q), 139.3 (s, C_q), 138.3 (s, CH), 136.5 (s, C_q), 135.8 (s, C_q), 135.4 (s, CH), 134.4 (s, CH), 134.3 (s, CH), 134.1 (s, CH), 133.5 (s, CH), 132.5 (s, CH), 131.7 (s, CH), 131.3 (s, CH), 131.2 (s, CH), 131.0 (s, C_q), 130.9 (s, CH), 130.3 (s, CH), 130.3 (s, C_q), 130.3 (s, C_q), 129.4 (s, CH), 128.9 (s, CH), 128.8 (s, CH), 128.6 (s, CH), 128.4 (s, CH), 128.4 (s, CH), 128.3 (s, CH), 128.3 (s, CH), 127.2 (s, CH), 126.7 (s, C_q), 123.8 (s, CH), 122.7 (s, CH), 122.2 (s, CH), 118.2 (s, CH), 117.1 (s, CH), 112.0 (s, CH), 103.2 (s, CH), 35.2 (s, C_q), 35.0 (s, C_q), 34.8 (s, C_q), 34.3 (s, C_q), 32.3 (s, CH₃), 32.0 (s, CH₃), 30.1 (s, CH₃), 29.8 (s, CH₃), 16.1 (d, *J* = 21.8 Hz, CH₃); ³¹P{¹H} NMR (243 MHz, C₆D₆, 295 K) δ [ppm] = 47.1 (dd, *J* = 199.9 Hz, 17.5 Hz, 1P), 44.2 (dd, *J* = 100.9 Hz, 17.3 Hz, 1P); ²⁹Si (IG) NMR (119 MHz, C₆D₆, 295 K) δ [ppm] = –67.7 (ddd, *J* = 34.6 Hz, 7.4 Hz, 7.2 Hz); MS (LIFDI⁺): [M]⁺, calcd.: 1104.38, found: 1104.45; Anal. Calcd for C₆₅H₇₁N₂O₂P₂SiRh: C, 70.64; H, 6.48; N, 2.53 found: C, 70.85; H, 6.71; N, 2.51.

Synthesis of Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-cyclopentadienyl Rhodium (2-Cp). In a J. Young NMR tube, to an orange solution of **2-Cl** (30.0 mg, 26.7 μ mol, 1.00 equiv) in 1 mL of thf was added a solution of NaCp (2 M in thf, 16.0 μ L, 32.0 μ mol, 1.20 equiv) and a few drops of C₆D₆ to monitor the reaction via NMR spectroscopy. The dark red solution was shaken for 20 h at room temperature, after which NMR spectroscopy indicated 80% conversion of the starting material. Subsequently, more NaCp was added (2 M in thf, 6.00 μ L, 12.0 μ mol, 0.45 equiv) in two portions and the mixture reacted at room temperature for additional 3 h, before NMR spectroscopy indicated full conversion. The reaction was condensed to dryness and the brown residue was washed with 2 $\times$ 1.5 mL of *n*-pentane to remove impurities, before it was extracted with benzene (1.5 mL). The extract was filtered through a syringe filter, before lyophilization yielded the target compound as a red-brown powder (20.1 mg, 17.4 μ mol, 65%). ¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.48 (dd, *J* = 7.8 Hz, 4.7 Hz, 1H), 8.22 (t, *J* = 7.3 Hz, 1H), 7.87 (broad, s, 2H), 7.69 (t, *J* = 8.7 Hz, 2H), 7.65–7.63 (m, 2H), 7.37 (t, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 1.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.19–7.17 (m, 1H), 7.13 (broad, 2H), 7.09–7.06 (m, 1H), 7.02–6.99 (m, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 6.97–6.92 (m, 4H), 6.85 (d, *J* = 1.3 Hz, 1H), 6.78 (dd, *J* = 11.7 Hz, 8.2 Hz, 2H), 6.54 (t, *J* = 7.4 Hz, 1H), 6.47 (t, *J* = 7.1 Hz, 1H), 6.40 (t, *J* = 7.3 Hz, 1H), 6.32 (t, *J* = 7.4 Hz, 2H), 6.18 (t, *J* = 6.5 Hz, 2H), 4.93 (s, 5H), 1.55 (s, 9H), 1.46 (s, 9H), 1.36 (s, 9H), 1.16 (s, 9H); ¹³C{¹H}(³¹P)

NMR (151 MHz, C_6D_6 , 295 K) δ [ppm] = 153.2 (s, C_q), 151.9 (s, C_q), 147.0 (s, C_q), 145.3 (s, C_q), 143.8 (s, C_q), 142.1 (s, C_q), 141.3 (s, C_q), 140.3 (s, C_q), 140.3 (s, C_q), 138.5 (s, C_q), 136.3 (s, CH), 135.1 (s, CH), 133.6 (s, C_q), 133.4 (s, CH), 133.1 (s, CH), 132.9 (s, C_q), 132.2 (s, C_q), 131.9 (s, CH), 131.9 (s, CH), 131.6 (s, C_q), 130.2 (s, C_q), 130.2 (s, CH), 130.1 (s, CH), 129.9 (s, CH), 129.4 (s, CH), 129.2 (s, CH), 128.0 (s, CH), 127.9 (s, CH), 127.9 (s, CH), 127.8 (s, CH), 127.6 (s, CH), 127.0 (s, CH), 123.1 (s, CH), 122.0 (s, CH), 118.8 (s, CH), 113.4 (s, C_q), 112.7 (s, CH), 111.6 (s, CH), 105.3 (s, CH), 103.0 (s, CH), 96.7 (s, Cp-CH), 35.0 (s, C_q), 35.0 (s, C_q), 34.9 (s, C_q), 34.5 (s, C_q), 32.5 (s, CH_3), 32.3 (s, CH_3), 30.3 (s, CH_3), 30.0 (s, CH_3); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6 , 295 K) δ [ppm] = 26.6 (dd, J = 177.6 Hz, 36.0 Hz, 1P), 19.0 (dd, J = 158.1 Hz, 36.0 Hz, 1P); ^{29}Si (IG) NMR (119 MHz, C_6D_6 , 295 K) δ [ppm] = -72.1 (ddd, J = 20.8 Hz, 16.2 Hz, 6.5 Hz); MS (LIFDI): $[M]^+$, calcd.: 1154.40; found: 1154.47; Anal. Calcd for $C_{69}H_{73}N_2O_2P_2SiRh$: C, 71.74; H, 6.37; N, 2.42 found: C, 71.56; H, 6.38; N, 2.47.

Synthesis of Bis(2,4-di-tert-butyl-(2-diphenylphosphanyl)amido)-phenolato)silane-hydrido Rhodium (2-H). To a solution of 2-Cl (92.0 mg, 81.7 μ mol, 1.00 equiv) in benzene (2 mL), $n-BuEt_3$ (1 M in toluene) (81.7 μ L, 81.7 μ mol, 1.00 equiv) was added, resulting in gas evolution, precipitation and a color change from orange to brown. The suspension was filtered through a syringe filter and the filtrate was condensed to dryness to give 2-H as a brown solid (65.3 mg, 59.8 μ mol, 73%). 1H NMR (600 MHz, C_6D_6 , 295 K) δ [ppm] = 8.08 (ddd, J = 8.1 Hz, 5.1 Hz, 1.2 Hz, 1H), 7.77–7.74 (m, 2H), 7.70 (ddd, J = 8.6 Hz, 4.6 Hz, 1.1 Hz, 1H), 7.47 (dd, J = 11.6 Hz, 8.2 Hz, 1.4 Hz, 2H), 7.39 (d, J = 2.2 Hz, 1H), 7.33 (d, J = 2.3 Hz, 1H), 7.30–7.23 (m, SH), 7.08–7.05 (m, 1H), 7.01–6.96 (m, 1H), 6.93–6.90 (m, 5H), 6.78–6.72 (m, 6H), 6.70–6.67 (m, 1H), 6.60–6.54 (m, 3H), 6.36 (td, J = 7.9 Hz, 2.1 Hz, 2H), 1.55 (s, 9H), 1.49 (s, 9H), 1.22 (s, 9H), 0.95 (s, 9H), -6.40 (ddd, J = 126.0 Hz, 33.1 Hz, 2.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6 , 295 K) δ [ppm] = 159.3 (s, C_q), 146.7 (s, C_q), 146.5 (s, C_q), 143.2 (s, C_q), 142.6 (s, C_q), 140.8 (s, C_q), 140.6 (s, C_q), 138.7 (s, C_q), 135.9 (s, C_q), 135.3 (s, CH), 134.1 (s, CH), 133.5 (d, J = 1.5 Hz, C_q), 133.2 (s, C_q), 133.0 (s, C_q), 133.0 (s, CH), 132.4 (s, CH), 131.3 (s, C_q), 131.2 (s, CH), 130.6 (s, CH), 130.1 (s, CH), 129.7 (s, CH), 129.4 (s, CH), 129.3 (d, J = 3.0 Hz, C_q), 129.0 (s, CH), 128.1 (d, J = 3.0 Hz, C_q), 128.1 (s, CH), 127.8 (d, J = 3.0 Hz, CH), 127.5 (s, CH), 127.4 (d, J = 3.0 Hz, C_q), 127.3 (s, CH), 127.0 (s, CH), 126.4 (s, CH), 124.5 (s, C_q), 122.9 (s, CH), 121.7 (s, CH), 121.4 (s, CH), 116.9 (s, CH), 115.2 (s, CH), 110.5 (s, CH), 101.7 (s, CH), 34.2 (s, C_q), 33.8 (s, C_q), 33.5 (s, C_q), 33.1 (s, C_q), 31.2 (s, CH_3), 30.8 (s, CH_3), 28.9 (s, CH_3), 28.7 (s, CH_3); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6 , 295 K) δ [ppm] = 43.0 (dd, J = 115.3 Hz, 15.7 Hz, 1P), 38.4 (dd, J = 180.1 Hz, 15.8 Hz, 1P); ^{29}Si (IG) NMR (119 MHz, C_6D_6 , 295 K) δ [ppm] = -67.1 (ddd, J = 35.4 Hz, 8.6 Hz, 4.4 Hz); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3054 (vw), 2948 (w), 2900 (w), 2862 (w), 1914 (w), 1578 (w), 1561 (vw), 1477 (w), 1462 (m), 1434 (m), 1416 (m), 1389 (w), 1358 (w), 1339 (vw), 1297 (w), 1282 (w), 1267 (w), 1220 (m), 1200 (w), 1157 (vw), 1127 (vw), 1110 (vw), 1094 (w), 1026 (w), 997 (m), 955 (w), 939 (w), 914 (w), 871 (m), 845 (w), 788 (w), 738 (w), 690 (m), 676 (m), 656 (w); MS (LIFDI): $[M]^+$, calcd.: 1090.3659; found: 1090.4135; Anal. Calcd for $C_{64}H_{69}N_2O_2P_2SiRh$: C, 70.45; H, 6.37; N, 2.57 found: C, 70.11; H, 6.63; N, 2.63.

Synthesis of Bis(2,4-di-tert-butyl-(2-diphenylphosphanyl)amido)-phenolato)silane-ethenylbenzeneyl Rhodium (2- C_6H_5 Ph). In a J. Young NMR tube, 2-H (13.5 mg, 12.4 μ mol, 1.00 equiv) and phenylacetylene (1.50 μ L, 13.7 μ mol, 1.10 equiv) were dissolved in C_6D_6 . After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting solid was dried *in vacuo* overnight to give 2- C_6H_5 Ph as a brown solid (14.1 mg, 12.0 μ mol, 97%). 1H NMR (600 MHz, C_6D_6 , 295 K) δ [ppm] = 8.17 (ddd, J = 8.1 Hz, 5.0 Hz, 1.2 Hz, 1H), 7.99–7.96 (m, 2H), 7.86–7.81 (m, 3H), 7.59 (ddd, J = 16.4 Hz, 12.7 Hz, 6.6 Hz, 1H), 7.40–7.37 (m, 2H), 7.29–7.26 (m, 4H), 7.17–7.16 (m, 4H), 7.10 (dd, J = 8.4 Hz, 7.1 Hz, 1.4 Hz, 1H), 7.06 (d, J = 2.2 Hz, 1H), 7.02–6.98 (m, 4H), 6.95–6.86 (m, 4H), 6.80–6.77 (m, 3H), 6.67 (tq, J = 7.4 Hz, 1.5 Hz, 1H), 6.57 (dd, J = 11.6 Hz, 6.2 Hz, 2H), 6.52 (td, J = 7.3 Hz, 1.6 Hz,

1H), 6.44 (td, J = 7.5 Hz, 2.2 Hz, 2H), 6.39 (dt, J = 7.5 Hz, 4.1 Hz, 2H), 6.01 (ddd, J = 16.5 Hz, 7.7 Hz, 1.6 Hz, 1H), 1.48 (s, 9H), 1.29 (s, 9H), 1.25 (s, 9H), 1.00 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6 , 295 K) δ [ppm] = 161.71 (d, J = 28.7 Hz, CH), 158.7 (s, C_q), 146.5 (s, C_q), 146.5 (s, C_q), 142.8 (s, C_q), 140.9 (s, C_q), 140.6 (s, C_q), 139.1 (s, C_q), 138.4 (s, C_q), 137.0 (s, CH), 135.0 (s, C_q), 134.4 (s, CH), 134.2 (s, CH), 133.3 (s, C_q), 133.2 (s, CH), 132.3 (s, C_q), 132.1 (s, CH), 132.0 (s, CH), 131.6 (s, CH), 130.6 (s, CH), 129.9 (s, CH), 129.6 (s, CH), 129.5 (s, C_q), 129.0 (d, J = 2.4 Hz, C_q), 128.5 (s, C_q), 128.3 (s, CH), 128.3 (s, CH), 127.8 (d, J = 11.8 Hz, CH), 127.4 (s, CH), 127.3 (s, CH), 127.3 (s, CH), 127.2 (s, CH), 127.0 (s, C_q), 126.8 (s, C_q), 126.6 (s, CH), 126.2 (s, C_q), 126.1 (s, CH), 124.9 (s, CH), 124.2 (s, CH), 122.7 (s, CH), 121.9 (s, CH), 121.7 (s, CH), 117.6 (s, CH), 116.2 (s, CH), 110.8 (s, CH), 101.9 (s, CH), 33.8 (s, C_q), 33.7 (s, C_q), 33.6 (s, C_q), 33.1 (s, C_q), 31.1 (s, CH_3), 30.9 (s, CH_3), 28.9 (s, CH_3), 28.6 (s, CH_3); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6 , 295 K) δ [ppm] = 46.1 (dd, J = 199.2 Hz, 19.4 Hz), 42.1 (dd, J = 99.1 Hz, 19.4 Hz); ^{29}Si (IG) NMR (119 MHz, C_6D_6 , 295 K) δ [ppm] = -68.5 (ddd, J = 33.0 Hz, 11.3 Hz, 6.4 Hz); MS (LIFDI): $[M]^+$, calcd.: 1192.4128; found: 1192.4750; Anal. Calcd for $C_{72}H_{77}N_2O_2P_2SiRh$: C, 72.47; H, 6.34; N, 2.35 found: C, 73.21; H, 6.24; N, 1.96.

Synthesis of Bis(2,4-di-tert-butyl-(2-diphenylphosphanyl)amido)-phenolato)silane-bis(cyclohexyl isocyanide-chlorido Rhodium (3-Cl). In a J. Young NMR tube, 2-Cl (21.8 mg, 19.4 μ mol, 1.00 equiv) and cyclohexyl isocyanide (3.88 μ L, 31.2 μ mol, 1.61 equiv) were dissolved in C_6D_6 (0.75 mL). After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting orange solids were washed with *n*-pentane (3 $\times$ 5 mL). The orange solid was dried *in vacuo* to give 3-Cl in 85% yield (22.2 mg, 16.5 μ mol). 1H NMR (600 MHz, C_6D_6 , 295 K) δ [ppm] = 8.52–8.49 (m, 4H), 7.96 (bs, 4H), 7.82 (dd, J = 8.2 Hz, 2.6 Hz, 2H), 7.25 (ddd, J = 8.5 Hz, 7.2 Hz, 1.6 Hz, 2H), 7.13–7.09 (m, 2H), 7.07 (t, J = 7.4 Hz, 4H), 7.04–7.00 (m, 6H), 6.94 (d, J = 2.1 Hz, 2H), 6.69 (t, J = 7.4 Hz, 2H), 6.46 (d, J = 8.1 Hz, 7.1 Hz, 1.1 Hz, 2H), 6.69 (d, J = 2.2 Hz, 2H), 2.74 (d, J = 11.9 Hz, 2H), 1.51–1.48 (m, 2H), 1.38 (s, 18H), 1.27 (s, 18H), 1.17 (bs, 6H), 0.93–0.86 (m, 2H), 0.66–0.56 (m, 6H), 0.45 (d, J = 13.4 Hz, 2H), -0.11 (qd, J = 12.7 Hz, 3.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, C_6D_6 , 295 K) δ [ppm] = 156.1 (s, C_q), 145.1 (s, C_q), 141.5 (s, C_q), 140.6 (s, C_q), 136.5 (s, C_q), 135.6 (s, CH), 135.1 (s, CH), 134.7 (s, CH), 132.9 (s, C_q), 132.9 (s, CH), 131.9 (s, C_q), 130.0 (s, CH), 129.6 (s, CH), 128.6 (s, CH), 127.7 (s, CH), 127.4 (s, CH), 122.7 (s, C_q), 122.3 (s, CH), 109.9 (s, CH), 103.0 (s, CH), 57.0 (s, C_q), 55.1 (s, CH), 34.8 (s, C_q), 34.7 (s, CH_2), 34.1 (s, C_q), 32.3 (s, CH_2), 31.7 (s, CH_2), 30.5 (s, CH_2), 30.4 (s, CH_2); $^{31}P\{^1H\}$ NMR (243 MHz, C_6D_6 , 295 K) δ [ppm] = 4.7 (d, J = 102.5 Hz); ^{29}Si (IG) NMR (119 MHz, C_6D_6 , 295 K) δ [ppm] = -86.7 (d, J = 21.0 Hz); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2941 (s), 2904 (m), 2858 (m), 2184 (s), 2164 (s), 2150 (w), 2033 (vw), 1575 (w), 1562 (w), 1468 (s), 1446 (s), 1434 (s), 1425 (s), 1388 (m), 1359 (w), 1348 (w), 1306 (m), 1291 (m), 1271 (m), 1235 (m), 1205 (m), 1157 (m), 1127 (w), 1116 (w), 1091 (m), 1028 (m), 1000 (m), 922 (vw), 893 (m), 849 (m), 790 (m), 774 (m), 747 (m), 693 (m), 680 (m), 670 (m), 656 (vw); MS (LIFDI): $[M-Cl-NCN]^+$, calcd.: 1198.4472; found: 1198.4499; Anal. Calcd for $C_{78}H_{80}ClN_2O_2P_2SiRh$: C, 69.71; H, 6.75; N, 4.17 found: C, 67.34; H, 6.68; N, 4.57.

Synthesis of Bis(2,4-di-tert-butyl-(2-diphenylphosphanyl)amido)-phenolato)silane-bis(cyclohexyl isocyanide-hydrido Rhodium (3-H). In a J. Young NMR tube, 2-H (25.0 mg, 22.9 μ mol, 1.00 equiv) and cyclohexyl isocyanide (8.10 μ L, 65.1 μ mol, 2.84 equiv) were dissolved in benzene (1.5 mL). After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting in a bright yellow powder, which was washed with *n*-pentane (2 $\times$ 1 mL) to remove excess cyclohexyl isocyanide. The product was dried *in vacuo* to yield the title compound in 70% yield (21.0 mg, 16.0 μ mol). 1H NMR (600 MHz, C_6D_6 , 295 K) δ [ppm] = 8.03–8.00 (m, 4H), 7.74 (d, J = 8.0 Hz, 1H), 7.61–7.57 (m, 3H), 7.30–7.26 (m, 2H), 7.22 (td, J = 7.6 Hz, 1.4 Hz, 1H), 7.14–7.08 (m, 8H), 7.03–6.98 (m, 7H), 6.84 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 1.8 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.69 (d, J = 1.9 Hz, 1H), 6.15 (d, J = 2.0 Hz, 1H), 2.80–2.76 (m, 1H), 2.46 (bs, 1H), 1.68–1.65 (m, 2H), 1.47

(s, 9H), 1.38 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H), 1.22–1.21 (m, 3H), 0.95–0.87 (m, 4H), 0.81–0.80 (m, 6H), 0.60 (d, $J = 10.0$ Hz, 4H), 0.14 (qd, $J = 11.5$ Hz, 3.2 Hz, 2H), –7.28 (dt, $J = 12.9$ Hz, 7.5 Hz, 1H); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 295 K) $\delta(\text{ppm}) = 21.1$ (d, $J = 119.3$ Hz, 2P); ^{29}Si (1G) NMR (119 MHz, C_6D_6 , 295 K) δ [ppm] = –75.5 (d, $J = 21.3$ Hz); MS (LIFDI): $[\text{M}+1]^+$, calc.: 1309.55, found: 1309.61; Anal. Calcd for $\text{C}_{78}\text{H}_{91}\text{N}_4\text{O}_3\text{P}_2\text{SiRh}$ x C_6H_6 : C, 72.71; H, 7.05; N, 4.04 found: C, 72.61; H, 6.95; N, 4.22.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.5C00368>.

Experimental and computational details including NMR spectra, IR spectra, and crystallographic data (PDF)

Accession Codes

Deposition Numbers 2418933–2418937 and 2426618 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

The authors declare no competing financial interest.

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Supporting Information:

Co-Ligand-Dependent Rh(I)–Si(IV) Interactions in Silicon Z-Type Complexes

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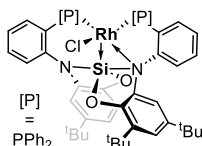
1. Experimental Procedures

a. Materials and General Methods

All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques using flame dried glassware or by working in a glovebox (Sylatech Glovebox) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å). Argon was dried by passing over two columns of phosphorus pentoxide. Commercially available chemicals were used as received. Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane **1** was synthesized according to literature known procedures.¹ All NMR spectra were recorded on a Bruker Avance III 600 MHz or a Bruker Avance II 400 MHz spectrometer at room temperature (295 K). All hetero-nuclei spectra were obtained with ¹H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ¹H and ¹³C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants J in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublets of doublets, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. All NMR-spectra were processed with Bruker TopSpin 4.3.0. ESI-MS spectra were measured on a Bruker ApexQe FT-ICR instrument, while LIFDI-MS spectra were measured on a JEOL AccuTOF GCx instrument. Elemental analysis (C, H, N) was measured on an Elementar vario MICRO Cube machine. Systematically low values for Carbon can be explained by the formation of SiC during the combustion process. IR spectra were recorded on an Agilent Cary 630 spectrometer equipped with diamond ATR units inside a nitrogen filled glovebox. Plots were generated using OriginPro 2024.

b. Syntheses

Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-chlorido rhodium (I) – 2-CI

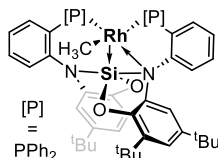


An orange solution of **1** PNO⁴² (500 mg, 506 μ mol, 1.01 eq) and [Rh(COD)Cl]₂ (124 mg, 751 μ mol, 0.50 eq) in benzene (50 mL) was stirred at room temperature overnight. The resulting red/orange suspension was condensed to dryness, yielding the target complex as an orange powder, which was further washed with *n*-pentane (3 x 5 mL) and dried *in vacuo* (470 mg, 444 μ mol, 83 %).

Crystals suitable for X-ray diffraction were obtained by layering a saturated solution in toluene with *n*-pentane at room temperature.

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.14-8.12 (m, 1H), 8.06-8.04 (m, 2H), 7.92-7.86 (m, 3H), 7.39-7.35 (m, 2H), 7.33 (s, 2H), 7.24-7.21 (m, 1H), 7.14-7.09 (m, 3H), 7.05-6.92 (m, 8H), 6.79 (t, J = 7.6 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 6.62 (t, J = 7.5 Hz, 1H), 6.51-6.48 (m, 3H), 6.41-6.38 (m, 2H), 6.30-6.27 (m, 2H), 1.54 (s, 9H), 1.47 (s, 9H), 1.27 (s, 9H), 0.95 (s, 9H); **¹³C{¹H} NMR** (151 MHz, C₆D₆, 295 K) δ [ppm] = 156.5 (s, C_q), 147.4 (s, C_q), 144.6 (s, C_q), 142.4 (s, C_q), 141.4 (d, J = 34.7 Hz, C_q), 138.4 (s, C_q), 138.0 (s, CH), 134.8 (s, C_q), 134.3 (s, C_q), 133.6 (s, C_q), 133.3 (s, CH), 132.8 (s, CH), 132.4 (s, CH), 132.0 (s, CH), 131.5 (d, J = 2.1 Hz, C_q), 131.3 (d, J = 15.4 Hz, CH), 131.1 (s, C_q), 130.3 (d, J = 11.7 Hz, CH), 123.0 (s, CH), 123.0 (s, C_q), 128.7 (s, CH), 128.4 (s, CH), 128.1 (s, CH), 127.6 (s, C_q), 127.4 (s, C_q), 127.3 (s, CH), 127.2 (s, CH), 127.0 (d, J = 10.5 Hz, CH), 127.0 (s, CH), 126.2 (s, CH), 125.5 (d, J = 3.4 Hz, C_q), 125.1 (s, C_q), 123.7 (s, CH), 121.9 (s, CH), 120.9 (s, CH), 117.9 (s, CH), 115.7 (s, CH), 111.1 (s, CH), 102.6 (s, CH), 77.4 (d, J = 14.2 Hz, CH), 34.0 (s, C_q), 33.8 (s, C_q), 33.6 (s, C_q), 33.1 (s, C_q), 31.1 (s, CH₃), 30.8 (s, CH₃), 28.9 (s, CH₃), 28.8 (s, CH₃); **³¹P{¹H} NMR** (243 MHz, C₆D₆, 295 K) δ [ppm] = 57.5 (dd, J = 143.6 Hz, 24.6 Hz, 1P), 39.6 (dd, J = 172.2 Hz, 24.6 Hz, 1P); **²⁹Si (IG) NMR** (119 MHz, C₆D₆, 295 K) δ [ppm] = -68.4 (ddd, J = 22.4 Hz, 7.3 Hz, 6.9 Hz); **HR-MS** (ESI⁺): [M+Na]⁺, calcd.: 1147.3616, found: 1147.3165; **Anal.** calcd. for C₆₈H₆₈ClN₂O₂P₂SiRh: C, 68.29; H, 6.09; N, 2.49 found: C, 67.16; H, 5.99; N, 2.77.

Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-methyl rhodium (I) – 2-CH₃

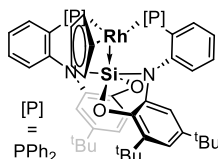


An orange solution of **2-Cl** (100 mg, 88.8 μmol , 1.00 eq) in 5 mL of toluene was cooled to -40°C , before MeLi (1.6 M in Et₂O, 56.1 μL , 89.7 μmol , 1.01 eq) was added, followed by 0.5 mL of Et₂O. The red reaction mixture was stirred while warming to room temperature for 1 h, before it was condensed to dryness under reduced pressure. The residue was washed with 2x2 mL of *n*-pentane to remove impurities, before it was extracted with benzene (4 mL). The extract was filtered through a syringe filter, before lyophilization yielded the target compound as a beige solid (59.0 mg, 53.4 μmol , 60%).

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.16 (dd, J = 7.6 Hz, 5.0 Hz, 1H), 7.90-7.87 (m, 2H), 7.84 (dd, J = 8.3 Hz, 4.8 Hz, 1H), 7.56 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 2.0 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.34 (d, J = 2.1 Hz, 1H), 7.31-7.28 (m, 1H), 7.29 (d, J = 1.9 Hz, 1H), 7.23 (dd, J = 11.4 Hz, 7.4 Hz, 2H), 7.19-7.17 (m, 1H), 7.14-7.11 (m, 1H), 7.06-7.01 (m, 4H), 6.95 (t, J = 7.3 Hz, 2H), 6.92 (d, J = 2.0 Hz, 1H), 6.82-6.79 (m, 2H), 6.65 (t, J = 7.5 Hz, 1H), 6.59-6.56 (m, 2H), 6.50 (t, J = 7.4 Hz, 1H), 6.45 (t, J = 7.2 Hz, 2H), 6.36 (t, J = 7.1 Hz, 2H), 1.50 (s, 9H), 1.47 (s, 9H), 1.28 (s, 9H), 0.99 (s, 9H), 0.54 (pseudo-t, J = 3.9 Hz, 3H); ¹³C{¹H}[³¹P] NMR (151 MHz, C₆D₆, 295 K): δ [ppm] = 160.6 (s, C_q), 148.2 (s, C_q), 146.9 (s, C_q), 144.0 (s, C_q), 142.6 (s, C_q), 142.1 (s, C_q), 139.3 (s, C_q), 138.3 (s, CH), 136.5 (s, C_q), 135.8 (s, C_q), 135.4 (s, CH), 134.4 (s, CH), 134.3 (s, CH), 134.1 (s, CH), 133.5 (s, CH), 132.5 (s, CH), 131.7 (s, CH), 131.3 (s, CH), 131.2 (s, CH), 131.0 (s, C_q), 130.9 (s, CH), 130.3 (s, CH), 130.3 (s, C_q), 130.3 (s, C_q), 129.4 (s, CH), 128.9 (s, CH), 128.8 (s, CH), 128.6 (s, CH), 128.4 (s, CH), 128.3 (s, CH), 128.3 (s, CH), 127.2 (s, CH), 126.7 (s, C_q), 123.8 (s, CH), 122.7 (s, CH), 122.2 (s, CH), 118.2 (s, CH), 117.1 (s, CH), 112.0 (s, CH), 103.2 (s, CH), 35.2 (s, C_q), 35.0 (s, C_q), 34.8 (s, C_q), 34.3 (s, C_q), 32.3 (s, CH₃), 32.0 (s, CH₃), 30.1 (s, CH₃), 29.8 (s, CH₃), 16.1 (d, J = 21.8 Hz, CH₃); ³¹P{¹H} NMR (243 MHz, C₆D₆, 295 K): δ [ppm] = 47.1 (dd, J = 199.9 Hz, 17.5 Hz, 1P), 44.2 (dd, J = 100.9 Hz, 17.3 Hz, 1P); ²⁹Si (IG) NMR (119 MHz, C₆D₆, 295 K): δ [ppm] = -67.7 (ddd, J = 34.6 Hz, 7.4 Hz, 7.2 Hz); MS (LIFDI⁺): [M]⁺, calcd.: 1104.38, found: 1104.45; Anal. calcd. for C₆₈H₇₁N₂O₂P₂SiRh: C, 70.64; H, 6.48; N, 2.53 found: C, 70.85; H, 6.71; N, 2.51.

* These signals are covered by the deuterated solvent signal, but can be observed via the DEPT135 NMR experiment.

Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-cyclopentadienyl rhodium (I) – 2'-Cp

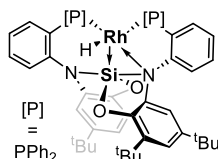


In a J. Young NMR tube, to an orange solution of **2-Cl** (30.0 mg, 26.7 μmol , 1.00 eq) in 1 mL of thf was added a solution of NaCp (2 M in thf, 16.0 μL , 32.0 μmol , 1.20 eq) and a few drops of C₆D₆ to monitor the reaction via NMR spectroscopy. The dark red solution was shaken for 20 h at room temperature, after which NMR spectroscopy indicated 80% conversion of the starting material. Subsequently, more NaCp was added (2 M in thf, 6.00 μL , 12.0 μmol , 0.45 eq) in two portions and the mixture was reacted at room temperature for additional 3 h, before NMR spectroscopy indicated full conversion. The reaction was condensed to dryness and the brown residue was washed with 2x1.5 mL of *n*-pentane to remove impurities, before it was extracted with benzene (1.5 mL). The extract was filtered through a syringe filter, before lyophilization yielded the target compound as a red-brown powder (20.1 mg, 17.4 μmol , 65%).

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.48 (dd, *J* = 7.8 Hz, 4.7 Hz, 1H), 8.22 (t, *J* = 7.3 Hz, 1H), 7.87 (broad, s, 2H), 7.69 (t, *J* = 8.7 Hz, 2H), 7.65-7.63 (m, 2H), 7.37 (t, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 1.2 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.19-7.17 (m, 1H), 7.13 (broad, 2H), 7.09-7.06 (m, 1H), 7.02-6.99 (m, 1H), 6.98 (d, *J* = 1.6 Hz, 1H), 6.97-6.92 (m, 4H), 6.85 (d, *J* = 1.3 Hz, 1H), 6.78 (dd, *J* = 11.7 Hz, 8.2 Hz, 2H), 6.54 (t, *J* = 7.4 Hz, 1H), 6.47 (t, *J* = 7.1 Hz, 1H), 6.40 (t, *J* = 7.3 Hz, 1H), 6.32 (t, *J* = 7.4 Hz, 2H), 6.18 (t, *J* = 6.5 Hz, 2H), 4.93 (s, 5H), 1.55 (s, 9H), 1.46 (s, 9H), 1.36 (s, 9H), 1.16 (s, 9H); **¹³C{¹H}(³¹P) NMR** (151 MHz, C₆D₆, 295 K) δ [ppm] = 153.2 (s, C_q), 151.9 (s, C_q), 147.0 (s, C_q), 145.3 (s, C_q), 143.8 (s, C_q), 142.1 (s, C_q), 141.3 (s, C_q), 140.3 (s, C_q), 140.3 (s, C_q), 138.5 (s, C_q), 136.3 (s, CH), 135.1 (s, CH), 133.6 (s, C_q), 133.4 (s, CH), 133.1 (s, CH), 132.9 (s, C_q), 132.2 (s, C_q), 131.9 (s, CH), 131.9 (s, CH), 131.6 (s, C_q), 130.2 (s, C_q), 130.2 (s, CH), 130.1 (s, CH), 129.9 (s, CH), 129.4 (s, CH), 129.2 (s, CH), 128.0 (s, CH), * 127.9 (s, CH), * 127.9 (s, CH), * 127.8 (s, CH), 127.6 (s, CH), 127.0 (s, CH), 123.1 (s, CH), 122.0 (s, CH), 118.8 (s, CH), 113.4 (s, C_q), 112.7 (s, CH), 111.6 (s, CH), 105.3 (s, CH), 103.0 (s, CH), 96.7 (s, Cp-CH), 35.0 (s, C_q), 35.0 (s, C_q), 34.9 (s, C_q), 34.5 (s, C_q), 32.5 (s, CH₃), 32.3 (s, CH₃), 30.3 (s, CH₃), 30.0 (s, CH₃); **³¹P{¹H} NMR** (243 MHz, C₆D₆, 295 K) δ [ppm] = 26.6 (dd, *J* = 177.6 Hz, 36.0 Hz, 1P), 19.0 (dd, *J* = 158.1 Hz, 36.0 Hz, 1P); **²⁹Si (IG) NMR** (119 MHz, C₆D₆, 295 K) δ [ppm] = -72.1 (ddd, *J* = 20.8 Hz, 16.2 Hz, 6.5 Hz); **MS** (LIFDI): [M]⁺, calcd.: 1154.40, found: 1154.47; **Anal.** calcd. for C₆₉H₇₃N₂O₂P₂SiRh: C, 71.74; H, 6.37; N, 2.42 found: C, 71.56; H, 6.38; N, 2.47.

* These signals are covered by the deuterated solvent signal, but can be observed via the DEPT135 NMR experiment.

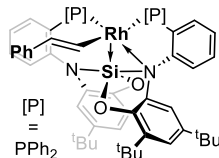
Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl)amido)phenolato)silane-hydrido rhodium (I) – 2-H



To a solution of **2-Cl** (92.0 mg, 81.7 μmol, 1.00 eq) in benzene (2 mL), NaBHEt₃ (1 M toluene) (81.7 μl, 81.7 μmol, 1.00 eq) was added, resulting in gas evolution, precipitation and a color change from orange to brown. The suspension was filtered through a syringe filter and the filtrate was condensed to dryness to give **2-H** as a brown solid (65.3 mg, 59.8 μmol, 73%).

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.08 (ddd, *J* = 8.1 Hz, 5.1 Hz, 1.2 Hz, 1H), 7.77-7.74 (m, 2H), 7.70 (ddd, *J* = 8.6 Hz, 4.6 Hz, 1.1 Hz, 1H), 7.47 (ddd, *J* = 11.6 Hz, 8.2 Hz, 1.4 Hz, 2H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.30-7.23 (m, 5H), 7.08-7.05 (m, 1H), 7.01-6.96 (m, 1H), 6.93-6.90 (m, 5H), 6.78-6.72 (m, 6H), 6.70-6.67 (m, 1H), 6.60-6.54 (m, 3H), 6.36 (td, *J* = 7.9 Hz, 2.1 Hz, 2H), 1.55 (s, 9H), 1.49 (s, 9H), 1.22 (s, 9H), 0.95 (s, 9H), -6.40 (ddd, *J* = 126.0 Hz, 33.1 Hz, 22.4 Hz, 1H); **¹³C{¹H}(³¹P) NMR** (151 MHz, C₆D₆, 295 K) δ [ppm] = 159.3 (s, C_q), 146.7 (s, C_q), 146.5 (s, C_q), 143.2 (s, C_q), 142.6 (s, C_q), 140.8 (s, C_q), 140.6 (s, C_q), 138.7 (s, C_q), 135.9 (s, C_q), 135.3 (s, CH), 134.1 (s, CH), 133.5 (d, *J* = 1.5 Hz, C_q), 133.2 (s, C_q), 133.0 (s, C_q), 133.0 (s, CH), 132.4 (s, CH), 131.3 (s, C_q), 131.2 (s, CH), 130.6 (s, CH), 130.1 (s, CH), 129.7 (s, CH), 129.4 (s, CH), 129.3 (d, *J* = 3.0 Hz, C_q), 129.0 (s, CH), 128.1 (d, *J* = 3.0 Hz, CH), 128.1 (s, CH), 127.8 (d, *J* = 3.0 Hz, CH), 127.5 (s, CH), 127.4 (d, *J* = 3.0 Hz, C_q), 127.3 (s, CH), 127.0 (s, CH), 126.4 (s, CH), 124.5 (s, C_q), 122.9 (s, CH), 121.7 (s, CH), 121.4 (s, CH), 116.9 (s, CH), 115.2 (s, CH), 110.5 (s, CH), 101.7 (s, CH), 34.2 (s, C_q), 33.8 (s, C_q), 33.5 (s, C_q), 33.1 (s, C_q), 31.2 (s, CH₃), 30.8 (s, CH₃), 28.9 (s, CH₃), 28.7 (s, CH₃); **³¹P{¹H} NMR** (243 MHz, C₆D₆, 295 K) δ [ppm] = 43.0 (dd, *J* = 115.3 Hz, 15.7 Hz, 1P), 38.4 (dd, *J* = 180.1 Hz, 15.8 Hz, 1P); **²⁹Si (IG) NMR** (119 MHz, C₆D₆, 295 K) δ [ppm] = -67.1 (ddd, *J* = 35.4 Hz, 8.6 Hz, 4.4 Hz); **IR (ATR):** $\tilde{\nu}$ [cm⁻¹] = 3054 (vw), 2948 (w), 2900 (w), 2862 (w), 1914 (w), 1578 (w), 1561 (vw), 1477 (w), 1462 (m), 1434 (m), 1416 (m), 1389 (w), 1358 (w), 1339 (vw), 1297 (w), 1282 (w), 1267 (w), 1220 (w), 1200 (w), 1157 (vw), 1127 (vw), 1110 (vw), 1094 (w), 1026 (w), 997 (m), 955 (w), 939 (w), 914 (w), 871 (m), 845 (w), 788 (w), 738 (w), 690 (m), 676 (m), 656 (w); **MS** (LIFDI): [M]⁺, calcd.: 1090.3659, found: 1090.4135; **Anal.** Calcd. for C₆₄H₆₉N₂O₂P₂SiRh: C, 70.45; H, 6.37; N, 2.57 found: C, 70.11; H, 6.63; N, 2.63.

