Aminopyridinato-Ligand-Stabilized Lanthanoid Complexes: Synthesis, Reactivity, Ethylene and Isoprene Polymerization

DISSERTATION

Zur Erlangung des akademischen Grades eines
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Für meine Eltern
in Dankbarkeit

„Aller Anfang ist leicht, und die letzten Stufen werden am schwersten und seltensten erstiegen.“

Johann Wolfgang von Goethe

Abbreviations

Å	Ångström
ApH	aminopyridine
Ap*H	(2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine
br	broad
*i*Bu	*iso*-butyl
BuLi	*n*-butyllithium
°C	degree celsius
calcd	calculated
CCTP	coordinative chain transfer polymerization
Cp	cyclopentadienyl
δ	chemical shift (ppm)
d	doublet
equiv	equivalent
Et	ethyl
h	hours
J	coupling constant (Hz)
KKTP	koordinative Kettentransfer Polymerisation
Me	methyl
NMR	nuclear magnetic resonance
Ln	rare earth metal, Sc, Y
Ph	phenyl
ppm	parts per million
*i*Pr	*iso*-propyl
py	2-pyridyl
q	quartet
s	singlet
sept	septett
t	triplet
thf	tetrahydrofurane
TIBAO	tetraisobutylalumoxane

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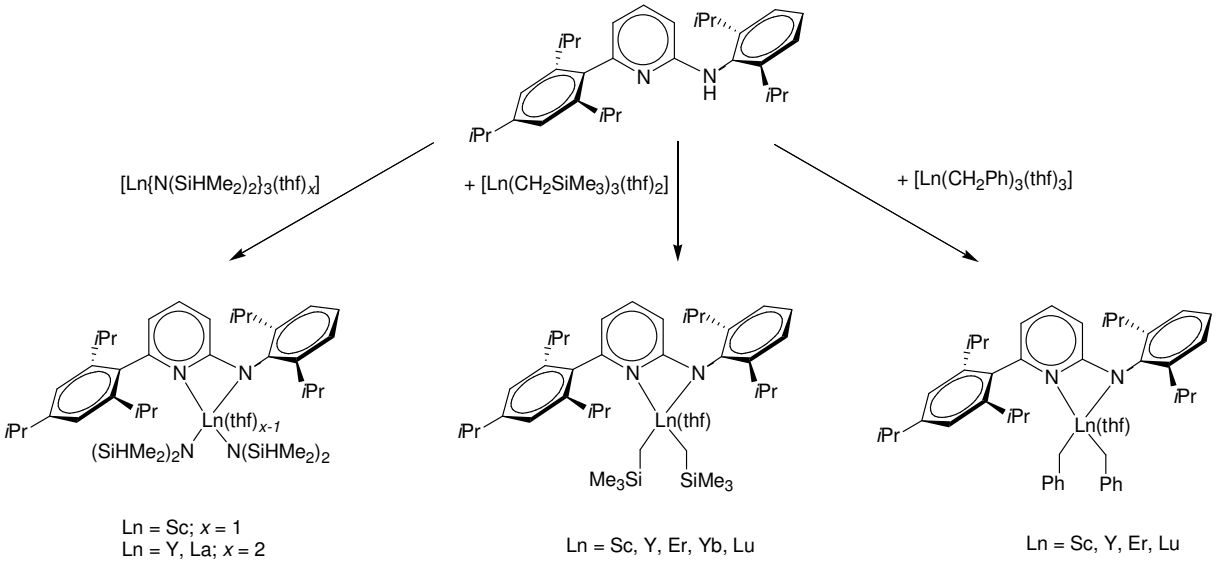
1. Zusammenfassung

Gegenstand der vorliegenden Arbeit war die Synthese und vollständige Charakterisierung Aminopyridinato-Ligand-stabilisierter Komplexe der Lanthanoide. Die Synthese der Lanthanoidkomplexe erfolgte mittels Amin- oder Alkaneliminierung. Die somit erhaltenen Verbindungen wurden hinsichtlich ihrer Eigenschaft als Precursoren für die Polymerisation von Ethylen oder Isopren und ihrer Fähigkeit Hydrido-Komplexe oder Kationen zu bilden untersucht.



Schema 1.1. Synthese der Aminopyridinato-Ligand-stabilisierten Lanthanoidkomplexe.

Frühere Arbeiten in der eigenen Arbeitsgruppe haben ergeben, dass Aminopyridinat-stabilisierte Organoyttrium-Kationen sehr hohe Aktivitäten in der Ethylenpolymerisation in Gegenwart von Aluminiumalkylen aufweisen. In dieser Arbeit konnte gezeigt werden, dass der dabei verwendete Precursorkomplex [Ap*Y(CH_2SiMe_3)$_2$(thf)] mit Phenylsilan oder Wasserstoff selektiv zu einem neuartigen dreikernigen Lanthanoid-Alkyl-Hydrido-Cluster reagiert. Das entsprechende Lutetiumderivat reagiert analog zur Yttriumverbindung. Die Lanthanoid-Alkyl-Hydrido-Cluster wurden mittels Einkristallröntgenstrukturanalyse charakterisiert und das Vorhandensein der Hydridliganden durch ^{1}H-NMR-Spektroskopie eindeutig nachgewiesen.

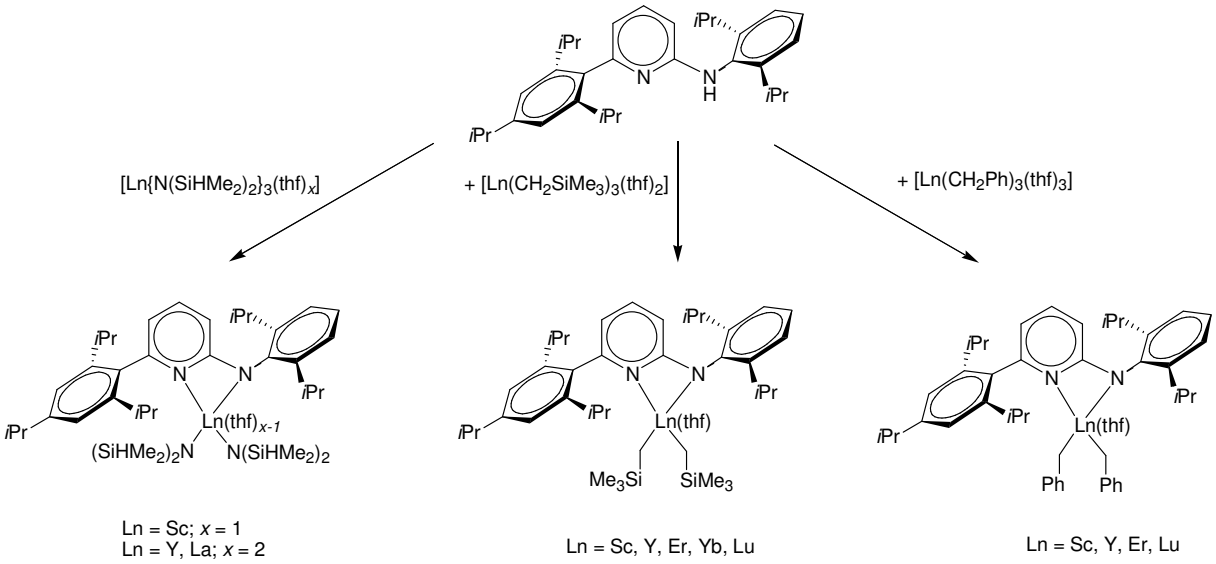
Dialkylkomplexe, stabilisiert durch Aminopyridinato-Liganden, reagieren mit Aniliniumborat unter Alkaneliminierung zu Organolanthanoid-Kationen. Diese wurden durch Stabilisierung mit THF isoliert und charakterisiert. Die Dibenzylkomplexe des Scandiums und Erbiums

wurden durch Einkristallstrukturanalysen charakterisiert. Die Dialkylkomplexes des Scandiums sind selektive und aktive Katalysatoren für die 3,4-selektive Polymerisation von Isopren nach Aktivierung mit Boraten. Dabei konnte, durch geeignete Polymerisationsbedingungen (Wahl des Cokatalysators, Polymerisationstemperatur), sogar isotaktisch angereichertes 3,4-Polyisopren erhalten werden. Das Aminopyridinat-stabilisierte Diamid des Scandiums polymerisiert Isopren in der Gegenwart von Aniliniumborat und Trialkylaluminiumverbindungen mit hohem *cis*-1,4-Anteil. Die Dialkylverbindungen des Yttrium, Erbium und Lutetium eignen sich ebenfalls als Prekatalysatoren für die Initiierung der Polymerisation von Isopren. Dabei nimmt der 3,4-Polyisoprenanteil mit der Zunahme des Ionenradius des dreiwertigen Lanthanoids ab, wobei sich der *cis*-1,4-Anteil erhöht. Durch die Zugabe von Aluminiumalkylen zu dem Katalysator/Cokatalysatorsystem wird eine teilweise drastische Veränderung der Mikrostruktur des erhaltenen Polyisoprens, in Abhängigkeit der Größe des Alkylliganden am Aluminiumatom und der Polymerisationstemperatur, beobachtet. Die hergestellten Aminopyridinato-Ligand-stabilisierten Bis(trimethylsilylmethyl)komplexe eignen sich auch als Prekatalysatoren (mit Außnahme der Ytterbiumverbindung) zur Polymerisation von Ethylen in Gegenwart von Ammoniumboraten und Aluminiumalkylen. Im Gegensatz zur Scandiumverbindung weisen die Verbindungen des Erbium, Lutetium und Yttrium Eigenschaften eines KKTP Katalysators auf. Die Aktivität ist dabei von der Größe des Lanthanoidions abhängig, die höchste Aktivität wird für das Organoerbium-Kation beobachtet.

Da die verwendeten Trialkyllanthanoidkomplexe extrem luft- und feuchtigkeitsempfindlich sowie thermisch instabil sind, wurde nach einem alternativen Zugang dafür gesucht. Dabei erwiesen sich Triamidkomplexe der Zusammensetung $[Ln\{N(SiHMe_2)_2\}_3(thf)_x]$ (x = 1, 2) als geeignete Ausgangsverbindungen, da sie einfach darzustellen beziehungsweise kommerziell erhältlich und thermisch stabil sind. Die Reaktion dieser Triamide mit den in dieser Arbeit verwendeten sterisch anspruchsvollen Aminopyridinliganden führt unter Amineliminierung zu den monosubstituierten Aminopyridinato-Komplexen. Diese eignen sich jedoch nicht als Ausgangsmaterialien für die Generierung von Katalysatoren für die koordinative Kettentransfer Polymerisation. NMR Untersuchungen zur Reaktivität gegenüber Triethylaluminium und Diisobutylaluminiumhydrid zeigten, dass ein irreversibler Transfer des Aminopyridinato-Liganden vom Lanthanoidmetal auf das Aluminiumatom stattfindet. Dieser Ligandentransfer verhindert den Einsatz dieser Amidkomplexe als Precursormaterialien für die KKTP, da sie während des Alkylierungsschrittes deaktiviert werden.

Summary

The aim of the present thesis was the synthesis and complete characterization of aminopyridinato-ligand-stabilized complexes of the lanthanoids. The lanthanoid complexes were synthesized by amine or alkane elimination. The thus obtained compounds were investigated in regard to their properties as precatalysts for the polymerization of ethylene or isoprene und their ability to form hydrido complexes or cations.



Schema 1.1. Synthesis of the aminopyridinato-ligand-stabilized lanthanoid complexes.

Previous investigations carried out in our group have shown that aminopyridinate-stabilized organoyttrium cations exhibit very high activity in the polymerization of ethylene in the presence of aluminium alkyl compounds. This work showed that the thereby used precursor [Ap*Y(CH_2SiMe_3)$_2$(thf)] can selectively react with phenylsilane or hydrogen to a novel trinuclear lanthanoid alkyl hydrido cluster. The corresponding lutetium derivative reacts analogous to the yttrium compound. The lanthanoid alkyl hydrido clusters were characterized by X-ray structure analyses, and the presence of the hydrid ligands were clearly proved by ^{1}H NMR spectroscopy.

Dialkyl complexes, stabilized by aminopyridinato ligands, react with anilinium borate to yield organolanthanoid cations after alkane elimination. They were isolated and characterized as thf adducts. The dibenzyl complexes of scandium and erbium were characterized by single crystal structure analyses. The dialkyl complexes of scandium are selective and active catalysts for the 3,4-selective polymerization of isoprene after activation with borates. We

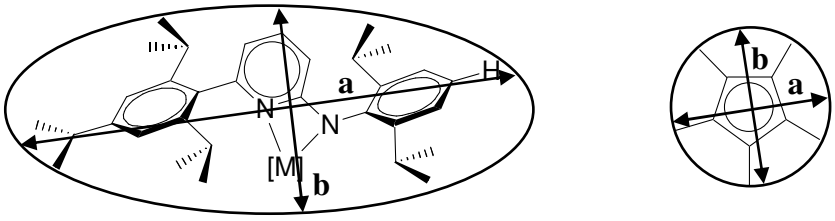
could even obtain isotactically enriched 3,4-polyisoprene through appropriate choice of the polymerization conditions (cocatalyst, polymerization temperature). The aminopyridinate-stabilized diamide of scandium can polymerize isoprene in the presence of anilinium borate and trialkylaluminium compounds, to obtain a polymer with a high *cis*-1,4-content. The dialkyl compounds of yttrium, erbium and lutetium are also suitable precatalysts for the initiation of the polymerization of isoprene. Although the 3,4-polyisoprene content decreased with an increased ionic radius of the trivalent lanthanoid, the *cis*-1,4-content increased. Addition of aluminium alkyl compounds leads to drastical changes of the microstructure of the obtained polymer which depends on the sterical demand of the alkyl ligand of the aluminium compound and the polymerization temperature. The synthesized aminopyridinato-ligand-stabilized bis(trimethylsilylmethyl) complexes are also suitable precatalysts (with exception of the ytterbium compound) for the polymerization of ethylene in the presence of ammonium borates and aluminium alkyl compounds. In contrast to the scandium derivative, the erbium, lutetium and yttrium compounds show characteristics of a CCTP catalyst. The activity is significantly dependent on the size of the lanthanoid ion, the highest activity was observed for the organoerbium cation.

Because of the extreme air and moisture sensitivity as well as the thermal instability of the used trialkyl lanthanoid complexes, we searched for an alternative starting material. Hence, the triamide complexes of the composition $[Ln\{N(SiHMe_2)_2\}_3(thf)_x]$ (x = 1, 2) proved to be suitable starting materials due to their facile synthesis and thermal stability. The reaction of these triamides with the bulky aminopyridines, used in this work, lead to the monosubstituted aminopyridinate-complexes after amine elimination. These are not suitable starting materials for the generation of catalysts for the coordinative chain transfer polymerization. NMR investigations of the reactivity with triethylaluminium and diisobutylaluminium revealed a fast and irreversible transfer of the aminopyridinato-ligand from the lanthanoid metal to the aluminium atom. This ligand transfer precludes the use of these amide complexes as suitable precursors for the CCTP, because of their deactivation during the alkylation step.

2. Introduction

The early work in organometallic chemistry of group 3 and the lanthanoids was strongly dominated by complexes supported by cyclopentadienyl ligands with various substituents and modifications.[1] Cyclopentadienyl organo rare earth metal complexes have become an interesting class of catalysts for a variety of transformations such as the hydroamination and olefin polymerization.[2] In order to develop new and more active catalysts, cyclopentadienyl-free complexes became of interest.[3]

One example for a cyclopentadienyl alternative ligand is the aminopyridinato ligand, which has extensively been used to stabilize lanthanoid complexes during the renaissance[4] of amido[5] metal chemistry. Aminopyridinato ligands are an important subclass of amido ligands and are derived from deprotonated 2-aminopyridines. The first strained η^2-coordinated aminopyridinato complex $[Ru(PhNpy)_2(PPh_3)_2]$ was published in 1984 by Cotton et al.,[6] the first early transition metal complex, a vanadium compound, was published by Gambarotta et al. in 1991,[7] and the first corresponding group 3 metal complex was described by Kempe et al. in 1997.[8] The aminopyridinato ligand used to stabilize this yttrium complex exhibits a relatively low steric demand. Thus, the chemistry of the corresponding rare earth complexes is limited, because of the preferred formation of ate-complexes.[4,8,9] In order to minimize this feature, bulkier aminopyridinato ligands were tailored by the introduction of 2,6-substituted (Me, *i*Pr) phenyl groups at the amido nitrogen atom and at the 6-position of the pyridine ring.



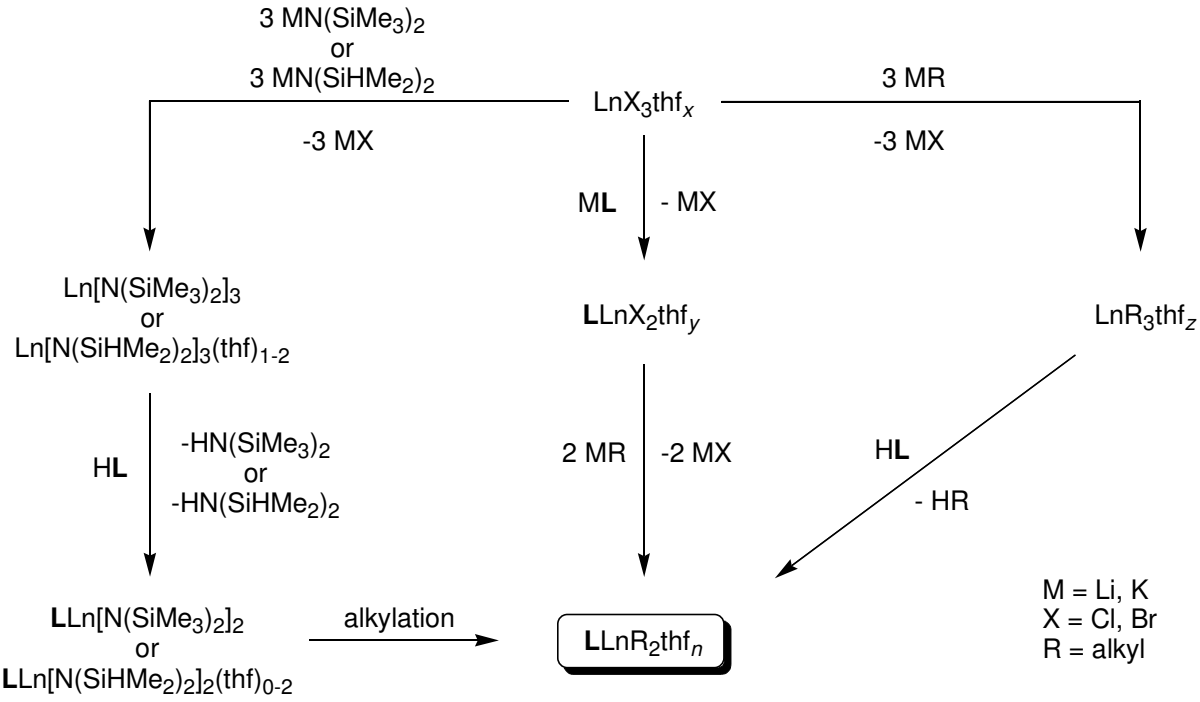
Scheme 2.1. Comparison of the steric demand of deprotonated Ap*H with Cp*.

The maximum atom-to-atom distances of the deprotonated bulky aminopyridinato ligand Ap*H (determined by X-ray structure analyses of the lithium salt)[10] are a = 15 Å and approximately perpendicular to it, b = 8 Å (Scheme 2.1). Comparison of these distances with those of the bulky, η^5-coordinated Cp* ligand,[11] which has distances of a = b = 6.2 Å for

both directions, indicates that deprotonated Ap*H would be a suitable ligand for metal ions with a huge coordination sphere, for example lanthanoids.

The synthesis of these bulky aminopyridines is achieved from 2,6-dibromopyridine by introduction of a substituted phenyl group via Kumada coupling and in a second step by the introduction of the aniline derivative in the 2-position of the pyridine ring via Pd-catalyzed aryl amination (Hartwig-Buchwald amination). This modular approach allows us to a fine tune of the steric bulk of the corresponding ligand. This approach in combination with the ionic radii of the group 3 or lanthanoid metals, which is a second tuneable parameter (the ionic radii for Ln^{3+} differ from Sc with 0.74 Å to La with 1.03 Å, for the coordination number 6),[12] is a powerful tool for finding the optimal ligand-metal ion combination, for homogeneous catalysis.

A very interesting group of compounds in terms of olefin polymerization are lanthanoid dialkyl complexes of the type [**L**LLnR$_2$thf$_x$], where **L** is a monoanionic ligand and R an alkyl ligand, because of their potential for the formation of lanthanoid alkyl cations.[3] Different established synthetic protocols for the synthesis of such complexes are shown in Scheme 2.2.



Scheme 2.2. Synthetic routes to [**L**LnR$_2$thf$_n$].

The most commonly used starting material for the preparation of dialkyl lanthanoid compounds are trivalent halides, which are often used as the thf adducts, due to an enhanced solubility in hydrocarbon solvents. Classical salt elimination reactions generate ligand-metal halide precursors. Standard alkylation procedures may subsequently convert these precursors

into the desired organometallic compounds. However, this route may cause problems, due to metal halide occlusion, formation of ate-complexes, and facile ligand redistribution.[13] These problems occur espacially often for the larger lanthanoid metals. Another method to introduce ligands is the amine elimination route which involves $Ln[N(SiMe_3)_2]_3$[14] or, especially for more bulky ligands, $Ln[N(SiHMe_2)_2]_3(thf)_{1\text{-}2}$[15] as precursors. However, this method is less successful than the amine elimination reactions of group 4 metal complexes, since the steric bulk of the used amido ligands ($-N(SiMe_3)_2$ and $-N(SiHMe_2)_2$) raises the barrier for the amine elimination. In addition, common routes for the conversion of the resulting metal amides into organometallic compounds are rare. Alkane elimination is an elegant route that allows to avoid the above mentioned problems. The latter directly affords a rare earth metal alkyl derivative which can be subsequently reacted with ligands that contain acidic protons (H**L**). The most common "homoleptic" metal alkyl species, $Ln(CH_2SiMe_3)_3(thf)_x$,[16] which have extensively been studied in alkane elimination reactions, were either generated in situ[17] or isolated (only available for the small and intermediate size metals, Sc,Y,Sm-Lu). Recent investigations afforded new types of homoleptic lanthanoid metal alkyl species, for example $Ln(CH_2Ph)_3(thf)_3$,[18] $Ln(AlMe_4)_3$,[19] $Ln[CH(SiMe_3)_2]_3$[20] or $Ln(o\text{-}CH_2C_6H_4NMe_2)_3$[21] which are available for the entire series and hence are very useful starting materials for alkane elimination reactions.

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3. Overview of Thesis Results

This thesis comprises four publications, which are presented in chapter 4 to 7.

3.1. Selective Assembly of Trinuclear Rare Earth Alkyl Hydrido Clusters Supported by Aminopyridinato Ligands

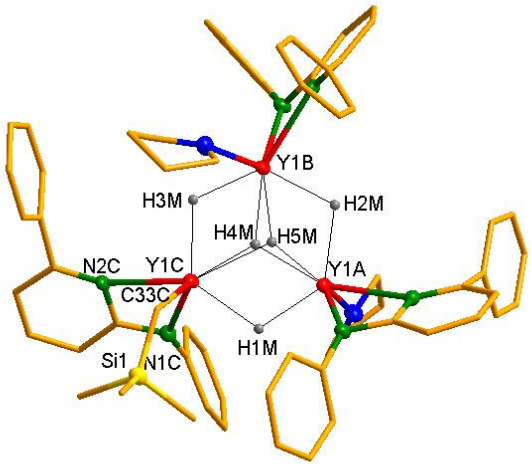

Figure 3.1. X-ray structure of the trinuclear rare earth alkyl hydrido cluster $[(Ap^*Y)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)_2(CH_2SiMe_3)(thf)_2]$.

Recently, our group reported on aminopyridinate dialkyl yttrium complexes which can be converted to the corresponding organoyttrium cations by abstraction of one of the two alkyl functions using ammonium borates. The reactions of the bis(alkyl) complexes $[Ap^*Ln(CH_2SiMe_3)_2(thf)]$ (Ln = Y, Lu) with both $PhSiH_3$ and H_2 result in selective assembly of the novel trinuclear rare earth alkyl hydrido clusters $[(Ap^*Ln)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)_2(CH_2SiMe_3)(thf)_2]$ (Figure 3.1). Both cluster compounds are single-component ethylene polymerization catalysts.

3.2. Synthesis and Structure of Aminopyridinate-Stabilized Yttrium and Lanthanum Amides and their Reactivity towards Alkylaluminium Compounds

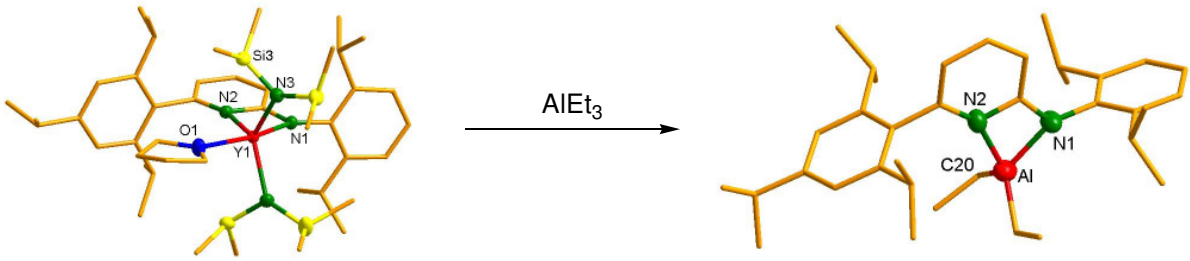

Figure 3.2. Aminopyridinato-ligand transfer from Y to Al.

Due to the very high moisture, air and temperature sensitivity of the aminopyridinate-stabilized alkyl complexes we became interested in the synthesis of aminopyridinate-stabilized (amido)lanthanoid complexes as suitable precursors for CCTP.

The bulky aminopyridines (2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine and [6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-(2,4,6-trimethyl-phenyl)-amine were introduced by amine elimination reaction with $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Y, La) to obtain the corresponding (mono)aminopyridinate complexes. Single crystal X-ray analyses were carried out for the yttrium derivatives. The complexes are not able to undergo coordinative chain transfer polymerization with ethylene in the presence of alkylaluminium compounds as the corresponding dialkyl complexes do. Investigations of the reactions of the lanthanoid aminopyridinate complexes with triethylaluminium or diisobutylaluminium hydride reveal a fast transfer of the aminopyridinato ligand to the aluminium atom (Figure 3.2). The products of this transfer reaction are aminopyridinate-stabilized dialkylaluminium compounds. One example of these aluminium complexes was characterized by X-ray crystal structure analysis.

3.3. Scandium Aminopyridinates: Synthesis, Structure and Isoprene Polymerization

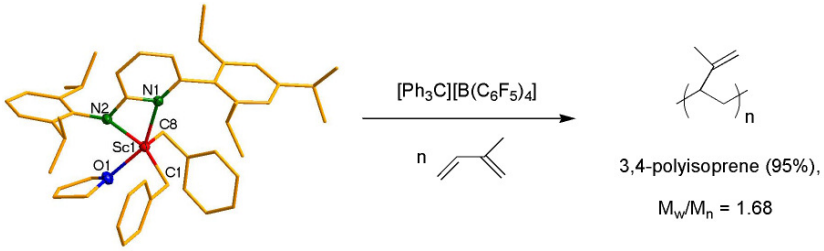

Figure 3.3. Aminopyridinate-stabilized scandium alkyl catalyzed 3,4-selective polymerization of isoprene.

