Dissertation

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Synthesis and Characterization of five-coordinated indium amidinates

Reviewer: Prof. Dr. Gerald Linti
Prof. Dr. Dr. Hans-Jörg Himmel

To my Parents,
Siamak, and
Arash.

Two roads diverged in a yellow wood and I took the one less traveled by and that has made all the difference.
“Robert Frost”

Summary:

The focus of this work is synthesis, characterization and exploring the reactivity of new indium amidinate compounds of the type R_2InX (R = R"NCR'NR"; R' = Ph, R" = $SiMe_3$, iPr, dipp; X = Br, Cl) with the coordination number of five and R_3In (R = $Me_3SiNCPhNSiMe_3$) with the coordination number of six. By using amidinates as chelating ligands the electron deficiency of indium atom will be resolved. Additionally, by using different substituents the study of the different synthesized indium amidinates has become possible. The selected method for the synthesis allows the carbodiimides to react with organolithium compounds to get the corresponding lithium amidinates. Afterwards the resulting lithium amidinates take part in transmetalation reactions with $InBr_3$ and $InCl_3$. The study of the reactivity of indium amidinate complexes including nucleophilic reactions as well as their reduction were also examined. Beside crystal structure analysis, nuclear magnetic resonance spectroscopy as well as elemental analysis has been applied to characterize the compounds.

Zusammenfassung:

Die vorliegende Arbeit befasst sich mit der Synthese und Strukturuntersuchung neuartiger Indiumamidinate von der Typ R_2InX (R = R"NCR'NR"; R' = Ph, R" = $SiMe_3$, iPr, dipp; X = Br, Cl) mit der Koordinationsnummer 5 sowie R_3In (R = $Me_3SiNCPhNSiMe_3$) mit der Koordinationsnummer 6. Durch die bereits verwendeten Synthesemethoden sollen Carbodiimiden mit Organo-Lithium-Verbindungen die entsprechenden Lithiumamidinate erhalten und mittels Transmetallierung mit $InBr_3$ and $InCl_3$ in Indiumamidinate überführt werden. Alle erfassten Strukturen wurden durch Kristallstrukturanalyse, NMR-Spektroskopie, sowie Elementaranalyse geprüft.

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List Of abbreviations

^{t}Bu	$C(CH_3)_3$
Cp*	Pentamethylcyclopentadien
Cy	Cyclohexyl
δ	chemical shift (NMR)
Dipp	2,6-*di*-isopropylphenyl
Et	ethyl
Eq.	equivalent
J	coupling constant
LiBr	lithium bromide
Me	methyl
MHz	mega hertz
NMR	Nucleic Magnetic Resonance
Ph	phenyl
THF	*tetra*-Hydrofuran
iPr	isopropyl
Nacnac	β-diiminate of acetylacetone
OTF	triflate
Xyl	xylene

1. Introduction

Indium, the fourth element in the third main group of the periodic system, was first discovered by German chemists Ferdinand Reich and Theodor Richter in 1863 in Freiberg, Saxony. By seeing an indigo blue spectral line at the absorption spectrum of sphalerite, they noticed the presence of an unknown element, which was later called Indium. Indium is a silvery white soft metal that comes with the lighter homologous boron, aluminium and gallium and the heavier thallium in the same group. With atomic number of 49, indium crystallizes in the tetragonal crystal system and exists in two natural isotopes $^{113}_{49}In$ (with abundance of 4.4%) and $^{115}_{49}In$ (with abundance of 95.7%). The latter with a half-life time of 600 billion years has a very weak radioactivity.[1][2]

The concentration of indium in the continental earth's crust is 50 ppb, which makes its late discovery reasonable. Most commonly, indium occurs together with zinc deposits (e.g. 0.03% of zinc blende). So it is a by-product the of the zinc production. By electrolysis of its salt solutions the purified indium could be later isolated.[3]

Indium is among the world's shortest natural sources with about 11000 tons. Simultaneously its high demand has made it one of the most expensive metals ever.

The leading producer of indium is China with 390 tons in 2012, followed by canada, Japan and South Korea each with 70 tons. Its price ranges from 94 US$ per kg in 2002 to 382 US$ in 2006 and 918 US$ in 2009 per kg. In 2014 the price per kg was about 750 US$. The fluctuation in prices is due to differences in supply and demand. [4]

Because of the low melting point of indium (156.6 °C), lower than thallium and tin but higher than gallium, it was highly used in bearing alloys in aircraft engines, specially during the world war II. But the most important industrial use of indium is in indium tin oxide (ITO) as transparent conductive coatings in liquid crystal displays (LCDs) and in solar panels. The semi conductively characteristic of indium in III/V compounds such as indium (III)phosphides and aresenides makes it an important part of the photo voltaic cells.[5] Indiumnitrid plays a significant role in LEDs by altering the wavelength of the radiated light range from ultra violet to infra red.[6]

Although indium has a very wide industrial application, it can be also useful in medicine. Indium leukocyte scintigraphy is a medical imaging technique, which can help to find areas localized with white blood cells, to chose the better antibiotic therapy. By taking the patient’s white cells, labeling them with ^{111}In and then re-inject them back, gamma radiation will be emitted and the monitoring of white blood cells will be possible.[7]

Because of the vast demand of indium in many fields and lack of indium natural resources, which are rarely enough for the next 14 years, it is necessary to produce the needed indium by efficient recycling, which is mainly done in Japan.[5]

Figure 1: indium metal [8]

atomic number	49
stable isotopes	$^{113}_{49}In$ (4.4%) $^{115}_{49}In$ (95.7%)
relative atomic weight	114,818
Oxidation numbers	+/-0, +1, +2, +3
ionization energies (kJ/mol)	1st: 558.3 2nd: 1820.7 3rd: 2704
Electronegativity Pauli scale	1.78
atomic radius empirical (pm)	167
covalent radius (pm)	142
Van der Waals radius (pm)	193
melting point (K(°C))	429.75 (156.60)
boiling point (K(°C))	2345 (2072)

Table 1: some selected characteristics of indium [9]

There are two important oxidation states for indium: ±0 and +3. As a matter of fact indium occurs in its most compounds as In(III)-ion by losing its electrons in the outer shells. By losing just one electron from the p-orbital, indium(I)-ion will be stabilized by the relativistic effect. This effect is higher in the heavier homologues of the group 13 as seen in the following sequence:

Stability: $Al^I < Ga^I < In^I < Tl^I$

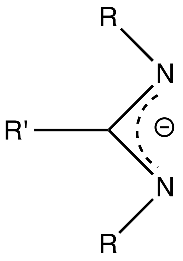
The indium (I)-halogenides are very temperature resistant but they will disproportionate to metallic indium and indium (III) by solvation in water.

Normally, Indium (II) compounds are compoundswith mixed oxidation states, containing indium (I) and indium (III). For example in In_2Cl_4 in which In-In are not directly connected to each other and the correct formulation will be as $In^+(InCl_4)^-$.[3]

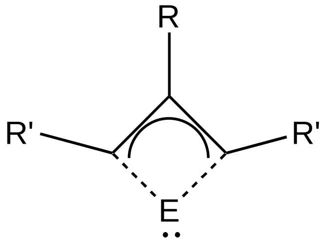
On the other hand gallium (I) compounds are very instable and disproportionate in metallic gallium and gallium (III). However thallium (III) compounds act as oxidizing agents and thallium (I) compounds are very stable. The only exceptions in this case are arene complexes such as pentamethylcyclopentadienyl –derivates (ECp*, E= In, Ga). In this case InCp* is more stable than GaCp* and undergoes a variety of reactions for synthesis of indium clusters. [10][11][12]

1.1 Amidinates and guanidinates, NCN ligands:

The NCN ligands, amidinates and guanidinates, possess two nitrogen donor atoms and a delocalized lone electron pair.



These ligands possess one single bridging carbon atom. The ligand acts as a N, N'-chelate and by coordination of two nitrogen atoms to one metal atom the four-membered ring is formed. The bite angles in the four-membered rings will be smaller than those in five and six-membered rings. It should be mentioned that the steric properties of these ligands are affected by the smaller bite angles. That means that the substituents on the nitrogen atoms will be oriented bit further away from the di-coordinate center in comparison with five and six-membered rings.[13] By using bulky aryl groups such as dipp, the coordinated chelate site is stabilized. By altering the substituents different ligands with different properties are obtained.

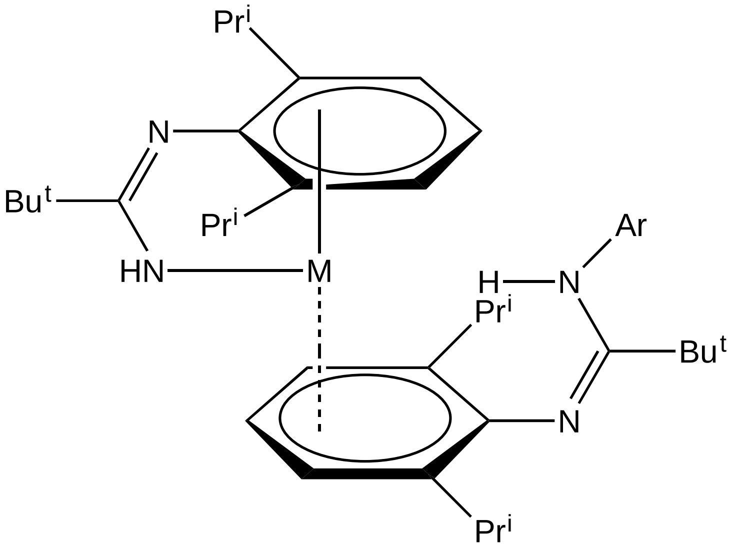


R' = $SiMe_3$, iPr, dipp

Figure 2: it is guanidinate, if R is amino-based analogous. It is amidinate analogous, if R is not amino-based or if the substituent is another pnictogen.

The guanidinates are more electron rich than the amidinates because of the amino substituent on the bridging position of the NCN.

As reported the synthesis and isolation of the univalent In[(dipp)NC{N(Cy)$_2$}N(dipp)][14] and Ga[(dipp)NC{N(Cy)$_2$}N(dipp [14] complexes possessing four membered ring with NCN chelating ligands is only possible by using the bulky guanidinate ligands.[15] In thallium guanidinates, a different structure is obtained in which the metal atom is connected to the one of the dipp ligands by one of the nitrogen atoms. This kind of coordination (pseudo-5-membered ring coordination) is seen by larger size cations like thallium (I) and indium (I). (compound **1.1**) This kind of coordination allows the complex be less strained. This effect is also observed by indium (I) amidinates when the NCN ligand is less electron rich or sterically demanding. [14][15] [16]



M = In, Tl

1.1

The group 13 amidinates and guanidinates act as precursors to group 13 nitrides. They are novel catalysts and in the case of aluminium precursors they can act as precursors to thin metal films.[17] The group 13 nitrides, such as mixed aluminium/gallium nitrides, are direct band gap semiconductors and are applied in the high-frequency LEDs and diode lasers.[18]

The first amidinates of group 13 elements were described by Hausen et. al. in 1978.[19] They were dimethylaluminum-N,N'-dimethylethyl und dimethylgallium-N,N'-dimethylethyl amidinates as shown in figure 4:

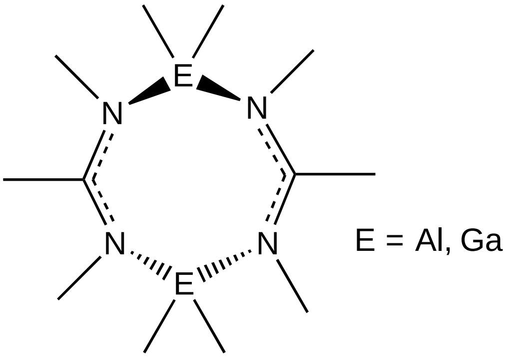
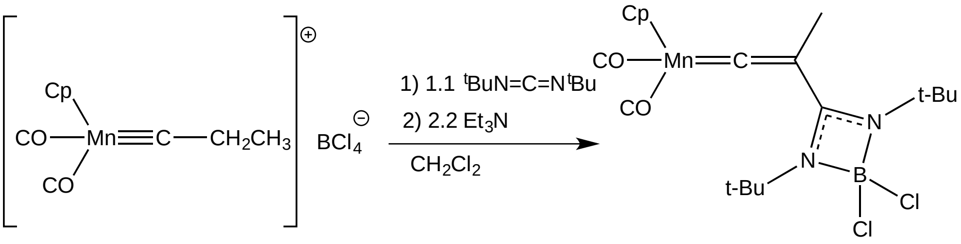


Figure 4

The next amidinate was synthesized and characterized in 1994 by Geoffrey et al.[20] This first boron amidinate was prepared by treating $[Cp(CO)_2Mn{\equiv}CCH_2CH_3]^+BCl_4^-$ with 1.1 eq. ditertbutylcarbodiimide and 2.2 eq. Et_3N in dichloromethane, unexpectedly. (equation 1)



(1)

In 1996 while searching for a new starting material for semi-conductors, Richeson et al. got the first indium amidinate (figure 5) by treating indium(III)chloride and two eq. of lithiumdicyclohexylneopentylamidinate by salt elimination.[21]

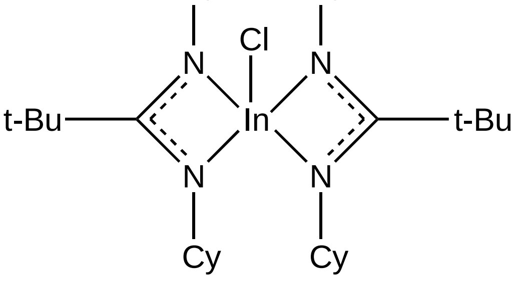


Figure 5

Shortly after that a bis(amidinato) chloro complex is synthesized by Richeson et al. In this indium amidinate the two indium atoms were connected through four bridging dicyclohexylmethyl amidinates and there is one chlor atom on each indium atom. (figure 6) [22]

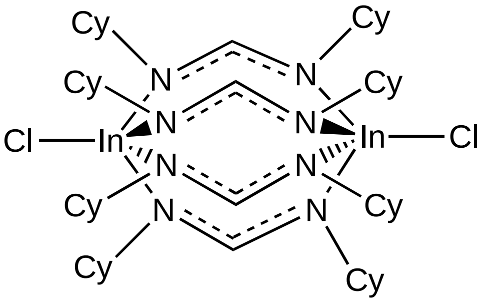


Figure 6

In 1996 Wallbridge et al. synthesized and characterized the new crystals of alkyl gallium amidinates.[23] Depending on stoichiometry of the reaction different mono-, bis- and trisamidinatogallium compounds were yielded (figure 7).

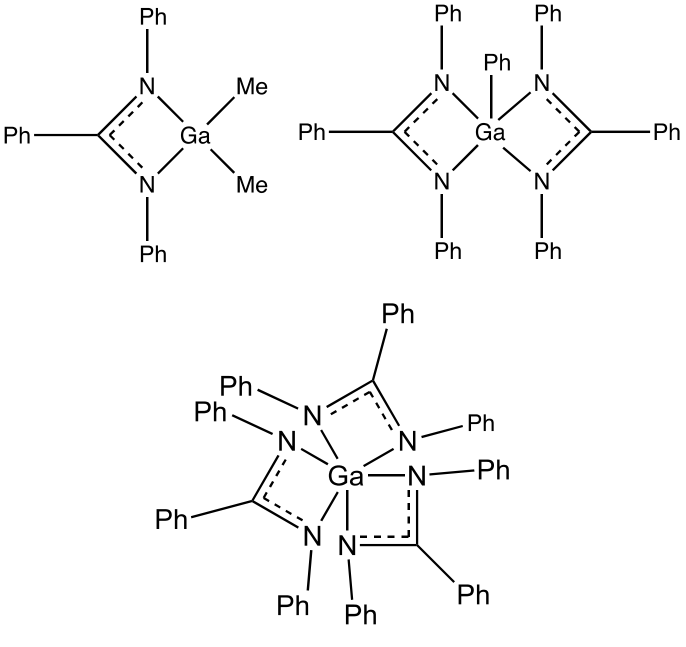
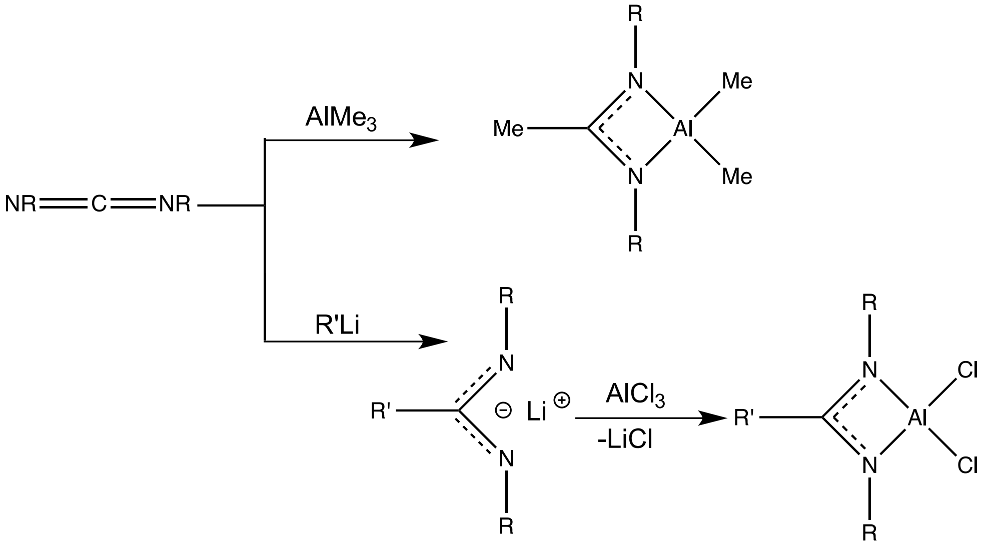


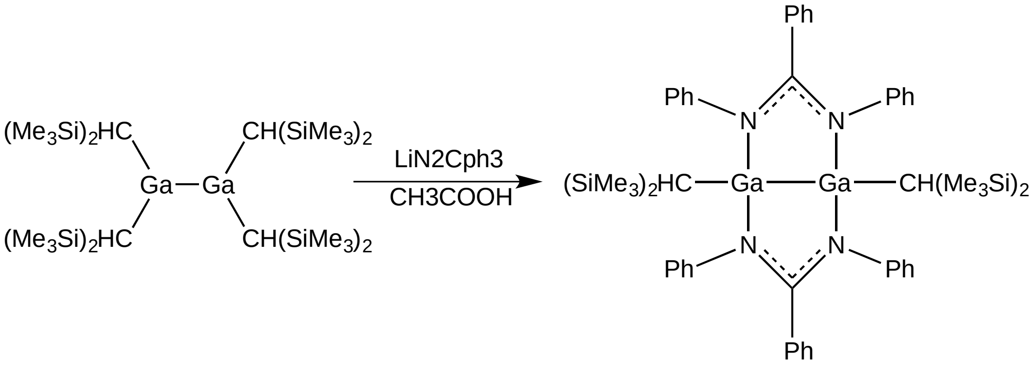
Figure 7

The first dialkylaluminium amidinate and dichloroaluminium amidinate were characterized by Jordan et al. one year later in 1997. They were synthesized either by adding aluminium alkyl to the carbodiimides or through treatment of the aluminium(III)chloride with one lithiumamidinate and subsequent alkylation (equation 2).[24] The same reaction was done by Jordan et al. with gallium instead of aluminium.[25]



(2)

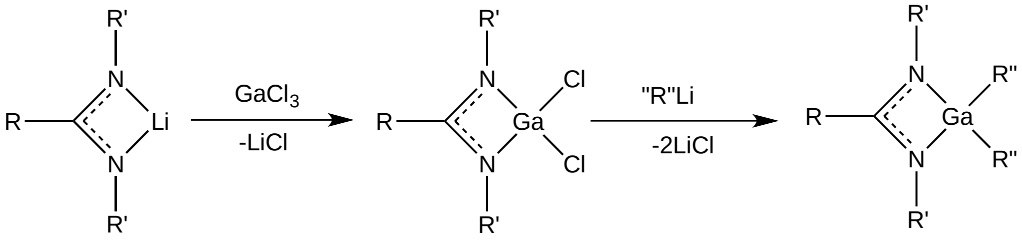
There are also subvalent compounds of gallium such as alkylated gallium(II)-amidinate which was described by Uhl et al.[26] (equation 3)



(3)

In this way of synthesis the digallane $Ga_2[CH(SiMe_3)_2]_4$ was treated with acetic acid and Lithium-N,N’-diphenylbenzylamidinate yielding the alkylated amidinate.[26]

