

Rare-Earth Metal Phenyl(trimethylsilyl)amide Complexes

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The reactions of common rare-earth metal chloride, borohydride, and triflate precursors – $\text{LnCl}_3(\text{thf})_x$, $\text{Ln}(\text{BH}_4)_3(\text{thf})_3$, and $\text{Ln}(\text{OTf})_3$ – with alkali metal amide complexes $\text{M}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ ($\text{M}[\text{NRR}']$; $\text{M} = \text{Li}, \text{K}$) were investigated in thf or hexane as a solvent. A diverse range of products was obtained comprising alkali metal-free mono(rare-earth metal) complexes $\text{Y}[\text{NRR}']\text{Cl}_2(\text{thf})_3$ and $\text{Ln}[\text{NRR}']_2(\text{BH}_4)(\text{thf})$ ($\text{Ln} = \text{Nd}, \text{La}$), as well as the mononeodymium ate complex $\{\text{Nd}[\text{NRR}']_2(\text{BH}_4)_2\}\{\text{Li}(\text{thf})_4\}$ and polymeric ate complexes

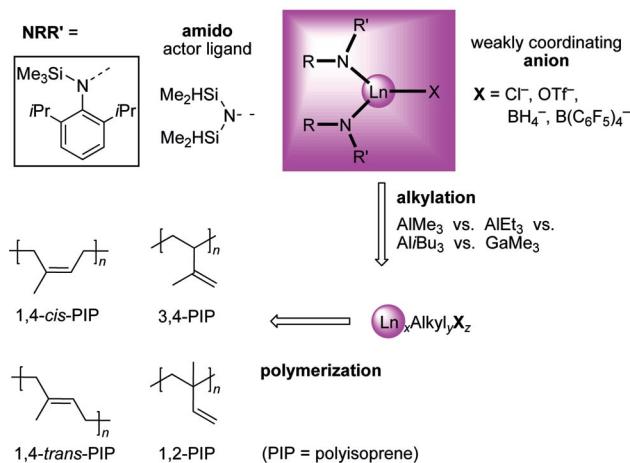
$\{\text{La}[\text{NRR}']_2(\text{thf})(\mu\text{-Cl})\text{K}(\text{thf})_2(\mu\text{-Cl})\}_n$ and $\{\text{Nd}[\text{NRR}']_2(\mu\text{-BH}_4)\text{Li}(\text{thf})_2(\mu\text{-BH}_4)\}_n$. All compounds were characterized by NMR (^1H and ^{13}C) and FTIR spectroscopy, elemental and X-ray structure analyses. The lithium salts $\text{Li}[\text{NRR}'](\text{thf})_3$ and $\text{Li}_4(\text{OTf})_4(\text{thf})_6$ were isolated as side products and structurally characterized. The homoleptic complex $\text{La}[\text{NRR}']_3$ was prepared following two synthesis protocols in hexane, either by reacting $\text{Ln}[\text{NRR}']_2(\text{BH}_4)(\text{thf})$ with 1 equiv. of $\text{K}[\text{NRR}']$ or treatment of $\text{LaCl}_3(\text{thf})_{1.25}$ with 3 equiv. of $\text{K}[\text{NRR}']$.