Aminopyridinato-ligand-stabilized organoyttrium cations show high activity in the polymerization of ethylene, whereas Al-terminated polyethylene was produced with a molecular weight distribution of <1.1. Because of this feature, we became interested in the ability of such cations to polymerize dienes, especially isoprene. Alkane elimination reactions of $[Sc(CH_2SiMe_3)_3(thf)_2]$ or $[Sc(CH_2Ph)_3(thf)_3]$ with aminopyridines ((2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine, [6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-(2,4,6-trimethyl-phenyl)-amine and (2,6-diisopropyl-phenyl)-[6-(2,6-dimethyl-phenyl)-pyridin-2-yl]-amine) led to selective formation of dialkyl complexes of scandium stabilized by one aminopyridinato ligand. The reaction of these compounds with anilinium borate leads to the elimination of one of the two alkyl functions and affords organoscandium cations. The amine elimination reaction of $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ with the aminopyridine Ap*H yields the corresponding mono(aminopyridinate) complex. Single-crystal X- ray analyses were carried out for the compounds $[Ap^*Sc(CH_2Ph)_2(thf)]$, $[Ap^*Sc(CH_2Ph)(thf)_3][B(C_6H_5)_4]$ and $[Ap^*Sc\{N(SiHMe_2)_2\}_2]$. The aminopyridinate-stabilized scandium dialkyles $[ApScR_2(thf)]$ (R = CH_2SiMe_3, CH_2Ph) are initiators for the controlled 3,4-selective isoprene polymerization after activation with perfluorinated tetraphenyl borates. Variation of the polymerization temperature as well as the addition of different alkylaluminium compounds influence the microstructure of the obtained polymer. Bis(dimethylsilyl)amides of scandium polymerize isoprene in the presence of anilinium borate and alkylaluminium compounds with high *cis*-1,4-selectivity.

3.4. Aminopyridinate-Stabilized Lanthanoid Complexes: Synthesis, Structure and Polymerization of Ethylene and Isoprene

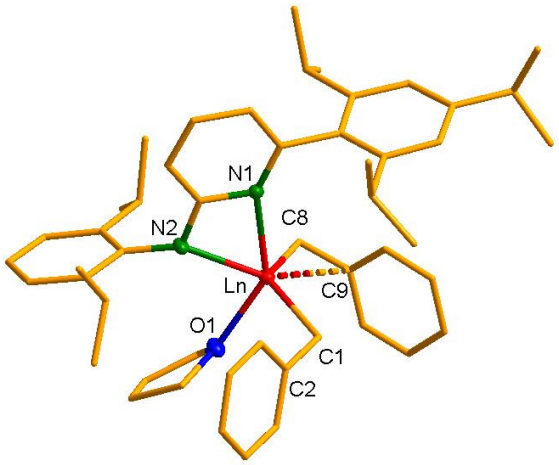

Figure 3.4. X-ray structure of the dibenzyl complexes $[Ap^*Ln(CH_2Ph)_2thf]$, Ln = Y, Er, Lu.

Our next goal was to investigate the influence of the lanthanoid metal ion size on the activity and selectivity of the polymerization catalysis of ethylene and isoprene. A series of aminopyridinate-stabilized lanthanoid dialkyl complexes has been synthesized and characterized. The complexes were prepared by alkane elimination reacting $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Er, Yb, Lu) or $[Ln(CH_2Ph)_3(thf)_3]$ (Ln = Y, Er, Lu) with one equivalent of the bulky aminopyridine (2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine. Single crystal X-ray analyses were carried out for all of the benzyl derivatives (Figure 3.4). The reaction of these compounds with anilinium borate leads to the elimination of one of the two alkyl functions and affords organolanthanoid cations. The aminopyridinate-stabilized lanthanoid dialkyles can initiate the polymerization of isoprene after activation with perfluorinated tetraphenyl borates. The obtained polymers have a 3,4-content of 60 % to 95 %. The metal ion size as well as the addition of aluminium alkyl compounds influence the microstructure of the obtained polymer. Aminopyridinate-stabilized organolanthanoid cations of Sc, Lu, Er and Y can polymerize ethylene in the presence of small amounts of aluminium alkyl compounds. The Lu, Er and Y complexes act as a CCTP catalyst and the erbium compound exhibits the highest activity.

3.5. Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and are published, accepted or to be submitted as indicated below. In the following, the contributions of all the co-authors to the different publications are specified. The asterisk denotes the corresponding author.

Chapter 4

This work is published in *Organometallics* **2008**, *27*, 2905-2907 with the title

"Selective Assembly of Trinuclear Rare Earth Alkyl Hydrido Clusters Supported by Aminopyridinato Ligands"

Dmitrii M. Lyubov, Christian Döring, Georgii K. Fukin, Anton V. Cherkasov, Andrei S. Shavyrin, Rhett Kempe*, and Alexander A. Trifonov*

Dmitrii Lyubov and I synthesized and characterized all of the compounds. Two of the X-ray structure analyses, included in this work, were done by me, and the other two were done by Georgii Fukin. Anton Cherkasov and Andrei Shavyrin did the ethylene polymerization experiments. The publication was written by Alexander Trifonov. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 5

This work is published in *Eur. J. Inorg. Chem.* **2009**, 412-418 with the title
"Synthesis and Structure of Aminopyridinate-Stabilized Yttrium and Lanthanum Amides and their Reactivity towards Alkylaluminium Compounds"
C. Döring, R. Kempe*

I have synthesized and characterized all of the compounds presented in this work and the publication was written by me. Rhett Kempe supervised this work and was involved in scientific discussions, comments and correction of the manuscript.

Chapter 6

This work is published in *Eur. J. Inorg. Chem.* **2009**, 4255-4264 with the title
„Scandium Aminopyridinates: Synthesis, Structure and Isoprene Polymerization"
Christian Döring, Winfried P. Kretschmer, Tobias Bauer, Rhett Kempe*

I have synthesized and characterized all of the compounds presented in this work and the publication was written by me. Tobias Bauer helped with the development of the polymerization protocol during his lab courses. Winfried Kretschmer and Rhett Kempe were involved in scientific discussions, comments and correction of the manuscript.

Chapter 7

This work is to be submitted with the title
„Aminopyridinate-Stabilized Lanthanoid Complexes: Synthesis, Structure and Polymerization of Ethylene and Isoprene"

Christian Döring, Winfried P. Kretschmer, Rhett Kempe*

I have synthesized and characterized all of the compounds presented in this work and the publication was written by me. I also did the isoprene polymerization experiments and analyses; Winfried Kretschmer did the ethylene polymerization experiments and analyses. Rhett Kempe were involved in scientific discussions, comments and correction of the manuscript.

4. Selective Assembly of Trinuclear Rare Earth Alkyl Hydrido Clusters Supported by Aminopyridinato Ligands

Dmitrii M. Lyubov,[a] Christian Döring,[b] Georgii K. Fukin,[a] Anton V. Cherkasov,[a] Andrei V. Shavyrin,[a] Rhett Kempe,*[b] and Alexander A. Trifonov*[a]

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Published in: *Organometallics* **2008**, *27*, 2905-2907.

Abstract: The reactions of the bis(alkyl) complexes [Ap*Ln(CH_2SiMe_3)$_2$(thf)] (Ln = Y, Lu) with both $PhSiH_3$ and H_2 result in selective assembly of the novel trinuclear rare earth alkyl hydrido clusters [(Ap*Ln)$_3$(μ_2-H)$_3$(μ_3-H)$_2$(CH_2SiMe_3)(thf)$_2$]. Both cluster compounds are single-component ethylene polymerization catalysts.

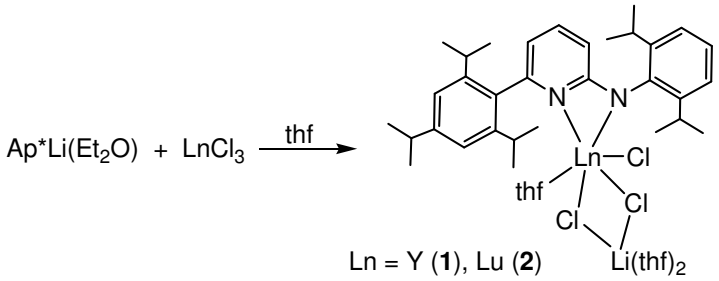
4.1. Introduction

Rare earth-metals hydrides possess an intriguing variety of unique structural and chemical properties.[1] The rapid development of this area, stimulated by promising catalytic activity of hydrido complexes, has resulted in considerably contributons to organolanthanoid chemistry.[2] Until recently rare earth-metals hydrides were represented exclusively by sandwich-[1] and half-sandwich-type ("constrained geometry")[3] monohydride, and very few classes of their non-cyclopentadienyl analogues are known.[4] Assembly of the anionic trinuclear tetrahydride lanthanoid species {[Cp_2LnH]$_3$H}{Li(thf)$_4$} was reported by Evans in the early 1980s.[1b-d] The first „mono(cyclopentadienyl) dihydrido" complexes were published in 2001, and their stoichiometric and catalytic chemistry was developed by Hou and co-workers.[5] The synthesis of rare earth polyhydrido species in coordination environments alternative to that of cyclopentadienyl still remains a challenge.[4] Sterically demanding amidopyridinato ligands[6] were successfully used as a suitable coordination environment for

stabilization of monomeric lanthanoid species, and our work has been aimed at the synthesis of related polyhydrido complexes. Herein we report on the selective formation, structure, and properties of trinuclear rare earth alkyl hydrido clusters.

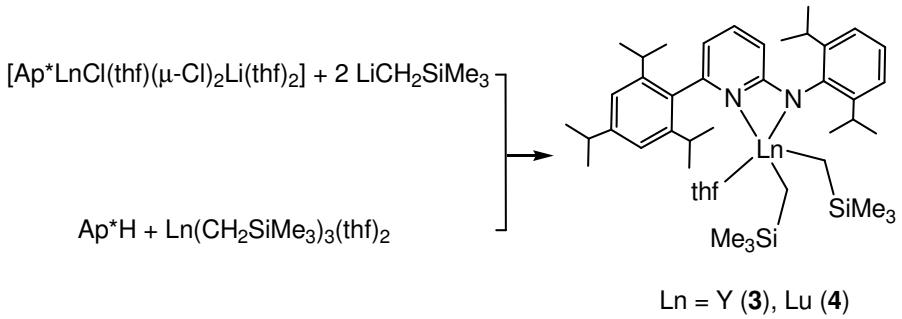
4.2. Results and Disscussion

Bulky (2,6-diisopropylphenyl)[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine (Ap*-H) was used as the ligand precursor for the preparation of the aminopyridinate dichloride, dialkyl, and alkyl hydrido complexes of yttrium and lutetium. Reactions of anhydrous $LnCl_3$ (Ln = Y, Lu) with an equimolar amount of $Ap^*Li(Et_2O)$[6b] in thf at 20 °C afforded the ate-complexes $[Ap^*LnCl(thf)(\mu\text{-}Cl)_2Li(thf)_2]$ (Ln = Y (**1**), Lu (**2**)) (Scheme 1), which were isolated after recrystallization from thf-hexane mixtures as pale yellow crystals in 78 and 85 % yields, respectively. Complex **1** has been characterized by X-ray diffraction study, which revealed its monomeric structure (see the Supporting Information).



Scheme 1. Synthesis of **1** and **2**.

Alkylation of complexes **1** and **2** with 2 equivalents of $LiCH_2SiMe_3$ in hexane at 0ºC allowed the synthesis of the salt-free dialkyl complexes $[Ap^*Ln(CH_2SiMe_3)_2(thf)]$ (Ln = Y (**3**), Lu (**4**)), which were obtained after recrystallization from pentane (**3**) or hexane (**4**) at -20ºC in 68 and 75% yields, respectively (Scheme 2). Complexes **3**[6c] and **4** were also synthesized through alkane elimination from trialkyl complexes and parent aminopyridine in hexane at 0ºC.



Scheme 2. Synthesis of **3** and **4**.

Crystallization of **3** and **4** by slow cooling of their concentrated pentane or hexane solutions to -20 ºC resulted in single crystals of solvates containing one molecule of solvent per one molecule of complex. X-ray crystal structure investigations have revealed that **3** and **4** are isostructural monomeric complexes (Figure 1). The coordination sphere of the metal atom consists of two nitrogen atoms of the bidentate aminopyridinato ligand, two carbon atoms of the alkyl groups and one oxygen atom of the thf molecule, resulting in a formal coordination number 5.

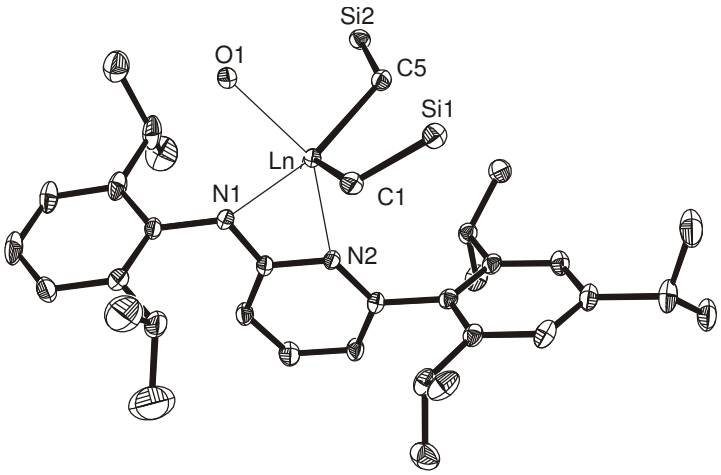
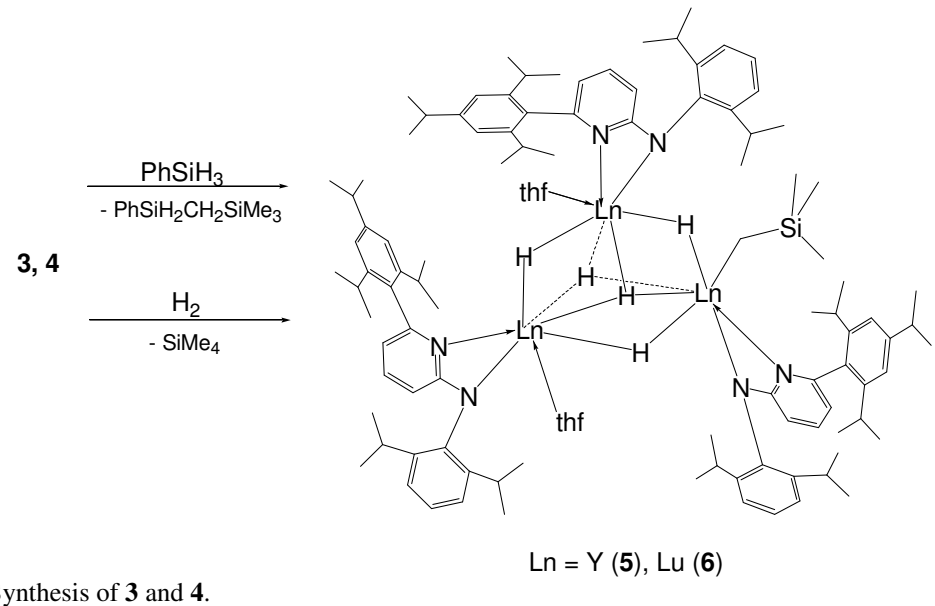


Figure 1. ORTEP drawing of **3** and **4** with 30% thermal ellipsoids. The Me groups in Me_3Si and CH_2 groups of thf are omitted. Selected bond lengths (Å) and angles (deg): for **3**, M-N(1) 2.316(4), M-N(2) 2.415(4), M-C(1) 2.370(5), M-C(5) 2.383(5), M-O 2.337(3), C-Ln-C 113.20(19), N-Ln-N 57.33(14); for **4**: M-N(1) 2.272(2), M-N(2) 2.371(2), M-C(1) 2.320(3), M-C(5) 2.332(3), M-O 2.2907(19), C-Ln-C 113.10(9), N-Ln-N 58.44(7).

The Y-C bond lengths in complex **3** are slightly longer compared to the appropriate distances in five-coordinated dialkyl yttrium compounds[7a-c] and are very close to the values reported for a related five-coordinated complex supported by a bulky amidinate ligand (2.374(4), 2.384(4) Å).[7d] In complex **4**, which is a rather rare example of a five-coordinated dialkyl lutetium complex, the Lu-C bond lengths are close to the distances previously reported for an analogue containing an anilido-pyridine-imine ligand (2.329(6), 2.349(6) Å).[7e] Complex **4**

despite the low coordination number of its central metal atom, is surprisingly stable at room temperature in C_6D_6 solution: no evidence of decomposition has been observed over 1 month. The stability of complex **3** is somewhat lower: under the similar conditions over 1 week, ~10% of the compound was decomposed. In the ^1H NMR spectrum of complex **4** at 20°C the hydrogen atoms of methylene groups attached to the lutetium atom appear as a singlet at -0.63 ppm; in the $^{13}C\{^1H\}$ NMR spectrum the appropriate carbons give rise to a singlet at 46.1 ppm. The most common synthetic route to lanthanoid hydrido complexes is σ-bond metathesis reaction of parent alkyls under treatment with dihydrogen[2c,f] or phenylsilane.[8] Hou and co-workers have demonstrated that hydrogenolysis of the cyclopentadienyl-supported dialkyl complexes $Cp'Ln(CH_2SiMe_3)_2(thf)$ ($Cp' = C_5Me_4SiMe_3$, Ln = Sc, Y, Gd, Dy, Ho, Er, Tm) affords the tetranuclear polyhydrido clusters $[Cp'Ln(\mu\text{-}H)_2]_4(thf)_n$, while the reaction with $PhSiH_3$ in the case of lutetium results in the formation of the dimeric alkyl-hydrido complex $[Cp'Lu(\mu\text{-}H)(CH_2SiMe_3)(thf)]_2$.[5] We have found that the reactions of **3** and **4** with both $PhSiH_3$ (1:2 molar ratio, 0°C) and H_2 (5 atm., 15°C, 24 h) smoothly occur in hexane under the aforementioned conditions and result in formation of unusual trinuclear alkyl hydrido clusters $[(Ap^*Ln)_3(\mu_2\text{-}H)_3(\mu_3\text{-}H)_2(CH_2SiMe_3)(thf)_2]$ (Ln = Y (**5**), Lu (**6**)) which were isolated after recrystallization from hexane at -20°C in 58 and 64 % yields, respectively (Scheme 3). Surprisingly, all attempts to remove the remaining alkyl group and to obtain polyhydrido clusters consisting of Ap^*LnH_2 units failed: the use of a 10-fold molar excess of $PhSiH_3$ or an increase in the reaction time with H_2 afforded only complexes **5** and **6**. Until recently very few examples of dimeric alkyl hydrido rare earth complexes have been described[5c,8,9] and to the best of our knowledge complexes **5** and **6** present the first examples of alkyl hydrido clusters.



Ln = Y (**5**), Lu (**6**)

Scheme 3. Synthesis of **3** and **4**.

Complexes **5** and **6** crystallize from hexane as solvates with one molecule of the solvent per unit. Exposure of complexes **5** and **6** at room temperature to dynamic vacuum (1 h) allowed us to remove hexane and to obtain nonsolvated compounds. Complexes **5** and **6** are extremely air and moisture sensitive crystalline solids; they are highly soluble in hexane and pentane. Complexes **5** and **6** can be kept in the solid state or in C_6D_6 solutions under dry argon or in sealed evacuated tubes at 20°C for several weeks without decomposition. Clear yellow single-crystal samples of **5** suitable for an X-ray crystal structure determination were obtained by slowly cooling its hexane solution to -20°C. X-ray single-crystal structure analysis has shown that **5** adopts a trimeric structure (Figure 2), where three Ap*Y fragments are bound by three μ_2-H and two μ_3-H ligands, while the alkyl group remains terminal. The coordination sphere of two yttrium atoms is determined by two nitrogen atoms of Ap* ligands, four hydrido ligands, and the oxygen atom of the coordinated thf molecule. In the coordination environment of the third yttrium atom there is no thf molecule, but it is covalently bound to the CH_2SiMe_3 group. The hexanuclear Y_3H_3 core is nearly planar (the maximum deviation from the Y_3H_3 plane is 0.132 Å), and two remaining hydrogen ligands are situated above and under this plane (1.023, 1.089 Å). The Y-(μ_2-H) distances are 2.08-2.16 Å, whereas the Y-(μ_3-H) distances are in the range of 2.19-2.42 Å. The Y-Y distances in complex **5** (3.5158(4), 3.4408(4), and 3.5058(4) Å) are noticeably shorter compared to the related distances in dimeric hydrides supported by bulky guanidinate ligands (3.6522(5)[10] and 3.6825(5) Å[4b]). The Y-C bond in **5** (2.402(5) Å) is slightly elongated compared to that in the starting dialkyl derivative **3**.

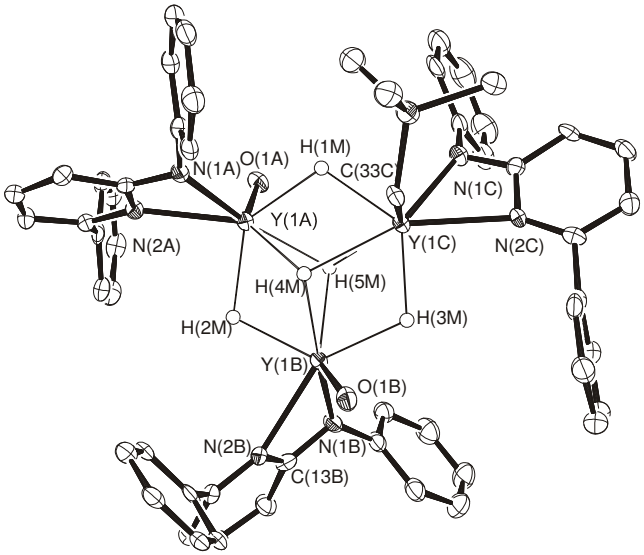


Figure 2. ORTEP drawing of **5** with 30% thermal ellipsoids. The *i*Pr groups and CH_2 groups of THF are omitted. Selected bond lengths (Å) and angles (deg): Y(1A)-N(1A) 2.323(2), Y(1A)-O(1A) 2.3496(19), Y(1A)-N(2A)

2.459(2), Y(1A)-Y(1B) 3.4408(4), Y(1A)-Y(1C) 3.5158(4), Y(1B)-N(1B) 2.307(2), Y(1B)-O(1B) 2.3510(19), Y(1B)-N(2B) 2.477(2), Y(1B)-Y(1C) 3.5058(4), Y(1C)-N(1C) 2.331(2), Y(1C)-C(33C) 2.402(3), Y(1C)-N(2C) 2.503(2), Y(1B)-Y(1A)-Y(1C) 60.512(8), N(1A)-Y(1A)-N(2A) 56.70(8), N(1B)-Y(1B)-N(2B) 56.64(7), N(1C)-Y(1C)-N(2C) 56.40(7).

The Ap* ligands appear as complex sets of signals in the ^{1}H NMR spectra (C_7D_8, -80 to -60ºC); however, the fact that the para protons of the pyridyl fragments give rise to three signals (**5**, 6.67, 6.78, and 6.83 ppm (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz); **6**, 6.62, 6.73, and 6.78 ppm (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.2 Hz)) reflects that their nonequivalence resulted from the unsymmetric structures of **5** and **6**. Three slightly broadened singlets (9.08, 12.25, and 12.37 ppm) with an integral intensity ratio 3:1:1 in the ^{1}H NMR spectrum of **6** correspond to the hydrido ligands. Apparently the signal at 9.08 ppm is due to μ_2-bridging ligands, while the signals at 12.25 and 12.37 ppm correspond to the μ_3-hydrido ligands situated in the apical positions of the trigonal bipyramid $Lu_3(\mu_3\text{-}H)_2$. The signals of the hydrido ligands of **6** are substantially shifted to the low field compared to the positions of respective signals of the reported cyclopentadienyl polyhydrido clusters (8.81 ppm),[5c] which corresponds to the tendency observed in the series of yttrium hydrides supported by cyclopentadienyl, cyclopentadienylamido, amidinate, and guanidinate ligands.[4b] In the ^{1}H NMR spectra of **5** the μ_2-bridging hydrido ligands appear as a triplet of doublets at 5.66 ppm with intensity corresponding to three protons. The multiplicity of this signal results from the coupling of each hydrido ligand with two neighbouring yttrium nuclei ($^1J_{YH}$ = 20.8 Hz) and with the third yttrium atom ($^1J_{YH}$ = 5.8 Hz) situated across the planar Y_3H_3 core. Unfortunately, the signals corresponding to the μ_3-hydrido ligands cannot be attributed unambiguously, since they overlap with signals of aromatic protons. Nevertheless, the existence of the cross-peaks in the COSY spectrum of **5** between the triplet of doublets at 5.66 ppm and the multiplet between 6.9 and 7.3 ppm gives evidence of the location of these signals in the area 6.9-7.3 ppm. The protons of the methylene group attached to the metal atom are nonequivalent in both **5** and **6** and appear in the ^{1}H NMR spectra at 293 K as a set of two doublets (at -1.10 and -0.03 ppm ($^2J_{HH}$ = 9.0 Hz) for **5** and at -1.35 and -0.42 ($^2J_{HH}$ = 9.7 Hz) for **6**). Thus, the ^{1}H NMR spectra of **5** and **6** prove that the trimeric structures of these compounds are retained in solutions in noncoordinating solvents.

Complexes **5** and **6** catalyze ethylene polymerization (20ºC, ethylene pressure 0.5 atm) but are inactive in styrene polymerization. The ethylene polymerization activity of complex **5** was found to be 560 g mmol^{-1} bar^{-1} h^{-1}, but the catalyst was deactivated in 3 h. The lutetium

complex **6** was less active (168 g $mmol^{-1}$ bar^{-1} h^{-1}) but did not demonstrate loss of the reaction rate over 1 day.

4.3. Conclusion

In summary, it was found that the reactions of dialkyl complexes [Ap*Ln(CH_2SiMe_3)$_2$(thf)] (Ln = Y, Lu) with both $PhSiH_3$ and H_2 result in selective assembly of the novel trinuclear rare earth alkyl hydrido clusters [(Ap*Ln)$_3$(μ_2-H)$_3$(μ_3-H)$_2$(CH_2SiMe_3)(thf)$_2$]. The yttrium complex has been structurally characterized. Both compounds show moderate activity in ethylene polymerization. Further studies on the synthesis and reactivity of this novel family of alkyl hydrido clusters are currently in progress.

4.4. Acknowledgment

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Supporting Information Available: Text, tables, figures, and CIF files giving detailed information on the synthesis and characterization of the lanthanoid complexes described here and crystallographic details of the structures determined by X-ray crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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4.6. Supporting Information

General remarks: All experiments were performed in evacuated tubes, using standard Schlenk-tube or glove-box techniques, with rigorous exclusion of traces of moisture and air. After drying over KOH, thf was purified by distillation from sodium/benzophenone ketyl, hexane and toluene by distillation from sodium/triglyme benzophenone ketyl prior to use. C_7D_8 was dried with sodium/benzophenone ketyl and condensed in vacuo prior to use. Ap'H and KAp' (Ap'-H = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine) were synthesized according to previously published procedures.[1,2] Anhydrous YCl_3[3] was prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purification. NMR spectra were recorded on a Bruker DPX 200, Bruker ARX 250, Bruker Avance III 400, Varian Inova 400 or on a Varian Inova 300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced internally using the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls on FSM 1201 and Specord M80 instruments. Lanthanoid metal analysis were carried out by complexometric titration. The C, H elemental analysis was made in the microanalytical laboratory of IOMC and at Bayreuth University using a Vario elementar EL *III* elemental analyser.

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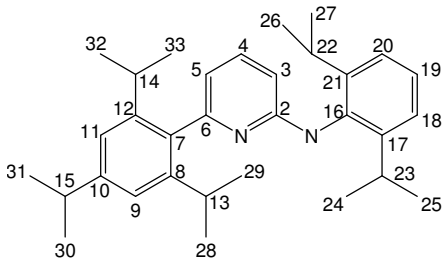

Scheme 1. Numbering of the carbon atoms in Ap*-ligand.

