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Thema

METALLKOMPLEXE
ALS KATALYSATOREN
FÜR SELEKTIVE
OLEFINOLIGOMERISIERUNGEN

Gutachter: Prof. Dr. Manfred Döring
Prof. Dr. Lutz H. Gade

METAL COMPLEXES AS CATALYSTS FOR SELECTIVE OLEFIN OLIGOMERISATIONS

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Non domandarci la formula che mondi possa aprirti,
sì qualche storta sillaba e secca come un ramo.
Codesto solo possiamo dirti,
ciò che non *siamo, ciò che* non *vogliamo.*

[Eugenio Montale – Ossi di Seppia]

Die vorliegende Arbeit wurde am Institut für Technische Chemie (ITC-CPV) des Forschungszentrums Karlsruhe in der Zeit von September 2001 bis September 2004 durchgeführt.

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Darüber hinaus wurden die Liganden **24c**,**d** und **16a**, und die Metallkomplexe **27c**,**d** und **17a** von Dr. Bluhm zur Verfügung gestellt, ebenso wie die Ligandvorläufer **15c** und **23a** von Dr. Michael Ciesielski und der Ligand **24f** von Frau Daniela Pufky.

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Publications:

1. "**New iron-based bis(imino)pyridine and acetyliminopyridine complexes as single-site catalysts for the oligomerization of ethylene**". Bluhm M.E., Folli C., Döring M.; *J. Mol. Catal. A*, 2004, 212, 13-18.

2. "**Substituierte 2-Aminoacrylsäure-imonoester**". Kröger M., Folli C., Döring M.; zum Patent eingereicht.

3. "**Nitrogen and phosphorus-coordinated nickel(II) complexes as single-site catalysts for the oligomerization of ethylene**". Bluhm M.E., Folli C., Walter O., Döring M.; in preparation.

4. "**Nickel(II) complexes as single-site catalysts for the dimerization of *α*-olefins**". Bluhm M.E., Folli C., Kröger M., Pufky D., Walter O., Döring M.; in preparation.

5. "**Cyclohexenoxide/CO_2 copolymerisation with zinc complexes of new 2-amido-acrylic acid-iminoester ligands**". Kröger M., Folli C., Döring M.; in preparation.

Abbreviations

B.p.	boiling point
calcd.	calculated
DMF	dimethylformamide
DMSO	diethylsulphoxide
EAO	ethylaluminoxane
EASC	ethylaluminium sesquichloride
eq	equivalent
Et	ethyl
M	molar
MAO	methylaluminoxane
Me	methyl
Mes	mesityl (2,4,6-trimethylphenyl)
MMAO	modified methylaluminoxane
M.p.	melting point
Ph	phenyl
r.t.	room temperature
R	organic substituent
THF	tetrahydrofuran
TOF	turnover frequency
TON	turnover number

Contents

1'. Kurzfassung

Aufgrund der Wichtigkeit von α-Olefinoligomeren als Zwischenprodukte und Building-Blocks für Polymere in der Chemischen Industrie, werden ständig neue single-site Katalysatoren mit verbesserter Aktivität und Selektivität gesucht. In diesem Zusammenhang wurde die Darstellung neuartiger organischer Liganden und deren Metallkomplexe für die Ethylen- und Propylenoligomerisierung untersucht.

Eine Reihe dreizähniger Iminoliganden, einschließlich der 2,6-Bis(imino)pyridine **1**-**2**, des 2,6-Diacetyl-monoiminopyridins **3**, der Iminophosphine **16** und der Imidazo[1,5-*a*]pyridine **23c** und **24a**, wurde synthetisiert. Veränderungen des Ligandgerüsts und der Substituenten ergaben eine breite Vielfalt verschiedener N,N,N- N,N,O- oder N,N,P-Liganden. Deren Eisen(II)-Komplexe **5**-**7** und **17** waren in Gegenwart des Cokatalysators MAO als Katalysatoren der Ethylenoligomerisierung aktiv und führten zu linearen Olefinen.

Außerdem wurden verschiedene Klassen zweizähniger Liganden mit variablen sterischen und elektronischen Eigenschaften für entsprechenden Nickelkomplexe hergestellt, wie z. B. die Imidazo[1,5-*a*]pyridine **23a**-**b** und **24b**-**f**, die 3-Aminoacrylate **28**, **29**, und **31**, die 3-Aminoiminoacrylate **35** und **37**. Besonders die unterschiedlich substituierten 3-Aminoiminoacrylate erforderten die Entwicklung und Optimierung neuer Synthesewege. **23a**, **24b**-**d**, **40** und **42** wurden als zweizähnige neutrale N,N-Liganden für die Darstellung der entsprechenden Nickel(II)-Dibromidkomplexe genutzt. Die potentiell aciden Liganden wurden durch Natrium-bis(trimethylsilyl)amid deprotoniert und anschließend mit $[(PPh_3)_2Ni(Mes)Br]$ umgesetzt. Zwei verschiedene Typen neutraler Nickel(II)-Komplexe wurden gewonnen: Einmal (**45** und **46**) koordiniert der Ligand einzähnig über die CN-Gruppe und zum anderen (**47**-**50** und **53**) als zweizähniger Chelatligand am Nickelzentrum.

Die Nickelkomplexe, die für die Ethylenoligomerisierung getestet wurden, zeigten die besten Ergebnisse in Anwesenheit von MAO als Cokatalysator. Aufgrund von Kettenwanderung am Nickelzentrum wurden nicht nur lineare Olefine, sondern auch verzweigte Isomere produziert. Die Propylendimerisierungstests ergaben mit EASC als Cokatalysator die besten Ergebnisse. Die Hauptprodukte waren im allgemeinen Dimere, wobei der C_6-Anteil ungefähr 90% betrug. Innerhalb den Dimeren waren primär Methylpentene, danach lineare Hexene und schließlich eine geringe Menge an Dimethylbutenen enthalten.

1. Abstract

Due to the importance of α-olefin oligomers as intermediates and polymer building blocks for the chemical industry, new single-site catalysts systems that are more active and more selective are constantly being sought. Inserted in this context, we investigated the syntheses of novel organic ligands and the respective metal complexes, to be applied for ethylene and propylene oligomerisation.

A group of tridentate imino-ligands was synthesised, which includes the 2,6-bis(imino)pyridines **1**-**2**, the 2,6-diacetyl-monoiminopyridine **3**, the iminophosphines **16**, and the imidazo[1,5-*a*]pyridines **23c** and **24a**, and others, obtaining a range of different N,N,N- or N,N,O- or N,N,P-ligands through variation of the coordinating backbone and of the substituents. The corresponding iron(II) complexes were then prepared and tested for the ethylene oligomerisation in the presence of MAO as co-catalyst. The 2,6-bis(imino)pyridyl-, the 2,6-diacetyl-monoiminopyridyl-, and the iminophosphine iron(II) complexes **5**-**7**, **17** were active catalysts and gave only linear olefins.

Furthermore, different classes of bidentate ligands for nickel(II) complexes were synthesised, which are easily tuneable in their steric and electronic properties; for instance the imidazo[1,5-*a*]pyridines **23a**-**b** and **24b**-**f**, the 3-aminoacrylates **28**, **29**, and **31**, the 3-aminoiminoacrylates **35** and **37**. In particular, the syntheses of the differently substituted 3-aminoiminoacrylates required to be developed and optimised according to the different substituents at the acrylic backbone and at the aryl rings. The bidentate N,N-ligands **23a**, **24b**-**d**, **40**, and **42** were used in their neutral form to yield the corresponding nickel(II) dibromide complexes. The rest of the ligands was deprotonated with sodium bis(trimethylsilyl)amide to yield their monoanionic form that next reacted with $[(PPh_3)_2Ni(Mes)Br]$. Two different classes of neutral nickel(II) complexes were obtained: in one class (**45** and **46**) the ligands actually coordinate as monodentate through their CN-group, while in the latter class of complexes (**47**-**50** and **53**) the ligands coordinate as bidentate chelate to the nickel centre. The nickel complexes tested for ethylene oligomerisation gave the best results in the presence of MAO as co-catalyst. Due to the chain-running at the nickel centre, not only linear olefins were formed, but also branched isomers. The propylene dimerisation tests gave the best results with EASC as co-catalyst, and the main products generally consisted of dimers, the fraction C_6 always being about 90%. Among the dimers, methylpentenes were the main products in most cases, followed by linear hexenes and small amounts of dimethylbutenes.

2. Introduction and objective

In catalysis with transition metal complexes, insertion-type C-C linkage of olefins resulting in the formation of oligomers or polymers represents one of the most important reactions. As a recent development, polymerisation of olefins to high-molecular-weight polymers and/or to narrow-weight distributed oligomers by late transition metal complexes is gaining considerable attention. These reactions are often performed with nickel or palladium single-site catalysts, but other metals have also been applied, and recently highly active ethylene polymerisation or oligomerisation catalysts based on iron or cobalt complexes have been reported[1,2].

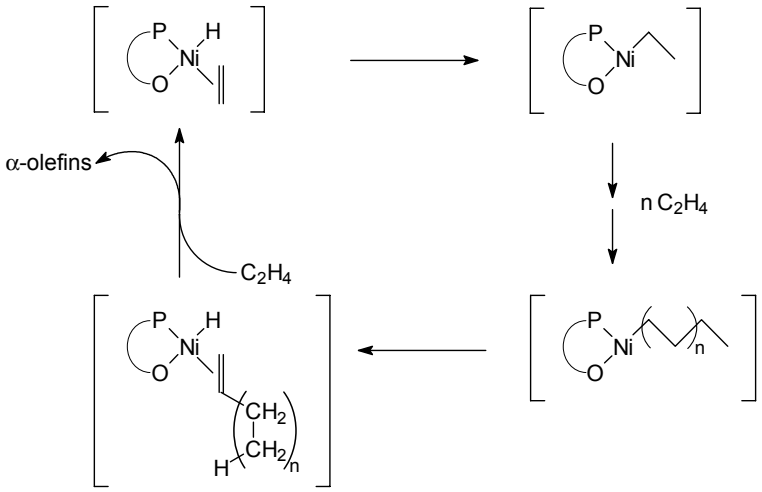
Most often, the catalysts employed contain ligands with Group V or VI donors which co-ordinate not only in the catalyst precursor, but also in the active species, in contrast to ligands that are merely intended to stabilise the catalyst precursors. The former ligands control catalyst selectivity and activity via steric and electronic interactions[3,4].

Compared to early metal systems, later transition metal complexes attract attention as olefin polymerisation catalysts due to their lower electrophilicity and, hence, higher heteroatom tolerance. This significantly decreases the susceptibility of late-metal catalysts to poisoning by polar monomers or polar impurities in the monomer feed[5]. The late transition metals can be stabilised by various heterodonor ligands and give mono- or binuclear complexes with several coordination modes.

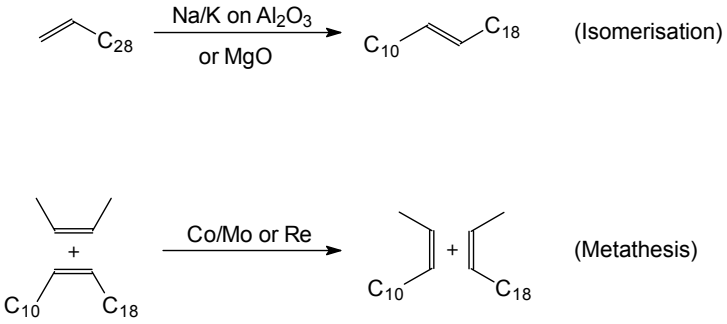
Alpha-olefins are very versatile intermediates and building blocks for chemical industry and widely used primarily as co-monomers for the production of linear low-density polyethylene (C_4-C_8) and manufacture of surfactants (C_{12}-C_{20}), plasticisers (C_6-C_{10}), and synthetic lubricants of various applications (automotive, aviation, refrigerating, transformer, cable, cosmetic and other oils). They are also used as a stock for the production of additives, cutting fluids and a variety of fine chemicals.

Today the predominant route to α-olefins is oligomerisation of ethylene, which is readily available by steam-cracking of light naphtha, gas-oil, or wet natural gases. In addition, the high product quality as compared to that of classical routes via wax cracking makes oligomerisation the preferred process. Worldwide production of linear α-olefins through ethylene oligomerisation presently is about two million tons per year.

One of the currently most common oligomerisation methods is the Shell Higher Olefin Process (SHOP). Catalysts used in industry for SHOP include neutral Ni(II) complexes that bear phosphorus/oxygen-chelating bidentate mono-anionic ligands[6,7]. The linear α-olefins produced are obtained in a Schulz-Flory type of distribution[8] with up to 99% linearity and 96-98% terminal olefins over the whole range from C_4 to C_{30+}. Since such catalysts exhibit a very low selectivity for the length of the oligomers formed, the SHOP process requires the combination of three reactions to meet the market needs for linear α-olefins for detergents (C_{12}-C_{20}): therefore, the process includes oligomerisation, isomerisation, and metathesis. (Schemes 2.1. and 2.2.)



Scheme 2.1. Proposed mechanism for the formation of linear α-olefins in the SHOP process.



Scheme 2.2. Examples of isomerisation and metathesis reactions in the SHOP process.

The mechanism proposed for the formation of linear α-olefins is shown in Scheme 2.1.: ethylene insertion into the nickel-hydride bond generates an ethyl complex; additional ethylene insertions yield nickel alkyls of various lengths, and subsequent β-hydride elimination produces an α-olefin hydride complex. Chain transfer in these systems likely

occurs by associative olefin exchange between free ethylene and nickel-ligated α-olefin, thus regenerating the nickel-hydride ethylene complex. Due to the selectivity of these systems for ethylene insertion, the formation of branched species by reinsertion of the α-olefin product is minimal.

After that, the oligomers mixture has to be separated by distillation into the desired product fractions. The lower C_4-C_{10} α-olefins and the C_{20+} fractions are combined to be isomerised to internal linear olefins (Scheme 2.2.) and then subjected to a metathesis reaction which yields a mixture of olefins with odd and even carbon chain lengths, where about 11-15% of the desired C_{11}-C_{14} linear internal olefins are contained. The undesired fractions can be recycled subsequently.

Additionally, it has been recently reported that cationic Ni(II) and Pd (II) α-diimine complexes are even effective ethylene oligomerisation and polymerisation catalysts[3] (Figure 2.1.).

In the early 1990ies Brookhart and co-workers introduced the first late transition metal complexes which were both highly stable and highly active for olefin polymerisation.

Ni(II) or Pd(II) complexes form cations by combination with MAO and polymerise ethylene to highly branched polymers with molecular weights of up to one million. Branching takes place by “chain-running”: the nickel or palladium runs along the carbon atoms of the polymer chain before a new insertion happens.

Electrophilicity of the late metal centre in these cationic complexes results in rapid rates of olefin insertion, while the use of non-coordinating counterions provides for an accessible coordination site for the incoming olefins. The use of bulky aryl-substituted α-diimine ligands favours insertion over chain transfer, because β-hydride elimination is prevented. The easily varied steric properties of such ligands are an important feature of the above-described catalyst systems.

Both the molecular weight and degree of branching in the resulting polyethylenes can be controlled by choice of α-diimine substituents.

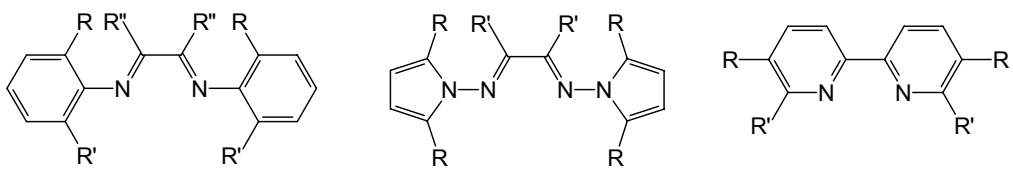
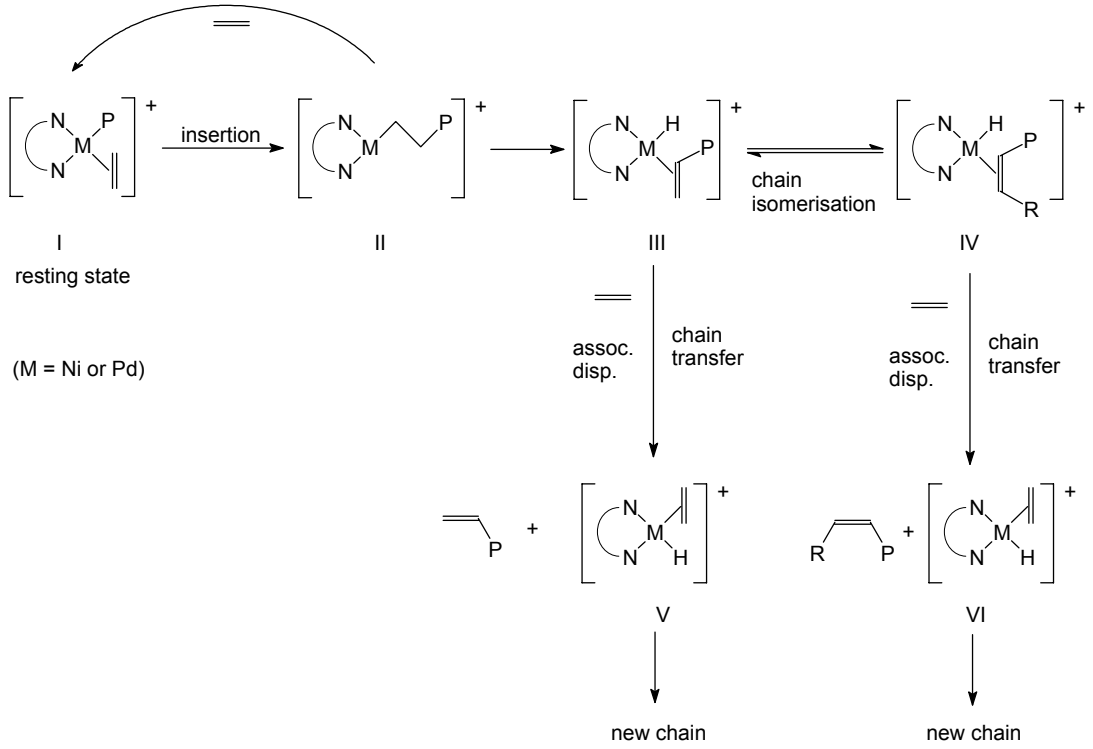
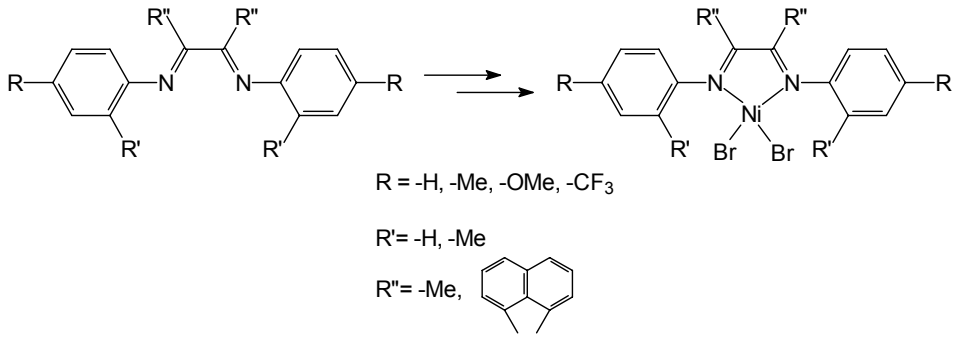


Figure 2.1. Examples of α-diimine ligands used for ethylene polymerisation/oligomerisation.



Scheme 2.3. Mechanism for olefin polymerisation/oligomerisation.



Scheme 2.4. Structure of the α-diimine ligands and their coordination mode in transition metal complexes.

Production of a high-molecular-weight polymer by the complexes mentioned results from slow chain transfer relative to chain propagation. In these d^8 square planar systems, chain transfer is proposed to occur by associative olefin displacement and is inhibited by the axial bulk provided by the *ortho*-substituents of the aryl rings. By eliminating the steric bulk of the *ortho*-substituents, rates of associative chain transfer are substantially increased, resulting in oligomerisation rather than polymerisation reactions: the α-diimine nickel complexes thus obtained represent a new class of highly active Ni(II) catalysts for the preparation of α-olefins ranging from C_4-C_{26}, with a high selectivity for linear *α*-olefins (94%).[3] Therefore, the control of the associative olefin exchange by varying the axial steric

and electronic characteristics represents a general methodology for the design of late metal catalysts for olefin oligomerisation or polymerisation.

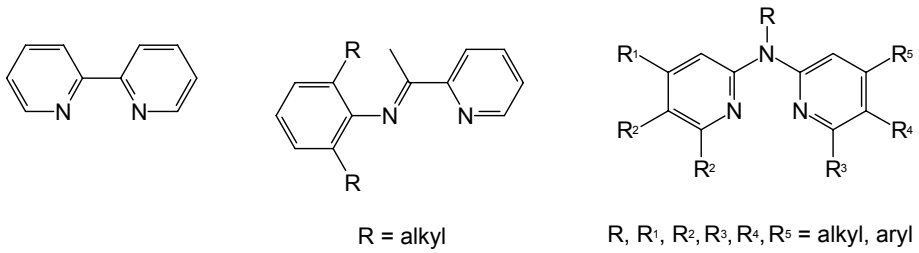
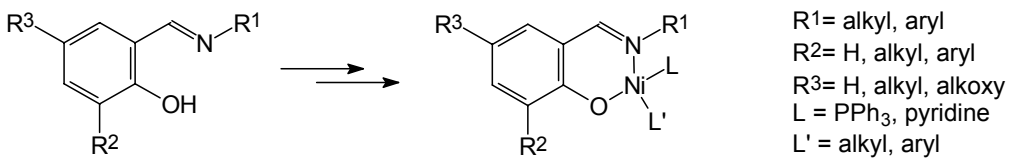


Figure 2.2. Structure of some nitrogen-based bidentate ligands.

Later, some other neutral and cationic nickel(II) and palladium(II) complexes were introduced, which behave as efficient catalysts for the oligomerisation of ethylene and contain bipyridylamines or unsymmetrical bidentate ligands that possess both the pyridyl and the imine functions[9] (Figure 2.2.).

The group 8 transition metal complexes based on salicylaldiminato ligands published by Grubbs in 1998 represent another class of interesting novel catalysts[10] (Scheme 2.5.). These single-site catalysts with non-symmetric chelating structures show high activities (that rival those of metallocenes) and have the advantageous properties of diversity and tunability by changing the substituents, which will sterically and electronically affect oligomerisation and polymerisation reactions (R^1 to R^3, Scheme 2.5.), including functional groups containing heteroatoms. Each substituent, R^1 to R^3, has specific, independent, and additive effects on the reactions.
In contrast to the α-diimine nickel complexes, these catalysts produce low-branched polyethylenes with a narrow molecular weight distribution.



Scheme 2.5. Structure of the salicylaldiminato ligands, and their metal complexes.

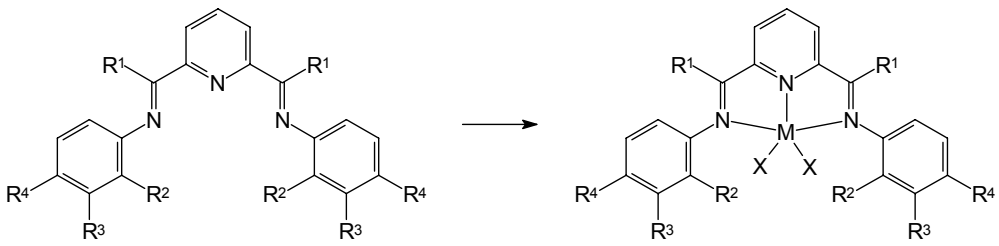
In 1998 Brookhart's and Gibson's groups independently and simultaneously unveiled an extremely active ethylene polymerisation system based on five-coordinate iron(II) and cobalt(II) complexes bearing bis(imino)pyridyl ligands[11,12] in the presence of aluminoxane

activators (Scheme 2.6.). This discovery was made all the more impressive by the fact that there had not been any literature precedents for any non-ferrocene iron complex acting as a catalyst precursor for ethylene polymerisation. In many cases, the activities of the bis(imino)pyridyl precursors are comparable or even higher than those obtained with group 4 metallocenes under analog conditions and, in general, iron(II) catalysts are more active by at least one order of magnitude than cobalt(II) analogues.

In contrast to the nickel and palladium systems, there is no chain-running and the polyethylene is strictly linear.

As observed for the α-diimine complexes, the aryl groups on the imine nitrogen atoms are roughly perpendicular to the ligand coordination plane. The protective bulk of the *ortho*-substituents above and below the metal centre again is critical to the molecular weight of the resulting ethylene polymer. The polyethylenes obtained are highly crystalline with a broad molecular weight distribution.

By reducing the steric bulk of these bis(imino)pyridines the resultant iron catalysts oligomerise ethylene to linear α-olefins with remarkably high activity and selectivity, while maintaining desirable oligomer distributions[12,13].



Scheme 2.6. Bis(imino)pyridine ligands and their metal complexes used for the oligomerisation of ethylene.

There is increasing interest in the development of catalysts for the linear dimerisation and trimerisation of propylene and ethylene, in particular to 1-hexene due to the importance of this co-monomer in the production of LLDPE polyethylene.

The trimerisation route largely avoids the production of unwanted olefins that conventional transition metal oligomerisation processes produce. Of the systems known to trimerise ethylene, most are based on homogeneous chromium catalysts. Wasserscheid's tridentate PNP and SNS ligands[14] are of particular interest: their corresponding chromium(III) complexes catalyse ethylene trimerisation with high activity and selectivity to 1-hexene when activated with methylaluminoxane (Figure 2.3.). The phosphine and thioether groups

operate as soft donor ligands that easily produce facile association-dissociation equilibriums.

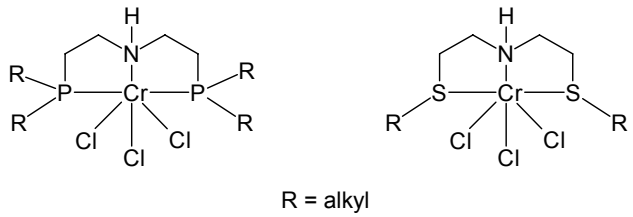


Figure 2.3. Wasserscheid's chromium catalyst precursors for ethylene trimerisation.

Due to the importance of ethylene polymers and oligomers, new single-site catalyst systems that are economical and/or more selective are constantly being sought.

Within the framework of the state of the art described above, my research work mostly proceeded in the following directions. Single-site catalysts precursors of the Brookhart's type were synthesised to be tested for ethylene oligomerisation/polymerisation. Emphasis was put on the effect of electron-donating and electron-withdrawing groups attached to the iminophenyl substituents[15]. Furthermore, other new ligands were prepared to attain modifications of the ligand backbone and their influence on the catalyses, in comparison to the known ligands, was verified.

Novel classes of versatile bidentate and tridentate ligands and their corresponding late transition metal complexes were developed to be tested for the oligomerisation of ethylene in the attempt of finding new and better catalysts for the olefin oligomerisation processes, to realise the selective formation of n-butene and n-hexene.

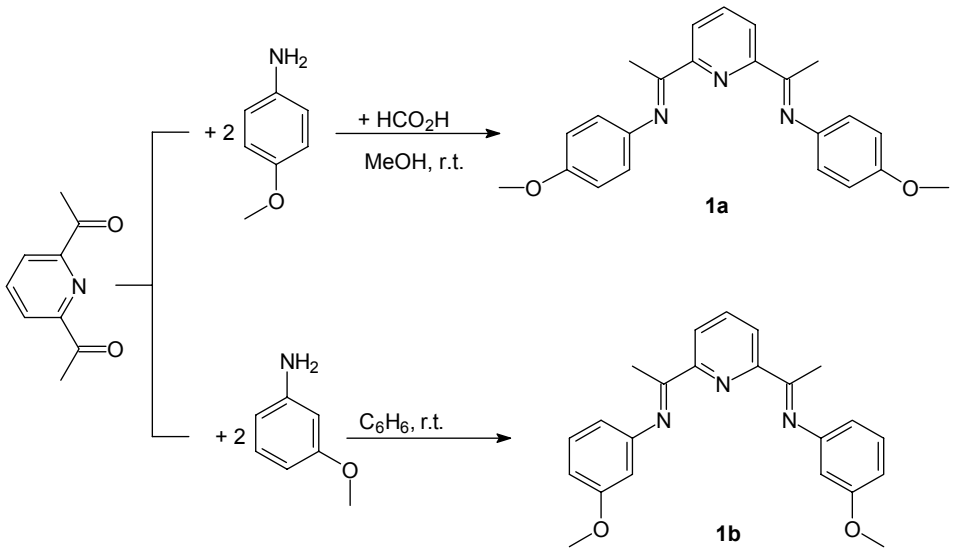
3. Description of the results

3.1. 2,6-Bis(imino)pyridyl and 2,6-diacetyl-monoiminopyridyl ligands and their iron complexes

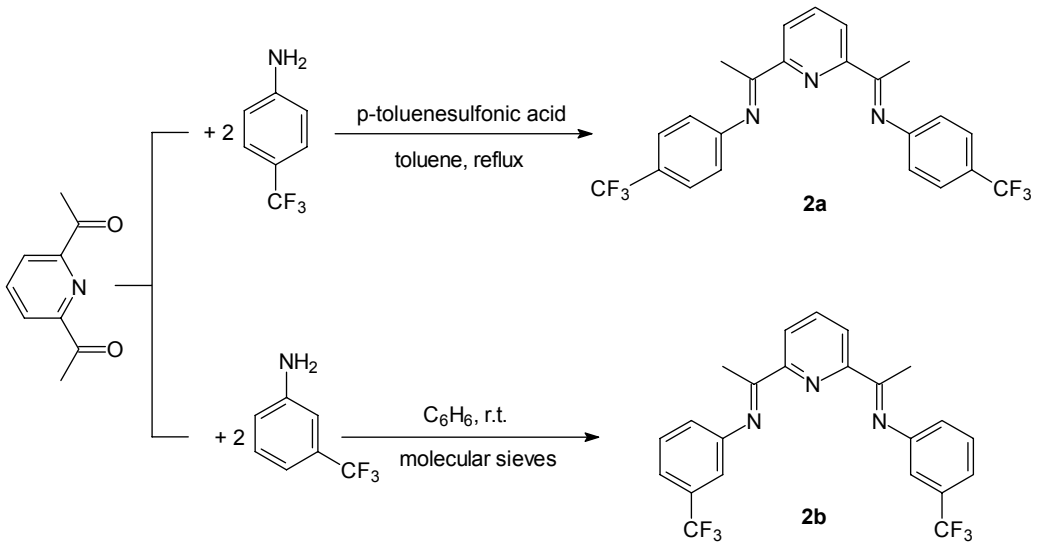
As described in the introduction, recently developed bis(imino)pyridyl iron complexes proved to be very highly active and selective catalyst precursors for olefin oligomerisation in combination with the co-catalysts MAO or MMAO. Nevertheless, both Brookhart and Gibson mostly investigated the effect of alkyl substituents in the *ortho*-position of the aryl ring, while few studies only were published on the influence of electron-withdrawing or electron-donating groups on the catalytic properties of the respective iron complexes. Several modifications of the bis(imino)pyridyl backbone have already been described in literature[13b], which mostly lead to a decrease of catalytic activity. Recently, fluoro-substituted bis(imino)pyridines and their iron complexes were synthesised and tested in ethylene oligomerisation[16]: in the presence of MMAO, they mainly produced short oligomers (C_4-C_8) with a high selectivity for linear α-olefins.

We developed bis(imino)pyridyl **1**, **2** and diacetyl-monoiminopyridyl **3** ligands with substituents that especially influenced the electronic properties of the ferrous precursor complexes **5-7** and we investigated their influence on the catalytic performance[17].

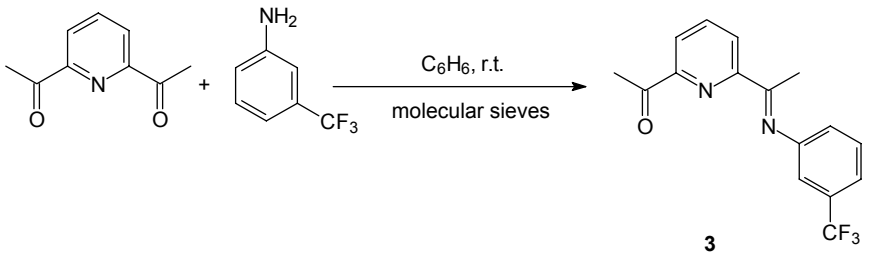
Schiff base condensation of 2,6-diacetylpyridine with *p*-methoxyaniline produced the title compound **1a**, through a modified version of procedures reported in literature[18] (Scheme 3.1.1.).



Scheme 3.1.1. Syntheses of methoxy-substituted 2,6-bis(imino)pyridyl ligands.



Scheme 3.1.2. Syntheses of trifluoromethyl-substituted 2,6-bis(imino)pyridyl ligands.



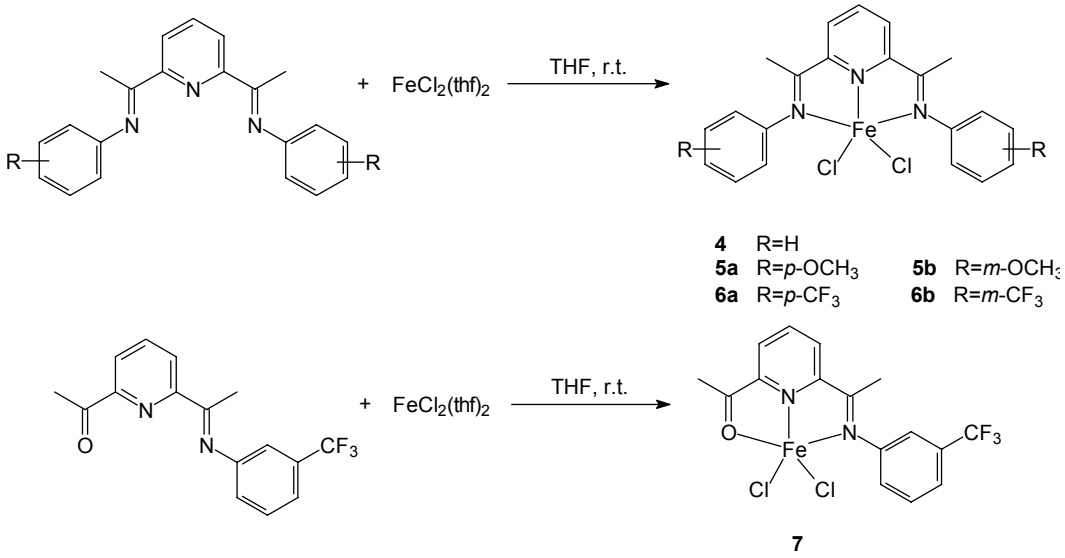
Scheme 3.1.3. Synthesis of an 2,6-diacetyl-monoiminopyridyl ligand.

The novel *m*-trifluoromethyl- and *m*-methoxy substituted 2,6-bis(imino)pyridines **2** as well as the new 2,6-diacetyl-monoiminopyridine **3** were obtained from 2,6-diacetylpyridine and the appropriate amount of anilines by a reaction adapted from Iovel et al.[19] who described the condensation of pyridine aldehydes with trifluoromethylanilines in benzene at room temperature in the presence of molecular sieves (Schemes 3.1.2. and 3.1.3.).

A different synthesis was required for the *p*-trifluoromethyl substituted bis(iminopyridine) **2a** which was obtained by refluxing the reactants in toluene in the presence of *p*-toluensulfonic acid[20]. The yields were not optimised and were fairly low for **2a** (8%) and higher (up to 90%) for **1a**.

Preparation of ligands with mixed methoxy- and trifluoromethyl substituents failed because of the decomposition of the reactants and the formation of by-products.

The tridentate ligands **1-3** were finally reacted under argon with $FeCl_2(thf)_2$[21] to the five-coordinate iron(II) complexes **5-7** (Scheme 3.1.4.). The iron complex **4,** whose bis(imino)pyridyl ligand was synthesised according to literature[22], was prepared for comparison in the catalytic ethylene oligomerisation tests (Chapter 3.8.).



Scheme 3.1.4. Synthesis of the iron(II) complexes.

3.2. Tridentate bis-benzylideneimines and their iron complexes

After Brookhart's and Gibson's discovery of the first non-ferrocene iron complexes active in the oligomerisation/polymerisation of olefins, several classes of ethylene polymerisation catalysts based on tridentate ligand complexes of iron have been developed in addition to the bis(imino)pyridine complexes. These include monoanionic as well as neutral ligands, like furan and pyrrole derivatives[23].

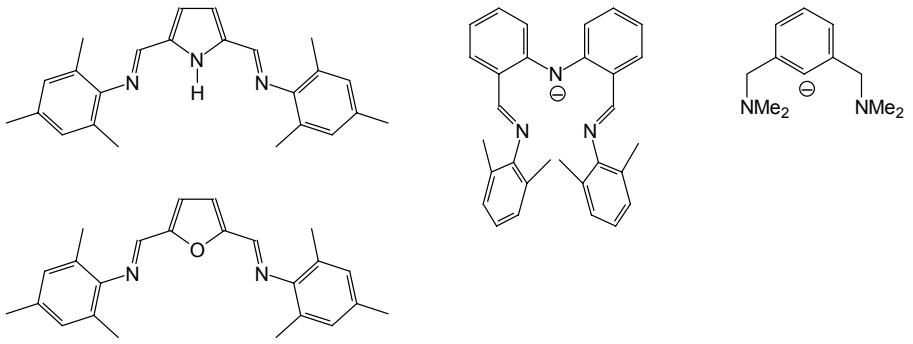
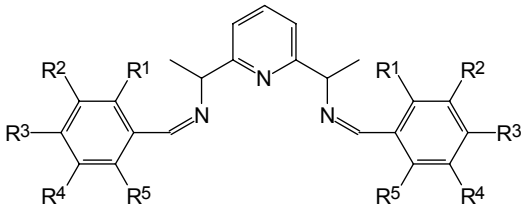


Figure 3.2.1. Examples of tridentate ligands for ethylene polymerisation iron catalysts.

We developed novel 2,6-bis(benzylideneimino)pyridyl ligands **8** with substituents in the aryl rings, which influence both the electronic and steric properties. The resultant ligands

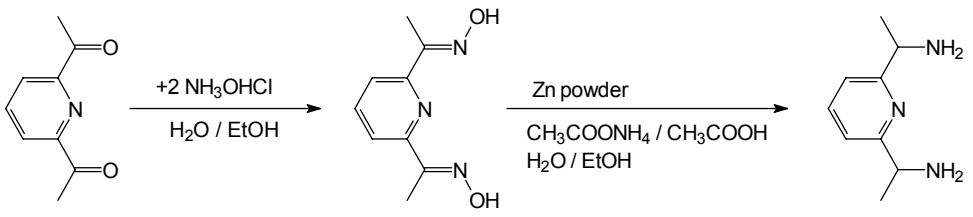
were reacted with $FeCl_2(thf)_{1.5}$ to the corresponding iron(II) complexes which were then tested as procatalysts for ethylene oligomerisation.



8a-h

	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**
-R[1]	-Cl	-Cl	-Br	-F	$-CH_3$	$-CH_3$	-H	-H
-R[2]	-H	-H	-H	-F	-H	-H	-H	
-R[3]	-H	-H	-H	-F	-H	$-CH_3$	$-C_6H_5$	
-R[4]	-H	-H	-H	-F	-H	-H	-H	-H
-R[5]	-H	-Cl	-H	-F	-H	$-CH_3$	-H	-H

Figure 3.2.2. 2,6-Bis(benzylideneimino)pyridyl ligands **8a-h** with different substituents at the phenyl ring.



9 **10**

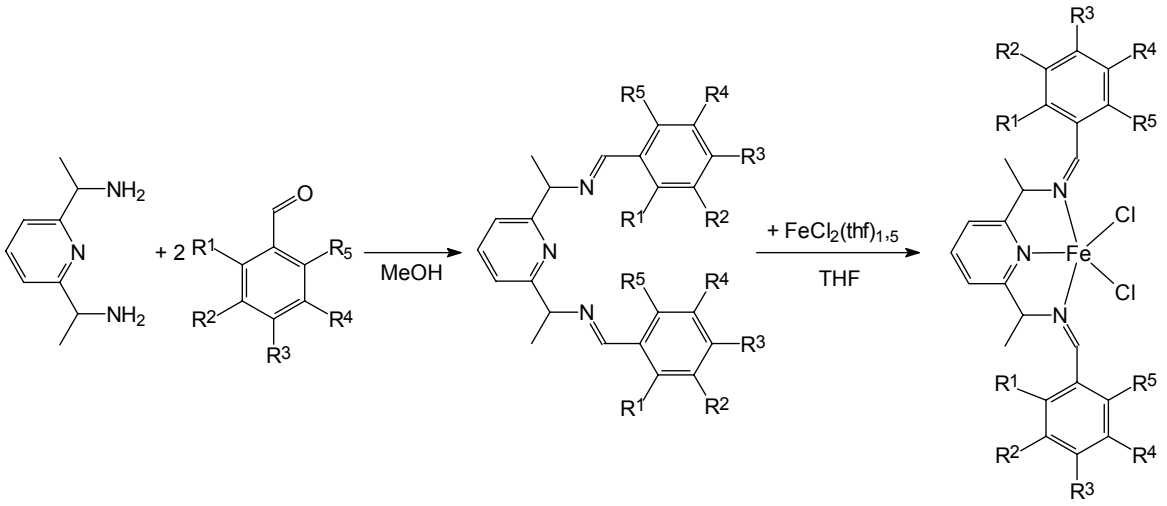
Scheme 3.2.1. Synthesis of the diamine **10**.

Pyridinylamines can be obtained from appropriate acetylpyridines by reaction with hydroxylamine hydrochloride in water/ethanol, followed by the reduction of the dioximes with zinc powder.

We synthesised the novel diamine **10** from 2,6-diacetylpyridine in two steps according to Scheme 3.2.1. using an adapted version of La Forge[24]. The diamine **10** was subsequently stirred in methanol with various substituted benzaldehydes **11a-h** to produce the Schiff bases **8a-h** (Scheme 3.2.2., Table 3.2.1.).

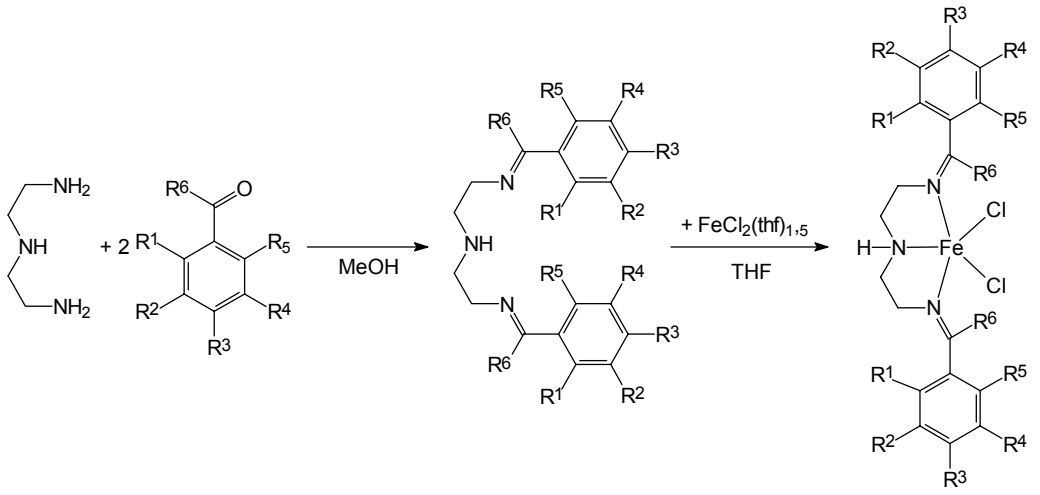
In an analogous way, bis(benzylideneimino)amines **13a-c** were obtained by condensation of diethylentriamine with the appropriate benzaldehydes (Scheme 3.2.3.).

The 2,6-bis(benzylideneimino)pyridyl ligands **8** and bis(benzylideneimino)amine ligands **13** were reacted under argon with $FeCl_2(thf)_{1.5}$ to the iron(II) complexes **12** and **14** (Schemes 3.2.2. and 3.2.3.).



10 **11a-h** **8a-h** **12a-h**

Scheme 3.2.2. Synthesis of the iron(II) complexes **12a-h**.



13a-d **14a-d**

	13/14a	**13/14b**	**13/14c**	**13/14d**
-R^1	-Cl	-Br	-CH_3	-H
-R^2	-H	-H	-H	-H
-R^3	-H	-H	-CH_3	-H
-R^4	-H	-H	-H	-H
-R^5	-Cl	-H	-CH_3	-H
-R^6	-H	-H	-H	-CH_3

Scheme 3.2.3. Synthesis of the iron(II) complexes **14a-d**.

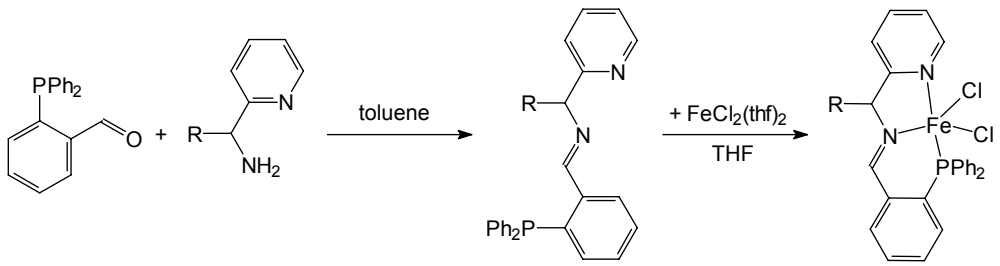
Table 3.2.1. Reaction data for the preparation of ligands **8** and **13**.

	8a	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**13a**	**13b**	**13c**
Temp. (°C)	reflux	reflux	reflux	25	reflux	reflux	reflux	reflux	reflux	reflux	reflux
Time (h)	3	5	4	5	5	6	3	4	5	5	5
Yield (%)	99	99	60	89	58	73	81	99	96	98	99

3.3. Iminophosphine ligands and their iron complexes

Iminoarylenephosphines of structure type **16**, briefly named iminophosphines, form a class of relatively widely investigated compounds. Among them, P,N,N-tridentate iminophosphines are described in literature mostly as ligands for metals from groups 6, 8 and 10 (Mo, Ru, Pd, Pt)[25]; in recent times only, studies have been published about the capability of their resultant complexes to act as catalysts. These compounds have been tested mainly for olefin hydrogenation, oxidation, and epoxidation reactions[26], whilst their potential as olefin oligomerisation/polymerisation catalysts has not yet been investigated in detail, although a number of phosphorus/nitrogen-based ligands are known to form complexes active in olefin oligomerisation or polymerisation[27].

Therefore, we synthesised some 2-picolyliminophosphines **16** which bear different substituents R in their picolylimino-backbone and made them react with $FeCl_2(thf)_2$[21] to give iron(II) complexes **17** (Scheme 3.3.1.). These iron complexes were then tested for the oligomerisation of ethylene with the purpose of verifing their potential as catalyst.



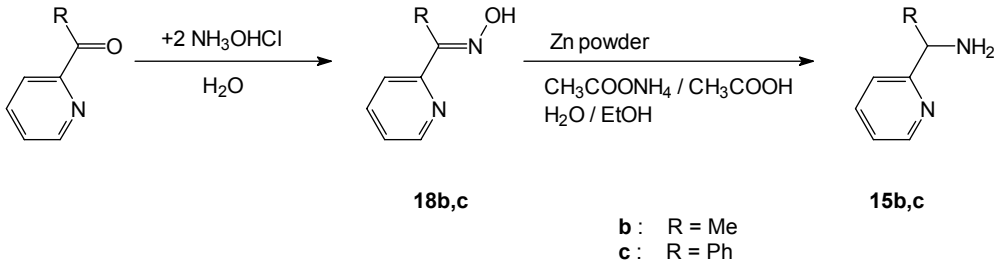
15a-c **16a-c** **17a-c**

	17a	**17b**	**17c**
-R	-H	$-CH_3$	$-C_6H_5$

Scheme 3.3.1. Synthesis of the iminophosphine ligands **16** and their iron(II) complexes **17**.

For this purpose, 2-(diphenylphosphino)benzaldehyde was condensed with differently substituted picolylamines **15** to give the 2-picolyl substituted iminophopsphine **16a** and the new **16b** and **16c**. A modified version of procedures described in literature[28] for the synthesis of iminophosphines was employed.

The amine **15a** is commercially available, whilst the latter two compounds **15b** and **15c** were produced in two steps from the related ketones with an adapted version of La Forge's[24] reaction with hydroxylamine hydrochloride in water, followed by reduction of the oximes **18b**,**c** with Zn powder (Scheme 3.3.2.).



Scheme 3.3.2. Synthesis of the substituted picolylamines **15b**,**c**.

3.4. Bidentate and tridentate imidazo[1,5-*a*]pyridyl ligands and the respective nickel and iron complexes

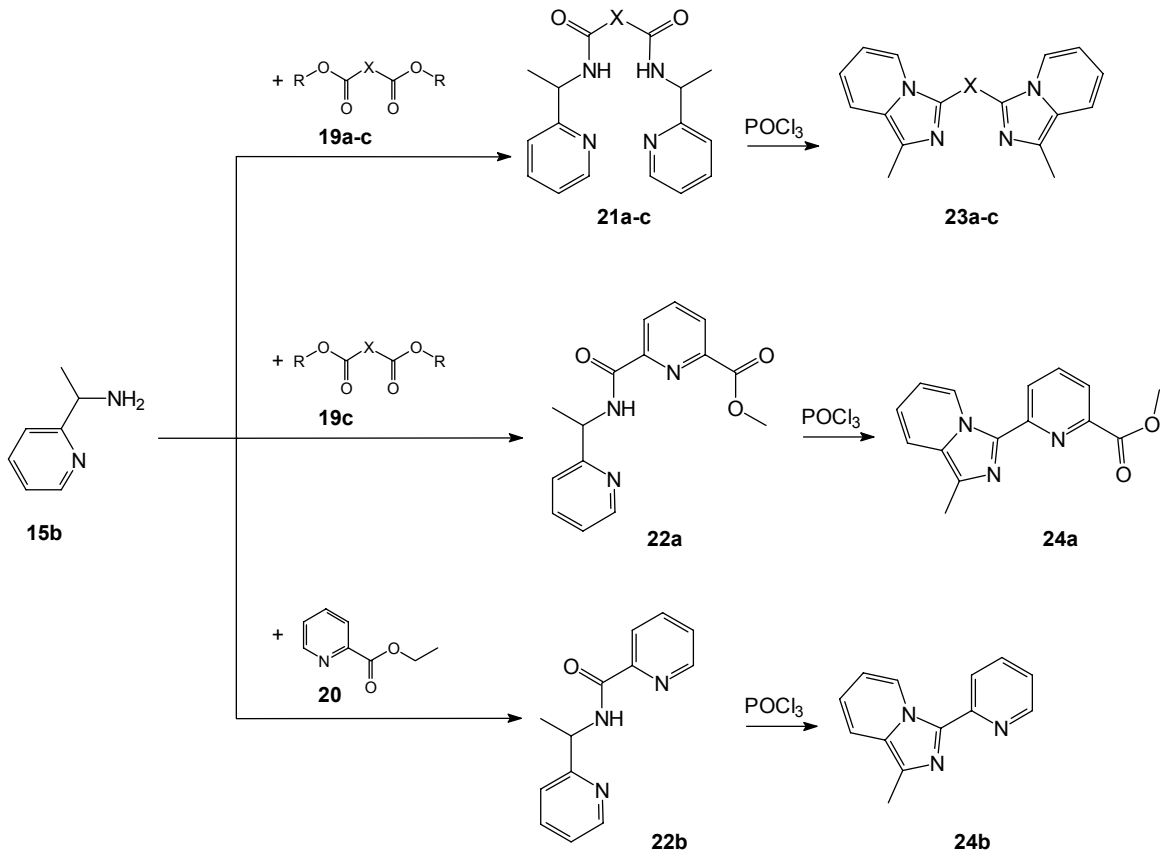
A number of differently substituted imidazo[1,5-*a*]pyridines **23**-**24** was synthesised using various methods.

In Method A, an appropriate carboxylate or bicarboxylate was condensed with 1-pyridin-2-ylethanamine **15b** and afterwards the amides **21**-**22** obtained were subjected to a dehydration reaction in the presence of $POCl_3$ to form the hetero-bicycle and, hence, the imidazopyridines **23a-c**, **24a**,**b** (Scheme 3.4.1.).

Method B was taken from literature: it was developed by Ciesielsky and Döring[29,30] and consists of the oxidative dehydrogenation of suitable Schiff bases **25** with the generation of a C-N bond between the imino-carbon atom and the nitrogen atom of the 2-pyridyl group in **25**, leading to the formation of the five-membered heterobicycles[30] **24c-e**. The reaction was performed in the presence of a catalytic amount of $CuCl_2$ and base (sodium hydroxide) with bubbling air in the reaction mixture (Scheme 3.4.2.).

Method A

	19/21/23a	19/21/23b	19/21/23c
R	C_2H_5	C_2H_5	CH_3
X	—	CH_2	



Scheme 3.4.1. Syntheses of the imidazo[1,5-*a*]pyridines **23a-c**, **24a**,**b** by condensation.

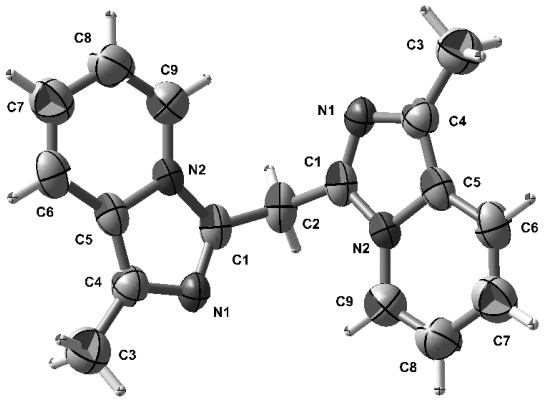


Figure 3.4.1. Crystal structure of compound **23b**. Crystals suitable for X-ray diffractometry were obtained in toluene/hexane=1:15. Selected bond lengths (Å) and angles (deg): C(1)-C(2), 1.501(2); C(1)-N(1), 1.320(3); C(1)-N(2), 1.368(2); N(1)-C(4), 1.371(2); C(4)-C(5), 1.380(3); N(2)-C(5), 1.409(2); C(5)-C(6), 1.411(3); C(6)-C(7), 1.350(3); C(7)-C(8), 1.420(3); C(8)-C(9), 1.343(3); N(2)-C(9), 1.382(2); C(4)-C(3), 1.489(3); C(1)-C(2)-C(1), 113.2(2); C(2)-C(1)-N(1), 126.1(2).

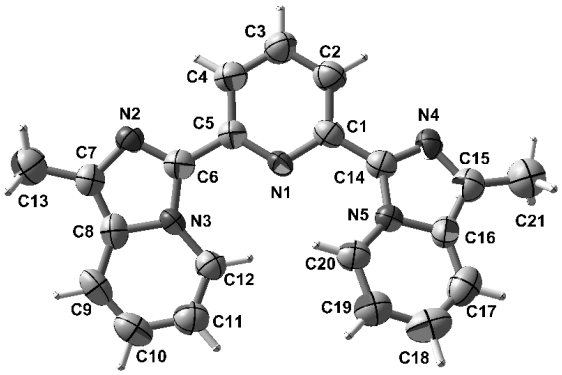
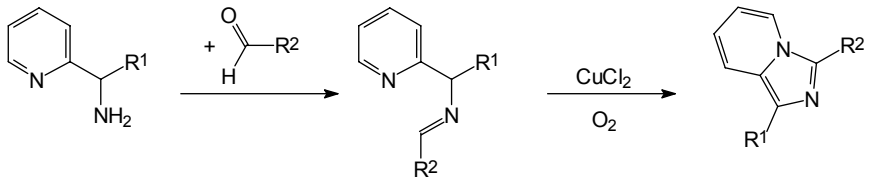


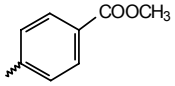
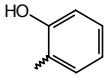
Figure 3.4.2. Crystal structure of compound **23c**. Crystals suitable for X-ray diffractometry were obtained in ethylacetate. Selected bond lengths (Å): C(6)-N(2), 1.331(4); C(7)-N(2), 1.358(3); C(8)-C(7), 1.366(4); N(3)-C(8), 1.413(4); C(9)-C(8), 1.411(4); C(10)-C(9), 1.355(4); C(11)-C(10), 1.411(4); C(12)-C(11), 1.352(5); N(3)-C(12), 1.387(3); C(6)-N(3), 1.379(4); C(5)-C(6), 1.459(4); N(1)-C(5), 1.349(3); C(1)-N(1), 1.357(4); C(14)-C(1), 1.456(4).

Method B



15b,d **25** **24c-e**

	15b	**15d**
R^1	CH_3	

	24c	**24d**	**24e**
R^1			CH_3
R^2	$CH(CH_3)_3$		

Scheme 3.4.2. Synthesis of the imidazo[1,5-*a*]pyridines **24c-e** by copper-catalysed oxidation.

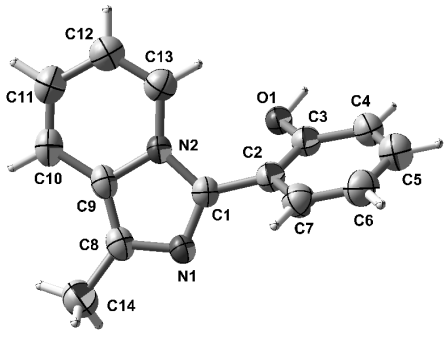


Figure 3.4.3. Crystal structure of compound **24e**. Crystals suitable for X-ray diffractometry were obtained from ethanol/water. Selected bond lengths (Å): C(1)-N(1), 1.332(2); N(2)-C(1), 1.362(2); C(13)-N(2), 1.385(2); C(9)-N(2), 1.407(2); C(12)-C(13), 1.346(2); C(11)-C(12), 1.432(2); C(10)-C(11), 1.351(2); C(9)-C(10), 1.422(2); C(8)-C(9), 1.377(2); N(1)-C(8), 1.373(2).