Introduction

Heteroleptic rare-earth metal complexes bearing amido and chloro ligands not only display useful synthesis precursors according to protonolysis (that is amine elimination) reactions,^[1] but can also be directly converted into efficient polymerization catalysts by reaction with organoaluminum compounds.^[2] Recently, we described such a silylamide-based *chlorination–alkylation* sequence which led to the precipitation and isolation of amorphous solids $[\text{Ln}_a\text{Al}_b\text{Me}_c\text{Cl}_d]_n$ ($a + b = 1$, $a > b$; $c + d = 3$, $d > c$) supposedly the active species in 1,3-diene polymerization.^[3] In this previous paper we also addressed the implications of the rare-earth metal cation size – neodymium showing the highest activity – the solvent effect (toluene vs. hexane), and the superior activation (“*cis-directing*”) behavior of the chloro ligand to the borato ($[\text{B}(\text{C}_6\text{F}_5)_4]$) ligand. Due to extensive ligand redistribution reactions it was difficult to control the $\text{Ln}/\text{Me}/\text{Cl}$ ratio in the precipitates of such organoaluminum-mediated $\text{Ln-NR}_2 \rightarrow \text{Ln-alkyl}$ transformations, which crucially affects the polymer characteristics. Additionally, occlusion of nitrogen- and aluminum-containing co-products was attributed to instant and rapid precipitation. The originally used mixed silylamide/chloride complexes were obtained by reaction of $\text{LnCl}_3(\text{thf})_x$ with 2 equiv. $\text{LiN}(\text{SiHMe}_2)_2$, which for scandium and yttrium, however, afforded a mixture of the tris(amido) derivatives $\text{Ln}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})_x$ and dimeric $[\text{Ln}\{\text{N}(\text{SiHMe}_2)_2\}_2]_2(\mu\text{-}$

$\text{Cl})(\text{thf})_2$. For the larger rare-earth metal center neodymium, even a trimetallic cluster, $[\text{Nd}\{\text{N}(\text{SiHMe}_2)_2\}(\text{thf})_2\text{-Nd}[\text{N}(\text{SiHMe}_2)_2]_2(\mu_2\text{-Cl})_2(\mu_3\text{-Cl})_2\{\mu\text{-N}(\text{SiHMe}_2)_2\}]_n$, was obtained. In order to avoid uncontrolled ligand redistribution already at this early stage we set out to investigate the accessibility of well-defined mixed silylamide/chloride complexes derived from the bulky phenylsilylamido ligand $[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$.^[4–11] At the same time, we wanted to further examine the effect of anions X different from chloro, e.g., OTf^- and BH_4^- . Scheme 1 summarizes these ideas of new precursor complexes with fixed $\text{N}/\text{Ln}/\text{X}$ ratios of relevance for 1,3-diene polymerization according to *cationization–alkylation* sequences.

AmidoAnionAlkylation Interplay in Isoprene Polymerization



Scheme 1. AmidoAnionAlkylation (AAA) interplay in rare-earth metal precatalysts for isoprene polymerization.

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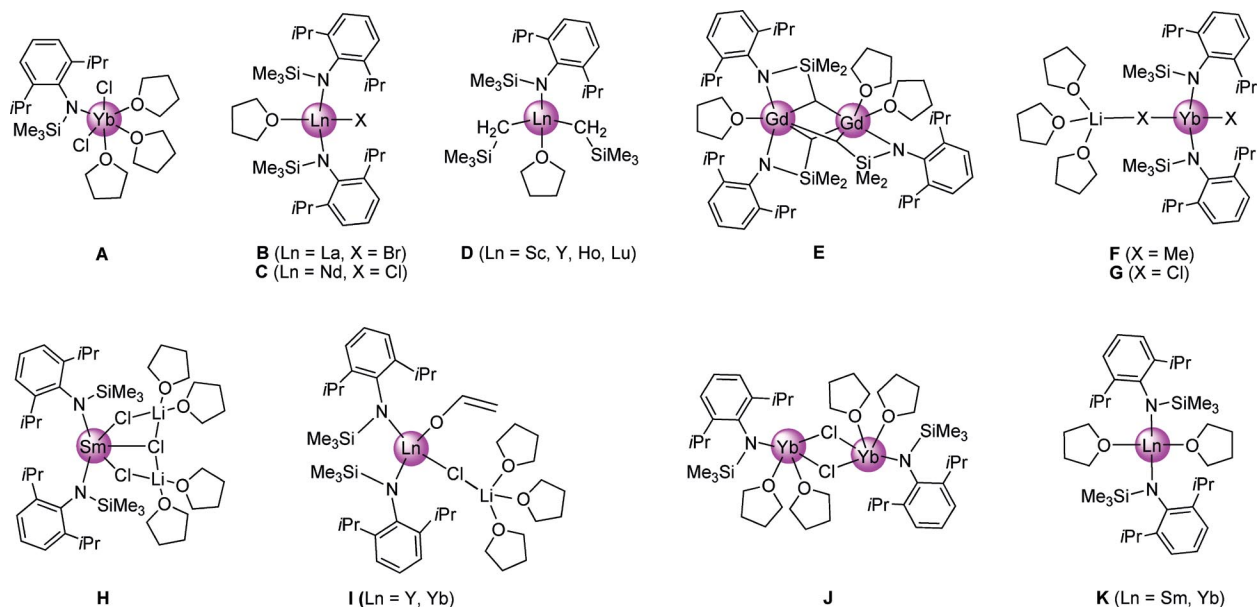


