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

DISSERTATION

Zur Erlangung des akademischen Grades eines
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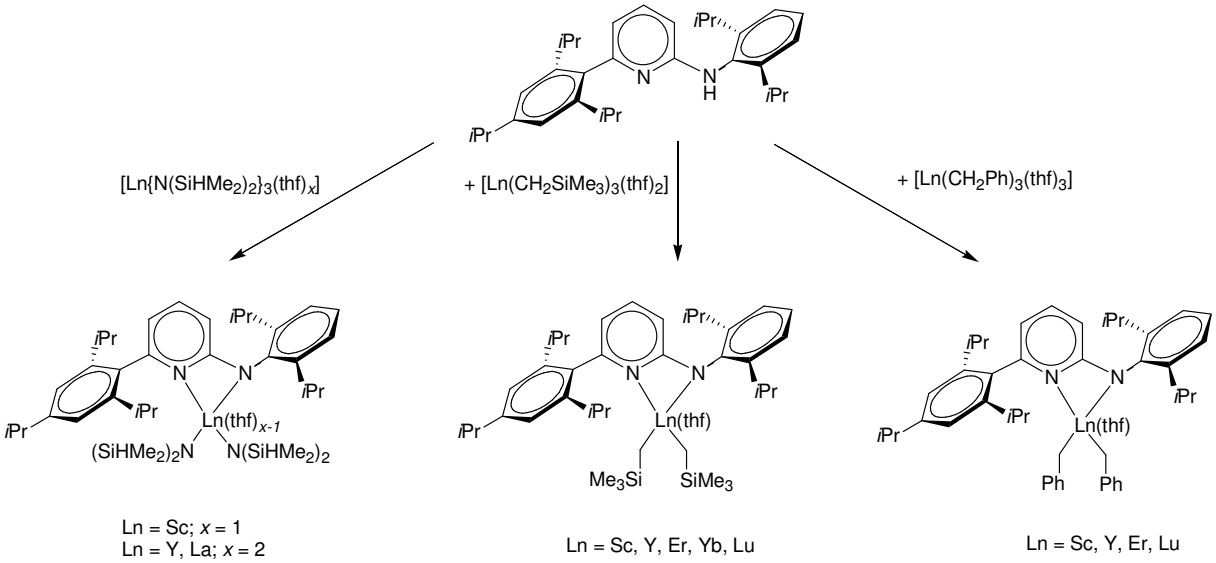
1. Zusammenfassung

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



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

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

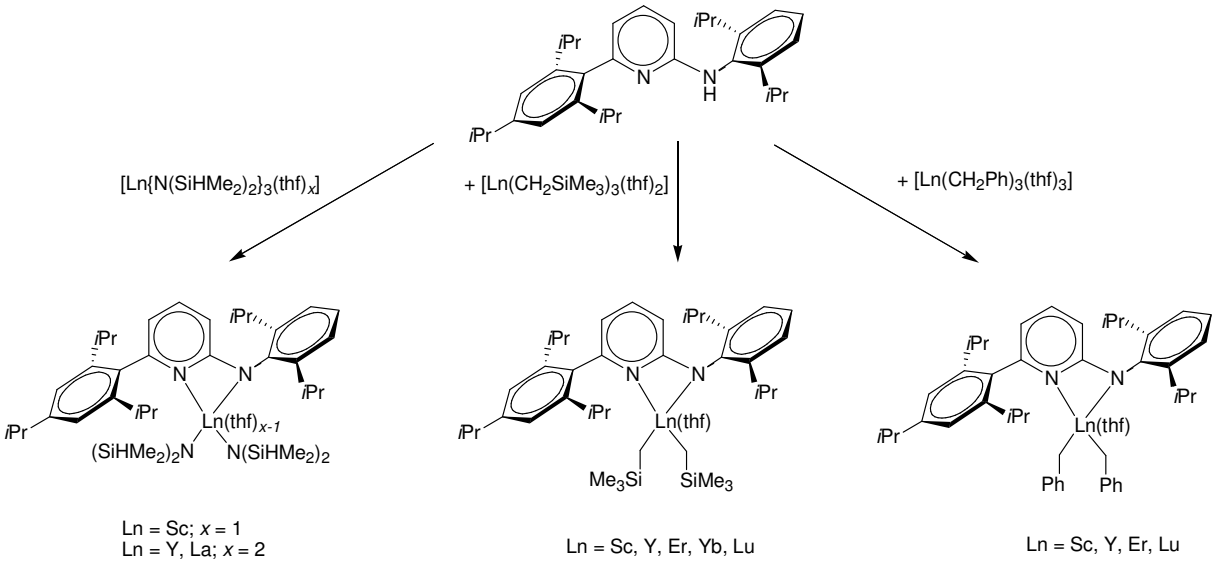
Dialkylkomplexe, stabilisiert durch Aminopyridinato-Liganden, reagieren mit Aniliniumborat unter Alkaneliminierung zu Organolanthanoid-Kationen. Diese wurden durch Stabilisierung mit THF isoliert und charakterisiert. Die Dibenzylkomplexe des Scandiums und Erbiums