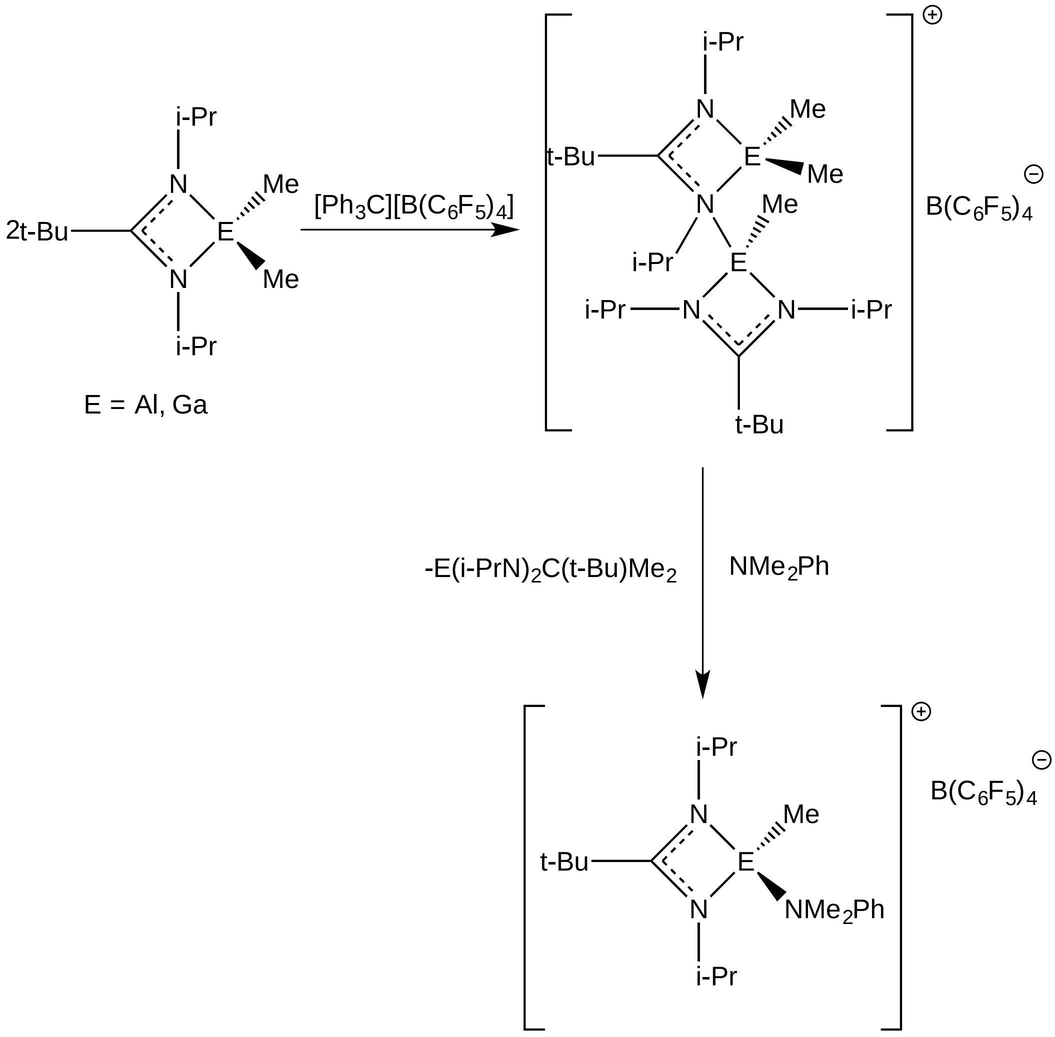
In the same year the synthesis and characterization of dialkyl gallium amidinate was performed by Jordan et. al by adding gallium gallium(III)chloride to the corresponding lithium amidinate and subsequent Grignard or organo lithium reaction. (equation 4)[25]



(4)

In 2000 the cationic gallium and aluminium amidinate complexes were synthesized by Jordan et al. using $[Ph_3C]^+[B(C_6F_5)_4]^-$.[27]

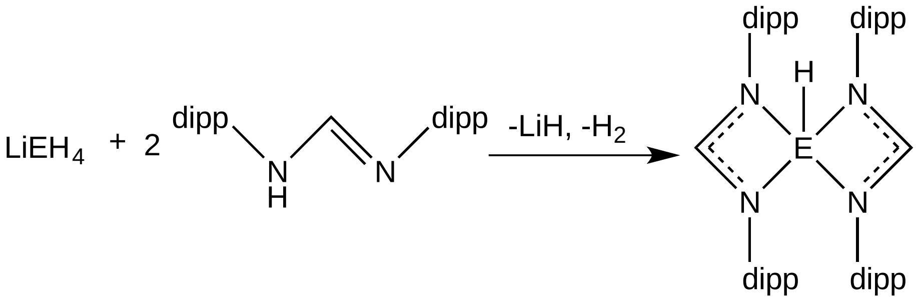
In this reaction one methyl anion was eliminated from the methyl triel amidinate and Ph_3CCH_3 and the corresponding triel amidinate cation were formed. In the next step another methyl triel amidinate was coordinated to these cations. By applying an appropriate donor group the desired amidinate was yielded. (equation 5)



(5)

In 2002 the synthesis of a bridiging tetramethyldialuminium diamidinate was performed by Coles et al.[28]

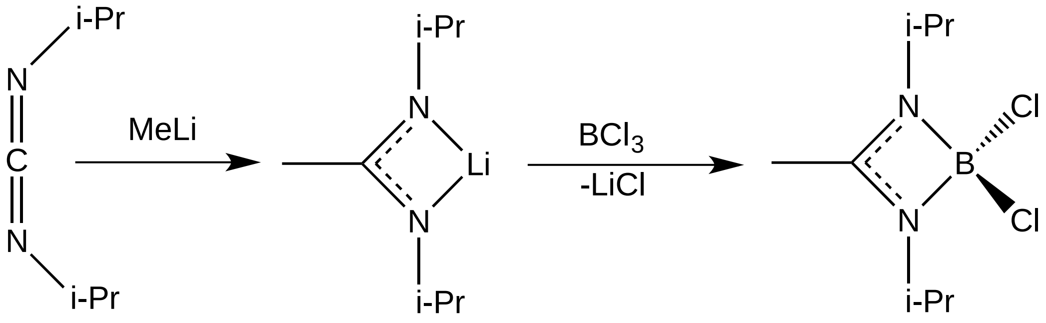
In the 2004 the first indium hydride, which was stabilized through amidinate ligands, was produced by Jones et al. By treating lithium indium hydride with two eq. Bis(2,6-Diisopropylphenyl)formamidine the product was yielded This product was not air sensitive in comparison to other sensitive indium hydrides before (equation 6).[29]



(6)

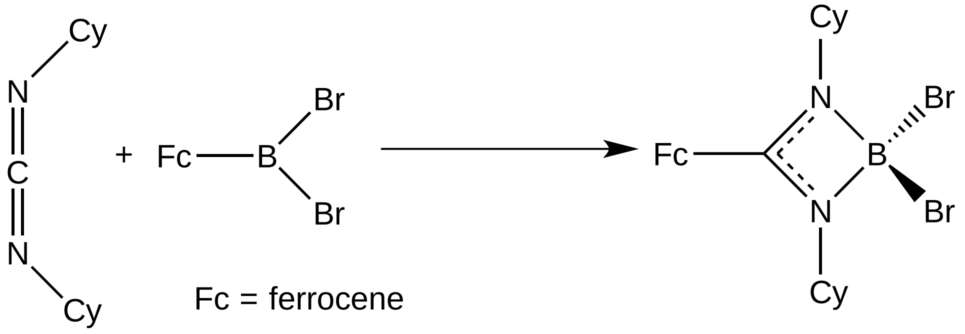
E= Al, Ga, In

In 2005 this experiment was transferred to gallium and aliminium successfully.[30] In the same year Cowley et al. produced a range of this kind of boron amidinates through different reactions shown bellow. (equations 7,8,9)[31]



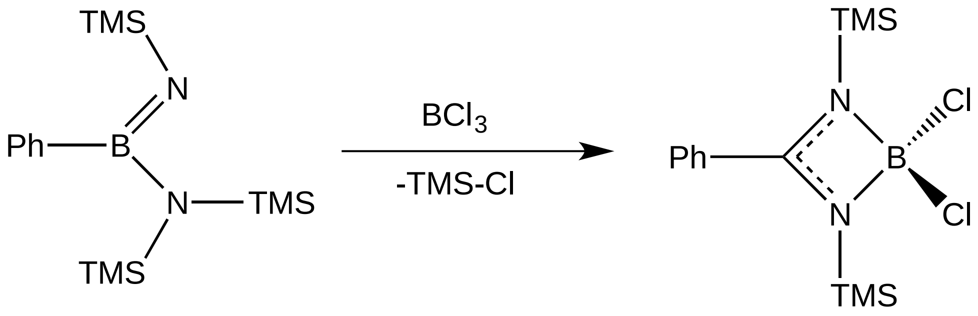
(7)

Salt elimination from lithium amidinates and bor halogenides



(8)

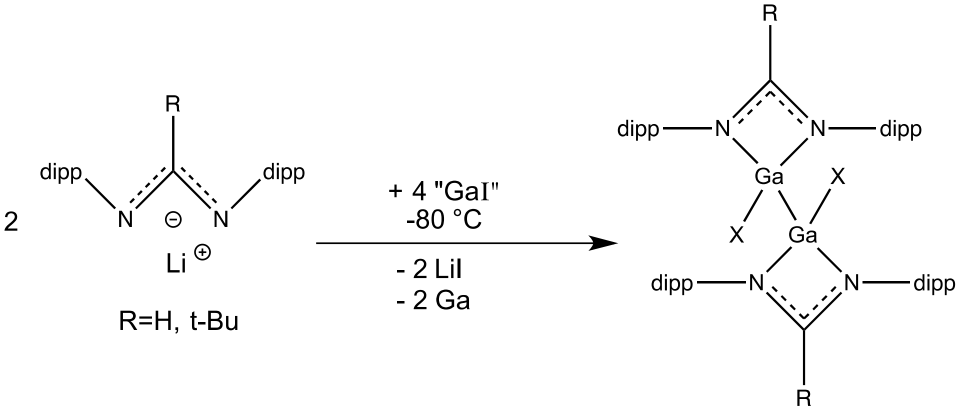
insertion of carbodiimides in bor-ferrocene binding



(9)

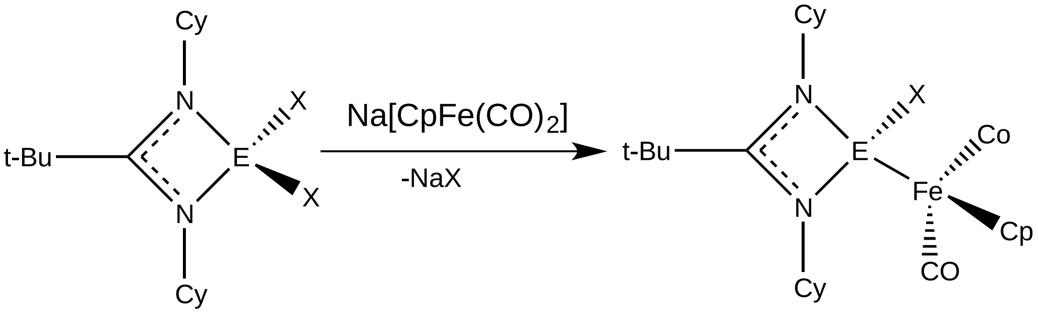
elimination of trimethylsilyl halogenides from N,N,N'-tris(trimethylsilyl)-benzamidine with bor halogenides

In 2005 the synthesis of two gallium amidinate compounds with the oxidation state of +II was reported by Jones et al.[32] By using bulky groups such as 2,6-Diisopropylphenyl (dipp) and GaI as gallium source the new gallium amidinate was yielded. (equation 10)



(10)

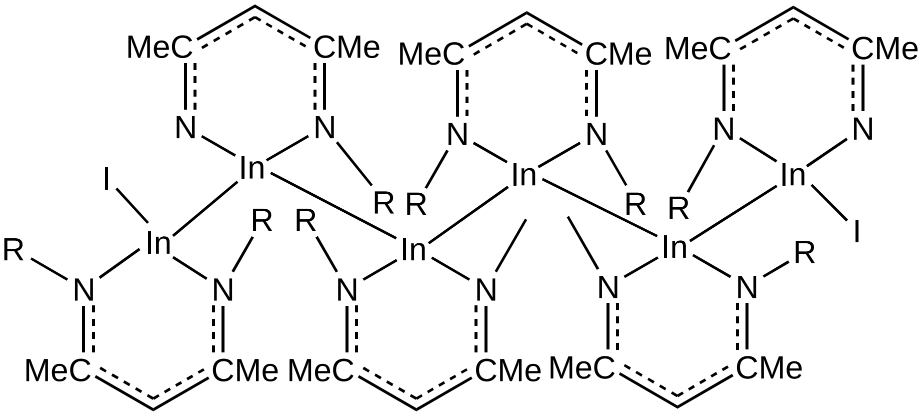
In 2006 the first aluminium-, gallium- and indium amidinate with one E-Fe binding were characterized by Jones et al. (equation 11)[33]



E = Al, X = Cl
E = Ga, X = Cl
E = In, X = Br

(11)

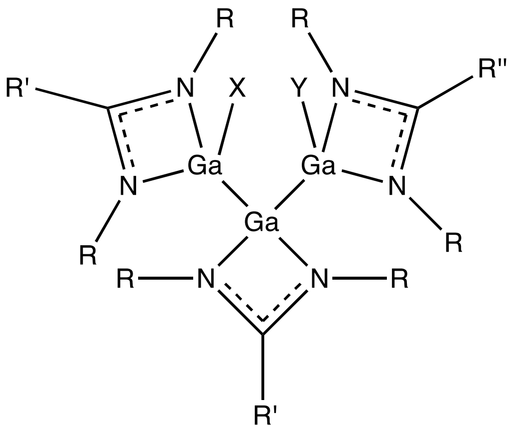
In 2006 the first hexa-indium complex were synthesized by Hitchcock et al. By treating indium(I)iodide with a protonated N-xylyl β-diketiminate and potassium base in THF, a hexa-indium chain was yielded. In this chain there are five indium-indium single bonds. The terminal indium atoms were connected to iodides and one β-diketiminate was bound to each indium atom. (figure 8)[34]



R = xyl

Figure 8

In 2011 Linti and Zessin characterized the new crystals of trigallanes with different substituents which were the first trigallanes stabilized through amidinate ligands. (figure 9)[35][36]



R = Cy, ^{i}Pr, ^{t}Bu
R' = ^{t}Bu, Me
R'' = ^{t}Bu, Me
X = I, Et, N=CMe$_2$
Y = I, H

Figure 9: structure of the trigallane amidinate

1. 2 Abstract

The focus of this work is synthesis, characterization and exploring the reactivity of new indium amidinate compounds of the type R_2InX (R = R”NCR’NR”; R’ = Ph, R” = $SiMe_3$, iPr, dipp; X = Br, Cl) with the coordination number of five and R_3In (R = $Me_3SiNCPhNSiMe_3$) with the coordination number of six. By using amidinates as chelating ligands the electron deficiency of indium atom will be resolved, in addition by using different substituents the study of the different synthesized indium amidinates has become possible.

The selected method for the synthesis allows the carbodiimides to react with organolithium compounds to get the corresponding lithium amidinates. Afterwards the resulting lithium amidinates take part in transmetalation reactions with $InBr_3$ and $InCl_3$.

Since the obtained indium amidinate compounds are very sensitive to the air moisture and hydrolysis, all the reactions were performed under argon flow and in vacuum to avoid the air moisture. In some experiments the reaction flask had to be protected towards light.

The study of the reactivity of indium amidinate complexes including nucleophilic reactions as well as their reduction were also examined.

Beside crystal structure analysis, nuclear magnetic resonance spectroscopy as well as elemental analysis has been applied to chracterize the compounds.

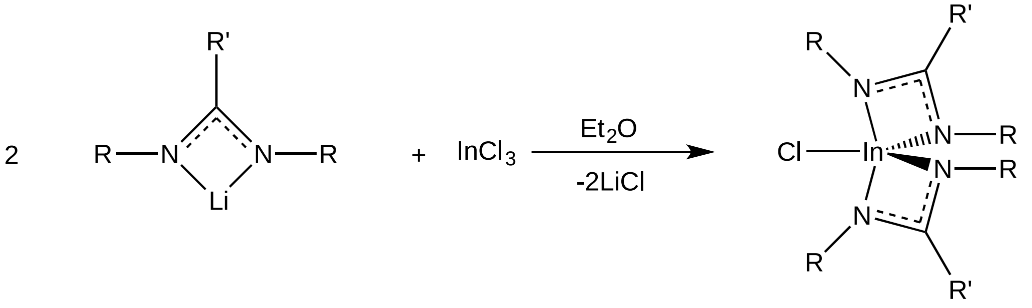
2 Five and six coordinated Indium (III) amidinates

2.1 Introduction

Because of the big demand in organic and inorganic complexes of the group 13 elements such as aluminium, gallium and indium in the industry and electronics, there is a rising interest in preparing and synthesizing them, as well as in characterization of these complexes.[37] The reason of the comprehensive study of using bidentate ligands in synthesis of indium compounds is to find out the relation between the geometry of indium amidinate ligands and the coordination surroundings of indium. These ligands have been applied in synthesis of a large number of mono and dinuclear transition metal complexes.[38]

An ideal system is created for studying the impact of the steric bulky groups on the product by changing the organic substituents on the nitrogen atoms and on the carbon atom of the bridging position (NCN). By using ^{t}Bu groups as substituent new bulky indium amidinates were obtained.

In 1996 Richeson et al. synthesized and characterized the first monomeric In(III) complexes of the formula $In[RNC(R')NR]_2Cl$ (R = Cyclohexyl, $SiMe_3$; R’ = Me, ^{t}Bu)[21][22] with the coordination number of five. (equation 12)

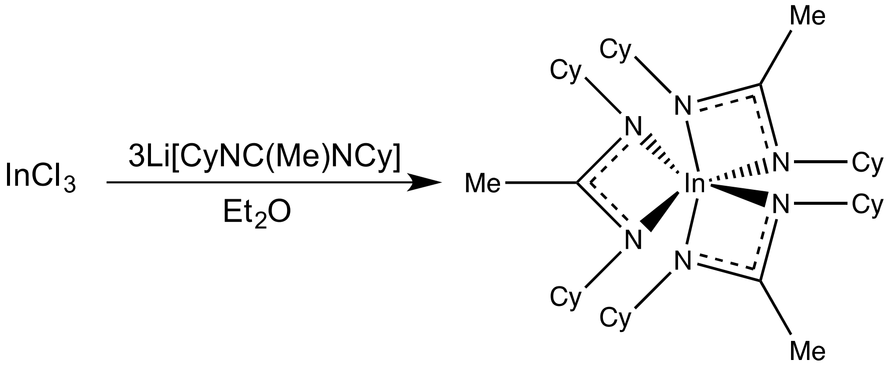


R = $SiMe_3$, Cyclohexyl
R' = Me, ^{t}Bu (12)

By reacting dicyclohexylcarbodiimide and 1,3-bis(trimethylsily)carbodiimide with MeLi in two different experiments the corresponding lithium salts of Li[CyN(CMe)NCy] and $Li[Me_3SiN(CMe)NSiMe_3]$ are prepared. By treating these ligands with $InCl_3$ in 2:1 stoichiometry the new indium amidinate species shown in equation 12 are yielded.

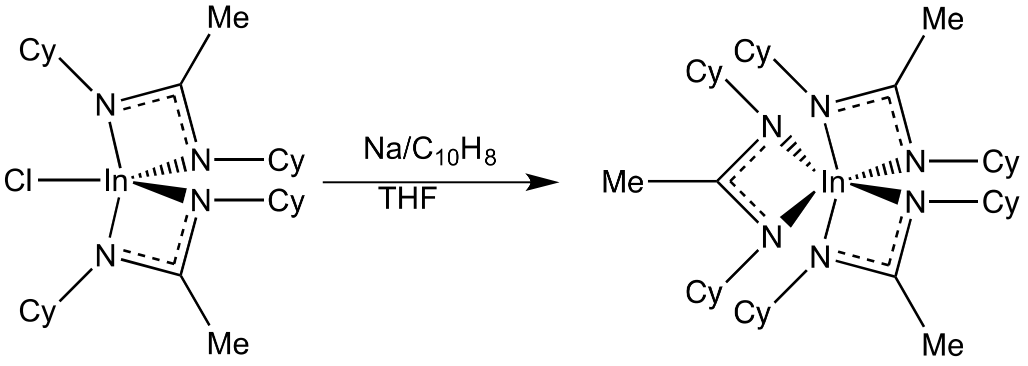
In order to have a bigger range of indium amidinate ligands and to be able to study the influence of different substituents positioned on the bridging site, ^{t}Bu groups are being used as new substituents. The reaction yielded in two new bulky members of indium amidinate ligands, $In[CyNC(CMe_3)NCy]_2Cl$ and $In[SiMe_3N(CMe_3)NSiMe_3]_2Cl$. (equation 12)

By treating 3 equiv Li[CyNC(Me)NCy] with $InCl_3$ the six coordinated indium complex of $In\{2[N(CH_2C_7H_5)]NC_5H_4\}_3$ was synthesized. (equation 13)



(13)

In another experiment Richeson et. al tried to reduce the $In[CyNC(CMe_3)NCy]_2Cl$ complex with $Na/C_{10}H_8$ to study the stabilization effect of reduced indium center. The $In[CyNC(Me)NCy]_3$ formula of this complex was confirmed by using microanalysis method and was likely the product of the disproportionation of the reduced indium complex. The results obtained from NMR spectroscopy showed that dicyclohexylamidinate ligands are all equivalent. (equation 14)



(14)

In this part of the work the indium amidinate complexes of type R_2InX with coordination number of five and R_3In with coordination number of six were synthesized.