Figure 1. Structurally characterized rare-earth metal(III) complexes **A**,^[5] **B**,^[6] **C**,^[7] **D**,^[8] **E**,^[8] **F**,^[9] **G**,^[5] **H**,^[5] and **I**^[10] featuring the [N(SiMe₃)-(C₆H₃iPr₂-2,6)] ligand. Depicted are also two lanthanide(II) derivatives, **J**^[5] and **K**.^[11]

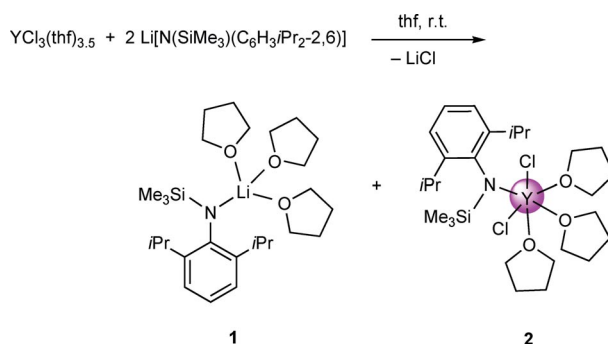
In 1995, Schumann et al. initially reported on lanthanide(III) amide complexes featuring [N(SiMe₃)(C₆H₃R₂-2,6)] (R = *i*Pr, Me, H) ligands.^[7] Bulky *i*Pr groups in 2,6-position of the aryl ligand facilitated the isolation of Nd[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂Cl(thf) (**C**, Figure 1) with a defined NR₂/Cl ratio of 2:1 in high yield and free of ligand redistribution products. It can be anticipated that this bulky amido ligand sterically saturates the large neodymium cation efficiently, making it less accessible for AlMe₃. This might slow down the alkylation reaction and facilitate the formation of well-defined and aluminum-free [Me₂NdCl]_{*n*}. In the present work we studied the accessibility of analogous phenyltrimethylsilylamide complexes Ln[N(SiMe₃)(C₆H₃iPr₂)]₂X for several rare-earth metal centers (Ln = Nd, La, Y) with varying anions (X = Cl, BH₄, OTf). Keeping in mind that the synthesis of such complexes is hampered by salt incorporation (**F** and **H**, Figure 1) or even C–H activation (**E**, Figure 1), the effect of solvent and distinct alkali metal amide precursors on the product formation was investigated.

Results and Discussion

Heteroleptic Complexes with Amido and Chloro Ligands

Salt metathesis reactions of some lanthanide chlorides with Li[N(SiMe₃)(C₆H₃R₂-2,6)] (R = H, Me, *i*Pr) have been reported previously by Schumann et al.^[7] Crucial for the product formation and in particular for the number of Ln-coordinating amido ligands is hereby the type of substitution of the aryl moiety in the 2- and 6-positions. Hydrogen substituents led to the isolation of the tris(amido) complexes Ln[N(SiMe₃)(C₆H₅)]₃(thf)_{*x*}, methyl groups gave the ate species Nd[N(SiMe₃)(C₆H₃Me₂-2,6)]₂(thf)(μ-Cl)₂Li(thf)₂, while the bulkier *i*Pr substituents afforded heterolep-

tic ate-free complex **C** (Figure 1). From the analogous reaction of YbCl₃ with 2 equiv. of Li[N(SiMe₃)(C₆H₃iPr₂-2,6)] compound **G** (Figure 1) was isolated and structurally characterized.^[5] The latter result confirmed that there is basically enough space around the Yb³⁺ ion to coordinate two amido ligands. In our hands, the 2-equiv. reaction for the larger Y³⁺, however, gave the mono(amido) derivative **2** (Scheme 2, Figure 2).