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

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

Summary

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



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

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

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

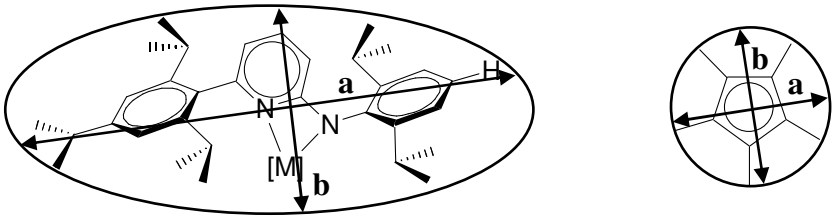
could even obtain isotactically enriched 3,4-polyisoprene through appropriate choice of the polymerization conditions (cocatalyst, polymerization temperature). The aminopyridinate-stabilized diamide of scandium can polymerize isoprene in the presence of anilinium borate and trialkylaluminium compounds,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

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

2. Introduction

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

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



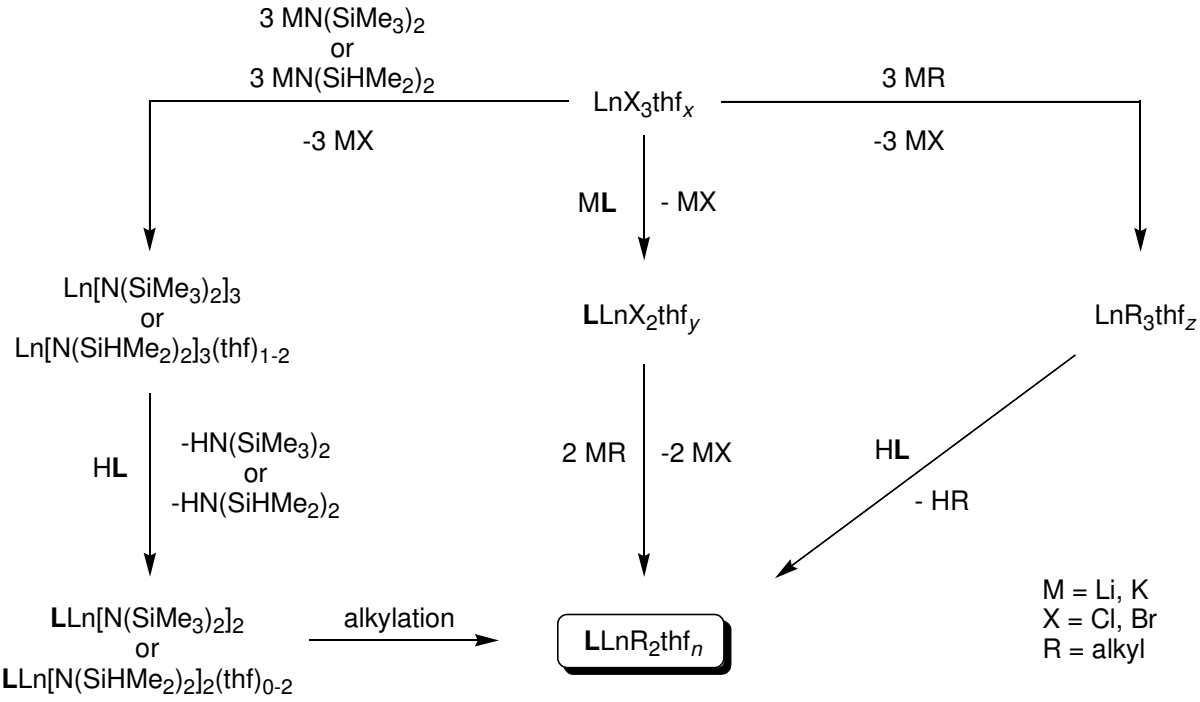
Scheme 2.1. Comparison of the steric demand of deprotonated Ap*H with Cp*.

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

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

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

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



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

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

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

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