N-Ligand Stabilized Lanthanide Complexes

DISSERTATION

Zur Erlangung des akademischen Grades eines
Doktors der Naturwissenschaften (Dr. rer. nat.)
im Fach Chemie der Fakultät für Biologie, Chemie und Geowissenschaften
der Universität Bayreuth

vorgelegt von
M. Sc. Sadaf Qayyum
geboren in Kamrial, Attock/Pakistan

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This thesis fulfills the requirements of the doctoral degree of the Faculty of Biology, Chemistry and Geological Sciences at the University of Bayreuth.

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Examination Committee:

Chairman: Prof. Dr. Karl Heinz Seifert
1. Referee: Prof. Dr. Rhett Kempe
2. Referee: Prof. Dr. Brend Wrackmeyer
Prof. Dr. Thomas Hellweg

The following work was undertaken during the period October 2004 to June 2009 at the Lehrstuhl für Anorganische Chemie II der Universität Bayreuth under the supervision of Prof. Dr. Rhett Kempe.

To my family

Table of Contents

1. Summary

A series of lanthanide complexes stabilized by N-ligands has been synthesized. Most of these complexes have been structurally characterized. The overall results emphasize the importance of the steric bulk of the applied ligands to stabilize various lanthanide complexes with a distinct reactivity.

To highlight and compare the steric bulk of an aminopyridinato with those of amidinate ligands mononuclear seven coordinated complexes of lanthanum were synthesized by salt elimination route. X-ray crystal structure analyses were carried out to compare the steric demand of the two amido ligands. A similar overall primary coordination site bulkiness for both ligands and distinct differences regarding this bulkiness for different directions were observed. A better shielding of the second coordination sphere was observed for the aminopyridinate.

Based on their steric demand mono(aminopyridinato) organoyttrium complexes were selectively synthesized in very good yields by alkane elimination from trialkylyttrium complexes. The corresponding yttrium cations were accessible by abstracting one of the two alkyls using ammonium borates. Based on the appropriate steric bulk of the used aminopyridinato ligand these yttrium cations show very high ethylene polymerization activity at 80 °C in the presence of small amounts of aluminium alkyls. During these polymerizations a reversible polyethylene chain transfer between the organoyttrium cation and aluminium compounds was observed. The chain transfer catalyst system described here is able to produce relatively long chain (up to 4000 g mol^{-1}) Al-terminated polyethylene with a molecular weight distribution < 1.1.

Instead of salt elimination or alkane elimination, aminopyridinato lanthanide complexes are accessible even under solventless conditions at elevated temperatures. The direct reaction between ytterbium metal and bulky aminopyridines was an effective way to synthesize true homoleptic monomeric aminopyridinato complexes of ytterbium. A systematic steric variation leads to bis- or tris(aminopyridinato)ytterbium complexes. The divalent ytterbium complexes show interesting intermolecular agostic interactions. Such agostic interactions do not persist if salt metathesis reactions are carried out in THF, since coordination of THF blocks the vacant site responsible for such interactions. A further increase in the steric bulk of the applied ligands leads to mixed amido/ iodo complexes in the salt metathesis reaction.

The attempted reduction of these mixed amido/ iodo rare earth metal complexes using KC_8 led to the formation of bis(aminopyridinato) complexes which have been characterized by X-

ray diffraction studies, NMR spectroscopic investigations and elemental analyses. Most likely reduction took place followed by disproportionation and the formation of bis(aminopyridinates).

Due to enhanced reactivity and, in particular, the rarity of cyclopentadienyl free rare earth metal hydrido complexes we became interested to synthesize bis(aminopyridinato)lanthanide hydrido complexes. Slight variation in the steric bulk enabled us to selectively synthesize the corresponding bis(aminopyridinato)lanthanide halide precursors. Due to the specific steric "pressure" the same coordination number was observed for La and Sc despite the large difference in their ionic radii. Since the most common synthetic route to the hydrido complexes is σ-bond metathesis reaction of parent alkyl complex with phenyl silane, we synthesized bis(aminopyridinato)lanthanide alkyl complexes. Corresponding hydrides generated by reaction of alkyl complexes with $PhSiH_3$ undergo a very fast intramolecular metallation reaction at room temperature. The intramolecular C-H activation is highly dependent on the size of the used lanthanides. For larger lanthanides the rate of decomposition of the parent alkyl is fast enough that it precludes the isolation of stable alkyl complexes. However gradual decrease of the metal atom size enables the isolation of stable alkyl complexes which then may undergo intramolecular C-H activation via a transient hydride species at reasonable rates at room temperature.

Zusammenfassung

Eine Serie N-ligand-stabilisierter Lanthanoidkomplexe wurde synthetisiert. Die meisten dieser Komplexe wurden strukturell charakterisiert. Im Großen und Ganzen heben die Ergebnisse dieser Arbeit die Bedeutung des sterischen Anspruchs der eingesetzten Liganden zur Stabilisierung verschiedener LanthanoidKomplexe mit einer speziellen Reaktivität betont .

Um den sterischen Anspruch von Aminopyridinatliganden im Vergleich zu Aminidinatliganden herauszustellen und zu vergleichen, wurden mononukleare, siebenfach koordinierte Komplexe des Lanthans über eine Salzeliminierungsroute hergestellt. Einkristall-Röntgenstrukturananlysen dieser Komplexe wurden durchgeführt, um den sterischen Anspruch der zwei Amidoliganden zu vergleichen. Ein ähnlicher allgemeiner primärer Koordinationsanspruch konnte für beide Liganden ermittelt werden und gleichzeitig wurden starke Unterschiede bezüglich des sterischen Anspruchs in verschiedene Richtungen festgestellt. Eine bessere Abschirmung der sekundären Koordinationssphäre wurde für Aminopyridinate beobachtet.

Basierend auf ihrem sterischen Anspruch, konnten Mono(aminopyridinato)-Organoyttrium-Komplexe selektiv und in guten Ausbeuten über eine Alkaneliminierungsreaktion mit Trialkylyttriumverbindungen hergestellt werden. Die entsprechenden Yttriumkationen waren zugänglich durch Abstraktion von einer oder zwei Alkyleinheiten mittels Ammoniumboraten. Basierend auf dem entsprechenden sterischen Anspruch der eingesetzten Liganden weisen diese Yttriumkationen bei 80 °C und in Gegenwart von geringen Mengen an Aluminiumalkylen eine sehr hohe Aktivität in der Ethylenpolymerisation auf. Während dieser Polymerisationen wurde ein reversibely Polyethylen-Kettentransfer zwischen dem Organoyttriumkation und den Aluminiumverbindungen beobachtet. Das hier beschriebene Kettentransfer-Katalysatorsystem ist in der Lage, relativ langkettiges (bis zu 4000g/mol) Al-terminiertes Polyethylen mit einer Molekulargewichtsverteilung <1.1 zu produzieren.

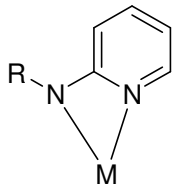
Neben der Salz- oder Alkaneliminierungroute können Aminopyridinato-Lanthanoidkomplexe auch unter lösungsmittelfreien Bedingungen bei erhöhten Temperaturen hergestellt werden. Die direkte Reaktion von metallischem Ytterbium und sterisch anspruchsvollen Aminopyridinatoliganden ist eine effiziente Methode, um monomere homoleptische Aminopyridinatokomplexe des Ytterbium herzustellen. Eine systematische Variation des sterischen Anspruchs des Liganden führt zu Bis- oder Tris(aminopyridinato)-Ytterbiumkomplexen. Die divalenten Ytterbiumkomplexe weisen interessante intermolekulare agostische Wechselwirkungen auf. Solche agostischn Wechselwirkungen können allerdings

nicht beobachtet werden, wenn die Synthese der Komplexe durch Salzmethathese in THF durchgeführt wird, da die Koordination eines THF-Moleküls die für diese Wechselwirkung verantwortliche freie Koordinationsstelle besetzt. Eine Erhöhung des sterischen Anspruchs der eingesetzten Liganden führt zu gemischten Amido/Iodo-Komplexen über eine Salzmetathesereaktion. Der Versuch diese gemischten Amido/Iodo-Seltenerdkomplexe mit KC_8 zu reduzieren führte zur Bildung von Bis(aminopyridinato)komplexen, die über Einkristall-Röntgenstrukturanalyse, NMR-Untersuchungen sowie Elementaranalyse charakterisiert wurden. Höchstwahrscheinlich erfolgte hier die Reduktion des Komplexes, gefolgt von einer Disproportionierung und der Bildung der Bis(aminopyridinate).

Wegen der erhöhten Reaktivität und insbesondere wegen der Seltenheit von Cyclopentadienyl-freien Seltenerdmetall-Hydridokomplexen waren wir daran interessiert, Bis(aminopyridinato)-Lanthanoidhydridkomplexe herzustellen. Kleine Variationen im sterischen Anspruch des Liganden ermöglichten die selektive Synthese der entsprechenden Bis(aminopyridinato) Lanthanoidhalogenid-Precursoren. Wegen des spezifischen sterischen „Drucks“ des N-Liganden konnte die gleiche Koordinationszahl sowohl für La als auch für Sc beobachtet werden, trotz ihrer stark unterschiedlichen Ionenradien. Da die meistverwendete Methode für die Herstellung von Hydridokomplexen eine σ-Bindungsmetathese von Alkylkomplexen mit Phenylsilanen ist, wurden zuerst Bis(aminopyridinato)-Lanthanoidalkylkomplexe hergestellt und mit $PhSiH_3$ umgesetzt. Die entsprechend gebildeten Hydride reagieren jedoch sehr schnell weiter in einer intramolekularen Metallierungsreaktion. Diese intramolekulare C-H-Bindungsaktivierung ist sehr stark von der Größe des eingesetzten Lanthanoids abhängig. Für große Lanthanoide ist die Zerfallsrate des Alkylkomplexes so schnell, dass eine Isolierung des entsprechenden Alkylkomplexes unmöglich ist. Jedoch führt eine sukzessive Verringerung der Größe des Metalls zu einer erhöhten Stabilität und ermöglicht somit die Isolierung stabiler Alkylkomplexe, die anschließend zu Hydridokomplexen umgesetzt werden können und in einer intramolekularen C-H-Bindungsaktivierung weiterreagieren.

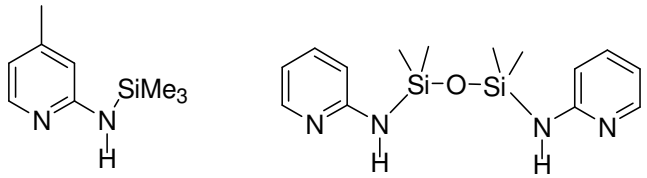
2. Introduction

During the renaissance of amido[1,2] metal chemistry, aminopyridinato ligands (Ap)[3] have been used extensively to stabilize lanthanide (Ln) complexes. These compounds (Scheme 1) have been shown to exhibit unusual stoichiometric and catalytic reactivity.[4]



Scheme 1. An aminopyridinato ligand in its strained η^2 binding mode, typical for early transition metals and lanthanides ([Ln] = lanthanide moiety; R = aryl, silyl or alkyl substituent).

The steric bulk of aminopyridinato ligands is rather small in comparison to the related cyclopentadienyl ligands[5] and the closely related silyl-substituted amidinates,[6,7] especially in the plane perpendicular to the pyridine moiety. This, in turn, gives rise to highly nitrogen coordinated lanthanide complexes. Therefore, the chemistry of aminopyridinato ligands differs dramatically from these two types in cases such as group-3 or lanthanide chemistry where steric bulk is important for the stabilization of reactive transition metal complexes.[8] For instance, the reactions of silyl substituted aminopyridinates derived from **1** (Scheme 2) with lanthanide trihalides gave ate complexes.[9] However, monochloro compounds were formed if 2 equiv. of cyclopentadienyl ligands[10] or silyl-substituted amidinates[6,7] were used instead of **1**. Some of the limitations of simple aminopyridinato ligands can be overcome by using bis(aminopyridinato) ligands such as deprotonated **2**. Reaction of dilithiated **2** (generated in situ) with $LnCl_3$ gave different products depending on the size of the lanthanide ion. For instance, when Ln = Y and Sm, the monochloro complexes could be synthesized however, similar reactions for the larger Nd and La ions again resulted in the formation of ate complexes.



1 **2**

Scheme 2. Silyl substituted aminopyridines.

The motivation for the present studies was not only to overcome the problems resulted due to the formation of ate complexes but also to study and evaluate the steric bulk effectively to synthesize selectively mono- or bis(aminopyridinato)lanthanide complexes. It also presents the versatility of methods to access such complexes. The mono(aminopyridinato)ligand stabilized yttrium cations show very high ethylene polymerization activity in the presence of small amounts of aluminum alkyl compounds at elevated temperature. Reversible polyethylene chain transfer between the organoyttrium cations and the aluminum compounds can be observed. Since the β-H elimination is nearly suppressed even at 100 °C, relatively high molecular weight Al-terminated polymer chains with very narrow polydispersity can be produced. It also presents the accessibilty of lanthanide complexes without any coordinating solvents. For instance, a solvent free bis(aminopyridinato)ytterbium^{II} complex was synthesized under solventless conditions at elevated temperature which shows interesting intermolecular agostic interactions in the solid state. An ambitious undertaking was the synthesis of compounds comprising direct Ln-Ln bonds that did not succeed but yielded interesting results. It was useful enough to reflect that how difficult it would be to synthesize such complexes.

Another focus of this work was the synthesis of non-metallocene hydride complexes. Even after a lapse of twenty five years of the pioneering works on the synthesis of the first molecular lanthanide hydrido complexes[11] these compounds still attract considerable attention[12] and remain one of the most promising classes of compounds for various catalytic applications.[13] However in contrast to hydride complexes supported by cyclopentadienyl ligands,[10,14] only relatively few examples of their non-cyclopentadienyl analogues have been reported in the literature.[15] Sterically demanding aminopyridinato ligands were successfully used for the stabilization of monomeric lanthanide species and the observed intramolecular C-H activation has been discussed in detail.

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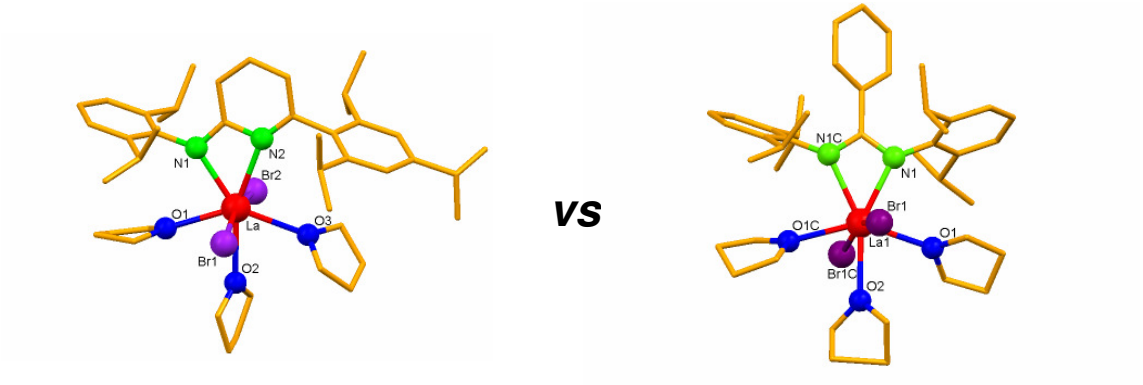
3. Overview of Thesis –Results

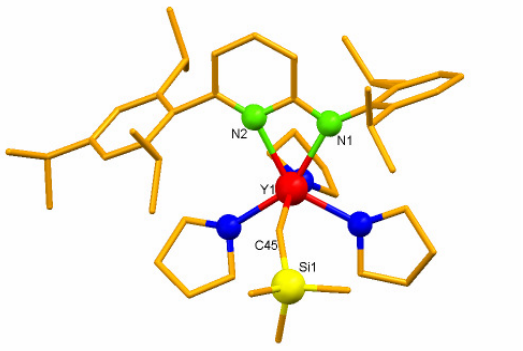
This thesis comprises five publications which are presented in chapter 4 to 8.

3.1. Lanthanum Dibromide Complexes of Sterically Demanding Aminopyridinato and Amidinate Ligands



The syntheses and structures of $[Ap^*LaBr_2(THF)_3]$ and $[Am^*LaBr_2(THF)_3]$ (Ap*-H = {(2,6-diisopropyl-phenyl)[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine}, Am*-H = N,N′-bis-(2,6-diisopropylphenyl)benzamidine) have been discussed. X-ray crystal structure analyses of the two seven coordinated complexes were carried out to compare the steric demand of the two amido ligands. A similar overall primary coordination site bulkiness for both ligands and distinct differences regarding this bulkiness for different directions were observed. A better shielding of the second coordination sphere was observed for the aminopyridinate.

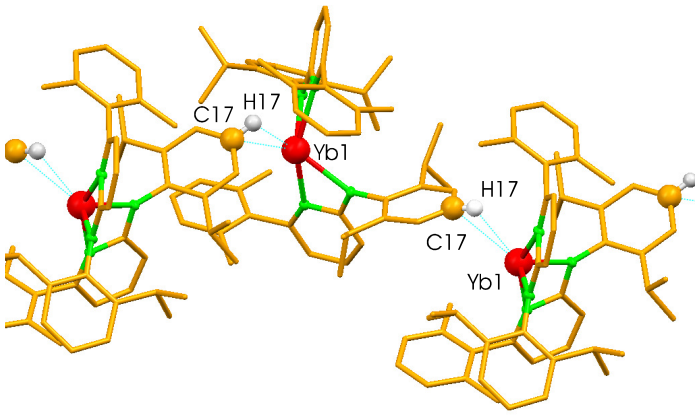
3.2. Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution



The reversible PE chain transfer (PE = polyethylene) between organoyttrium cations (see picture) and aluminum alkyls at elevated temperatures, to synthesize functionalized PE

materials with a very narrow molecular-weight distribution and relatively high molecular weights is described. Aminopyridinato ligands are the key to this lanthanide-catalyzed version of Ziegler's Aufbau reaction. Aminopyridinato ligand stabilized organoyttrium cations are accessible in very good yields via alkane elimination from trialkylyttrium complexes with sterically demanding aminopyridines followed by abstraction of one of the two alkyl functions using ammonium borates. At 80 °C and in the presence of small amounts of aluminum alkyl compounds very high ethylene polymerization activities are observed when very bulky aminopyridinato ligands are used. During these polymerizations a reversible polyethylene chain transfer between the organoyttrium cations and aluminum alkyls is observed. The chain transfer catalyst system described here is able to produce relatively long chains (up to 4000 g/mol) Al-terminated polyethylene with a molecular weight distribution < 1.1. In the synthesis of higher molecular PE a slight increase in polydispersity with increasing chain length (15600 g/mol, ~ 1.4) is observed due to reduced reversibility caused by higher viscosity and precipitation of the Al-terminated polymer chains (temperature of 80 - 100 °C).

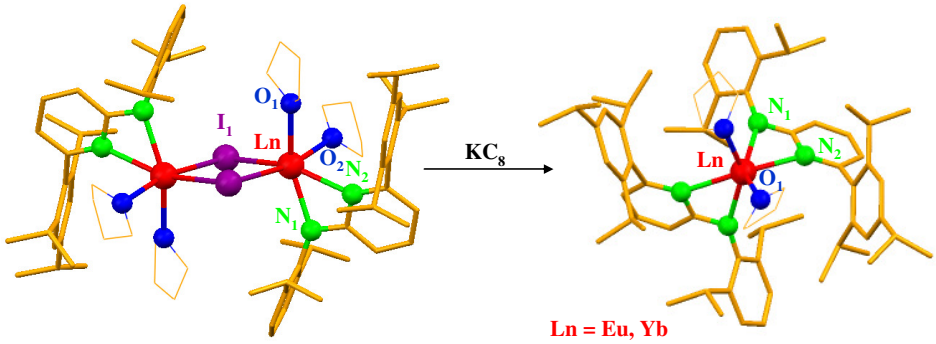
3.3. Small Steric Variations in Ligands with Large Synthetic and Structural Consequences



In this chapter the ability of aminopyridinato ligands to access aminopyridinato lanthanide complexes under solventless conditions at elevated temperatures is explored. The direct reaction between ytterbium metal and bulky aminopridinato ligands is an effective way to synthesize true homoleptic monomeric aminopyridinato complexes of ytterbium. A systematic steric variation leads to bis- or tris(aminopyridinato)ytterbium complexes. The divalent ytterbium complexes show interesting intermolecular agostic interactions in the solid state. Such agostic interactions do not persist if synthesized by salt metathesis reactions in

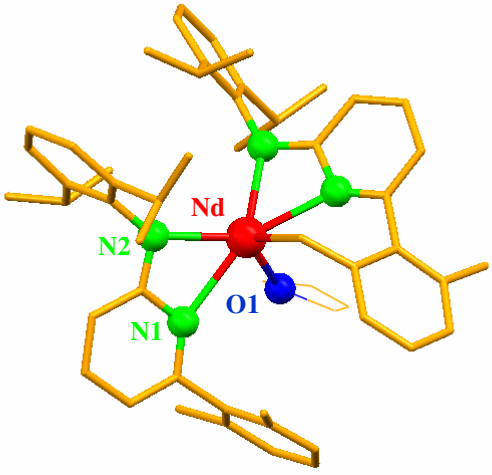
THF, since coordination of THF blocks the vacant site responsible for such interactions. A further increase in the steric bulk of the applied ligands leads to mixed amido/ iodo complexes in salt metathesis reaction.

3.4. Attempted Reduction of Divalent Rare Earth Iodo Aminopyridinates



Since unsupported metal bonds between lanthanides are unknown. We started to investigate and synthesize compounds containing unsupported Ln-Ln bonds and therefore attempted to reduce divalent iodo lanthanide complexes. The attempted reduction of these mixed amido/ iodo rare earth metal complexes using KC_8 led to the formation of bis(aminopyridinato) complexes which have been characterized by X-ray diffraction studies, NMR spectroscopic investigations and elemental analyses. Most likely reduction took place followed by disproportionation and the formation of bis(aminopyridinates).

3.5. Intramolecular C-H Bond Activation by Lanthanide Complexes Bearing a Bulky Aminopyridinato Ligand



Due to the enhanced reactivity and in particular rarity of cyclopentadienyl-free rare earth metal hydrido complexes we became interested to synthesize bis(aminopyridinato)lanthanide

hydrido complexes. Slight variation in the steric bulk of the ligand enabled us to selectively synthesize the corresponding bis(aminopyridinato)lanthanide halide precursors. Due to the low steric "pressure" towards the additional coordination sites the same coordination number was observed for instance for La and Sc despite the large difference in their ionic radii. Since the most common synthetic route to these hydrido complexes is σ-bond metathesis reaction of parent alkyl complex with phenylsilane, we synthesized bis(aminopyridinato) lanthanide alkyl complexes. Corresponding hydrides generated by reaction of alkyl complexes with $PhSiH_3$ undergo a very fast intramolecular metallation reaction at room temperature. The intramolecular C-H activation is highly dependent on the size of the used lanthanides. For larger lanthanides the rate of decomposition of the parent alkyl complex is fast enough that it precludes the isolation of stable alkyl complexes. However gradual decrease of the metal atom size enables the isolation of stable alkyl complexes which then may undergo intramolecular C-H activation via a transient hydride species at reasonable rates at room temperature.

3.6. Individual Contribution to Joint Publications

The results presented in this thesis were obtained in collaboration with others and published 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 *Z. Anorg. Allg. Chem.*, **2006,** *632,* 1936-1938, under the title, **"Lanthanum Dibromide Complexes of Sterically Demanding Aminopyridinato and Amidinate Ligands".** Winfried P. Kretschmer*, Auke Meetsma , Bart Hessen, Natalie M. Scott, Sadaf Qayyum, Rhett Kempe*.

Winfried P. Kretschmer synthesized and characterized the mono(amidinate) lanthanum dibromide complex.

Auke Meetsma did the X-ray analysis.

Bart Hessen provided the lab facility.

Natalie M. Scott did some initial work.

I synthesized and characterized the mono(aminopyridinato) lanthanum dibromide complex presented in this work.

Rhett Kempe supervised this work and was involved in scientific discussions, comments and the publication was written jointly with Rhett Kempe and Winfried P. Kretschmer.

Chapter 5

This work is published in *Chem. Eur. J.* **2006**, *12,* 8969-8978, under the title, **"Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution".** Winfried P. Kretschmer*, Auke Meetsma, Bart Hessen, Thomas Schmalz, Sadaf Qayyum and Rhett Kempe*.

Winfried P. Kretschmer synthesized and characterized the corresponding cations and the aluminium compound, did the polymerization experiments and polymer analysis.

Bart Hessen provided the polymerization and GPC facility.

Auke Meetsma did the X-ray analyses.

I have synthesized the organic ligands required to do this work.

Thomas Schmalz synthesized some of the compounds.

Rhett Kempe supervised this work and was involved in scientific discussions and suggestions.

The publication was written jointly with Rhett Kempe and Winfried P. Kretschmer.

Chapter 6

This work is published in *Eur. J. Inorg. Chem.* **2008**, 557-562, under the title, **"Steric Variations in Ligands with Large Synthetic and Structural Consequences"**. Sadaf Qayyum, Kristina Haberland, Craig M. Forsyth, Peter C. Junk, Glen B. Deacon* and Rhett Kempe*.

I synthesized and characterized all the complexes presented in this work and the publication is written by me.

Kristina Haberland did some initial work within the scope of her diploma requirements.

Craig M. Forsyth did the X-ray analyses.

Peter C. Junk, Glen B. Deacon and Rhett Kempe were the motive of idea of this work and supervised this work.

Chapter 7

This work is accepted in *Z. Anorg. Allg. Chem*. **2009,** under the title, **"Attempted Reduction of Divalent Rare Earth Iodo Aminopyridinates"** Sadaf Qayyum, Awal Noor, Germund Glatz, Rhett Kempe*.

I synthesized and characterized all the compounds and the publication was written by me. Awal Noor helped me to perform the reduction reactions.

Germund Glatz did the X-ray analyses.

Rhett Kempe supervised this work and was involved in scientific discussions and suggestions.

Chapter 8

This work is to be submitted to *Eur. J. Inorg. Chem.* under the title, **"Intramolecular C-H Bond Activation by Lanthanide Complexes Bearing a Bulky Aminopyridinato Ligand"**

Sadaf Qayyum, Grigorii G. Skvortsov, Georgii K. Funkin, Alexander A. Trifonov*, Winfried P. Kretschmer, Christian Döring and Rhett Kempe*.

I synthesized and characterized most of the compounds presented in this work, did the kinetic experiments and the publication was written by me.

Grigorii G. Skvortsov performed the syntheses of $[Ap_3La]$, $[Ap_2SmCl(thf)]$ and the C-H activation complexes of La and Nd.

Georgii K. Funkin did the NMR studies for compounds synthesized at the G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences Russia.

Winfried P. Kretschmer did NMR experiment with hydrogen and corrected the manuscript.

Christian Döring did the X-ray analyses.

Alexander Trifonov and Rhett Kempe supervised this work and were involved in scientific discussions and suggestions.

4. Lanthanum Dibromide Complexes of Sterically Demanding Aminopyridinato Ligands[1)]

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Dedicated to Professor Glen Deacon on the Occasion of his 70th Birthday

Keywords: Amidinate Ligands / Aminopyridinato ligands / Lanthanides / Lanthanum.

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Abstract: It is reported on the synthesis and structure of [Ap*$LaBr_2(THF)_3$] and [Am*$LaBr_2(THF)_3$] (Ap*-H = {(2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)-pyridin-2-yl]-amine}, Am*-H = *N,N`*-bis-(2,6-diisopropylphenyl)benzamidine). X-ray crystal structure analyses of the two seven coordinated complexes were carried out to compare the steric demand of the two amido ligands. A similar overall primary coordination site bulkiness for both ligands and distinct differences regarding this bulkiness for different directions were observed. A better shielding of the second coordination sphere was observed for the aminopyridinate.

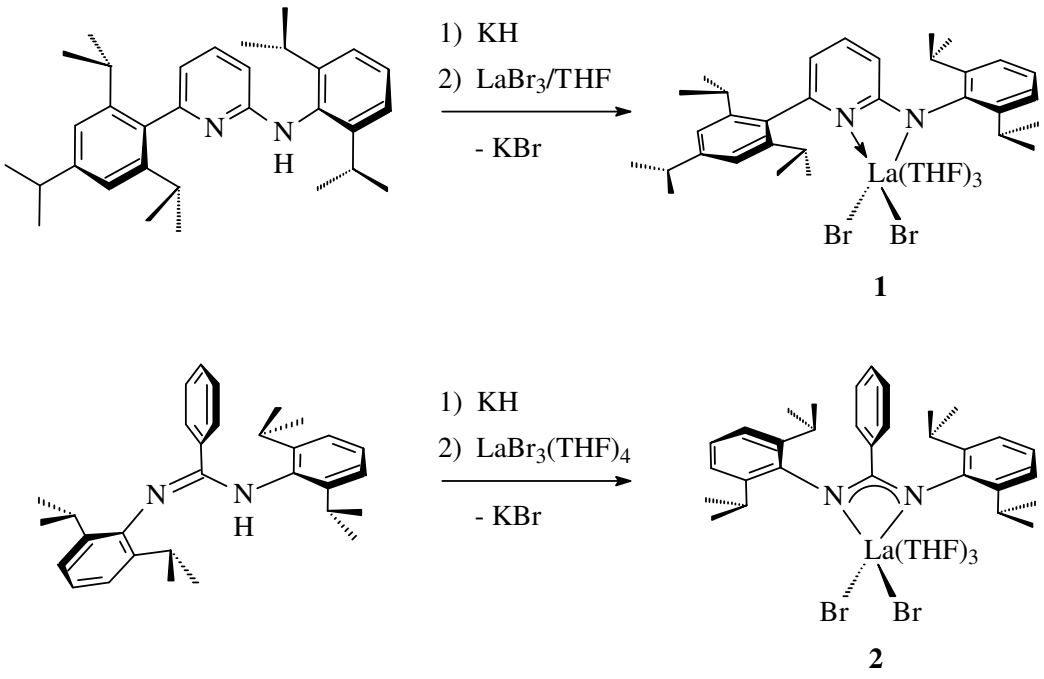
4.1. Introduction

Recently, sterically demanding *N,N*-bidentate anionic ligands became very popular in amido[1,2] lanthanide chemistry. Among such ligands selected amidinate[3] and

1) Paper presented at the XVIIIth Tage der Seltenen Erden (Terrae Rarae 2005) at Bonn-Röttgen/Germany, November 30th - December 2nd, 2005 (www.Terrae-rarae.de).

aminopyridinato[4,5] ligands are of special interest since they bind a large variety of rare earth metals forming species of the type [(L)LnX_2(THF)$_n$] (L = *N*,*N*-bidentate mono anionic amido ligands, Ln lanthanide metal, X = halide, n = 1,2,3,...)[6,7]. In this communication we report on synthesis and structure of [Ap*LaBr_2(THF)$_3$] and [Am*LaBr_2(THF)$_3$] (Ap*-H = {(2,6-diisopropyl-phenyl)-[6-(2,4,6-triisopropyl-phenyl)- pyridin-2-yl]-amine}, Am*-H = *N,N`*-bis-(2,6-diisopropylphenyl)-benzamidine).

Both compounds are accessible via salt elimination reaction in moderate to good yields. The reaction of Ap*-H or Am*-H with KH leads to the potassiated aminopyridinate or amidinate, respectively, which then can undergo transmetalation (Scheme 1). For **1** no reaction is observed with lithiated Ap*-H. The potassium salt of Ap*-H is a polymer and the lithium salt a three coordinated monomer. Additional coordination of one solvent molecule was found for the lithium salt[8]. This observation is in contrast to the reaction of lithiated Am*-H with [$LaBr_3$(THF)$_4$]. We succeeded in the formation of the corresponding lanthanum amidinate; however no complete LiBr separation could be achieved. Furthermore, no formation of a bis(aminopyridinato) complex could be observed by reacting two equiv. of Ap*K with $LaBr_3$.



Scheme1. Synthesis of **1** and **2**.

NMR spectroscopy of the two lanthanum complexes revealed the coordination of three additional THF ligands. Due to the additional coordination of three THF ligands we expected mononuclear seven coordinated compounds in solution. Such complexes should be ideal to

compare the steric bulk of the aminopyridinate and the amidinate ligand since the angles between the ancillary ligands are quite sensitive to the steric "pressure" of the amido ligands in at least two directions. Crystals of **1** and **2** suitable for X-ray crystal structure analysis could be grown from hexane (**1**) or THF (**2**) solutions. The molecular structures of **1** and **2** (ORTEP plots) are shown in Figure 1 and 2, respectively.