Scheme 2. Reaction of YCl₃(thf)_{3.5} with 2 equiv. of Li[N(SiMe₃)-(C₆H₃iPr₂-2,6)].

NMR investigations of the crude reaction product indicated a mixture of compounds, from which complex **2** could be isolated by extraction with hexane, and unequivocally characterized. The observed product mixture points toward the additional formation of ate complexes analog to compound **G** (Figure 1),^[5] which considerably affects the reproducibility of compound **2**. In the same reaction, excess lithium amide co-crystallized as the tris(thf) adduct Li[N(SiMe₃)(C₆H₃iPr₂-2,6)](thf)₃ (**1**) (Scheme 2, Figure 2). In accordance with the previously reported ytterbium derivative (**A**, Figure 1) compound **2** can be synthesized in higher yield by use of 1 equiv. of Li[N(SiMe₃)(C₆H₃iPr₂-2,6)].

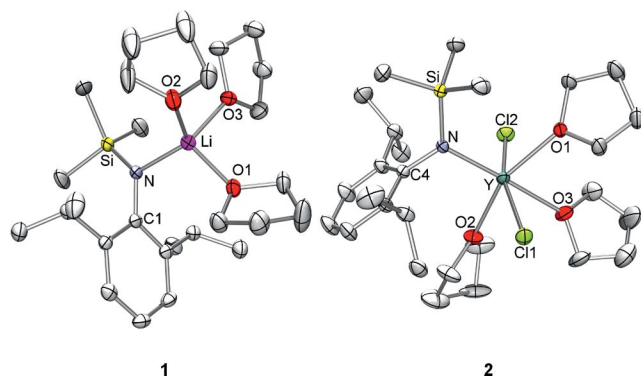


Figure 2. Solid-state structures of complexes $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)](\text{thf})_3$ (**1**) and $\text{Y}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]\text{Cl}_2(\text{thf})_3$ (**2**). Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

However, the obtained crystalline product **2** was still contaminated with small amounts of the lithium amide as indicated by its microanalysis and NMR spectra.

X-ray structural data of $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]$ derivatives have been reported previously. When crystallized from non-donor solvents such as hexane the dimeric species $\{\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]\}_2$ was obtained featuring a four-membered $[\text{Li}-\text{N}]_2$ ring and close $\text{Li}\cdots\text{H}$ and $\text{Li}\cdots\text{C}$ contacts.^[12] Monomeric complex $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)](\text{py})(\text{OEt}_2)$ features a lithium center which is coordinated in an approximate trigonal-planar fashion exhibiting additional short contacts to the *ipso* carbon atoms of the phenyl ring.^[13] In complex **1** the coordination sphere of the lithium atom is fully saturated by three thf molecules. The Li–N distances are comparable for all three complexes [**1**, 1.986(4) Å; $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)](\text{py})(\text{OEt}_2)$,^[13] 1.916(9) Å; $\{\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]\}_2$, 1.961(4) Å], and the Li–N–C angles lie in the range of 108.4(2)° (**1**) to 109.1(2)° ($\{\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]\}_2$).^[12]

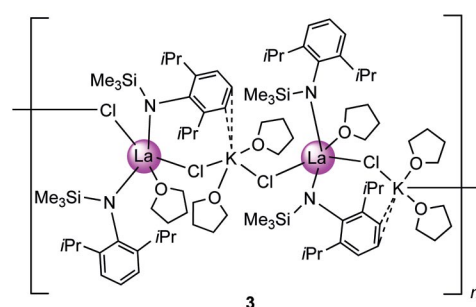
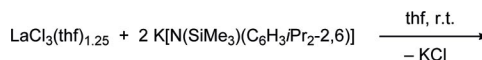
Compound **2** crystallizes in the monoclinic space group $P2_1/n$ (see Figure 2, Tables 1 and 7) and is isostructural to the yttrium compound **A** (Figure 1).^[5] The coordination geometry is best described as distorted octahedral. As expected the bond angles are all similar and the difference in the Ln–N and Ln–Cl distances between the Yb and Y derivatives follows the trend in the respective ionic radii (Table 1).