The five coordinated indium amidinates are divided into two groups:

a) R_2InX (R = $Me_3SiNCR'NSiMe_3$, R' = Phenyl, X = Br, Cl)

b) R_2InX (R = R”NCR’NR”, R” = dipp, ipr, R’ = Phenyl, X = Br, Cl)

The trisamidinate R_3In (R = $Me_3SiNCR'NSiMe_3$, R’ = Phenyl) is the only complex synthesized that possess a six coordinated indium central.

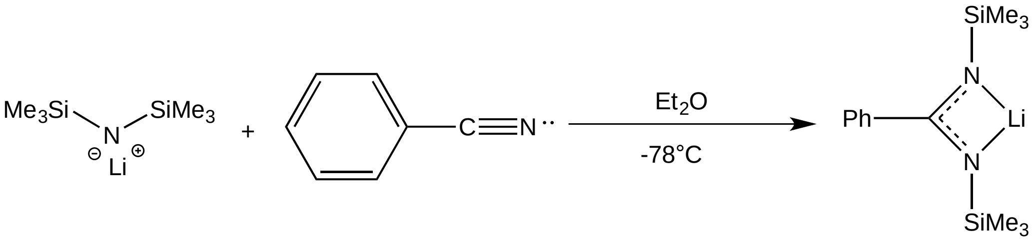
The spectroscopic characterization as well as the elemental analysis confirms the formula of these indium amidinate complexes. All the complexes are characterized by X-ray crystallography.

2.2 Synthesis of In[SiMe$_3$NC(Ph)NSiMe$_3$]$_3$

2.2.1 Reaction of Li[SiMe$_3$NC(Ph)NSiMe$_3$] with InCl$_3$

Li[SiMe$_3$NC(Ph)NSiMe$_3$ was prepared by dropwise addition of n-butyl lithium to the hexamethyldisilazanide in n–hexane at -78°C. The white-milky suspension was allowed to warm up to the room temperature and stirred over night. All the volatiles were removed and the white residue was used for the next step without any work up.

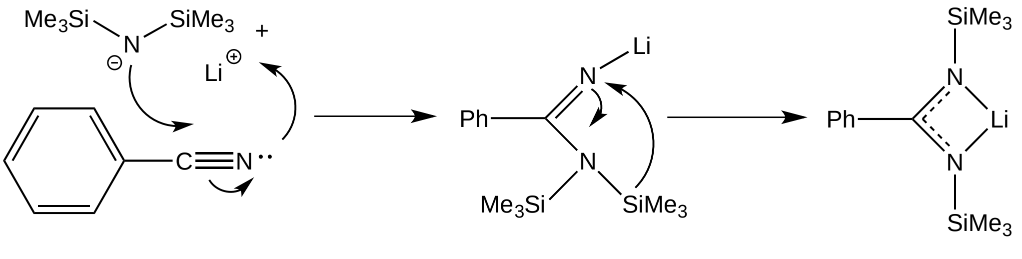
At the next step lithium hexamethyldisilazanide was dissolved in diethyl ether and benzonitrile was added slowly to this solution at -78°C. (equation 15) The suspension was allowed to warm up to the room temperature and stirred over night.



(15)

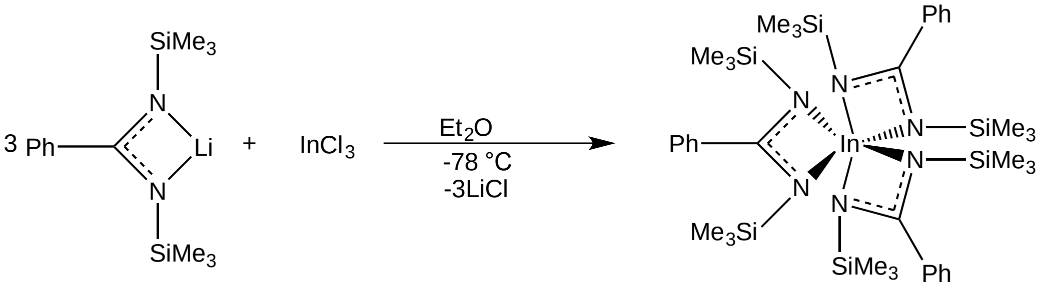
1 **2**

According to Boere et al. the reaction mechanism is the nucleophilic addition of the lithium hexamethyldisilazanide to benzonitrile that yields the symmetric lithium amidinate. The obtained lithium amidinate was not detected directly. However the rearrangement reactions of this kind are well known. (equation 16)[39] [40] [41]



(16)

The brown-orange solution of **2** was then treated without further work up with $InCl_3$ in 3:1 stoichiometry in diethyl ether at -78 °C. (equation 17) The resulted suspension was allowed to warm up to the ambient temperature and stirred over night. An orange suspension with white precipitation of LiCl was observed the following day.



(17)

2 **3**

After removal of the all the volatiles under vacuum and extracting the white residue first with n-hexane solvent and then with toluene solvent, the pale yellow crystals of $In[SiMe_3NC(Ph)NSiMe_3]_3$ (**3**) were formed in the n-hexane solvent with a yield of 43%.

2.2.2 Spectroscopic characterization of 3

In the ^{1}H-NMR-spectrum of $In[SiMe_3NC(Ph)NSiMe_3]_3$ (**3**) the signals for the 6 hydrogen atoms in *ortho* position of the phenyl groups are found at δ = 7.47 in form of a multiplet and for the 9 hydrogen atoms in the *meta* and *para* position of the phenyl groups are seen at the range of δ = 6.96-6.92 in form of a multiplet . Having 15 hydrogen atoms in the aromatic range confirms the existence of three phenyl rings in the complex. In addition a sharp singlet is seen at δ = 0.15 for the 54 hydrogen atoms of the $SiMe_3$ groups that are all equivalent.

In the ^{13}C-NMR-spectrum there is a low field shift for the ring carbon atom of NCN at δ = 181.3. Four different peaks are found for the four different aryl-carbon atoms at δ = 141.5 (*ipso*), δ = 128.3 (*para*), δ = 127.7 (*meta*) and δ = 126.2 (*ortho*). A single peak for $SiMe_3$ carbon atom is seen at δ = 2.9. All peaks correlate with the peaks seen in ^{1}H-NMR spectroscopy and with data obtained from the similar gallium amidinates synthesized before.[42] The nuclear resonance magnetic spectroscopy data confirms that the molecule is symmetrical. The fact that only one peak is seen for $SiMe_3$ groups shows that there is a free rotation around the N-Si bounding.

2.2.3 Crystal structure of 3

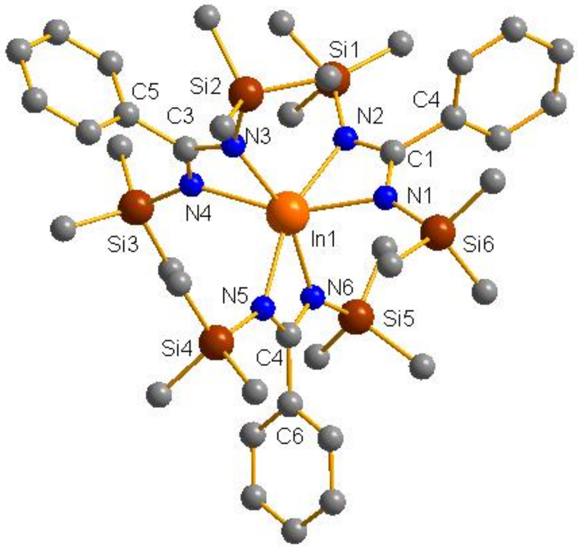


Figure 10 Molecule structure and atom-numbering scheme of **3**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: In1-N1 2.25 (3), In1-N2 2.26 (4), In1-N3 2.30(3), In1-N4 2.25 (3), In1-N5 2.26(4), In1-N6 2.27 (4), N1-C1 1.31 (5), N1-Si6 1.75 (3), N2-C1 1.32 (5), N2-Si1 1.74 (4), N3-C2 1.32 (5), N3-Si2 1.76 (3), N4-C2 1.33 (5), N4-Si3 1.73 (4), N5-C3 1.34 (5), N5-Si4 1.75 (4), N6-C3 1.34 (7), N6-Si5 1.74 (2), C1-C4 1.53(7), C2-C5 1.51 (6), C3-C6 1.51 (8).

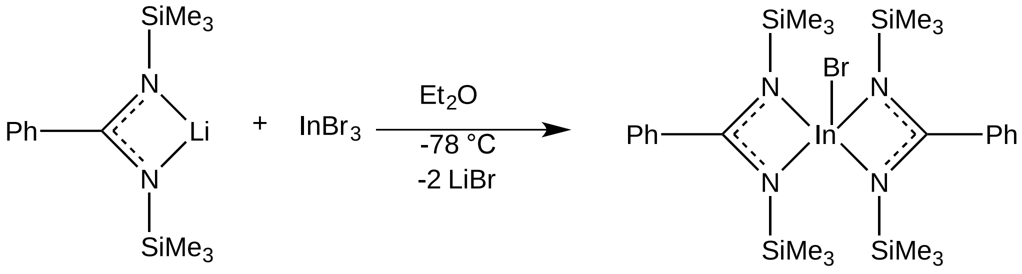
N1InN2 60.1(1), N3In1N4 59.9(1), N6In1N5 60.6(1), N1C1N2 117.8 (3), N3C2N4 117.9(4), N6C3N5 117.1(4), N1In1N4 155.5 (1), N1In1N6 93.3 (1), N2In1N4 101.8(1), N2In1N6 101.7 (1), N3In1N5 105.7 (1), N4In1N5 96.6 (1), In1N1Si6 136.9 (2), In1N2Si1 136.0(2), In1N3Si2 139.3(12), In1N4Si3 137.5(2), In1N5Si4 139.4(2), In1N6Si5 140.1(2), C1N2Si1 133.0(3), C1N1Si6 131.4 (3), C2N4Si3 129.6(3), C2N3Si2 129.4 (3), C3N6Si5 128.2 (3), N1In1N3 102.7(1), N1In1N5 105.1 (1), N2In1N3 94.2 (1), N2In1N5 157.8 (1), N3In1N6 161.6(1), N4In1N6 107.3(1), In1N1C1 91.5(3).

The molecular structure of In[$SiMe_3NC(Ph)NSiMe_3$]$_3$ (**3**) as well as the atom numbering scheme are shown in figure 10. The selected bond lengths and angles are also described above. The complex **3** crystallized in the monoclinic space group C 1/c. The structural analysis showed that the complex has a distorted octahedral symmetry possessing one unique amidinate ligand as seen and discussed by NMR data. The central indium atom is surrounded with six nitrogen atoms. The In-N bond distances do not differ significantly from each other (In1-N1 [2.25(3) Å], In1-N2 [2.26(4) Å], In1-N3 [2.30(3) Å], In1-N4 [2.25(3) Å], In1-N5 [2.26(4) Å], In1-N6 [2.27(4) Å]). These bond distances are almost similar to those In-N bonds in six coordinated In(dpt)$_3$ synthesized by Barron etal. (In1-N1 [2.259(9) Å], In1-N3 [2.22(1) Å], In1-N5 [2.24(1) Å], In1-N2 [2.26(1) Å], In1N4 [2.23(9) Å], In1-N6 [2.21(1) Å]).[43] The slight difference in In-N bond distances is because of the bulky substituents in the complex **3**.The (N1In1N4 155.5(1)°, N2In1N5 (157.84(2)°) and N3In1N6 (161.58(13)°) angles show the distorted geometry. This distortion is less than distortion seen for the six coordinated In(dpt)3 (N1In1N4 (148.9(4)°), N2In1N5 (144.1(4)°) and N3In1N6 (151.5(4)°)).[43] The phenyl groups are all planar. (Σ angles = 359, 359.9 and 359.9 for the three phenyl rings). The three-bite angles are almost the same N1In1N2 (60.1(1)°), N3In1N4 (59.9(1)°), N5In1N6 (60.6(1)°). The N-Si bond distances are all the same and the bonds are all equivalent (N1Si6 [1.75(3) Å], N2Si1 [1.74(4) Å], N3Si2 [1.76(3) Å], N4Si3 [1.73(4) Å], N5Si4 [1.75(4) Å], N6Si5 [1.74(2) Å]) which correlates with the data resulted from ^{1}H-NMR spectroscopy.

2.3 Synthesis of In[SiMe$_3$NC(Ph)NSiMe$_3$]$_2$Br

2.3.1 Reaction of Li[SiMe$_3$NC(Ph)NSiMe$_3$] with InBr$_3$

By treating lithium hexamethyldisilazanide (prepared by combination of the hexamethyldisilazanide with n-butyl lithium) with benzonitrile an orange solution of Li[SiMe$_3$NC(Ph)NSiMe$_3$] was formed. This was treated with 1 equivalent InBr$_3$ in diethyl ether at -78 °C. (equation 18) By allowing the suspension to be warmed up to the room temperature and stirring it over night an orange solution with white precipitation of LiBr was obtained.



(18)

2 **4**

Then all the volatiles were removed and the remaining white residue was extracted first with n-hexane and then with toluene solvent. The crystals of **4** were obtained from the toluene fraction with the yield of 15%.

2.3.2 Spectroscopic characterization of 4

The ^{1}H-NMR-spectrum of **4** shows two peaks for the aromatic hydrogens of the phenyl groups. The multiplet peak for the 4 hydrogens in *ortho*-position of phenyl groups is seen at δ = 7.36. The 6 hydrogen atoms in *meta*- and *para*-positions are found at δ = 6.96 in form of a multiplet peak. A sharp singlet is found at δ = 0.12 for the 36 hydrogen atoms of $SiMe_3$ groups. This reveals that all the hydrogens of the $SiMe_3$ groups are equivalent.

In the ^{13}C-NMR-spectrum the signal for the NCN carbon atom is seen at δ = 173.4 and for the ipso-carbon atom it is found at δ = 149.2. There are 3 peaks found for the aromatic *ortho*-, *meta*- and *para* carbon atoms at δ = 127.0, δ = 127.7 and δ = 128.2 respectively. A single peak is seen for the carbon atoms of the $SiMe_3$ groups at δ = 2.86 as expected from the ^{1}H-NMR-spectrum.

The ^{1}H-NMR and ^{13}C-NMR spectrum data correlates with the spectrum of the **3**.

2.3.3 Crystal structure of 4

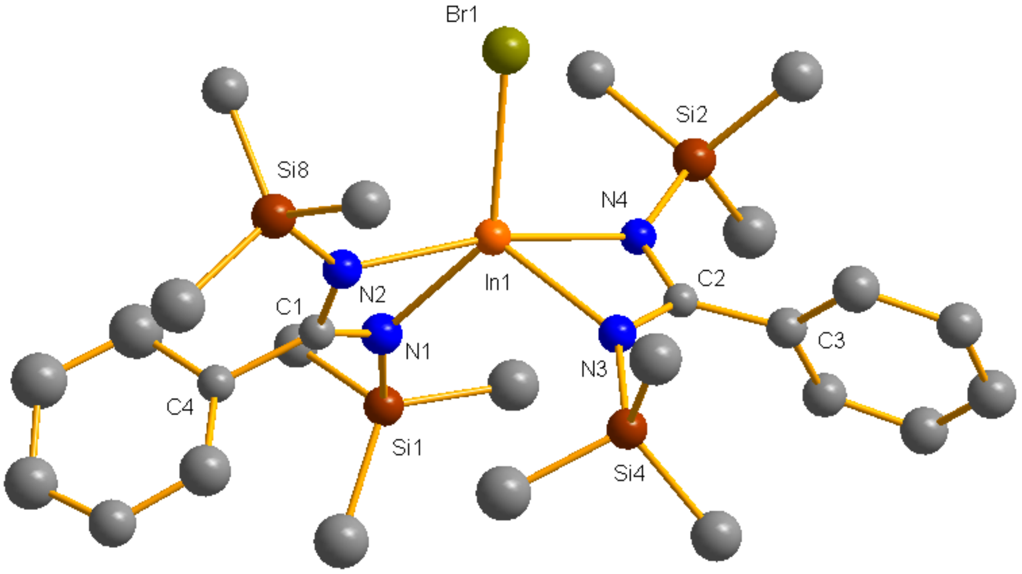


Figure 11 Molecule structure and atom-numbering scheme of **4**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:

In1-N1 2.22 (2), In1-N2 2.24(2), In1-N3 2.20(2), In1-N4 2.23(2), In1-Br1 2.539(2), N1-C1 1.411(19), N1-Si1 1.752(18), N2-C1 1.280(2), N2-Si8 1.726 (18), N3-C2 1.35 (2), N3-Si4 1.753(14), N4-C2 1.351(19), N4-Si2 1.728(15), N5-C3 1.340(5), N5-Si4 1.752(4), N6-C3 1.340(7), N6-Si5 1.745(2), C1-C4 1.49(2), C2-C3 1.44(2).

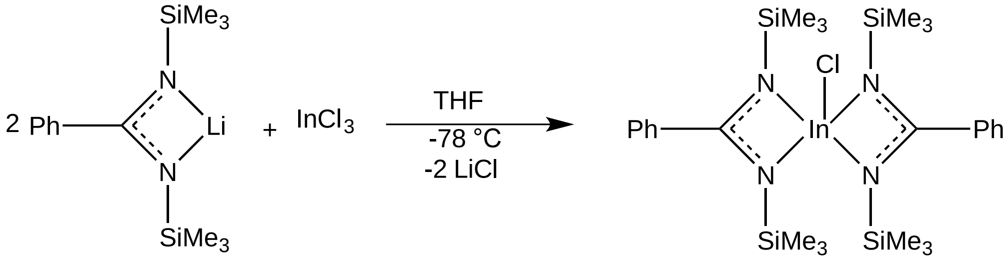
N1InN2 61.5(6), N3In1N4 62.1(5), N2In1N4 167.7(5), Br1In1N2 97.7(4), Br1In1N4 94.3(4), Br1In1N1 136.5(4), Br1In1N3 114.5(4), In1N2Si8 136.2(10), In1N1Si1 134.0(8), In1N3Si4 134.2(9), In1N4Si2 136.2(8), N2C1N1 115.8(13), N4C2N3 115.4(15), N4C2C3 122.6(14), N2C1C4 125.4(13).

The complex of **4** crystallized in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The molecule geometry as well as the atom-numbering scheme is shown in figure 11. Through structural analysis it is released that the complex has distorted trigonal bipyramidal structure (TBP) with an indium atom in center and two amidinates and one bromide group. The selected bond distances and angles are shown above. The NIn1Br1 part deviates from an ideal trigonal bipyramid with N2In1N4 (167.7(5)°) and N2In1Br1 (97.7(4)°) and N4In1Br1 (94.3(4)°) angles. As seen the In-N bond distances are slightly different from each other. (In1-N2 [2.24 (2) Å], In1-N1 [2.22(2) Å], In1-N3 [2.20(2) Å], In1-N4 [2.23(2) Å]). The In1N2 and In1N4 bond distances (bonds in axial positions) are slightly larger than In1N2 and In1N3 bond distances (bonds in equatorial positions), which is expected for the distorted trigonal bipyramidal symmetry. The bonds in axial position have p hybridization therefore are longer than bonds in equatorial position with sp^2 hybridization.[45] The bond distances are in good agreement with those in $InCl[C_6H_{11}NC(CH_3)NC_6H_{11}]_2$ complex In1N1 [2.198(3) Å] and In1N4 [2.188(3) Å] (bonds in equatorial positions) and In1N2 [2.236(3) Å] and InN3 [2.239(3) Å] (bonds in axial positions).[21] The In1Br1 bond distance [2.539(2) Å] is in good agreement with the In-Br bond distance in **3** [2.567(4) Å] and with the In-Br bond distance in *o*-$[C_6H_4(InBr(THF)_2)]_2$ [2.547(1) Å].[46] The bite angles are almost the same with N1In1N2 (61.5(6)°) and N3In1N4 (62.1(5)°). By comparing these values with the bite angles in $InCl[C_6H_{11}NC(CH_3)NC_6H_{11}]_2$ (N1In1N2 60.2(1)° and N3In1N4 (59.8(1)°)[21], it is noticed that these angles are a slightly larger in complex **4.**

2.4 Synthesis of In[SiMe$_3$NC(Ph)NSiMe$_3$]$_2$Cl

2.4.1 Reaction of Li[SiMe$_3$NC(Ph)NSiMe$_3$] with InCl$_3$

By treating lithium hexamethyldisilazanide with benzonitrile a pale yellow solution of **2** was formed. This product was treated with InCl$_3$ in 2:1 ratio in THF at -78 °C (equation 19). By allowing the suspension to warm up to ambient temperature and stirring it further over night a yellow solution with white precipitation of LiCl was obtained. After extracting the yellow solution with n-hexane, toluene and THF, the crystals of **5** were obtained from the toluene fraction with the yield of 22%.