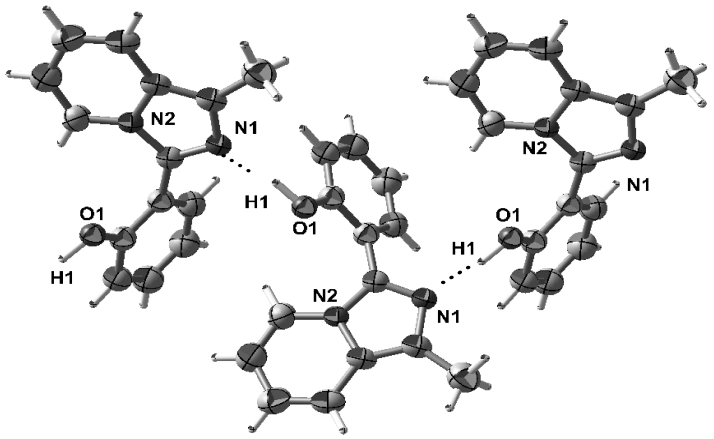
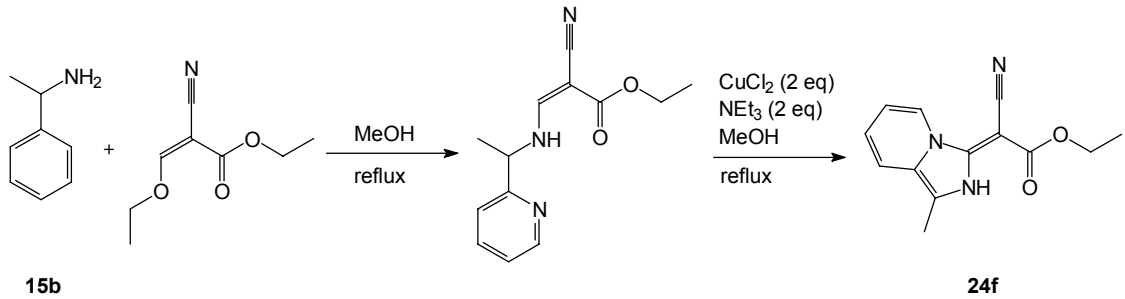


Figure 3.4.4. Crystal structure of compound **24e**. Intermolecular hydrogen bonds are shown by a broken line; selected atom distances (Å): N(1)-H(1)', 1.746; N(1)-H(1), 4.794.

Method C



15b **24f**

Scheme 3.4.3. Synthesis of the imidazo[1,5-*a*]pyridine **24f** by stoichiometric copper-mediated oxidation.

One potential bidentate anionic imidazopyridyl ligand **24f** was obtained by copper-mediated oxidation[31] under an argon atmosphere using stoichiometric amounts of $CuCl_2$ and a base (Scheme 3.4.3.).

Bidentate neutral N,N-ligands **23a** and **24b-d** were reacted with $NiBr_2(dme)$[3d] in DMF to provide the nickel(II) complexes **26a** and **27b-d** (Scheme 3.4.3.).

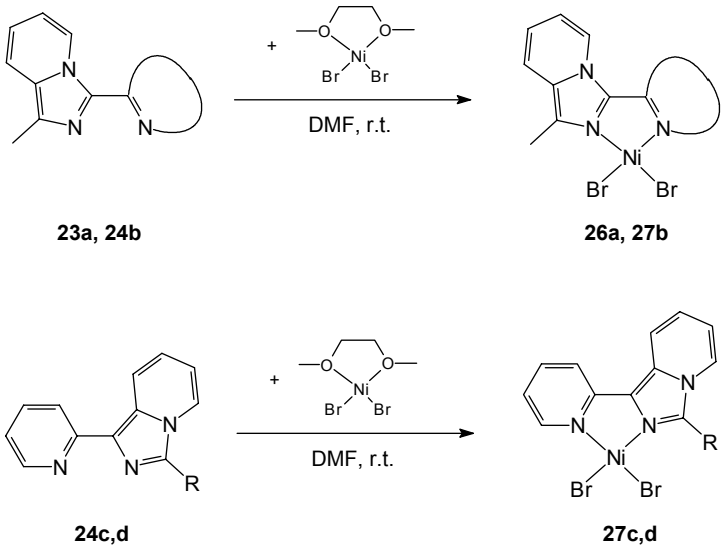
Compounds **23b** and **24f** were deprotonated with sodium bis(trimethylsilyl)amide and then reacted with $[(PPh_3)_2Ni(Mes)Br]$[32] to give the chelating neutral nickel complexes **26b** and **27f** (Scheme 3.4.4.).

The potassium salt[33] of compound **24e** was reacted as bidentate anionic ligand with $[(PPh_3)_2Ni(C_6H_5)Br]$[34] to give the nickel complex **27e** (Scheme 3.4.5.).

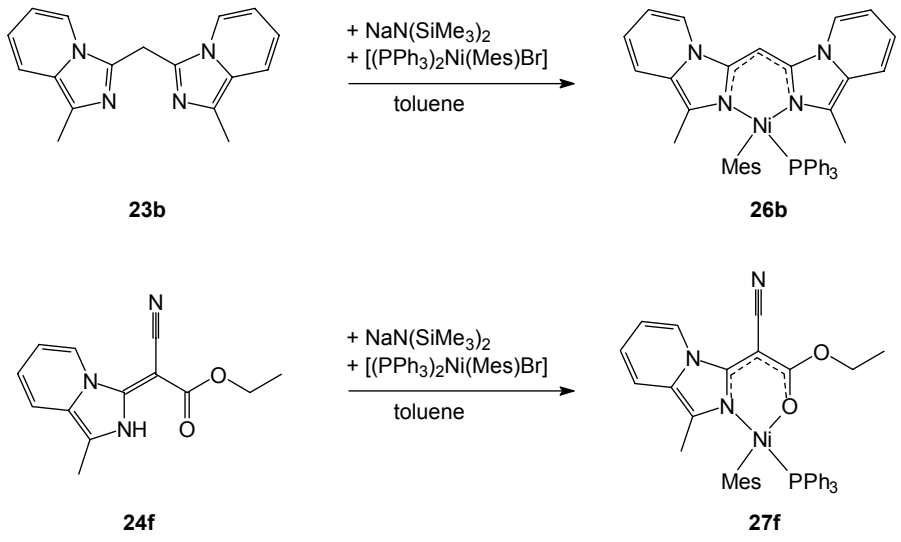
The nickel(II) complexes **27b-d** are dark green, tetrahedral, and paramagnetic, as confirmed by the fact that it was impossible to measure NMR spectra. In contrast to this,

the nickel complexes **26a**,**b** and **27e**,**f** are yellow, square-planar or distorted square-planar, and diamagnetic or lightly paramagnetic.

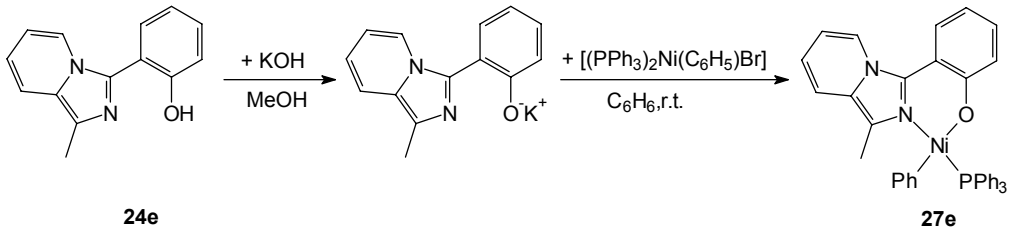
Finally, the iron(II) complexes **26c** and **27a** were obtained by reaction of the tridentate ligands **23c** and **24a** with $FeCl_2(thf)_{1.5}$ (Scheme 3.4.6.).



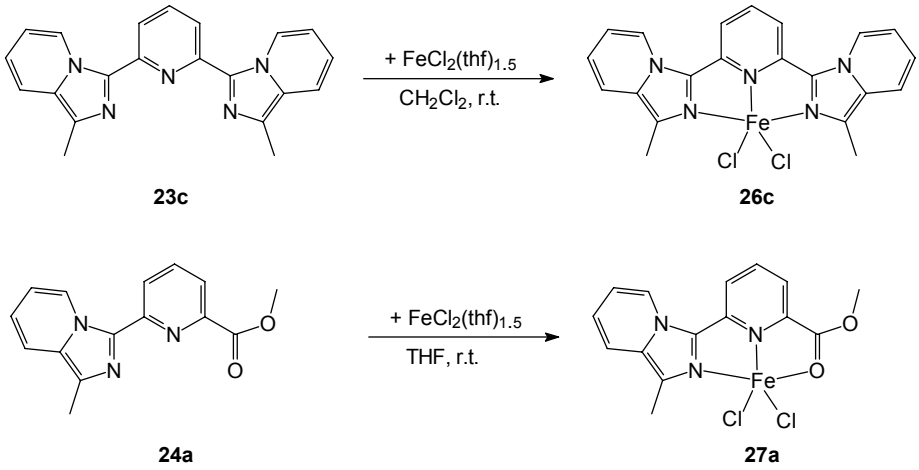
Scheme 3.4.4. Synthesis of the nickel(II) complexes **26a** and **27b-d**.



Scheme 3.4.5. Synthesis of the nickel(II) complex **26b** and **27f**.



Scheme 3.4.6. Synthesis of the nickel(II) complex **27e**.



23c **26c**

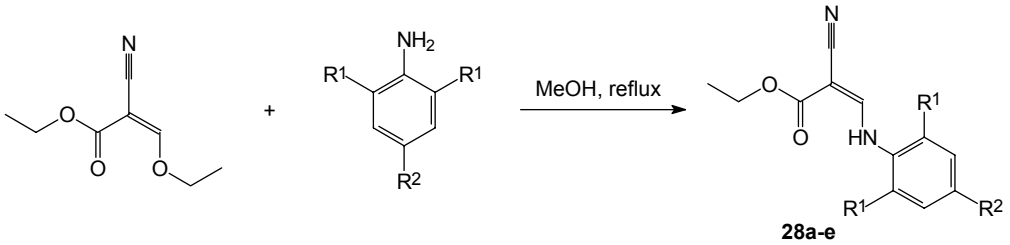
24a **27a**

Scheme 3.4.7. Synthesis of the iron(II) complexes **26c** and **27a**.

That way, a series of catalysts precursors was obtained, all of which contained the imidazo[1,5-*a*]pyridyl function but possessed different characteristics. Compounds **26a** and **27c-d** are analogous to Brookhart's α-diimine nickel-complexes which give highly branched polyethylenes of high molecular weight[2,3], while the complex **27d** equals Grubbs' salicylaldiminato catalysts[10] which produce less branched polyethylenes.
In the complex **26b**, the ring around the metal centre is extended from five to six members to verify a possible influence of the ring size on the catalytic activity. This complex also is analogous to the known β-diketiminato metal complexes (vide infra, Chapter 3.6.).
Finally, the iron complexes **26c** and **27a** exhibit correlation to Brookhart's 2,6-bis(imino)pyridyl catalysts[13] which just generate highly linear oligomers/polymers.

3.5. 3-Aminoacrylate ligands

A set of differently substituted 3-aminoacrylates **28**, **29**, and **31** was synthesised by aminolysis of the Claisen adducts[35]. Such bidentate N,O-ligands are a very versatile group of substances that can be used as monoanionic ligands: indeed, a wide series of ligands may be obtained by varying the amine or changing the substituents at the backbone, including groups with a different electronic behaviour. The late transition metal complexes resulting from these ligands were subsequently tested for olefin oligomerisation and polymerisation catalyses.



	28a	28b	28c	28d	28e
R^1	H	H	CH_3	CH_2CH_3	$CH(CH_3)_2$
R^2	CH_3	OCH_3	H	H	H

Scheme 3.5.1. Synthesis of cyano-substituted aminoacrylates **28a-e**.

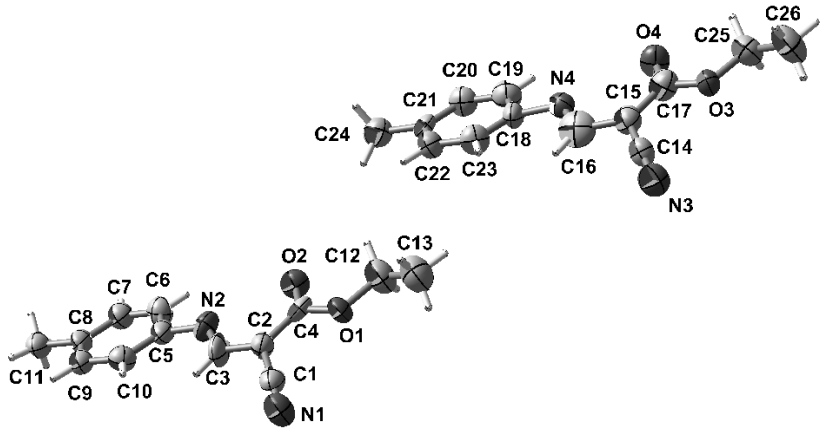


Figure 3.5.1. Crystal structure of the ethyl 2-cyano-3-[(4-methylphenyl)amino]acrylate **28a**. Crystals suitable for X-ray diffractometry were obtained in ethanol/water = 10/3. Selected bond lengths (Å): C(1)-N(1), 1.149(1); C(2)-C(1), 1.432(2); C(4)-C(2), 1.465(2); O(1)-C(4), 1.351(1); C(3)-C(2), 1.364(1); N(2)-C(3), 1.294(1); C(5)-N(2), 1.431(1).

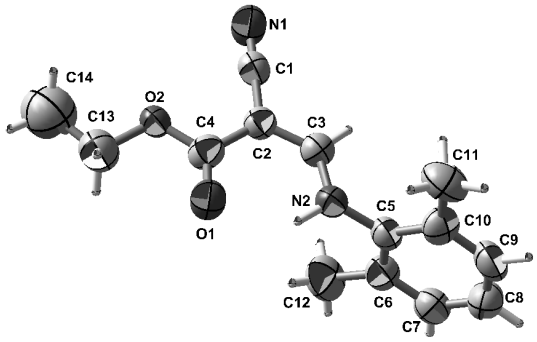
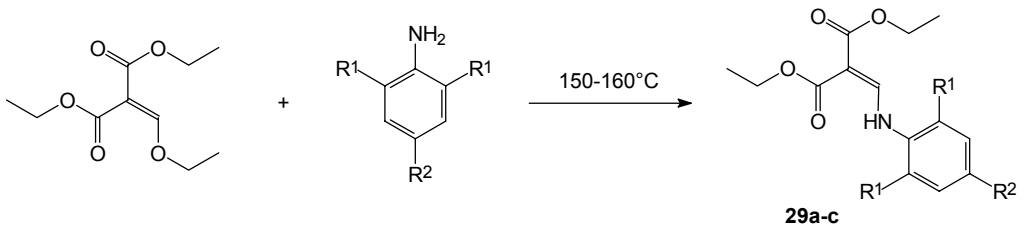


Figure 3.5.2. Crystal structure of the ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]acrylate **28c**. Crystals suitable for X-ray diffractometry were obtained in ethanol/water = 10/3. Selected bond lengths (Å): C(4)-O(1), 1.220(3); C(2)-C(4), 1.452(3); C(1)-C(2), 1.419(3); N(1)-C(1), 1.147(3); C(3)-C(2), 1.396(3); N(2)-C(3), 1.314(3); C(5)-N(2), 1.443(3).

Cyano-substituted aminoacrylates **28** were prepared easily by condensation of ethyl (ethoxymethylene)cyanoacetate with diverse anilines in refluxing methanol using an adapted version of similar reactions already described in literature[35] (Scheme 3.5.1.).

The above-described procedure was not effective for obtaining analogous substances with an ester group instead of a nitrile; for the synthesis of compounds **29**, the reactants had to be heated under stronger conditions in an apparatus fitted for distilling away the ethanol produced along the reaction (Scheme 3.5.2.).



	29a	**29b**	**29c**
R^1	H	CH_2CH_3	$CH(CH_3)_2$
R^2	CH_3	H	H

Scheme 3.5.2. Synthesis of ester-substituted aminoacrylates **29a-c**.

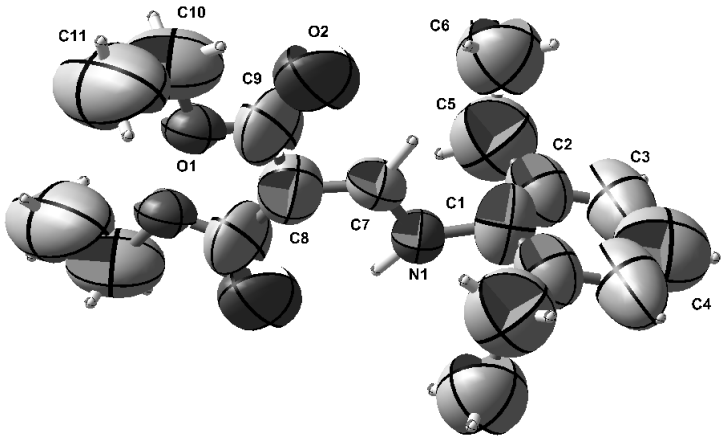
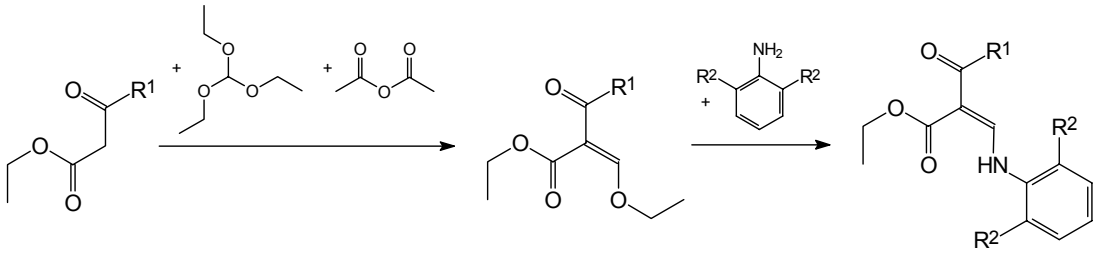


Figure 3.5.3. Crystal structure of compound **29b**. Crystals suitable for X-ray diffractometry were obtained in hexane. Selected bond lengths (Å) and angles (deg): C(1)-N(1), 1.494(8); N(1)-C(7), 1.340(8); C(7)-C(8), 1.460(1); C(8)-C(9), 1.432(7); C(9)-O(2), 1.219(6); C(9)-O(1), 1.308(6); C(1)-N(1)-C(7), 115.1(5); N(1)-C(7)-C(8), 116.6(5); C(7)-C(8)-C(9), 134.8(4); C(8)-C(9)-O(2), 123.0(6); O(2)-C(9)-O(1), 121.6(7); C(8)-C(9)-O(1), 115.2(4).

Finally, a third modification of the backbone was obtained: the acyl-substituted aminoacrylates **31** were synthesised in a two-step reaction from the β-keto-esters using an adapted version of a procedure described in literature[36] for similar compounds (Scheme 3.5.3.).

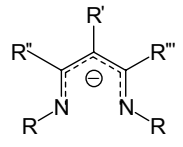


	31a	31b
R^1	CH_3	n-C_3H_7
R^2	CH_3	CH_3

Scheme 3.5.3. Synthesis of acyl-substituted aminoacrylates **31a-c**.

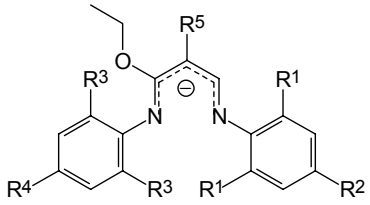
3.6. 3-Aminoiminoacrylate ligands

Although N,N-bidentate ligands are widely used systems in coordinating chemistry, β-diketiminato ligands **I** have received only recent, but significantly increasing, attention[37]. The R groups on nitrogen may be hydrogen or alkyl, aryl, or silyl groups; the R groups may also be linked with the R"/R"' groups to form either neighbouring fused six-membered or five-membered heterocyclic rings.



I

The β-dialdiminato/diketiminato ligands **I** have been made, with R', R", and R"' being hydrogens, alkyl, or aryl groups. Various derived metal complexes have been published, some of them are active in olefin polymerisation processes, e.g. Ti, Zr, Cr, Ni, Pd.



II

In particular, Ni(II) complexes of $(2,6\text{-}^{i}Pr_2(C_6H_3)NC(CH_3))_2CH$ were applied in ethylene oligomerisation[38].

β-Diketiminates have an important role as spectator ligands by virtue of their strong bonding to metal, their tunable and extensive steric demand, and their diversity of bonding modes. Many of these complexes are coordinatively unsaturated, and this feature is one of the key to their ability of functioning as catalysts for processes as varied as olefin oligo-, poly-, and co-polymerisation.

As extension of the class of well-known *β*-diketiminates, I have synthesised novel 3-aminoiminoacrylates that yield by deprotonation the monoanionic ligands of the typical structure **II**. An alkoxyl and a second functional group R^5 (i.e. nitrile or ester) are bound to the ligand backbone, noticeably modifying the electron distribution in the metallacycle of the resulting complex, in comparison to the classical *β*-diketiminates.

A wide range of modifications is possible on both the steric demand and electronic properties of these novel ligands, by varying the substituents at the backbone. This versatility allows to prepare bulky-substituted chelating ligands with interesting coordination properties and potential applications in catalysis as well as in bioinorganic chemistry.

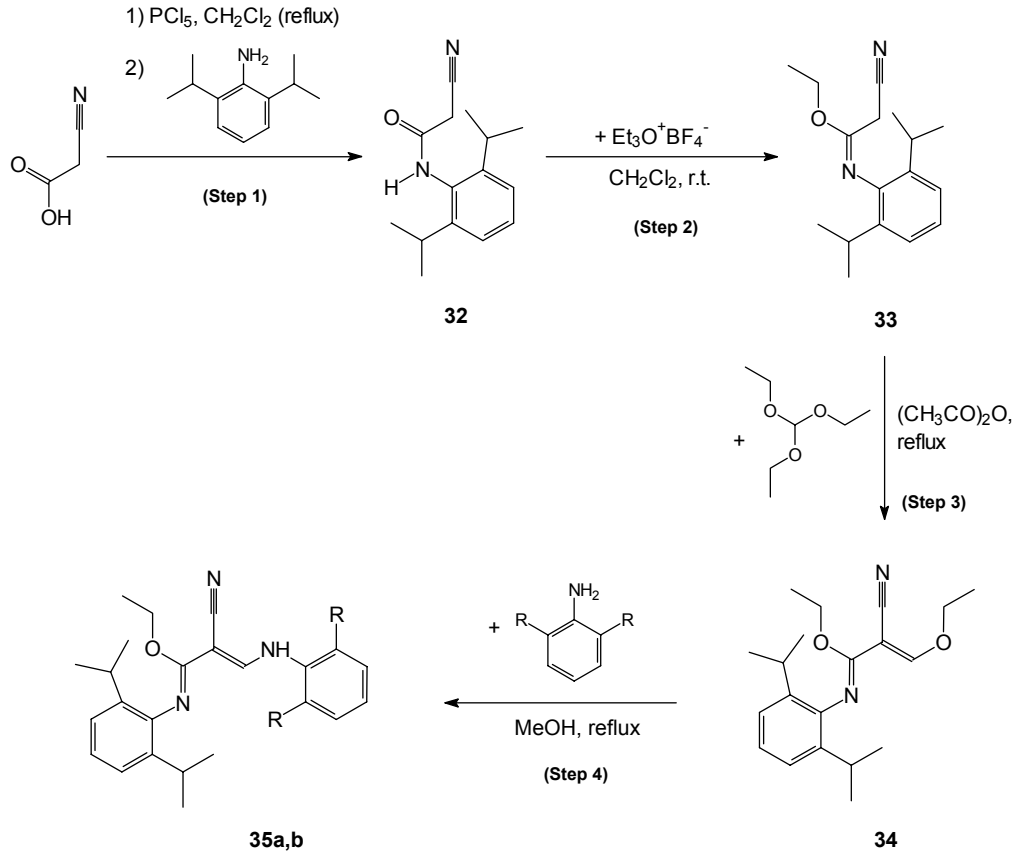
The primary 3-aminoiminoacrylates were obtained by diverse multi-step syntheses. These reactions required to be developed and optimised with respect to the different substituents R^5 in the acrylic backbone.

Cyano-substituted 3-aminoiminoacrylates **35** were obtained by a four-step reaction, where the first step[39] consisted of a chlorination of cyanoacetic acid, followed by condensation with 2,6-diisopropylaniline (Scheme 3.6.1.). The obtained amide **32** was subjected to conversion with an oxonium salt to form the related iminoester[40] **33**.

Compound **33** was then boiled at reflux with triethyl orthoformate in the presence of acetic anhydride as solvent, this being a typical Claisen's reaction[41]. The ethoxymethylene group in compound **34** was finally reacted with appropriate substituted anilines in refluxing methanol to give the final products **35a**,**b** (Method A, Scheme 3.6.1.) which could be obtained in good yields (Table 3.6.1.).

The above-described method was not successful if the substituent at the backbone was an ester- in place of a cyano-group, because decomposition occurred in step 3, as the iminoester function was not stable under the reaction conditions. Therefore, other reaction paths were investigated to find an alternative efficient synthesis.

Method A



	35a	35b
R	CH_3	$CH(CH_3)_2$

Scheme 3.6.1. Synthesis of cyano-substituted 3-amino-iminoacrylates **35a-b**.

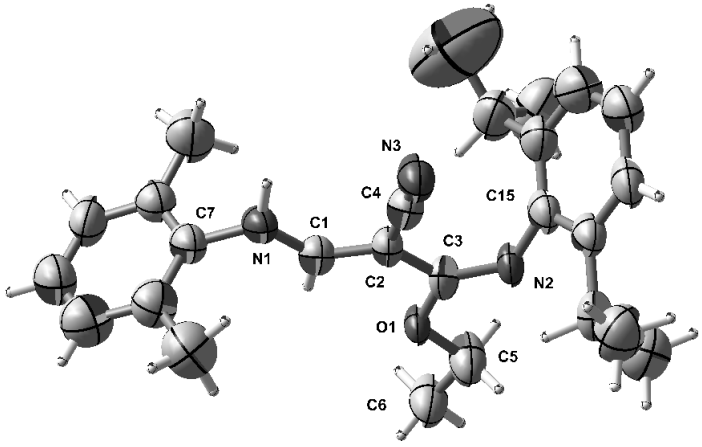


Figure 3.6.1. Crystal structure of compound **35a**. Crystals suitable for X-ray diffractometry were obtained in hexane. Selected bond lengths (Å) and angles (deg): N(1)-C(7), 1.449(2); C(1)-N(1), 1.327(3); C(2)-C(1), 1.374(3); C(4)-C(2), 1.428(3); N(3)-C(4), 1.157(3); C(3)-C(2), 1.465(3); O(1)-C(3), 1.361(2); N(2)-C(3), 1.275(2); C(15)-N(2), 1.419(3); C(7)-N(1)-C(1), 121.5(2); N(1)-C(1)-C(2), 127.5(2); C(1)-C(2)-C(4), 118.8(2); C(1)-C(2)-C(3), 121.4(2); C(2)-C(3)-N(2), 129.5(2); C(3)-N(2)-C(15), 123.7(2).

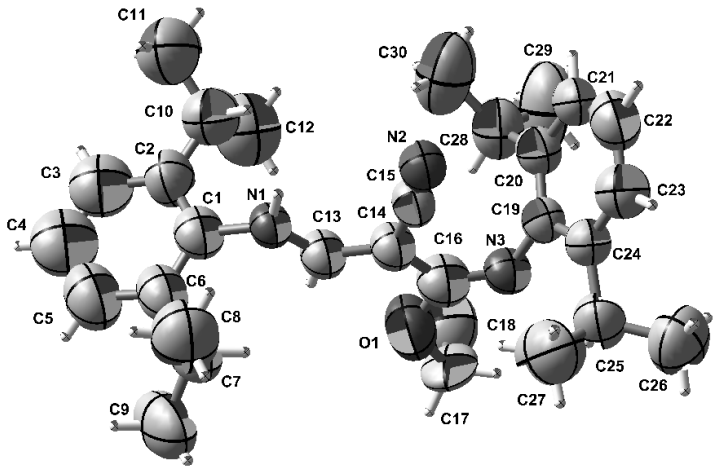
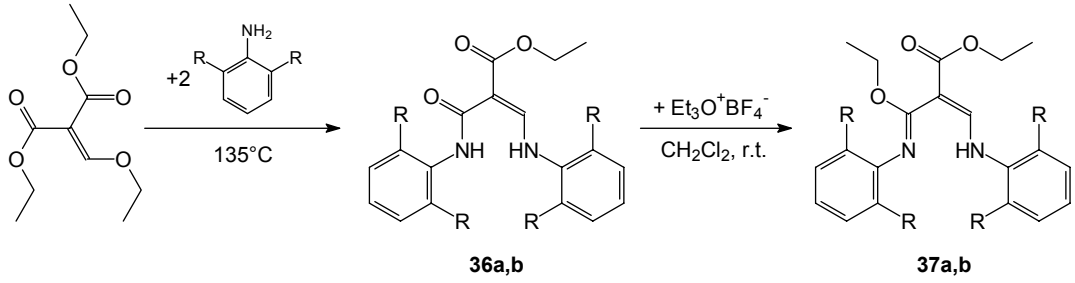


Figure 3.6.2. Crystal structure of compound **35b**. Crystals suitable for X-ray diffractometry were obtained in methanol/water. Selected bond lengths (Å) and angles (deg): C(15)-N(2), 1.143(2); C(14)-C(15), 1.423(3); C(13)-C(14), 1.375(3); N(1)-C(13), 1.324(2); C(1)-N(1), 1.446(2); C(16)-C(14), 1.470(3); O(1)-C(16), 1.354(3); N(3)-C(16), 1.269(3); C(19)-N(3), 1.414(2); C(1)-N(1)-C(13), 122.5(2); N(1)-C(13)-C(14), 127.4(2); C(13)-C(14)-C(15), 117.3(2); C(13)-C(14)-C(16), 120.4(2); C(14)-C(16)-N(3), 130.6(2); C(16)-N(3)-C(19), 120.8(2).

Method B



	36/37a	36/37b
R	CH_3	$CH(CH_3)_2$

Scheme 3.6.2. Synthesis of ester-substituted 3-amino-iminoacrylates **37a-b**, with identically substituted aryl rings.

Method B was found to be very successful in cases where the ensuing compounds **37a,b** bear two identically substituted aryl rings. The simple route consists of a twofold condensation[42] in the absence of any solvent at high temperature with simultaneous distillation of the produced ethanol, which yields the 3-aminoiminoacrylamides **36a,b**, followed by reaction with an oxonium salt[40] to provide the 3-aminoiminoacrylates **37a,b** in a similar way as described for Method A.

Several attempts were made to prepare the substance **35b** - or an analogous one - using Method B starting from ethyl (ethoxymethylene)cyanoacetate, but they failed due to the impossibility of obtaining the intermediate 3-aminoacrylamide: in fact, even when operating with a large excess of the appropriate aniline and/or with acid catalysis and/or for longer reaction times, condensation took place at the ethoxymethylene group only and just 2-cyano-3-aminoacrylates were obtained.

It was furthermore focussed on two different reaction routes for the generation of ester-substituted 3-aminoiminoacrylates bearing two diverse aryl rings **37c-e**.

In Method C (Scheme 3.5.3.), diethyl (ethoxymethylene)malonate was condensed[43] in succession with two different anilines to the 3-aminoacrylamides **38**, whereas the intermediates **29** occurred. The second condensation (amide formation, i.e. from **29** to **38**) required stronger reaction conditions than the first one.

Method D, on the other hand, employed diethyl malonate which was first condensed with one equivalent of an aniline sort[44]. The amide obtained subsequently reacted with triethyl orthoformate and the second aniline[42,45].

The last step was identical for both Method C and Method D and always consisted of the conversion to the corresponding 3-aminoiminoacrylates[40] **37c-e**.

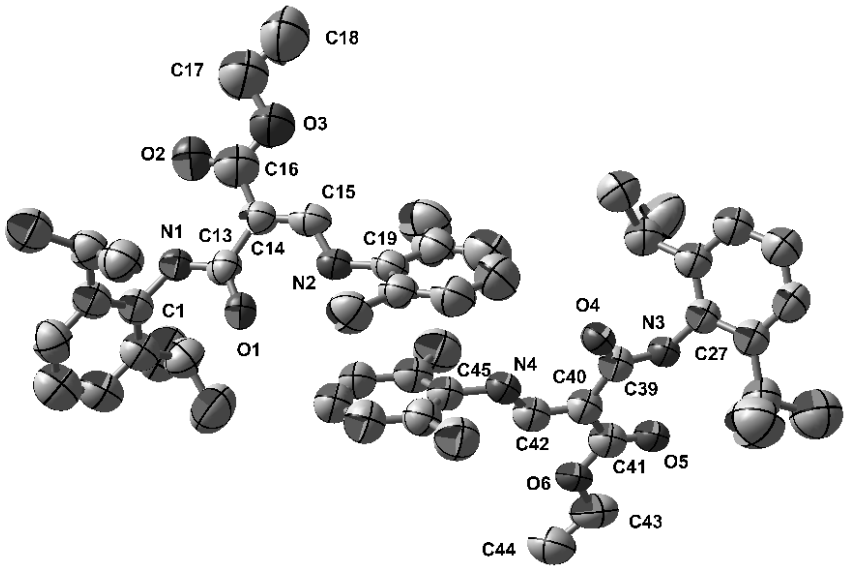
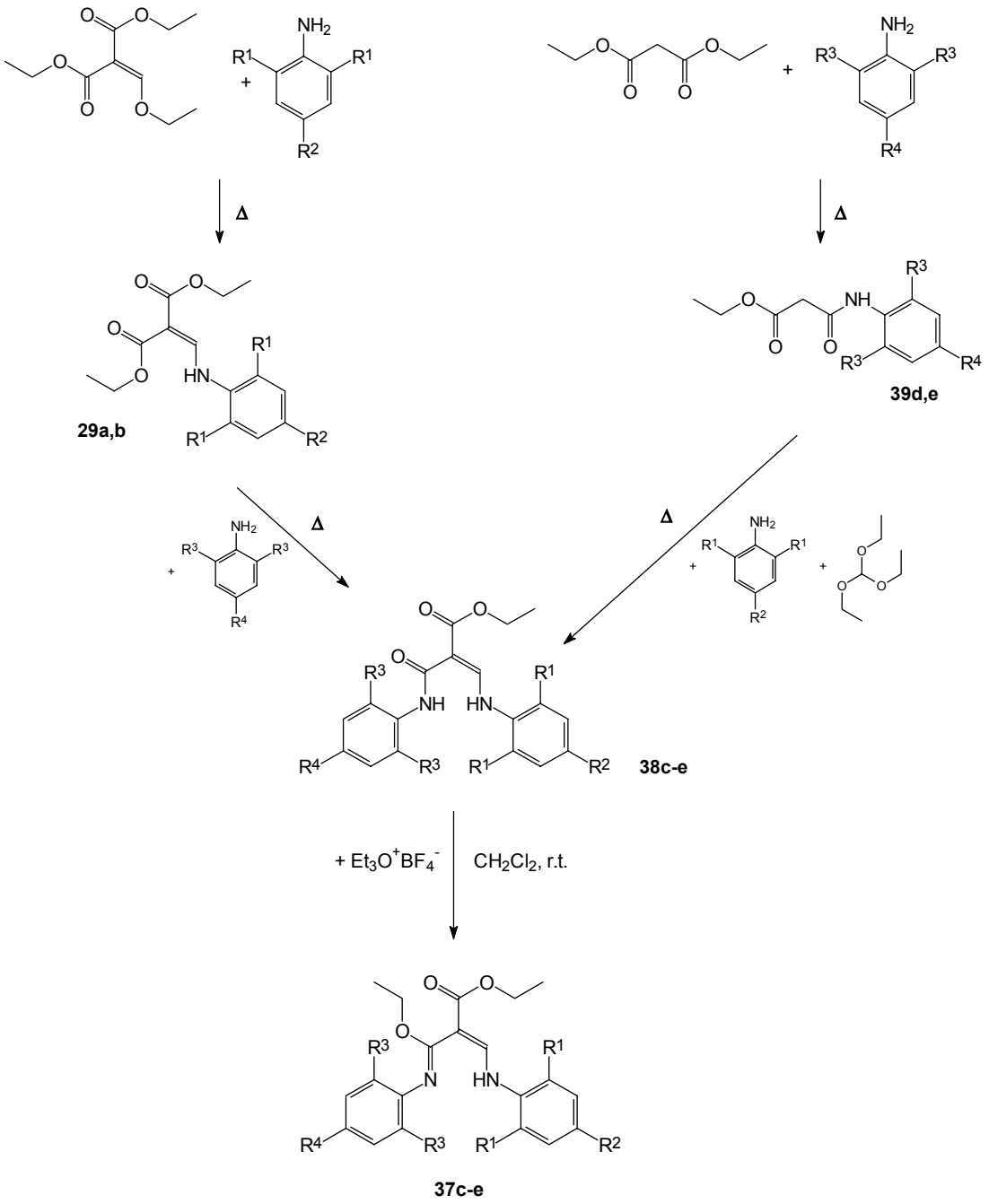


Figure 3.6.3. Crystal structure of compound **38e**. Crystals suitable for X-ray diffractometry were obtained in hexane. Selected bond lengths (Å) and angles (deg): N(1)-C(1), 1.435(3); C(13)-N(1), 1.346(3); O(1)-C(13), 1.241(3); C(14)-C(13), 1.475(3); C(16)-C(14), 1.459(4); C(15)-C(14), 1.372(4); N(2)-C(15), 1.327(3); C(19)-N(2), 1.430(3); N(1)-C(13)-C(14), 118.3(2); C(13)-C(14)-C(16), 121.0(3); C(13)-C(14)-C(15), 119.7(2); C(14)-C(15)-N(2), 126.2(2).

Method C

Method D



	37c	37d	37e
R¹	CH_2CH_3	H	CH_3
R²	H	CH_3	H
R³	H	CH_3	$CH(CH_3)_2$
R⁴	CH_3	H	H

Scheme 3.6.3. Syntheses of ester-substituted 3-amino-iminoacrylates **37c-e** with differently substituted aryl rings.

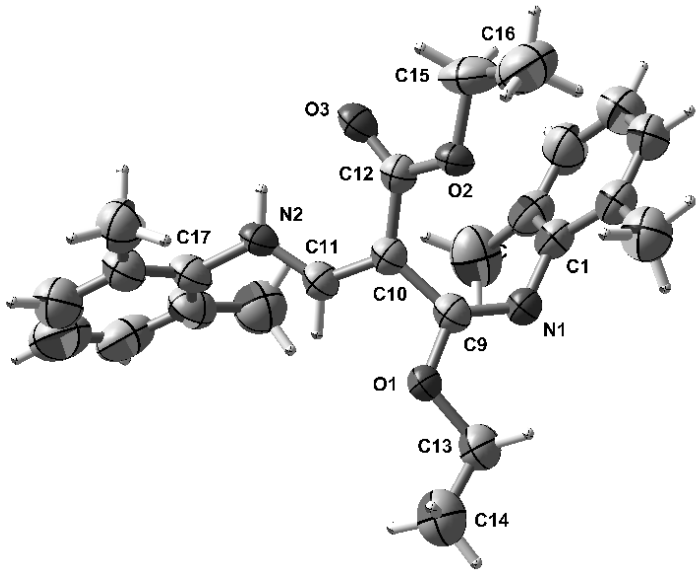


Figure 3.6.4. Crystal structure of compound **37a**. Crystals suitable for X-ray diffractometry were obtained in hexane/ethylacetate = 4/1. Selected bond lengths (Å) and angles (deg): N(2)-C(17), 1.433(2); C(11)-N(2), 1.337(2); C(10)-C(11), 1.370(2); C(12)-C(10), 1.455(2); C(9)-C(10), 1.478(2); O(1)-C(9), 1.362(1); N(1)-C(9), 1.271(2); C(1)-N(1), 1.410(2); N(2)-C(11)-C(10), 128.2(1); C(11)-C(10)-C(12), 119.5(1); C(9)-N(1)-C(1), 122.4(1); C(11)-C(10)-C(9), 118.1(1); C(10)-C(9)-N(1), 129.8(1).

Table 3.6.1. Yields of the products described in Methods A-D.

Method A	**32**	**33**	**34**	**/**	**35a**	**35b**
Time	0.5 h	5 d	5.5 h	/	0.5 h	0.5 h
Yield (%)	95	46	64	/	60 (17)[*]	57 (16)[*]
Method B	**36a**	**36b**	**/**	**/**	**37a**	**37b**
Time	20 h	38 h	/	/	7 d	9 d
Yield (%)	87	68	/	/	65 (57)[#]	60 (41)[#]
Method C	**29a**	**29b**	**38d**	**38c**	**37d**	**37c**
Time	5 h	5 h	16 h	30 h	12 d	35 d
Yield (%)	85	83	96	46	18 (15)[#]	57 (22)[#]
Method D	**39d**	**39e**	**38d**	**38e**	**37d**	**37e**
Time	20 h	19 h	4 h	5 h	12 d	30 d
Yield (%)	94	93	50	70	18 (8)[§]	26 (17)[‡]

[*]Yield calculated for the initial cyanoacetic acid. [#]Yield calculated for the initial diethyl (ethoxymethylene) malonate. [§]Yield calculated for the initial 2,6-dimethylaniline. [‡]Yield calculated for the initial 2,6-diisopropylaniline.

Method C has proved to be more efficient than Method D, as the overall yields are higher (Table 3.6.1.) and because the first step in Method D requires a large excess of diethyl malonate to prevent the prompt formation of diamide, while the other reactions can be performed in equimolar amounts.

Moreover, it emerges that the reaction with triethyloxonium tetrafluoroborate gives much higher yields in case of ester-substituted 3-aminoiminoacrylates with two identical anilines (**37a**,**b**): the reaction appears to be much slower when the amides contain two differently-substituted aryl rings, and the reactants need to be stirred for some weeks to achieve reasonable product yields.

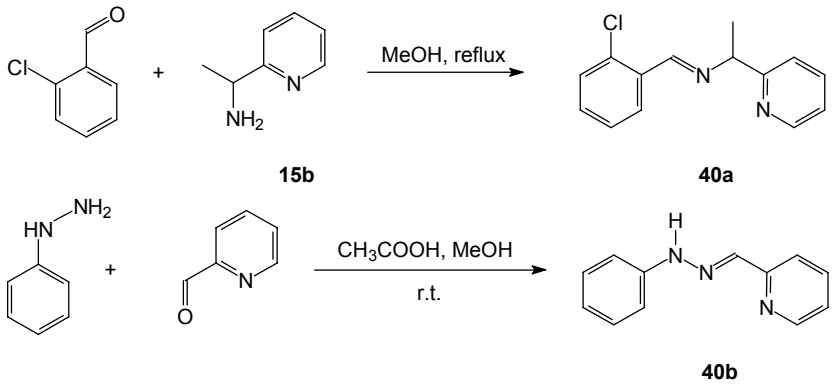
3.7. Additional bidentate N,N- ligands

In addition to the compounds described above, some further bidentate ligands were synthesised and used for preparing the corresponding nickel(II) complexes.

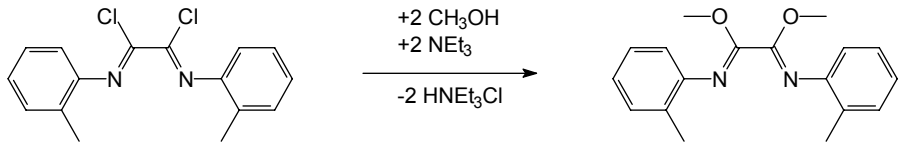
A bidentate neutral N,N-ligand **40a** was obtained by condensation of chlorobenzaldehyde with 1-pyridin-2-ylethanamine **15b** in refluxing methanol (Scheme 3.5.5.).[46] The 2-pyridine-2-carboxaldehyde hydrazone **40b** as well was synthesised by condensation according to literature.[47]

The bis(imino)oxalate **42** was synthesised from the corresponding diimidoyl dichloride of oxalic acid **41** according to literature[48] (Scheme 3.7.2.).

Lastly, an amidoiminomalonate **44** was synthesised from diethyl malonate by twofold condensation with diisopropylaniline, followed by a reaction with an oxonium salt[40] (Scheme 3.7.3.).

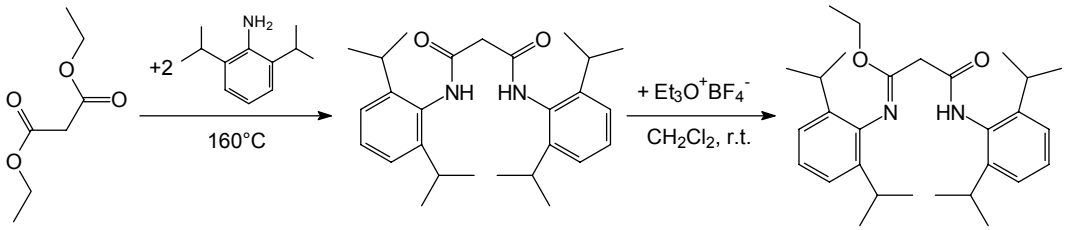


Scheme 3.7.1. Syntheses of the *N,N*-ligands **40a**,**b**.



41 **42**

Scheme 3.7.2. Synthesis of dimethyl bis(imino)oxalate **42**.



43 **44**

Scheme 3.7.3. Synthesis of the amidoiminomalonate **44**.

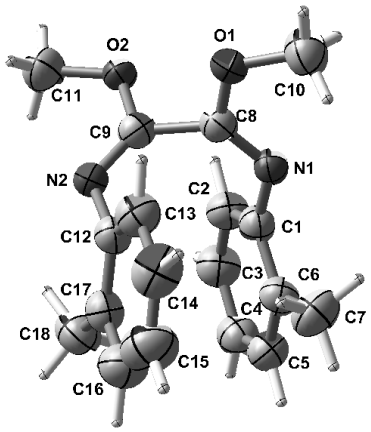


Figure 3.7.1. Crystal structure of dimethyl bis(imino)oxalate **42**. Crystals suitable for X-ray diffractometry were obtained in methanol. Selected bond lengths (Å): C(1)-N(1), 1.420(1); C(8)-N(1), 1.262(1); O(1)-C(8), 1.346(1); C(9)-C(8), 1.514(1); O(2)-C(9), 1.346(1); N(2)-C(9), 1.262(1); C(12)-N(2), 1.420(1).

3.8. Nickel complexes of nitrogen- and oxygen-based ligands

The compounds described in Chapters 3.5.-3.7. were used as ligands for nickel(II) complexes: all of them were employed in their monoanionic form, except for the substances **40** and **42** which were taken as neutral ligands.

As regards the aminoacrylate derivatives, it was intended to test them as bidentate chelating ligands with the aim of verifying the influence of the different substituents: both

the steric bulk at the aryl rings and electronic effects of the ligand backbone affect the activity and selectivity of the corresponding nickel catalyst precursors in olefin oligomerisation.

For this purpose, ligand deprotonation was performed with sodium bis(trimethylsilyl)amide to create their monoanionic forms that then reacted with *trans*-bromomesityl-bis-(triphenylphosphino)nickel(II) $[(PPh_3)_2Ni(Mes)Br]$[32] (Scheme 3.8.1.). Surprisingly, the results of X-ray diffractometry revealed that the monoanionic ligand derived from compound **35b** coordinated to nickel through its cyano-group and not as chelating ligand as had been expected (Figure 3.8.1.). The NMR spectra (pp. 98-100) in solution agree with the structure measured in the solid state.

The X-ray structure of the complex **45b** shows that the nickel atom is tetra-coordinated with a distorted square-planar conformation being assumed: in fact, the angles N(1)-Ni-C(31) and P(1)-Ni-P(2) were measured to be 172.5(1) and 173.4(4)°, respectively. The bond length within the molecule between nickel and the nitrogen atom is 1.888(3) Å; the nickel-phosphorus distances are 2.243(1) and 2.252(1) Å, while the shorter nickel carbon distance is 1.919(3) Å. The bond lengths in the ligand in its free and coordinated forms are slightly different (Figures 3.6.2. and 3.8.1.), showing a certain degree of mesomerism.

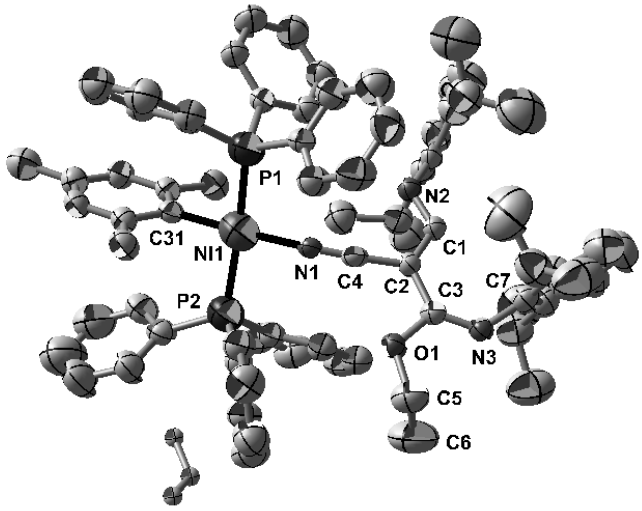
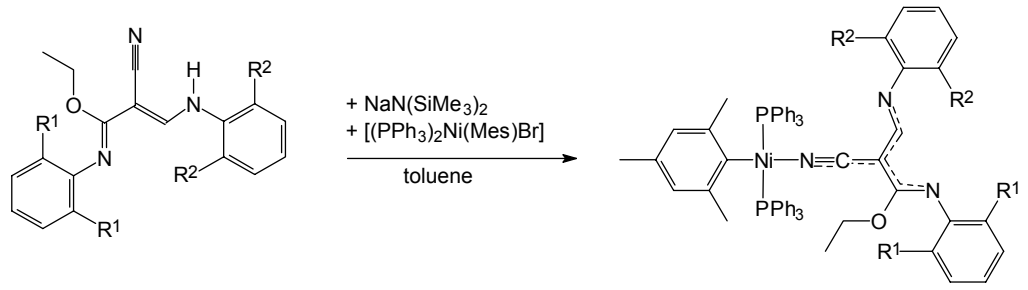


Figure 3.8.1. Crystal structure of the nickel(II) complex **45b**. Red crystals suitable for X-ray diffractometry were obtained in hexane/pentane/toluene = 10/3/1. Selected bond lengths (Å) and angles (deg): C(3)-N(3), 1.264(4); C(2)-C(3), 1.448(4); C(4)-C(2), 1.409(4); N(1)-C(4), 1.152(4); C(1)-C(2), 1.432(4); N(2)-C(1), 1.280(4); NI(1)-N(1), 1.888(3); P(2)-NI(1), 2.243(1); C(31)-NI(1), 1.919(3); P(1)-NI(1), 2.252(1); N(1)-NI(1)-P(2), 89.73(8); P(2)-NI(1)-C(31), 90.55(9); C(31)-NI(1)-P(1), 87.82(9); P(1)-NI(1)-N(1), 92.72(8); N(1)-NI(1)-C(31), 172.5(1); P(2)-NI(1)-P(1), 173.4(4).



35a,b **45a,b**

	35/45a	**35/45b**
R^1	$CH(CH_3)_2$	$CH(CH_3)_2$
R^2	CH_3	$CH(CH_3)_2$

Scheme 3.8.1. Synthesis of the nickel(II) complexes **45**.

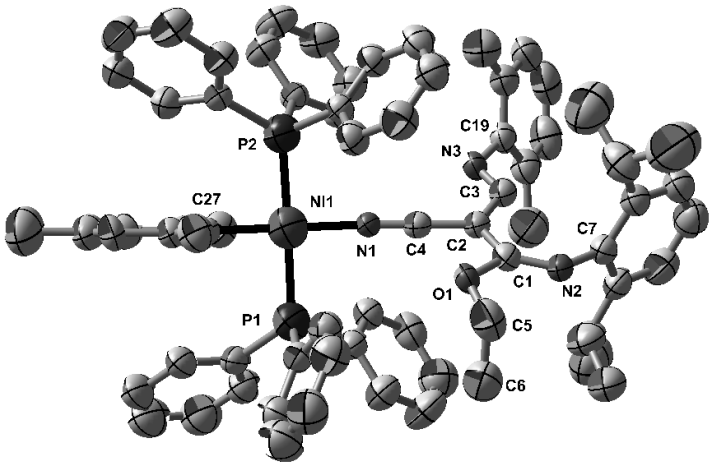


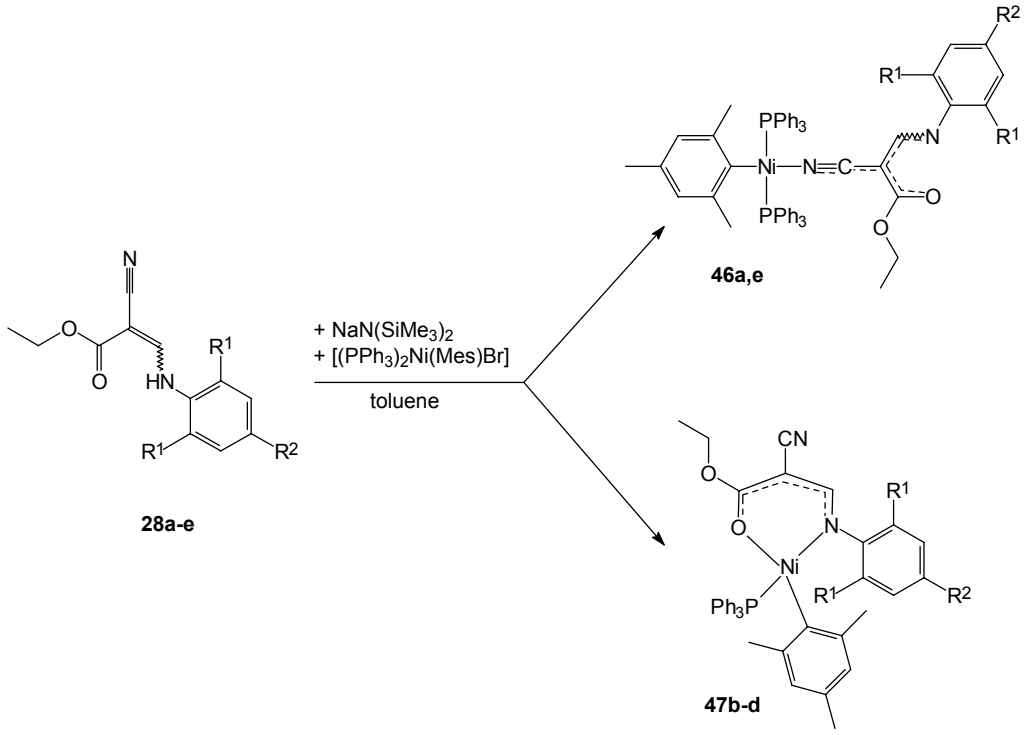
Figure 3.8.2. Crystal structure of the nickel(II) complex **45a**. Red crystals suitable for X-ray diffractometry were obtained in pentane/toluene = 15/1. Selected bond lengths (Å) and angles (deg): C(4)-N(1), 1.157(2); C(2)-C(4), 1.401(3); C(3)-C(2), 1.427(3); N(3)-C(3), 1.289(3); C(1)-C(2), 1.445(3); O(1)-C(1), 1.386(2); N(2)-C(1), 1.278(3); NI(1)-N(1), 1.894(2); NI(1)-P(2), 2.239(1); NI(1)-C(27), 1.899(2); NI(1)-P(1), 2.233(1); N(3)-C(3)-C(2), 123.1(2); C(3)-C(2)-C(1), 125.8(2); C(2)-C(1)-N(2), 132.8(2); C(2)-C(4)-N(1), 178.8(2); N(1)-NI(1)-P(2), 91.00(5); P(2)-NI(1)-C(27), 89.18(6); C(27)-NI(1)-P(1), 89.73(6); P(1)-NI(1)-N(1), 90.13(5); N(1)-NI(1)-C(27), 179.1(1); P(2)-NI(1)-P(1), 177.4(2).

To my knowledge, no examples of any similar complex have been found in literature so far: other potential N,N- and N,O-chelating compounds were published, which bear a nitrile function at their backbone, but they are always reported to coordinate to the metal centre as bidentate chelating ligands[49] and not as monodentate.

The ligand **35a**, similar to **35b**, produced an equivalent complex (Figure 3.8.2.).

It must be noted that the compounds **35a**,**b** when reacting with $ZnEt_2$ and acetic acid origin chelated zinc(II) complexes[50] that are active in the co-polymerisation of epoxide and CO_2.

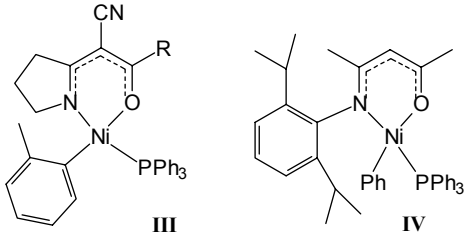
The 3-aminoacrylates **28a**,**e** behaved in the same manner as the corresponding imino ligands **35** when reacting to nickel(II), and gave analogous complexes (Scheme 3.8.2.). Conversely, under similar reaction conditions, the 3-aminoacrylates **28b-d** by releasing the phosphine ligand provided the formerly expected chelating complexes, where the nickel atom was bonded to the amide-nitrogen and the carboxylate-oxygen. The different ligands yielded the mentioned complexes in a definite and reproducible manner.



	28/46a	28/46e	28/47b	28/47c	28/47d
R¹	H	$CH(CH_3)_2$	H	CH_3	CH_2CH_3
R²	CH_3	H	OCH_3	H	H

Scheme 3.8.2. Syntheses of the nickel(II) complexes **46** and **47**.

Crystals of the complexes **47b-d** could be obtained and their structure was revealed by X-ray diffractometry (Figures 3.8.3. and 3.8.4.). The nickel(II) complex **47b** coordinates in an equivalent way as the reported **III**[49b] and **IV**[51]. The triphenylphosphine ligand occupies the *trans*-position to the coordinated nitrogen atom, while the mesityl group attached to the nickel centre is bound in *trans*-position to the oxygen. The Ni-O, Ni-N, Ni-C, and Ni-P



distances in complex **47b** are similar to those of known nickel complexes[49,51-52].

In the complex **47b**, the bond lengths between nickel and the nitrogen atom and between nickel and the oxygen atom in the molecule are 1.947(3) and 1.940(3) Å, respectively, and therefore almost identical within the standard deviation range. The same holds for the carbon-carbon distances in the metallacycle, that amount to C(1)-C(2) 1.399(5) and C(2)-C(3) 1.410(5) Å. The nickel-phosphorus distance is 2.188(1), while the nickel-carbon bond length measures 1.892(4) Å; both distances are markedly shorter than in the complexes binding two triphenylphosphines. In the complex **47b**, the bite angle O(1)-Ni-N(1) is 92.0(1)°. The metallacycle is planar and the metal centre shows a distorted square-planar surrounding with the angles of the four ligands totalling 360.8°; the angles N(1)-Ni-P(1) and O(1)-Ni-C(14) are 171.7(1) and 171.7(2)°, respectively. The plane of the mesityl ring is oriented almost perpendicularly to the metallacycle plane, the dihedral angle being 80.4°.

Attempts to crystallise complexes **46a**,**e** were not successful, but their structure can be nonetheless determined. The ESI mass spectra of **45a**,**b** - whose crystal structures were unambiguously determined (Figures 3.8.1. and 3.8.2.) - and **46a**,**e** clearly showed the molecular peak corresponding to the complex bearing two triphenylphosphines $[(PPh_3)_2Ni(Mes)L]$, while such peak was always absent in the case of compounds **47b-d** $[(PPh_3)Ni(Mes)L]$, where the molecular peak indicated the presence of only one triphenylphosphine.

Furthermore, ^1H NMR and IR spectra were measured. In the region 2198-2207 cm^{-1}, IR spectra of complexes **45a**,**b** and **46a**,**e** showed a weaker absorption band for the C≡N bond, compared with the complexes **47b-d** and **27f** which, on the other hand, exhibited strong absorptions in the range of 2173-2204 cm^{-1}.