Table 1. Selected bond lengths [Å] and angles [°] for **2** and **A**.

	2 (Ln = Y)	A (Ln = Yb)
Ln–N	2.260(2)	2.218(5)
Ln–Cl1	2.54945(5)	2.550(2)
Ln–Cl2	2.5793(5)	2.544(2)
N–Ln–Cl1	98.51(4)	97.8(2)
N–Ln–Cl2	98.97(4)	98.6(2)
Cl1–Ln–Cl2	162.38(2)	163.40(6)
Ln–N–Si	124.1(3)	123.78(7)

Attempted preparation of the chloro analog of $\text{La}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]_2\text{Br}(\text{thf})$ (**B**, Figure 1), following the same reaction procedure described for **C** (Figure 1) utilizing $\text{LaCl}_3(\text{thf})_{1.25}$ and 2 equiv. of $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]$ in

thf, gave also a product mixture. Lithium complex **1** was the only compound that crystallized from the hexane fractions. Exchanging the lithium amide for the potassium congener $\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]$ according to the procedure for the preparation of **B** (Figure 1)^[6] did not yield the anticipated monomeric species. Instead, crystals of polymeric $\{\text{La}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]_2(\text{thf})(\mu\text{-Cl})\text{K}(\text{thf})_2(\mu\text{-Cl})\}_n$ (**3**) could be grown directly from the reaction mixture (Scheme 3). ^1H and ^{13}C NMR spectroscopic measurements of the crude reaction mixture further confirmed compound **3** as the main reaction product.



Scheme 3. Reaction of $\text{LaCl}_3(\text{thf})_{1.25}$ with 2 equiv. of $\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3i\text{Pr}_2-2,6)]$.

An X-ray structure analysis revealed that compound **3** crystallizes as bent polymer chains of alternating lanthanum and potassium metal centers bridged via chlorido ligands. The geometry of the five coordinate lanthanum metal center can best be described as heavily distorted trigonal bipyramidal with O1 from thf and N1 from one amido ligand at the apical positions and N2 of the second amido as well as the two bridging chloro ligands Cl(1/2) in the equatorial plane. A deviation of the ideal symmetry is apparent from a bond angle of 145.46(8)° along the N1–La–O1 axis and the bond angles of Cl1–La–Cl2 [132.08(3)°], Cl2–La–N2 [126.16(7)°], and Cl1–La–N2 [96.10(7)°] of the trigonal basis. The potassium centers are coordinated by the two bridging chlorides [$\text{K}-\text{Cl}(1/2)$, 2.997(2) and 3.059(2) Å] as well as two thf molecules [$\text{K}-\text{O}(2/3)$, 2.731(3) and 2.697(3) Å]. Furthermore an interaction of K with the π -system of one phenyl ring (C3 and C4) in the ligand backbone is indicated. Similar potassium arene interactions were reported for $\text{K}[\text{La}(\text{OC}_6\text{H}_3i\text{Pr}_2-2,6)_4]$ ^[14] with K–C interatomic distances of 3.235(2) Å and 3.330(4) Å which are about the same as in **3** [$\text{K}-\text{C}3$, 3.212(4) Å and $\text{K}-\text{C}4$ 3.366(4) Å]. In the latter publication these interactions are described as rather modest compared to the potassium–arene interactions in other systems ranging from 3.018(8) Å in $\text{K}[\text{Er}(\text{OC}_6\text{H}_3i\text{Pr}_2-2,6)_4]$ ^[14] to 3.59 Å [$\text{K}(\text{dibenzo-18-crown-6})(\text{GaMe}_2\text{NCS})(\text{C}_6\text{H}_6)_2$].^[15] A section of the polymeric structure of **3** is shown in Figure 3 and selected bond lengths and angles are listed in Table 2.