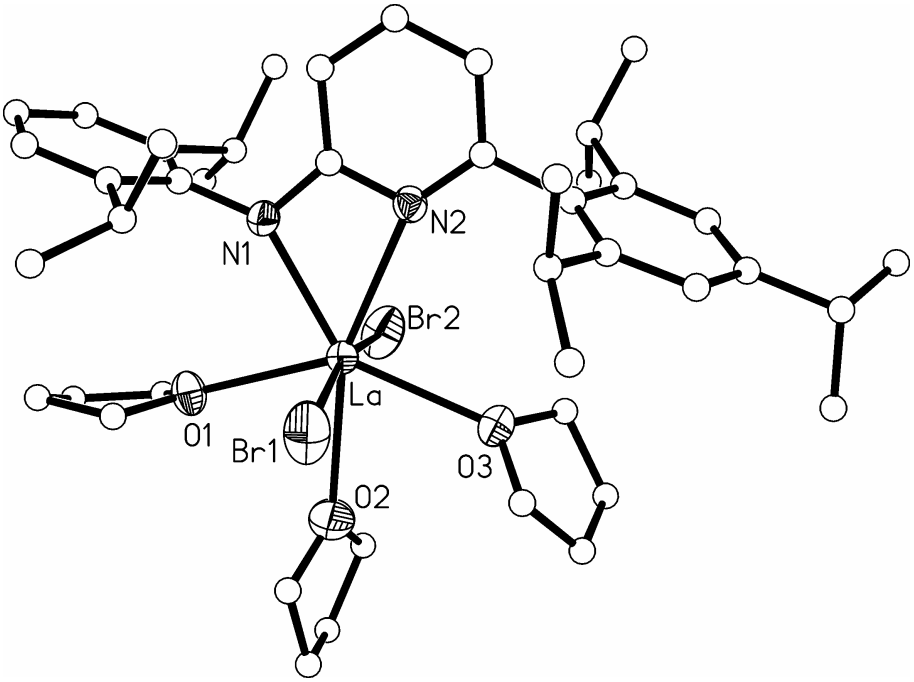
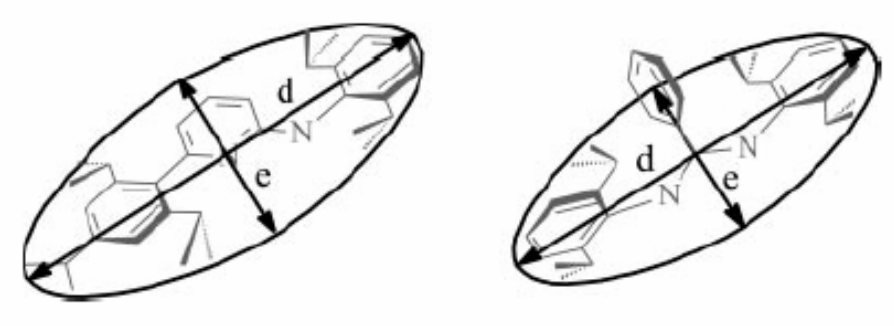


Figure 1. Molecular structure of **1** (ellipsoids [non carbon atoms] correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: La–N1 2.447(3), La–O1 2.560(2), La–O3 2.579(2), La–O2 2.634(3), La–N2 2.645(3), La–Br1 2.9028(6), La–Br2 2.9116(6); N1–La–O1 76.60(9), N1–La–O3 142.25(9), O1–La–O3 140.96(8), N1–La–O2 146.27(10), O1–La–O2 69.68(10), O3–La–O2 71.44(10), N1–La–N2 52.98(8), O1–La–N2 129.56(8), O3–La–N2 89.31(9), O2–La–N2 160.75(9), N1–La–Br1 96.58(7), O1–La–Br1 91.08(6), O3–La–Br1 87.98(7), O2–La–Br1 83.62(10), N2–La–Br1 95.61(6), N1–La–Br2 96.55(7), O1–La–Br2 88.29(6), O3–La–Br2 83.95(7), O2–La–Br2 83.38(10), N2–La–Br2 95.29(6), Br1–La–Br2 166.342(17), O1–La–O3 140.96(8).

Both compounds are monomeric in the solid state and the coordination can be described best as pentagonal bipyramides in which the two bromo ligands occupy the axial positions. The equatorial sites are populated by the three oxygen atoms of the THF ligands as well as the two N-atoms. The two N-atoms in **2** are equally bonded to the metal center [La–N 2.5254(18) Å], while the La–N distances of **1** [La–N1 2.447(3) Å; La–N2 2.645(3) Å] indicate a localization

of the anionic function at the amido N-atom. The binding of Ap* to the lanthanum atom is described best as a donor functionalized amido metal bond. The maximum atom to atom distances in accordance to Scheme 2 express the overall steric bulk of the two amido ligands or the second coordination sphere bulkiness. These distances are: d = 15.1 Å, e = 8.8 Å for **1** and d = 11.9 Å, e = 8.6 Å for **2**. Which means **1** is the more demanding in this regard.



Scheme 2. Description of the steric demand of the amido ligands by using the parameter d and e (maximum H–atom–H–atom distances perpendicular to each other).

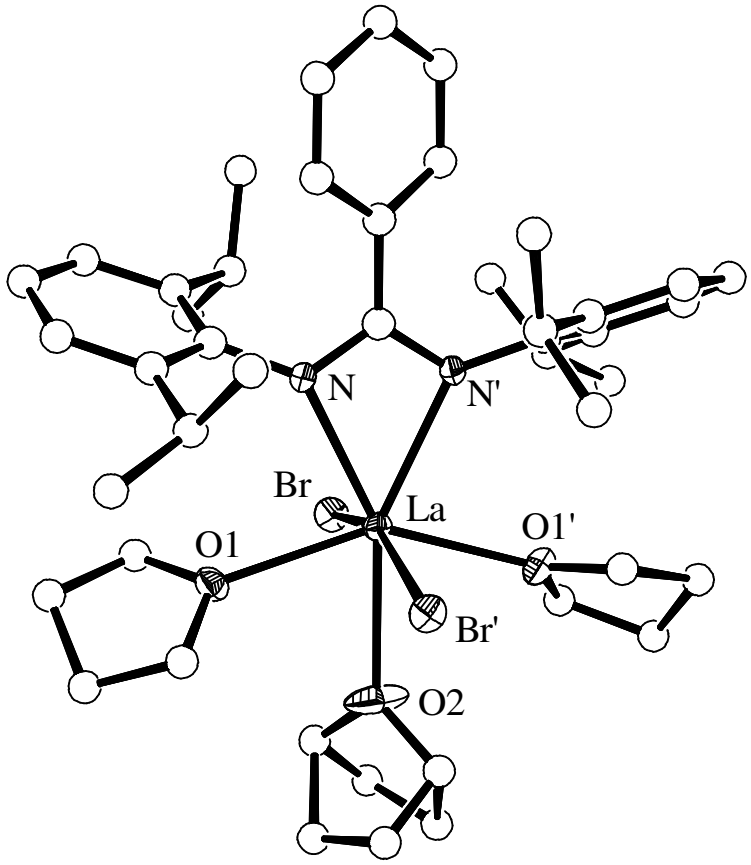


Figure 2. Molecular structure of **2** (ellipsoids [non carbon atoms] correspond to the 50% probability level); selected bond lengths [Å] and angles [°]: La–N 2.5254(18), La–O1 2.5571(17), La–O2 2.620(3), La–Br 2.9053(2); N–La–Br 99.18(4), N'–La–Br 99.44(4), N–La–O1 80.46(6), N–La–O2 153.84(4), N–La–O1' 132.77(6), N'–La–O1 132.77(6), N'–La–O2 153.84(4), O1–La–O2 73.38(4), O1–La–O1' 146.77(6), N–La–N' 52.33(6), O1–La–Br 85.62(4), O2–La–Br 79.62(1), Br–La–Br' 159.24(1).

Furthermore, the Br–La–Br bond angles and the nearly linear O–La–O angle can be used to describe the steric "pressure" which is put on the ancillary ligands (bromo and THF ligands). We call this the primary coordination site bulkiness. For **1** these angles are: Br1–La–Br2 166.342(17)°, O1–La–O3 140.96(8)°and for **2**: Br–La–Br`159.24(1)°, O1–La–O1` 146.77(6)°. The aminopyridinato ligand is sterically more demanding in d-direction which could be understood by the fact that the 2,6-isopropylphenyl substituent linked to the pyridine ring is pointing downwards (Figure 1). In e-direction the amidinate ligand is bulkier. The differences in the Br–La–Br und O–La–O angles are similar 7.1° and 5.8°, respectively. Thus we assume a similar overall primary coordination site bulkiness for both ligands but distinct differences in the d- and e-directions. The consequences of these differences in terms of the

reactivity of the corresponding early transition metal and lanthanide complexes are going to be investigated.

Table 3. Details of the X-ray crystal structure analyses.

compound	**1**	**2**
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	Pbcn
a, Å	14.455(3)	17.0544(9)
b, Å	17.772(4)	17.393(1)
c, Å	18.361(4)	14.6421(8)
β, deg	95.13(3)	
V, $Å^3$	4697.9(16)	4343.2(4)
Z	4	4
crystal size, mm	0.48 x 0.36 x 0.34	0.49 x 0.46 x 0.39
ρ_{calcd}, g cm^{-3}	1.372	1.460
μ, mm^{-1} (Mo Kα)	2.647	2.862
T, K	193(2)	100(1)
θ range, deg	1.60 to 26.31	2.34 to 29.68
no. of reflecions unique	9341	5384
no. of reflections obs. [I > 2σ (I)]	8148	4661
no. of parameters	469	358
wR^2 (all data)	0.0849	0.0618
R value [I>2σ (I)]	0.0333	0.0286

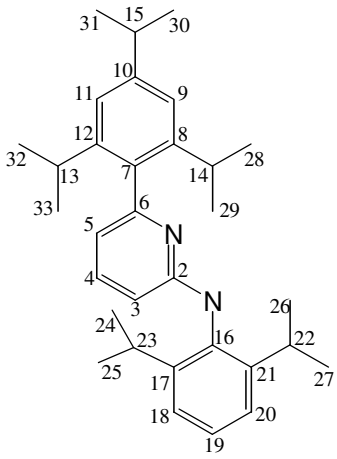
4.2. Experimental Section

All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried (CaH_2) and distilled prior to use. NMR spectra were obtained using either a Brucker ARX 250, Brucker DRX 500, Varian Unity Inova 400 or VXR 300 spectrometer. Chemical shifts are reported in ppm relative to the deuteurated solvent. Elemental analyses were carried out using an Elementar Vario EL III. Ap*-H[8] and Am*-H[7b] were synthesized following literature procedures. [$LaBr_3(THF)_4$] was prepared by continuous extraction of anhydrous $LaBr_3$ with THF. [9] All other starting materials were

purchased from commercial suppliers. X-ray crystal structure analyses were performed using a STOE-IPDS II (**1**) or a Brucker SMART APEX CCD (**2**) equipped with a low temperature unit. Structure solution and refinement was accomplished using SIR97[10], SHELXL97[11] and WinGX[12]. Crystallographic details are summarized in Table 1. CCDC-602184 (compound **1**) and CCDC -602602 (compound **2**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336-033; e-mail: deposit@-ccdc.cam.ac.uk).

Preparation of the lanthanide complexes

[Ap*LaBr$_2$(thf)$_3$] (1): $LaBr_3$ (0.80 g, 2.10 mmol), [K(Ap*)] (1.04 g, 2.10 mmol) and THF (40 mL) were added to a flask, and the mixture was stirred for 15 h. The solvent was removed under vacuum and hexane was added (30 mL). The yellow reaction mixture was filtered and on standing at room temperature for 24 h, yellow crystals (partially suitable for X-ray analysis) of **1** were formed (0.80 g, 40%). (Found: C, 54.03; H, 6.70; N, 2.70. $C_{44}H_{67}Br_2LaN_2O_3$ requires C, 54.44; H, 6.96; N, 2.89%). ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 1.17 (d, 6H, $H^{28,29,32,33}$), 1.22 (d, 6H, $H^{30,31}$), 1.29 (d, 6H, $H^{24,25,26,27}$), 1.44 (br, 4H, β-CH_2, thf), 1.49 (d, 6H, $H^{24,25,26,27}$), 1.57 (d, 6H, $H^{28,29,32,33}$), 2.78 (sept, 1H, H^{15}), 3.44 (sept, 2H, $H^{13,14}$), 3.58 (br, 12H, α-CH_2, thf), 4.22 (sept, 2H, $H^{22,23}$), 5.78 (d, 1H, H^3), 6.03 (d, 1H, H^5), 6.86 (t, 1H, H^4), 7.18 (m, 2H, $H^{18,20}$), 7.24 (m, 1H, H^{19}), 7.29 ppm (m, 2H, $H^{9,11}$). ^{13}C NMR (C_6D_6, 298 K): δ = 21.36 ($C^{28,29,32,33}$), 24.39 ($C^{24,25,26,27}$), 24.64 ($C^{28,29,32,33}$), 25.23 (β-CH_2, thf), 25.98 ($C^{24,25,26,27}$), 26.17 ($C^{30,31}$), 28.64 ($C^{22,23}$), 30.81 ($C^{13,14}$), 34.75 (C^{15}), 70.65 (α-CH_2, thf), 107.70 (C^3), 111.18 (C^5), 121.04 ($C^{9,11}$), 124.10 ($C^{18,20}$), 125.60 (C^{19}), 137.83 (C^7), 138.75 (C^4), 144.45 ($C^{17,21}$), 147.13 (C^{16}), 148.66 ($C^{8,12}$), 149.07 (C^{10}), 155.92 (C^6), 170.77 (C^2) ppm.



[Am*LaBr$_2$(THF)$_3$] (2): Am*-H (0.88 g, 2.00 mmol) was added to a slurry of KH (0.08 g, 2.00 mmol) in THF (25 mL) and stirred to become a clear solution. After adding [$LaBr_3(THF)_4$] (1.33 g, 2.00 mmol) the mixture was heated under reflux for several minutes to become slurry again. The hot mixture was filtered and slowly cooled to room temperature.

After a few hours yellow crystals of the title complex were formed which were filtered of and dried under reduced pressure (1.68 g, 88%). (Found: C, 51.94; H, 6.39; N, 2.82. $C_{43}H_{63}Br_2LaN_2O_3$ requires C, 54.10; H, 6.65; N, 2.93%). ^{1}H NMR (400 MHz, THF-d_8, 298 K): δ = 0.70 (d, 12H, ^3J(H,H) = 6.6 Hz, CH_3), 1.18 (d, 12H, ^3J(H,H) = 6.6 Hz, CH_3), 1.72 (br, 12H; β-CH_2, thf), 3.56 (br, 12H; α-CH_2, thf), 3.71 (sept, 4 H, ^3J(H,H) = 6.6 Hz, CHMe$_2$), 6.69 – 6.97 (m, 11H, C_6H_5, C_6H_3) ppm. ^{13}C NMR (100 MHz, THF-d_8, 298 K): δ = 25.19 (*C*H$_3$), 26.56 (*C*H$_3$), 27.34 (thf), 29.68 (*C*HMe$_2$), 69.22 (thf), 124.98 (Ar *C*), 125.14 (Ar *C*), 127.93 (Ar *C*), 130.23 (Ar *C*), 133.23 (Ar *C*), 143.56 (Ar *C*), 147.40 (Ar *C*), 174.25 (N*C*N) ppm.

Acknowledgments

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5. Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular Weight Distribution

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Keywords: Aluminum / Chain Transfer / Lanthanides / Polymerization / Yttrium

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Abstract: Aminopyridinato ligand stabilized organoyttrium cations are accessible in very good yield through alkane elimination from trialkyl yttrium complexes with sterically demanding aminopyridines followed by abstraction of one of the two alkyl functions using ammonium borates. At 80 °C and in the presence of small amounts of aluminum alkyl compounds very high ethylene polymerization activities are observed if very bulky aminopyridinato ligands are used. During these polymerizations a reversible polyethylene chain transfer is observed between the organoyttrium cations and aluminum alkyls. The chain transfer catalyst system described here is able to produce relatively long chain (up to 4000 g/mol) Al terminated polyethylene with a molecular weight distribution < 1.1. In the synthesis of higher molecular PE a slight increase in polydispersity with increasing chain length (15600 g/mol, ~ 1.4) is observed due to reduced reversibility caused by higher viscosity and precipitation of polymer chains (temperature of 80 - 100 °C).

5.1. Introduction

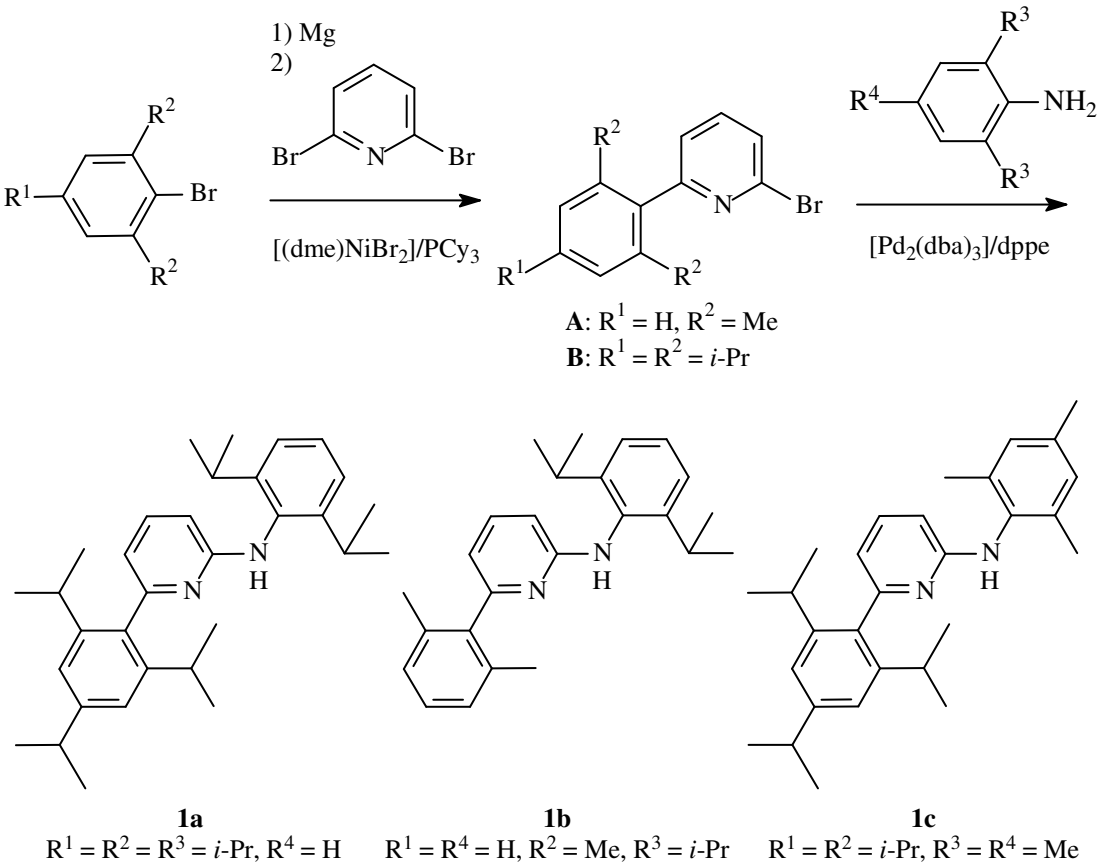
The unusual large coordination sphere and the high Lewis acidity of the lanthanides give rise to a unique coordination chemistry, for instance between Ln and main group alkyls.[1,2] The optimization of such coordinative interactions between "[Cp_2SmPE]" (Cp = cyclopentadienyl,

PE = polyethylenyl) and "[PE_2Mg]" allows for the synthesis of well defined PE materials and di-block copolymers by reversible chain transfer.[3] Lanthanide alkyls like "[Cp_2SmPE]" are usually less efficient in ethylene insertion than organolanthanide cations.[4] Early and late transition metal PE chain transfer catalysts on the other hand are limited to rather low molecular weight polymers. Such systems transfer efficiently at room temperature and are able to polymerize with a polydispersity less than 1.1, up to a molecular weight of 1200g/mol.[5] We report here on aminopyridinato ligand[6] stabilized organoyttrium cations and the reversible PE chain transfer between these cations and aluminum to synthesize aluminum terminated PE chains with a very narrow molecular weight distribution. The rather high thermal stability of these cations in combination with a suppressed *ß*-H transfer allows for the synthesis of relatively high molecular weight Al-terminated PE, functionalized polyethylene blocks to build novel polymer architectures.[7] More than 50 years ago, Karl Ziegler and co-workers discovered the Aufbaureaktion,[8] -the insertion of ethylene into an aluminum alkyl bond at very high ethylene pressures. The "Nickeleffekt"[9] and the following explorations of the influence of other metals with regard to ethylene insertion led to the transition metal catalyzed ethylene polymerization.[10] We report here on a lanthanide-catalyzed version of the Aufbaureaktion.

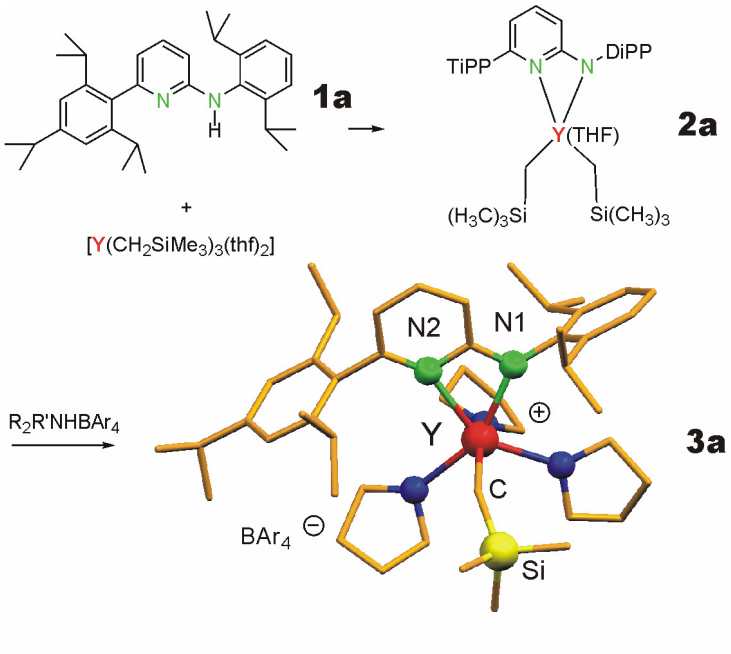
5.2. Results and Discussion

Synthesis and Structure of the Organoyttrium Cations

The reaction of the sterically demanding aminopyridine[11] **1a** (Scheme 1) with one equiv. [$Y(CH_2SiMe_3)_3(thf)_2$] (Me = methyl, thf = tetrahydrofuran) leads to the dialkyl **2a** in good yield (Scheme 2). The ^1H and ^{13}C NMR signals of the CH_2 group of the two alkyl ligands show coupling constants of $^2J(^{89}Y,^1H)$ = 3 Hz or $^1J(^{89}Y,^{13}C)$ = 39.7 Hz, as well as $^2J(^{29}Si,^1H)$ = 8.3 Hz or $^1J(^{29}Si,^{13}C)$ = 46.5 Hz. The ^{29}Si NMR spectrum of **2a** shows a doublet at - 4.3 ppm with a coupling constant $^2J(^{89}Y,^{29}Si)$ of 1.9 Hz. The reaction of **2a** with ammonium borates leads selectively and quantitatively to an elimination of one of the two alkyl ligands. The organoyttrium cation **3a** which was obtained in the presence of THF by using the anilinum borate $[C_6H_5NH(CH_3)_2]^+[B(C_6H_5)_4]^-$ was characterized by X-ray crystal structure analysis. The molecular structure is shown in (Scheme 2). Crystallographic details are summarized in Table.



Scheme 1. Synthesis of sterically demanding aminopyridines **1a** - **1c**.



Scheme 2. Synthesis of **2a** and **3a** and molecular structure of the cation of **3a** [TiPP = 2,4,6-tri(*iso*-propyl)phenyl, DiPP = 2,6-di(*iso*-propyl)phenyl, R = CH_3, R' = C_6H_5, Ar = C_6H_5]. Two independent cations per asymmetric unit were found; selected bond lengths [Å] and

angles [°]: Y–N1 2.302(3), Y–N2 2.421(3), Y–C 2.382(4), N1–Y–N2 57.41(11) Y–C–Si 143.8 (2). The compounds **2b** and **2c** as well as **3b** and **3c** are synthesized analogously to **2a** and **3a** using **1b** and **1c**, respectively, (Scheme 1) instead of **1a**.

Table 1. Details of the X-ray crystal structure analyses of **3a**, **3c** and **4**.

Compound	**3a**	**3c**	**4**
crystal system	triclinic	triclinic	triclinic
space group	P-1	P-1	P-1
a [Å]	13.258(2)	11.8440(6)	9.201(1)
b [Å]	20.221(3)	14.7060(7)	10.786(1)
c [Å]	27.745(4)	18.8650(10)	20.025(2)
α [°]	71.180(2)	76.945(4)	99.345(2)
β [°]	80.953(2)	84.642(4)	101.742(2)
γ [°]	86.622(2)	84.478(4)	93.622(2)
V, [Å^3]	6952.6(18)	3177.4(3)	1910.4(3)
crystal size, [mm^3]	0.5 x 0.4 x 0.2	0.6 x 0.5 x 0.3	0.4 x 0.3 x 0.1
ρ_{calcd}, [g cm^{-3}]	1.156	1.176	1.038
μ, [cm^{-1}] (Mo Kα)	9.02	9.82	0.80
T, [K]	100(1)	193(1)	100(1)
θ range, [°]	2.39-29.15	1.43-25.75	2.29-28.08
reflections unique	27688	11992	6856
refl. obs. [I > 2σ (I)]	17070	9619	4253
no. of parameters	1523	694	402
wR^2 (all data)	0.1887	0.1609	0.1297
R value [I>2σ (I)]	0.0636	0.0681	0.0597

The mean Y–C bond length [2.382(4) Å] of **3a** is slightly shorter than the expected value of a Y–C bond of a -$CH_2Si(CH_3)_3$ ligand (2.401 Å),[12] and goes along with an expected shortening due to the cationic nature of the yttrium center. The mean Y–C–Si angle [143.8(2)°] of **3a** is around 10° larger than the mean observed value of these ligands (134.3°).[13] NMR investigations of the organoyttrium cation **3a** revealed similar coupling patterns as for **2a**. Furthermore a good thermal stability of **3a** was observed via NMR spectroscopy. Over a period of several days at room temperature no decomposition was detected.

Analogue to the synthesis of **2a** reaction of **1b** or **1c** (Scheme 1) with $[Y(CH_2SiMe_3)_3(thf)_2]$ led to the corresponding dialkyls **2b** and **2c**, respectively. Almost quantitative yields are observed via NMR spectroscopy. These dialkyls form organoyttrium cations in the presence of ammonium borates. The reaction of **2b** and **2c** with $\{[PhNMe_2H][B(C_6H_5)_4]\}$ gave rise to **3b** and **3c**, respectively (Scheme 1 and Scheme 2). X-ray crystal structure analysis of **3c** was determined (Figure 1). Crystallographic details are listed in Table.

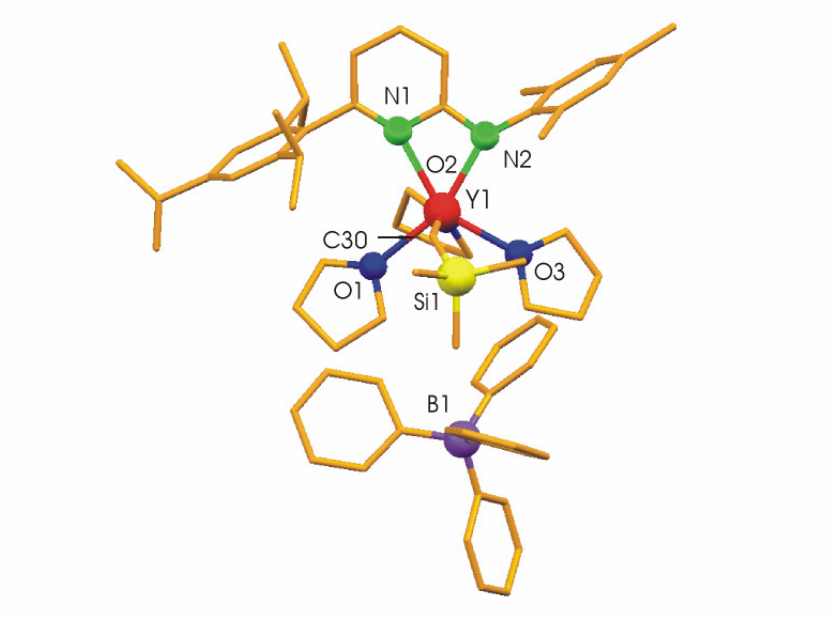


Figure1. Molecular structure of **3c**. Selected bond parameters lenghts [Å] and angles [°]: C30–Y1 2.376(4), N1–Y1 2.427(3), N2–Y1 2.273(3), Y1–O3 2.322(3), Y1–O2 2.374(3), Y1–O1 2.361(3), O2–Y1–C30 159.34(13), O3–Y1–O1 109.88(10), N2–Y1–N1 57.81(10).

In analogy to the trialkyl yttrium $[Y(CH_2SiMe_3)_3(thf)_2]$, the aluminum trialkyl $\{Al[CH_2CH(CH_3)_2]_3\}$ reacts almost quantitatively with one equiv. of **1a** to give rise to the aminopyridinato ligand stabilized aluminum dialkyl **4**. X-ray crystal structure analysis of **4** was determined (Figure 2). Crystallographic details are listed in Table.

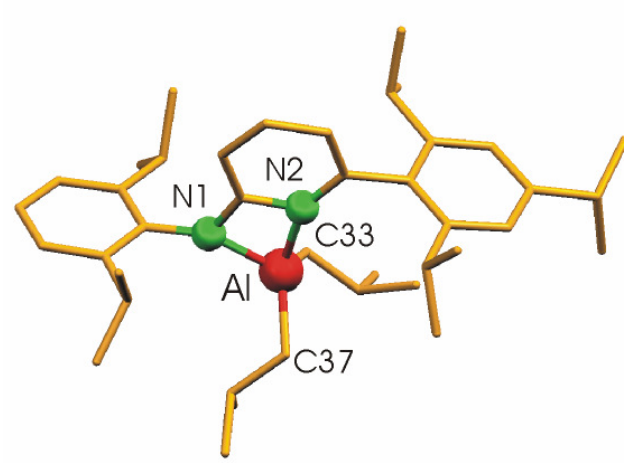


Figure 2. Molecular structure of **4**. Selected bond parameters lenghts [Å] and angles [°]: Al–N1 1.935(2), Al–N2 1.991(2), Al–C33 1.965(3), Al–C37 1.963(3), N1–Al–N2 68.77(8), C33–Al–C37 120.34(12).

Organoyttrium Catalyzed Ethylene Polymerization – Dependence of the Activity on the Steric Bulk of the Aminopyridinato Ligand:

The Ap-ligand-stabilized (Ap = aminopyridinato) organoyttrium cations can polymerize ethylene with a very high activity[14] in the presence of small amounts of aluminum alkyls (Table, first entry). The presence of aluminum alkyl is essential to observe polymerization activity (Table, entry 1). The efficient steric shielding of the metal centre and/or the Y–N bonds seems to be important to observe the very high activities.

Table 2. Ethylene polymerization activity - dependence of the steric bulk of the Ap ligand.[a]

Entry	**ligand**	$\mathbf{m_{Pol.}}$	**activity**	$\mathbf{M_w}$	$\mathbf{M_w/M_n}$
		[g]	$[kg_{PE}mol_{Kat}^{-1}h^{-1}bar^{-1}]$	$[gmol^{-1}]$	
1	**1a**	13.4	1072	66500[b]	3.2
2	**1b**	5.0	400	46100[b] (10800[c])	4.3 (1.5)
3	**1c**	5.4	432	263900[b] (16300[c])	28.8 (2.4)

[a] Conditions: Dialkyl (**2a**-**c**): 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, aluminum alkyl: TIBAO (tetra-*iso*-butyl alumoxane), Y/Al = 1/20, 260 ml toluene, temperature: 80 °C, pressure: 5 bar, time: 15 min. [b] Bimodal. [c] M_w of the main fraction (>90%).

The reduction of the steric demand of the Ap ligand [**1b** compared to **1a** for instance (Scheme 1) 2,6-dimethyl-phenyl instead of 2,4,6-triisopropylphenyl substituents at the pyridine ring of

the Ap ligand] goes along with a decrease of the ethylene polymerization activity by about 60%. The same behaviour was found for the inversion of the substitution patterns of the sterically less demanding version [**1c** versus **1b**; 2,4,6-trimethyl-phenyl at the amido N-atom instead at the pyridine ring (Scheme 1)]. Coordination chemical studies show that less bulky aminopyridinato ligands like **1b** and **1c** have the tendency to form bis(aminopyridinato) complexes.[11b] We did not observe such species during the formation of the corresponding cations **3b** and **3c** but can not rule out completely that under catalytic conditions bis(aminopyridinato) complexes are formed via ligand redistribution and PE elimination. Such species can not catalyze chain growth any more since they no longer have a metal carbon bond to insert ethylene, and thus may contribute to the slightly decreased activity.

Temperature Dependence of the Organoyttrium Catalyzed Ethylene Polymerization :

Since the organoyttrium cations based on **1a** showed the highest ethylene polymerization activity we proceeded to explore these catalyst systems in more detail. An extremely unusual temperature dependence was observed (Table, Figure 3).

Table 3. Temperature dependence of the ethylene polymerization using organoyttrium cations based on **1a**.[a]

Entry	**T**	**$m_{pol.}$**	**activity**	**M_w**	**M_w/M_n**
	[°C]	[g]	[$kg_{PE}mol_{cat}^{-1}h^{-1}bar^{-1}$]	[$gmol^{-1}$]	
1	30	0.5	40	67900[b] (1950)[c]	43.0 (1.3)
2	50	2.5	200	76400[d]	19.1
3	80	13.4	1072	66500[d]	3.2
4	100	10.1	808	15600	1.4

[a] Conditions: **2a**: 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, aluminum alkyl: TIBAO, Y/Al = 1/20, 260 ml toluene, pressure: 5 bar, time: 15 min. [b] Contains a small amount of high molecular PE. [c] M_w of the main fraction (>95%). [d] Bimodal distribution.