Finally, the structure of complexes **46a**,**e** was confirmed by their behaviour in oligomerisation catalysis, since they showed catalytic properties similar to the procatalysts **45a**,**b**, while the complexes **47b-d** behaved differently (vide infra, Chapter 3.11.).

Even though compounds **28a-e** are very similar to each other, they yield different complexes under the same reaction conditions. A factor which may explain this behaviour is the fact that the stability of the complexes binding one or two triphenylphosphines is significantly influenced by small changes in the ligand structures, the energy levels corresponding to the two possible structures being very close to each other. In case of the anionic ligands derived from **35a**,**b** and **28a**,**e**, the form $[(PPh_3)_2Ni(Mes)L]$ is, therefore, more stable, whereas in the case of **28b-d**, the form $[(PPh_3)Ni(Mes)L]$ is favoured. Neither

transformations of the complexes $[(PPh_3)_2Ni(Mes)L]$ in $[(PPh_3)Ni(Mes)L]$ through release of triphenylphosphine were observed under the investigated conditions, nor the reverse reaction in the presence of an excess of phosphine.

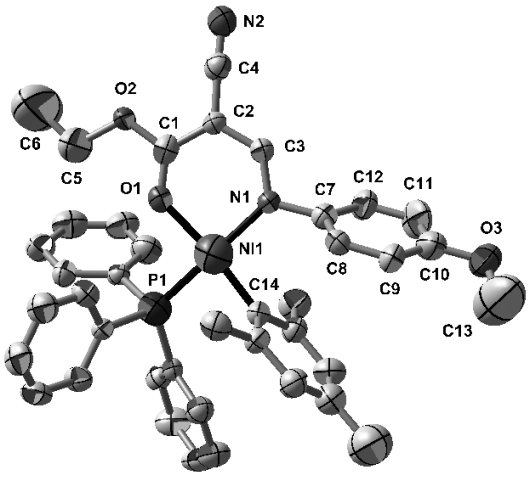


Figure 3.8.3. Crystal structure of the nickel(II) complex **47b**. Red crystals suitable for X-ray diffractometry were obtained in hexane/pentane/toluene = 3/1/1. Selected bond lengths (Å) and angles (deg): C(1)-O(1), 1.254(5); C(1)-C(2), 1.399(5); C(2)-C(3), 1.410(5); C(3)-N(1), 1.313(4); NI(1)-O(1), 1.940(3); NI(1)-N(1), 1.947(3); NI(1)-C(14), 1.892(4); NI(1)-P(1), 2.188(1); O(1)-C(1)-C(2), 125.1(4); C(1)-C(2)-C(3), 121.8(4); C(2)-C(3)-N(1), 128.2(4); O(1)-NI(1)-N(1), 92.0(1); N(1)-NI(1)-C(14), 93.8(1); C(14)-NI(1)-P(1), 88.0(1); P(1)-NI(1)-O(1), 87.0(1); O(1)-NI(1)-C(14), 171.7(2); P(1)-NI(1)-N(1), 171.7(1).

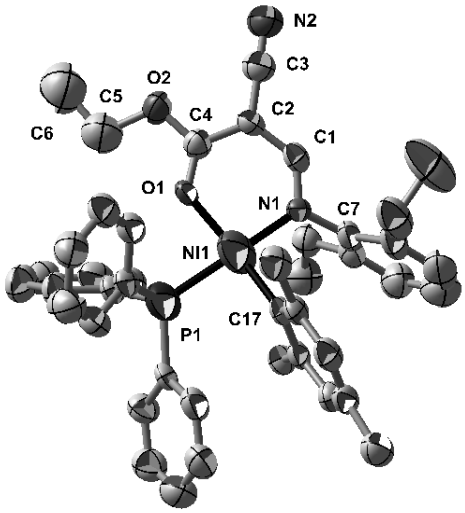


Figure 3.8.4. Crystal structure of the nickel(II) complex **47d**. Red crystals suitable for X-ray diffractometry were obtained in pentane/toluene = 8/1. Selected bond lengths (Å) and angles (deg): C(4)-O(1), 1.244(5); C(2)-C(4), 1.404(6); C(1)-C(2), 1.406(6); N(1)-C(1), 1.309(5); NI(1)-O(1), 1.941(3); NI(1)-N(1), 1.936(4); NI(1)-C(17), 1.904(4); NI(1)-P(1), 2.185(2); O(1)-C(4)-C(2), 124.9(4); C(4)-C(2)-C(1), 121.0(4); C(2)-C(1)-N(1), 127.8(4); N(1)-NI(1)-O(1), 91.3(1); O(1)-NI(1)-P(1), 86.4(1); P(1)-NI(1)-C(17), 88.4(1); C(17)-NI(1)-N(1), 94.7(2); N(1)-NI(1)-P(1), 173.2(1); O(1)-NI(1)-C(17), 169.9(2).

Complexes **47b-d** are not stable in solution for a long time. For example, complex **47c** was dissolved in pentane/hexane/toluene = 10/2/1 and, within a few days, red crystals of **47c** grew. After one month, they slowly disappeared and were replaced by pale turquoise crystals of **47'c** (Figure3.8.5.): the mesityl group had reacted with the electrophilic carbon atom of the nitrile group of another ligand molecule, thus giving rise to a new N,N-bidentate ligand, through a Grignard analogous reaction.

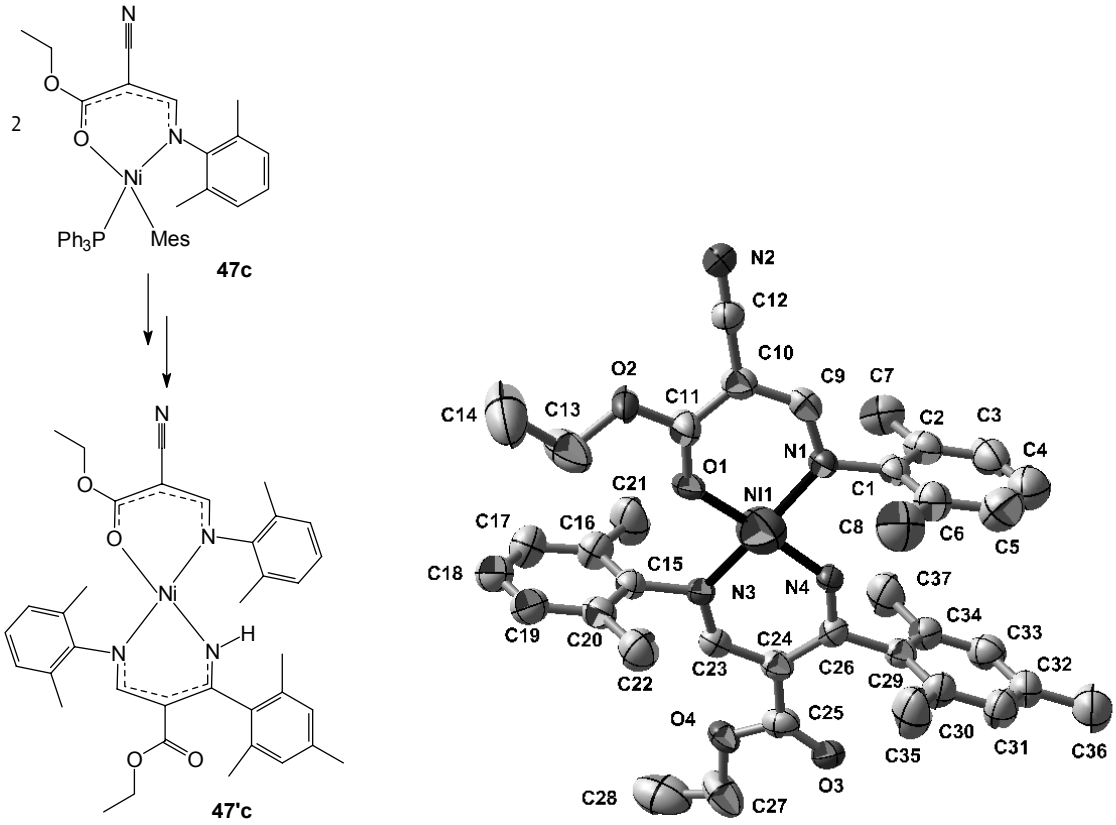
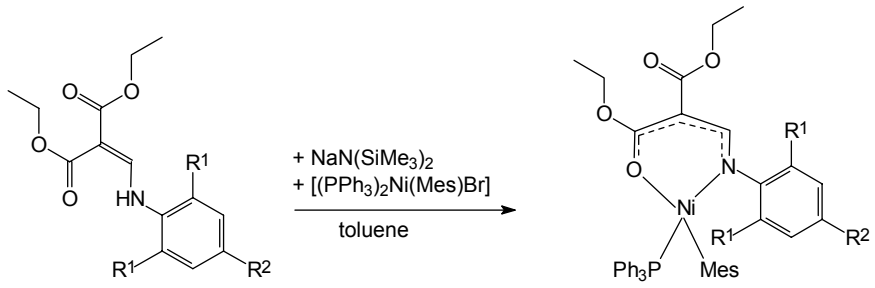


Figure 3.8.5. Crystal structure of the nickel(II) complex **47'c**. Green crystals formed in pentane/hexane/toluene= 10/2/1. Selected bond lengths (Å) and angles (deg): O(1)-C(11), 1.255(2); C(10)-C(11), 1.404(2); C(9)-C(10), 1.405(2); N(1)-C(9), 1.314(2); O(3)-C(25), 1.206(2); C(24)-C(25), 1.466(2); C(23)-C(24), 1.404(2); N(3)-C(23), 1.321(2); C(26)-C(24), 1.410(2); N(4)-C(26), 1.317(2); NI(1)-N(3), 1.891(1); NI(1)-N(4), 1.831(1); NI(1)-N(1), 1.930(1); NI(1)-O(1), 1.881(1); N(1)-NI(1)-O(1), 91.63(5); N(4)-NI(1)-N(3), 90.38(5); N(3)-NI(1)-O(1), 87.90(5); N(4)-NI(1)-N(1), 90.38(5); N(1)-NI(1)-N(3), 176.0(1); O(1)-NI(1)-N(4), 175.4(1).

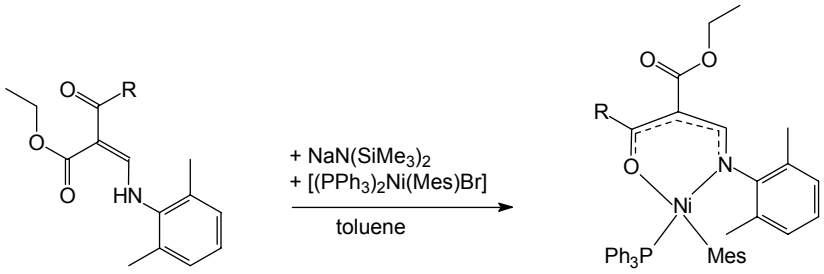
In the case of the anionic ligands derived from **29**, **31**, and **37**, the molecule does not contain any other good coordinating functions which could bind to the nickel ion like the cyano-group does: for this reason, only chelate complexes were obtained. In case of the nickel(II) complexes **49**, the anionic ligand coordinates through the keto-function, because this oxygen atom has a stronger nucleophilic character than the ester one[35c].



29a-c **48a-c**

	29/48a	**29/48b**	**29/48c**
R^1	H	CH_2CH_3	$CH(CH_3)_2$
R^2	CH_3	H	H

Scheme 3.8.3. Synthesis of the nickel(II) complexes **48**.



31a,b **49a,b**

	31/49a	**31/49b**
R	CH_3	*n*-C_3H_7

Scheme 3.8.4. Synthesis of the nickel(II) complexes **49**.

The complexes **49** have the same kind of structure as **47**.

In the complex **49b**, the triphenylphosphine occupies the *trans*-position to the coordinating nitrogen atom, while the mesityl group attached to Ni is bound in *trans*-position to the oxygen of the ketone group. The Ni-O, Ni-N, Ni-C and Ni-P distances in complex **49b** are slightly shorter than in the nickel complexes **47b**.

In the complex **49b**, the bond lengths between nickel and the nitrogen atom and between nickel and the oxygen atom within the molecule are 1.909(6) and 1.915(5) Å, respectively, and, hence, almost identical within the standard deviation range. The carbon-carbon distances in the metallacycle are 1.446(10) and 1.391(11) Å for C(1)-C(2) and C(2)-C(3), respectively. The nickel-phosphorus distance is 2.184(3), while the nickel-carbon bond length measures 1.882(7) Å. In the complex **49b**, the bite angle O(1)-Ni-N(1) is 90.4(2)°. The metallacycle is planar and the metal centre shows a distorted square-planar

surrounding with the angles of the four ligands totalling 360.5°; the angles N(1)-Ni-P(1) and O(1)-Ni-C(14) amount to 176.6(2) and 171.0(3)°, respectively. The plane of the mesityl ring is oriented perpendicularly to the metallacycle plane, the dihedral angle being 90.0°.

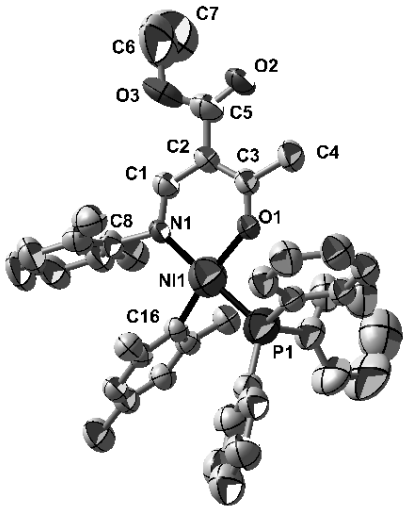


Figure 3.8.6. Crystal structure of the nickel(II) complex **49a**. Red crystals suitable for X-ray diffractometry were obtained in pentane/hexane/toluene = 10/2/1. Selected bond lengths (Å) and angles (deg): C(1)-N(1), 1.309(2); C(2)-C(1), 1.420(2); C(3)-C(2), 1.395(3); O(1)-C(3), 1.271(2); NI(1)-N(1), 1.937(2); O(1)-NI(1), 1.901(1); P(1)-NI(1), 2.190(1); C(16)-NI(1), 1.903(2); N(1)-NI(1)-O(1), 90.55(6); O(1)-NI(1)-P(1), 86.41(4); P(1)-NI(1)-C(16), 88.24(5); C(16)-NI(1)-N(1), 95.48(6); N(1)-NI(1)-P(1), 174.0(1); C(16)-NI(1)-O(1), 170.3(1).

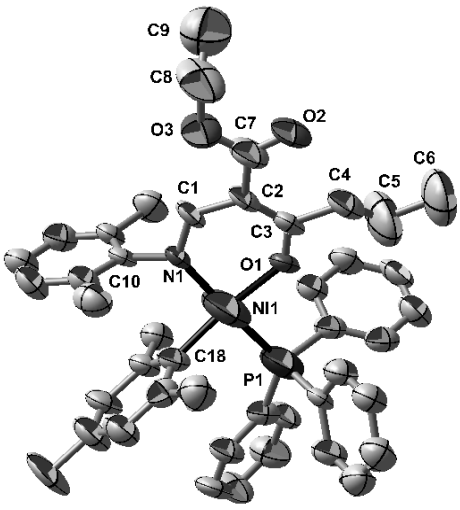
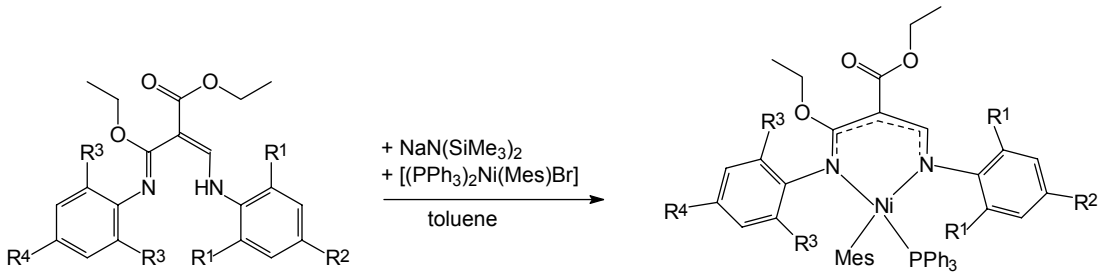


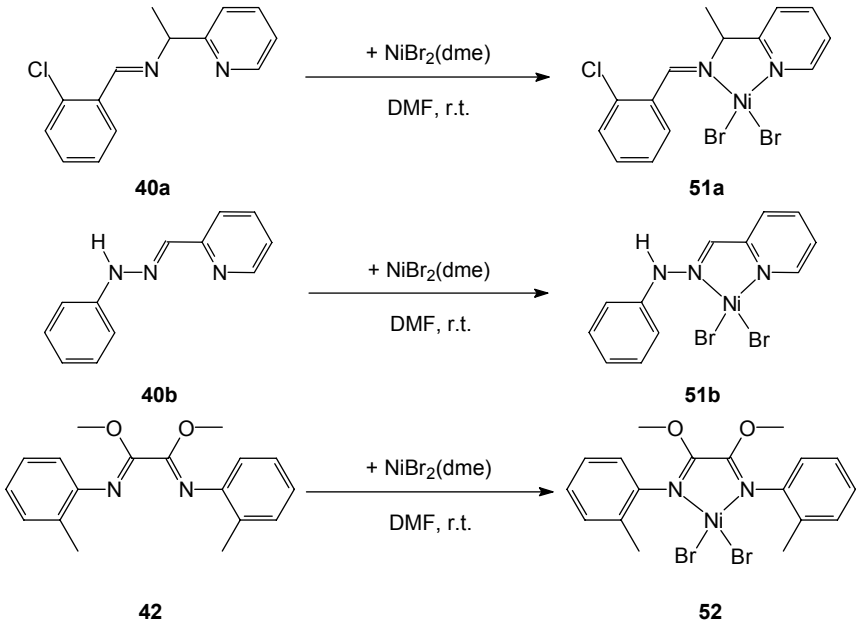
Figure 3.8.7. Crystal structure of the nickel(II) complex **49b**. Red crystals suitable for X-ray diffractometry were obtained in pentane/toluene = 7/1. Selected bond lengths (Å) and angles (deg): C(1)-N(1), 1.327(9); C(2)-C(1), 1.446(10); C(3)-C(2), 1.391(11); O(1)-C(3), 1.270(9); NI(1)-N(1), 1.909(6); NI(1)-O(1), 1.915(5); NI(1)-P(1), 2.184(3); NI(1)-C(18), 1.882(7); N(1)-NI(1)-O(1), 90.4(2); O(1)-NI(1)-P(1), 88.1(2); P(1)-NI(1)-C(18), 89.0(2); C(18)-NI(1)-N(1), 93.0(3); N(1)-NI(1)-P(1), 176.6(2); C(18)-NI(1)-O(1), 171.0(3).



37a-e **50a-e**

	37/50a	**37/50b**	**37/50c**	**37/50d**	**37/50e**
R^1	CH_3	$CH(CH_3)_2$	CH_2CH_3	H	CH_3
R^2	H	H	H	CH_3	H
R^3	CH_3	$CH(CH_3)_2$	H	CH_3	$CH(CH_3)_2$
R^4	H	H	CH_3	H	H

Scheme 3.8.5. Synthesis of the nickel(II) complexes **50**.

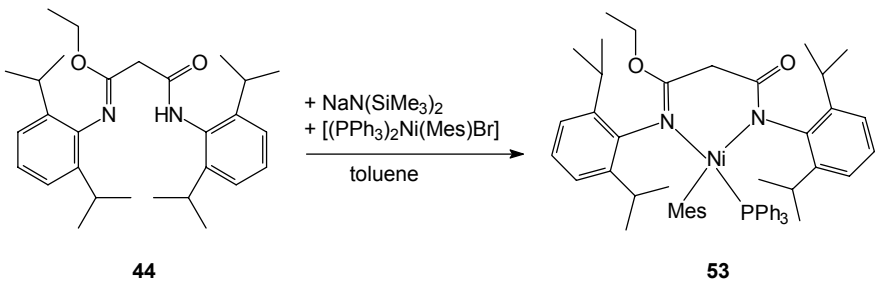


40a **51a**

40b **51b**

42 **52**

Scheme 3.8.5. Syntheses of the nickel(II) complexes **51** and **52**.



44 **53**

Scheme 3.8.6. Synthesis of the nickel(II) complex **53**.

Complexes **50a**,**e** and **53** were prepared analogously to the anionic ligands described above, by reaction of their anions with $[(PPh_3)_2Ni(Mes)Br]$ (Schemes 3.8.5. and 3.8.6.).

Finally, complexes **51** and **52** were obtained from the neutral ligands **40** and **42**, respectively, by a simple reaction with $NiBr_2(dme)$ in DMF at room temperature (Scheme 3.8.5.).

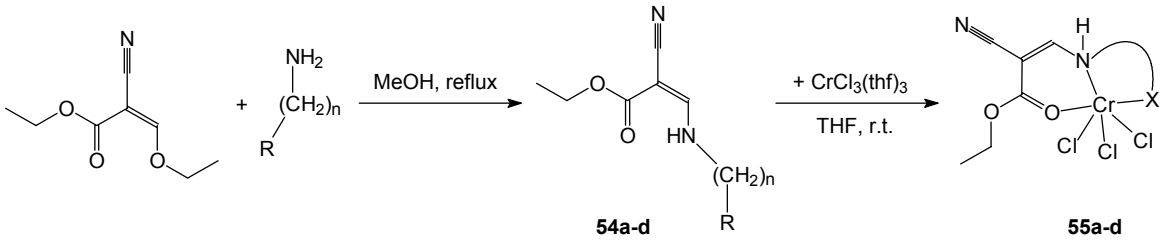
While the complexes **51b** and **53** are greenish-yellow and yellow, respectively, and approximately square-planar, the complexes **51a** and **52** are dark green and pale blue, respectively, and consistently tetrahedral and paramagnetic, as was confirmed by NMR measurements.

3.9. Tridentate 3-aminoacrylate ligands and their chromium complexes

At last, a set of tridentate aminoacrylate ligands was prepared, which bear different heteroatoms as third coordinating function.

The compounds **54a-d** were synthesised using the same method than the one employed for the aminoacrylates **28** described in Chapter 3.5.: ethyl (ethoxymethylene)cyanoacetate was subjected to a reaction with the suitable amines in refluxing methanol (Scheme 3.9.1.).

The resulting tridentate N,N,O-, P,N,O-, and S,N,O- ligands successively reacted with $CrCl_3(thf)_3$ in tetrahydrofuran at room temperature to produce the chromium complexes **55a-d** which were tested as catalysts for olefin oligomerisation.



	54a	54b	54c	54d
n	1	2	2	2
R			PPh_2	SEt

Scheme 3.9.1. Synthesis of the ligands **54** and their chromium complexes **55**.

3.10. Catalytic ethylene oligomerisation with iron and chromium complexes

All iron and chromium complexes described in the previous sections were tested for ethylene oligomerisation in the presence of MAO as co-catalyst (Table 3.10.1.).

Iron(II) complexes **4**-**7** are active compounds in combination with the co-catalyst MAO in the ethylene oligomerisation. The reaction temperature rises in all catalytic experiments with **4**-**7**. Catalytic activity decreases or completely stops when the reaction vessel is cooled and kept at room temperature during the reaction.

The products of these oligomerisation attempts are mainly dimers, trimers, and tetramers, with approximately 90% of the product being in the range of C_4-C_8 (at 3 bar pressure). Mostly hexenes are formed with the procatalysts **4**, **5b**, and **6**, while butenes predominate when using the diacetyl-monoiminopyridyl complex **7** and 2,6-bis(imino)pyridyl complex **5a** (Table 3.10.2., Figures 3.10.1. and 3.10.2.).

The distribution of oligomers obtained in the catalysed ethylene oligomerisation with **4**-**7** follows Schulz-Flory rules for oligomers $C_{>4}$, which are characterised by the constant[8,53] α representing the probability of chain propagation:

α = rate of propagation/[(rate of propagation) + (rate of chain transfer)] =

= (moles of C_{n+2}) / (moles of C_n)

The α value can be determined by the molar ratio of the C_{12} and C_{14} fractions (Figure 3.10.3.); the α values obtained for the catalytic oligomerisation runs with **4**, **5**, **6**, and **7** range between 0.30 and 0.39. Pressure changes hardly affect the α values (runs 3, 5), which is in agreement with previous observations in other 2,6-bis(imino)pyridyl complexes[2,11]. All α values found in the catalytic runs 1-9 are much lower than those reported for ethylene oligomerisation catalysed by the *o*-monoalkyl-substituted iron complexes[2,11] (which reach α values of 0.70-0.85). This can be explained by the absence of any substituent at the *o*-position of the aryl rings in our iron complexes **4**-**7**. In fact, α was reported to range from 0.33 to 0.34 for *o*-fluoro substituted 2,6-bis(imino)pyridines, which is in line with the results of our catalyst precursors due to the small size of the fluoro group.

The unsubstituted iron(II) procatalyst **4** provides for one of the highest turnover numbers of all catalysts tested, but it shows a poor selectivity in the production of α-olefins.

The main effect of the *m*-substituents (both methoxy **5b** and trifluoromethyl **6b**) on the catalysis consists in a slight decrease in the catalytic activity (runs 1, 4, and 7) compared to the unsubstituted 2,6-bis(imino)pyridyl complex **4**. This is associated with a parallel small

improvement in the *α*-olefin selectivity, which nevertheless remains quite low. Conversely, the influence of the different substituents apparently is significantly stronger in the *para*- than in the *meta*-position.

Table 3.10.1. Results of oligomerisation of ethylene with iron and chromium catalysts.

No.	Cat[a]	Loading (µmol)	Time (h)	*p* (bar)	*T* (°C)	Solvent	Yield (g)[b]	TON (x 10^3)	TOF (x 10^3/h)	α	% *α*-olefins[b]
1	**4**	10	2	3	22-75	toluene	11.4	40.8	20.4	0.36	28
2	**5a**	10	2.5	3	22-60	toluene	1.0	3.7	1.5	0.39	77
3	**5a**	10	1	30	22-60	toluene	0.3	0.89	0.89	0.30	88
4	**5b**	10	2.5	3	22-75	toluene	12.0	43.0	17.2	0.39	29
5	**5b**	10	1.2	30	25-100	toluene	9.9	35.5	29.6	0.35	82
6	**6a**	10	2	3	22-75	toluene	7.8	27.9	13.9	0.36	27
7	**6b**	9.3	2.5	3	22-75	toluene	9.3	35.8	14.3	0.30	36
8	**7**	10	2.75	3	22-70	toluene	2.5	9.0	3.3	0.39	77
9	**7**	10	1.5	30	22-70	toluene	10.5	37.3	24.9	0.36	82
10	**12a**	10	1	3	22	toluene	—	—	—	—	—
11	**12b**	10	1	3	22	toluene	—	—	—	—	—
12	**12c**	10	1	3	22	toluene	—	—	—	—	—
13	**12d**	10	1	3	22	toluene	—	—	—	—	—
14	**12d**	10	1	30	24-30	toluene	0.006	0.02	0.02	0.27	100
15	**12d**	10	1	20	70	toluene	—	—	—	—	—
16	**12e**	10	1	3	22	toluene	—	—	—	—	—
17	**12f**	10	1	3	22	toluene	—	—	—	—	—
18	**12g**	10	1	3	22	toluene	—	—	—	—	—
19	**12h**	10	1	3	22	toluene	—	—	—	—	—
20	**14a**	10	1	3	22	toluene	—	—	—	—	—
21	**14b**	10	1	3	22	toluene	—	—	—	—	—
22	**14c**	10	1	3	22	toluene	—	—	—	—	—
23	**14d**	10	1	30	28-34	toluene	0.28	0.98	0.98	—	100
24	**14d**	10	1	20	70	toluene	0.06	0.23	0.23	—	100
25	**17a**	10	1	30	22	toluene	—	—	—	—	—
26	**17b**	10	1	30	22-30	toluene	0.5	1.9	1.9	0.51	99
27	**17c**	10	1	30	22-30	toluene	1.8	6.4	6.4	0.42	99
28	**26c**	1.5	1	1	22	toluene	—	—	—	—	—
29	**27a**	10	1	30	25	toluene	—	—	—	—	—
30	**55a**	10	1	30	22	toluene	—	—	—	—	—
31	**55b**	10	1	30	22	toluene	—	—	—	—	—
32	**55c**	10	1	30	23-29	toluene	—	—	—	—	—
33	**55d**	10	1	30	22	toluene	—	—	—	—	—

[a] All procatalysts were first dissolved in 30 ml of solvent in an ultrasonic bath and then activated with approximately 100 eq MAO (0.6 ml of a 10 wt% MAO solution in toluene). [b] The yield and the 1-olefin content of C_4-C_{18} were determined by GC using calibration curves with standard solutions.

A substantial dissimilarity in the behaviour of methoxy- and trifluoromethyl-substituted ligands is observed for the catalyst precursors **5a** and **6a**, where the aryl rings bear the functional groups at the *para*-position. The activity of the *p*-trifluoromethyl-substituted catalyst **6a** is far higher than that of the *p*-methoxy-substituted one (runs 2 and 6). In this case, too, a decrease in the catalytic activity corresponds to an increase in the selectivity for α-olefins, the best selectivity being reached by **5a** (77%).

Table 3.10.2. Yield (%) of oligomers in the experiments with catalyst precursors **4**-**7** at 3 bar.

Fraction (%)	1	2	4	6	7	8
C_4	27.6	51.4	26.8	31.3	35.2	49.3
C_6	45.4	31.1	45.2	41.2	42.3	31.0
C_8	16.2	11.8	16.1	15.4	13.7	12.8
C_{10}	7.2	4.0	7.4	7.6	6.0	4.6
C_{12}	2.5	1.2	2.8	3.0	2.2	1.4
C_{14}	1.0	0.5	1.1	1.1	0.5	0.6
C_{16}	0.3	0.1	0.4	0.3	0.1	0.2
C_{18}	—	—	0.1	0.1	—	0.1

Table 3.10.3. Yield (%) of oligomers in the experiments with catalyst precursors **4**-**7**, **12d**, and **14d** at 30 bar.

Fraction (%)	3	5	9	14	23	24
C_4	51.9	61.6	46.7	78.5	78.7	55.5
C_6	41.2	31.2	35.3	21.5	11.6	27.2
C_8	5.5	5.9	12.4	—	9.7	17.3
C_{10}	0.9	1.0	3.4	—	—	—
C_{12}	0.3	0.2	1.4	—	—	—
C_{14}	0.1	0.1	0.5	—	—	—
C_{16}	0.03	—	0.2	—	—	—
C_{18}	—	—	0.1	—		

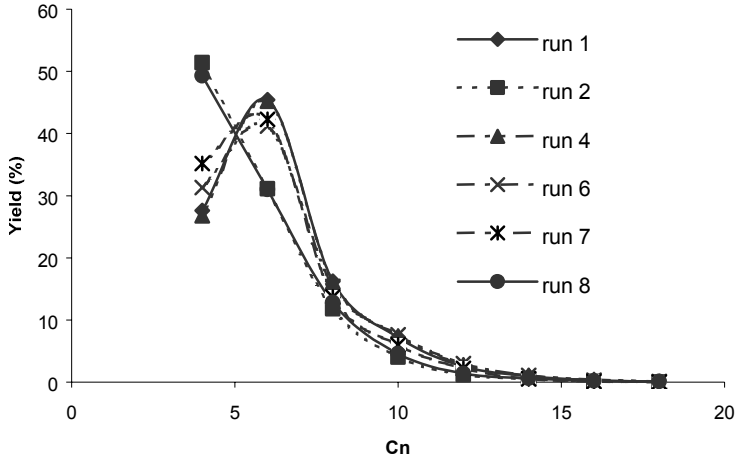


Figure 3.10.1. Oligomer distribution for catalyst precursors **4**-**7** at 3 bar: yield of each oligomer fraction vs. carbon number.

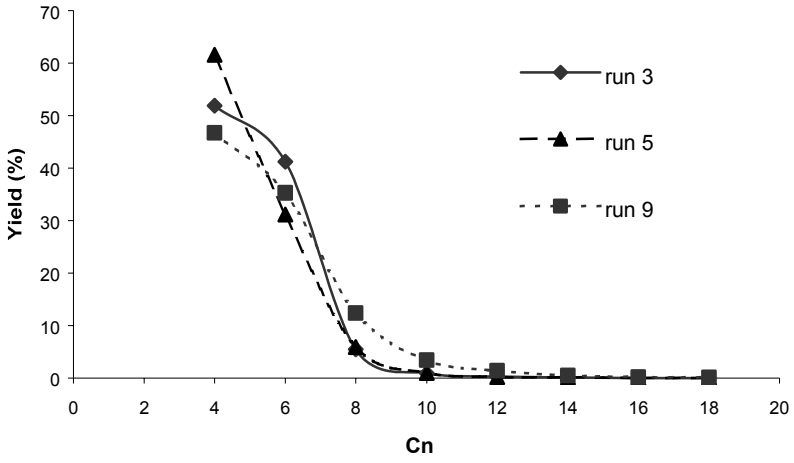


Figure 3.10.2. Oligomer distribution for catalyst precursors **4-7** at 30 bar: yield of each oligomer fraction vs. carbon number.

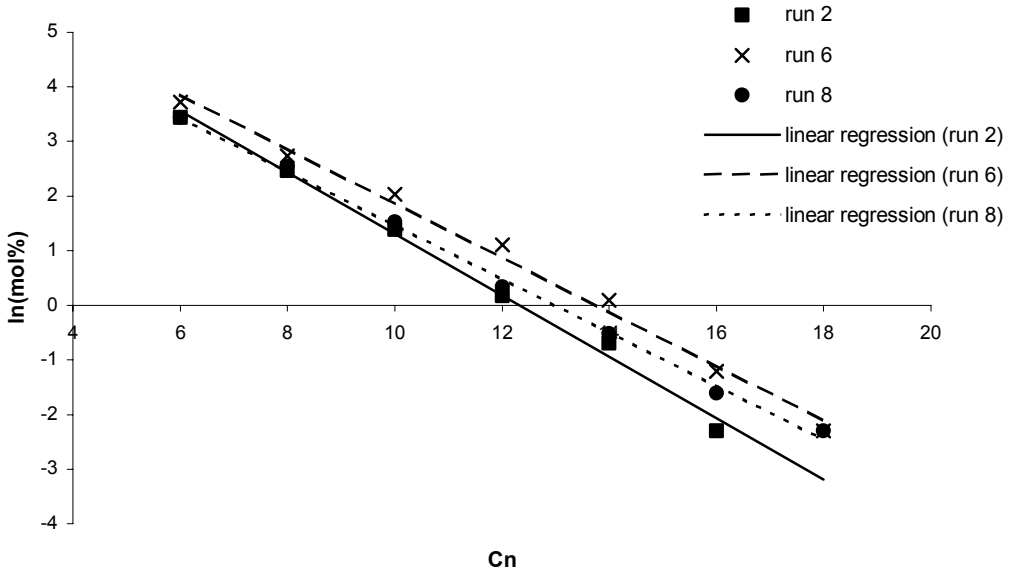


Figure 3.10.3. Schulz-Flory distribution for catalyst precursors **4-7** at 3 bars: ln mol% of each fraction vs. carbon number.

The *m*-trifluoromethyl-substituted 2,6-diacetyl-monoiminopyridyl complex **7** (run 8) exhibits a lower catalytic activity than the analogous 2,6-bis(imino)pyridyl **6b**. This behaviour might probably be explained by the reduced steric bulk at one side of the complex, and the different electronic properties of the ketone in the ligand backbone, that differ from those of to the arylimino-group.

None of the above catalysts **4-7** produced branched isomers, but only linear olefins due to the absence of chain-running during the oligomerisation reaction.

Olefins ranging from C_4-C_{18} are produced in all experiments but turnover numbers vary in the range of 1,000 to 43,000. Additionally, variations of the catalyst ligands, temperature, and pressure significantly influence the α-olefins selectivity and formation of the main olefin species in the products. Complexes **4-7** exhibit small Schultz-Flory α values, thus confirming small chain propagation.

Although the substituted pyridyl backbone is very similar in the 2,6-bis(benzylideneimino)pyridyl complexes **12** and the previously described 2,6-bis(imino)pyridyl complexes **4-6**, reactivity towards olefin oligomerisation appeared to be very different under the same conditions. In fact, complexes **12** show very low or no activity for the oligomerisation of ethylene in the presence of MAO as co-catalyst (Table 3.10.1., runs 10-19). Even the attempts of increasing the steric hindrance of the substituents in the aryl groups (complexes **12f-12h**) or of drastically changing the electronic properties of the substituents (complexes **12d**) did not bring about any significant improvement of the catalytic activity. Equally poor performances were obtained with bis(benzylideneimine)amine iron(II) complexes **14**. Only when the catalyses were performed under higher pressure (runs 14 and 23) an extremely small amount of oligomers - mostly butene - was yielded, while an increase in the temperature did not result in any improvement (runs 15 and 24). These results indicate that such iron complexes are not suitable for ethylene oligomerisation.

The findings obtained for the complexes **12** and **14** and from comparison with the formerly reported ethylene polymerisation/oligomerisation catalysts based on tridentate ligand complexes of iron[11-12,23] (Figure 3.2.1., Chapter 3.2.) show that the catalytic activity is probably dependent on the double-bond location in the ligand backbone. It appears that these iron(II) complexes are more active when the coordinating nitrogen atoms are connected through conjugated double bonds and/or are included in aromatic structures: this does not apply to complexes **12-14**.

To the best of our knowledge, only one example of a non-conjugated system applied in ethylene oligomerisation was recently published[54], where iron complexes analogous to **14** were described. In that case, catalyses were performed at temperatures ranging from 120 to 210°C and pressures as high as 18 bar in the presence of EAO as co-catalyst, the activity of the catalyst precursors turning out only very low to moderate. This is in line with the results of our catalytic tests.

Table 3.10.4. Yield (%) of oligomers in the experiments 26-27.

Fraction (%)	26	27
C_4	87.4	95.3
C_6	8.1	4.2
C_8	2.6	0.5
C_{10}	1.1	0.05
C_{12}	0.5	0.02
C_{14}	0.3	—

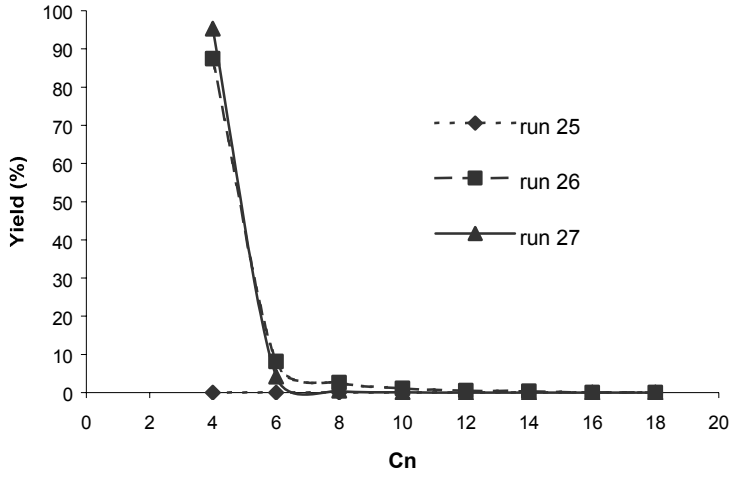


Figure 3.8.4. Oligomer distribution in experiments 25-27: yield of each oligomer fraction vs. carbon number.

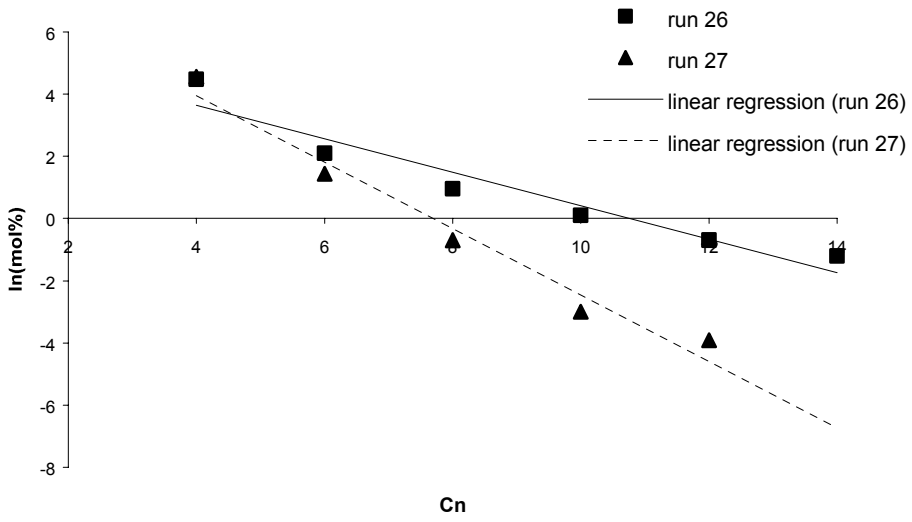


Figure 3.10.5. Oligomer distribution in experiments 25-27: ln mol% of each fraction vs. carbon number.

However, the presence of conjugated double bonds in the ligand backbone is not sufficient to ensure a good activity in the ethylene oligomerisation process: in fact, imidazo[1,5-*a*]pyridine iron(II) complexes **26c** and **27a** were observed to be inactive under the test conditions (runs 28 and 29). The electronic characteristics of the aromatic hetero-bicycle likely play an important role in determining the catalytic properties.

The last class of ethylene polymerisation catalysts tested is based on P,N,N-tridentate ligand complexes of iron(II): the catalytic activity of the iminophosphine-based catalyst precursors **17** correlates with the bulk of the substituent at the picolylamine backbone (Table 3.10.1., runs 25-27). The complex **17a** which does not bear any substituent does not exhibit any activity for ethylene oligomerisation under the tested conditions, while the methyl-substituted **17b** and phenyl-substituted **17c** are active. And indeed, the larger is the substituent at the backbone, the higher is the activity of the catalyst. To a certain extent, oligomer yields are lower than in the case of 2,6-bis(imino)pyridyl catalysts **4-6**, but the selectivity is definitely higher, the catalysts **17** giving up to 99% α-olefins.

Complexes **17b**,**c** mainly dimerise ethylene, yielding about 90% C_4 and only small amounts of heavier fractions (Table 3.10.4., Figure 3.10.4.). The oligomer distribution slightly deviates from the Schulz-Flory distribution (Figure 3.10.5.).

The chromium complexes **55** were intended to be used as ethylene trimerisation catalyst precursors in analogy with Wasserscheid's trimerisation chromium(III) catalysts based on heterodonor tridentate P,N,P- and S,N,S-ligands[14]. However, all complexes **55** were inactive and did not produce any oligomers under the test conditions.

3.11. Catalytic ethylene oligomerisation with nickel complexes

All nickel(II) complexes described in Chapters 3.4. and 3.8. were tested for the oligomerisation of ethylene (Tables 3.11.1. and 3.11.2.).

All complexes that bind ligands containing one or two imidazo[1,5-*a*]pyridine groups were found to be inactive for the catalysis (Table 3.11.1., runs 1-10) in the presence of both MAO or EASC as co-catalyst. Even when increasing the pressure from 1 to 30 bar (runs 2, 3, 8-10) catalytic performances were not improved.

Nickel(II) and palladium(II) complexes of α-diimines and 2-iminopyridines have already been reported about as suitable catalysts for ethylene oligomerisation/polymerisation[3,55] to produce oligomers in the range C_4-C_{26} with a low selectivity for both oligomers length and

branching. The bis(imino)oxalate nickel(II) procatalyst **52** is formally analogous to the published α-diimine complexes, but it bears methoxy-groups attached to the imino-backbone instead of the usual alkyl or aryl substituents. The electron-withdrawing methoxy-groups strongly influence the catalytic activity of this procatalyst in the presence of MAO as co-catalyst (Table 3.11.6., entry 39), rendering it largely smaller than that of the previously described α-diimine complexes[3]. The distribution of the produced oligomers is affected, too: in fact, procatalyst **52** was more selective towards the production of short olefins with high selectivity for butenes (89%) at 3 bar ethylene pressure, while only small amounts of C_6-C_8 were formed (10.3%) together with negligible quantities of C_{10}-C_{18}. Higher ethylene pressure had minor effects on the catalyst activity: overall activity was reduced slightly and the percentage of hexenes produced increased (17% vs. 6.5%), while the butenes decreased (78%).

The 2-iminopyridine nickel(II) procatalyst **51a** is active for ethylene oligomerisation when activated with MAO, but both its selectivity for formed oligomers and the *α*-selectivity are low, a broad spectrum of oligomers in the range of C_4-C_{26} being obtained (Table 3.11.5., entry 36). The oligomer distribution obtained in the oligomerisation catalysis with **51a** follows Schulz-Flory rules[3,53] for oligomers higher than C_4, which can be characterised by the constant α (see Chapter 3.10.). In this case, oligomers with a higher molecular weight are obtained and, in fact, α has a value as high as 0.80.

Table 3.11.1. Results of oligomerisation of ethylene with nickel(II) catalysts.

No.	Cat[a]	Loading (μmol)	Cocat.	Time (h)	*p* (bar)	*T* (°C)	Solvent	Yield (g)	TON (x 10^3)	TOF (x 10^3/h)	A[b]	% *n*-olefins[b]	% *iso*-olefins[b]
1	**26a**	1.5	MAO	1	1	22	toluene	—	—	—	—	—	—
2	**26a**	10	EASC	1.25	30	27-32	toluene	—	—	—	—	—	—
3	**26b**	10	EASC	1	30	25-64	toluene	—	—	—	—	—	—
4	**27b**	10	MAO	1	1	22	toluene	—	—	—	—	—	—
5	**27c**	1.5	MAO	1	1	22	toluene	—	—	—	—	—	—
6	**27d**	1.5	MAO	1	1	22	toluene	—	—	—	—	—	—
7	**27e**	10	MAO	1	1	22	toluene	—	—	—	—	—	—
8	**27e**	10	EASC	1	30	25-62	toluene	—	—	—	—	—	—
9	**27f**	10	MAO	1	30	25-31	toluene	—	—	—	—	—	—
10	**27f**	10	EASC	1	30	25-62	toluene	—	—	—	—	—	—

[a] All procatalysts were dissolved in 30 ml of the specified solvent and then activated either with 100 eq of MAO (0.6 ml of a 10 wt% MAO solution in toluene) or with 300 eq of EASC (3.3 ml of a 25 wt% solution in toluene). [b] α is the probability of chain propagation

Table 3.11.2. Results of the oligomerisation of ethylene with nickel(II) catalysts.

No.	Cat[a]	Loading (µmol)	Cocat.	Time (h)	*p* (bar)	*T* (°C)	Solvent	Yield (g)[b]	TON (x 10^3)	TOF (x 10^3/h)	α[c]	% *n*-olefins[b]	% *iso*-olefins[b]
11	**45a**	10	MAO	1	30	25-33	toluene	0.65	2.33	2.33	—	71	29
12	**45b**	10	—	1	30	25	toluene	0.08	0.29	0.29	—	43	57
13	**45b**	10	MAO	1	30	25-45	toluene	6.46	23.06	23.06	0.04	27	73
14	**45b**	10	EASC	1	30	25-74	toluene	—	—	—	—	—	—
15	**46a**	10	MAO	0.5	30	23-35	toluene	1.88	6.7	13.41	0.04	27	73
16	**46e**	10	MAO	1	30	22-25	toluene	31.80	113.49	113.49	0.11	22	78
17	**47b**	14	MAO	1	30	23-28	toluene	—	—	—	—	—	—
18	**47b**	10	EASC	1	30	25-70	toluene	—	—	—	—	—	—
19	**47c**	10	MAO	1	30	25-31	toluene	—	—	—	—	—	—
20	**47c**	10	EASC	1	30	25	toluene	—	—	—	—	—	—
21	**47d**	10	EASC	1	30	25-70	toluene	—	—	—	—	—	—
22	**48a**	10	MAO	1	30	23-42	toluene	7.51	26.79	26.79	—	24	76
23	**48b**	10	MAO	1	30	23	toluene	4.43	15.80	15.80	—	58	42
24	**48c**	10	—	1	30	23-30	toluene	13.06	46.61	46.61	—	30	70
25	**48c**	10	MAO	1	30	23-70	toluene	25.95	92.59	92.59	—	28	72
26	**48c**	10	EASC	1	30	25-72	toluene	—	—	—	—	—	—
27	**49a**	10	MAO	1	30	25-43	toluene	6.78	24.19	24.19	0.08	20	80
28	**49a**	10	EASC	1	30	25-70	toluene	—	—	—	—	—	—
29	**49b**	10	MAO	1	30	25-34	toluene	14.3	50.93	50.93	0.09	24	76
30	**49b**	10	EASC	1	30	25-70	toluene	—	—	—	—	—	—
31	**50a**	10	MAO	1	30	23	toluene	—	—	—	—	—	—
32	**50b**	10	EASC	1	30	25-70	toluene	—	—	—	—	—	—
33	**50c**	10	EASC	1	30	25-70	toluene	—	—	—	—	—	—
34	**50d**	10	EASC	1	30	25-71	toluene	—	—	—	—	—	—
35	**50e**	10	EASC	1	30	25-72	toluene	—	—	—	—	—	—
36	**51a**	10	MAO	1	30	22-30	CH_2Cl_2	2.70	9.53	9.53	0.80	33	67
37	**51b**	10	MAO	1	30	25-30	toluene	—	—	—	—	—	—
38	**51b**	10	EASC	1.5	30	26-32	toluene	1.52	5.43	3.62	—	15	85
39	**52**	10	MAO	4.5	3	22	toluene	0.08	0.28	0.06	0.26	58	42
40	**52**	10	MAO	1	30	22-31	toluene	0.08	0.04	0.04	0.24	40	60
41	**53**	10	MAO	1	24	25-47	toluene	5.8	20.53	20.53	0.11	54	46
42	**53**	10	EASC	1	30	27-70	toluene	—	—	—	—	—	—

[a] All procatalysts were dissolved in 30 ml of the specified solvent, and then activated either with 100 eq of MAO (0.6 ml of a 10 wt% MAO solution in toluene) or 300 eq of EASC (3.3 ml of a 25 wt% solution in toluene). [b] The yield and the olefin content of C_4-C_{26} were determined by GC using calibration curves with standard solutions. [c] α is the probability of chain propagation

The 2-pyridine-2-carboxaldehyde hydrazone nickel(II) complex **51b** represents an additional modification of the widely investigated *α*-diimine catalysts. Complex **51b** was not active in ethylene oligomerisation in the presence of MAO, but it produced olefins in

the range of C_4-C_{10} when activated with EASC at 30 bar ethylene pressure. Dimers and trimers were the prevailing products (46.9% and 48.7%, respectively).

For all procatalysts **51-52**, the α-selectivity is low to moderate (15 to 58%), which is due to their ability of reversibly eliminating *β*-hydrogens after ethylene insertion, reinserting the olefin with the opposite regiochemistry, and, hence, giving isomers after chain transfer or leading to the isomerisation of *α*-olefins by a re-uptake mechanism. The ability of Ni(II) complexes to isomerise *α*-olefins is well known[3].

Procatalysts **45a**,**b** and **46a**,**e** (with the CN-bounded ligands) are effective for ethylene oligomerisation when activated with MAO (runs 11, 13, 15, and 16), mostly yielding dimers. The more sterically hindered **45b** and **46a** are the most active complexes of this group, thus indicating the importance of bulky substituents at the aryl rings, even if they are relatively distant from the catalytic metal centre. However, the presence of an imidoate group in place of an ester generally undermines the catalytic performances.

The higher the activity is, the lower is the selectivity for the produced olefins; in fact, **45b** (run 13) only yields C_4-C_6 with 95.9% butenes, while **46e** (run 16) gives C_4-C_{10} with 89.1% butenes. The selectivity for *α*-olefins in general is rather poor; in fact, it is only about 25% but reaches 71% in case of the less active **45a**.

The choice of the co-catalyst is important in these catalyses, as shown for the complex **45b** (runs 12-14). In fact, it shows a good catalytic activity in the presence of MAO, whereas it is about 100 times less active in the absence of any co-catalyst. On the other hand, it becomes completely inactive when EASC is used, under the reaction conditions investigated.

Table 3.11.3. Yield (%) of oligomers in the experiments 11-13, 15, 16.

Fraction (%)	11	12	13	15	16
C_4	100	100	95.9	95.9	89.1
C_6	—	—	4.1	4.1	9.9
C_8	—	—	—	—	0.9
C_{10}	—	—	—	—	0.1

Table 3.11.4. Yield (%) of oligomers in the experiments 22-25, 27.

Fraction (%)	22	23	24	25	27
C_4	92.5	100	98.2	89.5	91.7
C_6	6.5	—	1.8	9.5	7.7
C_8	1.0	—	—	1.0	0.6
C_{10}	0.06	—	—	0.04	—
C_{12}	0.02	—	—	—	—
C_{14}	0.01	—	—	—	—

Table 3.11.5. Yield (%) of oligomers in the experiments 29, 36, 38-40.

Fraction (%)	29	36	38	39	40	41
C_4	92.2	9.3	46.9	89.0	78.0	88.7
C_6	7.1	16.7	48.7	6.5	17.0	9.9
C_8	0.7	16.2	3.0	3.8	4.6	1.2
C_{10}	—	11.4	1.4	0.23	0.4	0.14
C_{12}	—	9.5	—	0.16	—	0.03
C_{14}	—	8.4	—	0.15	—	0.01
C_{16}	—	6.4	—	0.10	—	0.01
C_{18}	—	5.2	—	0.07	—	—
C_{20}	—	4.8	—	—	—	—
C_{22}	—	4.5	—	—	—	—
C_{24}	—	4.1	—	—	—	—
C_{26}	—	3.3	—	—	—	—

Complexes **47b-d** as well as **27f** differ from **45-46**, as in the former the ligands are chelate-coordinated and do not bind to the metal via their cyano-group. In this case, the resulting nickel complexes are completely inactive in ethylene oligomerisation, no matter what co-catalyst was used (runs 17-21). The same behaviour was noticed with N,N-chelate complexes **50**.

Though complexes **47** and **48-49** share the same coordinating mode - all of them are N,O-chelates - and have similar structure, they exhibit very different catalytic properties. While **47** are completely inactive, **48-49** can oligomerise ethylene and reach good TOF (Table 3.11.2., runs 17-29). Apparently, the presence of the non coordinating cyano-group in place of an ester acts as an inhibiting factor in the catalysis. The chelate complexes **48a-c** are active when MAO is employed as co-catalyst at 30 bar (runs 22, 23, and 25). The catalyst precursor **48c** which bears the most bulky groups (i.e. *iso*-propyl) at the 2,6-positions of the aryl ring is in his category even the most active for oligomerisation. The main products are dimers ranging from 89.5% for **48c** (C_4-C_{10}) to 100% for **48b** (only C_4). The procatalyst **48a** produces the brightest range of oligomers (C_4-C_{14}), although it is more selective for butenes than **48c** (92.5% vs. 89.5%). Selectivity towards α-olefins again is scanty and varies in the range of 24-58%.

The procatalyst **48c** maintains a good catalytic activity even in the absence of any co-catalyst (run 24), its TOF being just half of the value reached in the presence of MAO (4.7×10^4 h^{-1} vs. 9.3×10^4 h^{-1}). It becomes fully inactive when EASC is employed (run 26).

Structures of the chelate precursors **49a**,**b** are similar to that of **48** illustrated above, but they have a ketone instead of an ester group as coordinative active group. When activated

with MAO, both complexes **49a** and **49b** can oligomerise ethylene to C_4-C_{14} (runs 27 and 29), the main fraction consisting of butenes (92%).

The length of the alkyl chain influences the activity. In fact, the TOF of **49b** which bears a *n*-propyl chain is twice the value of **49a** which just has a methyl group ($5.1x10^4$ h^{-1} vs. $2.4x10^4$ h^{-1}). Selectivities are very similar to each other.

Finally, the amidoiminomalonate complex **53** was tested for ethylene oligomerisation, which is characterised by a different substitution pattern at the ligand backbone and bears an amide and an imidoate function, but no substituents in the middle position of the backbone. This complex shows good performances in the presence of MAO as co-catalyst, yielding oligomers in the range of C_4-C_{16} with prevailing dimers (run 41). Moreover, it possesses one of the best α-selectivities (54%) of all procatalysts tested, although the selectivity for dimerisation is not very satisfactory (88.7%).

In the end, 3-aminoacrylate, 3-aminoiminoacrylate, and amidoiminomalonate nickel(II) complexes form a versatile class of successful ethylene oligomerisation catalysts, where the catalytic properties are though strongly affected by many factors like the coordination mode (as chelate or monodentate ligand), the steric hindrance of the substituents at the aryl rings, electronic characteristics of the functional groups at the backbone (ester, nitrile or simply hydrogen) and the groups sideways to the atoms that coordinate to the metal (ester, ketone or imidoate).

The best results are obtained in the presence of MAO as co-catalyst. The best activity for ethylene oligomerisation is shown by the CN-coordinated 2-cyano-3-aminoacrylate nickel(II) complex **46e** (TOF 1.13 x 10^5 h^{-1}), followed by the chelate ester-substituted 3-aminoacrylate **48c** (TOF 9.3 x 10^4 h^{-1}), while the most selective catalysts for *n*-olefins are the non-chelate 2-cyano-3-aminoiminoacrylate nickel(II) complex **45a** (71%) and the chelate ester-substituted 3-aminoacrylate **48b** (58%).

3.12. Catalytic propylene dimerisation with nickel complexes

Few technical processes are used in the industry for the dimerisation of propylene. The non-regioselective olefin dimerisation[56] (Dimersol, Institut Français du Pétrole), performed in the absence of any phosphine ligand, affords propene dimers with a composition of 22% *n*-hexenes, 72% 2-methylpentenes and 6% 2,3-dimethylbutenes;

dimers form 80% of the oligomers mixture, a small amount of trimers (18%) and tetramers (2%) being produced too. The process works at 50°C under a pressure sufficient to maintain the reactants in the liquid phase. The catalyst results from the interaction of a nickel organic salt, soluble in a paraffinic hydrocarbon solvent, and an ethylaluminium chloro compound; the active species is formed in situ inside the dimerisation reactor.

Regioselective dimerisation of propene to 2,3-dimethylbutenes is currently operated by Sumitomo[57] and BP Chemicals[58] with tricyclohexylphosphine and Ziegler-type catalysts. In the Sumitomo process very high selectivities in 2,3-dimethylbutenes (up to 85%) are obtained at 20-50°C and by using toluene as a solvent. On the other hand, the BP Chemical process operates without any solvent, at lower temperature, and with a simpler catalyst composition, giving a lower selectivity for 2,3-dimethylbutenes.

Some of the nickel(II) complexes described in Chapter 3.8. were also tested for the dimerisation of propylene. The tested procatalysts were not catalytically active when treated with MAO (Table 3.12.1., runs 5, 8, and 14); nevertheless, they exhibited good performances when activated with EASC, with the TOF ranging from 7,500 to 63,000 h^{-1}.

Dependence of the activity on the organoaluminum activator corresponds to what is reported in literature for the dimerisation of propylene by *β*-ketiminate nickel(II) complexes[59] (TOF up to 1.3 x 10^5 h^{-1}).

All catalysts tested behaved in a similar way and the main products generally consisted of dimers, the fraction C_6 always reaching about 85-95% (Tables 3.12.3. to 3.12.5.). The prevailed tendency to dimerisation rather than higher oligomerisation is representative of those nickel catalysts in the activation of olefins because of their strong propensity to *β*-elimination.