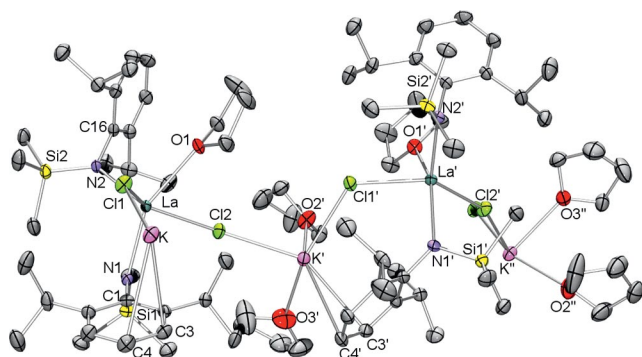


Figure 3. Solid-state structure of complex $\{ \text{La}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2(\text{thf})(\mu\text{-Cl})\text{K}(\text{thf})_2(\mu\text{-Cl}) \}_n$ (**3**). Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for **3**.

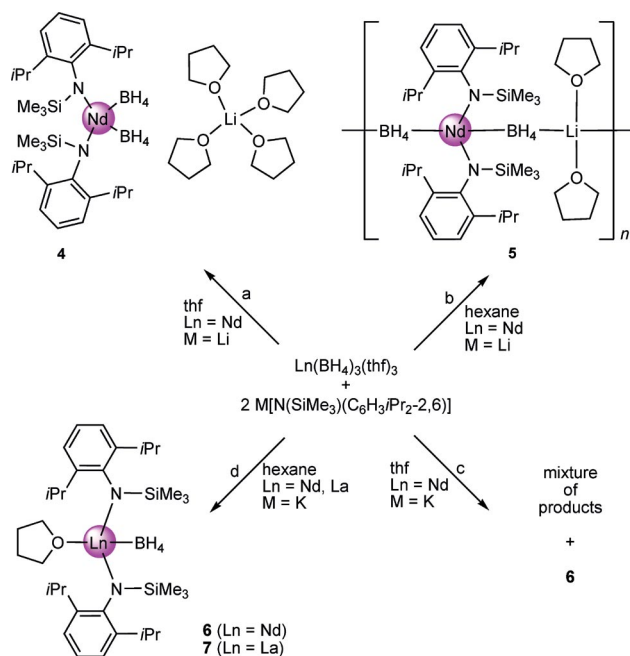
Bond lengths		Bond angles	
La–Cl1	2.7449(8)	Cl1–La–Cl2	132.08(3)
La–Cl2	2.8479(8)	N1–La–N2	114.51(9)
La–N1	2.424(3)	O1–La–N1	145.46(8)
La–N2	2.367(3)	O1–La–N2	99.53(8)
La–O1	2.611(2)	Cl1–La–O1	80.73(6)
K–Cl1	2.997(2)	Cl1–La–N2	96.10(7)
K–Cl2	3.059(2)	Cl2–La–N2	126.16(7)
K–C3	3.212(4)	La–Cl2–K	124.45(3)
K–C4	3.366(4)	La–Cl1–K	157.37(4)

Heteroleptic Complexes with Amido and Borohydrido Ligands

Complexes $\text{Ln}(\text{BH}_4)_3(\text{thf})_3$ not only display versatile synthesis precursors^[16] but also are employed as precatalysts in polymerization reactions.^[17] Following the idea of employing anions different from chloride (Scheme 1) we treated the neodymium tris(borohydride) complex $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ with 2 equiv. of $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ (**a**, Scheme 4).

Instant reaction was indicated by a color change of the solution from purple to blue. Blue crystals of $[\text{Nd}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)\}_2(\text{BH}_4)_2][\text{Li}(\text{thf})_4]$ (**4**) could be harvested directly from the thf reaction mixture in high yield and separated from co-crystallized colorless $\text{LiBH}_4(\text{thf})_x$.^[18] The exact molecular composition of the obtained product could be derived from a single crystal structure determination showing two $[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ ligands and two BH_4 anions coordinated to the neodymium metal center. The anionic fragment $\{[\text{Nd}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)\}_2(\text{BH}_4)_2]\}$ of ate complex **4** is charge balanced by a $\text{Li}(\text{thf})_4$ ion (Figure 4).