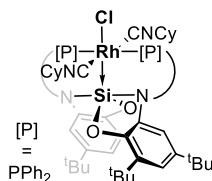
Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl-amido)phenolato)silane-ethenylbenzenylo rhodium (I) – 2-C₂H₂Ph



In a J. Young NMR tube, **2-H** (13.5 mg, 12.4 μ mol, 1.00 eq) and phenylacetylene (1.50 μ l, 13.7 μ mol, 1.10 eq) were dissolved in C₆D₆. After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting solid was dried *in vacuo* overnight to give **2-C₂H₂Ph** as a brown solid (14.1 mg, 12.0 μ mol, 97 %). Suitable crystals for scXRD were grown by vapor diffusion using toluene as solvent and *n*-pentane as anti-solvent.

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.17 (ddd, *J* = 8.1 Hz, 5.0 Hz, 1.2 Hz, 1H), 7.99-7.96 (m, 2H), 7.86-7.81 (m, 3H), 7.59 (ddd, *J* = 16.4 Hz, 12.7 Hz, 6.6 Hz, 1H), 7.40-7.37 (m, 2H), 7.29-7.26 (m, 4H), 7.17-7.16 (m, 4H), 7.10 (ddt, *J* = 8.4 Hz, 7.1 Hz, 1.4 Hz, 1H), 7.06 (d, *J* = 2.2 Hz, 1H), 7.02-6.98 (m, 4H), 6.95-6.86 (m, 4H), 6.80-6.77 (m, 3H), 6.67 (tq, *J* = 7.4 Hz, 1.5 Hz, 1H), 6.57 (dd, *J* = 11.6 Hz, 7.6 Hz, 2H), 6.52 (td, *J* = 7.3 Hz, 1.6 Hz, 1H), 6.44 (td, *J* = 7.5 Hz, 2.2 Hz, 2H), 6.39 (dt, *J* = 7.5 Hz, 4.1 Hz, 2H), 6.01 (ddd, *J* = 16.5 Hz, 7.7 Hz, 1.6 Hz, 1H), 1.48 (s, 9H), 1.29 (s, 9H), 1.25 (s, 9H), 1.00 (s, 9H); **¹³C{¹H}[³¹P] NMR** (151 MHz, C₆D₆, 295 K) δ [ppm] = 161.71 (d, *J* = 28.7 Hz, CH), 158.7 (s, C_q), 146.5 (s, C_q), 146.5 (s, C_q), 142.8 (s, C_q), 140.9 (s, C_q), 140.6 (s, C_q), 139.1 (s, C_q), 138.4 (s, C_q), 137.0 (s, CH), 135.0 (s, C_q), 134.4 (s, CH), 134.2 (s, CH), 133.3 (s, C_q), 133.2 (s, CH), 132.3 (s, C_q), 132.1 (s, CH), 132.0 (s, CH), 131.6 (s, CH), 130.6 (s, CH), 129.9 (s, CH), 129.6 (s, CH), 129.5 (s, C_q), 129.0 (d, *J* = 2.4 Hz, C_q), 128.5 (s, C_q), 128.3 (s, CH), 127.8 (d, *J* = 11.8 Hz, CH), 127.4 (s, CH), 127.3 (s, CH), 127.2 (s, CH), 127.0 (s, C_q), 126.8 (s, C_q), 126.6 (s, CH), 126.2 (s, C_q), 126.1 (s, CH), 124.9 (s, CH), 124.2 (s, CH), 122.7 (s, CH), 121.9 (s, CH), 121.7 (s, CH), 117.6 (s, CH), 116.2 (s, CH), 110.8 (s, CH), 101.9 (s, CH), 33.8 (s, C_q), 33.7 (s, C_q), 33.6 (s, C_q), 33.1 (s, C_q), 31.1 (s, CH₃), 30.9 (s, CH₃), 28.9 (s, CH₃), 28.6 (s, CH₃); **³¹P{¹H} NMR** (243 MHz, C₆D₆, 295 K) δ [ppm] = 46.1 (dd, *J* = 199.2 Hz, 19.4 Hz), 42.1 (dd, *J* = 99.1 Hz, 19.4 Hz); **²⁹Si (IG) NMR** (119 MHz, C₆D₆, 295 K) δ [ppm] = -68.5 (ddd, *J* = 33.0 Hz 11.3 Hz, 6.4 Hz); **MS** (LIFDI): [M]⁺, calc.: 1192.4128, found: 1192.4750; **Anal.** Calcd. for C₇₂H₇₅N₂O₂P₂SiRh: C, 72.47; H, 6.34; N, 2.35 found: C, 73.21; H, 6.24; N, 1.96.

Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanyl-amido)phenolato)silane-bisdicyclohexyl isocyanide-chlorido rhodium (I) – 3-Cl

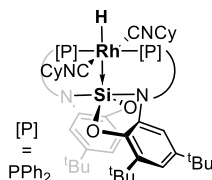


In a J. Young NMR tube, **2-Cl** (21.8 mg, 19.4 μ mol, 1.00 eq) and cyclohexyl isocyanide (3.88 μ l, 31.2 μ mol, 1.61 eq) were dissolved in C₆D₆ (0.75 mL). After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting orange solids were washed with *n*-pentane (3 $\times$ 5 mL). The orange solid was dried *in vacuo* to give **3-Cl** in 85 % yield (22.2 mg, 16.5 μ mol). Suitable crystals for scXRD were grown by vapor diffusion using toluene as solvent and *n*-pentane as anti-solvent.

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.52-8.49 (m, 4H), 7.96 (bs, 4H), 7.82 (dd, *J* = 8.2 Hz, 2.6 Hz, 2H), 7.25 (ddd, *J* = 8.5 Hz, 7.2 Hz, 1.6 Hz, 2H), 7.13-7.09 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 4H), 7.04-7.00 (m, 6H), 6.94 (d, *J* = 2.1 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 2H), 6.74 (ddd, *J* = 8.1 Hz, 7.1 Hz, 1.1 Hz, 2H), 6.69 (d, *J* = 2.2 Hz, 2H), 2.46 (t, *J* = 11.9 Hz, 2H), 1.51-1.48 (m, 2H), 1.38 (s, 18H), 1.27 (s, 18H), 1.17 (bs, 6H), 0.93-0.86 (m, 2H), 0.66-0.56 (m, 6H), 0.45 (d, *J* = 13.4 Hz, 2H), -0.11 (qd, *J* = 12.7 Hz, 3.6 Hz, 2H); **¹³C{¹H}[³¹P] NMR** (151 MHz, C₆D₆, 295 K) δ

[ppm] = 156.1 (s, C_q), 145.1 (s, C_q), 141.5 (s, C_q), 140.6 (s, C_q), 136.5 (s, C_q), 135.6 (s, CH), 135.1 (s, CH), 134.7 (s, CH), 132.9 (s, C_q), 132.9 (s, CH), 131.9 (s, C_q), 130.0 (s, CH), 129.6 (s, CH), 128.6 (s, CH), 127.7 (s, CH), 127.4 (s, CH), 122.7 (s, C_q), 122.3 (s, CH), 109.9 (s, CH), 103.0 (s, CH), 57.0 (s, C_q), 55.1 (s, CH), 34.8 (s, C_q), 34.7 (s, CH₂), 34.1 (s, C_q), 32.3 (s, CH₃), 31.7 (s, CH₂), 30.5 (s, CH₂), 30.4 (s, CH₃); ³¹P{¹H} NMR (243 MHz, C₆D₆, 295 K) δ(ppm) = 4.7 (d, J = 102.5 Hz); ²⁹Si (IG) NMR (119 MHz, C₆D₆, 295 K) δ [ppm] = -86.7 (d, J = 21.0 Hz); IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2941 (s), 2904 (m), 2858 (m), 2184 (s), 2164 (s), 2150 (w), 2033 (vw), 1575 (w), 1562 (w), 1468 (s), 1446 (s), 1434 (s), 1425 (s), 1388 (m), 1359 (w), 1348 (w), 1306 (m), 1291 (m), 1271 (m), 1235 (m), 1205 (m), 1157 (m), 1127 (w), 1116 (w), 1091 (m), 1028 (m), 1000 (m), 922 (vw), 893 (m), 849 (m), 790 (m), 774 (m), 747 (m), 693 (m), 680 (m), 670 (m), 656 (vw); MS (LIFDI): [M-Cl-CNCy]⁺, calc.: 1198.4472, found: 1198.4499; Anal. Calcd. for C₇₈H₉₀ClN₄O₂P₂SiRh: C, 69.71; H, 6.75; N, 4.17 found: C, 67.34; H, 6.68; N, 4.57.

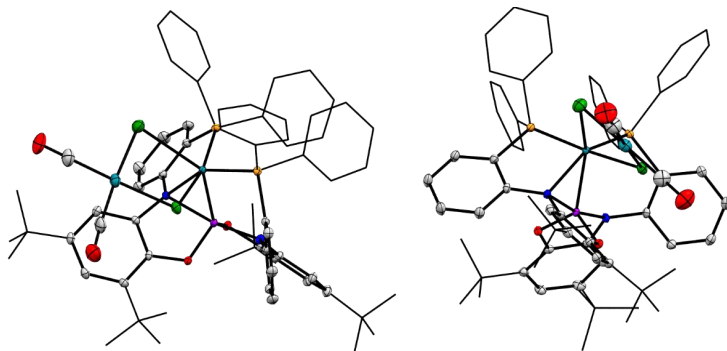
Bis(2,4-di-*tert*-butyl-(2-diphenylphosphanylamido)phenolato)silane-bisdicyclohexyl isocyanide-hydrido rhodium (I) – 3-H



In a J. Young NMR tube, **2-H** (25.0 mg, 22.9 μmol, 1.00 eq) and cyclohexyl isocyanide (8.10 μl, 65.1 μmol, 2.84 eq) were dissolved in benzene (1.5 mL). After subsequent NMR analysis showed quantitative conversion, the solvent was removed *in vacuo* and the resulting in a bright yellow powder, which was washed with *n*-pentane (2 × 1 mL) to remove excess cyclohexyl isocyanide. The product was dried *in vacuo* to yield the title compound in 70% yield (21.0 mg, 16.0 μmol).

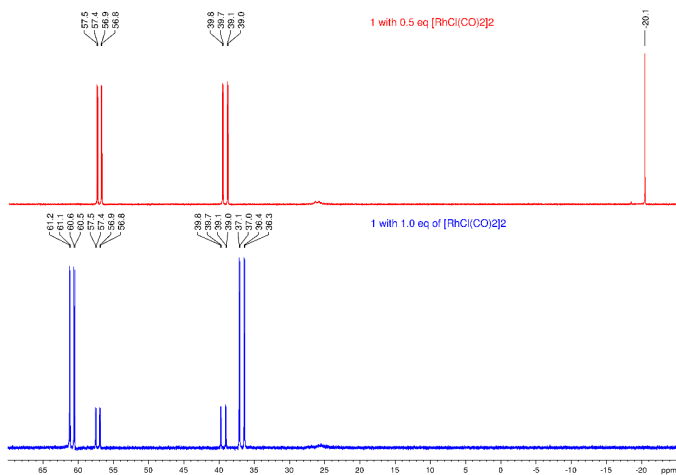
Due to the reactive nature of the product in solution, no ¹³C NMR data could be obtained.

¹H NMR (600 MHz, C₆D₆, 295 K): δ [ppm] = 8.03-8.00 (m, 4H), 7.74 (d, J = 8.0 Hz, 1H), 7.61-7.57 (m, 3H), 7.30-7.26 (m, 2H), 7.22(td, J = 7.6 Hz, 1.4 Hz, 1H), 7.14-7.08 (m, 8H), 7.03-6.98 (m, 7H), 6.84 (t, J = 7.4 Hz, 1H), 6.73 (d, J = 1.8 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.69 (d, J = 1.9 Hz, 1H), 6.15 (d, J = 2.0 Hz, 1H), 2.80-2.76 (m, 1H), 2.46 (bs, 1H), 1.68-1.65 (m, 2H), 1.47 (s, 9H), 1.38 (s, 9H), 1.37 (s, 9H), 1.35 (s, 9H), 1.22-1.21 (m, 3H), 0.95-0.87 (m, 4H), 0.81-0.80 (m, 6H), 0.60 (d, J = 10.0 Hz, 4H), 0.14 (qd, J = 11.5 Hz, 3.2 Hz, 2H), -7.28 (dt, J = 12.9 Hz, 7.5 Hz, 1H); ³¹P{¹H} NMR (162 MHz, C₆D₆, 295 K) δ(ppm) = 21.1 (d, J = 119.3 Hz, 2P); ²⁹Si (IG) NMR (119 MHz, C₆D₆, 295 K) δ [ppm] = -75.5 (d, J = 21.3 Hz); MS (LIFDI): [M+1]⁺, calc.: 1309.55, found: 1309.61; Anal. Calcd. for C₇₈H₉₁N₄O₂P₂SiRh x C₆H₆: C, 72.71; H, 7.05; N, 4.04 found: C, 72.61; H, 6.95; N, 4.22.

Reaction of **1** with $[(\text{CO})_2\text{RhCl}]$ – Formation of **2-Cl** and **2-(μ-Cl)₂-Rh-(CO)₂**Figure S 1: Solid-state structure of **2-(μ-Cl)₂-Rh-(CO)₂** (vibrational ellipsoids displayed at 50%, hydrogens for clarity)-

In a J. Young NMR tube, **1** (11.8 mg, 12.0 μmol, 1.00 eq) and di-μ-chloro-tetracarbonyldirhodium(I) (2.50 mg, 6.42 μmol, 0.54 eq) were dissolved in C_6D_6 (0.5 mL), which led to the immediate formation of CO. Subsequent NMR spectroscopic analysis showed 85% conversion to complex **2-Cl**. After 16 h, the solution was again investigated by NMR spectroscopy, but silane **1** was still detected in the mixture. Addition of an excess of di-μ-chloro-tetracarbonyldirhodium(I) (2.50 mg, 6.42 μmol, 0.54 eq) and investigation of the red suspension by NMR spectroscopy revealed full consumption of **1**, but also the formation of an unknown species alongside **2-Cl**. The liquid phase was decanted, filtered and crystallized by gas phase diffusion of *n*-pentane into the saturated benzene solution at room temperature. After 7 days, dark red crystals, suitable for scXRD analysis formed, revealing **2-(μ-Cl)₂-Rh-(CO)₂** as the product of the reaction of di-μ-chloro-tetracarbonyldirhodium(I) and **2-Cl**.

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, C_6D_6 , 295 K) $\delta(\text{ppm})$ = 60.9 (dd, J = 154.4 Hz, 27.6 Hz, 1P), 36.7 (dd, J = 169.8 Hz, 27.6 Hz, 1P).

Figure S 2: Stacked $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (243 MHz) of the reaction sequence, forming **2-Cl** and **2-(μ-Cl)₂-Rh-(CO)₂** (C_6D_6 , 295 K).

2. Computational Details

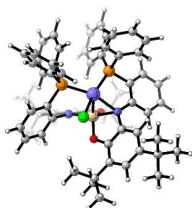
a. Structure Optimization

All computations have been performed using the Orca 5.0.3 program package.²⁻³ Geometry optimizations were carried out with Grimme's PBEh-3c/def2-mSVP, including the geometrical counter-poise correction scheme (gCP), atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ), using *VeryTightSCF* settings.⁴⁻⁹ As in all following calculations (except the QTAIM analysis), ECP was used for Rh (def2-ECP).¹⁰ All obtained structures have been approved to be energetic minima on the potential energy surface by analytical calculation of harmonic frequencies at the PBEh-3c level. Structures with imaginary frequencies $>10\text{ cm}^{-1}$ have been reoptimized with *TightOPT* settings. Unscaled ZPEs and thermal corrections at 298 K from the rigid-rotor harmonic oscillator (RRHO) approximation¹¹ were later used for the calculation of thermodynamic values. For the Coulomb Integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^{8,9,12} As starting geometries, VSEPR structures preoptimized with UFF were used.¹³

b. Cartesian Coordinates

Cartesian coordinates (reported in Å) and energies (in hartree) of all stationary points discussed in the reaction profile in the main text. Reported at the PBEh-3c level of theory.

2-Cl E = -4275.425489313808



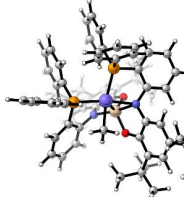
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P	8.55885736580655	3.09253195247823	16.90707150609060
Si	6.27872429411199	4.50602631111270	14.87231640414862
N	8.18915268481624	4.88644102614787	14.65967784726494
O	6.02712282915336	5.21737309764086	13.36927142017855
O	5.99071399790591	5.54845703995072	16.16435568818103
N	4.69340867028090	3.71843994860836	15.15386236978572
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2-CH₃

E = -3855.476654973829

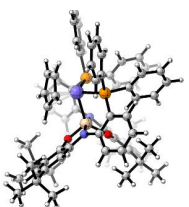


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O	8.13921310391286	0.58017731498970	16.5930940350271	H	6.92700708164870	-0.04635587132711	19.67915363081307
N	7.97543794881695	1.73857864416861	17.19084299571522	H	9.68960312915853	-0.07306425481933	11.35481722028400
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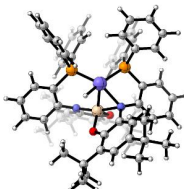


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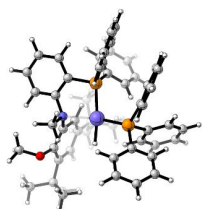


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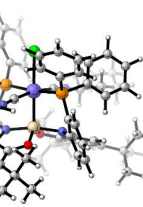


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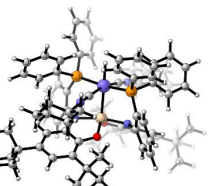
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H -5.33028050209881	2.65544426210392	20.16682981918962	H -4.19337525502072	4.61241607751251	19.09830588324887
H -4.11737272608467	4.71186094776720	20.85207914840043			
H -0.02453970067217	12.93046252545798	16.68014197788987			
H 1.29609323572396	15.01507296641758	16.38084519094204			

c. ETS-NOCV Calculations

For energy decomposition analysis (EDA), using the Extended Transition State (ETS) method¹⁴ combined with the natural orbitals for chemical valence (NOCV) concept,¹⁵ calculations were performed at the BP86-D3BJ/TZ2P level^{6, 16-17} as implemented in the AMS2023.104 software package.¹⁸

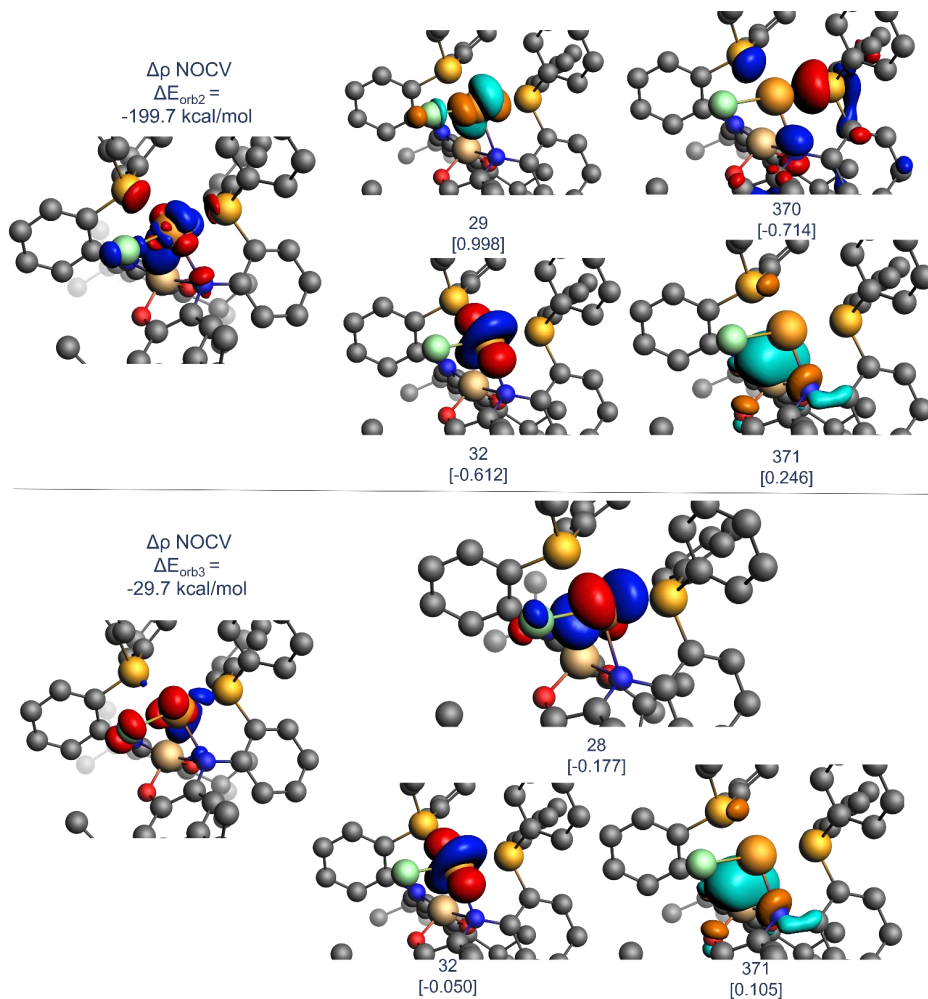


Figure S 3: Deformation density $\Delta\rho$ of ETS-NOCV orbitals that reflect Rh-Si interactions in **2-Cl**, as calculated at the BP86-D3BJ/TZ2P//PBEh-3c level of theory (charge flow from red to blue). Additionally shown are the corresponding symmetrized fragment orbitals (SFOs) with the highest eigenvalues v (symbolizing charge flow). Hydrogen atoms are omitted for clarity.

d. NBO Calculations

Natural Bond Orbital (NBO) calculations were conducted on PBE0-D4/def2-TZVPP level of theory,^{8, 19-21} using NBO 6.0.18a as included in Orca 5.0.3.²² ECP for Rh was employed.¹⁰ Wiberg bond indices were calculated using the BNDIDX keyword. NBOs were rendered and plotted using Chemcraft.²³ For the NBO analysis of **3-X**, the basis set def2-TZVP was used due to the increased size of the system.

NBO analysis for complex **2-Cl**:

Important NBOs of **2-Cl** that take major roles in the N-Rh-Si interaction are listed below and displayed in figure S4.

Table S1: List of selected NBOs in complex **2-Cl** with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
94	1.93	LP (Rh)	4d (100%)
96	1.69	LP (Rh)	4d (100%)
97	1.99	LP (Cl)	3s (79%), 3p (21%)
99	1.97	LP (Cl)	3s (1%), 3p (99%)
100	1.61	LP (Cl)	3s (17%), 3p (83%)
111	1.82	BD (Rh-P2)	29% Rh 5s (52%), 4d (48%) 71% P 3s (31%), 3p (68%)
112	1.81	BD (Rh-P1)	32% Rh 5s (47%), 4d (53%) 68% P 3s (30%), 3p (70%)
119	1.79	BD (Si-N1)	14% Si 3s (41%), 3p (58%) 86% N 2s (31%), 2p (69%)
281	0.47	LV (Si)	3s (35%), 3p (64%)
282	0.38	LV (Si)	3s (24%), 3p (76%)
283	0.32	LV (Si)	3p (100 %)
285	0.32	BD* (Rh-P2)	71% Rh 5s (52%), 4d (48%) 29% P 3s (31%), 3p (68%)
286	0.42	BD* (Rh-P1)	68% Rh 5s (47%), 4d (53%) 32% P 3s (30%), 3p (70%)
293	0.37	BD* (Si-N1)	86% Si 3s (41%), 3p (58%) 14% N 2s (31%), 2p (69%)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] ≥ 1 kcal/mol for selected bonding interactions between the listed NBOs:

• $\Delta E^{(2)}$ 94 (LP _{Rh}) $\rightarrow$ 283 (LV _{Si})	3.3
• $\Delta E^{(2)}$ 96 (LP _{Rh}) $\rightarrow$ 293 (BD* _{Si-N1})	66.5
• $\Delta E^{(2)}$ 97 (LP _{Cl}) $\rightarrow$ 283 (LV _{Si})	1.2
• $\Delta E^{(2)}$ 99 (LP _{Cl}) $\rightarrow$ 283 (LV _{Si})	1.2
• $\Delta E^{(2)}$ 99 (LP _{Cl}) $\rightarrow$ 293 (BD* _{Si-N1})	1.6
• $\Delta E^{(2)}$ 100 (LP _{Cl}) $\rightarrow$ 283 (LV _{Si})	3.0
• $\Delta E^{(2)}$ 104 (LP _{Rh}) $\rightarrow$ 274 (LV _{Si})	2.65
• $\Delta E^{(2)}$ 111 (BD _{Rh-P2}) $\rightarrow$ 281 (LV _{Si})	17.7
• $\Delta E^{(2)}$ 111 (BD _{Rh-P2}) $\rightarrow$ 282 (LV _{Si})	23.3
• $\Delta E^{(2)}$ 111 (BD _{Rh-P2}) $\rightarrow$ 283 (LV _{Si})	2.8
• $\Delta E^{(2)}$ 111 (BD _{Rh-P2}) $\rightarrow$ 293 (BD* _{Si-N1})	25.6
• $\Delta E^{(2)}$ 112 (BD _{Rh-P1}) $\rightarrow$ 281 (LV _{Si})	10.0
• $\Delta E^{(2)}$ 112 (BD _{Rh-P1}) $\rightarrow$ 282 (LV _{Si})	21.7
• $\Delta E^{(2)}$ 112 (BD _{Rh-P1}) $\rightarrow$ 293 (BD* _{Si-N1})	32.4
• $\Delta E^{(2)}$ 119 (BD _{Si-N1}) $\rightarrow$ 285 (BD* _{Rh-P2})	54.6
• $\Delta E^{(2)}$ 119 (BD _{Si-N1}) $\rightarrow$ 286 (BD* _{Rh-P2})	7.7

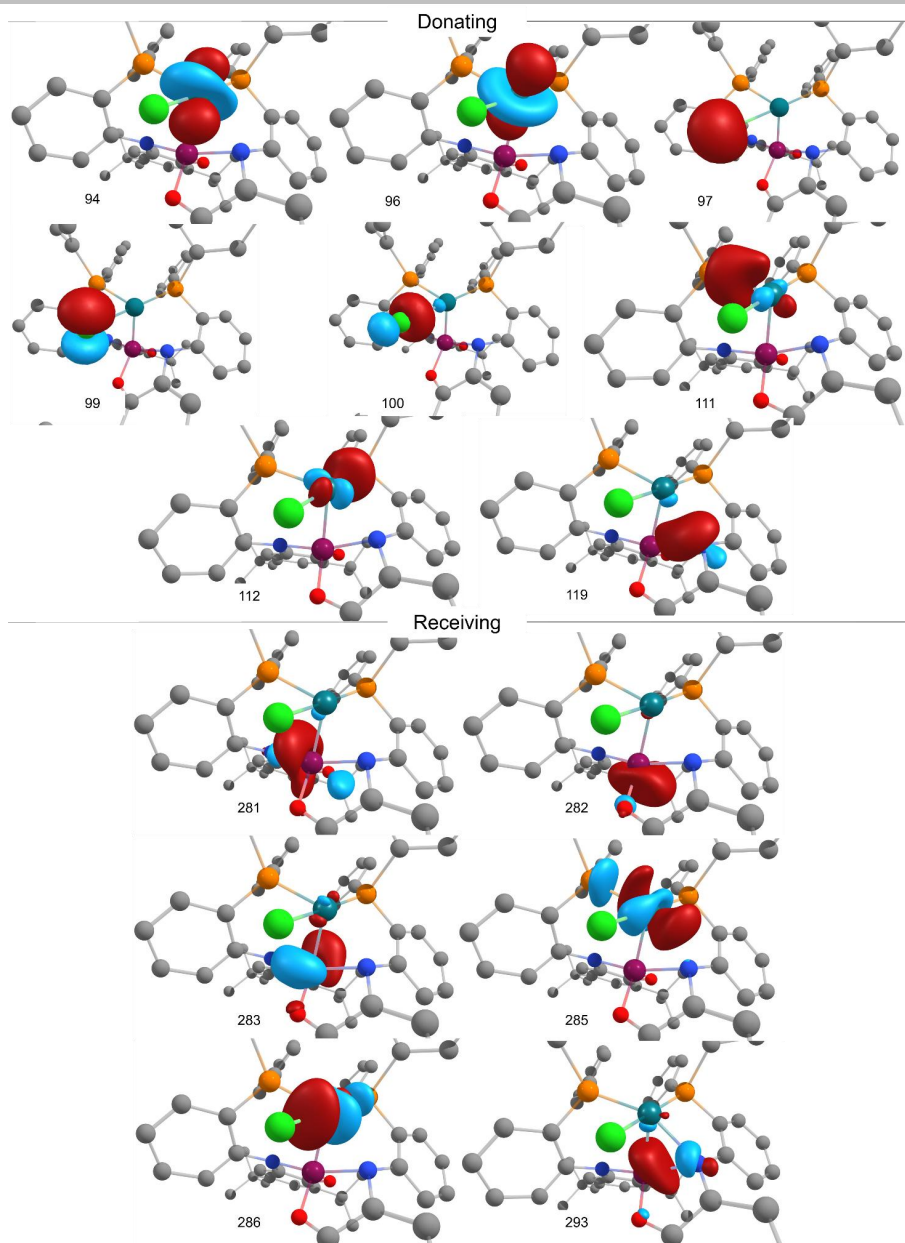


Figure S 4: Selected NBOs (PBE0-D4/def2-TZVP//PBEh-3c) of 2-Cl, displayed at 0.1 a.u.. Hydrogen atoms are hidden for clarity.

NBO analysis for complex 2-CH₃:

Important NBOs of 2-CH₃ that take major roles in the Rh-Si interaction are listed below and displayed in figure S6.

Table S 2: List of selected NBOs in complex 2-CH₃ with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
89	1.94	LP (Rh)	4d (100%)
90	1.93	LP (Rh)	4d (100%)
91	1.91	LP (Rh)	4d (100%)
92	1.67	LP (Rh)	4d (100%)
104	1.79	BD (Rh-C1)	37% Rh 5s (45%), 4d (55%) 63% C 2s (23%), 2p (77%)
105	1.81	BD (Rh-P2)	28% Rh 5s (54%), 4d (46%) 72% P 3s (33%), 3p (67%)
115	1.81	BD (Si-N1)	14% Si 3s (42%), 3p (57%) 86% N 2s (32%), 2p (67%)
277	0.47	LV (Si)	3s (34%), 3p (65%)
278	0.38	LV (Si)	3s (24%), 3p (76%)
279	0.32	LV (Si)	3p (100 %)
281	0.46	BD* (Rh-C1)	63% Rh 5s (45%), 4d (55%) 37% C 2s (23%), 2p (77%)
292	0.36	BD* (Si-N1)	86% Si 3s (42%), 3p (57%) 14% N 2s (32%), 2p (67%)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] for selected bonding interactions (≥ 1 kcal/mol) between the listed NBOs:

• $\Delta E^{(2)}$ 90 (LP _{Rh}) → 279 (LV _{Si})	4.9
• $\Delta E^{(2)}$ 91 (LP _{Rh}) → 279 (LV _{Si})	1.5
• $\Delta E^{(2)}$ 92 (LP _{Rh}) → 277 (LV _{Si})	38.4
• $\Delta E^{(2)}$ 92 (LP _{Rh}) → 278 (LV _{Si})	23.0
• $\Delta E^{(2)}$ 92 (LP _{Rh}) → 292 (BD* _{Si-N1})	73.2
• $\Delta E^{(2)}$ 104 (BD _{Rh-C1}) → 277 (LV _{Si})	26.2
• $\Delta E^{(2)}$ 104 (BD _{Rh-C1}) → 278 (LV _{Si})	37.0
• $\Delta E^{(2)}$ 104 (BD _{Rh-C1}) → 279 (LV _{Si})	13.9
• $\Delta E^{(2)}$ 104 (BD _{Rh-C1}) → 292 (BD* _{Si-N1})	67.5
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 277 (LV _{Si})	25.1
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 278 (LV _{Si})	29.7
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 279 (LV _{Si})	1.0
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 292 (BD* _{Si-N1})	30.2

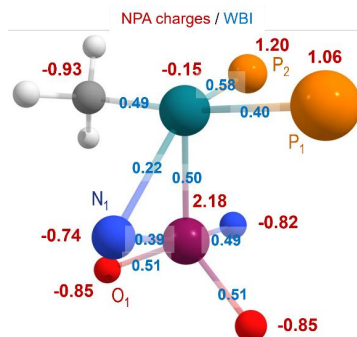


Figure S 5: Natural charges (red) and WBIs (blue) of the central C-Rh-P-P-Si-NONO unit in compound 2-CH₃. (PBE0-D4/def2-TZVPP//PBEh-3c)

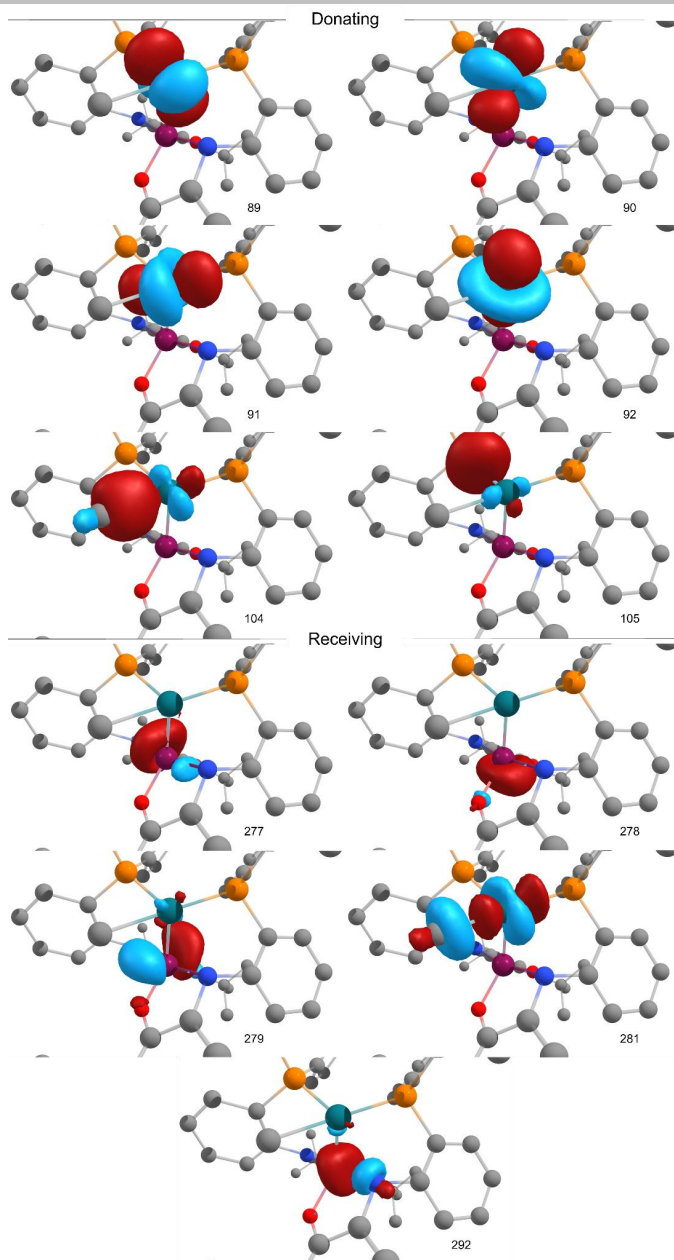


Figure S 6: Selected NBOs (PBE0-D4/def2-TZVPP//PBEh-3c) of 2-CH_3 , displayed at 0.1 a.u.. Hydrogen atoms are hidden for clarity.

NBO analysis for complex 2-Cp:

Important NBOs of **2-Cp** that take major roles in the Rh-Si interaction are listed below and displayed in figure S8.

Table S 3: List of selected NBOs in complex **2-Cl** with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
93	1.94	LP (Rh)	4d (100%)
94	1.93	LP (Rh)	4d (100%)
95	1.91	LP (Rh)	4d (100%)
96	1.64	LP (Rh)	4d (100%)
108	1.80	BD (Rh-P1)	31% Rh 5s (49%), 4d (51%) 69% P 3s (32%), 3p (68%)
109	1.77	BD (Rh-P2)	31% Rh 5s (50%), 4d (50%) 69% P 3s (32%), 3p (68%)
290	0.84	LV (Si)	3s (69%), 3p (31%)
291	0.38	LV (Si)	3s (32%), 3p (68%)
292	0.35	LV (Si)	3p (100 %)
293	0.29	LV (Si)	3p (100 %)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] for selected bonding interactions between the listed NBOs:

• $\Delta E^{(2)}$ 93 (LP _{Rh}) → 290 (LV _{Si})	7.1
• $\Delta E^{(2)}$ 93 (LP _{Rh}) → 292 (LV _{Si})	1.0
• $\Delta E^{(2)}$ 93 (LP _{Rh}) → 293 (LV _{Si})	0.8
• $\Delta E^{(2)}$ 94 (LP _{Rh}) → 290 (LV _{Si})	2.0
• $\Delta E^{(2)}$ 94 (LP _{Rh}) → 293 (LV _{Si})	2.0
• $\Delta E^{(2)}$ 95 (LP _{Rh}) → 290 (LV _{Si})	1.1
• $\Delta E^{(2)}$ 96 (LP_{Rh}) → 290 (LV_{Si})	103.6
• $\Delta E^{(2)}$ 96 (LP _{Rh}) → 291 (LV _{Si})	4.8
• $\Delta E^{(2)}$ 108 (BD _{Rh-P1}) → 290 (LV _{Si})	156.0
• $\Delta E^{(2)}$ 108 (BD _{Rh-P1}) → 291 (LV _{Si})	24.2
• $\Delta E^{(2)}$ 108 (BD _{Rh-P1}) → 292 (LV _{Si})	3.3
• $\Delta E^{(2)}$ 108 (BD _{Rh-P1}) → 293 (LV _{Si})	1.3
• $\Delta E^{(2)}$ 109 (BD _{Rh-P2}) → 290 (LV _{Si})	203.4
• $\Delta E^{(2)}$ 109 (BD _{Rh-P2}) → 291 (LV _{Si})	29.6
• $\Delta E^{(2)}$ 109 (BD _{Rh-P2}) → 293 (LV _{Si})	1.2

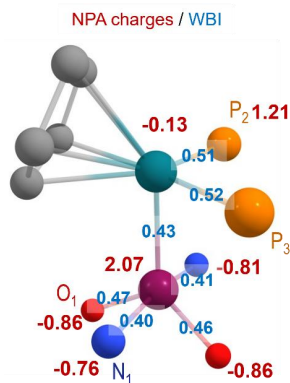


Figure S 7: Natural charges (red) and WBIs (blue) of the central Cp-Rh-P-P-Si-NONO unit in compound **2-Cp**. (PBE0-D4/def2-TZVPP/PBEh-3c)

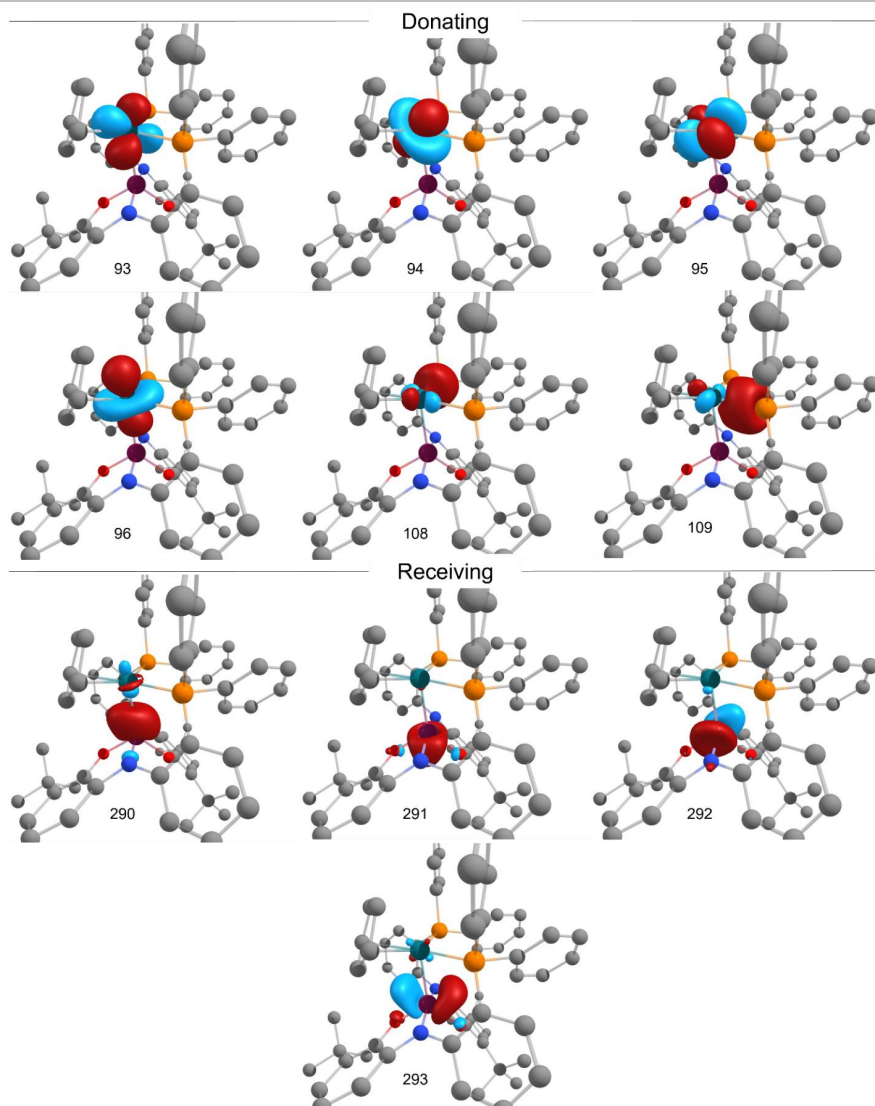


Figure S 8: Selected NBOs (PBE0-D4/def2-TZVPP//PBEh-3c) of **2-Cp**, displayed at 0.1 a.u.. Hydrogen atoms are hidden for clarity.