Among the dimers, methylpentenes are the main products in most cases (Table 3.12.2.), followed by hexenes. Mostly internal olefins were produced. The GC-spectra of the fractions C_6 usually showed the presence of many different isomers, thus indicating that the catalysts are able to isomerise the olefin produced.

When the propylene pressure was increased, catalytic activity was improved, too (Table 3.12.1., runs 18 and 19). In case of complex **50a**, the higher pressure also influences the ratio of the dimers produced: at lower pressure, the catalyst is more selective for methylpentenes.

Even complexes that were not active in ethylene oligomerisation tests nevertheless provided for good results with propylene. For example, complexes **50a**,**b** were not effective in oligomerising ethylene, but they worked when using propylene and exhibited

rather good TOF ($1.3x10^4$ h^{-1} and $3.7x10^4$ h^{-1}, respectively at 3 bar pressure). The increased steric hindrance of the isopropyl groups at the aryl rings in the procatalyst **50b** provides for an improvement in the catalytic performance, compared to the **50a** which bear less bulky methyl groups. However, **50a** exhibited the highest selectivity for methylpentenes.

Furthermore a comparison between **48c** and **50b** (which both have isopropyl groups at the aryl rings) suggests that the presence of an ester group at the coordinative position inhibits the catalysis. This trend goes in the opposite direction than what was observed in case of ethylene oligomerisation with the same catalysts. An analoguous example can be found in literature, where neutral *β*-ketiminato nickel(II) complexes of general structures [(Ar-N=CH-Ar-O)(PPh_3)(Ph)Ni] or [(Ar-N-C(CH_3)=CH-C(O)CH_3)(PPh_3)(Ph)Ni] are described as good catalysts for norbornene polymerisation in the presence of MMAO, but were inactive when ethylene was used[51].

Table 3.12.1. Results of propylene dimerisation with nickel(II) catalysts.

No.	Cat[a]	Loading (µmol)	Cocat.	Time (h)	*p* (bar)	*T* (°C)	Yield (g)[b]	TON (x 10^3)	TOF (x 10^3/h)
1	**26b**	10	EASC	1	8	25-44	22.0	52.41	52.41
2	**27e**	10	EASC	1	8	26-36	3.1	7.47	7.47
3	**27f**	10	EASC	1.2	9.5	25-43	15.5	36.93	30.77
4	**45a**	10	EASC	1	8	24-36	9.7	23.09	23.09
5	**45b**	10	MAO	1	8	24	—	—	—
6	**45b**	10	EASC	0.8	8	26-52	12.6	30.00	36.15
7	**46a**	10	EASC	1	8	25-49	14.0	33.25	33.25
8	**46e**	10	MAO	1	8	25	—	—	—
9	**46e**	10	EASC	1	8	25-50	7.8	18.56	18.56
10	**47b**	10	EASC	1	8	25	11.8	28.09	28.09
11	**47c**	14	EASC	1	9.5	25-54	23.4	39.76	39.76
12	**47d**	10	EASC	1	8	26-44	19.0	45.25	45.25
13	**48b**	10	EASC	1	8	24-44	8.0	18.93	18.93
14	**48c**	10	MAO	1	8	26	—	—	—
15	**48c**	10	EASC	1	8	25	11.5	27.43	27.43
16	**49a**	10	EASC	1	9.5	25-54	26.5	63.06	63.06
17	**49b**	10	EASC	1	8	26-42	7.7	18.34	18.34
18	**50a**	10	EASC	1	8	27-50	5.4	12.88	12.88
19	**50a**	10	EASC	1	9.5	25-52	17.1	40.73	40.73
20	**50b**	10	EASC	1	8	26-43	15.7	37.41	37.41
21	**53**	10	EASC	1	8	25-50	11.5	27.34	27.34

[a] All procatalysts were first dissolved in 30 ml of toluene in an ultrasonic bath and then activated with 300 eq of EASC (3.3 ml of a 25 wt% solution in toluene). [b] The yield and the olefin content of C_6-C_{27} were determined by GC using calibration curves with standard solutions.

Table 3.12.2. Distribution of dimers (mol%).

No.	Catalyst	1-Hexene[a]	Hexenes[b]	Methylpentenes	Dimethylbutenes
1	**26b**	0.0	32.7	66.5	0.8
2	**27e**	0.0	14.1	85.9	0.0
3	**27f**	0.0	32.7	66.5	0.8
4	**45a**	0.06	38.0	61.6	0.4
6	**45b**	0.05	39.4	58.1	2.5
7	**46a**	0.07	38.0	59.3	2.7
9	**46e**	0.07	43.0	53.9	3.1
10	**47b**	0.0	41.0	50.9	8.1
11	**47c**	0.0	28.9	67.9	3.2
12	**47d**	0.0	33.0	65.8	1.2
13	**48b**	0.08	39.4	60.1	0.5
15	**48c**	0.0	30.2	68.3	1.5
16	**49a**	0.0	32.9	65.5	1.6
17	**49b**	0.0	31.1	67.7	1.2
18	**50a**	0.06	20.1	73.9	6.0
19	**50a**	0.0	33.2	65.0	1.8
20	**50b**	0.06	35.7	63.1	1.2
21	**53**	0.0	33.6	64.5	1.9

[a] Calculated over the all C_6. [b] 1-Hexene included.

Table 3.12.3. Yield (%) of oligomers in the experiments 1-4, 6, and 7.

Fraction (%)	1	2	3	4	6	7
C_6	91.6	3.0	91.4	84.8	93.0	87.6
C_9	4.1	5.6	3.6	5.5	6.7	5.5
C_{12}	2.7	39.7	2.7	5.1	0.2	4.5
C_{15}	0.9	37.8	0.9	2.0	—	1.1
C_{18}	0.7	9.1	0.9	1.8	—	1.1
C_{21}	—	2.6	0.3	0.5	—	0.1
C_{24}	—	1.7	0.2	0.3	—	0.1
C_{27}	—	0.5	—	—	—	—

Table 3.12.4. Yield (%) of oligomers in the experiments 9-14.

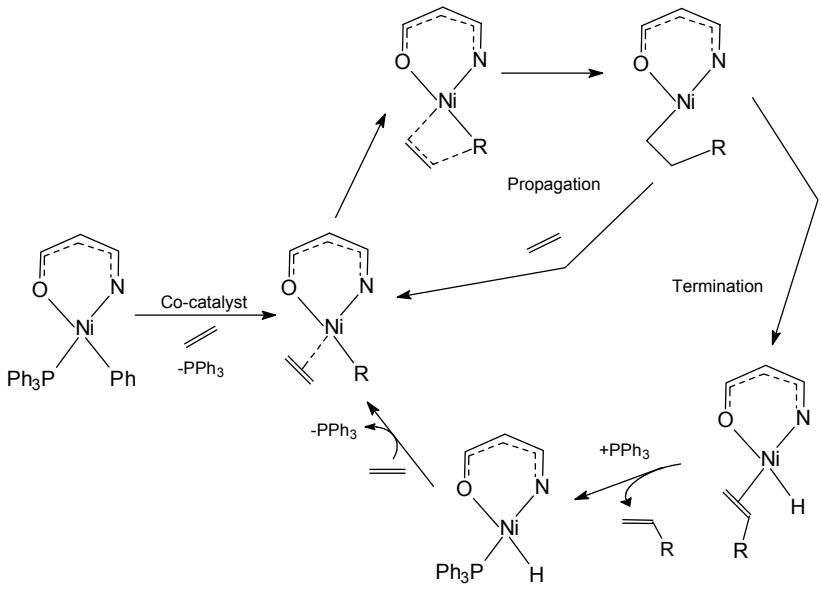
Fraction (%)	9	10	11	12	13	15
C_6	87.5	95.7	91.5	89.8	86.0	92.2
C_9	6.1	2.8	5.5	5.5	6.1	4.5
C_{12}	3.9	1.5	2.2	3.0	4.6	2.2
C_{15}	0.8	—	0.3	0.9	1.3	0.5
C_{18}	1.6	—	0.5	0.8	1.3	0.6
C_{21}	—	—	—	—	0.3	—
C_{24}	—	—	—	—	0.3	—

Table 3.12.5. Yield (%) of oligomers in the experiments 16-21.

Fraction (%)	16	17	18	19	20	21
C_6	92.0	95.2	95.2	92.5	89.6	84.7
C_9	4.2	3.3	3.2	4.4	4.1	7.5
C_{12}	2.4	1.2	1.7	1.9	3.5	4.7
C_{15}	0.7	0.1	—	0.5	1.2	1.4
C_{18}	0.7	0.2	—	0.7	1.1	1.7
C_{21}	—	—	—	0.3	—	
C_{24}	—	—	—	0.2	—	

Other examples of catalysts with a completely different behaviour in the ethylene and propylene oligomerisation are the imidazo[1,5-*a*]pyridyl chelate complexes **26b** and **27f** which also exhibit a high TOF ($5.2x10^4$ h^{-1} and $3.1x10^4$ h^{-1}, respectively). The procatalyst mostly dimerised propylene: in particular, **26b** gave oligomers in the range of C_6-C_{18}, while **27f** yielded olefins up to C_{24}. Among the C_6, the main products consisted of methylpentenes. Surprisingly, the imidazo[1,5-*a*]pyridyl complex **27e** exhibited a quite different catalytic performance, since it was less active ($7.5x10^3$ h^{-1}) and oligomerised propylene mostly to tetramers (39.7%) and pentamers (37.8%) (Table 3.12.3.). According to Zhang et al.[60] the catalyst activity depends on the metal atom net charge: the weaker electron-donating ability of a ligand connected to the central nickel atom of a catalyst results in an increase in the net charge on the nickel atom and, hence, a decrease in polymerisation/oligomerisation activity. Since the electron-donating ability of a phenyl substituent in **27e** is lower than that of a mesityl, this could partly explain the drop in catalytic activity which, nonetheless, depends also on the imidazopyridyl ligand. At any rate, the identity of the aryl ring connected to the nickel centre usually does not exhibit any influence on the oligomer distribution[61]. In fact, the length of the oligomers produced depends on the ratio between chain growth and chain termination by β-hydrogen transfer or abstraction. According to the mechanism model proposed for these types of nickel catalysts in the presence of a co-catalyst[5,62] (Scheme 3.12.1.) the phenyl/mesityl group does not have any influence on the chain length and, in fact, these steps are controlled by the chelate ligand.

The cyano-coordinated complexes **45a**,**b** and **46a**,**e** also produced mostly dimers in good yields (Table 3.12.3., runs 4 and 6) and exhibited better selectivities for linear hexenes (Table 3.12.2., runs 4, 6, 7, and 9). In this case, **45b** was the most active and most selective towards dimers (93.0%) in this class of complexes, the trend being opposite to that of ethylene oligomerisation, where **46e** was the best of this group.



Scheme 3.12.1. Mechanism of the olefin oligomerisation.

The procatalysts **47b-d** did not work for ethylene oligomerisation, but they could perform propylene dimerisation when activated with EASC (runs 10-12). The most selective procatalyst for dimers was **47b** which produces olefins in the range of C_6-C_{12} only. Appearently, also in this case the catalytic activity is influenced by the steric hindrance of the substituents at the aryl rings.

The behaviour of the chelate **47b-d** and the non-chelate **45-46** was very similar in the propylene dimerisation both as regards the activity and the selectivity.

When using complex **53**, a lower fraction of dimers was obtained (84.7%), but the ratio of linear C_6 did not change significantly in comparison with the other procatalysts tested.

At 8 bar propylene pressure, the overall most active nickel catalyst was the imidazopyridyl complex **26b** (5.2×10^4 h^{-1}), while the best selectivity for dimers was shown by the 3-aminoacrylate complexes **47b** (95.7%). The complex **46e** exhibited the highest selectivity for hexenes among the dimers (43.0%), while **50a** and **48c** were the most selective towards methylpentenes (73.9 and 68.3%, respectively).

Additionlly, a few tests with 1-hexene were performed for verifying whether these complexes could be active in the oligomerisation of higher α-olefins (Table 3.12.6.). Two procatalysts were tested in the presence of EASC and gave oligomers in the range of C_{12}-C_{24} with rather low yields. The main products consisted of dimers and the oligomer distribution was affected by the identity of the ligand (runs 22 and 23) and by the

oligomerisation conditions (runs 23 and 24): when the reaction was performed in bulk more dimers were obtained than in the case when the 1-hexane was diluted in toluene.

In the tests with the undiluted olefin the yields were little better, but the complexes **27f** and **47c** behaved also as isomerisation catalysts for the 1-hexane and yielded a mixture of internal olefins. When using **27f** the hexene distribution at the end of the catalysis corresponded to 0.9% 1-hexene, 0.2% *cis*-2-hexene, 19.4% *trans*-2-hexene, and 79.6% *trans*-3-hexene. On the other hand, when using **47c** the following distribution resulted: 1.0% 1-hexene, 15.5% *cis*-2-hexene, 63.4% *cis*-3-hexene, and 20.1% *trans*-3-hexene.

Table 3.12.6. Results of hexene oligomerisation with nickel(II) catalysts.

No.	Cat[a]	Loading (µmol)	Cocat.	Time (h)	*T* (°C)	Solvent	Yield (g)[c]	TON (x 10^3)	TOF (x 10^3/h)
22	**27f**[a]	10	EASC	1	25-29	—	0.7	0.84	0.84
23	**47c**[a]	10	EASC	1	24-28	—	1.3	1.58	1.58
24	**47c**[b]	10	EASC	1	23-28	toluene	0.3	0.32	0.32

[a] The procatalysts were first dissolved in 30 ml of 1-hexene in an ultrasonic bath and then activated with 360 eq of EASC. [b] The procatalyst was first dissolved in 30 ml of toluene in an ultrasonic bath; after that, 5 ml of 1-hexene were added and the catalysis was activated with 360 eq of EASC. [c] The yield and the olefin content of C_6-C_{24} were determined by GC using calibration curves with standard solutions.

Table 3.12.7. Yield (%) of oligomers in the experiments 22-24.

Fraction (%)	22	23	24
C_{12}	41.6	88.4	68.2
C_{18}	32.3	7.0	27.0
C_{24}	26.2	4.6	4.8

4. Conclusions

In this work novel bidentate and tridentate ligands, and their metal complexes were synthesised, which were finally tested to catalyse olefin oligomerisation in the presence of a co-catalyst (MAO, EASC).

First, a group of tridentate imino-ligands was synthesised, which includes the 2,6-bis(imino)pyridines **1**-**2**, the 2,6-diacetyl-monoiminopyridine **3**, the 2,6-bis(benzylideneimino)pyridines **8**, the bis(benzylideneimino)amines **13**, the iminophosphines **16**, and the imidazo[1,5-*a*]pyridines **23c** and **24a**. That way, it was possible to obtain a range of different N,N,N- or N,N,O- or N,N,P-ligands through variation of the coordinating backbone and of the substituents.

All the above-mentioned ligands were used to prepare the corresponding iron(II) complexes, which were then tested for the ethylene oligomerisation, in the presence of MAO as co-catalyst.

The 2,6-bis(imino)pyridyl-, the 2,6-diacetyl-monoiminopyridyl- and the iminophosphine iron(II) complexes **5**-**7**, **17** gave the best results in the oligomerisation catalysis. Complexes **5**-**7** showed activities about 1-30 x 10^3 h^{-1} and produced oligomers in the range C_4-C_{18}, whose distribution follows Schulz-Flory rules from C_6 onwards. This catalysts only gave linear olefins, while the selectivity towards α-olefins (27 to 88%) was dependent on the ligand substituents and on the ethylene pressure. On the other hand the procatalyst **17b-c** were less active (1 x 10^3 h^{-1}), but much more selective for ethylene dimerisation, producing up to 95% 1-butene.

Different classes of bidentate ligands for nickel(II) complexes were synthesised, which are easily tunable in their steric and electronic properties. These ligands include the imidazo[1,5-*a*]pyridines **23a**-**b** and **24b**-**f**, the 3-aminoacrylates **28**, **29**, and **31**, the 3-aminoiminoacrylates **35** and **37**, and the amidoiminomalonate **44**.

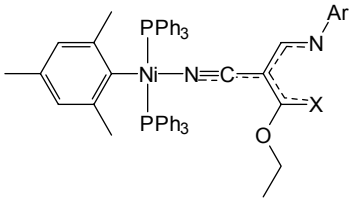
In particular, the syntheses of the differently substituted 3-aminoiminoacrylates **35** and **37** required to be developed and optimised according to the different substituents at the acrylic backbone and at the aryl rings. Cyano-substistuted 3-aminoiminoacrylates **35** were obtained through a four-steps reaction, where the first step consisted of a chlorination of cyanoacetic acid, followed by condensation with 2,6-diisopropylaniline. The obtained amide underwent conversion with an oxonium salt to the related iminoester **33** which was then boiled at reflux with triethyl orthoformate in the presence of acetic anhydride as

solvent, in a typical Claisen's reaction. The ethoxymethylene group in the obtained intermediate **34** finally reacted with appropriate substituted anilines in refluxing methanol, producing the final products **35** in good yields.

The ester-substituted 3-aminoimininoacrylates **37** were obtained instead through a twofold condensation of a substituted aniline with diethyl ethoxymethylenemalonate in absence of any solvent at high temperature, with simultaneous distillation of the produced ethanol, followed by reaction with an oxonium salt to provide the final products. Ester-substituted 3-aminoiminoacrylates bearing unlike substituents at the aryl rings were obtained by two different multi-step methods, which always involve the conversion of the 3-aminoacrylamides to the 3-aminoiminoacrylates by reaction with a triethyloxonium salt as last step.

The neutral bidentate N,N-ligands **23a**, **24b-d**, **40**, and **42** were used to form the corresponding nickel(II) dibromide complexes.

On the other hand, the potential acidic ligands were deprotonated with sodium bis(trimethylsilyl)amide to yield their monoanionic form that next reacted with $[(PPh_3)_2Ni(Mes)Br]$. Two different classes of neutral nickel(II) complexes were obtained: in one class (**45** and **46**), the nickel centre binds to the cyano-group of the ligand, which coordinates as monodentate; in the latter class of complexes (**47-50** and **53**), the ligands form bidentate chelate nickel complexes.



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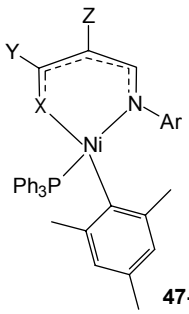


47-50

	45	**46**
X	N—Ar	O

	47	**48**	**49**	**50**
X	O	O	O	N—Ar
Y	OEt	OEt	Alkyl	OEt
Z	CN	C(O)OEt	C(O)OEt	C(O)OEt

Figure 4.1. Structures of the nickel(II) complexes **45-50**.

The nickel complexes were tested in ethylene oligomerisation. The best results were obtained using MAO as co-catalyst. The best active catalysts were the non-chelate cyano-coordinated 3-aminoiminoacrylate- and 3-aminoacrylate complexes, together with the chelating ester- substituted 3-aminoacrylate-, the acyl-substituted 3-aminoacrylate- and the amidoiminomalonate. Their activities ranged from 2,300 to 113,500 h^{-1}, and the main products consisted of dimers (89-100%). Due to the chain-running at the nickel centre, not only α-butene was formed. The same factor determined the formation of branched isomers among the higher olefins (30-80%).

Some of the synthesised nickel(II) complexes were tested for propylene dimerisation, too. The procatalysts **26b**, **27f**, **45-50**, and **53** worked well when activated with EASC, but were inactive when MAO was used in its place.
All the tested catalysts behaved in a similar way and the main products generally consisted of dimers, being the fraction C_6 always about 90%. Among the dimers, methylpentenes were the main products in most cases, followed by linear hexenes and small amounts of dimethylbutenes. An exception was represented by the imidazo[1,5-*a*]pyridyl complex **27e**: they interestingly produced mostly propylene tetramers and pentamers, though exhibiting lower activity.
The overall most active nickel catalyst in this case was the imidazopyridyl complex **26b** (5.2 x 10^4 h^{-1}), while the best selectivity for dimers was shown by the cyano-substituted 3-aminoacrylate chelate complexes **47b** (96%), the acyl-substituted 3-aminoacrylate **49b** (95%), and the 3-aminoiminoarylate complex **50a** (95%). On the other hand, **46e** had the highest selectivity for hexenes among the dimers (43%), while **50a** and was the most selective towards methylpentenes (74%).

5. Experimental

5.1. General

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques.

NMR spectra were recorded on a Bruker spectrometer 250 MHz (^{1}H) and 62.9 MHz (^{13}C) at 293 K. The signals of the not-completely deuterated portion of deuterated chloroform ($CDCl_3$), or hexadeuterated dimethylsulphoxide ($(CD_3)_2SO$), or high-field signal of the octadeuterated tetrahydrofurane (THF-d_8) were taken as internal standard in the ^{1}H NMR spectra; in the ^{13}C NMR spectra the signal of the deuterated solvent was used.

IR spectra were recorded with a Perkin Elmer System 2000 FT-IR.

Mass spectra were obtained using electron ionisation (EI), electron spray ionisation (ESI), or field ionisation (FI).

Melting points were determined with a (Büchi B-545) melting point apparatus and are uncorrected.

Elemental analyses were performed in a Vario EL III, CHNOS-elemental analyser from Elementar Analysesysteme GmbH, and the results are obtained as average of three measurements.

The reaction mixtures were analysed by GC-MS with a gas-phase chromatograph 5890 (column DP 5; length 30 m, diameter 0.25 μm) and a with a mass spectrometer 5970 from Hewlett Packard.

The X-ray structures were obtained by collecting the intensity data for the compounds on a Siemens Smart CCD 1000 diffractometer using graphite-monochromated Mo-K_α radiation. The X-ray analyses were performed with an irradiation time of 10 to 40 s per frame, collecting a full sphere of data. Data were corrected for Lorentz and polarisation effects, an experimental absorption correction was performed with SADABS[63]. Structure solution and refinement was performed with SHELX-97[64] (For further details see the crystallographic appendix 7.1.).

Oligomer products were analysed by GC with a flame ionisation detector, using a 50 m DB1 column, injector temperature 40°C and the following temperature program: 40°C/5 min, 40–300°C, 5°C/10 min. The individual products were integrated, using *n*-tridecane as internal standard.

All chemicals were obtained commercially and used as received unless stated otherwise.

Following compounds were synthesised according to literature:
N-{1-[6-(*N*-phenylethanimidoyl)pyridin-2-yl]ethylidene}aniline[21]
2-(1-methylimidazo[1,5-*a*]pyridin-3-yl)phenol **24b**[28]
3-*tert*-butyl-1-pyridin-2-ylimidazo[1,5-*a*]pyridine **24c**[28]
methyl 4-(1-pyridin-2-ylimidazo[1,5-*a*]pyridin-3-yl)benzoate **24d**[28]
$[(PPh_3)_2Ni(Mes)Br]$[30] $[(PPh_3)_2Ni(C_6H_5)Br]$[31]
pyridine-2-carbaldehyde phenylhydrazone **40b**[43]
dimethyl-*N,N'*-bis(2-methylphenyl)ethane diimidoate **42**[35]

Following compounds were put at disposal within our team:
1-phenyl-1-pyridin-2-ylmethanamine **15c**
1,1'-dimethyl-[3,3']bi(imidazo[1,5-*a*]pyridinyl) **23a**
ethyl cyano(1-methylimidazo[1,5-*a*]pyridin-3(2*H*)-ylidene)acetate **24f**
N,N'-bis(2-methylphenyl)ethane diimidoylchloride **28**

5.2. Syntheses of the ligands

5.2.1. Syntheses of the 2,6-bis(imino)pyridyl and 2,6-diacetyl-monoiminopyridyl ligands

5.2.1.1. ***2,6-Bis[1-(4-methoxyphenylimino)ethyl]pyridine*** **1a**: 2,6-Diacetylpyridine (0.38 g, 2 mmol) and *p*-anisidine (0.67 g, 5 mmol) were dissolved in 16 ml of methanol under stirring. Formic acid (97%, 0.3 ml) was added to this solution and a beige precipitate slowly formed from the brown solution. The reaction mixture was stirred for 8 h at room temperature, then the precipitate was collected by vacuum filtration and washed with methanol. The dried solid was a fluorescent greenish-yellow powder, yield: 0.78 g (2 mmol, 91%). – ^{1}H NMR (THF-d_8) δ 8.35 (d, 2H, H_{Pyr}), 7.89 (t, 1H, H_{Pyr}), 6.85 (q, 8H, H_{Aryl}), 3.78 (s, 6H, OCH_3), 2,42 (s, 6H, N=CCH_3); ^{13}C NMR (THF-d_8) δ 164.6, 154.6, 153.9, 141.3, 134.5, 119.8, 118.8, 112.0, 52.7, 13.1. – EI$^+$-MS m/z = 373 (M^+). – M.p. = 199°C.

5.2.1.2. ***2,6-Bis[1-(3-methoxyphenylimino)ethyl]pyridine*** **1b**: 2,6-Diacetylpyridine (0.74 g, 4.5 mmol) was stirred with *m*-anisidine (1.83 g, 15 mmol) in 20 ml of dry benzene at ambient temperature in the presence of 8.5 g of molecular sieves. The reaction was performed under argon in a closed flask for approximately 50 d. Then the reaction mixture was filtered, the solvent was removed under reduced pressure and a yellow oil was

obtained. A few ml of *n*-hexane were added to the oil and the mixture was stored at 5°C overnight. A yellow precipitate formed, which was filtered and washed with hexane. Yield: 1.1 g (3 mmol, 66%). – ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2H, H_{Pyr}), 7.80 (t, 1H, H_{Pyr}), 7.22 (t, 2H, H_{Aryl}), 6.61 (d, 2H, H_{Aryl}), 6.38–6.34 (m, 4H, H_{Aryl}), 3.76 (s, 6H, OCH_3), 2.34 (s, 6H, N=CCH_3); ^{13}C NMR ($CDCl_3$) δ 167.9, 160.7, 155.8, 153.1, 137.2, 130.3, 122 7, 111.9, 109.6, 105.3, 55.6, 16.6. – EI$^+$-MS m/z = 373 (M^+). – M.p. = 133 – 135°C.

5.2.1.3. ***2,6-Bis[1-(4-trifluoromethylphenylimino)ethyl]pyridine*** **2a**: 2,6-Diacetyl-pyridine (0.38 g, 2 mmol), 4-trifluoromethylaniline (2.4 g, 15 mmol) and a few milligrams of *p*-toluenesulfonic acid were heated under reflux in 50 ml of toluene for 15 h. Then the brown reaction mixture was concentrated and dissolved in a mixture of hexane/ethylacetate = 1:1. Filtration over silica gel and removal of the solvents gave brown oil, which was stored at 5°C over night. Colourless crystals of **2b** formed, which were filtered and washed with *n*-hexane, yield: 0.08 g (0.2 mmol, 8%). – ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2H, 3-H_{Pyr}), 7.82 (t, 1H, 4-H_{Pyr}), 7.53 (d, 4H, H_{Aryl}), 6.82 (d, 4H, H_{Aryl}), 2.31 (s, 6H, N=CCH_3); ^{13}C NMR ($CDCl_3$) δ 166.5, 153.5, 152.9, 135.6, 125.4 (q), 125.1 (q), 124.9 (q), 121.3, 117.8, 15.0. – EI$^+$-MS m/z = 449 (M^+); FI$^+$-HR-MS: m/z 449.1327 (calcd.), found 449.1260 for $C_{23}H_{17}N_3F_6$, δ = 6.7 mDa. – M.p. = 141°C.

5.2.1.4. ***2,6-Bis[1-(3-trifluoromethylphenylimino)ethyl]pyridine*** **2b**: 2,6-Diacetyl-pyridine (0.82 g, 5 mmol) was stirred with 3-trifluoromethylaniline (1.62 g, 10 mmol) in 25 ml of dry benzene at ambient temperature in the presence of 2.8 g of molecular sieves. The reaction was performed under argon in a closed flask for 48 h. The molecular sieves were removed by filtration, the reaction mixture was concentrated and a few ml of dichloromethane were added. The obtained pale yellow crystals were filtered and dried. Yield: 0.36 g (0.8 mmol, 16%). – ^{1}H NMR ($CDCl_3$) δ 8.08 (d, 2H, H_{Pyr}), 7.89 (t, 1H, H_{Pyr}), 7.48-6.94 (m, 8H, H_{Aryl}), 2.36 (s, 6H, N=CCH_3). – EI$^+$-MS m/z = 449 (M^+).

5.2.1.5. ***1-(6-{N-[3-(Trifluoromethyl)phenyl]ethanimidoyl}pyridin-2-yl)ethanone*** **3**: 2,6-Diacetyl-pyridine (1.63 g, 10 mmol) was stirred with 3-trifluoromethylaniline (1.61 g, 10 mmol) in 20 ml of dry benzene at room temperature in the presence of 11 g of molecular sieves. The reaction was performed under argon in a closed flask for approximately 80 d. Then the reaction mixture was filtered, the solvent was removed under reduced pressure and a yellow oil was obtained. The product was stored at 5°C. Slowly a yellow precipitate formed which was filtered and washed with methanol. Yield: 2.1 g (7 mmol, 70%). – ^{1}H NMR ($CDCl_3$) δ 8.38 (d, 1H, H_{Pyr}), 8.06 (d, 1H, H_{Pyr}), 7.88 (t, 1H, H_{Pyr}), 7.43 (t, 1H, H_{Aryl}), 7.32 (d, 1, H_{Aryl}), 7.04 (s, 1H, H_{Aryl}), 6.94 (d, 1H, H_{Aryl}), 2.71 (s,

3H, O=CC*H*$_3$), 2.35 (s, 3H, N=CC*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 200.2, 168.3, 155.8, 152.8, 151.8, 137.8, 131.9 (q), 130.0, 125.1, 124.5 (q), 123.2, 122.9, 120.8 (q), 116.5 (q), 26.0, 16.6. – EI$^+$-MS *m*/*z* = 306 (M^+); FI$^+$-HR-MS: *m*/*z* 306.0980 (calcd.), found 306.0917 for $C_{16}H_{13}N_3OF_3$, δ = 6.3 mDa. – M.p. = 116-118°C.

5.2.2. Syntheses of the 2,6-bis(benzylideneimino)pyridyl ligands

5.2.2.1. ***1-[6-(N-Hydroxyethanimidoyl)pyridin-2-yl]ethanone oxime* 9:** An aqueous solution (120 ml) of hydroxylamine hydrochloride (17.54 g, 0.25 mol) was dropped into a solution of 2,6-diacetylpyridine (16.32 g, 0.10 mol) in 250 ml of ethanol. The mixture was then heated at reflux for 4 h.; after that, the solvent was removed under reduced pressure and a pale orange precipitate was obtained, which was finally filtered and dried under vacuum. Yield: 19.23 g (0.10 mol, 99.5%). – ^{1}H NMR (DMSO-d_6) δ 11.52 (s, 2H, O*H*), 7.80 (m, 3H, H_{Pyr}), 2.24 (s, 6H, C*H*$_3$). – FI$^+$-HR-MS: *m/z* 193.0851 (calcd.), found 193.0847 for $C_9H_{11}N_3O_2$, δ = –0.4 mDa. – M.p. 236.5-238°C.

5.2.2.2. ***1-[6-(1-Aminoethyl)pyridin-2-yl]ethanamine* 10:** A mixture containing the dioxime **9** (19.3 g, 0.10 mol), ammonium acetate (30.8 g, 0.40 mol), glacial acetic acid (24.0 g, 0.40 mol), 135 ml of distilled water, and 80 ml of ethanol was heated to 70°C. Then the addition of zinc powder (52.4 g, 0.80 mol) was started in small portions and the mixture was further heated at reflux: the zinc powder was added to the refluxing mixture in 50 min with stirring. After that, the reaction mixture was kept at reflux for additional 2 h, it was then allowed to cool to 60°C, the unconverted zinc was filtered off and was washed with 50% aqueous ethanol (3 x100 ml): the combined filtrates were treated with 80 ml of concentrated HCl and the volume of the obtained colourless solution was evaporated to 100 ml under reduced pressure and cooled at –20°C overnight. The precipitated white zinc complex of the diamine was filtered and taken up into 35 ml of water at 3°C, finally treated with 200 g of 50% ice-cooled KOH solution while the flask was cooled in an ice bath. The separated yellowish oil was dissolved in 100 ml of THF; then the KOH solution was extracted with THF (6 x 50 ml). The aqueous filtrate was slowly treated with KOH to pH 14, while the flask was cooled in an ice bath: a white precipitate formed, which was filtered and washed with THF (2x100 ml) (the obtained organic phase was collected for further treatments). The KOH solution was extracted with THF (7 x 50 ml); finally, all the THF solutions were combined and dried twice over KOH and twice over Na_2SO_4. The

solvent was removed under reduced pressure and a pale yellow oil was obtained, which underwent a distillation in vacuum ($5.5 \cdot 10^{-2}$ Torr). The pure diamine was a colourless oil. Yield: 10.12 g (0.06 mol, 61.0%). – ^{1}H NMR ($CDCl_3$) δ 7.52 (t, 1H, H_{Pyr}), 7.05 (d, 2H, H_{Pyr}), 4.08 (q, 2H, C*H*), 2.69 (s, 4H, NH_2), 1.36 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 164.41, 137.08, 118.09, 52.21, 24.27. – FI$^+$-HR-MS: *m/z* 166.1329 (calcd.), found 166.1334 for $C_9H_{15}N_3$, δ = 0.5 mDa. – B.p. 55°C/$5.5 \cdot 10^{-2}$ Torr.

5.2.2.3. ***N-(2-Chlorobenzylidene)-N-[1-(6-{1-[(2-chlorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8a:** A solution of 2-chlorobenzaldehyde (0.85 g, 6 mmol) in 10 ml of methanol was added dropwise to a solution of the diamine **10** (0.50 g, 3 mmol) in 15 ml of methanol while stirring at room temperature. The mixture was boiled at reflux for 3 h; after that it was cooled to room temperature, the solvent was removed under reduced pressure and an orange solid resulted, which was dried under vacuum. Yield: 1.23 g (3 mmol, 99%). – ^{1}H NMR ($CDCl_3$) δ 8.89 (s, 2H, N=C*H*), 8.15 (d, 2H,3-H_{Pyr}), 7.67 (t, 1H, H_{Pyr}), 7.45-7.26 (m, 8H, H_{Aryl}), 4.77 (q, 2H, C*H*), 1.65 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 164.3, 161.5, 137.7, 136.7, 135.1, 132.0, 131.4, 129.9, 126.7, 118.9, 69.6, 23.2. – EI$^+$-MS *m/z* = 410 (M^+).

5.2.2.4. ***N-(2,6-Dichlorobenzylidene)-N-[1-(6-{1-[(2,6-dichlorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8b**: A solution of 2,6-chlorobenzaldehyde (1.05 g, 6 mmol) in 10 ml of methanol was added dropwise to a solution of the diamine **10** (0.50 g, 3 mmol) in 10 ml of methanol while stirring at room temperature. The mixture was refluxed for 5 h; after that it was cooled to room temperature, the solvent was removed under reduced pressure and a yellow solid was obtained and subsequently dried under vacuum. Yield: 1.42 g (3 mmol, 99%). – ^{1}H NMR ($CDCl_3$) δ 8.63 (s, 2H, N=C*H*), 7.68 (t, 1H, H_{Pyr}), 7.48 (d, 2H, H_{Pyr}), 7.36 (d, 4H, H_{Aryl}), 7.24 (t, 2H, H_{Aryl}), 4.81 (q, 2H, C*H*), 1.71 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 162.2, 156.5, 137.2, 134.7, 133.5, 130.2, 128.6, 119.4, 72.4, 23.6. – FI$^+$-HR-MS: *m/z* 477.0333 (calcd.), found 477.0302 for $C_{23}H_{19}Cl_4N_3$, δ = –3.1 mDa.

5.2.2.5. ***N-(2-Bromobenzylidene)-N-[1-(6-{1-[(2-bromobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8c**: 2-Bromobenzaldehyde (1.11 g, 6 mmol) was added dropwise to a solution of the diamine **10** (0.50 g, 3 mmol) in 20 ml of methanol while stirring at room temperature. The mixture was refluxed for 4 h; after that it was cooled to room temperature, the volume of the solvent was reduced under reduced pressure and cooled in ice. A pale yellow precipitate formed, which was filtered off. Yield: 0.89 g (2 mmol, 60%). – ^{1}H NMR ($CDCl_3$) δ 8.75 (s, 2H, N=C*H*), 8.06 (d, 2H, H_{Pyr}), 7.84 (t, 1H, H_{Pyr}), 7.60-7.18 (m, 8H, H_{Aryl}), 4.70 (q, 2H, C*H*), 1.57 (d, 6H, CH_3). – EI$^+$-MS *m/z* = 500 (M^+).

5.2.2.6. ***N-(Pentafluorobenzylidene)-N-[1-(6-{1-[(pentafluorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8d**: Pentafluorobenzaldehyde (0.78 g, 4 mmol) was added dropwise to a solution of the diamine **10** (0.33 g, 2 mmol) in 20 ml of methanol in a Schlenk flask under argon. The solution was stirred at room temperature for 5 h; after that, the solvent was evaporated under vacuum and a yellow oil was obtained. Yield: 0.93 g (1.8 mmol, 89%). – ^{1}H NMR ($CDCl_3$) δ 8.56 (s, 2H, N=C*H*), 7.70 (t, 1H, H_{Pyr}), 7.45 (d, 2H, H_{Pyr}), 4.71 (q, 2H, C*H*), 1.66 (d, 6H, CH_3). – FI$^+$-HR-MS: *m/z* 521.0950 (calcd.), found 521.0966 for $C_{23}H_{13}F_{10}N_3$, δ = 1.6 mDa.

5.2.2.7. ***N-(2-Methylbenzylidene)-N-[1-(6-{1-[(2-methylbenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8e**: A solution of *o*-tolualdehyde (0.64 g, 5.3 mmol) in 15 ml of methanol was added dropwise to a solution of the diamine **10** (0.44 g, 2.6 mmol) in 10 ml of methanol while stirring at room temperature. The mixture was refluxed for 5 h; after that, it was cooled to room temperature, the solvent was removed under reduced pressure and a yellow-greenish solid was yielded and subsequently dried under vacuum. Yield: 0.57 g (1.5 mmol, 58%). – ^{1}H NMR ($CDCl_3$) δ 8.77 (s, 2H, N=C*H*), 7.97 (d, 2H, H_{Aryl}), 7.67 (t, 1H, H_{Pyr}), 7.47 (d, 2H, H_{Pyr}), 7.31-7.17 (m, 6H, H_{Aryl}), 4.70 (q, 2H, C*H*), 2.55 (s, 6H, CH_3), 1.66 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 163.3, 159.1, 137.7, 134.5, 137.2, 130.8, 130.2, 127.9, 126.1, 119.2, 72.2, 24.2, 19.5. – EI$^+$-MS *m/z* = 370 (M^+).

5.2.2.8. ***N-(2-Mesitylmethylene)-N-[1-(6-{1-[(2-mesitylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8f**: A solution of mesitaldehyde (0.90 g, 6 mmol) in 10 ml of methanol was added dropwise to a solution of the diamine **10** (0.50 g, 3 mmol) in 10 ml of methanol while stirring at room temperature. The mixture was refluxed for 6 h; after that, it was cooled to room temperature and small white crystals formed from the solution. They were filtered and dried in air. Yield: 0.94 g (2 mmol, 73%). – ^{1}H NMR ($CDCl_3$) δ 8.70 (s, 2H, N=C*H*), 7.59 (t, 1H, H_{Pyr}), 7.39 (d, 2H, H_{Pyr}), 6.79 (s, 4H, H_{Aryl}), 4.57 (q, 2H, C*H*), 2.33 (s, 12H, CH_3), 2.20 (s, 6H, CH_3), 1.55 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 163.2, 159.7, 140.1, 137.9, 136.2, 134.6, 129.0, 119.4, 71.3, 24.0, 22.2, 18.4. – EI$^+$-MS *m/z* = 426 (M^+).

5.2.2.9. ***N-(1,1'-Biphenyl-4-ylmethylene)-N-[1-(6-{1-[(1,1'-biphenyl-4-ylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8g**: A solution of 4-biphenylcarboxaldehyde (1.10 g, 6 mmol) in 10 ml of methanol was added dropwise to a solution of the diamine **10** (0.50 g, 3 mmol) in 10 ml of methanol while stirring at room temperature. The mixture was heated at reflux for 3 h and a white solid slowly precipitated from the colourless solution. The solid was filtered off and dried in vacuum. Yield: 1.21 g (2 mmol, 81%). – ^{1}H NMR

($CDCl_3$) δ 8.44 (s, 2H, N=C*H*), 7.90-7.15 (m, 21H, $H_{Aryl+Pyr}$), 4.67 (q, 2H, C*H*), 1.61 (d, 6H, CH_3). – EI$^+$-MS *m/z* = 494 (M^+).

5.2.2.10. ***N-(2-Naphthylmethylene)-N-[1-(6-{1-[(2-naphthylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine*** **8h**: A solution of 2-naphthaldehyde (0.94 g, 6 mmol) in 20 ml of methanol was added dropwise to a solution of the diamine **10** (0.50 g, 3 mmol) in 10 ml of methanol while stirring at room temperature. The mixture was refluxed for 4 h; after that, it was cooled to room temperature and a white solid precipitated from the solution, which was filtered off. Yield: 1.32 g (3 mmol, 99%). – ^{1}H NMR ($CDCl_3$) δ 8.54 (s, 2H, N=C*H*), 8.27 (s, 2H, $H_{Naphthyl}$), 8.05-7.66 (m, 8H, $H_{Naphthyl}$), 7.56 (t, 1H, H_{Pyr}), 7.51-7.40 (m, 4H, $H_{Naphthyl}$), 7.17 (d, 2H, H_{Pyr}), 4.69 (q, 2H, C*H*), 1.61 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 164.2, 160.1, 134.7, 136.2, 134.4, 133.2, 131.4, 131.2, 128.8, 128.0, 127.5, 126.5, 124.6, 118.9, 71.3, 20.2. – EI$^+$-MS *m/z* = 442 (M^+).

5.2.3. Syntheses of the bis(benzylideneimino)amine ligands

5.2.3.1. ***N-(2,6-Dichlorobenzylidene)-N'-{2-[(2,6-dichlorobenzylidene)amino]ethyl}ethane-1,2-diamine*** **13a**: A solution of 2,6-dichlorobenzaldehyde (1.76 g, 10 mmol) in 15 ml of methanol was added dropwise to a solution of diethylentriamine (0.52 g, 5 mmol) in 10 ml of methanol while stirring at room temperature. The solution was refluxed for 5 h; then the solvent was evaporated under vacuum and a yellow oil was obtained. Yield: 1.91 g (5 mmol, 96%). – ^{1}H NMR (C_6D_6) δ 8.34 (s, 2H, N=C*H*), 6.96 (d, 4H, H_{Aryl}), 6.51 (d, 2H, H_{Aryl}), 3.76 (t, 4H, CH_2), 3.01 (t, 4H, CH_2), 1.78 (sb, 1H, N*H*). – EI$^+$-MS *m/z* = 418 (M^+).

5.2.3.2. ***N-(2-Bromobenzylidene)-N'-{2-[(2-bromobenzylidene)amino]ethyl}ethane-1,2-diamine*** **13b**: 2-Bromobenzaldehyde (1.95 g, 10 mmol) was added dropwise to a solution of diethylentriamine (0.56 g, 5 mmol) in 25 ml of methanol while stirring at room temperature. The solution was refluxed for 5 h; then the solvent was evaporated under vacuum and a yellow oil was yielded. Yield: 2.21 g (5 mmol, 98%). – ^{1}H NMR (C_6D_6) δ 8.69 (s, 2H, N=C*H*), 8.31 (d, 2H, H_{Aryl}), 7.86 (d, 2H, H_{Aryl}), 7.14-6.71 (m, 8H, H_{Aryl}), 3.65 (t, 4H, CH_2), 2.88 (t, 4H, CH_2), 1.25 (bs, 1H, N*H*). – EI$^+$-MS *m/z* = 438 (M^+).

5.2.3.3. ***N-(Mesitylmethylene)-N'-{2-[(mesitylmethylene)amino]ethyl}ethane-1,2-diamine*** **13c**: Mesitaldehyde (1.46 g, 10 mmol) was added dropwise to a solution of diethylentriamine (0.51 g, 5 mmol) in 25 ml of methanol while stirring at room

temperature. The solution was refluxed for 5 h; evaporation of the solvent under vacuum yielded a pale yellow oil. Yield: 1.71 g (5 mmol, 99%). – ^{1}H NMR (C_6D_6) δ 8.58 (s, 2H, N=C*H*), 6.78 (s, 4H, H_{Aryl}), 3.77 (t, 4H, CH_2), 3.05 (t, 4H, CH_2), 2.47 (s, 12H, CH_3), 2.18 (s, 6H, CH_3), 1.76 (sb, 1H, N*H*). – EI$^+$-MS *m/z* = 364 (M^+); EI$^+$-HR-MS: *m/z* 363.2674 (calcd.), found 363.2698 for $C_{24}H_{33}N_3$, δ = 2.4 mDa.

5.2.3.4. ***N-(1-phenylethylidene)-N'-{2-[(1-phenylethylidene)amino]ethyl}ethane-1,2-diamine*** **13d**: Acetophenone (4.44 g, 36 mmol) was added dropwise to a solution of diethylentriamine (2.00 g, 18 mmol) in 50 ml of methanol; the mixture was refluxed 5 h, then the solvent was removed under vacuum. Yield 5.25 g (17 mmol, 95%). – ^{1}H NMR (C_6D_6) δ 7.95 (d, 4H, H_{Aryl}), 7.27-7.23 (m, 6H, H_{Aryl}), 3.55 (t, 4H, CH_2), 3.26 (t, 4H, CH_2), 2.17 (bs, 1H, N*H*), 1.84 (s, 6H, CH_3). – EI$^+$-MS *m/z* = 308 (M^+).

5.2.4 Syntheses of the iminophosphine ligands

5.2.4.1. ***1-Pyridin-2-ylethanone oxime*** **18b**: Hydroxylamine hydrochloride (36.6 g, 0.53 mol) and sodium acetate (36.0 g, 0.44 mol) were dissolved in 250 ml of water. The solution was warmed up to 55-60°C and 2-acetyl pyridine (42.9 g, 0.35 mol) was added within 20 minutes. Then the mixture was stirred for 1 h at 60°C. After cooling to room temperature, the mixture was neutralised with NaOH to pH 6-7 and the oxime precipitated. The oxime was filtered off and the crude product was recrystallised from water/ethanol = 5/3. Yield: 43.2 g (0.32 mol, 90%). – ^{1}H NMR ($CDCl_3$) δ 9.21 (bs, 1H, O*H*), 8.70 (d, 1H, H_{Pyr}), 7.89 (d, 1H, H_{Pyr}), 7.73 (t, 1H, H_{Pyr}), 7.24 (t, 1H, H_{Pyr}), 2.39 (s, 3H, CH_3). – EI$^+$-MS *m/z* = 136 (M^+).

5.2.4.2. ***1-Pyridin-2-ylethanamine*** **15b**: A mixture containing the oxime **18b** (40.8 g, 0.30 mol), ammonium acetate (46.2 g, 0.60 mol), glacial acetic acid (36.0 g, 0.60 mol), 200 ml of water and 70 ml of ethanol was heated to 70°C. Then zinc powder (78.5 g, 1.20 mol) was added in small portions to the refluxing mixture within 90 min. The mixture was refluxed additional 90 min. After that, it was cooled down to 50°C and the unconverted zinc was filtered away. The zinc powder was washed with 50% aqueous ethanol (2 x 120 ml). The combined filtrates were treated with 120 ml of concentrated hydrochloric acid. The volume of the resulting colourless solution was reduced to 100 ml; after that, the mixture was cooled at –20°C overnight. The precipitated white zinc complex of the amine was filtered off and the first filtrate was collected. The zinc complex was

taken up in 100 ml of water (at 3°C) and treated with 340 g of an ice-cooled 50% potassium hydroxide solution, while the flask was cooled in an ice-bath. The separated oil was dissolved in 120 ml of THF. Then, the KOH solution was extracted with THF (3 x 90 ml). The combined organic extracts were dried twice over KOH. The THF solution was finally dried twice over Na_2SO_4. The first filtrate was slowly treated with KOH to pH 14 (the flask being cooled in an ice bath) while the amine was separated as an oil from the aqueous solution. The crude amine was dissolved in THF and the KOH solution was extracted twice with THF. All THF solutions were dried with KOH (twice) and Na_2SO_4 (twice). Finally the THF solutions were combined and the solvent was removed under reduced pressure. A pale yellow oil was obtained, which was subjected to a vacuum distillation (p 5 mbar; bp_5 63°C). The pure amine is a colourless oil. Yield: 25.7 g (0.21 mol, 75%). – ^{1}H NMR ($CDCl_3$) δ 8.36 (d, 1H, H_{Pyr}), 7.45 (t, 1H, H_{Pyr}), 7.12 (d, 1H, H_{Pyr}), 6.95 (t, 1H, H_{Pyr}), 3.96 (q, 1H, C*H*), 1.85 (s, 2H, NH_2), 1.24 (d, 3H, CH_3). – EI$^+$-MS *m/z* = 122 (M^+).

5.2.4.3. ***N-[2-(Diphenylphosphino)benzylidene]-N-(pyridin-2-ylmethyl)amine*** **16a**: In a Schlenk-flask a solution of 2-(diphenylphosphino)-benzaldehyde (0.50 g, 1.7 mmol) in 50 ml of methanol was cooled to 0°C, then 2-picolylamine (0.19 g, 1.7 mmol) was added dropwise. The reaction mixture was stirred further 10 min at 0°C, and the solvent was finally removed in vacuo. Yield: 0.65 g (1.7 mmol, 98%). – ^{1}H NMR ($CDCl_3$) δ 8.69 (d, 1H), 7.97 (d, 1H), 7.76 (t, 1H), 7.68-7.49 (m, 9H), 7.35-7.21 (m, 7H), 5.14 (s, 2H, CH_2); ^{31}P NMR (C_6D_6) δ 12.8. – EI$^+$-MS *m/z* = 380 (M^+).

5.2.4.4. ***N-[2-(Diphenylphosphino)benzylidene]-N-(1-pyridin-2-ylethyl)amine*** **16b**: 1-Pyridin-2-ylethanamine **15b** (0.20 g, 1.6 mmol) was added dropwise to a solution of 2-(diphenylphosphino)-benzaldehyde (0.45 g, 1.5 mmol) in 35 ml of toluene. The mixture was refluxed for 3 h; after that, the solvent was removed in vacuo and an oil was obtained. Yield: 0.53 g (1.3 mmol, 89%). – ^{1}H NMR ($CDCl_3$) δ 8.88 (d, 1H), 8.42 (d, 1H), 7.93 (d, 1H), 7.47 (t, 2H), 7.30-7.20 (m, 12H), 7.02 (t, 1H), 6.81 (t, 1H), 4.05 (q, 1H, C*H*), 1.30 (d, 3H, CH_3); ^{31}P NMR ($CDCl_3$) δ –11.34. – FI$^+$-HR-MS: *m/z* 394.1599(calcd.), found 394.1571 for $C_{26}H_{23}N_2P$, δ = –2.8 mDa.

5.2.4.5. ***N-{[2-(Diphenylphosphino)phenyl]methylene}-N-[phenyl(pyridin-2-yl) methyl]amine*** **16c:** 1-Phenyl-1-pyridin-2-ylmethanamine **15c** (0.29 g, 1.6 mmol) was dropped into a solution of 2-(diphenylphosphino)-benzaldehyde (0.45 g, 1.5 mmol) in 25 ml of toluene at room temperature with stirring. Heat was applied and the reaction was run in an argon atmosphere at 85°C for 7 h, and finally under reflux for 1 h. After that, the

solvent was removed under vacuum and an orange oil was obtained. Yield: 0.59 g (1.3 mmol, 83%). – ^{1}H NMR (CD_2Cl_2) δ 8.90 (d, 1H), 8.34 (d, 1H), 7.94 (d, 1H), 7.49-6.98 (m, 20H), 6.81 (d, 1H), 5.52 (s, 1H, C*H*); ^{31}P NMR (CD_2Cl_2) δ –11.45. – FI^{+}-HR-MS: *m/z* 456.1755 (calcd.), found 456.1667 for $C_{31}H_{25}N_2P$, δ = –8.8 mDa.

5.2.5. Syntheses of the imidazo[1,5-a]pyridyl ligands

5.2.5.1. ***N,N'-Bis(1-pyridin-2-ylethyl)malonamide*** **21b**: Diethyl malonate (1.05 g, 6.5 mmol) was stirred under argon with an excess of 1-pyridin-2-ylethanamine **15b** (2.05 g, 16.8 mmol) at 170°C for 10 h. After that, the mixture was allowed to cool to ambient temperature and the ethanol was removed under reduced pressure. The product was used for the following step without any further purification. Yield: 1.93 g (6.2 mmol, 95%). – ^{1}H NMR ($CDCl_3$) δ 8.50 (d, 2H, H_{Pyr}), 8.13 (d, 2H, N*H*), 7.60 (dt, 2H, H_{Pyr}), 7.22 (d, 2H, H_{Pyr}), 7.14 (dt, 2H, H_{Pyr}), 5.11 (p, 2H, C*H*), 3.28 (s, 2H, CH_2), 1.46(d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 166.6, 161.0, 149.1, 136.8, 122.3, 121.1, 50.3, 43.3, 22.1. – EI^{+}-MS *m/z* = 312 (M^{+}).

5.2.5.2. ***1-Methyl-3-[(1-methylimidazo[1,5-a]pyridin-3-yl)methyl]imidazo[1,5-a] pyridine*** **23b**: A mixture containing the bis-amide **21b** (6.2 mmol, 1.93 g), an excess of phosphorus oxychloride (10 ml, 100 mmol) and 15 ml of toluene was stirred for 4 h under argon (exclusion of moisture) while refluxing. The excess of $POCl_3$ and the solvent were removed under reduced pressure; after that, 50 ml of distilled water were added, the mixture was neutralised with sodium hydroxide to pH 7-8 and extracted with ethyl acetate. The extracts were collected and the solvent was removed. The resulting solid was re-crystallised from hot ethyl acetate. Brown crystals slowly grew, which were filtered and dried. Yield: 1.14 g (4.1 mmol, 67%). – ^{1}H NMR ($CDCl_3$) δ 8.13 (d, 2H, H_{Pyr}), 7.20 (d, 2H, H_{Pyr}), 6.50 (dt, 2H, H_{Pyr}), 6.41 (dt, 2H, H_{Pyr}), 4.81 (s, 2H, CH_2), 2.43(s, 6H, CH_3). – EI^{+}-HR-MS: *m/z* 276.1375 (calcd.), found 276.1341 for $C_{17}HR_{16}N_4$, δ = –3.4 mDa.

5.2.5.3. ***N-[1-(6-{1-[(Pyridin-2-ylcarbonyl)amino]ethyl}pyridin-2-yl)ethyl]pyridine-2-carboxamide*** **21c**: A mixture of dimethyl pyridine-2,6-dicarboxylate (1,36 g, 7 mmol) and the amine **15b** (2,56 g, 21 mmol) was stirred under argon for 7 h at 170°C. After cooling the mixture to 120°C, 20 ml of cyclohexane were added; then the mixture was cooled to 5°C and a yellow solid precipitated, which was filtered and dried under vacuum. Yield: 2.58 g (6.9 mmol, 99%). – ^{1}H NMR ($CDCl_3$) δ 9.47 (d, 2H, N*H*), 8.61 (d, 2H, H_{Pyr}),

8.32 (d, 2H, H_{Pyr}), 7.99 (t, 1H, H_{Pyr}), 7.77 (dt, 2H, H_{Pyr}), 7.47 (d, 2H, H_{Pyr}), 7.28 (dt, 2H, H_{Pyr}), 5.44 (p, 2H, C*H*), 1.74 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 162.9, 161.0, 149.0, 148.7, 138.8, 137.6, 124.8, 122.6, 121.8, 50.0, 22.2. – EI$^+$-MS *m/z* = 375 (M^+).

5.2.5.4. ***1-Methyl-3-[6-(1-methylimidazo[1,5-a]pyridin-3-yl)pyridin-2-yl]imidazo [1,5-a]pyridine*** **23c**: A mixture containing the amide **21c** (4,00 g, 10 mmol), 15 ml of phosphorus oxychloride (15 ml, 160 mmol) and 40 ml of toluene was stirred under reflux for 7 h under argon. After cooling to ambient temperature, the excess of $POCl_3$ and the solvent were removed under reduced pressure and then 50 ml of distilled water were added. The mixture was neutralised with sodium acetate and sodium hydroxide to pH 6-7 and a dark yellow precipitate was obtained, which was filtered and recrystallised from ethyl acetate. Yield: 2.82 g (8 mmol, 78%). – ^{1}H NMR ($CDCl_3$) δ 9.51 (d, 2H, H_{Pyr}), 8.20 (d, 2H, H_{Pyr}), 7.91 (t, 1H, H_{Pyr}), 7.51 (d, 2H, H_{Pyr}), 6.80 (t, 2H, H_{Pyr}), 6.63 (d, 2H, H_{Pyr}), 2.64 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 148.8, 137.7, 133.9, 129.5, 129.4, 124.8, 120.7, 118.8, 118.0, 113.7, 12.5. – FI$^+$-HR-MS: *m/z* 339.1484 (calcd.), found 339.1426 for $C_{21}H_{17}N_5$, δ = –5.8 mDa.

5.2.5.5. ***Methyl 6-{[(1-pyridin-2-ylethyl)amino]carbonyl}pyridine-2-carboxylate*** **22a**: A mixture of dimethyl pyridine-2,6-dicarboxylate (1,60 g, 8 mmol) and the amine **15b** (1.00 g, 8 mmol) in equimolar amounts was stirred under argon for 4 h at 170°C. After cooling the mixture to room temperature, the methanol was removed under vacuum.The product was used for the further reaction without any purification. – ^{1}H NMR ($CDCl_3$) δ 8.96 (d, 1H, N*H*), 8.56 (d, 1H, H_{Pyr}), 8.30 (d, 1H, H_{Pyr}), 8.24 (d, 1H, H_{Pyr}), 7.95 (t, 1H, H_{Pyr}), 7.60 (t, 1H, H_{Pyr}), 7.28 (t, 1H, H_{Pyr}), 7.14 (d, 1H, H_{Pyr}), 5.30 (m_5, 1H, C*H*), 3.95 (s, 3H, CH_3), 1.58 (d, 3H, CH_3). – EI$^+$-HR-MS: *m/z* 285.1113 (calcd.), found 285.1063 for $C_{15}H_{15}N_3O_3$, δ = –5.0 mDa.