(19)

2 **5**

2.4.2 Spectroscopic characterization of 5

The ^{1}H-NMR-spectrum of **5** shows two peaks for the aromatic hydrogens of phenyl groups. The peak seen for the *ortho*-position of the aromatic ring is at the range of δ = 7.12-7.13 with the intensity of 4 in form of multiplets. For the *meta*- and *para*- positions of the aromatic ring the peak found is at the range of δ = 6.93 - 6.99 in form of a multiplet peak with the intensity of 6. This reveals that 2 phenyl groups attached to carbon atoms of NCN are equivalent. A singlet is found at δ = 0.13 for the 36 hydrogen atoms of the SiMe$_3$ groups. Finding just one peak for the SiMe$_3$ groups proves the equality of these groups on both amidinate ligands of the complex. Analyzing the crystal structure of the complex can also prove this fact.

The ^{13}C-NMR-spectrum of **5** shows one signal for the NCN carbon atom at δ = 177.8 and one for *ipso*-carbon at δ = 137.6. The aromatic *ortho*-, *meta*- and *para* carbon atoms are found at δ = 126.2, δ = 126.4 and δ = 126.5 respectively. A single peak for the carbon atoms of the $SiMe_3$-groups is found at δ = 1.3. All these ^{13}C-NMR data correlate with the data resulted from the peaks of ^1H-NMR-spectrum and proves that the phenyl and $SiMe_3$ groups on both amidinate groups are equivalent.

Comparing these spectra with those obtained from the analogous $In[SiMe_3NC(Ph)NSiMe_3]_2Br$(**4**) no significant differences are seen except the chemical shifts of hydrogen atoms of $SiMe_3$ groups are slightly different. This is because of the difference in the electronegativity of Br and Cl that causes the chemical shifts occur in lower field region in case of complex **5**.

2.4.3 Crystal structure of 5

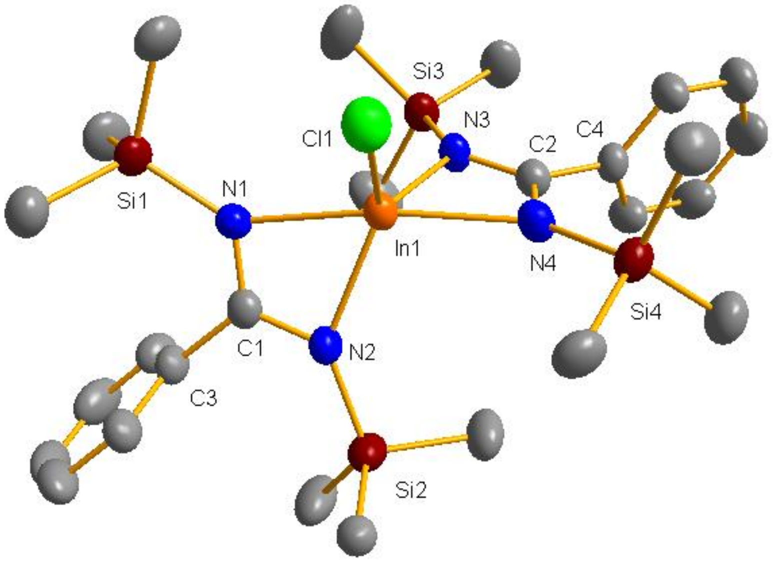


Figure 12 Molecule structure and atom-numbering scheme of **5.** Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:

In1Cl1 2.376(2), In1N1 2.24(4), In1N2 2.20(5), In1N3 2.20(4), In1N4 2.24(4), N1C1 1.322(8), N2C1 1.343(7), N3C2 1.336(6), N4C2 1.327(7), N1Si1 1.749(5), N2Si2 1.744(5), N3Si3 1.746(5), N4Si4 1.747(5), C1C3 1.499(7), C2C4 1.491(7).
N1In1N2 61.6(2), N3In1N4 61.4(2), Cl1In1N1 100.1(1), Cl1In1N3 120.2(1), Cl1In1N2 127.7(1), Cl1In1N4 95.2(1), In1N1Si1 139.2(3), In1N3Si3 132.8(2), In1N4Si4 136.1(3), In1N2Si2 137.4(2), N1C1N2 116.9(5), N3C2N4 116.4(5), N1In1N4 164.7(2), N3In1N2 112.2(2).

The molecule geometry as well as the atom-numbering scheme is shown in figure 13. The selected bond distances and angles are also shown above. The complex of **5** crystalized from toluene in the monoclinic space group P2$_1$/n with four molecules in the unit cell. The indium atom of complex **5** is coordinated in a distorted trigonal bipyramidal manner by two amidinates and a chlorine atom. As expected for the trigonal bipyramidal symmetrythe In1N1 [2.24(4) Å] and In1N4 [2.24(4) Å] bond distances (bonds in axial positions) are longer than

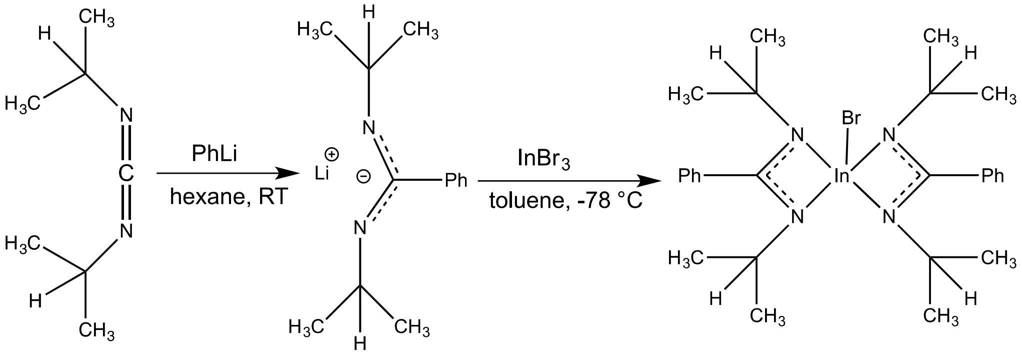
In1N2 [2.20(5) Å] and In1N3 [2.20(4) Å] bond distances (bonds in equatorial positions).[46] The N2In1N3 (112.2(2)°) as well as N2In1Cl1 (127.7(1)°) and Cl1In1N3 (120.2(1)°) angles show the distortion of trigonal bipyramidal symmetry. The bite angles in **5**, N1In1N2 (61.6(2)°) and N1In1N4 (61.4(2)°), are the same and very close to those in $[PhCN_2(SiMe_3)_2]_2InBr$ (**4**). The In1Cl1 bond distance 2.38(2) lies in the range of some other In(III) complexes such as $InCl_5^{2-}$ 2.415(12), $[InCl_4(H_2O)_2]^-$ [2.485(2) Å], [2.456(7) Å] [49] and [2.417(3) Å]. [50] Comparing the In1Cl1 bond distance with that of in neutral adducts, it is noticed that the In-Cl bond distance is almost the same as in $InCl_3.2Ph_3P$ [2.377(5) Å] and [2.382(5) Å] [51] and shorter than [2.396(5) Å] and [2.465(1) Å] in $InCl_3$.terpy.[52]

Comparing the two indium amidinate complexes $[PhCN_2(SiMe_3)_2]_2InBr$ and $[PhCN_2(SiMe_3)_2]_2InCl$ it is noticed that both complexes do have distorted trigonal bipyramidal geometry. N2In1N4 (167.7(5)°) in **4** is about 3° larger than N1In1N4 (164.7(2)°) in **5.** By comparing Br1In1N2 (97.7(4)°) Br1In1N4 (94.3(4)°) angles and Cl1In1N1 (100.1(1)°) Cl1In1N4 (95.2(1)°) angles, we see that the deviation from 90° in **5** is more than in **4**. The bite angles are almost the same. There are N1In1N2 (61.5(6)°) and N3In1N4 (62.1(5)° in **4** and N1In1N2 (61.6(2)°) and N3In1N4 (61.4(2)°) in **5**. The In-N bond distances differ slightly one other.

2.5 Synthesis of In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br

2.5.1. Reaction of Li[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$)] with InBr$_3$

By treating bis-2,6-diisopropylcarbodiimide with one equivalent phenyl lithium at -78 °C in n-hexane and stirring the solution over night, a yellow solution of Li[CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$)] (**6**) resulted. By treating **6** with one equivalent InBr$_3$ at -78 °C and allowing the mixture to warm up to the room temperature and stir further, a yellow solution with a white precipitation was obtained. (equation 20)



(20)

6 **7**

After extracting the yellow solution with n-hexane and toluene, the crystals of In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br **7** were isolated from the n-hexane fraction at -25 °C with the yield of 20%.

2.5.2 Spectroscopic characterization of 7

In the ^1H-NMR-spectrum of **7** the characteristic signals for the hydrogen atoms of the phenyl ring are seen. For the 6 hydrogen atoms in *meta*- and *para*-positions a multiplet peak is seen in the range of δ = 6.95 - 6.64 and for the 4 hydrogen atoms in the *ortho*-position the multiplet peak is found at the range of δ = 7.26-7.22. A symmetric septet peak occurred at δ = 3.5 with the intensity of 4 which is characteristic for the hydrogen atom bound at tertiary carbon atom of isopropyl substituents. At δ = 1.24 a doublet with the intensity of 24 is seen that belongs to the hydrogen atoms of the methyl groups on the isopropyl substituents. Finding just one doublet and one septet proves that all the isopropyl substituents are equivalent and in the same chemical environment. These results are in a good agreement with the results obtained from the ^1H-NMR of the amido guanidinate with isopropyl substituents $[Me_2NC(N^iPr)_2]_2AlCl$.[53]

The ^{13}C-NMR-spectrum of **7** shows a signal for carbon atom of the NCN group of the amidinate at δ = 170.4 and one for the *ipso*-carbon at δ = 140.5. Three peaks are found for the aromatic *ortho*-, *meta*- and *para* carbon atoms of phenyl groups at δ = 127.7, δ = 126.8 and δ = 126.2 respectively. This proves that the phenyl groups are equivalent and the data correlates with the date revealed from ^1H-NMR spectrum. The peaks for the *C*HMe$_2$ and CH*Me$_2$* carbon atoms are seen at δ = 46.6 and δ = 24.4 respectively which come in agreement with the similar compounds synthesized by Richeson et al.[21][22]

2.5.3 Crystal structure of 7

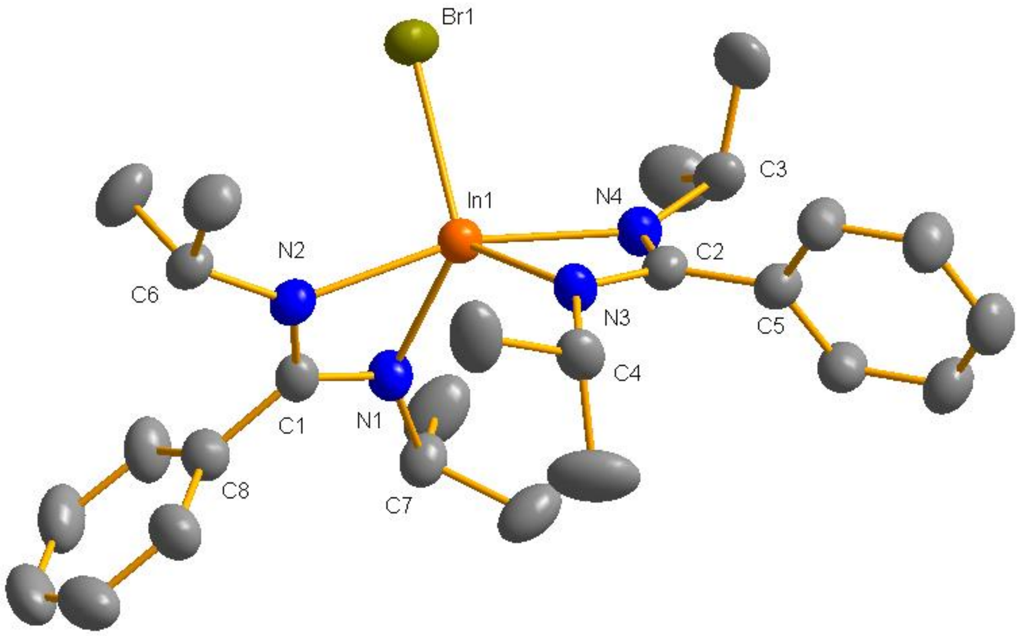


Figure 13 Molecule structure and atom-numbering scheme of **7**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:

In1-Br1 2.528(1), In1-N1 2.179(6), In1-N2 2.231(5), In1-N3 2.186(5), In1-N4 2.227(5), N1-C1 1.327(8), N2-C1 1.343(10), N3-C2 1.344(8), N4-C2 1.342(9), N3-C4 1.470(8), N4-C3 1.469(8), N1-C7 1.473(10), N2-C6 1.450(9), C1-C8 1.492(10), C2-C5 1.471(9).

N1In1N2 60.8(2), N3In1N4 60.6(2), N1In1N3 115.7(2), N2In1Br1 98.5 (2), N4In1Br1 98.6(2), N1In1Br1 122.9(2), N3In1Br1 121.4(1), N1C1N2 113.4(6), N2C2N3 112.1(6), In1N4C3 141.4(5), In1N1C7 140.2(5), C1N1C7 124.3(6), C1N2C6 121.8(6), N2C1C8 123.3(7), N4C2C5 123.9(6).

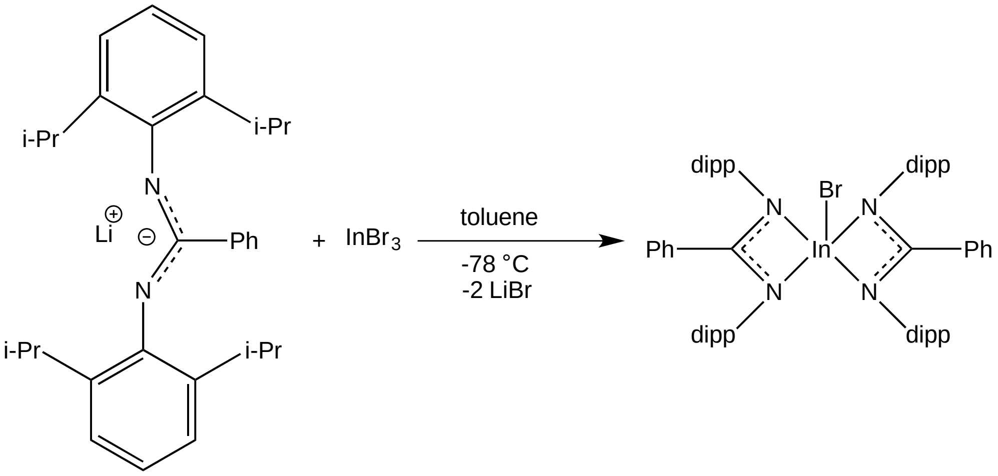
The molecule geometry as well as the atom-numbering scheme is shown in figure 14. The selected bond distances and angles are also shown above. The complex **7** crystalized from n-hexane in the triclinic space group P1 with two molecules in the unit cell. The indium atom is coordinated in a distorted trigonal bipyramidal manner by two amidinates and a bromine atom. The

In1N1 [2.179(6) Å] and In1N3 [2.186(5) Å] do have shorter bond distances than the In1N2 [2.231(5) Å] and In1N4 [2.227(5) Å], so the first two In-N bonds are in equatorial position and the other two in axial, which correlates with the data obtained by similar complexes prepared yet.[45] The equatorial groups N2Br1N3 are coplanar with the sum of the angles equal to 360°. The In1-Br1 bond distance [2.528(1) Å] is shorter than In1-Br1 bond distance in **4** [(2.539(2) Å]. Comparing the In-N bond distances in both amidinate complexes, it is seen that those bonds are also shorter in $[PhCN_2(i\text{Pr})_2]_2InBr$ (**7**). This is because of the steric effect of the bulky groups of $SiMe_3$. The bite angles are almost the same, N1InN2 (60.8(2)°) and N3In1N4 (60.6(2)°). The N1In1N3 angle (115.7(2)°) deviate slightly from 120° which confirms the Bent rule.[54][55] The Br1In1N4 (122.9(2)°) and Br1In1N1 (121.4(2)°) are larger than expected. The reason is that nitrogen is more electronegative than brom atom and this causes less p-character in the indium-brom bond, which causes a larger BrInN angle. The nitrogen centers in amidinate rings deviate slightly from planarity, the sum of angles around N1 and N2 atoms are 358.9 and 354.6 respectively due to the steric congestion around the metal center.

2.6 Synthesis of In[(dipp)NC(Ph)N(dipp)]$_2$Br

2.6.1 Reaction of Li[(dipp)NC(Ph)N(dipp)] with InBr$_3$

By treating bis-2,6-diisopropyphenylcarbodiimide with one equivalent phenyl lithium at -78 °C in n-hexane and stirring the solution over night, a pale yellow solution of [PhCN(dipp)$_2$]Li was obtained. **8** was dissolved in toluene and treated with one equivalent InBr$_3$ at -78 °C. (equation 21) The mixture was allowed to warm up to the room temperature and stirred over night. At the next day a yellow solution with white precipitation was obtained. After removing of all the volatiles under vacuum the residue is extracted once with 15 mL n-hexane and once with 15 mL toluene. The pale yellow crystals of the **9** were isolated from the n-hexane fraction at -25 °C after a few weeks with the yield of 41%. .



(21)

8 **9**

2.6.2 Spectroscopic characterization of 9

In the ^{1}H-NMR-spectrum of **9** the signal for the 10 hydrogen atoms of the phenyl rings are observed as a doublet peak for the hydrogens in para position with the intensity of two at δ = 7.69 and as multiplet peaks for hydrogens in ortho and meta positions at δ = 7.31 with the intensity of 8. The hydrogen peaks in the *para* positions of the aromatic ring of dipp groups are found at the range of δ = 7.06-7.03 with the intensity of 4 in a form of a multiplet. The hydrogen peaks in the *meta* positions of the aromatic ring of the dipp groups are seen at the range of δ = 6.94-6.92 with the intensity of 8 in a form of a doublet of doublets (dd). For the isopropyl groups the two characteristic peaks are seen as doublet and septet: The Septet peak occurs at δ = 3.40 with the intensity of 8. The doublet peak is found at the range of δ = 1.39-0.95 with the intensity of 48 H. The ^{1}H-NMR data correlate with the data obtained from the similar indium amidinate complexes synthesized.[32]

The signals for the NCN carbon atom and for the *ipso*-carbon in aromatic ring are seen at δ = 170.8 and δ = 151.7. There are several peaks shown for the carbon atoms of the aromatic rings, both for phenyl rings and the aromatic rings of the dipp groups. The peaks for the aromatic carbon atoms of the dipp groups are found at δ = 143.9, δ = 138.3 and δ = 134.3. There are three other peaks for the carbon atoms of the phenyl ring seen at δ = 128.3, δ = 127.3 and δ = 126.6 for the *para*-, *met*a-, and *ortho*-carbon atoms respectively. The peaks for the CHMe_2 are observed one at δ = 23.4 and the other one at δ = 23.7. For the *C*HMe$_2$ two peaks are found, one at δ = 27.6 and the other one at δ = 27.9. Data obtained from C-NMR correlate with the data obtained from ^{1}H-NMR and again with the data reported.[32]

2.6.3 Crystal structure of 9

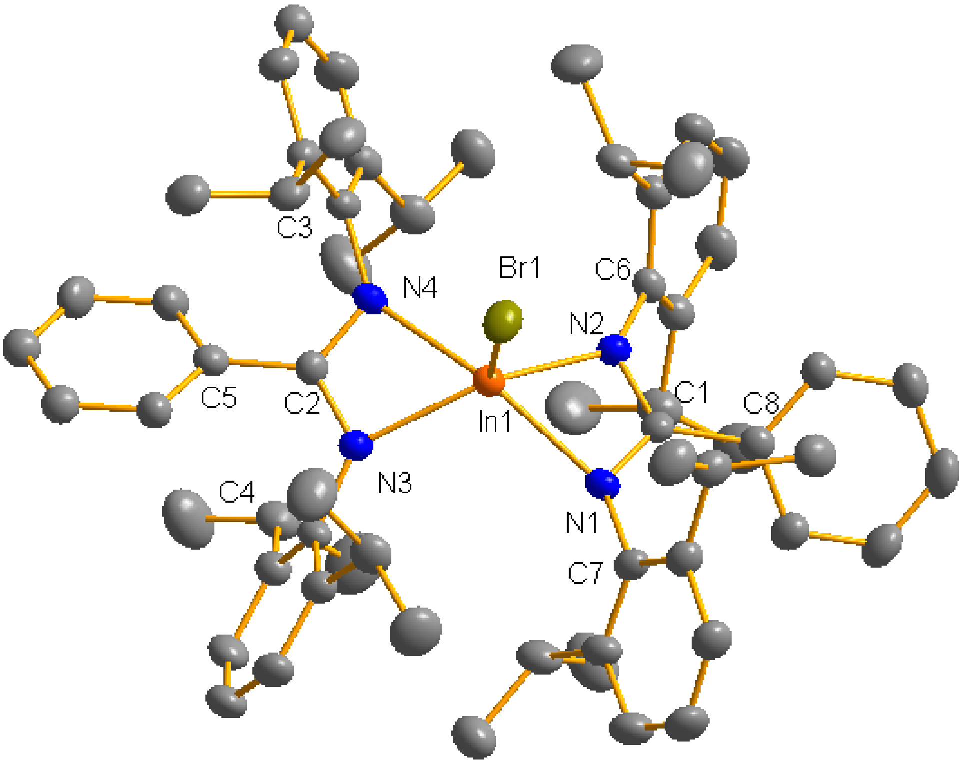


Figure 14 Molecule structure and atom-numbering scheme of **7**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:

In1Br1 2.508(2), In1N1 2.249(3), In1N2 2.183(3), In1N4 2.249(3), In1N3 2.183(3), N1C1 1.333(4), N2C1 1.348(4), N3C2 1.333(4), N4C2 1.348(4), N1C7 1.436(4), N2C6 1.423(4), N4C3 1.436(4), N3C4 1.423(4).