Synthesis of 1: To a solution of Ap*H 1.00 g (2.19 mmol) in diethyl ether (30 mL) 1.46 mL a solution of BuLi in hexane (1.5 M) was added. Reaction mixture was stirred for 0.5 h and all the volatiles were removed in vacuum and the solid residue was dissolved in thf (15 mL). This solution was added to a suspension of 0.43 g (2.19 mmol) of anhydrous YCl_3 in thf (15 mL) at room temperature and the reaction mixture was stirred for 1 h. thf was removed in vacuum and the solid was extracted with toluene (2 × 30 mL). Crystals of **1** were obtained as pale yellow microcrystalline solid by crystallization from thf/hexane mixture, yield 1.49 g (78%). ^{1}H NMR (200 MHz, C_6D_6, 293 K): δ 1.06 (d, $^3J_{HH}$=6.5 Hz, 12 H, $H^{28,29,32,33}$), 1.26 (m, 18 H, $H^{24,25,26,27,30,31}$), 1.37 (br s, 12H, β-CH_2 thf), 2.85 (sept, $^3J_{HH}$ = 6.5 Hz, 1H, H^{15}), 2.99 (sept, $^3J_{HH}$ = 7.5 Hz, 2H; $H^{13,14}$), 3.32 (sept, $^3J_{HH}$ = 6.5 Hz, 2H, $H^{22,23}$), 3.57(br s, 12H, α-CH_2 thf), 5.86 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H^3), 6.56 (d, $^3J_{HH}$ = 7.0 Hz, 1H, H^5), 7.00 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, H^4), 7.11 (br m, 3H, $H^{18,19,20}$), 7.21 (br m, 2H, $H^{9,11}$). ^{13}C NMR (50 MHz, C_6D_6, 293 K): δ 23.5 (s, β-CH_2 thf), 24.0, 24.1 (s, $C^{24,25,26,27}$), 24.4 (s, $C^{30,31}$), 25.4 (s, $C^{28,29,32,33}$), 28.4 (s, $C^{22,23}$), 30.6 (s, $C^{13,14}$), 34.6 (s, C^{15}), 67.7 (s, α-CH_2 thf), 103.6 (s, C^3), 115.1 (s, C^5), 120.4 (s, $C^{9,11}$), 123.9 (s, $C^{18,20}$), 125.3 (s, C^{19}), 134.8 (s, C^7), 137.1 (s, C^4), 137.5 (s, C^{16}), 146.4 (s, $C^{17,21}$), 147.8 (s, $C^{8,12}$), 148.3 (s, C^{10}), 159.5 (s, C^6), 168.5 (s, C^2). ^{7}Li NMR (C_6D_6, 293 K, 77.7 MHz): δ 2.0 (s). Anal. Calcd for $C_{44}H_{67}Cl_3LiN_2O_3Y$ (874.22 g·mol^{-1}): C, 60.45; H, 7.72; N, 3.20; Y, 10.17%. Found: C, 60.13; H, 7.89; N, 3.25; Y, 10.08%.

Synthesis of 2: Complex Ap*LuCl(thf)(μ-Cl_2)Li(thf)$_2$ was obtained from 0.86 g Ap*H (1.88 mmol), 1.26 mL BuLi (solution in hexane, 1.5 M) and 0.53 g (1.88 mmol) anhydrous $LuCl_3$ following the same experimental procedure as for **1**. Complex **2** was isolated as a pale yellow microcrystalline solid by crystallization from thf/hexane mixture, yield 1.53 g (85%). ^{1}H NMR (C_5D_5N, 293 K, 200 MHz): δ 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $H^{28,29,32,33}$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, $H^{30,31}$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, $H^{24,25,26,27}$), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, $H^{24,25,26,27}$), 1.44 (d, $^3J_{HH}$ = 6.8 Hz, 6 H, $H^{28,29,32,33}$), 1.56 (br s, 12H, β-CH_2 thf), 2.65 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, H^{15}), 3.60 (m, together 14H, $H^{13,14}$ and α-CH_2 thf), 4.43 (sept, $^3J_{HH}$ = 6.8

Hz, 2H, $H^{22,23}$), 5.79 (d, $^3J_{HH}$ = 8.3 Hz, 1H, H^3), 6.03 (d, $^3J_{HH}$ = 7.0 Hz, 1H, H^5), 7.11 (dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, H^4), 7.22 (br m, 3H, $H^{18,19,20}$), 7.44 (br m, 2H, $H^{9,11}$). ^{13}C NMR (50 MHz, C_5D_5N, 293 K): δ 22.8 (s, β-CH_2 thf), 23.8, 24.1 (s, $C^{24,25,26,27}$), 25.6 (s, $C^{28,29,32,33}$), 26.2 (s, $C^{30,31}$), 27.1 (s, $C^{22,23}$), 29.8 (s, $C^{13,14}$), 33.9 (s, C^{15}), 67.6 (s, α-CH_2 thf), 107.1 (s, C^3), 110.4 (s, C^5), 120.3 (s, $C^{9,11}$), 123.4 (s, $C^{18,20}$), 123.9 (s, C^{19}), 134.8 (s; C^7), 135.6 (s, C^4), 145.4 (s, $C^{17,21}$), 146.2 (s, $C^{8,12}$), 146.5 (s, C^{16}), 147.6 (s, C^{10}), 156.0 (s, C^6), 170.4 (s, C^2). ^{7}Li NMR (77.7 MHz, C_5D_5N, 293 K): δ 6.7 (s). Anal. Calcd for $C_{44}H_{67}Cl_3LiLuN_2O_3$ (960.28 g·mol^{-1}): C, 55.03; H, 7.03; N, 2.92; Lu, 18.22%. Found: C, 54.86; H, 7.12; N, 2.97; Lu, 18.24%.

Synthesis of 3: Method a) To a suspension of **1** (0.520 g, 0.59 mmol) in hexane (20 mL) a solution of Me_3SiCH_2Li (0.112g, 1.19 mmol) in hexane (15 mL) was added at 0˚C. Reaction mixture was stirred for 1 h, the solution was filtered and concentrated approximately to 1/10 of its initial volume and kept overnight at -20˚C. Complex **3** was isolated as pale-yellow crystals, yield 0.32 g (68%). Crystals suitable for X-Ray analysis were obtained by cooling concentrated pentane solution from 20˚C to -20˚C. ^{1}H NMR (200MHz, C_6D_6, 293 K): δ -0.42 (d, $^2J_{YH}$ = 3.0 Hz, 4H, YCH_2), 0.18 (s, 18H, Si(CH_3), 1.05 (br s, 4H, β-CH_2 thf), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $H^{28,29,32,33}$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $H^{30,31}$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $H^{24,25,26,27}$), 2.85 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, H^{15}), 2.99 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $H^{13,14}$), 3.32 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $H^{22,23}$), 3.57(br s, 12H, α-CH_2 thf), 5.86 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H^3), 6.56 (d, $^3J_{HH}$ = 7.0 Hz, 1H, H^5), 7.00 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, H^4), 7.11 (br m, 3H, $H^{18,19,20}$), 7.21 (br m, 2H, $H^{9,11}$). ^{13}C NMR (C_6D_6, 293 K, 50 MHz): δ 3.8 (s, Si(CH_3), 23.5 (s, $C^{28,29,32,32}$), 24.0 (s, $C^{24,25,26,27}$), 24.1 (s, $C^{28,29,32,33}$), 24.4 (s, $C^{24,25,26,27}$), 25.4 (s, $C^{\beta\text{- thf}}$), 26.3 (s, $C^{30,31}$), 28.4 (s, $C^{22,23}$), 30.6 (s, $C^{13,14}$), 34.6 (s, C^{15}), 39.6 (d, $^1J_{YC}$=39.8 Hz, YCH_2), 69.2 (s, α-CH_2 thf), 106.4 (s, C^3), 111.0 (s, C^5), 120.9 (s, $C^{9,11}$), 123.9 (s, $C^{18,20}$), 124.6 (s, C^{19}), 135.7 (s, C^7), 139.1 (s, C^4), 143.7 (s, $C^{17,21}$), 144.2 (s, C^{16}), 147.8 (s, $C^{8,12}$), 149.3 (s, C^{10}), 155.7 (s, C^6), 169.4 (d, $^1J_{YC}$ = 2.8 Hz, C^2). Anal. Calcd for $C_{44}H_{73}N_2OSi_2Y$ (791.14 g·mol^{-1}): C, 66.80; H, 9.30; N, 3.54; Y, 11.24%. Found: C, 66.98; H, 9.43; N, 3.48; Y, 11.37%.

Method b): To a solution of $(Me_3SiCH_2)_3Y(thf)_2$ (0.53 g, 1.07 mmol) in hexane (10 mL) a solution of Ap*H (0.49 g, 1.07 mmol) in hexane (30 mL) was added at 0˚C. Reaction mixture was stirred at 0˚C for 1h, concentrated approximately to 1/10 of its initial volume and kept over night at -20˚C. Yield 0.61 g (72%).

Synthesis of 4: Method a): To a suspension of **2** 0.630 g (0.66 mmol) in hexane (20 mL) a solution of Me_3SiCH_2Li 0.112g (1.19 mmol) in hexane (15 mL) was added at 0˚C. Reaction mixture was stirred for 1 h then solution was filtered and concentrated approximately to 1/10 of its initial volume and kept overnight at -20˚C. Complex **4** was isolated as a pale-yellow crystalline solid, yield 0.43 g (75%). Crystals suitable for X-Ray analysis were obtained by cooling concentrated solution from 20˚C to -20˚C. ^{1}H NMR (200 MHz, C_6D_6, 293 K): δ -0.63 (s, 4H, LuC*H*$_2$), 0.19 (s, 18H, Si(C*H*$_3$), 1.10 (br s, 4H β-CH$_2$ thf), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12H, H^{28,29,30,31,32,33}), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 6H, H^{24,25,26,27}), 1.35 (d, $^3J_{HH}$ = 6.8 Hz, 6H, H^{24,25,26,27}), 1.61 (d, $^3J_{HH}$ = 6.8 Hz, 6H, H^{28,29,32,33}) 2.91 (sept, $^3J_{HH}$ = 6.8 Hz, 1H, H^{15}), 3.12 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, H^{13,14}), 3.45 (sept, $^3J_{HH}$ = 6.8Hz, 2H, H^{22,23}), 3.64 (br s, 4H, α-CH$_2$ thf), 5.65 (d, $^3J_{HH}$ = 9.4 Hz, 1H, H^3), 6.15 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H^5), 6.77 (dd, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 7.8 Hz, 1H, H^4), 7.15 (br m, 3H, H^{18,19,20}), 7.28 (br m, 2H, H^{9,11}). ^{13}C NMR (C_6D_6, 293 K, 50 MHz): δ 4.1 (s, Si(*C*H$_3$), 23.3 (s, C^{28,29,32,33}), 24.0 (s, C^{24,25,26,27}), 24.2 (s, C^{28,29,32,33}), 24.6 (s, C^{24,25,26,27}), 24.8 (s, β-CH$_2$ thf), 26.6 (s, C^{30,31}), 28.5 (s, C^{22,23}), 30.7 (s, C^{13,14}), 34.8 (s, C^{15}), 46.1 (s, Lu*C*H$_2$) C 70.1 (s, α-CH$_2$ thf), 106.7 (s, C^3), 111.6 (s, C^5), 121.0 (s, C^{9,11}), 123.9 (s, C^{18,20}), 124.9 (s, C^{19}), 135.6 (s, C^7), 139.3 (s, C^4), 144.1 (s, C^{17,21}), 144.6 (s, C^{16}), 146.4 (s, C^{8,12}), 149.4 (s, C^{10}), 155.9 (s, C^6), 168.7 (s, C^2). Anal. Calcd for $C_{44}H_{73}LuN_2OSi_2$ (876.47 g mol^{-1}): C, 60.25; H, 8.39; N, 3.19; Lu, 19.95%. Found: C,60.08; H, 8.56; N, 3.03; Lu, 19.92%.

Method b): To a solution of $(Me_3SiCH_2)_3Lu(thf)_2$ (0.39 g, 0.67 mmol) in hexane (10 mL) a solution of Ap*H (0.31 g, 0.67 mmol) in hexane (30 mL) was added at 0˚C. Reaction mixture was stirred at 0˚C for 1h, concentrated approximately to 1/10 of its initial volume and kept overnight at -20˚C. Yield 0.47 g (80%).

Synthesis of 5: To a solution of **3** (0.370 g, 0.47 mmol) in hexane (20 mL) phenylsilane (0.102 g, 0.95 mmol) was added at 0˚C. Reaction mixture was stirred at 0˚C for 1h and kept over night at -20˚C. The volatiles were removed in vacuum and the solid residue was dried for 3h. The solid was redissolved in hexane (10 mL) and cooled over night at -20˚C. **5** was isolated as yellow crystalline solid (0.180 g, 58%). ^{1}H NMR (400 MHz, C_7D_8, 293 K): -1.10 (d, $^2J_{HH}$ = 9.0 Hz, 1H, YC*H*$_2$), -0.13 (s, 9H, Si(C*H*$_3$)), -0.03 (d, $^2J_{HH}$ = 9.0 Hz, 1H, YC*H*$_2$), 0.75–1.49 (complex m, together 98H, CH(C*H*$_3$) and *β*-C*H*$_2$ thf), 2.61–3.83 (complex m, 23H, C*H*(CH$_3$) and *α*-C*H*$_2$ thf), 5.59 (d, $^3J_{HH}$=8.4 Hz, 1H, H^3), 5.66 (td, $^1J_{YH}$ = 20.8 Hz, $^1J_{YH}$ = 5.8 Hz, 3H, Y-μ^{2}H), 5.75 (d, $^3J_{HH}$=8.4 Hz, 2H; H^3), 5.93, 6.03, 6.11 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H^5), 6.67, 6.78, 6.83 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz, 1H; H^4), 6.94–7.30 (m, together 20H, H^{9,11,18,19,20} and Yμ-^{3}H) ppm. ^{13}C NMR (100 MHz, C_7D_8, 293 K): 3.8 (s; Si(*C*H$_3$), 22.4, 23.3, 23.4, 23.5, 23.6, 24.0, 24.1, 24.2, 24.3, 24.4, 24.5, 24.6, 24.8, 24.9, 25.0, 25.2, 25.3, 25.5,

25.9, 26.1, 26.2, 26.6, 26.9, 27.0, 27.3, 27.8 (s, $C^{24,25,26,27,28,29,32,32}$ and β-CH_2 thf), 28.2, 28.3, 28.4, 28.5, 28.6, 28.8 (s, $C^{22,23}$), 30.0, 30.1, 30.2, 30.7, 30.8, 31.1 (s, $C^{13,14}$), 34.6, 34.7, 34.8 (s, C^{15}), 41.8 (d, $^1J_{YC}$ = 39.8 Hz; YCH_2), 70.6, 70.7 (s, α-CH_2 thf), 108.0, 109.1, 109.8 (s, C^3), 110.6, 110.7, 111.0 (s, C^5), 119.9, 120.5, 120.6, 120.7, 121.0, 121.8 (s, $C^{9,11}$), 123.3, 123.6, 123.7, 123.8, 123.9, 124.3 (s, $C^{18,20}$), 124.6, 124.7, 125.1 (s, C^{19}), 135.1, 136.8, 136.9 (s, C^7), 138.1, 138.6, 138.7 (s, C^4), 142.5, 142.6, 143.2, 143.5, 143.7, 144.0 (s, $C^{17,21}$), 145.4, 145.5, 145.8 (s, C^{16}), 146.4, 146.5, 146.7, 147.7, 147.8, 147.9 (s, $C^{8,12}$), 148.5, 149.0, 149.2 (s, C^{10}), 155.8, 156.1, 156.6 (s, C^6), 170.7, 170.9, 171.6 (d, $^1J_{YC}$ = 2.8 Hz, C^2) ppm. ^{89}Y NMR (19.6 MHz, C_7D_8, 293 K): 503, 515, 755 ppm. Elemental analysis (%) calcd for $C_{114}H_{175}N_6O_2SiY_3$ (1955.45 g·mol^{-1}): C 69.98, H 9.02, N 4.30, Y 13.63; found: C 69.74, H 8.82, N 4.29, Y 13.54.

Synthesis of 6: To a solution of **4** (0.43 g, 0.49 mmol) in hexane (20 mL) phenylsilane (0.106 g, 0.99 mmol) was added at 0˚C. Reaction mixture was stirred at 0˚C for 1h and kept over night at -20˚C. Solvent was removed in vacuum and the solid residue was dried for 3h. The solid was redissolved in hexane (10 mL) and cooled overnight at -20˚C. **6** was isolated as yellow crystalline solid (0.23 g, 64%). ^{1}H NMR (400 MHz, C_7D_8, 293 K): -1.35 (d, $^2J_{HH}$ = 9.7 Hz, 1H, LuCH_2), -0.42 (d, $^2J_{HH}$ = 9.7 Hz, 1H, LuCH_2), -0.16 (s, 9H; Si(CH_3), 0.73-1.48 (complex m, together 98H; CH(CH_3) and β-CH_2 thf), 2.56–3.84 (compl m, 23H; CH(CH_3) and α-CH_2 thf), 5.55 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H^3), 5.71 (d, $^3J_{HH}$ = 8.5 Hz, 2H, H^3), 5.94, 6.06, 6.13 (d, $^3J_{HH}$ = 7.2 Hz, 1H, H^5), 6.62, 6.73, 6.78 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, H^4), 6.93-7.35 (compl m, 15H, $H^{9,11,18,19,20}$), 9.08 (s, 3H, LuH), 12.25 (s, 1H, LuH), 12.37 (s, 1H, LuH) ppm. ^{13}C NMR (100 MHz, C_7D_8, 293 K,): 4.0 (s, Si(CH_3), 22.8, 23.3, 23.4, 23.5, 23.6, 24.1, 24.2, 24.3, 24.4, 24.6, 24.7, 24.9, 25.0, 25.1, 25.4, 25.6, 26.0, 26.1, 26.4, 26.5, 26.6, 26.7, 27.0, 27.1, 27.2, 27.4 (s, $C^{24,25,26,27,28,29,32,32}$ and β-CH_2 thf), 28.3, 28.4, 28.5, 28.6, 28.8, 28.9 (s, $C^{22,23}$), 30.1, 30.2, 30.3, 30.9, 31.1, 31.3 (s, $C^{13,14}$), 34.8, 34.9, 35.0 (s, C^{15}), 45.8 (s, LuCH_2), 71.0, 71.1 (s, CH_2 α- thf), 108.5, 109.8, 110.6 (s, C^3), 111.2, 111.3, 111.8 (s, C^5), 120.1, 120.6, 120.7, 120.8, 121.0, 121.1 (s, $C^{9,11}$), 123.4, 123.8, 123.9, 124.1, 124.2, 124.5 (s, $C^{18,20}$), 124.9, 125.0, 125.0 (s; C^{19}), 136.9, 137.0, 137.6 (s, C^7), 138.1, 138.4, 138.6 (s, C^4), 143.1, 143.7, 143.8, 144.0, 144.2, 144.4 (s, $C^{17,21}$), 145.2, 146.0, 146.2 (s, C^{16}), 146.5, 146.6, 147.2, 147.8, 147.9, 148.4 (s, $C^{8,12}$), 148.7, 149.1, 149.3 (s, C^{10}), 156.2, 156.5, 156.9 (s, C^6), 170.2, 170.5, 171.4 (s, C^2) ppm. Elemental analysis (%) calcd for $C_{114}H_{175}Lu_3N_6O_2Si$ (2213.18 g·mol^{-1}): C 61.83, H 7.96, N 3.79, Lu 23.70; found: C 61.63, H 8.08, N 3.71, Lu 23.64.

Catalytic tests procedures

Catalytic tests with ethylene and propylene were carried out under rigorously anaerobic conditions in sealed glass manometric system (ethylene: toluene 5 mL, catalyst concentration $2.29 \cdot 10^{-3}$ mol/L (**5**), $1.76 \cdot 10^{-3}$ mol/L(**6**) 20ºC, ethylene pressure - 0.5 atm; propylene: toluene 5 mL, catalyst concentration $1.31 \cdot 10^{-3}$(**5**), $1.66 \cdot 10^{-3}$(**6**) mol/L, 0ºC, propylene pressure - 0.5 atm). The reactions were monitored by monomer consumption. Catalysts efficiencies were estimated by both monomer consumption and by quenching the polymerization reaction after measured time intervals and weighing the quantitaty of polymer produced. The polymers were washed with dilute HCl, methanol and dried in vacuo to constant weight.

Crystal structure determinations.

Crystal data for **1**: $C_{40}H_{59}YN_2O_2Cl_2Li$, M_r=759.70, triclinic, space group P-1, a=12.8280(9), b=13.4100(9), c=15.7150(10) Å, α=71.150(5)°, β=84.948(5)°, γ=65.743(5)°, V=2329.4(3) Å^3, Z=2, T=191(2) K, F_{000}=804, μ=1.396 mm^{-1}, θ=1.37-26.05°, reflection collected 30654, independent reflections 8810 [R_{int}=0.1147], GOF=0.934, R=0.0630 (I>2σ(I)), wR^2=0.1345 (all data), largest diffraction peak and hole 0.738/-0.335 eÅ^{-3}.

Crystal data for **3**: $C_{49}H_{79}YN_2OSi_2$, M_r=857.23, monoclinic, space group C2/c, a=36.3320(10), b=12.8360(5), c=23.8650(8) Å; β=106.057(3), V=10695.4(6) Å^3, Z=8, T=133(2) K, F_{000}=3696, μ=1.167 mm^{-1}, θ=1.69-22.00°, reflection collected 41022, independent reflections 6556 [R_{int}=0.0822], GOF=1.154, R=0.0650 (I>2σ(I)), wR^2=0.1437 (all data), largest diffraction peak and hole 0.718/-0.443 e Å^{-3}.

Crystal data for **4**: $C_{50}H_{87}LuN_2OSi_2$, M_r=963.37, monoclinic, space group C2/c, a=36.236(2), b=12.7914(7), c=23.7867(14) Å; β=105.6250(10), V=10617.9(11) Å^3, Z=8, T=100(2) K, F_{000}=4064, μ=1.938 mm^{-1}, θ=1.70-26.00°, reflection collected 31529, independent reflections 10443 [R_{int}=0.0379], GOF=1.061, R=0.0384 (I>2σ(I)), wR^2=0.0990 (all data), largest diffraction peak and hole 2.161/-0.835 e Å^{-3}.

Crystal data for **5**: $C_{117}H_{178}Y_3N_6O_2Si$, M_r=1995.47, monoclinic, space group P2(1)/n, a=25.7685(16), b=15.7564(10), c=29.3881(18) Å; β=106.5990(10)°, V=11434.9(12) Å^3, Z=4, T=100(2) K, F_{000}=4276, μ=1.569 mm^{-1}, θ=2.06-24.00°, reflection collected 80930,

independent reflections 17842 [R_{int}=0.0844], GOF=1.015, R=0.0540 (I>2σ(I)), wR^2=0.1344 (all data), largest diffraction peak and hole 1.213/-0.563 e $Å^{-3}$.

CCDC-681734 (**1**), CCDC-681735 (**3**), CCDC-681736 (**4**) and CCDC-681737 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Low-temperature diffraction data of **1**, **3** were collected on a STOE-IPDS II device equipped with an Oxford Cryostream low-temperature unit; **4** and **5** on a Bruker-AXS Smart Apex diffractometer.

Compound	**Ap*YCl(thf)(μ-Cl)$_2$Li(thf)$_2$, (1)**	**Ap*Y(CH$_2$SiMe$_3$)$_2$ thf ·C$_5$H$_{12}$, (3)**
Formula	$C_{40}H_{59}Cl_2LiN_2O_2Y$	$C_{49}H_{79}N_2OSi_2Y$
M_r	759.70	857.23
Crystal size, mm^3	0.39×0.17×0.11	0.28×0.20×0.18
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a, Å	12.8280(9)	36.3320(10)
b, Å	13.4100(9)	12.8360(5)
c, Å	15.7150(10)	23.8650(8)
α, °	71.150(5)	-
β, °	84.948(5)	106.057(3)
γ, °	65.743(5)	-
Cell volume, $Å^3$	2329.4(3)	10695.4(6)
Z	2	8
T, K	191(2)	133(2)
F_{000}	804	3696
μ, mm^{-1}	1.396	1.167
2θ range, °	3.30-52.11	3.30-52.11
Reflection collected	30654	41022
Reflections unique	8810	6556
R_{int}	0.1147	0.0822
GOF	0.934	1.154
Refl. obs. (I>2σ(I))	5771	5330
Parameters	491	471
wR_2 (all data)	0.1345	0.1437
R value (I>2σ(I))	0.0630	0.0650
Largest diff. peak and hole	0.738/-0.335	0.718/-0.443

Compound	**Ap*Lu(CH_2SiMe_3)$_2$ thf ·C_6H_{14}, (4)**	**(Ap*)$_3$Y$_3$(CH_2SiMe_3) thf$_2$H$_5$·2C_6H_{14}, (5)**
Formula	$C_{50}H_{87}LuN_2OSi_2$	$C_{117}H_{178}N_6O_2SiY_3$
M_r	963.37	1995.47
Crystal size, mm^3	0.25×0.15×0.10	1.42×0.48×0.41
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$
a, Å	36.236(2)	25.7685(16)
b, Å	12.7914(7)	15.7564(10)
c, Å	23.7867(14)	29.3881(18)
α, °	-	-
β, °	105.6250(10)	106.5990(10)
γ, °	-	-
Cell volume, Å^3	10617.9(11)	11434.9(12)
Z	8	4
T, K	100(2)	100(2)
F_{000}	4064	4276
μ, mm^{-1}	1.938	1.569
2θ range, °	3.29-52.17	3.30-52.11
Reflection collected	31529	80930
Reflections unique	10443	17842
R_{int}	0.0379	0.0844
GOF	1.061	1.015
Refl. obs. (I>2σ(I))	8360	12486
Parameters	613	1188
wR_2 (all data)	0.0990	0.1344
R value (I>2σ(I))	0.0384	0.0540
Largest diff. peak and hole	2.161/-0.835	1.213/-0.563

5. Synthesis and Structure of Aminopyridinate-Stabilized Yttrium and Lanthanum Amides and their Reactivity towards Alkylaluminium Compounds

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Keywords: aluminium, aminopyridinato ligands, ligand transfer, rare earth metals, silylamide route

Abstract: A series of aminopyridinate-stabilized (amido)lanthanoid complexes has been synthesized and characterized. The bulky aminopyridines (2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine (**1a)** and [6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-(2,4,6-trimethyl-phenyl)-amine (**1b)** were introduced by amine elimination reaction with $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Y, La, thf = tetrahydrofurane, Me = methyl) to obtain the corresponding (mono)aminopyridinate complexes. Single crystal X-ray analyses were carried out for the yttrium derivatives. The complexes are not able to undergo coordinative chain transfer polymerization with ethylene in the presence of alkylaluminium compounds as the corresponding dialkyl complexes do. Investigations of the reactions of the lanthanoid aminopyridinate complexes with triethylaluminium or diisobutylaluminium hydride reveal a fast transfer of the aminopyridinato ligand to the aluminium atom. The products of this transfer reaction are aminopyridinate-stabilized dialkylaluminium compounds. One example of these aluminium complexes was characterized by X-ray crystal structure analysis.

5.1. Introduction

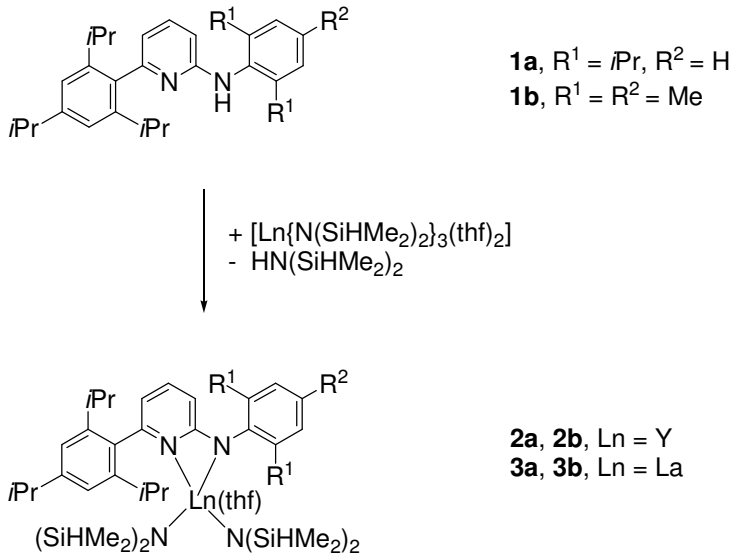
Coordinative chain transfer polymerisation[1] (CCTP) is an excellent tool to polymerize ethylene and α-olefines like propylene in a highly controlled and efficient fashion. A variety

of systems are described in the literature which are capable of catalyzing this type of polymerization with various alkyl main group and zinc compounds.[2] We recently described an yttrium-based system, which catalyzes chain growing at aluminium.[3] This catalyst system is able to produce very narrowly molecular weight distributed polyethylene – less than 1.1 M_w/M_n – up to a molecular weight of about 4000 g/mol, and a polydispersity index of about 1.3 is observed for higher molecular weight polymers. Due to the interesting features of this catalyst system, we became interested in the investigation of the behaviour of other rare earth metals in this type of polymerization. The yttrium catalyst system was generated from a trisalkyl precursor, namely $[Y(CH_2SiMe_3)_3(thf)_2]$.[4] Unfortunately, such precursors are not available for all rare earth metals.[5] Triamides of group 3 elements and the rare earth metals with the composition $[Ln\{N(SiHMe_2)_2\}_3(thf)_n]$ (n = 1, 2) are excellent starting materials to introduce a multiplicity of ligands, especially bulky ones[6,7,13,14] by the silylamide route. These tris(disilylamides) have the advantage to be available as salt-free derivatives for the whole series of lanthanoids (Sc, Y, La-Lu).[7b,8,21] Recently, the thf-free triamides $[Y\{N(SiHMe_2)_2\}_3]$[9] and $[La\{N(SiHMe_2)_2\}_3]$[10] were introduced. The lanthanum complex is accessible by the conversion of $[La\{N(SiMe_3)_2\}_3]$ with the amine $HN(SiHMe_2)_2$ in pentane; the driving force of this reaction is the stronger acidity of $HN(SiHMe_2)_2$. The yttrium triamide was obtained from the reaction of $[YMe_3]_n$ and 3 equiv. of the amine $HN(SiHMe_2)_2$. Herein we report the synthesis and structure of aminopyridinato-ligand-stabilized[3,11,12,18,19] disamides of yttrium and lanthanum as well as ligand transfer reactions with alkylaluminium compounds, which are the reason for these compounds not being suitable as starting materials for the generation of catalysts for CCTP.