5.2.5.6. ***Methyl 6-(1-methylimidazo[1,5-a]pyridin-3-yl)pyridine-2-carboxylate*** **24a**: A mixture containing the amide **22a** (2.30 g, 8 mmol), 4.1 ml of phosphorus oxychloride and 12 ml of toluene was refluxed for 2.5 h under argon. The mixture was then cooled to room temperature and the excess of $POCl_3$ and the solvent were removed under reduced pressure. Water was added (20 ml), the mixture was neutralised with sodium acetate and sodium hydroxide to pH 8 and extracted with ethyl acetate (6x15 ml). The extracts were dried over sodium sulphate and the solvent was removed. The resulting residue was purified by fractionated crystallisation in ethylacetate; the first crystallised solid was filtered away and the mother liquor was evaporated under vacuum yielding the product as a yellow solid. Yield: 0.53 g (2 mmol, 25%). – ^{1}H NMR ($CDCl_3$) δ 10.07 (d, 1H, H_{Pyr}), 8.71

(d, 1H, H_{Pyr}), 7.97-7.85 (m, 2H, H_{Pyr}), 7.47 (d, 1H, H_{Pyr}), 6.94-6.79 (m, 2H, H_{Pyr}), 3.98 (s, 3H, CH_3), 2.63 (s, 3H, CH_3). – EI^+-HR-MS: *m/z* 267.1008 (calcd.), found 267.0962 for $C_{15}H_{13}N_3O_2$, δ = –4.6 mDa.

5.2.5.7. ***N-(1-Pyridin-2-ylethyl)pyridine-2-carboxamide*** **22b**: The amine **15b** (4.89 g, 40 mmol) and ethyl picolinate (6.05 g, 40 mmol) were stirred under argon for 7 h at 200°C. The ethanol was then removed under reduced pressure and the residue was fractionated in vacuo (10^{-3} mbar, bp_{10-3} : 160°C). The amide was a colourless oil. Yield: 5.78 g (25 mmol, 63%). – ^{1}H NMR ($CDCl_3$) *δ* 8.96 (d, 1H, N*H*), 8.46 (d, 1H, H_{Pyr}), 8.44 (d, 1H, H_{Pyr}), 8.05 (d, 1H, H_{Pyr}), 7.66 (dt, 1H, H_{Pyr}), 7.49 (dt, 1H, H_{Pyr}), 7.24 (dt, 1H, H_{Pyr}), 7.17(d, 1H, H_{Pyr}), 7.02 (dt, 1H, H_{Pyr}), 5.24 (p, 1H, C*H*), 1.48 (d, 3H, CH_3); ^{13}C NMR ($CDCl_3$) *δ* 163.5, 161.1, 150.0, 149.2, 148.1, 137.1, 136.6, 126.0, 122.2, 122.0, 121.1, 50.0, 22.2. – EI^+-MS *m/z* = 227 (M^+).

5.2.5.8. ***1-Methyl-3-pyridin-2-ylimidazo[1,5-a]pyridine*** **24b**: A mixture containing the amide **22b** (5.78 g, 25 mmol), 10 ml of phosphorus oxychloride and 25 ml of toluene was refluxed for 2 h under argon. The mixture was then cooled to room temperature and the excess of $POCl_3$ and the solvent were removed under reduced pressure. Water was added (65 ml), the mixture was neutralised with sodium acetate and sodium hydroxide to pH 8 and extracted with ethyl acetate (5x30 ml). The extracts were dried over sodium sulphate and the solvent was removed. The obtained residue was a viscous yellow-brown oil. The crude heterocycle was isolated by means of column chromatography (alumina pH 9, ethyl acetate). Finally, the crude product was recrystallised from cyclohexane/diethylether. Yield: 1.11 g (5.3 mmol, 21%). – ^{1}H NMR ($CDCl_3$) *δ* 9.87 (d, 1H, H_{Pyr}), 8.61 (d, 1H, H_{Pyr}), 8.36 (d, 1H, H_{Pyr}), 7.76 (t, 1H, H_{Pyr}), 7.45 (d, 1H, H_{Pyr}), 7.17 (t, 1H, H_{Pyr}), 6.80 (t, 1H, H_{Pyr}), 6.70 (t, 1H, H_{Pyr}), 2.61 (s, 3H, CH_3). – EI^+-HR-MS: *m/z* 209.0953 (calcd.), found 209.0934 for $C_{13}H_{11}N_3$, δ = –1.9 mDa. – M.p. 59°C.

5.2.6. Syntheses of the bidentate 3-aminoacrylate ligands

5.2.6.1. ***Ethyl 2-cyano-3-[(4-methylphenyl)amino]acrylate*** **28a:** A mixture of equimolar amounts of ethyl(ethoxymethylene)cyanoacetate (5.25 g, 30 mmol) and p-toluidine (3.25 g, 30 mmol) in 30 ml of methanol was refluxed for 15 min. The reaction mixture was then cooled to room temperature and the volume of the solvent was reduced to 10 ml under reduced pressure: the needle shaped colourless crystals that formed were

filtered and washed with hexane. Yield: 6.64 g (29 mmol, 96%). – ^{1}H NMR ($CDCl_3$) δ 10.63 (d, 1H, N*H*), 7.75 (d, 1H, N-C*H*), 7.10 (d, 2H, H_{Aryl}), 6.90 (d, 2H, H_{Aryl}), 4.20 (q, 2H, CH_2), 2.26 (s, 3H, CH_3), 1.27 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.96, 152.41, 136.18, 130.86, 130.77, 118.05, 117.54, 75.18, 61.43, 21.12, 14.61. – FI^{+}-HR-MS: *m/z* 230.1055 (calcd.), found 230.1024 for $C_{13}H_{14}N_2O_2$, δ = –3.1 mDa. – M.p. 128.7-128.9°C.

5.2.6.2. ***Ethyl 2-cyano-3-[(4-dimethoxyphenyl)amino]acrylate*** **28b**: A mixture of ethyl (ethoxymethylene)cyanoacetate (2.80 g, 16 mmol) and p-anisidine (2.05 g, 16 mmol) in 10 ml of methanol was refluxed for 45 min. Afterwards, the solution obtained was cooled to room temperature and a pale grey solid precipitated, which was filtered and washed with hexane. Yield: 3.84 g (15 mmol, 96%). – ^{1}H NMR ($CDCl_3$) δ 10.69 (d, 1H, N*H*), 7.75 (d, 1H, N-C*H*), 7.03 (d, 2H, H_{Aryl}), 6.91 (d, 2H, H_{Aryl}), 4.28 (q, 2H, CH_2), 3.81 (s, 3H, OCH_3), 1.35 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.1, 158.1, 152.8, 132.2, 119.2, 118.6, 115.5, 74.6, 61.4, 55.9, 14.6. – FI^{+}-HR-MS: *m/z* 246.1004 (calcd.), found 246.0987 for $C_{13}H_{14}N_2O_3$, δ = –1.7 mDa. – M.p. 106.1-107.1°C.

5.2.6.3. ***Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]acrylate*** **28c**: 2,6-Dimethylaniline (3.72 g, 30 mmol) was added dropwise to a solution of ethyl (ethoxymethylene)cyanoacetate (5.23 g, 30 mmol) in 10 ml of methanol. The mixture was refluxed for 20 min; after that, it was cooled to room temperature and small colourless crystals grew from the solution, which were filtered off and washed with hexane. Yield: 6.11 g (25 mmol, 83%). – ^{1}H NMR ($CDCl_3$) δ 10.17 (d, 1H, N*H*), 7.28 (d, 1H, N-C*H*), 7.07-7.00 (m, 3H, H_{Aryl}), 4.16 (q, 2H, CH_2), 2.21 (s, 6H, CH_3), 1.25 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 166.3, 158.9, 136.9, 132.9, 129.0, 127.8, 117.0, 74.1, 60.8, 18.3, 14.4. – IR (KBr): ν 3196 cm^{-1} (N─H), 2213 (C≡N), 1691 (C=C─N), 1599 (N─H). – FI^{+}-HR-MS: *m/z* 244.1212 (calcd.), found 244.1160 for $C_{14}H_{16}N_2O_2$, δ = –5.2 mDa. – M.p. 138.2-139.5°C.

5.2.6.4. ***Ethyl 2-cyano-3-[(2,6-diethylphenyl)amino]acrylate*** **28d**: A mixture of ethyl (ethoxymethylene)cyanoacetate (3.02 g, 18 mmol) and 2,6-diethylaniline (2.69 g, 18 mmol) in 10 ml of methanol was refluxed for 30 min. After that the reaction mixture was cooled to room temperature and stored overnight at +5°C: needle-shaped colourless crystals grew from the solution, which were then filtered and washed with hexane. Some more product was yielded by reducing the volume of the filtrate. Yield: 4.08 g (15 mmol, 86%). – ^{1}H NMR ($CDCl_3$) δ 10.24 (d, 1H, N*H*), 7.86 (d, 1H, N-C*H*), 7.34-7.13 (m, 3H,

H_{Aryl}), 4.26 (q, 2H, OCH_2), 2.62 (q, 4H, CH_2), 1.37 (t, 3H, CH_3), 1.21 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.9, 159.2, 140.1, 135.7, 128.6, 127.2, 116.9, 73.4, 60.9, 24.7, 14.7, 14.3. – FI$^+$-HR-MS: *m/z* 272.1525 (calcd.), found 272.1477 for $C_{16}H_{20}N_2O_2$, δ = –4.8 mDa. – M.p. 114.6-115.9°C.

5.2.6.5. ***Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]acrylate*** **28e**: Ethyl (ethoxymethylene)cyanoacetate (5.20 g, 30 mmol) was added to a solution of 2,6-diisopropylaniline (5.93 g, 30 mmol) in 100 ml of methanol. The mixture was refluxed for 10 min; the solvent was then removed under reduced pressure and the resulting residue was recrystallised from ethylacetate. The colourless crystals were filtered and washed with hexane. Yield: 3.75 g (12 mmol, 42%). – ^{1}H NMR ($CDCl_3$) δ 10.15 (d, 1H, N*H*), 7.72 (d, 1H, N-C*H*), 7.30-7.11 (m, 3H, H_{Aryl}), 4.19 (q, 2H, CH_2), 2.98 (m, 2H, C*H*), 1.29 (t, 3H, CH_3), 1.15 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 166.7, 159.9, 145.0, 134.4, 129.3, 124.5, 117.4, 74.3, 61.3, 28.8, 24.0, 14.7. – IR (KBr): ν 3202 cm^{-1} (N─H), 2216 (C≡N), 1674 (C=C─N), 1623 (C=C). – FI$^+$-HR-MS: *m/z* 300.1838 (calcd.), found 300.1745 for $C_{18}H_{24}N_2O_2$, δ = 9.3 mDa. – M.p. 157-158 °C.

5.2.6.6. ***Diethyl {[(4-methylphenyl)amino]methylene}malonate*** **29a**: A mixture of diethyl ethoxymethylenemalonate (4.06 g, 18.4 mmol) and p-toluidine (1.98 g, 18.3 mmol) in 5 ml of ethanol was heated at 140°C for 5 h, while the ethanol produced was distilled away along the reaction. The resulting thick oil was stored overnight at –30°C and a solid formed, which was ground in a mortar, then mixed with 20 ml of cold hexane and stirred for 1 h. Finally, the white powder was filtered. Yield: 4.34 g (15.6 mmol, 85%). – ^{1}H NMR ($CDCl_3$) δ 10.98 (d, 1H, N*H*), 8.50 (d, 1H, C*H*), 7.17 (d, 2H, H_{Aryl}), 7.03 (d, 2H, H_{Aryl}), 4.30 (q, 2H, CH_2), 4.24 (q, 2H, CH_2), 2.33 (s, 3H, CH_3), 1.38 (t, 3H, CH_3), 1.32 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.5, 166.1, 152.5, 137.3, 135.1, 130.7, 117.6, 93.4, 60.6, 60.3, 21.1, 14.8, 14.7. – FI$^+$-HR-MS: *m/z* 277.1314 (calcd.), found 277.1193 for $C_{15}H_{19}NO_4$, δ = –12.1 mDa. – M.p. 47.5-47.7°C.

5.2.6.7. ***Diethyl {[(2,6-diethylphenyl)amino]methylene}malonate*** **29b**: A solution of 2,6-diethylaniline (2.79 g, 18.3 mmol) in 5 ml of ethanol was dropped into diethyl ethoxymethylenemalonate (4.00 g, 18.1 mmol) while stirring at room temperature. The mixture was then heated at 150°C for 5 h and the ethanol produced was distilled away along the reaction. At the end, an oil remained, which was stored overnight at –30°C where it solidified. The solid was then ground in a mortar, taken in 10 ml of cold hexane, stirred for 30 min and finally filtered. A white powder resulted. Yield: 4.78 g (15.0 mmol, 83%). – ^{1}H NMR ($CDCl_3$) δ 10.50 (d, 1H, N*H*), 8.04 (d, 1H, C*H*), 7.26-7.13 (m, 3H, H_{Aryl}), 4.33 (q,

2H, CH_2), 4.19 (q, 2H, CH_2), 2.64 (q, 4H, CH_2), 1.40 (t, 3H, CH_3), 1.27 (t, 3H, CH_3), 1.22 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.6, 166.0, 160.0, 139.8, 137.2, 128.0, 127.5, 91.9, 60.4, 60.0, 25.2, 15.1, 14.7. – FI$^+$-HR-MS: *m/z* 319.1784 (calcd.), found 319.1744 for $C_{18}H_{25}NO_4$, δ = –4.0 mDa. – M.p. 77.4-78.4°C.

5.2.6.8. ***Diethyl {[(2,6-diisopropylphenyl)amino]methylene}malonate*** **29c**: A mixture of diethyl ethoxymethylenemalonate (3.31 g, 15 mmol) and 2,6-diisopropylaniline (2.96 g, 15 mmol) was heated at 150°C for 4 h while the ethanol produced along the reaction was distilled away. An oil resulted, which was stored overnight at –30°C; the formed solid was ground in a mortar, then mixed with 10 ml of cold hexane and stirred for 30 min. The white powder was finally filtered. Yield: 3.73 g (10.7 mmol, 71%). – ^{1}H NMR ($CDCl_3$) δ 10.41 (d, 1H, N*H*), 7.92 (d, 1H, C*H*), 7.27-7.11 (m, 3H, H_{Aryl}), 4.26 (q, 2H, CH_2), 4.11 (q, 2H, CH_2), 3.04 (m, 2H, C*H*), 1.33 (t, 3H, CH_3), 1.18 (t, 3H, CH_3), 1.16 (d, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.4, 160.2, 144.3, 135.6, 128.2, 124.0, 91.4, 60.1, 28.4, 23.7, 14.4. – FI$^+$-HR-MS: *m/z* 347.2097 (calcd.), found 347.2111 for $C_{20}H_{29}NO_4$, δ = 1.4 mDa. – M.p. 77.0-77.8°C.

5.2.6.9. ***Ethyl 2-acetyl-3-[(2,6-dimethylphenyl)amino]acrylate*** **31a**: A mixture of ethyl acetoacetate (4.87 g, 37 mmol), triethyl orthoformate (10.31 g, 68 mmol) and acetic anhydride (3.96 g, 38 mmol) was refluxed for 70 min and then the volatile components were removed in vacuo (typically 60°C/0.2mmHg). The residual liquid consists largely of the ethyl 2-acetyl-3-ethoxyacrylate **30a** and was used without purification. It was heated to 150°C and hot 2,6-dimethylaniline (9.00 g, 74 mmol) was quickly added. The mixture was kept at reflux for further 20 min, then it was allowed to partially cool and 50 ml of cold hexane were added under vigorously stirring. The mixture was stored overnight at –30°C and big colourless crystals formed, which were filtered and washed with hexane. Yield: 4.28 g (16 mmol, 44%). – ^{1}H NMR ($CDCl_3$) δ 12.31 (d, 1H, N*H*), 8.08 (d, 1H, C=C*H*), 7.12 (bs, 3H, H_{Aryl}), 4.20 (q, 2H, OCH_2), 2.57 (s, 3H, C(O)CH_3), 2.31 (s, 6H, CH_3), 1.29 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 200.5, 167.3, 159.5, 138.1, 132.8, 129.3, 127.5, 101.6, 60.0, 31.4, 18.8, 14.8. – EI$^+$-HR-MS: *m/z* 261.1365 (calcd.), found 261.1351 for $C_{15}H_{19}NO_3$, δ = –1.4 mDa. – M.p. 56.0-56.7°C.

5.2.6.10. ***Ethyl 2-butyryl-3-[(2,6-dimethylphenyl)amino]acrylate*** **31b**: A mixture of ethyl butyrylacetate (3.01 g, 18 mmol), triethyl orthoformate (5.44 g, 36 mmol) and acetic anhydride (1.86 g, 18 mmol) was refluxed for 5.5 h, and then the volatile components were removed in vacuo (60°C/0.2 mmHg). The residual liquid consisted largely of the ethyl 2-butyryl-3-ethoxyacrylate **30b** and was used without purification. It was heated to 150°C

and 2,6-dimethylaniline (2.30 g, 26 mmol) was quickly added. The mixture was kept at reflux for further 25 min, then it was allowed to cool and it was stored overnight at –30°C, where it solidified. The solid was pulverised, mixed with 20 ml of cold hexane and then stirred 15 min in an ice-bath. The white solid was finally filtered and washed with hexane. Yield: 0.74 g (3 mmol, 14%). – ^{1}H NMR ($CDCl_3$) δ 12.31 (d, 1H, N*H*), 8.08 (d, 1H, C=C*H*), 7.12 (sb, 3H, H_{Aryl}), 4.20 (q, 2H, OCH_2), 2.96 (t, 2H, C(O)CH_2), 2.31 (s, 6H, CH_3), 1.70 (m_6, 2H, CH_2), 1.29 (t, 3H, CH_3), 1.00 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 202.8, 167.0, 159.2, 137.8, 132.5, 128.9, 127.0, 101.1, 59.6, 44.2, 18.5, 18.4, 14.5, 14.1. – EI$^+$-HR-MS: *m/z* 289.1678 (calcd), found 289.1703 for $C_{17}H_{23}NO_3$, δ = 2.5 mDa. – M.p. 63.5-64.2°C.

5.2.7. Syntheses of the 3-aminoiminoacrylate ligands

5.2.7.1. ***2-Cyano-N-(2,6-diisopropylphenyl)acetamide*** **32:** Cyanoacetic acid (12.76 g, 0.15 mol) was added to a stirred suspension of phosphorus pentachloride (31.27 g, 0.15 mol) in dichloromethane (450 ml) at ambient temperature. The reaction mixture was heated under reflux for 30 min. After cooling, 2,6-diisopropylaniline (17.73 g, 0.10 mol) was added in 10 min and the reaction mixture was heated 2 h under reflux. It was then cooled in an ice/water bath, and water (200 ml) was added. After stirring for 30 min, the reaction mixture was neutralized by the addition of a sodium carbonate solution. The water phase was extracted twice with dichloromethane; the organic phases were then collected and dried over Na_2SO_4. The solvent was removed under reduced pressure and the obtained white solid was recrystallised from toluene and dried in vacuum. Yield: 23.3 g (0.095 mol, 95%). – ^{1}H NMR ($CDCl_3$) δ 7.73 (s, 1H, N*H*), 7.28-7.07 (m, 3H, H_{Aryl}), 3.33 (s, CH_2), 2.87 (m_7, 2H, C*H*), 1.07 (d, 12H, CH_3). – EI$^+$-MS *m/z* = 244 (M^+). – M.p. 160-162 °C.

5.2.7.2. ***Ethyl 2-cyano-N-(2,6-diisopropylphenyl)ethanimidoate*** **33:** A mixture of 2-cyano-*N*-(2,6-diisopropylphenyl)acetamide **32** (14.70 g, 60 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (66 ml, 66 mmol) was stirred 5 d at ambient temperature. The solvent was removed under vacuum and the residue was washed twice with abs. diethylether. Then the residue was taken up in 60 ml of abs. diethylether and cooled to 0°C. Triethylamine (9.2 ml, 66 mmol) was slowly added, and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue

was washed three times with abs. diethylether. The diethylether solutions were collected, dried over Na_2SO_4, and the solvent was removed under reduced pressure. Distillation of the residue (13.7 g) gave the pure product. Yield: 7.52 g (28 mmol, 46%). – ^{1}H NMR (DMSO-d_6) δ 7.18-6.97 (m, 3H, H_{Aryl}), 4.35 (q, 2H, OCH_2), 3.40 (s, 2H, CH_2), 2.72 (m$_7$, 2H, CH), 1.34 (t, 3H, CH_3), 1.14 (d, 6H, CH_3), 1.06 (d, 6H, CH_3); ^{13}C NMR (DMSO-d_6) δ 151.84, 142.00, 137.54, 124.24, 123.40, 115.21, 62.87, 27.98, 23.52, 22.78, 19.57, 14.30. – EI$^+$-MS *m/z* = 273 (M$^+$). – B.p. 103 °C.

5.2.7.3. ***Ethyl 2-cyano-3-ethoxy-N-(2,6-diisopropylphenyl)prop-2-enimidoate*** **34:** A mixture of ethyl- 2-cyano-*N*-(2,6-diisopropylphenyl)ethanimidoate **33** (7.3 g, 26 mmol), triethyl orthoformate (3.8 g, 26 mmol), and acetic anhydride (5.47 g, 54 mmol) was refluxed for 5.5 h. The solvent was removed under reduced pressure and the residual thick oil was distilled. Yield: 5.4 g (16 mmol, 64%). – ^{1}H NMR (DMSO-d_6) δ 7.88 (s, 1H, C=CH), 7.13-6.97 (m, 3H, H_{Aryl}), 4.29 (q, 2H, CH_2), 4.21 (q, 2H, CH_2), 2.80 (m$_7$, 2H, CH), 1.33 (t, 3H, CH_3), 1.15-1.05 (m, 15H, CH_3); ^{13}C NMR (DMSO-d_6) δ 171.6, 149.5, 143.4, 137.4, 123.9, 123.0, 112.1, 84.1, 72.9, 62.2, 28.1, 23.2, 15.3, 14.5 . – EI$^+$-MS *m/z* = 329 (M$^+$). – B.p. 125-130 °C.

5.2.7.4. ***Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]-N-(2,6-diisopropylphenyl) prop-2-enimidoate*** **35a**: A mixture of **34** (0.66 g, 2.0 mmol) and 2,6-dimethylaniline (0.25 g, 2.1 mmol) was dissolved in 7 ml of methanol and refluxed for 30 min. The solution was then stored overnight at –20 °C and the product crystallized. The formed crystals were filtered and washed with hexane. Yield: 0.48 g (1.2 mmol, 60%). – ^{1}H NMR ($CDCl_3$) δ 7.45 (d, 1H, C=CH), 7.06-6.95 (m, 6H, H_{Aryl}), 4.28 (q, 2H, CH_2), 2.96 (m$_7$, 1H, CH), 2.87 (m$_7$, 1H, CH), 2.19 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 1.30 (t, 3H, CH_3), 1.18 (d, 3H, CH_3), 1.12 (d, 3H, CH_3), 1.10 (d, 3H, CH_3), 1.07(d, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 155.8, 150.9, 142.8, 141.4, 133.8, 133.4, 129.2, 127.8, 127.5, 124.4, 124.0, 123.3, 115.1, 75.6, 62.2, 29.0, 28.6, 24.3, 23.8, 23.3, 22.9, 18.8, 18.6, 14.9. – IR (KBr): ν 3185 cm^{-1} (N─H), 2204 (C≡N), 1619(C=N), 1589 (C=C). – EI$^+$-HR-MS: *m/z* 403.2624 (calcd.), found 403.2656 for $C_{30}H_{41}N_3O$, δ = 3.2 mDa. – M.p. 195 °C.

5.2.7.5. ***Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]-N-(2,6-diisopropylphenyl)prop-2-enimidoate*** **35b**: A mixture of **34** (1.51 g, 4.6 mmol) and 2,6-diisopropylaniline (0.93 g, 4.7 mmol) in 10 ml of methanol was refluxed for 30 min. The reaction mixture was then stored overnight at 5 °C and the product crystallized. The colourless crystals were filtered and washed with hexane. Yield: 1.21 g (2.6 mmol, 57%). – ^{1}H NMR ($CDCl_3$) δ 7.53 (d, 1H, C=CH), 7.28-7.02 (m, 6H, H_{Aryl}), 4.37 (d, 1H, NH), 3.72 (q, 2H, CH_2), 3.04

(m_7, 2H, C*H*), 2.89 (m_7, 2H, C*H*), 1.18 (t, 3H, CH_3), 1.13 (d, 6H, CH_3), 1.10 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 156.8, 145.4, 145.0, 139.0, 135.9, 128.7, 124.4, 124.2, 123.3, 29.1, 28.8, 28.7, 24.3, 24.0, 23.9, 23.3, 22.9, 15.6. – IR (KBr): ν 3185 cm^{-1} (N─H), 2198 (C≡N), 1647 (C=N), 1587 (C==C). – EI$^+$-HR-MS: *m/z* 459.3250 (calcd.), found 459.3255 for $C_{30}H_{41}N_3O$, δ = 0.5 mDa. – M.p. 157 °C.

5.2.7.6. ***Ethyl 3-[(2,6-dimethylphenyl)amino]-2-{[(2,6-dimethylphenyl)amino] carbonyl}acrylate*** **36a**: A mixture of diethyl ethoxymethylenemalonate (3.00 g, 13.6 mmol) and 2,6-dimethylaniline (3.35 g, 27.4 mmol) was heated at 135°C for 20 h in an apparatus fitted for the distillation of the ethanol produced along the reaction. The mixture was then allowed to partially cool and 70 ml of cold hexane were added; the mixture was stirred in an ice-bath for 1 h, then the white precipitate was filtered and washed with hexane. Colourless crystals were obtained by recrystallisation in hexane. Yield: 4.32 g (11.8 mmol, 87%). – ^{1}H NMR ($CDCl_3$) δ 11.80 (d, 1H, N*H*), 10.22 (s, 1H, N*H*), 8.16 (d, 1H, NC*H*), 7.10 (bs, 6H, H_{Aryl}), 4.25 (q, 2H, CH_2), 2.33 (s, 6H, CH_3), 2.32 (s, 6H, CH_3), 1.32 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.1, 168.0, 158.5, 138.6, 135.8, 132.9, 129.3, 128.4, 127.0, 126.9, 100.0, 91.2, 60.4, 19.1, 19.0, 14.8. – EI$^+$-HR-MS: *m/z* 366.1943 (calcd.), found 366.1926 for $C_{22}H_{26}N_2O_4$, δ = –1.7 mDa. – M.p. 125.1-125.7°C.

5.2.7.7. ***Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(2,6-dimethylphenyl)amino]acrylate*** **37a**: A mixture of 3-[(2,6-dimethylphenyl)amino]-2-{[(2,6-dimethylphenyl)amino]carbonyl}acrylate **36a** (3.00 g, 8.2 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (12.34 g, 9.3 mmol) was stirred 7 d at ambient temperature. The solvent was removed under vacuum and the residue was washed twice with abs. diethylether. Then the residue was taken up in 40 ml of abs. diethylether and cooled to 0°C. Triethylamine (1.3 ml, 9.3 mmol) was slowly added and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with abs. diethylether. The diethylether solutions were collected and dried over Na_2SO_4; after that, the solvent was removed under reduced pressure. A yellow oil was obtained, which was mixed with 10 ml of hexane and stored overnight at -30°C: the precipitate formed was filtered and recrystallised in hexane/ethylacetate = 4/1, where big colourless rhomboidal crystals grew. Yield: 2.11 g (5.3 mmol, 65%). – ^{1}H NMR ($CDCl_3$) δ 9.74 (d, 1H, N*H*), 7.01 (sb, 3H, H_{Aryl}), 6.94 (d, 2H, H_{Aryl}), 6.82 (d, 1H, C=C*H*), 6.78 (t, 1H, H_{Aryl}), 4.36 (q, 2H, OCH_2), 4.08 (q, 2H, OCH_2), 2.09 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 1.39 (t, 3H, CH_3), 1.25 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 157.0, 153.5, 146.2, 138.4, 133.1, 129.0, 128.4, 128.3, 126.5, 122.4,

100.0, 93.2, 62.2, 59.9, 19.0, 18.4, 14.8, 14.6. – EI^+-HR-MS: *m/z* 394.2256 (calcd.), found 394.2257 for $C_{24}H_{30}N_2O_3$, δ = -0.1 mDa. – M.p. 69.6-71.0°C.

5.2.7.8. ***Ethyl 3-[(2,6-diisopropylphenyl)amino]-2-{[(2,6-diisopropylphenyl)amino] carbonyl}acrylate*** **36b**: A mixture of diethyl ethoxymethylenemalonate (5.01 g, 23 mmol) and 2,6-diisopropylaniline (9.04 g, 46 mmol) was heated at 135°C for 38 h, while the ethanol produced along the reaction was distilled away. The mixture was then allowed to partially cool and 20 ml of cold hexane were added under vigorously stirring. After that, it was stored overnight at –30°C and a white precipitate was collected and filtered. Yield: 7.43 g (16 mmol, 68%). – ^{1}H NMR ($CDCl_3$) *δ* 11.90 (d, 1H, N*H*), 10.10 (s, 1H, N*H*), 8.07 (d, 1H, NC*H*), 7.33-7.18 (m, 6H, H_{Aryl}), 4.25 (q, 2H, CH_2), 3.20 (m_7, 2H, C*H*), 3.19 (m_7, 2H, C*H*), 1.31 (t, 3H, CH_3), 1.23 (d, 24H, CH_3); ^{13}C NMR ($CDCl_3$) *δ* 169.3, 169.1, 159.7, 146.7, 144.4, 136.5, 132.3, 128.2, 128.1, 124.4, 123.7, 91.0, 60.4, 29.4, 28.9, 24.1, 14.8. – EI^+-HR-MS: *m/z* 478.3195 (calcd.), found 478.3201 for $C_{30}H_{42}N_2O_3$, δ = -0.6 mDa. – M.p. 182.0-182.7°C.

5.2.7.9. ***Ethyl 2-{ethoxy[(2,6-diisopropylphenyl)imino]methyl}-3-[(2,6-diisopropyl phenyl)amino]acrylate*** **37b**: A mixture of ethyl 3-[(2,6-diisopropylphenyl)amino]-2-{[(2,6-diisopropylphenyl)amino]carbonyl}acrylate **36b** (4.00 g, 8 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (12.45 g, 9 mmol) was stirred 9 d at ambient temperature. The solvent was removed under vacuum and the residue was washed twice with abs. diethylether. Then the residue was taken up in 30 ml of abs. diethylether and cooled to 0°C. Triethylamine (1.3 ml, 9 mmol) was slowly added and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with abs. diethylether. The diethylether solutions were collected, dried over Na_2SO_4, and the solvent was removed under reduced pressure. An oil was obtained, out of which small crystals slowly grew. The solid was finally filtered. Yield: 2.57 g (5 mmol, 60%). – ^{1}H NMR ($CDCl_3$) *δ* 9.63 (d, 1H, N*H*), 7.26-6.89 (m, 6H, H_{Aryl}), 6.61 (d, 1H, C=C*H*), 4.34 (q, 2H, OCH_2), 4.18 (q, 2H, OCH_2), 2.97 (m_7, 2H, C*H*), 2.74 (m_7, 2H, C*H*), 1.38 (t, 3H, CH_3), 1.30 (t, 3H, CH_3), 1.12 (d, 6H, CH_3), 1.05 (d, 12H, CH_3), 1.02 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) *δ* 168.8, 157.4, 155.9, 154.9, 144.9, 143.3, 137.5, 127.9, 123.5, 122.8, 122.7, 91.9, 61.8, 59.6, 28.0, 24.1, 23.4, 22.3, 14.5, 14.4. – EI^+-HR-MS: *m/z* 506.3508 (calcd.), found 506.3554 for $C_{32}H_{46}N_2O_3$, δ = 4.6 mDa. – M.p. 102.8-103.3°C.

5.2.7.10. ***Ethyl 3-[(2,6-diethylphenyl)amino]-2-{[(4-methylphenyl)amino]carbonyl} acrylate*** **38c**: A mixture of diethyl {[(2,6-diethylphenyl)amino]methylene}malonate **29b**

(1.20 g, 4 mmol) and p-toluidine (0.44 g, 4 mmol) was heated at 135°C for 30 h, while the ethanol produced along the reaction was distilled away. After that, the mixture was allowed to partly cool and 10 ml of hexane where added while vigorously stirring. The mixture was stirred further 30 min in an ice-bath and the precipitate formed was filtered and purified by column chromatography (on silica, eluant ethylacetate:hexane = 1:4). Yield: 0.67 g (2 mmol, 46%). – ^{1}H NMR ($CDCl_3$) δ 11.78 (d, 1H, N*H*), 10.89 (s, 1H, C(O)N*H*), 8.08 (d, 1H, C=C*H*), 7.53 (d, 2H, H_{Aryl}), 7.24-7.13 (m, 5H, H_{Aryl}), 4.23 (q, 2H, OCH_2), 2.69 (q, 4H, CH_2), 2.33 (s, 3H, CH_3), 1.30 (t, 3H, CH_3), 1.25 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.7, 167.6, 158.8, 139.5, 137.2, 135.9, 133.1, 129.4, 127.6, 127.1, 120.6, 91.0, 60.1, 24.9, 20.9, 14.9, 14.5. – EI$^+$-HR-MS: *m/z* 380.2100 (calcd.), found 380.2075 for $C_{23}H_{28}N_2O_3$, δ = –2.5 mDa.

5.2.7.11. ***Ethyl 3-[(2,6-diethylphenyl)amino]-2-{ethoxy[(4-methylphenyl)imino] methyl}acrylate*** **37c**: A mixture of ethyl 3-[(2,6-diethylphenyl)amino]-2-{[(4-methylphenyl)amino]carbonyl}acrylate **38c** (0.60 g, 2 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (2.35 g, 2 mmol) was stirred 35 d at ambient temperature. The solvent was then evaporated under vacuum and the residue was washed with abs. diethylether, after that it was taken in 20 ml of abs. diethylether and cooled to 0°C. Triethylamine (0.5 ml) was slowly added and the mixture was stirred at room temperature for 2 h. The ether phase was separated and the residue again washed with abs. ether. The ether solutions were collected and the solvent was evaporated under vacuum. The resulting solid was recrystallised from diethylether. Yield 0.37 g (0.9 mmol, 57%). – ^{1}H NMR ($CDCl_3$) δ 9.58 (d, 1H, N*H*), 7.18-6.89 (m, 5H, H_{Aryl}), 6.78 (d, 1H, C=C*H*), 6.71 (d, 2H, H_{Aryl}), 4.29 (q, 2H, OCH_2), 4.01 (q, 2H, OCH_2), 2.44 (q, 4H, CH_2), 2.28 (s, 3H, CH_3), 1.35 (t, 3H, CH_3), 1.20 (t, 3H, CH_3), 1.13 (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.5, 159.5, 154.6, 147.1, 139.9, 137.5, 131.8, 129.6, 127.4, 127.2, 122.0, 93.0, 62.3, 60.0, 25.0, 21.2, 15.0, 14.7, 14.6. – EI$^+$-HR-MS: *m/z* 408.2413 (calcd.), found 408.2433 for $C_{25}H_{32}N_2O_3$, δ = 2.0 mDa.

5.2.7.12. ***Ethyl 2-{[(2,6-dimethylphenyl)amino]carbonyl}-3-[(4-methylphenyl) amino]acrylate*** **38d [Method C]**: A mixture of equimolar amounts of diethyl {[(4-methylphenyl)amino]methylene}malonate **29a** (2.00 g, 7.2 mmol) and 2,6-dimethylaniline (0.88 g, 7.2 mmol) was heated at 155°C for 16 h in an apparatus fitted for the distillation of the ethanol produced along the reaction. Then the mixture was allowed to partially cool and 40 ml of hexane were added; the mixture was further stirred 1 h in an ice-bath and finally stored at –30°C. The colourless crystals formed were finally filtered. Yield: 2.44 g

(6.9 mmol, 96%). – ^{1}H NMR ($CDCl_3$) δ 12.38 (d, 1H, N*H*), 10.20 (s, 1H, N*H*), 8.56 (d, 1H, C=C*H*), 7.16 (d, 2H, H_{Aryl}), 7.10 (sb, 3H, H_{Aryl}), 7.02 (d, 2H, H_{Aryl}), 4.31 (q, 2H, OCH_2), 2.33 (s, 3H, CH_3), 2.29 (s, 6H, CH_3), 1.39 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.6, 167.6, 151.1, 137.1, 135.6, 134.5, 134.4, 130.3, 128.0, 126.8, 117.1, 99.6, 60.2, 20.9, 18.7, 14.6. – EI$^+$-HR-MS: *m/z* 352.1787 (calcd.), found 352.1765 for $C_{21}H_{24}N_2O_3$, δ = –2.2 mDa. – M.p. 128.1-129.3°C.

5.2.7.13. ***Ethyl 3-[(2,6-dimethylphenyl)amino]-3-oxopropanoate*** **39d**: A mixture of diethylmalonate (48.0 g, 0.30 mol) and 2,6-dimethylaniline (12.01 g, 0.10 mmol) was heated at 160°C for 20 h in an apparatus fitted for the distillation of the ethanol produced along the reaction. Then the mixture was cooled to room temperature, mixed with 80 ml of cold hexane, stirred in an ice-bath for 1 h and the white solid was finally filtered. Yield: 22.14 g (0.09 g, 94%). – ^{1}H NMR ($CDCl_3$) δ 8.48 (s, 1H, N*H*), 7.07-6.98 (m, 3H, H_{Aryl}), 4.20 (q, 2H, OCH_2), 3.44 (s, 2H, CH_2C=O), 2.16 (s, 6H, CH_3), 1.26 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.6, 163.5, 135.2, 133.6, 128.1, 127.3, 61.4, 41.4, 18.3, 14.1. – EI$^+$-HR-MS: *m/z* 235.1208 (calcd.), found 235.1200 for $C_{13}H_{17}NO_3$, δ = –0.8 mDa. – M.p. 88.7-89.9°C

5.2.7.14. ***Ethyl 2-{[(2,6-dimethylphenyl)amino]carbonyl}-3-[(4-methylphenyl) amino]acrylate*** **38d [Method D]**: A mixture of ethyl 3-[(2,6-dimethylphenyl)amino]-3-oxopropanoate **39d** (1.25 g, 5.3 mmol), p-toluidine (0.60 g, 5.5 mmol) and triethyl orthoformate (0.83 g, 5.5 mmol) was heated at 160°C for 4 h in an apparatus fitted for the distillation of the ethanol produced along the reaction. The mixture was then allowed to partially cool and mixed with 10 ml of hexane in an ice-bath for 30 min. A white solid precipitated, which was filtered and recrystallised from ethylacetate/hexane. Yield: 0.94 g (2.7 mmol, 50%). – ^{1}H NMR ($CDCl_3$) δ 12.38 (d, 1H, N*H*), 10.20 (s, 1H, N*H*), 8.56 (d, 1H, C=C*H*), 7.16 (d, 2H, H_{Aryl}), 7.10 (sb, 3H, H_{Aryl}), 7.02 (d, 2H, H_{Aryl}), 4.31 (q, 2H, OCH_2), 2.33 (s, 3H, CH_3), 2.29 (s, 6H, CH_3), 1.39 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.6, 167.6, 151.1, 137.1, 135.6, 134.5, 134.4, 130.3, 128.0, 126.8, 117.1, 99.6, 60.2, 20.9, 18.7, 14.6. – EI$^+$-HR-MS: *m/z* 352.1787 (calcd.), found 352.1765 for $C_{21}H_{24}N_2O_3$, δ = –2.2 mDa. – M.p. 128.1-129.3°C.

5.2.7.15. ***Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(4-methylphenyl) amino]acrylate*** **37d**: A mixture of ethyl 2-{[(2,6-dimethylphenyl)amino]carbonyl}-3-[(4-methylphenyl)amino]acrylate **38d** (1.60 g, 4.5 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (6.68 g, 5.0 mmol) was stirred 12 d at ambient temperature. The solvent was removed under vacuum and the residue was washed twice with abs. diethylether. Then, the residue was taken up in 40 ml of abs.

diethylether and cooled to 0°C. Triethylamine (0.7 ml, 5.0 mmol) was slowly added and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with abs. diethylether. The diethylether solutions were collected, dried over Na_2SO_4, and the solvent was removed under reduced pressure. A yellow oil remained, which was mixed with 10 ml of hexane and stored overnight at –30°C: finally, the small yellow crystals formed were filtered. Yield: 0.30 g (0.8 mmol, 18%). – ^{1}H NMR ($CDCl_3$) δ 10.06 (d, 1H, N*H*), 7.14 (d, 1H, C=C*H*), 7.05 (d, 2H, H_{Aryl}), 7.00 (d, 2H, H_{Aryl}), 6.82 (t, 1H, H_{Aryl}), 6.54 (d, 2H, H_{Aryl}), 4.39 (q, 2H, OCH_2), 4.12 (q, 2H, OCH_2), 2.28 (s, 3H, CH_3), 2.13 (s, 6H, CH_3), 1.42 (t, 3H, CH_3), 1.26 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.2, 157.0, 146.8, 146.1, 137.6, 133.4, 130.2, 128.1, 127.9, 122.2, 116.5, 94.1, 61.9, 59.8, 20.7, 18.5, 14.5, 14.3. – EI$^+$-HR-MS: *m/z* 380.2100 (calcd.), found 380.2067 for $C_{23}H_{28}N_2O_3$, δ = –3.3 mDa. – M.p. 60.6-61.5°C.

5.2.7.16. ***Ethyl 3-[(2,6-diisopropylphenyl)amino]-3-oxopropanoate*** **39e**: A mixture of 2,6-diisopropylaniline (15.00 g, 76 mmol) and diethyl malonate (50.00 g, 309 mmol) was heated at 160°C for 19 h while distilling the ethanol produced along the reaction. A thick oil resulted, which was then mixed with 170 ml of cold hexane, stirred for 1 h, and finally filtered. The operation was repeated with further 150 ml of hexane and, finally, a white powder was yielded and recrystallised in ethanol/water = 3/1. Yield: 13.19 g (45 mmol, 60%). – ^{1}H NMR ($CDCl_3$) δ 8.53 (s, 1H, N*H*), 7.31 (t, 1H, H_{Aryl}), 7.19 (d, 2H, H_{Aryl}), 4.28 (q, 2H, OCH_2), 3.53 (s, 2H, CH_2C=O), 3.05 (m$_7$, 2H, C*H*), 1.35 (t, 3H, CH_3), 1.20 (d, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 169.9, 164.4, 146.0, 130.9, 128.4, 123.5, 61.8, 41.2, 28.8, 23.6, 14.1. – EI$^+$-HR-MS: *m/z* 291.1834 (calcd.), found 291.1788 for $C_{17}H_{25}NO_3$, δ = –4.6 mDa. – M.p. 127.2-127.9°C.

5.2.7.17. ***Ethyl 2-{[(2,6-diisopropylphenyl)amino]carbonyl}-3-[(2,6-dimethylphenyl) amino]acrylate*** **38e**: A mixture of ethyl 3-[(2,6-diisopropylphenyl)amino]-3-oxopropanoate **39e** (2.10 g, 7 mmol), 2,6-dimethylaniline (0.90 g, 7 mmol) and triethyl orthoformate (1.10 g, 7 mmol) was heated at 130°C for 5 h in an apparatus fitted for the distillation of the ethanol produced along the reaction. An oil resulted, which solidified at room temperature. The white solid was ground in a mortar, mixed with 50 ml of cold hexane, then stirred for 30 min and finally filtered. Yield: 2.07 g (5 mmol, 70%). – ^{1}H NMR ($CDCl_3$) δ 11.90 (d, 1H, N*H*), 10.12 (s, 1H, N*H*), 8.19 (d, 1H, C=C*H*), 7.33-7.09 (m, 6H, H_{Aryl}), 4.27 (q, 2H, OCH_2), 3.20 (m$_7$, 2H, C*H*), 2.33 (s, 6H, CH_3), 1.34 (t, 3H, CH_3), 1.25 (bd, 12H, CH_3); ^{13}C NMR ($CDCl_3$) δ 168.8, 168.7, 158.0, 146.2, 138.2, 132.3, 131.8, 129.0, 127.8, 126.5, 123.3, 90.7, 60.0, 28.9, 24.2, 23.2, 18.6, 14.5. – EI$^+$-HR-MS:

m/z 422.2569 (calcd.), found 422.2599 for $C_{26}H_{34}N_2O_3$, δ = 3.0 mDa. – M.p. 120.3-121.0°C.

5.2.7.18. ***Ethyl 2-[[(2,6-diisopropylphenyl)imino](ethoxy)methyl]-3-[(2,6-dimethyl phenyl)amino]acrylate*** **37e**: A mixture of ethyl 2-{[(2,6-diisopropylphenyl)amino] carbonyl}-3-[(2,6-dimethylphenyl)amino]acrylate **38e** (1.43 g, 3 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (4.97 g, 4 mmol) was stirred 30 d at ambient temperature. The solvent was removed under vacuum and the residue was washed twice with abs. diethylether. After that, the residue was taken up in 20 ml of abs. diethylether and cooled to 0°C. Triethylamine (0.6 ml) was slowly added and the mixture was stirred at room temperature for 2 h. The organic phase was separated and the residue was washed three times with abs. diethylether. The diethylether solutions were collected and the solvent was removed under reduced pressure. An oil resulted, out of which small colourless crystals slowly grew. The crystals were filtered and washed with cold diethylether. Yield: 0.40 g (0.9 mmol, 26%). – ^{1}H NMR ($CDCl_3$) *δ* 9.62 (d, 1H, N*H*), 7.10-6.90 (m, 6H, H_{Aryl}), 6.60 (d, 1H, C=C*H*), 4.34 (q, 2H, OCH_2), 4.20 (q, 2H, OCH_2), 2.98 (m_7, 2H, C*H*), 1.88 (s, 6H, CH_3), 1.38 (t, 3H, CH_3), 1.31 (t, 3H, CH_3), 1.12 (d, 6H, CH_3), 1.04 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) *δ* 168.8, 156.0, 153.6, 143.4, 138.0, 137.8, 133.0, 128.4, 126.3, 123.0, 122.6, 92.2, 61.7, 59.7, 27.9, 24.1, 22.3, 17.8, 14.5, 14.4. – EI$^+$-HR-MS: *m/z* 450.2882 (calcd.), found 450.2905 for $C_{28}H_{38}N_2O_3$, δ = 2.3 mDa.

5.2.8. Synthesis of a bidentate pyridinylethylamine ligand

5.2.8.1. ***N-[(2-Chlorophenyl)methylene]-N-(1-pyridin-2-ylethyl)amine*** **40:** A solution of 2-chlorobenzaldehyde (2.1 g, 15 mmol) in 20 ml of methanol was added dropwise to a solution of 1-pyridine-2-ylethanamine **15b** (1.8 g, 15 mmol) in 15 ml of methanol while stirring at ambient temperature. The mixture was then refluxed for 5 h. The solvent was removed under vacuum and a dark yellow oil resulted. Yield: 3.2 g (13 mmol, 85%). – ^{1}H NMR ($CDCl_3$) *δ* 8.28 (s, 1H, N=C*H*), 8.50 (d, 1H, N=C*H*), 8.11 (t, 1H, H_{Aryl}), 7.58 (t, 1H, H_{Aryl}), 7.47 (d, 1H, H_{Aryl}), 7.29-7.16 (m, 3H, H_{Aryl}), 7.07 (t, 1H, H_{Aryl}), 4.70 (q, 1H, C*H*), 1.59 (d, 3H, CH_3). – EI$^+$-HR-MS: *m/z* 244.0767 (calcd.), found 244.0724 for $C_{14}H_{13}ClN_2$, δ = 2.3 mDa.

5.2.9. Synthesis of an amidoiminomalonate ligand

5.2.9.1. ***N,N'-bis(2,6-diisopropylphenyl)malonamide*** **43**: A mixture of diethyl malonate (10.10 g, 0.062 mol) and 2,6-diisopropylaniline (25.00 g, 0.127 mol) was heated at 160°C for about 10 h in an equipment fitted for the distillation of the ethanol produced along the reaction. The mixture was then cooled to room temperature and the solid mass was reduced to a powder which was mixed with 200 ml of cold hexane and stirred for 1 h. Finally, the microcrystalline pale-pink powder was filtered and washed with hexane. Yield: 23.79 g (56 mmol, 90%). – ^{1}H NMR ($CDCl_3$) δ 8.48 (s, 2H, N*H*), 7.20 (t, 1H, H_{Aryl}), 7.10 (d, 4H, H_{Aryl}), 3.62 (s, 2H, CH_2), 2.98 (m_7, 4H, C*H*), 1.11 (d, 24H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.1, 145.9, 130.7, 128.5, 123.5, 42.7, 28.9, 23.6. – EI$^+$-HR-MS: *m/z* 422.2933 (calcd), found 422.2910 for $C_{27}H_{38}N_2O_2$, δ = –2.3 mDa. – M.p. 270.3-271.7°C.

5.2.9.2. ***Ethyl N-(2,6-diisopropylphenyl)-3-[(2,6-diisopropylphenyl)amino]-3-oxopropanimidoate*** **44**: A mixture of *N*,*N*'-bis(2,6-diisopropylphenyl)malonamide **43** (10.00 g, 24 mmol) and a 1.0M solution of triethyloxonium tetrafluoroborate in dichloromethane (74.08 g, 56 mmol) was stirred 20 d at ambient temperature. The solvent was then evaporated under vacuum and the residue was washed with 160 ml of absolute diethylether and filtered. After that, it was taken in 60 ml of abs. diethylether, cooled to 0°C and triethylamine (7.5 ml, 54 mmol) was slowly added. The mixture was stirred at room temperature for 2 h and then it was filtered. The ether phases were collected and the solvent was removed under reduced pressure; the residue consisted of a white solid, which was recrystallised from toluene/hexane = 3/1. Yield: 6.97 g (15 mmol, 64%). – ^{1}H NMR ($CDCl_3$) δ 7.59 (s, 1H, N*H*), 7.34-7.02 (m, 6H, H_{Aryl}), 4.50 (q, 2H, OCH_2), 3.25 (s, 2H, CH_2), 3.08 (m_7, 2H, C*H*), 2.87 (m_7, 2H, C*H*), 1.47 (t, 3H, CH_3), 1.21 (d, 12H, CH_3), 1.20 (d, 6H, CH_3), 1.16 (d, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.4, 154.9, 146.2, 137.8, 131.0, 128.6, 123.8, 123.7, 123.6, 123.2, 62.6, 38.4, 28.8, 28.3, 23.4, 22.7, 14.5. – EI$^+$-HR-MS: *m/z* 450.3246 (calcd.), found 450.3172 for $C_{29}H_{42}N_2O_2$, δ = –7.4 mDa. – M.p. 158.2-159.9°C.

5.2.10. Syntheses of the tridentate 3-aminoacrylate ligands

5.2.10.1. ***Ethyl 2-cyano-3-[(pyridin-2-ylmethyl)amino]acrylate*** **54a**: A mixture of ethyl (ethoxymethylene)cyanoacetate (2.00 g, 12 mmol) and 1-pyridin-2-ylmethanamine (1.32 g, 12 mmol) in 10 ml of methanol was refluxed for 20 min. After that, the volume of

the solvent was decreased under reduced pressure to approximately 3 ml and it was stored overnight at –30°C. The precipitate was filtered and washed with hexane. Yield: 2.35 g (10 mmol, 88%). – ^{1}H NMR ($CDCl_3$) δ 8.57 (d, 1H, H_{Pyr}), 8.00 (d, 1H, C=C*H*), 7.79 (t, 1H, H_{Pyr}), 7.35-7.29 (m, 2H, H_{Pyr}), 4.68 (d, 2H, NCH_2), 4.14 (q, 2H, OCH_2), 1.22 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.6, 159.6, 155.3, 150.0, 137.5, 123.5, 122.0, 116.8, 73.8, 61.0, 53.6, 14.8. – EI$^+$-HR-MS: *m/z* 231.1008 (calcd.), found 231.0957, for $C_{12}H_{13}N_3O_2$, δ = –5.1 mDa.

5.2.10.2. ***Ethyl 2-cyano-3-[(2-pyridin-2-ylethyl)amino]acrylate*** **54b**: A mixture of equimolar amounts of ethyl (ethoxymethylene)cyanoacetate (3.00 g, 17 mmol) and 2-(2-aminoethyl)pyridine (2.24 g, 17 mmol) in 10 ml of methanol was refluxed for 20 min. After that, the volume of the solvent was diminished under reduced pressure to approximately 3 ml and it was stored overnight at –30°C. The pale yellow precipitate was filtered and washed with hexane. Yield: 2.14 g (9 mmol, 50%). – ^{1}H NMR ($CDCl_3$) δ 8.57 (d, 1H, H_{Pyr}), 7.82-7.73 (m, 2H, C=C*H* and H_{Pyr}), 7.32-7.26 (m, 2H, H_{Pyr}), 4.12 (q, 2H, OCH_2), 3.80 (q, 2H, NCH_2), 3.18 (t, 2H, CH_2), 1.21 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.8, 159.5, 158.0, 149.7, 137.1, 124.0, 122.3, 117.0, 72.0, 60.7, 48.8, 37.8, 14.8. – EI$^+$-HR-MS: *m/z* 245.1164 (calcd.), found 245.1174, for $C_{13}H_{15}N_3O_2$, δ = –1.0 mDa.

5.2.10.3. ***Ethyl 2-cyano-3-{[2-(diphenylphosphino)ethyl]amino}acrylate*** **54c**: A mixture of equimolar amounts of ethyl (ethoxymethylene)cyanoacetate (0.37 g, 2 mmol) and 2-(diphenylphosphino)ethylamine (0.50 g, 2 mmol) in 10 ml of methanol was stirred and heated at reflux for 30 min. After that, the volume of the solvent was diminished under reduced pressure to approximately 2 ml and 5 ml of hexane were added while stirring. The mixture was stored overnight at –30°C and then the white precipitate was filtered. Yield: 0.65 g (2 mmol, 84%). – ^{1}H NMR ($CDCl_3$) δ 8.94 (sb, 1H, N*H*), 7.90 (d, 1H, C=C*H*), 7.72-7.31 (m, 10H, H_{Aryl}), 4.10 (q, 2H, OCH_2), 3.68 (m, 1H, CH_2), 3.39 (m, 1H, CH_2), 2.58 (m, 1H, CH_2), 2.40 (m, 1H, CH_2), 1.22 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.9, 158.8, 136.8, 136.6, 132.8, 132.5, 129.2, 128.9, 128.7, 118.6, 71.5, 60.6, 47.1 (d), 30.0 (d), 14.3. – EI$^+$-HR-MS: *m/z* 352.1341 (calcd.), found 352.1378, for $C_{20}H_{21}N_2O_2P$, δ = 3.7 mDa.

5.2.10.4. ***Ethyl 2-cyano-3-{[2-(ethylthio)ethyl]amino}acrylate*** **54d**: To a solution of 2-(ethylthio)ethylamine hydrochloride (1.42 g, 10 mmol) and sodium hydroxide (0.40 g, 10 mmol) in 80 ml of methanol, ethyl (ethoxymethylene)cyanoacetate (1.69 g, 10 mmol) was added at room temperature. The reaction mixture was refluxed for 20 min and then concentrated under vacuum to circa 10 ml. Under stirring and cooling in an ice-bath, 100 ml of distilled water were slowly dropped into the reaction mixture. The resulting

white precipitate was filtered, repeatedly washed with water and dried in vacuo. Yield: 1.88 g (8 mmol, 82%). – ^{1}H NMR ($CDCl_3$) δ 9.04 (bs, 1H, N*H*), 7.26 (d, 1H, C=C*H*), 4.16 (q, 2H, OCH_2), 3.44 (q, 2H, NCH_2), 2.66 (t, 2H, SCH_2), 2.49 (q, 2H, SCH_2), 1.25 (t, 3H, CH_3), 1.20 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 165.7, 160.0, 117.1, 72.14, 60.9, 49.3, 32.4, 26.4, 15.1, 14.8. – EI$^+$-HR-MS: *m/z* 228.0932 (calcd), found 228.0927, for $C_{10}H_{16}N_2O_2S$, δ = –0.5 mDa.

5.3. Syntheses of the metal complexes

5.3.1. Syntheses of iron(II) complexes

General procedure for the synthesis of the iron(II) complexes **4**–**7**: The appropriate ligand was added to a suspension of $FeCl_2(thf)_2$ in absolute THF in a Schlenk-flask under argon. The mixture was stirred for 3 h at room temperature, then the solvent was removed and finally the product was dried in vacuum.

5.3.1.1. ***2,6-Bis[1-(phenylimino)ethyl]pyridyliron(II) chloride*** **4**: 2,6-Bis [(phenylimino)ethyl]pyridine (200 mg, 0.64 mmol), $FeCl_2(thf)_2$ (173 mg, 0.64 mmol), THF 30 ml. Compound **4** was obtained as a dark blue powder. Yield 251 mg (0.56 mmol, 89%). – FI$^+$-HR-MS: *m/z* 439.0305 (calcd.), found 439.0225 for $C_{21}H_{19}N_3Cl_2Fe$, δ = 8.0 mDa. – $C_{21}H_{19}N_3Cl_2Fe$: calcd. C 57.30, H 4.35, N 9.54, found C 57.0, H 4.52, N 9.28.

5.3.1.2. ***2,6-Bis[1-(4-methoxyphenylimino)ethyl]pyridyliron(II) chloride*** **5a**: 2,6-Bis[1-(4-methoxyphenylimino)ethyl]pyridine **1a** (150 mg, 0.42 mmol), $FeCl_2(thf)_2$ (109 mg, 0.42 mmol), THF 30 ml. Compound **5a** was obtained as a dark blue powder. Yield 189 mg (0.38 mmol, 90%). – FI$^+$-HR-MS: *m/z* 499.0517 (calcd.), found 499.0475 for $C_{23}H_{23}N_3O_2Cl_2Fe$, δ = 0.8 mDa. – $C_{23}H_{23}N_3O_2Cl_2Fe$: calcd. C 55.22, H 4.63, N 8.40, found C 55.44, H 4.92, N 8.11.

5.3.1.3. ***2,6-Bis[1-(3-methoxyphenylimino)ethyl]pyridyliron(II) chloride*** **5b**: 2,6-Bis[1-(3-methoxyphenylimino)ethyl]pyridine **1b** (200 mg, 0.54 mmol), $FeCl_2(thf)_2$ (145 mg, 0.54 mmol), THF 30 ml. Compound **5b** was obtained as a dark blue powder. Yield 208 mg (0.42 mmol, 77%). – $C_{23}H_{23}N_3O_2Cl_2Fe$: calcd. C 55.22, H 4.63, N 8.40, found C 55.16, H 4.65, N 8.15.

5.3.1.4. ***2,6-Bis[1-(4-trifluoromethylphenylimino)ethyl]pyridyliron(II) chloride*** **6a**: 2,6-Bis[1-(4-trifluoromethylphenylimino)ethyl]pyridine **2a** (100 mg, 0.22 mmol), $FeCl_2(thf)_2$ (60 mg, 0.22 mmol), THF 30 ml. Compound **6a** was obtained as a dark blue

powder. Yield 114 mg (0.2 mmol, 89%). – FI^+-HR-MS: *m*/*z* 575.0053 (calcd.), found 574.9968 for $C_{23}H_{17}N_3F_6Cl_2Fe$, δ = 8.5 mDa. – $C_{23}H_{17}N_3F_6Cl_2Fe$: calcd. C 47.94, H 2.97, N 7.29, found C 47.64, H 2.72, N 6.98.