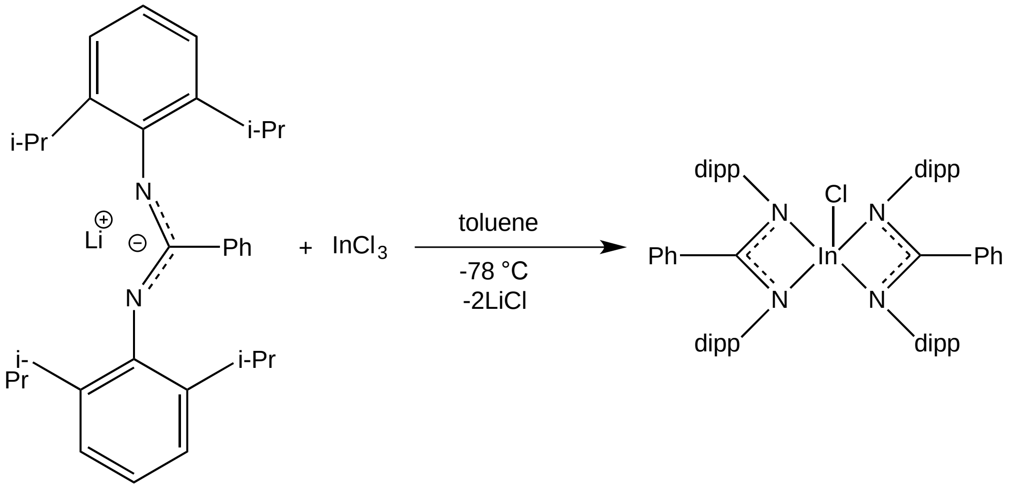
N4In1N3 60.07(9), N1In1N2 60.07(9), N1In1N4 156.7(1), Br1In1N2 109.31(6), N2In1N3 141.4(1), N3In1Br1 109.31(6).

The complex **9** crystallized from n-hexane in the monoclinic space group C 1 2/c1 with four molecules in the unit cell. The molecule geometry as well as the atom-numbering scheme is shown in figure 14. The selected bond distances and angles are also shown above. The indium atom is coordinated in a distorted trigonal bipyramidal manner by two amidinates and a bromine atom possessing C_2 symmetry. In Complex **9** the equatorial plane consists of three groups (e.g. N2, N3 and Br1) that are coplanar with the sum of appropriate angles equal to 360°. The axial In-N bonds [2.249(3) Å] are larger than those in equatorial position [2.183(3) Å] as expected. That is because the orbitals involved in the In-N bonds in axial position of five-coordinated indium amidinate complexes are p orbitals but those in equatorial position have sp^2 hybridization (more s character). Therefore they are shorter than axial ones. The angle between the axial groups N1In1N4 (156.7(1)°) shows the distorted geometry. The bite angle is (60.07(9)°) which is comparable with the bite angle in compound **10** (60.1(3)°). The In1Br1 bond distance is [2.508(2) Å] which is smaller than that in $In[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2]_2Br$ [2.528(2) Å] and in $In[SiMe_3NC(Ph)NSiMe_3]_2Br$ [2.539(2) Å]. This can be explained by the steric effects of the $SiMe_3$ groups.

2.7 Synthesis of In[(dipp)NC(Ph)N(dipp)]$_2$Cl

2.7.1 Reaction of Li[(dipp)NC(Ph)N(dipp)] with InCl$_3$

By treating bis-2,6-diisopropyphenylcarbodiimide with one equivalent phenyl lithium at -78 °C in n-hexane and stirring the solution over night, a yellow suspension of Li[(dipp)NC(Ph)N(dipp)] (**8**) was obtained. **8** was dissolved in 15 mL toluene and treated with one equivalent InCl$_3$ at -78 °C. (equation 22) The mixture was allowed to warm up to the room temperature and stir over night. At the following day an orange-yellow solution with a white precipitation resulted. After removing of all the volatiles under vacuum the residue is extracted once with 15 mL n-hexane and once with 15 mL toluene. The pale yellow crystals of **10** were isolated from the n-hexane fraction at -35 °C after few weeks.



(22)

8 **10**

2.7.2 Spectroscopic characterization of 10

In the ^{1}H-NMR-spectrum the hydrogen peaks for the phenyl ring are found at the range of δ = 7.68-7.29 with the intensity of 10 in form of a multiplet. The hydrogen peaks for the *para* and *ortho* positions of the aromatic ring of dipp group are found at the range of δ = 7.06-7.04 with the intensity of 4 in form of multiplet and the peaks for the hydrogens in the *meta* position of the aromatic ring of the dipp group are seen at the range of δ = 6.95-6.69 with the intensity of 8 in form of a multiplet. For the hydrogen atoms of the isopropyl substituents there are two doublets and two septets found. Two Septet peaks are seen at δ = 3.58 and δ = 3.26 each with the intensity of 4. This is because of the different distances of the amidinate backbones from the chlor atom and therefore being in two different chemical environment. The two doublet peaks are seen at δ = 1.38 and at δ = 0.90 each with the intensity of 24.

In the ^{13}C-NMR spectrum of **10** there is a peak at δ = 168.7 which belongs to the NCN carbon atom. The peak at δ = 160.3 shows the *ipso*-carbon atom. The carbon atoms of the phenyl ring and the dipp substituents are responsible for the several peaks seen in the corresponding range. The peaks found for the carbon atoms of the dipp substituents are at δ = 145.5, δ = 138.0 and δ = 136.7. The peaks found for the carbon atoms of the phenyl rings are seen at δ = 128.4, δ = 128.0 and δ = 127.7 for the *para*-, *meta*-, and *ortho*- carbon atoms. These peaks are in a good agreement with the peaks found for the similar gallium[56] and indium compounds.[32] There are two peaks for at δ = 23.7 and δ = 23.4 which belong to the carbon atoms of $\mathrm{CH}Me_2$ and two other peaks at δ = 27.6 and δ = 27.9 for the carbon atoms of $C\mathrm{HMe_2}$. The data obtained correlates well with the data obtained from the ^{1}H-NMR and ^{13}C-NMR of **9**.

2.7.3 Crystal structure of 10

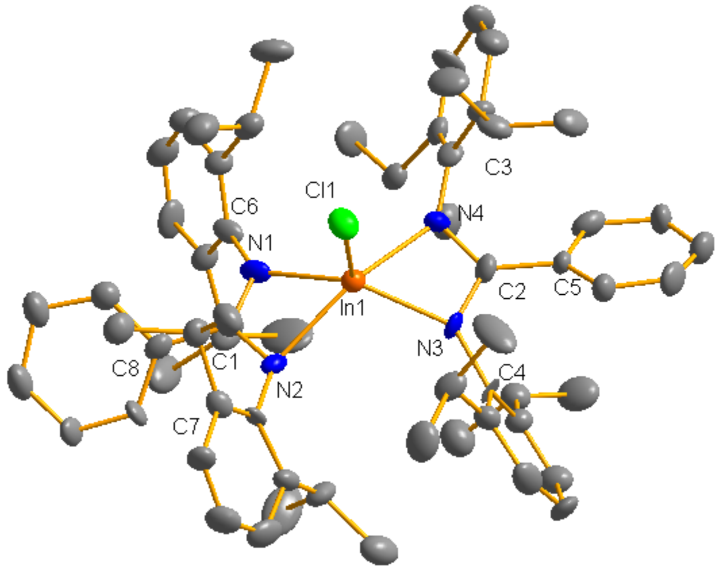


Figure 15 Molecule structure and atom-numbering scheme of **10**. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]:

In1-Cl1 2.366(10), In1-N1 2.221(10), In1-N2 2.160(7), In1-N3 2.266(11), In1-N4 2.205(10), N1-C1 1.314(14), N1-C6 1.375(13), N2-C1 1.335(14), N2-C7 1.459(15), N3-C4 1.475(11), N4-C3 1.415(16), C1-C8 1.467(16), C2-C5 1.506(15).

N1In1N2 60.1(3), N3In1N4 60.5 (4), N1In1Cl1 109.2(3), N2In1Cl1 102.9(3), N3In1Cl1 108.9(3), N4In1Cl1 99.8(3), N1C1N2 116.1(10), N3C2N4 106.7(9), N1C1C8 123.8(10), N4C2C5 129.9(12).

The complex of **10** crystalized from n-hexane in the monoclinic space group C1/c1 with four molecules in the unit cell. The molecule geometry as well as the atom-numbering scheme is shown in figure 15. The selected bond distances and angles are also shown above. The indium atom is a five-coordinated center with two amidinates and one chlor atom. The In1Cl1 bond distance is [2.366(10) Å], which can be comparable the with In-Cl bond distance in bis(amidinato)indium halide complexes $[InCl([N(Cy)_2CBu^t)_2]$[21], [2.405(10) Å); and InCl[(N($C_6H_3Pr^i_2$-2,6)$_2$CH)2][32], [2.357(1) Å]. Comparing the In1Cl1 bond distance with a number of inorganic In(III) complexes, we see that it is shorter than that in $InCl_5^{2-}$ [2.415(12) Å][49], $[InCl_4(H_2O)_2]^-$ [2.485(2) Å] [50]. Comparing it with the In-Cl bond distance in neutral complexes, it is in a good agreement with $InCl_3$.2Ph_3P [2.377(5) Å][51] and [2.394(1) Å].[57] In organoindium complexes, which are strongly distorted TBP, this value is higher for $[(CH_3)_2InCl]_2$ [2.673(9) Å], [2.954(6) Å] and [3.450(9) Å].[58] Comparing the In-N bond distances in two chelating amidinates, it is noticed that two of the In-N bond distances are longer that the others, which are in axial position, and the other two are in equatorial positions as expected. It seems that there is less delocalization of backbones of the amidinates, as the N-C distances among each of NCN groups apparently differ from each other. The In-N bonds distances as well as the N-C bond distances are slightly longer that those described in InCl[(N($C_6H_3Pr^i_2$-2,6)$_2$CH)2]][32], due to using steric phenyl groups instead of hydrogen atom attaching to the NCN fragment. The bite angles are almost the same in both amidinate groups (N1In1N2 (60.1(3)°), N3In1N4 (60.5 (4)°) and this value correlate with the values obtained from similar experiments.[32] The nitrogen centers of the amidinate groups are almost coplanar with the sum of the angles 359.9° and 352.4° for N1 and N2 respectively. The phenyl substituents are also coplanar with the sum of the angles 359.8° and 359.7°. The N1In1N4 angle (113.4(4)°) deviate from the 120° which can be explained by Bent rule. [54][55] The N1In1Cl1 (109.2(3)°) and N4In1Cl1 (99.8(3)°) angles deviate from the ideal angle and are larger than expected.

3 Reactions of the five coordinated indium complexes of type R_2InX (R = R"NCR'NR", R" = dipp, ipr, R' = Phenyl, X = Br, Cl)

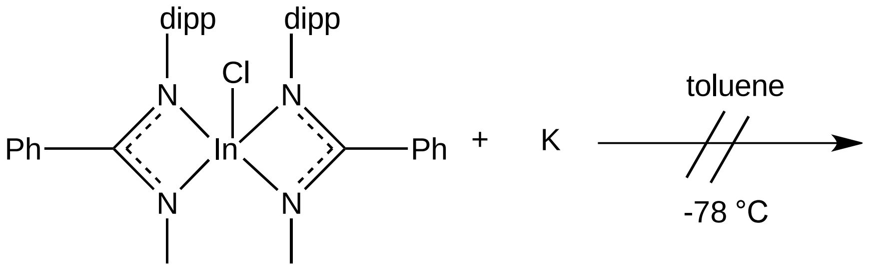
3.1 Reaction of, $In[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2]_2Br$, $In[(dipp)NC(Ph)N(dipp)]_2Br$ and $In[(dipp)NC(Ph)N(dipp)]_2Cl$ with potassium

After synthesizing the five-coordinated indium amidinates and possessing different substituents on the nitrogen atoms, it was time to reduce these compounds with an appropriate reducing agent to obtain the corresponding indium clusters. In this project the selected reducing agent was potassium.

Finely divided potassium metal was added to the indium amidinate compound and suspended in toluene and heated under reflux for several days.

Unfortunately the attempts were unsuccessful. Using bulky substituents around the indium center made the approach of two indium atoms and the overlap of their orbitals impossible. (equations 23-25)

By performing the ^{1}H-NMR und ^{13}C-NMR spectroscopy it is revealed that the products possess only the NMR resonance of the substrate five-coordinated indium complexes.



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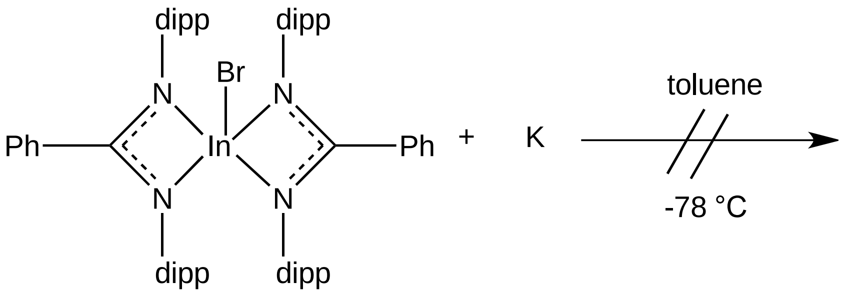

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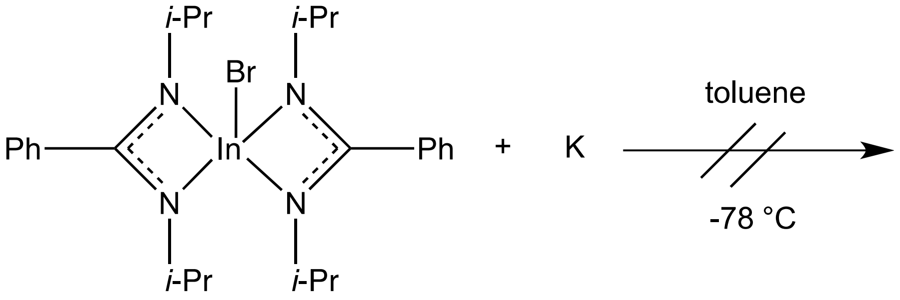


(25)

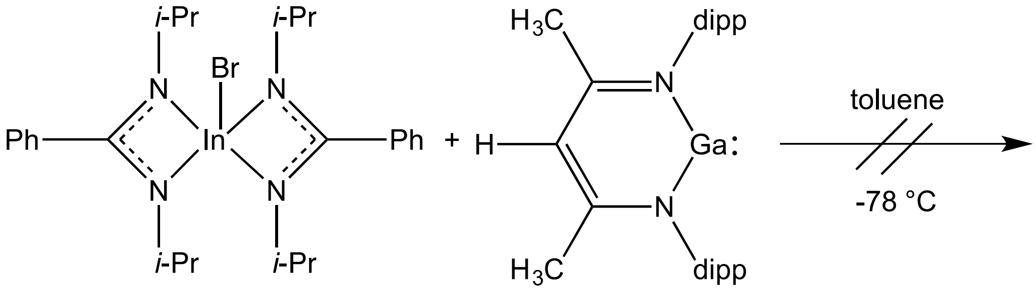
There is still additional work to be performed in this field. Choosing other effective reducing agents such as potassium graphite or changing the substituents to the less bulky ones may affect the resulted products.

3.2 Reaction of In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br, In[(dipp)NC(Ph)N(dipp)]$_2$Br and In[(dipp)NC(Ph)N(dipp)]$_2$Cl with Ganacnac

The ligands of β-diketiminates do have a large application in lots of the reactions in the field of chemistry. They can be easily synthesized by the condensation reaction of the acetyl acetone with aniline or diisopropylaniline derivates, they are soluble in the most of the organic solvents and can be crystalized very fast.[59] The metals of the group 13 have a special place in the developing the chemistry of the stabilized β-diketiminate trieles.[60][61] By reaction of the lithium-β-diketiminate with GaI and addition of the Potassium to the mixture for the reduction, the Ga (I)- β-diketiminate ligands are synthesized. The Ga (I) center is very reactive, though because of the shielding effect of the diisopropyl groups, it is well stabilized. These ligands and their orbitals are very similar to the N-heterocyclic carbenes (NHC) and can undergo the similar reactions. The Ga (I) heterocyclic ligands can undergo a series of the complex building reactions with transition metals. [62][63]

In this part of the research the focus of the work was to isolate compounds with Ga-In binding by reacting Ganacnac and the five coordinated indium ligands having dipp or isopropyl groups.

The crystals of **7**, **9** and **10** were suspended in toluene and were treated with 1 equivalent Gananac dissolved in toluene at -78°C.) (equations 26-28)The mixtures were allowed to warm up to the room temperature and stir over night. After removing of all the volatiles under vacuum the residues were extracted once with n-hexane and once with toluene.



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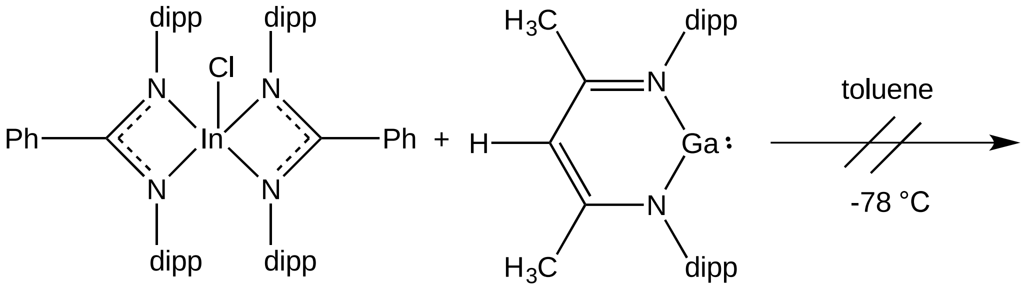

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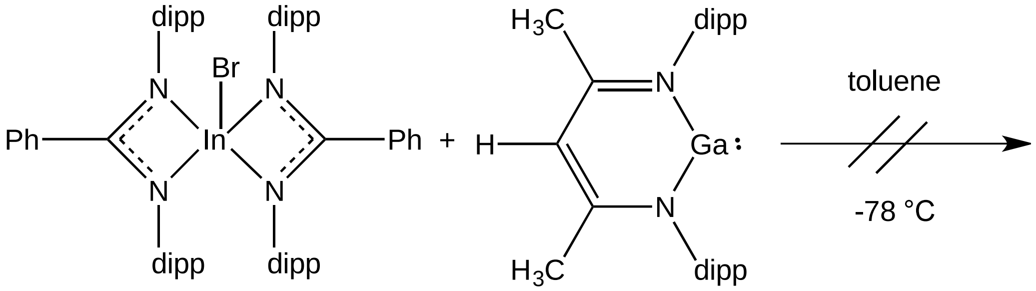


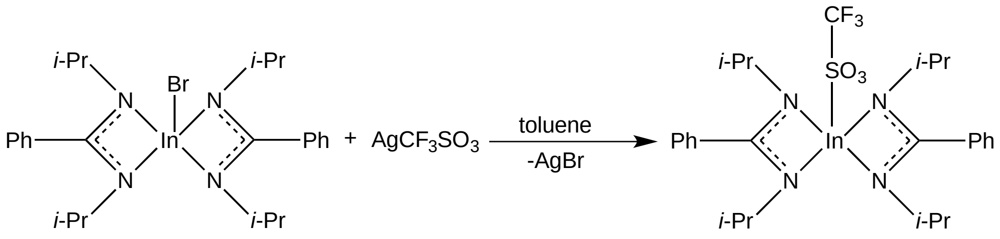
(28)

Unfortunately all the attempts were unsuccessful. One of the limitations on the synthesis was the bulky steric groups attaching to both of the ligands. By comparing the ^{1}H-NMR and ^{13}C-NMR of the resulted solutions with the substrates, it is revealed that the substrates remained unchanged and no new reaction has taken place. No new isolated crystals were obtained in all of these reactions.