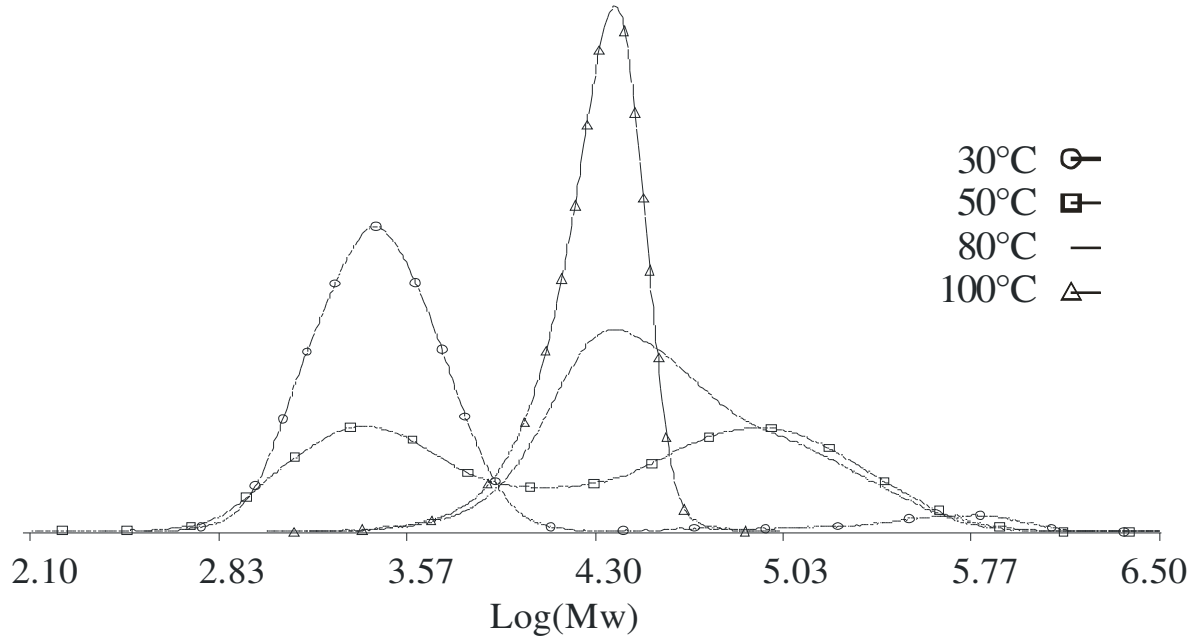
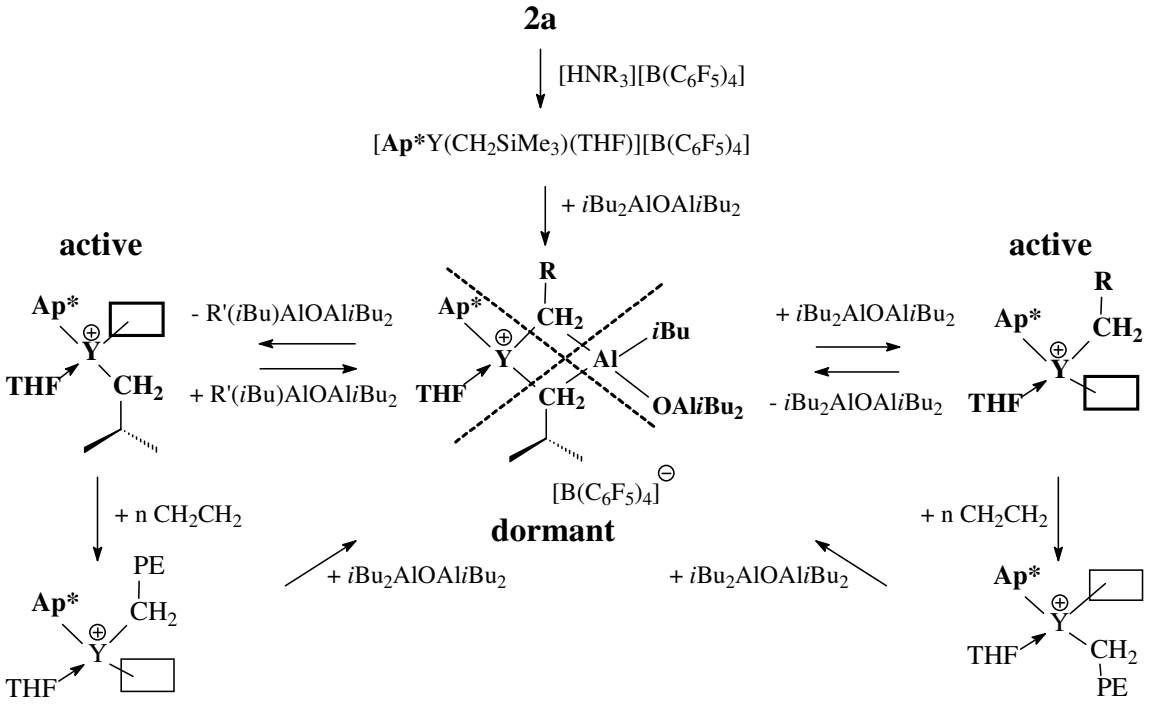


Figure 3. Molecular weight distribution (SEC) of the polymerization experiments listed inTable 3.

At 30 °C a mainly monomodal distribution with a relatively low molecular weight was observed. At 50 °C a polymer with a bimodal distribution is observed. One of the distributions shows a molecular weight similar to the main fraction of the 30 °C run and the second a significant higher M_w. At 80 °C an overlapping bimodal distribution can bee seen with again an increase of the mean molecular weight with increasing temperature. At 100 °C the polymerization under the given conditions (Table 3) produces again a monomodal distribution.



Scheme 3. Proposed mechanism for the organoyttrium cation catalyzed ethylene polymerization.

The overall trend from 30 to 80 °C is an unusual increase in activity together with an increase in the molecular weight. These observations could be explained by a reversible chain transfer[3] between the organoyttrium cation–responsible for chain growth–and the aluminum center–responsible for chain storage in combination with (partial) precipitation of the Al-terminated PE (Scheme 3). At 30 °C a relatively slow chain growing proceeds (blocking of the active side by strongly bonded aluminum alkyls at low temperature) giving rise to a short, narrowly distributed and soluble Al terminated main fraction. At 50 and 80 °C chain growth proceeds much faster, and since the same number of chains is grown, longer chains that precipitate are produced. Substantial amounts of precipitated polymer were observed at 50 and 80 °C with only traces for the 30 °C run. After precipitation, two fractions are observed (bimodal distribution) the fraction still soluble under the applied condition and the precipitated fraction; the fraction that most likely continues to grow. The improved solubility at 80 °C in comparison to 50 °C leads to overlapping bimodal distribution at this temperature and to a monomodal distribution at 100 °C (Figure 3). NMR spectroscopy of the obtained polymers (after hydrolytic workup) revealed that saturated polymers with *iso*-propyl end groups are observed (Figure 4). Even at 100 °C nearly no *β*-H elimination takes place indicating that chain transfer is much faster than *β*-H elimination. Raising the aluminum to

yttrium ratio (Table 4) goes along with an increase of the intensity of the end group proton NMR signal in comparison to the PE signal (Figure 5). The PE signal also becomes very narrow indicating a very narrow molecular weight distribution if the appropriate aluminum to yttrium ratio is used.

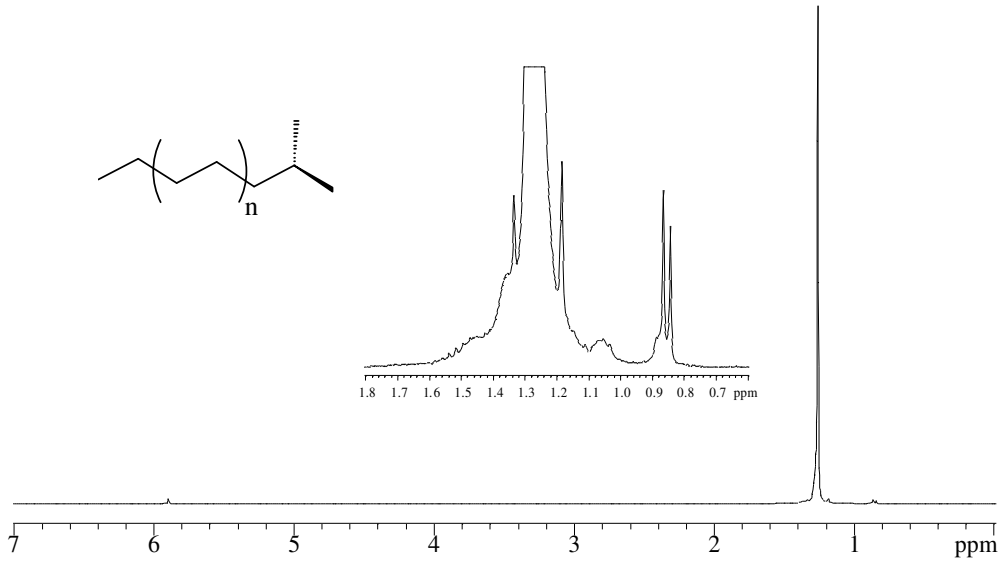


Figure 4. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of *iso*-propyl terminated PE (Table 3, entry 4)

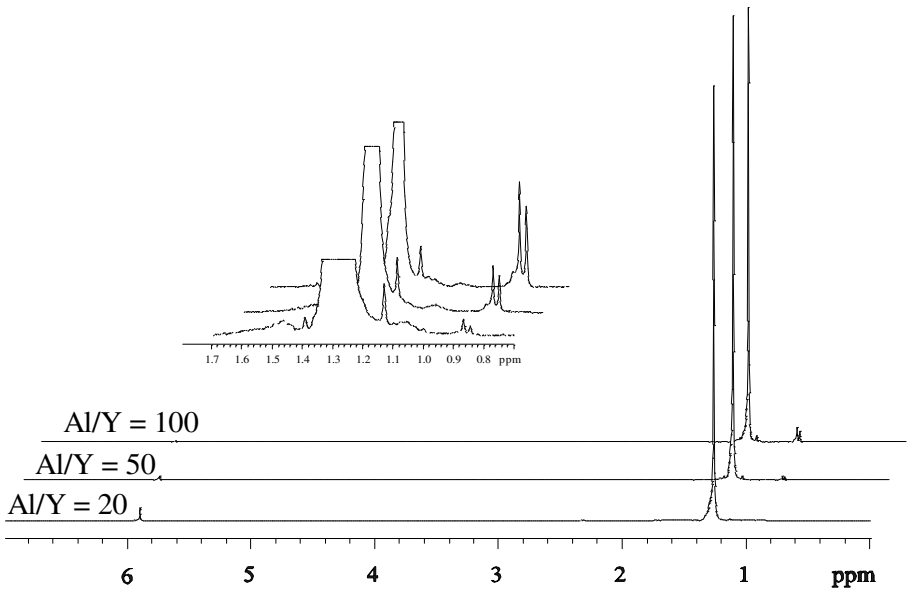
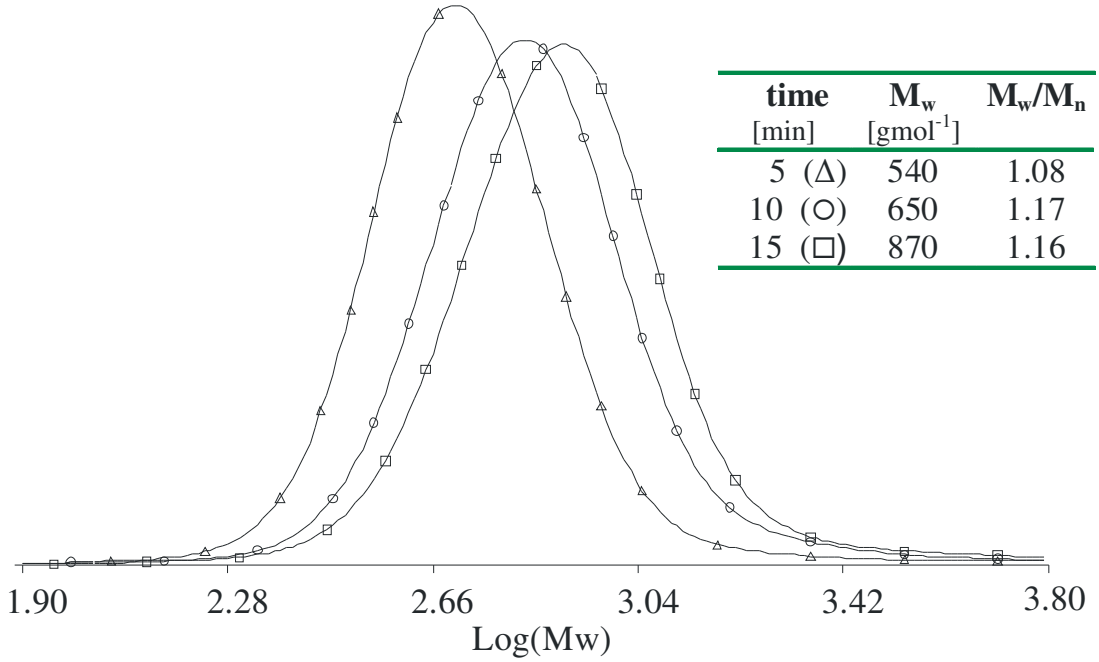


Figure 5. ^{1}H NMR spectra ($C_2D_2Cl_4$, 120 °C) of PE produced by polymerization runs (Table 4)

Time Dependence of the Chain Growth:

In the organoyttrium cation catalyzed ethylene polymerization between two major periods can be distinguished. In the first, the "homogeneous" period slow continuous ethylene

consumption together with an increase of the molecular weight but without significant broadening[15] of the distribution can be observed (Figure 6).



time [min]	M_w [gmol^{-1}]	M_w/M_n
5 (Δ)	540	1.08
10 (○)	650	1.17
15 (□)	870	1.16

Figure 6. Time-dependent increase of the molecular weight of the polymers (SEC). **2a**: 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, aluminum alkyl: TIBAO, Y/Al = 1/150, 260 mL toluene, pressure: 5 bar.

With ongoing chain growth partial polymer precipitation occurs together with a strong increase in ethylene uptake, second "heterogeneous" period. In Figure 7 the molecular weight distribution before, at and after the precipitation point is shown. It can be seen that polymerization continues up to the precipitation point without significant broadening of the molecular weight. Behind the precipitation point a bimodal distribution is observed. It seems - as mentioned above – that only the precipitated chain grows, while the molecular weight of the lower M_n fraction is nearly not raised with increasing time. This indicates that with reduced reversibility due to higher viscosity fast multiple ethylene insertion into the active organoyttrium species (Scheme 3) occurs, which then precipitates with an attached polymer chain and continues to grow heterogeneously.

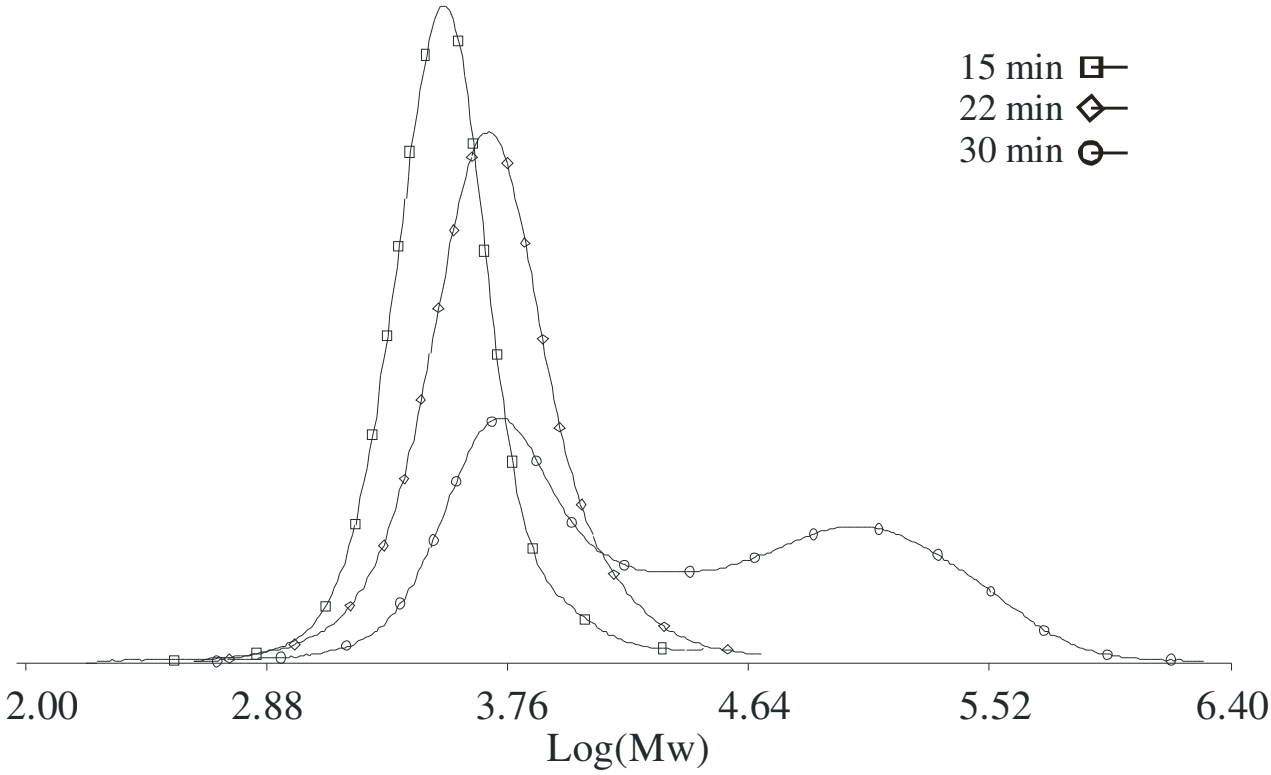


Figure 7. Influence of the polymer precipitation on the molecular weight distribution (SEC); before (15 min), at the beginning (22 min) and after (30 min) precipitation (Table 4, entries 4, 6 and 7).

Dependence of the Ethylene Polymerization from the used Aluminum Alkyl and the Aluminum-to-Yttrium Ratio

Reaction temperature, polymerization time and the aluminum to yttrium ratio can be tuned to ensure the Al terminated PE stays soluble during the polymerization process and allows for the synthesis of very narrowly distributed polymers (Table 4, entries 4 and 5, Figure 8). The stability of the organoyttrium cations in combination with nearly suppressed *β*-H elimination at even 100 °C allows for the synthesis of relatively long chain polymers having a polydispersity < 1.1. Increasing viscosity and precipitation of the Al terminated polymer chains results in a reduction of the reversibility of the chain transfer and thus broader polydispersities are observed.

Table 4. Ethylene polymerization catalyzed by **2a** as a function of the aluminum-to-yttrium ratio.[a]

Entry	**Al/Y**	**$m_{pol.}$**	**activity**	**M_w**	**M_w/M_n**
	[mol/mol]	[g]	[$kg_{PE}\ mol_{cat}^{-1}\ h^{-1}\ bar^{-1}$]	[$gmol^{-1}$]	
1	0	0	0	n.d.	n.d.
2	5	13.5	1080	88100	2.3
3	20	13.4	1072	66500[b]	3.2
4	50	4.7	376	3940	1.09
5	100	2.1	168	1460	1.05
6	50[c]	7.5	409	5920	1.4
7	50[d]	14.5	580	73900	7.7
8	100[d]	6.0	240	5830	1.3

[a] Conditions: **2a**: 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, aluminum alkyl: TIBAO, 260 mL toluene, pressure: 5 bar. [b] Bimodal. [c] 22 min run time. [d] 30 min run time.

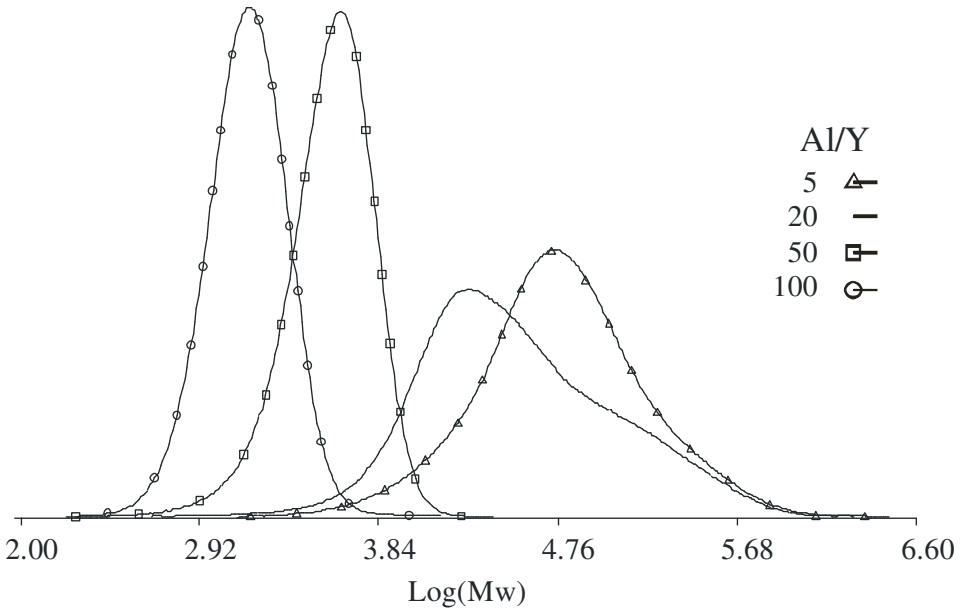


Figure 8. Molecular - weight distribution (SEC) of the polymerization experiments listed in Table 4 (entries 2-5).

The Mortreux system which allows working at elevated temperatures, shows mainly α-olefin side products at 100 °C.[3a] Transition metal based chain transfer catalyst systems[5] are described to work at room temperature which restricts the production of long chain polymers most likely due to solubility problems. Molecular weights with a dispersity of around 1.1 up

to a M_w of about 1200 g/mol are described for these catalyst systems which correspond to about 43 ethylene insertions per growing chain.

Table 5. Ethylene polymerization catalyzed by **2a**:influence of the aluminum alkyl.[a]

Entry	**Al-alkyl**	**Al:Y**	$\mathbf{m_{pol.}}$	**activity**	$\mathbf{M_w}$	$\mathbf{M_w/M_n}$
		[mol/mol]	[g]	[$kg_{PE}\ mol_{Kat}^{-1} h^{-1} bar^{-1}$]	[$g\ mol^{-1}$]	
1	TOA	100	0.5	40	n.d.	n.d.
2	TIBA	100	0.9	80	n.d.	n.d.
3	TIBA[b]	100	4.3	129	2660	1.2
4	TOAO	100	1.9	152	2580	1.1
5	TIBAO	100	2.1	168	1460	1.05
6	TPPAO	5	4.6	368	111000	2.1
7	TPPAO	50	1.9	152	2770	1.2

[a] Conditions: **2a**: 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, pressure: 5 bar, time: 15 min. [b] 100 °C, 10 bar, 20 min.

As shown in Table the organoyttrium cation catalyzed chain growth on aluminum is not limited to TIBAO, but can be carried out with a wide variety of aluminum alkyls. However the use of partially hydrolyzed Al-alkyls seems to have a strong beneficial effect on the ethylene polymerization activity. This behaviour can best be explained by the stronger coordination of the aluminum trialkyls at the organoyttrium cation,[1,2] compared to the less electron rich aluminoxanes. This results in a shifting of the equilibrium between "free" organoyttrium, able to insert ethylene, and the yttrium-aluminum complex responsible chain transfer (Scheme 3). Aluminum cations stabilized by aminopyridinato ligands are nearly inactive in ethylene polymerization. The activation of **4** using ammonium borates (10 µmol, ammonium borate: $[R_2N(CH_3)H]^+[B(C_6F_5)_4]^-$ (R = $C_{16}H_{31}$–$C_{18}H_{35}$), Al/B = 1/1.1, aluminum alkyl: TIBAO, Al/Al = 1/20, 260 mL toluene, pressure: 5 bar, 15 min) under the same conditions applied for **2a** (Table, entry 3) results in an activity of 8 $kg_{PE}\ mol_{Cat}^{-1}\ h^{-1}\ bar^{-1}$. In other words the yttrium free catalyst system is not able to accomplish the chain growth that leads to polymeric materials described above. By varying the substituents at the aluminum alkyl, and the workup, alcohol derivatives are accessible for instance (Figure 9-Figure 11).

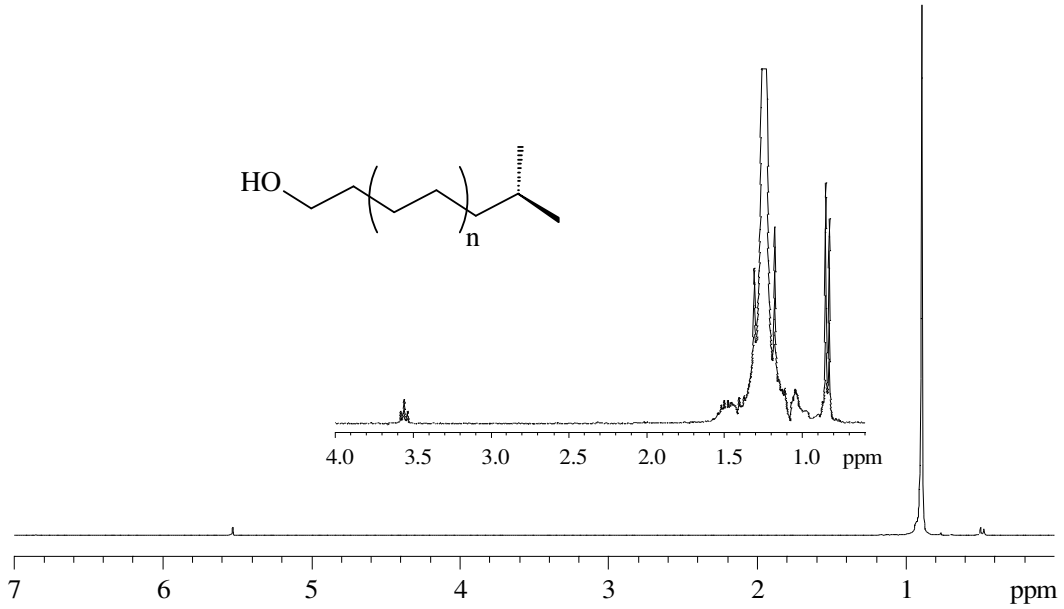


Figure 9. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE after oxidative workup (Table 4, entry 6).

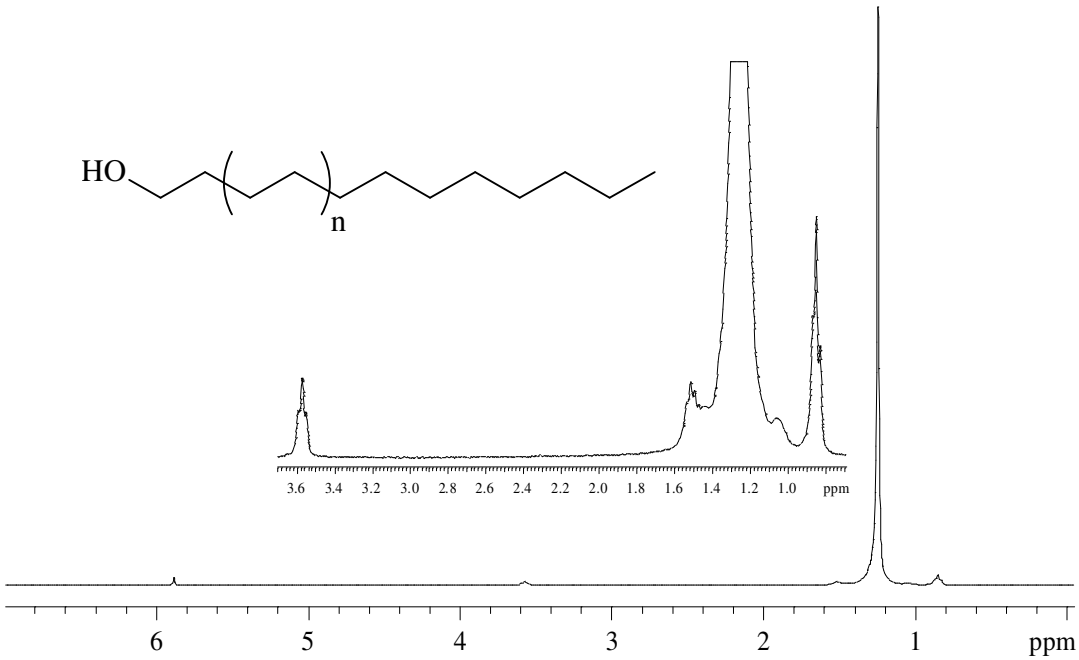


Figure 10. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE after oxidative workup (Table 5, entry 4).

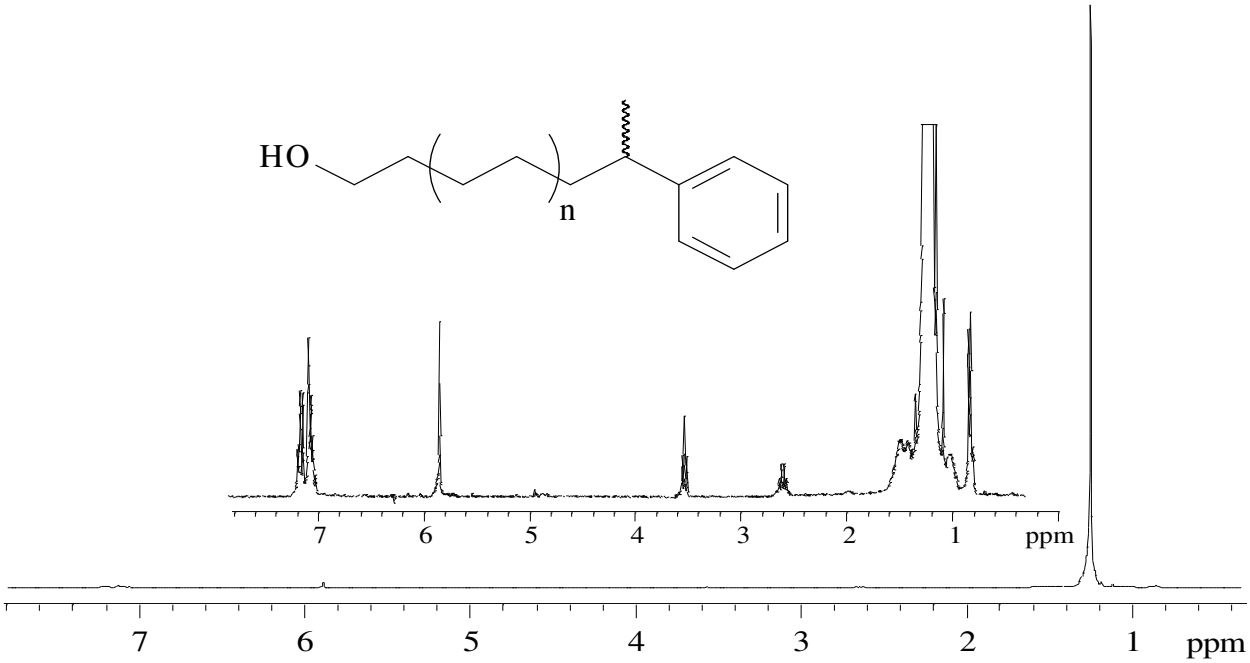


Figure 11. ^{1}H NMR spectrum ($C_2D_2Cl_4$, 120 °C) of PE after oxidative workup (Table 5, entry 6).

5.3. Conclusions

Aminopyridinato ligand stabilized organoyttrium cations can show a very high ethylene polymerization activity in the presence of small amounts of aluminum alkyl compounds (trialkyls and aluminoxanes) at elevated temperature. A reversible polyethylene chain transfer between the organoyttrium cations and the aluminum compounds is observed. Since *β*-H elimination is nearly suppressed even at 100 °C relatively high molecular weight Al-terminated polymer chains with a very narrow polydispersity can be produced.

5.4. Experimental Section

General Considerations

All manipulations of air-or moisture-sensitive compounds were carried out under N_2 using glove-box, standard Schlenk or vacuum line techniques. Solvents and reagents were purified by distillation from $LiAlH_4$, potassium, Na/K alloy or sodium ketyl of benzophenone under nitrogen immediately before use. Toluene (Aldrich, anhydrous, 99.8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å). Ethylene (AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scavenger and molecular sieves (Aldrich, 4Å).

NMR spectra were recorded on a Varian Gemini 400 (^{1}H: 400 MHz, ^{13}C: 100.5 MHz) or Varian VXR-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz) spectrometer. The ^{1}H and ^{13}C NMR spectra, measured at 25 °C and 120 °C, were referenced internally using the residual solvent resonances, and the chemical shifts are (δ) reported in ppm. The polymer samples were prepared by dissolving 15 mg of the polymer in 0.5 mL CD_2Cl_2 at 100 °C for 3 h before measuring.

Gel permeation chromatography (GPC) analysis was carried out on a Polymer Laboratories Ltd. (PL-GPC210) 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) and polystyrene (M_w = 100000 – 500000 g/mol) standards. The reported values are the average of at least two independent determinations.

Ligand and Complex Synthesis:

N,N-Dimethylanilinium(tetrapentafluorophenyl)borate ([$PhNMe_2H$][$B(C_6F_5)_4$], Strem), N,N,N-trialkylammonium(tetrapentafluorophenyl)borate ([R_2NMeH][$B(C_6F_5)_4$], R = $C_{16}H_{31}$ – $C_{18}H_{35}$, 6.2 wt-% $B(C_6F_5)_4^-$ in Isopar, DOW Chemicals), trimethyl aluminum (TMA, 2.0 M in toluene, Aldrich), tri-*iso*-butyl aluminum (TIBA, 25 wt-% in toluene, Aldrich), tri-*n*-octyl aluminum (TOA, 25 wt-% in toluene, Aldrich) and TIBA (Witco) were used as received.