5.2. Results and Discussion

Metal Complex Synthesis

The reaction of $[Y\{N(SiMe_3)_2\}_3]$ with 1 equiv. of the sterically demanding aminopyridines **1a** and **b** in thf at 60°C showed no conversion (monitored by ^1H NMR spectroscopy). Even after 3 days at 100°C in toluene no aminopyridinate complexes were observed. This well-documented inertness of the bulky triamide led us to the replacement of $[Y\{N(SiMe_3)_2\}_3]$ with $[Ln\{N(SiHMe_2)_2\}_3(thf_2]$.[8]



Scheme 1. Synthesis of aminopyridinate stabilized bisamides **2a**, **2b** and **3a**, **3b**.

The reaction of the aminopyridine ligands **1** with 1 equiv. of $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Y, La) yielded after amine elimination the corresponding disamides **2** and **3,** respectively (Scheme 1). The conversion of **1a,b** with $[La\{N(SiHMe_2)_2\}_3(thf)_2]$ at room temperature is nearly quantitative within 2 hours, whereas the reaction of $[Y\{N(SiHMe_2)_2\}_3(thf)_2]$ at 60°C takes 12 h to obtain complete conversion. The complexes **2** and **3** were characterized by NMR spectroscopy and elemental analysis. Furthermore, the structure of **2a** and **2b** was determined by X-ray crystallography. Suitable single crystals of **2a,b** were obtained by cooling a saturated hexane solution to -30° C. The complexes **2a** and **2b** crystallize as light-yellow prisms in the monoclinic space group $P2_1/c$. The molecular structures are depicted in Figures 1 (**2a**) and 2 (**2b**); crystallographic details are summarized in Table 1. In both compounds the metal atom has a coordination number of 5 and is coordinated by two bis(dimethylsilyl)amido ligands, one aminopyridinato and one thf ligand. The average metal-nitrogen bond length between both $\{N(SiHMe_2)_2\}$ groups and the yttrium atom with 2.243(3) (**2a**) and 2.243(7) Å (**2b**) are comparable to the average Y-N bond length of 2.260(4) Å in $[Y\{N(SiHMe_2)_2\}_3(thf)_2]$,[21] but is shorter than the Ln-N_{amido} distances of the aminopyridinato ligand.

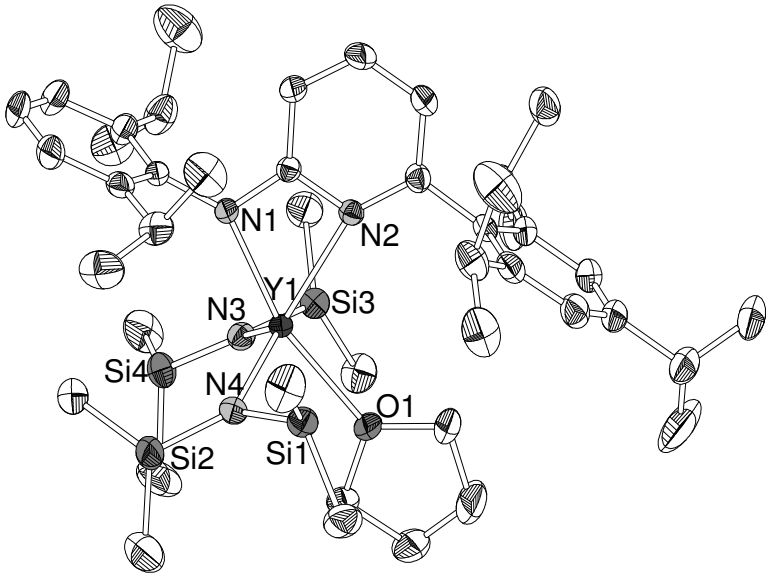


Figure 1. ORTEP diagram of the molecular structure of **2a** in the solid state (ellipsoids set at 40% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Y-N1 2.325(3), Y-N2 2.443(3), Y-N3 2.252(3), Y-N4 2.243(3), Y-O 2.409(2), Y-Si1 3.0970(11), Y-Si2 3.6559(14), Y-Si3 3.0830(11), Y-Si4 3.6402(14), Si1-N4-Si2 121.26(19), Si3-N3-Si4 124.99(19), Y-N4-Si2 135.74(18), Y-N4-Si1 102.74(14).

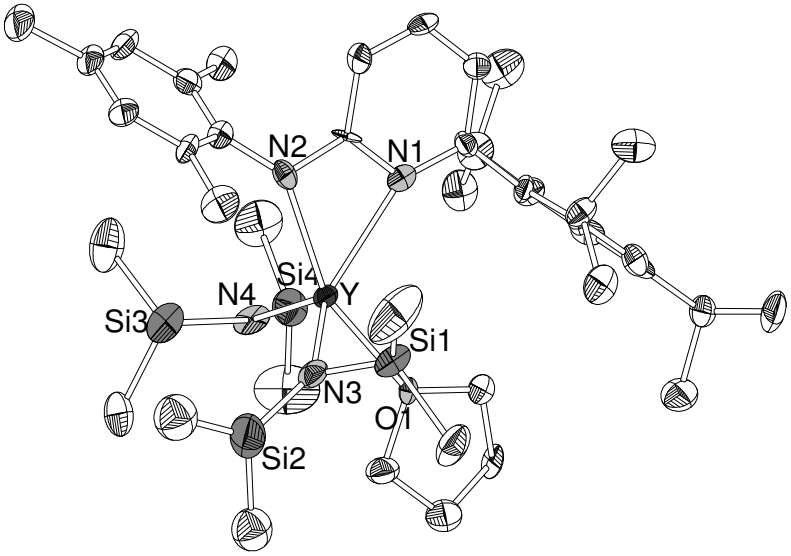


Figure 2. ORTEP diagram of the molecular structure of **2b** in the solid state (ellipsoids set at 40% probability level). H atoms and disordered methyl groups on Si2 have been omitted for clarity. Selected bond lengths [Å] and angles [°]:Y-N1 2.490(8), Y-N2 2.324(7), Y-N3 2.265(7), Y-N4 2.220(7), Y-O 2.390(5), Y-Si1 3.083(3) Y-Si2 3.630(3), Y-Si3 3.223(3), Y-Si4 3.306(3), Y-N3-Si1 101.7(3), Y-N3-Si2 133.2(4), Y-N4-Si3 111.3(4), Y-N4-Si4 114.4(3), Si1-N3-Si2 125.0(4), Si3-N4-Si4 132.0(5).

One of the silicon atoms of both $\{N(SiHMe_2)_2\}$ ligands of **2a** has a shorter distance to the metal centre than the other one: [Y-Si1 3.0970(11) and Y-Si3 3.0830(11) Å vs. Y-Si2 3.6559(14) and Y-Si4 3.6402(14) Å]. As a result, the Y-N-Si angle is becoming smaller and

larger, respectively [Y-N4-Si1 102.74(14)° vs. Y-N4-Si2 135.74(18)°]. These features are an indicator for a monoagostic β-Si-H interaction (Figure 3b) of both dimethylsilylamido ligands as it is observed, for instance, for the complexes $[Ln\{N(SiHMe_2)_2\}_2\{CH(PPh_2NSiMe_3)_2\}]$[7b], $[Y(Mes_2N_2NMe)\{N(SiHMe_2)_2\}(thf)]$[13] (Mes=2,4,6-trimethylphenyl), $[Cp_2{*}Y\{N(SiHMe_2)_2\}]$[14] (Cp*=$C_5Me_5$), $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$[8].

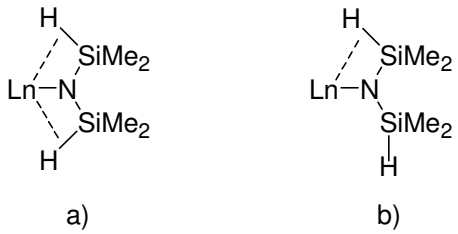


Figure 3. Diagostic (a) and monoagostic (b) interactions of the silylamido ligand.

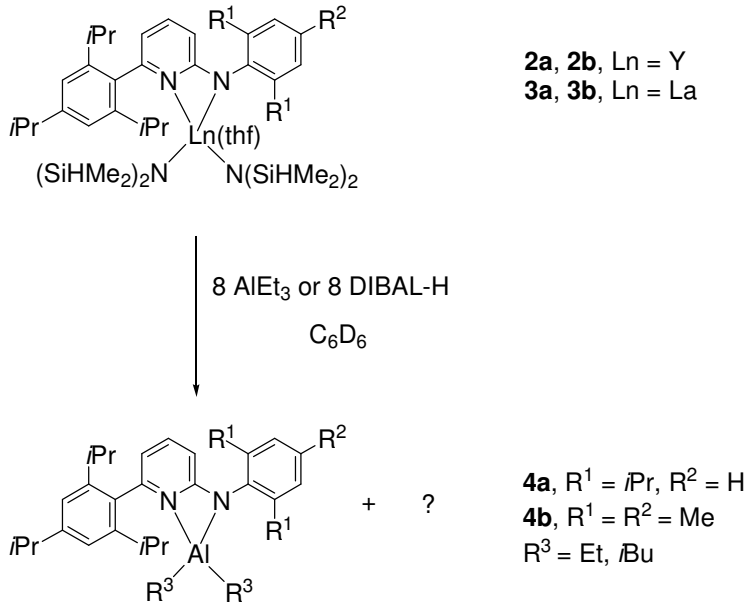
However in solution only one set of signals is observed for the dimethylsilylamido ligands (a doublet at δ = 0.24 ppm and a septet at δ = 4.92 ppm). Both $\{N(SiHMe_2)_2\}$ ligands of compound **2b** show different agostic β-Si-H interactions. One of the amido ligands has the same monoagostic β-Si-H interaction as it is observed for complex **2a** [Y-Si1 3.083(3) Å vs. Y-Si2 3.630(3) Å, Y-N3-Si1 101.7(3)° vs. Y-N3-Si2 133.2(4)°]. The other bis(dimethylsilyl)amido ligand reveals a weak diagostic β-Si-H interaction (Figure 3a). In this case both metal-silicon bond lengths differ only negligibly [Y-Si3 3.223(3) and Y-Si4 3.306(3) Å], the Y-N-Si angles [111.2(4) und 114.4(3)°] are also nearly equal, and the N-Si-N angle of 132.0(5)° is larger than the comparable angle of the other bis(dimethylsilyl)amido ligand of **2b** [125.0(4)°].

In comparison to other complexes with diagostic β-Si-H interactions the Si-N-Si bond angle is only marginally enlarged, {153.3(2)° for *rac*-$[\{Me_2Si(2\text{-}Me\text{-}C_9H_6)_2\}Y\{N(SiHMe_2)_2\}]$[15] and 139.8(1)° for $[(Me_4C_5H)Y\{N(SiHMe_2)_2\}]$[16]}. The occurrence of a weak diagostic interaction of one of the bis(dimethylsilyl)amido ligands of compound **2b** could be explained by the lower steric demand of ligand **1b** compared to **1a**. A theoretical discussion on a diagostic β-Si-H interaction was given by Hieringer et al.[17]

CCTP Activity of the Aminopyridinate-Stabilized Amido Complexes and Ligand Transfer to Aluminium Atom

We reported on aminopyridinate-stabilized alkylyttrium compounds, which are highly active ethylene polymerization catalysts (CCTP mechanism) in the presence of ammonium borates and alkylaluminium compounds or alumoxanes.[3] The aminopyridinate-stabilized

dialkylyttrium compounds have a constitution similar to compounds **2** and **3**, but with two alkyl {CH_2SiMe_3} groups instead of the amide ligands {$N(SiHMe_2)_2$} of **2** and **3**. In the presence of alkylaluminium compounds (which are planned to act as alkylating agents and as transfer reagents) and ammonium borates, complex **2a** showed no ethylene CCTP activity. From this result we reasoned that in the presence of an alkylaluminium compound, **2** and **3** rather undergo a deactivation reaction than an alkylation. During the investigations of the reaction of **2a** with triethylaluminium or diisobutylaluminium hydride a transfer of the aminopyridinato ligand from the yttrium to the aluminium atom was observed (Scheme 2).



Scheme 2. Aminopyridinato ligand transfer from Y to Al.

The ligand transfer was observed by ^{1}H NMR spectroscopy (Figure 4). For that 20 µmol of **2a** was dissolved in 0.5 mL deuterated benzene in a NMR tube, and 8 equiv. of triethylaluminium were added. Two ^{1}H NMR spectra were measured, after 5 min and at 60°C after 12 h. After 5 min, a conversion from the starting compound **2a** to an uncharacterized species was observed (Figure 4, top). After 12 h at 60 °C, a complete transfer to the aluminium atom was observed by ^{1}H NMR spectroscopy (Figure 4, centre). To prove the formation of **4a** (Scheme 2), we independently synthesized the aminopyridinate-stabilized dialkyl aluminium complexes **4**. The same ligand transfer is observed if only 4 equiv. of the alkylaluminium compound were added.

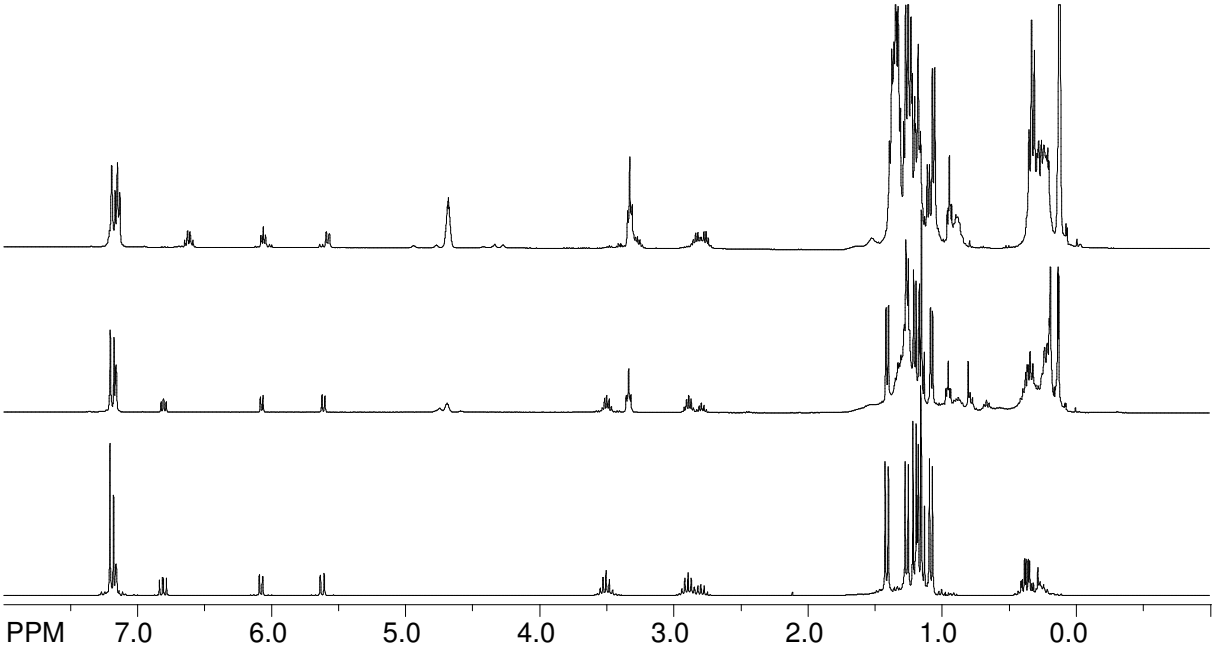


Figure 4. ^{1}H NMR spectra (C_6D_6, 298 K) of a mixture of **2a** + 8 equiv. $AlEt_3$ (top) at room temp. after 5 min and (centre) at 60 °C indicative of **4a** being the only aminopyridinate; (bottom) ^{1}H NMR spectra (C_6D_6, 298 K) of **4a**

The ^{1}NMR spectrum of compound **4a** shows two different signals for both CH_2 groups of the ethyl ligands, with a very small difference in chemical shift. They were detected as quartets at δ = 0.36 and 0.37 ppm, respectively. Due to the lower steric demand of **1b** and thereby increased rotation of the ethyl ligand, only one signal for the methylene groups of compound **4b** was observed as a quartet at δ = 0.33 ppm. Furthermore, compound **4a** was characterized by an X-ray structure analysis (Figure 5).

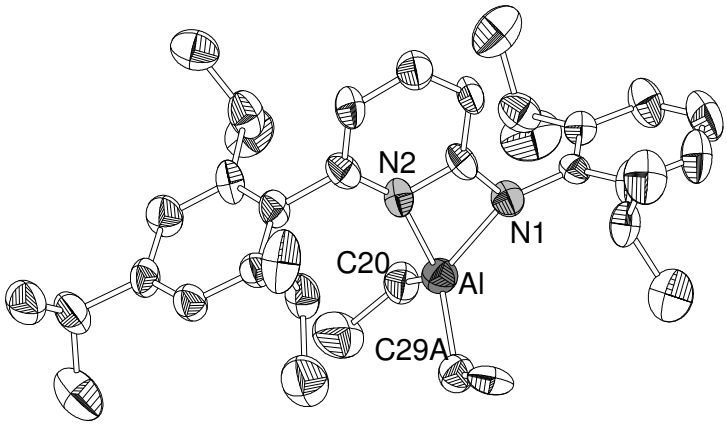


Figure 5. ORTEP diagram of the molecular structure of **4a** in the solid state (ellipsoids set at 40% probability level). H atoms and disordered ethyl group have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Al-N1 1.929(5), Al-N2 1.970(5), Al-C20 1.945(6), Al-C29A 1.914(18), N1-Al-N2 69.1(2), C20-Al-C29A 110.6(5).

Compound **4a** crystallizes in the triclinic space group $P\bar{1}$. The complex is mononuclear involving a strained η^2 coordination of the Ap (aminopyridinato) ligand. The Al-N bond lengths are quite similar and thus indicative of a binding mode with a high degree delocalization of the anionic function of the Ap ligands. (Ap)aluminium complexes which are η^2 coordinated are rare [3,12g,18,19].

Table 1. Details of the X-ray crystal structure analyses.

Compound	**2a**	**2b**	**4a**
Formula	$C_{44}H_{79}N_4OSi_4Y$	$C_{41}H_{72}N_4OSi_4Y$	$C_{36}H_{53}AlN_2$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	12.5412(6)	19.3700(14)	11.614(3)
b [Å]	21.7430(7)	11.6850(8)	12.113(3)
c [Å]	19.1632(9)	21.9730(14)	13.879(3)
α [°]	90	90	73.788(19)
β [°]	98.900(4)	103.091(6)	80.996(18)
γ [°]	90	90	66.882(18)
Z	4	4	2
μ [mm^{-1}]	1.256	1.335	0.083
V [$Å^3$]	5162.6(4)	4844.1(6)	1721.9(7)
Crystal size [mm^3]	0.61×0.60×0.58	0.23×0.20×0.14	0.33×0.23×0.07
T [K]	193(2)	173(2)	173(2)
θ range [°]	1.43-25.83	1.60-25.46	1.53-22.42
Reflections, unique	9776	9195	6514
Reflections, observed [$I>2\sigma(I)$]	8599	2290	1475
Parameters	500	480	372
wR_2 (all data)	0.1342	0.1252	0.1171
R value [$I>2\sigma(I)$]	0.0604	0.0601	0.0822

5.3. Conclusions

The results reported herein demonstrate that reactions of the trisamide complexes $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Y, La) with bulky aminopyridines selectively lead to the formation of mono(aminopyridinate) bis(dimethylsilyl)amides. They react with alkylaluminium compounds by transfer of the aminopyridinato ligand from the rare earth to the aluminium atom. Such a transfer reaction prohibits their use as precursors for CCTP, since the pre-catalysts are deactivated during the alkylation step. For alkyl precursors, which are suitable starting material for the generation of CCTP catalysts, the organo rare earth cation must be generated before the reaction with aluminium can take place. After the cation is generated, a highly electrophillic rare earth metal and aluminium compete for the coordination

of the aminopyridinato ligand, and the rare earth cation wins.[3] In the neutral, state the electrophilicity is much lower, and ligand transfer takes place.

5.4. Experimental Section

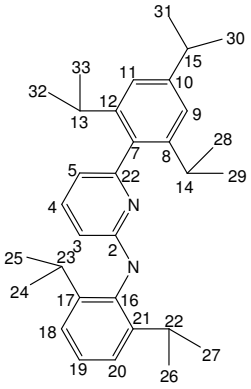
General Considerations

All reactions and manipulations involving air-sensitive compounds were performed under dry argon by using standard Schlenk and glovebox techniques. Non-halogenated solvents were dried with sodium/benzophenone ketyl and halogenated solvents with P_2O_5. Deuterated solvents were obtained from Cambridge Isotope Laboratories, degassed, dried with molecular sieves and distilled prior to use. Starting materials **1a**[20] and **1b**[3] were synthesized according to literature methods. [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] were prepared by a modified literature procedure[21] using K[N(SiHMe$_2$)$_2$][22] instead of Li[N(SiHMe$_2$)$_2$]. All other chemicals were purchased from commercial sources in purities >97% and used without further purification, if not otherwise stated. NMR spectra were obtained with either a Varian INOVA 300 or a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out with a Vario elementar EL *III* apparatus. X-ray crystal structure analyses were performed with a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[23] SHELXL-97[24] and WinGX[25]. Crystallographic details are summarized in Table 1. CCDC-702054 (**2a**), -702056 (**2b**) and -702055 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

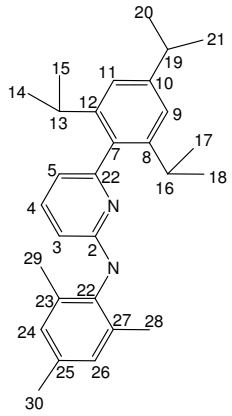
Synthesis of the Complexes

Synthesis of 2a: thf (20 mL) was added to a mixture of [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1.26 g, 2.00 mmol) and **1a** (913 mg, 2.00 mmol). The resulting solution was stirred at 60 °C overnight. All volatiles were removed in vacuo to yield **2a** as a pale yellow powder in excellent yield (1.65 g, 94%). Elemental analysis for $C_{44}H_{79}N_4OSi_4Y$ (881.4): calcd. C 59.96, H 9.03, N 6.36; found C 59.42, H 8.88, N 5.88. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.24 (d, 24H, ^3J(H,H) = 2.5 Hz, Si(CH_3)$_2$), 1.17 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.22 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.24 (br, 4H, β-CH_2, THF), 1.25 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.41 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.46 (d, 6H, ^3J(H,H) = 6.8 Hz,

CH(CH_3)$_2$), 2.80 (sept, 1H, ^3J(H,H) = 6.7 Hz, 15-H) 3.10 (sept, 2H, ^3J(H,H) = 6.7 Hz, 13,14/22,23-H), 3.58 (br, 4H, α-CH_2, THF), 3.71 (sept, 2H, ^3J(H,H) = 6.7 Hz, 13,14/22,23-H), 4.92 (sept, 4H, ^3J(H,H) = 3.0 Hz, ^1J(Si,H) = 84 Hz, Si*H*), 5.73 (d, 1H, ^3J(H,H) = 8.7 Hz, 3-H), 5.97 (d, 1H, ^3J(H,H) = 7.1 Hz, 5-H), 6.66 (dd, 1H, ^3J(H,H) = 8.1 Hz, ^3J(H,H) = 7.0 Hz, 4-H), 7.10-7.28 ppm (m, 5H, 9,11,18,19,20-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.8, 24.6, 24.8, 25.1, 25.7, 26.3, 26.5, 28.7, 31.0, 35.2, 71.2, 109.7, 112.1, 121.4, 124.9, 125.3, 137.6, 138.7, 144.8, 145.8, 147.6, 149.7, 156.6, 171.4 ppm; ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = -22.9 ppm.



Synthesis of 2b: [Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1.26 g, 2.00 mmol) and **1b** (829 mg, 2.00 mmol) were dissolved together in thf (20 mL). After stirring the mixture at 60°C for 12 h all volatiles were removed. The residue was redissolved in a minimum amount of pentane and crystallized at -30° C to afford a pale yellow crystalline material. Yield 940 mg (56%). Elemental analysis for $C_{41}H_{73}N_4OSi_4Y$ (839.3): calcd. C 58.67, H 8.77, N 6.68; found C 59.20, H 8.52, N 6.46. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.28 (d, 24H, ^3J(H,H) = 2.9 Hz, Si(CH_3)$_2$), 1.15 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.18 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.23 (m, 4H, β-CH_2, THF), 1.35 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 2.26 (s, 3H, 30-H), 2.49 (s, 6H, 28,29-H), 2.75 (sept, 1H, ^3J(H,H) = 6.7 Hz, 19-H), 3.13 (sept, 2H, ^3J(H,H) = 6.7 Hz, 13,16-H), 3.37 (m, 4H, α-CH_2, THF), 4.94 (sept, 4H, ^3J(H,H) = 3.1 Hz, ^1J(Si,H) = 83 Hz, Si*H*), 5.82 (d, 1H, ^3J(H,H) = 8.7 Hz, 3-H), 5.97 (d, 1H, ^3J(H,H) = 7.0 Hz, 5-H), 6.75 (dd, 1H, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 7.0 Hz, 4-H), 6.98 (s, 2H, 9,11/24,26-H), 7.06 ppm (s, 2H, 9,11/24,26-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.9, 20.9, 21.4, 22.2, 24.2, 24.8, 25.7, 26.8, 30.9, 35.1, 70.7, 107.2, 111.4, 121.2, 130.0, 132.6, 133.3, 137.9, 138.9, 144.3, 147.9, 149.8, 156.0, 168.9 ppm; ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = -27.0 ppm.



Synthesis of 3a: A mixture of $[La\{N(SiHMe_2)_2\}_3(thf)_2]$ (680 mg, 1.00 mmol) and **1a** (457 mg, 1.00 mmol) were dissolved together in toluene (20 mL) and stirred for 2 hours. All volatiles were removed and the residue was extracted with 20 mL of hexane. Removal of the solvent afforded spectroscopically pure **3a** as a yellow powder. Yield 430 mg (46%). Elemental analysis for $C_{44}H_{79}N_4OSi_4La$ (931.4): calcd. C 56.74, H 8.55, N 6.02; found C 56.19, H 8.60, N 6.01. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.20 (d, 24H, ^3J(H,H) = 2.7 Hz, Si(CH_3)$_2$), 1.17 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.22 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.23 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.24 (br, 4H, β-CH_2, THF), 1.39 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.43 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 2.79 (sept, 1H, ^3J(H,H) = 6.7 Hz, 15-H), 3.12 (sept, 2H, ^3J(H,H) = 6.7 Hz, 13,16-H), 3.38 (br, 4H, α-CH_2, THF), 3.58 (sept, 2H, ^3J(H,H) = 6.7 Hz, 13,16-H), 4.90 (br, 4H, SiH, ^3J(H,H) = 2.7 Hz, ^1J(Si,H) = 81 Hz, SiH), 5.73 (d, 1H, ^3J(H,H) = 8.3 Hz, 3-H), 5.95 (d, 1H, ^3J(H,H) = 7.1 Hz, 5-H), 6.70 (dd, 1H, ^3J(H,H) = 8.3 Hz, ^3J(H,H) = 7.1 Hz, 4-H), 7.08-7.27 ppm (m, 5H, 9,11,18,19,20-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.4, 24.8, 25.0, 25.3, 25.6, 26.0, 26.1, 29.1, 31.0, 35.1, 70.5, 109.4, 110.7, 121.5, 124.6, 124.7, 137.8, 138.6, 144.0, 146.5, 147.5, 149.4, 156.3, 170.3 ppm; ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = -25.8 ppm.