NBO analysis for complex 2-H:

Important NBOs of **2-H** that take major roles in the Rh-Si interaction are listed below and displayed in figure S10.

Table S 4: List of selected NBOs in complex **2-H** with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
88	1.95	LP (Rh)	4d (100%)
89	1.94	LP (Rh)	4d (100%)
90	1.92	LP (Rh)	4d (100%)
91	1.70	LP (Rh)	4d (100%)
104	1.68	BD (Rh-H1)	48% Rh 5s (48%), 4d (52%) 52% H 1s (100%)
105	1.83	BD (Rh-P2)	28% Rh 5s (52%), 4d (48%) 72% P 3s (33%), 3p (67%)
273	0.71	LV (Si)	3s (71%), 3p (29%)
274	0.39	LV (Si)	3s (29%), 3p (71%)
275	0.36	LV (Si)	3p (100 %)
276	0.34	LV (Si)	3p (100 %)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] for selected bonding interactions between the listed NBOs:

• $\Delta E^{(2)}$ 88 (LP _{Rh}) → 273 (LV _{Si})	1.5
• $\Delta E^{(2)}$ 88 (LP _{Rh}) → 275 (LV _{Si})	1.7
• $\Delta E^{(2)}$ 89 (LP _{Rh}) → 276 (LV _{Si})	6.4
• $\Delta E^{(2)}$ 90 (LP _{Rh}) → 275 (LV _{Si})	1.2
• $\Delta E^{(2)}$ 91 (LP_{Rh}) → 273 (LV_{Si})	167.4
• $\Delta E^{(2)}$ 91 (LP _{Rh}) → 274 (LV _{Si})	12.5
• $\Delta E^{(2)}$ 104 (BD_{Rh-H1}) → 273 (LV_{Si})	397.9
• $\Delta E^{(2)}$ 104 (BD _{Rh-H1}) → 274 (LV _{Si})	39.8
• $\Delta E^{(2)}$ 104 (BD _{Rh-H1}) → 276 (LV _{Si})	12.4
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 273 (LV _{Si})	81.4
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 274 (LV _{Si})	16.4
• $\Delta E^{(2)}$ 105 (BD _{Rh-P2}) → 275 (LV _{Si})	1.0

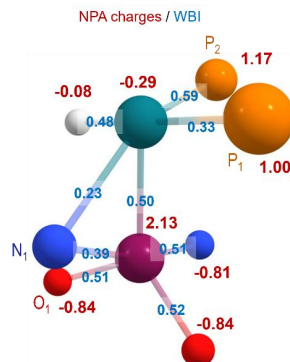


Figure S 9: Natural charges (red) and WBIs (blue) of the central H-Rh-P-P-Si-NONO unit in compound **2-H**. (PBE0-D4/def2-TZVPP//PBEh-3c)

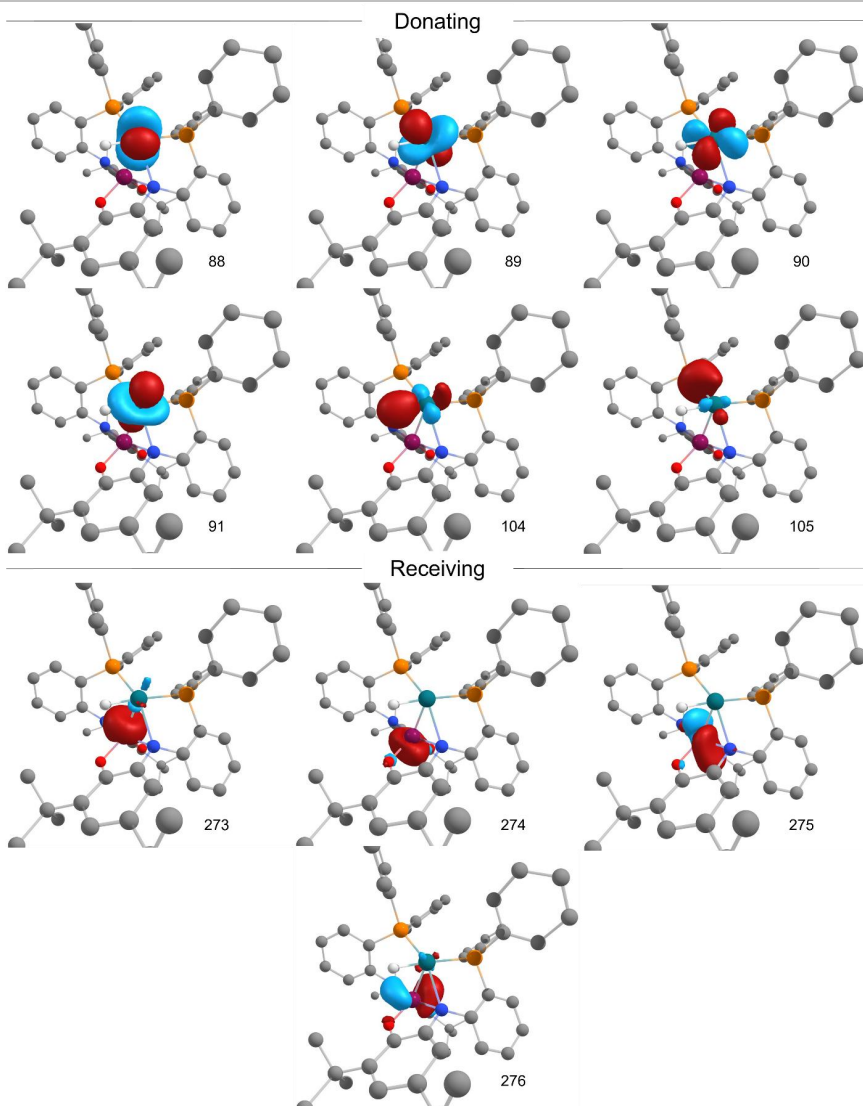


Figure S 10: Selected NBOs (PBE0-D4/def2-TZVPP//PBEh-3c) of **2-H**, displayed at 0.1 a.u.. Hydrogen atoms (with exception of the hydride) are hidden for clarity.

NBO analysis for model complex [HRh(PPh₃)(PNOMe₂)]:

To evaluate the effect that the Z-type interaction has for the stability of **2-H**, a similar model compound was designed that mimics the coordination geometry of **2-H** in the absence of the Rh-Si interaction. The compound with selected natural charges obtained by NPA and WBIs is depicted in figure S 9.

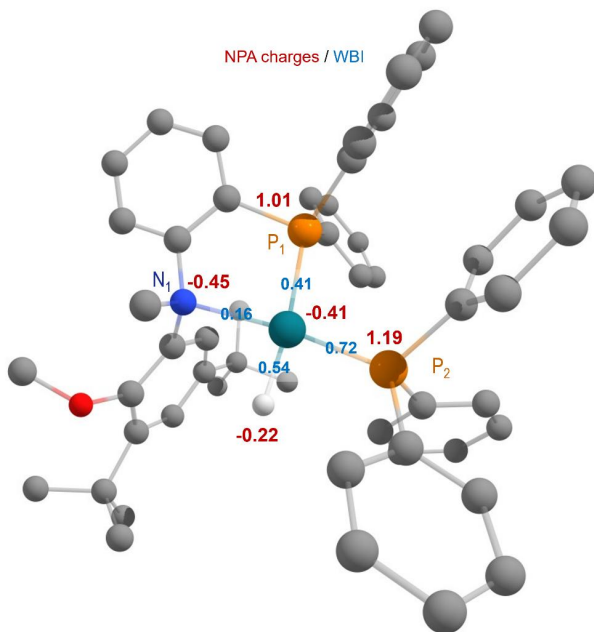


Figure S 11: Natural charges (red) and WBIs (blue) in compound [HRh(PPh₃)(PNOMe₂)] (PBE0-D4/def2-TZVPP//PBEh-3c; hydrogen atoms except the hydride are omitted for clarity).

NBO analysis for complex 3-Cl:

Important NBOs of **3-Cl** that take major roles in the Rh-Si interaction are listed below and displayed in figure S12.

Table S 5: List of selected NBOs in complex **3-Cl** with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
109	1.96	LP (Rh)	4d _{xz} (100%)
110	1.89	LP (Rh)	4d _{yz} (100%)
111	1.88	LP (Rh)	4d _{xy} (100%)
112	1.99	LP (Cl)	3s (84%), 3p (16%)
115	1.75	LP (Cl)	3s (14%), 3p (86%)
116	1.30	LP (P2)	3s (15%), 3p (85%)
130	1.86	BD (Rh-P1)	39% Rh 5s (35%), 4d (65%) 61% P 3s (31%), 3p (68%)
131	1.77	BD (Rh-Si)	71% Rh 5s (29%), 4d (70%) 29% Si 3s (53%), 3p (46%)
341	0.40	LV (Si)	3s (48%), 3p (52%)
342	0.37	LV (Si)	3p (100%)
343	0.30	LV (Si)	3p (100 %)
347	0.40	BD* (Rh-Si)	29% Rh 5s (29%), 4d (70%) 71% Si 3s (53%), 3p (46%)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] ≥ 1 kcal/mol for selected bonding interactions between the listed NBOs:

- $\Delta E^{(2)}$ 109 (LP_{Rh}) $\rightarrow$ 342 (LV_{Si}) 1.0
- $\Delta E^{(2)}$ 130 (BD_{Rh-P1}) $\rightarrow$ 341 (LV_{Si}) 9.5
- $\Delta E^{(2)}$ 130 (BD_{Rh-P1}) $\rightarrow$ 342 (LV_{Si}) 1.2
- $\Delta E^{(2)}$ 130 (BD_{Rh-P1}) $\rightarrow$ 347 (BD*_{Rh-Si}) 114.1
- $\Delta E^{(2)}$ 112 (LP_{Cl}) $\rightarrow$ 347 (BD*_{Rh-Si}) 5.1
- $\Delta E^{(2)}$ 115 (LP_{Cl}) $\rightarrow$ 347 (BD*_{Rh-Si}) 56.4
- $\Delta E^{(2)}$ 116 (LP_{P2}) $\rightarrow$ 341 (LV_{Si}) 1.3
- $\Delta E^{(2)}$ 116 (LP_{P2}) $\rightarrow$ 342 (LV_{Si}) 2.5
- $\Delta E^{(2)}$ 116 (LP_{P2}) $\rightarrow$ 343 (LV_{Si}) 1.5
- $\Delta E^{(2)}$ 116 (LP_{P2}) $\rightarrow$ 347 (BD*_{Rh-Si}) 34.96

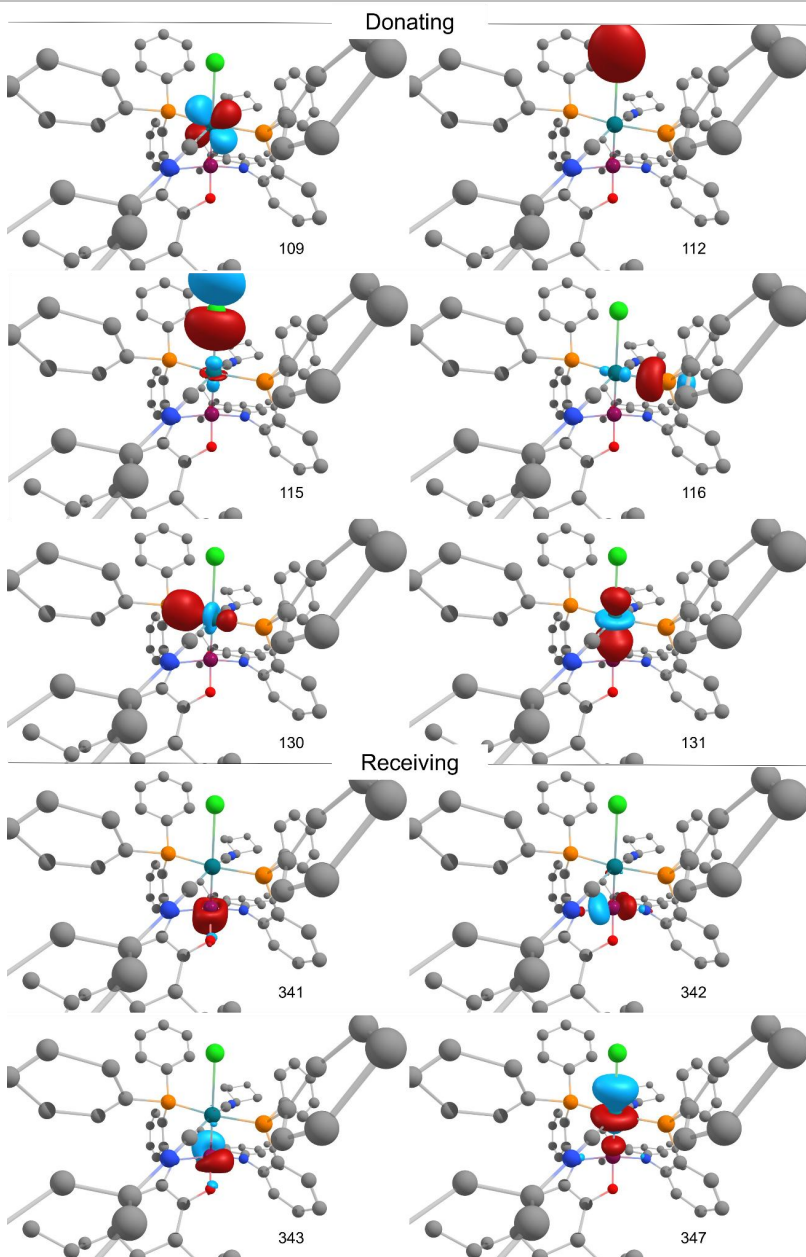


Figure S 12: Selected NBOs (PBE0-D4/def2-TZVP//PBEh-3c) of **3-ClI**, displayed at 0.05 - 0.1 a.u.. Hydrogen atoms are hidden for clarity.

NBO analysis, WBIs and NPA analysis for complex 3-H:

Important NBOs of **3-H** that take major roles in the Rh-Si interaction are listed below and displayed in figure S14.

Table S 6: List of selected NBOs in complex **3-Cl** with occupation, type and hybridization.

NBO	Occupation	Type	Hybridization
104	1.95	LP (Rh)	4d (100%)
105	1.88	LP (Rh)	4d (100%)
106	1.88	LP (Rh)	4d (100%)
107	1.70	LP (Rh)	5s (1%) 4d (99%)
108	1.26	LP (H)	1s (100%)
109	1.30	LP (P2)	3s (16%), 3p (84%)
122	1.77	BD (Rh-P1)	34% Rh 5s (53%), 4d (47%) 66% P 3s (32%), 3p (68%)
123	1.84	BD (Rh-C1)	28% Rh 5s (45%), 4d (55%) 72% C 2s (61%), 2p (39%)
333	0.96	LV (Si)	3s (67%), 3p (32%)
334	0.39	LV (Si)	3s (33%), 3p (67%)
335	0.37	LV (Si)	3p (100 %)
336	0.29	LV (Si)	3p (100 %)

Second order perturbation theory stabilization energies $\Delta E^{(2)}$ [kcal/mol] ≥ 1 kcal/mol for selected bonding interactions between the listed NBOs:

• $\Delta E^{(2)}$ 107 (LP _{Rh}) → 333 (LV _{Si})	100.4
• $\Delta E^{(2)}$ 107 (LP _{Rh}) → 334 (LV _{Si})	6.3
• $\Delta E^{(2)}$ 122 (BD _{Rh-P1}) → 333 (LV _{Si})	286.0
• $\Delta E^{(2)}$ 122 (BD _{Rh-P1}) → 334 (LV _{Si})	43.5
• $\Delta E^{(2)}$ 122 (BD _{Rh-P1}) → 335 (LV _{Si})	1.5
• $\Delta E^{(2)}$ 123 (BD _{Rh-C1}) → 333 (LV _{Si})	169.0
• $\Delta E^{(2)}$ 123 (BD _{Rh-C1}) → 334 (LV _{Si})	29.4
• $\Delta E^{(2)}$ 123 (BD _{Rh-C1}) → 335 (LV _{Si})	1.5
• $\Delta E^{(2)}$ 123 (BD _{Rh-C1}) → 336 (LV _{Si})	3.3
• $\Delta E^{(2)}$ 108 (LP _{H1}) → 333 (LV _{Si})	670.7
• $\Delta E^{(2)}$ 108 (LP _{H1}) → 334 (LV _{Si})	41.9
• $\Delta E^{(2)}$ 109 (LP _{P2}) → 333 (LV _{Si})	32.2
• $\Delta E^{(2)}$ 109 (LP _{P2}) → 334 (LV _{Si})	4.2
• $\Delta E^{(2)}$ 109 (LP _{P2}) → 335 (LV _{Si})	2.2
• $\Delta E^{(2)}$ 109 (LP _{P2}) → 336 (LV _{Si})	1.0

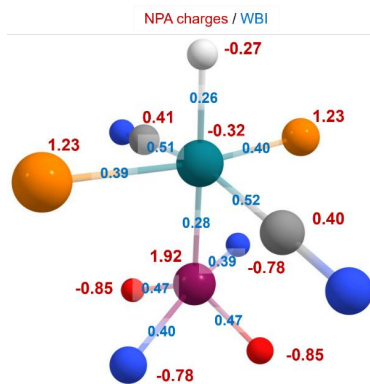


Figure S 13: Natural charges (red) and WBIs (blue) of the central H-Rh-P-P-Si-NONO unit in compound **3-H**. (PBE0-D4/def2-TZVP//PBEh-3c)

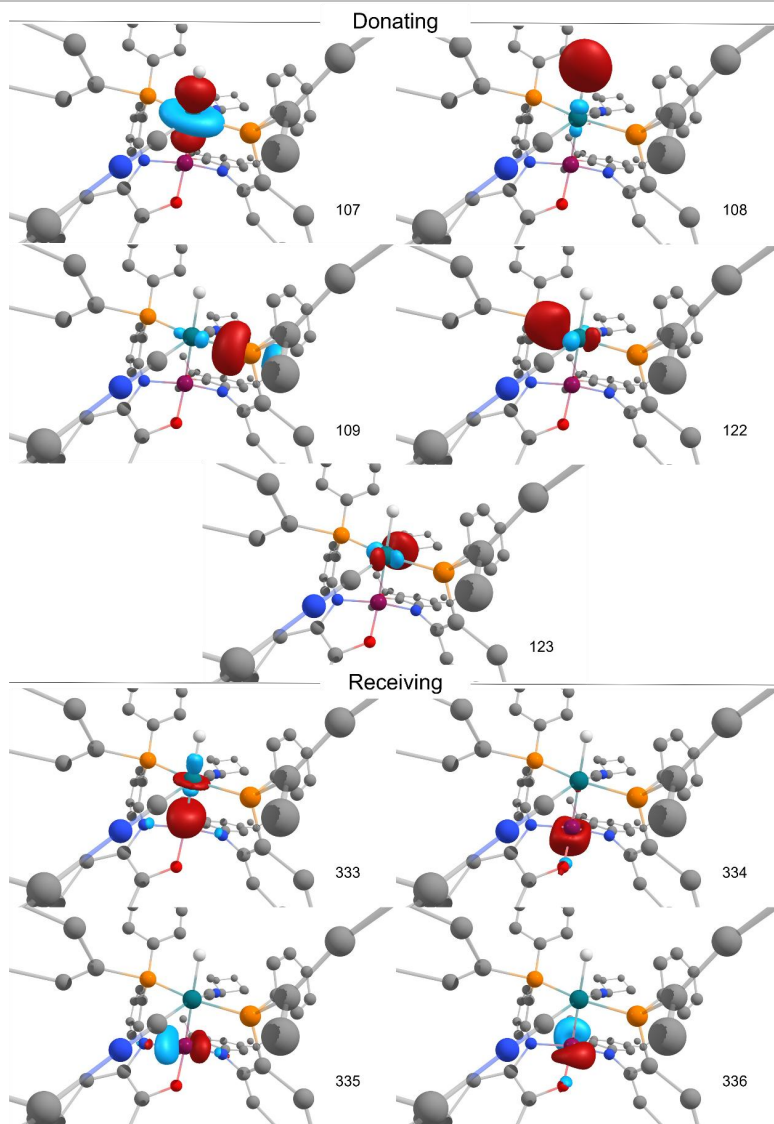


Figure S 14: Selected NBOs (PBE0-D4/def2-TZVP//PBEh-3c) of **3-H**, displayed at 0.1 a.u.. Hydrogen atoms (except Rh-H) are hidden for clarity.

Natural Bond Orbital QTAIM analyses were performed on the PBE0/DKH-def2-TZVP (Rh: SARC-DKH-TZVP) electron densities,^{19-21, 24} using the AIMAll software with default integration.²⁵ A variety of descriptors have been used in the context of Bader's theory of AIM, to describe and compare the nature of chemical bonds.²⁶⁻²⁹ The main components considered are the electron density, $\rho(r_{BCP})$, and the Laplacian of the density, $\nabla^2\rho(r_{BCP})$ at the bond critical points (bcp's). Positive Laplacians, as found at the bcp's the Si-O/N bonds suggest closed shell (ionic) interactions, whereas the opposite is found for the Rh-Si bond in **2-Cp** and **3-Cl**, meaning shared (covalent) interactions. The total electronic energy density $H(r_{BCP})$ serves as a criterion for the bond classification, with negative values for shared-type (covalent) atomic interactions (typical covalent single bonds ≈ -0.35) and positive values in closed-shell bonds.³⁰ In addition, the ratio of $G(r_{BCP})/\rho(r_{BCP})$ (Lagrangian kinetic energy per electron) indicates the kind of interatomic interactions, with a value <1 for shared interaction (Rh-Si and Rh-P) and >1 for closed-shell (ionic) bonding (Si-O/N and Rh-N).³¹⁻³² The ellipticity ($\epsilon=\lambda_1/\lambda_2-1$) of a bond quantifies the anisotropy of the electron density, with deviations from a cylindrical distribution leading to values larger than zero. This can be observed for highly asymmetric Si-N1 bond in **2-Cl**, which aligns well with the calculated NBO of this bond (NBO 119) The delocalization index is yet another indicator for covalent bonding.

Table S 7: Result for the QTAIM analysis of **2-Cl**, **2-Cp** and **3-Cl**.

QTAIM								Bader charge analysis	
2-Cl	$\rho(r_{BCP})$	$\nabla^2\rho(r_{BCP})$	$H(r_{BCP})$	$G(r_{BCP})$	$G(r_{BCP})/\rho(r_{BCP})$	$\epsilon=\lambda_1/\lambda_2-1$	DI		Q
Si-Rh	0.0926	0.020	-0.062	0.068	0.734	0.144	0.396	Si	3.05
Si-N	0.0869/ 0.1169	0.208/ 0.429	-0.042/ -0.053	0.094/ 0.161	1.082/ 1.377	0.689/ 0.135	0.227 0.331	N	-1.35/ -1.52
Si-O	0.1302/ 0.1297	0.704/ 0.699	-0.049/ -0.049	0.225 0.223	1.728/ 1.719	0.084/ 0.087	0.224/ 0.225	O	-1.39/ -1.39
Rh-P	0.1103/ 0.1156	0.136/ 0.119	-0.045/ -0.051	0.079/ 0.080	0.716/ 0.692	0.111/ 0.046	0.966/ 0.989	Rh	-0.13
Rh-N	0.0837	0.323	-0.016	0.096	1.147	0.400	0.660	P	+1.88/ +1.90
Rh-Cl	0.0842	0.250	-0.020	0.083	0.986	0.119	0.822		
2-Cp									
Si-Rh	0.0848	-0.120	-0.056	0.026	0.307	0.0730	0.525	Si	2.87
Si-N	0.0979/ 0.0961	0.292/ 0.285	-0.045/ -0.044	0.118/ 0.115	1.205/ 1.197	0.072/ 0.151	0.285/ 0.300	N	-1.46/ -1.46
Si-O	0.1202/ 0.1211	0.614/ 0.629	-0.045/ -0.045	0.199/ 0.202	1.658/ 1.668	0.068/ 0.078	0.337/ 0.328	O	-1.39/ -1.39
Rh-P	0.1078/ 0.1068	0.128/ 0.127	-0.044/ -0.043	+0.076/ +0.075	0.705/ 0.702	0.070/ 0.065	0.988/ 0.957	Rh	-0.15
								P	+1.87/ +1.87
3-Cl									
Si-Rh	0.0873	-0.121	-0.060	0.030	0.339	0.035			
Si-N	0.0990/ 0.0982	0.309/ 0.299	-0.045/ -0.044	0.122/ 0.119	1.229/ 1.216	0.153/ 0.149			
Si-O	0.1169/ 0.1179	0.589/ 0.599	-0.044/ -0.044	0.191/ 0.194	1.634/ 1.643	0.074/ 0.077			
Rh-P	0.0945/ 0.0929	0.131/ 0.136	-0.033/ -0.032	0.066/ 0.066	0.396/ 0.708	0.018/ 0.016			
Rh-Cl	0.0546	0.159	-0.010	0.050	0.910	0.062			

3. X-Ray Diffraction

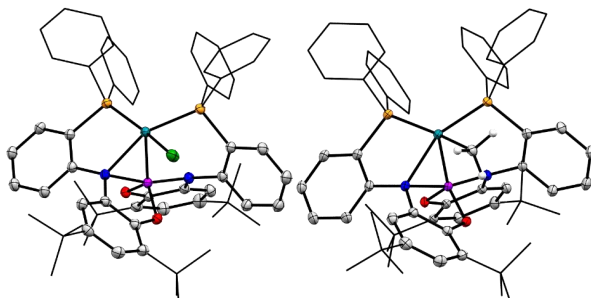
a. General

Suitable crystals for single-crystal structure determination were taken directly from the mother liquor, taken up in perfluorinated polyether oil and fixed on a cryo loop. Full shells of intensity data were collected at low temperatures with a Bruker D8 Venture diffractometer, dual source (Mo- K_α radiation, microfocus X-ray tube, Photon III detector, temperature 100 K). Data were processed with the standard Bruker (SAINT, APEX3) software package.³³⁻³⁴ Multiscan absorption correction was applied using the SADABS program.³⁵⁻³⁶ The structures were solved by intrinsic phasing³⁷⁻³⁸ and refined by full-matrix least-squares methods against F^2 using the SHELXTL software package (Version 2018/3).³⁹⁻⁴² Graphical handling of the structural data during solution and refinement was performed with shelXle.⁴³ All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Some parts of the disorder model were introduced by the program DSR.⁴⁴⁻⁴⁵

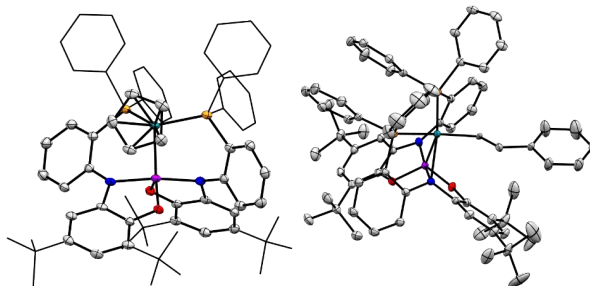
For the structure of **2-C₆H₅Ph**, four distorted molecules of co-crystallized toluene, for **2-Cp** two distorted molecules of Et₂O, for **2-CH₃** eight distorted molecules of toluene as well as two molecules of diethylether, for **3-Cl**, four distorted molecules of co-crystallized *n*-pentane and two molecules of thf and for **2-(μ -Cl)₂-Rh(CO)₂** four disordered molecules of benzene were treated with the SQUEEZE procedure as implemented in PLATON.⁴⁶⁻⁴⁷ Finalisation of gathered data was done using final cif tool.⁴⁸

For data visualization, Mercury 2024.1.0 was used.⁴⁹⁻⁵² The thermal displacement ellipsoids are shown at the probability level of 50%. CCDC numbers 2418933-2418937 and 2426618 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>.

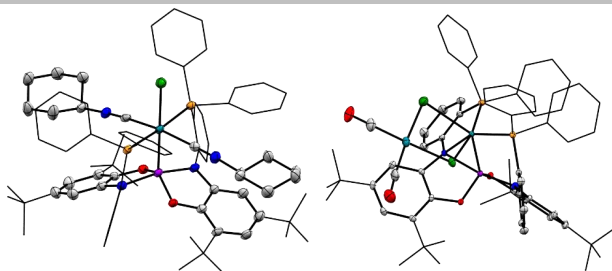
b. Summarized Data



Compound CCDC number	2-Cl 2418933	2-CH₃ 2418935
Identification code	mo_na275_3_0ma_a	mo_na637_a_sq
Empirical formula	C ₁₄₀ H ₁₆₀ Cl ₂ N ₄ O ₄ P ₄ Rh ₂ Si ₂	C ₆₅ H ₇₁ N ₂ O ₂ P ₂ RhSi
Formula weight	2527.58	1105.17
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	<i>C2/c</i> (15)	<i>C2/c</i> (15)
<i>a</i> [Å]	39.626(5)	39.701(6)
<i>b</i> [Å]	12.1783(14)	12.2754(16)
<i>c</i> [Å]	30.472(4)	29.987(5)
α [°]	90	90
β [°]	118.411(9)	118.138(13)
γ [°]	90	90
Volume [Å ³]	12934(3)	12887(4)
<i>Z</i>	4	8
ρ_{calc} [g cm ⁻³]	1.298	1.139
μ [mm ⁻¹]	0.421	0.373
<i>F</i> (000)	5304	4640
Crystal size [mm ³]	0.179×0.175×0.160	0.430×0.330×0.224
Radiation	Mo- <i>K</i> α (λ = 0.71073 Å)	Mo- <i>K</i> α (λ = 0.71073 Å)
2 θ range [°]	4.07 to 63.30 (0.68 Å)	4.30 to 59.15 (0.72 Å)
Index ranges	−58 ≤ <i>h</i> ≤ 58 −17 ≤ <i>k</i> ≤ 17 −44 ≤ <i>l</i> ≤ 45	−55 ≤ <i>h</i> ≤ 55 −17 ≤ <i>k</i> ≤ 17 −41 ≤ <i>l</i> ≤ 41
Reflections collected	416707	249540
Independent reflections	21691 [<i>R</i> _{int} = 0.1068, <i>R</i> _{sigma} = 0.0365]	18064 [<i>R</i> _{int} = 0.0614, <i>R</i> _{sigma} = 0.0237]
Data/Restraints/Parameters	21691/194/808	18064/420/751
Goodness-of-fit on <i>F</i> ²	1.138	1.037
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0484, <i>wR</i> ₂ = 0.1116	<i>R</i> ₁ = 0.0270, <i>wR</i> ₂ = 0.0678
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0607, <i>wR</i> ₂ = 0.1200	<i>R</i> ₁ = 0.0331, <i>wR</i> ₂ = 0.0707
Largest peak/hole [e Å ⁻³]	1.45/−0.80	0.42/−0.47



Compound CCDC number	2-Cp 2418934	2-C₂H₂Ph 2418936
Identification code	mo_na616_2_a_sq	mo_naja18_a_sq
Empirical formula	C ₁₄₂ H ₁₅₆ N ₄ O ₅ P ₄ Rh ₂ Si ₂	C _{72.01} H _{74.28} N ₂ O ₂ P ₂ RhSi
Formula weight	2384.58	1192.68
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	14.011(3)	13.203(3)
<i>b</i> [Å]	19.608(5)	14.939(4)
<i>c</i> [Å]	25.391(6)	20.682(3)
α [°]	105.649(7)	95.353(5)
β [°]	103.514(10)	99.188(9)
γ [°]	96.376(9)	114.096(9)
Volume [Å ³]	6417(3)	3618.8(13)
<i>Z</i>	2	2
ρ_{calc} [g cm ⁻³]	1.234	1.095
μ [mm ⁻¹]	0.381	0.337
<i>F</i> (000)	2508	1251
Crystal size [mm ³]	0.33×0.12×0.04	0.308×0.280×0.130
Radiation	Mo- <i>K</i> α (λ = 0.71073 Å)	Mo- <i>K</i> α (λ = 0.71073 Å)
2 θ range [°]	3.79 to 50.35 (0.84 Å)	3.92 to 60.30 (0.71 Å)
Index ranges	-16 ≤ <i>h</i> ≤ 16 -23 ≤ <i>k</i> ≤ 23 -30 ≤ <i>l</i> ≤ 30	-18 ≤ <i>h</i> ≤ 18 -21 ≤ <i>k</i> ≤ 21 -29 ≤ <i>l</i> ≤ 29
Reflections collected	256702	300856
Independent reflections	22923	21353 [<i>R</i> _{int} = 0.0641, <i>R</i> _{sigma} = 0.0272]
Data/Restraints/Parameters	22923/198/1498	21353/1313/966
Goodness-of-fit on <i>F</i> ²	1.034	1.034
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0389, <i>wR</i> ₂ = 0.0897	<i>R</i> ₁ = 0.0312, <i>wR</i> ₂ = 0.0781
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0539, <i>wR</i> ₂ = 0.0980	<i>R</i> ₁ = 0.0369, <i>wR</i> ₂ = 0.0815
Largest peak/hole [e Å ⁻³]	0.75/-0.86	0.62/-0.59



Compound CCDC number	3-Cl 2418937	2-(μ-Cl)₂-Rh(CO)₂ 2426618
Identification code	mo_naja21_3_a_sq	mo_na643_a_sq
Empirical formula	C ₆₃ H ₁₀₂ ClN ₄ O ₂ P ₂ RhSi	C ₆₆ H ₆₈ Cl ₂ N ₂ O ₄ P ₂ Rh ₂ Si
Formula weight	1416.07	1319.97
Temperature [K]	120(2)	100(2)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [Å]	14.677(5)	22.586(5)
<i>b</i> [Å]	17.879(7)	12.462(2)
<i>c</i> [Å]	19.675(7)	24.336(4)
α [°]	68.56(2)	90
β [°]	69.779(15)	103.709(5)
γ [°]	73.78(2)	90
Volume [Å ³]	4440(3)	6655(2)
<i>Z</i>	2	4
ρ_{calc} [g cm ⁻³]	1.059	1.318
μ [mm ⁻¹]	0.314	0.687
<i>F</i> (000)	1500	2712
Crystal size [mm ³]	0.21×0.18×0.12	0.11×0.10×0.07
Radiation	Mo-K α (λ = 0.71073 Å)	Mo-K α (λ = 0.71073 Å)
2 θ range [°]	4.22 to 57.82 (0.74 Å)	3.69 to 58.26 (0.73 Å)
Index ranges	-18 ≤ <i>h</i> ≤ 19 -22 ≤ <i>k</i> ≤ 24 0 ≤ <i>l</i> ≤ 26	-30 ≤ <i>h</i> ≤ 30 -17 ≤ <i>k</i> ≤ 17 -33 ≤ <i>l</i> ≤ 33
Reflections collected	22926	607185
Independent reflections	22926 [<i>R</i> _{int} = 0.1141, <i>R</i> _{sigma} = 0.0543]	17886 [<i>R</i> _{int} = 0.1030, <i>R</i> _{sigma} = 0.0245]
Data/Restraints/Parameters	22926/730/1009	17886/204/764
Goodness-of-fit on <i>F</i> ²	1.036	1.042
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0696, <i>wR</i> ₂ = 0.1692	<i>R</i> ₁ = 0.0350, <i>wR</i> ₂ = 0.0945
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0933, <i>wR</i> ₂ = 0.1812	<i>R</i> ₁ = 0.0441, <i>wR</i> ₂ = 0.1009
Largest peak/hole [e Å ⁻³]	2.09/-1.41	1.22/-2.37

c. Metric Oxidation States

Metric oxidation states (MOS) of the ligand fragments based on the model of Brown are calculated using the bond lengths that were obtained from scXRD analysis of compound **2-Cl** and **2-Cp**.⁵³

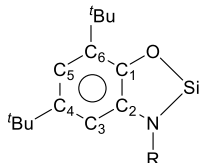


Figure S 15: Numbering scheme for the carbon atoms in compound **2-Cl**, as suggested by Brown.⁵³

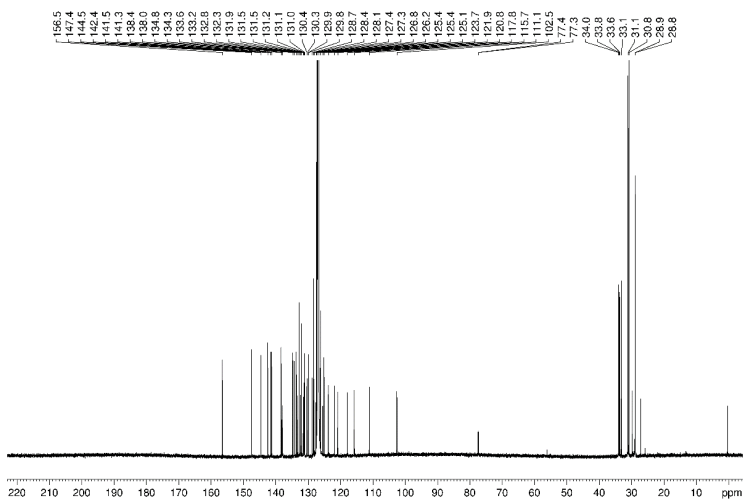
Table S 8: Average bond lengths (Å) and resulting MOS for complexes **2-Cl**, **2-Cp** (only one molecule in the asymmetric unit was considered) and **3-Cl**.