5.3.1.5. ***2,6-Bis[1-(3-trifluoromethylphenylimino)ethyl]pyridyliron(II) chloride*** **6b**: 2,6-Bis[1-(3-trifluoromethylphenylimino)ethyl]pyridine **2b** (54 mg, 0.12 mmol), $FeCl_2(thf)_2$ (33 mg, 0.12 mmol), THF 15 ml. Compound **6b** was obtained as a dark blue powder. Yield 44 mg (0.08 mmol, 64%). – FI^+-HR-MS: *m*/*z* 575.0053 (calcd.), found 575.0061 for $C_{23}H_{17}N_3F_6Cl_2Fe$, δ = 0.8 mDa. – $C_{23}H_{17}N_3F_6Cl_2Fe$: calcd. C 47.94, H 2.97, N 7.29, found C 47.50, H 3.02, N 7.03.

5.3.1.6. ***1-{6-[N-(3-trifluoromethyl)ethanimidoyl]pyridin-2-yl}ethanone iron(II) chloride*** **7**: 1-{6-[*N*-(3-Trifluoromethyl)ethanlimidoyl]pyridin-2-yl}ethanone **3** (150 mg, 0.49 mmol), $FeCl_2(thf)_2$ (133 mg, 0.49 mmol), THF 30 ml. Compound **7** was obtained as a dark blue powder. Yield 127 mg (0.29 mmol, 60%). – ESI^+-MS: *m*/*z* = 446 ($M^+ + NH_4^+$). – $C_{16}H_{13}N_2OF_3Cl_2Fe$: calcd. C 44.37, H 3.02, N 6.46, found C 44.67, H 3.28, N 6.11.

General procedure for the synthesis of the iron(II) complexes **12a**-**h**: A solution of the appropriate ligand in dry THF was added to a suspension of $FeCl_2(thf)_{1.5}$ in absolute THF in a Schlenk-flask under argon. The mixture was stirred for 4 h at room temperature, then the solvent was removed and finally the product was dried under vacuum.

5.3.1.7. ***N-(2-Chlorobenzylidene)-N-[1-(6-{1-[(2-chlorobenzylidene)amino]ethyl} pyridin-2-yl)ethyl]amine iron(II) chloride*** **12a**: *N*-(2-Chlorobenzylidene)-*N*-[1-(6-{1-[(2-chlorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine **8a** (409 mg, 1.0 mmol), $FeCl_2(thf)_{1.5}$ (231 mg, 0.98 mmol), THF 25 ml. Compound **12a** was obtained as a brown powder. Yield 519 mg (0.97 mmol, 98%). – IR (KBr): *v* 3428 cm^{-1} (C=N), 3066 (C–H, *aryl*), 2975, 2928 (C–H, CH_3) 1694 (C=C), 1632 (C=C), 1591 (C=C), 1390 (C–H, CH_3), 1053 (C–Cl), 758 (C–H, *aryl*). – ESI^+-MS: *m*/*z* = 537 (M^+). – $C_{23}H_{21}N_3Cl_4Fe$: calcd. C 51.43, H 3.94, N 7.82; found C 51.16, H 4.09, N 7.55.

5.3.1.8. ***N-(2,6-Dichlorobenzylidene)-N-[1-(6-{1-[(2,6-dichlorobenzylidene)amino] ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12b**: *N*-(2,6-Dichlorobenzylidene)-*N*-[1-(6-{1-[(2,6-dichlorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine **8b** (479 mg, 1.0 mmol), $FeCl_2(thf)_{1.5}$ (236 mg, 1.0 mmol), THF 35 ml. Compound **12b** was obtained as a brown powder. Yield 559 mg (0.92 mmol, 92%). – IR (KBr): *v* 3424 cm^{-1} (C=N), 3072 (C–H, *aryl*), 2977 (C–H, CH_3), 1708 (C=N), 1648 (C=C), 1578 (C=C), 1389 (C–H, CH_3),

1096 (C–Cl), 780 (C–H, *aryl*). – ESI$^+$-MS: *m*/*z* = 604 (M^+ – 2H), *m*/*z* = 570 (M^+ – Cl). – $C_{23}H_{19}N_3Cl_6Fe$: calcd. C 45.59, H 3.16, N 6.93; found C 45.23, H 3.51, N 6.63.

5.3.1.9. ***N-(2-Bromobenzylidene)-N-[1-(6-{1-[(2-bromobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12c**: *N*-(2-Bromobenzylidene)-*N*-[1-(6-{1-[(2-bromobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine **8c** (400 mg, 0.80 mmol), $FeCl_2(thf)_{1.5}$ (188 mg, 0.80 mmol), THF 25 ml. Compound **12c** was obtained as a dark-red powder. Yield 441 mg (0.70 mmol, 88%). – ESI$^+$-MS: *m*/*z* = 591 (M^+ – Cl). – $C_{23}H_{21}N_3Br_2Cl_2Fe$: calcd. C 44.13, H 3.38, N 6.71; found C 44.44, H 3.46, N 6.51.

5.3.1.10. ***N-(Pentafluorobenzylidene)-N-[1-(6-{1-[(pentafluorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12d**: *N*-(Pentafluorobenzylidene)-*N*-[1-(6-{1-[(pentafluorobenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine **8d** (297 mg, 0.57 mmol), $FeCl_2(thf)_{1.5}$ (135 mg, 0.58 mmol), THF 30 ml. Compound **12d** was obtained as a brown powder. Yield 325 mg (0.50 mmol, 88%). – IR (KBr): *v* 3401 cm^{-1} (C=N), 2964 (C–H, *CH_3*), 1711 (C=N), 1651 (C=C), 1501 (C=C), 1262 (C–F), 808 (C–H, *pyridine*). – ESI$^+$-MS: *m*/*z* = 648 (M^+).

5.3.1.11. ***N-(2-Methylbenzylidene)-N-[1-(6-{1-[(2-methylbenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12e**: *N*-(2-Methylbenzylidene)-*N*-[1-(6-{1-[(2-methylbenzylidene)amino]ethyl}pyridin-2-yl)ethyl]amine **8e** (370 mg, 1.0 mmol), $FeCl_2(thf)_{1.5}$ (232 mg, 0.99 mmol), THF 25 ml. Compound **12e** was obtained as a reddish-brown powder. Yield 490 mg (0.98 mmol, 99%). – IR (KBr): *v* 3438 cm^{-1} (C=N), 3060 (C–H, *aryl*), 2972, 2927 (C–H, *CH_3*) 1692 (C=C), 1626 (C=C), 1601 (C=C), 1381 (C–H, *CH_3*), 757 (C–H, *aryl*). – ESI$^+$-MS: *m*/*z* = 460 (M^+ – Cl). – $C_{25}H_{27}N_3Cl_2Fe$: calcd. C 60.51, H 5.48, N 8.47; found C 60.27, H 5.74, N 8.29.

5.3.1.12. ***N-(2-Mesitylmethylene)-N-[1-(6-{1-[(2-mesitylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12f**: *N*-(2-Mesitylmethylene)-*N*-[1-(6-{1-[(2-mesitylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine **8f** (300 mg, 0.70 mmol), $FeCl_2(thf)_{1.5}$ (166 mg, 0.70 mmol), THF 35 ml. Compound **12f** was obtained as an orange powder. Yield 340 mg (0.62 mmol, 88%). – ESI$^+$-MS: *m*/*z* = 516 (M^+ – Cl). – $C_{29}H_{35}N_3Cl_2Fe$: calcd. C 63.06, H 6.39, N 7.61; found C 62.74, H 6.04, N 7.38.

5.3.1.13. ***N-(1,1'-Biphenyl-4-ylmethylene)-N-[1-(6-{1-[(1,1'-biphenyl-4-ylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12g**: *N*-(1,1'-Biphenyl-4-ylmethylene)-*N*-[1-(6-{1-[(1,1'-biphenyl-4-ylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine **8g** (400 mg, 0.81 mmol), $FeCl_2(thf)_{1.5}$ (191 mg, 0.81 mmol), THF 30 ml. Compound **12g** was obtained as a brownish-red powder. Yield 471 mg (0.76 mmol, 94%). – ESI$^+$-MS:

m/*z* = 620 (M^+). – $C_{35}H_{31}N_3Cl_2Fe$: calcd. C 67.76, H 5.04, N 6.77; found C 67.41, H 4.73, N 6.41.

5.3.1.14. ***N-(2-Naphthylmethylene)-N-[1-(6-{1-[(2-naphthylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine iron(II) chloride*** **12h**: *N*-(2-Naphthylmethylene)-*N*-[1-(6-{1-[(2-naphthylmethylene)amino]ethyl}pyridin-2-yl)ethyl]amine **8h** (440 mg, 1.0 mmol), $FeCl_2(thf)_{1.5}$ (234 mg, 1.0 mmol), THF 60 ml. Compound **12h** was obtained as a dark-red powder. Yield 498 mg (0.88 mmol, 88%). – ESI^+-MS: *m*/*z* = 568 (M^+). – $C_{31}H_{27}N_3Cl_2Fe$: calcd. C 65.52, H 4.79, N 7.39; found C 65.28, H 5.00, N 7.01.

General procedure for the synthesis of the iron(II) complexes **14a-c**: A solution of the appropriate ligand in absolute THF was added to a suspension of $FeCl_2(thf)_{1.5}$ in absolute THF in a Schlenk-flask under argon. The mixture was stirred overnight at room temperature, then the solvent was removed and finally the product was dried under vacuum.

5.3.1.15. ***N-(2,6-Dichlorobenzylidene)-N'-{2-[(2,6-dichlorobenzylidene)amino]ethyl}ethane-1,2-diamine iron(II) chloride*** **14a**: *N*-(2,6-Dichlorobenzylidene)-*N*'-{2-[(2,6-dichlorobenzylidene)amino]ethyl}ethane-1,2-diamine **13a** (850 mg, 2.04 mmol), $FeCl_2(thf)_{1.5}$ (479 mg, 2.04 mmol), THF 35 ml. Compound **14a** was obtained as a yellow powder. Yield 1075 mg (1.98 mmol, 97%). – ESI^+-MS: *m*/*z* = 544 (M^+). – $C_{18}H_{17}N_3Cl_6Fe$: calcd. C 39.75, H 3.15, N 7.73; found C 39.34, H 3.53, N 7.49.

5.3.1.16. ***N-(2-Bromobenzylidene)-N'-{2-[(2-bromobenzylidene)amino]ethyl}ethane-1,2-diamine iron(II) chloride*** **14b**: *N*-(2-Bromobenzylidene)-*N*'-{2-[(2-bromobenzylidene)amino]ethyl}ethane-1,2-diamine **13b** (901 mg, 2.1 mmol), $FeCl_2(thf)_{1.5}$ (484 mg, 2.1 mmol), THF 35 ml. Compound **14b** was obtained as a pale-orange powder. Yield 1035 mg (1.8 mmol, 89%). – ESI^+-MS: *m*/*z* = 564 (M^+). – $C_{18}H_{19}N_3Br_2Cl_2Fe$: calcd. C 38.34, H 3.40, N 7.45; found C 38.02, H 3.08, N 7.24.

5.3.1.17. ***N-(Mesitylmethylene)-N'-{2-[(mesitylmethylene)amino]ethyl}ethane-1,2-diamine iron(II) chloride*** **14c**: *N*-(Mesitylmethylene)-*N*'-{2-[(mesitylmethylene)amino]ethyl}ethane-1,2-diamine **13c** (700 mg, 1.9 mmol), $FeCl_2(thf)_{1.5}$ (452 mg, 1.9 mmol), THF 35 ml. Compound **14c** was obtained as a greenish-yellow powder. Yield 884 mg (1.8 mmol, 94%). – IR (KBr): *v* 3420 cm^{-1} (N–H), 3263 (C=N), 2957, 2941, 2918 (C–H, CH_2, CH_3) 1683 (C=C), 1648 (C=C), 1611 (C=C), 1432 (C–H, CH_2, CH_3), 852 (C–H, *aryl*). – ESI^+-MS: *m*/*z* = 490 (M^+). – $C_{24}H_{33}N_3Cl_2Fe$: calcd. C 58.79, H 6.78, N 8.57; found C 58.49, H 6.40, N 8.19.

5.3.1.18. ***N-(1-Phenylethylidene)-N'-{2-[(1-phenylethylidene)amino]ethyl}ethane-1,2-diamine*** **14d**: *N*-(1-Phenylethylidene)-*N*'-{2-[(1-phenylethylidene)amino]ethyl}ethane-1,2-diamine **13d** (1.50 g, 5 mmol), $FeCl_2(thf)_{1.5}$ (1.15 g, 5 mmol), THF 75 ml. Compound **14d** was obtained as a brown powder. Yield 1.89 g (4 mmol, 89%). – IR (KBr): *v* 3400 cm^{-1} (C=N), 3121 (N–H), 2895 (C–H, CH_3), 1683 (C=N), 1598 (C=C), 1490 (C=C), 1448 (C–H, CH_3), 760 (C–H, *phenyl*), 693 (C–H, *phenyl*). – ESI^+-MS: *m*/*z* = 434 (M^+). – $C_{20}H_{25}N_3Cl_2Fe$: calcd. C 55.33, H 5.80, N 9.68; found C 55.03, H 5.44, N 9.65.

5.3.1.19. ***N-[2-(Diphenylphosphino)benzylidene]-N-(pyridin-2-ylmethyl)amine iron(II) chloride*** **17a**: A solution of *N*-[2-(diphenylphosphino)benzylidene]-*N*-(pyridin-2-ylmethyl)amine **16a** (655 mg, 1.7 mmol) in 20 ml of absolute dichloromethane was added to a suspension of $FeCl_2(thf)_{1.5}$ (400 mg, 1.7 mmol) in 20 ml of absolute dichloromethane in a Schlenk-flask under argon. The mixture was stirred 18 h at room temperature, then the solvent was removed and finally the product was dried under vacuum. Compound **17a** was obtained as a reddish-violet powder. Yield 725 mg (1.4 mmol, 84%). – IR (KBr): *v* 3426 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2962 (C–H, CH_2), 1696 (C=C), 1617 (C=C), 1480 (C=N), 1435 (P–Ph, PPh_2), 751 (C–H, *aryl*). – ESI^+-MS: *m*/*z* = 507 (M^+). – $C_{25}H_{21}N_2Cl_2FeP$: calcd. C 59.20, H 4.17, N 5.52; found C 59.11, H 4.09, N 5.29.

5.3.1.20. ***N-[2-(Diphenylphosphino)benzylidene]-N-(1-pyridin-2-ylethyl)amine iron(II) chloride*** **17b**: A solution of *N*-[2-(diphenylphosphino)benzylidene]-*N*-(1-pyridin-2-ylethyl)amine **16b** (409 mg, 1.0 mmol) in 20 ml of absolute THF was added dropwise to a suspension of $FeCl_2(thf)_2$ (264 mg, 0.97 mmol) in 20 ml of absolute THF in a Schlenk-flask under argon. The mixture was stirred 2 h at room temperature, then the volume of the solvent was reduced under vacuum to 5 ml and 20 ml of absolute hexane were added. A violet solid precipitated from the solution and was filtered, washed with hexane, and then dried in vacuo. Yield 303 mg (0.58 mmol, 60%). – IR (KBr): *v* 3413 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2964 (C–H, CH_3), 2927 (C–H, *CH*), 1627 (C=C), 1481 (C=C), 1436 (P–Ph, PPh_2), 749 (C–H, *aryl*). – ESI^+-MS: *m*/*z* = 521 (M^+). – $C_{26}H_{23}N_2Cl_2FeP$: calcd. C 59.92, H 4.45, N 5.37; found C 59.72, H 4.45, N 4.99.

5.3.1.21. ***N-{[2-(Diphenylphosphino)phenyl]methylene}-N-[phenyl(pyridin-2-yl) methyl]amine iron(II) chloride*** **17c**: A solution of *N*-{[2-(diphenylphosphino) phenyl]methylene}-*N*-[phenyl(pyridin-2-yl)methyl]amine **16c** (490 mg, 1.1 mmol) in 30 ml of absolute THF was added dropwise to a suspension of $FeCl_2(thf)_2$ (290 mg, 1.1 mmol) in 20 ml of absolute THF in a Schlenk-flask under argon. The mixture was

stirred 2.5 h at room temperature, then the volume of the solvent was reduced under vacuum to 10 ml and 20 ml of absolute hexane. A violet precipitate appeared from the solution, which was filtered off, washed with n-hexane and dried in vacuo. Yield 450 mg (0.77 mmol, 72%). – IR (KBr): *v* 3447 cm^{-1} (C=N), 3055 (C–H, *aryl*), 2865 (C–H, *CH*), 1618 (C=C), 1480 (C=C), 1436 (P–Ph, *PPh_2*), 772 (C–H, *aryl*), 747 (C–H, *phenyl*), 696 (C–H, *phenyl*). – ESI^+-MS: *m*/*z* = 547 (M^+ – Cl), *m*/*z* = 511 (M^+ – 2Cl). – $C_{31}H_{25}N_2Cl_2FeP$: calcd. C 63.84, H 4.32, N 4.80; found C 64.12, H 4.70, N 4.54.

5.3.1.22. ***1-Methyl-3-[6-(1-methylimidazo[1,5-a]pyridin-3-yl)pyridin-2-yl]imidazo[1,5-a]pyridine iron(II) chloride*** **26c**: 1-Methyl-3-[6-(1-methylimidazo[1,5-*a*]pyridin-3-yl)pyridin-2-yl]imidazo[1, 5-*a*]pyridine **23c** (0.30 g, 0.9 mmol) was dissolved in 30 ml of absolute dichloromethane in an argon atmosphere and a solution of $FeCl_2(thf)_{1.5}$ (0.21 g, 0.9 mmol) in 10 ml of absolute dichloromethane was added; the mixture was stirred at room temperature under an argon atmosphere in a closed flask for 1 h. A brown-reddish solid precipitated, which was filtered off under argon, and finally dried under vacuum. Yield: 0.23 g (0.5 mmol, 57%). – ESI^+-MS: *m*/*z* = 465 (M^+ – H), *m*/*z* = 430 (M^+ – Cl). – $C_{21}H_{17}N_5Cl_2Fe$: calcd. C 54.11, H 3.68, N 15.02; found C 54.07, H 3.73, N 14.96.

5.3.1.23. ***Methyl 6-(1-methylimidazo[1,5-a]pyridin-3-yl)pyridine-2-carboxylate iron(II) chloride*** **27a**: A solution of methyl 6-(1-methylimidazo[1,5-*a*]pyridin-3-yl)pyridine-2-carboxylate **24a** (0.27 g, 1 mmol) in 15 ml of absolute tetrahydrofuran was slowly dropped into a solution of $FeCl_2(thf)_{1.5}$ (0.23 g, 1 mmol) in 25 ml of absolute THF. The solution was stirred at room temperature for 4 h, after that the solvent was evaporated under vacuum and a dark brown powder resulted. Yield: 0.39 g (0.98 mmol, 98%). – IR (KBr): *v* 3428 cm^{-1} (C=N), 3078 (C–H, *aryl*), 2963 (C–H, *CH_3*), 1699 (C=O), 1635 (C=C), 1593 (C=C), 1492 (C=N), 1433 (C–H, *CH_3*), 1257 (C–O–C), 1092 (C–O), 1016 (C–O–C), 765 (C–H, *pyridine*), 740 (C–H, *imidazopyr*). – ESI^+-MS: *m*/*z* = 393 (M^+ – H), 358 (M^+ – Cl). – $C_{15}H_{13}N_3Cl_2FeO_2$: calcd. C 45.72, H 3.33, N 10.66; found C 45.89, H 3.68, N 10.87.

5.3.2. Syntheses of chromium(III) complexes

General procedure for the syntheses of chromium(III) complexes **55a-d**: A solution of the appropriate tridentate ligand in 20 ml of absolute THF was added dropwise to a

solution of $CrCl_3(thf)_3$ in 20 ml of absolute THF in a Schlenk flask under argon. The mixture was stirred overnight at room temperature, then the solvent was removed under vacuum and the product was stored under argon.

5.3.2.1. ***Ethyl 2-cyano-3-[pyridine-2-ylmethyl)amino]acrylate chromium(III) trichloride*** **55a**: Ethyl 2-cyano-3-[pyridine-2-ylmethyl)amino]acrylate **54a** (0.20 g, 0.9 mmol), $CrCl_3(thf)_3$ (0.32 g, 0.9 mmol). Complex **55a** was obtained as a dark-grey powder. Yield: 0.29 g (0.8 mmol, 88%). – IR (KBr): *v* 3260 cm^{-1} (N–H), 3064 (C–H, *pyridine*), 2977 (C–H, CH_2, CH_3), 2214 (C≡N, s), 1683 (C=C–N), 1630 (C=C), 1581 (C=C), 1562 (C=N, *pyridine*), 1467 (C–H, CH_2, CH_3), 1378 (C–H, CH_3), 1264 (C–O–C), 1102 (C–O), 1040 (C–O–C), 762 (C–H, *pyridine*), 723 (C–H, CH_2). – ESI^+-MS: *m/z* = 390 (M^+). – $C_{12}H_{13}N_3Cl_3CrO_2$: calcd. C 36.99, H 3.36, N 10.79; found C 36.98, H 3.69, N 10.48.

5.3.2.2. ***Ethyl 2-cyano-3-[pyridine-2-ylethyl)amino]acrylate chromium(III) trichloride*** **55b**: Ethyl 2-cyano-3-[pyridine-2-ylethyl)amino]acrylate **54b** (0.20 g, 0.8 mmol), $CrCl_3(thf)_3$ (0.30 g, 0.8 mmol). Complex **55b** was obtained as a dark grey powder. Yield: 0.30 g (0.7 mmol, 91%). – IR (KBr): *v* 3267 cm^{-1} (N–H), 2964 (C–H, CH_2, CH_3), 2211 (C≡N, s), 1679 (C=C–N), 1621 (C=C), 1561 (C=N, *pyridine*), 1469 (C–H, CH_2, CH_3), 1379 (C–H, CH_3), 1262 (C–O–C), 1102 (C–O), 1020 (C–O–C), 766 (C–H, *pyridine*). – ESI^+-MS: *m/z* = 404 (M^+). – $C_{13}H_{15}N_3Cl_3CrO_2$: calcd. C 38.68, H 3.75, N 10.41; found C 38.37, H 3.91, N 10.22.

5.3.2.3. ***Ethyl 2-cyano-3-{[2-(diphenylphosphino)ethyl]amino}acrylate chromium (III) trichloride*** **55c**: Ethyl 2-cyano-3-{[2-(diphenylphosphino)ethyl]amino} acrylate **54c** (0.20 g, 0.6 mmol), $CrCl_3(thf)_3$ (0.21 g, 0.6 mmol). Complex **55c** was obtained as a dark grey powder. Yield: 0.27 g (0.5 mmol, 93%). – IR (KBr): *v* 3271 cm^{-1} (N–H), 3058 (C–H, *phenyl*), 2964 (C–H, CH_2, CH_3), 2239 (C≡N, s), 1677 (C=C–N), 1626 (C=C), 1434 (P–Ph, PPh_2), 1379 (C–H, CH_3), 1261 (C–O–C), 1096 (C–O), 1022 (C–O–C), 742 (C–H, *phenyl*), 693 (C–H, *phenyl*). – ESI^+-MS: *m/z* = 511 (M^+). – $C_{20}H_{21}N_2Cl_3CrO_2P$: calcd. C 47.03, H 4.14, N 5.48; found C 46.88, H 4.33, N 5.23.

5.3.2.4. ***Ethyl 2-cyano-3-{[2-(ethylthio)ethyl]amino}acrylate chromium(III) trichloride*** **55d**: Ethyl 2-cyano-3-{[2-(ethylthio)ethyl]amino}acrylate **54d** (0.20 g, 0.9 mmol), $CrCl_3(thf)_3$ (0.33 g, 0.9 mmol). Complex **55d** was obtained as a dark grey powder. Yield: 0.31 g (0.8 mmol, 95%). – IR (KBr): *v* 3281 cm^{-1} (N–H), 2979 (C–H, CH_2, CH_3), 2242 (C≡N, s), 1682 (C=C–N), 1627 (C=C), 1449 (C–H, CH_2, CH_3), 1379 (C–H,

CH₃), 1257 (C–O–C), 689 (C–S). – ESI⁺-MS: *m/z* = 387 (M^+). – $C_{10}H_{16}N_2Cl_3CrO_2S$: calcd. C 31.06, H 4.17, N 7.24; found C 31.35, H 4.33, N 6.88.

5.3.3. Synthesis of nickel(II) complexes

5.3.3.1. ***1,1'-Dimethyl-3,3'-biimidazo[1,5-a]pyridylnickel(II) dibromide*** **26a**: Dimethoxyethylnickel dibromide (0.26 g, 0.8 mmol) was dissolved in 15 ml of absolute DMF, then 1,1'-dimethyl-3,3'-biimidazo[1,5-*a*]pyridine (0.22 g, 0,8 mmol) was added. The mixture was stirred in a closed Schlenk flask under an argon atmosphere at room temperature for 7 d. A yellow solid precipitated out of the solution; it was filtered under argon and dried in vacuo. Yield: 0.20 g (0.4 mmol, 49%). – ^{1}H NMR ($CDCl_3$) δ 8.06 (bs, 2H, H_{Aryl}), 7.48 (d, 2H, H_{Aryl}), 6.79-6.78 (m, 4H, H_{Aryl}), 2.68 (bs, 3H, CH_3). – IR (KBr): *v* 3467 cm^{-1} (C=N), 3112 (C–H, *heterocycle*), 2917 (C–H, *CH₃*), 1629 (C=C), 1545 (C=C), 1510 (C=N), 1379 (C–H, *CH₃*), 750 (C–H, *heterocycle*). – ESI⁺-MS: *m*/*z* = 479 (M^+ – 2H), 321 (M^+ – 2Br).

5.3.3.2. ***1-Methyl-3-[(1-methylimidazo[1,5-a]pyridin-3-yl)methyl]imidazo[1,5-a] pyridylmesityl(triphenylphosphino)nickel(II)*** **26b**: 1-Methyl-3-[(1-methylimidazo[1,5-*a*]pyridin-3-yl)methyl]imidazo[1,5-a]pyridine **23b** (0.08 g, 0.3 mmol) was dissolved in 25 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.51 g, 0.4 mmol) was added. That solution was dropped into a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.24 g, 0.3 mmol) in 15 ml of absolute toluene. The mixture was stirred at room temperature for 17 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 25 ml of absolute pentane were added and a pale green precipitate formed, which was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.10 g (1 mmol, 45%). – ^{1}H NMR ($CDCl_3$) δ 8.06 (bs, 2H, H_{Aryl}), 7.68 (bs, 2H, H_{Aryl}), 7.56-7.10 (m, 15H, H_{Phenyl}), 6.53 (bs, 2H, H_{Aryl}), 6.43 (bs, 2H, H_{Aryl}), 4.79 (s, 2H, $H_{Mesityl}$), 3.11 (bs, 1H, C*H*), 2.50 (s, 6H, CH_3), 1.69 (s, 6H, CH_3), 1.27 (s, 3H, CH_3). – IR (KBr): *v* 3455 cm^{-1} (C=N), 2963, 2917 (C–H, *CH₃*), 1631 (C=C), 1435 (P–Ph, *PPh₃*), 1102 (C–N), 847 (C–H, *mesityl*), 738 (C–H, *heterocycle*), 707 (C–H, *heterocycle*). – ESI⁺-MS: *m*/*z* = 715 (M^+). – $C_{44}H_{41}N_4NiP$: calcd. C 73.86, H 5.78, N 7.83; found C 73.53, H 5.49, N 8.18.

5.3.3.3. ***1-Methyl-3-pyridin-2-ylimidazo[1,5-a]pyridylnickel(II) dibromide*** **27b**: Dimethoxyethylnickel dibromide (0.23 g, 0.7 mmol) was dissolved in 6 ml of

dimethylformamide; after that, 1-methyl-3-pyridin-2-ylimidazo[1,5-*a*]pyridine **24b** (0.16 g, 0.7 mmol) dissolved in 10 ml of dimethylformamide was added. The mixture was stirred at room temperature in an argon atmosphere in a closed flask along 5 h. After that the solvent was removed in high vacuum and a green solid resulted. Yield: 0.31 g (0.7 mmol, 98%). – ESI^+-MS: *m*/*z* = 346 (M^+ – Br). – $C_{13}H_{11}N_3Br_2Ni$: calcd. C 36.50, H 2.59, N 9.82; C 36.71, H 2.68, N 9.87.

5.3.3.4. ***3-tert-Butyl-1-pyridin-2-ylimidazo[1,5-a]pyridylnickel(II) dibromide*** **27c**: A solution of dimethoxyethylnickel dibromide (0.24 g, 0.8 mmol) in 5 ml of dimethylformamide was added to a solution of 3-*tert*-butyl-1-pyridin-2-ylimidazo[1,5-*a*]pyridine **24c** (0.20 g, 0.8 mmol) in 12 ml of dimethylformamide. The mixture was stirred under argon at ambient temperature for 4 h, then the solvent was evaporated under vacuum and a greenish-yellow powder was obtained. Yield: 0.36 g (0.8 mmol, 96%). – ^1H NMR ($CDCl_3$) δ 7.80 (d, 1H, NC*H*), 7.39-7.16 (m, 15H, H_{Phenyl}), 6.78-6.67 (m, 3H, H_{Aryl}), 5.83 (s, 2H, $H_{Mesityl}$), 4.14 (q, 2H, CH_2), 2.47 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.20 (t, 3H, CH_3), 0.89 (t, 3H, CH_3). – IR (KBr): ν 3413 cm^{-1} (C=N), 2969 (C–H, *CH_3*), 1644 (C=C), 1604 (C=C), 1481 (C–H, *CH_3*), 741 (C–H, *aryl*). – ESI^+-MS: *m*/*z* = 536 (M^+). – $C_{19}H_{15}N_3Br_2NiO_2$: calcd. C 42.59, H 2.82, N 7.84; found C 42.19, H 3.09, N 8.08.

5.3.3.5. ***Methyl 4-(1-pyridin-2-ylimidazo[1,5-a]pyridin-3-yl)benzoate nickel(II) dibromide*** **27d**: A solution of ethyl 4-(1-pyridin-2-ylimidazo[1,5-*a*]pyridin-3-yl)benzoate **24d** (0.30 g, 0.9 mmol) in 5 ml of dimethylformamide was added to a solution of dimethoxyethylnickel dibromide (0.28 g, 0.9 mmol) in 7 ml of dimethylformamide. The mixture was stirred 3 h at ambient temperature under argon, then the solvent was evaporated under vacuum and a green solid resulted. Yield: 0.49 g (0.9 mmol, 98%). – ^1H NMR ($CDCl_3$) δ 7.80 (d, 1H, NC*H*), 7.39-7.16 (m, 15H, H_{Phenyl}), 6.78-6.67 (m, 3H, H_{Aryl}), 5.83 (s, 2H, $H_{Mesityl}$), 4.14 (q, 2H, CH_2), 2.47 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.20 (t, 3H, CH_3), 0.89 (t, 3H, CH_3). – IR (KBr): ν 3383 cm^{-1} (C=N), 1712 (C=O), 1657 (C=C), 1518 (C=C), 1485 (C–H, *CH_3*), 1283 (C–O–C), 830 (C–H, *aryl*), 747 (C–H, *imidazopyr*). – ESI^+-MS: *m*/*z* = 470 (M^+). – $C_{16}H_{17}N_3Br_2Ni$: calcd. C 40.90, H 3.65, N 8.94; found C 41.21, H 4.03, N 9.29.

5.3.3.6. ***2-(1-Methylimidazo[1,5-a]pyridin-3-yl)benzenolatephenyl(triphenylphosphino)nickel(II)*** **27e**: 2-(1-Methylimidazo[1,5-*a*]pyridin-3-yl)phenol **24e** (0.12 g, 0.5 mmol) was dissolved in 20 ml of absolute methanol; then KOH (0.03 g, 0.5 mmol) was added. The resulting solution was stirred at room temperature for 2 h, and then filtered; finally, the solvent was evaporated under vacuum. The yellow powder obtained was mixed

to a solution of *trans*[NiBr(Ph)(PPh_3)$_2$] (0.33 g, 0.4 mmol) in 15 ml of dry benzene. The mixture was stirred at room temperature for 24 hours, then it was filtered on celite under argon and concentrated in vacuo to 5 ml. After that, 20 ml of absolute hexane were added to the reaction and a yellow solid precipitated, which was isolated by filtration under argon and dried in high vacuum. Yield: 0.11 g (0.2 mmol, 40%). – ^{1}H NMR ($CDCl_3$) δ 7.72-7.63 (m, 9H, H_{Aryl}), 7.58-7.46 (m, 13H, H_{Aryl}), 7.37-7.19 (m, 6H, H_{Aryl}), 1.26 (s, 3H, CH_3). – IR (KBr): ν 3434 cm^{-1} (C=N), 3053 (C–H, *aryl*), 2962 (C–H, *CH_3*), 1636 (C=C, *heterocycle*), 1596 (C=C), 1470 (C=C), 1437 (P–Ph, *PPh_3*), 1261 (C–O), 1119 (C–N), 722 (C–H, *phenyl*). – ESI$^+$-MS: *m*/*z* = 622 (M^++ H), 644 (M^+ + Na). – $C_{38}H_{31}N_2NiOP$: calcd. C 73.46, H 5.03, N 4.51; found C 73.09, H 4.78, N 4.29.

5.3.3.7. ***Ethyl cyano(1-methylimidazo[1,5-a]pyridin-3(2H)-ylidene)acetatemesityl (triphenylphosphino)nickel(II)*** **27f**: Ethyl cyano(1-methylimidazo[1,5-*a*]pyridin-3(*2H*)-ylidene)acetate **24f** (0.11 g, 0.4 mmol) was dissolved in 15 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.70 g, 0.5 mmol) was added. That mixture was dropped into a solution of [(PPh_3)$_2$NiMesBr] (0.33 g, 0.4 mmol) in 20 ml of absolute toluene. The mixture was stirred at room temperature for 3 d, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 25 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.09 g (0.1 mmol, 31%). – ^{1}H NMR ($CDCl_3$) δ 7.39-7.06 (m, 18H, $H_{Phenyl+Pyr}$), 6.59 (t, 1H, H_{Pyr}), 6.05 (s, 2H, H_{Mes}), 4.27 (q, 2H, CH_2), 2.75 (s, 6H, CH_3), 2.01 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 0.62 (t, 3H, CH_3). – IR (KBr): ν 3437 cm^{-1} (C=N), 3055 (C–H, *aryl*), 2964, 2923 (C–H, *CH_3*), 2174 (C≡N, s), 1742 (C=O), 1581 (C=C), 1497 (C=C), 1435 (P–Ph, *PPh_3*), 1374 (C–H, *CH_3*), 1261 (C–O), 1094 (C–O), 1029 (C–O–C), 846 (C–H, *mesityl*), 729 (C–H, *heterocycle*), 694 (C–H, *heterocycle*). – ESI$^+$-MS: *m*/*z* = 682 (M^+). – $C_{40}H_{38}N_3NiO_2P$: calcd. C 70.40, H 5.61, N 6.16; found C 70.03, H 5.30, N 5.82.

5.3.3.7. ***Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]-N-(2,6-diisopropylphenyl) prop-2-enimidoatetoluyl-bis-(triphenylphosphino)nickel(II)*** **45a**: Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]-N-(2,6-diisopropylphenyl)prop-2-enimidoate **35a** (0.13 g, 0.3 mmol) was dissolved in 10 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.50 g, 0.3 mmol) was added. The resulting solution was added dropwise to a solution of [(PPh_3)$_2$Ni(Mes)Br] (0.26 g, 0.3 mmol) in 10 ml of absolute toluene. The mixture was stirred under argon at room temperature for 17 h, then it

was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 15 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.14 g (0.1 mmol, 38%). – ^{1}H NMR ($CDCl_3$) δ 7.56-7.07 (m, 37H, H_{Phenyl}+NC*H*), 6.10 (s, 2H, H_{Mes}), 4.34 (q, 2H, CH_2), 3.10 (s, 6H, CH_3), 2.94 (m_7, 2H, C*H*), 2.16 (s, 6H, CH_3), 1.98 (s, 3H, CH_3), 1.38 (t, 3H, CH_3), 1.20 (d, 6H, CH_3), 1.17 (d, 6H, CH_3). – IR (KBr): ν 3448 cm^{-1} (C=N), 3058 (C–H, *aryl*), 2964 (C–H, *CH_3*), 2204 (C≡N, w), 1647 (C=C), 1621 (C=C), 1589 (C=C, *phenyl*), 1478 (C=C), 1435 (P–Ph, *PPh_3*), 1370 (C–H, *$C(CH_3)_2$*), 1273 (C–O–C), 1095 (C–O), 1027 (C–O–C), 847 (C–H, *mesityl*), 796 (C–H, *aryl*), 773 (C=C–H), 693 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 1105 (M^+).

5.3.3.8. ***Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]-N-(2,6-diisopropyl phenyl)prop-2-enimidoatemesityl-bis-(triphenylphosphino)nickel(II)*** **45b**: Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]-N-(2,6-diisopropylphenyl)prop-2-enimidoate **35b** (0.38 g, 0.8 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.23 g, 0.8 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.66 g, 0.8 mmol) in 35 ml of absolute toluene. The mixture was stirred under argon at room temperature for 23 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 50 ml of absolute hexane and 15 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.27 g (0.2 mmol, 27%). – ^{1}H NMR (DMSO-d_6) δ 7.49-7.17 (m, 37H, H_{Phenyl}+NC*H*), 6.08 (s, 2H, H_{Mes}), 3.32 (s, 24H, CH_3), 2.86 (bs, 4H, C*H*), 2.72 (bs, 2H, CH_2), 2.29 (bs, 6H, CH_3), 2.02 (bs, 3H, CH_3), 1.23 (bs, 3H, CH_3). – IR (KBr): ν 3436 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2961, 2911 (C–H, *CH_3*), 2198 (C≡N, w), 1618 (C=C), 1456 (C=C), 1434 (P–Ph, *PPh_3*), 1363 (C–H, *$C(CH_3)_2$*), 1262 (C–O–C), 1093 (C–O), 1028 (C–O–C), 846 (C–H, *mesityl*), 803 (C–H, *aryl*), 693 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 1161 (M^+). – $C_{75}H_{81}N_3NiOP_2$: calcd. C 77.58, H 7.03, N 3.62; found C 77.43, H 6.91, N 3.32.

5.3.3.9. ***Ethyl 2-cyano-3-[(4-methylphenyl)amino]acrylatemesityl-bis-(triphenyl phosphino)nickel(II)*** **46a**: Ethyl 2-cyano-3-[(4-methylphenyl)amino]acrylate **28a** (0.29 g, 1.3 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.86 g, 1.3 mmol) was added. After that [$(PPh_3)_2$Ni(Mes)Br] (1.00 g, 1.3 mmol) in 50 ml of absolute toluene was added dropwise to the resultant solution. The mixture was stirred under argon at room temperature for 24 h,

then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 5 ml. After that, 50 ml of absolute hexane were added and a dark yellow precipitate formed, which was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.69 g (0.7 mmol, 58%). – ^{1}H NMR ($CDCl_3$) δ 7.60 (bs, 1H, NC*H*), 7.52-7.16 (m, 30H, H_{Phenyl}), 6.54 (d, 2H, H_{Aryl}), 6.43 (d, 2H, H_{Aryl}), 5.75 (s, 2H, $H_{Mesityl}$), 2.82 (q, 2H, CH_2), 2.64 (q, 2H, CH_2), 2.06 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 0.75 (t, 3H, CH_3). – IR (KBr): ν 3463 cm^{-1} (C=N), 3042 (C–H, *aryl*), 2963 (C–H, *CH_3*), 2200 (C≡N, w), 1671 (C=C), 1629 (C=C), 1479 (C=C), 1434 (P–Ph, *PPh_3*), 1379 (C–H, *CH_3*), 1261 (C–O–C), 1094 (C–O), 1027 (C–O–C), 843 (C–H, *mesityl*), 817 (C–H, *aryl*), 694 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 932 (M^+). – $C_{54}H_{54}N_2NiO_2P_2$: calcd. C 73.40, H 6.16, N 3.17; found C 73.13, H 6.04, N 3.54.

5.3.3.9. ***Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]acrylatemesityl-bis-(triphenylphosphino)nickel(II)*** **46e**: Ethyl 2-cyano-3-[(2,6-diisopropylphenyl)amino]acrylate **28e** (0.21 g, 0.7 mmol) was dissolved in 15 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.06 g, 0.7 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.55 g, 0.7 mmol) in 30 ml of absolute toluene. The mixture was stirred under argon at room temperature for 21 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 5 ml of absolute hexane and 30 ml of absolute pentane were added and the bright yellow precipitate formed was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.17 g (0.2 mmol, 24%). – ^{1}H NMR (DMSO-d_6) δ 7.47-7.14 (m, 34H, H_{Aryl}+NC*H*), 6.19 (s, 2H, H_{Mes}), 3.32 (s, 12H, CH_3), 2.86 (bs, 4H, C*H*), 2.77 (bs, 2H, CH_2), 2.28 (bs, 6H, CH_3), 2.02 (bs, 3H, CH_3), 0.62 (t, 3H, CH_3). – IR (KBr): ν 3434 cm^{-1} (C=N), 3055 (C–H, *aryl*), 2962 (C–H, *CH_3*), 2207 (C≡N, w), 1615 (C=C), 1480 (C=C), 1435 (P–Ph, *PPh_3*), 1370 (C–H, *$C(CH_3)_2$*), 1262 (C–O–C), 1094 (C–O), 1027 (C–O–C), 844 (C–H, *mesityl*), 694 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 1001 (M^+). – $C_{63}H_{64}N_2NiO_2P_2$: calcd. C 75.53, H 6.44, N 2.80; found C 75.20, H 6.10, N 2.47.

5.3.3.10. ***Ethyl 2-cyano-3-[(4-methoxyphenyl)amino]acrylatemesityl(triphenylphosphino)nickel(II)*** **47b**: Ethyl 2-cyano-3-[(4-methoxyphenyl)amino]acrylate **28b** (0.17 g, 0.7 mmol) was dissolved in 15 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.00 g, 0.7 mmol) was added. That resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.52 g, 0.7 mmol) in 20 ml of absolute toluene. The mixture was stirred under argon at room temperature for

16 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 20 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.32 g (0.5 mmol, 71%). – ^{1}H NMR ($CDCl_3$) δ 7.61 (d, 1H, NC*H*), 7.40-7.20 (m, 15H, H_{Aryl}), 6.44 (d, 2H, H_{Aryl}), 6.28 (d, 2H, H_{Aryl}), 5.78 (d, 2H, H_{Mes}), 3.59 (s, 3H, CH_3), 2.83 (q, 2H, CH_2), 2.63 (s, 6H, CH_3), 1.86 (s, 3H, CH_3), 0.75 (t, 3H, CH_3). – IR (KBr): ν 3465 cm^{-1} (C=N), 3055 (C–H, *aryl*), 2960, 2911 (C–H, CH_3), 2832 (C–H, OCH_3), 2198 (C≡N, s), 1664, 1618 (C=C), 1479 (C=C, *phenyl*), 1429 (P–Ph, PPh_3), 1372 (C–H, CH_3), 1095 (C–O), 1029 (C–O–C), 843 (C–H, *mesityl*), 832 (C–H, *aryl*), 749 (C–H, *phenyl*), 696 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 685 (M^+). – $C_{40}H_{39}N_2NiO_3P$: calcd. C 70.09, H 5.74, N 4.09; found C 69.89, H 5.79, N 4.12.

5.3.3.11. ***Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]acrylatemesityl(triphenyl phosphino)nickel(II)*** **47c**: Ethyl 2-cyano-3-[(2,6-dimethylphenyl)amino]acrylate **28c** (0.17 g, 0.7 mmol) was dissolved in 15 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.10 g, 0.8 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.55 g, 0.7 mmol) in 30 ml of absolute toluene. The mixture was stirred under argon at room temperature for 17 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 5 ml of absolute hexane and 20 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.23 g (0.3 mmol, 48%). – ^{1}H NMR (DMSO-d_6) δ 7.50-7.15 (m, 16H, H_{Phenyl}+NC*H*), 6.73-6.62 (m, 3H, H_{Aryl}), 5.77 (s, 2H, H_{Mes}), 3.32 (s, 6H, CH_3), 3.01 (q, 2H, CH_2), 2.09 (s, 6H, CH_3), 1.87 (s, 3H, CH_3), 0.67 (t, 3H, CH_3). – IR (KBr): ν 3456 cm^{-1} (C=N), 3057 (C–H, *aryl*), 2962, 2914 (C–H, CH_3), 2205 (C≡N, s), 1703 (C=O), 1615 (C=C), 1435 (P–Ph, PPh_3), 1371 (C–H, CH_3), 1267 (C–O–C), 1094 (C–O), 1019 (C–O–C), 844 (C–H, *mesityl*), 747 (C–H, *phenyl*), 695 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 684 (M^+). – $C_{41}H_{41}N_2NiO_2P$: calcd. C 72.05, H 6.05, N 4.10; found C 71.84, H 5.91, N 3.94.

5.3.3.12. ***Ethyl 2-cyano-3-[(2,6-diethylphenyl)amino]acrylatemesityl(triphenyl phosphino)nickel(II)*** **47d**: Ethyl 2-cyano-3-[(2,6-diethylphenyl)amino]acrylate **28d** (0.20 g, 0.7 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.08 g, 0.7 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.56 g, 0.7 mmol) in 15 ml of absolute toluene. The mixture was stirred under argon at room temperature for

17 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 25 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.30 g (0.4 mmol, 58%). – ^{1}H NMR ($CDCl_3$) δ 7.41-7.16 (m, 16H, H_{Phenyl}+NC*H*), 6.82 (t, 1H, H_{Aryl}), 6.66 (d, 2H, H_{Aryl}), 5.78 (s, 2H, $H_{Mesityl}$), 2.99 (q, 2H, CH_2), 2.57 (q, 2H, CH_2), 2.50 (s, 6H, CH_3), 1.89 (s, 3H, CH_3), 1.03 (t, 3H, CH_3), 0.79 (t, 3H, CH_3). – IR (KBr): *v* 3461 cm^{-1} (C=N), 3064 (C–H, *aryl*), 2960, 2933 (C–H, *CH_3, CH_3*), 2206 (C≡N, s), 1614 (C=C), 1498 (C=C), 1431 (P–Ph, *PPh_3*), 1367 (C–H, *CH_3*), 1273 (C–O–C), 1094 (C–O), 1019 (C–O–C), 845 (C–H, *mesityl*), 745 (C–H, *phenyl*), 694 (C–H, *phenyl*). – ESI$^+$-MS: *m*/*z* = 711 (M^+). – $C_{43}H_{45}N_2NiO_2P$: calcd. C 72.59, H 6.37, N 3.94; found C 72.24, H 6.13, N 3.63.

5.3.3.13. ***Diethyl {[(4-methylphenyl)amino]methylene}malonatemesityl(triphenyl phosphino)nickel(II)*** **48a**: Diethyl {[(4-methylphenyl)amino]methylene}malonate **29a** (0.08 g, 0.3 mmol) was dissolved in 25 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.47 g, 0.3 mmol) was added. The resulting solution was added dropwise to a solution of [(PPh_3)$_2$Ni(Mes)Br] (0.22 g, 0.3 mmol) in 10 ml of absolute toluene. The mixture was stirred under argon at room temperature for 48 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 25 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.10 g (0.1 mmol, 48%). – ^{1}H NMR ($CDCl_3$) δ 8.23 (d, 1H, NC*H*), 7.32-7.07 (m, 15H, H_{Phenyl}), 6.97 (d, 2H, H_{Aryl}), 6.83 (d, 2H, H_{Aryl}), 5.78 (s, 2H, $H_{Mesityl}$), 4.11 (q, 2H, CH_2), 3.09 (q, 2H, CH_2), 2.93 (s, 6H, CH_3), 2.46 (s, 6H, CH_3), 1.83 (s, 3H, CH_3), 1.16 (t, 3H, CH_3), 0.72 (t, 3H, CH_3). – ESI$^+$-MS: *m*/*z* = 717 (M^+). – $C_{42}H_{44}NNiO_4P$: calcd. C 70.41, H 6.19, N 1.95; found C 70.19, H 5.99, N 1.73.

5.3.3.14. ***Diethyl {[(2,6-diethylphenyl)amino]methylene}malonatemesityl(triphenyl phosphino)nickel(II)*** **48b**: Diethyl {[(2,6-diethylphenyl)amino]methylene}malonate **29b** (0.14 g, 0.4 mmol) was dissolved in 10 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.66 g, 0.4 mmol) was added. The resulting solution was added dropwise to a solution of [(PPh_3)$_2$Ni(Mes)Br] (0.35 g, 0.4 mmol) in 10 ml of absolute toluene. The mixture was stirred under argon at room temperature for 22 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 30 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo and finally stored under argon.

Yield: 0.14 g (0.2 mmol, 40%). – ^{1}H NMR ($CDCl_3$) δ 7.92 (d, 1H, NC*H*), 7.42-7.10 (m, 15H, H_{Phenyl}), 6.75 (t, 1H, H_{Aryl}), 6.61 (d, 2H, H_{Aryl}), 5.72 (s, 2H, $H_{Mesityl}$), 4.03 (q, 2H, CH_2), 2.91 (q, 2H, CH_2), 2.78 (q, 2H, CH_2), 2.50 (q, 2H, CH_2), 2.41 (s, 6H, CH_3), 1.82 (s, 6H, CH_3), 1.10 (t, 3H, CH_3), 0.96 (t, 3H, CH_3), 0.75 (t, 3H, CH_3). – IR (KBr): ν 3443 cm^{-1} (C=N), 3056 (C–H, *aryl*), 2965, 2933 (C–H, *CH_2, CH_3*), 1698 (C=O), 1600 (C=C), 1462 (C–H, *CH_2, CH_3*), 1435 (P–Ph, *PPh_3*), 1381 (C–H, *CH_3*), 1241 (C–O–C), 1071 (C–O), 1027 (C–O–C), 845 (C–H, *mesityl*), 789 (C–H, *aryl*), 747 (C–H, *phenyl*), 722 (C–H, *CH_2*), 695 (C–H, *phenyl*). – ESI$^+$-MS: *m*/*z* = 758 (M^+). – $C_{45}H_{50}NNiO_4P$: calcd. C 71.25, H 6.64, N 1.85; found C 70.89, H 6.51, N 1.77.

5.3.3.15. ***Diethyl {[(2,6-diisopropylphenyl)amino]methylene}malonatemesityl(triphenylphosphino)nickel(II)*** **48c**: Diethyl {[(2,6-diisopropylphenyl)amino]methylene} malonate **29c** (0.22 g, 0.6 mmol) was dissolved in 10 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.00 g, 0.7 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.48 g, 0.6 mmol) in 10 ml of absolute toluene. The mixture was stirred under argon at room temperature for 23 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to circa 3 ml. After that, 30 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.16 g (0.2 mmol, 34%). – ^{1}H NMR ($CDCl_3$) δ 7.86 (d, 1H, NC*H*), 7.33-7.09 (m, 15H, H_{Phenyl}), 6.93 (t, 1H, H_{Aryl}), 6.81 (d, 2H, H_{Aryl}), 5.80 (s, 2H, $H_{Mesityl}$), 4.03 (q, 2H, CH_2), 3.61 (m_7, 2H, C*H*), 3.05 (q, 2H, CH_2), 2.46 (s, 6H, CH_3), 1.84 (s, 3H, CH_3), 1.09 (t, 3H, CH_3), 0.91 (d, 6H, CH_3), 0.89 (d, 6H, CH_3), 0.67 (t, 3H, CH_3). – IR (KBr): ν 3468 cm^{-1} (C=N), 3057 (C–H, *aryl*), 2962 (C–H, *CH_3*), 1697 (C=O), 1599 (C=C), 1461 (C–H, *CH_3*), 1436 (P–Ph, *PPh_3*), 1381 (C–H, *$C(CH_3)_2$*), 1260 (C–O–C), 1070 (C–O), 1029 (C–O–C), 846 (C–H, *mesityl*), 802 (C–H, *aryl*), 744 (C–H, *phenyl*), 693 (C–H, *phenyl*). – ESI$^+$-MS: *m*/*z* = 787 (M^+). – $C_{47}H_{54}NNiO_4P$: calcd. C 71.77, H 6.92, N 1.78; found C 71.61, H 6.43, N 1.63.

5.3.3.15. ***Ethyl 2-acetyl-3-[(2,6-dimethylphenyl)amino]acrylatemesityl(triphenylphosphino)nickel(II)*** **49a**: Ethyl 2-acetyl-3-[(2,6-dimethylphenyl)amino]acrlate **31a** (0.17 g, 0.6 mmol) was dissolved in 10 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.03 g, 0.7 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.50 g, 0.6 mmol) in 15 ml of absolute toluene. The mixture was stirred under argon at room temperature for 19 h, then it was filtered on celite under argon and the filtrate was concentrated under

vacuum to 3 ml. After that, 5 ml of absolute hexane and 25 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.08 g (0.1 mmol, 19%). – ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 1H, NC*H*), 7.39-7.16 (m, 15H, H_{Phenyl}), 6.78-6.67 (m, 3H, H_{Aryl}), 5.83 (s, 2H, $H_{Mesityl}$), 4.14 (q, 2H, CH_2), 2.47 (s, 6H, CH_3), 2.11 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.20 (t, 3H, CH_3), 0.89 (t, 3H, CH_3). – IR (KBr): ν 3441 cm^{-1} (C=N), 3055 (C–H, *aryl*), 2964, (C–H, *CH_3*), 1688 (C=C), 1635 (C=C), 1480 (C–H, *CH_3*), 1435 (P–Ph, *PPh_3*), 1262 (C–O–C), 1094 (C–O), 1022 (C–O–C), 843 (C–H, *mesityl*), 803 (C–H, *aryl*), 740 (C–H, *phenyl*), 694 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 700 (M^+). – $C_{42}H_{44}NNiO_3P$: calcd. C 72.02, H 6.33, N 2.00; found C 71.67, H 5.98, N 1.79.

5.3.3.16. ***Ethyl 2-butyryl-3-[(2,6-dimethylphenyl)amino]acrylatemesityl(triphenyl phosphino)nickel(II)*** **49b**: Ethyl 2-butyryl-3-[(2,6-dimethylphenyl)amino]acrylate **31b** (0.20 g, 0.7 mmol) was dissolved in 10 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.04 g, 0.7 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.52 g, 0.7 mmol) in 10 ml of absolute toluene. The mixture was stirred under argon at room temperature for 5 d, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 3 ml. After that, 20 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.08 g (0.1 mmol, 16%). – ^{1}H NMR ($CDCl_3$) δ 7.79 (d, 1H, NC*H*), 7.38-7.16 (m, 15H, H_{Phenyl}), 6.79-6.65 (m, 3H, H_{Aryl}), 5.84 (s, 2H, $H_{Mesityl}$), 4.14 (q, 2H, CH_2), 2.50 (t, 2H, CH_2), 2.46 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 1.94 (s, 3H, CH_3), 1.22 (t, 3H, CH_3), 0.74 (m_6, 2H, CH_2), 0.49 (t, 3H, CH_3). – IR (KBr): ν 3446 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2964, 2935 (C–H, *CH_2, CH_3*), 1706 (C=O), 1583 (C=C), 1457 (C–H, *CH_2, CH_3*), 1434 (P–Ph, *PPh_3*), 1387 (C–H, *CH_3*), 1272 (C–O–C), 1072 (C–O), 1035 (C–O–C), 846 (C–H, *mesityl*), 786 (C–H, *aryl*), 693 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 728 (M^+). – $C_{44}H_{48}NNiO_3P$: calcd. C 72.54, H 6.64, N 1.92; found C 72.18, H 6.33, N 1.68.

5.3.3.17. ***Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(2,6-dimethylphenyl)amino]acrylatemesityl(triphenylphosphino)nickel(II)*** **50a**: Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(2,6-dimethylphenyl)amino]acrylate **37a** (0.29 g, 0.7 mmol) was dissolved in 15 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (1.15 g, 0.8 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.58 g, 0.7 mmol) in 15 ml of absolute toluene. The mixture was stirred under argon at room temperature for 16 h, then it

was filtered on celite under argon and the filtrate was concentrated under vacuum to 1 ml. After that, 30 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.33 g (0.4 mmol, 53%). – ^{1}H NMR ($CDCl_3$) δ 7.32-7.06 (m, 15H, H_{Phenyl}), 6.94 (t, 1H, H_{Aryl}), 6.67 (d, 2H, H_{Aryl}), 6.63 (bs, 1H, NC*H*), 5.79 (s, 2H, $H_{Mesityl}$), 4.28 (q, 2H, CH_2), 2.61 (q, 2H, CH_2), 2.45 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.08 (s, 6H, CH_3), 1.92 (s, 3H, CH_3), 1.31 (t, 3H, CH_3), 0.53 (t, 3H, CH_3). – IR (KBr): ν 3449 cm^{-1} (C=N), 3058 (C–H, *aryl*), 2968, 2923 (C–H, *CH_3*), 1642 (C=O), 1610 (C=C), 1465 (C–H, *CH_3*), 1435 (P–Ph, *PPh_3*), 1379 (C–H, *CH_3*), 1238 (C–O–C), 1086 (C–O), 1037 (C–O–C), 844 (C–H, *mesityl*), 804 (C–H, *aryl*), 693 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 834 (M^+). – $C_{51}H_{55}N_2NiO_3P$: calcd. C 73.48, H 6.65, N 3.36; found C 73.12, H 6.38, N 3.10.

5.3.3.18. ***Ethyl 2-{ethoxy[(2,6-diisopropylphenyl)imino]methyl}-3-[(2,6-diisopropyl phenyl)amino]acrylatemesityl(triphenylphosphino)nickel(II)*** **50b**: Ethyl 2-{ethoxy[(2,6-diisopropylphenyl)imino]methyl}-3-[(2,6-diisopropylphenyl)amino]acrylate **37b** (0.23 g, 0.4 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.68 g, 0.5 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.35 g, 0.4 mmol) in 10 ml of absolute toluene. The mixture was stirred under argon at room temperature for 17 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 25 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.12 g (0.1 mmol, 28%). – ^{1}H NMR (DMSO-d_6) δ 7.62 (s, 1H, NC*H*), 7.63-7.16 (m, 21H, H_{Aryl}), 6.08 (s, 2H, H_{Mes}), 3.32 (s, 24H, CH_3), 2.97 (bs, 4H, C*H*), 2.88 (bs, 2H, CH_2), 2.72 (bs, 2H, CH_2), 2.28 (bs, 6H, CH_3), 1.93 (bs, 3H, CH_3), 1.22 (bs, 3H, CH_3), 1.08 (bs, 3H, CH_3). – ESI$^+$-MS: m/z = 946 (M^+). – $C_{59}H_{71}N_2NiO_3P$: calcd. C 74.92, H 7.57, N 2.96; found C 74.72, H 7.53, N 2.91.

5.3.3.19. ***Ethyl 3-[(2,6-diethylphenyl)amino]-2-{ethoxy[(4-methylphenyl)imino] methyl}acrylatemesityl(triphenylphosphino)nickel(II)*** **50c**: Ethyl 3-[(2,6-diethylphenyl) amino]-2-{ethoxy[(4-methylphenyl)imino]methyl}acrylate **37c** (0.10 g, 0.3 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.37 g, 0.3 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.20 g, 0.3 mmol) in 5 ml of absolute toluene. The mixture was stirred under argon at room temperature for 18 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml.