3.3 Reaction of In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br (7) with AgCF$_3$SO$_3$

The next step was to react the R$_2$InX (R = R"NCR'NR", R" = *i*Pr, R' = Phenyl, X = Br), which is less steric hindered, with silver trifluoromethanesulfonate or silver triflate.

By reaction of In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br with AgCF$_3$SO$_3$ in 1:1 stoichiometry in toluene at -78 °C and allowing the mixture to warm up to the room temperature and stir over night, a milky-yellow suspension with a grey-black precipitation was obtained. The Schlenk flask was protected from light all the time. (equation 29)



(29)

7 **11**

After removing of all the volatiles under vacuum the residue was extracted with THF. Pale yellow crystals of the **11** were isolated from the THF fraction at -35 °C with the yield of 54%.

3.3.1 Spectroscopic characterization of 11

There are two peaks found for the hydrogen atoms of the phenyl groups. The multiplet peak for the hydrogen atoms in *ortho* position are found at the range of δ = 7.26-7.24 with the intensity of 4. The peaks for the hydrogen atoms of the phenyl groups in *meta*- and *para*- positions are seen at the range of δ = 7.08-7.07, which are characteristics for the aromatic groups. Characteristic peak for the isopropyl groups are seen as a septet peak at δ = 3.7 with the intensity of 4 and as a doublet peak for the $CH(CH_3)_2$ groups at δ = 1.52 with the intensity of 24. By comparing the resulted ^{1}H-NMR with the data resulted from the ^{1}H-NMR of the similar complex $In[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2]_2Br$ we notice that the peaks are shifted to the high field in the complex with the triflate ligand. That is due to the different electronegativity of the triflate group in comparison with the bromide atom.

The ^{13}C-NMR-spectrum of **11** shows two signals for the NCN carbon atom and for that of *ipso*-carbon in aromatic ring at δ = 173.8 and δ = 154.5 respectively. The aromatic *ortho*-, *meta*- and *para* carbon atoms are found at δ = 127.1, δ = 126.9 and δ = 126.7. The peak for the CF_3 group can not be seen properly and is hidden among the peaks of solvent (toluene) between δ = 125.2 and δ = 128.1. Additionally one peak is found for the $CHMe_2$ at δ = 46.9 and one peak for the $CHMe_2$ at δ = 24.0 as expected for the ^{13}C-NMR spectrum of the isopropyl groups.

3.3.2 Crystal structure of In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$SO$_3$CF$_3$ (11)

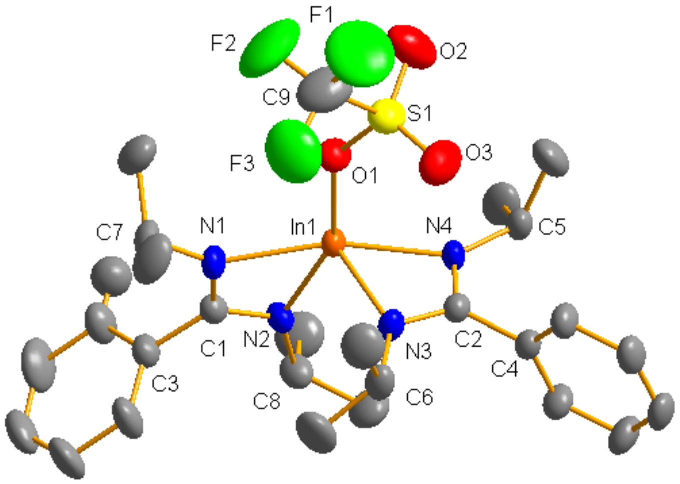


Figure 16 Molecule structure and atom-numbering scheme of **11**. Hydrogen atoms and solvent molecule have been omitted for clarity. Selected bond lengths [Å] and angles [°]:

In1N1 2.240(5), In1N2 2.180(4), In1N3 2.175(4), In1N4 2.231(4), In1O1 2.240(4), N1C1 1.323(7), N2C1 1.339(7), N3C2 1.328(7), N4C2 1.335(7), N1C7 1.465(7), N2C8 1.447(7), N3C6 1.473(7), N4C5 1.469(7), O1S1 1.469 (7), O2S1 1.421(6), O3S1 1.418(5), S1C9 1.806(11), F1C9 1.315(11), F2C9 1.321(12), F3C9 1.359(12).

N1In1N2 60.6(2), N2In1N3 60.8 (2), N1In1N4 164.4(2), N1C1N2 113.7(5), N3C2N4 113.8(4), O1In1N1 95.3(2), O1In1N4 97.1(2)

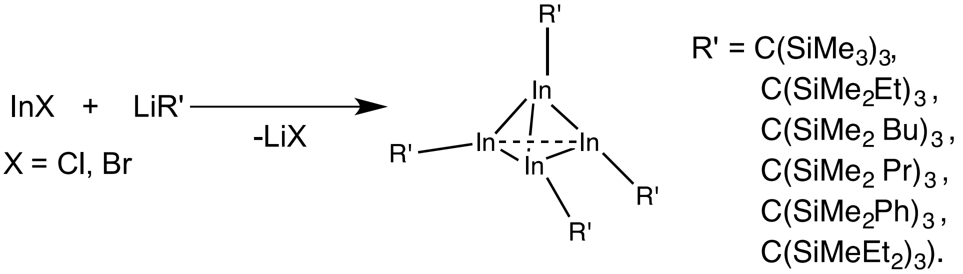
The In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$SO$_3$CF$_3$ (**11**)crystalized from THF in the monoclinic space group P 2$_1$/n with four molecules in the unit cell with one molecule THF per unit. The molecule geometry as well as the atom-numbering scheme is shown in figure **16**. The selected bond distances and angles are also shown above. The indium atom is coordinated in a distorted trigonal bipyramidal manner with two chelating amidinates and one triflate group. Studying the In-N bonds, it is seen that two of In-N bonds (In1N1 [2.240(5) Å], In1N4 [2.231(4) Å]) are longer than the other bonds (In1N2

[2.180(4) Å], In1N3 [2.175(4) Å]). The former are in axial position and the latter in equatorial one.[45]

Comparing these bonds with those in **7**, it is noticed that the bonds in **7** are slightly longer than in **11**. The reason is likely due to more electronegativity of the triflate in comparison with the bromine atom. The elongation of the indium-nitrogen bonding can be explained by the bent rule. [54][55] The s-character will be more distinctive towards electropositive atoms and therefore we notice more p-character towards In-N bindings. The In1O1 bond distance [2.240(4) Å] is shorter than In1Br1 bond distance in **7** [2.528(1) Å] as expected. N1In1N4 angle (164.4(2)°) in **11** is about 2° larger than that in **7** (162.9(2)°). The bite angles N1In1N2 (60.6(2)°) and N3In1N4 (60.8(2)°) are exactly the same as in the $In[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2]_2Br$ complex (N1In1N2 (60.8(2)°) and N3In1N4 (60.6(2)°). The planarity of the phenyl groups are confirmed by the sum of the angles (360° and 359.9°).

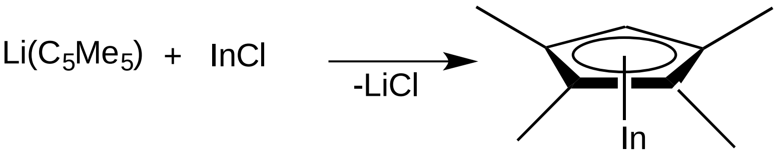
4 Subvalent organic indium complexes

Subvalent organic indium complexes possess fascinating characteristics. Uhl and Cowley synthesized the alkyl substituted indium tetrahedranes In_4R_4 [(R = $C(SiMe_3)_3$, $C(SiMe_2Et)_3$, $C(SiMe_2\,Bu)_3$, $C(SiMe_2\,Pr)_3$, $C(SiMe_2Ph)_3$, $C(SiMeEt_2)_3$), $Si(SiMe_3)_3$, which was directly generated from the reaction of monovalent InCl or InBr with the corresponding Lithium compounds. (equation 30) [64] [65] [66][67]



(30)

In the same way pentamethylcyclopentadienyl indium (InCp*) was isolated. These complexes can be sublimated easily and occur as monomers in gas phase. (equation 31)[11]



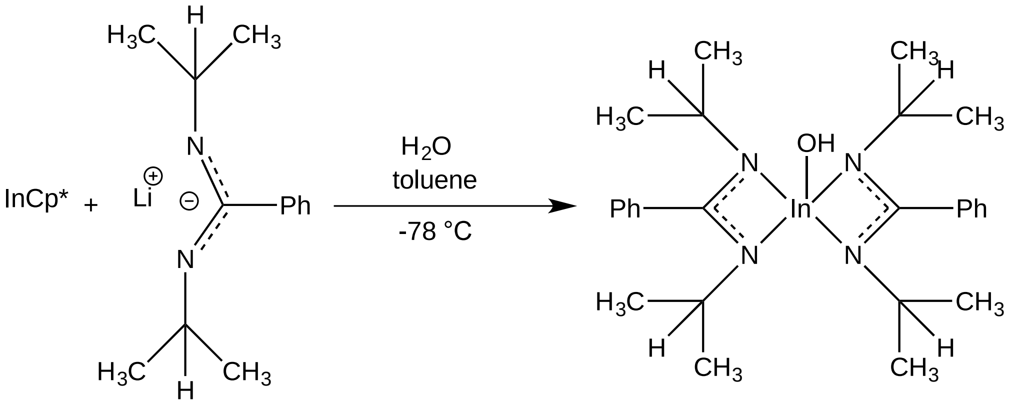
(31)

These complexes act as very good precursors for the low valent indium compounds and can be used for new transition metal complexes.[68]

In this part of the work the focus of the research is to react the InCp* with the **6** and **8** to obtain the corresponding low valent Indium complexes.

4.1 Reaction of InCp* with 6 and 8

The InCp* was dissolved in toluene. 1 equivalent **6** was dissolved in toluene. The two solutions were added at -78 °C under argon flow. (equation 32) The mixture is then allowed to warm up to the ambient temperature and stir over night. At the next day the mixture was black which showed that disproportionation occurred and indium metal was precipitated. All the volatiles were then removed under vacuum and the remaining residue was first extracted with n-hexane and then with toluene solvents. The two resulted fractions were reduced and the pale-yellow solutions were kept at -35 °C for several months. The ^{1}H-NMR and ^{13}C-NMR spectroscopy were done with the n-hexane-fraction.



(32)

6 **12**

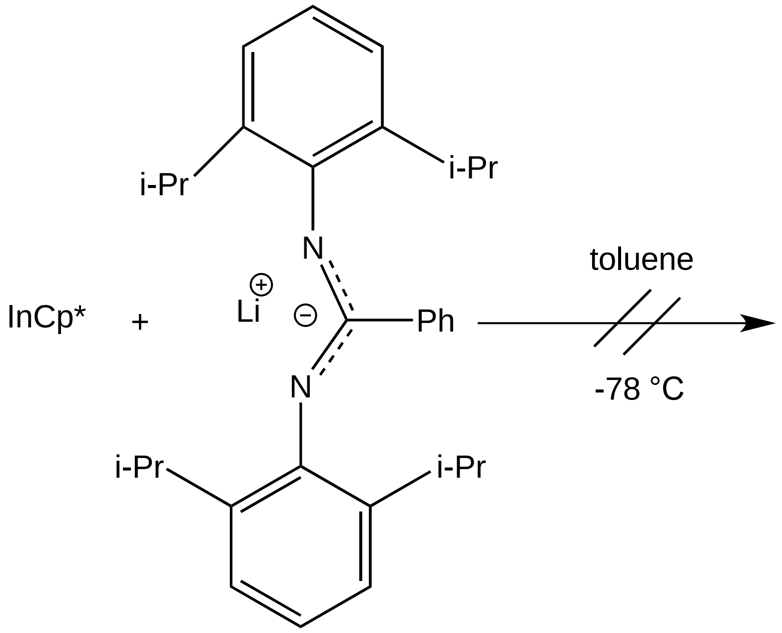
By comparing the ^{1}H- NMR and ^{13}C-NMR spectrum of the **12** with those of **7**, it is noticed that the results are identical with a very slight low field shift for the spectrum of **12**, which can be caused by having OH group instead of bromide at the indium atom. The peak for the OH group can be seen as a wide peak at δ = 4.38. Unfortunately the crystals of **12** could not be measured.

4.1.1 Spectroscopic characterization of 12

The ^{1}H-NMR-spectrum of **12** shows the characteristic signals for the hydrogen atoms of phenyl ring. For the hydrogen atoms in the *ortho*-position the peak is seen at the range of δ = 7.27-7.26 with the intensity of 4 in form of a multiplet. The other peak for the hydrogens in *meta*- and *para*- positions is found at the range of δ = 7.10- 7.04 in form of a multiplet with the intensity of 6. The peak for the OH group is found at δ = 4.38 as wide singlet with the intensity of one. The characteristic peaks for isopropyl groups are found as one septet and one doublet. The septet is found at δ = 3.50 with the intensity of 4 and the doublet is found at δ = 1.33 with the intensity of 24. The data resulted correlate well with the data obtained from 1H-NMR of **7**.

The ^{13}C-NMR-spectrum of **12** shows a signal for NCN carbon atom at δ = 167.4 and one for the *ipso*-carbon at δ = 140.5. The aromatic *ortho*-, *meta*- and *para* carbon atoms are found at δ = 125.7, δ = 126.9 and δ = 127.9. There is one peak found for $C\mathrm{HMe}_2$ at δ = 46.9 and one peak for the $\mathrm{CH}Me_2$ at δ = 24.3.

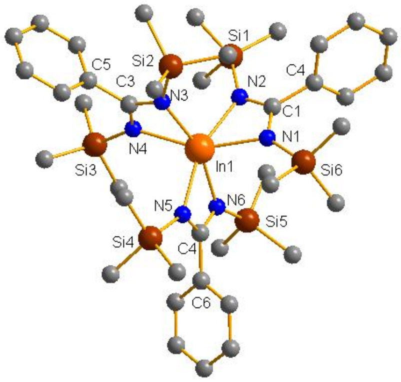
In another reaction InCp* was dissolved in toluene. 1 equivalent of **8** was dissolved in toluene. The two solutions were added at -78 °C under argon flow. (equation 33) The mixture is then allowed to warm up to the ambient temperature and stir over night. All the volatiles were then removed under vacuum and the remaining residue was first extracted with n-hexane and then with toluene solvents. The two resulted fractions were reduced and the yellow solutions were kept at -35 °C for several months. The ^{1}H-NMR and ^{13}C-NMR spectroscopy were done with the both fractions. It is shown that the resulted products are the same as substrates and no new reaction has taken place.



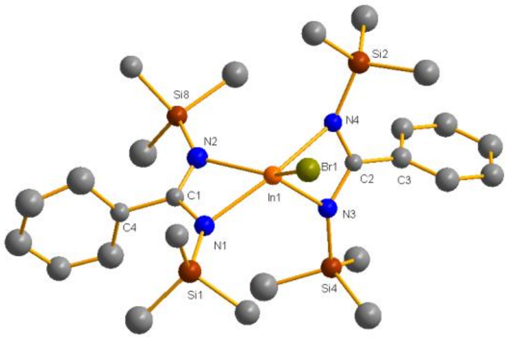
(33)

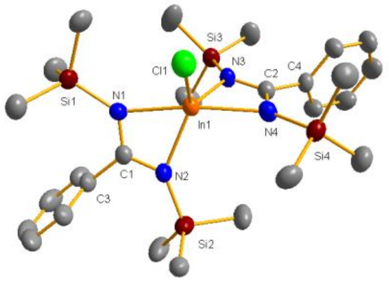
5 Conclusion

By the reaction of lithium amidinates with $InCl_3$ and $InBr_3$ the new five and six coordinated indium amidinate complexes of type R_2InX (R = R”NCR’NR”; R’ = Ph, R” = $SiMe_3$, iPr, dipp; X = Br, Cl) and R_3In(R = $Me_3SiNCPhNSiMe_3$) are synthesized and characterized.



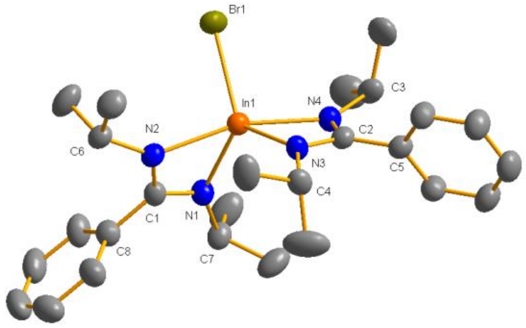
In[SiMe$_3$NC(Ph)NSiMe$_3$]$_3$ **(3)**



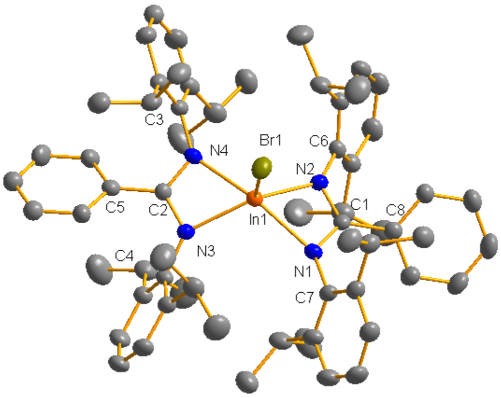


In[SiMe$_3$NC(Ph)NSiMe$_3$]$_2$Br **(4)**

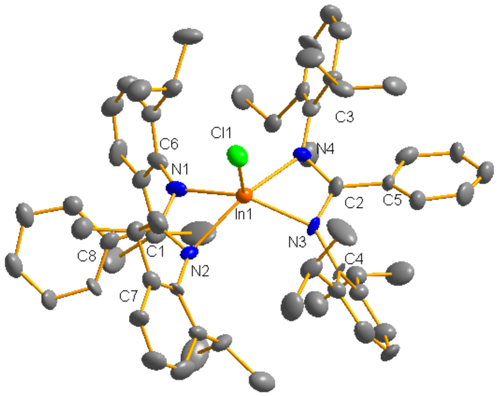
In[SiMe$_3$NC(Ph)NSiMe$_3$]$_2$Cl **(5)**



In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br **(7)**



In[(dipp)NC(Ph)N(dipp)]$_2$Br **(9)**

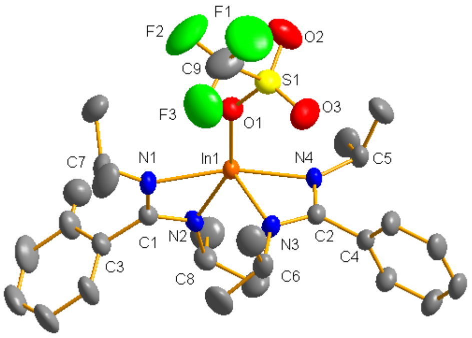


In[(dipp)NC(Ph)N(dipp)]$_2$Cl **10**

Figure 17

Using different bulky substituents at the nitrogen atoms helps to stabilize the crystal structure of these indium amidinate complexes.

By reacting silver triflate with the In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br **(7)** complex the bromide can be substituted with the triflate (SO$_3$CF$_3$) group through nucleophilic reaction by sustaining the oxidation state of the indium atom. (figure 18)



In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$SO$_3$CF$_3$ **(11)**

Figure 18

Trying to reduce the indium amidinates with potassium as well as reacting them with Ganacnac was unsuccesseful. In all the reactions the substrates stayed unchainged because of the steric hindrance of the bulky groups attached to the nitrogen atom.

By trying to react the lithium amidinate with InCp* in the presence of moist the corresponding 5 coordinated indium amidinate In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$OH **(12)** is formed. However the crystals were not measurable.

The chemistry of indium compounds offers an extensive and vast undiscovered research area. It would be a challenge to find a suitable reduction method for such complexes as well as to synthesize new subvalent indium sources.

6 Experimental Section

6. 1 General experimenting conditions, measuring and analyzing methods

All experiments were carried out under purified argon or in vacuum by using schlenk techniques, because of the high sensitivity of the most used substances towards air and/or moisture. All the used equipment were heated while applying a vacuum by a vacuum pump and then filled with argon.