	2-Cl		2'-Cp	
	amp-N1	amp-N2	amp-N1	amp-N2
d(C1-O)	1.374(2)	1.385(2)	1.373(3)	1.374(3)
d(C2-N)	1.430(2)	1.404(2)	1.403(3)	1.395(3)
d(C1-C2)	1.398(3)	1.409(3)	1.399(4)	1.400(4)
d(C2-C3)	1.389(3)	1.388(3)	1.388(4)	1.401(4)
d(C3-C4)	1.399(3)	1.403(3)	1.400(4)	1.399(4)
d(C4-C5)	1.402(3)	1.393(3)	1.392(4)	1.398(4)
d(C5-C6)	1.399(3)	1.405(3)	1.401(4)	1.400(4)
d(C6-C1)	1.395(3)	1.392(3)	1.394(4)	1.394(4)
MOS	-2.15	-2.14	-2.08	-1.98

	3-Cl	
	amp-N1	amp-N2
d(C1-O)	1.373(4)	1.364(4)
d(C2-N)	1.388(4)	1.385(4)
d(C1-C2)	1.406(4)	1.409(5)
d(C2-C3)	1.397(5)	1.384(5)
d(C3-C4)	1.392(5)	1.414(5)
d(C4-C5)	1.396(5)	1.396(5)
d(C5-C6)	1.410(5)	1.411(5)
d(C6-C1)	1.389(4)	1.403(5)
MOS	-1.97	-1.94

¹H NMR spectrum of compound 10 in CDCl₃. The spectrum shows peaks in the aromatic region (6.5-8.1 ppm) and aliphatic region (0.9-2.0 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
8.12	1.00
8.04	1.17
7.92	1.38
7.84	1.35
7.91	2.45
7.90	2.08
7.89	1.38
7.88	1.35
7.86	2.08
7.35	1.05
7.21	1.00
7.14	1.00
7.12	2.08
7.11	1.05
7.09	1.00
7.04	1.00
7.00	1.00
6.99	2.08
6.77	1.05
6.75	1.00
6.74	1.00
6.62	1.00
6.51	1.00
6.50	1.00
6.48	1.00
6.39	1.00
1.54	8.81
1.47	9.41
1.27	9.22
0.95	9.95



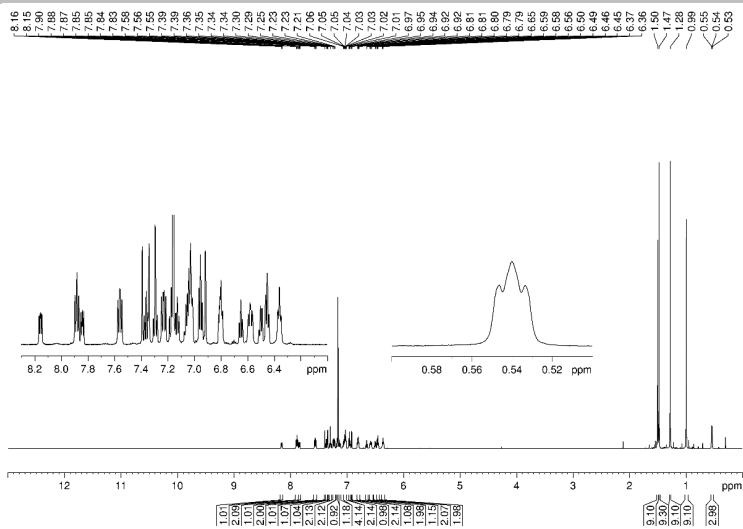


Figure S 20: ^1H NMR spectrum (600 MHz) of **2-CH₃** in C_6D_6 at 295 K.

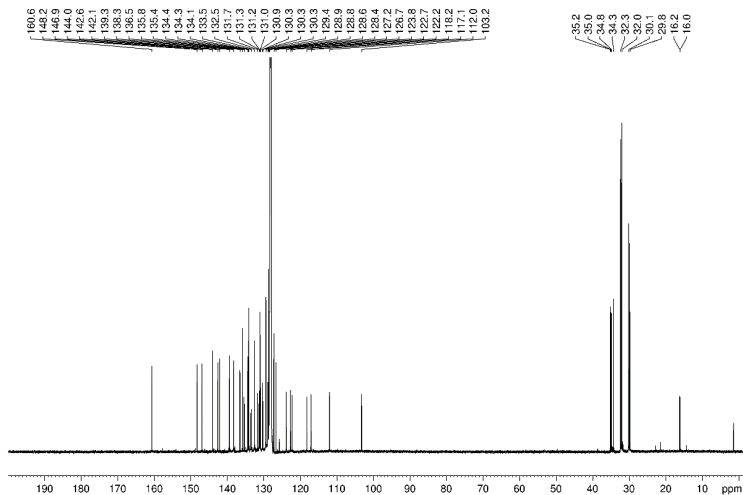


Figure S 21: $^{13}\text{C}\{^1\text{H}\}[^{31}\text{P}]$ NMR spectrum (151 MHz) of **2-CH₃** in C_6D_6 at 295 K.

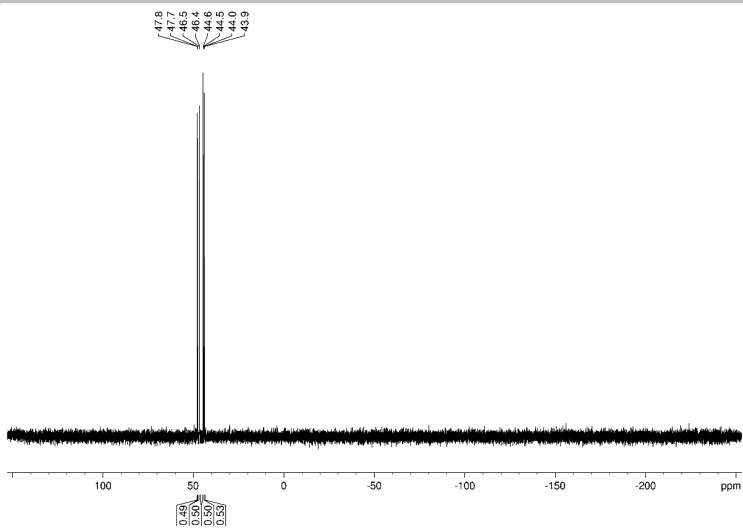


Figure S 22: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of **2-CH₃** in C_6D_6 at 295 K.

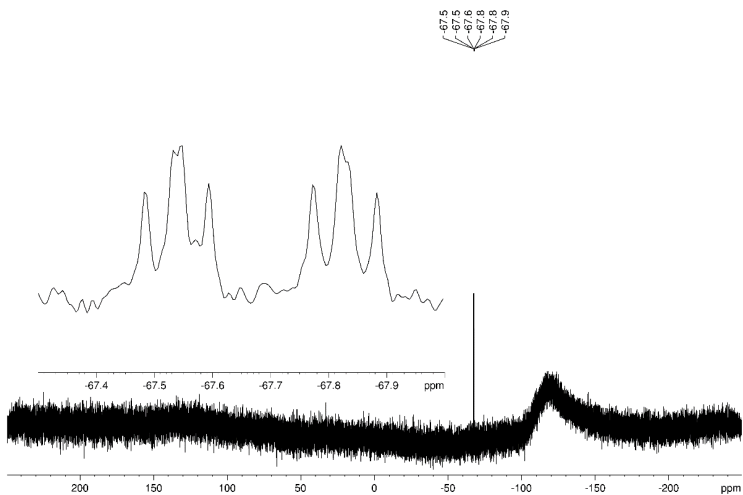


Figure S 23: ^{29}Si (IG) NMR spectrum (119 MHz) of **2-CH₃** in C_6D_6 at 295 K.

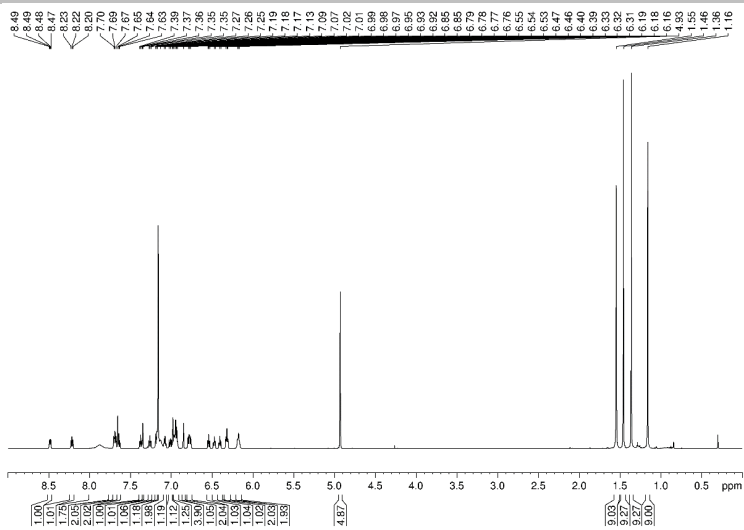


Figure S 24: ^1H NMR spectrum (600 MHz) of **2'-Cp** in C_6D_6 at 295 K.

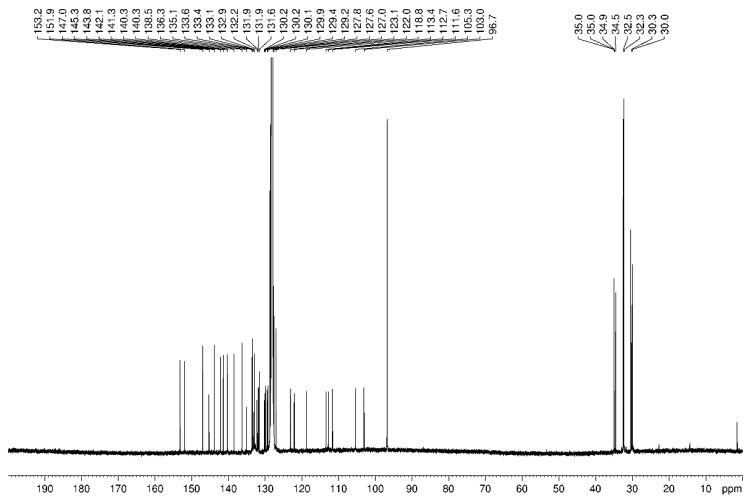


Figure S 25: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (151 MHz) of **2'-Cp** in C_6D_6 at 295 K.

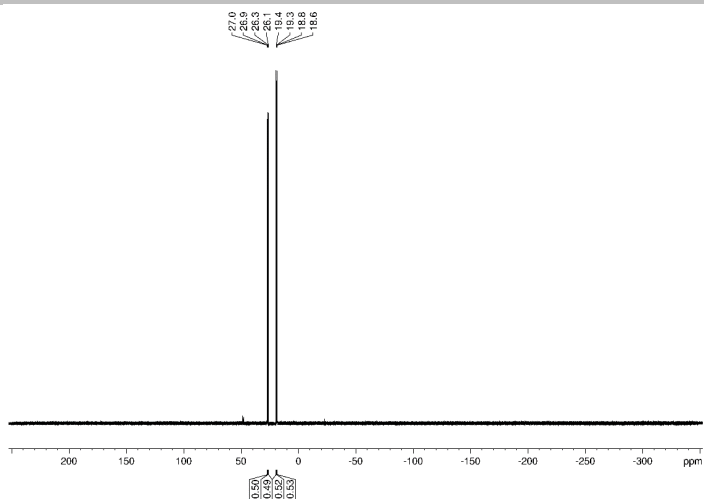


Figure S 26: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of $2'\text{-Cp}$ in C_6D_6 at 295 K.

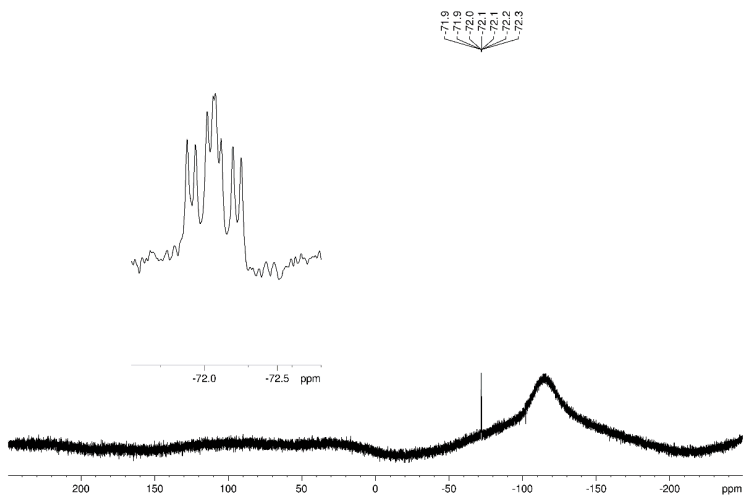


Figure S 27: ^{29}Si (IG) NMR spectrum (119 MHz) of $2'\text{-Cp}$ in C_6D_6 at 295 K.

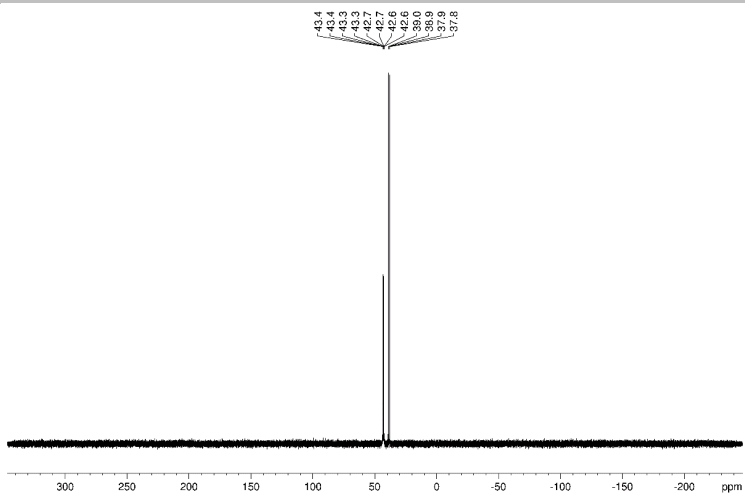


Figure S 30: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of **2-H** in C_6D_6 at 295 K

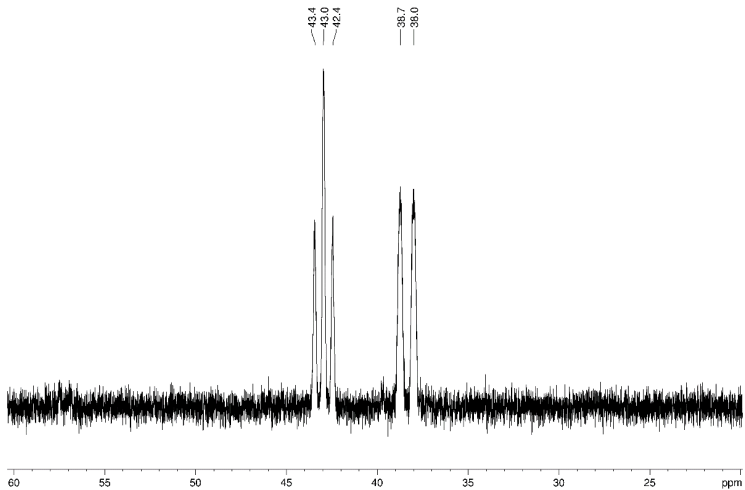


Figure S 31: ^{31}P NMR spectrum (243 MHz) of **2-H** in C_6D_6 at 295 K.

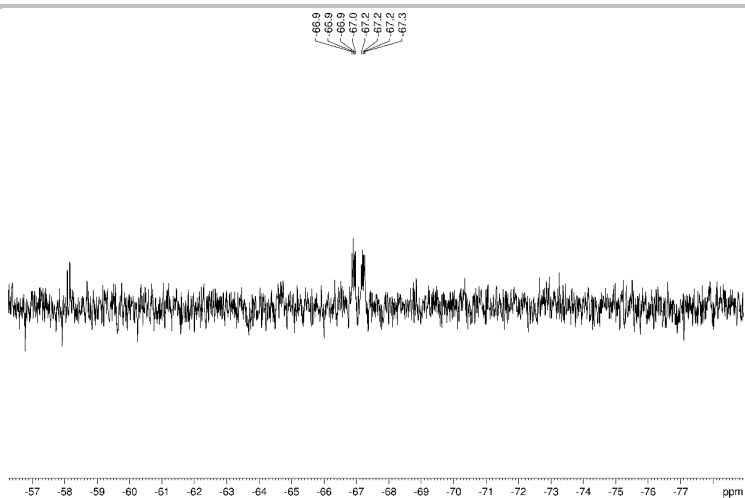


Figure S 32: ^{29}Si (IG) NMR spectrum (119 MHz) of **2-H** in C_6D_6 at 295 K.

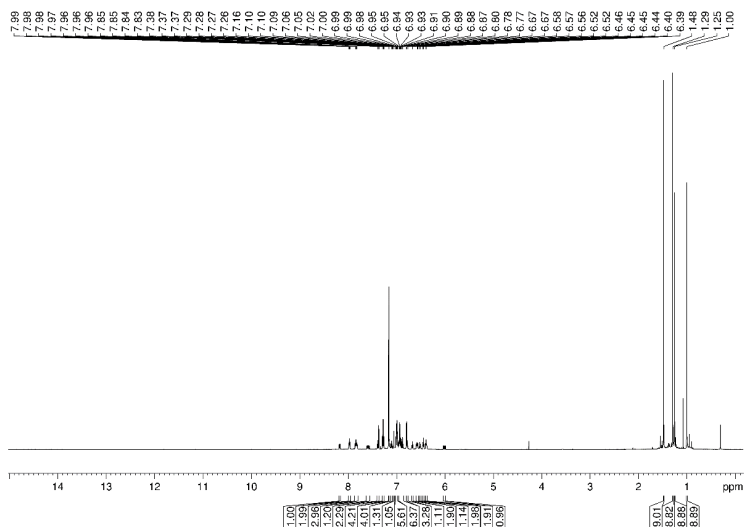


Figure S 33: ^1H NMR spectrum (600 MHz) of **2-C₂H₂Ph** in C_6D_6 at 295 K.

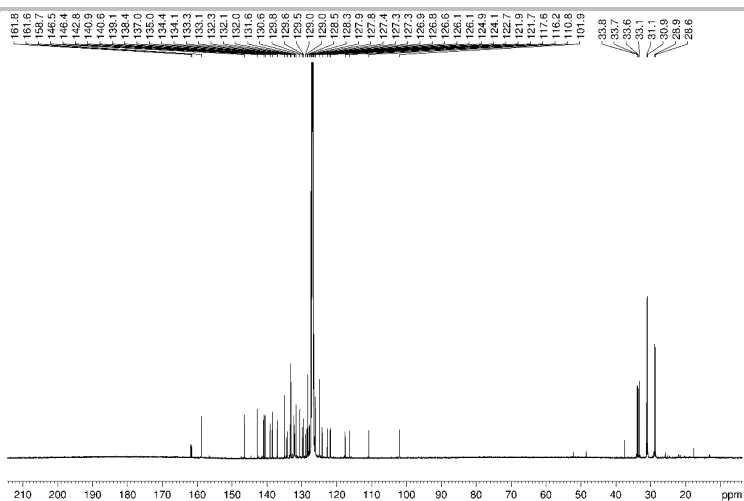


Figure S 34: $^{13}\text{C}\{^1\text{H}\}[^{31}\text{P}]$ NMR spectrum (151 MHz) of **2-C₂H₂Ph** in C_6D_6 at 295 K.

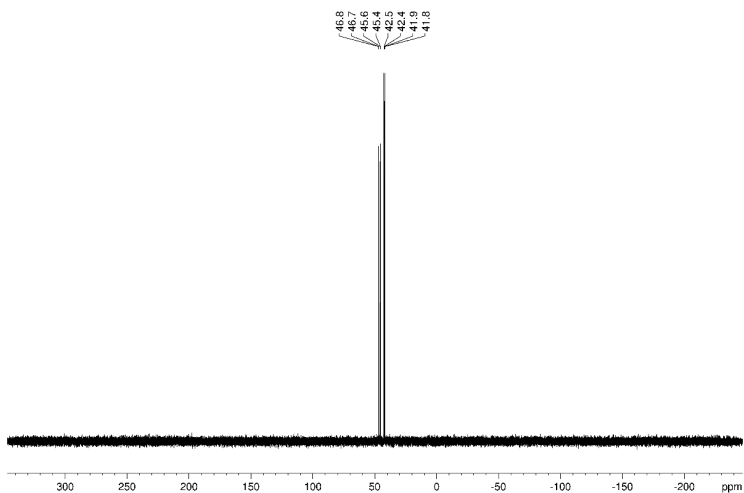


Figure S 35: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of **2-C₂H₂Ph** in C_6D_6 at 295 K.

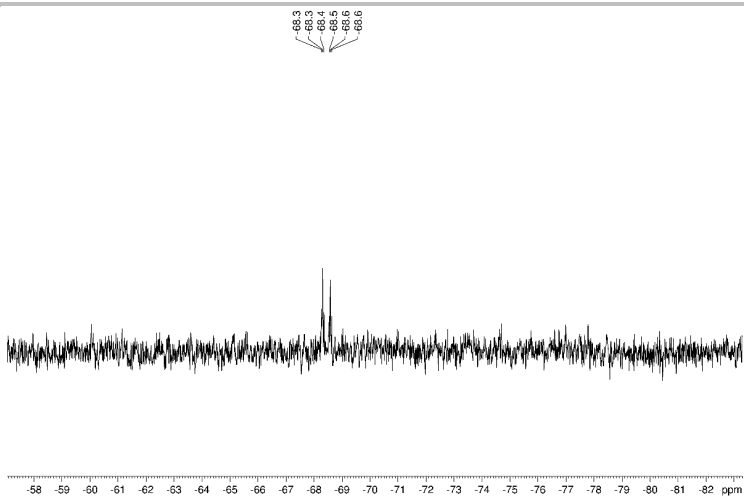


Figure S 36: ^{29}Si (IG) NMR spectrum (119 MHz) of **2-C₂H₂Ph** in C_6D_6 at 295 K.

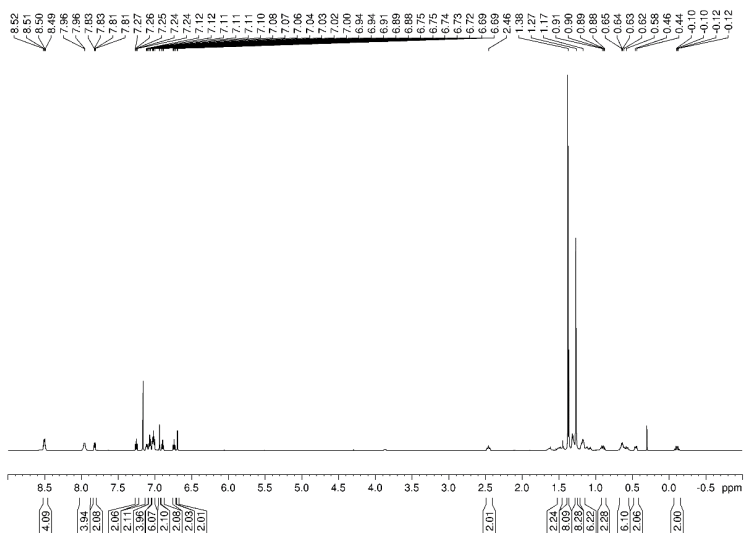


Figure S 37: ^1H NMR spectrum (600 MHz) of **3-Cl** in C_6D_6 at 295 K.

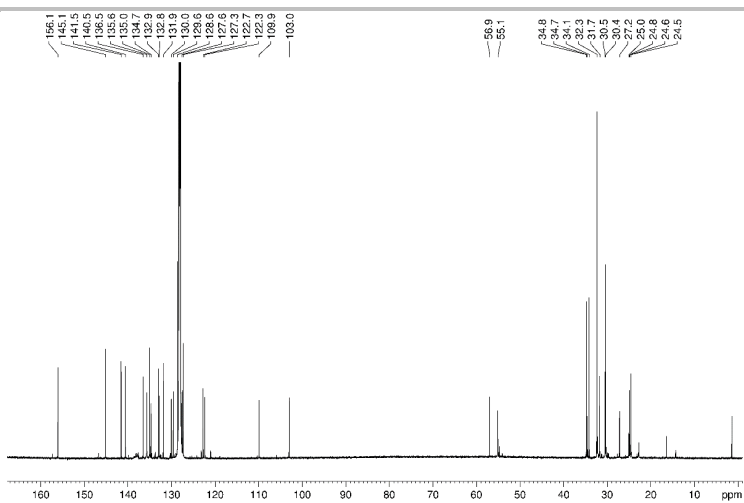


Figure S 38: $^{13}\text{C}\{^1\text{H}\}[^{31}\text{P}]$ NMR spectrum (151 MHz) of **3-Cl** in C_6D_6 at 295 K.

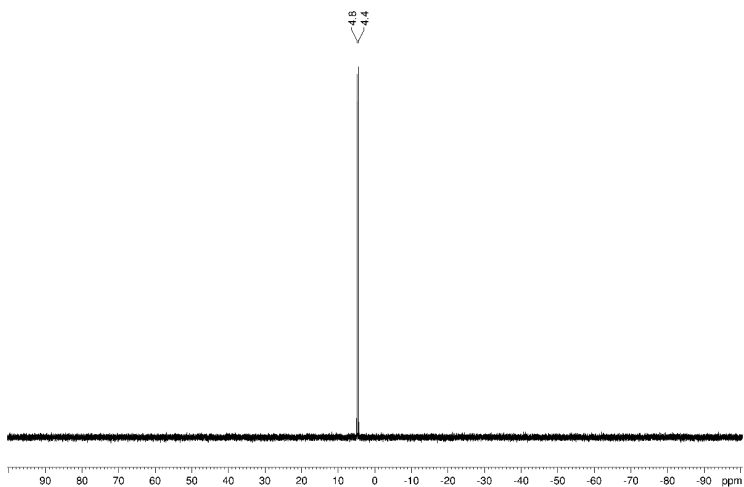


Figure S 39: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (243 MHz) of **3-Cl** in C_6D_6 at 295 K.

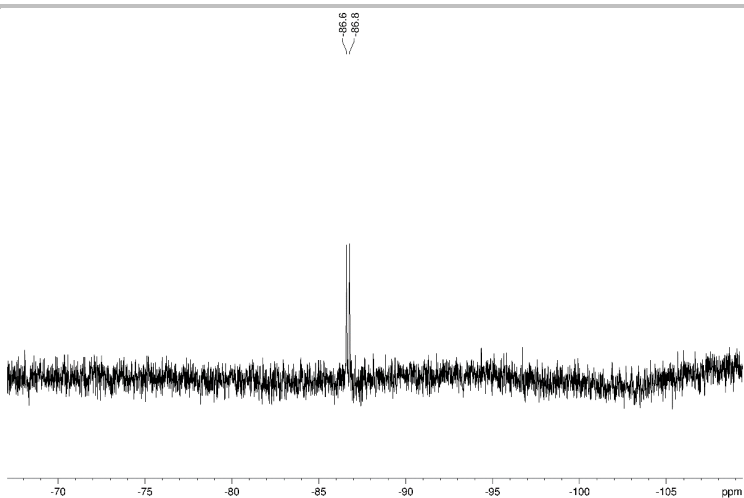


Figure S 40: ²⁹Si (IG) NMR spectrum (119 MHz) of 3-Cl in C₆D₆ at 295 K.

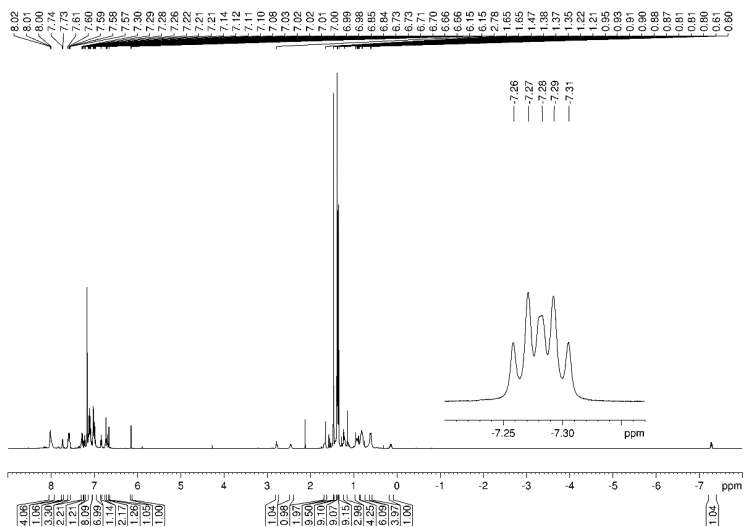


Figure S 41: ¹H NMR spectrum (600 MHz) of 3-H in C₆D₆ at 295 K.

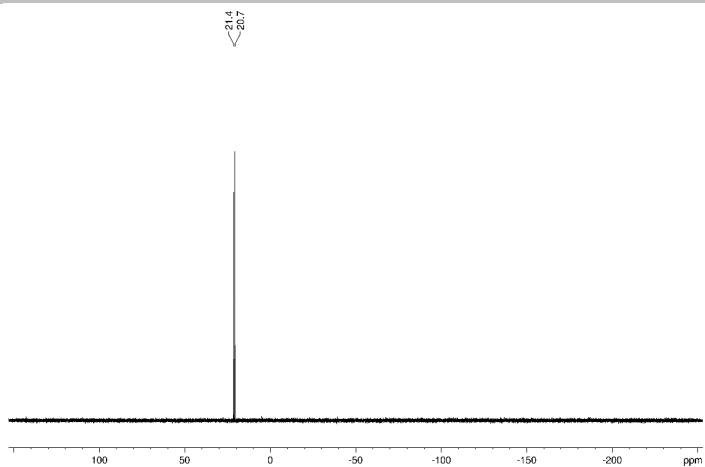


Figure S 42: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (161 MHz) of **3-H** in C_6D_6 at 295 K.

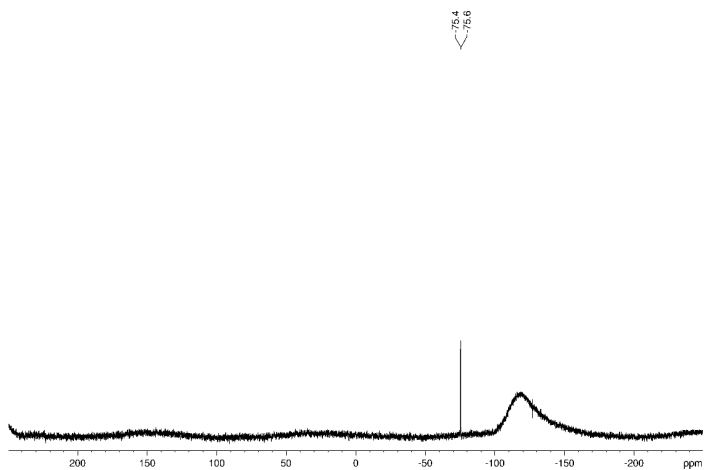


Figure S 43: ^{29}Si (1G) NMR spectrum (119 MHz) of **3-H** in C_6D_6 at 295 K.

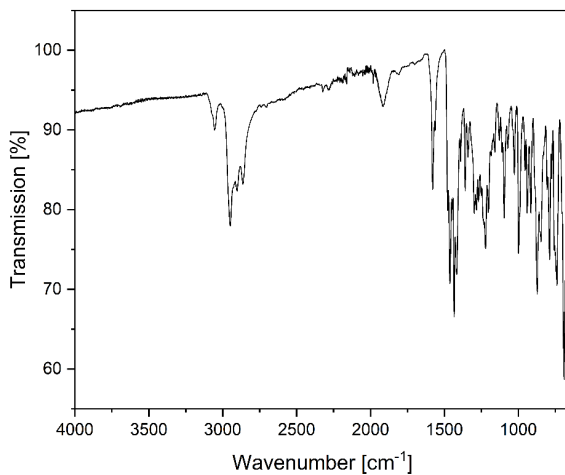


Figure S 44: IR (ATR) spectrum of **2-H** under nitrogen atmosphere at 298 K.

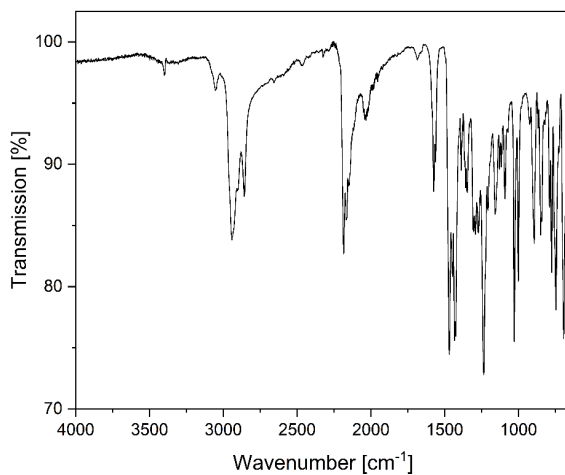


Figure S 45: IR (ATR) spectrum of **3-Cl** under nitrogen atmosphere at 298 K.

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3.3.4. MOLYBDENUM COMPLEXES OF A SILICON Z-TYPE LIGAND ⁱⁱⁱ

PREFACE

While the hitherto reported chemistry of Z-type complexes mainly focussed on late transition metals due to their ability to donate electron density from their filled d-orbitals to the Lewis acidic center, much less is known about possible Z-type interactions of low oxidation state early transition metals. Given their potential to fixate and activate dinitrogen (N₂),^[200–202] their inclusion into this thriving field promises valuable insights, especially taking into account the catalytic activity of reported N₂ Z-type complexes of late transition metals.^[195,201] With this large gap in the field of Z-type chemistry, we were curious whether we could expand the coordination chemistry of σ -accepting ligands to incorporate molybdenum, a metal famous for its ability to activate small molecules like N₂.^[301–308] The pronounced *effective* Lewis acidity of the ambiphilic bis(phosphanyl-amidophenolato)silane PNO₂Si makes this ligand a compelling candidate for probing the limits of Z-type chemistry.

TOWARDS A MOLYBDENUM (0) Z-TYPE COMPLEX

We began our studies by evaluating the reactivity of PNO₂Si towards Mo(III) and Mo(IV) halide precursors, like MoX₃(thf)₃ (X = Cl, I) and MoCl₄(solv)₂ (solv = MeCN, Et₂O). Although used as prominent precursors for L₃ or L₂X ligand systems, none of the mentioned Mo compounds reacted with the L₂Z ligand.

However, reaction of PNO₂Si with the Mo(0) precursor molybdenum hexacarbonyl [Mo(CO)₆] in C₆D₆ at 100 °C slowly furnished a new broad signal in the ³¹P{¹H} NMR spectrum (δ = 43.1 ppm) over the course of 44 h. The identification of the formed product as a C₂ symmetric complex was further backed-up by ¹H- and ¹³C{¹H} NMR spectroscopy, with the latter also indicating the presence of two

ⁱⁱⁱThe results described in this section were obtained during a stay in the group of Prof. Dr. CHRISTOPHER “KIT” CUMMINS at the Massachusetts Institute of Technology as part of a mutual collaboration.

chemically inequivalent sets of CO ligands (223.5 and 208.3 ppm). Due to symmetric coupling to the two phosphines of PNO_2Si , both resonances split into triplets ($^2J = 12.9, 7.9 \text{ Hz}$). The presence of carbonyl ligands was further underlined by two broad resonances at 1873 and 1840 cm^{-1} in the IR spectrum. Interestingly, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum displayed a single resonance at -66.5 ppm that splits into a triplet due to $^2J_{^{31}\text{P},^{29}\text{Si}}$ coupling (3.9 Hz), hinting the presence of a $\text{Mo} \rightarrow \text{Si}$ interaction in the formed complex.

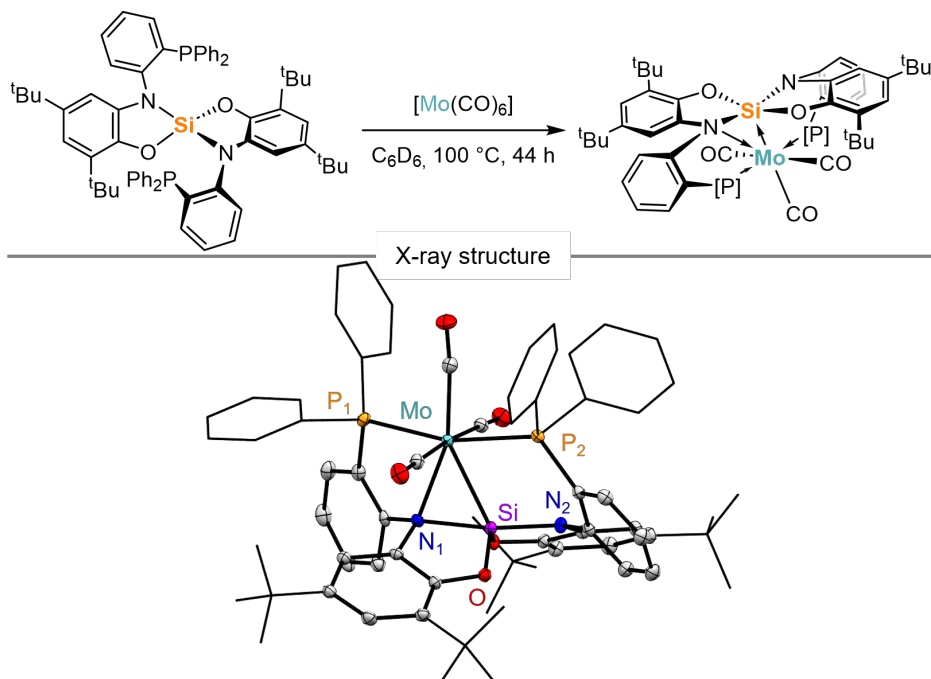


FIG. 3.6.: Synthesis of $\text{Mo}(0)$ Z-type complex $\text{trans}[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ and its solid-state structure (vibrational ellipsoids displayed at 50%, hydrogen atoms and solvent molecules omitted for clarity).

This spectroscopic observation was then ultimately confirmed by the scXRD structure of complex $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ (FIG. 3.6), displaying a Mo-Si bond length of $2.5988(3) \text{ \AA}$. The ratio $r = 0.98$ of the bond length and the sum of covalent radii of Mo and Si lays in the typical range of a dative Z-type interaction. Most

notably, the solid-state structure of $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ does not fully match the spectroscopic characterization in solution. While three carbonyl ligands can be observed (two *cis* to Si, one *trans* to Si), a hepta-coordinated Mo center is formed, by two phosphine arms, which are located *trans* to each other, and additional $\text{N}_1 \rightarrow \text{Mo}$ coordination ($d = 2.3162(9) \text{ \AA}$) by one amidophenolate (amp), as already observed for the rhodium complexes of PNO_2Si .

However, in contrast to the complexes in chapter section 3.3.3, a dynamic equilibrium between $\text{N}_1 \rightarrow \text{Mo}$ and energetically equivalent $\text{N}_2 \rightarrow \text{Mo}$ coordination can be observed in solution, explaining the presence of just one broad signal in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and the pseudo- C_2 symmetry observed in the other spectra. DFT computations at the $\omega\text{b97X-V/def2-TZVPP}(\text{SMD}=\text{benzene})//\text{PBEh-3c}$ level of theory further support a dynamic equilibrium at room temperature with a barrier of $\Delta G^\ddagger = 66.7 \text{ kJ/mol}$ and a transient penta-coordinated $\text{Mo}(0)$ complex.