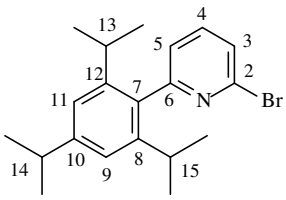
[$Y(CH_2SiMe_3)_3(thf)_2$],[16] N,N-dimethylanilinium(tetraphenyl)borate ([$C_6H_5NH(CH_3)_2$] [$B(C_6H_5)_4$]),[17] tetra-*iso*-butyl aluminoxane ([*i*-$Bu_2Al]_2O$, TIBAO),[18] tetra-*n*-octyl aluminoxane ([$Oct_2Al]_2O$, TOAO),[18] tetra-(2-phenyl-)propyl aluminoxane ([$CH_3CH(Ph)CH_2]_2Al\}_2O$, TPPAO),[18] **1a** and **1b**[11a] were prepared according to published procedure.

Preparation of 1-MgBr-[2,4,6-(*i*-Pr)$_3$C$_6$H$_2$]:

Magnesium turnings (0.94 g, 38.7 mmol) were added to 1-Br-[2,4,6-(*i*-Pr)$_3$C$_6$H$_2$] (35.2 mmol, 9.97 g) in THF (30 mL) and activated using 1,2-dibromoethane. When the resulting suspension was stirred, an exothermic reaction took place and an ice bath was used to cool the mixture if it became too vigorous. After 2 h the reaction mixture was cooled, stirred overnight, filtered and the filtrate directly used in the preparation of **B**.

Preparation of B:

2,6-Dibromopyridine (7.91 g, 33.4 mmol), THF (35 mL), tricyclohexylphosphine (0.075 mmol) and [(dme)$NiBr_2$] (0.012 g, 0.0375 mmol) were added together in a Schlenk flask under argon. The above described Grignard reagent was then added to the stirred suspension resulting in a beige precipitate. The reaction mixture was kept at 50 °C for 72 h. Water and $CHCl_3$ were added and the resulting suspension transferred to a separating funnel. The organic phase was collected and the residue extracted with $CHCl_3$ (2x). The combined organic phases were washed with a saturated NaCl solution and dried over Na_2SO_4. The solvent was removed to afford a white precipitate, which was recrystallized from hexane (20 mL) (7.05 g, yield 58%). M.p. 232-233 °C Elemental anal. for . $C_{20}H_{26}BrN$ (360.3): calcd. C 66.67, H 7.27, N 3.89; found C 67.56, H 7.48, N 3.78.

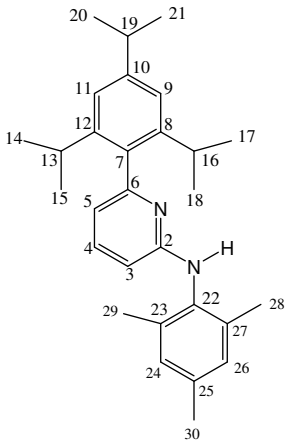


^{1}H NMR (250.13 MHz, $CDCl_3$, 298K): δ = 1.00-1.30 (m, 18H, CH_3), 2.44 (sept, 2H, $H^{13,15}$), 2.88 (sept, 1H, H^{14}), 7.02 (s, 2H, $H^{9,11}$), 7.21 (d, ^3J = 7.4 Hz, 1H, H^5), 7.43 (d, ^3J = 8.0 Hz, 1H, H^3), 7.59 (dd, ^3J = 8.0 Hz, ^3J = 7.4 Hz, 1H, H^4) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 298K): δ = 23.8 (s, CH_3), 24.1 (s, CH_3), 24.2 (s, CH_3), 30.4 (s, $C^{13,15}$), 34.4 (s, C^{14}), 120.8 (s, $C^{9,11}$), 123.9 (s, $C^{3,5}$), 125.9 (s, $C^{3,5}$), 134.9 (s, C^7), 137.9 (s, C^4), 141.5 (s,C^2), 146.1 (s, $C^{8,12}$), 149.3 (s, C^{10}), 161.3 (s, C^6) ppm.

Preparation of 1c:

B (2.75 g, 7.63 mmol), 1,3-bis(diphenyl-phosphino)propane (0.12 g, 0.28 mmol), tris(dibenzylideneacetone) dipalladium(0) (0.13 g, 0.14 mmol) and sodium *tert*-butoxide (0.83 g, 8.6 mmol) were loaded into a Schlenk tube. After adding 2,4,6-trimethyl-phenyl-amine (1.03 g, 7.63 mmol) in toluene (30 mL) the resulting mixture was heated at ~95 °C for 24 h. The reaction mixture was cooled to room temperature, and subsequently water (50 mL) and diethyl ether (50 mL) were added. The organic phase was separated and the remaining residue extracted with diethyl ether (3 x 20 mL). The combined organic phases were washed with a saturated NaCl solution and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting red solid was purified using column chromatography (SiO_2/CH_2Cl_2) Recrystallization at –30 °C from pentane or hexane afforded white crystalline materials. yield: 2.05 g (65%).

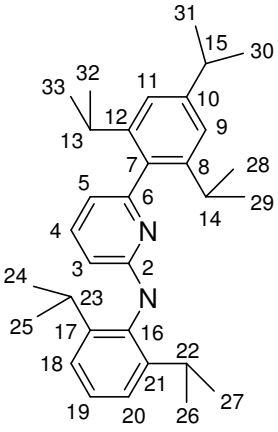
Elemental anal. for $C_{29}H_{38}N_2$ (M_w = 414.63 g/mol) C 84.01, H 9.24, N 6.76; found: C 84.10, H 9.35, N 6.20%.



^{1}H NMR (250.13 MHz, $CDCl_3$, 298K): δ = 1.12 (d, ^{3}J = 6.9 Hz, 6H, $H^{14,15,17,18}$), 1.18 (d, ^{3}J = 6.9 Hz, 6H, $H^{14,15,17,18}$), 1.26 (d, ^{3}J = 7.0 Hz, 6H, $H^{20,21}$), 2.20 (s, 6H, $H^{28,29}$), 2.30 (s, 3H, H^{30}), 2.69 (sept, ^{3}J = 6.9 Hz, 2H, $H^{13,16}$), 2.91 (sept, ^{3}J = 7.0 Hz, 1H, H^{19}), 5.92 (dd, ^{3}J = 8.3 Hz, ^{4}J = 0.8 Hz, 1H, H^{3}), 5.97 (br, 1H, H^{NH}), 6.61 (dd, ^{3}J = 7.2 Hz, ^{4}J = 0.8 Hz, 1H, H^{5}), 6.95 (s, 2H, $H^{9,11/24,26}$), 7.05 (s, 2H, $H^{9,11/24,26}$), 7.37 (dd, ^{3}J = 8.3 Hz, ^{3}J = 7.2 Hz, 1H, H^{4}) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$, 298K): δ = 18.2 (s, $C^{28,29}$), 20.9 (s, C^{30}), 24.0 (s, $C^{14,15/17,18/20,21}$), 24.1 (s, $C^{14,15/17,18/20,21}$), 24.5 (s, $C^{14,15/17,18/20,21}$), 30.3 (s, $C^{13,16}$), 34.5 (s, C^{19}), 103.1 (s, C^{3}), 114.8 (s, C^{5}), 120.7 (s, $C^{9,11/24,26}$), 129.2 (s, $C^{9,11/24,26}$), 134.3 (s, C^{7}), 136.3 (s, C^{10}), 136.7 (s, $C^{8,12/27,29}$), 137.4 (s, C^{25}), 146.0 (s, $C^{8,12/27,29}$), 148.3 (s, C^{4}), 157.7 (s, C^{6}), 158.6 (s, C^{2}) ppm. (two signals seem to be isochronic)

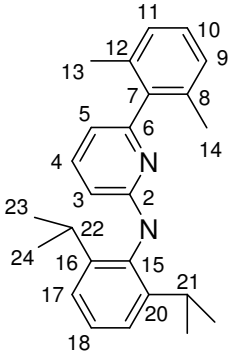
Synthesis of bis(trimethylsilylmethyl)-aminopyridinato-yttrium(tetrahydrofurane) complexes 2a – 2c:

0.1 mmol of the desired amino pyridine ligand Ap'H (**1a**, 45.6 mg; **1b**, 41.5 mg; **1c**, 33.0 mg; Scheme 1) was dissolved in toluene (2 mL) and slowly added to a ice cooled solution of $[Y(CH_2SiMe_3)_3(thf)_2]$ (49.5 mg, 0.1 mmol) in toluene (2 mL). After stirring for 30 min all volatile was removed, to yield the corresponding, spectroscopically pure $[Ap'Y(CH_2SiMe_3)_2(thf)]$ (based on ^{1}H NMR, **2a** – **2c**, Scheme 2) as pale yellow residue in almost quantitative yield.

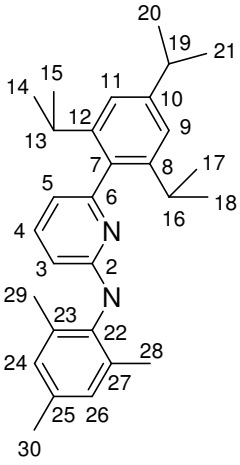


2a: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.42 (d, 4H, ^{2}J(Y,H) = 3.0 Hz, H^{YCH2}), 0.18 (s, 18H, H^{SiMe3}), 1.05 (br, 4H, β-CH_2, thf), 1.16 (d, 6H, ^{3}J(H,H) = 6.8 Hz, $H^{28,29,32,33}$), 1.18 (d, 6H, ^{3}J(H,H) = 6.8 Hz, $H^{30,31}$), 1.24 (d, 6H, ^{3}J(H,H) = 6.8 Hz, $H^{24,25,26,27}$), 1.32 (d, 6H, ^{3}J(H,H) = 6.8 Hz, $H^{24,25,26,27}$), 1.56 (d, 6H, ^{3}J(H,H) = 6.8 Hz, $H^{28,29,32,33}$), 2.88 (sept, 1H, ^{3}J(H,H) = 6.8 Hz, H^{15}), 3.11 (sept, 2H, ^{3}J(H,H) = 6.8 Hz, $H^{13,14}$), 3.42 (sept, 2H, ^{3}J(H,H) = 6.8 Hz, $H^{22,23}$), 3.60 (br, 4H, α-CH_2, thf), 5.65 (d, 1H, ^{3}J(H,H) = 8.4 Hz, H^{3}), 6.09 (d, 1H, ^{3}J(H,H) = 7.2 Hz, H^{5}), 6.75 (dd, 1H, ^{3}J(H,H) = 8.4 Hz, ^{3}J(H,H) = 7.2 Hz, H^{4}), 7.10 (m, 2H, $H^{18,20}$), 7.16 (m, 1H, H^{19}), 7.25 (m, 2H, $H^{9,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.1 (s, C^{SiMe3}), 23.6 (s, $C^{28,29,32,33}$), 24.3 (s, $C^{24,25,26,27}$), 24.4 (s, $C^{28,29,32,33}$), 24.9 (s, $C^{24,25,26,27}$), 25.2 (s, β-CH$_2$, thf), 26.7 (s, $C^{30,31}$), 28.8 (s, $C^{22,23}$), 30.9 (s, $C^{13,14}$), 35.0 (s, C^{15}), 39.8 (d, ^{1}J(Y,C) = 39.7 Hz, ^{1}J(Si,C) = 46.5 Hz, C^{YCH2}), 69.2 (s, α-CH$_2$, thf), 106.7 (d, ^{3}J(Y,C) = 1.6 Hz, C^{3}), 111.2 (s,

C^5), 121.2 (s, $C^{9,11}$), 124.2 (s, $C^{18,20}$), 124.9 (s, C^{19}), 136.0 (s, C^7), 139.4 (s, C^4), 144.0 (s, $C^{17,21}$), 144.5 (d, ^2J(Y,C) = 0.9 Hz, C^{16}), 146.7 (s, $C^{8,12}$), 149.6 (s, C^{10}), 156.0 (d, ^2J(Y,C) = 1.0 Hz, C^6), 169.6 (d, ^2J(Y,C) = 2.6 Hz, C^2) ppm.



2b: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.46 (d, 4H, ^2J(Y,H) = 3.3 Hz, H^{YCH2}), 0.21 (s, 18H, H^{SiMe3}), 1.16 (br, 4H, β-CH_2, thf), 1.18 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{22,23,25,26}$), 1.22 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{22,23,25,26}$), 2.36 (s, 6H, $H^{13,14}$), 3.39 (sept, 2H, ^3J(H,H) = 7 Hz, $H^{21,24}$), 3.70 (br, 4H, α-CH_2, thf), 5.59 (d, 1H, ^3J(H,H) = 8.4 Hz, H^3), 5.81 (d, 1H, ^3J(H,H) = 6.6 Hz, H^5), 6.79 (dd, 1H, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.6 Hz, H^4), 7.08 (m, 2H, $H^{17,19}$), 7.15 (m, 2H, $H^{10,18}$), 7.18 (m, 2H, $H^{9,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.2 (s, C^{SiMe3}), 20.7 (s, $C^{13,14}$), 24.3 (s, $C^{22,23,25,26}$), 24.8 (s, $C^{22,23,25,26}$), 25.3 (s, β-CH_2, thf), 28.7 (s, $C^{21,24}$), 39.2 (d, ^1J(Y,C) = 39.2 Hz, C^{YCH2}), 69.4 (s, α-CH_2, thf), 106.1 (s, C^3), 108.3 (s, C^5), 121.1 (s, $C^{17,19}$), 124.9 (s, C^{18}), 128.1 (s, $C^{9,11}$), 128.7 (s, C^{10}), 135.8 (s, C^7), 140.6 (s, C^4), 144.0 (s, $C^{16,20}$), 144.2 (s, C^{15}), 156.0 (s, C^6), 169.6 (s, C^2) ppm.

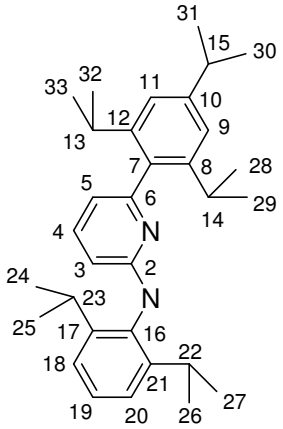


2c: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.41 (d, 4H, ^2J(Y,H) = 3.1 Hz, H^{YCH2}), 0.22 (s, 18H, H^{SiMe3}), 1.18 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{14,15,17,18}$), 1.24 (br, 4H, β-CH_2, thf), 1.32 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{14,15,17,18}$), 1.55 (d, 6H, ^3J(H,H) = 6.6 Hz, $H^{20,21}$), 2.22 (s, 3H, H^{30}), 2.25 (s, 6H, $H^{28,29}$), 2.89 (sept, 1H, ^3J(H,H) = 6.6 Hz, H^{19}), 3.12 (sept, 2H, ^3J(H,H) = 7.0 Hz, $H^{13,16}$), 3.61 (br, 4H, α-CH_2, thf), 5.70 (d, 1H, ^3J(H,H) = 8.4 Hz, H^3), 6.12 (d, 1H, ^3J(H,H) = 6.9 Hz, H^5), 6.84 (dd, 1H, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 6.9 Hz, H^4), 6.88 (s, 2H, $H^{24,26}$), 7.25 (s, 2H, $H^{9,11}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.2 (s, C^{SiMe3}), 19.1 (s, $C^{28,29}$), 20.9 (s, C^{30}), 23.6 (s, $C^{14,15,17,18}$), 24.4 (s, $C^{14,15,17,18}$), 25.2 (s, β-CH_2, thf), 26.7 (s, $C^{20,21}$), 30.9 (s, $C^{13,16}$), 35.0 (s, C^{19}), 39.8 (d, ^1J(Y,C) = 39.1 Hz, C^{YCH2}), 69.2 (s, α-CH_2, thf), 105.1 (s, C^3), 111.0 (s, C^5), 121.2 (s, $C^{9,11}$), 129.6 (s, $C^{24,26}$), 132.6 (s, C^{25}), 133.0 (s, $C^{23,27}$), 136.0 (s, C^7), 139.8 (s, C^4), 144.0 (s, C^{22}), 146.7 (s, $C^{8,12}$), 149.6 (s, C^{10}), 156.1 (d, C^6), 169.7 (s, C^2) ppm.

Synthesis of *3a:*

$[Y(CH_2SiMe_3)_3(thf)_2]$ (150 mg, 0.30 mmol) was dissolved in toluene (1 mL), before a solution of **1a** (1 mL, 0.3 M in toluene, 0.30 mmol) was added. After stirring the mixture for 5 min it was combined with a suspension of $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (134 mg, 0.30

mmol) in toluene/THF (1.5 mL, 60/40 mol-%), and repeatedly shaken until a clear solution was observed. The slightly yellow oil was layered with hexane (3.5 mL) and kept at RT overnight. After 12 h colorless crystals were obtained, which were decantated from the mother liquor and dried. Yield: 247 mg (68%) of **3a** · $(C_6H_{14})_{0,5}$. Elemental anal. for $[C_{48}H_{78}N_2O_3SiY][C_{24}H_{20}B](C_6H_{14})_{0.5}$ (M_w = 1210.47 g/mol) (calc.) found: C(74.42) 75.11, H(8.74) 8.53, N(2.31) 2.09, Y(7.34) 7.10%.

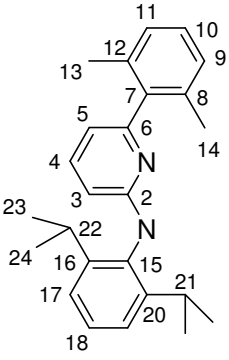


3a: ^{1}H NMR (400 MHz, THF-d_8, 298K): δ = -0.61 (d, 2H, ^2J(Y,H) = 3.0 Hz, H^{YCH2}), -0.18 (s, 9H, H^{SiMe3}), 1.03 (d, 12H, ^3J(H,H) = 7.0 Hz, $H^{28,29,30,31,32,33}$), 1.20 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{24,25,26,27}$), 1.27 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{24,25,26,27}$), 1.30 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{28,29,32,33}$), 1.73 (m, 12H, β-CH_2, thf), 2.82 (sept, 2H, ^3J(H,H) = 7.0 Hz, $H^{13,14}$), 2.93 (sept, 2H, ^3J(H,H) = 7.0 Hz, H^{15}), 3.22 (sept, 2H, ^3J(H,H) = 7.0 Hz, $H^{22,23}$), 3.57 (m, 12H, α-CH_2, thf), 5.74 (dd, 1H, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 0.7 Hz, H^3), 6.22 (dd, 1H, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 0.7 Hz, H^5), 6.66 (tt, 4H, ^3J(H,H) = 7.0 Hz, ^4J(H,H) = 1.4 Hz, H^{BC6H5}), 6.80 (m, 8H, ^3J(H,H) = 7.0 Hz, H^{BC6H5}), 7.12 – 7.22 (m, 13H; $H^{9,11,18,19,20/BC6H5}$), 7.25 (dd, 1H, ^{3}J(H,H) = 8.8 Hz, ^3J(H,H) = 7.0 Hz, H^4) ppm. ^{13}C NMR (100 MHz, THF-d_8, 298K): δ = 5.1 (s, C^{SiMe3}), 24.7 (s, $C^{28,29,32,33}$), 25.5 (s, $C^{24,25,26,27}$), 25.6 (s, $C^{30,31}$), 26.6 (s, $C^{24,25,26,27}$), 27.3 (br, β-CH$_2$, thf), 27.6 (s, $C^{28,29,32,33}$), 29.8 (s, $C^{22,23}$), 32.3 (s, $C^{13,14}$), 36.4 (s, C^{15}), 41.0 (d, ^2J(Y,C) = 42.9 Hz, C^{YCH2}), 69.2 (s, α-CH$_2$, thf), 110.1 (s, C^3), 114.6 (s, C^5), 122.9 (s,$C^{9,11}$), 123.1 (s, C^{BC6H5}), 126.3 (s, $C^{18,20}$), 126.7 (m, C^{BC6H5}), 127.2 (s, C^{19}), 137.2 (s, C^7), 138.1 (m, C^{BC6H5}), 141.4 (s, C^4), 144.8 (s, C^{16}), 145.5 (s, $C^{17,21}$), 148.7 (s, $C^{8,12}$), 152.3 (s, C^{10}), 156.4 (s, C^6), 166.2 (q, ^1J(C,B) = 49.0 Hz, C^{BC6H5}), 172.5 (s, C^2) ppm.

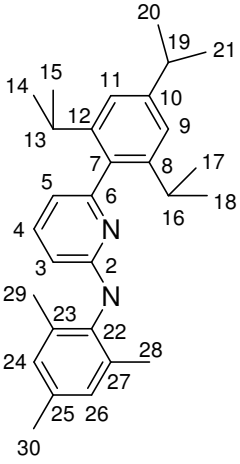
Synthesis of 3b and 3c:

$[Y(CH_2SiMe_3)_3(thf)_2]$ (55 mg, 0.11 mmol) was dissolved in benzene/THF (0.5 mL, 80/20 V-%), before a solution of **1b** or **1c** (0.5 mL, 0.22 M IN benzene, 0.11 mmol) was added. After stirring the mixture for 5 min it was combined with a suspension of $[C_6H_5NH(CH_3)_2][B(C_6H_5)_4]$ (49 mg, 0.11 mmol) in benzene/THF (0.5 mL, 80/20 V-%), and repeatedly shaken until a clear solution was observed. The slightly yellow oil was layered with hexane (3.5 mL) and kept at RT. After 3 days pale yellow crystals were observed, which were decantated from the mother liquor and dried. Yield: 75 mg (61%) of **3b**. Elemental anal. for $[C_{41}H_{64}N_2O_3SiY][C_{24}H_{20}B]$ (M_w = 1069.18 g/mol) (calc.)found: C(73.02) 72.92, H(7.92) 7.75, N(2.61) 2.35%. Yield: 95 mg (73%) of **3c**. Elemental anal. for

$[C_{45}H_{72}N_2O_3SiY][C_{24}H_{20}B]$ (Mw =1125,28 g/mol) (calc.)found: C(73.65) 73.89, H(8.24) 8.26, N(2.49) 2.27%.



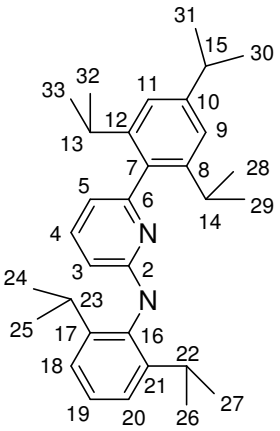
3b: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.61 (d, 2H, ^2J(Y,H) = 3.1 Hz, H^{YCH2}), 0.06 (s, 9H, H^{SiMe3}), 1.04 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{22,23,25,26}$), 1.19 (d, 6H, ^3J(H,H) = 6.6 Hz, $H^{22,23,25,26}$), 1.41 (br, β-CH_2, thf), 2.00 (s, 6H, $H^{13,14}$), 3.14 (sept, 2H, ^3J(H,H) = 6.6 Hz, $H^{21,24}$), 3.49 (br, α-CH_2, thf), 5.54 (d, 1H, ^3J(H,H) = 8.4 Hz, H^3), 5.67 (d, 1H, ^3J(H,H) = 7.0 Hz, H^5), 6.70 (dd, 1H, ^3J(H,H) = 8.4 Hz, ^3J(H,H) = 7.0 Hz, H^4), 6.90 (d, 2H, ^3J(H,H) = 7.7 Hz, $H^{9,11,17,19}$), 7.02 (t, 1H, ^3J(H,H) = 7.7 Hz, $H^{10,18}$), 7.12 – 7.25 (m, 15H; $H^{9,11,17\text{-}20,BC6H5}$), 7.89 (br, 8H, $H^{o\text{-}BC6H5}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.1 (s, C^{SiMe3}), 20.5 (s, $C^{13,14}$), 24.5 (s, $C^{22,23,25,26}$), 25.3 (s, $C^{22,23,25,26}$), 25.6 (s, β-CH_2, thf), 28.1 (s, $C^{21.24}$), 39.6 (d, ^1J(Y,C) = 43.7 Hz, C^{YCH2}), 68.8 (s, α-CH_2, thf), 107.9 (s, C^3), 110.1 (s, C^5), 122.2 (s, C^{BC6H5}), 124.1 (s, C^{18}), 124.8 (s, $C^{17,19}$), 126.0 (m, C^{BC6H5}), 129.2 (s, $C^{9,11}$), 136.0 (s, C^7), 137.1 (m, C^{BC6H5}), 139.6 (s, C), 140.3 (s, C), 140.6 (s, C^4), 142.5 (s, $C^{16,20}$), 143.8 (s, C^{15}), 154.7 (s, C^6), 165.0 (q, ^1J(C,B) = 49.9 Hz; C^{BC6H5}), 170.3 (s, C^2) ppm.



3c: ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.61 (d, 2H, ^2J(Y,H) = 3.0 Hz, H^{YCH2}), 0.08 (s, 9H, H^{SiMe3}), 1.04 (d, 6H, ^3J(H,H) = 6.6 Hz, $H^{14,15,17,18}$), 1.21 (d, 6H, ^3J(H,H) = 6.6 Hz, $H^{14,15,17,18}$), 1.22 (d, 6H, ^3J(H,H) = 6.6 Hz, $H^{20,21}$), 1.37 (br, β-CH_2, thf), 2.08 (s, 6H, $H^{28,29}$), 2.25 (s, 3H, H^{30}), 2.74 (sept, 1H, ^3J(H,H) = 6.6 Hz, H^{19}), 2.78 (sept, 2H, ^3J(H,H) = 6.6 Hz, $H^{13,16}$), 3.44 (br, α-CH_2, thf), 5.67 (d, 1H, ^3J(H,H) = 8.8 Hz, H^3), 6.00 (d, 1H, ^3J(H,H) = 6.9 Hz, H^5), 6.71 (dd, 1H, ^3J(H,H) = 8.8 Hz, ^3J(H,H) = 6.9 Hz, H^4), 6.90 (s, 2H, $H^{9,11,24.26}$), 7.06 (s, 2H, $H^{9,11,24.26}$), 7.12 – 7.28 (m, 12H; $H^{\cdot BC6H5}$), 7.91 (br, 8H, $H^{o\text{-}BC6H5}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 4.2 (s, C^{SiMe3}), 19.4 (s, $C^{28,29}$), 20.9 (s, C^{30}), 23.6 (s, $C^{14,15,17,18}$), 24.3 (s, $C^{14,15,17,18}$), 25.6 (s, β-CH_2, thf), 26.6 (s, $C^{20,21}$), 30.7 (s, $C^{13,16}$), 34.7 (s, C^{19}), 39.0 (d, ^1J(Y,C) = 43.7 Hz, C^{YCH2}), 69.1 (s, α-CH_2, thf), 106.7 (s, C^3), 112.2 (s, C^5), 121.3 (s, $C^{9,11}$), 122.3 (s, C^{BC6H5}), 126.1 (m, C^{BC6H5}), 130.2 (s, $C^{24,26}$), 132.6 (s, C^{25}), 134.0 (s, $C^{23,27}$), 135.4 (s, C^7), 137.1 (m, C^{BC6H5}), 140.1 (s, C^4), 142.1 (s, C^{22}), 147.2 (s, $C^{8,12}$), 150.7 (s, C^{10}), 154.7 (s, C^6), 165.0 (q, ^1J(C,B) = 49.1 Hz; C^{BC6H5}), 168.6 (d, ^2J(Y,C) = 2.3 Hz; C^2) ppm.

NMR tube reactions of 2a with $[PhNMe_2H][B(C_6F_5)_4]$ - formation of 3a:

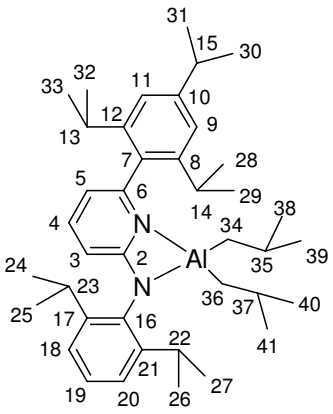
A NMR tube was charged with **2a** (16 mg, 20 µmol), THF (20 µL) and deutero-benzene (0.5 mL) together with $[PhNMe_2H][B(C_6F_5)_4]$ (16 mg, 20 µmol). Afterwards the tube was sealed and shaken for 5 min to become a clear solution before measurement.



3a': ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = -0.51 (d, ^2J(Y,H) = 3.1 Hz, 2H; H^{YCH2}), 0.0 (br, 18H; $H^{SiMe3,SiMe4}$), 1.01 (d, 6H, ^3J(H,H) = 6.2 Hz, $H^{28,29,30,31,32,33}$), 1.03 (d, 6H, ^3J(H,H) = 6.2 Hz, $H^{28,29,30,31,32,33}$), 1.20 (d, 6H, ^3J(H,H) = 7.0 Hz, $H^{28,29,32,33}$), 1.22 (d, 12H, ^3J(H,H) = 7.0 Hz, $H^{24,25,26,27}$), 1.42 (br, β-CH_2, thf), 2.52 (s, 6H, H^{NMe2}), 2.77 (sept, 3H, ^3J(H,H) = 7.0 Hz, $H^{13,14,15}$), 3.15 (sept, 2H, ^3J(H,H) = 7.0 Hz, $H^{22,23}$), 3.54 (br, α-CH_2, thf), 5.56 (d, 1H, ^3J(H,H) = 8.7 Hz, H^3), 5.99 (d, 1H, ^3J(H,H) = 7.3 Hz, H^5), 6.63 (d, 1H, ^3J(H,H) = 7.7 Hz, $H^{o\text{-}C6H5N}$), 6.64 (dd, 1H, ^3J(H,H) = 8.7 Hz, ^3J(H,H) = 7.3 Hz, H^4), 6.79 (m, 1H, $H^{p\text{-}C6H5N}$), 7.08 (s, 2H, $H^{9,11}$), 7.12–7.25 (m, 5H; $H^{18,19,20,\ C6H5N}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 0.0 (s, C^{SiMe4}), 3.9 (s, C^{SiMe3}), 23.2 (s, $C^{28,29,32,33}$), 24.1 (s, $C^{24,25,26,27}$), 24.3 (s, $C^{30,31}$), 25.3 (s, $C^{24,25,26,27}$), 25.6 (br, β-CH$_2$, thf), 26.3 (s, $C^{28,29,32,33}$), 28.2 (s, $C^{22,23}$), 30.7 (s, $C^{13,14}$), 34.7 (s, C^{15}), 40.2 (s, C^{NMe2}), 41.2 (d, ^2J(Y,C) = 42.9 Hz, C^{YCH2}), 68.8 (s, α-CH$_2$, thf), 108.5 (s, C^3), 112.7 (s, C^5), 113.0 (s, C^{NC6H5}), 117.0 (s, C^{NC6H5}), 121.4 (s, $C^{9,11}$), 124.9 (s, $C^{18,20}$), 126.2 (s) 129.3 (s, C^{NC6H5}), 135.1 (s, C^{19}), 135.8 (br, C^{BC6F5}), 137.7 (s, C^7), 138.2 (br, C^{BC6F5}), 139.8 (s, C^4), 142.5 (s, C^{16}), 143.7 (s, $C^{17,21}$), 147.1 (s, $C^{8,12}$), 147.9 (br, C^{BC6F5}), 150.2 (br, C^{BC6F5}), 151.1 (s, C^{10}), 154.5 (s, C^6), 170.5 (s, C^2) ppm. ^{19}F NMR (470 MHz, C_6D_6, 298 K): δ = -167.1 (t, ^3J(F,F) = 18.3 Hz, *m*-F), -163.1 (t, ^3J(F,F) = 21.8 Hz, *p*-F), -132.5 (br, *o*-F) ppm.

Synthesis of bis(alkyl)-aminopyridinato-aluminum complex 4:

A Schlenk vessel was charged with **1a** (45.6 mg, 0.1 mmol) and toluene (2 mL) before tri-*iso*-butyl-aluminum (TIBA, 25 wt-% in toluene, 1 mL, 0.1 mmol) was added. After stirring for 30 min all volatile was removed, to yield the corresponding, spectroscopic pure **4** as colorless oil in almost quantitative yield. For X-ray analysis of **4** the residue was dissolved in 3 mL hexane. Slow evaporation of the solvent over a period of 5 days leaves colorless crystals. Elemental anal. for $C_{40}H_{61}AlN_2$ (M_w = 596.92 g/mol) (calc.)found: C(80.49) 80.53, H(10.30) 10.41, N(4.69) 4.53%.