After that, 15 ml of absolute pentane were added and the yellow precipitated formed was filtered under argon, dried in vacuo, and finally stored under argon. Yield: 0.20 g (0.2 mmol, 91%). – ^{1}H NMR ($CDCl_3$) δ 7.32-6.54 (m, 23H, $H_{Phenyl+Aryl}$+NC*H*), 5.73 (s, 2H, $H_{Mesityl}$), 3.98 (q, 2H, CH_2), 2.61 (q, 2H, CH_2), 2.43 (q, 4H, CH_2), 2.41 (s, 6H, CH_3), 2.29 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.06 (t, 3H, CH_3), 0.89 (t, 3H, CH_3), 0.67 (t, 3H, CH_3). – IR (KBr): ν 3459 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2964 (C–H, *CH_2, CH_3*), 1646 (C=O), 1479 (C–H, *CH_2, CH_3*), 1435 (P–Ph, *PPh_3*), 1094 (C–O), 1029 (C–O–C), 847 (C–H, *mesityl*), 804 (C–H, *aryl*), 692 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 847 (M^+).

5.3.3.20. ***Ethyl 2-{ethoxy[(2,6-dimethylphenyl)imino]methyl}-3-[(4-methylphenyl) amino]acrylatemesityl(triphenylphosphino)nickel(II)*** **50d**: Ethyl 2-{ethoxy[(2,6-dimethyl phenyl)imino]methyl}-3-[(4-methylphenyl)amino]acrylate **37d** (0.14 g, 0.4 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.54 g, 0.4 mmol) was added. The resulting mixture was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.29 g, 0.4 mmol) in 20 ml of absolute toluene. The mixture was stirred under argon at room temperature for 23 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 15 ml of absolute pentane were added and the yellow precipitate was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.07 g (0.1 mmol, 23%). – ^{1}H NMR ($CDCl_3$) δ 7.29-6.91 (m, 15H, H_{Phenyl}), 6.70-6.49 (m, 8H, H_{Aryl}+NC*H*), 5.79 (s, 2H, $H_{Mesityl}$), 4.30 (q, 2H, CH_2), 2.63 (q, 2H, CH_2), 2.45 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 2.18 (s, 6H, CH_3), 1.90 (s, 3H, CH_3), 1.33 (t, 3H, CH_3), 0.54 (t, 3H, CH_3). – IR (KBr): ν 3456 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2964 (C–H, *CH_3*), 1636 (C=O), 1480 (C–H, *CH_3*), 1435 (P–Ph, *PPh_3*), 1095 (C–O), 1029 (C–O–C), 847 (C–H, *mesityl*), 804 (C–H, *aryl*), 744 (C–H, *aryl*), 693 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 819 (M^+).

5.3.3.21. ***Ethyl 2-[[(2,6-diisopropylphenyl)imino](ethoxy)methyl]-3-[(2,6-dimethyl phenyl)amino]acrylatemesityl(triphenylphosphino)nickel(II)*** **50e**: Ethyl 2-[[(2,6-diisopropylphenyl)imino](ethoxy)methyl]-3-[(2,6-dimethylphenyl)amino]acrylate **37e** (0.09 g, 0.2 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.34 g, 0.2 mmol) was added. The resulting solution was added dropwise to a solution of [$(PPh_3)_2$Ni(Mes)Br] (0.15 g, 0.2 mmol) in 20 ml of absolute toluene. The mixture was stirred under argon at room temperature for 2 d, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 15 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo and finally stored under argon.

Yield: 0.07 g (0.1 mmol, 41%). – ^{1}H NMR ($CDCl_3$) δ 7.03-6.55 (m, 22H, $H_{Phenyl+Aryl}$+NC*H*), 5.80 (s, 2H, $H_{Mesityl}$), 4.22 (q, 2H, CH_2), 3.55 (m_7, 2H, C*H*), 2.71 (q, 2H, CH_2), 2.46 (s, 6H, CH_3), 1.91 (s, 6H, CH_3), 1.84 (s, 3H, CH_3), 1.14 (t, 3H, CH_3), 0.86 (s, 6H, CH_3), 0.82 (s, 6H, CH_3), 0.79 (t, 3H, CH_3). – IR (KBr): ν 3455 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2963 (C–H, CH_3), 1635 (C=O), 1481 (C–H, CH_3), 1435 (P–Ph, PPh_3), 1095 (C–O), 1029 (C–O–C), 847 (C–H, *mesityl*), 805 (C–H, *aryl*), 693 (C–H, *phenyl*). – ESI$^+$-MS: m/z = 889 (M^+).

5.3.3.22. ***N-[(2-Chlorophenyl)methylene]-N-(1-pyridin-2-ylethyl)aminenickel(II) dibromide*** **51a**: *N*-[(2-Chlorophenyl)methylene]-*N*-(1-pyridin-2-ylethyl)amine **40a** (0.20 g, 0.8 mmol) was added dropwise to a solution of dimethoxyethylnickel(II) dibromide (0.25 g, 0.8 mmol) in 10 ml of dimethylformamide in a Schlenk flask in an argon atmosphere. The mixture was stirred for 3 h at room temperature, then the solvent was removed in high vacuum and a dark green residue resulted, which was stored under argon. Yield: 0.26 g (0.6 mmol, 69%). – ESI$^+$-MS m/z = 463 (M^+). – $C_{14}H_{13}N_2ClBr_2Ni$: calcd. C 36.30, H 2.82, N 6.05, found C 36.57, H 3.01, N 6.14.

5.3.3.23. ***Pyridine-2-carbaldehydephenylhydrazonenickel(II) dibromide*** **51b**: Pyridine-2-carbaldehyde phenylhydrazone **40b** (0.25 g, 1.3 mmol) was added dropwise to a solution of dimethoxyethylnickel(II) dibromide (0.39 g, 1.23 mmol) in 10 ml of absolute tetrahydrofurane and 3 ml of dimethylformamide in a Schlenk flask under an argon atmosphere. The mixture was stirred for 2 h at room temperature, then the solvent was removed in high vacuum and the dark green residue resulted was mixed with 5 ml of tetrahydrofurane and 20 ml of pentane. The precipitated solid was filtered under argon and dried in vacuo. Yield: 0.34 g (0.8 mmol, 64%). – ^{1}H NMR (DMSO-d_6) δ 10.7 (bs, 1H, N*H*), 8.44 (bs, 1H, H_{Pyr}), 7.88 (bs, 1H, H_{Pyr}), 7.82 (bs, 1H, C*H*), 7.70 (t, 1H, H_{Pyr}), 7.17 (t, 3H, $H_{Pyr+Phenyl}$), 7.04 (d, 2H, H_{Phenyl}), 6.72 (t, 1H, H_{Phenyl}). – IR (KBr): ν 3369 cm^{-1} (C=N), 1655 (C=C), 1607 (C=C), 1493 (C=C), 770 (C–H, *aryl*), 749 (C–H, *pyridine*), 692 (C–H, *aryl*). – ESI$^+$-MS m/z = 416 (M^+). – $C_{12}H_{11}N_3Br_2Ni$: calcd. C 34.67, H 2.67, N 10.11; found C 35.01, H 2.93, N 10.38.

5.3.3.24. ***Dimethyl-N,N'-bis(2-methylphenyl)ethanediimidoatenickel(II) dibromide*** **52**: A solution of dimethyl-*N,N'*-bis(2-methylphenyl)ethane diimidoate **42** (1.10 g, 3.7 mmol) in 15 ml of DMF was added dropwise to a solution of dimethoxyethylnickel(II) dibromide (1.15 g, 3.7 mmol) in 20 ml of dimethylformamide in an argon atmosphere. The

mixture was stirred for 5 h at room temperature. Then the solvent was removed under vacuum and a pale blue powder was obtained. The nickel complex was stored under argon. Yield: 1.80 g (3.5 mmol, 95%). – IR (KBr): *v* 3360 cm^{-1} (C=N), 3021 (C–H, *aryl*), 2945 (C–H, *CH_3*), 1650 (C=C), 1596 (N=C–O), 1488 (C=C), 1445 (C–H, *CH_3*), 1385 (C–H, *CH_3*), 1206 (C–O–C), 1045 (C–O–C), 756 (C–H, *aryl*). – ESI^+-MS: *m/z* 515 (M^+). – $C_{18}H_{20}N_2O_2Br_2Ni$: calcd. C 41.99, H 3.92, N 5.44, found C 42.18, H 4.21, N 5.73.

5.3.3.25. ***N-(2,6-diisopropylphenyl)-3-[(2,6-diisopropylphenyl)amino]-3-oxopropan imidoatemesityl(triphenylphosphino)nickel(II)*** **53**: Ethyl *N*-(2,6-diisopropylphenyl)-3-[(2,6-diisopropylphenyl)amino]-3-oxopropanimidoate **44** (0.21 g, 0.4 mmol) was dissolved in 20 ml of absolute toluene, then a 0.6M solution of sodium bis(trimethylsilyl)amide in toluene (0.65 g, 0.4 mmol) was added. The resulting solution was added dropwise to a solution of $[(PPh_3)_2Ni(Mes)Br]$ (0.35 g, 0.4 mmol) in 20 ml of absolute toluene. The mixture was stirred under argon at room temperature for 18 h, then it was filtered on celite under argon and the filtrate was concentrated under vacuum to 2 ml. After that, 20 ml of absolute pentane were added and the yellow precipitate formed was filtered under argon, dried in vacuo and finally stored under argon. Yield: 0.16 g (0.2 mmol, 41%). – ^1H NMR ($CDCl_3$) δ 7.77-6.91 (m, 21H, $H_{Aryl+Phenyl}$), 6.10 (s, 2H, H_{Mes}), 3.10 (s, 6H, CH_3), 3.03 (bs, 1H, C*H*), 2.92 (bs, 1H, C*H*), 2.62 (bs, 2H, CH_2), 2.36 (s, 2H, CH_2), 1.98 (s, 3H, CH_3), 1.20 (bs, 12H, CH_3), 1.09 (bs, 12H, CH_3), 0.97 (bs, 3H, 1.20 (bs, 12H, CH_3). – IR (KBr): *v* 3359 cm^{-1} (C=N), 3054 (C–H, *aryl*), 2964 (C–H, *CH_3*), 2869 (C–H, *CH*), 1595 (C=C), 1550 (C(O)–N), 1480 (C=C), 1459 (C–H, *CH_2, CH_3*), 1435 (P–Ph, *PPh_3*), 1385 (C–H, *$C(CH_3)_2$*), 1260 (C–O–C), 1095 (C–O), 846 (C–H, *mesityl*), 801 (C–H, *aryl*), 744 (C–H, *phenyl*), 693 (C–H, *phenyl*). – ESI^+-MS: *m/z* = 889 (M^+). – $C_{56}H_{67}N_2NiO_2P$: calcd. C 75.59, H 7.59, N 3.15; found C 75.21, H 7.23, N 2.78.

5.4. Oligomerisation procedures

5.4.1. Ethylene oligomerisation tests with iron complexes

5.4.1.1. ***Low-pressure tests***: The procatalyst was dissolved in 30 ml of solvent in a Schlenk-flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 ml glass reactor was evacuated and then filled with argon. The procatalyst solution was added under argon into the reactor vessel. Under

stirring the cocatalyst MAO (0.6 ml, approximately 100 eq of a 10 wt% MAO solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 3 bars with ethylene. The reactor pressure maintained constant throughout the oligomerisation run by manually controlled addition of ethylene. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

5.4.1.2. ***High-pressure tests***: Same procedure as described for low-pressure tests. Instead of a glass reactor, was a 150 ml stainless steel reactor with cooling mantle used. After the reactor was closed it was pressurized to 30 bars with ethylene. The temperature of the reaction was controlled by cooling the reactor vessel with water.

5.4.2. Ethylene oligomerisation tests with chromium complexes

5.4.2.1. ***High-pressure tests***: The procatalyst was dissolved in 30 ml of solvent in a Schlenk-flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 ml stainless steel reactor with cooling mantle was evacuated and then filled with argon. The procatalyst solution was added under argon into the reactor vessel. Under stirring the cocatalyst MAO (0.6 ml, approximately 100 eq of a 10 wt% MAO solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 30 bars with ethylene. The reactor pressure maintained constant throughout the oligomerisation run by manually controlled addition of ethylene. The temperature of the reaction was controlled by cooling the reactor vessel with water. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

5.4.3. Ethylene oligomerisation tests with nickel complexes

5.4.3.1. ***Low-pressure tests***: The procatalyst was dissolved in 30 ml of solvent in a Schlenk-flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 ml glass reactor was evacuated and then filled with argon. The procatalyst solution was added under argon into the reactor vessel. Under stirring the cocatalyst MAO (0.6 ml, approximately 100 eq of a 10 wt% MAO solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized either to 1 or 3 bars (see Chapter 3.11.) with ethylene. The reactor pressure maintained constant throughout the oligomerisation run by manually controlled addition of ethylene. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

5.4.3.2. ***High-pressure tests***: Same procedure as described for low-pressure tests. Instead of a glass reactor, was a 150 ml stainless steel reactor with cooling mantle used. After the reactor was closed it was pressurized to 30 bars with ethylene. The temperature of the reaction was controlled by cooling the reactor vessel with water. The experiments were performed either with MAO (0.6 ml, approximately 100 eq of a 10 wt% solution in toluene) or with ethylaluminum sesquichloride (3.3 ml, 300 eq of a 25 wt% solution in toluene) as cocatalyst.

5.4.4. Propylene oligomerisation tests with nickel complexes

5.4.4.1. ***High-pressure tests***: The procatalyst was dissolved in 30 ml of solvent in a Schlenk-flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 ml stainless steel reactor with cooling mantle was evacuated and then filled with argon. The procatalyst solution was added under argon into the reactor vessel. Under stirring the cocatalyst ethylaluminum sesquichloride (3.3 ml, 300 eq of a 25 wt% ethylaluminum sesquichloride solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 30 bars with ethylene. The reactor pressure maintained constant throughout the oligomerisation run by manually controlled addition of ethylene. The temperature of

the reaction was controlled by cooling the reactor vessel with water. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

6. References

1. (a) Britovsek G.J.P., Gibson V.C., Wass D.F., *Angew. Chem.*, 1999, 111, 448-468; (b) Mecking S., *Coordination Chemistry Reviews*, 2000, 203, 325-351.

2. (a) Small B.L., Brookhart M., Bennett A.M.A., *J. Am. Chem. Soc.*, 1998, *120*, 4049-4050; (b) Britovsek G.J.P., Gibson V., Kimberly B.S., Maddox P.J., McTavish S.J., Solan G.A., White A.J.P., Williams D.J., *Chem. Commun.*, 1998, (7), 849-850; (c) Small B.L., Brookhart M., *J. Am. Chem. Soc.*, 1998, 120, 7143-7144.

3. (a) Johnson L.K., Killian C.M., Brookhart M., *J. Am. Chem. Soc.*, 1995, 117, 6414-6415; (b) Johnson L.K., Mecking S., Brookhart M., *J. Am. Chem. Soc.*, 1996, 118, 267-268; (c) Killian C.M., Tempel D.J., Johnson L.K., Brookhart M., *J. Am. Chem. Soc.*, 1996, 118, 11664-11665; (d) Killian C.M., Johnson L.K., Brookhart M., *Organometallics*, 1997, 16, 2005-2007; (e) Tempel D., Brookhart M., *Organometallics*, 1998, 17(11), 2290-2296; (f) Svejda S.A., Brookhart M., *Organometallics*, 1999, 18, 65-74.

4. (a) Mecking S., Johnson L.K., Wang L., Brookhart M., *J. Am. Chem. Soc.*, 1998, 120(5), 888-899.

5. Younkin T.R., Connor E.F., Henderson J.I., Freidrich S., Grubbs R.H., Bansleben D.A., *Science*, 2000, 287, 460-462.

6. (a) Vogt D., in *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH Publishers: 1996, Vol. 1, pp 245-256; (b) Parshall, G. W.; Ittel, S. D. In *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*; John Wiley & Sons: New York 1992, pp 68-72; (c) Skupinska, J. *Chem. Rev.* 1991, 91(4), 613-648.

7. (a) Peuckert M., Keim W., *Organometallics* 1983, 2, 594-597; (b) Keim W.; Behr, A.; Limbacker B., Kruger C., *Angew. Chem. Int. Ed. Engl.* 1983, 22, 503; (c) Keim W.; Behr A.; Kraus G. *J. Organomet. Chem.* 1983, 251(3), 377-391; (d) Peuckert M., Keim W., *J. Mol. Cat.* 1984, 22, 289; (e) Keim W., Schulz R. P., *J. Mol. Cat.* 1994, 92(1), 21-33.

8. (a) Flory P.J., *J. Am. Chem. Soc.*, 1940, 62, 1561; (b) Schulz G.V., *Z. Phys. Chem., Abstr.*, 1935, B30, 379; (c) Schulz G.V., *Z. Phys. Chem., Abstr.*, 1935, B43, 25.

9. (a) Plentz Meneghetti S., Lutz P.J., Kress J., *Organometallics*, 1999, 18, 2734-2737; (b) Schareina T., Hillebrand G., Fuhrmann H., Kempe R., *Eur. J. Inorg. Chem.*, 2001, 2421-2426.

10. (a) Wang C., Friedrich S.K., Younkin T.R., Li R.T., Grubbs R.H., Bansleben D.A., Day M.W., *Organometallics*, 1998, 17(15), 3149-3151; (b) Makio H., Kashiva N., Fujita T., *Adv. Synth. Catal.*, 2002, 344(5), 477-493.

11. (a) Britovsek G.J.P., Gibson V.C., Kimberley B.S., Maddox P.J., McTavish S.J., Solan G.A., White A.J.P., Williams D.J., *Chem. Commun.*, 1998, 849-850; (b) Britovsek G.J.P., Gibson

V.C., Wass D.F., *Angew. Chem.*, 1999, 111, 448-468; (c) Britovsek G.J.P., Bruce M., Gibson V.C., Kimberley B.S., Maddox P.J., Mastroianni S., McTavish S.J., Redshaw C., Solan G.A., Strömberg S., White A.J.P., Williams D.J., *J. Am. Chem. Soc.*, 1999, 121, 8728-8740; (d) Britovsek G.J.P., Mastroianni S., Solan G.A., Baugh S.P.D., Redshaw C., Gibson V.C., White A.J.P., Williams D.J., Elsegood M.R.J., *Chem. Eur. J.*, 2000, 6(12), 2221-2231.

12. (a) Small B.L., Brookhart M., Bennett A.M.A., *J. Am. Chem. Soc.*, 1998, 120, 4049-4050; (b) Small B.L., Brookhart M., *J. Am. Chem. Soc.*, 1998, 120, 7143-7144; (c) Small B.L., Brookhart M., *Macromolecules*, 1999, 32, 2120-2130.

13. (a) Ittel S.D., Johnson L.K., Brookhart M., *Chem. Rev.*, 2000, 100(4), 1169-1203; (b) Gibson V.C., Spitzmesser S.K., *Chem. Rev.*, 2003, 103(1), 283-315.

14. (a) McGuinness D.S., Wasserscheid P., Keim W., Hu C., Englert U., Dixon J.T., Grove C., *Chem. Commun.*, 2003, 334-335; (b) McGuinness D.S., Wasserscheid P., Keim W., Morgan D., Dixon J.T., Bollmann A., Maumela H., Hess F., Englert U., *J. Am. Chem. Soc.*, 2003, 125, 5272-5273.

15. Bluhm M.E., Folli C., Döring M., *J. Mol. Catal. A*, 2004, 212(1-2), 13-18.

16. Chen Y., Quian C., Sun J., *Organometallics*, 2003, 22(6), 1231-1236.

17. Bluhm M., Folli C., Döring M., *Book of Abstracts, 13th Int. Symposium on Homogeneous Catalysis*, 2002, 306.

18. (a) Alyea E.C., Merrel P.H., *Syn. React. Inorg. Metal-Org. Chem.*, 1974, 4(6), 535-544; (b) Meehan P.R., Alyea E.C., Ferguson G., *Acta Crystallogr. C Cryst. Struct. Commun.*, 1997, 53(7), 888-890; (c) Vance A.L., Alcock N.W., Heppert J.A., Busch D.H., *Inorg. Chem.*, 1998, 37(26), 6912-6920.

19. Iovel I., Golomba L., Belyakov S., Kemme A., Lukevics E., *Appl. Organometallic Chem.*, 2001, 15(9), 733.

20. This compound is mentioned, but not further described as regards the synthesis, in: Johnson K.J., Feldman J., Kreutzer A., McLain S.J., Bennett A.M.A., Coughlin E.B., Donald T.S., Nelson L.T.J., Parthasarathy A., Shen X., Tam W., Wang Y., *US Patent* 5,714,556.

21. Herzog S., Gustav K., Krüger E., Oberender H., Schuster R.Z., *Z. Chem.*, 1963, 3(11), 428-429.

22. Chiericato G. Jr., Arana C.R., Casado C., Cuadrado I., Abruna H.D., *Inorg. Chim. Acta*, 2000, 300, 32-42.

23. (a) Tohi Y., Matsui S., Fujita T., WO Patent Application 9965951 to Mitsui Chemicals, Inc., Japan. Priority date June 16, 1998; (b) Tohi Y., Matsui S., Fujita T., WO Patent Application 9965952 to Mitsui Chemicals, Inc., Japan. Priority date June 16, 1998; (c) Matsui S., Nitabaru M., Tsoru K., Fujita T., Suzuki Y., Takagi Y., Tanaka H, WO Patent Application 9954364 to Mitsui Chemicals, Inc., Japan. Priority date Sept. 4, 1998.

24. La Forge F.B., *J. Am. Chem. Soc.*, 1928, 50, 2477-2483.

25. (a) Rauchfuss T.B., *J. Organomet. Chem.*, 1978, 162(2), C19-C22; (b); Wong W.K., Gao J., Wong W.T., *Polyhedron*, 1993, 12(9), 1047-1053; (c) Yang C., Cheung Y.K., Yao J., Wong Y.T., Jia G., *Organometallics*, 2001, 20(3), 424-429.

26. (a) Stoop R.M., Bachmann S., Valentini M., Mezzetti A., *Organometallics*, 2000, 19(20), 4117-4162; (b) Wong W.-K., Chen X.-P., Pan W.-X., Guo J.-P., Wong W.-Y., *Eur. J. Inorg. Chem.*, 2002, (1), 231-237; (c) Masson J.-P., Bahsoun A.A., Youinou M.-T., Osborn J.A., *C. R. Chimie*, 2002, 5(4), 303-308; (d) Li C.-B., Pan W.-X., Wong W.-K., Li J.-L., Qiu X.-Q., Chen X.-P., *J. Mol. Catal. A*, 2003, 193(1-2), 71-75.

27. (a) Bonnet M.C., Dahan F., Ecke A., Keim W., Schulz R.P., Tkatchenko I., *J.C.S. Chem. Commun.*, 1994, (5), 615-616; (b) Po R., Cardi N., Santi R., Romano A.M., Zannoni C., Spera S., *J. Polym Sci.A*, 1998, 36(12), 2119-2126; (c) Guan Z., *PCT Int. Appl.*, WO 2000059956; (d) Muller G., Klinga M., Leskela M., Rieger B., *Z., Anorg. Allg. Chem.*, 2002, 628(13), 2839-2846.

28. (a) Shirakawa E., Yoshida H., Takaya H., *Tetrahedron Lett.* 1997, 38(21), 3759-3762; (b) Antonaroli S., Crociani B., *J. Organomet. Chem.*, 1998, 560, 137-146.

29. (a) Döring M., Ciesielski M., Görls H., *J. Inorg. Biochem.*, 1999, 74, 117; (b) Ciesielski M., Walter O., Döring M., *J. Inorg. Biochem.*, 2001, 86, 475.

30. Bluhm M.E., Ciesielski M., Görls H., Döring M., *Angew. Chem. Int. Ed.*, 2002, 41(16), 2962-2965.

31. Pufky D., Ciesielski M., Döring M., *Tetrahedron*, in press.

32. Klein A., *Z. Anorg. Allg. Chem.*, 2001, 627, 645-650.

33. (a) Crane J.D., Hughes R., Sinn E., *Inorg. Chim. Acta*, 1995, 237, 181-185; (b) Wang C., Friedrich S., Younkin T.R., Li R.T., Grubbs R.H., Bansleben D.A., Day M.W., *Organometallics*, 1998, 17(15), 3149-3151.

34. Hidai M., Kashiwagi T., Ikeuchi T., Uchida Y., *J. Organometal. Chem.*, 1971, 30, 279-282.

35. (a) Jäger E.G., *Z. Anorg. Allg. Chem.*, 1968, 359(3-4), 147-159; (b) Kristen H., Hamann O., *Pharmazie*, 1976, 31(4), 222-224; (c) Jäger E.-G., Kirchhof B., Schmidt E., Remde B., Kipke A., Müller R., *Z. Anorg. Allg. Chem.*, 1982, 485, 141-172.

36. Ife R.J., Brown T.H., Keeling D.J., Leach C.A., Meeson M.L., Pearsons M.E., Reavill D.R., Theobald C.J., Wiggall K.J., *J. Med. Chem.*, 1992, 35, 3413-3422.

37. Bourget-Merle L., Lappert M.F., Severn J.R., *Chem. Rev.*, 2002, 102, 3031-3065.

38. Wiencko H.L., Kogut E., Warren T.H., *Inorg. Chim. Acta*, 2003, 345, 199-208.

39. Kuo E.A., Hambelton P.T., Kay D.P., Evans P.L., Matharu S.S., Little E., McDowall N., Jones C.B., Hedgecock J.R., Yea C.M., Chan A.W.E., Hairsine P.W., Ager I.R., Tully W.R., Williamson R.A., Westwood R., *J. Med. Chem.*, 1996, 39, 4608-4621.

40. Ahlbrecht H., Vonderheid C., *Chem. Ber.*, 1973, 106, 2009-2016.

41. (a) Claisen L., *Berichte*, 1893, 26(3), 2729-2735; (b) Claisen L., Haase E., *Berichte*, 1895, 28(1), 35-41; (c) Claisen L., *Liebig's Annalen*, 1897, 297, 1-99; (d) Reidlinger C., Dworczak R., Junek H., Graubaum H., *Monatsh. Chem.*, 1998, 129, 1313-1318; (e) Cuvigny T., Normant H., *Bull. Soc., Chim. Fr.*, 1961, 2423-2432.

42. Price C.C., Boekelheide V., *J. Am. Chem. Soc.*, 1946, 68, 1246-1250.

43. (a) Price C.C., Roberts R.M., *J. Am. Chem. Soc.*, 1946, 68, 1204-1208; (b) Snyder H.R., Jones R.E., *J. Am. Chem. Soc.*, 1946, 68, 1253-1255.

44. Hodgkinson A.J., Staskun B., *J. Org. Chem.*, 1969, 34(6), 1709-1713.

45. Wolfbeis O.S., *Chem. Ber.*, 1981, 114(11), 3471-3484.

46. Barth J.A., *Organikum*, J. A. Barth Verlag (Heidelberg), 1996, 430-431.

47. Barchiesi E., Bradamante S., Carfagna C., Ferraccioli R., *Perkin Trans. 2*, 1988, (8), 1565-1572.

48. Wuckelt J., *Beiträge zur Reaktivität und Koordinationschemie von Bis(imidoyl)chloriden der Oxalsäure*, Dissertation, Jena, 1998.

49. (a) Fritschi H., Leutenegger U., Siegmann K., Pfaltz A., *Helv. Chim. Acta*, 1988, 71, 1541-1552; (b) Kläui W., Bongards J., Reiß G.J., *Angew. Chem. Int. Ed.*, 2000, 39(21), 3894-3896.

50. Döring M., Kröger M., *Zinkkomplex substituierter 2-Amido-Acrylsäure-Iminoester und dessen Verwendung*, Patent Application (Ger) 102004037201.2.

51. Zhang D., Jin G.-X., Wenig L.-H., Wang F., *Organometallics*, 2004, 23(13), 3270-3275.

52. (a) Feldman J., McLain S.J., Parthasarathy A., Marshall W.J., Calabrese J.C., Arthur S.D., *Organometallics*, 1997, 16(8), 1514-1516; (b) Foley S.R., Stockland R.A.Jr., Shen H., Jordan R.F., *J. Am. Chem. Soc.*, 2003, 125, 4350-4361.

53. (a) Schulz G.V., *Z. Phys. Chem. Abt. B*, 1935, 30, 379-398; (b) Schulz G.V., *Z. Phys. Chem. Abt. B*, 1935, 43, 25-46; (c) Flory P.J., *J. Am. Chem. Soc.*, 1940, 62, 1561-1565; (d) Henrici-Olivé G., Olivé S., *Adv. Polym. Sci.*, 1974, 15, 1-30.

54. Wang M., Dai D., Zhu H.-J., Wang H., Sun L.-C., *Chem. Res. Chinese U.*, 2003, 19(2), 231-234.

55. Plentz Meneghetti S., Lutz P.J., Kress J., *Organometallics*, 1999, 18, 2734-2737.

56. (a) Benedek W.J., Mauleon J.-L., *Hydrocarbon Process.*, 1980, 59(5), 143; (b) Boucher J.F., Follain G., Fulop D., Gaillard J., *Oil Gas J.*, 1982, 80, 84-86; (c) Chauvin Y., Gaillard J., Léonard J., Bonnifay P., Andrews J.W., *Hydrocarbon Process.*, 1982, 61(5), 110-112; (d) Gaillard J., *Pet. Tech.*, 1985, 314, 20-27.

57. (a) Nomura K., Itagaki M., Ishino M., Yamamoto M., Suzukamo G., *Catal. Lett.*, 1997, 47, 47-49; (b) Itagaki M., Suzukamo G., Nomura K., *Bull. Chem. Soc. Jpn.*, 1998, 71, 79-82; (c) Sato H., Tojima H., Ikimi K., *J. Mol. Catal.*, 1999, 144, 285-293.

58. Olivier-Bourbigou H., Saussine L., in *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; VCH Publishers: 1996, Vol. 1, pp 257-259.

59. Wu S., Lu S., *Appl. Catal. A*, 2003, 246, 295-301.

60. Zhang T., Guo D., Jie S., Sun W.-H., Li T., Yiang X., *J. Polym. Sci. A*, 2004, 42(19), 4765-4774.

61. Desjardins S.Y., Cavell K.J., Jin H., Skelton B.W., White A.H., *J. Organomet. Chem.*, 1996, 515, 233-243.

62. (a) Chan M.S.W., Deng L., Ziegler T., *Organometallics*, 2000, 19(14), 2741-2750; (b) Michalak A., Ziegler T., *Organometallics*, 2003, 22(10), 2069-2079.

63. SADABS, Siemens area detector absorption correction programme, Siemens, 1997.

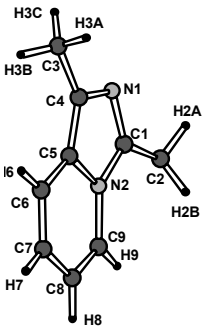
64. (a) SHELX-97, Sheldrick G.M., Universität Göttingen, 1997; (b) xpma, Zsolnai L., Huttner G., Universität Heidelberg, 1997; (c) Winray, Soltek R., Universität Heidelberg, 1997.

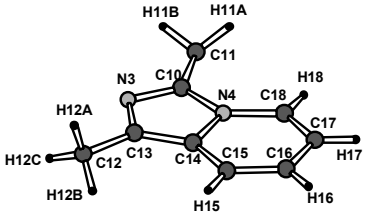
7. Appendix

7.1. Crystal structures

Table 7.1.1.1. Crystallographic data of the ligand **23b**. (Twice 0.5 molecules in the independent unit of cell)

Compound	**23b**
Empirical formula	$C_{17}H_{16}N_4$
Formula weight	276.34
Crystal size	0.25 × 0.30 × 0.25 mm^3
Crystal system	orthorhombic
Space group	C222 (1) (No. 20)
Unit cell dimensions	a = 1399.13(1)
	b = 1399.05(1)
	c = 1434.37(1) pm
	α = 90.0
	β = 90.0
	γ = 90.0 °
Volume	2807.7(5) × 10^6 pm^3
Z	Z = 8
Density (calculated)	1.307 g/cm^3
Temperature	200 K
θ-Range	2.06≤ θ ≤ 28.31 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Number of	
reflections measured	17319
unique reflections	3452
reflections observed	2142 (I > 2 σ)
Parameters refined	199
Residual electron density	0.145 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0409 (I > 2σ)
	R_W = 0.0971 (all data on F^2)





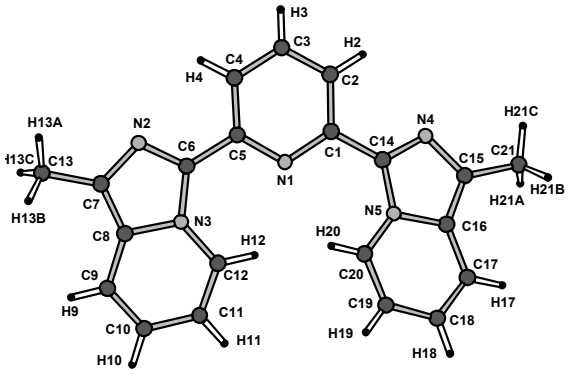
Standard deviations are given in parentheses.

Table 7.1.1.2. Selected bond lengths [Å] and angles [deg] for **23b**.

N(1)-C(1)	1.320(3)	C(1)-N(2)-C(5)	106.86(16)
N(1)-C(4)	1.371(2)	C(9)-N(2)-C(5)	121.05(17)
N(2)-C(1)	1.368(2)	C(10)-N(3)-C(13)	106.96(17)
N(2)-C(9)	1.382(2)	C(10)-N(4)-C(18)	132.13(17)
N(2)-C(5)	1.409(2)	C(10)-N(4)-C(14)	106.79(15)
N(3)-C(10)	1.320(3)	C(18)-N(4)-C(14)	121.08(17)
N(3)-C(13)	1.366(2)	N(1)-C(1)-N(2)	111.09(16)
N(4)-C(10)	1.367(2)	N(1)-C(1)-C(2)	126.11(16)
N(4)-C(18)	1.388(2)	N(2)-C(1)-C(2)	122.79(16)
N(4)-C(14)	1.412(2)	C(1)#1-C(2)-C(1)	113.2(2)
C(1)-C(2)	1.501(2)	N(1)-C(4)-C(5)	110.05(17)
C(2)-C(1)#1	1.501(2)	N(1)-C(4)-C(3)	122.28(18)
C(3)-C(4)	1.489(3)	C(5)-C(4)-C(3)	127.65(18)
C(4)-C(5)	1.380(3)	C(4)-C(5)-N(2)	105.03(17)
C(5)-C(6)	1.411(3)	C(4)-C(5)-C(6)	136.67(18)
C(6)-C(7)	1.350(3)	N(2)-C(5)-C(6)	118.28(17)
C(7)-C(8)	1.420(3)	C(7)-C(6)-C(5)	119.8(2)
C(8)-C(9)	1.343(3)	C(6)-C(7)-C(8)	120.4(2)
C(1)-N(1)-C(4)	106.96(17)	C(9)-C(8)-C(7)	120.8(2)
C(1)-N(2)-C(9)	132.09(17)	C(8)-C(9)-N(2)	119.57(19)

Table 7.1.2.1. Crystallographic data of the ligand **23c**.

Compound	**23c**
Empirical formula	$C_{21}H_{17}N_5$
Formula weight	339.40
Crystal size	0.20 × 0.20 × 0.03 mm^3
Crystal system	orthorhombic
Space group	Pca2 (1) (No. 29)
Unit cell dimensions	a = 718.1(3)
	b = 1099.4(5)
	c = 2107.1(1) pm
	α = 90.0
	β = 90.0
	γ = 90.0 °
Volume	1663.5(1) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.355 g/cm^3
Temperature	200 K
θ-Range	1.85≤ θ ≤ 28.30 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-9 ≤ h ≤ 8, -14 ≤ k ≤ 14, -25 ≤ l ≤ 27
Number of	
reflections measured	16976
unique reflections	3976
reflections observed	1967 (I > 2 σ)
Parameters refined	242
Residual electron density	0.166 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0484 (I > 2σ)
	R_w = 0.1166 (all data on F^2)



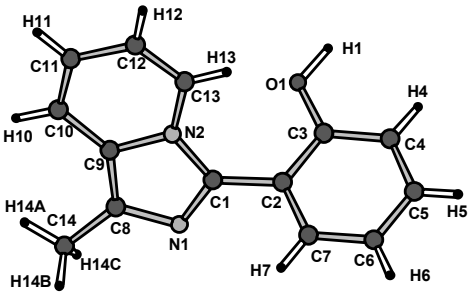
Standard deviations are given in parentheses.

Table 7.1.2.2. Selected bond lengths [Å] and angles [deg] for **23c**

N(1)-C(5)	1.349(3)	C(6)-N(2)-C(7)	107.5(3)
N(1)-C(1)	1.357(4)	C(6)-N(3)-C(12)	132.3(3)
N(2)-C(6)	1.331(4)	C(6)-N(3)-C(8)	106.2(2)
N(2)-C(7)	1.358(3)	C(12)-N(3)-C(8)	121.5(3)
N(3)-C(6)	1.379(4)	N(1)-C(1)-C(2)	122.2(3)
N(3)-C(12)	1.387(3)	N(1)-C(1)-C(14)	118.5(3)
N(3)-C(8)	1.413(4)	C(2)-C(1)-C(14)	119.3(3)
N(4)-C(14)	1.332(4)	C(3)-C(2)-C(1)	119.6(3)
N(4)-C(15)	1.365(4)	C(2)-C(3)-C(4)	119.2(3)
N(5)-C(20)	1.375(4)	C(3)-C(4)-C(5)	118.8(3)
N(5)-C(14)	1.379(4)	N(1)-C(5)-C(4)	122.7(3)
N(5)-C(16)	1.398(3)	N(1)-C(5)-C(6)	119.3(3)
C(1)-C(2)	1.389(4)	C(4)-C(5)-C(6)	118.0(2)
C(1)-C(14)	1.456(4)	N(2)-C(6)-N(3)	110.2(3)
C(2)-C(3)	1.371(4)	N(2)-C(6)-C(5)	123.4(3)
C(3)-C(4)	1.378(4)	N(3)-C(6)-C(5)	126.4(3)
C(4)-C(5)	1.394(4)	N(2)-C(7)-C(8)	110.3(3)
C(5)-C(6)	1.459(4)	N(2)-C(7)-C(13)	121.9(3)
C(7)-C(8)	1.366(4)	C(8)-C(7)-C(13)	127.8(3)
C(7)-C(13)	1.496(4)	C(7)-C(8)-C(9)	136.5(3)
C(8)-C(9)	1.411(4)	C(7)-C(8)-N(3)	105.8(3)
C(9)-C(10)	1.355(4)	C(9)-C(8)-N(3)	117.8(3)
C(10)-C(11)	1.411(4)	C(10)-C(9)-C(8)	120.3(3)
C(11)-C(12)	1.352(5)	C(9)-C(10)-C(11)	120.4(3)
C(5)-N(1)-C(1)	117.4(2)	C(12)-C(11)-C(10)	121.2(3)

Table 7.1.3.1. Crystallographic data of the ligand **24e**.

Compound	**24e**
Empirical formula	$C_{14}H_{12}N_2O$
Formula weight	224.26
Crystal size	1.00 × 0.40 × 0.20 mm^3
Crystal system	monoclinic
Space group	P2 (1) / c (No. 14)
Unit cell dimensions	a = 938.56(8)
	b = 1228.23(1)
	c = 1023.63(9) pm
	α = 90.0
	β = 97.7560(1)
	γ = 90.0 °
Volume	1169.21(2) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.274 g/cm^3
Temperature	200 K
θ-Range	2.19≤ θ ≤ 28.27 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 16, -13 ≤ l ≤ 13
Number of	
reflections measured	11972
unique reflections	2838
reflections observed	2266 (I > 2 σ)
Parameters refined	162
Residual electron density	0.175 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0427 (I > 2σ)
	R_w = 0.1073 (all data on F^2)



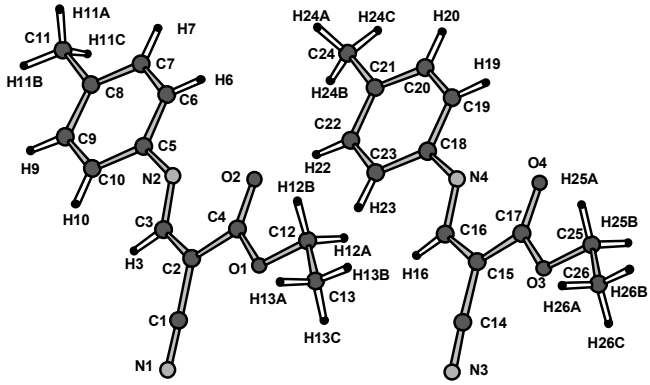
Standard deviations are given in parentheses.

Table 7.1.3.2. Selected bond lengths [Å] and angles [deg] for **24e**

O(1)-C(3)	1.3500(14)	C(3)-O(1)-H(1)	111.7(12)
O(1)-H(1)	0.95(2)	C(1)-N(1)-C(8)	107.79(10)
N(1)-C(1)	1.3317(15)	C(1)-N(2)-C(13)	130.30(10)
N(1)-C(8)	1.3727(15)	C(1)-N(2)-C(9)	107.55(10)
N(2)-C(1)	1.3615(15)	C(13)-N(2)-C(9)	122.02(10)
N(2)-C(13)	1.3846(16)	N(1)-C(1)-N(2)	109.94(10)
N(2)-C(9)	1.4069(15)	N(1)-C(1)-C(2)	125.30(11)
C(1)-C(2)	1.4731(15)	N(2)-C(1)-C(2)	124.61(11)
C(2)-C(7)	1.3943(17)	C(7)-C(2)-C(3)	119.21(11)
C(8)-C(9)	1.3768(18)	C(7)-C(2)-C(1)	119.22(11)
C(8)-C(14)	1.4918(18)	C(3)-C(2)-C(1)	121.55(10)
C(9)-C(10)	1.4224(17)	O(1)-C(3)-C(4)	122.56(11)
C(10)-C(11)	1.351(2)	O(1)-C(3)-C(2)	118.22(10)
C(10)-H(10)	0.9300	N(1)-C(8)-C(9)	109.24(10)
C(11)-C(12)	1.432(2)	N(1)-C(8)-C(14)	122.12(12)
C(11)-H(11)	0.9300	C(9)-C(8)-C(14)	128.64(12)
C(12)-C(13)	1.3457(18)	C(8)-C(9)-N(2)	105.48(10)
C(12)-H(12)	0.9300	C(8)-C(9)-C(10)	136.51(12)
C(13)-H(13)	0.9300	N(2)-C(9)-C(10)	117.98(11)
C(14)-H(14A)	0.9600	C(11)-C(10)-C(9)	119.63(12)
C(14)-H(14B)	0.9600	C(10)-C(11)-C(12)	120.46(12)
C(14)-H(14C)	0.9600	C(13)-C(12)-C(11)	121.00(13)
		C(12)-C(13)-N(2)	118.85(12)

Table 7.1.4.1. Crystallographic data of the ligand **28a**. (Two molecules in the independent unit of the elementary cell)

Compound	**28a**
Empirical formula	$C_{26}H_{26}N_4O_4$
Formula weight	458.51
Crystal size	0.20 × 0.10 × 0.10 mm^3
Crystal system	monoclinic
Space group	P2 (1) / c (No. 14)
Unit cell dimensions	a = 929.53(1)
	b = 2456.6(3)
	c = 1065.24(1) pm
	α = 90.0
	β = 97.328(2)
	γ = 90.0 °
Volume	2432.1(4) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.252 g/cm^3
Temperature	200 K
θ-Range	1.66≤ θ ≤ 28.36 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-11 ≤ h ≤ 12, -32 ≤ k ≤ 32, -13 ≤ l ≤ 14
Number of	
reflections measured	26464
unique reflections	5999
reflections observed	1143 (I > 2 σ)
Parameters refined	316
Residual electron density	0.538 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0775 (I > 2σ)
	R_W = 0.3166 (all data on F^2)



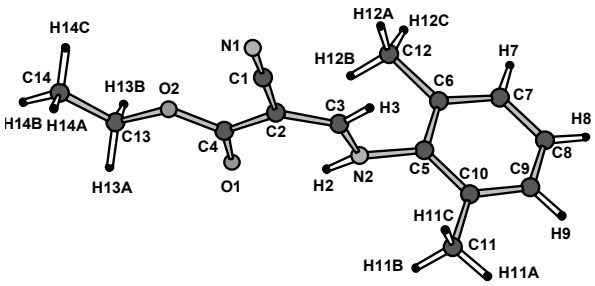
Standard deviations are given in parentheses.

Table 7.1.4.2. Selected bond lengths [Å] and angles [deg] for **28a**

O(1)-C(4)	1.351(12)	C(4)-O(1)-C(12)	115.7(9)
O(1)-C(12)	1.476(12)	C(17)-O(3)-C(25)	117.3(9)
O(2)-C(4)	1.205(13)	C(3)-N(2)-C(5)	127.0(11)
O(3)-C(17)	1.328(12)	C(16)-N(4)-C(18)	121.3(10)
O(3)-C(25)	1.449(12)	N(1)-C(1)-C(2)	177.9(13)
O(4)-C(17)	1.235(12)	C(3)-C(2)-C(1)	118.0(11)
N(1)-C(1)	1.149(14)	C(3)-C(2)-C(4)	121.1(11)
N(2)-C(3)	1.294(13)	C(1)-C(2)-C(4)	120.7(10)
N(2)-C(5)	1.431(13)	N(2)-C(3)-C(2)	127.5(12)
N(3)-C(14)	1.156(14)	O(2)-C(4)-O(1)	125.0(12)
N(4)-C(16)	1.308(13)	O(2)-C(4)-C(2)	123.5(11)
N(4)-C(18)	1.447(13)	O(1)-C(4)-C(2)	111.5(10)
C(1)-C(2)	1.432(16)	C(6)-C(5)-C(10)	118.6(10)
C(2)-C(3)	1.364(12)	C(6)-C(5)-N(2)	118.5(11)
C(2)-C(4)	1.465(15)	C(10)-C(5)-N(2)	122.8(10)
C(5)-C(6)	1.359(15)	C(5)-C(6)-C(7)	121.8(12)
C(5)-C(10)	1.400(14)	C(6)-C(7)-C(8)	121.5(11)
C(6)-C(7)	1.358(15)	C(7)-C(8)-C(9)	118.2(11)
C(7)-C(8)	1.379(15)	C(7)-C(8)-C(11)	121.3(10)
C(8)-C(9)	1.390(15)	C(9)-C(8)-C(11)	120.5(11)
C(8)-C(11)	1.513(15)	C(8)-C(9)-C(10)	120.2(11)
C(9)-C(10)	1.404(13)	C(5)-C(10)-C(9)	119.6(10)
C(12)-C(13)	1.478(14)	C(13)-C(12)-O(1)	106.7(10)

Table 7.1.5.1. Crystallographic data of the ligand **28c**.

Compound	**28c**
Empirical formula	$C_{14}H_{16}N_2O_2$
Formula weight	244.29
Crystal size	0.30 × 0.30 × 0.25 mm^3
Crystal system	monoclinic
Space group	P2 (1) / n (No. 14)
Unit cell dimensions	a = 1058.91(7)
	b = 799.86(5)
	c = 1696.3(1) pm
	α = 90.0
	β = 108.063(1)
	γ = 90.0 °
Volume	1365.9(2) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.188 g/cm^3
Temperature	200 K
θ-Range	2.03≤ θ ≤ 28.26 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 10, -22 ≤ l ≤ 22
Number of	
reflections measured	14154
unique reflections	3316
reflections observed	2447 (I > 2 σ)
Parameters refined	175
Residual electron density	0.775 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0690 (I > 2σ)
	R_w = 0.2086 (all data on F^2)



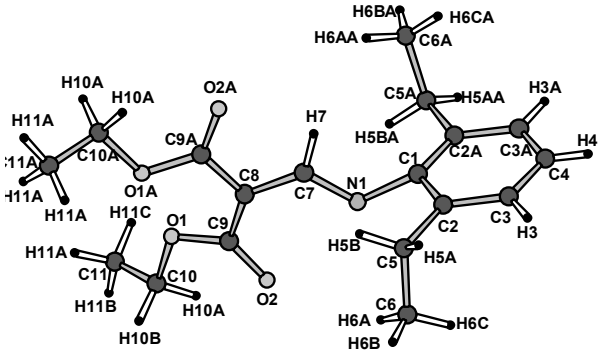
Standard deviations are given in parentheses.

Table 7.1.5.2. Selected bond lengths [Å] and angles [deg] for **28c**

O(1)-C(4)	1.220(3)	C(5)-N(2)-H(2)	122.9(18)
O(2)-C(4)	1.341(3)	N(1)-C(1)-C(2)	179.2(3)
O(2)-C(13)	1.455(3)	C(3)-C(2)-C(1)	117.42(19)
N(1)-C(1)	1.147(3)	C(3)-C(2)-C(4)	122.91(18)
N(2)-C(3)	1.314(3)	C(1)-C(2)-C(4)	119.38(18)
N(2)-C(5)	1.443(3)	N(2)-C(3)-C(2)	125.5(2)
N(2)-H(2)	0.94(3)	N(2)-C(3)-H(3)	117.2
C(1)-C(2)	1.419(3)	C(2)-C(3)-H(3)	117.2
C(2)-C(3)	1.396(3)	O(1)-C(4)-O(2)	124.4(2)
C(2)-C(4)	1.452(3)	O(1)-C(4)-C(2)	122.8(2)
C(3)-H(3)	0.9300	O(2)-C(4)-C(2)	112.75(17)
C(5)-C(6)	1.397(3)	C(6)-C(5)-C(10)	122.2(2)
C(5)-C(10)	1.400(3)	C(6)-C(5)-N(2)	117.29(18)
C(6)-C(7)	1.386(3)	C(10)-C(5)-N(2)	120.5(2)
C(6)-C(12)	1.508(3)	C(7)-C(6)-C(5)	118.7(2)
C(7)-C(8)	1.378(4)	C(7)-C(6)-C(12)	120.7(2)
C(8)-C(9)	1.377(4)	C(5)-C(6)-C(12)	120.6(2)
C(9)-C(10)	1.398(3)	C(8)-C(7)-C(6)	120.3(2)
C(10)-C(11)	1.501(3)	C(9)-C(8)-C(7)	120.5(2)
C(13)-C(14)	1.468(4)	C(8)-C(9)-C(10)	121.7(2)
		C(9)-C(10)-C(5)	116.7(2)
C(4)-O(2)-C(13)	115.02(17)	C(9)-C(10)-C(11)	121.9(2)
C(3)-N(2)-C(5)	121.01(18)	C(5)-C(10)-C(11)	121.4(2)
C(3)-N(2)-H(2)	112.9(18)	O(2)-C(13)-C(14)	107.0(2)

Table 7.1.6.1. Crystallographic data of the ligand **29b**. (Half a molecule in the independent unit of the elementary cell).

Compound	**29b**
Empirical formula	$C_9H_{12}N_{0.5}O_2$
Formula weight	159.19
Crystal size	0.50 × 0.60 × 0.60 mm^3
Crystal system	tetragonal
Space group	P4 (1) 2 (1) 2 (No. 92)
Unit cell dimensions	a = 1228.03(6)
	b = 1228.03(6)
	c = 1166.21(8) pm
	α = 90.0
	β = 90.0
	γ = 90.0 °
Volume	1758.71(2) × 10^6 pm^3
Z	Z = 8
Density (calculated)	1.202 g/cm^3
Temperature	200 K
θ-Range	2.35≤ θ ≤ 28.27 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 15, -15 ≤ l ≤ 15
Number of	
reflections measured	21311
unique reflections	2172
reflections observed	1533 (I > 2 σ)
Parameters refined	126
Residual electron density	0.435 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.1038 (I > 2σ)
	R_W = 0.3773 (all data on F^2)



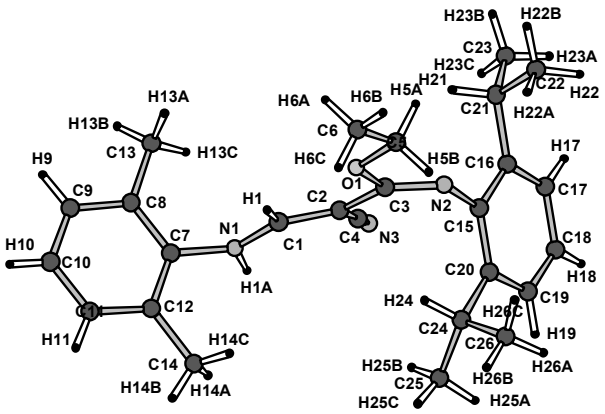
Standard deviations are given in parentheses.

Table 7.1.6.2. Selected bond lengths [Å] and angles [deg] for **29b**.

O(1)-C(9)	1.308(6)	C(9)-O(1)-C(10)	114.4(5)
O(1)-C(10)	1.458(7)	C(7)-N(1)-C(1)	115.1(5)
O(2)-C(9)	1.219(6)	C(2)-C(1)-N(1)	115.8(4)
N(1)-C(7)	1.340(8)	C(2)#1-C(1)-N(1)	118.9(4)
N(1)-C(1)	1.494(8)	C(1)-C(2)-C(3)	117.2(6)
C(1)-C(2)	1.380(5)	C(1)-C(2)-C(5)	121.7(5)
C(2)-C(3)	1.403(8)	C(3)-C(2)-C(5)	121.0(6)
C(2)-C(5)	1.514(9)	C(4)-C(3)-C(2)	122.2(7)
C(3)-C(4)	1.337(10)	C(6)-C(5)-C(2)	111.4(6)
C(5)-C(6)	1.474(10)	N(1)-C(7)-C(8)	116.6(5)
C(7)-C(8)	1.460(10)	C(9)#1-C(8)-C(9)	126.8(5)
C(8)-C(9)	1.432(7)	C(9)#1-C(8)-C(7)	98.4(3)
C(10)-C(11)	1.353(11)	C(9)-C(8)-C(7)	134.8(4)
		O(2)-C(9)-O(1)	121.6(7)
		O(2)-C(9)-C(8)	123.0(6)
		O(1)-C(9)-C(8)	115.2(4)
		C(11)-C(10)-O(1)	112.5(6)

Table 7.1.7.1. Crystallographic data of the ligand **35a**

Compound	**35a**
Empirical formula	$C_{26}H_{33}N_3O$
Formula weight	403.55
Crystal size	0.30 × 0.30 × 0.10 mm^3
Crystal system	monoclinic
Space group	P2 (1) / n (No. 14)
Unit cell dimensions	a = 1393.9(1)
	b = 815.48(8)
	c = 2158.6(2) pm
	α = 90.0
	β = 107.220(2)
	γ = 90.0 °
Volume	2343.9(4) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.144 g/cm^3
Temperature	200 K
θ-Range	1.56≤ θ ≤ 28.29 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-18 ≤ h ≤ 18, -10 ≤ k ≤ 10, -28 ≤ l ≤ 28
Number of	
reflections measured	27426
unique reflections	5778
reflections observed	2661 (I > 2 σ)
Parameters refined	287
Residual electron density	0.402 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0556 (I > 2σ)
	R_w = 0.1772 (all data on F^2)



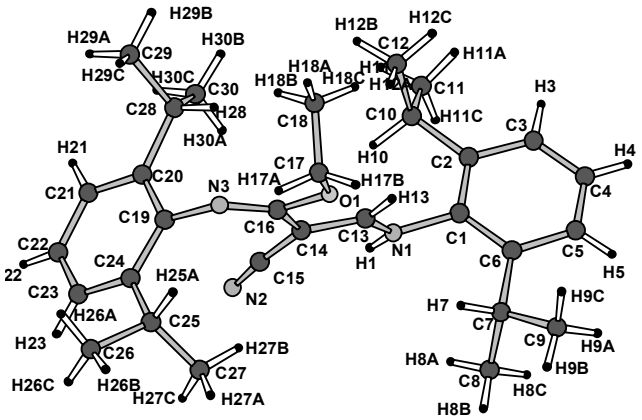
Standard deviations are given in parentheses.

Table 7.1.7.2. Selected bond lengths [Å] and angles [deg] for **35a**.

O(1)-C(3)	1.361(2)	C(3)-O(1)-C(5)	115.98(15)
O(1)-C(5)	1.452(2)	C(1)-N(1)-C(7)	121.55(17)
N(1)-C(1)	1.327(3)	C(1)-N(1)-H(1A)	118.3
N(1)-C(7)	1.449(2)	C(7)-N(1)-H(1A)	119.1
N(1)-H(1A)	0.9349	C(3)-N(2)-C(15)	123.69(18)
N(2)-C(3)	1.275(2)	N(1)-C(1)-C(2)	127.53(19)
N(2)-C(15)	1.419(3)	N(1)-C(1)-H(1)	116.2
N(3)-C(4)	1.157(3)	C(2)-C(1)-H(1)	116.2
C(1)-C(2)	1.373(3)	C(1)-C(2)-C(4)	118.83(18)
C(1)-H(1)	0.9300	C(1)-C(2)-C(3)	121.39(18)
C(2)-C(4)	1.428(3)	C(4)-C(2)-C(3)	119.74(16)
C(2)-C(3)	1.465(3)	N(2)-C(3)-O(1)	119.50(18)
C(5)-C(6)	1.485(3)	N(2)-C(3)-C(2)	129.53(18)
C(15)-C(16)	1.412(3)	O(1)-C(3)-C(2)	110.96(15)
C(16)-C(17)	1.388(3)	N(3)-C(4)-C(2)	175.3(2)
C(16)-C(21)	1.520(3)	O(1)-C(5)-C(6)	108.00(17)
C(17)-C(18)	1.376(3)	C(8)-C(7)-C(12)	122.33(19)
C(18)-C(19)	1.376(3)	C(8)-C(7)-N(1)	119.0(2)
C(19)-C(20)	1.394(3)	C(12)-C(7)-N(1)	118.62(19)
C(20)-C(24)	1.519(3)	C(7)-C(8)-C(9)	117.9(2)
C(21)-C(23)	1.519(3)	C(7)-C(8)-C(13)	122.2(2)
C(21)-C(22)	1.521(3)	C(20)-C(15)-C(16)	121.38(19)
C(24)-C(25)	1.492(4)	C(20)-C(15)-N(2)	120.49(19)
C(24)-C(26)	1.492(3)	C(16)-C(15)-N(2)	117.92(19)

Table 7.1.8.1. Crystallographic data of the ligand **35b**

Compound	**35b**
Empirical formula	$C_{30}H_{41}N_3O$
Formula weight	459.66
Crystal size	0.20 × 0.20 × 0.08 mm^3
Crystal system	monoclinic
Space group	P2 (1) / n (No. 14)
Unit cell dimensions	a = 1368.4(2)
	b = 1250.2(1)
	c = 1781.8(2) pm
	α = 90.0
	β = 112.173(2)
	γ = 90.0 °
Volume	2823.1(6) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.081 g/cm^3
Temperature	200 K
θ-Range	1.62≤ θ ≤ 28.30 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-17 ≤ h ≤ 18, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23
Number of	
reflections measured	32550
unique reflections	6868
reflections observed	3896 (I > 2 σ)
Parameters refined	363
Residual electron density	0.479 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0672 (I > 2σ)
	R_w = 0.2174 (all data on F^2)



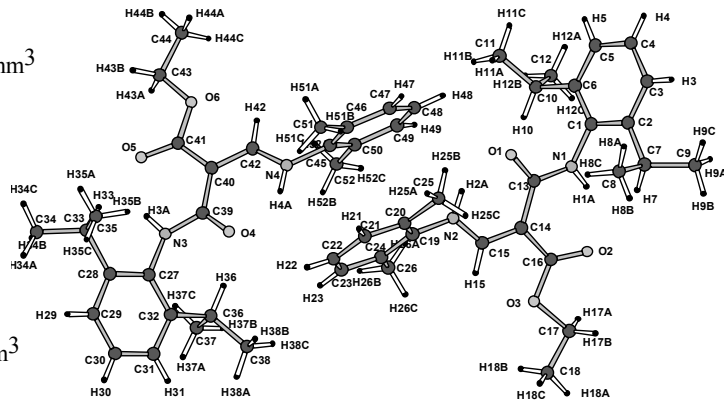
Standard deviations are given in parentheses.