In order to understand the bonding scenario in complex *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$, a series of computational bond analyses was launched. Analysis of the *Intrinsic Bond Orbitals* (IBOs) at the $\text{PBE0-DKH/def2-TZVP//PBEh-3c}$ level of theory, revealed an IBO that depicts the $\text{Mo} \rightarrow \text{Si}$ interaction from a filled d-orbital of the divalent $\text{Mo}(0)$ into the empty σ^* orbital of the silane (FIG. 3.7 A). Similarly, a *Natural Bond Orbital* (NBO) for the Mo-Si bond was found, with major contributions of Mo (84%; 93% d-character, see FIG. 3.7 B). The natural electron configuration of Mo, based on *Natural Population Analysis* (NPA) was determined to be 5s (0.44), 4d (6.78) and therefore supports the formulation of a d^6 metal center. The slightly increased electron count can be attributed to the three surrounding strongly donating carbonyl ligands at Mo and is also reflected in the negative natural charge at Mo (-1.27). The NPA charge at Si in complex *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ is with 2.20 slightly reduced compared to the free silane (2.35), reflecting the charge flow from Mo to the Lewis acidic center. However, this effect is less pronounced compared to the other Z-type complexes of this ligand with $\text{Pd}(0)$ or $\text{Rh}(\text{I})$. Similarly, the *Wiberg Bond Index* (WBI) of the Mo-Si bond is with 0.31 lower compared to the Z-type interactions with $\text{Pd}(0)$

(section 3.3.1, WBI = 0.43) and Rh(I) (section 3.3.3, WBI = 0.47), indicating a weaker interaction. The reason behind this weakened interaction undoubtedly comes from the reduced amount of d-electrons at the metal center in combination with strong π -accepting CO ligands. Despite being less expressed than other Z-type interactions of PNO_2Si , the Mo-Si interaction appears to be slightly stronger than the N_1 -Mo bond, which WBI is calculated to 0.30. The fact that the dynamic structure switch in solution still takes place, although the WBI of the conformationally stable N_1 -Rh interaction in $[\text{PNO}_2\text{SiRhCl}]$ is significantly lower (0.23, section 3.3.3) indicates a strong dependency of this molecular motion on either the positioning of the phosphines or the strength of Z-type interaction. In analogy to the Rh system, the coordination of the amp- N_1 to the metal center slightly weakens the respective Si- N_1 bond (WBI = 0.43, compared to WBI (Si- N_2) = 0.50).

ETS-NOCV analysis at the BP86-D3BJ/TZ2P//PBEh-3c level of theory shed light into the importance of the Z-type interaction for the overall stability of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$. The deformation density $\Delta\rho_1$, shown in FIG. 3.7 C, showcases the charge flow (red→blue) from the filled d-orbital at Mo to the Si center, with only minor influences of the N_1 -Mo bond. The eigenvalue of the corresponding NOCV pair, which reflects the amount of charge transferred, is outstandingly high ($|v| = 0.97$) and the orbital interaction energy ($\Delta E_{\text{orb}1} = -68 \text{ kcal/mol}$) is even higher than in the respective Pd complex (section 3.3.1), despite the fact that in the latter case additional charge flow from the phosphines to Pd was observed.

For a deeper understanding of the differences between the Mo→Si and N_1 →Mo interactions, QTAIM analysis at the PBE0-DKH/def2-TZVP//PBEh-3c level of theory was conducted. In line with the results above, electron density at the bond critical point (bcp) for the Mo-Si bond ($\rho(r_{\text{bcp}}) = 0.0642$) is lower compared to other Z-type complexes of this ligand ($\text{M} = \text{Pd}(0), \text{Rh}(\text{I})$). Its negative Laplacian ($\nabla^2\rho(r_{\text{bcp}}) = -0.025$), shown in FIG. 3.7 D, alongside other bond criteria (*Cramer and Kraka energy density* $H(r_{\text{bcp}})$ and *Lagrangian kinetic energy per electron* $G(r_{\text{bcp}})/\rho(r_{\text{bcp}})$) indicate a shared covalent interaction. In contrast, the N_1 →Mo

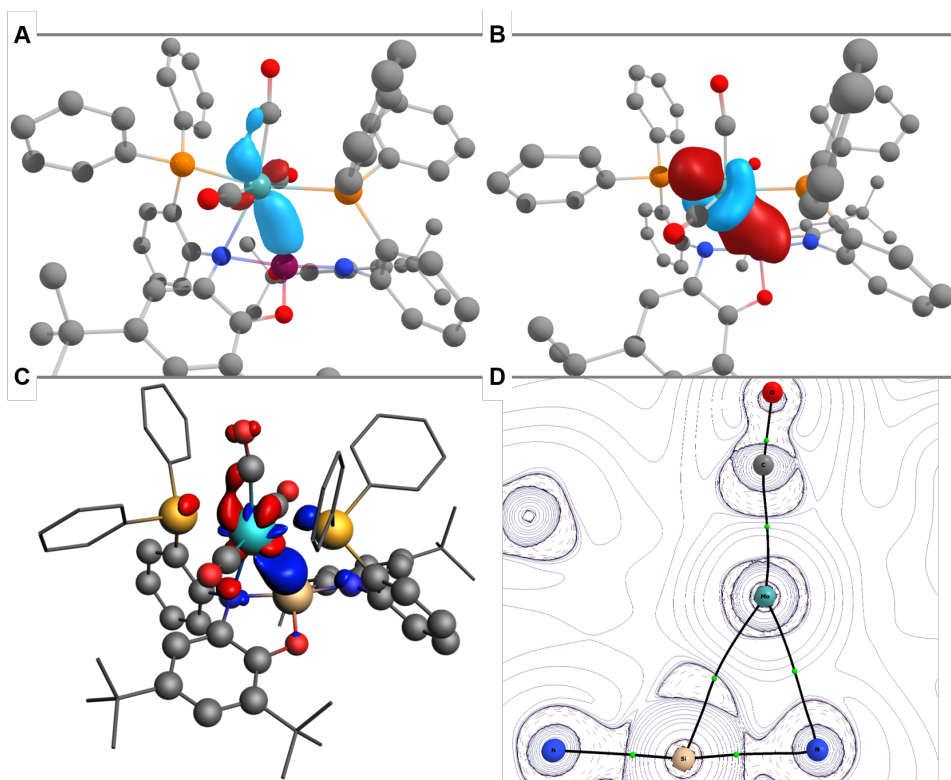


FIG. 3.7.: Theoretical bond analyses in complex *trans*-[PNO₂SiMo(CO)₃]: A) IBO showcasing the Mo-Si interaction. B) NBO of the Mo-Si bond C) ETS-NOCV deformation density $\Delta\rho_1$ (E_{orb1}) of the NOCV orbital corresponding to the Mo-Si interaction (charge flow from red to blue). D) N₁-Si-Mo plane with the Laplacian of the electron density, bond paths and bond critical points (bcp), as obtained by QTAIM analysis.

interaction, which has a similar electron density at its bcp ($\rho(r_{bcp}) = 0.0623$), can be better described as an ionic closed shell interaction according to the criteria above, likely owing to the greater electronegativity difference between the involved elements.

Although *trans*-[PNO₂SiMo(CO)₃] was formed in respectable yields by the reaction of PNO₂Si with [Mo(CO)₆], the long reaction times and substantial release of CO gas rendered the synthesis of large quantities difficult. In an attempt to

facilitate the synthesis, the reactivity of PNO_2Si towards the $\text{Mo}(\text{CO})_3$ synthon $[\eta^6\text{-(toluene)Mo}(\text{CO})_3]$ in C_6D_6 was evaluated.

In contrast to the reaction with $[\text{Mo}(\text{CO})_6]$, consumption of the silane was already observed at lower temperature (70°C), however to a hitherto unobserved species. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displayed two doublets at 41.1 and 27.5 ppm, accounting for two chemically inequivalent phosphines, which - based on the coupling constant ($^2J_{^{31}\text{P},^{31}\text{P}} = 25.3\text{ Hz}$) - are located *cis* to each other at the Mo center. Interestingly, *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ formed with prolonged reaction times alongside the unknown *cis*- $\text{PNO}_2\text{SiMoL}_x$ species, as indicated by NMR spectroscopy. Elevated temperatures (100°C) sped-up the conversion of the *cis*- $\text{PNO}_2\text{SiMoL}_x$ species to *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$, although even after prolonged heating ($>24\text{ h}$) substantial amounts of the *cis*-species remained present in solution (ca. 15%). Based on the ability of this unknown species to slowly convert into *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$, its chemical identity is presumed to be the respective *cis*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ complex (see FIG. 3.8). This assumption is backed up by DFT computed thermodynamics ($\omega\text{b97X-V/def2-TZVPP(SMD=benzene)}/\text{PBEh-3c}$), which favour the *trans*- isomer by $\Delta G^0 = 12.8\text{ kJ/mol}$. It is speculated that the *cis* $\rightarrow$ *trans* isomerization takes place through the temporary loss of CO ($\Delta G^0 = 109.0\text{ kJ/mol}$), therefore requiring elevated temperatures.

The formation of *cis*- $\text{PNO}_2\text{Si}[\text{Mo}]$ -complexes is not a singularity. Although *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ is poorly soluble in MeCN, prolonged refluxing cleanly furnished an asymmetric *cis*-coordinated species, as judged by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy ($\delta = 58.5$ and 32.6 ppm , $^2J_{^{31}\text{P},^{31}\text{P}} = 93.0\text{ Hz}$). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of this compound hinted the presence of two chemically inequivalent CO ligands at Mo, as well as one coordinating molecule of MeCN, which was further supported by ^1H NMR spectroscopy, leaving no doubt that the formed complex can be described as *cis*- $[\text{PNO}_2\text{SiMo}(\text{CO})_2(\text{MeCN})]$. Although no solid-state structure was obtained, a Mo $\rightarrow$ Si interaction was suggested by the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of the compound, displaying a doublet of doublets ($\delta = -61.0\text{ ppm}$, $^2J_{^{29}\text{Si},^{31}\text{P}} = 20.4, 9.8\text{ Hz}$) due to

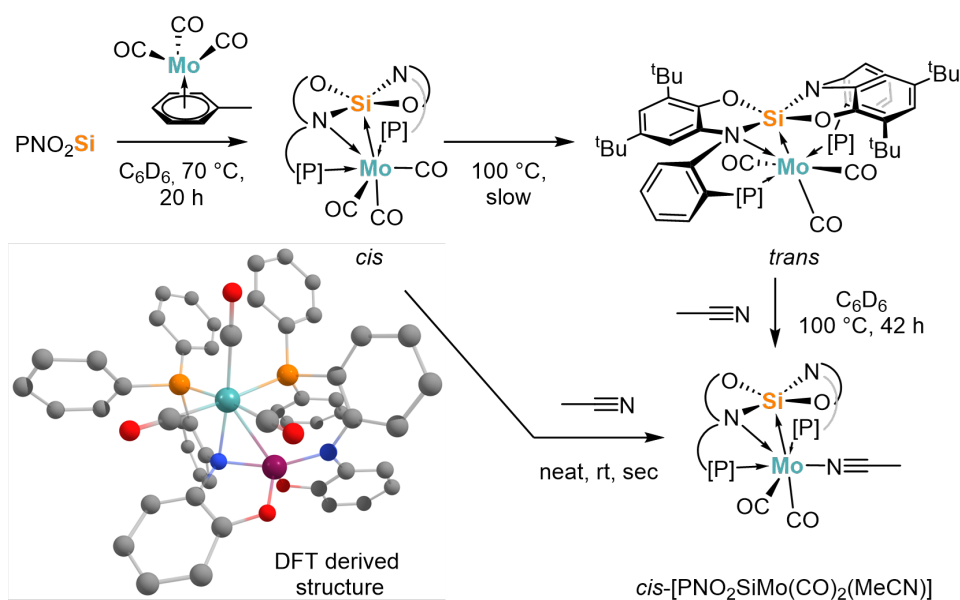


FIG. 3.8.: Reaction of PNO_2Si with $[\eta^6\text{-(toluene)Mo(CO)}_3]$, forming $\text{cis-[PNO}_2\text{SiMo(CO)}_3]$, subsequent isomerization to $\text{trans-[PNO}_2\text{SiMo(CO)}_3]$ and reactivity with MeCN, forming $\text{cis-[PNO}_2\text{SiMo(CO)}_2(\text{MeCN})]$. The inset shows the DFT-optimized structure of $\text{cis-[PNO}_2\text{SiMo(CO)}_3]$ (PBEh-3c, $t\text{Bu}$ groups and hydrogen atoms omitted for clarity).

coupling of the ^{29}Si nucleus with the two inequivalent ^{31}P nuclei through the Mo-Si bond. It is to be noted that $\text{cis-[PNO}_2\text{SiMo(CO)}_3]$ also reacts with MeCN to form $\text{cis-[PNO}_2\text{SiMo(CO)}_2(\text{MeCN})]$, only with the difference that the reaction takes place at room temperature within seconds, suggesting an elevated barrier for the $\text{cis} \leftrightarrow \text{trans}$ barrier in transient $[\text{PNO}_2\text{SiMo(CO)}_2]$.

OXIDATION CHEMISTRY OF $\text{TRANS-[PNO}_2\text{SiMo(CO)}_3]$

Aiming for the removal of the tightly bound CO ligands in $\text{trans-[PNO}_2\text{SiMo(CO)}_3]$ in order to access N_2 - and nitrido complexes after subsequent reduction, the oxidation chemistry of this unique Z-type Mo complex was investigated. Exposure of $\text{trans-[PNO}_2\text{SiMo(CO)}_3]$ to an excess of iodine in thf at room temperature led

to the formation of a dark green solution accompanied by fast conversion of the initial Mo(0) complex to a single C_2 symmetric complex, as judged by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy ($\delta = 72.2$ ppm). However, prolonged reaction times or elevated temperatures gradually changed the color of the reaction mixture to red and gave rise to a new set of signals in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, namely two singlets at 68.0 and -23.4 ppm. The multiplicity of the signals as well as the significant high-field shift of one of the phosphine resonances suggested the formation of a Mo-complex, in which only one phosphine arm of the silane coordinates to the Mo center. This was ultimately confirmed by the solid-state structure of the final product of the reaction, shown in FIG. 3.9. A pseudo octahedral Mo(II)(CO) $_2$ I complex had formed, which is additionally coordinated by one phosphine arm of the silane, the amp-N $_1$ and the lone pair of an alkoxy-silicate, which formed through an iodide induced ring-opening of a thf molecule. Matching the spectroscopic observation, the second phosphine arm is not coordinated to the metal center and is located below the silicate plane. It is assumed that during the reaction, a MoI $_2$ (CO) $_2$ complex forms, which then slowly reacts with thf to the final product.

Oxidation of complex *trans*-[PNO $_2$ SiMo(CO) $_3$] with AgOTf in thf also resulted in formation of a dark green solution, which quickly solidified due to solvent polymerization. Reasoning this by the higher nucleophilicity of thf compared to CF $_3$ SO $_3^-$, the assumption was made that a similar initial species was produced as in the oxidation reaction with I $_2$. Switching the solvent of the reaction to C $_6$ D $_6$ eliminated the problem of nucleophilic ring-opening reactions and resulted in the formation of a dark green solution. Similar to the oxidation with I $_2$, a single resonance in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum was detected at $\delta = 71.1$ ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum displayed a single triplet ($\delta = 233.7$ ppm, $^2J_{^{13}\text{C},^{31}\text{P}} = 25.2$ Hz), accounting for CO ligands in a symmetric coordination environment, which was confirmed by the solid-state structure, as obtained by scXRD analysis (FIG. 3.10). A Mo(II)(CO) $_2$ -complex had formed, with two triflate anions coordinating the silane, forming a dianionic silicate, which coordinates the Mo(II)(CO) $_2$ fragment

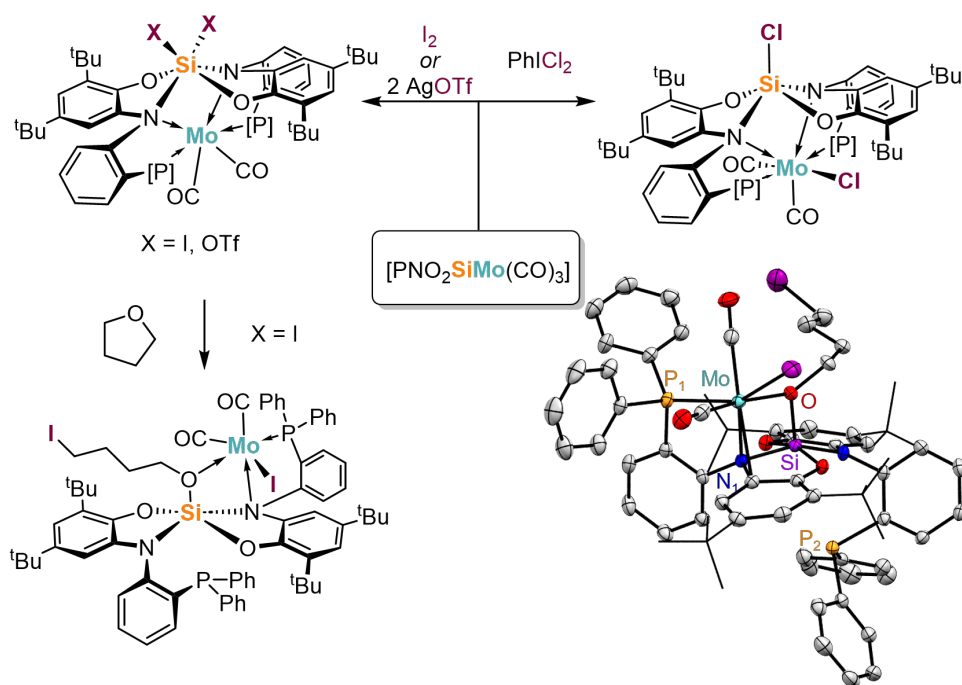


Fig. 3.9.: Oxidation chemistry of Mo(0) Z-type complex $trans\text{-}[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ and the solid-state structures of the ring-opening product after oxidation with I_2 in thf (vibrational ellipsoids displayed at 50%, hydrogen atoms and solvent molecules omitted for clarity).

with its phosphines and the nitrogen atoms of the amps. The broad signal of the triflates in the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum suggest a dynamic triflate exchange and an equilibrium between the hexa-coordinated silicate $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ and the penta-coordinated silicate $[(\text{TfO})\text{PNO}_2\text{SiMo}(\text{CO})_2][\text{TfO}]$. In line with this hypothesis, no signal in the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum was observed, due to extensive dynamic-caused broadening.

Intriguingly, the structure of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ is closely related to the structure of the Pd(II) complex $[(\text{TfO})_2\text{-Si}(\text{PNO})_2\text{Pd}]$, the product of the reaction of AgOTf with the Z-type Pd(0) complex $[\text{PNO}_2\text{SiPd}]$ (see section 3.3.2). This can be explained by the isolobal relationship of the $d^8\text{-Pd-}$ and the $L_2\text{-d}^4\text{-Mo}$ fragment.

Since $[(\text{TfO})_2\text{-Si}(\text{PNO})_2\text{Pd}]$ also displays a strong absorption in the UV-Vis due to a strong LMCT from the amidophenolates to the empty d-orbital at Pd(II), we were curious whether the dark green coloration of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ also originates from a similar charge transfer. Therefore, the vertical excitation profile of the Mo(II) complex was calculated using TD-DFT (CAM-B3LYP/def2-TZVPP(SMD=thf)//PBEh-3c). In accordance with the experimental observations, a low energetic excited state was found, with an excitation wavelength of 605 nm. A closer look in the *Natural Transition Orbitals* (NTOs) of this excited state however revealed the nature of this transition to be a d $\rightarrow$ d-transition, which should be forbidden by the LAPORTE rule. The intensity of this transition can however be explained when the molecular orbitals (MOs) are considered instead of the NTOs. While the LUMO of complex $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ really is an empty Mo-centered d-orbital, the most important donating MOs (HOMO (61%), HOMO-2 (11%) and HOMO-4 (13%)) all display electron density in the π -system of the amp residues in addition to localization at the d-orbital at Mo. This additional p-character of the donating MOs could break the symmetry of the transition.

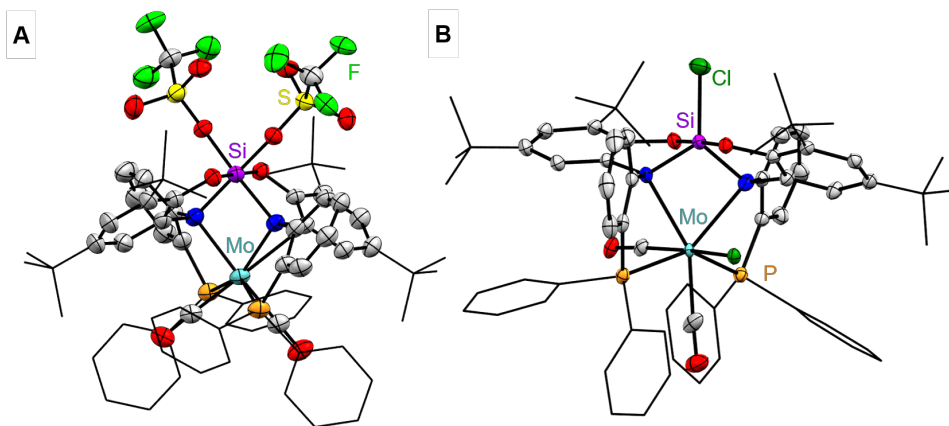


FIG. 3.10.: Solid-state structures of the products after oxidation of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ with AgOTf (A) and PhICl₂ (B) (vibrational ellipsoids displayed at 50%, hydrogen atoms and solvent molecules omitted for clarity).

Given the unsuccessful attempts to access to Mo(III) or Mo(IV) complexes of PNO_2Si without CO ligands through oxidation with I_2 or AgOTf , the reaction of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ with stronger oxidants was evaluated. Addition of two equivalents of a chilled (-15°C) solution of iodobenzene dichloride (PhICl_2) in thf to a solution of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ resulted in the immediate formation of a red-brown solution. Investigation of the reaction contents by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed the formation of an oxidized Mo complex, which, in contrast to the oxidation reactions described above, contained two chemically inequivalent phosphines that both coordinated the oxidized Mo center, as judged by their chemical coupling ($\delta = 85.7$ and 62.3 ppm, $^2J_{^{31}\text{P},^{31}\text{P}} = 38.1$ Hz). The absence of dark coloration, together with an unprecedented $^{31}\text{P}\{^1\text{H}\}$ NMR pattern for oxidized $\text{PNO}_2\text{Si-Mo}$ complexes, indicated successful oxidation to a putative Mo(IV) species lacking CO ligands. IR spectroscopy of the reaction mixture however revealed the presence of distinct CO stretching bands, therefore rendering the successful oxidation to a Mo(IV) complex unlikely. Single crystals of the reaction mixture, investigated by scXRD, ultimately revealed the solid-state structure of the product (FIG. 3.10 B). Similar to the other oxidation reactions, the oxidation yielded a dicarbonyl-Mo(II) complex and did not proceed further. In contrast to the other oxidation products, only one chloride coordinates the silane, forming a penta-coordinated silicate, while the other chloride coordinates to the Mo(II) center, breaking the C_2 symmetry of the system.

The altered coordination environment at the Mo center in $[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$ also changed the chemistry of the complex. In contrast to the other dicarbonyl-Mo(II) complexes, $[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$ was not stable when exposed to vacuum, which resulted in the loss of one carbonyl ligand, as judged by IR and NMR spectroscopy. This process however is not fully selective and was therefore not further investigated.

CONCLUSION TO THE MOLYBDENUM CHEMISTRY OF PNO₂Si

In this section, the coordination chemistry of PNO₂Si with molybdenum was explored. The first Mo(0) Z-type complex *trans*-[PNO₂SiMo(CO)₃] was synthesized by the reaction of the ambiphilic silane PNO₂Si and molybdenum hexacarbonyl. Investigation by spectroscopy and quantum chemical calculations revealed the presence of a Z-type interaction, which strength-wise ranks lowest upon the interactions reported in this work. The coordination isomer of this complex, *cis*-[PNO₂SiMo(CO)₃] was observed as an intermediate in the synthesis, when [η^6 -(toluene)Mo(CO)₃] was used as the precursor. This coordination mode of PNO₂Si was then further investigated by the model complex *cis*-[PNO₂SiMo(CO)₂(MeCN)], the product of the reaction of *trans*-[PNO₂SiMo(CO)₃] and MeCN.

Aiming for the removal of the CO ligands, the oxidation chemistry of *trans*-[PNO₂SiMo(CO)₃] was investigated. Although oxidants were used in excess, only di- and monocarbonyl Mo(II) complex were obtained and characterized. Dependent on the nucleophilicity of the formed anion, these Mo(II) complexes adopt different geometries. Weakly coordinating triflates, product of the oxidation with AgOTf, formed a hexa-coordinated silicato Mo(II) complex, reminiscent of the respective Pd(II) complex in section 3.3.2. The same structural motif in the two triflate complexes was explained by the isolobal relationship between the L₂-d⁴ and d⁸ fragment, also partially explaining the origin of the strong coloration of the Mo(II) complex. Oxidation with iodine in thf presumably also forms the structurally related di-iodo silcato Mo(II) dicarbonyl complex, before the nucleophilic iodides in this intermediate ring-open thf, forming an alkoxy-silicato Mo(II) complex. When the anion exceeds a certain threshold of nucleophilicity, only one anion coordinates to the silane, while the other coordinates to the Mo center, as observed in the solid-state structure of the reaction product of *trans*-[PNO₂SiMo(CO)₃] and PhICl₂.

The results in this section conclude the following:

- Mo(0) carbonyl complexes of PNO₂Si are the first isolated and studied Mo Z-type complexes and expand the small field of reported d⁶ Z-type complexes.
- The chemistry of PNO₂Si is limited to Mo(0) and Mo(II) complexes. Higher oxidation states of Mo appear to be infeasible in combination with this electron-rich silane. Z-type interactions however, can only be observed for Mo(0) complexes.
- In order to access N₂-Mo(0) Z-type complexes, different synthetic routes that circumvent the use of CO ligands must be evaluated.

3.3.5. AN AMBIPHILIC TIN Z-TYPE LIGAND ^{IV}

PREFACE

The ability of a ligand to switch its coordination mode based on the needs at the metal center is a valuable concept that could prove fruitful for several catalytic processes. While there are some reports of systems that change their coordination mode from L- to X-,^[309] reports where a Z-type ligand switches to a L-type ligand are scarce and rely on Lewis base coordination at group 13 ligands in low oxidation states, exploiting their inherent ambiphilic nature.^[310]

Electron-rich amidophenolates can partially donate electron density towards the central element in group 14 compounds of this ligand class, as already observed by increased metrical oxidation states (MOS) in the Pd complexes of PNO₂Si (compare section 3.3.1). This concept was ultimately exploited by the ligand-centered oxidation and subsequent Lewis base triggered electromerism in section 3.3.2. Switching to the heavier central atom tin, the partially reduced Sn(II) oxidation state should be energetically feasible and stabilized.^[289] Making use of this energetically smoothed energy landscape, a L/Z-type switch, coupling the redox non-innocence of the amp fragment and Sn, appears feasible. In fact, this concept was already exploited for element-ligand cooperative bond activation of allyl-halogenides by bis(amidophenolato)stannanes.^[105] Even Sn(IV)/Sn(II) electromerism without the presence of an additional metal was speculated in these complexes,^[106] encouraging the design of an ambiphilic, electron-rich stannane as a Z-type ligand with the potential of subsequent Z/L-type switching.

SYNTHESIS ATTEMPTS OF PNO₂Sn

In order to design an ambiphilic stannane, we evaluated a similar approach to the established silane synthesis in section 3.3.1, choosing 2,4-di-tert-butyl-6-(2-(diphen-

^{iv}The results described in this section were partially obtained by B. Sc. LOUSIA A. BRAND under my direct supervision as part of her Bachelor's thesis.

ylphosphaneyl)phenyl)aminophenol (PNO-H₂) as a suited ligand framework for Sn. A CD₂Cl₂ solution of PNO-H₂ was exposed to tetrakis(dimethylamido)stannane (Sn(NMe₂)₄), forming a pale yellow solution (FIG. 3.11). Investigation by ³¹P{¹H} NMR spectroscopy revealed the formation of an asymmetric bis-phosphine species as the major product of the reaction ($\delta = -13.9$ and -26.3 ppm), with the phosphine, resonating at higher fields, coordinating to the Sn center, as judged by the ¹¹⁹Sn-satellites ($J = 360$ Hz).

The solid-state structure obtained by scXRD analysis confirmed this assumption (FIG. 3.12 A). A Sn(IV) center is octahedrally coordinated by the oxygen and nitrogen of one fully deprotonated κ^2 -PNO fragment, a chloride and by a partially deprotonated second κ^3 PNO-H fragment, where in addition to O[−] and the NH, coordination of the phosphine takes place ($d(\text{Sn-P}) = 2.6359(9)$ Å). The second phosphine arm in [ClSn(PNO)(PNO-H)] is coordinated to the protonated amine by a hydrogen bond.

Without any “classic” chloride sources present during the reaction, it was obvious that the chloride was a product of the reaction with intermediates in the reaction and the chlorinated solvent. Therefore, in a second isolation attempt, MeCN was chosen as the solvent and the reaction temperatures were lowered to -40 °C. Despite the absence of a possible chloride source, a similar signal pattern was observed in the ³¹P{¹H} NMR spectrum, although in low intensity since the product precipitated quickly. Crystals obtained from a concentrated solution in diethyl ether were analyzed by scXRD, revealing the solid-state structure as depicted in FIG. 3.12 B. The structure shows a neutral penta-coordinated stannane with two fully deprotonated PNO units and a *N,N*-dimethylacetimidamide coordinated to the Lewis acid. The latter presumably formed through Lewis acid catalyzed nucleophilic insertion of dimethylamine at a Sn-coordinated molecule of MeCN, showcasing the vivid reactivity of the used Sn precursor or rather the formed intermediates of the reaction.

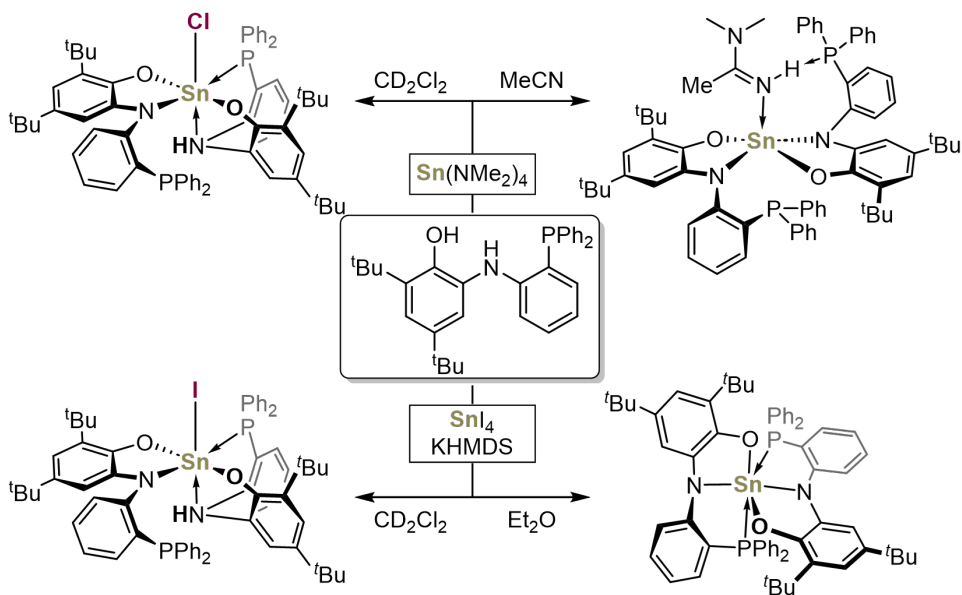


FIG. 3.11.: Reactivity of PNO-H₂ towards different Sn(IV) precursors in different solvents.

Given the reactive nature of intermediates formed in the reactions with $\text{Sn}(\text{NMe}_2)_4$, we investigated SnI_4 as a possible precursor for the attempted synthesis of PNO_2Sn . In the absence of a base, PNO-H₂ was oxidized by SnI_4 , therefore KHMDS (HMDS = hexamethyldisilazid) was added in stoichiometric amounts to a reaction solution in CD_2Cl_2 . Interestingly, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated the formation of a species with similar NMR properties like $[\text{ClSn}(\text{PNO})(\text{PNO}-\text{H})]$, displaying two resonances at $\delta = -20.3$ and -23.3 ppm, the latter with ^{117}Sn - and ^{119}Sn -satellites ($J = 818, 857$ Hz). Single crystals of this compound then further underlined these assumptions, revealing a structure similar to $[\text{ClSn}(\text{PNO})(\text{PNO}-\text{H})]$, with a partially protonated PNO-H fragment and an iodide coordinated to the octahedral Sn(IV) center (FIG. 3.12 C).

In order to drive the deprotonation of the amines to completeness, the polarity of the reaction solvent was lowered, effectively increasing the basicity of the employed base. In fact, the reaction of PNO-H₂, SnI_4 and KHMDS in Et_2O resulted in the

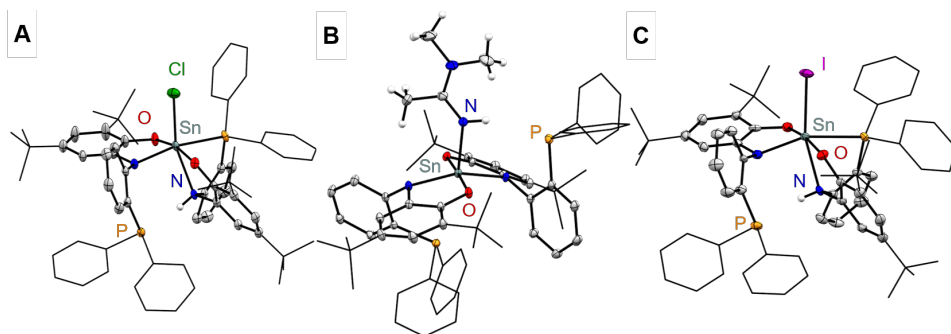


FIG. 3.12.: Solid-state structures of the products of the reactions of PNO- H_2 with $Sn(NMe_2)_4$ in CD_2Cl_2 (A), in MeCN (B), or with SnI_4 and KHMDS in diethyl ether (C) (vibrational ellipsoids displayed at 50%, hydrogen atoms, except for the NH proton and solvent molecules omitted for clarity).

precipitation of a yellow solid, which was washed with excess Et_2O before it was extracted with benzene. $^{31}P\{^1H\}$ NMR-analysis of the extracted solution revealed the clean formation of a novel C_2 -symmetric species with a single resonance at $\delta_{31P} = -24.2$ ppm, displaying ^{117}Sn - and ^{119}Sn -satellites ($J = 315, 330$ Hz), which suggested the formation of a hexa-coordinated stannane. Coordination of the phosphines to the $Sn(IV)$ center was further underlined by the signal in the $^{119}Sn\{^1H\}$ NMR, a triplet at $\delta = -345.8$ ppm ($^1J = 330$ Hz).

Analysis of the solid-state structure of PNO_2Sn (obtained by scXRD analysis, Fig. 3.13 A) is in line with the spectroscopic observations. Two fully deprotonated κ^3 -PNO ligands coordinate the $Sn(IV)$, forming exclusively the hexa-coordinated *mer*-isomer, with two dative $P \rightarrow Sn$ bonds ($d(Sn-P)_{avg} = 2.6514(7)$ Å). The fact that in the stannane, in contrast to its silicon relative, coordination of the phosphines to the Lewis acidic center is observed could be explained by the increased size of the central atom, which lowers the ring-strain after coordination.

Evaluating potential electromerism in compound PNO_2Sn , the MOS of the amiodiphenolates were calculated based on the experimental bond lengths. While this resulted in slightly increased values (-1.81 and -1.89), especially when compared to silane PNO_2Si (MOS = -2.29), the overall representation of this molecule as a

diamagnetic Sn(IV) species is favored. While the coloration of PNO_2Sn left room for speculations whether an open-shell Sn(II) state plays a role in the description of the electronic structure of this complex, the comparison of the recorded UV-Vis spectrum with TD-DFT computed spectra of both electromers ($S = 0$ and $S = 1$) also ruled in favor of a singlet Sn(IV) complex (FIG. 3.13 B). These findings are in line with previous reports that excluded electromerism in hyper-coordinated stannanes.^[106]

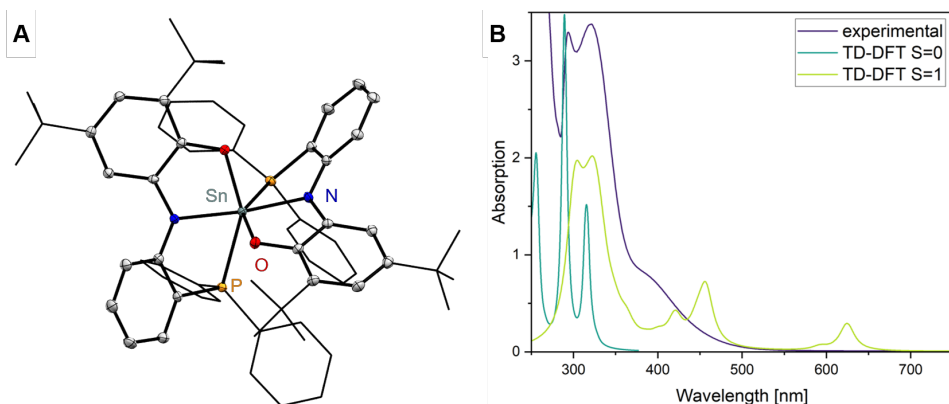


FIG. 3.13.: A) Solid-state structure of PNO_2Sn (vibrational ellipsoids displayed at 50%, hydrogen atoms and solvent molecules omitted for clarity). B) Comparison of experimental (thf , $2 \cdot 10^{-5} \text{ mol L}^{-1}$) and computational (CAM-B3LYP/def2-TZVPP(SMD=thf)//PBEh-3c) UV-Vis spectra.

While PNO_2Sn did not show reactivity towards weak nucleophiles like thf , acetonitrile or benzaldehyde due to competitive phosphine coordination at the Lewis acidic Sn(IV), reactivity was observed when a solution of PNO_2Sn in C_6D_6 was exposed to HNTf_2 . A down-field shifted singlet ($\delta_{31\text{P}} = -9.9 \text{ ppm}$ with ^{117}Sn - and ^{119}Sn -satellites ($J = 808, 846 \text{ Hz}$) was observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, indicating the formation of a novel symmetric species with both phosphines coordinating to Sn(IV). Analysis by scXRD confirmed these assumptions (FIG. 3.14). After protonation of both amido positions in PNO_2Sn a rearrangement took place, forming the *fac*-isomer of the dicationic complex $[(\text{PNO-H})_2\text{Sn}]^{2+}$. The protonated

amp-NHs still coordinate the Sn(IV) center through their lone pair, while one bistriflimide anion is stabilizing this configuration through two H-bonds.

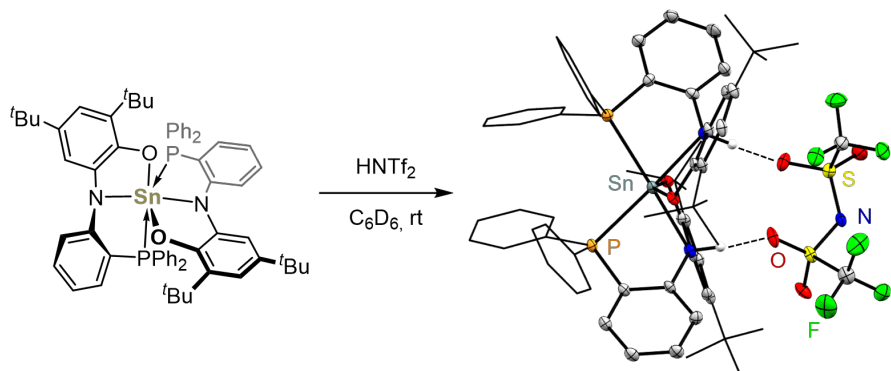


FIG. 3.14.: Reactivity of PNO₂Sn towards HNTf₂ and solid-state structure of the product (vibrational ellipsoids displayed at 50%, carbon-bound hydrogen atoms, solvent molecules and the second [NTf₂]⁻ are omitted for clarity).