^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.47 (dd, 2H, ^{2}J(H,H) = 14.0 Hz, ^{3}J(H,H) = 7.9 Hz, H^{AlCH2}), 0.54 (dd, 2H, ^{2}J(H,H) = 14.0 Hz, ^{3}J(H,H) = 7.3 Hz, H^{AlCH2}), 0.91 (d, 6H, ^{3}J(H,H) = 6.6 Hz, H^{38-41}), 1.05 (d, 6H, ^{3}J(H,H) = 6.6 Hz, $H^{24-33,38-41}$), 1.06 (d, 6H, ^{3}J(H,H) = 6.6 Hz, $H^{24-33,38-41}$), 1.15 (d, 6H, ^{3}J(H,H) = 6.6 Hz, $H^{24-33,38-41}$), 1.21 (d, 6H, ^{3}J(H,H) = 7.0 Hz, $H^{24-33,38-41}$), 1.31 (d, 6H, ^{3}J(H,H) = 7.0 Hz, $H^{24-33,38-41}$), 1.41 (d, 6H, ^{3}J(H,H) = 7.0 Hz, $H^{24-33,38-41}$), 2.04 (m, 2H, ^{3}J(H,H) = 6.6 Hz, $H^{35,37}$), 2.80 (sept, 1H, ^{3}J(H,H) = 6.6 Hz, H^{15}), 2.90 (sept, 2H, ^{3}J(H,H) = 6.6 Hz, $H^{13,14}$), 3.55 (sept, 2H, ^{3}J(H,H) = 7.0 Hz, $H^{22,23}$), 5.62 (dd, 1H, ^{3}J(H,H) = 8.4 Hz, ^{4}J(H,H) = 0.9 Hz, H^{3}), 6.08 (dd, 1H, ^{3}J(H,H) = 7.3 Hz, ^{4}J(H,H) = 0.9 Hz, H^{5}), 6.80 (dd, 1H, ^{3}J(H,H) = 8.4 Hz, ^{3}J(H,H) = 7.3 Hz, H^{4}), 7.13 (br, 2H, $H^{18,20}$), 7.19 (br, 3H, $H^{9,11,19}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 22.2 (br, C^{AlCH2}), 22.8 ($C^{28,29,32,33}$), 24.2 ($C^{24,25,26,27}$), 24.6 ($C^{28,29,32,33}$), 24.9 ($C^{24,25,26,27}$), 26.4 ($C^{38,39,40,41}$), 26.5 ($C^{38,39,40,41}$), 27.8 ($C^{30,31}$), 28.4 ($C^{35,37}$), 28.7 ($C^{22,23}$), 30.8 ($C^{13,14}$), 34.9 (C^{15}), 104.9 (C^{3}), 111.5 (C^{5}), 121.0 ($C^{9,11}$), 124.4 ($C^{18,20}$), 126.3 (C^{19}), 138.3 (C^{7}), 139.4 (C^{4}), 141.0 ($C^{17,21}$), 145.7 (C^{16}), 146.8 ($C^{8,12}$), 150.2 (C^{10}), 154.7 (C^{6}), 167.3 (C^{2}) ppm.

Polymerization Studies:

General description of polymerization experiments: The catalytic ethylene polymerization reactions were performed in a stainless steel 1 L autoclave (Medimex) in semi-batch mode (ethylene was added by replenishing flow to keep the pressure constant). The reactor was temperature and pressure controlled and equipped with separated toluene, catalyst and cocatalyst injection systems and a sample outlet for continuous reaction monitoring. At 5 bar of ethylene pressure multiple injection of the catalyst with a pneumatically operated catalyst injection system was used. During a polymerization run the pressure, the ethylene flow, the inner and the outer reactor temperature and the stirrer speed were monitored continuously. In a typical semi-batch experiment, the autoclave was evacuated and heated for 1 h at 125 °C prior to use. The reactor was then brought to desired temperature, stirred at 600 rpm and charged with toluene (230 mL) together with trialkylammonium (tetrapentafluorophenyl)borate (11 μmol, 0.12 g) and the required amount of aluminum scavenger (1 mL of a 0.1 M stock solution). After pressurizing with ethylene to reach 5 bar total pressure the autoclave was equilibrated for 5 min. Subsequently aminopyridinato yttrium dialkyl complex (1 mL, 0.01 M stock solution in toluene) together with toluene (30 mL) was injected, to start the reaction. During the run the ethylene pressure was kept constant to within

0.2 bar of the initial pressure by replenishing flow. After the desired reaction time the reactor was vented and the residual aluminum alkyls were destroyed by addition of ethanol (100 mL). In the case of subsequent oxidation, the reactor was vented and stirred for 1 h at 80 °C under an atmosphere of dry air before ethanol (100 mL) was added. Polymeric product was collected, stirred for 30 min in acidified ethanol and rinsed with ethanol and acetone on a glass frit. The polymer was initially dried on air and subsequently in vacuum at 80 °C.

Synthesis of the catalyst stock solutions: The complexes **2a** – **2c** were prepared as described above. For catalytic ethylene conversion the pale yellow residues were dissolved in toluene (10 mL) and used without further purification.

X-ray crystal structure analysis

Data collection was accomplished using either a Bruker SMART APEX CCD or a Stoe IPDSII diffractometer equipped with a low temperature unit (λ(MoK$\overline{\alpha}$) = 0.71073 Å). Details of the X-ray crystal structure analyses are listed in Table. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-285279 (compound **3a**), CCDC-605499 (compound **3c**), CCDC-294801 (compound **4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; web: www.ccdc.cam.ac.uk/conts/retrieving.html.

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6. Small Steric Variations in Ligands with Large Synthetic and Structural Consequences

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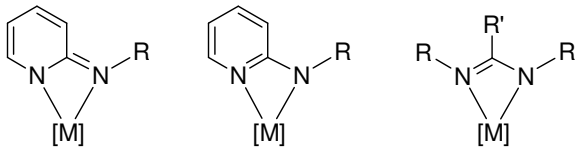
Abstract: The reaction of ytterbium metal with the aminopyridines 2,6-(diisopropylphenyl)-[6-(2,6-dimethylphenyl)pyridin-2-yl]amine (**1**, Ap`H) and (2,4,6-trimethylphenyl)-[6-(2,4,6-trimethylphenyl)pyridin-2-yl]amine (**2**, $Ap^{Me}H$) at elevated temperature under vacuum in the presence of mercury gave rise to divalent [Yb(Ap`)$_2$] (**3**) and trivalent [Yb(Ap^{Me})$_3$] (**4**), respectively. The single-crystal X-ray structure analysis of **3** revealed a four-coordinate ytterbium atom with two chelating (*N,N`*) Ap` ligands inclined to each other at an angle of 126.93(7)° (Cl–Yb–C26). Additionally the complex forms intermolecular C_{Aryl}–H agostic interactions [Yb1···C17 2.981(2) Å and Yb1···H17 2.56(3) Å] (all H atoms refined). Complex **4** contains a six-coordinate ytterbium atom having three chelating (*N,N`*) $Ap^{Me}$ ligands and has distorted octa-hedral stereochemistry. The reaction of the potassium salts of Ap`H (**5**) and $Ap^{Me}H$ (**6**) with [$YbI_2(thf)_4$] in THF gave rise to the divalent lanthanide complexes [Yb(Ap`)$_2$(thf)] (**7**), and [Yb($Ap^{Me}$)$_2$(thf)$_2$] (**8**), respectively, and **7** was also obtained by redox transmetallation/ligand exchange from Yb metal, $HgPh_2$ and Ap`H. X-ray crystal structures show that **7** and **8** have five- and six-coordinate ytterbium atoms and distorted trigonal-

bipyramidal and distorted octahedral stereochemistry, respectively, the difference in coordination number reflecting the difference in steric demand of the Ap` and Ap^{Me} ligands.

6.1. Introduction

Agostic bonding has been found to play a major role in the ligand reactivity of transition metal complexes, particularly in α-olefin polymerization.[1,2] The nature of the interaction was interpreted by Brookhart and Green in terms of a three-centre, two-electron bond between the C-H bond and a vacant d-orbital of the transition metal atom.[3,4] The presence of an agostic interaction is commonly indicated by the resulting geometric deformation of the agostic ligand, as shown by an elongation of the C-H bond, rather short M···H contacts, and a distortion of the ligand spatial arrangement.[5,6] Aminopyridinato ligands[7,8] are of interest due to the flexibility of their binding mode (amidopyridine vs. aminopyridinato form)[9] and the ligand "asymmetry". Such ligands (Scheme 1, left) are structurally related to amidinates[10] (Scheme 1, right).



Scheme 1: Aminopyridinate form (left), amidopyridine form (centre) and amidinate ligands (right)

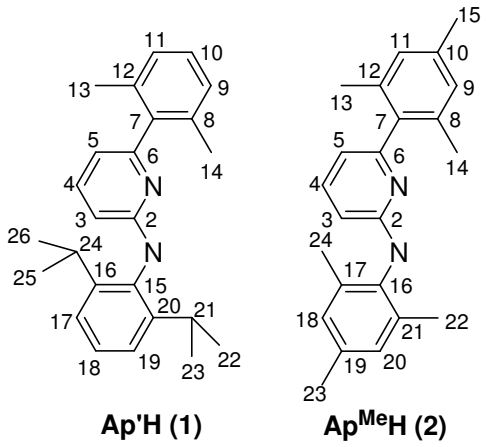
We have begun investigations of very bulky versions of such ligands.[11] Here we report that small variations in very bulky ligands have large synthetic and structural consequences including a rare example of a C^{Aryl}-H intermolecular agostic interaction and a small steric range in which such an interaction could be stabilized.

6.2. Results and Discussion

The aminopyridines **1**[11a] and **2**[12] [Equation (1), Scheme 2] were prepared by palladium-catalyzed arylamination,[13] and appeared suitable for conversion into the corresponding (amidopyridine)lanthanide complexes by reaction of lanthanoid metals with the ligands at elevated temperatures.

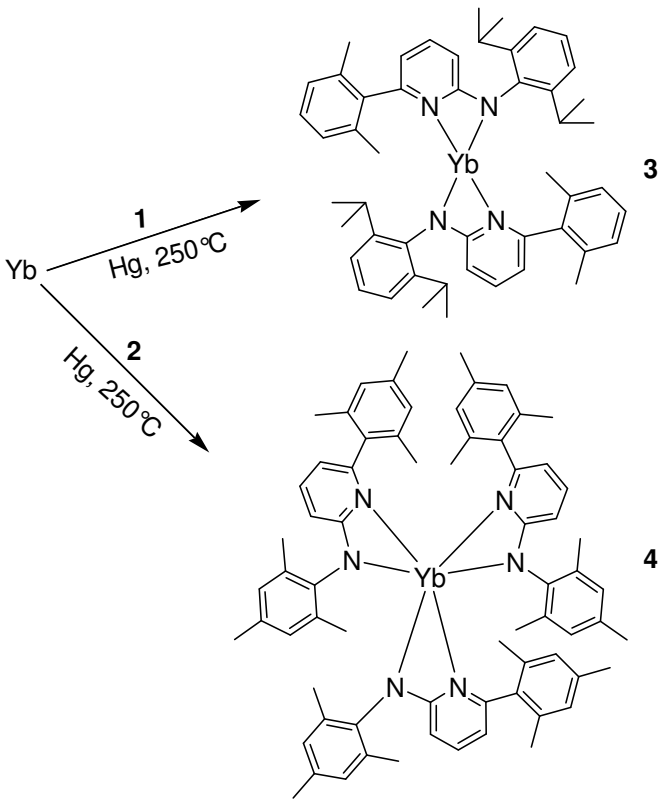
$$Ln + n\ ApH \longrightarrow LnAp_n + n/2\ H_2 \qquad (1)$$

(Ap = Ap` or Ap^{Me})



Scheme 2. 2,6-dialkylphenyl substituted aminopyridines and the numbering scheme used for NMR assignments.

This "direct" synthetic method[14] is especially valuable for homoleptic lanthanoid organoamides and phenolates[15] and has recently been extended to analogous alkaline earth complexes.[16] Direct reaction of **1** with ytterbium metal activated by mercury metal under vacuum at 250 °C gave rise to divalent [Yb(Ap`)$_2$] (**3**) (Scheme 3). Mercury assists by way of metal surface amalgamation/cleaning, while the molten ligand possibly acts initially as a solvent until the reaction mixture solidifies.



Scheme 3. Synthesis of the Ytterbium complexes **3** and **4**.

Suitable crystals of **3** could be grown during the complex synthesis. For crystallographic details see Table 1. The molecular structure of divalent homoleptic **3** (Figure 1) exhibits a bent structure as observed for the metallocenes [Yb{η-$C_5H3(1,3\text{-}SiMe_3)_2\}_2$][17] and [Ln(η-$C_5Me_5)_2$] (Ln = Sm,[18,19] Eu[19]). The C1–Yb–C26 angle for **3** is 126.93°, rather small when compared with the centroid-Yb-centroid angle of bulky [Yb{η-$C_5H_3(1,3\text{-}SiMe_3)_2\}_2$] (138.0°). The ytterbium atom is four-coordinate with two chelating Ap` ligands. The Yb–N bond lengths suggest that both ligands are in the amidopyridine form.

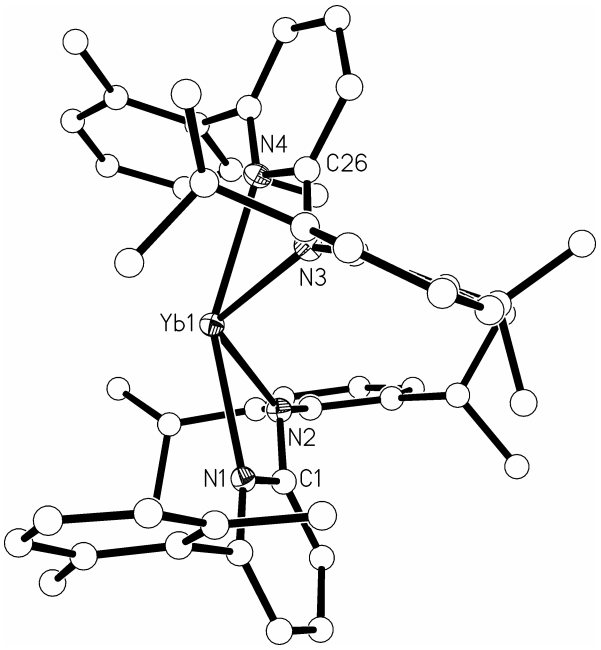


Figure 1. Molecular structure of [Yb(Ap`)$_2$] (**3**). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Yb1 2.4323(18), N2–Yb1 2.4041(18), N3–Yb1 2.3708(18), N4–Yb1 2.4489(18); N1–Yb1–N2 56.05(6), N1–Yb1–N3 105.89(6), N1–Yb1–N4 151.90(6), N2–Yb1–N3 116.20(6), N2–Yb1–N4 109.36(6), N3–Yb1–N4 56.02(6), C1–Yb1–C26 126.93(6).

This open sandwich structure leaves a vacant face on the Yb atom. To compensate for this, there is a close contact between a carbon–hydrogen bond of one of the phenyl rings of one YbAp`$_2$ molecule and a neighbouring Yb atom, with Yb1···C17 bonding distances of 2.981(2) Å and Yb1···H17 distances of 2.56(3) Å (all H atoms refined; Figure 2). Sterically crowded homoleptic (NacNac)Yb^{II} complexes adopt a highly symmetric non-bent structure.[20] Thus, we conclude that for anionic bidentate *N,N* ligands the thermodynamically more stable form is the highly symmetric and not the bent conformation. The ligand inclination may result from these unique intermolecular agostic interactions. Structurally characterized mononuclear

homoleptic (amidinato/aminopyridinato/amidopyridine)Yb^{II} complexes have not yet been described to the best of our knowledge.

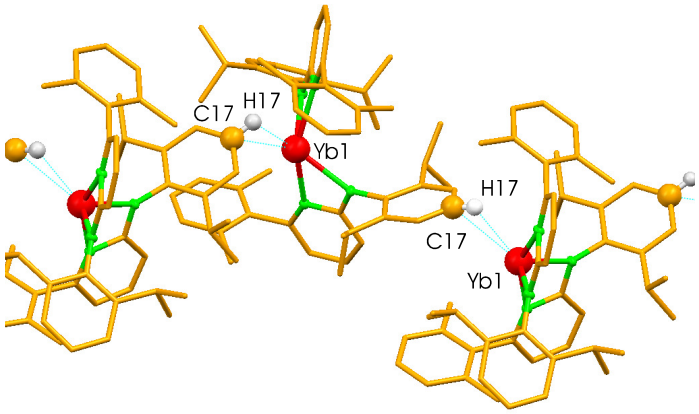


Figure 2. X-ray structure of **3** showing intermolecular agostic interactions (Yb1···H17 2.981(2) Å and Yb1···H17 distances 2.56(3) Å).

Reduction of the steric bulk, by applying **2** - a ligand which is smaller than **1** - according to Equation (1) led to a trivalent homoleptic Yb complex (Scheme 3). The formation of bis- or tris(amidopyridine)ytterbium complexes and thus the formation of di- or trivalent complexes can be explained in terms of the steric bulk of the corresponding ligands. The rare earth metal atom can bind three ligands of the less bulky version, Ap^{Me}, and thus the thermodynamically favoured trivalent oxidation state is accessible. Ytterbium can only bind two ligands of the slightly bulkier version, and thus the redox process stops at the oxidation state of two. X-ray analysis of **4** (for crystal and refinement data, see Table 1) reveals a distorted octahedral coordination for the ytterbium atom (Figure 3).

Table 1. Details of the X-ray crystal structure analyses of **3, 4, 7** and **8**.

	3	**4**	**7**·$2C_7H_8$	**7**·$0.5C_6H_{14}$	**8**·C_6H_{14}
Empirical formula	$C_{50}H_{58}N_4Yb$	$C_{69}H_{75}N_6Yb$	$C_{68}H_{82}N_4OYb$	$C_{57}H_{73}N_4OYb$	$C_{30}H_{40}N_2OYb$
Formula weight	888.04	1161.39	1144.42	1003.23	531.16
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	P2(1)/c	P-1	P2(1)/n	P2(1)/c	P2/c
a [Å]	12.1463(3)	11.4580(7)	11.1460(7)	10.8483(2)	12.4800(7)
b [Å]	22.6968(6)	11.4970(7)	27.6330(19)	24.2933(5)	12.2840(8)
c [Å]	15.5101(4)	26.6150(18)	19.960(15)	19.7081(3)	18.6520(12)
α [°]	90	101.131(5)	90	90	90
β [°]	95.608(1)	90.670(5)	103.037(5)	101.643(1)	104.689(5)
γ [°]	90	118.141(4)	90	90	90
V [Å^3]	4255.4(19)	3011.8(3)	5991.3(7)	5087.02(16)	2766.0(3)
Z	4	2	4	4	4
Crystal size [mm]	0.18 x 0.10 x 0.08	0.19 x 0.18 x 0.17	0.17x0.15x 0.10	0.25 x 0.25 x 0.25	0.39 x 0.17 x 0.11
ρ_{calcd} [g cm^{-3}]	1.386	1.281	1.269	1.310	1.276
μ_{calcd} [mm^{-1}] (Mo-K_α)	2.236	1.598	1.605	1.880	1.734
T [K]	123(2)	193(2)	193(2)	123(2)	193(2)
θ range [°]	1.60-30.00	1.57-25.82	1.28-25.85	2.51-27.50	1.66-25.71
No. of obsd. refl. [I > 2σ(I)]	11605	5573	6844	10516	3364
No. of unique refl.	12400	11144	11392	11681	5237
No.of parameters	728	685	667	581	303
R value [I>2σ(I)]	0.0321	0.0606	0.0408	0.0379	0.0447
*w*R^2	0.0590	0.1193	0.0993	0.0793	0.0860

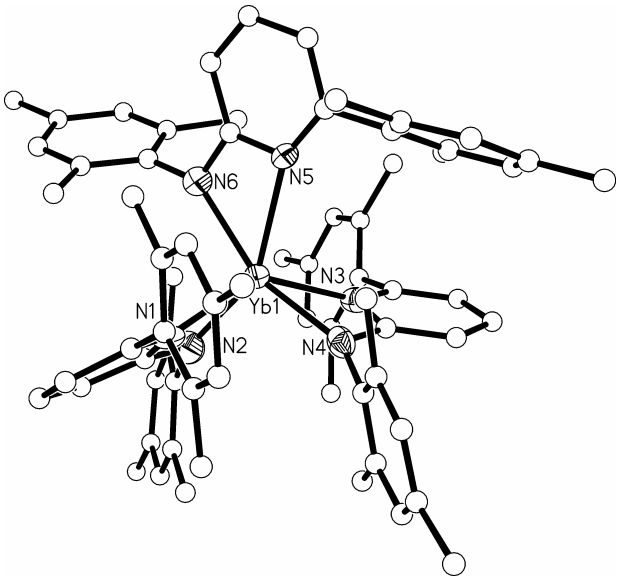
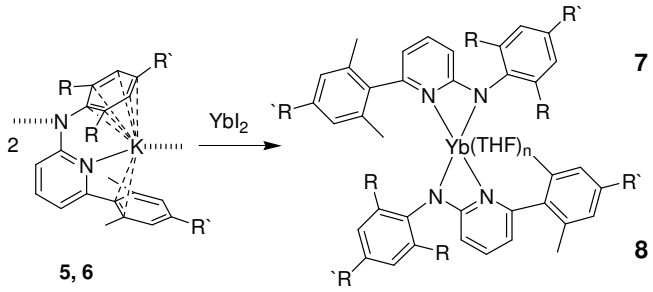


Figure 3. Molecular structure of [Yb(Ap^{Me})$_3$] (**4**). Selected bond lengths [Å] and angles [°]: N1–Yb1 2.357(8), N2–Yb1 2.264(7), N3–Yb1 2.395(7), N4–Yb1 2.263(7), N5–Yb1 2.543(7), N6–Yb1 2.299(7); N4–Yb1–N2 106.1(2), N4–Yb1–N6 158.4(2), N2–Yb1–N6 95.5(3), N4–Yb1–N1 92.5(3), N2–Yb1–N1 58.4(3), N6–Yb1–N1 98.7(2) N4–Yb1–N3 59.0(3), N2–Yb1–N3 98.9(3), N6–Yb1–N3 118.7(3), N1–Yb1–N3 138.8(2), N4–Yb1–N5 102.1(2), N2–Yb1–N5 151.2(2), N6–Yb1–N5 56.3(2), N1–Yb1–N5 115.6(2), N3–Yb1–N5 100.2(2).

It is noteworthy to mention that the ligands are coordinated in the amidopyridine binding mode to the metal atom. The different bond lengths for Yb–$N1_{pyridine}$ [2.357(8) Å] and Yb–$N2_{amido}$ [2.264(7) Å] indicate an amidopyridine binding mode where the anionic function is localized at the amido N-atom. A similar situation is noticeable with the bond length Yb–$N5_{pyridine}$ [2.543(7) Å] and Yb–$N6_{amido}$ [2.299(7) Å]. The ligand N3, N4 is also in the amidopyridine form, but the difference in appropriate bond lengths is smaller (0.13 Å). It is noteworthy that, for one of the ligands, the Yb–$N_{pyridine}$ bond (2.543 Å) is much longer than the averaged Yb–$N_{pyridine}$ bond for the two others (2.376 Å) indicating weak bonding due to steric saturation. Ligands N3, N4 and N1, N2 are the ligands containing the respective donor atoms.

Salt metathesis reactions of **5** (potassium salt of **1**)[11a] with [$YbI_2(thf)_4$] in THF solution resulted in the formation of the bis(amidopyridine)Yb^{II} complex **7** (Scheme 4). In addition, **7** was prepared from Yb metal by redox transmetallation/ligand exchange in THF [Equation (2)].

$$Yb + 2\,Ap'H + HgPh_2 \xrightarrow{THF} [Yb(Ap')_2(thf)] + 2PhH + Hg^{\circ} \qquad (2)$$



Scheme 4. Synthesis of **7** and **8** (**5, 7**: n = 1, R = *i*-Pr; R` = H: **6, 8**: n = 2, R =R`= Me) by metathesis reactions

X-ray quality crystals of **7**·$2C_7H_8$ were grown from concentrated toluene solution. In addition, crystals of **7**·$0.5C_6H_{14}$ were grown from hexane. In the case of the sterically more demanding ligand Ap`, only one thf molecule coordinates to the central metal atom. The resulting five coordination can be best described as very distorted trigonal-bipyramidal, with the N2, N4 and O1 atoms in the Yb plane and N1 and N3 apical [N1–Yb1–N3 157.59(14)°] (Figure 4). The Yb–$N_{pyridine}$ [2.479(4), 2.466(4) Å] bonds are significantly longer than the Yb–N_{amido} bonds [2.380(4), 2.384(3) Å] indicating an amidopyridine bonding mode.

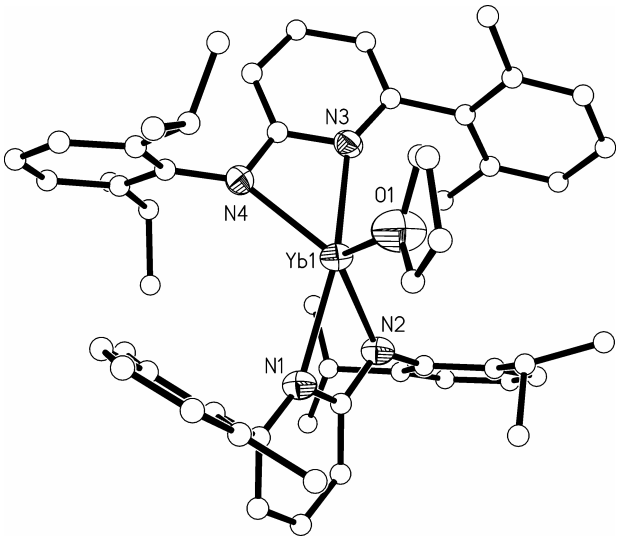


Figure 4. Molecular structure of [Yb(Ap`)$_2$(thf)] (**7**). Hydrogen atoms and two toluene molecule are omitted for clarity; Selected bond lengths [Å] and angles [°]: N1–Yb1 2.479(4), N2–Yb1 2.380(4), N3–Yb1 2.466(4), N4–Yb1 2.384(3), O1–Yb1 2.362(4); N4–Yb1–N1 113.38(15), O1–Yb1–N1 101.37(15), O1–Yb1– N4 114.73(16), N3–Yb1–N1 157.59(14), N4–Yb1–N3 55.82(15), O1–Yb1–N3 101.05(15), N2–Yb1–N1 56.17(14), N2–Yb1–N4 126.99(15), O1–Yb1–N2 118.28(16), N2–Yb1–N3 112.02(16).

The reactant **6** was prepared in a similar fashion to **5**[11a] and was treated with $[YbI_2(thf)_4]$ in THF. Product **8** was extracted with hexane, and crystallisation afforded red crystals. Complex **8** was characterized by X-ray crystal-structure analysis and contains one hexane molecule per Yb atom in the crystal lattice. Crystal and refinement details are listed in Table 1. The molecular structure of **8** is shown in Figure 5.

The reduction of the steric bulk of the amidopyridine from **7** to **8** allows for the coordination of the two thf ligands which bind to the metal centre in a *cisoid* manner, and the coordination arrangement can be best described as distorted octahedral. The Yb–$N_{pyridine}$ (2.544 Å), Yb–N_{amide} (2.396 Å) and Yb–O distances are comparable to other related thf complexes,[11b] and the bonding mode is amidopyridine in character. Considering the lability of the coordinated thf molecules, it is surprising that the Yb–O distance (Figure 5) lies close to the mean value for those in all previously reported Yb–O_{thf} interactions (2.43 Å).[21] The small chelating angle N_{amido}–Yb–$N_{pyridine}$ (average 54.76°) underlines the strained nature of the amidopyridine ligand binding. The Yb–$N_{pyridine}$ and Yb–O_{thf} bonds of **8** are longer than those of **7** by amounts consistent with a change of one in the coordination number,[22] but the differences in the Yb–N_{amido} distances is much smaller (ca. 0.02 Å).

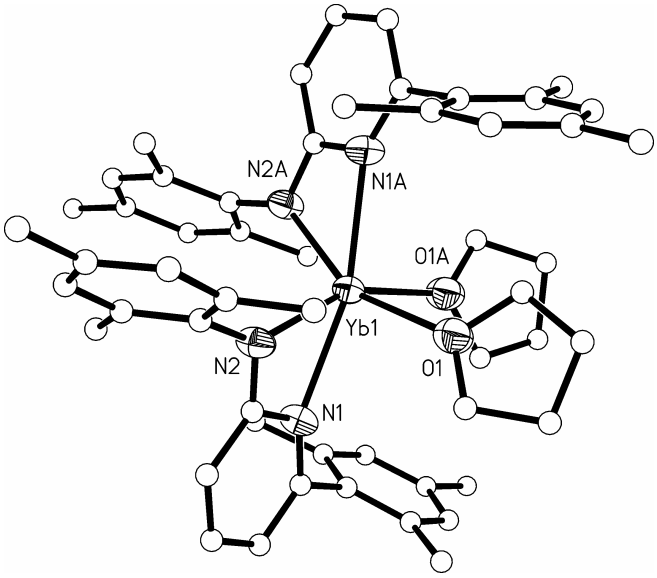


Figure 5. Molecular structure of $[Yb(Ap^{Me})_2(thf)_2]$ (**8**)**.** Hydrogen atoms and hexane molecule are omitted for clarity; Selected bond lengths [Å] and angles [°]: N1–Yb1 2.544(4), N2–Yb1 2.396(5), O1–Yb1 2.428(4); N2–Yb1–N2A 105.7(2), N2–Yb1–N1 54.76(15), O1A–Yb1–O1 78.1(2)

The nature of the products depends highly on the size of the ligands as the steric bulk is in the order Ap*-H > Ap`-H > $Ap^{Me}$-H. In the present study, the formation of the solvent-free complexes **3** and **4** has been enforced by the use of solvent-free conditions. The smallest ligand, $Ap^{Me}$-H, yields a six-coordinate $Yb^{III}$ complex, and the slightly bulkier Ap`-H yields a 4-coordinate Yb^{II} complex with rare intermolecular agostic interactions. This indicates that the coordination sphere is large enough to induce the presence of an agostic interaction but not large enough to accommodate a third ligand. Agostic complexes are often unstable, and substrate coordination and/or chelation generally seem to be necessary to bring the C-H bond and the coordinatively unsaturated metal centre into close proximity.[23] The reaction of the sterically more demanding aminopyridine Ap*-H (**9**), {(2,6-diisopropylphenyl)[6-(2,4,6-triisopropylphenyl)pyridin-2-yl]amine}[11a] directly with Yb metal mainly gave starting material. Salt metathesis reactions of the potassium salt of **9** with $[YbI_2(thf)_4]$ in THF solution resulted in the formation of a heteroleptic ytterbium iodide dimer $[Yb_2(Ap^*)_2I_2(thf)_4]$,[11b] notably with an Ap*/Yb ratio of 1:1. This outcome is driven by the extreme bulk of Ap* and contrasts the present metathesis reactions (Scheme 4).

6.3. Conclusions

The direct reaction between lanthanoid metal and bulky aminopyridines is an effective and simple way to synthesize true homoleptic “monomeric” amidopyridine complexes of Yb. The complexes predominantly adopt the amidopyridine binding mode. Relatively less bulky **2** results in the formation of a six-coordinate trivalent Yb complex, whereas more bulky **1** afforded a low-coordinate divalent Yb compound showing intermolecular C_{Aryl}-H agostic interactions, which do not persist in THF, from which five-coordinate $[Yb(Ap`)_2(thf)]$ (**7**) is isolated. A further increase of the steric bulk leads to different chemistry, such as mixed amido/iodo complexes in salt metathesis chemistry. Further studies are directed towards the exploration of the differences in reactivity of the low-valent ytterbium complexes introduced here.

6.4. Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon or N_2, using standard Schlenk and glovebox techniques. Non halogenated solvents were distilled from sodium/benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled from

sodium/benzophenone prior to use. All chemicals were purchased from commercial vendors and used without further purification. Ytterbium metal was obtained from Santoku. NMR spectra were obtained using either a 250 or 400 MHz Bruker ARX spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. X-ray crystal structure analyses were performed with a STOE-IPDS II or an Enraf–Nonius KAPPA CCD diffractometer equipped with a low-temperature unit. Structure solution and refinement were accomplished using SIR97,[24] SHELXL-97[25] and WinGX.[26] Crystallographic details are summarized in Table 1. Elemental analyses were carried out with Vario Elementar EL III or Leco CHNS-932 elemental analysers. CCDC-663340 to -663344 contains 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 [Yb(Ap`)$_2$] (3):** Ap`H (0.50 g, 1.4 mmol), Yb powder (0.40 g, 2.31 mmol) and a drop of mercury metal were heated together at 250 °C in a vacuum sealed glass tube for 16 days. The glass tube was gradually cooled to room temperature. After the cooling some red crystals of [Yb(Ap`)$_2$] were observed and were handpicked for X-ray crystallography. Yield (0.476 g, 77%). $C_{50}H_{58}N_4Yb$ (888.04): Calcd. C 67.62, H 6.58, N 6.31; found. C 68.13, H 6.40 , N 5.87. ^{1}H NMR (C_6D_6, 296 K): δ = 1.04 [br d, 12H, H^{22,23,25,26} Me$_2$(CH)], 1.32 [br d, 12H, H^{22,23,25,26} Me$_2$(CH)], 1.56 [br s, 6H, H^{13,14} Me(Ar)], 2.11 [br s, 6H, H^{13,14} Me(Ar)], 3.41 [br m, 4H, H^{21,24}], 5.60 [d, 2H, H^3 m-H(py)], 5.67 [dd, 2H, H^5 m-H(py)], 6.72 [t, 2H, H^4 p-H(py)], 7.26-7.32 [m, 12H, H^{9,10,11,17,18,19} H(Ar)] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.6 (s, C^{13,14}), 24.3 (C^{22,23,25,26}), 25.3 (C^{22,23,25,26}), 25.8 (s, C^{13,14}), 25.71 (C^{21,24}), 27.5 (C^{21,24}), 96.94 (C$^{3\ or\ 5}$), 106.73 (C$^{3\ or\ 5}$), 123.51 (C$^{17,19)}$), 123.73 (C^{9,11}), 124.4 (C^{18}), 137.1 (C^{10}), 138.0 (C^{16,20}), 142.6(C^7), 143.1 (C^4), 145.4 (C^{15}), 146.8 (C^{8,12}), 155.5 (C^6), 169.1 (C^2) ppm.