Synthesis of 3b: $[La\{N(SiHMe_2)_2\}_3(thf)_2]$ (680 mg, 1.00 mmol) and **1b** (415 mg, 1.00 mmol) were dissolved together in toluene (20 mL). After stirring the mixture for 2 hours all volatiles were removed and the residue was extracted with 20 mL of hexane. Removal of the solvent afforded spectroscopically pure **3b** as a yellow powder. Yield 521 mg (59%). Elemental analysis for $C_{41}H_{73}N_4OSi_4La$ (889.2) C 55.37, H 8.27, N 6.30; found C 55.26, H 8.25, N 6.12. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.24 (d, 24H, ^3J(H,H) = 1.7 Hz, Si(CH_3)$_2$), 1.16 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.19 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 1.24 (br, 4H, β-CH_2, THF), 1.36 (d, 6H, ^3J(H,H) = 6.7 Hz, CH(CH_3)$_2$), 2.27 (s, 3H, 30-H), 2.45 (s, 6H, 28,29-H), 2.76 (sept, 1H, ^3J(H,H) = 6.7 Hz, 19-H) 3.15 (sept, 2H, ^3J(H,H) = 6.7 Hz, 13,16-H), 3.27

(br, 4H, α-CH_2, THF), 4.93 (sept, 4H, ^3J(H,H) = 2.7 Hz, ^1J(Si,H) = 81 Hz, Si*H*), 5.81 (d, 1H, ^3J(H,H) = 8.8 Hz, 3-H), 5.96 (d, 1H, ^3J(H,H) = 6.9 Hz, 5-H), 6.79 (dd, 1H, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 6.9 Hz, 4-H), 6.97 (s, 2H, 9,11-H), 7.07 ppm (s, 2H, 24,26-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.5, 20.6, 21.4, 24.8, 24.9, 25.7, 26.4, 31.0, 35.1, 70.0, 107.3, 110.6, 121.3, 130.0, 132.1, 132.7, 138.1, 138.7, 145.3, 147.8, 149.4, 156.1, 168.3 ppm; ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = -26.1 ppm.

Synthesis of 4a: A Schlenk vessel was charged with **1a** (91.0 mg, 0.20 mmol) and toluene (3 mL) before a triethylaluminium solution (0.20 mL, 0.20 mmol, 1.0 M $AlEt_3$ in toluene) was added. After stirring the mixture for 1 h all volatiles were removed *in vacuo* to yield **4a** as colorless oil in almost quantitative yield. Elemental analysis for $C_{36}H_{53}N_2Al$ (540.8) C 79.95, H 9.88, N, 5.18; found C 79.33, H 10.20, N 5.48. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.36 (q, 2H, ^3J(H,H) = 8.1 Hz, AlCH_2CH$_3$), 0.37 (q, 2H, ^3J(H,H) = 8.1 Hz, AlCH_2CH$_3$), 1.07 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.15 (t, 6H, ^3J(H,H) = 8.1 Hz, AlCH$_2$CH_3), 1.16 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.19 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.25 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.40 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 2.79 (sept, 1H, ^3J(H,H) = 6.8 Hz, 15-H), 2.88 (sept, 2H, ^3J(H,H) = 6.8 Hz, 13,14/22,23-H), 3.50 (sept, 2H, ^3J(H,H) = 6.8 Hz, 13,14/22,23-H), 5.61 (d, 1H, ^3J(H,H) = 8.6 Hz, 3-H), 6.07 (d, 1H, ^3J(H,H) = 7.0 Hz, 5-H), 6.80 (dd, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 7.1 Hz, 4-H), 7.17 (br, 2H, 18,20-H), 7.19 ppm (br, 3H, 9,11,19-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 1.8, 9.2, 22.7, 24.2, 24.4, 24.7, 26.4, 28.6, 30.9, 34.8, 104.4, 111.3, 120.9, 124.3, 126.3, 133.4, 138.3, 141.4, 145.6, 146.9, 150.3, 154.8, 167.2 ppm.

Synthesis of 4b: To a stirred solution of **1b** (83.0 mg, 0.20 mmol) in toluene (3 mL) was added a triethylaluminium solution (0.20 mL, 0.20 mmol, 1.0 M $AlEt_3$ in toluene). After stirring the mixture for 1 h all volatiles were removed *in vacuo* to yield **4b** as colorless oil in almost quantitative yield. Elemental analysis for $C_{33}H_{47}AlN_2$ (498.7) C 79.47, H 9.50, N 5.62; found C 79.23, H 9.55, N 5.72. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.33 (q, 4H, ^3J(H,H) = 8.1 Hz, AlCH_2CH$_3$), 1.11 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.16 (t, 6H, ^3J(H,H) = 8.1 Hz, AlCH$_2$CH_3), 1.20 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 1.42 (d, 6H, ^3J(H,H) = 6.8 Hz, CH(CH_3)$_2$), 2.20 (s, 3H, 30-H), 2.27 (s, 6H, 28,29-H), 2.80 (sept, 1H, ^3J(H,H) = 6.9 Hz, 9-H), 2.90 (sept, 2H, ^3J(H,H) = 6.8 Hz, 13,16-H), 5.64 (dd, 1H, ^4J(H,H) = 0.8 Hz, ^3J(H,H) = 8.6 Hz, 3-H), 6.09 (dd, 1H, ^4J(H,H) = 0.8 Hz, ^3J(H,H) = 7.2 Hz, 5-H), 6.83 (dd, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 7.2 Hz, 4-H), 6.85 (s, 2H, 9,11-H), 7.19 ppm (s, 2H, 24,26-H); ^{13}C NMR (75 MHz,

C_6D_6, 298 K): δ = 0.2, 8.9, 18.8, 20.9, 22.7, 24.2, 26.5, 30.9, 34.8, 104.0, 111.1, 120.9, 129.6, 133.4, 134.0, 134.2, 138.4, 141.4, 146.9, 150.2, 154.2, 165.6 ppm.

5.5. Acknowledgments

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5.6. References

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6. Scandium Aminopyridinates: Synthesis, Structure and Isoprene Polymerization

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Abstract: Alkane elimination reactions of $[Sc(CH_2SiMe_3)_3(thf)_2]$ or $[Sc(CH_2Ph)_3(thf)_3]$ with aminopyridines (**1a** = (2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine, **1b** = [6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-(2,4,6-trimethyl-phenyl)-amine, **1c** = (2,6-diisopropyl-phenyl)-[6-(2,6-dimethyl-phenyl)-pyridin-2-yl]-amine) led to selective formation of dialkyl complexes of scandium stabilized by one aminopyridinato ligand (= Ap). The reaction of these compounds with anilinium borate leads to the elimination of one of the two alkyl functions and affords organoscandium cations. The amine elimination reaction of $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ with the aminopyridine **1a** yields the corresponding mono(aminopyridinate) complex. Single-crystal X- ray analysis were carried out for the compounds $[Ap^*Sc(CH_2Ph)_2(thf)]$ **3a**, $[Ap^*Sc(CH_2Ph)(thf)_3][B(C_6H_5)_4]$ **4a** and $[Ap^*Sc\{N(SiHMe_2)_2\}_2]$ **6a** (Ap*-H = **1a**). The aminopyridinate-stabilized scandium dialkyles $[ApScR_2(thf)]$ (R = CH_2SiMe_3, CH_2Ph) are initiators for the controlled 3,4-selective isoprene polymerization after activation with perfluorinated tetraphenyl borates. Variation of the polymerization temperature as well as the addition of different alkylaluminium compounds influence the microstructure of the obtained polymer. Bis(dimethylsilyl)amides of scandium polymerize isoprene in the presence of anilinium borate and alkylaluminium compounds with high cis-1,4-selectivity.

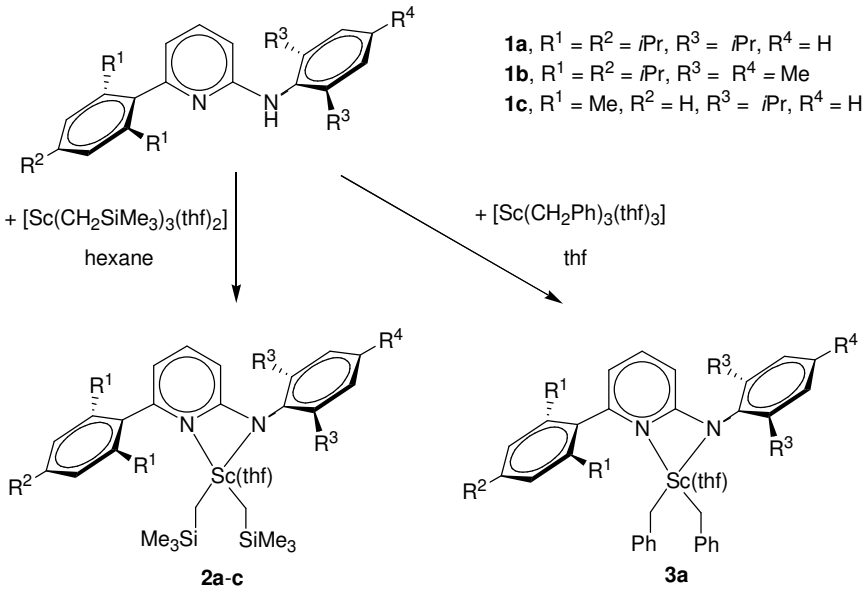
6.1. Introduction

Isoprene polymerization catalyzed by organolanthanoid cations has gained a lot of attention recently after the initial reports published by Okuda and coworker as well as Hou and coworker simultaneously.[1] Rare earth metal-alkyl(halogenide) complexes of the type [(**L**)LnR$_2$(D)] (R = CH_2SiMe_3, $AlMe_4$, *o*-$CH_2C_6H_4NMe_2$, μ_3-C_3H_5, Cl, D = thf) where **L** is a cyclopentadienyl[2] or an anionic N- ligand,[3,4] are known to catalyze or initiate isoprene polymerization.[5] Very interesting in terms of stereoselectivity are the precursors [{$Me_2Si(C_5Me_4)$-(PHCy)}YCH_2SiMe_3]$_2$ (Cy = cyclohexyl)[1b] or [(PhC(NC_6H_4*i*Pr_2-2,6)$_2$)Y(*o*-$CH_2C_6H_4NMe_2$)$_2$][4] which show, in the combination with [Ph_3C][$B(C_6F_5)_4$], very high regio- and stereoselectivities (3,4-selectivity: >99%, mmmm > 99 %). Furthermore, the yttrium amidinate complex switches the stereoselectivity drastically from 3,4-isospecific to *cis*-1,4-selective by addition of $AlMe_3$. Recently Zimmermann et al. described half-sandwich complexes of the type [(C_5Me_5)Ln($AlMe_4$)$_2$] (Ln = Y, La, Nd) which, upon activation with fluorinated borates or boranes, are highly active catalysts for the living *trans*-1,4-selective (up to 99.5%) polymerization of isoprene.[2b] Although 3,4-polyisoprene is used as an important component of high-performance rubber for example in tires,[6] the number of 3,4-selective catalyst systems is smaller in contrast to systems which yield high *cis*-1,4-polyisoprene (natural rubber),[2d,3e,4,7,8] most likely since isoprene prefers to coordinate in most of the catalytically active systems in the thermodynamically more stable *cis*-1,4-mode.[3a,9]

Herein we report the synthesis and the structure of dialkyl and bis(dimethylsilylamide) complexes of scandium stabilized by aminopyridinato ligands[10,11] (= Ap) and their catalytic properties in the isoprene polymerization in the presence of borates. Furthermore, the influence of the aminopyridinato ligand, the polymerization temperature, the catalyst concentration and various aluminium alkyls on the polymerization will be discussed.

6.2. Results and Discussion

Metal Complex Synthesis and Structure



Scheme 1. Synthesis of aminopyridinate-stabilized dialkyls **2a**, **2b**, **2c** and **3a**.

Similarly to the synthesis of aminopyridinate yttrium dialkyls $[ApY(CH_2SiMe_3)_2(thf)]$[12] the corresponding scandium complexes were successfully prepared (Scheme 1). Only very recently the first scandium aminopyridinate, a homoleptic compound, was described.[13] The reaction of the aminopyridines **1a-c** with one equivalent of $[Sc(CH_2SiMe_3)_3(thf)_2]$ yielded after tetramethylsilane elimination the corresponding scandium compounds **2a-c** (Scheme 1, left side) which were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The ^1H NMR spectra of the compounds **2a-c** exhibit the characteristic splitting pattern of each aminopyridinato ligand as it was observed for the already described analogous yttrium compounds. In contrast to the yttrium derivatives the methylene groups of the alkyl ligand exhibit an AB-system (doublets at 0.01 and 0.09 ppm for **2a**; -0.01 and 0.07 ppm for **2b** and 0.01 and 0.07 ppm for **2c**) in the ^1H NMR spectrum. This effect can be attributed to the smaller coordination sphere of the scandium ion and hindered rotation of the aminopyridinato ligands therewith. The aminopyridine **1a** reacts also with one equivalent of the tribenzyl complex $[Sc(CH_2Ph)_3(thf)_3]$ to afford after toluene elimination the aminopyridinate-stabilized dibenzyl complex **3a**. Suitable single crystals for X-ray structure analysis of this compound were obtained by cooling a saturated pentane solution to 0°C. The compound **3a** crystallizes in the monoclinic space group *C*2/*c*. The molecular structure is depicted in Figure 1; crystallographic details are summarized in Table 5. The metal centre has a coordination number of five and is coordinated by one aminopyridinato ligand, one thf ligand and two benzyl ligands which show in the solid state different coordination modes. One of the two benzyl ligands has an η^1-coordination (Sc1-C1-C2 121.88(16)), whereas the other ligand exhibits an η^2-coordination which is indicated by the Sc1-C8-C9 angle of 88.50(15)° and a

shortened distance of the scandium atom to the *ipso*-carbon atom of this ligand (Sc1-C9 2.657(2) Å).

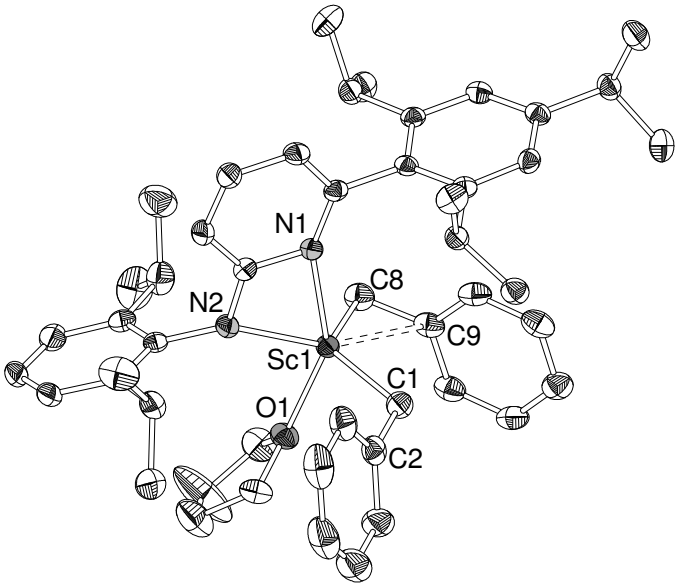
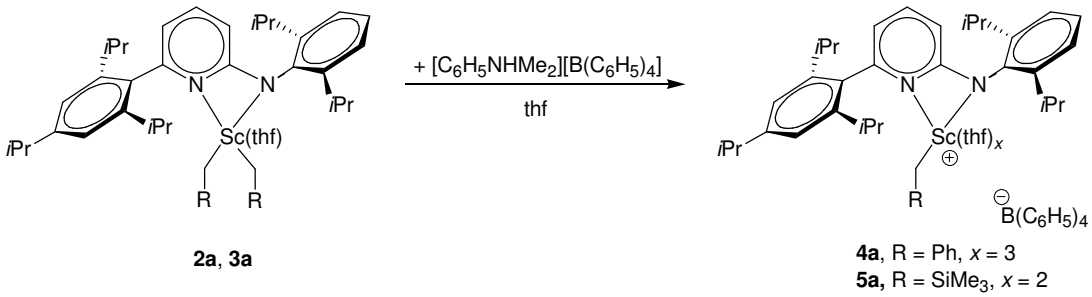


Figure 1. ORTEP diagram of the molecular structure of **3a** in the solid state (ellipsoids set at 50% probability level). H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc1-N1 2.286(2), Sc1-N2 2.1290(19), Sc1-C1 2.245(3), Sc1-C8 2.256(3), Sc1-C9 2.657(2), N1-Sc1-N2 61.31(7), Sc1-C1-C2 121.88(16), Sc1-C8-C9 88.50(15).

The dialkyl complexes **2a** and **3a** react with one equivalent of anilinium borate to afford after alkane elimination the organoscandium cations **4a** and **5a** respectively which were isolated in the presence of thf (Scheme 2). The composition of the compounds was determined by NMR spectroscopy and elemental analyses. Furthermore, compound **4a** was characterized by an X-ray structure analysis. Suitable single crystals were obtained by slow diffusion of pentane into a thf/toluene (1:1) solution of **4a**. The compound crystallizes in the triclinic space group $P\bar{1}$ as yellow plates. Crystallographic details are summarized in Table 5 and the molecular structure of **4a** is presented in Figure 2.

The cation of **4a** shows a distorted octahedral coordination of the scandium atom indicated by O-Sc-C_{benzyl} angles of 89.51(17) and 95.94(18)°. The metal atom is coordinated by three thf, one benzyl [η^1-coordination, Sc1-C1-C2 121.2(4)°] and one aminopyridinato ligand. The thf ligands show a meridonal arrangement and the methylene group of the benzyl ligand is in *trans*-position to the pyridine nitrogen atom of the aminopyridinato ligand.



2a, **3a**

4a, R = Ph, *x* = 3
5a, R = $SiMe_3$, *x* = 2

Scheme 2. Synthesis of organoscandium cations **4a** and **5a**.

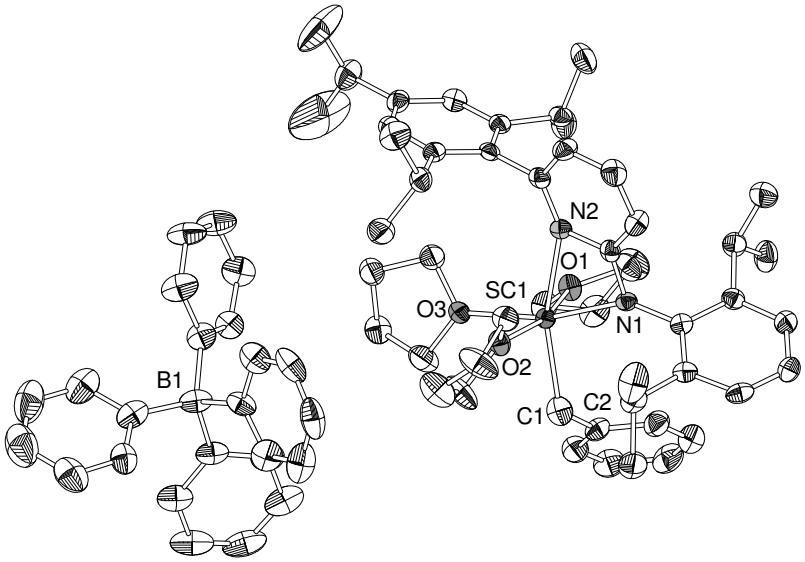
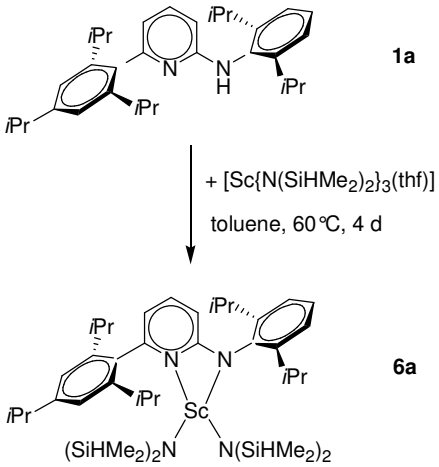


Figure 2. ORTEP diagram of the molecular structure of **4a** in the solid state (ellipsoids set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc1-C1 2.234(6), Sc1-N1 2.188(4), Sc1-N2 2.358(4), Sc1-O1 2.177(3), Sc1-O2 2.192(3), Sc1-O3 2.217(3), Sc1-C1-C2 121.2(4), O1-Sc1-C1 95.15(17), O2-Sc1-C1 89.51(17), O3-Sc1-C1 95.94(18).

As we reported recently, the bulky aminopyridines **1a,b** react with triamide precursors, namely $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$ (Ln = Y, La).[14] Similarly the compound $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ reacts with the aminopyridine **1a** in toluene at 60°C within four days to afford the diamide **6a** (Scheme 3).



Scheme 3. Synthesis of the aminopyridinate-stabilized diamide **6a**.

Figure 5 depicts the molecular structure of **6a**, crystallographic details are summarized in Table 5. The structure of **6a** demonstrates that the thf ligand present in the starting compound was eliminated due to the steric demand of the aminopyridinato ligand. The metal atom displays a distorted tetrahedral geometry and is coordinated by four nitrogen atoms [N1-Sc-N4 116.33(5)°, N3-Sc-N4 107.36(6)°, N2-Sc-N3 109.49(6)°] (two from the aminopyridinato and two from the bis(dimethylsilyl)amido ligand respectively). Both scandium to nitrogen bond distances between the $\{N(SiHMe_2)_2\}$ groups and the scandium atom of **6a** (2.0573(15) and 2.0409(14) Å) are only marginally shorter than the average of Sc-N bond distances of 2.069(2) Å in $[Sc\{N(SiHMe_2)_2\}_3(thf)]$.[15] Both $\{N(SiHMe_2)_2\}$ ligands exhibit an asymmetrical coordination to the metal centre which is caused by a Sc···(Si-H) interaction of both bis(dimethylsilyl)amido ligands respectively. As a result, the Sc-N-Si angles within each of amido ligands are different [Sc-N3-Si1 100.93(7)° vs. Sc-N3-Si2 129.36(9)° and Sc-N4-Si3 99.40(7)° vs. Sc-N4-Si4 131.32(8)°]. This bending towards the scandium centre also results in different Sc-Si distances of each $\{N(SiHMe_2)_2\}$ ligands respectively (Sc-Si1 2.9003(6) and Sc-Si3 2.8642(6) Å vs. Sc-Si2 3.4117(6) and Sc-Si4 3.4208(6) Å). The very short Sc-Si3 distance of 2.8642(6) Å is the shortest up till now known scandium silicon distance for an agostic interaction and is very close to the known distance of Sc-Si σ-bonds in $[(C_5H_5)_2Sc\{Si(SiMe_3)_3\}thf]$[16] with 2.863(2) Å and $[(C_5Me_5)_2Sc(SiH_2SiPh_3)]$[17] with 2.797(1) Å. Proton NMR spectra of **6a** were recorded in toluene-d_8 in the temperature range of 23 to 100°C (Figure 3). The room temperature ^1H NMR spectrum reveals two doublets for the methyl groups of the silylamide group but only one septet for the SiH protons. The same splitting pattern was observed at -80°C. Above 20°C, the signals for the SiMe groups begin to broaden and at 100°C only one doublet is observed.

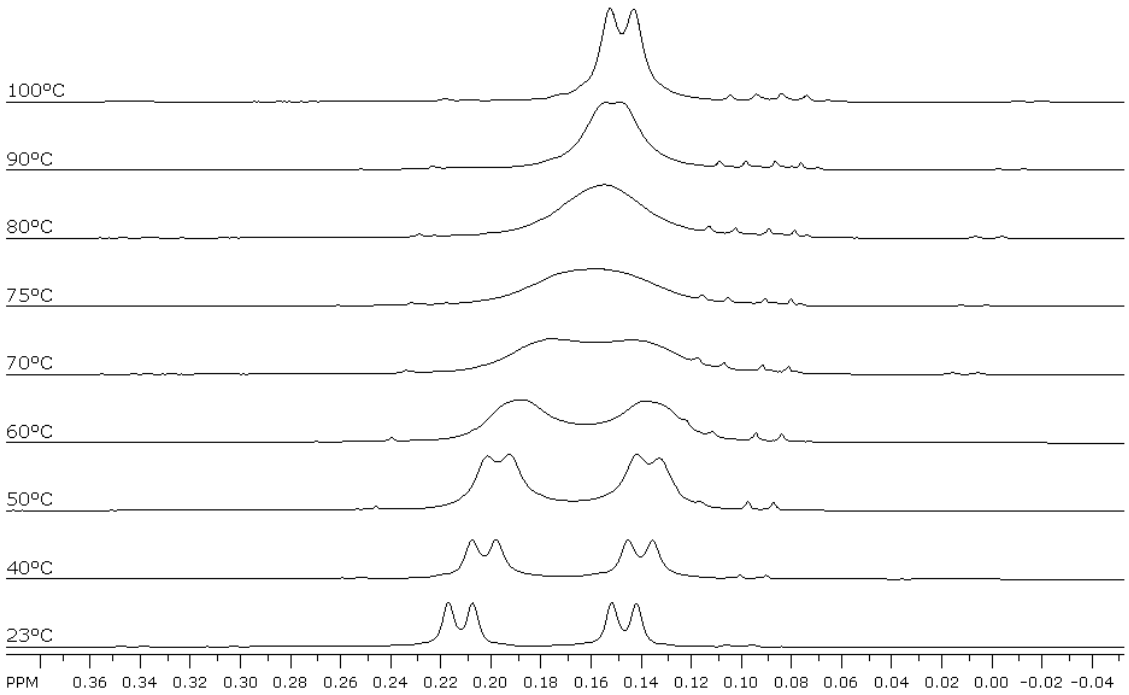


Figure 3. ^{1}H NMR spectra of **6a** in toluene-d_8 at different temperatures.

The rate constants for this exchange were determined by NMR simulation using the program DNMR3.[18] From the Eyring equation, the activation parameters for this process were calculated ($\Delta G^{\ddagger}$ = 73.9 ± 0.9 kJ mol^{-1}; $\Delta H^{\ddagger}$ = 49.2 ± 0.3 kJ mol^{-1}; $\Delta S^{\ddagger}$ = 71.9 ± 1.0 J mol^{-1} K^{-1}, T_c = 348 K; Figure 4). The activation energy of $\Delta G^{\ddagger}$ = 73.9 kJ mol^{-1} for this process is similar to that found in [(etbmp)Sc{N(SiHMe$_2$)$_2$}(thf)] (etbmp = 1,4-dithiabutanediyl-bis(6-*tert*-butyl-4-methylphenol) with $\Delta G^{\ddagger}$ = 69.79 kJ mol^{-1} and T_c = 330 K.[19]

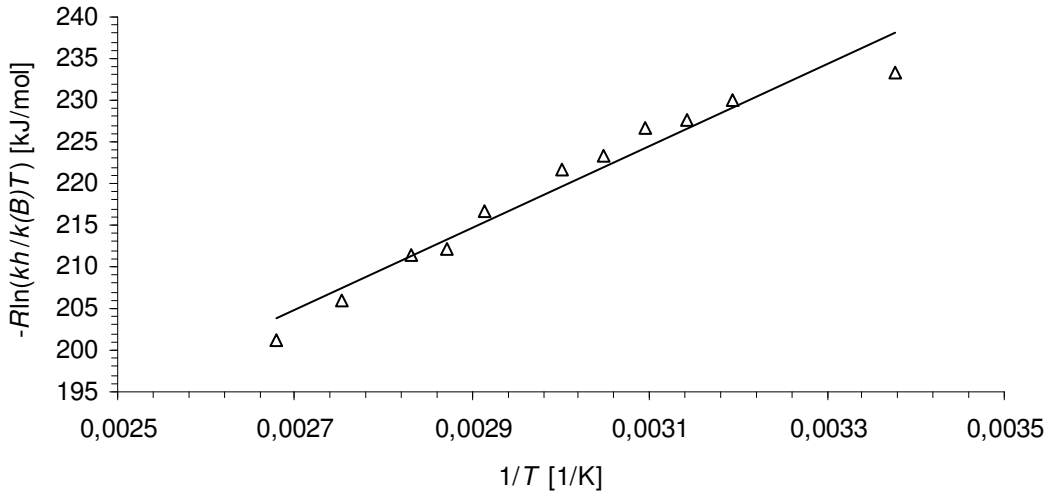


Figure 4. Eyring plot ($-R\ln(kh/k_BT) = -\Delta S^{\ddagger} + \Delta H^{\ddagger}/T$) for the coalescence of the SiMe signals.