COORDINATION CHEMISTRY OF PNO₂Sn

With an ambiphilic stannane in hand, we explored the potential of PNO₂Sn as a Z-type ligand in the coordination chemistry of late transition metals. Although it is the heavier analogue of PNO₂Si, coordination of the phosphines to the Sn(IV) center significantly alters the stannane's reactivity. Before metal complexation can occur, the Sn–P bond must be cleaved - often requiring elevated temperatures that are not compatible with delicate transition metal precursors. Additionally, partial transmetalation of the amidophenolates from tin to the target metal may take place, as stannanes are well-known for their effectiveness as transmetallation reagents. This was observed in the reaction of PNO₂Sn with [Rh(COD)Cl]₂ (COD = cyclooctadiene). After heating the reaction to 80 °C, multiple species formed as judged by NMR spectroscopy. Single crystals of one species formed and were analyzed by scXRD, revealing a complex structure in which a (PNO)SnCl₂ frag-

ment coordinates a (PNO-H)-Rh fragment through a P→Rh and a Z-type Rh→Sn interaction (see FIG. 5.1 in section 5.5).

By offering the ambiphilic Z-type ligand a suitable Lewis base, de-coordination of the phosphines from the Lewis acidic center should be facilitated. This approach was effectively tested by the reaction of PNO₂Sn with (DMS)AuCl (DMS = dimethylsulfide) in dcm. ³¹P{¹H} NMR spectroscopy revealed the immediate consumption of the stannane, forming a single symmetric species (δ = 30.2 ppm). Orange crystals of the complex formed after gas phase diffusion of *n*-pentane into the concentrated dcm solution and were analyzed by scXRD (FIG. 3.15).

As envisioned, the chloride coordinates to the Sn(IV) center, forming a penta-coordinated stannate. Both phosphines are located below the plane, symmetrically coordinating the Au cation ($\angle(\text{P-Au-P}) = 170.45(2)^\circ$). With a bond length of 3.2457(5) Å ($r = 1.18$), a Au-Sn Z-type interaction appears to be unlikely and would probably require the abstraction of the chloride, which quenches the Lewis acidity. The herein observed reactivity towards (DMS)AuCl perfectly matches the reactivity of the lighter homologue PNO₂Si, which also forms a structurally related penta-coordinated chlorido-silicate Au(I) complex (section 5.5).

Lastly, the complexation of Pd(0) was evaluated. Since a related approach to the synthesis of the silane Pd(0) complex through reductive elimination after coordination of CpPd(allyl) failed due to thermal sensitivity of this precursor, Pd₂dba₃ (dba = dibenzylideneacetone) was employed as a robust Pd(0) source. Multiple solvents were evaluated for the reaction, which proceeded slowly at room temperature. After 24 h in CD₂Cl₂, 40% conversion of PNO₂Sn to a new species was observed in the ³¹P{¹H} NMR spectrum. The formed species was detected as a singlet at $\delta = -0.2$ ppm and therefore with a similar chemical shift like [PNO₂SiPd] ($\delta = 4.5$ ppm), indicating a related chemical identity of the formed complex. Based on the ¹¹⁹Sn-satellites of the signal ($^2J = 130$ Hz), which exhibit a significantly lower coupling constant than the $^1J_{119\text{Sn},31\text{P}}$ couplings observed in the structurally characterized Sn(IV) complexes above - and more closely resemble typical $^2J_{119\text{Sn},31\text{P}}$

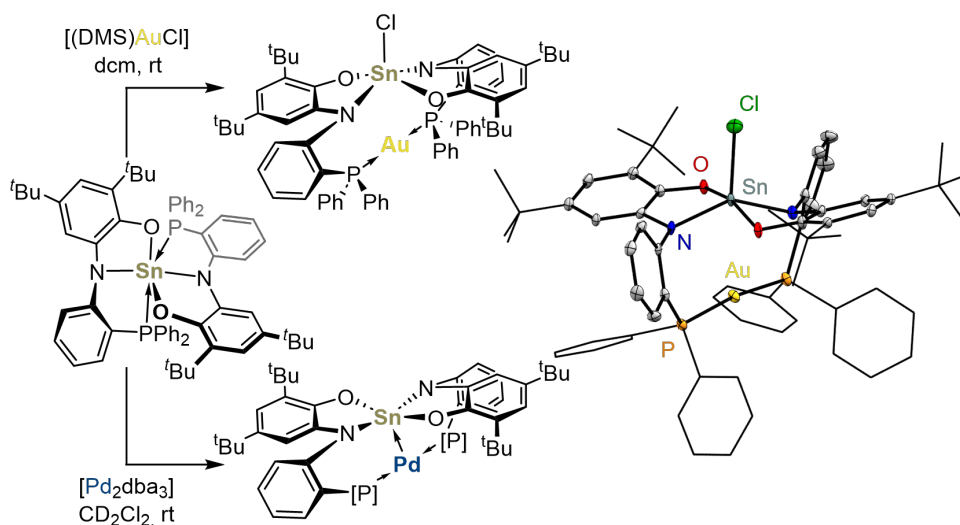


FIG. 3.15.: Coordination chemistry of PNO₂Sn with d¹⁰-metal fragments and solid-state structure of [Cl-Sn(PNO)₂Au(I)] (vibrational ellipsoids displayed at 50%, hydrogen atoms and solvent molecules are omitted for clarity).

values - a T-shaped geometry thus appears reasonable. The satellites furthermore hint at the expected Pd→Sn Z-type interaction. LIFDI-MS analysis of the reaction mixture further confirmed the presence of a species with the expected composition of [PNO₂SnPd], matching the expected isotope pattern. While all spectroscopic findings support the successful synthesis of [PNO₂SnPd], ultimate proof by scXRD analysis is still pending.

CONCLUSION TO THE Z-TYPE CHEMISTRY OF TIN

In this section, the heavier homologue of the versatile ambiphilic Z-type ligand PNO₂Si, PNO₂Sn was synthesized and first impressions regarding its coordination chemistry with late transitions were gathered. Despite their relationship in the periodic table of elements, the chemistry of Sn and the employed phosphanyl-amidophenol PNO-H₂ significantly deviated from the respective silicon chemistry. Numerous combinations of Sn(IV) precursors, bases and solvent systems were

evaluated until finally PNO_2Sn precipitated from the reaction of PNO-H_2 with KHMDs and SnI_4 in diethyl ether. Unlike its silane relative, the tin center in PNO_2Sn is not tetrahedrally coordinated, since due to the increased size of Sn additional coordination of the phosphines to the Lewis acidic center is observed in solution and the solid-state. Potential Sn(II)/Sn(IV) electromerism was ruled out by structural parameters as well as the optical properties of this compound, partially reasoned by stabilization of the Sn(IV) state by phosphine coordination. Still, electromerism could be easily tangible in Z-type complexes of PNO_2Sn .

Albeit the initial pre-coordination of the phosphines, PNO_2Sn formed coordination compounds with Au(I) (through reaction with $(\text{DMS})\text{AuCl}$) and with Pd(0) (through reaction with Pd_2dba_3). The geometries of these complexes closely resembled the respective silane derivatives, underlining the possible application of PNO_2Sn as a Z-type ligand. Given the decreased electronegativity of Sn, more covalent Z-type interactions are expected for the respective bimetallic complexes, although this still needs further validation and is subject of ongoing research.

4 | REFLECTION AND SUMMARY

Effective Lewis acidity refers to the perturbative influence of a Lewis acid on the electronic structure of a coordinated substrate. Although this concept is still being established, the present cumulative dissertation comprises both published and unpublished advancements in its targeted application in the fields of catalysis and coordination chemistry. This dissertation describes in particular how the *effective* Lewis acidity of group 14 Lewis superacids can be exploited for catalysis of the ring-closing metathesis (RCM) of C-O bonds in oligo- and polyethers. Furthermore, it discusses the pronounced electronic changes at transition metal centers, caused by the effective Lewis acidity of coordinating ambiphilic Z-type ligands. In the following paragraphs, the results discussed in section 3.3.5 will be summarized, compared, and contextualized.

Catalytic activity of silane Lewis superacids in the RCM of oligo- and polyethers was visited in section 3.2. While section 3.2.1 explored the general reactivity and clarified the reaction mechanism, section 3.2.2 focused on expanding this reaction to a variety of polyethylene oxide (pEO) derivatives, exploring boundaries and substantially improving the depolymerization.

First, the polymeric Lewis superacidic bis(perchlorocatecholato)silane $[\text{Si}(\text{cat}^{\text{Cl}})_2]_n$ was investigated regarding its catalytic potential in the C-O bond metathesis of 1,5-dimethoxypentane, surpassing previously reported catalysts in terms of reactivity. Even oligoethers (e.g., diglyme) that have been regarded as challenging substrates for this reaction, due to their propensity of chelation, were efficiently converted to 1,4-dioxane. Upon optimization of the reaction conditions, a range of

structurally diverse substrates was examined. Notably, a chemoselective conversion of 18-crown-6 in the presence of other derivatives was achieved, offering a promising approach to selectively modulate the distribution of these macrocycles. A key highlight of this section was the RCM of pEO, a ubiquitous class of polymers (FIG. 4.1). The observed chemoselective conversion in the presence of polystyrene demonstrated the potential of this system for the upcycling of pEO, even within polymer blends or composite materials. In addition, cross-linking of polymer chains was identified as a competing side reaction, thereby presenting a plausible toolbox to introduce vitrimeric features through dynamic covalent chemistry.

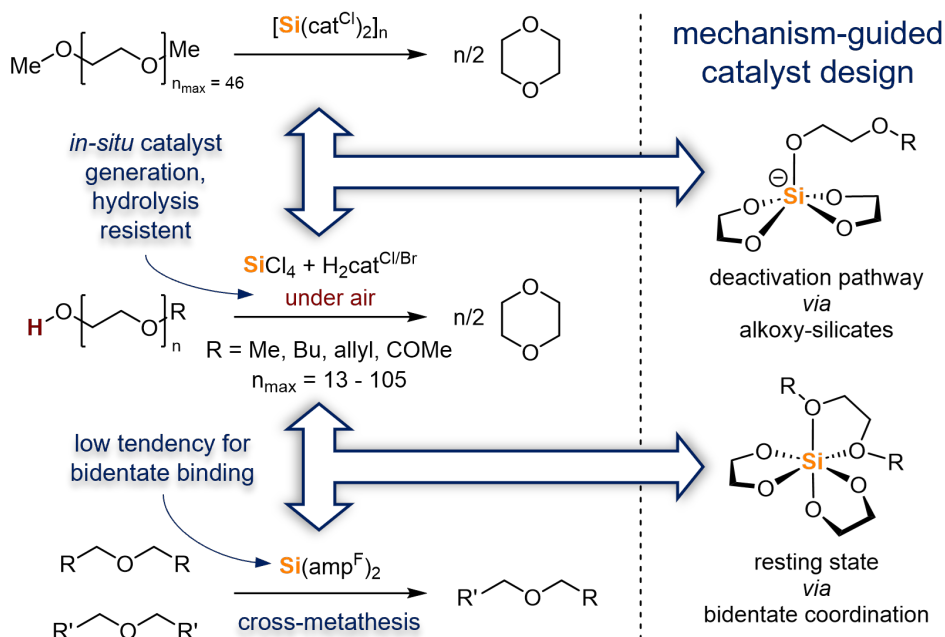


FIG. 4.1.: Key findings of this work regarding the RCM of oligo- and polyethers summarized as a flowchart, showcasing the mechanism-guided catalyst evolution for this reaction, ultimately discovering catalytically active systems for the cross-metathesis of C-O bonds.

Since the RCM in pEO represented an opportunity for a circular economy of this polymer, paving the way for a sustainable future of material design, this disserta-

tion further focussed on expanding the applicability of this process. Specifically the sensitivity to air and the inability to convert hydroxy-functionalized pEO derivatives rendered this approach impracticable for potential industrial applications.

In section 3.2.2, a series of differently capped pEOs with varying chain lengths were evaluated in the silicon catalyzed RCM. While a broad tolerance of functional groups and chain lengths was demonstrated, correlations between chain-length and yield gave insights into plausible deactivation pathways of the catalyst. Similarly, elevated pEO concentrations increased reaction yields, substantiating a beneficial effect of high local concentrations of ether functionalities in close proximity to the Lewis acid. This was taken advantage of when the solvent-free depolymerization of pEO was demonstrated, eradicating the need of environmentally problematic chlorinated solvents.

A striking observation was made when the homologue of $\text{Si}(\text{cat}^{\text{Cl}})_2$, $\text{Ge}(\text{cat}^{\text{Cl}})_2$, which is known tolerate hydroxyl functionalities, exhibited only slightly higher turnover numbers (TONs) in the RCM of hydroxy-terminated pEOs. Ruling out hydrolysis as the leading cause of reactivity quenching, the formation of an anionic alkoxy-silicate was identified as a plausible deactivation pathway in the RCM of pEOs (FIG. 4.1). Regeneration of these silicates by reactions with electrophiles (HNTf_2 , MeI) experimentally validated this theory and disclosed a potential remedy for the depolymerization of hydroxy-functionalized polyethers.

Having identified the catalytically inactive species, an approach was taken to circumvent its formation by increasing the acidity of the reaction medium. This was achieved by an *in-situ* generation of $\text{Si}(\text{cat}^{\text{Cl}})_2$ from the respective catechol and SiCl_4 , generating HCl as a side product (FIG. 4.1). While this approach naturally increased the feasibility of the process, avoiding the handling of air-sensitive $[\text{Si}(\text{cat}^{\text{Cl}})_2]_n$, it also significantly increased the TON of the catalyst and expanded the scope of this reaction to hydroxy-terminated pEOs, successfully eradicating this limitation.

As a final step, the mechanism of the RCM was elucidated by combining experimental observations with DFT calculations using 18-crown-6 as a model substrate. The calculations indicate the formation of a monodentately coordinated $\text{Si}(\text{cat}^{\text{Cl}})_2$ -18-crown-6 adduct, in which the C–O bond is substantially polarized by the *effective* Lewis acidity of the silane. This polarization facilitates a cascade of intramolecular $\text{S}_{\text{N}}2$ reactions *via* transient zwitterionic silicato-dioxanium intermediates.

For linear polyethers - as opposed to the mechanism proposed for cyclic oligoethers - the initial intramolecular nucleophilic attack yields an ion pair consisting of an alkoxy silicate and a dioxanium cation. This ion pair must undergo an intermolecular reaction to liberate dioxane and regenerate the catalytically active species, which explains the increased efficiency observed in concentrated reaction media. If the dioxanium ion reacts with an external nucleophile in solution, the silicate must correspondingly react with a different electrophile to close the catalytic cycle.

The monodentate coordination to the Lewis acid is not the most energetically favored mode of binding. Instead, the formation of a bidentate *cis*-adduct of $\text{Si}(\text{cat}^{\text{Cl}})_2$ is favored energetically and can also be observed by NMR spectroscopy as the resting state of the reaction (FIG. 4.1). A comparison of binding thermodynamics of various Lewis acids with diglyme (bis(2-methoxyethyl) ether) revealed a low tendency of $\text{Si}(\text{cat}^{\text{Cl}})_2$ to engage in bidentate coordination. Through computational screening of suitable catalysts, with high *effective* Lewis acidity and a minimized propensity of bidentate substrate coordination, $\text{Si}(\text{amp}^{\text{F}})_2$ was selected as a promising candidate. In line with theoretical predictions, this catalyst exhibited significantly improved yields in the degradation of diglyme, outperforming $\text{Si}(\text{cat}^{\text{Cl}})_2$. With this mechanism-guided designed catalyst, even the ambitious cross-metathesis of mono-ethers, a side reaction already observed in the depolymerization of pEO, was realized.

Group 14 based Z-type ligands and their coordination chemistry were discussed in section 3.3. Deliberately using of the high *effective* Lewis acidity of tetrrels, two ambiphilic Z-type ligands were synthesized. While silane PNO_2Si was

easily approachable in a two step synthesis from the respective aminophenol, as described in section 3.3.1, the synthesis of the heavier homologue PNO_2Sn required a precisely designed combination of Sn(IV) precursor, base, and solvent to successfully isolate this derivative, as described in section 3.3.5. Due to the increased size of the central atom, phosphine coordination was observed in PNO_2Sn , whereas PNO_2Si formed an FLP. This significantly impacted the coordination chemistry of PNO_2Sn , necessitating decoordination of the phosphine prior to transition metal complexation, thereby resulting in prolonged reaction times or the need for elevated temperatures. One way to overcome this limitation was discovered by using Lewis bases to ease the decoordination of the phosphines, as observed in the reaction with $(\text{DMS})\text{AuCl}$, resulting in the formation of a chlorido-stannate Au(I) complex (FIG. 4.2). Although no metal-Lewis acid interaction was observed in this complex due to the chloride-induced quenching of the Lewis acidity, the fact that the silane PNO_2Si formed the structurally related chlorido-silicato Au(I) complex highlights the principal comparability of both systems, despite their structural difference in the absence of transition metals.

While this dissertation reports the coordination chemistry of a broad range of transition metals (Au , Rh , Mo), it particularly focused on the chemistry of palladium in combination with *effective* Z-type ligands (FIG. 4.2). Both ambiphilic ligands investigated in this work formed T-shaped Pd(0) complexes with strong $\text{Pd} \rightarrow \text{E}$ ($\text{E} = \text{Si}$, Sn) interactions, as described in section 3.3.1 and section 3.3.5. Silane complex $[\text{PNO}_2\text{SiPd}]$ was extensively studied in section 3.3.1. A strong $\text{Pd} \rightarrow \text{Si}$ Z-type interaction, caused by the *effective* Lewis acidity of Si , was observed in the solid-state, in solution and *in silico*. In-depth quantum chemical analysis of the electronic structure revealed a push-pull stabilization of the d^{10} fragment by the two phosphines and the σ -accepting silane. This Z-type interaction exceeded the strength of the P-Pd bonds and surpassed previously reported silanes. Through the strong Z-type interaction and the accompanying electron deficiency of this divalent Pd(0) complex, $[\text{PNO}_2\text{SiPd}]$ acted as an electrophile with its LUMO

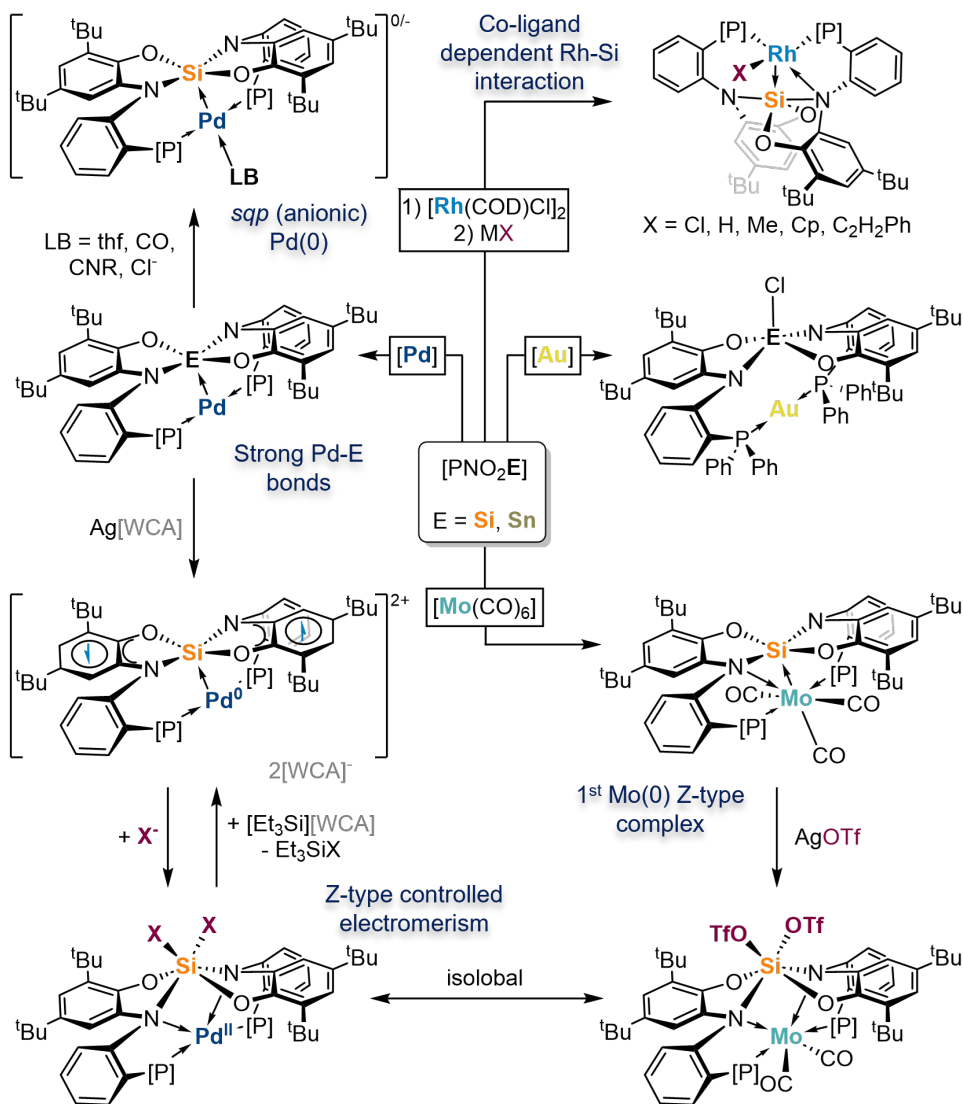


FIG. 4.2.: Key findings of this work regarding the coordination chemistry of ambiphilic group 14 based ligands. Emphasised is the altered reactivity of the coordinated transition metal, caused by the Z-type interaction with the *effective* Lewis acid.

located at the Pd atom. Reactions with Lewis bases (thf, CO, and cyclohexyl isocyanide) formed square planar (*sqp*) Pd(0) complexes (FIG. 4.2). These complexes mimicked the geometry of divalent Pd(II) complexes, but represent the first examples of *sqp* Pd(0), expanding the narrow field of *sqp*-d¹⁰ complexes. Through reaction with a chloride source, even an elusive anionic *sqp* Pd(0) complex (the first of its kind), which was often speculated as a fleeting intermediate in the AMATORE-JUTAND cross-coupling cycle, was isolated and characterized. Successful synthesis of this electron-rich complex was reasoned by stabilization of the anionic charge and the surplus of electron density through the *effective* Lewis acid. Elevated rates in the oxidative addition of PhI were in fact observed for this anionic Pd(0) complex in the first minutes of the reaction. However, speculations regarding the generality of the observed effect must not ignore the unique nature of the product after the oxidative addition, resulting from migration of the phenyl group to Si in the Pd(II) complex.

The oxidation chemistry of [PNO₂SiPd] was visited in section 3.3.2. Two-electron oxidation in the presence of Lewis bases resulted in the formation of silicato-Pd(II) complexes that exhibited strong coloration due to an LMCT from the electron-rich amidophenolate to the empty d-orbital. Oxidation in the absence of Lewis basic functionalities with silver salts of the weakly coordinating perfluorinated tetra-*tert*-butoxide aluminate [Al(O^tBu^F)₄][−], however resulted in ligand-centered oxidation of [PNO₂SiPd], forming an open-shell dicationic Pd(0) complex (FIG. 4.2). Its electronic structure was investigated by (VT)-EPR spectroscopy in conjunction with computational studies, revealing weak anti-ferromagnetic coupling of the two amidophenolate-centered radicals, forming an open-shell singlet ground state at low temperatures. Quantum chemical bond analyses corroborated the significant stabilization of this highly electrophilic Pd(0) complex by the strong Z-type interaction of the silane, which *effective* Lewis acidity naturally increased after oxidation.

Reaction of the open-shell dicationic Pd(0) complex with Lewis bases gave rise to the first example of Pd(0)/Pd(II) pseudo-electromerism (FIG. 4.2). After coordination of the Lewis base to Si, resulting in loss of the stabilizing Z-type interaction, an intramolecular rearrangement of electron density from the Pd(0) center to the oxidized ligand-backbone takes place, resulting in the formation of a diamagnetic Pd(II) complex. Full reversibility of this process was achieved by silylium mediated abstraction of the Lewis base from the respective silicato Pd(II) complex, providing the first example of Z-type controlled electromerism. Modulating the spin and oxidation states of a metal center through second-sphere coordination introduces a novel concept with potential to enable a wide range of promising future applications.

Systematic studies on the relationship between Z-type interactions and the coordination environment of the transition metal were presented in section 3.3.3, which explored the chemistry of a series of Rh(I)-silane complexes. Reaction of ambiphilic silane with $[\text{Rh}(\text{COD})\text{Cl}]_2$ furnished the respective Rh-Cl complex, the first example of a Rh(I)-silane Z-type complex. This complex corroborated the flexible coordination behavior of PNO_2Si , adopting a C_1 -symmetry in which additional coordination of the amp- N_1 was observed (FIG. 4.2). Bond analyses revealed a Rh-Si interaction, which surpassed previously reported Rh(I) Z-type interactions, comparable in strength to silyl-Rh bonds.

Transmetallation gave rise to a series of X-Rh(I)-complexes ($\text{X} = \text{Cl}, \text{Me}, \text{H}, \text{C}_2\text{H}_2\text{Ph}, \text{Cp}$). By fundamentally analyzing these related complexes, both structurally and computationally, insights into the nature of the Rh $\rightarrow$ Si interaction were gained, underlining its dependency on the respective co-ligand X at Rh. Co-ligands capable of donating electron density into Si-centered orbitals through good overlap of the involved Rh-X bond orbitals increase the Rh-Si bond strength. Thereby, the respective co-ligand gets energetically stabilized, which was most prominently demonstrated by the isolation of an inert Rh-H complex, where the hydride experienced substantial stabilization by the σ -accepting silane. However, this stabilization

is strongly dependent on the geometry of the complex, as substantiated by the reaction with isocyanides that forced the complex into a C_{2v} geometry with the hydride located *trans* to the silane center. Missing the stabilizing effect that occurred through overlap of the s-orbital and the Rh-Si bond in the initial complex, vivid reactivity of the hydride was observed in the octahedral Rh(I) complex.

The results in section 3.3.3 fundamentally explored the relationship between a Z-type interaction and co-ligands at the respective metal center, providing valuable insights into stabilizing effects. These findings emphasize careful design of future Rh-Z-type systems for catalytic applications in order to prevent highly stabilized intermediates when the Z-type interaction exceeds certain levels.

Z-type chemistry hitherto focused on electron-rich late transition metals that easily donate electron density from their filled d-orbitals into the LUMO of the Lewis acid. This dissertation reports a paradigm shift by presenting the first examples of molybdenum(0) Z-type complexes using the ambiphilic silane PNO_2Si in section 3.3.4. Through reaction of this ligand with a suitable $Mo(CO)_3$ synthon, a tricarbonyl-Mo(0)-silane complex (*trans*- $[PNO_2SiMo(CO)_3]$, Fig. 4.2) was isolated and studied. While analysis by scXRD revealed a Mo-Si bond in the solid-state, NMR spectroscopy further confirmed a Mo→Si interaction in this complex. Similar to the Rh(I) chemistry of PNO_2Si , additional coordination of the Mo center by one $amp-N_1$ can be observed in the solid-state, whereas NMR spectroscopy indicated a dynamic equilibrium with an averaged C_2 symmetry in solution. DFT-based bond analyses elucidated the Mo-Si Z-type interaction, the first of its kind, which in terms of strength naturally ranks lowest when compared to the d^8 - and d^{10} -interactions in this work.

Exploring possible synthetic pathways to a N_2 -Mo-Z-type complex for subsequent catalytic applications, the oxidation chemistry of *trans*- $[PNO_2SiMo(CO)_3]$ was studied in this dissertation. Interestingly, oxidation reactions never surpassed the Mo(II)-state, giving rise to a series of dicarbonyl-Mo(II)-silicato complexes and thereby sketching the limitations of the employed electron-rich silane. A rich coor-

dination chemistry with several unique structural motives was observed for these complexes, which was reasoned by different nucleophilicities of the respective Lewis bases (Cl^- , I^- , OTf^-). For the latter case, a hexa-coordinated triflate-silicate complex of a Mo(II)(CO)_2 fragment was isolated that structurally and electronically closely resembled its isolobal Pd(II) counterpart (FIG. 4.2), highlighting the similarities of these elements despite their separation in the periodic table. The expansion of Z-type chemistry to group 8 metals demonstrated in this dissertation encourages further research on this hitherto neglected area of the periodic table. It also draws a border, rendering Z-type interactions of metals with less than three fully occupied d-orbitals unlikely.

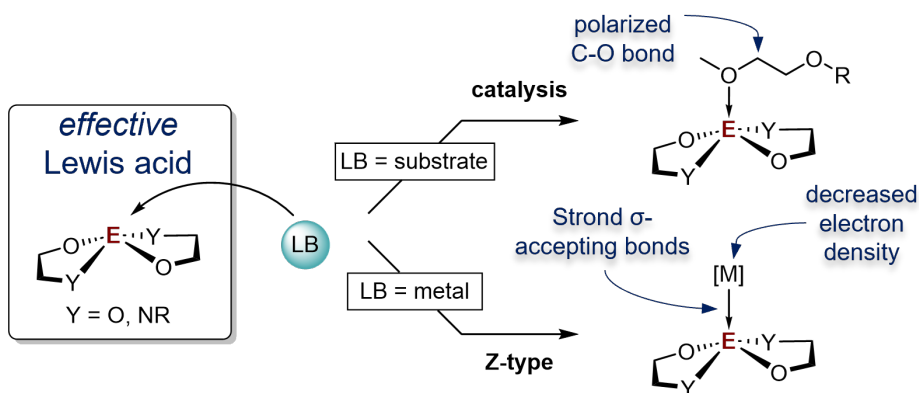


FIG. 4.3.: Overall conclusion on the concept of using effective group 14 Lewis acids for bond activation in catalysis and for strong Z-type interactions with transition metals.

To conclude, this dissertation provided insights into the potential that highly *effective* Lewis acids hold for applications in catalysis and coordination chemistry (FIG. 4.3). The contributions of this dissertation to the field of metathesis reactions clearly showcase that through careful ligand design, silicon can act as suitable and sustainable catalyst in its natural oxidation state thanks to its *effective* Lewis acidity. Application of this reaction in the depolymerization of polyethers created new opportunities for a circular economy of this widely used polymer class. In the

second part of this dissertation, several contributions to the Z-type chemistry of Pd, Rh, and Mo were made, providing rare examples of group 14 Lewis acids used as Z-type ligands. The obtained insights emphasize the benefits of *effective* Lewis acidity in the area of ambiphilic ligands. This dissertation contributes to a deeper understanding of the relationship between Lewis acids and the resulting Z-type interactions, demonstrating how these can be harnessed to induce reactivity in transition metals that would otherwise be inaccessible without this unique class of ligands.

5 | EXPERIMENTAL AND COMPUTATIONAL DETAILS

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5.1. GENERAL REMARKS ON EXPERIMENTAL WORK

All experiments were carried out under a dry and oxygen-free argon atmosphere by using standard Schlenk techniques, using flame dried glassware, or by working in a glovebox (SYLATECH GB 1950-E or VAC Genesis) under a nitrogen atmosphere. Solvents were dried by applying standard procedures, freshly degassed and stored over molecular sieves (3 Å resp. 4 Å).

Commercially available chemicals were used as received, unless stated otherwise. $[\eta^6\text{-(toluene)Mo(CO)}_3]$, bis(2,4-di-tert-butyl-(2-diphenylphosphanylamido)phenolato)silane and PhICl_2 were synthesized according to literature-known procedures.^[266,311,312]

NMR spectra were recorded on Bruker instruments (Avance III 600 MHz, Ultra-Shield 600 MHz, Avance Neo 500 MHz, Avance II 400 MHz, Avance-III HD Nanobay 400 MHz or Ascend 400 MHz) at room temperature (295 K or 298 K). Hetero-nuclei spectra were obtained with ^1H broadband or composite pulse decoupling (cpd), unless noted otherwise. Referencing of the chemical shifts in ^1H and ^{13}C NMR spectra was accomplished by residual solvent signals. Chemical shifts δ are given in ppm (parts per million); coupling constants J in Hz (Hertz). Observed signal patterns are noted according to their multiplicities in the standard fashion (e.g. s = singlet, d = doublet, dd = doublets of doublets, pt = pseudo-triplet, etc.). Overlapping signals with indistinct shapes are described as m = multiplet. All NMR spectra were processed with Bruker TopSpin 4.3.0.

Electron Spray Ionization (ESI) high resolution mass spectra (HR-MS) and *Liquid Injection Field Desorption Ionization* (LIFDI) mass spectra were recorded at the Department of Organic Chemistry at Heidelberg University under supervision of Dr. JÜRGEN GROSS on a Bruker ApexQe FT-ICR and a JOEL AccuTOF GCx instrument. Elemental analyses (EA) (C, H, N) were measured by the staff of the microanalytical laboratory of the chemical institutes of Heidelberg University by an Elementar vario MICRO Cube machine.

IR spectra were measured on an Agilent Cary 630 FTIR spectrometer equipped with a diamond ATR unit inside a nitrogen-filled glovebox.

UV-Vis-NIR spectra were recorded on a Agilent Cary 5000 spectrometer, in Normag quartz glass cuvettes under inert atmosphere. The spectra were baseline corrected by subtraction of the background spectrum of the respective solvent. Plots were generated using OriginPro 2024.

5.2. CRYSTALLOGRAPHIC DATA ACQUISITION AND STRUCTURE REFINEMENT

Single crystal X-Ray diffraction (scXRD) was performed on a Bruker D8 VENTURE dual wavelength Mo/Cu four-circle diffractometer with a microfocus sealed X-ray tube using a mirror optics as monochromator and a Bruker PHOTON II or PHOTON III detector. The diffractometers were equipped with Oxford Cryostream 700 low temperature devices. All measurements were carried out at low temperatures with molybdenum K_{α} ($\lambda = 0.7107 \text{ \AA}$) radiation. Data were processed with the standard Bruker (SAINT, APEX5) software package.^[313,314] Multiscan absorption correction was applied using the SADABS program.^[315,316] The structures were solved by direct methods using SHELXT and refined by full-matrix least-squares methods against F^2 by SHELXL-2019/2.^[317–319] Structural data was graphically handled using shelXle.^[320] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms bound to carbon were input at calculated positions and refined with a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Parts of the disorder models were introduced by the program DSR.^[321,322] In structures with highly disordered solvent molecules, these were accounted for with the PLATON SQUEEZE method.^[323,324] Parts of this report and the CIF file were generated using FinalCif.^[325] Structures were visualized using Mercury 2024.1.0, displaying thermal displacement ellipsoids at 50% probability.^[326–329]

5.3. COMPUTATIONAL DETAILS

All calculations were performed using the Orca 5.0.4 program package,^[330,331] unless stated otherwise. Geometry optimizations were carried out with GRIMME's

PBEh-3c/def2-mSVP method, including the geometrical counter-poise correction scheme (gCP), atom-pairwise dispersion correction and the Becke-Johnson damping scheme (D3BJ).^[332–337] *VeryTightSCF* settings were used. ECPs were used for Mo, Sn and I (def2-ECP).^[338] Calculated geometries were confirmed as energetic minima by frequency calculations at the same level of theory as the optimization calculation. Enthalpies at 298 K were computed at the same level of theory using the rigid-rotor harmonic oscillator (RRHO) approximation.^[339] For the Coulomb integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[336,337,340]

For precise energies, single point energies were calculated after successful geometry optimization, using HEAD-GORDON's ω b97x-V method with the def2-TZVPP basis set (including DFT-NL dispersion correction).^[338,341–344] Solvation corrected energies were calculated using the SMD solvation module with the conductor-like polarizable continuum model, CPCM.^[345] For the Coulomb integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[336,337,340] All calculations were carried out using *VeryTightSCF* settings.

TD-DFT calculations for the vertical excitation profiles of the first 30 excited states were conducted using the hybrid exchange-correlation functional CAM-B3LYP with the def2-TZVPP basis set at *VeryTightSCF* settings.^[336,346] Solvent effects were accounted for by the SMD solvation module, using thf as the solvent.^[345] For the Coulomb integral, the RI approximation (RIJCOSX) was applied along with the corresponding auxiliary basis sets.^[336,337,340] Natural transition orbitals (NTOs) were calculated by setting *DONTO* = *TRUE*.^[347,348] Calculated spectra were plotted using ChemCraft with Gaussian line broadening.^[349]

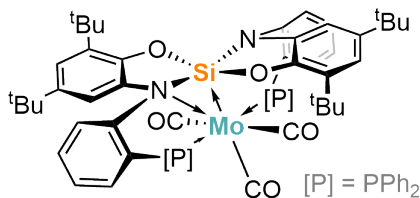
Natural Bond Orbital (NBO) calculations were conducted on PBE0-D4/def2-TZVPP level of theory wavefunctions,^[342,350,351] using the program NBO 6.0.18a as included in Orca 5.0.4.^[352] Wiberg bond indices were calculated using the BNDIDX keyword. NBOs were rendered and plotted using Chemcraft.^[349]

PBE0/DKH-def2-TZVP (Mo: SARC-DKH-TZVP) electron densities were used for plotting of the intrinsic bond orbitals (IBOs) as implemented in Orca 5.0.4.,^[342,350,351,353,354] and for QTAIM analysis with the AIMAll software, using default integration settings.^[355]

Energy decomposition analysis (EDA), using the Extended Transition State (ETS) method combined with the natural orbitals for chemical valence (NOCV) concept was calculated within the AMS2025.103 software package at the BP86-D3BJ/TZ2P level of theory, with *Frozen Core* set to *None* and *Numerical Quality* set to *Good*.^[334,356–360]

5.4. SYNTHETIC PROCEDURES AND CHARACTERIZATION

TRANS-[PNO₂SiMo(CO)₃]



(A) From [Mo(CO)₆]

In a 50 mL round bottom flask with a teflon valve, PNO₂Si (200 mg, 203 μmol, 1.00 eq) and freshly sublimed Mo(CO)₆ (107 mg, 405 μmol, 2.00 eq) were suspended in 5 mL of benzene. The mixture was heated in an oil bath at 100 °C for 3 days. After 3 h and 22 h the reaction was quickly cooled to rt, opened to a N₂ line with over pressure bubbler in order to release an excess of CO, before it was closed again and heating was continued. After analysis of an aliquot by NMR spectroscopy only revealed 50% conversion, an excess of Mo(CO)₆ (140 mg, 530 μmol, 2.61 eq) was added to the reaction mixture and heating was continued for 60 h, before 1 mL of thf was added to the reaction mixture, followed by 18 h of heating. The solvent of the reaction was removed under reduced pressure. The residue was picked up in 8 mL of thf, transferred back to the reaction vessel and heated at

100 °C for 26 hours. All reaction contents were condensed to dryness and the dry residue was heated at 60 °C *in vacuo* in order to remove volatile Mo species. Inside a glovebox, the red-orange residue was picked up in 3 mL of toluene, transferred to a 20 mL vial and subsequently condensed to dryness. The residue was suspended in 1 mL of *n*-pentane. The red solution phase was decanted and this process was repeated once more, before the beige solid (160 mg, 137 µmol, 68%) was dried *in vacuo*.

(B) From [η^6 -(toluene)-Mo(CO)₃]

In a 50 mL round bottom flask with a teflon valve, PNO₂Si (200 mg, 203 µmol, 1.00 eq) and [η^6 -(toluene)-Mo(CO)₃] (76.0 mg, 235 µmol, 1.25 eq) were suspended in 8 mL of benzene. The yellow solution was stirred at 100 °C for 18 h, before it was cooled down to room temperature. Afterwards, the reaction mixture was lyophilized and the orange residue was heated to 80 °C *in vacuo* to remove any volatile molybdenum compounds. The orange powder was suspended in 5 mL of MeCN, filtered and washed with additional 5 mL of MeCN and 5 mL of –20 °C cold *n*-pentane. Drying the yellow solid *in vacuo* yielded *trans*-[PNO₂SiMo(CO)₃] as a beige powder (171 mg, 147 µmol, 72%).