Previously reported $\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2\text{Cl}(\text{thf})$ (**C**, Figure 1) is somewhat comparable to **4** featuring also a four-coordinate Nd metal center.^[7] Both complexes display distorted tetrahedral coordination geometries as evidenced, e.g., by the large angle N1–Nd–N2 of 129.64(5)° in **4** [C: N1–Nd–N2 116.60(7)°, largest deviation: N2–Nd–O 121.03(6)°]. However, complexes **4** and **C** show distinct Nd–N distances of 2.370(2)/2.350(2) Å and 2.276(2)/2.264(2) Å,



Scheme 4. Synthesis protocols for mixed amide/borohydride complexes of neodymium and lanthanum.

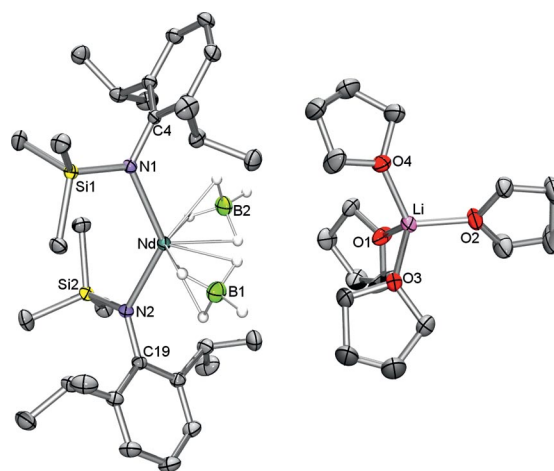


Figure 4. Solid-state structure of complex $[\text{Nd}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)\}_2(\text{BH}_4)_2][\text{Li}(\text{thf})_4]$ (**4**). Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are except for the BH_4 moieties omitted for clarity.

respectively (Table 3). Short contacts between the neodymium center and the *ipso* carbon atoms of the aryl moiety were observed in **C** [2.814(2) Å, 3.129(2) Å] but do not prevail in **4**. A similar ate species was found for the neodymium borohydride guanidinate complex $[(\text{Me}_3\text{Si})_2\text{NC}(\text{N-Cy})_2]_2\text{-Nd}(\mu\text{-BH}_4)_2\text{Li}(\text{thf})_2$.^[19,20] However, in the latter complex the BH_4 ligands are bridging the neodymium and lithium metal centers giving rise to markedly longer Nd–B distances of 2.739(1) and 2.925(1) Å than in **4** [2.631(3) Å, 2.631(2) Å]. The tridentate coordination mode of the BH_4 ligands is further corroborated by the IR spectrum of **4** (B-H 2432 cm^{-1} , strong singlet; B-H_b 2213 cm^{-1} , broad).^[21]

Table 3. Selected bond lengths [Å] and angles [°] for **4** and **C**.

	4	C
Nd–N1	2.3700(15)	2.276(2)
Nd–N2	2.3498(15)	2.264(2)
Nd–B1	2.631(3)	–
Nd–B2	2.631(2)	–
Nd–C _{ipso}	3.394(3); 3.387(2)	2.814(2); 3.129(2)
N1–Nd–N2	129.64(5)	116.60(7)
Nd–N1–Si1	115.45(7)	125.7(1)
Nd–N2–Si2	115.05(8)	139.4(1)
Nd–N1–C _{ipso}	124.9(2)	113.4(1)
Nd–N2–C _{ipso}	125.5(2)	96.7(1)
N1–Nd–N2	129.64(5)	116.60(7)

Having in mind that chloro complex **C** is hexane soluble^[7] we anticipated that performing the reaction of $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ with $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_{2-2,6})]$ in hexane might lead to an ate complex free species via precipitation of the lithium borohydride by-product. Moreover, the neodymium precursor of choice already carries three molecules of thf to a) enhance the solubility in hexane and b) make further addition of thf, which would support ate complex formation, unnecessary.