Synthesis of [Yb(Ap^{Me})$_3$] (4): Yb powder (0.262 g, 1.51 mmol), Ap^{Me}H (0.500 g, 1.51 mmol), and mercury metal (two drops) were heated together at 250 °C in a vacuum sealed glass tube for 9 days. The glass tube was gradually cooled to 150 °C over one day and further cooling to room temperature yielded light orange crystals of [Yb(Ap^{Me})$_3$]. Yield: (0.200 g, 60%). $C_{69}H_{75}N_6Yb$ (1161.41): Calcd. C 71.36, H 6.51, N 7.24; found. C 72.02 , H 7.35 , N 6.92. ^{1}H NMR (C_6D_6, 298 K): (Paramagnetic species) δ = -5.20 [br, s], 1.11 [d], 2.19 [m], 11.96 [s], 20.17 [s], 34.95 [br, s], 67.05 [br, s] ppm.

Synthesis of [(Ap^{Me}K)] (6): Ap^{Me}H, (3.00 g, 9.08 mmol), and KH (0.364 g, 9.08 mmol) were loaded into a Schlenk flask in the glove box. Ether (50 mL) was added to the above reaction mixture at 0 °C. The yellow reaction mixture was stirred overnight at room

temperature. The mixture was filtered and the volume reduced in vacuum to dryness. The resulting yellow precipitate was washed with hexane. The precipitate was dried under vacuum. Yield (3.240 g, 97%). $C_{23}H_{25}N_2K$ (368.56): Calcd. C 74.95, H 6.84, N 7.60; found. C 74.70 , H 6.73 , N 7.03. ^{1}H NMR (C_6D_6, 298 K): δ = 2.02 [s, 6H, $H^{13,14,22,24}$ *o*-Me], 2.17 [s, 6H, $H^{13,14,22,24}$ *o*-Me], 2.24 [s, 3H, $H^{15 \text{ or } 23}$ *p*-Me], 2.33 [s, 3H, $H^{15 \text{ or } 23}$ *p*-Me], 5.74 [dd, 1H, $H^{3/5}$ *m*-H(py)], 5.77 [dd, 1H, $H^{3/5}$ *m*-H(py)], 6.85 [s, 2H, $H^{18, 20}$ H(Ar)], 6.96 [s, 2H, $H^{9,11}$ H(Ar)], 6.98 [t, 1H, H^4 P-H(py)], ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.2 (d, $C^{13,14,22,24}$), 20.1 (d, $C^{13,14,22,24}$), 20.9 ($C^{15,23}$), 21.2 ($C^{15,23}$), 103.9 (d, $C^{3/5}$), 105.4 (d, $C^{3/5}$), 129.3 (d, $C^{9,11}$), 129.4 (C^{19}), 129.5 ($C^{18,20}$), 131.2 ($C^{17,21}$), 135.2 ($C^{8,12}$), 135.5 (C^7), 138.1 (C^{10}), 140.1 (C^{22}), 141.3 (C^4), 158.4 (C^6), 165.5 (C^2) ppm.

Synthesis of [Yb(Ap`)2(thf)] (7). Method I (Toluene Co-Crystallized): $[YbI_2(thf)_4]$ (1.072 g, 1.50 mmol) and **4** (1.10 g, 3.00 mmol) were placed into a Schlenk flask in a glove box; thf (40 mL) was added to the dark maroon-coloured reaction mixture which was stirred overnight. The solvent was evaporated under vacuum. The product was extracted with toluene (30 mL). The mixture was filtered and the filtrate concentrated to afford dark red crystals suitable for Xray analysis after 24 h at -20 °C. Yield (0.600 g, 45%). $C_{54}H_{66}N_4OYb$ (960.17): calcd. C 67.55, H 6.93, N 5.84; found C 66.99, H 6.76, N 5.65. ^{1}H NMR (C_6D_6, 298 K): δ = 1.13 [d, 12H, ^{H22,23,25,26} Me_2(CH)], 1.29 [br. m, 16H, $H^{22,23,25,26}$ Me_2(CH), β-CH_2, thf], 1.90 [s, 12 H, $H^{13,14}$ Me(Ar)], 3.41 [br. s, 8H, $H^{21,24}$, α-CH_2, thf], 5.70 [dd, 2 H, H^3 *m*-H(py)], 6.82 [dd, 2 H, H^5 *m*-H(py)], 6.96 [t, 2H, H^4 *p*-H(py)], 7.26-7.32 [m, 12 H, $H^{9,10,11,17,18,19}$ H(Ar)] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.8 (d, $C^{13,14}$), 24.5 ($C^{22,23,25,26}$), 24.8 ($C^{22,23,25,26}$), 25.5 (Cβ-thf), 28.4 ($C^{21,24}$), 31.9 ($C^{21,24}$), 68.0 (Cα-thf), 105.9 ($C^{3/5}$), 123.4 ($C^{17,19}$), 123.8 ($C^{9,11}$), 128.2 (C^{18}), 135.8 (C^{10}), 138.2 ($C^{16,20}$), 142.2 (C^7), 142.3 (C^4), 143.5 (C^{15}), 146.9 ($C^{8,12}$), 155.8 (C^6), 168.9 (C^2) ppm. Analysis and NMR samples toluene-free. **Method II (Hexane Co-Crystallized):** A mixture of Yb metal (1.04 g, 6.0 mmol), $HgPh_2$ (0.71 g 2.0 mmol) and Ap`H (1.37 g, 4.0 mmol) in thf (40 mL) was heated to 65 °C while being stirred for 24 h. After cooling, the reaction mixture was filtered and the red-orange solution concentrated to dryness. Recrystallization of the residue from hexane gave the title compound as red needles Yield (1.24 g, 62%). 1H NMR (C_6D_6, 298 K): δ = 0.94 [m, 2H, CH_2 (hexane)], 1.14 [br. s, 12H, $H^{22,23,25,26}$ Me_2(CH)], 1.27 [br. m, 21H, $H^{22,23,25,26}$ Me_2(CH), β-CH_2, CH_2 / CH_3(hexane)], 1.88 [br. s, 12H, $H^{13,14}$ Me(Ar)], 3.40 [br. s, 8H, $H^{21,24}$, α-CH_2, thf], 5.71 [dd, ^3J = 6.9, ^4J = 0.9 Hz, 4 H, H^3 or 5 *m*-H(py)], 6.81 [br. s, 6H, $H^{17,18,19}$ H(Ar)], 6.99 [br. m, 2H, H^4 *p*-H(py)], 7.29 [br. m, 6H, $H^{9,10,11}$ H(Ar)] ppm.

Synthesis of [Yb(Ap^{Me})$_2$(thf)$_2$] (8): [YbI_2 (THF)$_4$] (1.072 g, 1.50 mmol) and **6**, (1.100 g, 3.00 mmol), were loaded into a Schlenk flask in the glove box. THF (40 mL) was added to the above reaction mixture having dark maroon colour at the time of addition. The reaction was stirred overnight. The solvent was removed under vacuum and hexane (30 mL) was added. The mixture was filtered and the filtrate was concentrated to afford dark red crystals suitable for X-ray analysis after 24 h at -20 °C. Yield (1.00 g, 86%). $C_{54}H_{66}N_4O_2Yb.C_6H_{14}$ (1062.34): Calcd. C 67.84, H 7.59, N 5.27; found. C 67.57, H 7.87, N 5.72. ^{1}H NMR (C_6D_6, 298 K): δ = 1.23 [br, s, 8H, β-CH_2, thf], 2.05 [s, 12H, $H^{13,14,22,24}$ *o*-Me], 2.12 [s, 6H, $H^{15,23}$ *p*-Me], 2.20 [s, 12H, $H^{13,14,22,24}$ *o*-Me], 2.38 [s, 6H, $H^{15,23}$ *p*-Me], 3.33 [br s, 8H, α-CH_2, thf], 5.81 [dd, 4H, $H^{3/5}$ *m*-H(py)],], 6.69 [s, 4H, $H^{18,20}$ H (Ar)], 6.93 [t, 2H, H^4 *p*-H(py)], 6.96 [s, 4H, $H^{9,11}$ H (Ar)],ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 19.2 (d, $C^{13,14,22,24}$), 20.1 (d, $C^{13,14,22,24}$), 21.2 ($C^{15,23}$), 23.0 ($C^{15,23}$), 25.4 (β-CH_2, thf), 68.3 (α-CH_2, thf), 105.9 (d, $C^{3/5}$), 105.7 (d, $C^{3/5}$), 129.3 (d, $C^{9,11}$), 130.0 ($C^{18,20}$), 132.5 ($C^{17,21}$), 135.8 (C^{19}), 136.1 ($C^{8,12}$), 137.9 (C^7), 138.1 (C^{10}), 140.1 (C^{22}), 147.5 (C^4), 156.3 (C^6), 167.9 (C^2) ppm.

Attempted synthesis of [Yb(Ap^*)$_2$] (10): Yb powder (0.189 g, 1.09 mmol) Ap^*H (0.500 g, 1.09 mmol), and mercury metal (two drops) were heated together at 250 °C in a vacuum sealed glass tube for 15 days. Progressive heating at 270 °C and at 300 °C failed to achieve any reaction.

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7. Attempted Reduction of Divalent Rare Earth Iodo Aminopyridinates

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Keywords: Aminopyridinato ligands / Europium / N ligands / Reduction / Ytterbium

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Abstract: Rare examples of amido-iodo complexes of selected divalent lanthanides can be synthesized by using deprotonated Ap^*H {Ap^*H = 2,6-diisopropylphenyl)-[6-(2,4,6-triisopropylphenyl)-pyridin-2-yl]-amine} as a stabilizing ligand. Reaction of $[Ap^*K]_n$ with $[LnI_2(thf)_n]$ (Ln = Eu, Yb, n = 4, 5) in THF leads to $[Ln(Ap^*)I(thf)_2]_2$ (Ln = Eu, Yb). An attempted reduction of these divalent heteroleptic complexes with KC_8 to synthesize complexes containing an unsupported Ln-Ln bond resulted in the formation of $[Ln(Ap^*)_2(thf)_2]$. These lanthanide complexes were characterized by X-ray structure analysis.

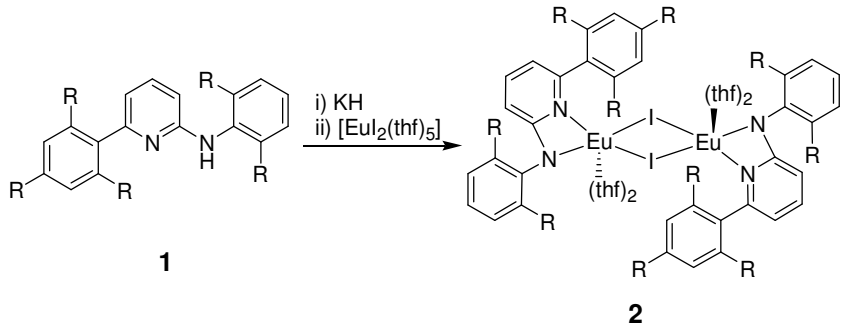
7.1. Introduction

Unsupported rare earth transition metal bonds are rare[1,2,3,4] and unsupported bonds between lanthanides are unknown. Inspired by the beautiful work of Jones and Stasch[5] and the analogy between alkaline earth metals and two valent rare earth metals, we became interested in reducing divalent iodo lanthanide complexes in order to synthesize compounds containing unsupported Ln-Ln bonds. We recently started a research programme using bulky aminopyridinates[6] and expected $[Ln(Ap^*)I(thf)_2]_2$ (Ln = Eu, Yb = **2**, **3**) to be good starting materials for such reductions. Divalent "heteroleptics" have been well documented in the case of donor-functionalized Cp-ligands but rarely described for alkoxy and amido ligands.[7] Here we report on the attempted reduction of **2** and **3**.

7.2. Results and Discussion

The potassium salt of $[Ap^*K]_n$ (**1**) reacts with $[EuI_2(thf)_5]$ and $[YbI_2(thf)_4]$ in a salt metathesis reaction affording **2** and **3** respectively without the formation of any ate complexes, as shown in Scheme 1.[6c] Crystals of compound **2** suitable for X-ray analysis were grown from toluene

solution at room temperature. Experimental details of the X-ray single crystal structure analysis are summarized in Table 1. The molecular structure of **2** is shown in Figure 1.



1 **2**

Scheme 1. Synthesis of **2**. (R = isopropyl).

These investigations revealed **2** to be a dinuclear mono(aminopyridinato) complex and the coordination around each europium metal can be best described as distorted octahedral (Figure 1).

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

Compound	**2·C_7H_8**	**4**	**5·C_6H_{14}**
Formula	$C_{43.5}H_{63}EuIN_2O_2$	$C_{72}H_{102}EuN_4O_2$	$C_{78}H_{116}N_4O_2Yb$
*F*w	924.82	1207.54	1314.79
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	P2(1)/n	P2(1)/n
a / Å	10.6650(9)	14.3710(5)	13.4190(7)
b / Å	14.5630(13)	16.9360(7)	20.8430(11)
c / Å	14.9830(12)	34.2400(16)	25.9170(12)
α /°	75.076(7)	90.00	90.00
β /°	74.266(6)	98.854(3)	98.798(4)
γ /°	79.523(7)	90.00	90.00
V / Å^3	2148.6(3)	8234.3(6)	7163.5(6)
Z	2	4	4
d(calcd)/(g/cm^3)	1.430	0.974	1.219
μ /mm^{-1}	2.213	0.798	1.35
2θ range /°	2.89-51.94	2.41-52.11	3.18-52.02
ωR^2 (all data)	0.0799	0.1004	0.1296
R value	0.0305	0.0427	0.0600

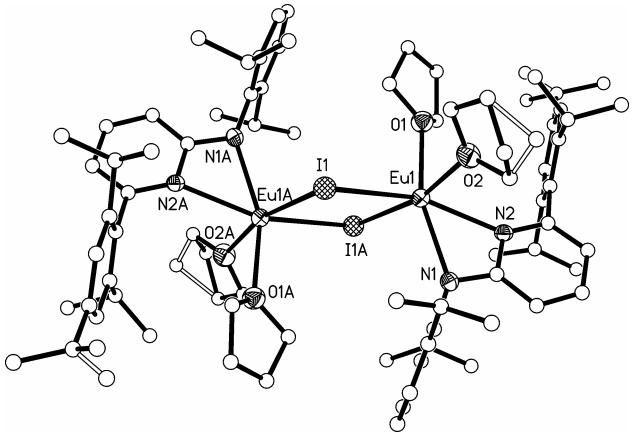
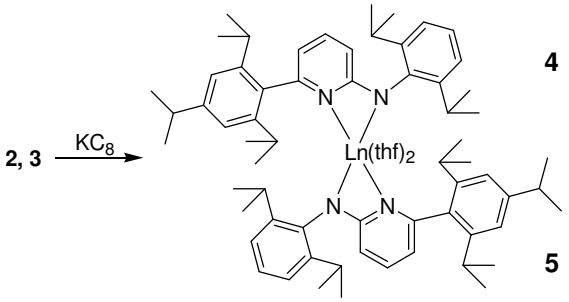


Figure 1. Molecular structure of $[Eu(Ap^{*})I(thf)_2]_2$ (**2**). One toluene molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Eu1 2.481(3), N2–Eu1 2.583, O1–Eu1 2.569(3), O2–Eu1 2.574(3), I1–Eu1 3.246(4), I1–Eu1 3.248(4), Eu1–I1 3.248(4); Eu1–I1–Eu1 90.073(11), N1–Eu1–O11 152.94(9), N1–Eu1–O2 95.10(9), O1–Eu1–O2 91.02(9), N1–Eu1–N2 53.44(9), O1–Eu1–N2 101.58(9), O2–Eu1–N2 82.57(9), N1–Eu1–I1 101.40(7), O1–Eu1–I1 105.45(6), O2–Eu1–I1 83.94(7), N2–Eu1–I1 149.90(6), N1– Eu1–I1 96.76(7), O1–Eu1–I1 80.14(6), O2–Eu1–I1 167.53(7), N2–Eu1–I1 107.69(6), I1–Eu1–I1 89.927(11).

The N–Eu–N angle (53.44 (9)°) underlines the strained nature of the aminopyridinato coordination and the different Eu–N distances indicate a localization of the anionic function of the ligand at the amido-N atom a classic amido–metal bond and a standard pyridine–europium bond.[8] The attempted reduction of complexes **2** and **3** using KC_8 to synthesize complexes with metal–metal bond led to the formation of monomeric bis(aminopyridinato) complexes **4** and **5**, respectively (Scheme 2).



Scheme 2. Synthesis of **4**, **5** (**4** Ln = Eu; **5** Ln = Yb).

In comparison to **4** which is paramagnetic and gives only broad signals in ^{1}H NMR spectrum, complex **5** exhibits rather well resolved signals. Complexes **4** and **5** were further confirmed regarding their molecular structures by X-ray analysis (Figure 2 and Figure 3), respectively. Crystals of **4** and **5** suitable for X-ray analysis were grown from hexane solutions at -84 °C. However, the crystals are quite sensitive to temperature and get dissolved once the temperature rises above 0 °C.

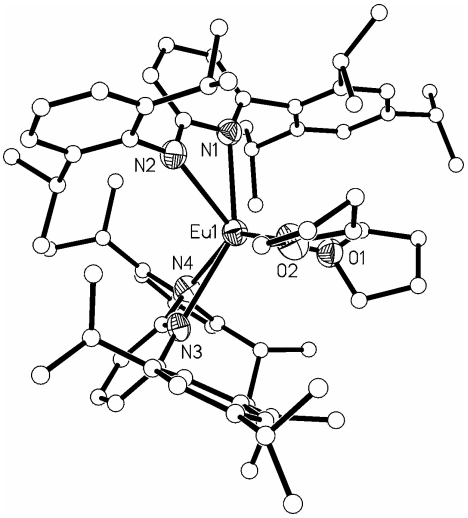


Figure 2. Molecular structure of [Eu(Ap*)$_2$(thf)$_2$] (**4**). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–Eu1 2.671(6), N2–Eu1 2.526(6), N3–Eu1 2.691(6), N4–Eu1 2.547(6), O1–Eu1 2.590(6) O2–Eu1 2.589(6); N2–Eu1–N4 111.8(2), N2–Eu1–O1 142.79(19), N4–Eu1–O1 94.92(19), N2–Eu1–O2 93.9(2), N4–Eu1–O2 140.93(19), O1–Eu1–O2 79.15(19), N2–Eu1–N1 52.3(2), N4–Eu1–N1 105.7(2), O1–Eu1–N1 96.70(19), O2–Eu1–N1 113.30(19), N2–Eu1–N3 106.5(2), N4– Eu1–N3 52.1(2), O1–Eu1–N3 110.42(17), O2–Eu1–N3 93.54(19), N1–Eu1–N3 145.1(2).

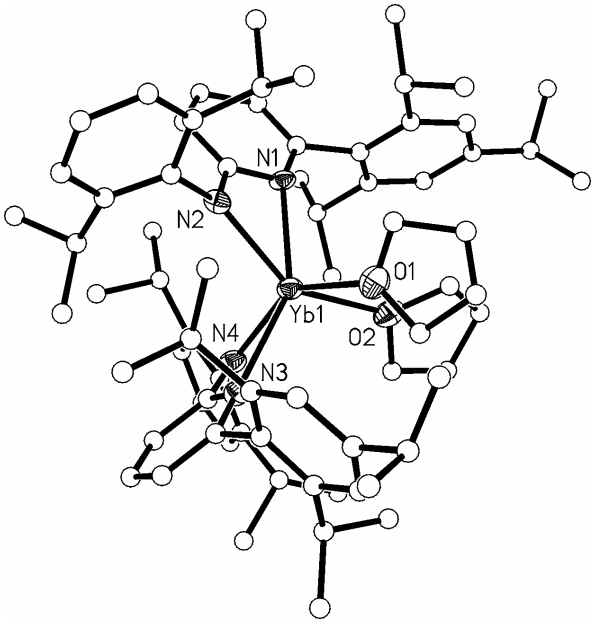


Figure 3. Molecular structure of $[Yb(Ap^{*})_2(thf)_2]$ (**5**). One hexane molecule and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Yb1–N2 2.431(6), Yb1–O1 2.438(6) Yb1–O2 2.446(6), Yb1–N4 2.464(7), Yb1–N1 2.511(5), Yb1–N3 2.511(6); N2–Yb1–O1 98.7(2), N2–Yb1–O2 145.8(2), O1–Yb1–O2 76.4(2), N2–Yb1–N4 110.3(2), O1–Yb1–N4 143.4(2), O2–Yb1–N4 90.4(2), N2–Yb1–N1 55.09(19), O1–Yb1–N1 107.1(2), O2–Yb1–N1 93.4(2), N4–Yb1–N1 107.6(2), N2–Yb1–N3 105.12(19), O1–Yb1–N3 97.5(2), O2–Yb1–N3 109.1(2), N4–Yb1–N3 54.40(19), N1–Yb1–N3 150.0(2).

Table 2. Comparison of bond lengths (Å) between selected atoms.

Selected atoms	**2**	**3**[6c]	**4**		**5**	
M–N_{amide}	2.481(3)	2.423(4)	2.528(3)	2.541(3)	2.431(6)	2.464(7)
M–$N_{pyridine}$	2.583(3)	2.508(4)	2.672(3)	2.679(3)	2.511(5)	2.511(6)
M–O	2.569(3)	2.574(3) 2.432(4)	2.445(4)	2.578(2)	2.595(3)	2.438(6) 2.446(8)

Despite the steric crowding around the metal atoms two thf ligands in each case additionally coordinate the metal in a *cisoid* manner and the coordination arrangement can be best described as distorted octahedral. The average Eu–$N_{pyridine}$ (2.681 Å), Eu–N_{amide} (2.536 Å) and Eu–O (2.586 Å) distances in **4** are long in comparison to the Yb–$N_{pyridine}$ (2.511 Å), Yb–N_{amide} (2.448 Å) and Yb–O (2.442 Å) distances in **5** which looks in accordance with the differences in the ionic radii of Eu^{+2} (1.31Å) and Yb^{+2} are (1.16 Å) with the coordination number six.[9] The amido ligand binds in the amidopyridine bonding mode. The average Eu–$N_{pyridine}$ and Eu–N_{amido} bonds of **4** are longer by (0.1 Å and 0.05 Å) than those of **2** by amounts consistent with an increase of the steric bulk but the differences in the Yb–O distances is much smaller

(ca. 0.02 Å). However, the bond lengths for these atoms are comparable in **3**[6c] and **5** (Table 2). The coordination of two thf ligands in **4** is in contrast to the literature results where a coordination of only one thf ligand was observed for comparatively less bulky version of the aminopyridinato ligands. [6h]

7.3. Conclusions

Based on the steric demand of the aminopyridinato ligand mono(aminopyridinato) complexes of di-valent lanthanides have been selectively synthesized. The reduction of these rare earth metal complexes using KC_8 led to the formation of bis(aminopyridinato) complexes which have been characterized by X-ray diffraction studies, NMR spectroscopic investigations and elemental analysis. Most likely reduction took place followed by disproportionation and the formation of bis(aminopyridinates).

7.4. Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon or N_2, using standard Schlenk and glovebox techniques. Non halogenated solvents were distilled from sodium benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled from sodium benzophenone prior to use. All chemicals were purchased from commercial vendors and used without further purification. Ytterbium metal was obtained from Santoku. Compound **3**[6c], $[YbI_2(thf)_4]$[10] and KC_8[11] were prepared following literature procedures. NMR spectra were obtained using a 400 MHz spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. X-ray crystal structure analyses were performed by using a STOE-IPDS II equipped with a low-temperature unit. Structure solution and refinement were accomplished using SIR9[12] SHELXL-97[13] and WinGX[14]. Crystallographic details are summarized in Table 1. Elemental analyses were carried out by Vario elementar EL *III* elemental analyser. Crystallographic data (excluding structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-724671 (compound **2·C_7H_8**), CCDC-724672 (compound **4**) and CCDC-724673 (compound **5·C_6H_{14}**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; web: www.ccdc.cam.ac.uk/conts/retrieving.html.

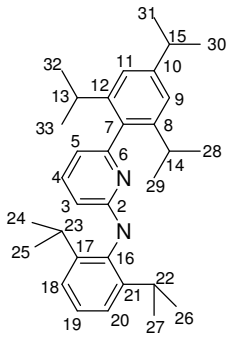


Figure 4. Numbering scheme for the ligand.

Synthesis of [Eu(Ap*)I(thf)$_2$]$_2$ (2): THF (30 mL) was added to Ap*K (0.993 g, 2 mmol) and [EuI$_2$(thf)$_5$] (1.532 g, 2 mmol) in a Schlenk flask at room temperature. The resulting yellow reaction mixture was then stirred for 20 hours. The solvent was evaporated under vacuum. The product was extracted with toluene (30 mL). The filtrate was concentrated to afford bright yellow crystals suitable for X-ray analysis after 24 hours at room temperature. Crystals dried under vacuum for two hours for elemental analysis. Yield (0.900 g, 51%). $C_{80}H_{118}N_4O_4Eu_2I_2$ (1757.55): Calcd. C 54.67, H 6.77, N 3.19; found C 54.39, H 6.22, N 3.32. ^{1}H NMR (400 MHz, C_6D_6, 298 K): (Paramagnetic) δ = 0.108 (br, s), 1.08 (d), 1.27 (m), 2.10 (br, s), 3.0 (s), 3.32 (s), 5.87 (br, s), 6.60 (br, s).

Synthesis of [Eu(Ap*)$_2$(thf)$_2$] (4): **2** (0.836 g, 0.457 mmol) was dissolved in THF (10 mL) and added to freshly prepared KC_8 (0.136 g, 1 mmol) in THF (30 mL) at -30 °C. The reaction mixture was then stirred over night at room temperature. The suspension was turbid reddish in colour. Hexane (30 mL) was added for extraction of the product. The yellow orange solution was filtered and the filtrate was concentrated to small volume to afford bright yellow crystals suitable for X-ray analysis after 48 hours at -80 °C. Yield (0.230 g, 40%). $C_{72}H_{102}N_4O_2Eu$ (1207.57): Calcd. C 71.61, H 8.51, N 4.64; found C 70.70, H 9.12, N 4.29. ^{1}H NMR (400 MHz, C_6D_6, 298 K): (Paramagnetic) δ = 0.28 (br, s), 2.19 (m), 2.88 (s), 3.0 (s), 3.37 (s), 5.90 (s), 6.45 (br, s), 7.35 (br, s).

Synthesis of [Yb(Ap*)$_2$(thf)$_2$] (5): **3** (1.106 g, 0.615 mmol) was dissolved in THF (10 mL) and was added to freshly prepared KC_8 (0.136 g, 1 mmol) in THF (30 mL) at -30 °C. The reaction mixture was then stirred for 20 hours. The solvent was evaporated under vacuum. The product was extracted with toluene (30 mL) and the filtrate was concentrated to afford red crystals suitable for X-ray analysis after 24 hours at room temperature. Crystals dried under vacuum for one hour for elemental analysis. Yield (0.209 g, 28%). $C_{72}H_{102}N_4O_2Yb_2$ (1228.65): Calcd. C 70.38, H 8.37, N 4.56; found C 69.82, H 8.19, N 4.15. ^{1}H NMR (400

MHz, C_6D_6, 298 K): δ = 1.13-1.31 {m, 68H, (60H, CH(C*H*$_3$)$_2$, $H^{24,25,26,27,28,29,30,31,32,33}$, 8H, β-C*H*$_2$, thf)}, 2.57 (sept, 2H, C*H*$(CH_3)_2$, H^{15}), 2.94 (sept, 4H, C*H*$(CH_3)_2$, $H^{13,14}$), 3.39 (br, s, 8H, α-C*H*$_2$, thf), 3.49 (sept, 4H, C*H*$(CH_3)_2$, $H^{22,23}$), 5.74 (d, 2H, H^3), 5.93 (d, 2H, H^5), 6.74 (dd, 2H, H^4), 7.12-7.34 (m, Ar, 10H, $H^{9,11,18,19,20}$) ppm. ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ = 21.39 (s, $C^{22,23}$), 25.6 (s, $C^{30,31}$), 25.7(s, $C^{28,29,32,33}$), 25.9 (s, β-*C*H$_2$, thf), 28.0 (s, $C^{24,25,26,27}$), 30.3 (s, $C^{13,14}$), 34.7 (s, C^{15}), 70.1 (s, α-*C*H$_2$, thf), 107.6 (s, C^3), 108.2 (s, C^5), 122.5 (s, $C^{9,11}$), 123.8 (s, $C^{18,20}$), 125.6 (s, C^4), 129.2 (s, C^7), 137.0 (s, $C^{17,21}$), 138.4 (s, C^{19}), 144.0 (s, C^{10}), 147.0 (s, $C^{8,12}$), 155.9 (s, C^6), 170.0 (s, C^2) ppm.

Acknowledgments

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8. Intramolecular C-H Bond Activation by Lanthanide Complexes Bearing a Bulky Aminopyridinato Ligand

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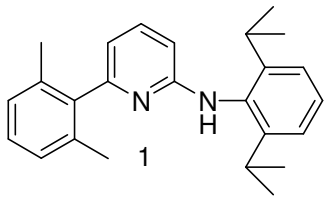
Abstract: The present work is aimed towards the synthesis of C-H activation products of various group 3 and lanthanide metals bearing a bulky aminopyridinato ligand, (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine (**1**, Ap'H). Deprotonation of **1** using KH leads to polymeric $[Ap'K]_n$ (**2**), which undergoes clean salt metathesis reaction with MX_3 [M = Sc, Nd and Sm, and X = Cl or M = La and X = Br] forming mono thf adducts $[Ap'_2ScCl(thf)]$ (**3**), $[Ap'_2LaBr(thf)]$ (**4**), $[Ap'_2NdCl(thf)]$ (**5**), and $[Ap'_2SmCl(thf)]$ (**6**). However, reacting **2** with $LuCl_3$ leads to mono- as well as bis(aminopyridinato) lutetium complexes $[Ap'LuCl_2(thf)_2]$ (**7**) and $[Ap'_2LuCl(thf)]$ (**8**) respectively, while the analogous reaction with $LaCl_3$ at 50 °C produces the tris(aminopyridinato) lanthanum complex $[Ap'_3La]$ (**9**). For the selective synthesis of **8** in good yield amine elimination route was adopted. X-ray diffraction studies revealed a distorted octahedral coordination for the bis(aminopyridinato) complexes **3**, **4** and **6**, despite the differences in their ionic radii. Alkylation of the bis(aminopyridinato) monohalide complexes with equimolar amount of $LiCH_2SiMe_3$ in hexane allowed the isolation of the corresponding alkyl derivatives for smaller metals like Sc and Lu affording $[Ap'_2ScCH_2SiMe_3(thf)]$ (**10**) and $[Ap'_2LuCH_2SiMe_3(thf)]$ (**11**), respectively. However, lanthanides with large ionic radii such as La and Nd resulted in the formation of methyl group C-H bond activation products $[Ap'(Ap'_{-H})La(thf)_2]$ (**12**) and $[Ap'(Ap'_{-H})Nd(thf)]$ (**13**), respectively. Most likely an alkyl species was formed which then undergoes intramolecular C-H activation and C-H activation runs fast with regard to the rate of alkyl complex formation. The alkylation of **6** (Sm) with $LiCH_2SiMe_3$ did not give a clear product.

The reaction of **11** with $PhSiH_3$ (Ph = phenyl) led via intramolecular C-H bond activation to [Ap'(Ap'$_{-H}$)Lu(thf)] (**14**). In this case most likely a hydride species was formed which then undergoes rapid C-H activation. The alkyl complex **10** (Sc) did not react with $PhSiH_3$. The molecular structures of **11**, **12** and **13** have been confirmed by X-ray crystal structure analysis.

8.1. Introduction

The activation of C-H bonds and in particular the activation of the C–H bonds of inert alkyls by transition metal and lanthanide complexes is a reaction of general interest due to its relevance for the functionalization of organic molecules.[1] The chemistry of lanthanide metals is characterized by their high electrophilicity, their tendency to high coordination numbers and their unique feature of varying the sizes of the rare earth atom[2] with a nearly identical coordination chemical behavior. Complexes of these metals are strong Lewis acids which may attack the electron density of C-H bonds, thus forming agostic[3] interactions and activate C-H bonds. Watson has even shown that methane, itself, could be activated by lanthanocene complexes such as $(Cp^*)_2LuCH_3$ (Cp* = pentamethylcyclopentadienyl).[4] Consequently, intermolecular alkyl group C-H activation of spectator ligands of lanthanide complexes has been observed for a variety of ligands, for instance, for methyl groups of the Cp* ligand.[5] Similar alkyl group C-H activation reactions have been described for non-metallocene lanthanide complexes.[6]

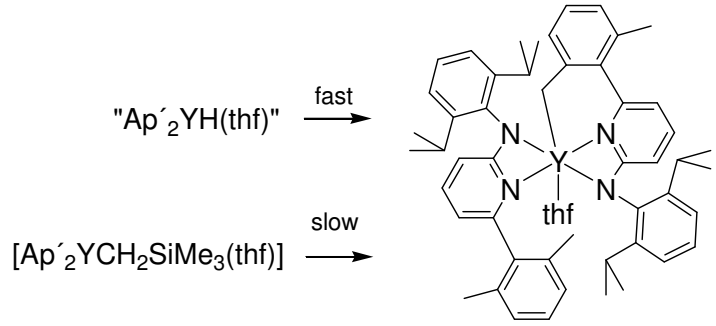
Aminopyridinato ligands[7] have been used successfully for the stabilization of early transition metals and lanthanides and we started recently a research program to investigate the reactivity of metal complexes coordinated by very bulky aminopyridinates.[8] In the course of these studies we observed that alkyl and hydrido yttrium complexes supported by the aminopyridinato ligand Ap' (Ap'H = (2,6-diisopropylphenyl)-[6-(2,6-dimethylphenyl)-pyridin-2-yl]-amine, Chart 1) undergo methyl group C-H activation of one of the methyl groups of the 2,6-dimethylphenly moiety of the Ap' ligand.[8i]



1

Chart 1. Used aminopyridine (Ap'H).