Table 7.1.8.2. Selected bond lengths [Å] and angles [deg] for **35b**.

O(1)-C(16)	1.354(3)	C(25)-C(26)	1.555(6)
O(1)-C(17)	1.470(5)	C(28)-C(29)	1.501(4)
N(1)-C(13)	1.324(2)	C(28)-C(30)	1.522(4)
N(1)-C(1)	1.446(2)		
N(1)-H(1)	0.87(2)	C(16)-O(1)-C(17)	119.9(4)
N(2)-C(15)	1.143(2)	C(13)-N(1)-C(1)	122.49(17)
N(3)-C(16)	1.269(3)	C(13)-N(1)-H(1)	120.2(15)
N(3)-C(19)	1.414(2)	C(1)-N(1)-H(1)	116.3(15)
C(2)-C(3)	1.399(3)	C(16)-N(3)-C(19)	120.79(16)
C(2)-C(10)	1.497(4)	C(6)-C(1)-N(1)	119.0(2)
C(6)-C(7)	1.507(4)	C(2)-C(1)-N(1)	118.30(19)
C(7)-C(8)	1.511(5)	N(1)-C(13)-C(14)	127.39(18)
C(7)-C(9)	1.533(4)	N(1)-C(13)-H(13)	116.3
C(10)-C(12)	1.495(5)	C(14)-C(13)-H(13)	116.3
C(10)-C(11)	1.512(4)	C(13)-C(14)-C(15)	117.32(16)
C(13)-C(14)	1.375(3)	C(13)-C(14)-C(16)	120.43(17)
C(13)-H(13)	0.9300	C(15)-C(14)-C(16)	122.23(16)
C(14)-C(15)	1.423(3)	N(2)-C(15)-C(14)	172.39(18)
C(14)-C(16)	1.470(3)	N(3)-C(16)-O(1)	120.14(18)
C(17)-C(18)	1.426(10)	N(3)-C(16)-C(14)	130.56(18)
C(20)-C(21)	1.393(3)	O(1)-C(16)-C(14)	109.30(17)
C(20)-C(28)	1.519(3)	C(18)-C(17)-O(1)	100.9(5)
C(24)-C(25)	1.526(3)	C(20)-C(19)-C(24)	121.22(18)
C(25)-C(27)	1.434(6)	C(20)-C(19)-N(3)	120.72(18)

Table 7.1.9.1. Crystallographic data of the ligand **38e**. (Two molecules in the independent part of the elementary cell)

Compound	**38e**
Empirical formula	$C_{52}H_{68}N_4O_6$
Formula weight	845.10
Crystal size	0.60 × 0.60 × 0.60 mm^3
Crystal system	monoclinic
Space group	P2 (1) / c (No. 14)
Unit cell dimensions	a = 1586.9(2)
	b = 1866.5(2)
	c = 1805.4(2) pm
	α = 90.0
	β = 114.510(2)
	γ = 90.0 °
Volume	4865.8(10) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.154 g/cm^3
Temperature	200 K
θ-Range	1.65≤ θ ≤ 28.48 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-21 ≤ h ≤ 21, -24 ≤ k ≤ 24, -23 ≤ l ≤ 23
Number of	
reflections measured	56304
unique reflections	11849
reflections observed	6762 (I > 2 σ)
Parameters refined	621
Residual electron density	0.573 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0723 (I > 2σ)
	R_W = 0.2118 (all data on F^2)



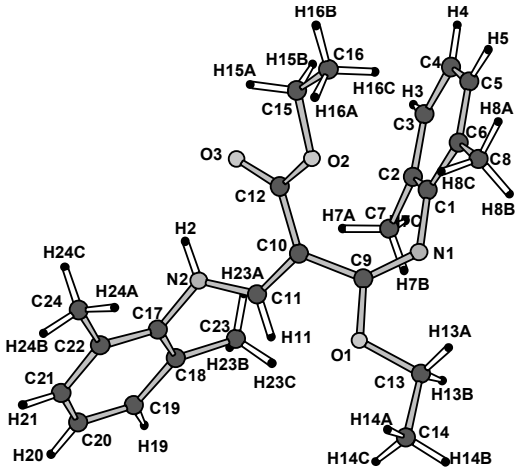
Standard deviations are given in parentheses.

Table 7.1.9.2. Selected bond lengths [Å] and angles [deg] for **38e**.

O(1)-C(13)	1.241(3)	C(16)-O(3)-C(17)	106.9(4)
O(2)-C(16)	1.217(4)	C(13)-N(1)-C(1)	123.0(2)
O(3)-C(16)	1.341(4)	C(15)-N(2)-C(19)	125.8(2)
O(3)-C(17)	1.525(7)	C(6)-C(1)-N(1)	120.1(2)
O(4)-C(39)	1.239(3)	C(2)-C(1)-N(1)	117.8(2)
O(5)-C(41)	1.218(3)	O(1)-C(13)-N(1)	120.8(2)
O(6)-C(41)	1.346(3)	O(1)-C(13)-C(14)	120.9(2)
O(6)-C(43)	1.471(4)	N(1)-C(13)-C(14)	118.3(2)
N(1)-C(13)	1.346(3)	C(15)-C(14)-C(16)	119.2(2)
N(1)-C(1)	1.435(3)	C(15)-C(14)-C(13)	119.7(2)
N(2)-C(15)	1.327(3)	C(16)-C(14)-C(13)	121.0(3)
N(2)-C(19)	1.430(3)	N(2)-C(15)-C(14)	126.2(2)
N(3)-C(39)	1.353(3)	O(2)-C(16)-O(3)	120.9(3)
N(3)-C(27)	1.427(3)	O(2)-C(16)-C(14)	126.3(3)
N(4)-C(42)	1.320(3)	O(3)-C(16)-C(14)	112.8(3)
N(4)-C(45)	1.443(3)	C(18)-C(17)-O(3)	103.8(6)
C(13)-C(14)	1.475(3)	C(24)-C(19)-C(20)	121.5(3)
C(14)-C(15)	1.372(4)	C(24)-C(19)-N(2)	121.3(3)
C(14)-C(16)	1.459(4)	C(20)-C(19)-N(2)	117.2(2)
C(17)-C(18)	1.418(10)		

Table 7.1.10.1. Crystallographic data of the ligand **37a**.

Compound	**37a**
Empirical formula	$C_{24}H_{30}N_2O_3$
Formula weight	394.50
Crystal size	0.50 × 0.55 × 0.60 mm^3
Crystal system	monoclinic
Space group	C2 / c (No. 15)
Unit cell dimensions	a = 2661.4(3)
	b = 1194.4(1)
	c = 1681.7(2) pm
	α = 90.0
	β = 120.014(1)
	γ = 90.0 °
Volume	4455.1(8) × 10^6 pm^3
Z	Z = 8
Density (calculated)	1.176 g/cm^3
Temperature	200 K
θ-Range	1.84≤ θ ≤ 28.30 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-33 ≤ h ≤ 33, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22
Number of	
reflections measured	25721
unique reflections	5425
reflections observed	3950 (I > 2 σ)
Parameters refined	281
Residual electron density	0.227 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0433 (I > 2σ)
	R_w = 0.1180 (all data on F^2)



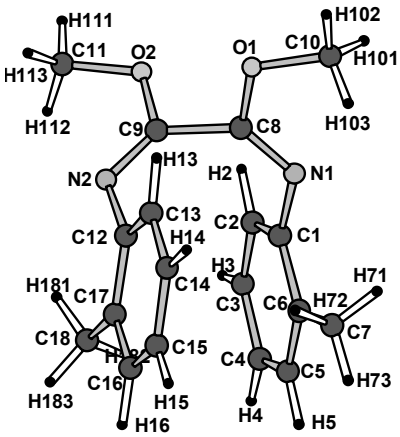
Standard deviations are given in parentheses.

Table 7.1.10.2. Selected bond lengths [Å] and angles [deg] for **37a**.

O(1)-C(9)	1.3625(14)	C(9)-N(1)-C(1)	122.39(10)
O(1)-C(13)	1.4505(15)	C(11)-N(2)-C(17)	122.23(11)
O(2)-C(12)	1.3420(14)	C(11)-N(2)-H(2)	118.2(11)
O(2)-C(15)	1.4531(16)	C(17)-N(2)-H(2)	119.5(11)
O(3)-C(12)	1.2201(14)	C(2)-C(1)-N(1)	122.51(12)
N(1)-C(9)	1.2711(16)	C(6)-C(1)-N(1)	117.11(12)
N(1)-C(1)	1.4103(16)	N(1)-C(9)-O(1)	119.15(11)
N(2)-C(11)	1.3373(16)	N(1)-C(9)-C(10)	129.78(11)
N(2)-C(17)	1.4334(16)	O(1)-C(9)-C(10)	111.04(10)
N(2)-H(2)	0.852(17)	C(11)-C(10)-C(12)	119.47(11)
C(2)-C(7)	1.503(2)	C(11)-C(10)-C(9)	118.15(11)
C(6)-C(8)	1.504(2)	C(12)-C(10)-C(9)	122.33(10)
C(9)-C(10)	1.4774(16)	N(2)-C(11)-C(10)	128.22(11)
C(10)-C(11)	1.3704(17)	N(2)-C(11)-H(11)	115.9
C(10)-C(12)	1.4552(17)	C(10)-C(11)-H(11)	115.9
C(11)-H(11)	0.9300	O(3)-C(12)-O(2)	122.43(11)
C(13)-C(14)	1.500(2)	O(3)-C(12)-C(10)	123.77(11)
C(15)-C(16)	1.481(2)	O(2)-C(12)-C(10)	113.70(10)
C(18)-C(23)	1.500(2)	O(1)-C(13)-C(14)	107.46(11)
C(22)-C(24)	1.502(2)	O(2)-C(15)-C(16)	108.72(12)
		C(22)-C(17)-C(18)	121.86(12)
C(9)-O(1)-C(13)	115.65(9)	C(22)-C(17)-N(2)	118.33(12)
C(12)-O(2)-C(15)	115.36(10)	C(18)-C(17)-N(2)	119.77(12)

Table 7.1.11.1. Crystallographic data of the ligand **42**.

Compound	**42**
Empirical formula	$C_{18}H_{20}N_2O_2$
Formula weight	296.36
Crystal size	0.80 × 0.80 × 0.50 mm^3
Crystal system	monoclinic
Space group	P2 (1) / n (No. 14)
Unit cell dimensions	a = 811.73(8)
	b = 1879.8(2)
	c = 1075.4(1) pm
	α = 90.0
	β = 91.972(1)
	γ = 90.0 °
Volume	1639.1(3) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.201 g/cm^3
Temperature	200 K
θ-Range	2.17 ≤ θ ≤ 28.28 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 24, -13 ≤ l ≤ 13
Number of	
reflections measured	16946
unique reflections	3964
reflections observed	3478 (I > 2 σ)
Parameters refined	279
Residual electron density	0.212 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0421 (I > 2σ)
	R_w = 0.1124 (all data on F^2)



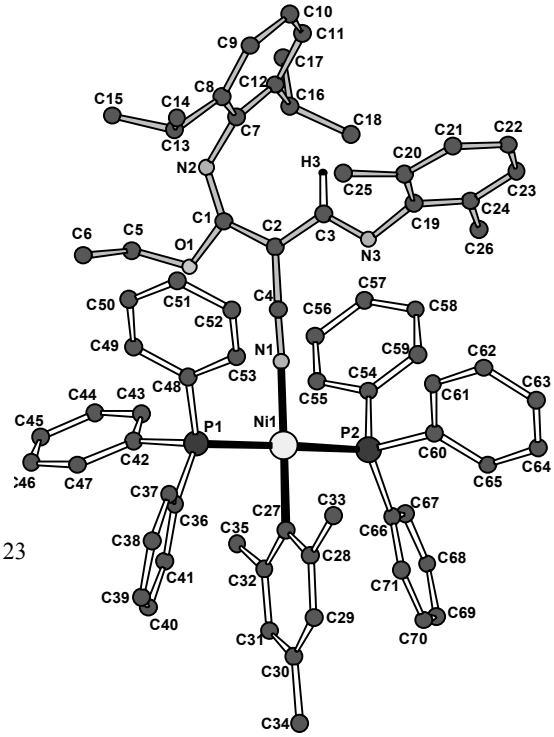
Standard deviations are given in parentheses.

Table 7.1.11.2. Selected bond lengths [Å] and angles [deg] for **42**.

O(1)-C(8)	1.3463(13)	C(8)-O(1)-C(10)	116.28(9)
O(1)-C(10)	1.4419(14)	C(9)-O(2)-C(11)	116.20(9)
O(2)-C(9)	1.3462(13)	C(8)-N(1)-C(1)	120.64(9)
O(2)-C(11)	1.4421(15)	C(9)-N(2)-C(12)	119.24(9)
N(1)-C(8)	1.2621(14)	C(2)-C(1)-C(6)	120.10(10)
N(1)-C(1)	1.4203(14)	C(2)-C(1)-N(1)	121.59(10)
N(2)-C(9)	1.2617(14)	C(6)-C(1)-N(1)	118.14(10)
N(2)-C(12)	1.4199(14)	C(3)-C(2)-C(1)	120.39(11)
C(1)-C(2)	1.3928(16)	C(4)-C(3)-C(2)	120.01(12)
C(1)-C(6)	1.4030(15)	C(5)-C(4)-C(3)	119.43(11)
C(2)-C(3)	1.3908(17)	C(4)-C(5)-C(6)	121.82(11)
C(3)-C(4)	1.3856(18)	C(5)-C(6)-C(1)	118.23(11)
C(4)-C(5)	1.3842(18)	C(5)-C(6)-C(7)	121.23(11)
C(5)-C(6)	1.3941(17)	C(1)-C(6)-C(7)	120.55(11)
C(6)-C(7)	1.5006(17)	N(1)-C(8)-O(1)	122.98(10)
C(8)-C(9)	1.5138(14)	N(1)-C(8)-C(9)	127.72(10)
C(12)-C(13)	1.3963(17)	O(1)-C(8)-C(9)	109.30(9)
C(12)-C(17)	1.4026(16)	N(2)-C(9)-O(2)	123.42(10)
C(13)-C(14)	1.3872(18)	N(2)-C(9)-C(8)	127.19(10)
C(14)-C(15)	1.378(2)	O(2)-C(9)-C(8)	109.38(9)
C(15)-C(16)	1.387(2)	C(13)-C(12)-N(2)	120.41(10)
C(16)-C(17)	1.3907(18)	C(17)-C(12)-N(2)	119.01(10)
C(17)-C(18)	1.5025(19)	C(16)-C(17)-C(18)	121.00(12)
		C(12)-C(17)-C(18)	121.34(11)

Table 7.1.12.1. Crystallographic data of the complex **45a**.

Compound	**45a**
Empirical formula	$C_{71}H_{73}N_3NiOP_2$
Formula weight	1104.97
Crystal size	0.30 × 0.20 × 0.20 mm^3
Crystal system	monoclinic
Space group	P2 (1) / c (No. 14)
Unit cell dimensions	a = 1497.8(1)
	b = 2413.1(2)
	c = 1746.9(1) pm
	α = 90.0
	β = 101.839(1)
	γ = 90.0 °
Volume	6179.6(7) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.188 g/cm^3
Temperature	200 K
θ-Range	1.39 ≤ θ ≤ 28.32 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-19 ≤ h ≤ 19, -31 ≤ k ≤ 32, -23 ≤ l ≤ 23
Number of	
reflections measured	74003
unique reflections	15125
reflections observed	8752 (I > 2 σ)
Parameters refined	724
Residual electron density	0.253 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0413 (I > 2σ)
	R_w = 0.1087 (all data on F^2)



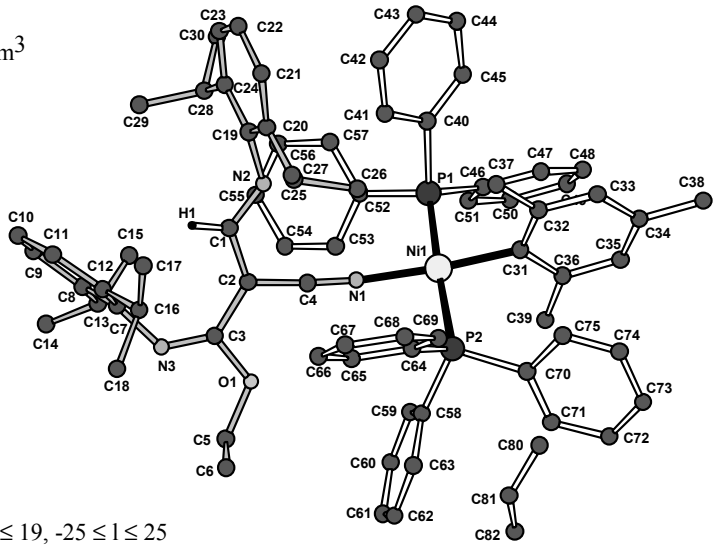
Standard deviations are given in parentheses.

Table 7.1.12.2. Selected bond lengths [Å] and angles [deg] for **45a**.

Ni(1)-N(1)	1.8945(17)	C(13)-C(14)	1.528(4)
Ni(1)-C(27)	1.899(2)	C(16)-C(17)	1.507(4)
Ni(1)-P(1)	2.2331(6)	C(16)-C(18)	1.506(4)
Ni(1)-P(2)	2.2393(6)		
O(1)-C(1)	1.386(2)	N(1)-Ni(1)-C(27)	179.06(8)
O(1)-C(5)	1.441(3)	N(1)-Ni(1)-P(1)	90.13(5)
N(1)-C(4)	1.157(2)	C(27)-Ni(1)-P(1)	89.73(6)
N(2)-C(1)	1.278(3)	N(1)-Ni(1)-P(2)	91.00(5)
N(2)-C(7)	1.413(3)	C(27)-Ni(1)-P(2)	89.18(6)
N(3)-C(3)	1.289(3)	P(1)-Ni(1)-P(2)	177.40(2)
N(3)-C(19)	1.416(3)	C(4)-N(1)-Ni(1)	177.60(16)
C(1)-C(2)	1.445(3)	C(1)-N(2)-C(7)	123.62(19)
C(2)-C(4)	1.401(3)	C(3)-N(3)-C(19)	119.36(18)
C(2)-C(3)	1.427(3)	N(2)-C(1)-C(2)	132.8(2)
C(5)-C(6)	1.492(4)	O(1)-C(1)-C(2)	109.49(17)
C(7)-C(12)	1.402(3)	C(4)-C(2)-C(3)	116.81(19)
C(7)-C(8)	1.406(3)	C(4)-C(2)-C(1)	117.38(18)
C(8)-C(9)	1.386(3)	C(3)-C(2)-C(1)	125.80(19)
C(8)-C(13)	1.513(3)	N(3)-C(3)-C(2)	123.13(19)
C(9)-C(10)	1.378(3)	N(1)-C(4)-C(2)	178.8(2)
C(10)-C(11)	1.380(4)	O(1)-C(5)-C(6)	111.3(2)
C(11)-C(12)	1.385(3)	C(17)-C(16)-C(18)	110.4(2)
C(12)-C(16)	1.514(3)	C(17)-C(16)-C(12)	113.5(2)
C(13)-C(15)	1.529(4)	C(18)-C(16)-C(12)	112.5(2)

Table 7.1.13.1. Crystallographic data of the complex **45b**. (It crystallises with 0.4 molecules of pentane per unit)

Compound	**45b**
Empirical formula	$C_{77}H_{85.8}N_3NiOP_2$
Formula weight	1189.94
Crystal size	0.30 × 0.25 × 0.10 mm^3
Crystal system	triclinic
Space group	P-2 (1) (No. 2)
Unit cell dimensions	a = 1267.37(9)
	b = 1470.2(1)
	c = 1880.8(1) pm
	α = 101.815(1)
	β = 91.609(1)
	γ = 102.356(1) °
Volume	3341.3(4) × 10^6 pm^3
Z	Z = 2
Density (calculated)	1.183 g/cm^3
Temperature	200 K
θ-Range	1.63 ≤ θ ≤ 28.31 °
Scan	ω-Scan, Δ ω=0.40 °
Index ranges	-16 ≤ h ≤ 16, -19 ≤ k ≤ 19, -25 ≤ l ≤ 25
Number of	
reflections measured	40555
unique reflections	16042
reflections observed	6611 (I > 2 σ)
Parameters refined	777
Residual electron density	0.975 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0480 (I > 2σ)
	R_W = 0.1326 (all data on F^2)



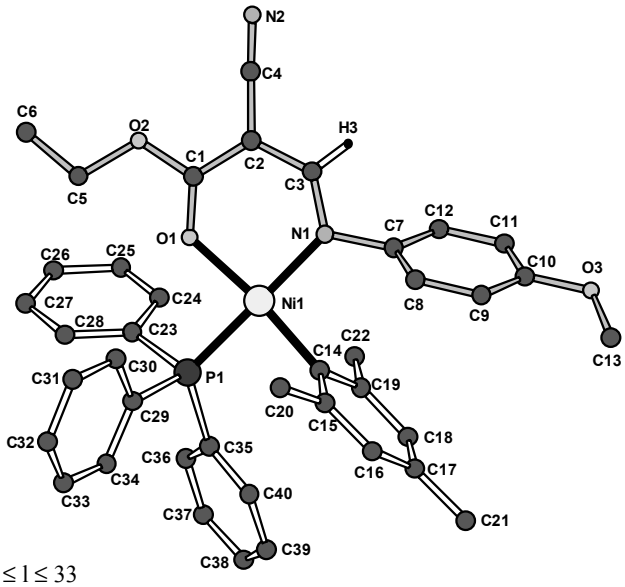
Standard deviations are given in parentheses.

Table 7.1.13.2. Selected bond lengths [Å] and angles [deg] for **45b**.

Ni(1)-N(1)	1.888(3)	N(1)-Ni(1)-C(31)	172.50(12)
Ni(1)-C(31)	1.919(3)	N(1)-Ni(1)-P(2)	89.73(8)
Ni(1)-P(2)	2.2436(10)	C(31)-Ni(1)-P(2)	90.55(9)
Ni(1)-P(1)	2.2516(10)	N(1)-Ni(1)-P(1)	92.72(8)
P(1)-C(52)	1.816(3)	C(31)-Ni(1)-P(1)	87.82(9)
P(1)-C(40)	1.829(3)	P(2)-Ni(1)-P(1)	173.39(4)
P(1)-C(46)	1.832(3)	C(3)-O(1)-C(5)	117.4(3)
P(2)-C(70)	1.819(3)	C(4)-N(1)-Ni(1)	168.6(3)
P(2)-C(58)	1.831(3)	C(1)-N(2)-C(19)	122.1(3)
P(2)-C(64)	1.834(3)	C(3)-N(3)-C(7)	126.3(3)
O(1)-C(3)	1.376(3)	N(2)-C(1)-C(2)	121.2(3)
O(1)-C(5)	1.429(4)	C(4)-C(2)-C(1)	114.3(3)
N(1)-C(4)	1.152(4)	C(4)-C(2)-C(3)	119.1(3)
N(2)-C(1)	1.280(4)	C(1)-C(2)-C(3)	125.7(3)
N(2)-C(19)	1.418(4)	N(3)-C(3)-O(1)	118.5(3)
N(3)-C(3)	1.264(4)	N(3)-C(3)-C(2)	132.0(3)
N(3)-C(7)	1.405(4)	O(1)-C(3)-C(2)	109.5(3)
C(1)-C(2)	1.432(4)	N(1)-C(4)-C(2)	175.2(3)
C(2)-C(4)	1.409(4)	O(1)-C(5)-C(6)	111.9(3)
C(2)-C(3)	1.448(4)	C(12)-C(7)-N(3)	120.4(3)
C(5)-C(6)	1.476(5)	N(3)-C(7)-C(8)	18.5(3)
C(8)-C(13)	1.512(5)	C(24)-C(19)-N(2)	119.3(3)
		C(20)-C(19)-N(2)	118.5(3)

Table 7.1.14.1. Crystallographic data of the complex **47b**.

Compound	**47b**
Empirical formula	$C_{40}H_{39}N_2NiO_3P$
Formula weight	685.41
Crystal size	$0.25 \times 0.07 \times 0.07$ mm^3
Crystal system	monoclinic
Space group	P2 (1) / c (No. 14)
Unit cell dimensions	a = 1522.03(8)
	b = 961.62(5)
	c = 2491.5(1) pm
	$\alpha = 90.0$
	$\beta = 106.896(1)$
	$\gamma = 90.0$ °
Volume	$3489.2(3) \times 10^6$ pm^3
Z	Z = 4
Density (calculated)	1.305 g/cm^3
Temperature	200 K
θ-Range	$1.40 \le \theta \le 28.28$ °
Scan	ω-Scan, $\Delta\omega$=0.45 °
Index ranges	$-20 \le h \le 20$, $-12 \le k \le 12$, $-32 \le l \le 33$
Number of	
reflections measured	41775
unique reflections	8602
reflections observed	3102 ($I > 2\sigma$)
Parameters refined	437
Residual electron density	0.436×10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	$R_1 = 0.0500$ ($I > 2\sigma$)
	$R_w = 0.1232$ (all data on F^2)



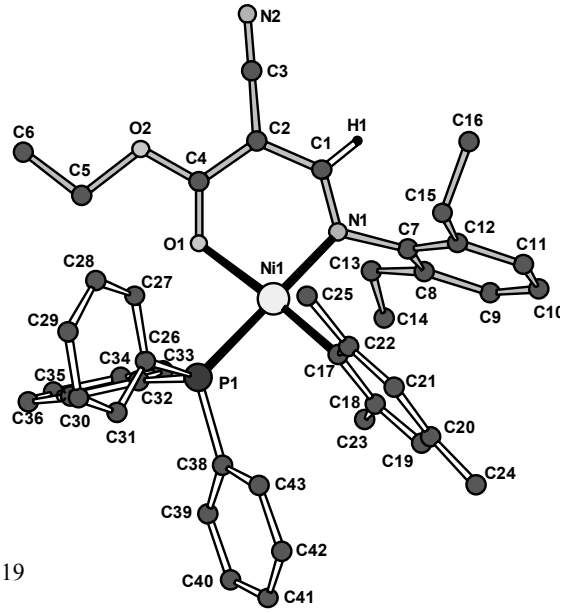
Standard deviations are given in parentheses.

Table 7.1.14.2. Selected bond lengths [Å] and angles [deg] for **47b**.

Ni(1)-C(14)	1.892(4)	C(14)-Ni(1)-O(1)	171.66(15)
Ni(1)-O(1)	1.940(3)	C(14)-Ni(1)-N(1)	93.81(14)
Ni(1)-N(1)	1.947(3)	O(1)-Ni(1)-N(1)	92.03(12)
Ni(1)-P(1)	2.1877(12)	C(14)-Ni(1)-P(1)	88.03(11)
P(1)-C(35)	1.821(4)	O(1)-Ni(1)-P(1)	87.04(9)
P(1)-C(29)	1.825(4)	N(1)-Ni(1)-P(1)	171.71(10)
P(1)-C(23)	1.827(4)	C(35)-P(1)-C(29)	103.57(17)
O(1)-C(1)	1.254(5)	C(35)-P(1)-C(23)	102.35(18)
O(2)-C(1)	1.342(5)	C(29)-P(1)-C(23)	103.22(18)
O(2)-C(5)	1.459(5)	C(35)-P(1)-Ni(1)	122.87(13)
O(3)-C(10)	1.386(5)	C(29)-P(1)-Ni(1)	114.33(13)
O(3)-C(13)	1.410(5)	C(23)-P(1)-Ni(1)	108.28(13)
N(1)-C(3)	1.313(4)	C(1)-O(1)-Ni(1)	128.9(3)
N(1)-C(7)	1.450(5)	C(10)-O(3)-C(13)	117.4(4)
N(2)-C(4)	1.159(5)	C(3)-N(1)-C(7)	112.8(3)
C(1)-C(2)	1.399(5)	C(3)-N(1)-Ni(1)	123.1(3)
C(2)-C(3)	1.411(5)	C(7)-N(1)-Ni(1)	123.5(3)
C(2)-C(4)	1.425(6)	O(1)-C(1)-O(2)	119.4(4)
C(5)-C(6)	1.409(6)	O(1)-C(1)-C(2)	125.1(4)
C(7)-C(8)	1.381(5)	O(2)-C(1)-C(2)	115.5(4)
C(7)-C(12)	1.386(5)	C(1)-C(2)-C(3)	121.8(4)
C(8)-C(9)	1.398(5)	C(1)-C(2)-C(4)	120.9(4)
C(9)-C(10)	1.384(6)	C(3)-C(2)-C(4)	117.3(4)
C(10)-C(11)	1.363(6)	N(1)-C(3)-C(2)	128.2(4)
		N(2)-C(4)-C(2)	177.7(5)

Table 7.1.15.1. Crystallographic data of the complex **47d**.

Compound	**47d**
Empirical formula	$C_{43}H_{45}N_2NiO_2P$
Formula weight	711.49
Crystal size	$0.25 \times 0.20 \times 0.10$ mm^3
Crystal system	triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	a = 1082.2(5)
	b = 1215.7(6)
	c = 1463.2(7) pm
	α = 99.202(7)
	β = 94.050(7)
	γ = 98.805(7) °
Volume	$1868.8(15) \times 10^6$ pm^3
Z	Z = 2
Density (calculated)	1.264 g/cm^3
Temperature	200 K
θ-Range	$1.42 \le \theta \le 28.45$ °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 16$, $-19 \le l \le 19$
Number of	
reflections measured	18820
unique reflections	8853
reflections observed	4789 ($I > 2\sigma$)
Parameters refined	472
Residual electron density	1.061×10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	$R_1 = 0.0725$ ($I > 2\sigma$)
	$R_w = 0.1971$ (all data on F^2)



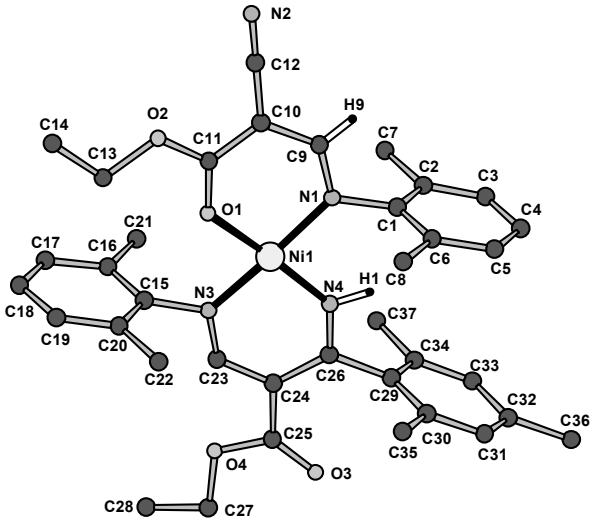
Standard deviations are given in parentheses.

Table 7.1.15.2. Selected bond lengths [Å] and angles [deg] for **47d**.

Ni(1)-C(17)	1.904(4)	N(1)-Ni(1)-P(1)	173.16(10)
Ni(1)-N(1)	1.936(4)	O(1)-Ni(1)-P(1)	86.44(9)
Ni(1)-O(1)	1.941(3)	C(4)-O(1)-Ni(1)	128.1(3)
Ni(1)-P(1)	2.1847(15)	C(4)-O(2)-C(5)	113.2(7)
P(1)-C(38)	1.820(4)	C(1)-N(1)-C(7)	114.5(3)
P(1)-C(26)	1.824(4)	C(1)-N(1)-Ni(1)	123.3(3)
P(1)-C(32)	1.824(4)	C(7)-N(1)-Ni(1)	121.8(3)
O(1)-C(4)	1.244(5)	N(1)-C(1)-C(2)	127.8(4)
O(2)-C(4)	1.340(5)	C(4)-C(2)-C(1)	121.0(4)
O(2)-C(5)	1.488(9)	C(4)-C(2)-C(3)	120.5(4)
N(1)-C(1)	1.309(5)	C(1)-C(2)-C(3)	117.9(4)
N(1)-C(7)	1.449(5)	N(2)-C(3)-C(2)	179.7(4)
N(2)-C(3)	1.146(5)	O(1)-C(4)-O(2)	120.1(4)
C(1)-C(2)	1.406(6)	O(1)-C(4)-C(2)	124.9(4)
C(2)-C(4)	1.404(6)	O(2)-C(4)-C(2)	114.9(4)
C(2)-C(3)	1.422(6)	C(6)-C(5)-O(2)	106.1(11)
C(5)-C(6)	1.485(14)	C(8)-C(7)-N(1)	118.3(4)
C(12)-C(15)	1.510(7)	C(12)-C(7)-N(1)	120.7(4)
C(15)-C(16)	1.509(7)	C(7)-C(8)-C(13)	120.3(4)
		C(9)-C(8)-C(13)	120.6(4)
C(17)-Ni(1)-N(1)	94.70(15)	C(11)-C(12)-C(15)	120.9(5)
C(17)-Ni(1)-O(1)	169.89(15)	C(7)-C(12)-C(15)	121.8(4)
N(1)-Ni(1)-O(1)	91.34(13)	C(14)-C(13)-C(8)	115.7(4)
C(17)-Ni(1)-P(1)	88.44(12)	C(16)-C(15)-C(12)	111.5(5)

Table 7.1.16.1. Crystallographic data of the complex **47'c**.

Compound	**47'c**
Empirical formula	$C_{37}H_{42}N_4NiO_4$
Formula weight	665.46
Crystal size	0.70 × 0.30 × 0.15 mm^3
Crystal system	triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	a = 822.72(6)
	b = 996.29(7)
	c = 2213.8(2) pm
	α = 82.085(1)
	β = 82.423(1)
	γ = 80.269(1) °
Volume	1760.4(2) × 10^6 pm^3
Z	Z = 2
Density (calculated)	1.255 g/cm^3
Temperature	200 K
θ-Range	1.87 ≤ θ ≤ 28.30 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -28 ≤ l ≤ 28
Number of	
reflections measured	21021
unique reflections	8368
reflections observed	6499 (I > 2 σ)
Parameters refined	440
Residual electron density	0.368 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0331 (I > 2σ)
	R_w = 0.0925 (all data on F^2)



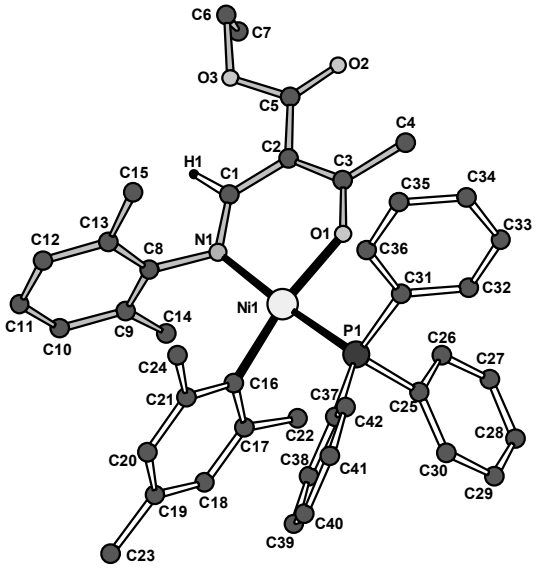
Standard deviations are given in parentheses.

Table 7.1.16.2. Selected bond lengths [Å] and angles [deg] for **47'c**.

Ni(1)-N(4)	1.8310(12)	N(4)-Ni(1)-O(1)	175.44(6)
Ni(1)-O(1)	1.8810(11)	N(4)-Ni(1)-N(3)	90.38(5)
Ni(1)-N(3)	1.8910(12)	O(1)-Ni(1)-N(3)	87.90(5)
Ni(1)-N(1)	1.9303(12)	N(4)-Ni(1)-N(1)	90.38(5)
O(1)-C(11)	1.2544(18)	O(1)-Ni(1)-N(1)	91.63(5)
O(2)-C(11)	1.3357(18)	N(3)-Ni(1)-N(1)	176.00(5)
O(3)-C(25)	1.2056(19)	C(11)-O(1)-Ni(1)	130.08(10)
O(4)-C(25)	1.3619(18)	C(9)-N(1)-C(1)	113.26(12)
N(1)-C(9)	1.3143(18)	C(9)-N(1)-Ni(1)	124.15(10)
N(1)-C(1)	1.4437(18)	C(23)-N(3)-C(15)	112.12(12)
N(2)-C(12)	1.1450(19)	C(23)-N(3)-Ni(1)	126.43(10)
N(3)-C(23)	1.3209(18)	C(26)-N(4)-Ni(1)	134.33(11)
N(3)-C(15)	1.4453(18)	N(1)-C(9)-C(10)	127.10(13)
N(4)-C(26)	1.3175(18)	C(11)-C(10)-C(9)	120.71(14)
N(4)-H(1)	0.909(16)	C(11)-C(10)-C(12)	119.78(13)
C(9)-C(10)	1.405(2)	C(9)-C(10)-C(12)	119.41(13)
C(9)-H(9)	0.9300	O(1)-C(11)-C(10)	124.86(14)
C(10)-C(11)	1.404(2)	N(2)-C(12)-C(10)	179.02(17)
C(10)-C(12)	1.428(2)	N(3)-C(23)-C(24)	127.58(13)
C(23)-C(24)	1.404(2)	C(23)-C(24)-C(26)	120.13(13)
C(23)-H(23)	0.9300	C(23)-C(24)-C(25)	118.47(13)
C(24)-C(26)	1.410(2)	C(26)-C(24)-C(25)	121.40(13)
C(24)-C(25)	1.466(2)	N(4)-C(26)-C(24)	121.07(13)
C(26)-C(29)	1.4988(19)	N(4)-C(26)-C(29)	115.65(12)

Table 7.1.17.1. Crystallographic data of the complex **49a**.

Compound	**49a**
Empirical formula	$C_{42}H_{44}NNiO_3P$
Formula weight	700.46
Crystal size	0.40 × 0.40 × 0.30 mm^3
Crystal system	monoclinic
Space group	P2 (1) / c (No. 14)
Unit cell dimensions	a = 2049.3(1)
	b = 1759.0(1)
	c = 1014.35(7) pm
	α = 90.0
	β = 91.436(1)
	γ = 90.0 °
Volume	3655.3(4) × 10^6 pm^3
Z	Z = 4
Density (calculated)	1.273 g/cm^3
Temperature	200 K
θ-Range	1.53 ≤ θ ≤ 28.30 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-27 ≤ h ≤ 27, -23 ≤ k ≤ 23, -13 ≤ l ≤ 13
Number of	
reflections measured	43174
unique reflections	8977
reflections observed	7039 (I > 2 σ)
Parameters refined	448
Residual electron density	0.718 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.0368 (I > 2σ)
	R_w = 0.1032 (all data on F^2)



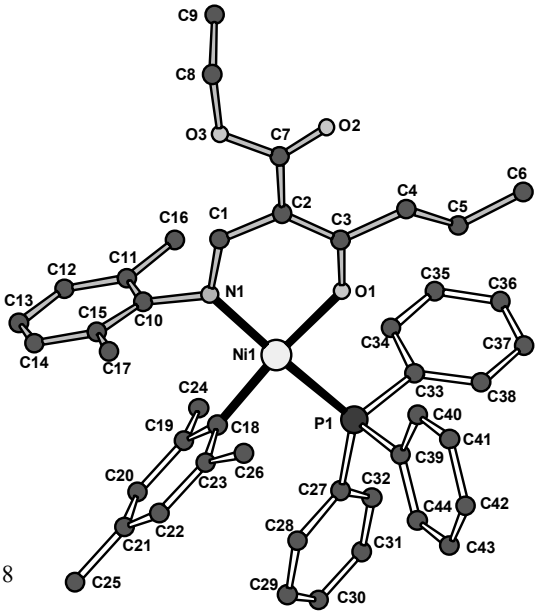
Standard deviations are given in parentheses.

Table 7.1.17.2. Selected bond lengths [Å] and angles [deg] for **49a**.

Ni(1)-O(1)	1.9005(13)	C(12)-C(13)	1.402(3)
Ni(1)-C(16)	1.9029(17)	C(13)-C(15)	1.498(3)
Ni(1)-N(1)	1.9372(15)		
Ni(1)-P(1)	2.1897(5)	O(1)-Ni(1)-C(16)	170.28(7)
P(1)-C(31)	1.8256(17)	O(1)-Ni(1)-N(1)	90.55(6)
P(1)-C(25)	1.826(2)	C(16)-Ni(1)-N(1)	95.48(6)
P(1)-C(37)	1.832(2)	O(1)-Ni(1)-P(1)	86.41(4)
O(1)-C(3)	1.271(2)	C(16)-Ni(1)-P(1)	88.24(5)
O(2)-C(5)	1.205(2)	N(1)-Ni(1)-P(1)	174.02(5)
O(3)-C(5)	1.348(3)	C(3)-O(1)-Ni(1)	133.15(12)
O(3)-C(6)	1.462(3)	C(1)-N(1)-C(8)	112.57(15)
N(1)-C(1)	1.309(2)	C(1)-N(1)-Ni(1)	123.61(12)
N(1)-C(8)	1.452(2)	N(1)-C(1)-C(2)	128.75(17)
C(1)-C(2)	1.420(2)	C(3)-C(2)-C(1)	121.44(16)
C(2)-C(3)	1.395(3)	C(3)-C(2)-C(5)	120.36(17)
C(2)-C(5)	1.467(3)	C(1)-C(2)-C(5)	118.16(17)
C(3)-C(4)	1.504(2)	O(1)-C(3)-C(2)	121.53(16)
C(6)-C(7)	1.433(7)	O(1)-C(3)-C(4)	113.97(17)
C(8)-C(13)	1.399(3)	O(2)-C(5)-C(2)	126.9(2)
C(8)-C(9)	1.403(3)	C(13)-C(8)-N(1)	117.88(18)
C(9)-C(10)	1.398(3)	C(9)-C(8)-N(1)	120.12(18)
C(9)-C(14)	1.496(3)	C(10)-C(9)-C(14)	119.7(2)
C(10)-C(11)	1.371(4)	C(8)-C(13)-C(15)	121.83(18)
C(11)-C(12)	1.377(4)	C(12)-C(13)-C(15)	120.8(2)

Table 7.1.18.1. Crystallographic data of the complex **49b**.

Compound	**49b**
Empirical formula	$C_{44}H_{47}NNiO_3P$
Formula weight	727.51
Crystal size	0.30 × 0.05 × 0.05 mm^3
Crystal system	triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	a = 1074.9(10)
	b = 1381.2(13)
	c = 1423.3(14) pm
	α = 100.83(2)
	β = 99.92(2)
	γ = 104.05(1) °
Volume	1960(3) × 10^6 pm^3
Z	Z = 2
Density (calculated)	1.233 g/cm^3
Temperature	200 K
θ-Range	1.50 ≤ θ ≤ 28.61 °
Scan	ω-Scan, Δ ω=0.45 °
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, -18 ≤ l ≤ 18
Number of	
reflections measured	24010
unique reflections	9499
reflections observed	3130 (I > 2 σ)
Parameters refined	467
Residual electron density	1.749 × 10^{-6} e/pm^3
Corrections	Lorentz and Polarisation, Exp. Absorption correction [20]
Structure solution	direct methods
Structure refinement	full matrix least square on F^2
Programs used	SHELX-97 [21], xpma [22], winray [23]
R indices	R_1 = 0.1058 (I > 2σ)
	R_w = 0.3194 (all data on F^2)

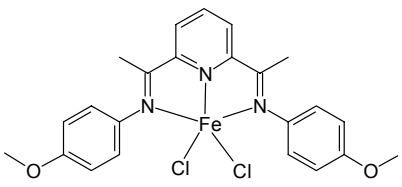


Standard deviations are given in parentheses.

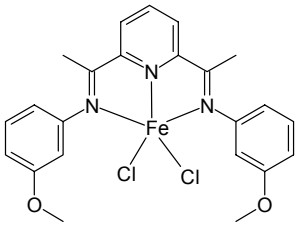
Table 7.1.18.2. Selected bond lengths [Å] and angles [deg] for **49b**.

Ni(1)-C(18)	1.882(7)	N(1)-Ni(1)-O(1)	90.4(2)
Ni(1)-N(1)	1.909(6)	C(18)-Ni(1)-P(1)	89.0(2)
Ni(1)-O(1)	1.915(5)	N(1)-Ni(1)-P(1)	176.57(18)
Ni(1)-P(1)	2.184(3)	O(1)-Ni(1)-P(1)	88.05(17)
O(1)-C(3)	1.270(9)	C(3)-O(1)-Ni(1)	131.2(5)
O(2)-C(7)	1.220(9)	C(1)-N(1)-C(10)	112.3(6)
O(3)-C(7)	1.333(10)	C(1)-N(1)-Ni(1)	125.3(5)
O(3)-C(8)	1.459(10)	N(1)-C(1)-C(2)	125.8(7)
N(1)-C(1)	1.327(9)	C(3)-C(2)-C(1)	121.5(7)
N(1)-C(10)	1.450(9)	C(3)-C(2)-C(7)	122.6(7)
C(1)-C(2)	1.446(10)	C(1)-C(2)-C(7)	115.8(7)
C(2)-C(3)	1.391(11)	O(1)-C(3)-C(2)	122.3(7)
C(2)-C(7)	1.454(11)	O(1)-C(3)-C(4)	115.0(7)
C(3)-C(4)	1.519(10)	C(2)-C(3)-C(4)	122.8(7)
C(4)-C(5)	1.454(12)	C(5)-C(4)-C(3)	115.5(8)
C(5)-C(6)	1.529(12)	C(4)-C(5)-C(6)	113.2(9)
C(8)-C(9)	1.474(17)	O(2)-C(7)-C(2)	126.4(8)
C(11)-C(16)	1.509(10)	O(3)-C(7)-C(2)	114.3(7)
C(15)-C(17)	1.496(11)	C(12)-C(11)-C(16)	118.8(7)
		C(10)-C(11)-C(16)	121.5(7)
C(18)-Ni(1)-N(1)	93.0(3)	C(10)-C(15)-C(17)	124.0(7)
C(18)-Ni(1)-O(1)	171.0(3)	C(14)-C(15)-C(17)	118.9(7)

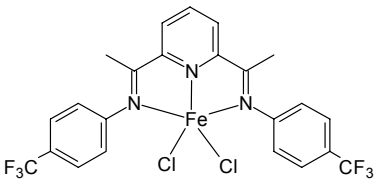
7.2. Structural formulas



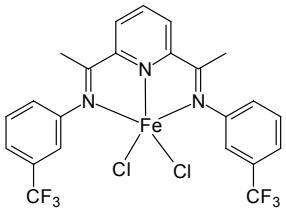
1a → 5a



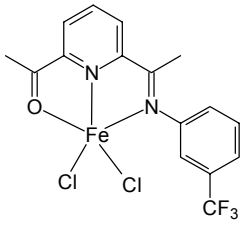
1b → 5b



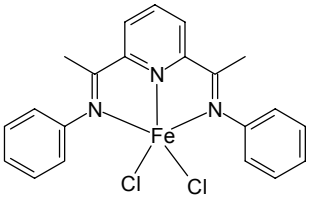
2a → 6a



2b → 6b



3 → 7



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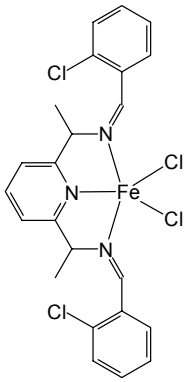
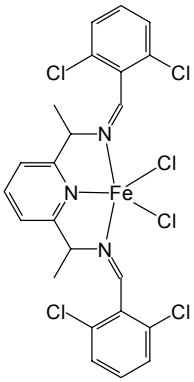
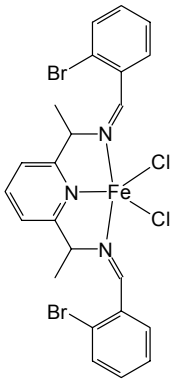


8a → 12a



8b → 12b



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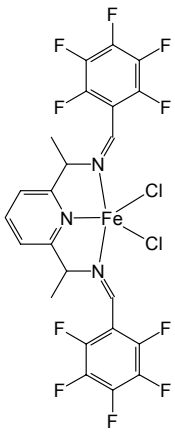

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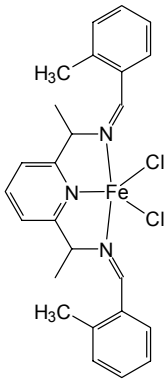
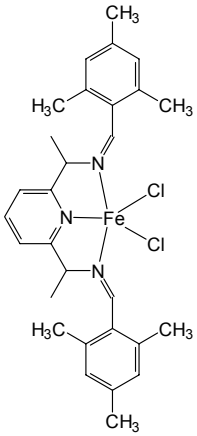


8e → 12e



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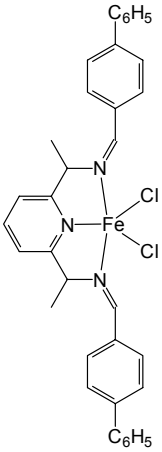
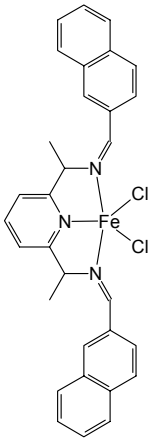
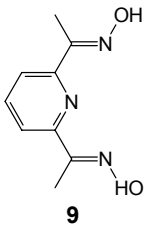


8g → 12g



8h → 12h



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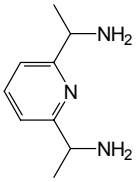

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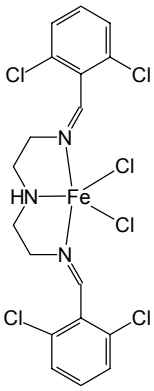
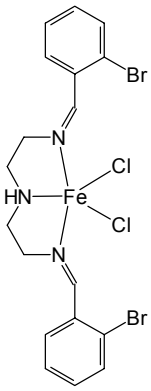
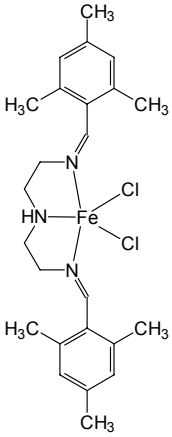


13a → 14a



13b → 14b



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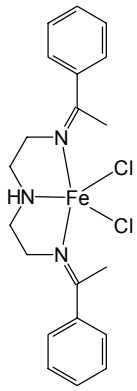
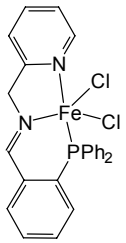
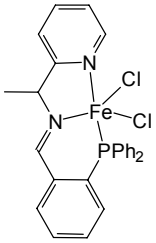


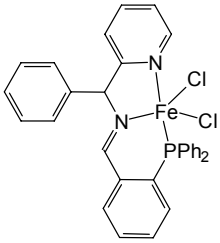
13d → 14d



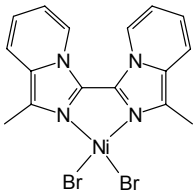
16a → 17a



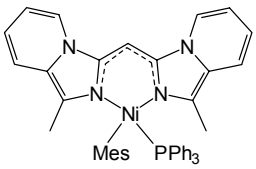
16b → 17b



16c → 17c



23a → 26a



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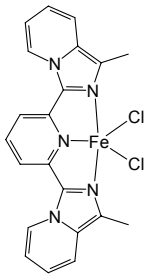
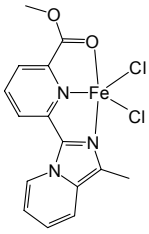
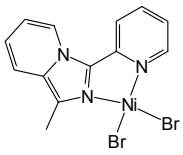


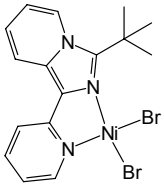
23c → 26c



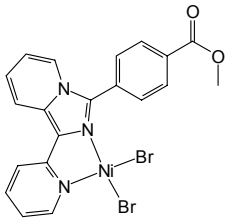
24a → 27a



24b → 27b



24c → 27c



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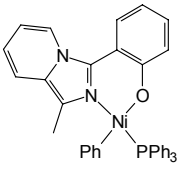
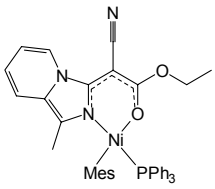
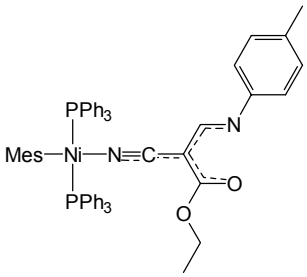


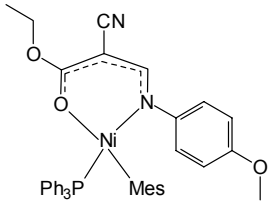
24e → 27e



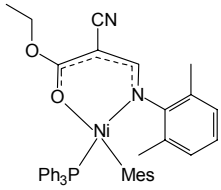
24f → 27f



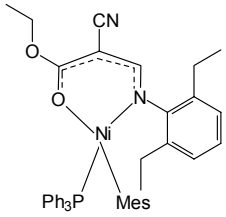
28a → 46a



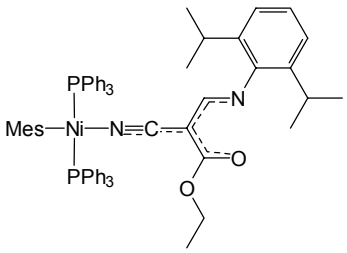
28b → 47b



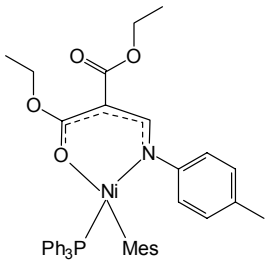
28c → 47c



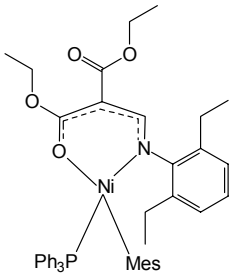
28d → 47d



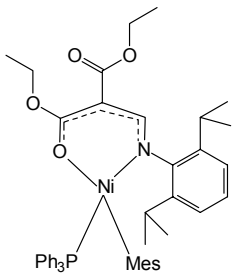
28e → 46e



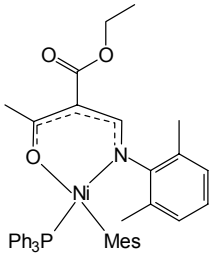
29a → 48a



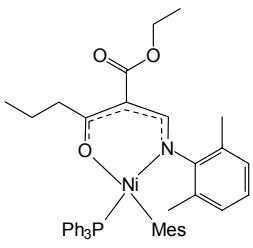
29b → 48b



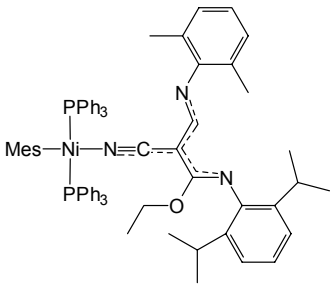
29c → 48c



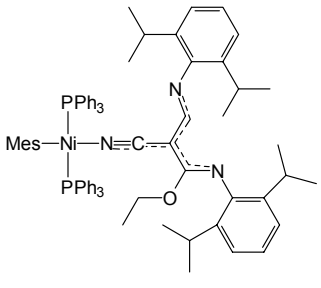
31a → 49a



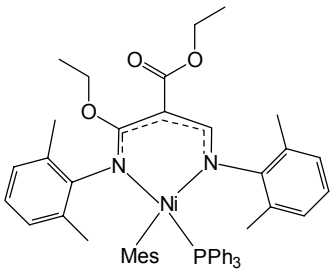
31b → 49b



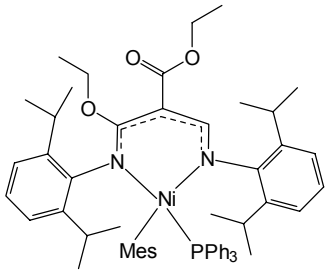
35a → 45a



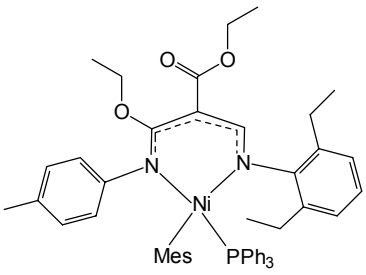
35b → 45b



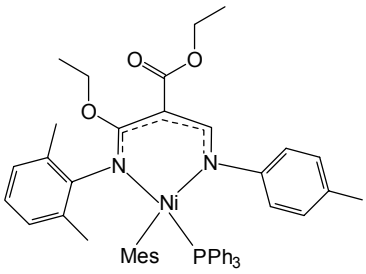
37a → 50a



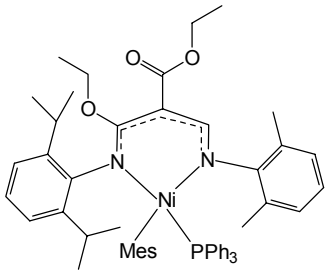
37b → 50b



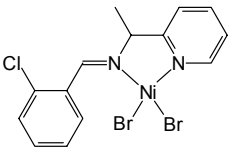
37c → 50c



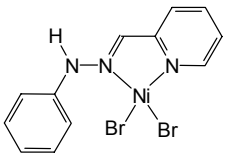
37d → 50d



37e → 50e



40a → 51a



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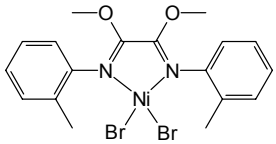
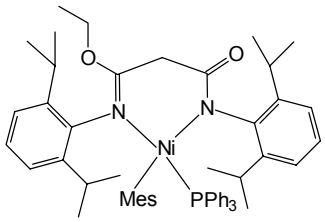
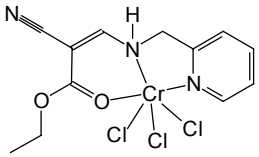


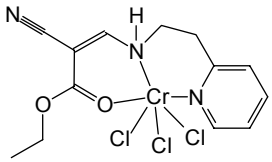
42 → 52



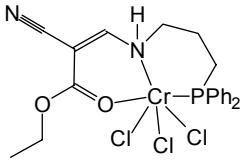
44 → 53



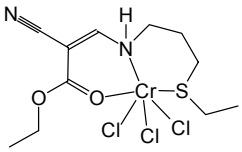
54a → 55a



54b → 55b



54c → 55c



54d → 55d

Legend for the metal complexes: **ligand → metal complex**

except for **23b**, **24e**-**f**, **28**-**37**, **44** where: **protonated ligand → metal complex**

Hiermit erkläre ich an Eides Statt, dass ich die vorliegende Arbeit selbständig und ohne unerlaubte Hilfsmittel durchgeführt habe.

Cristina Folli

Karlsruhe, im September 2004