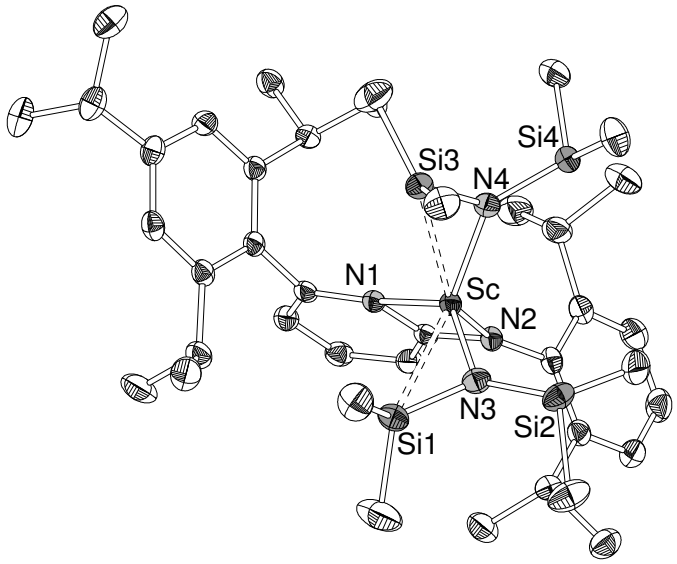


Figure 5. ORTEP diagram of the molecular structure of **6a** in the solid state (ellipsoids set at 50% probability level). H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Sc-N1 2.2548(14), Sc-N2 2.1320(14), Sc-N3 2.0573(15), Sc-N4 2.0409(14), Sc-Si1 2.9003(6), Sc-Si2 3.4117(6), Sc-Si3 2.8642(6), Sc-Si4 3.4208(6), Si1-N3-Si2 129.45(9), Sc-N3-Si1 100.93(7), Sc-N3-Si2 129.36(9), Si3-N4-Si4 128.64(9), Sc-N4-Si3 99.40(7), Sc-N4-Si4 131.32(8), N1-Sc-N4 116.33(5), N3-Sc-N4 107.36(6), N2-Sc-N3 109.49(6).

Polymerization of isoprene

The complexes **2**, **3a** and **6a** were tested as precatalysts for the polymerization of isoprene. The microstructure of the obtained polyisoprene was determined by ^{1}H and ^{13}C NMR spectroscopy. The results of the polymerization experiments are summarized in Table 1-4. The bis(trimethylsilylmethyl)scandium compounds **2a-c** polymerize isoprene in a 3,4-selective fashion (>93%) after activation with perfluorinated anilinium borate in chlorobenzene or toluene. A narrow molecular weight distribution of 1.26 to 1.33 is observed (Table 1, run 1-3). A marked decrease of the 3,4-polyisoprene content and broadening of the molecular weight distribution is observed when triisobutylaluminium (10 equivalents) was mixed with the polymerization catalyst. (Table 1, run 5-7). Detailed investigations of the influence of different aluminium alkyls or TIBAO (tetraisobutylalumoxane) on the microstructure of the obtained polymer were performed (Table 1, run 8-10). Switching from Al*i*Bu_3 to the shorter-chain aluminium compounds $AlEt_3$ and $AlMe_3$ results in a decrease of 3,4-polyisoprene content and increase of *cis*-1,4-polyisoprene content in the direct relation to the size of the alkyl groups at the aluminium metal; the molecular weight distributions are very broad due to a bimodal distribution. A similar influence of the aluminium alkyls on the microstructure of the polymer was also reported by Hou for an yttrium-amidinate isoprene polymerization catalyst.[4] When the polymerization temperature was increased to 40°C for

the system **2a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$/Al*i*Bu$_3$ a decrease of the 3,4-polyisoprene content to 62% together with a broadening of the molecular weight distribution were observed (Table 1, run 11). Decrease of the polymerization temperature (0°C) for this system leads to an increased 3,4-polyisoprene content going along with an isotactically enrichment (mm ≈ 100%, mmmm ≈ 30% and 35%, Table 1, run 12, 13). At even lower temperature of -14°C a relatively narrow molecular weight distribution was observed, indicative for the deactivation of other polymerization-active species or absence of such species at low temperature.

Table 1. Polymerization of isoprene with complexes **2** under various conditions[a]

Run	Cat.	Al-alkyl	T [°C]	Yield [%]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4 / *cis*-1,4
1[d]	**2a**	-	20	94	135	1.26	93/7
2	**2b**	-	20	100	141	1.27	97/3
3	**2c**	-	20	94	192	1.33	96/4
4[e]	**2a**	-	20	81	58	4.47	83/17
5	**2a**	Al*i*Bu$_3$	20	100[f]	137	3.84	80/20
6	**2b**	Al*i*Bu$_3$	20	98	144	3.08	91/9
7	**2c**	Al*i*Bu$_3$	20	100	144	2.59	89/11
8	**2a**	TIBAO	20	100	104	2.00	96/4
9	**2a**	AlEt$_3$	20	96	32	6.84[g]	81/19
10	**2a**	AlMe$_3$	20	90	25	6.10[g]	33/67
11	**2a**	Al*i*Bu$_3$	40	100	31	6.10[g]	62/38
12	**2a**	Al*i*Bu$_3$	0	100	147	3.54	96[h]/4
13	**2a**	Al*i*Bu$_3$	-14	100	225	1.75	96[i]/4
14	**2a**	-	0	99	80	2.35	96/4
15	-	Al*i*Bu$_3$	20	-	-	-	-

[a] Conditions: 10 mL C_6H_5Cl, Dialkyl (**2a-c**): 10µmol, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ 10µmol, isoprene: 10mmol, [Al]/[complex] = 10, reaction time: 20h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^{1}H and ^{13}C spectroscopy, no *trans*-1,4 polyisoprene were found. [d] 10 mL toluene used as solvent. [e] $[Ph_3C][B(C_6F_5)_4]$ was used as the activator, polymerization time 2h. [f] 98% conversion after 30 min. [g] bimodal distribution. [h] mm = 100%, mmmm = 30%. [i] mm = 100%, mmmm = 35 %.

To investigate the isoprene polymerization catalyzed by **2a** in more detail, the polymerizations were carried out at different monomer to catalyst ratios. The results are

summarized in Table 2. A plot of the concentration of **2a** against the average number molecular weight (M_n) affords a linear dependence, indicative for a controlled polymerization (Figure 6).

Table 2. Polymerization of isoprene with complex **2a** with different catalyst/monomer ratios.

Run	Concentration **2a** [µmol]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4 / *cis*-1,4
1	5	157	1.96	96/4
2	10	115	1.55	94/6
3	15	75	1.30	94/6

[a] Conditions: 10 mL C_6H_5Cl, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$, [**2a**]/[B] = 1, isoprene: 10mmol, reaction time: 20h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4 polyisoprene were found.

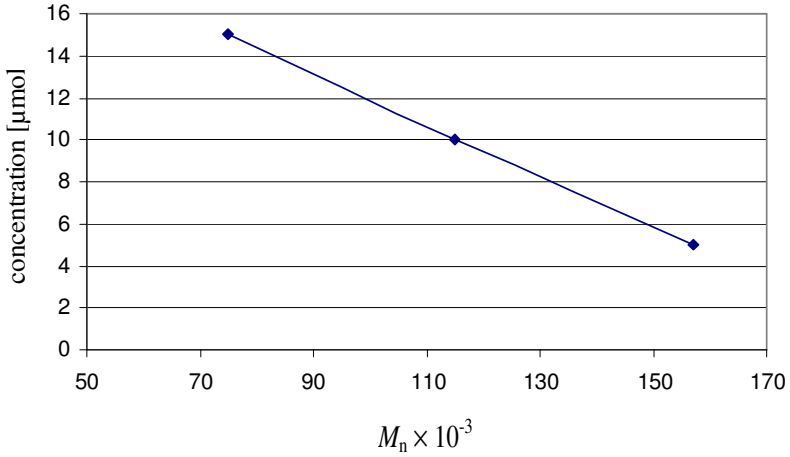


Figure 6. Plot of concentration of **2a** versus average number molecular weight (M_n) of the obtained polyisoprene.

The aminopyridinate-stabilized dibenzyl complex **3a** showed no activity in the polymerization of isoprene in the presence of anilinium borate or tris(pentafluorphenyl)borane (Table 3, run 1-2). However, if $[Ph_3C][B(C_6F_5)_4]$ is used as an activator a high stereo- and regioselectivity (95% 3,4-isoprene, mm = 100%, mmmm = 35%, Table 3, run 3) and a narrow molecular weight distribution of 1.68 is observed for the polymer. Isotactically enriched 3,4-polymerization of isoprene has been rarely described.[4,1b,8g] Addition of alkylaluminium compounds (Table 3, run 4-13) to the system **3a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ also leads to a polymerization active system with the same trend as it was observed for **2** as a precatalysts (the use of $[Ph_3C][B(C_6F_5)_4]$ as an activator leads to a similar selectivity like it was observed for the system **3a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$/$AlR_3$, but it highly increases the molecular

weight distribution, Table 3, run 4). The influence on the *cis*-1,4-selectivity in the presence of $AlMe_3$ is even more pronounced (67% *cis*-1,4-polyisoprene with **2a** vs. 90% with **3a**). If less than 10 equivalents of Al*i*Bu_3 were used a significantly narrower molecular weight distribution was observed. The presence of bimodal distributions for the system **3a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$/$AlR_3$ (R = Me, Et, *i*Bu) suggests also the presence of several polymerization-active species; because of its close relation to the yttrium amidinate system from Hou,[4] (addition of $AlMe_3$ switches the regio- and stereoselectivity) where a heterotrinuclear Y/Al complex is formed, we suggest that a similar species might be one of these active species in our system (Table 3, run 4, 9-11). The thf-stabilized organoscandium cation **4a** does not polymerize isoprene, even in the presence of 10 equivalents of Al*i*Bu_3.

We can not completely rule out the formation of aminopyridinate aluminium complexes under the polymerization conditions, but aminopyridinato ligand transfer from the lanthanoid to the aluminium centre is usually observed for neutral rare earth complexes and not for cations.[12,14]

Table 3. Polymerization of isoprene with complex **3a** under various conditions[a]

Run	Al-alkyl (equiv)	*T* [°C]	Yield [%]	$M_n \times 10^{-3}$[b]	M_w/M_n [b]	Microstructure [%] [c] 3,4 / *cis*-1,4
1	-	20	-	-	-	-
2[d]	-	20	-	-	-	-
3[e]	-	20	97	130	1.68	95[f]/5
4[e]	Al*i*Bu_3 (10)	20	100	33	9.48	81/19
5	Al*i*Bu_3 (10)	20	98	78	5.32[g]	76/24
6	Al*i*Bu_3 (5)	20	99	73	2.85	73/27
7	Al*i*Bu_3 (2)	20	100	139	2.10	77/23
8	Al*i*Bu_3 (1)	20	100	119	1.76	81/19
9	$AlEt_3$ (10)	20	99	63	3.86[g]	37/63
10	$AlMe_3$ (10)	20	96	67	4.51[g]	10/90
11	Al*i*Bu_3 (10)	0	100	153	3.43[g]	>99/0
12	Al*i*Bu_3 (10)	-14	100	129	2.40	>99/0

[a] Conditions: 10 mL C_6H_5Cl, **3a** 10µmol, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ 10µmol, isoprene: 10mmol, reaction time: 20h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4 polyisoprene were found. [d] $B(C_6F_5)_3$ was used as the activator. [e] $[Ph_3C][B(C_6F_5)_4]$ was used as the activator, 20mL C_6H_5Cl. [f] mm = 100%, mmmm = 35%. [g] bimodal distribution.

The diamide **6a** is also an effective precatalyst for the polymerization of isoprene. After alkylation with 10 equivalents of alkylaluminium compounds ($AlMe_3$ or $Al\textit{i}Bu_3$) the compound **6a** yields *cis*-1,4-enriched polyisoprene in the presence of $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (Table 4, run 3, 4). Aminopyridinato-ligand-stabilized yttrium or lanthanum diamides react with alkylaluminium compounds by transfer of the aminopyridinato ligand from the rare earth metal to the aluminium atom.[14] ^1H NMR spectroscopic investigations of the reaction of **6a** with an excess of trimethylaluminium (6 equivalents) reveal that the diamide **6a** react immediately with the alkylaluminium compound. The proton NMR spectrum showed the formation of a new aminopyridinato ligand containing species and one equivalent of $[Me_2Al\{\mu\text{-}N(SiHMe_2)_2\}]_2$. Furthermore, two equivalents of unreacted $AlMe_3$ were detected. This led to the conclusion that a bis(aluminate)scandium species of the type $[ApSc(AlMe_4)_2]$ had been formed. A similar formation of a bis(aluminate) complex was described by Anwander et al. in the reaction of $[Cp^*Ln\{N(SiHMe_2)_2\}_2]$ (Cp^* = pentamethylcyclopentadienyl, Ln = Y, Lu) with $AlMe_3$. [20] Unfortunately, we did not succeed to separate these species from the byproduct $[Me_2Al\{\mu\text{-}N(SiHMe_2)_2\}]_2$ in order to prove clearly the existence of the aminopyridinate bis(aluminate) complex. The NMR tube reaction of **6a** with trimethylaluminium also displayed the formation of $[ApAlMe_2]$ by ligand transfer[11g,14] (11% after 3.5 h, 40% after 10 d).

Further investigations revealed that the triamide $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ showed similar *cis*-1,4-selectivity under the same conditions for the polymerization of polyisoprene (Table 4, run 1, 2). A similar system ($[Nd\{N(SiMe_3)_2\}_3]/[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$) also showed 1,4-*cis*-selectivity for the polymerization of butadiene. [21]

Table 4. Polymerization of isoprene with bis(dimethylsilylamide)scandium complexes[a]

Run	Cat.	Yield [%]	$M_n \times 10^{-3}$[b]	M_w/M_n[b]	Microstructure [%][c] 3,4 / *cis*-1,4
1[d]	$[Sc\{N(SiHMe_2)_2\}_3(thf)]$	97	183	2.73	6/94
2[e]	$[Sc\{N(SiHMe_2)_2\}_3(thf)]$	91	64	2.81	7/93
3[d]	**6a**	100	206	2.22	22/78
4[e]	**6a**	100	241	2.32	4/96

[a] Conditions: 10 mL C_6H_5Cl, Cat. 10µmol, anilinium borate: $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ 10µmol, isoprene: 10mmol, reaction time: 20h. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy, no *trans*-1,4 polyisoprene were found. [d] $Al\textit{i}Bu_3$ (10 equiv) used for alkylation/activation, [e] $AlMe_3$ (10 equiv) used for alkylation/activation.

Table 5. Details of the X-ray crystal structure analyses.

Compound	**3a**	**4a**	**6a**
Formula	$C_{50}H_{65}N_2OSc \times C_5H_{12}$	$C_{75}H_{94}BN_2O_3Sc$	$C_{40}H_{71}N_4\ ScSi_4$
Crystal system	monoclinic	triclinic	monoclinic
Space group	*C*2/*c*	$P\bar{1}$	$P2_1/n$
a [Å]	36.4750(12)	13.6470(11)	11.6110(5)
b [Å]	12.9730(6)	15.2080(13)	18.8400(8)
c [Å]	23.8620(9)	19.1700(15)	21.6160(9)
α [°]	90	101.638(6)	90
β [°]	118.169(4)	98.954(6)	103.936(3)
γ [°]	90	113.099(6)	90
Z	4	2	4
μ [mm^{-1}]	0.186	0.152	0.295
Cell volume [$Å^3$]	9953.9(7)	3460.5(5)	4589.3(3)
Crystal size [mm^3]	0.55×0.29×0.21	0.35×0.35×0.11	0.24×0.13×0.12
T [K]	133(2)	133(2)	133(2)
θ range [°]	1.79-26.05	1.52-24.00	1.45-26.19
Reflections unique	9361	10851	8654
Refl. Obs. [$I>2\sigma(I)$]	5866	5776	7552
Parameters	532	742	458
wR_2 (all data)	0.123	0.206	0.109
R value [$I>2\sigma(I)$]	0.052	0.088	0.040

6.3. Conclusions

Mono(aminopyridinate)scandium complexes of the type $[ApScR_2(thf)_x]$ (R = CH_2SiMe_3, CH_2Ph, x = 1; R = $N(SiHMe_2)_2$, x = 0) were synthesized and characterized. The dialkyl complexes are active and selective catalysts for the controlled 3,4-selective polymerization of isoprene after activation by borates. Addition of alkylaluminium compounds to the catalyst system leads to drastical changes in the microstructure of the polymer which are depending from the sterical demand of the alkyl ligand of the aluminium and the polymerization temperature. The stereo- and regioselectivity can be improved by polymerization at low

temperatures. The highest stereo- and regioselectivity was observed for the catalyst/activator system **3a**/$[Ph_3C][B(C_6F_5)_4]$ (3,4-content 95%, mm = 100%, mmmm = 35%, M_w/M_n = 1.68), whereas the system **2a**/$[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ shows the narrowest molecular weight distribution (3,4-content 93%, M_w/M_n = 1.26). The ternary systems **6a**/AlR_3/ $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ and $[Sc\{N(SiHMe_2)_2\}_3(thf)]$/$AlR_3$/ $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (R = Me, *i*Bu) polymerize isoprene *cis*-1,4-selective.

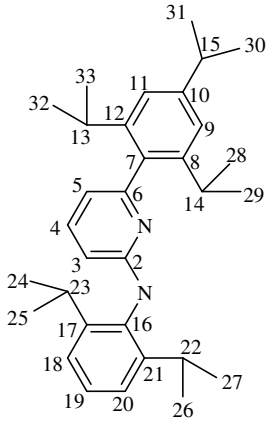
6.4. Experimental Section

General Procedures Synthesis and Structure

All reactions and manipulations involving air-sensitive compounds were performed under dry and oxygen free argon by using standard Schlenk and glovebox techniques. Non-halogenated solvents were dried with sodium/benzophenone ketyl and halogenated solvents with CaH_2. Deuterated solvents were obtained from Cambridge Isotope Laboratories, degassed, dried with molecular sieves and distilled prior to use. Starting materials **1a-c**,[12,22] tetra-isobutylaluminoxane ($[iBu_2Al]_2O$, TIBAO),[23] $[Sc(CH_2SiMe_3)_3(thf)_2]$,[24] $[Sc(CH_2Ph)_3(thf)_3]$,[25] $[Sc\{N(SiHMe_2)_2\}_3(thf)]$,[15] $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$[26] were synthesized according to literature methods. All other chemicals were purchased from commercial sources in purities >97% and used without further purification, if not otherwise stated. NMR spectra were obtained with either a Varian INOVA 300 or a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out with a Vario elementar EL III apparatus. The molecular weights (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) on an Agilent 1200 series (Column: PLgel Mixed-C) at 30°C using thf as eluent and a flow rate of 1mL/min against polystyrene standards. X-ray crystal structure analyses were performed with a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[27] SHELXL-97[28] and WinGX[29]. Crystallographic details are summarized in Table 5, CCDC-734318-734320 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

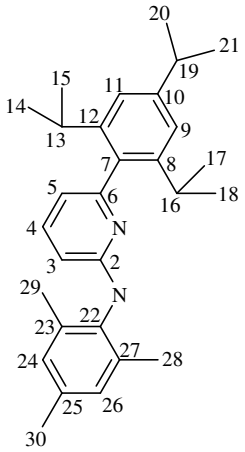
Synthesis of the Complexes

Synthesis of 2a: To a mixture of $[Sc(CH_2SiMe_3)_3(thf)_2]$ (451 mg, 1.00 mmol) and **1a** (457 mg, 1.00 mmol) was added hexane (20 mL) at room temperature. The reaction mixture was stirred for 1 h and filtered. Removal of all volatiles under vacuum yielded 610 mg (80%) of **2a** as a yellow crystalline material. Elemental analysis for $C_{44}H_{67}N_2OSi_2Sc$ (747.2): calcd. C 70.73, H 9.85, N 3.75; found C 70.57, H 10.12, N 3.48. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.01 (d, ^2J(H,H) = 11 Hz, 2H, CH_AH$_B$SiMe$_3$), 0.09 (d, ^2J(H,H) = 11 Hz, 2H, CH$_A$$H_B$SiMe$_3$), 0.14 (s, 18H, CH$_2SiMe_3$), 1.08 (br, 4H, β-C$H_2$, THF), 1.16 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.20 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.23 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.36 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.61 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.93 (sept, ^3J(H,H) = 6.8 Hz, 1H, 15-H), 3.16 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 3.44 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 3.81 (br, 4H, α-CH_2, THF), 5.63 (d, ^3J(H,H) = 8.5 Hz, 1H, 3-H), 6.16 (d, ^3J(H,H) = 7.1 Hz, 1H, 5-H), 6.74 (dd, ^3J(H,H) = 8.5 Hz, ^3J(H,H) = 7.1 Hz, 1H, 4-H), 7.16-7.30 ppm (m, 5H, 9,11,18,19,20-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.7, 23.3, 24.1, 24.5, 24.7, 25.3, 27.0, 28.6, 31.0, 35.1, 45.3, 71.5, 106.4, 112.3, 121.2, 124.3, 125.2, 135.8, 139.6, 144.3, 144.4, 146.7, 149.6, 156.0, 170.0 ppm; ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = -4.9 ppm.

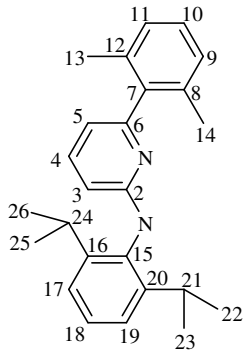


Synthesis of 2b: The compounds $[Sc(CH_2SiMe_3)_3(thf)_2]$ (451 mg, 1.00 mmol) and **1b** (415 mg, 1.00 mmol) were dissolved in hexane (20 mL). The resulting mixture was stirred for 1 h and filtered. The solvent was removed *in vacuo* to yield **2b** as a yellow crystalline compound (420 mg, 60%). Elemental analysis for $C_{41}H_{67}N_2OSi_2Sc$ (705.1): calcd. C 69.84, H 9.58, N 3.97; found C 69.44, H 9.56 N 3.92. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = -0.01 (d, ^2J(H,H) = 11 Hz, 2H, CH_AH$_B$SiMe$_3$), 0.07 (d, ^2J(H,H) = 11 Hz, 2H, CH$_A$$H_B$SiMe$_3$), 0.16 (s, 18H, CH$_2SiMe_3$), 1.03 (br, 4H, β-C$H_2$, THF), 1.19 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.35 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.59 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.18 (s, 6H,

28,29-H), 2.21 (s, 3H, 30-H), 2.92 (sept, ^{3}J(H,H) = 6.8 Hz, 1H, 19-H), 3.15 (sept, ^{3}J(H,H) = 6.8 Hz, 2H, 13,16-H), 3.74 (br, 4H, α-CH_2, THF), 5.64 (d, ^{3}J(H,H) = 8.5 Hz, 1H, 3-H), 6.20 (d, ^{3}J(H,H) = 7.1 Hz, 1H, 5-H), 6.84 (m, 3H, 4-H, 9,11/24,26-H), 7.29 ppm (s. 2H. 9,11/24,26-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.9, 19.0, 21.0, 23.3, 24.5, 24.6, 27.1, 31.0, 35.1, 45.3, 71.2, 104.2, 112.0, 121.1, 129.5, 133.0, 133.3, 135.8, 140.0, 143.7, 146.7, 149.6, 156.1, 167.9 ppm; ^{29}Si NMR (79 MHz, C_6D_6, 298 K): δ = -4.8 ppm.



Synthesis of 2c: [$Sc(CH_2SiMe_3)_3(thf)_2$] (270 mg, 0.60 mmol) and **1c** (215 mg, 0.60 mg) were dissolved in hexane (20 mL). The mixture was stirred for 1 h and filtered. All volatiles were removed under reduced pressure yielding **2c** (196 mg, 51%) as a yellow crystalline material. Elemental analysis for $C_{37}H_{55}N_2OSi_2Sc$ (649.0): calcd. C 68.47, H 9.16, N 4.32; found C 68.30, H 9.00, N 4.40. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.01 (d, ^{2}J(H,H) = 11 Hz, 2H, CH_AH$_B$SiMe$_3$), 0.07 (d, ^{2}J(H,H) = 11 Hz, 2H, CH$_A$$H_B$SiMe$_3$), 0.17 (s, 18H, CH$_2SiMe_3$), 1.09 (br, 4H, β-C$H_2$, THF), 1.16 (d, ^{3}J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.21 (d, ^{3}J(H,H) = 6.9Hz, 6H, CH(CH_3)$_2$), 2.40 (s, 6H, 13,14-H), 3.42 (sept, ^{3}J(H,H) = 6.9 Hz, 2H, 21,24-H), 3.82 (br, 4H, α-CH_2, THF), 5.58 (d, ^{3}J(H,H) = 8.6 Hz, 1H, 3-H), 5.86 (d, ^{3}J(H,H) = 7.1 Hz, 1H, 5-H), 6.80 (dd, ^{3}J(H,H) = 8.6 Hz, ^{3}J(H,H) = 7.1 Hz, 1H, 4-H), 7.03-7.20 ppm (m, 6H, 9,10,11,17,18,19-H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 3.8, 20.9, 24.1, 24.7, 25.2, 28.4, 44.5, 71.5, 105.6, 109.2, 124.2, 125.3, 127.8, 128.7, 135.9, 139.9, 140.8, 143.9, 144.3, 156.0, 169.5 ppm; ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ = -5.0 ppm.



Synthesis of 3a: [$Sc(CH_2Ph)_3(thf)_3$] (428 mg, 0.80 mmol) and **1a** (365 mg, 0.80 mmol) were dissolved in thf (20 mL) and stirred at room temperature for about 1h. All volatiles were removed under reduced pressure and the residue was extracted with hexane (40 mL). Removal of the solvent affords **3a** as a yellow spectroscopically pure compound (364 mg, 60%). Elemental analysis for $C_{50}H_{65}N_2OSc$ (755.0): calcd. C 79.54, H 8.68, N 3.71; found C 79.07, H 9.06, N 3.75. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 0.79 (br, 4H, β-CH_2, THF), 1.13 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.19 (d, ^3J(H,H) = 6.5 Hz, 12H, CH(CH_3)$_2$), 1.32 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.52 (d, ^3J(H,H) = 6.7 Hz, 6H, CH(CH_3)$_2$), 2.02 (dd, ^3J(H,H) = 8.8 Hz, 4H, CH_2Ph), 2.90 (sept, ^3J(H,H) = 6.8 Hz, 1H, 15-H), 3.23 (sept, ^3J(H,H) = 6.7 Hz, 2H, 13,14/22,23-H), 3.31 (br, 4H, α-CH_2, THF), 3.39 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 5.74 (d, ^3J(H,H) = 8.5 Hz, 1H, 3-H), 6.28 (d, ^3J(H,H) = 7.1 Hz, 1H, 5-H), 6.58 (d, ^3J(H,H) = 7.5 Hz, 4H, *o*-H), 6.76 (t, ^3J(H,H) = 7.1 Hz, 2H, *p*-H), 6.88 (t, ^3J(H,H) = 7.8 Hz, 1H, 4-H), 7.05 (t, ^3J(H,H) = 7.4 Hz, *m*-H), 7.16 (m, 3H, 18,19,20-H), 7.33 ppm (s, 2H, 9,11-H); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.6, 24.0, 24.4, 24.7, 24.9, 27.2, 28.6, 31.3, 34.0, 60.1, 71.5, 105.8, 112.3, 119.1, 121.2, 124.2, 124.6, 125.5, 129.0, 135.5, 139.9, 143.5, 144.4, 147.2, 150.1, 150.2, 155.7, 169.3 ppm.