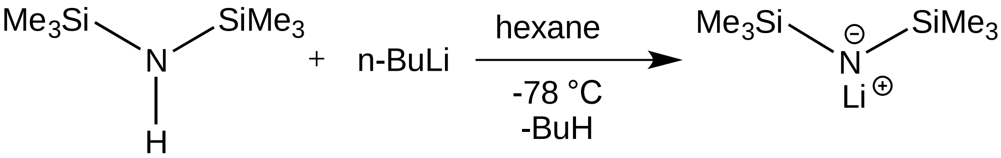
Solvents were dried by using usual lab techniques with sodium suspension (n-hexane, toluene, THF, diethyl ether) and degassed and stored under Argon atmosphere prior to use.

Solution NMR spectral data were collected on a Bruker Advance II 400 and a Bruker Advance III 600 with sample changer B-ACS 60. The standard solvent used was C_6D_6 (^1H, ^{13}C). Chemical shifts are reported in ppm downfield from $SiMe_4$ and were calibrated to the residual proton signal of the deuterated solvent.

For the single-crystal X-ray diffraction suitable crystals were mounted with perfluorated polyether oil on the tip of a glass fiber and cooled immediately on the goniometer head. Data were collected with Mo ($K\alpha$) radiation with STOE IPDS I Diffractometer. Structures were solved with the program SHELXTL (PC) and refined.[69] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon atoms were included as riding model with fixed isotropic U values in the final refinement. Program Diamond 3.1f with the application POV-Ray for windows version 3.6 was used for graphic epictions.

6.1.1 Lithium hexamethyldisilazide [70]

1.62 g (10.05 mmol) hexamethyldisilazanide was dissolved in 15 mL n-hexane in a schlenk flask and cooled to -78°C. 4.02 mL (10.05 mmol, 2.5 M in n-hexane) *n*-butyl lithium was added drop wise with stirring. After warming up the mixture to the ambient temperature, the milky-white suspension was allowed to stir overnight. All the volatile components were removed under vacuum. **1** was used for the next experiment without further work-up.

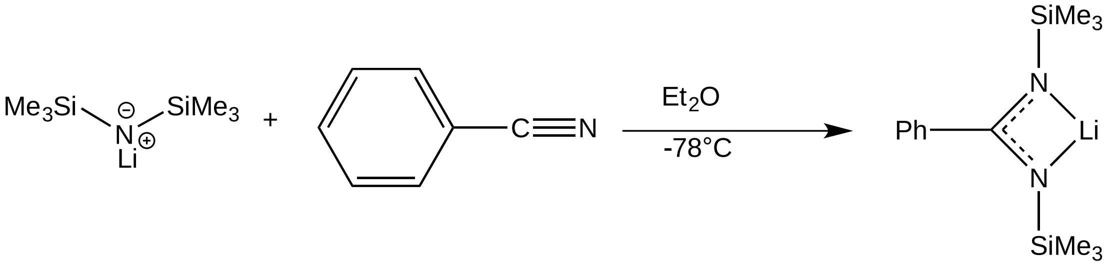


1

167.33 g/mol

6.1.2 Li[SiMe3NC(Ph)NSiMe3] [71][72]

The white powder of **1** was suspended in 20 mL diethyl ether and 1.00 eq (1.04, 10.05 mmol) benzonitril was added dropwise through a syringe at -78 °C with stirring. After warming up to the ambient temperature, the orange-brown mixture was allowed to stir over night. The solution was used directly for the next step.



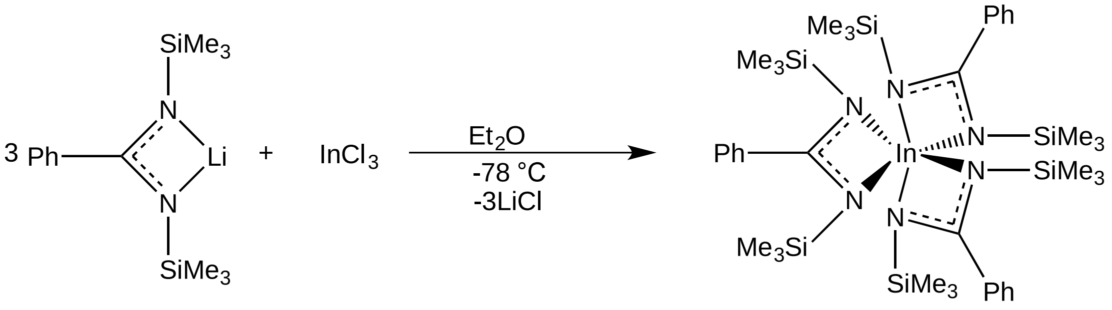
1

2

270.45 g/mol

6.1.3 In[SiMe$_3$NC(Ph)NSiMe$_3$]$_3$

2.70 g (10.0 mmol) of **2** were dissolved in 15 mL of diethyl ether and cooled to -78 °C. 1/3 Equivalents of $InCl_3$ (0.73 g, 3.35 mmol) were dissolved in 15 mL of diethyl ether and the solution was added drop wise with stirring to the cooled solution. After warming up to ambient temperature the orange suspension was allowed to stir overnight, further. All volatiles were removed under oil pump vacuum. The residue was first extracted with 15 mL n-hexane, then with 15 mL toluene. Pale yellow crystals of **3** formed from the n-hexane-fraction at -30°C; yield 3.16 g (0.4 mmol, 43 %)



2 **3**

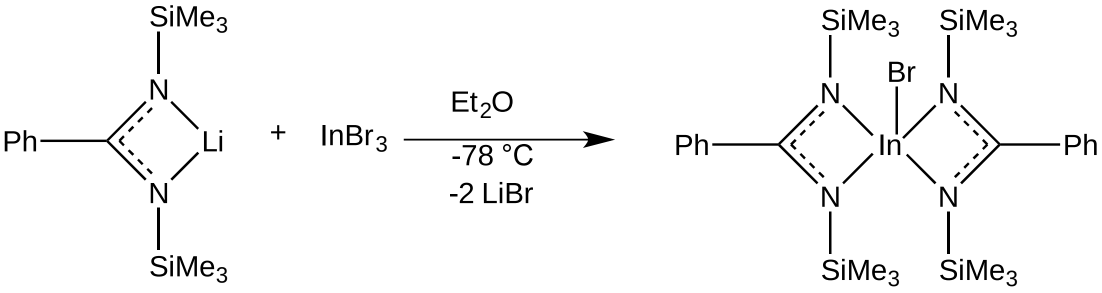
Elemental analysis for $C_{39}H_{69}InN_6Si_6$ (905.45 gmol^{-1}): calcd (%) C 50.60, H 7.57, N 9.57; found: C 50.17, H 6.76, N 10.97.

^{1}**H-NMR (400 MHz, C_6D_6)**: δ [ppm] = 7.47 (m, 6 H; *o*-Ph-*H*), 6.96 (m, 9 H; *m*-Ph-*H*/*p*-Ph-*H*), 0.15 (s, 54 H; SiMe$_3$)

^{13}**C NMR (100.56 MHz, C_6D_6)** δ = 181.3 (N*C*N), 141.5 (*ipso*-Ph-*C*), 128.3 (*p*-Ph-*C*), 127.7 (*m*-Ph-*C*), 126.2 (*o*-Ph-*C*), 2.9 (Si*Me*$_3$).

6.1.4 In[SiMe3NC(Ph)NSiMe3]2Br

2.70 g (10.0mmol) of **2** were dissolved in 15 mL of diethyl ether and cooled to -78 °C. 1.00 eq. (3.5 g, 10.05 mmol) of $InBr_3$ was dissolved in 15 mL of diethyl ether and the solution was added dropwise with stirring to the cooled solution. After warming up to ambient temperature the orange suspension was allowed to stir overnight, further. All volatiles were removed in vacuum. The white residue was first extracted with 15 mL n-hexane, then with 15 mL toluene. Pale yellow crystals of **4** were formed from the toluene-fraction at -35°C, yield 1.4 g (1.9 mmol, 15 %)



2 **4**

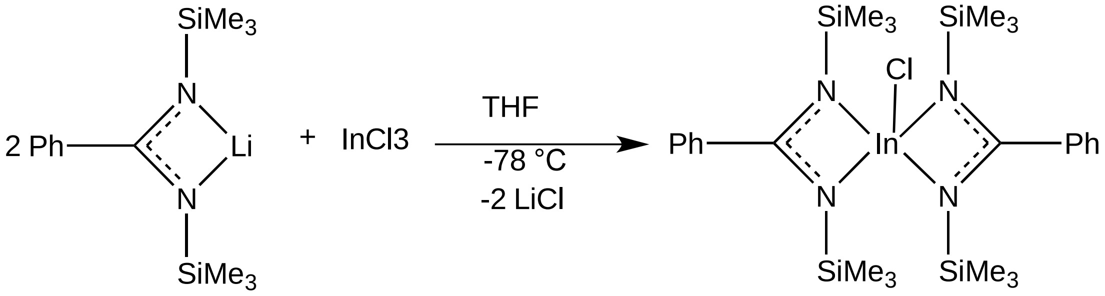
Elemental analysis for $C_{26}H_{46}BrInN_4Si_4$ (721.74 $gmol^{-1}$): calcd (%) C 31.79, H 4.72, N 5.70; found: C 32.80, H 4.89, N 6.15.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.36 (m, 4 H; *o*-Ph-*H*), 6.96 (m, 6 H; *m*-Ph-*H*/*p*-Ph-*H*), 0.12 (s, 36 H; $SiMe_3$)

^{13}C NMR (100.56 MHz, C_6D_6) δ = 181.3 (N*C*N), 141.5 (*ipso*-Ph-*C*), 128.2 (*p*-Ph-*C*), 127.7 (*m*-Ph-*C*), 127.0 (*o*-Ph-*C*), 2.9 (Si*Me*$_3$).

6.1.5 In[SiMe$_3$NC(Ph)NSiMe$_3$]$_2$Cl

2.70 g (10.mmol) of **2** were dissolved in 15 mL of diethyl ether and cooled to -78 °C. 0.5 equivalents (1.1 g, 5.04 mmol) of InCl$_3$ were dissolved in 15 mL of diethyl ether and the solution was added dropwise with stirring to the cooled solution. After warming up to ambient temperature the orange suspension was allowed to stir overnight, further. All volatiles were removed under vacuum. The white residue was first extracted with 15 mL n-hexane, then with 15 mL toluene and finally with 15 mLTHF. Pale yellow crystals of **5** were formed from the THF-fraction at -35°C, yield 1.5 g (2.2 mmol, 22.2 %)



2 **5**

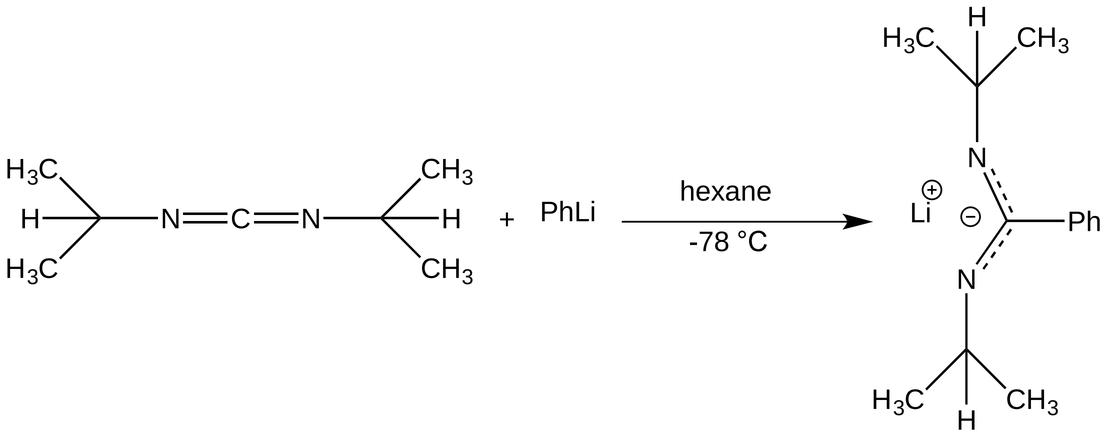
Elemental analysis calcd (%) for $C_{26}H_{46}ClInN_4Si_4$ (676.15 gmol^{-1}): C 36.70, H 5.45, N 6.58; found: C 36.59, H 5.44, N 5.82.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.13 – 7.12 (m, 4 H; *o*-Ph-*H*), 6.97- 6.95 (m, 6 H; *m*-Ph-*H*/*p*-Ph-*H*), 0.13 (s, 36 H; SiMe$_3$)

^{13}C NMR (100.56 MHz, C_6D_6) δ = 177.8 (N*C*N), 137.6 (*ipso*-Ph-*C*), 126.5 (*p*-Ph-*C*), 126.4 (*m*-Ph-*C*), 126.2 (*o*-Ph-*C*), 1.3 (Si*Me$_3$*).

6.1.6 $Li[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2)]$

1.26 g (10.0 mmol) of bis-2,6-diisopropylcarbodiimide were dissolved in 20 mL n-hexane in a schlenk flask and cooled to -78°C. 6. mL (10 mmol) of phenyl lithium (2.5 M in n-hexane) were added to the solution dropwise with stirring. After warming up to the ambient temperature, the white mixture was allowed to stir overnight, further. All volatile components were removed under vacuum and **6** was used for the next step without any work up.

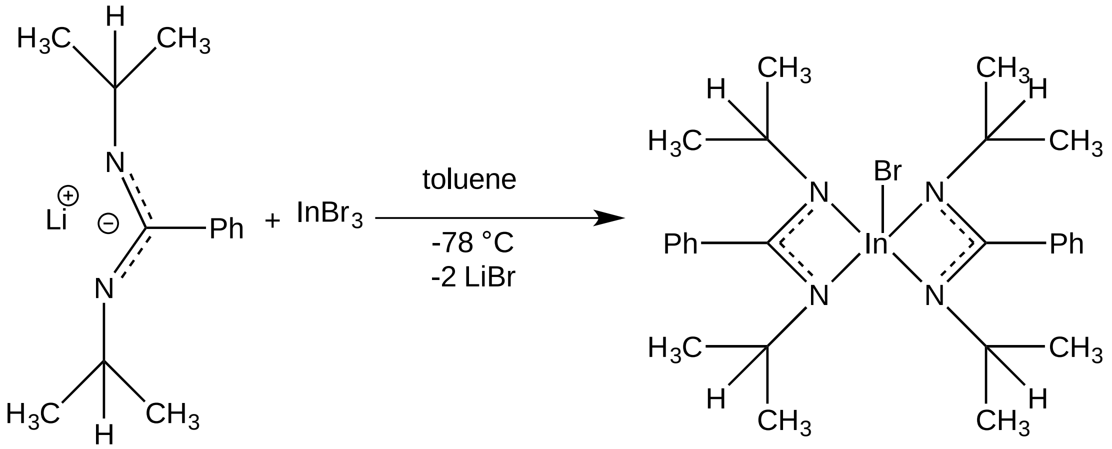


6

210 g/mol

6.1.7 $In[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2]_2Br$

2.1 g (10 mmol) of **6** were suspended in 15 mL toluene and cooled to -78 °C in a schlenk flask. The mixture of 3.5 g (1.00 eq., 10.05 mmol) of $InBr_3$ dissolved in 15 mL toluene was added dropwise with stirring to the cooled suspension. After warming up to ambient temperature the orange suspension was allowed to stir overnight, further. All volatiles were removed in vacuum. The white residue was first extracted with 15 mL n-hexane, then with 15 mL toluene. Pale yellow crystals of **7** were formed from the toluene-fraction at -35°C, yield 1.2 g (2.0 mmol, 20 %)



6 **7**

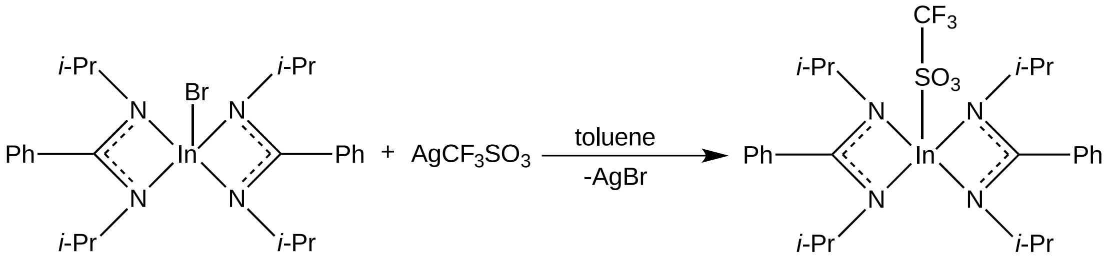
Elemental analysis for $C_{26}H_{40}BrInN_4$ (601.34 $gmol^{-1}$): calcd (%) C 51.76, H 6.68, N 9.29; found: C 49.81, H 6.06, N 8.52.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.26 – 7.22 (m, 4 H; *o*-Ph-*H*), 6.95- 6.64 (m, 6 H; *m*-Ph-*H*/*p*-Ph-*H*), 3.5 (sept, $^3J_{H-H}$= 6.6 Hz, 4H; C*H*Me2), 1.24 (d, $^3J_{H-H}$= 6.4 Hz, 24 H; CH(*CH_3*)2).

^{13}C NMR (100.56 MHz, C_6D_6) δ = 170.4 (N*C*N), 140.5 (*ipso*-Ph-*C*), 127.7 (*p*-Ph-*C*), 126.8 (*m*-Ph-*C*), 126.2 (*o*-Ph-*C*), 46.8 (*C*HMe2), 24.4 (CH*Me2*).

6.1.8 $\mathrm{In[(CH(CH_3)_2NC(Ph)N(CH(CH_3)_2]_2SO_3CF_3}$

1.3 mmol (0.78 g) of **7** were dissolved in 10 mL toluene. 1.3 mmol (0.33 g) silver trifluoromethanesulfonate were added to this solution at -78 °C. The flask was protected against light. The yellow suspension was allowed to warm up to room temperature and stir over night. All volatiles were removed from the grey-metallic suspension under vacuum. The residue was extracted with 15 mL THF. By keeping the reduced solution at -30 °C for some days the yellow crystals of **11** were obtained, yield 0.5 g (0.7 mmol, 54%).



7 **11**

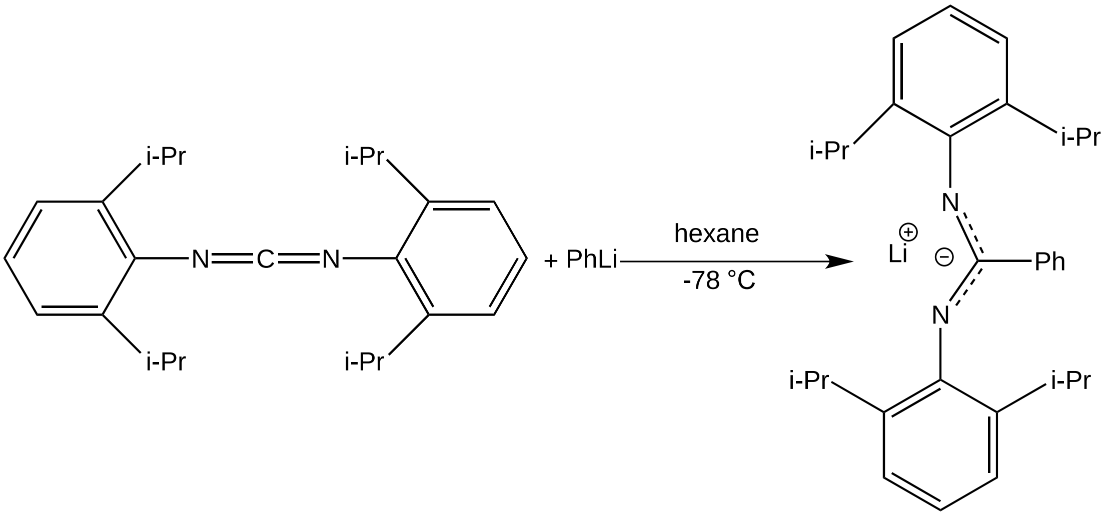
Elemental analysis for $C_{27}H_{38}F_3InN_4O_3S$ (685.19 gmol^{-1}): calcd (%) C 43.59, H 5.02, N 5.81; found: C 42.69, H 5.29, N 7.19.

^{1}H NMR (400 MHz, C_6D_6): δ [ppm] = 7.26 – 7.24(m, 4 H; *o*-Ph-*H*), 7.08- 7.07 (m, 6 H; *m*-APh-*H*/*p*-Ph-*H*), 3.7 (sept, $^3J_{H,H}$ = 6.4 H; C*H*Me$_2$), 1.25 (d, $^3J_{H,H}$= 6.3 Hz, 24 H; CH(CH_3)$_2$).

^{13}C NMR (100.56 MHz, C_6D_6) δ = 173.8 (N*C*N), 154.5 (*ipso*-Ph-*C*), 127.1 (*p*-Ph-*C*), 126.9 (*m*-Ph-*C*), 126.7 (*o*-Ph-*C*), 46.9 (*C*HMe$_2$), 24.6 (CH*Me$_2$*).