Crystals suitable for scXRD were obtained by gas phase diffusion of *n*-pentane into a saturated dcm solution at –35 °C.

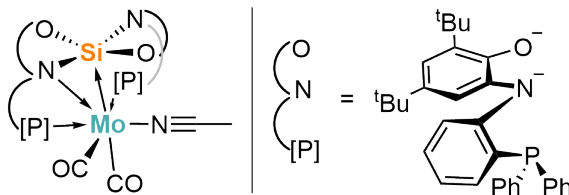
¹H NMR (500 MHz, C₆D₆, 298 K): δ [ppm] = 7.74-7.71 (m, 4H), 7.61-7.58 (m, 4H), 7.54 (dd, *J* = 8.2, 2.9 Hz, 2H), 7.42-7.39 (m, 2H), 7.07-7.04 (m, 4H), 7.00-6.97 (m, 8H), 6.94-6.88 (m, 4H), 6.75 (t, *J* = 7.6 Hz, 2H), 6.64 (d, *J* = 1.9 Hz, 2H), 1.33 (s, 18H), 1.14 (s, 18H).

¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ [ppm] = 223.5 (t, *J*_{31P,13C} = 13.0 Hz, C_q, CO), 208.3 (t, *J*_{31P,13C} = 8.0 Hz, C_q, 2CO), 156.5 (d, *J*_{31P,13C} = 19.5 Hz, C_q), 144.1 (s, C_q), 144.1 (s, C_q), 142.8 (s, C_q), 138.0 (d, *J*_{31P,13C} = 35.6 Hz, C_q), 137.9 (d, *J* = 42.8 Hz, C_q), 134.9 (s, C_q), 133.0 (d, *J*_{31P,13C} = 11.8 Hz, CH), 132.8 (s, CH), 132.6 (d, *J*_{31P,13C} = 10.6 Hz, CH), 132.0 (s, CH), 129.7 (s, CH), 129.5 (s, CH), 128.7-128.6 (m, CH), 128.5-128.3 (m, CH), 123.8 (s, CH), 115.4 (s, CH), 110.6 (s, CH), 34.7 (s, C_q), 34.7 (s, C_q), 31.9 (s, CH₃), 29.9 (s, CH₃).

³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ [ppm] = 43.1 (broad, s).

²⁹Si{¹H} NMR (79 MHz, C₆D₆, 298 K): δ [ppm] = –66.5 (t, *J*_{31P,29Si} = 3.9 Hz).

IR (ATR, thf film): $\tilde{\nu}$ [cm^{–1}] = 2952 (w), 1908 (vs), 1879 (vs), 1476 (m), 1433 (m), 1292 (m), 1228 (s), 1027 (s), 691 (s).

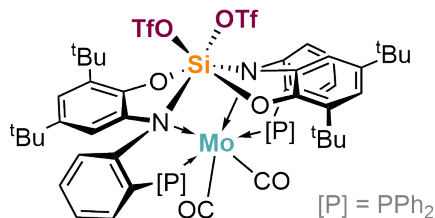
cis-[PNO₂SiMo(CO)₂(MeCN)]

In a J. Young NMR tube, *trans*-[PNO₂SiMo(CO)₃] (7.00 mg, 6.00 μmol, 1.00 eq) was dissolved in 0.45 mL of C₆D₆. To this, an excess of MeCN (2.46 mg, 60.0 μmol, 10.0 eq) was added. The resulting orange solution was heated in a steel block at 100 °C for 42 h. Afterwards, the reaction was analyzed by NMR spectroscopy, indicating quantitative formation of the title compound.

¹H NMR (400 MHz, C₆D₆, 298 K): δ[ppm] = 8.15-8.05 (m, 4H), 7.90 (dd, *J* = 7.8, 5.6 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 2H), 7.2 (t, *J* = 8.2 Hz, 1H), 7.36-7.33 (m, 2H), 7.27 (t, *J* = 7.0 Hz, 1H), 7.12-7.03 (m, 7H), 7.00-6.94 (m, 3H), 6.89-6.83 (m, 6H), 6.80-6.76 (m, 2H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.08 (d, *J* = 2.0 Hz, 1H), 1.44 (s, 9H), 1.39 (s, 9H), 1.24 (s, 9H), 1.00 (s, 9H), 0.18 (s, 3H).

¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ[ppm] = 226.7 (dd, *J*_{31P,13C} = 16.0, 9.7 Hz, C_q, CO), 215.5 (dd, *J*_{31P,13C} = 11.7, 4.1 Hz, C_q, CO), 162.0 (d, *J*_{31P,13C} = 28.0 Hz, C_q), 152.7 (d, *J*_{31P,13C} = 11.7 Hz, C_q), 147.0 (s, C_q), 145.0 (s, C_q), 144.8 (s, C_q), 142.9 (d, *J*_{31P,13C} = 45.4 Hz, C_q), 141.8 (s, C_q), 140.3 (s, C_q), 139.1 (s, C_q), 137.3 (d, *J*_{31P,13C} = 33.1 Hz, C_q), 135.7 (d, *J*_{31P,13C} = 24.8 Hz, C_q), 135.2 (s, C_q), 134.4 (d, *J*_{31P,13C} = 11.4 Hz, CH), 134.0 (s, C_q), 133.7 (d, *J*_{31P,13C} = 11.1 Hz, CH), 133.2 (d, *J*_{31P,13C} = 11.1 Hz, CH), 132.7 (s, CH), 132.5 (d, *J*_{31P,13C} = 9.7 Hz, CH), 132.0 (d, *J*_{31P,13C} = 10.7 Hz, CH), 131.6 (s, CH), 131.1 (s, CH), 130.3 (s, CH), 129.0 (s, CH), 128.9 (s, CH), 128.7 (s, CH), 128.5 (s, CH), 127.5 (s, CH), 127.4 (s, CH), 124.8 (d, *J*_{31P,13C} = 5.6 Hz, CH), 122.6 (s, C_q), 120.6 (d, *J*_{31P,13C} = 4.2 Hz, CH), 120.2 (d, *J*_{31P,13C} = 5.5 Hz, CH), 117.2 (s, CH), 116.9 (s, CH), 116.0 (s, C_q), 113.0 (s, CH), 106.1 (s, CH), 34.9 (s, 2C_q), 34.6 (s, C_q), 34.5 (s, C_q), 32.2 (s, CH₃), 32.2 (s, CH₃), 30.5 (s, CH₃), 29.7 (s, CH₃), 1.4 (s, CH₃). **³¹P{¹H} NMR** (162 MHz, C₆D₆, 298 K): δ[ppm] = 58.5 (d, *J* = 93.0 Hz, 1P), 32.6 (d, *J* = 93.0 Hz, 1P).

²⁹Si{¹H} NMR (79 MHz, C₆D₆, 298 K): δ[ppm] = -61.0 (dd, *J*_{31P,29Si} = 20.4, 9.8 Hz).

$[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ 

To a J. Young NMR tube, containing a solution of *trans*-[PNO₂SiMo(CO)₃] (24.0 mg, 20.6 μmol, 1.00 eq) in 0.45 mL C₆D₆, AgOTf (10.6 mg, 41.1 μmol, 2.00 eq) was added in one portion and the tube was shaken vigorously, resulting in the formation of a dark green suspension alongside with the precipitation of elemental silver. The reaction mixture was analyzed by NMR spectroscopy, stating full conversion of the starting material. The contents of the NMR tube, alongside with 0.4 mL of benzene were filtered through a PTFE syringe filter and added drop-wise to rapidly stirred *n*-pentane (10 mL). The precipitating dark green solid was allowed to settle, before the supernatant was carefully decanted with a pipette. The obtained solid was dried *in vacuo* to yield the target compound as as green powder (15.6 mg, 10.9 μmol, 53%). A second crop of product was obtained by concentrating the decanted organic phase to 0.2 mL, followed by the addition of 5 mL of *n*-pentane, resulting the precipitation of more dark green solid (7.6 mg). Combined Yield: 23.2 mg, 16.1 μmol, 79%.

Crystals suitable for scXRD were obtained by gas phase diffusion of *n*-pentane into a saturated *o*DFB solution at −15 °C.

¹H NMR (500 MHz, C₆D₆, 298 K): δ[ppm] = 8.76 (dd, *J* = 8.3, 3.6 Hz, 2H), 7.60 (d, *J* = 2.1 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.13-7.11 (m, 2H), 7.02-7.00 (m, 8H), 6.95-6.94 (m, 6H), 6.91 (d, *J* = 2.1 Hz, 2H), 6.81-6.77 (m, 4H), 6.59-6.56 (m, 4H), 1.22 (s, 18H), 1.13 (s, 18H).

¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ[ppm] = 233.7 (t, *J*_{31P,13C} = 25.0 Hz, C_q, CO), 152.5 (s, C_q), 143.1 (s, C_q), 138.0 (s, C_q), 135.7 (t, *J*_{31P,13C} = 5.7 Hz, CH), 134.1 (s, CH), 133.6 (s, CH), 132.9 (t, *J*_{31P,13C} = 5.9 Hz, CH), 131.7 (s, CH), 131.4 (s, CH), 130.7 (s, CH), 129.2 (t, *J*_{31P,13C} = 5.3 Hz, CH), 128.8 (t, *J*_{31P,13C} = 5.7 Hz, CH), 125.6 (s, CH), 125.0 (s, C_q), 123.5 (s, CH), 120.3 (q, *J*_{19F,13C} = 319 Hz, CF₃), 35.2 (s, C_q), 35.0 (s, C_q), 31.7 (s, CH₃), 29.7 (s, CH₃).

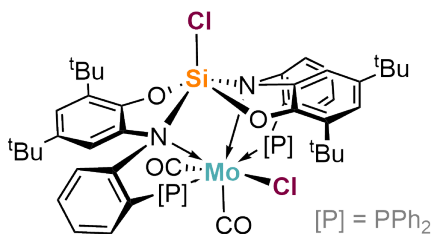
¹⁹F NMR (471 MHz, C₆D₆, 298 K): δ[ppm] = −74.8 (broad, s).

$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6 , 298 K): $\delta[\text{ppm}] = 71.1$ (s).

$^{29}\text{Si}\{^1\text{H}\}$ NMR (79 MHz, C_6D_6 , 298 K): not detected.

IR (ATR, thf film): $\tilde{\nu} [\text{cm}^{-1}] = 2956$ (m), 2866 (m), 1938 (m), 1867 (vs), 1480 (m), 1437 (m), 1295 (m), 1161 (s), 1066 (s), 1029 (s), 913 (m), 747 (m), 695 (m).

$[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$

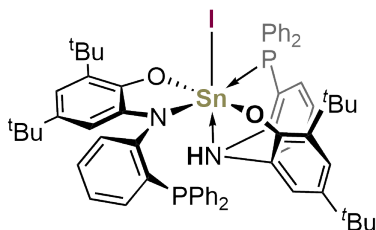


To a rapidly stirred solution of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ (30.0 mg, 25.7 μmol , 1.00 eq) in 1 mL of thf, which was cooled to -20°C , a cooled solution of PhICl_2 (14.1 mg, 51.4 μmol , 2.00 eq) in 0.5 mL of thf was added. The reaction mixture was stirred while reaching room temperature, resulting in a gradually color change from green to dark brown. The reaction was stirred for additional 10 min at room temperature, before all volatiles were removed *in vacuo*. The glassy residue was suspended in 2 mL of *n*-pentane, before the solvent was removed *in vacuo* to eliminate any traces of thf. This step was repeated once more. The grey-brown residue was then extracted with 3 x 4 mL of *n*-pentane. The combined pentane extracts were condensed to dryness, to yield 13.3 mg of a light-brown powder (11.0 μmol , 43%).

^1H NMR (400 MHz, C_6D_6 , 298 K): $\delta[\text{ppm}] = 8.27$ (dd, $J = 7.6, 5.0$ Hz, 2H), 8.04 (dd, $J = 12.0, 7.3$ Hz, 2H), 7.94 (dd, $J = 8.0, 4.8$ Hz, 1H), 7.73 (t, $J = 8.1$ Hz, 2H), 7.66-7.62 (m, 2H), 7.50 (t, $J = 8.4$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 1H), 7.24 (d, $J = 1.7$ Hz, 1H), 7.07-6.78 (m, 19H), 5.82 (d, $J = 1.5$ Hz, 1H), 5.31 (d, $J = 1.6$ Hz, 1H), 1.68 (s, 9H), 1.41 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K): $\delta[\text{ppm}] = 85.6$ (d, $J_{31\text{P},31\text{P}} = 38.1$ Hz, 1P), 62.3 (d, $J_{31\text{P},31\text{P}} = 38.1$ Hz, 1P).

IR (ATR, thf film, *in situ*): $\tilde{\nu} [\text{cm}^{-1}] = 3054$ (vw), 2950 (m), 2900 (w), 2861 (w), 1961 (m), 1934 (s), 1880 (vs), 1571 (w), 1482 (m), 1470 (m), 1435 (m), 1360 (w), 1260 (m), 1088 (w), 997 (w), 900 (w), 848 (w), 752 (w), 695 (w).

I-Sn(PNO)(PNO-H)

PNO-H₂ (200 mg, 415 μ mol, 1.00 eq), SnI₄^v (130 mg, 208 μ mol, 1.00 eq) and KHMDS (124 mg, 623 μ mol, 1.50 eq) were dissolved in dcm (6 mL). The dark brown solution was stirred at room temperature overnight. The resulting suspension was filtered, the residue was washed with dcm (2 mL) before the filtrate was concentrated *in vacuo*. Crystallization *via* gaseous diffusion of *n*-pentane into the dcm at -40°C yielded a precipitate, which was washed with *n*-pentane to receive a dark purple solid in 25 % yield (122 mg, 101 μ mol).

¹H NMR (400 MHz, CD₂Cl₂, 295 K): δ [ppm] = 8.91 (dd, J = 12.1, 5.5 Hz, 1H, N-H), 7.80 – 7.77 (m, 2H), 7.70 – 7.66 (m, 2H), 7.62 – 7.60 (m, 2H), 7.49 – 7.46 (m, 2H), 7.45 – 7.40 (m, 2H), 7.30 – 7.28 (m, 4H), 7.27 – 7.25 (m, 3H), 7.15 (dt, J = 7.5, 3.8 Hz, 2H), 7.13 – 7.09 (m, 2H), 7.06 – 7.03 (m, 2H), 6.90 (t, J = 7.1, 14.3 Hz, 2H), 6.83 (d, J = 2.1 Hz, 1H), 6.71 – 6.67 (m, 1H), 6.43 (d, J = 1.7 Hz, 1H), 6.37 (d, J = 1.8 Hz, 1H), 5.93 (t, J = 7.6, 15.6 Hz, 2H), 5.71 (d, J = 2.1 Hz, 1H), 1.18 (s, 9H, ^tBu-H), 1.04 (s, 9H, ^tBu-H), 0.90 (s, 9H, ^tBu-H), 0.82 (s, 9H, ^tBu-H).

¹³C{¹H, ³¹P} NMR (151 MHz, CD₂Cl₂, 295 K): δ [ppm] = 154.0 (s, C_q), 153.6 (s, C_q), 148.3 (s, C_q), 145.5 (s, ^{Ar}C_q), 141.4 (s, C_q), 138.4 (s, C_q), 138.4 (s, C_q), 137.8 (s, C_q), 136.5 (s, C_q), 136.2 (s, CH), 135.7 (s, 2 CH), 135.4 (s, CH), 134.3 (s, CH), 134.2 (s, CH), 133.9 (s, CH), 133.3 (s, CH), 132.8 (s, CH), 132.5 (s, CH), 131.2 (s, CH), 130.0 (s, CH), 129.5 (s, CH), 129.4 (s, CH), 129.2 (s, CH), 129.0 (s, CH), 128.1 (s, CH), 127.9 (s, CH), 127.2 (s, C_q), 126.6 (s, CH), 125.5 (s, CH), 125.5 (s, CH), 124.5 (s, C_q), 123.3 (s, CH), 121.9 (s, C_q), 119.7 (s, CH), 111.0 (s, CH), 107.4 (s, CH), 35.2 (s, C_q), 34.9 (s, C_q), 34.3 (C_q), 34.3 (s, C_q), 31.7 (s, CH₃), 31.6 (s, CH₃), 29.9 (s, CH₃), 29.4 (s, CH₃).

³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 295 K): δ [ppm] = -20.3 (d, J = 4.4 Hz, 1P), -23.3

^vSnI₄ was recrystallized from toluene at -40°C , subsequently dried *in vacuo* and stored at -40°C in the dark.

(d, $J = 4.6$ Hz, $J_{31\text{P},117\text{Sn}} = 818$ Hz, $J_{31\text{P},119\text{Sn}} = 857$ Hz, 1P).

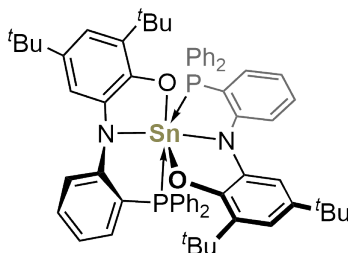
$^{119}\text{Sn}\{^1\text{H}\}$ NMR (224 MHz, CD_2Cl_2 , 295.0 K): δ [ppm] = -599.6 (dd, $J = 37.0$, 895.0 Hz).

MS (LIFDI; toluene) [m/z]: $[\text{M-I}]^+$ calcd.: 1206.29; found: 1206.33.

MS (ESI(-)) [m/z]: $[\text{M-I}]^-$ calcd.: 1205.29; found: 1205.28.

Elemental Analysis [%] calcd. for $\text{C}_{64}\text{H}_{69}\text{IN}_2\text{O}_2\text{P}_2\text{Sn} \times 1.5 \text{ CH}_2\text{Cl}_2$: C, 59.01; H, 5.44; N, 2.10; found C, 59.45; H, 5.63; N, 2.46.

Bis(2,4-DI-*TERT*-BUTYL-(2-DIPHENYLPHOSPHANYLAMIDO)PHENOLATO)STANNANE(IV)[PNO_2Sn]



PNO-H_2 (1.21 g, 2.51 mmol, 1.00 eq), recrystallized SnI_4 (787 mg, 1.26 mmol, 0.50 eq) and KHMDs (1.00 g, 5.03 mmol, 2.00 eq.) were suspended in diethyl ether (75 mL) and stirred overnight. The yellow precipitate was filtered and washed with diethyl ether (50 mL). After initial filtration, the product was extracted with hot benzene (150 mL) and separated from the potassium iodide by filtration. After lyophilization, the product was obtained as an orange solid in a yield of 64 % (867 mg, 804 μmol).

^1H NMR (400 MHz, C_6D_6 , 295 K): δ [ppm] = 8.19 (d, $J = 8.4$ Hz, 2H), 8.06 (d, $J = 2.3$ Hz, 2H), 7.43 (d, $J = 2.5$ Hz, 2H), 7.40-7.37 (m, 6H), 7.28-7.25 (m, 2H), 7.18 (q, $J = 5.8$ Hz, 4H), 7.10 (t, $J = 7.4$ Hz, 2H), 7.02 (t, $J = 7.4$ Hz, 4H), 6.88 (t, $J = 7.4$ Hz, 2H), 6.79 (t, $J = 7.4$ Hz, 4H), 6.72 (t, $J = 7.3$ Hz, 2H), 1.69 (s, 18H), 1.49 (s, 18H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 295 K): δ [ppm] = 155.2 (s, C_q), 150.0 (s, C_q), 137.9 (s, C_q), 137.0 (s, C_q), 135.6 (s, 2 CH), 134.2 (s, C_q), 133.5 (s, CH), 133.3 (s, CH), 131.4 (s, CH), 130.2 (s, CH), 128.9 (t, $J = 5.4$ Hz, CH), 128.7 (t, $J = 5.0$ Hz, CH), 128.0 (s, CH), 118.1 (t, $J = 3.6$ Hz, CH), 116.1 (s, CH), 115.6 (s, CH), 114.3 (s, C_q), 114.1 (s, C_q), 113.9 (s, CH), 35.5 (s, C_q), 34.8 (s, C_q), 32.4 (s, CH_3), 30.1 (s, CH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 295 K): δ [ppm] = -24.2 (s, $J_{31\text{P},117/119\text{Sn}} = 330$ Hz)

$^{119}\text{Sn}\{^1\text{H}\}$ NMR (224 MHz, C_6D_6 , 295 K): δ [ppm] = -345.8 (t, $J = 330$ Hz).

MS (LIFDI; toluene) $[m/z]$: $[M]^+$ calcd.: 1078.38; found: 1078.42.

Elemental Analysis [%] calcd. for $\text{C}_{64}\text{H}_{68}\text{N}_2\text{O}_2\text{P}_2\text{Sn}$: C, 71.31; H, 6.36; N, 2.60; found C, 68.85; H, 5.94; N, 2.62.

5.5. REACTIVITY STUDIES

OXIDATION OF *TRANS*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ WITH I_2

trans- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ (42.0 mg, 36.0 μmol , 1.00 eq) was dissolved in 1.5 mL of thf inside a J. Young NMR tube. To this orange solution, 0.47 mL of a I_2 solution (78.8 mM in thf, 9.13 mg, 36.0 μmol , 1.00 eq) was added with a syringe. The resulting dark green solution was slowly shaken at room temperature for 42 h by using the motor of a rotary evaporator. After NMR spectroscopy stated full conversion of the initially formed complex, all reaction contents were condensed to dryness. The residue was first washed with 4 mL of *n*-pentane and then extracted with 3.5 mL of Et_2O , yielding crude product.

Crystals suitable for scXRD were obtained by gas phase diffusion on *n*-pentane into the concentrated diethyl ether solution at -15°C .

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 298 K): δ [ppm] = 68.0 (s, 1P), -23.2 (s, 1P).

REACTIVITY OF PNO-H_2 WITH $\text{Sn}(\text{NMe}_2)_4$

(A) In DCM; Formation of $[\text{Cl-Sn}(\text{PNO})(\text{PNO-H})]$

In a J. Young tube, $\text{Sn}(\text{NMe}_2)_4$ (4.13 μL , 16.4 μmol , 1.05 eq) was added to a solution of PNO-H_2 (15.0 mg, 31.1 μmol , 2.00 eq) in CD_2Cl_2 . The off-white solution was subsequently analyzed by NMR spectroscopy. Crystallization by gas phase diffusion on *n*-pentane and MeCN into the concentrated solution at -40°C yielded crystals suitable for scXRD.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -13.9 (s, 1P), -26.3 (s, $J_{31\text{P}, 117/119\text{Sn}} = 731$ Hz, 1P).

(B) In MeCN; Formation of $[\text{PNO}_2\text{Sn-C}_4\text{N}_2\text{H}_{10}]$

To a solution of PNO-H_2 (15.0 mg, 31.1 μmol , 1.00 eq) in MeCN, $\text{Sn}(\text{NMe}_2)_4$ (4.08 μL , 15.6 μmol , 0.50 eq) was added at -40°C . The yellow reaction mixture was stirred

overnight, before the formed precipitate was isolated by filtration and subsequently dried *in vacuo*. The solid was dissolved in C_6D_6 for NMR spectroscopy.

$^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -13.6 (s, 1P), -26.6 (s, $J_{^{31}P,^{117}Sn} = 561$ Hz, $J_{^{31}P,^{119}Sn} = 582$ Hz, 1P).

Crystallization of the yellow solid from a concentrated diethyl ether solution at $-40^\circ C$ yielded crystals suitable for scXRD analysis.

FORMATION OF $[(PNO-H)_2Sn][NTf_2]_2$

To a solution of PNO_2Sn (10.0 mg, $9.28\ \mu mol$, 1.00 eq) in C_6D_6 , $HNTf_2$ was added in one portion (2.60 mg, $9.28\ \mu mol$, 1.00 eq). The resulting pale-yellow solution was kept at room temperature for 16 h before it was heated to $50^\circ C$ for additional 16 h. Subsequent analysis *via* NMR spectroscopy revealed partial conversion, after which a second equivalent of $HNTf_2$ (2.60 mg, $9.28\ \mu mol$, 1.00 eq) was added. The reaction was continued at room temperature overnight before final NMR spectra were measured.

$^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6 , 295 K): δ [ppm] = -9.9 (s, $J_{^{31}P,^{117}Sn} = 808$ Hz, $J_{^{31}P,^{119}Sn} = 846$ Hz).

Crystallization by gas phase diffusion on *n*-pentane into the concentrated solution at $-40^\circ C$ yielded crystals suitable for scXRD.

REACTION OF $[Rh(COD)Cl]_2$ AND PNO_2Sn

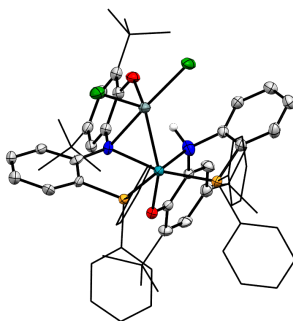


FIG. 5.1.: Solid-state structure of the reaction product of PNO_2Sn and $[Rh(COD)Cl]_2$. Vibrational ellipsoids dispalyed at 50%, hydrogen atoms (with the exception of the N-H) are omitted for clarity.

In a J. Young NMR tube, PNO_2Sn (10.0 mg, 9.28 μmol , 1.00 eq) was dissolved in 0.45 mL of C_6D_6 . Addition of $[\text{Rh}(\text{COD})\text{Cl}]_2$ resulted in the formation of a dark orange solution which was heated at 80 $^\circ\text{C}$ for two days. NMR analysis of the reaction mixture revealed a mixture of products. Slow evaporation of the solvent yielded crystals, suitable for scXRD analysis, as shown in Fig. 5.1.

FORMATION OF $[\text{Cl-Sn}(\text{PNO})_2\text{Au}]$

To a solution of PNO_2Sn (10.0 mg, 9.28 μmol , 1.00 eq) in dcm, $(\text{DMS})\text{AuCl}$ (1.73 mg, 9.28 μmol , 1.00 eq) was added. The resulting yellow solution was subsequently investigated *via* NMR spectroscopy.

$^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, dcm, 295 K): δ [ppm] = 30.2 (s).

MS (LIFDI; toluene) [m/z]: $[\text{M}]^+$ calcd.: 1310.31; found: 1310.38.

Crystallization by gas phase diffusion on *n*-pentane into the concentrated solution at -40 $^\circ\text{C}$ yielded crystals suitable for scXRD.

FORMATION OF $[\text{PNO}_2\text{SnPd}]$

PNO_2Sn (10.0 mg, 9.28 μmol , 1.00 eq) and Pd_2dba_3 (4.25 mg, 4.64 μmol , 0.50 q) were dissolved in CD_2Cl_2 in a J. Young tube. The dark red reaction mixture was shaken overnight, before NMR spectra were taken.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 295 K): δ [ppm] = -0.2 (s, $J_{^{31}\text{P},^{117/119}\text{Sn}} = 130$ Hz).

MS (LIFDI; toluene) [m/z]: $[\text{M}]^+$ calcd.: 1184.28; found: 1184.33.

FORMATION OF $[\text{Cl-Si}(\text{PNO})_2\text{Au}]$

To a solution of $\text{PNO}_2\text{SixHCl}$ (20.0 mg, 19.5 μmol , 1.00 eq) in CD_2Cl_2 , $(\text{PPh}_3)\text{AuNTf}_2$ (14.4 mg, 19.5 μmol , 1.00 eq) was added. The resulting orange solution was subsequently investigated *via* NMR spectroscopy.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 295 K): δ [ppm] = 29.7 (broad, s).

The spectra match the spectra obtained by reaction of $(\text{DMS})\text{AuCl}$ with PNO_2Si . Crystallization by gas phase diffusion on *n*-pentane into the concentrated solution at -40 $^\circ\text{C}$ yielded crystals suitable for scXRD (Fig. 5.2).

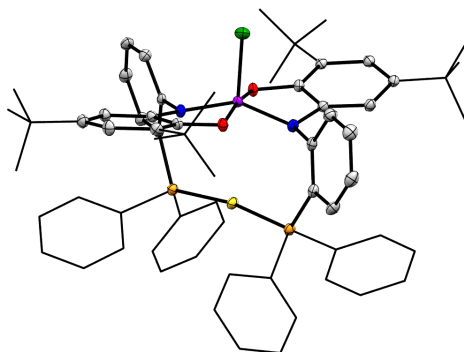


FIG. 5.2.: Solid-state structure of $[\text{Cl-Si}(\text{PNO})_2\text{Au}]$, the product of the reaction of PNO_2Si and $(\text{PPh}_3)\text{AuNTf}_2$. Vibrational ellipsoids displayed at 50%, hydrogen atoms and solvent molecules are omitted for clarity.

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A | APPENDIX

A.1. NMR SPECTRA	399
A.2. IR SPECTRA	410
A.3. CRYSTALLOGRAPHIC DATA	413

A.1. NMR SPECTRA

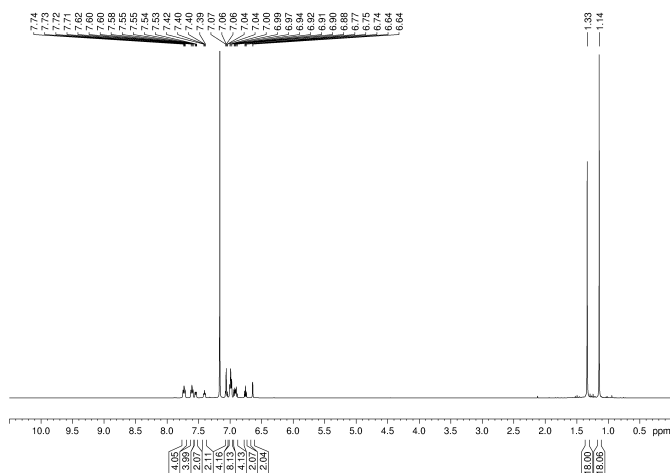


FIG. A.1.: ^1H NMR spectrum (500 MHz) of *trans*-[PNO₂SiMo(CO)₃] in C₆D₆ at 298 K.

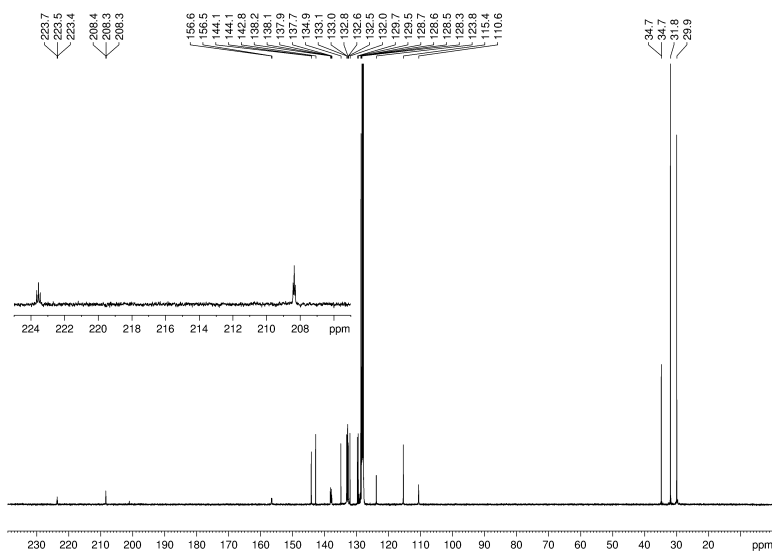


FIG. A.2.: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (126 MHz) of *trans*-[PNO₂SiMo(CO)₃] in C₆D₆ at 298 K.

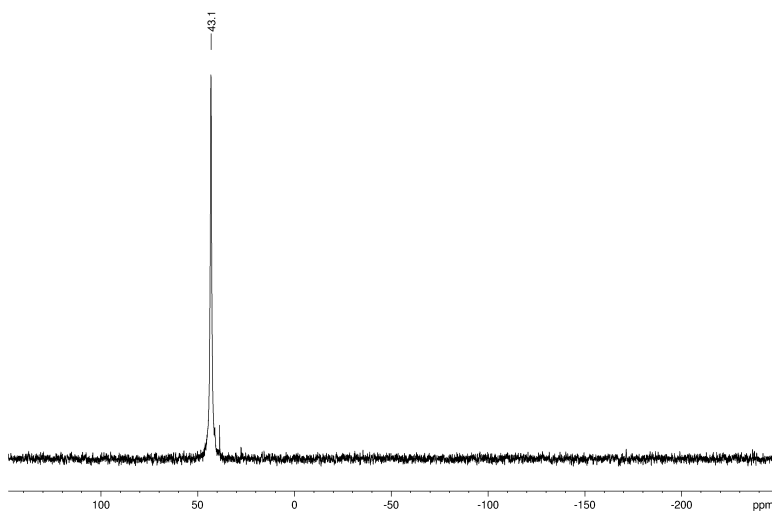


FIG. A.3.: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of *trans*-[PNO₂SiMo(CO)₃] in C₆D₆ at 298 K.

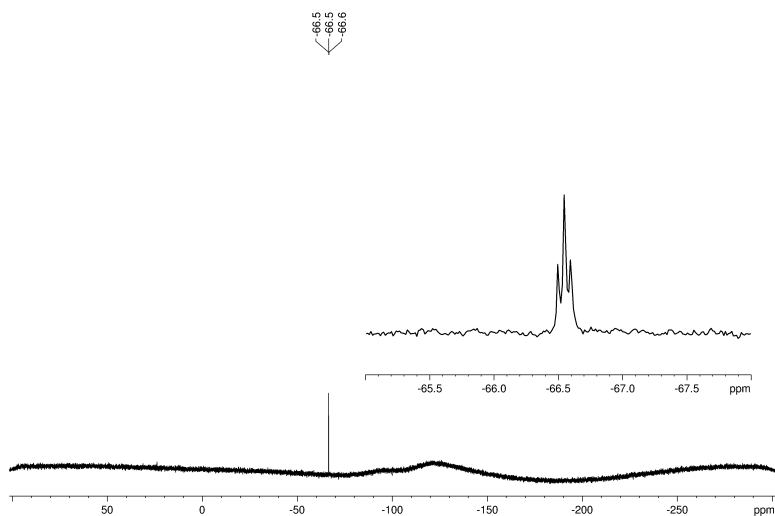


FIG. A.4.: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (79 MHz) of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ in C_6D_6 at 298 K.

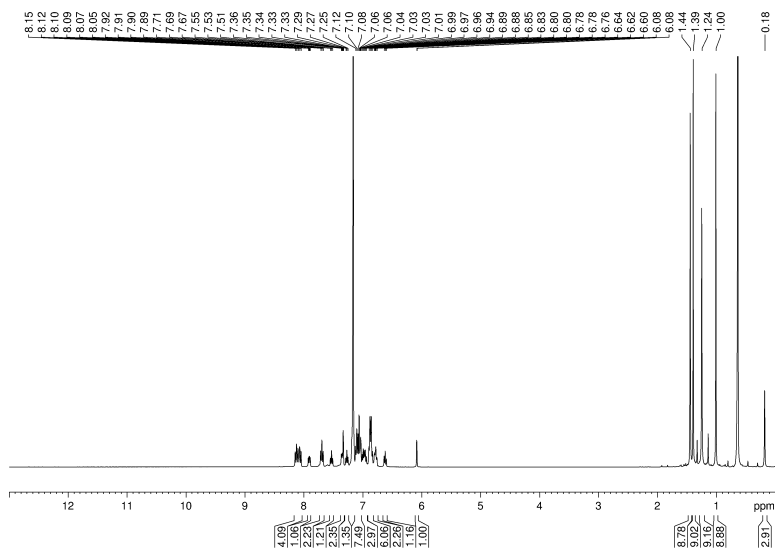


FIG. A.5.: ^1H NMR spectrum (400 MHz) of *cis*- $[\text{PNO}_2\text{SiMo}(\text{CO})_2(\text{MeCN})]$ in C_6D_6 at 298 K.

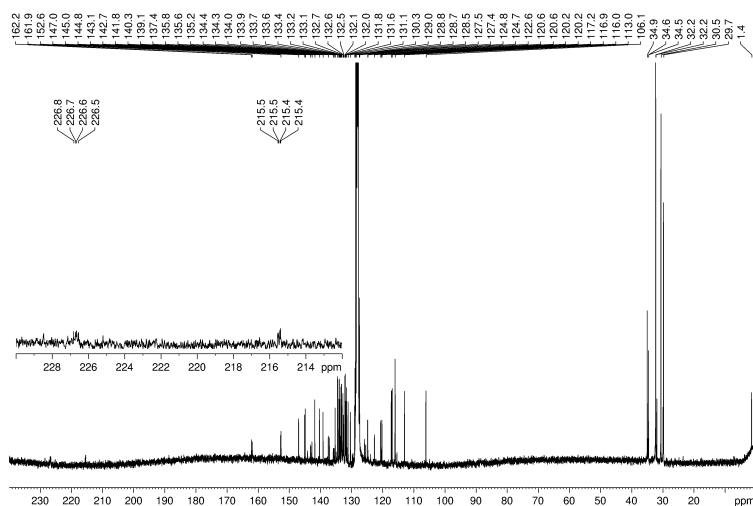


FIG. A.6.: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of *cis*-[PNO₂SiMo(CO)₂(MeCN)] in C₆D₆ at 298 K.

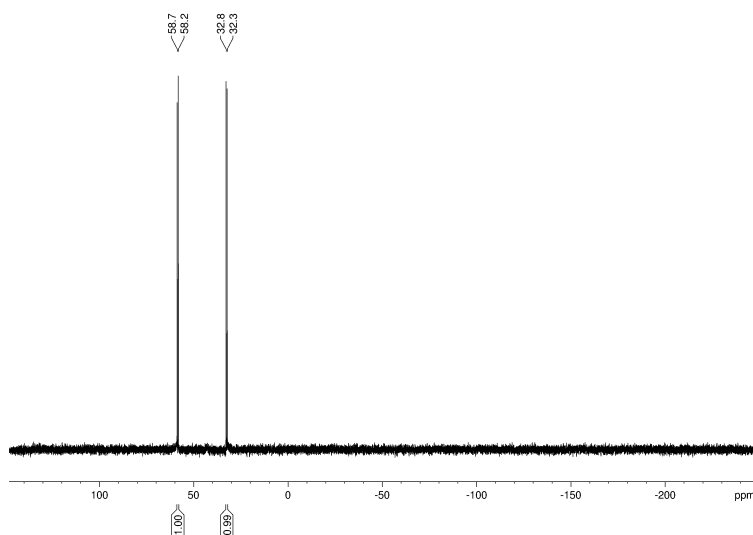


FIG. A.7.: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of *cis*-[PNO₂SiMo(CO)₂(MeCN)] in C₆D₆ at 298 K.

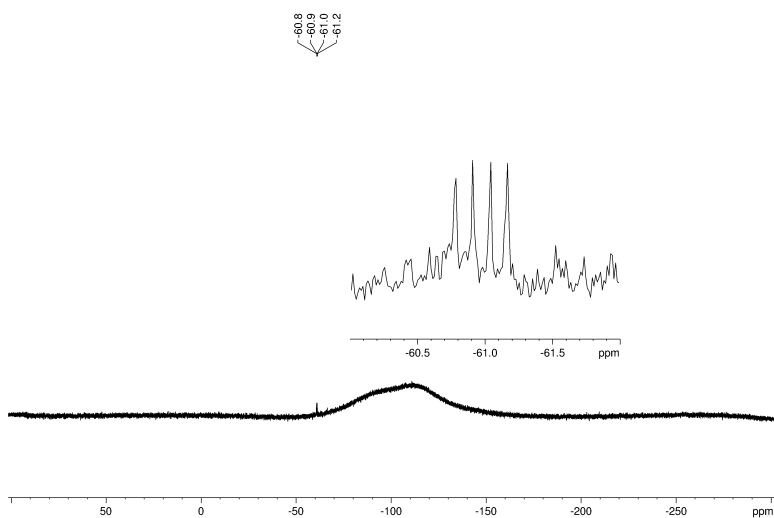


FIG. A.8.: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum (79 MHz) of *cis*-[PNO₂SiMo(CO)₂(MeCN)] in C₆D₆ at 298 K.