Synthesis of 4a: To a mixture of **3a** (76 mg, 0.10 mmol) and [$C_6H_5NH(CH_3)_2$][$B(C_6H_5)_4$] (44 mg, 0.10 mmol) were added thf (1.0 mL) and toluene (1.0 mL). The reaction mixture was shaken for 5 min to obtain a clear solution. Slowly diffusion of pentane into this solution over a period of 3 days affords **4a**·(OC_4H_8) as yellow crystalline plates which where decanted and washed twice with hexane (2×10 mL). Yield 54 mg (40%). Elemental analysis for [$C_{51}H_{74}N_2O_3Sc$][$C_{24}H_{20}B$] (OC_4H_8) (1199.4): calcd. C 79.11, H 8.57, N 2.34; found C 79.10, H 8.39, N 2.50. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ = 1.12-1.16 (m, 12H, CH(CH_3)$_2$), 1.22 (br, 12H, β-CH_2, THF), 1.31-1.35 (m, 12H, CH(CH_3)$_2$), 1.40 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.11 (br, 2H, CH_2Ph), 2.85 (sept, ^3J(H,H) = 6.7 Hz, 2H, 13,14/22,23-H), 3.02 (sept, ^3J(H,H) = 6.9 Hz, 1H, 15-H), 3.24 (br, 2H, 13,14/22,23-H), 3.47 (br, 12H, α-CH_2,

THF), 5.85 (d, ^3J(H,H) = 8.7 Hz, 1H, 3-H), 6.37 (d, ^3J(H,H) = 7.1 Hz, 1H, 5-H), 6.53 (d, ^3J(H,H) = 7.6 Hz, 2H, *o*-Benzyl), 6.86 (t, ^3J(H,H) = 7.3 Hz, 1H, *p*-Benzyl), 7.07-7.37 (m, 20H, *m*-Benzyl, 4,9,11,18,19,20-H, BC_6H_5), 7.83 ppm (br, 8H, *o*-BC_6H_5); ^{13}C NMR (100 MHz, C_6D_5Br, 298 K): δ = 22.9, 24.1, 24.6, 25.7, 26.3, 27.8, 30.5, 34.5, 40.3, 67.4, 68.1, 108.1, 112.7, 113.5, 116.7, 121.2, 125.0, 125.0, 129.1, 134.3, 135.3, 137.2, 137.8, 139.8, 142.2, 143.6, 146.6, 147.3, 150.8, 154.2, 164.5 (q, ^1J(C,B) = 49.3 Hz, BC_6H_5), 169.6 ppm.

Synthesis of 5a: The compounds **2a** (75 mg, 0.10 mmol) and $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (44 mg, 0.10 mmol) were dissolved in thf (5 mL). The mixture was stirred for 20 min. After removal of all volatiles the mixture was washed twice with hexane (2×10 mL) and the remaining yellow solid was dried in vacuo to yield **5a** as a yellow powder (74 mg, 70%). Elemental analysis for $[C_{44}H_{70}N_2O_2ScSi][C_{24}H_{20}B]$ (1051.3): calcd. C 77.69, H 8.63, N 2.66; found C 78.05, H 8.95, N 2.31. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.02 (s, 9H, $CH_2Si\mathit{Me_3}$), 0.36 (br, 2H, CH_2SiMe_3), 1.00-1.22 (m, 38H, β-CH_2, THF, $CH(CH_3)_2$), 2.66 (br, 2H, 13,14/22,23-H), 2.79 (sept, ^3J(H,H) = 6.9 Hz, 1H, 15-H), 3.00 (br, 2H, 13,14/22,23-H), 3.30 (br, 8H, α-CH_2, THF), 5.59 (d, ^3J(H,H) = 8.6 Hz, 1H, 3-H), 6.06 (d, ^3J(H,H) = 7.1 Hz, 1H, 5-H), 7.05-7.28 (m, 18H, 4,9,11,18,19,20-H, BC_6H_5), 7.95 ppm (br, 8H, *o*-BC_6H_5); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 3.4, 23.7, 24.6, 24.7, 25.5, 25.6, 26.5, 29.2, 31.2, 35.1, 40.6, 72.7, 108.5, 113.4, 121.7, 122.6, 125.4, 126.5, 127.3, 129.7, 137.4, 139.3, 141.7, 142.5, 147.2, 151.4, 154.9, 165.4 (q, ^1J(C,B) = 49.5 Hz, BC_6H_5), 169.7 ppm.

Synthesis of 6a: The compounds $[Sc\{N(SiHMe_2)_2\}_3(thf)]$ (797 mg, 1.55 mmol) and **1a** (708 mg, 1.55 mmol) were dissolved in toluene (20 mL). The reaction mixture was stirred at 60 °C for 4 days. All volatiles were removed and the residue was extracted with hexane (40 mL). The solvent was removed *in vacuo* to yield 925 mg (78%) of a yellow crystalline compound. Elemental analysis for $C_{40}H_{71}N_4Si_4Sc$ (765.3): calcd. C 62.78, H 9.35, N 7.32; found C 62.26, H 9.49, N 7.02. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.17 (d, ^3J(H,H) = 2.3 Hz, 12H, $Si(CH_3)_2$), 0.23 (d, ^3J(H,H) = 2.2 Hz, 12H, $Si(CH_3)_2$), 1.11-1.15 (m, 12H, $CH(CH_3)_2$), 1.27 (d, ^3J(H,H) = 6.9 Hz, 6H, 30,31-H), 1.40-1.42 (m, 12H, $CH(CH_3)_2$), 2.83 (sept, 1H, ^3J(H,H) = 6.9 Hz, 15-H), 2.95 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 3.60 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 4.92 (br, ^1J(Si,H) = 162 Hz, 4H, Si*H*), 5.63 (d, ^3J(H,H) = 8.6 Hz, 1H, 3-H), 6.02 (d, ^3J(H,H) = 7.0 Hz, 1H, 5-H), 6.67 (t, ^3J(H,H) = 7.8, 1H, 4-H), 7.14-7.28 ppm (m, 5H, 9,11,18,19,20-H); ^{1}H NMR (300 MHz, toluene-d_8, 373 K): δ = 0.15 (d, ^3J(H,H) = 2.8 Hz, 24H, $Si(CH_3)_2$) 1.09 (d, 6H, ^3J(H,H) = 6.8 Hz, $CH(CH_3)_2$), 1.11 (d,

^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.26 (d, ^3J(H,H) = 6.9 Hz, 6H, 30,31-H), 1.34 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.38 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.85 (sept, 1H, ^3J(H,H) = 6.9 Hz, 15-H), 2.94 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 3.52 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 4.86 (sept, ^3J(H,H) = 2.8 Hz, ^1J(Si,H) = 164 Hz, 4H, Si*H*), 5.66 (dd, ^3J(H,H) = 8.6 Hz, ^1J(H,H) = 0.9 Hz, 1H, 3-H), 6.01 (dd, ^3J(H,H) = 7.0 Hz, ^1J(H,H) = 0.9 Hz, 1H, 5-H), 6.80 (dd, ^3J(H,H) = 7.0, ^3J(H,H) = 8.6 Hz, 1H, 4-H), 6.96-7.22 ppm (m, 5H, 9,11,18,19,20-H); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 2.1, 2.8, 24.1, 24.2, 24.3, 25.4, 25.7, 28.3, 30.9, 34.7, 107.2, 111.5, 121.0, 124.3, 125.6, 135.3, 139.3, 142.7, 144.1, 146.4, 149.3, 156.3 168.6; ppm; ^{29}Si NMR (60 MHz, toluene-d_8, 298 K): δ = -19.3 ppm.

NMR tube reaction of 2a with [$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$]: The compounds **2a** (15 mg, 20 µmol) and [$C_6H_5NH(CH_3)_2$][$B(C_6F_5)_4$] (16 mg, 20 µmol) were dissolved in deuterated bromobenzene (0.5 mL) and thf (30 µL) was added. After 5 min the solution was transfered into a NMR tube equipped with a young valve. ^{1}H NMR (400 MHz, C_6D_5Br, 298 K): δ = 0.00 (s, 12H, $SiMe_4$), 0.11 (s, 9H, CH_2Si*Me*$_3$), 0.31 (br, 2H, C*H*$_2$SiMe$_3$), 1.10-1.13 (m, 12H, CH(CH_3)$_2$), 1.30-1.34 (m, 12H, CH(CH_3)$_2$), 1.36 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.64 (br, β-CH_2, THF), 2.78 (s, 6H, N*Me*$_2$), 2.88 (br, 2H, 13,14/22,23-H), 2.98 (sept, ^3J(H,H) = 6.9 Hz, 1H, 15-H), 3.22 (br, 2H, 13,14/22,23-H), 3.67 (br, α-CH_2, THF), 5.78 (d, ^3J(H,H) = 8.6 Hz, 1H, 3-H), 6.32 (d, ^3J(H,H) = 7.1 Hz, 1H, 5-H), 6.72 (d, ^3J(H,H) = 8.1 Hz, 2H, *o*-$C_6H_5NMe_2$), 6.83 (t, ^3J(H,H) = 7.3 Hz, 1H, *p*-$C_6H_5NMe_2$), 7.11 (dd, ^3J(H,H) = 8.6 Hz, ^3J(H,H) = 7.1 Hz, 1H, 4-H), 7.23 (s, 2H, 9,11-H), 7.27-7.33 ppm (m, 5H, 18,19,20-H, *m*-$C_6H_5NMe_2$); ^{13}C NMR (100 MHz, C_6D_5Br, 298 K): δ = 0.0, 3.6, 23.0, 24.2, 24.5, 24.7, 25.8, 26.4, 27.9, 30.6, 34.6, 40.4, 67.5, 108.2, 112.8, 113.6, 116.8, 121.3, 125.1, 129.2, 134.4, 135.4, 137.2, 137.8, 139.7, 139.9, 142.3, 143.7, 146.7, 147.5, 149.9, 150.9, 154.3, 169.7 ppm; ^{19}F NMR (376 MHz, C_6D_5Br, 298 K): δ = -132.4 (br d, ^3J(F,F) = 12.0 Hz, *o*-F), -162.7 (t, ^3J(F,F) = 21.0 Hz, *p*-F), -166.7 ppm (t, ^3J(F,F) = 18.9 Hz, *m*-F).

NMR tube reaction of 6a with $AlMe_3$: The complex **6a** (25 mg, 33 µmol) was dissolved in a NMR tube equipped with a young valve in C_6D_6 (0.5 mL). After the addition of 6 equivalents trimethylaluminium (19 µL, 0.2 mmol) the tube was sealed and shaken. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.34 (s, 24H, Al*Me*$_4$), -0.13-0.07 (br, 30H, Al*Me*$_3$, NAl*Me*$_2$), 0.19 (d, ^3J(H,H) = 3.0 Hz, 24H, Si(CH_3)$_2$), 1.08 (d, ^3J(H,H) = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.12 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.26 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.31 (d, ^3J(H,H) = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.32 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.76-2.95 (m,

3H, 13,14/22,23-H, 15-H), 3.37 (sept, ^{3}J(H,H) = 6.7 Hz, 2H, 13,14/22,23-H), 4.74 (sept, ^{1}J(Si,H) = 211 Hz, ^{3}J(H,H) = 3 Hz, 4H, Si*H*), 5.68 (d, ^{3}J(H,H) = 8.6 Hz, 1H, 3-H), 6.13 (d, ^{3}J(H,H) = 7.1 Hz, 1H, 5-H), 6.80 (dd, ^{3}J(H,H) = 7.1, ^{3}J(H,H) = 8.6 Hz, 1H, 4-H), 7.17 (s, 2H, 9,11-H), 7.23 ppm (s, 3H, 18,19,20-H).

Polymerization of isoprene: A detailed polymerization procedure (Table 1, run 4) is described as a typical example. In a glove box the complex **2a** (8 mg, 10 µmol) was dissolved in C_6H_5Cl (8 mL) and isoprene (680 mg, 1 mL, 10 mmol) was added. The mixture was placed in a water bath (20 C). Then $AlMe_3$ (100 µmol, 50 µL, 2.0 M in hexane) and a solution of $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (8 mg, 10 µmol) in C_6H_5Cl (2 mL) were added. After stirring for 20 h at room temperature the mixture was poured into a large quantity of acidified isopropanol containing 0.1 % (w/w) 2,6-di-*tert*-butyl-4-methylphenol as a stabilizing agent. The precipitated polymer was decanted, washed with isopropanol and dried in vacuo at 60°C to a constant weight to afford 680 mg of polyisoprene (100%). The microstructure of the polymer was examined by ^{13}C NMR spectroscopy in $CDCl_3$.

6.5. Acknowledgments

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7. Aminopyridinate-Stabilized Lanthanoid Complexes: Synthesis, Structure and Polymerization of Ethylene and Isoprene

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Abstract: A series of aminopyridinate-stabilized lanthanoid dialkyl complexes has been synthesized and characterized. The complexes were prepared by alkane elimination reacting $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Er, Yb, Lu) or $[Ln(CH_2Ph)_3(thf)_3]$ (Ln = Y, Er, Lu) with one equivalent of the bulky aminopyridine (2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine. Single-crystal X-ray analyses were carried out for all of the benzyl derivatives. The reaction of these compounds with anilinium borate leads to the elimination of one of the two alkyl functions and affords organolanthanoid cations. The aminopyridinate-stabilized lanthanoid dialkyles can initiate the polymerization of isoprene after activation with perfluorinated tetraphenyl borates. The obtained polymers have a 3,4-content of 60 % to 95 %. The metal ion size as well as the addition of aluminium alkyl compounds influences the microstructure of the obtained polymer. Aminopyridinate-stabilized organolanthanoid cations of Sc, Lu, Er and Y can polymerize ethylene in the presence of small amounts of aluminium alkyl compounds. The Lu, Er and Y complexes act as a CCTP catalyst and the erbium compound exhibits the highest activity.

7.1. Introduction

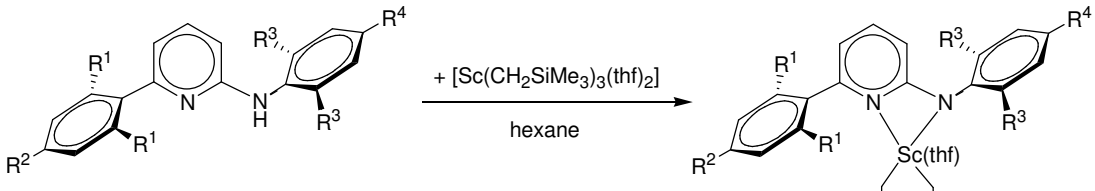
Cationic lanthanoid (group 3 and rare earth) metal alkyls are known to be useful initiators for the polymerization of olefins or 1,3-dienes.[1] Reaction of neutral di- or trialkyl complexes of

the lanthanoids with one equivalent of perfluorinated borate compounds is an established route to create an cationic rare earth metal alkyl species, which is active for polymerization.[2] Coordinative chain transfer polymerization[3] (CCTP) catalysis is an excellent tool to polymerize ethylene and α-olefines like propylene in a highly controlled and efficient fashion. A variety of systems are described which are capable of catalyzing this type of polymerization with various main group and Zn alkyls.[4] Very recently, we described an aminopyridinate-stabilized scandium system[9] which is an active precatalyst for the 3,4-selective polymerization of isoprene[5,6] and we further demonstrated that a similiar yttrium complex catalyzes chain growing at aluminium. Bambirra et al.[1h] as well as Okuda and coworkers[1i] imposingly demonstrated the relation between ethylene polymerization activity and the metal ion size. Thus, we became interested in comparing ethylene and isoprene polymerization catalysis for a variety of lanthanoid ions.

Herein we report the synthesis and structure of bis(trimethylsilylmethyl) and dibenzyl rare earth complexes stabilized by bulky aminopyridinato[7,8,9] (= Ap) ligands in addition, the performance of these compounds as precatalysts for the polymerization of ethylene and isoprene will be discussed. The focus will be put on the influence of the ionic radius of the lanthanoid on the activity and selectivity of the polymerization reactions as well as the ability of these compounds to mediate CCTP.

7.2. Results and Discussion

Metal Complex Synthesis



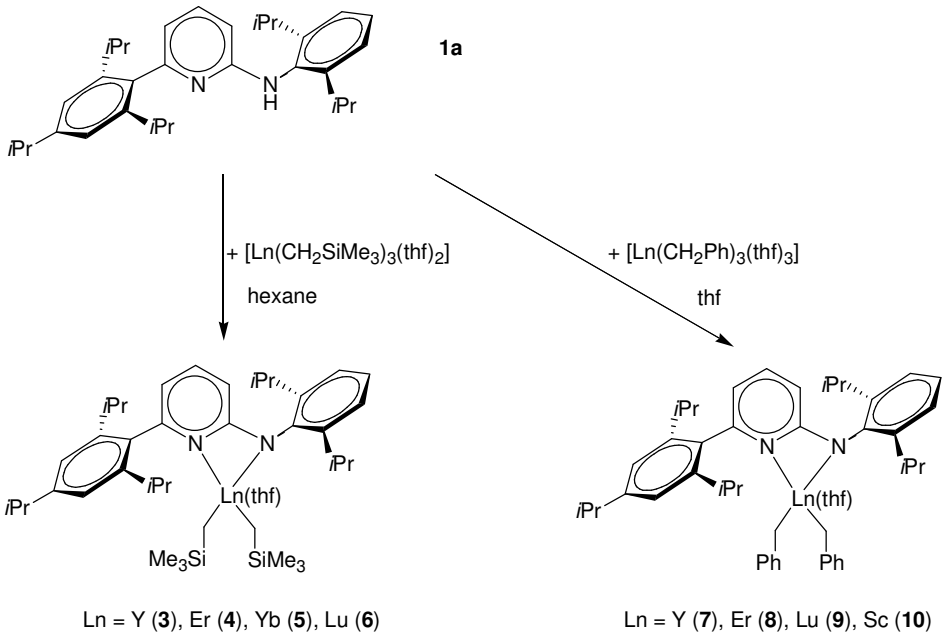
1a, $R^1 = R^2 = i$Pr, $R^3 = i$Pr, R^4 = H
1b, $R^1 = R^2 = i$Pr, $R^3 = R^4$ = Me
1c, R^1 = Me, R^2 = H, $R^3 = i$Pr, R^4 = H

2a-c

Scheme 1. Synthesis of aminopyridinate-stabilized scandium dialkyls **2a**-**c**.

As we reported recently a serious of aminopyridinate-stabilized bis(trimethylsilylmethyl) scandium complexes were synthesized (Scheme 1).[9] Similarly the reaction of the trialkyl precursor compounds $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Er, Yb, Lu) and $[Ln(CH_2Ph)_3(thf)_3]$

(Ln = Y, Er, Lu) with the aminopyridine ligand **1a** yield after alkane elimination selectively the corresponding dialkyl compounds **3**-**10** (Scheme 2).



Scheme 2. Synthesis of aminopyridinate-stabilized lanthanoid dialkyls **3**-**10**.

The compounds **3**, **6** and **10** were already described in earlier reports.[9,10,11] The erbium and ytterbium analogues were synthesized in the same way to yield the corresponding bis(trimethylsilylmethyl) compounds **4** and **5** (Scheme 2, left side) in moderate and very good yield (64% and 93%), respectively. The aminopyridine **1a** also reacts with one equivalent of the tribenzyl complexes $[Ln(CH_2Ph)_3(thf)_3]$ (Ln = Y, Er, Lu) to afford after toluene elimination the aminopyridinate-stabilized dibenzyl complexes **7**, **8**, **9** and **10** (Scheme 2, right side). The proton NMR spectra of **7** and **9** exhibit the characteristic splitting pattern of the aminopyridinato ligand. In contrast to the scandium analogue **10**[9] where the methylene group from the benzyl ligand exhibit an AB-system only one signal is observed in the ^{1}H NMR spectra of **7** and **9**, whereas the signal of **9** appears as a broad singulet. The ^{13}C NMR spectra show only one resonance for the methylene groups of the benzyl ligands at 54.1 (doublet, ^1J(Y,C) = 28.6 Hz) for **7** and 59.1 ppm for compound **9**, respectively. The compounds **7**-**9** were also characterized by X-ray structure analysis. Suitable crystals were obtained by cooling a saturated pentane or hexane solution to 0°C. The complexes **7**-**9** are isostructural and crystallize in the monoclinic space group *C*2/*c*. The structures are depicted in Figure 1 and Figure 2, crystallographic details are summarized in Table 4. The metal atoms are five-coordinated by one aminopyridinato ligand, one thf ligand and two benzyl ligands which show (in the solid state) different coordination modes. Similar to the scandium derivative **10**[9]

one of the two benzyl ligands has a η^1-coordination [Ln1-C1-C2: 116.0(3) (**7**), 116.2(4) (**8**), 119.5(5) (**9**) and 121.88(16)° (**10**)], whereas the other ligand exhibits an η^2-coordination which is indicated by the Ln1-C8-C9 angles of 83.2(3) (**7**), 84.4(4) (**8**), 85.4(4) (**9**) and 88.50(15)° (**10**) and a shortened distance of the lanthanoid atom to the *ipso*-carbon atom of this ligand [Ln1-C9: 2.675(4) (**7**), 2.677(6) (**8**) and 2.668(6) (**9**) Å]. Within the series **7**-**10** the N1-Ln1-N2 bite angle of the aminopyridinato ligand decreases with an increasing ionic radius of the metal centre[12] from scandium to yttrium [N1-Ln1-N2: 57.25(12) (**7**), 57.69(15) (**8**), 58.33(15) (**9**) and 61.31(7)° (**10**)]. Another significant effect of similar nature is the decreasing Ln1-C8-C9 angle of the η^2-coordinated benzyl ligand with increased ionic radius (Table 1).

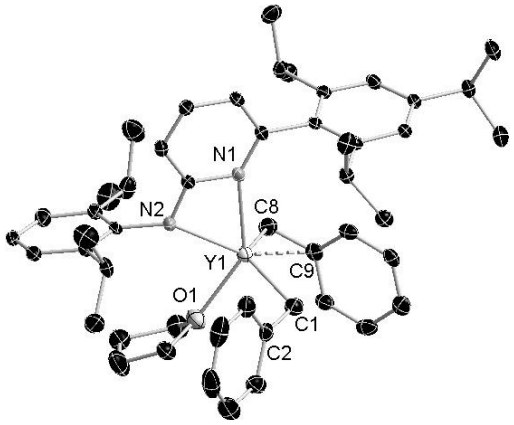


Figure 1. Molecular structure of **7** (ellipsoids set at 40% probability level). H atoms have been omitted for clarity.

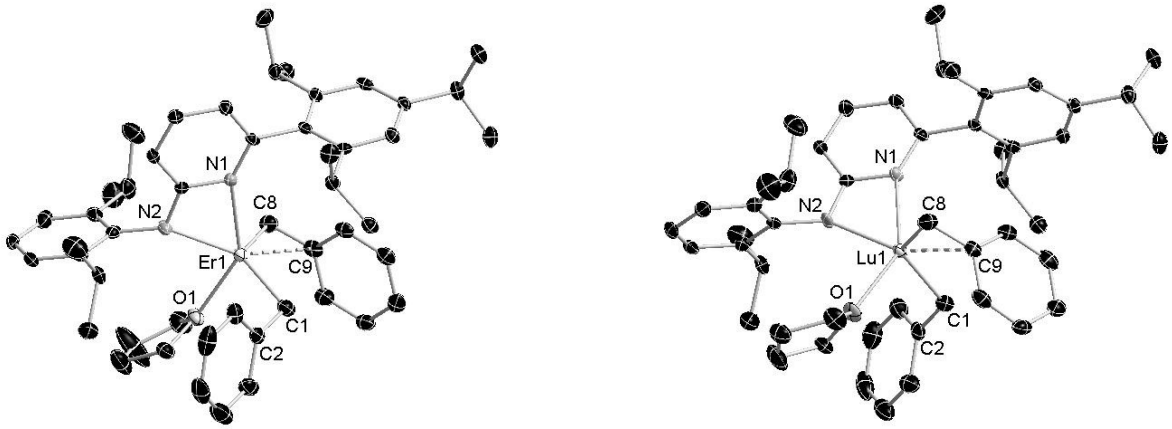
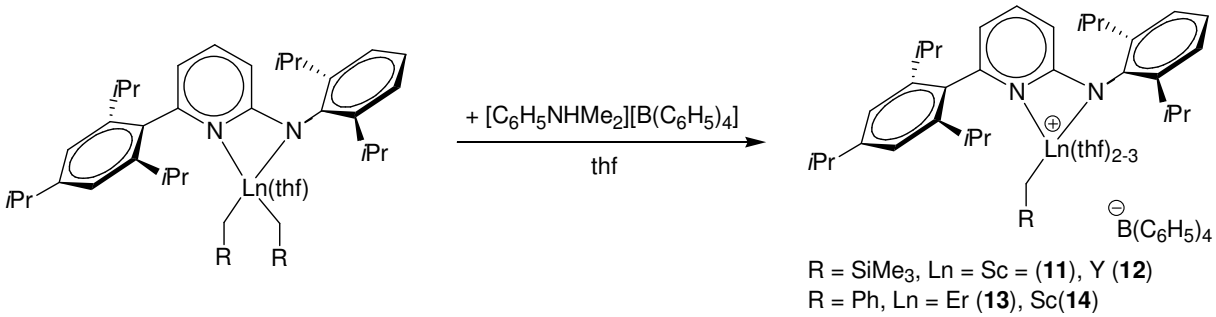


Figure 2. Molecular structure of **8** (left) and **9** (left) (ellipsoids set at 40% probability level). H atoms and solvent molecules have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for the complexes [Ap*Ln$(CH_2Ph)_2$(thf)] (Ln = Y, Er, Lu, Sc).

	Ln = Y (**7**)	Ln = Er (**8**)	Ln = Lu (**9**)	Ln = Sc (**10**)[a]
		bond length		
Ln1-N1	2.423(4)	2.403(4)	2.381(4)	2.286(2)
Ln1-N2	2.303(3)	2.287(4)	2.244(4)	2.129(2)
Ln1-O1	2.328(3)	2.310(4)	2.294(4)	2.1728(17)
Ln1-C1	2.414(5)	2.411(7)	2.351(7)	2.245(3)
Ln1-C8	2.436(5)	2.414(7)	2.365(7)	2.256(3)
Ln1-C9	2.675(4)	2.677(6)	2.668(6)	2.657(2)
		bond angles		
Ln1-C1-C2	116.0(3)	116.2(4)	119.5(5)	121.88(16)
Ln1-C8-C9	83.2(3)	84.4(4)	85.4(4)	88.50(15)
N1-Ln1-N2	57.25(12)	57.69(15)	58.33(15)	61.31(7)

[a] from ref.[9]



Scheme 3. Synthesis of organolanthanoid cations **11**-**14**.

The dialkyl complexes **2a**, **3** and **7**-**10** react with one equivalent of anilinium borate in thf to afford after alkane elimination the thf stabilized organolanthanoid cations **11**-**14** respectively (Scheme 3). The bis(trimethylsilylmethyl) complexes **11**, **12** and **14** have been already characterized in our previous reports.[9,10] The organoerbium cation **13** was characterized by an X-ray structure analysis. Suitable single crystals were obtained by slow diffusion of pentane into a thf solution of **13**. The compound crystallizes in the triclinic space group P-1, crystallographic details are summarized in Table 4 and the molecular structure is presented in Figure 3. The cation of **13** shows a distorted octahedral coordination of the erbium atom indicated by O-Er-C_{benzyl} angles of 90.1(2) and 94.8(2)°. The metal atom is coordinated by three thf, one benzyl [η^1-coordination, Er1-C1-C2 117.4(6)°] and one aminopyridinato ligand. The thf ligands show a meridonal arrangement and the methylene group of the benzyl ligand is in *trans*-position to the pyridine nitrogen atom of the aminopyridinato ligand.

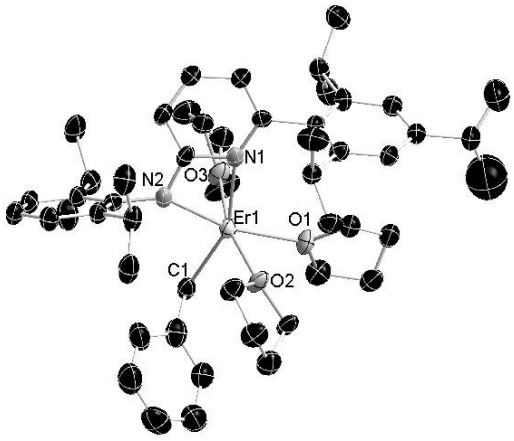


Figure 3. ORTEP diagram of the molecular structure of **13** in the solid state (ellipsoids set at 40% probability level). H atoms solvent molecule and anion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Er1-C1 2.418(8), Er1-N1 2.462(6), Er1-N2 2.325(6), Er1-O1 2.348(5), Er1-O2 2.317(5), Er1-O3 2.302(5), Er1-C1-C2 117.4(6), O1-Er1-C1 96.9(2), O2-Er1-C1 94.8(2), O3-Er1-C1 90.1(2).