The alkyl complex [Ap'$_2$YCH$_2$SiMe$_3$] undergoes this C-H activation rather slow and the corresponding hydride does it more than 500 times faster.

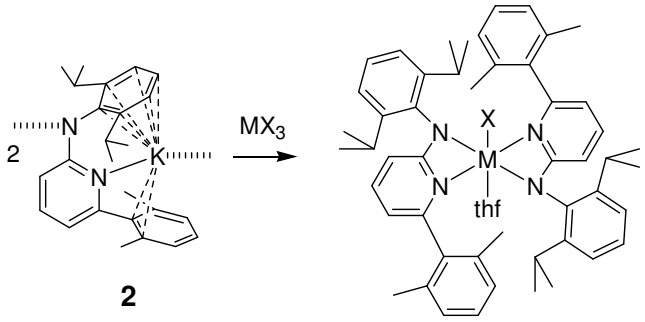


Scheme 1. Ligand metallation (methyl group C-H activation) reaction of Ap'$_2$Y-alkyl and -hydride complexes.

Since yttrium mimics the size of the late lanthanides quite well we became interested how this ligand metallation proceeds for early lanthanides as well as for Lu and Sc. Herein we report on synthesis and characterization of lanthanide monohalide complexes stabilized by bulky Ap' ligands, their alkylation with LiCH$_2$SiMe$_3$ which leads - depending from the size of the lanthanide ion - to C-H activation products or to (rather) stable alkyl complexes.

8.2. Results and Discussion

Polymeric **2** was prepared according to the literature reported procedure.[8a] Two equivalents of **2** were reacted with MX_3 [M = Sc, Nd, and Sm, and X = Cl or M = La and X = Br] in a salt metathesis reaction to afford the corresponding bis(aminopyridinato) complexes [Ap'$_2$ScCl(thf)] (**3**), [Ap'$_2$LaBr(thf)] (**4**), [Ap'$_2$NdCl(thf)] (**5**), and [Ap'$_2$SmCl(thf)] (**6**) in good yields (Scheme 2).

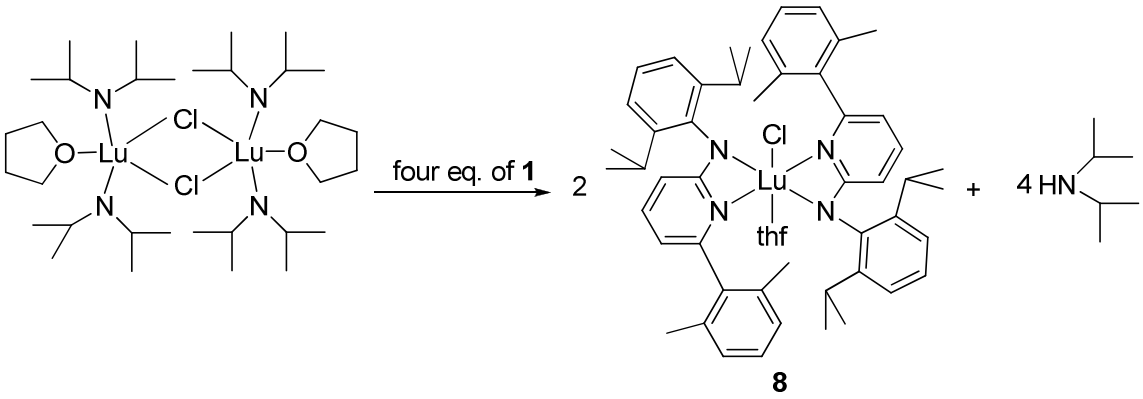


2

M = Sc, X = Cl (**3**),
M = La, X = Br (**4**),
M = Nd, X = Cl (**5**),
M = Sm, X = Cl (**6**),
M = Lu, X = Cl (**8**).

Scheme 2. Synthesis of bis(aminopyridinato) halide complexes.

However, in case of Lu both mono- as well as bis(aminopyridinato) lutetium complexes [Ap'$LuCl_2(thf)_2$] (**7**) and [Ap'$_2$LuCl(thf)] (**8**) were observed, respectively. Due to the poor solubility of **8** in hexane **7** can be separated easily if extracted with hexane in 24% yield. Residual **8** was extracted with toluene in a yield of 20%. Due to the poor yield of **8** we became interested in using the amine elimination route. Compound **8** was synthesized in very good yield (90%) by reacting four equivalents of **1** with $[(R_2N)_2LuCl(thf)]_2$ where R= diisopropyl (Scheme 3).



Scheme 3. Amine elimination synthesis of **8**.

A thf free derivative of compound **3** was isolated after work up in toluene. However, crystals suitable for X-ray analysis were grown from concentrated toluene solution after adding a few drops of THF which coordinates to the vacant site of the metal centre. Compound **4** is isolated as yellow crystalline material from hexane in moderate yield. Compound **6** and **8** were isolated as yellow crystals by slow diffusion of hexane or toluene into a saturated THF solution of these complexes. This series of compounds is a rare example of lanthanide complexes with the same ligand environment for which the same coordination number is observed despite their different ionic radii. The coordination of the bis(aminopyridinato) lanthanide halide complexes is best described as distorted octahedron arising from the two bidentate aminopyridinates, the chloro/bromo as well the thf ligand, as shown in Figure 1 till Figure 3 and Figure 5. Crystallographic details of all structures are listed in Table 1. It has been observed that in all cases the aminopyridinato ligands induce distortion from the ideal octahedral symmetry. $N_{pyridine}$-M-N_{amido} angles of 60.21°, 52.98°, 55.16°and 57.7° in **3**, **4**, **6** and **8**, respectively were observed and the longer M-$N_{pyridine}$ bond distances compared to M-N_{amido} bond length is indicative of the localization of the anionic function of the ligand at the amido N-atoms.[9]

Compound **7** is dimeric in solid state and the coordination around each Lu can be best described as distorted pentagonal bipyramidal (Figure 4). The two chloro ligands, the pair of nitrogen atoms and one thf ligand form the pentagonal (equatorial) plane and the remaining chloro and thf ligand occupy the axial positions of the polyhedron. The distortion is caused by the small N-Lu-N angle of 56.5(2)° due to the strained binding mode of the ligand. It leads to a situation in which all other angles in the pentagonal plane are over 72°. The N1–Lu–Cl2 and O2-Lu-Cl2 cis angles are 77.13(18) and 72.66(15)°. The N2–Lu–O2 angle is the widest [81.5(2)°]. The $O1_{ax}$-Lu–$O2_{eq}$ and Cl_{ax}-Lu-$O2_{eq}$ angles are 80.63(18)° and 90.05(14)°, respectively.

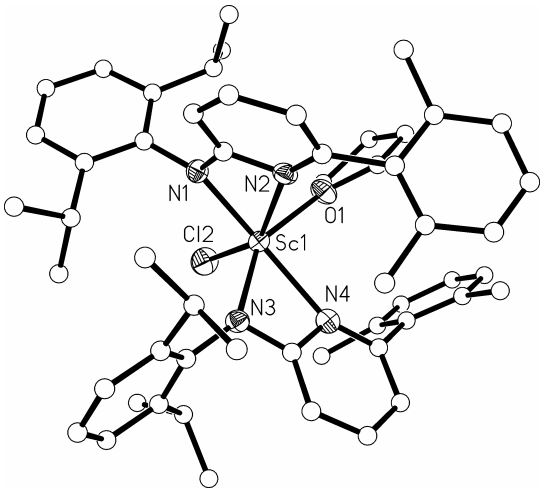


Figure 1. Molecular structure of **3**; Selected bond lengths [Å] and angles [°]: N1–Sc1 2.109(5), N2– Sc1 2.403(6), N3–Sc1 2.151(6), N4–Sc1 2.314(5), O1–Sc1 2.190(5) Cl2–Sc1 2.365(2); N1–Sc1–N3 105.9(2), N1–Sc1–O1 101.61(19), N3–Sc1–O1 149.00(18), N1–Sc1–N4 160.4(2), N3–Sc1–N4 60.57(19), O1–Sc1–N4 89.09(19), N1–Sc1–Cl2 92.25(16), N3–Sc1–Cl2 101.97(16), O1–Sc1–Cl2 90.88(15), N4–Sc1–Cl2 104.05(16), N1–Sc1–N2 59.85(19), N3–Sc1–N2 94.0(2), O1–Sc1–N2 87.57(19), N4–Sc1–N2 104.89(19), Cl2–Sc1–N2 150.99(14).

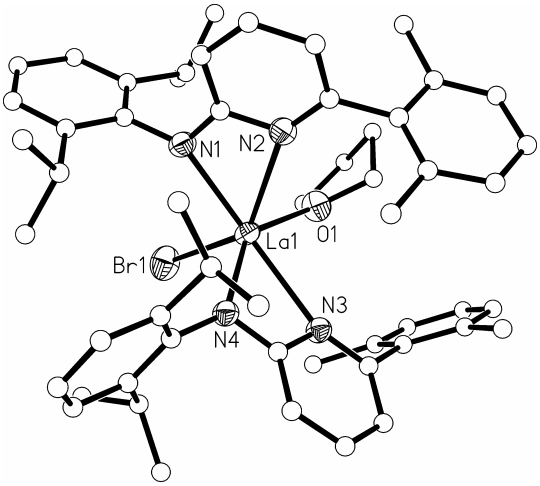


Figure 2. Molecular structure of **4**; Selected bond lengths [Å] and angles [°]: N1–La1 2.418(3), N2–La1 2.650(4), N3–La1 2.639(3), N4–La1 2.433(3), O1–La1 2.525(3), Br1–La1 2.8625(6) ; N1–La1–N4 104.46(11), N1–La1–O1 110.29(11), N4–La1–O1 144.13(11), N1–La1–N3 151.20(11), N4–La1–N3 53.04(11), O1–La1–N3 91.22(10), N1–La1–N2 52.92(12), N4–La1–N2 102.77(11), O1–La1–N2 91.42(10), N3–La1–N2 109.73(11), N1–La1–Br1 89.59(9), N4–La1–Br1 103.33(8), O1–La1–Br1 85.80(7), N3–La1–Br1 111.59(8), N2–La1–Br1 138.63(8).

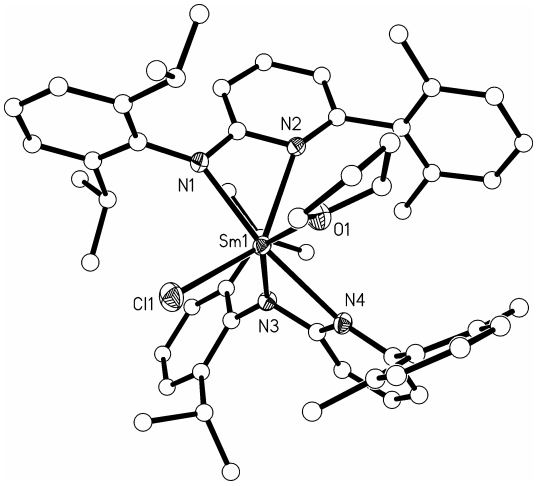


Figure 3. Molecular structure of **6**; Selected bond lengths [Å] and angles [°]: N1–Sm1 2.334(2), N2–Sm1 2.572(2), N3–Sm1 2.352(2), N4–Sm1 2.519(2), O1–Sm1 2.4064(18), Cl1–Sm1 2.5681(6) ; N1–Sm1–N4 156.85(7), N1–Sm1–O1 103.58(7), N4–Sm1–O1 89.57(7), N1–Sm1–N3 107.83(7), N4–Sm1–N3 55.63(7), O1–Sm1–N3 144.80(7), N1–Sm1–N2 54.69(6), N4–Sm1–N2 107.57(6), O1–Sm1–N2 88.88(6), N3–Sm1–N2 96.43(7), N1–Sm1–Cl1 89.50(5), N4–Sm1–Cl1 109.53(5), O1–Sm1–Cl1 90.98(5), N3–Sm1–Cl1 104.61(5), N2–Sm1–Cl1 142.90(5).

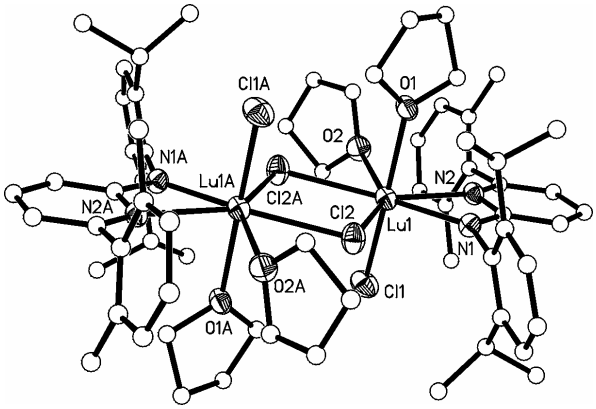


Figure 4. Molecular structure of **7**; Selected bond lengths [Å] and angles [°]: Lu1–N1 2.283(5), Lu1–O1 2.341(5), Lu1–O2 2.375(5), Lu1–N2 2.474(6), Lu1–Cl1 2.516(2), Lu1–Cl2 2.675(2), Lu1–Cl2 2.718(2), 3.556; N1–Lu1–O1 86.21(17), O1–Lu1–O2 80.63(18), N1–Lu1–N2 56.5(2), O1–Lu1–N2 85.93(17), O2–Lu1–N2 81.5(2), N1–Lu1–Cl1 98.79(12), O1–Lu1–Cl1 170.23(13), O2–Lu1–Cl1 90.05(14), N2–Lu1–Cl1 89.83(14), N1–Lu1–Cl2 77.13(18), O1–Lu1–Cl2 94.14(12), O2–Lu1–Cl2 144.41(14), Cl1–Lu1–Cl2 95.16(7), O1–Lu1–Cl2 85.57(12), O2–Lu1–Cl2 72.66(15), N2–Lu1–Cl2 153.81(14), Cl1–Lu1–Cl2 94.48(7), Cl2–Lu1–Cl2 71.85(7).

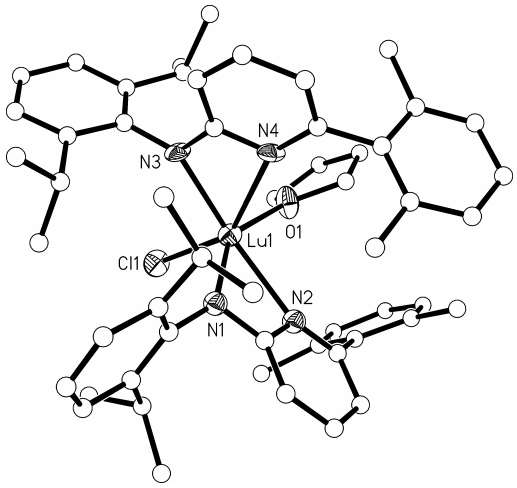
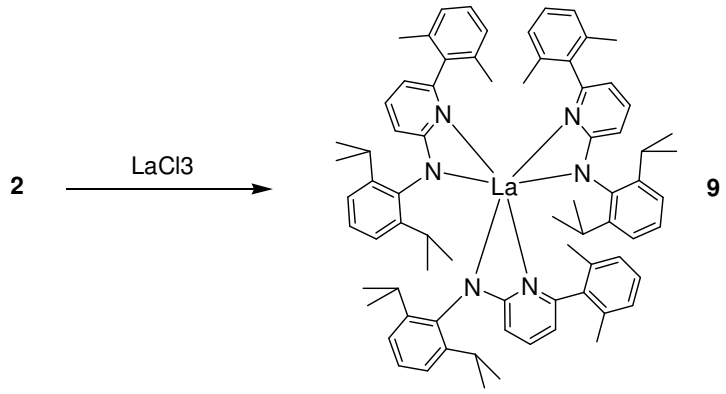


Figure 5. Molecular structure of **8**; Selected bond lengths [Å] and angles [°]: N1–Lu1 2.248(7), N2– Lu1– 2.422(8), N3–Lu1 2.246(8), N4–Lu1 2.462(10), O1–Lu1 2.297(6), Cl1–Lu1 2.479(3) ; N1–Lu1–N4 95.0(3), N1–Lu1–O1 147.8(3), N4–Lu1–O1 88.5(4), N1–Lu1–N3 105.8(3), N4–Lu1–N3 56.7(3), O1–Lu1–N3 102.8(3), N1–Lu1–N2 58.7(2), N4–Lu1–N2 107.1(3), O1–Lu1–N2 89.7(3), N3–Lu1–N2 158.6(3), N1–Lu1–Cl1 102.8(3), N4–Lu1–Cl1 146.8(19), O1–Lu1–Cl1 90.9(2), N3–Lu1–Cl1 91.3(2), N2–Lu1–Cl1 106.1(2).

Being structurally very similar, complexes **3** and **4** demonstrated different dynamic behaviour in solution. We essentially address this to the different radii of the lanthanide ions. In **3** the signals of the two methyl groups are well separated as two sharp peaks at room temperature. At 330 K a very slow exchange between two methyl groups is observed. The exchange becomes faster at 350 K but the signals still remain inequivalent. The ^{1}H NMR spectrum of compound **4** at room temperature consists of one broad signal corresponding to methyl group. The cooling of the toluene-d_8 solution to 273 K afforded the splitting of the above signal into two broad resonances. Further cooling resulted first in sharpening of these signals (253 K) and then again into the broadening and splitting of each of them to a new pair of signals (233 K). Most likely, two dynamic processes are present, first the exchange of the positions of the two Ap ligand and second the freezing out of the rotation of the 2,6-dimethylphenyl substituent.



Scheme 4. Synthesis of tris(aminopyridinato)lanthanum complex **9**.

Reacting two equivalents of **2** with $LaCl_3$ in THF at 65 °C without stirring it at room temperature leads to a homoleptic complex, [Ap'$_3$La] (**9**) in overall yield of 37 % (Scheme 4). Crystals of **9** suitable for X-ray analysis (crystallographic details are listed in Table 2) were grown by slow condensation of hexane into a saturated THF solution of **9**. The coordination around La can best be described as distorted octahedral as shown in Figure 6. The comparatively long bond distances of 2.745 Å (averaged value) for the La-$N_{pyridine}$ indicates steric overcrowding to accommodate the third ligand.

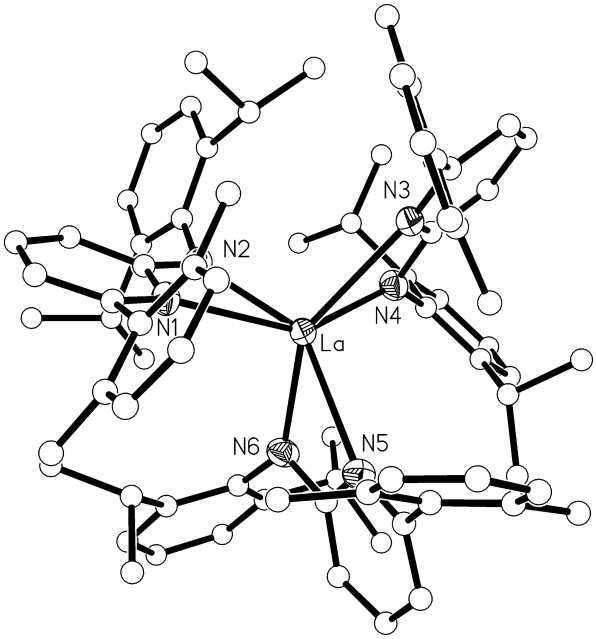
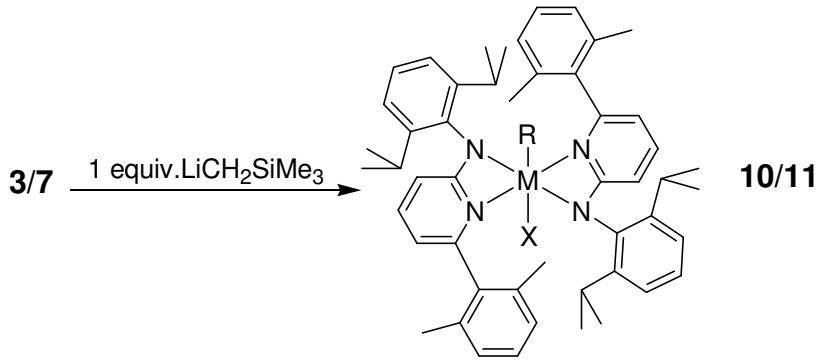


Figure 6. Molecular structure of **9**; Selected bond lengths [Å] and angles [°]: N1–La 2.7249(17), N2–La 2.4446(18), N3–La 2.7302(17), N4–La 2.4478(19), N5–La 2.7815(17), N6–La 2.4365(18), N4–La–N2 96.75(6), N4–La–N6 98.69(6), N2–La–N6 100.64(6), N4–La–N1 144.11(6), N2–La–N1 52.31(6), N6–La–N1 104.22(6) N4–La–N3 52.24(5), N2–La–N3 103.74(6), N6–La–N3 143.72(6), N1–La–N3 111.92(5), N4–La–N5 105.61(6), N2–La–N5 146.32(6), N6–La–N5 51.84(6), N1–La–N5 110.25(5), N3–La–N5 109.84(5).

As we have previously shown for yttrium[8i] that such bis(aminopyridinato) lanthanide halide complexes can be successfully alkylated using $LiCH_2SiMe_3$ and such alkyls then on reacting with $PhSiH_3$ (fast) or decomposition of the parent alkyl (slow) lead to intramolecular C-H bond activation products (Scheme 1). In order to investigate this behavior in terms of the size of used metal we extended our studies to various other lanthanides. We observed that **3** and **4** comprising of smaller lanthanides like Sc and Lu can be alkylated successfully by reacting them with one equivalent of $LiCH_2SiMe_3$ in hexane to give the corresponding alkyl complexes [Ap'$_2$ScCH$_2$SiMe$_3$] (**10**) and [Ap'$_2$LuCH$_2$SiMe$_3$(thf)] (**11**) in good yields of 62% and 86%, respectively (Scheme 5).



Scheme 5. Synthesis of **10** and **11** [**10**: M = (Sc, X = no thf); **11**: M = (Lu, X = thf), (R= $CH_2Si(CH_3)_2$].

In the ^{1}H NMR spectrum of complex **10** we observed a singlet at 0.13 ppm for the protons of the –$SiMe_3$ group and a broad singlet at 0.22 ppm for the methylene protons. In the ^{13}C NMR we observed a sharp signal for the –$SiMe_3$ group at 3.62 ppm however a signal for methylene carbon could not be observed. Complex **10** is quite stable in solution and doesn't show any detectable decomposition when its C_6D_6 solution was monitored for several weeks. Compound **11** was crystallized by slow cooling of its concentrated hexane solution when layered with THF to -20 ºC. X-ray analysis show one THF molecule per one molecule of [Ap'$_2$LuCH$_2$SiMe$_3$(thf)] in the crystal. The structure refinement data are listed in Table 3. The coordination sphere of the lutetium atom is set up by four nitrogen atoms of two aminopyridinato ligands, one carbon atom of the alkyl group and one oxygen atom of the THF molecule resulting in the coordination number of six. The Lu-C bond distance of 2.323(14) Å is slightly shorter than the values reported for related anilido phosphinimino (2.370 Å), 4,4,4``-tri-tert-butyl-2,2`:6`,2``-terpyridine (2.378 Å) and ß-ketoiminato (2.402 Å) ligand complexes.[10]

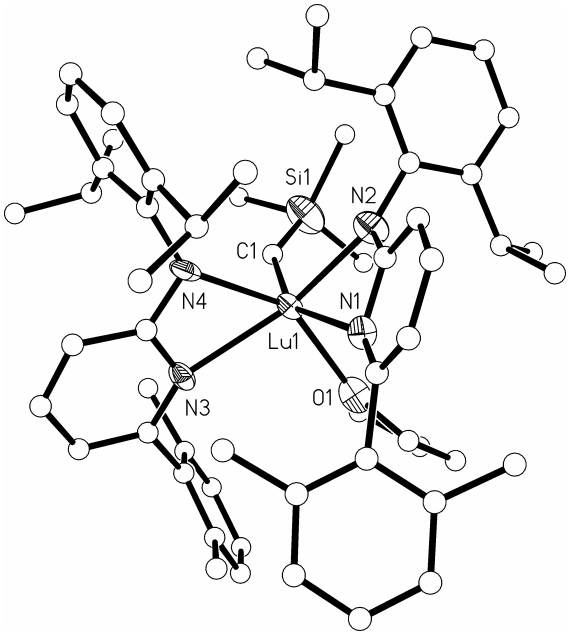
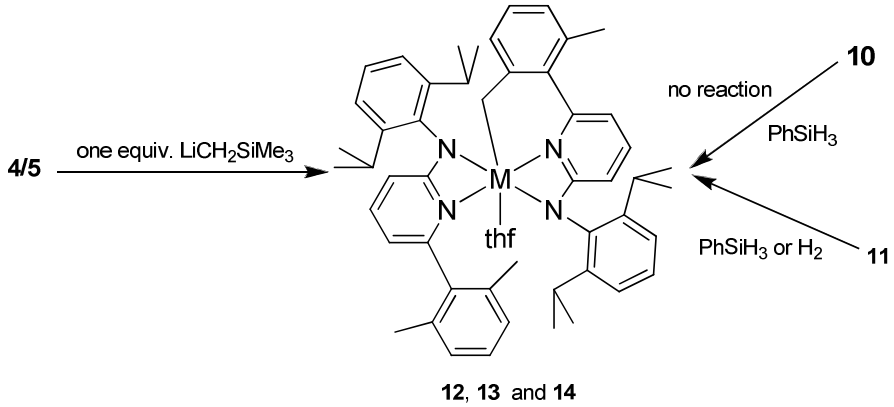


Figure 7. Molecular structure of **11** ; Selected bond lengths [Å] and angles [°]: N1–Lu1 2.536(9), N2–Lu1 2.242(9), N3–Lu1 2.426(9), N4–Lu1 2.310(10), O1–Lu1 2.294(9), C1–Lu1 2.323(14) ; N1–Lu1–N4 94.1(3), N1–Lu1–O1 84.3(3), N4–Lu1–O1 148.2(3), N1–Lu1–N3 108.3(3), N4–Lu1–N3 56.8(3), O1–Lu1–N3 93.5(3), N1–Lu1–N2 58.2(3), N4–Lu1–N2 101.3(3), O1–Lu1–N2 104.6(3), N3–Lu1–N2 155.3(3), N1– Lu1–C1 154.2(4), N4–Lu1–C1 100.1(4), Si1–Lu1–C1 149.8(7), O1–Lu1–C1 94.4(4), N3–Lu1–C1 97.5(4), N2–Lu1–C1 97.7(4).

In the ^{1}H NMR spectrum of complex **11** the hydrogen atoms of the methylene group attached to the lutetium atom appear as a broad singlet at –0.65 ppm whereas in the ^{13}C NMR the appropriate carbon appears at 47.8 ppm. Similarly in the ^{1}H NMR spectrum the nine protons of the $SiMe_3$ group appear as a singlet at 0.15 ppm. It is worthy to note that the signal sets corresponding to the aminopyridinate fragments in the ^{1}H NMR spectrum of **11** is quite different from its parent chloro complex **7**. In later the protons of the methyl substituents appear as a singlet at 2.90 ppm whereas the same group of protons in **11** gives two individual singlets at 1.46 and 2.46 ppm. This different behavior can be explained in terms of the steric bulk of the alkyl group introduced that slows down the ligand exchange process due to increased hindrance to rotation. Complex **11** does not coordinate THF during the course of the reaction and results in the THF adduct if a few drops of THF are added during crystallization process. Compound **11** can be stored in solid state without decomposition at – 20°C while in solution at room temperature it decomposes quite slowly eliminating $SiMe_4$ compared to its yttrium analogue.

In contrast to Sc and Lu the alkylation of the chloro complexes **4** and **5** comprising of larger lanthanides La and Nd with one equivalent of $LiCH_2SiMe_3$ did not yield the desired alkyl complexes and led directly to the intramolecular C-H bond activated products [Ap'(Ap$_{-H}$')La(thf)] (**12**) and [Ap'(Ap$_{-H}$')Nd(thf)] (**13**), in good yields of 61% and 63 %, respectively (Scheme 6).



Scheme 6. Synthesis of C-H activation complexes [**12**: M = La; **13**: M = Nd; **14**: M = Lu].

Orange crystals of **12** were grown by slow cooling of a concentrated THF:hexane (1:2) solution to -20 °C whereas brown crystals of **13** suitable for X-ray analysis were grown from a mixture of THF:pentane (1:10) at low temperature. The molecular structures of **12** and **13** are depicted in Figure 8 and Figure 9, respectively. In **12** one extra THF coordinates to the La compared to the parent **4** exceeding the coordination number to seven. Complex **13** shows strongly distorted octahedral coordination. The bond lengths of 2.601 (4) Å and 2.519 (10) Å in **12** and **13**, respectively between the corresponding metal (lanthanum/neodiumium) and the "benzylic" carbon are quite longer compared to previously reported Y-C bond [2.420(11) Å].[8i] Unlike the chloro compounds **4** and **5**, in complexes **12** and **13** one aminopyridinato ligand is bidentate, while the second one becomes tridentate due to metallation of the methyl group of one of the $Me_2C_6H_3$-fragments and formation of the new M-C σ-bond. The interesting features of **12** and **13** are the different ways of coordination of the aminopyridinato ligands. We have observed in the chloro complexes that both of the ligands have amidopyridine binding modes. The type of coordination of the bidentate Ap' ligand is similar to that observed in chloro complexes: one short M-N bond with amido nitrogen atom [La1-N1 2.489(3) Å and Nd1-N4 2.416(6)] Å and one long with the nitrogen atom of pyridine fragment [La1-N2 2.700(7) Å and Nd1-N3 2.556(8) Å]. In the tridentate Ap$_{-H}$' ligand formation of the M-C bond influences dramatically the bonding situation: the covalent bond

between metal and amido nitrogen atom [La1-N4 2.565(3) Å and Nd1-N1 2.499(7) Å] becomes longer than the coordination bond between metal and pyridine nitrogen atom [La1-N3 2.528(3) Å and Nd1-N2 2.448(7) Å) which means a switch from the amidopyridine to the aminopyridinato form is observed.[9]

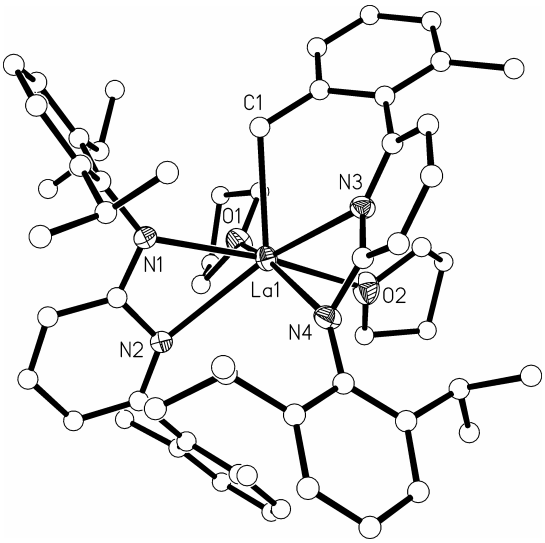


Figure 8. Molecular structure of **12**; Selected bond lengths [Å] and angles [°]: N1–La1 2.489(3), N2–La1 2.700(3), N3–La1 2.528(3), N4–La1 2.565(3), O1–La1 2.554(2), O2–La1 2.609(2), C1–La1 2.601(4); La–C1–C2 117.4(2), N1–La1–N4 107.81(9), N1–La1–O1 90.44(9), N4–La1–O1 155.45(9), N1–La1–N3 119.46(9), N4–La1–N3 52.97(8), O1–La1–N3 131.32(8), N1–La1–N2 51.83(9), N4–La1–N2 99.29(8), O1–La1–N2 78.87(8), N3–La1–N2 149.74(8), N1–La1–C1 70.5(3), N4–La1–C1 112.37(10), O1–La1–C1 87.36(10), N3–La1–C1 66.43(10), N2–La1–C1 125.78(10), N1–La1–O2 159.17(9), N4–La1–O2 88.91(9), O2–La1–N3 80.39(11), O2–La1–N2 114.44(8), O1–La1–C1 117.7(3), O1–La1–O2 70.21(8), C1–La1–O2 109.18(10).

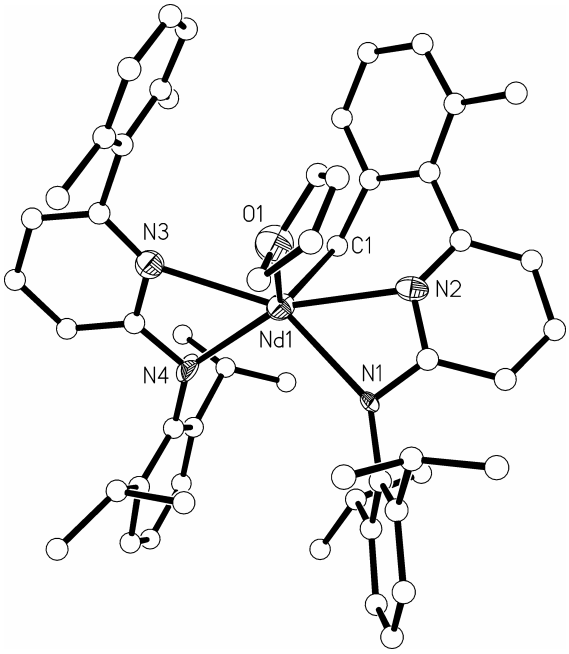


Figure 9. Molecular structure of **13**; Selected bond lengths [Å] and angles [°]: N1–Nd1 2.499(7), N2–Nd1 2.448(7), N3–Nd1 2.556(8), N4–Nd1 2.416(6), O1–Nd1 2.462(6), C1–Nd1 2.519(10) ; N1–Nd1–N4 107.8(2), N1–Nd1–O1 91.3(2), N4–Nd1–O1 127.8(2), N1–Nd1–N3 147.6(2), N4–Nd1–N3 54.4(2), O1–Nd1–N3 83.7(2), N1–Nd1–N2 53.8(2), N4–Nd1–N2 148.9(2), O1–Nd1–N2 81.0(2), N3–Nd1–N2 154.1(2), N1–Nd1–C1 107.9(3), N4–Nd1–C1 99.8(3), O1–Nd1–C1 120.2(3), N3–Nd1–C1 102.3(3), N2–Nd1–C1 68.6(3).