6.1.9 Li[(dipp)NC(Ph)N(dipp)]

1.82 g (5 mmol) of bis-2,6-diisopropylphenylcarbodiimide were dissolved in 20 mL of n-hexane in a schlenk flask and cooled to -78°C. 4.02 mL (5 mmol) phenyl lithium (2.5 M in n-hexane) were added dropwise to the solution with stirring. After warming up to the ambient temperature, the mixture was allowed to stir overnight, further. All volatile components were removed in vacuum. White-pale yellow powder of **8** was used for the next reaction without any work out.

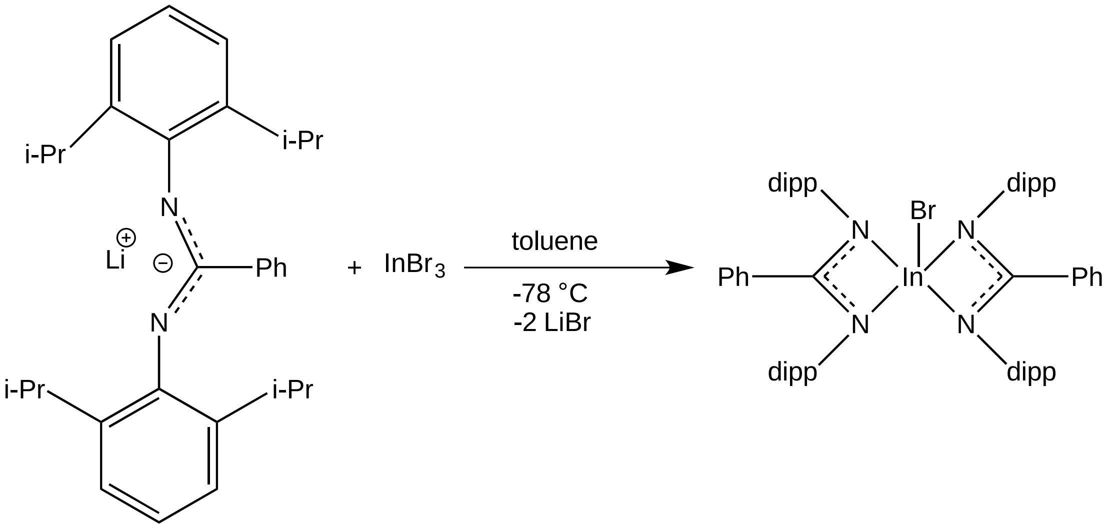


8

446.61 g/mol

6.1.10 In[(dipp)NC(Ph)N(dipp)]$_2$Br

2.23 g (5 mmol) of **8** were suspended in 15 mL toluene and cooled to -78 °C in a schlenk flask. The mixture of 1.78 g (1.00 eq., 5 mmol) of $InBr_3$ dissolved in 15 mL toluene were added dropwise with stirring. After warming up to ambient temperature the orange suspension was allowed to stir overnight. All volatiles were removed in vacuum. The yellow residue was first extracted with 15 mL n-hexane, then with 15 mL toluene. Pale yellow crystals of **9** were formed from the n-hexane-fraction at -35°C, yield 2.0 g (2.0 mmol, 41 %)



8 **9**

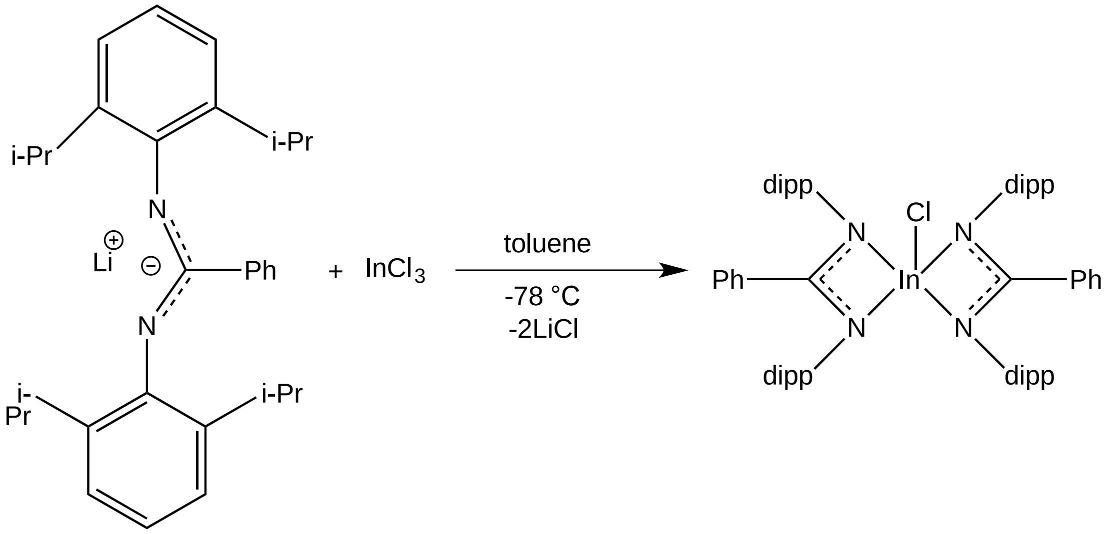
Elemental analysis for $C_{56}H_{73}BrInN_4$ (995.41 gmol^{-1}): calcd (%) C 69.20, H 7.49, N 5.21; found: C 68.77, H 8.22, N 4.98.

^{1}H-NMR (400 MHz, C_6D_6): δ = 7.69 (d, $^3J_{H-H}$ = 5.95 Hz, 2 H; p-C*H*(Ph)), 7.31 (m,8 H, *m*-CH(Ph)/*o*-CH(Ph)), 7.03-7.06 (m, $^3J_{H-H}$ = 7.8 Hz, 4 H; p-C*H*(dipp)), 6.94-6.92 (dd, $^3J_{H-H}$ = 7.7 Hz, 8 H; m-C*H*(dipp)/o-C*H*(dipp)), 3.40 (sept, $^3J_{H-H}$ =6.9 Hz, 8 H; C*H* Me$_2$), 1.39 (d, $^3J_{H-H}$ =6.7Hz, 24 H; CH*Me*), 0.95 (d, $^3J_{H-H}$ = 6.7 Hz, 24 H; CH*Me*).

^{13}C NMR (100.56 MHz, C$_6$D$_6$) δ = 170.8 (N*C*N), 151.7 (*ipso-C*), 143.8 (*C*-dipp), 138.0 (*C*-dipp), 134.3 (*C*-dipp), 128.3 (*p*-*C*(Ph)), 127.3 (*m*-*C*(Ph)), 126.6 (*o*-*C*(Ph)), 27,9 (*C*HMe2), 27.6 (*C*HMe2), 23.7 (CH*Me*$_2$), 23.4 (CH*Me*$_2$).

6.1.11 In[(dipp)NC(Ph)N(dipp)]$_2$Cl

2.7 g (6 mmol) of **8** were suspended in 15 mL of toluene and cooled to -78 °C in a schlenk flask. 1.35 g (6 mmol) of $InCl_3$ were dissolved in 15 mL toluene and added to the cooled solution dropwise with stirring. After warming up to the ambient temperature the orange suspension was allowed to stir overnight, further. All volatiles were removed in vacuum. The yellow residue was first extracted with 15 mL n-hexane, then with 15 mL toluene. Pale yellow crystals of **10** were formed from the n-hexane-fraction at -35°C, yield 0.9 g (0.9 mmol, 15 %)



8 **10**

Elemental analysis for $C_{62}H_{78}BrInN_4$ (1029.66 gmol^{-1}): calcd (%) C 72.19, H 7.82, N 5.43; found: C 71.99, H 7.56, N 5.52.

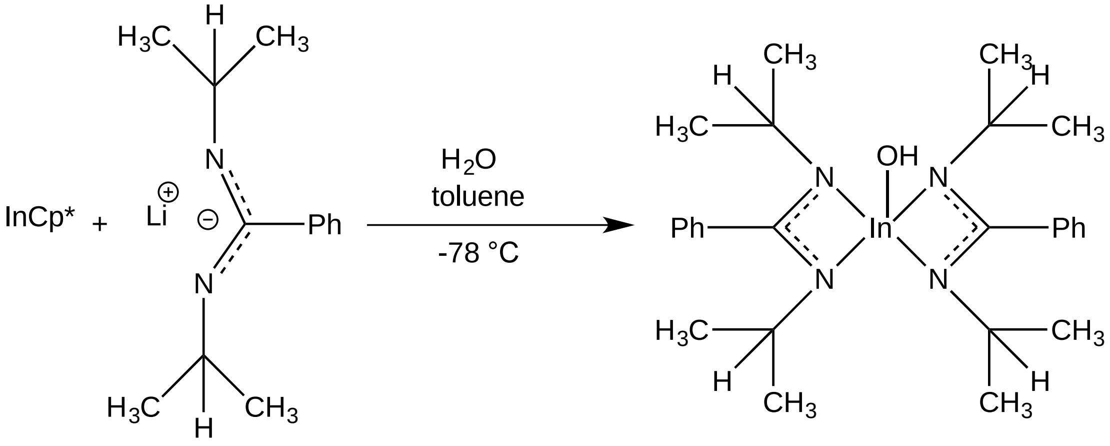
^{1}H-NMR (400 MHz, C_6D_6): δ = 7.68-7.29 (m, 10 H; C*H*(Ph)), 7.04-7.06 (m, $^3J_{H-H}$ = 8.3 Hz, 4 H; p-C*H*(dipp)), 6.95-6.69 (d, $^3J_{H-H}$ = 6.3 Hz, 8 H; m-C*H*(dipp)/o-C*H*(dipp)), 3.58 (sept, $^3J_{H-H}$ =7.7 Hz, 4 H; C*H* Me$_2$), 3.26 (sept, $^3J_{H-H}$ =6.8 Hz, 4 H; C*H* Me$_2$), 1.38 (d, $^3J_{H-H}$ =6.0Hz, 24 H; CH*Me*), 0.90

(d, $^{3}J_{H-H}$ = 6.9 Hz, 24 H; CH*Me*).

^{13}C NMR (100.56 MHz, C_6D_6) δ = 168.7 (N*C*N), 160.3 (*ipso*-*C*), 145.4 (*C*-dipp), 138.0 (*C*-dipp), 136.7 (*C*-dipp), 128.4 (*p*-*C*(Ph)), 128.0 (*m*-*C*(Ph)), 127.7 (*o*-*C*(Ph)), 27,9 (*C*HMe2), 27.6 (*C*HMe2), 24.0 (CHMe_2), 22.4 (CHMe_2).

6.1.12 In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$OH

5 mmol (1.25 g) InCp* was dissolved in 15 mL toluene. 5 mmol (1.05 g) [PhCN$_2$(dip)$_2$]Li was dissolved in 15 mmol toluene (pale yellow solution) and added to the InCp* solution by stirring at -78 °C. The suspension was allowed to warm up to the room temperature and stir over night, further. All volatiles were removed from the grey suspension. The residue was then extracted once with 15 mL n-hexane and once with 5 mL toluene. The solvents of both fractions were reduced and the remaining solution were kept at -35 °C for several months.



6

12

538.22 g/Mol

^{1}H NMR (400 MHz, C$_6$D$_6$): δ [ppm] = 7.26 – 7.22 (m, 4 H; *o*-Ph-*H*), 7.10- 7.04 (m, 6 H; *m*-Ph-*H*/*p*-Ph-*H*), 4.38 (s, 1H; O*H*), 3.5 (sept, $^3J_{H-H}$= 6.4 Hz 4H; C*H*Me$_2$), 1.33 (d, $^3J_{H-H}$= 6.3 Hz, 24 H; CH(*CH$_3$*)$_2$).

^{13}C NMR (100.56 MHz, C$_6$D$_6$) δ = 167.4 (NCN), 140.5 (*ipso*-Ph-*C*), 127.9 (*p*-Ph-*C*), 126.6 (*m*-Ph-*C*), 125.7 (*o*-Ph-*C*), 46.9 (*C*HMe$_2$), 24.3 (CH*Me$_2$*).

7 Literature

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8. Crystallographic appendix

Compound: In[SiMe$_3$NC(Ph)NSiMe$_3$]$_3$(3)

Summenformel	$C_{39}H_{69}InN_6Si_6$ (YRV67a)
Molare Masse [g/mol]	905.36
Kristallsystem	monoklin
Kristallgrößе [mm^3]	0.3 x 0.3 x 0.2
Temperature [K]	200(2)
Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	C 1/c
Zelldimension [pm]	a= 17.742(4) Å, b= 14.749 (3), c=39.506 (8) α= 90.00(0)°, β= 102.89(3)°, γ=90.00(0)°
V [Å^3]	10077.29 (387)
Z	8
ρ(calcd.)[g/cm^3]	835.802
μ[mm^{-1}]	0.643
F(000)	3824
2Θ$_{max}$[°]	28.13
Refl. gemessen	41154
Refl. unabhängig	23247
Refl. beobachtet	17244
Indexbereich h k l	-23 →23 -19 →19 -52 →52
Daten/Parameter/Restraints	17244/973/2
GOF	0.930
Final R [$I>2s(I)$]	0.0525
Final $w\,R_2$ [$I>2s(I)$]	0.1275
Final R [alle Daten]	0.0759
Final $w\,R_2$ [alle Daten]	0.1178
max/min Restelektronendichte [e/ Å^3]	0.816/-1.047

Compound: In[SiMe$_3$NC(Ph)NSiMe$_3$]$_2$Br (4)

Summenformel	C26H52BrInN4Si4 (YRV60)
Molare Masse [g/mol]	727.81
Kristallsystem	triklin
Kristallgrößе [mm^3]	0.37 x 0.30 x 0.15
Temperature [K]	200(2)

Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	$P\bar{1}$
Zelldimension [pm]	a= 12.161 (2), b= 13.014 (2), c=13.460 (3) α= 67.62(3)°, β= 75.13(3)°, γ=66.89(3)°
V [Å^3]	1797.26(83)
Z	2
ρ(calcd.)[g/cm^3]	1.34481
μ[mm^{-1}]	1.923
F(000)	752
$2\Theta_{max}$[°]	30.43
Refl. gemessen	21589
Refl. unabhängig	17488
Refl. beobachtet	11004
Indexbereich h	-17 → 17
k	-18 →18
l	-19 →19
Daten/Parameter/Restraints	17488/649/3
GOOF	0.676
Final *R* [*I>2s(I)*]	0.0426
Final wR_2 [*I>2s(I)*]	0.1007
Final *R* [alle Daten]	0.0796
Final wR_2 [alle Daten]	0.1205
max/min Restelektronendichte [e/ Å^3]	1.101/-1.475

Compound: $In[SiMe_3NC(Ph)NSiMe_3]_2Cl$ (5)

Summenformel	C26H46ClInN4Si4 (YRV28)
Molare Masse [g/mol]	677.3
Kristallsystem	monoklin
Kristallgröße [mm^3]	0.36 x 0.26 x 0.12
Temperature [K]	200(2)
Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	P 2_1/n
Zelldimension [pm]	a= 10.689 (2), b= 31.922 (6), c=11.526 (2) α= °, β= 116.48(3)°, γ= (3)°
V [Å^3]	3520.24(144)
Z	4

ρ(calcd.)[g/cm^3]	1.27788
μ[mm^{-1}]	0.904
F(000)	1408
2Θ$_{max}$[°]	30.546
Refl. gemessen	29179
Refl. unabhängig	9957
Refl. beobachtet	4802
Indexbereich h k l	-17 → 15 -45 →44 -16 →16
Daten/Parameter/Restraints	9957/338/0
GOOF	0.799
Final R [$I>2s(I)$]	0.0665
Final $w R_2$ [$I>2s(I)$]	0.1585
Final R [alle Daten]	0.1253
Final $w R_2$ [alle Daten]	0.1844
max/min Restelektronendichte [e/ Å^3]	1.719/-3.351

Compound: In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$Br (7)

Summenformel	C26H38BrInN4 (YRV132)
Molare Masse [g/mol]	601.33
Kristallsystem	triklin
Kristallgröβe [mm^3]	0.41 x 0.34 x 0.15
Temperature [K]	200(2)
Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	P1
Zelldimension [pm]	a= 10.144 (2), b= 10.670 (2), c=13.308 (4) α= 90.00(0)°, β= 95.7(3)°, γ=90.75(3)°
V [Å^3]	1425.82(52)
Z	2
ρ(calcd.)[g/cm^3]	1.40056
μ[mm^{-1}]	0.696
F(000)	612
2Θ$_{max}$[°]	30.51
Refl. gemessen	17201
Refl. unabhängig	7884

Refl. beobachtet	3822
Indexbereich h	-14 → 14
k	-14 →15
l	-18 →18
Daten/Parameter/Restraints	7884/298/0
GOOF	0.842
Final *R* [*I>2s(I)*]	0.662
Final *w* R_2 [*I>2s(I)*]	0.1785
Final *R* [alle Daten]	0.1276
Final *w* R_2 [alle Daten]	0.1497
max/min Restelektronendichte [e/ Å^3]	1.688/-2.096

Compound: In[(dipp)NC(Ph)N(dipp)]$_2$Br (9)

Summenformel	C62H78BrInN4 (YRV101)
Molare Masse [g/mol]	1074.01
Kristallsystem	monoklin
Kristallgröβe [mm^3]	0.34 x 0.26 x 0.20
Temperature [K]	200(2)
Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	C 1 2/c1
Zelldimension [pm]	a= 23.825 (5), b= 10.362 (2), c=26.225 (4) α= 90.00(0)°, β= 116.64(3)°, γ=90.00(0)°
V [Å^3]	5786.99(250)
Z	4
ρ(calcd.)[g/cm^3]	1.23265
μ[mm^{-1}]	1.138
F(000)	2248
2Θ_{max}[°]	30.54
Refl. gemessen	33082
Refl. unabhängig	8765
Refl. beobachtet	5086
Indexbereich h	-34 →34
k	-14 →14
l	-37 →37
Daten/Parameter/Restraints	8765/316/0
GOOF	0.844

Final *R* [*I>2s(I)*]	0.0416
Final *w* R_2 [*I>2s(I)*]	0.0845
Final *R* [alle Daten]	0.0877
Final *w* R_2 [alle Daten]	0.1000
max/min Restelektronendichte [e/ Å^3]	1.259/-1.611

Compound: In[(dipp)NC(Ph)N(dipp)]$_2$Cl (10)

Summenformel	C26H78ClInN4 (YRV95)
Molare Masse [g/mol]	1029.55
Kristallsystem	monoklin
Kristallgröβe [mm^3]	0.37 x 0.2 x 0.16
Temperature [K]	200(2)
Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	C 1/c1
Zelldimension [pm]	a= 23.927 (3), b= 10.3138 (13), c=26.1496(17) α= 90.00(=)°, β= 116.939(15)°, γ= 90.00(0)°
V [Å^3]	5752.92(133)
Z	4
ρ(calcd.)[g/cm^3]	1.18862
μ[mm^{-1}]	0.497
F(000)	2176
2Θ_{max}[°]	30.456
Refl. gemessen	33733
Refl. unabhängig	8697
Refl. beobachtet	6478
Indexbereich h k l	-34 → 34 -14 →14 -37 →35
Daten/Parameter/Restraints	8697/316/0
GOOF	0.966

Final R [$I>2s(I)$]	0.0645
Final $w R_2$ [$I>2s(I)$]	0.1520
Final R [alle Daten]	0.0855
Final $w R_2$ [alle Daten]	0.1621
max/min Restelektronendichte [e/ Å^3]	3.412/-1.519

Compound: In[(CH(CH$_3$)$_2$NC(Ph)N(CH(CH$_3$)$_2$]$_2$SO$_3$CF$_3$ (11)

Summenformel	C35H54F3InN4O5 (YRV136)
Molare Masse [g/mol]	814.7
Kristallsystem	monoklin
Kristallgröβe [mm^3]	0.520 x 0.380 x 0.202
Temperature [K]	200(2)
Wellenlänge	Mo Kα 0.71073 Å (Graphit Monochromator)
Raumgruppe	P 2$_1$/n
Zelldimension [pm]	a= 9.7436 (14), b= 14.206 (2), c=29.265 (4) α= 90.00(=)°, β= 97.25(2)°, γ= 90.00(0)°
V [Å^3]	4018.40(99)
Z	4
ρ(calcd.)[g/cm^3]	1.34656
μ[mm^{-1}]	0.696
F(000)	1696
$2\Theta_{max}$[°]	30.40
Refl. gemessen	34391
Refl. unabhängig	11072
Refl. beobachtet	5308
Indexbereich h k l	-13 → 13 -20 →20 -41 →41
Daten/Parameter/Restraints	11072/450/0
GOOF	0.886

Final R [$I>2s(I)$]	0.713
Final $w\ R_2$ [$I>2s(I)$]	0.1505
Final R [alle Daten]	0.1464
Final $w\ R_2$ [alle Daten]	0.1778
max/min Restelektronendichte [e/ Å^3]	1.697/-0.706

Eidesstattliche Versicherung gemäß § 8 der Promotionsordnung der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Universität Heidelberg

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Synthesis and Characterization of five-coordinated indium amidinates

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