Polymerization of ethylene

Table 2. Polymerization of ethylene catalyzed by **2**-**4** under various conditions.[a]

Run	Kat.	Al-alkyl (equiv)	m_{pol} [g]	M_n [g mol^{-1}]	M_w/M_n	Activity [kg_{PE} mol_{cat}^{-1} h^{-1} bar^{-1}]
1[b]	**3**	TIBAO(20)	13.4	20800[c]	3.2	1072
2[b]	**3**	TIBAO(50)	4.7	3610	1.09	376
3	**4**	TIBAO(20)	20.2	29600	2.0	1616
4	**4**	TIBAO(50)	13.6	14500	1.6	1088
5	**5**	TIBAO(20)	0.03	-	-	2
6	**5**	TIBAO(50)	0.03	-	-	2
7	**6**	TIBAO(20)	1.6	6000	1.5	128
8	**6**	TIBAO(50)	0.5	-	-	40
9	**2a**	TIBAO(20)	6.7	607100[c] (13100)[d]	3.33 (1.62)	536
10	**2a**	TIBAO(50)	6	610900[c] (13000)[d]	4.71 (1.77)	480
11	**2a**	TIBA(25)	3.9	5150	2.71	312
12	**2b**	TIBAO(50)	4.8	373500[c] (4280)[e]	16.1 (1.56)	384
13	**2c**	TIBAO(50)	3.9	39600	2.56	312

[a] Conditions: Dialkyl (**2**-**4**): 10 µmol, ammonium borate $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Y/B = 1/1.1, 260 mL toluene, time 15 min, temperature: 80°C, pressure: 5 bar . [b] from ref.[9] [c] Bimodal distribution. [d] M_w of the main fraction (98%). [e] M_w of the main fraction (83%).

We have recently demonstrated, that aminopyridinate-stabilized organoyttrium cations show attractive activities in the polymerization of ethylene in the presence of small amounts of

aluminium alkyl compounds.[10] We could also show the influence of the steric bulk of the aminopyridinato ligand on the polymerization activity for this yttrium-based system. Therefore, we wanted to investigate the polymerization activities for other lanthanoid aminopyridinate-stabilized complexes. The compounds **2a,b,c** and **4**-**6** were investigated as precatalysts for the controlled ethylene polymerization (CCTP). All of these dialkyl compounds except the ytterbium derivative **5** showed low to very good activities.[13] The erbium (**4**) and the lutetium (**6**) compounds revealed a similar dependency on the TIBAO concentration like it was already observed for the yttrium system. On the basis of this observation we suggest these compounds to be coordinative chain transfer polymerization catalysts. Whereas the lutetium compound **6** showed only low activities (Table 2, run 7, 8), the erbium dialkyl **4** revealed the highest activities up to 1616 kg_{PE} mol_{cat}^{-1} h^{-1} bar^{-1}. Because of the related ionic radii of erbium and yttrium (0.89 vs 0.90 Å, for coordination number 6),[12] both show high ethylene polymerization activities (Table 2, run 1-4). The average number molecular weight (M_n) of the polymer obtained with erbium compound **4** is higher compared to the polymer obtained with yttrium derivative **3** (29600 and 14500 g mol^{-1} for **4** vs. 20800 and 3610 g $mol^{-1}$for **3**), whereas the molecular weight distribution remains narrow (2.0 and 1.6, Table 2, run 3, 4). When the ionic radius is decreased to 0.86 Å (coordination number 6), in the case of lutetium, the polymerization activity significantly decreased and the obtained polymer show a molecular weight of 6000 g mol^{-1} and a relatively narrow molecular weight distribution of 1.5 (Table 2, run 7). When the scandium compound **2a** was used as a precatalyst, which comply with an ionic radius of 0.74 Å, a good activity for the polymerization of ethylene is observed. The obtained polymer revealed a bimodal distribution, but the main fraction has a content of 98 % (M_n = 13100, M_w/M_n = 1.62). In contrast to the ethylene polymerization catalysts **3**, **4** and **6**, the scandium compound **2a** did not show a significant dependency of the TIBAO concentration on the activity and the molecular weight (Table 2, run 9, 10). We suppose that the ion radius of the scandium metal is too small for the coordination of aluminium, which is necessary for the polyethylene chain transfer. Reduction of the steric demand of the aminopyridinato ligand leads to a decreased activity (Table 2, run 10, 12, 13), the same effect was observed for the yttrium compound, and was explained by ligand redistribution.[10]

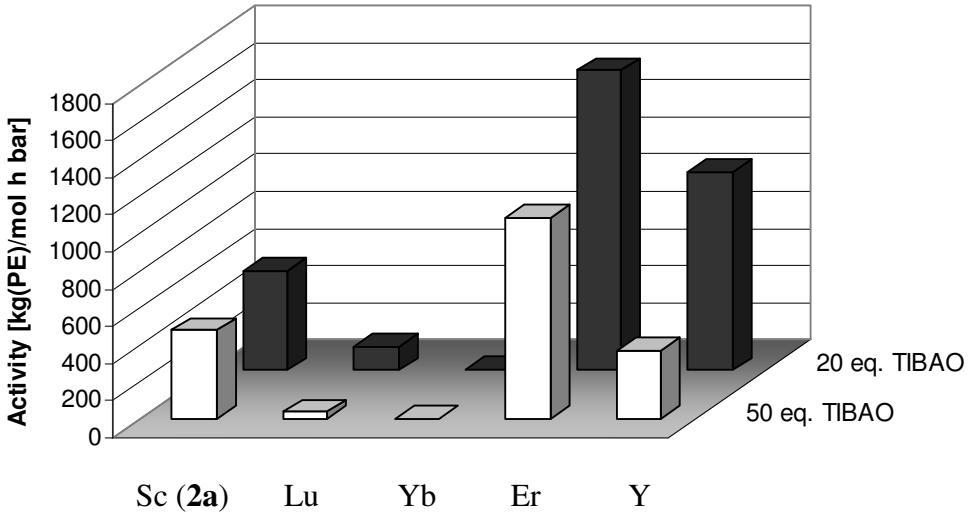


Figure 4. Influence of the metal ion size and the Al concentration on the ethylene polymerization activity.

Polymerization of isoprene

As we described very recently, the aminopyridinate-stabilized dialkyl compounds of scandium (**2a-c** and **10**) are active and selective catalysts for the controlled 3,4-selective polymerization of isoprene.[9] In order to investigate the influence of the metal centre on the selectivity of the isoprene polymerization we also tested the complexes **3**-**9** as precatalysts for the isoprene polymerization. The microstructure of the obtained polyisoprene was determined by ^{1}H and ^{13}C NMR spectroscopy. The results of the polymerization experiments are summarized in Table 3. The bis(trimethylsilylmethyl)lanthanoid compounds **3**, **4** and **6** polymerize isoprene after activation with perfluorinated anilinium borate in chlorobenzene or toluene (Table 3, run 1,2 and 4). Only the ytterbium derivative in this series is unable to initiate the polymerization of isoprene after activation (Table 3, run 3). Presumably a reduction of the ytterbium metal takes place. The microstructure of the polymer obtained with **2**-**4** and **6** as precatalysts depends significantly on the metal size: with an increasing ionic radii of the metal centre the *cis*-1,4-polyisoprene content is increasing and the 3,4- polyisoprene content is decreasing respectively [3,4-content: 60% (Y) < 80% (Er) < 86% (Lu) < 93% (Sc)]. The same influence of ionic radius of the central metal atom on the 3,4-selectivity was also observed by Cui and coworkers [the 3,4-content decreases from 88.5% (Sc) to 43.8% (Y)].[1a] GPC analyses of these polymers show bimodal molecular weight distributions. When the new dibenzyl complexes **7**-**9** are used as precatalysts for the polymerization of isoprene the same relation between the ionic radii and the microstructure, as it was described above for the bis(trimethylsilylmethyl)lanthanoid compounds, is observed (Figure 5). The molecular weight distribution of polyisoprene produced with the dibenzyl complex (**7**-**10**) is narrow and monodisperse, compared the molecular weight distribution of the polyisoprene produced with

the bis(trimethylsilylmethyl) complex (**3**-**6**), but become broader with an increasing ionic radii of the lanthanoid metal (1.68 (Sc) to 2.45 (Y)).

A marked decrease of the 3,4-polyisoprene content and broadening of the molecular weight distribution is observed when triisobutylaluminium (10 equivalents) was mixed with the polymerization catalyst (Table 3, run 7, 9 and 12). For complex **8** the polymerization was also carried out in the presence of trimethylaluminium to obtain a high *cis*-1,4 polyisoprene (92%). This effect of the aluminium alkyls on the microstructure of the polyisoprene was also observed for the scandium derivative **10** and an yttrium-amidinate isoprene polymerization catalyst described by Hou and coworker.[14]

Table 3. Effect of Ln size and alkyl ligand on the polymerization of isoprene.

Run	Cat.	Cocatalyst	Yield [%]	$M_n \times 10^{-3}$ [g mol^{-1}][b]	M_w/M_n [b]	Microstructure [c] *cis*-1,4/*trans*-1,4/3,4
1	**3**	A	100	86	3.82[d]	37/3/60
2	**4**	A	100	34	3.52[d]	13/7/80
3	**5**	A	-	-	-	-
4	**6**	A	100	104	2.98[d]	4/10/86
5[e]	**2a**	A	94	135	1.26	7/0/93
6	**7**	B	97	157	2.45	32/0/68
7	**7**	B/Al*i*Bu_3	99	86	2.66	42/0/58
8	**8**	B	100	222	1.80	13/3/84
9	**8**	B/Al*i*Bu_3	92	57	2.57	40/0/60
10	**8**	B/$AlMe_3$	92	112	2.90	92/0/8
11	**9**	B	96	168	1.65	7/0/93
12	**9**	B/Al*i*Bu_3	100	24	2.43	23/5/72
13[e]	**10**	B	97	130	1.68	5/0/95

[a] Conditions: 10 mL C_6H_5Cl, catalyst: 10µmol, cocatalyst: A = $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$, B = $[Ph_3C][B(C_6F_5)_4]$, [cat]/[cocat] 1:1, [Al]/[cat] = 10, isoprene: 10mmol, reaction time: 20h, temperature: 20°C. [b] Determined by GPC against polystyrene standards. [c] Determined by ^1H and ^{13}C spectroscopy. [d] bimodal distribution. [e] from ref.[9]

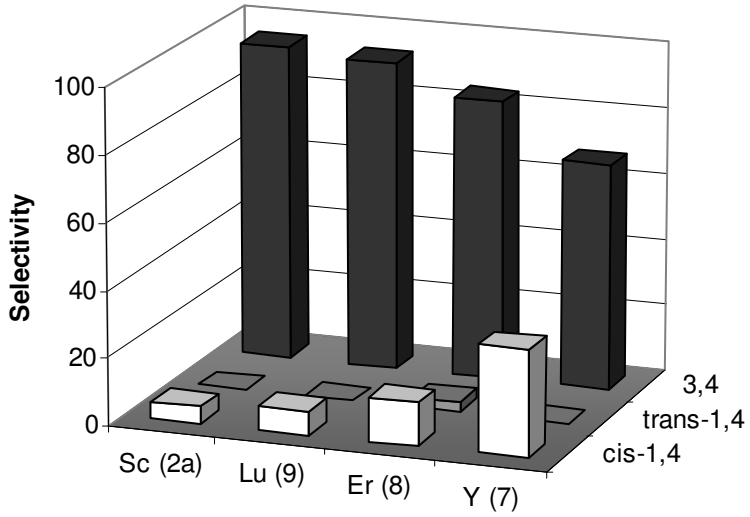


Figure 5. Influence of the metal centre on the microstructure of the obtained polyisoprene (Table 3, run 13, 11, 8, 6).

Table 4. Details of the X-ray crystal structure analyses.

Compound	**7**	**8**	**9**	**13**
Formula	$C_{50}H_{65}N_2OY$	$C_{50}H_{65}ErN_2O{\times}C_5H_{12}$	$C_{50}H_{65}LuN_2O{\times}C_6H_{14}$	$C_{73}H_{90}BErN_2O_3{\times}OC_4H_8$
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P\bar{1}$
a [Å]	36.7280(10)	36.7240(15)	36.8040(10)	13.6250(12)
b [Å]	13.0360(6)	13.0460(9)	13.0430(6)	15.2430(13))
c [Å]	24.1120(9)	24.1000(13)	24.0810(9)	19.1560(17)
α [°]	90	90	90	101.422(7)
β [°]	118.307(4)	118.352(5)	118.511(3)	99.138(6)
γ [°]	90	90	90	112.884(7)
Z	4	4	4	2
μ [mm^{-1}]	1.180	1.689	1.982	1.258
Cell volume [$Å^3$]	10164.0(7)	10161.3(10)	10157.8(7)	3468.0(5)
Crystal size [mm^3]	0.36×0.13×0.09	0.25×0.15×0.08	0.32×0.16×0.11	0.58×0.32×0.14
T [K]	133(2)	133(2)	133(2)	133(2)
θ range [°]	1.26-26.08	1.68-26.04	1.68-25.74	1.51-25.72
Reflections unique	8666	9423	9588	13035
Refl. Obs. [I>2σ(I)]	6447	6556	5852	7669
Parameters	487	572	548	785
wR_2 (all data)	0.150	0.105	0.087	0.154
R value [I>2σ(I)]	0.075	0.053	0.041	0.058

7.3. Conclusion

Mono(aminopyridinate)lanthanoid bis(trimethylsilylmethyl) and dibenzyl complexes have been synthesized and characterized. These dialkyl lanthanoid compounds with exception of the ytterbium compound are active catalysts for the polymerization of isoprene after activation with borates. The obtained polyisoprene has an enriched 3,4-content. The ionic radius of the lanthanoid metal is in relation to the *cis*-1,4 to 3,4-content ratio. Smaller metals, like scandium or lutetium predominantly afford polyisoprene with high 3,4-content (>90 %). The 3,4-content decreases to 68 % when yttrium is used as a precatalyst. Addition of trimethylaluminium to the erbium catalyst system leads to a drastical change of the microstructure. The aminopyridinate-stabilized lanthanoid bis(trimethylsilylmethyl) compounds show very high ethylene polymerization activities in the presence of aluminium compounds (trialkyls and aluminoxanes) and perfluorinated tetraphenyl borate. The activity is strongly influenced by the ionic radius of the lanthanoid metal. The highest activity was observed for the erbium compound. The ytterbium dialkyl is almost inactive under the same conditions.

7.4. Experimental Section

General Procedures Synthesis and Structure

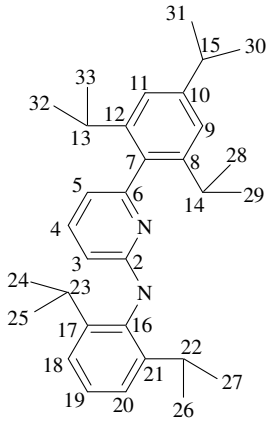
All reactions and manipulations involving air-sensitive compounds were performed under dry argon by using standard Schlenk and glovebox techniques. Non-halogenated solvents were dried with sodium/benzophenone ketyl and halogenated solvents with CaH_2. Deuterated solvents were obtained from Cambridge Isotope Laboratories, degassed, dried with molecular sieves and distilled prior to use. Starting materials **1a-c**,[10,15] tetra-isobutylaluminoxane ([*i*$Bu_2Al]_2O$, TIBAO),[16] [$Ln(CH_2SiMe_3)_3(thf)_2$],[17] [$Ln(CH_2Ph)_3(thf)_3$],[18] [$LScR_2(thf)$] (L = **1**, R = CH_2SiMe_3, CH_2Ph),[9] [Ap*$Y(CH_2SiMe_3)_2(thf)$],[10] [Ap*$Lu(CH_2SiMe_3)_2(thf)$],[11] [$C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$[19] were synthesized according to literature methods. All other chemicals were purchased from commercial sources in purities >97% and used without further purification, if not otherwise stated. NMR spectra were obtained with either a Varian INOVA 300 or a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out with a Vario elementar EL *III* apparatus. The molecular weights (M_w/M_n) of the isoprene polymers were determined

by gel permeation chromatography (GPC) on an Agilent 1200 series (Column: PLgel Mixed-C) at 30°C using thf as eluent and a flow rate of 1mL/min against polystyrene standards. The molecular weights (M_w/M_n) of the ethylene polymers were determined by gel permeation chromatography on a Polymer Laboratories Ltd. (PL-GPC210 or PL-GPC220) chromatograph at 150°C using 1,2,4-trichlorobenzene as the mobile phase. The samples were prepared by dissolving the polymer (0.1% weight/volume) in the mobile phase solvent in an external oven and were run without filtration. The molecular weight was referenced to polyethylene (M_w = 50000 g mol^{-1}) and polystyrene (M_w = 100000-500000 g mol^{-1}) standards. The reported values are the average of at least two independent determinations. X-ray crystal structure analyses were performed with a STOE-IPDS II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR97,[20] SHELXL-97[21] and WinGX[22]. Crystallographic details are summarized in Table 4, CCDC-xxxxxx contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of the Complexes

Synthesis of 4: Hexane (20 mL) was added to mixture of $[Er(CH_2SiMe_3)_3(thf)_2]$ (287 mg, 0.50 mmol) and **1a** (228 mg, 0.50 mmol). After stirring the mixture for two hours it was filtered. Evaporation of all volatiles yield **4** as an orange powder (280 mg, 64 %).

Elemental analysis for $C_{44}H_{73}N_2OSi_2Er$ (869.5): calcd. C 60.78, H 8.46, N 3.22; found C 61.17, H 8.42, N 3.61.



Synthesis of 5: The compounds $[Yb(CH_2SiMe_3)_3(thf)_2]$ (289 mg, 0.50 mmol) and **1a** (228 mg, 0.50 mmol) were dissolved in hexane (20 mL). The mixture was stirred for two

hours, subsequent filtration and removal off all volatile yield **5** as a red powder (405 mg, 93 %).

Elemental analysis for $C_{44}H_{73}N_2OSi_2Yb$ (875.3): calcd. C 60.38, H 8.41, N 3.20; found C 60.07, H 8.14, N 3.22.

Synthesis of 7: The compounds **[**$Y(CH_2Ph)_3(thf)_3$] (463 mg, 0.80 mmol) and **1a** (365 mg, 0.80 mmol) were dissolved in thf (20 mL) and the mixture was stirred for two hours. After removal of all volatiles the residue was extracted with hexane (40 mL). The solvent was removed under reduced pressure to yield **7** as a yellow powder (400 mg, 63%).

Elemental analysis for $C_{50}H_{65}N_2OY$ (799.0): calcd. C 75.16, H 8.20, N 3.51; found C 75.00, H 8.63, N 3.42. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.03 (br, 4H, β-CH_2, THF), 1.15 (d, ^3J(H,H) = 6.7 Hz, 6H, CH(CH_3)$_2$), 1.18 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.22 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.29 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.49 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.76 (s, 4H, CH_2Ph), 2.86 (sept, ^3J(H,H) = 6.9 Hz, 1H, 15-H), 3.13 (sept, ^3J(H,H) = 6.7 Hz, 2H, 13,14/22,23-H), 3.25br, 4H, α-CH_2, THF), 3.53 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 5.76 (d, ^3J(H,H) = 8.4 Hz, 1H, 3-H), 6.16 (d, ^3J(H,H) = 7.0 Hz, 1H, 5-H), 6.40 (d, ^3J(H,H) = 7.5 Hz, 4H, *o*-H), 6.65 (t, ^3J(H,H) = 7.3 Hz, 2H, *p*-H), 6.84 (dd, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 7.0 Hz, 1H, 4-H), 7.02 (t, ^3J(H,H) = 7.6 Hz, *m*-H), 7.11-7.23 (m, 3H, 18,19,20-H), 7.27 ppm (s, 2H, 9,11-H); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.7, 22.9, 24.1, 24.3, 24.7, 28.6, 30.9, 31.8, 34.9, 54.1 (d, ^1J(Y,C) = 28.6 Hz), 70.0, 106.7, 117.5, 121.1, 121.9, 124.0, 124.9, 129.2, 131.0, 135.8, 139.2, 144.1, 144.2, 147.0, 149.9, 151.1, 155.7, 170.2 ppm.

Synthesis of 8: A mixture of **[**$Er(CH_2Ph)_3(thf)_3$] (394 mg, 0.60 mmol) and **1a** (274 mg, 0.60 mmol) weredissolved in thf (20 mL). The resulting red solution was stirred for two hours. All volatiles were removed under reduced pressure and the residue was extracted with hexane (20 mL). Removal of the solvent yield **8** as an orange crystalline compound (447 mg, 85%).

Elemental analysis for $C_{50}H_{65}N_2OEr$ (877.3): calcd. C 68.45, H 7.47, N 3.19; found C 68.14, H 7.53, N 3.42.

Synthesis of 9: [$Lu(CH_2Ph)_3(thf)_3$] (532 mg, 0.80 mmol) and **1a** (365 mg, 0.80 mmol) were dissolved in thf (20 mL) and stirred over night. All volatiles were removed under reduced pressure and the residue was extracted with hexane (30 mL). Removal of the solvent affords **9**

as a yellow spectroscopically pure compound (400 mg, 56%). Elemental analysis for $C_{50}H_{65}N_2OLu$ (884.0): calcd. C 67.85, H 7.40, N 3.17; found C 67.63, H 7.74, N 3.33. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.87 (br, 4H, β-CH_2, THF), 1.15 (d, ^3J(H,H) = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.21 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.30 (d, ^3J(H,H) = 6.9 Hz, 6H, CH(CH_3)$_2$), 1.52 (d, ^3J(H,H) = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.64 (br s, 4H, CH_2Ph), 2.87 (sept, ^3J(H,H) = 6.9 Hz, 1H, 15-H), 3.17 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 3.19 (br, 4H, α-CH_2, THF), 3.48 (sept, ^3J(H,H) = 6.8 Hz, 2H, 13,14/22,23-H), 5.74 (d, ^3J(H,H) = 8.7 Hz, 1H, 3-H), 6.22 (d, ^3J(H,H) = 7.1 Hz, 1H, 5-H), 6.47 (d, ^3J(H,H) = 7.8 Hz, 4H, *o*-H), 6.69 (t, ^3J(H,H) = 7.3 Hz, 2H, *p*-H), 6.85 (t, ^3J(H,H) = 7.8 Hz, 1H, 4-H), 7.02 (t, ^3J(H,H) = 7.6 Hz, *m*-H), 7.10-7.19 (m, 3H, 18,19,20-H), 7.29 ppm (s, 2H, 9,11-H); ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.8, 24.2, 24.4, 24.9, 25.0, 27.0, 28.7, 31.1, 35.0, 59.1, 70.5, 106.8, 111.9, 118.2, 121.2, 123.4, 124.1, 125.3, 130.0, 135.8, 139.7, 144.0, 144.5, 147.1, 150.0, 151.3, 155.9, 169.0 ppm.

Synthesis of 13: To a mixture of **8** (132 mg, 0.15 mmol) and $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (64 mg, 0.15 mmol) were added thf (2.0 mL) and toluene (1.0 mL). The reaction mixture was stirred for 5 min to obtain a clear solution. Slowly diffusion of pentane into this solution over a period of 4 days affords **13**·(OC_4H_8) as yellow crystalline plates which were separated by decanting off the solution and washed twice with pentane (2×10 mL). Yield 84 mg (45%). Elemental analysis for $[C_{51}H_{74}N_2O_3Er][C_{24}H_{20}B]$ (OC_4H_8) (1321.7): calcd. C 71.79, H 7.78, N 2.12, found C 71.21, H 7.54, N 2.34.

Polymerization of ethylene

A detailed polymerization procedure (Table 2, run 1) is described as a typical example. The catalytic ethylene polymerization reactions were performed in a double-walled stainless steel 1 L autoclave, equipped with a mechanical stirrer. In a typical experiment, the autoclave was evacuated and heated for 2 h at 100°C prior to use. The reactor was then brought to 80°C, and charged with toluene (250 mL) together with trialkylammonium (tetrapentafluorophenyl)borate (11 mmol, 0.12 g) and the required amount of aluminium scavenger. After pressurizing with ethylene to reach the desired pressure, the autoclave was equilibrated for 5 min. Subsequently aminopyridinatolanthanoid dialkyl complex (1 mL, 0.01m stock solution in toluene) together with toluene (10 mL) was injected to start the reaction. During the run the ethylene pressure was kept constant. After 15 min the reactor was

vented and the residual aluminium alkyls were destroyed by addition of isopropanol (100 mL).

The precipitated polymer was decanted and washed with acidified isopropanol and again with isopropanol and dried at 80°C to a constant weight to afford 6.5 g of polyethylene.

Polymerization of isoprene

A detailed polymerization procedure (Table 3, run 8) is described as a typical example. In a glove box the complex **3** (8 mg, 10 µmol) was dissolved in C_6H_5Cl (8 mL) and isoprene (680 mg, 1 mL, 10 mmol) was added. The mixture was placed in a water bath (20°C). Then $AlMe_3$ (100 µmol, 50 µL, 2.0 M in hexane) and a solution of $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (8 mg, 10 µmol) in C_6H_5Cl (2 mL) were added. After stirring for 20 h at room temperature the mixture was poured into a large quantity of acidified isopropanol containing 0.1 % (w/w) 2,6-di-*tert*-butyl-4-methylphenol as a stabilizing agent. The precipitated polymer was decanted, washed with isopropanol and dried in vacuo at 60°C to a constant weight to afford 626 mg of polyisoprene (92%). The microstructure of the polymer was examined by ^{13}C NMR spectroscopy in $CDCl_3$.

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7.6. References

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8. List of Publications

1. T. Schaub, C. Döring, U. Radius, *Dalton Trans.* **2007**, *20*, 1993-2002.
"Efficient nickel mediated carbon-carbon bond cleavage of organonitriles"

The following publications have been published, are submitted or are to be submitted during the work on this thesis:

2. G. G. Skvortsov, G. K. Fukin, A. A. Trifonov, A. Noor, C. Döring, R. Kempe, *Organometallics* **2007**, *26*, 5770-5773.
"Intramolecular (sp^3-hybridized) C-H Activation: Yttrium Alkyls versus Transient Yttrium Hydrides"

3. Z. Garcia-Hernandez, B. Wrackmeyer, M. Herberhold, T. Irrgang, C. Döring, R. Kempe, *Z. Kristallogr. NCS* **2007**, *222*, 149-150.
"Crystal structure of 1,3-bis[seleno(phenyl)-η^5-phospha]-3-selena-4,5-[1,2-dicarba-*closo*-dodecaborano(12)]-cyclopentane, $Se[P(C_6H_5)Se]_2(C_2B_{10}H_{10})$"

4. A. Noor, C. Döring, R. Kempe, *Z. Kristallogr. NCS* **2008**, *223*, 515-516.
"Crystal structure of bis-(2,4,6-trimethylphenyl)-[6-(2,4,6-trimethylphenyl)pyridin-2-yl]amido-(μ-oxo)-hexachloroditantalum(V), $(C_{46}H_{50}N_4)Ta_2Cl_6O$"

5. S. Proch, J. M. Villanueva, T. Irrgang, C. Döring, R. Kempe, *Z. Kristallogr. NCS* **2008**, *223*, 55-56.
"Refinement of the crystal structure of aquazinc(II) glutamate hydrate, $Zn(H_2O)(C_5H_7NO_4) \cdot H_2O$"

6. A. M. Dietel, C. Döring, R. Kempe, *Z. Kristallogr. NCS* **2008**, *223*, 395-396.
"Crystal structure of bis(1,1,1,3,3,3-hexamethyl-disilylamide)bis((4,6-dimethyl-pyridin-2-yl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amide)diytterbium(II), $\{Yb(C_{27}H_{35}N_3)[N(Si(CH_3)_3)]_2\}_2$"

7. C. Döring, R. Kempe, *Z. Kristallogr. NCS* **2008**, *223*, 397-398.
"Crystal structure of tribenzyltris(tetrahydrofurano)neodymium(III), $[Nd(CH_2Ph)_3(OC_4H_8)_3]$"

8. D. M. Lyubov, C. Döring, G. K. Fukin, A. V. Cherkasov, A. S. Shavyrin, R. Kempe, A. A. Trifonov, *Organometallics* **2008**, *27*, 2905-2907.
"Selective Assembly of Trinuclear Rare earth Alkyl Hydrido Clusters Supported by Amidopyridinate Ligands"

9. A. M. Dietel, C. Döring, G. Glatz, M. V. Butovskii, O. Tok, F. M. Schappacher, R. Pöttgen, R. Kempe, *Eur. J. Inorg. Chem.* **2009**, 1051-1059.
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10. Declaration / Erklärung

I hereby declare that I have written this work by myself and that no other sources than those mentioned in this work have been used.

This work has so far neither been submitted to the Faculty of Biology, Chemistry and Earth Sciences at the University of Bayreuth nor to any other scientific institution for the purpose of a doctoral thesis.

Hiermit versichere ich an Eides statt, dass ich die vorliegende Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel und Quellen angefertigt habe.

Diese Arbeit wurde bisher weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht.

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Christian Döring