We observe a broad singlet at 1.35 ppm for the La-*CH*$_2$ protons in the ^{1}H NMR spectrum that coincides with the signal of coordinated THF. However the respective signal was observed as a singlet at 68.9 ppm in ^{13}C NMR spectrum. In case of **13** the paramagnetic nature of the complex excludes the observations of this resonance.

We know from our previous studies that such C-H activated products are accessible if the parent alkyl is reacted with equimolar amount of $PhSiH_3$ therefore for smaller scandium and lutetium the σ-bond metathesis reactions of alkyl complexes **10** and **11** with phenylsilane were employed as a synthetic approach to bis(aminopyridinato) lanthanide hydrides or intramolecular C-H bond activation products. We observed that **10** was quite inert towards phenylsilane and didn't undergo any observable change when the reaction was monitored by ^{1}H NMR. However stirring of **11** in toluene with phenylsilane for three days at room temperature and then cooling to -20 °C allowed the isolation of complex [Ap'(Ap$_{-H}$')Lu(thf)] (**14**) in 60 % yield (Scheme 6).

In order to understand the role of the size of the used lanthanide we studied the formation of complex **14** on NMR scale in benzene-d_6 at 296 K in the presence of phenylsilane. We observed that for lutetium the rate of formation of C-H activation product is about twenty times slower than for comparatively larger yttrium.[8i]

8.3. Conclusions

Several conclusions can be made from this study. The bulky aminopyridinato ligand Ap' affords isostructural bisaminopyridinate monohalide complexes from La to Sc despite of the large difference in the ionic radii of the metals. The corresponding alkyl complexes, synthesized via salt metathesis starting from the monohalides, can be instable and can undergo intramolecular methyl moiety C-H activation depending on the size of the used lanthanides. For larger lanthanides the rate of decomposition of the parent alkyl at room temperature is fast and precludes the isolation of these alkyls. Gradual decrease of the metal size enables the isolation of stable alkyl complexes. These rather stable alkyls may undergo intramolecular C-H activation via a transient hydride species at reasonable rates at room temperature.

Table 1. Crystallographic data and structure refinement details for **3**, **4**, and **6**.

	3	**4**·C_6H_{14}	**6**
Empirical formula	$C_{54}H_{66}N_4OScCl$	$C_{57}H_{72}N_4OLaBr$	$C_{54}H_{66}N_4OSmCl$
Formula weight	867.52	1048.01	972.91
T [K]	191(2)	191(2)	133(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P-1*	*P-1*	*P-1*
Unit cell dimensions [Å, deg]	*a* = 12.6930(11)	*a* = 12.2880(7)	*a* = 12.8440(7)
	b = 14.030(12)	*b* = 12.3570(7)	*b* = 13.9910(8)
	c = 14.1790(12)	*c* = 19.3060(11)	*c* = 14.2110(8)
	α = 73.880(10)	α = 99.975(5)	α = 104.986(4)
	β = 79.920(10)	β = 90.309(5)	β = 99.473(4)
	γ = 88.820(5)	γ = 113.791	γ = 90.957(4)
Volume, Å^3	2391.2(4)	2632.8(3)	2428.5(2)
Z	2	2	2
Density (calculated), g/cm^3	1.205	1.322	1.330
Absorption coefficient, mm^{-1}	0.252	1.611	1.305
F(000)	928	1048	1010
Crystal size, mm	0.22 x 0.17 x 0.15	0.21 x 0.20 x 0.19	0.49 x 0.36x 0.22
θ range for data collection, deg	1.51-25.69	1.82-24.69	1.51-25.75
Reflections collected	22008	28979	31719
Independent reflections	8473 R_{int} = 0.1566	8860 R_{int} = 0.808	9143 R_{int} = 0.4494
Completeness to θ	93.1	98.7	98.5
Data/restraints/ parameters	8473/ 0 / 550	8860 / 0 / 562	9143 / 0 / 562
Goodness-of-fit on F^2	1.063	0.919	1.058
Final R indices [I>2sigma(I)]	R_1 = 0.0870 wR_2 = 0.1935	R_1 = 0.0421 wR_2 = 0.0743	R_1 = 0.0269 wR_2 = 0.066
R indices (all data)	R_1 = 0.1922 wR_2 = 0.2217	R_1 = 0.0714 wR_2 = 0.0803	R_1 = 0.0321 wR_2 = 0.0705
Largest diff. peak and hole, eÅ^3	0.337 / -0.286	0.779 and -0.465	1.788 and -0.544

Table 2**.** Crystallographic data and structure refinement details for **7**, **8,** and **9**.

	7	**8**	**9**
Empirical formula	$C_{33}H_{45}Cl_2N_2O_2Lu$	$C_{54}H_{66}ClN_4OLu$	$C_{75}H_{87}N_6La$
Formula weight	747.58	997.53	1211.42
T [K]	193(2)	133(2)	191(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P2*(1)/*n*	*P-1*	*P2*(1)/*n*
Unit cell dimensions [Å, deg]	*a* = 10.222(5)	*a* = 12.7414(9)	*a* = 13.7710(4)
	b = 18.663(5)	*b* = 13.9751(13)	*b* = 22.5550(8)
	c = 17.437(7)	*c* = 14.1997(10)	*c* = 20.1650(7)
		α = 105.467(7)	
	β = 93.047(5)	β = 99.750(7)	β = 91.11(3)
		γ = 90.090(7)	
Volume, Å^3	3322(2)	2898.8(3)	6262.2(4)
Z	4	2	4
Density (calculated), g/cm^3	1.495	1.381	1.285
Absorption coefficient, mm^{-1}	0.71	2.155	0.73
F(000)	1512	1028	2554
Crystal size, mm	0.17 x 0.08 x 0.07	0.23 x 0.20 x 0.18	0.59 x 0.50 x 0.35
θ range for data collection, deg	1.60-26.15	1.51-25.70	1.35-25.74
Reflections collected	6538	6249	11821
Independent reflections	2790	4437	10335
	R_{int} = 0.000	R_{int} = 0.000	R_{int} = 0.068
Completeness to θ	98.3	68.5	98.7
Data/restraints/ parameters	6538/ 0 / 361	6249/ 0 / 544	11821/ 0 / 881
Goodness-of-fit on F^2	0.493	1.008	1.077
Final R indices [I>2sigma(I)]	R_1 = 0.0328	R_1 = 0.0572	R_1 = 0.0303
	wR_2 = 0.0488	wR_2 = 0.1356	wR_2 = 0.0720
R indices (all data)	R_1 = 0.1074	R_1 = 0.0756	R_1 = 0.0375
	wR_2 = 0.0638	wR_2 = 0.1387	wR_2 = 0.0757
Largest diff. peak and hole, eÅ^3	0.601 / -1.004	1.690 and -2.095	0.761 / -0.421

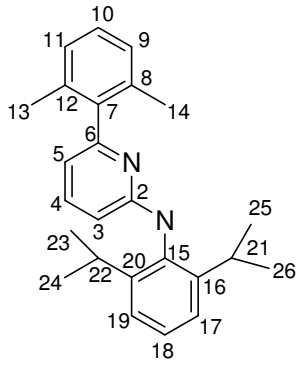
Table 3**.** Crystallographic data and structure refinement details for**, 11, 12** and **13**.

	11. C_4H_8O	**12**	**13**
Empirical formula	$C_{62}H_{85}N_4O_2LuSi$	$C_{58}H_{73}N_4O_2La$	$C_{54}H_{65}N_4ONd$
Formula weight	1121.40	997.11	930.34
T [K]	133(2)	133(2)	173(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P-1*	*P2*(1)/c	*P2*(1)
Unit cell dimensions [Å, deg]	*a* = 12.5940(10)	*a* = 12.2350(5)	*a* = 9.7600(6)
	b = 12.6940(13)	*b* = 23.4280(11)	*b* = 20.8890(12)
	c = 18.972(2)	*c* = 18.6550(8)	*c* = 12.2070(7)
	α = 75.789(8)		
	β = 89.453(5)	β = 103.847(3)	β = 107.083(4)
	γ = 83.858(7)		
Volume, $Å^3$	2922.9(5)	5191.9(4)	2378.9(2)
Z	2	4	2
Density (calculated), g/cm^3	1.274	1.276	1.299
Absorption coefficient, mm^{-1}	1.753	0.87	1.13
F(000)	1172	2088	970
Crystal size, mm	0.14 x 0.11 x 0.06	0.28 x 0.25x 0.23	0.15 x 0.15 x 0.11
θ range for data collection, deg	1.63-25.74	1.42-25.65	1.75-25.7
Reflections collected	9976	61178	25156
Independent reflections	5084	9754	8173
	R_{int} = 0.000	R_{int} = 0.073	R_{int} = 0.096
Completeness to θ	89.3	99.1	97.7
Data/restraints/ parameters	9976/ 0 / 638	9754 / 0 / 588	8173/ 0 / 522
Goodness-of-fit on F^2	0.803	0.901	0.995
Final R indices [I>2sigma(I)]	R_1 = 0.0705	R_1 = 0.038	R_1 = 0.0622
	wR_2 = 0.1129	wR_2 = 0.0826	wR_2 = 0.1025
R indices (all data)	R_1 = 0.1540	R_1 = 0.0610	R_1 = 0.0622
	wR_2 = 0.1361	wR_2 = 0.0870	wR_2 = 0.1098
Largest diff. peak and hole, $eÅ^3$	1.11 and -0.764	3.07 and -0.76	2.35 and -1.34

8.4. Experimental Section

General Procedures: All reactions and manipulations with air-sensitive compounds were performed under dry argon, using standard Schlenk and glovebox techniques. Non halogenated solvents were distilled from sodium benzophenone ketyl and halogenated solvents from P_2O_5. Deuterated solvents were obtained from Cambridge Isotope Laboratories and were degassed, dried and distilled prior to use. All chemicals were purchased from commercial vendors and used without further purification. NMR spectra were obtained using either a Bruker ARX 250 or Varian Inova Unity 400 spectrometer. Chemical shifts are reported in ppm relative to the deuterated solvent. X-ray crystal structure analyses were performed by using a STOE-IPDS I or II equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished using SIR9711, SHELXL-912 and WinGX13. Crystallographic details are summarised in Tabl 1, Table 2 and Table 3. Elemental analyses were carried out by Vario elementar EL *III* or Leco CHNS-932 elemental analyzer. CCDC-740977 to CCDC-740984 and CCDC-741180 contains the supplementary crystallographic details for this paper. These data can be obtained free of charge from Cambridge crystallographic Data centre via: www.ccdc.cam.ac.uk/conts/retrieving.html

Synthesis of lanthanide complexes



Scheme 7. Numbering scheme for NMR labelling.

Synthesis of 3: THF (40 mL) was added to $ScCl_3$ (0.302 g, 2.00 mmol) and **2** (1.586 g, 4.00 mmol) in a schlenk flask. The resulting bright yellow coloured reaction mixture was stirred overnight. The solvent was evaporated under vacuum and the product was extracted with toluene (30 mL). Toluene was fully evaporated and the resulting product was washed with hexane. Yield (0.9 g, 52%). $C_{54}H_{66}ClN_4ScO$ (867.5): Calcd. C 74.76, H 7.67, N 6.46; found.

C 74.26, H 8.01, N 6.46. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.81-1.26 [m, 24H, $H^{23,24,25,26}$], 1.47 [s, 6H, $H^{13,14}$], 2.34 [s, 6H, $H^{13,14}$], 3.28 [sept, 4H, $H^{21,22}$], 5.60 [d, 2H, H^3], 5.68 [d, 2H, H^5], 6.67 [dd, 2H, H^4], 7.02-7.18 [m, 12H, $H^{9,10,11,17,18,19}$] ppm ^{13}C NMR (C_6D_6, 298 K): δ = 19.2 [$C^{13,14}$], 24.7 [$C^{23,24,25,26}$], 29.9 [$C^{13,14}$], 104.8 [$C^{3/5}$], 110.6 [$C^{3/5}$], 124.1 [$C^{17,19}$], 124.4 [$C^{9,11}$], 129.2 [$C^{10,18}$], 135.7 [$C^{8,12}$], 137.3 [C^7], 141.6 [$C^{16,20}$], 144.0 [C^4], 144.5 [C^{15}], 156.1 [C^6], 168.7 [C^2] ppm.

Synthesis of 4: THF (40 mL) was added to $LaBr_3$ (0.757 g, 2.00 mmol) and **2** (1.58 g, 4.00 mmol) in a schlenk flask. The resulting bright yellow colour reaction mixture was stirred overnight. The solvent was removed under vacuum and the product was extracted with hexane (30 mL). The filtrate was concentrated to afford bright yellow crystals suitable for X-ray analysis after 48 h at room temperature. Yield (1.066 g, 53%). $C_{54}H_{66}N_4OLaBr$ (1005.94): Calcd. C 64.47, H 6.61, N 5.57; found. C 64.60, H 7.07, N 5.10. ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.96-1.39 [m, 28H, (4H, β-CH_2, thf) , 24H, $H^{23,24,25,26}$], 2.12 [br, s, 12H, $H^{13,14}$], 3.32 [br, s, 4H, α-CH_2, thf], 3.45 [sept, 4H, $H^{21,22}$], 5.57 [d, 2H, H^3], 5.75 [d, 2H, H^5], 6.70 [dd, 2H, H^4], 6.88-7.21 [m,12H, $H^{9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 20.6 [$C^{13,14}$], 25.0 [$C^{23,24,25,26}$], 25.3 [β-CH_2, thf], 28.7 [$C^{21,22}$], 70.1 [α-CH_2, THF], 107.7 [$C^{3/5}$], 109.8 [$C^{3/5}$], 124.2 [$C^{17,19}$], 124.9 [$C^{9,11}$], 127.8 [$C^{10,18}$], 136.3 [$C^{8,12}$], 139.5 [C^7], 140.3 [C^4], 144.0 [$C^{16,20}$], 144.8 [C^{15}], 155.8 [C^6], 170.4 [C^2] ppm.

Synthesis of 6: A solution of **2** (0.34 g, 0.86 mmol) in THF (30 mL) of was added to a suspension of $SmCl_3$ (0.11 g, 0.43 mmol) in THF (5 mL) and the reaction mixture was stirred for 7 h at 50 °C. After cooling to room temperature THF was evaporated in vacuum and the remaining residue was extracted with toluene (30 mL). The extracts were filtered and the solvent was removed under vacuum and the resulting yellow solid was redissolved in THF. Slow condensation of hexane into concentrated THF solution afforded complex **6** as yellow crystals. The crystals were washed with cold hexane and dried in vacuum at room temperature (45 min). Yield (0.33 g, 81%). $C_{54}H_{66}ClON_4Sm$ (972.94). Calcd. C 66.66, H 6.84 N 5.76; Found. C 66.11, H 6.88, N 5.64.

Synthesis of 7 and 8: THF (40 mL) was added to $LuCl_3$ (0.562 g, 2.00 mmol) and **2**, (1.58 g, 4.00 mmol) in a schlenk flask. The resulting yellow colour reaction mixture was stirred overnight. The solvent was removed under vacuum and hexane (30 mL) was added. The yellow reaction mixture was filtered and on standing at room temperature for 48 hours, yellow

crystals (suitable for X-ray analysis) of the title compound **7** were formed. Yield (0.37 g, 24%). $C_{66}H_{90}N_4O_4Cl_4Lu_2$ (1495.19): Calcd. C 53.02, H 6.07, N 3.75; found. C 52.85, H 5.96, N 3.74 .; ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.50-1.09 [br m, 24H, 24H, $H^{23,24,25,26}$], 1.22 [br s, 16H, (4H, β-CH_2, thf) $H^{13,14}$], 2.40 [br s, 12H, $H^{13,14}$], 3.76 [br, s, 8H, (16H ,α-CH_2, thf), 4.09 [sept, 4H, $H^{21,22}$)], 5.82 [br d, 4H, $H^{3/5}$], 6.87-7.25 [m,14H, $H^{4, 9, 10, 11, 17, 18, 19}$] ppm. ^{13}C NMR ($C_6D_6$, 298 K): δ = 23.83 [$C^{13,14}$], 24.88 [$C^{23,24,25,26}$], 25.2 and 25.4 [β-CH_2, THF], 28.7 [$C^{21,22}$], 71.9 [α-CH_2, thf], 106.7 [$C^{3/5}$], 107.5 [$C^{3/5}$], 124.1 [$C^{17,19}$], 125.2 [$C^{9,11}$], 127.4 [$C^{10,18}$], 128.2 [$C^{8,12}$], 139.9 [C^7], 140.8 [C^4], 143.1 [$C^{16,20}$], 145.8 [C^{15}], 155.1[C^6], 168.1 [C^2] ppm.

Toluene (30 mL) was added to the residue of the reaction Schlenck. The mixture was filtered and the filtrate was concentrated. A few drops of THF were added to afford bright yellow crystals of 8 suitable for X-ray analysis after 24 hours at room temperature. Yield (0.200 g, 20%). $C_{54}H_{66}N_4OLuCl$ (997.55): Calcd. C 65.02, H 6.67, N 5.62; found. C64.15, H6.80 , N5.33 ; ^{1}H NMR (400 MHz, C_7D_8, 298 K): δ = 0.88-1.11 [m, 28H, (4H, β-CH_2, thf), 24H, $H^{23,24,25,26}$], 2.92 [s, 12H, $H^{13,14}$], 3.28-3.59 [br, sept, 8H, (4H, α-CH_2, thf) (4H, $H^{21,22}$)], 5.79 [br d, 4H, $H^{3/5}$], 6.74-7.19 [m,14H, $H^{4, 9, 10, 11, 17, 18, 19}$] ppm. ^{13}C NMR ($C_7D_8$, 298 K): δ = 20.4 [$C^{13,14}$], 21.3 [$C^{23,24,25,26}$], 23.8 and 24.9 [β-CH_2, thf], 28.1 [$C^{21,22}$], 72.7 [α-CH_2, thf], 104.2 [$C^{3/5}$], 109.9 [$C^{3/5}$], 124.2 [$C^{17,19}$], 125.2 [$C^{9,11}$], 129.2 [$C^{10,18}$], 135.9 [$C^{8,12}$], 139.5 [C^7], 141.3 [C^4], 144.3 [$C^{16,20}$], 148.0 [C^{15}], 156.4 [C^6], 157.4 [C^2] ppm.

Selective Synthesis of 8: {[$(R_2N)_2LuCl]_2$}where R= diisopropyl (0.539 g, 1.11mmol) and **1** (0.800 g, 2.23mmol) were loaded together into a Schlenk flask in a glove box. Toluene (40 mL) was added to the yellow reaction mixture. The mixture was stirred overnight. Toluene was fully removed in vacuum to yield **8**. The product was washed with hexane. Yield (1.00 g, 90%).

Synthesis of 9: A solution of **2** (0.49 g, 1.24 mmol) in THF (30 mL) of was added to a suspension of $LaCl_3$ (0.152 g, 0.61 mmol) in THF (5 mL) and the reaction mixture was stirred for 20 h at 65 °C. After cooling to the room temperature THF was evaporated in vacuum and the remaining residue was extracted with toluene (30 mL). The solvent was removed under vacuum and the resulting solid residue was redissolved in THF. Slow condensation of hexane into the concentrated THF solution afforded complex **9** as brown crystals. The crystals were washed with cold hexane and dried in vacuum at room temperature. Yield (0.12 g, 32%). $C_{75}H_{87}N_6La$ (1211.44). Calcd. C, 74.36; H, 7.24; N 6.94; Found. C, 73.81; H, 7.42; N, 7.10.;

^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.57-1.16 [br m, 36H, $H^{23,24,25,26}$], 1.59 [brs, 6H, $H^{13,14}$], 2.13 [br s, 6H, $H^{13,14}$], 2.34 [brs, 6H, $H^{13,14}$], 2.83 [sept, 2H, $H^{21,22}$], 3.33 [sept, 4H, $H^{21,22}$], 5.57 [d, 3H, H^3], 5.78 [d, 3H, H^5], 6.61 [dd, 3H, H^4], 6.82-7.23 [m, 18H, $H^{9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 20.5 [$C^{13,14}$], 24.7, 26.5, 26.7 [$C^{23,24,25,26}$], 28.8, 29.1 [$C^{21,22}$], 109.0 [$C^{3/5}$], 112.0 [$C^{3/5}$], 124.5 [$C^{17,19}$], 125.0 [$C^{9,11}$], 125.3 [$C^{10,18}$], 138.1 [$C^{8,12}$], 140.9 [C^7], 144.0 [C^4], 145.7 [$C^{16,20}$], 145.9 [C^{15}], 156.0 [C^6], 171.0 [C^2] ppm.

Synthesis of 10: $LiCH_2SiMe_3$ (0.105 g, 1.11 mmol) in hexane (30 mL) was added to a stirred suspension of **3** (0.886 g, 1.11 mmol) in hexane and the reaction mixture was stirred for 24 h. The mixture was filtered and volume of the filterate was reduced under vacuum. A light yellow crystalline material deposited at -25 °C after standing over night. Yield (0.572 g, 62%). $C_{54}H_{69}N_4SiSc$ (847.19): Calcd. C 76.56, H 8.21, N 6.61; found C 77.25, H 7.82, N 6.72.; ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = 0.13 [s, 9H, $H^{CH2Si(CH3)3}$], 0.22 [s, 2H, $H^{CH2Si(CH3)3}$], 0.81-1.27 [m, 24H, $H^{23,24,25,26}$], 1.45 [s, 6H, $H^{13,14}$], 2.18 [s, 6H, $H^{13,14}$], 3.18-3.44 [sept, 4H, $H^{21,22}$], 5.62 [br, dd, 4H, $H^{3/5}$], 6.65 [br, dd, 2H, H^4], 7.01-7.37 [m, 12H, $H^{9,10,11,17,18,19}$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 3.62 [$C^{Si(CH3)3}$], 21.26 [$C^{13,14}$], 23.66 [$C^{13,14}$], 24.7 and 24.8 [$C^{23,24,25,26}$], 25.1 and 25.4 [$C^{21,22}$], 29.2 [$C^{21,22}$], 105.5 [$C^{3/5}$], 110.4 [$C^{3/5}$], 124.4 [$C^{17,19}$], 125.9 [$C^{9,11}$], 128.4 [$C^{10,18}$], 136.3 [$C^{8,12}$],139.4 [C^7], 142.8 [$C^{16,20}$], 144.1 [C^4], 144.1 [C^{15}], 144.5 [C^6], 169.2[C^2] ppm. (CH_2 signal could not be observed).

Synthesis of 11: $LiCH_2SiMe_3$ (0.094g, 1.00 mmol) in hexane (30 mL) was added to a stirred suspension of **8** (1.0 g, 1.00 mmol) in hexane and the reaction mixture was stirred for 24 h. The mixture was filtered and yellow crystals of **11** suitable for X-ray analysis were obtained by slow cooling of the concentrated THF/Hexane mixture (1:5). The crystals were dried under vacuum for two hours for elemental analysis. Yield (0.900 g, 86%). $C_{58}H_{77}N_4OSiLu$ (1049.31): Calcd. C 66.39, H 7.40, N 5.34; found C 66.73, H 7.29, N 5.71.; ^{1}H NMR (250 MHz, C_6D_6, 298 K): δ = - 0.65 [s, 2H, $H^{CH2Si(CH3)3}$], 0.15 [s, 9H, $H^{CH2Si(CH3)3}$], 0.92-1.22 [m, 24H, $H^{23,24,25,26}$], 1.40 [br s, 4H, β-CH_2, thf], 1.46 [s, 6H, $H^{13,14}$], 2.16 [s, 6H, $H^{13,14}$], 3.29 [sept, 4H, $H^{21,22}$], 3.59 [4H, α-CH_2, thf], 5.62 [d, 2H, $H^{3/5}$], 5.67 [d, 2H, $H^{3/5}$], 6.70 [br, dd, 2H, H^4], 6.96-7.22 [m, 12H, $H^{9,10,11,17,18,19}$) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 4.34 [$C^{Si(CH3)3}$], 19.5 [$C^{13,14}$], 21.1 [$C^{13,14}$], 24.1 [$C^{23,24,25,26}$], 24.7 [$C^{23,24,25,26}$], 25.0 [$C^{23,24,25,26}$], 25.7 [β-CH_2, thf], 28.0 [$C^{21,22}$], 29.3 [$C^{21,22}$], 47.8[CH_2], 68.4 [α-CH_2, thf], 106.3 [$C^{3/5}$], 109.8 [$C^{3/5}$], 124.1 [$C^{17,19}$], 124.4 [$C^{17,19}$], 125.4 [$C^{9,11}$], 127.8 [$C^{9,11}$], 128.5 [$C^{10,18}$], 135.7 [$C^{8,12}$], 136.2 [$C^{8,12}$], 139.4 [C^7], 140.8 [C^4], 144.1 [C^{15}], 144.2 [$C^{16,20}$], 156.0 [C^6], 168.0 [C^2] ppm.

Synthesis of 12: A solution of $LiCH_2SiMe_3$ (0.043 g, 0.46 mmol in toluene (30 mL) was added to a suspension of **4** (0.46 g, 0.46 mmol) in toluene (5 mL) and the reaction mixture was stirred for 30 minutes at room temperature and then for 1 h at 50 ˚C. After cooling to room temperature the mixture was filtered and toluene was removed in vacuum. The solid residue was dissolved in a THF/hexane mixture (~ 1:2). Slow cooling of the concentrated solution of **12** to –20 ˚C afforded brown crystals of **12.** The crystals were separated from the mother liquor by decantation, washed with cold hexane and dried in vacuum at room temperature. Yield (0.28 g, 61%). $C_{58}H_{73}N_4O_2La$ (997.1). Calcd. C 69.86, H 7.38, N 5.62; Found C 69.73, H 7.81, N 5.66.; ^{1}H NMR (400 MHz, C_6D_6, *J*/Hz): δ = 1.03, 1.21, 1.27 [d, 24H, H,^{23,24,25,26}], 1.35 [br s together, 10H, β-CH_2, thf, CH_2La], 2.27, 2.42 [s, 9H, H^{13,14}], 3.33 [br s, 2H, H^{21,22}], 3.48 [m, 2H, H^{21,22}], 3.51 [br s, 8H, α-CH_2, thf], 5.79, 5.81 [d, 2H, H^3, $J_{H\text{-}H}$ = 8.4], 5.94, 6.46 [d, 2 H, H^5, $J_{H\text{-}H}$ = 7.2], 6.56-7.35 [m, 14 H, H^{4,9,10,11,17,18,19}] ppm. ^{13}C NMR (100 MHz, C_6D_6, *J*/Hz): δ = 20.4, 22.4 [C^{13,14}], 24.1, 25.1 [C^{23,24,25,26}], 25.2 [β-*C*H$_2$, thf], 28.4, 28.5 [C^{21,22}], 68.8 [α-*C*H$_2$, thf], 68.9 [s, *C*H$_2$], 106.4, 108.4 [C^3], 108.0, 109.0 [C^5], 118.2, 122.8, 123.6, 123.8, 124.0, 127.4, 127.5, 127.6, 128.1 [C^{9,10,11,17,18,19}], 138.4, 139.3 [C^4], 134.3, 136.0, 141.7, 143.2, 143.6, 146.4, 147.1, 153.1[C^{7,8,12,15,16,20}], 153.7, 155.8 [C^6], 166.7, 170.4 [C^2] ppm.

Synthesis of 13: A solution of $LiCH_2SiMe_3$ (0.045 g, 0.48 mmol) in hexane (30 mL) was added to a suspension of **5** (0.464 g, 0.48 mmol) in hexane (20 mL) and the reaction mixture was stirred for 1 h. The mixture was filtered and hexane was removed in vacuum. The solid residue was dissolved in a THF/pentane mixture (~ 1:10). Slow cooling of the concentrated solution of **13** to –20 ˚C afforded brown crystals of **13.** The crystals were separated from the mother liquor by decantation, washed with cold hexane and dried in vacuum at room temperature. Yield (0.29 g, 63%). $C_{54}H_{65}N_4ONd$ (930.36). Calcd. C 69.71, H 7.04, N 6.02; Found C 69.05, H 7.44, N 6.04.

Synthesis of 14: A solution of $PhSiH_3$ (0.061 g, 0.57 mmol) in toluene (3 mL) was added to a solution of **11** (0.600 g, 0.57 mmol) in toluene (30 mL) at room temperature and the reaction mixture was stirred for 72 hours. The solution was concentrated to small volume and the solution was cooled at -25 °C affording yellow crystalline material. Yield (0.319 g, 60%). $C_{54}H_{65}N_4OLu$ (961.09): Calcd. C 67.48, H 6.82, N 5.83.; Found C 67.28, H 7.20, N 5.99.; ^{1}H NMR (400 MHz, C_7D_8, 298 K): δ = 0.80-1.58 [m, together 32H, H^{23,24,25,26} , β-CH$_2$, thf, CH_2Lu)], 1.78-2.33 [m, together 9H, H^{13,14}], 3.19-3.45 [br, sept, 8H, (4H, α-CH$_2$, thf) (4H,

$H^{21,22}$)], 5.64 [m, 4H, $H^{3/5}$], 6.63-7.27 [m, 14H, $H^{4,9,10,11,17,18,19}$] ppm. ^{13}C NMR (C_7D_8, 298 K): δ = 20.3, 20.5 [$C^{13,14}$], 23.0, 25.0 [$C^{23,24,25,26}$], 25.2 [β-CH_2, thf], 28.1, 28.6 [$C^{21,22}$], 68,6 [α-CH_2, thf], 72.1 [s, CH_2], 103.7, 108.8 [$C^{3/5}$], 110.1, 114.5 [$C^{3/5}$], 124.2, 124.3, 124.8, 125.0, 127.5, 127.7, 128.5, 129.7 [$C^{9,10,11,17,18,19}$], 134.7, 135.2 [C^4], 135.9, 136.0, 138.9, 139.5, 140.8, 141.8, 144.4 [$C^{7,8,12,15,16,20}$], 148.0, 156.3 [C^6], 159.3, 159.9 [C^2] ppm.

Alternative synthesis: A solution of **11** (0.025 mg, 22.3 mmol) in C_6D_6 (0.5 mL) was charged in a young valve equated NMR tube. The solution was cooled to -90 ºC and the Ar atmosphere was replaced by 4 bar of H_2. The tube was allowed to warm up to room temperature and measured continuously every 2h. After 12h the reaction was completed and an NMR spectrum similar to the one above was observed. No intermediate was detected.

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9. List of publications:

The following papers have been published/submitted during the work on this thesis:

1. Winfried P. Kretschmer, Auke Meetsma , Bart Hessen, Natalie M. Scott, Sadaf Qayyum, Rhett Kempe, *Z. Anorg. Allg. Chem.* **2006,** *632,* 1936-1938. "Lanthanum Dibromide Complexes of Sterically Demanding Aminopyridinato and Amidinate Ligands".

2. Winfried P. Kretschmer, Auke Meetsma, Bart Hessen, Thomas Schmalz, Sadaf Qayyum, Rhett Kempe. *Chem. Eur. J.* **2006**, *12,* 8969-8978. "Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution".

3. Sadaf Qayyum, Kristina Haberland, Craig M. Forsyth, Peter C. Junk, Glen B. Deacon, Rhett Kempe. *Eur. J. Inorg. Chem.* **2008**, 557-562. "Small Steric Variations in Ligands with Large Synthetic and Structural Consequences".

4. Sadaf Qayyum, Germund Glatz, Torsten Irrgang, Rhett Kempe, *Z. Kristallogr. NCS.* **2008**, *223,* 48-50. "Crystal structure of (4,6-dimethyl-pyridin-2-yl)-6-(2,4,6-triisopropyl-phenyl)-prridine -2-yl)-amine, ($C_{20}H_{26}$ N)(C_7H_8N)NH".

5. Sadaf Qayyum, Awal Noor, Germund Glatz, Rhett Kempe. *Z. Anorg. Allg. Chem.* **2009**, In press. "Attempted Reduction of Divalent Rare Earth Iodo Aminopyridinates".

6. Sadaf Qayyum, Grigorii G. Skvortsov, Georgii K. Funkin, Alexander A. Trifonov, Christian Döring, Rhett Kempe, *Eur. J. Inorg. Chem.* (submitted), "Intramolecular C-H Bond Activation by Lanthanide Complexes Bearing a Bulky Aminopyridinato Ligand".

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Declaration/Erklärung

Hereby I declare that this work has so for 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 doctorate.
Furthermore, I declare that I have written this work by myself and that I have not used any other sources, other than mentioned earlier in this work.

Hiermit erkläre ich, dass diese Arbeit bisher von mir weder an der Fakultät für Biologie, Chemie und Geowissenschaften der Universität Bayreuth noch einer anderen wissenschaftlichen Einrichtung zum Zwecke der Promotion eingereicht wurde. Ferner erkläre ich, dass ich diese Arbeit selbständig verfasst und keine anderen als die darin angegebenen Hilfsmittel benutzt habe.

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Sadaf Qayyum