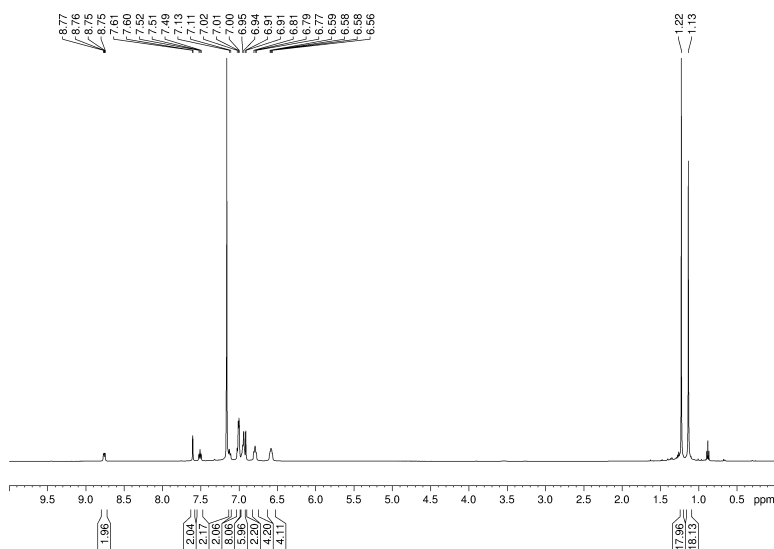


FIG. A.9.: ^1H NMR spectrum (500 MHz) of [(TfO)₂SiPNO₂Mo(CO)₂] in C₆D₆ at 298 K.

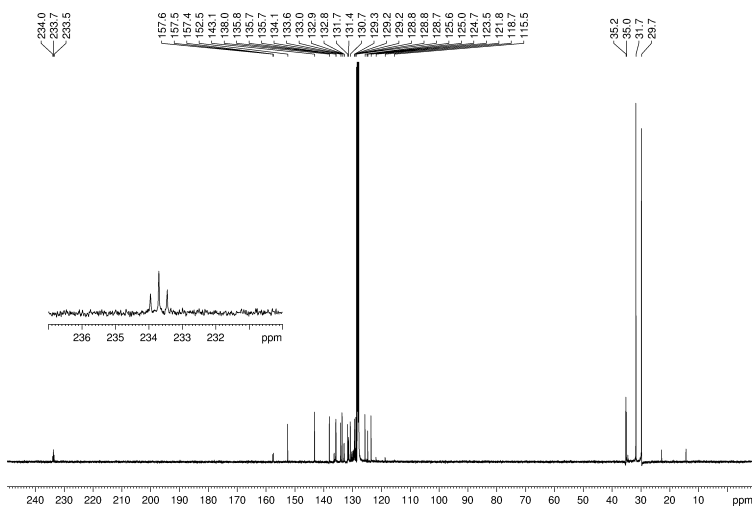


FIG. A.10.: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz) of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ in C_6D_6 at 298 K.

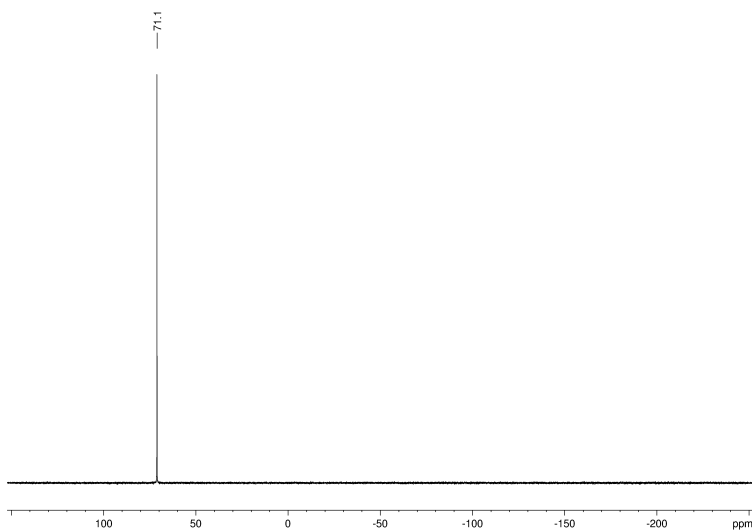


FIG. A.11.: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ in C_6D_6 at 298 K.

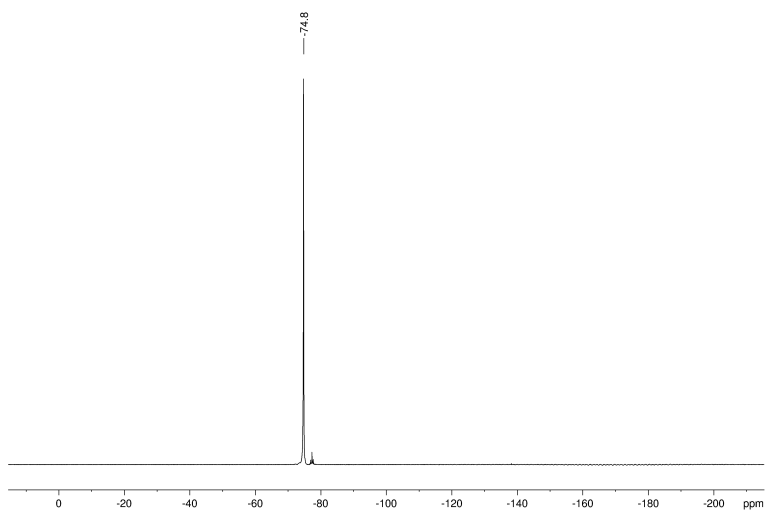


FIG. A.12.: ^{19}F NMR spectrum (471 MHz) of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ in C_6D_6 at 298 K.

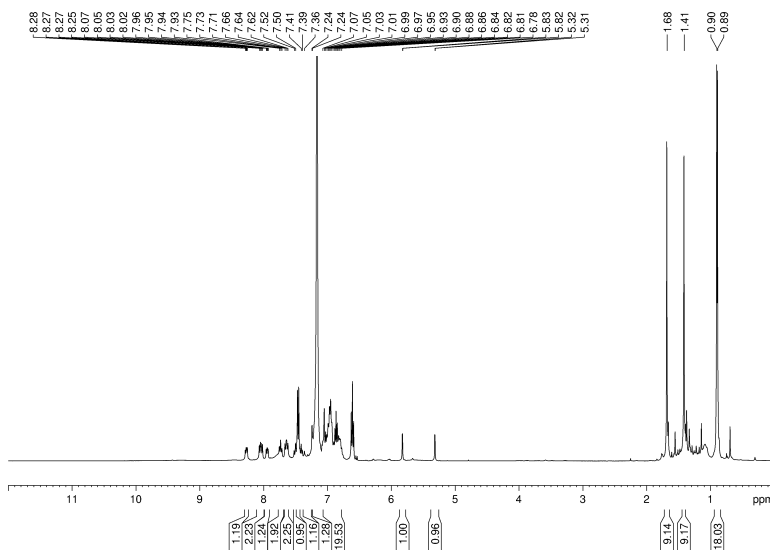
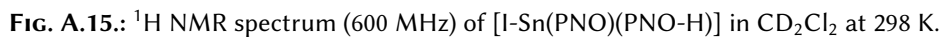
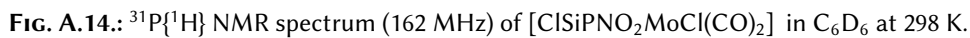


FIG. A.13.: ^1H NMR spectrum (400 MHz) of $[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$ in C_6D_6 at 298 K (contains PhI).



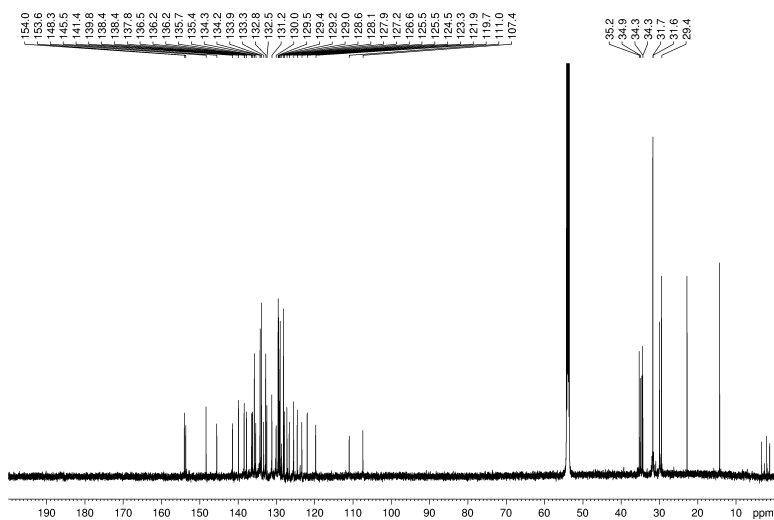


FIG. A.16.: $^{13}\text{C}\{^1\text{H}\}^{31}\text{P}$ NMR spectrum (151 MHz) of $[\text{I-Sn(PNO)(PNO-H)}]$ in CD_2Cl_2 at 298 K.

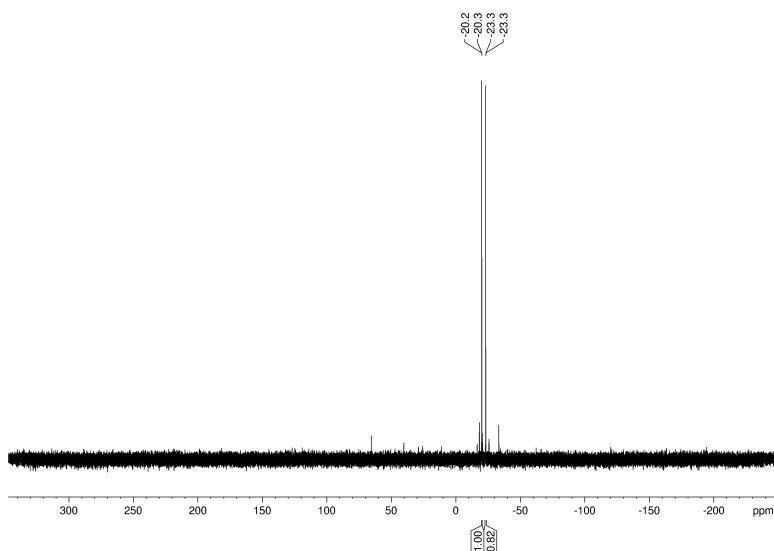


FIG. A.17.: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of $[\text{I-Sn(PNO)(PNO-H)}]$ in CD_2Cl_2 at 295 K.

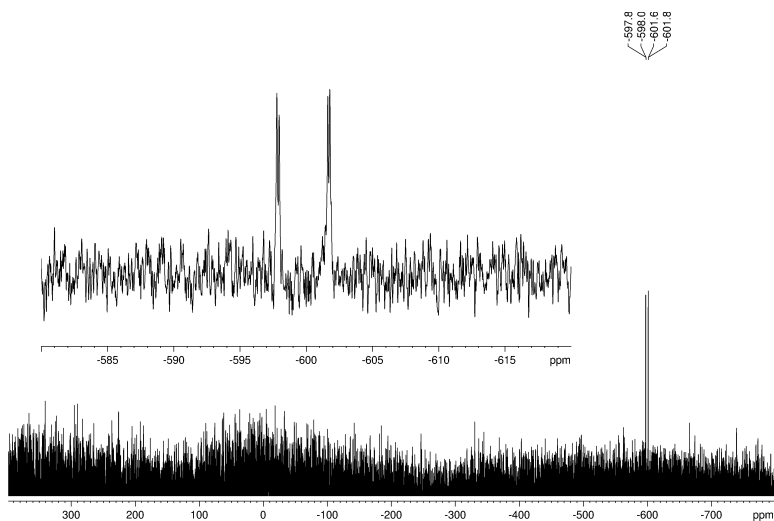


FIG. A.18.: $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum (224 MHz) of $[\text{I-Sn(PNO)(PNO-H)}]$ in CD_2Cl_2 at 295 K.

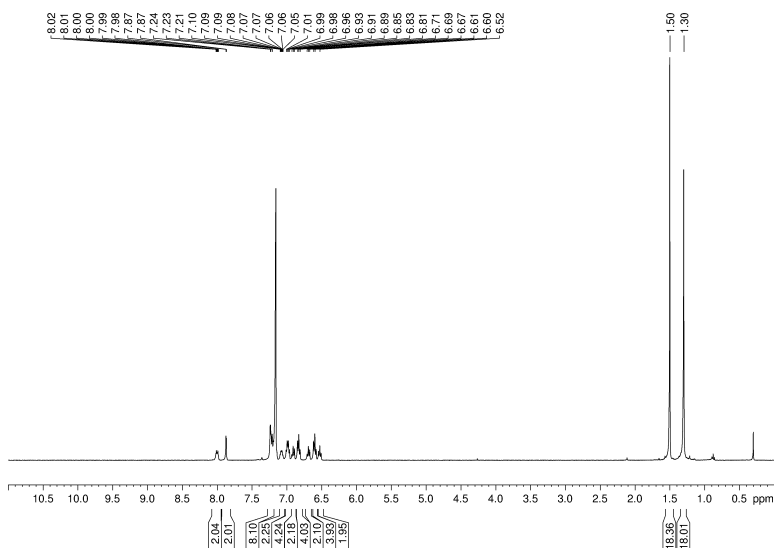


FIG. A.19.: ^1H NMR spectrum (400 MHz) of PNO_2Sn in C_6D_6 at 295 K.

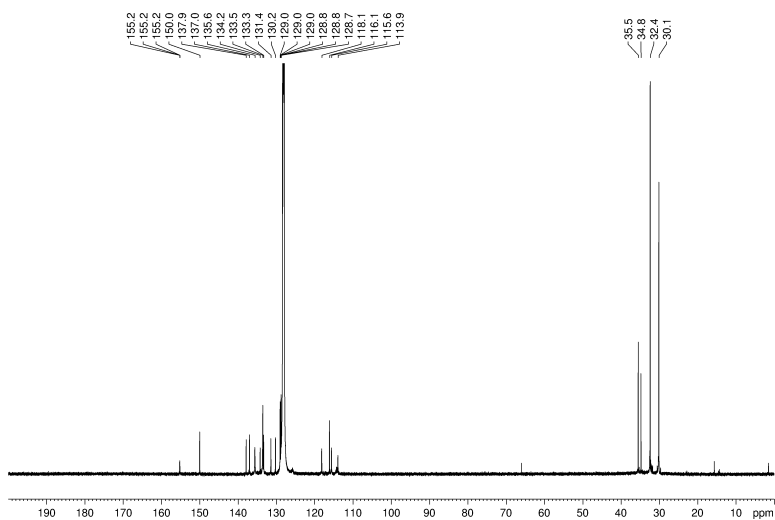


FIG. A.20.: $^{13}\text{C}\{^1\text{H}\}\{^{31}\text{P}\}$ NMR spectrum (151 MHz) of PNO_2Sn in C_6D_6 at 295 K.

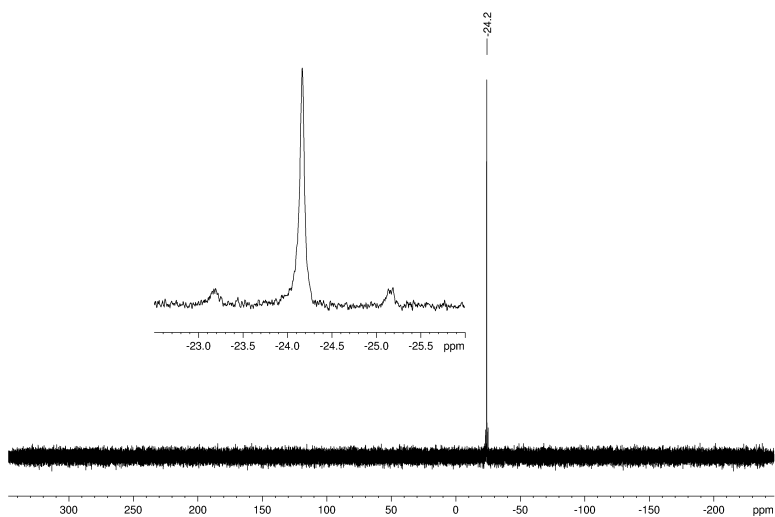


FIG. A.21.: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (162 MHz) of PNO_2Sn in C_6D_6 at 295 K.

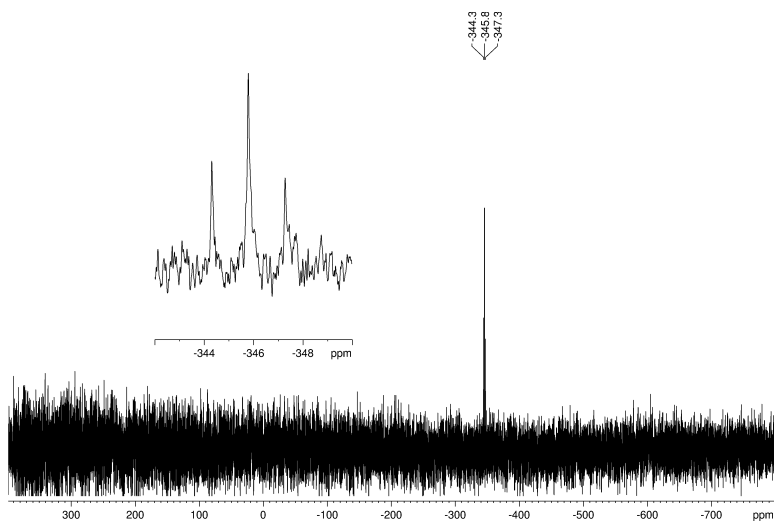


FIG. A.22.: $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum (224 MHz) of PNO_2Sn in C_6D_6 at 295 K.

A.2. IR SPECTRA

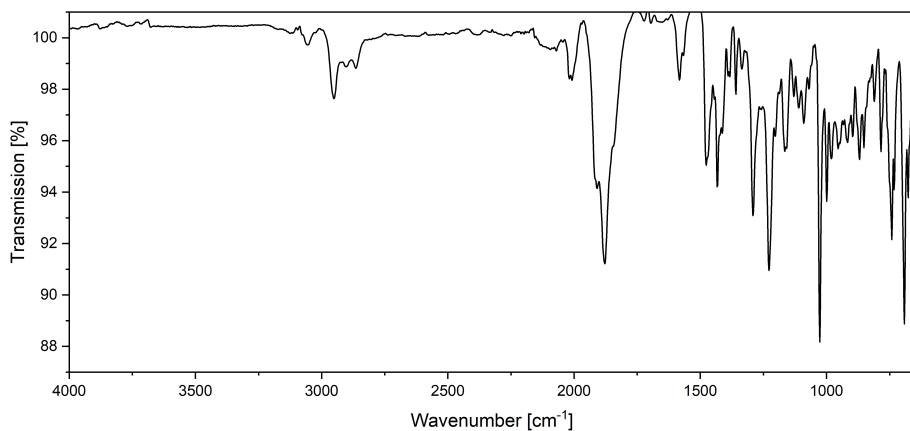


FIG. A.23.: IR (ATR) spectrum of *trans*- $[\text{PNO}_2\text{SiMo}(\text{CO})_3]$ as a thf film under nitrogen atmosphere at 295 K.

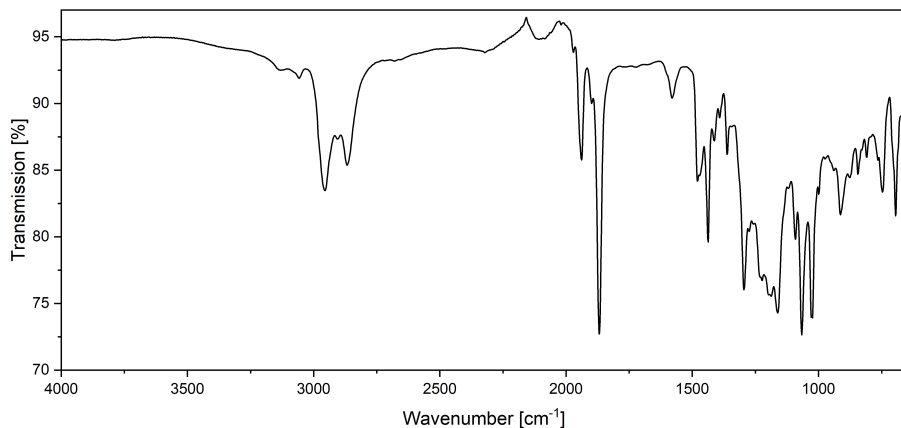


FIG. A.24.: IR (ATR) spectrum of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ as a thf film under nitrogen atmosphere at 295 K.

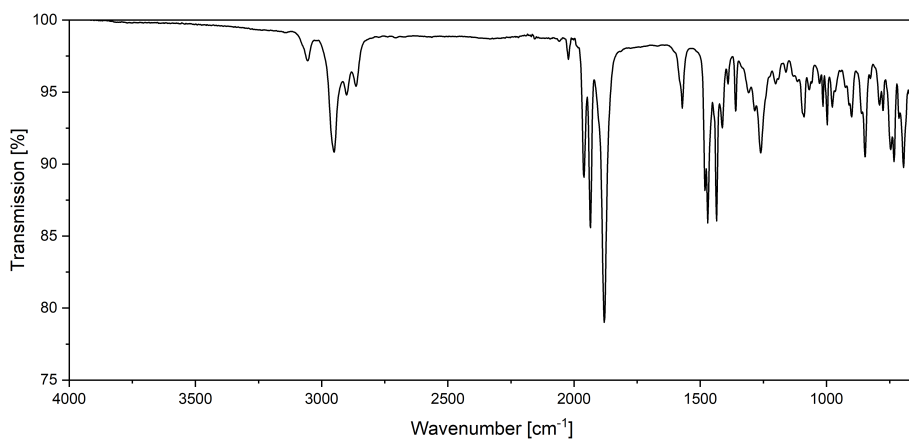


FIG. A.25.: IR (ATR) spectrum of $[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$ as a thf film of the reaction mixture after full conversion to the target molecule under nitrogen atmosphere at 295 K.

A.3. CRYSTALLOGRAPHIC DATA

TAB. A.1.: Collected data for crystal structures of *trans*-[PNO₂SiMo(CO)₃] and [(IC₄H₈O)-Si(PNO)₂MoI(CO)₂].

Compound	<i>trans</i> -[PNO ₂ SiMo(CO) ₃]	[RO-Si(PNO) ₂ MoI(CO) ₂]
Empirical formula	C ₇₀ H ₇₄ Cl ₆ MoN ₂ O ₅ P ₂ Si	C ₁₄₈ H ₁₇₂ I ₄ Mo ₂ N ₄ O ₁₂ P ₄ Si ₂
Formula weight	1421.98	3078.43
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> $\bar{1}$ (2)
a [Å]	23.1465(19)	10.6084(12)
b [Å]	18.8403(13)	15.2163(17)
c [Å]	17.1989(14)	48.105(5)
α [°]	90	97.410(4)
β [°]	100.872(3)	95.498(4)
γ [°]	90	98.555(5)
Volume [Å ³]	7365.6(10)	7562.0(15)
Z	4	2
ρ _{calc} [gcm ⁻³]	1.282	1.352
μ [mm ⁻¹]	0.502	1.096
F(000)	2944	3136
Crystal size [mm ³]	0.305×0.260×0.220	0.170×0.135×0.030
2 θ range [°]	4.19 to 61.02 (0.70 Å)	3.90 to 55.84 (0.76 Å)
Index ranges	-33 ≤ h ≤ 33 -26 ≤ k ≤ 26 -24 ≤ l ≤ 24	-13 ≤ h ≤ 13 -20 ≤ k ≤ 19 -63 ≤ l ≤ 63
Reflections (independent)	425831 (22479) <i>R</i> _{int} = 0.0518 <i>R</i> _{sigma} = 0.0182	368152 (36076) <i>R</i> _{int} = 0.0857 <i>R</i> _{sigma} = 0.0425
Completeness to θ = 25.242 °	99.9 %	100.0 %
Data / Restraints / Parameters	22479/818/ 964	36076/1190/ 1840
Goodness-of-fit on <i>F</i> ²	1.053	1.075
Final <i>R</i> indexes [I ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0277 w <i>R</i> ₂ = 0.0690	<i>R</i> ₁ = 0.0501 w <i>R</i> ₂ = 0.1135
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0326 w <i>R</i> ₂ = 0.0713	<i>R</i> ₁ = 0.0646 w <i>R</i> ₂ = 0.1208
Largest peak/hole [eÅ ⁻³]	0.49/-0.70	1.29/-2.57

TAB. A.2.: Collected data for crystal structures of $[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$ and $[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$.

Compound	$[(\text{TfO})_2\text{SiPNO}_2\text{Mo}(\text{CO})_2]$	$[\text{ClSiPNO}_2\text{MoCl}(\text{CO})_2]$
Empirical formula	$\text{C}_{74}\text{H}_{72}\text{F}_8\text{MoN}_2\text{O}_{10}\text{P}_2\text{S}_2\text{Si}$	$\text{C}_{71}\text{H}_{80}\text{Cl}_2\text{MoN}_2\text{O}_4\text{P}_2\text{Si}$
Formula weight	1551.42	1282.24
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	18.244(4)	12.257(3)
b [Å]	15.907(3)	27.122(6)
c [Å]	28.121(5)	19.643(4)
α [°]	90	90
β [°]	95.163(10)	101.441(9)
γ [°]	90	90
Volume [Å ³]	8127(3)	6400(2)
Z	4	4
ρ_{calc} [gcm ⁻³]	1.268	1.331
μ [mm ⁻¹]	0.338	0.408
F(000)	3200	2688
Crystal size [mm ³]	0.170×0.270×0.510	0.015×0.070×0.080
2 θ range [°]	2.94 to 51.53 (0.82 Å)	2.59 to 60.21 (0.71 Å)
Index ranges	$-22 \leq h \leq 22$ $-19 \leq k \leq 19$ $-34 \leq l \leq 34$	$-17 \leq h \leq 17$ $-38 \leq k \leq 38$ $-27 \leq l \leq 27$
Reflections (independent)	427682 (15560) $R_{\text{int}} = 0.0430$ $R_{\text{sigma}} = 0.0132$	265655 (18819) $R_{\text{int}} = 0.0836$ $R_{\text{sigma}} = 0.0358$
Completeness to $\theta = 25.242^\circ$	99.9 %	100.0 %
Data / Restraints / Parameters	15560 / 1575 / 1169	18819 / 528 / 887
Goodness-of-fit on F^2	1.115	1.244
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0589$ $wR_2 = 0.1247$	$R_1 = 0.0690$ $wR_2 = 0.1401$
Final R indexes [all data]	$R_1 = 0.0698$ $wR_2 = 0.1340$	$R_1 = 0.0801$ $wR_2 = 0.1441$
Largest peak/hole [eÅ ⁻³]	0.64/−0.57	0.81/−1.22

TAB. A.3.: Collected data for the crystal structures of **[Cl-Sn(PNO)(PNO-H)]** and **[PNO₂Sn-C₄N₂H₁₀]**.

Compound	[Cl-Sn(PNO)(PNO-H)]	[PNO₂Sn-C₄N₂H₁₀]
Empirical formula	C _{66.87} H _{73.07} Cl _{2.74} N ₃ O ₂ P ₂ Sn	C _{73.72} H _{92.29} N ₄ O _{3.43} P ₂ Sn
Formula weight	1228.64	1269.91
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> $\bar{1}$ (2)
a [Å]	13.4161(16)	13.480(2)
b [Å]	26.310(7)	14.3424(18)
c [Å]	20.038(5)	19.836(4)
α [°]	90	77.694(8)
β [°]	106.957(11)	74.563(7)
γ [°]	90	75.534(5)
Volume [Å ³]	6766(3)	3535.1(10)
<i>Z</i>	4	2
ρ_{calc} [gcm ⁻³]	1.206	1.193
μ [mm ⁻¹]	0.575	0.454
F(000)	2552	1340
Crystal size [mm ³]	0.265×0.220×0.216	0.39×0.24×0.20
2 θ range [°]	4.25 to 61.02 (0.70 Å)	3.83 to 64.13 (0.67 Å)
Index ranges	-18 ≤ <i>h</i> ≤ 19 -37 ≤ <i>k</i> ≤ 37 -28 ≤ <i>l</i> ≤ 28	-19 ≤ <i>h</i> ≤ 20 -20 ≤ <i>k</i> ≤ 21 0 ≤ <i>l</i> ≤ 29
Reflections (independent)	361872 (20646) <i>R</i> _{int} = 0.0824 <i>R</i> _{sigma} = 0.0290	24343 (24343) <i>R</i> _{int} = 0.0789 <i>R</i> _{sigma} = 0.0309
Completeness to $\theta = 25.242^\circ$	99.9 %	99.8 %
Data / Restraints / Parameters	20646/533/ 843	24343/255/ 855
Goodness-of-fit on <i>F</i> ²	1.076	1.120
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0373 <i>wR</i> ₂ = 0.0901	<i>R</i> ₁ = 0.0428 <i>wR</i> ₂ = 0.1042
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0462 <i>wR</i> ₂ = 0.0966	<i>R</i> ₁ = 0.0474 <i>wR</i> ₂ = 0.1061
Largest peak/hole [eÅ ⁻³]	0.86/-0.82	1.20/-1.13

TAB. A.4.: Collected data for crystal structures of [I-Sn(PNO)(PNO-H)] and [PNO₂Sn].

Compound	[I-Sn(PNO)(PNO-H)]	[PNO ₂ Sn] x 2(C ₆ F ₂ H ₄)
Empirical formula	C ₆₇ H ₇₂ IN ₂ O ₂ P ₂ Sn	C ₇₆ H ₇₆ F ₄ N ₂ O ₂ P ₂ Sn
Formula weight	1244.79	1306.01
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group (number)	<i>P</i> 2 ₁ / <i>n</i> (14)	<i>P</i> 2 ₁ / <i>n</i> (14)
a [Å]	13.624(2)	9.994(4)
b [Å]	27.719(5)	30.221(8)
c [Å]	15.768(2)	21.594(4)
α [°]	90	90
β [°]	94.436(12)	91.137(6)
γ [°]	90	90
Volume [Å ³]	5936.9(16)	6521(3)
Z	4	4
ρ _{calc} [gcm ⁻³]	1.393	1.330
μ [mm ⁻¹]	1.050	0.501
F(000)	2548	2712
Crystal size [mm ³]	0.20×0.08×0.04	0.27×0.25×0.22
2 θ range [°]	3.81 to 57.59 (0.74 Å)	4.01 to 59.15 (0.72 Å)
Index ranges	-18 ≤ h ≤ 18 -37 ≤ k ≤ 37 -21 ≤ l ≤ 21	-13 ≤ h ≤ 13 -41 ≤ k ≤ 41 -29 ≤ l ≤ 29
Reflections (independent)	177976 (15442) <i>R</i> _{int} = 0.0931 <i>R</i> _{sigma} = 0.0413	563891 (18283) <i>R</i> _{int} = 0.1087 <i>R</i> _{sigma} = 0.0277
Completeness to θ = 25.242 °	100.0 %	100.0 %
Data / Restraints / Parameters	15442/618/ 806	18283/518/ 869
Goodness-of-fit on <i>F</i> ²	1.024	1.129
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0373 w <i>R</i> ₂ = 0.0853	<i>R</i> ₁ = 0.0354 w <i>R</i> ₂ = 0.0805
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0493 w <i>R</i> ₂ = 0.0918	<i>R</i> ₁ = 0.0389 w <i>R</i> ₂ = 0.0826
Largest peak/hole [eÅ ⁻³]	1.51/-0.78	0.58/-1.43

TAB. A.5.: Collected data for crystal structures of [(PNO)SnCl₂Rh(PNO-H)] (FIG. 5.1) and [Cl-Sn(PNO)₂Au].

Compound	[(PNO)SnCl ₂ Rh(PNO-H)]	[Cl-Sn(PNO) ₂ Au]
Empirical formula	C ₆₄ H ₆₉ Cl ₂ N ₂ O ₂ P ₂ RhSn	C ₆₄ H ₆₈ AuClN ₂ O ₂ P ₂ Sn
Formula weight	1252.65	1310.25
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group (number)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> $\bar{1}$ (2)
a [Å]	24.986(14)	12.485(2)
b [Å]	12.309(5)	15.721(3)
c [Å]	19.411(11)	16.074(4)
α [°]	90	91.424(11)
β [°]	104.183(17)	93.365(11)
γ [°]	90	105.838(10)
Volume [Å ³]	5788(5)	3027.2(11)
Z	4	2
ρ_{calc} [gcm ⁻³]	1.437	1.437
μ [mm ⁻¹]	0.909	2.972
F(000)	2568	1316
Crystal size [mm ³]	0.15×0.08×0.07	0.51×0.21×0.19
2 θ range [°]	3.71 to 51.36 (0.82 Å)	4.10 to 59.38 (0.72 Å)
Index ranges	-30 ≤ h ≤ 30 -15 ≤ k ≤ 15 -23 ≤ l ≤ 23	-17 ≤ h ≤ 17 -21 ≤ k ≤ 21 -22 ≤ l ≤ 22
Reflections (independent)	217330 (10966) <i>R</i> _{int} = 0.1220 <i>R</i> _{sigma} = 0.0478	173408 (17115) <i>R</i> _{int} = 0.0596 <i>R</i> _{sigma} = 0.0317
Completeness to $\theta = 25.242^\circ$	100.0 %	99.9 %
Data / Restraints / Parameters	10966/180/ 719	17115/24/ 670
Goodness-of-fit on <i>F</i> ²	1.095	1.037
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0556 w <i>R</i> ₂ = 0.1197	<i>R</i> ₁ = 0.0298 w <i>R</i> ₂ = 0.0744
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0761 w <i>R</i> ₂ = 0.1329	<i>R</i> ₁ = 0.0344 w <i>R</i> ₂ = 0.0774
Largest peak/hole [eÅ ⁻³]	1.92/-1.38	1.91/-1.07

Tab. A.6.: Collected data for crystal structures of $[(\text{PNO-H})_2\text{Sn}][\text{NTf}_2]_2$ and $[\text{Cl-Si}(\text{PNO})_2\text{Au}]$.

Compound	$[(\text{PNO-H})_2\text{Sn}][\text{NTf}_2]_2$	$[\text{Cl-Si}(\text{PNO})_2\text{Au}]$
Empirical formula	$\text{C}_{69}\text{H}_{72}\text{Cl}_2\text{F}_{12}\text{N}_4\text{O}_{10}\text{P}_2\text{S}_4\text{Sn}$	$\text{C}_{65}\text{H}_{70}\text{AuCl}_3\text{N}_2\text{O}_2\text{P}_2\text{Si}$
Formula weight	1725.07	1304.57
Temperature [K]	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group (number)	$C2 (5)$	$P\bar{1} (2)$
a [Å]	24.225(3)	12.164(3)
b [Å]	17.495(2)	16.038(4)
c [Å]	19.396(3)	16.174(4)
α [°]	90	89.725(8)
β [°]	100.878(4)	85.496(6)
γ [°]	90	72.423(7)
Volume [Å ³]	8072.7(19)	2998.0(13)
Z	4	2
ρ_{calc} [gcm ⁻³]	1.419	1.445
μ [mm ⁻¹]	0.608	2.706
F(000)	3520	1328
Crystal size [mm ³]	0.03×0.13×0.21	0.323×0.231×0.226
2 θ range [°]	3.78 to 54.20 (0.78 Å)	4.17 to 57.55 (0.74 Å)
Index ranges	-31 ≤ h ≤ 31 -22 ≤ k ≤ 22 -24 ≤ l ≤ 24	-16 ≤ h ≤ 16 -21 ≤ k ≤ 21 -21 ≤ l ≤ 21
Reflections (independent)	185067 (17794) $R_{\text{int}} = 0.1214$ $R_{\text{sigma}} = 0.0580$	131982 (15594) $R_{\text{int}} = 0.0671$ $R_{\text{sigma}} = 0.0359$
Completeness to $\theta = 25.242^\circ$	99.9 %	99.9 %
Data / Restraints / Parameters	17794/1658/ 1125	15594/0/ 697
Goodness-of-fit on F^2	1.021	1.052
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0398$ $wR_2 = 0.0853$	$R_1 = 0.0201$ $wR_2 = 0.0487$
Final R indexes [all data]	$R_1 = 0.0561$ $wR_2 = 0.0923$	$R_1 = 0.0215$ $wR_2 = 0.0493$
Largest peak/hole [eÅ ⁻³]	1.41/-1.01	0.72/-0.97

LIST OF ABBREVIATIONS

Symbols

$\Delta\delta$ chemical shift difference.

oDCB *ortho*-dichlorobenzene.

oDFB *ortho*-difluorobenzene.

sqp square planar.

***i*Pr** *iso*-propyl.

***t*Bu** *tert*-butyl.

A

amp amidophenolate.

Ar aryl.

arb. unit arbitrary unit.

B

BCF tris(pentafluorophenyl)borane.

bcp bond critical point.

bpy 2,2'-bipyridine.

C

cat^X perhalogenated catecholate.

COD cyclooctadiene.

Cp^{*} pentamethyl cyclopentadienyl.

CPCM Conductor-like polarizable continuum model.

cpd composite pulse decoupling.

Cy cyclohexyl.

D

dba dibenzylideneacetone.

dcm dichloromethane.

DFT density functional theory.

DMAP 4-(dimethylamino)pyridine.

DMS dimethylsulfide.

E

EA elemental analysis.

EI electron ionization.

EPR electron paramagnetic resonance.

ESI electron spray ionization.

Et ethyl (group).

ETS-NOCV extended transition state - natural orbitals for chemical valence.

F

FIA fluoride ion affinity.

FLP frustrated Lewis pair.

G

GB GUTMANN-BECKETT.

GEI global electrophilicity index.

GNN graph neural network.

H

HIA hydride ion affinity.

HMDS hexamethyldisilazide.

HOMO highest occupied molecular orbital.

HSAB hard and soft Lewis acids and bases.

I

IR infrared.

IUPAC	International Union of Pure and Applied Chemistry.	R	
L		RCM	ring closing metathesis.
LIFDI	liquid injection field desorption ionization.	RRHO	rigid-rotor-harmonic-oscillator approximation.
LMCT	ligand to metal charge transfer.	S	
LUMO	lowest unoccupied molecular orbital.	scXRD	single crystal X-ray diffraction.
M		SET	single electron transfer.
Me	methyl (group).	SMD	solvation model based on density.
MO	molecular orbital.	T	
MOF	metal organic framework.	tbp	trigonal bipyramidal.
MOS	metrical oxidation state.	TD-DFT	time dependent density functional theory.
MS	mass spectrometry.	thf	tetrahydrofuran.
N		TOF	turn-over frequency.
NBO	natural bond orbital.	TON	turn-over number.
NHC	<i>N</i> -heterocyclic carbene.	U	
NMR	nuclear magnetic resonance.	UV-Vis	ultraviolet-visible.
NPA	natural population analysis.	V	
NTO	natural transition orbital.	VSEPR	valence shell electron pair repulsion.
O		VT	variable temperature.
OEEF	oriented external electric field.	W	
P		WBI	Wiberg bond index.
PEG	polyethylene glycol.	WCA	weakly coordinating anion.
pEO	polyethylene oxide.		
Ph	phenyl (group).		
PNO	2,4-di- <i>tert</i> -butyl-phosphanyl-amidophenolate.		
ppm	parts per million.		
py	pyridine.		
Q			
QTAIM	quantum theory of atoms in molecules.		

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*„Aber, wie das so ist hienieden:
manchmal scheints so, als sei es beschieden,
nur pöapö, das irdische Glück.
Immer fehlt dir irgendein Stück.
(...)
Etwas ist immer. Tröste dich.
Jedes Glück hat einen kleinen Stich.
Wir möchten so viel: Haben. Sein. Und gelten.
Dass einer alles hat – das ist selten.“*
— KURT TUCHOLSKY in “Das Ideal”



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