Accordingly, $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ was treated with 2 equiv. of the lithium amide salt $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_{2-2,6})]$ in hexane (**b**, Scheme 4). Again, color change of the suspension from pale purple to blue proved an instant reaction. Upon separation of the precipitate and concentrating of the solution in vacuo, blue crystals of compound **5** could be grown at -35°C from the hexane solution. Due to the paramagnetism of the neodymium metal center the ^1H and ^{13}C NMR spectra were not conclusive. Especially the proton resonances appeared well separated within a signal range from $\delta = 25$ to -10 ppm, however, could not be assigned.

The solid-state structure of **5** consists of polymeric chains of composition $\{\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_{2-2,6})]_2(\mu\text{-BH}_4)\text{Li}(\text{thf})_2(\mu\text{-BH}_4)\}_n$ with alternating neodymium and lithium metal centers bridged by borohydrido units (BH_4) (Figure 5, a). The bridging mode of the BH_4 moieties can be derived from the pattern of the B–H stretching bands as described by Marks et al.^[21] Two medium bands at 2360 and 2338 cm^{-1} and a very weak band at 2430 cm^{-1} in the IR spectrum of **5** are indicative of a mixed bridging mode. This means that the borohydrido ligands bind to the neodymium and lithium metal centers in a $\eta^2\text{-}\eta^2$ and a $\eta^2\text{-}\eta^1$ fashion (Figure 5, b).

Like in complex **4** (Figure 4) two borohydrido and two amido ligands accomplish a distorted tetrahedral geometry at the neodymium metal center in **5**. The Nd–N bond lengths are slightly shorter in **5** compared to **4** while the Nd– BH_4 distances are elongated due to the bridging nature of these moieties in **5**. Furthermore, in complex **5** the *ipso*-carbon atoms C1 and C16 of the phenyl rings are in close proximity to the neodymium center analogous to complex **C** while this interaction is not observed in **4** [Nd–C1 $2.847(2)\text{ Å}$, Nd–C16 $3.229(2)\text{ Å}$ in **5**; Nd–C1 $2.814(2)\text{ Å}$, Nd–C16 $3.129(2)\text{ Å}$ in **C**; Nd–C1 $3.394(2)\text{ Å}$, Nd–C16 $3.387(2)\text{ Å}$ in **4**]. The pronounced $\text{Nd}\cdots\text{C1}_{ipso}$ interaction is

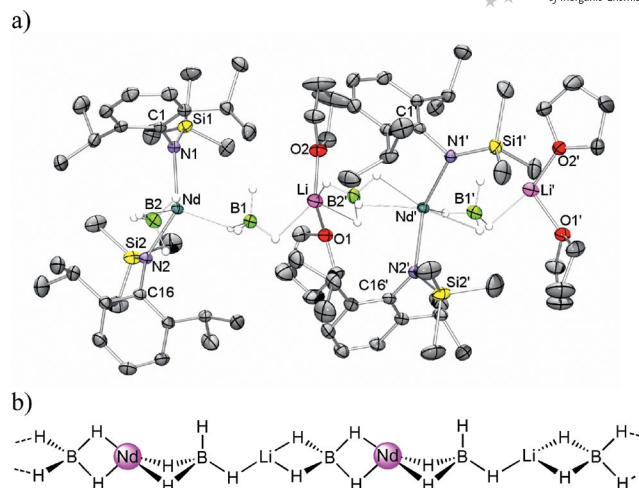


Figure 5. a) Section of the molecular structure of complex $\{\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_{2-2,6})]_2(\mu\text{-BH}_4)\text{Li}(\text{thf})_2(\mu\text{-BH}_4)\}_n$ (**5**). Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms except for the BH_4 moiety are omitted for clarity. b) Borohydrido bridging modes in **5** as suggested by FTIR spectroscopy.

further evidenced by an acute angle Nd–N1–C1 of $97.03(9)^\circ$ and by the markedly distorted tetrahedral bonding angles N1–Nd–B1 of $98.88(5)^\circ$ and N2–Nd–B2 of $99.25(5)^\circ$. The lithium metal centers also adopt a distorted tetrahedral geometry: two thf molecules and two bridging borohydrido ligands show bond angles ranging from $103.92(3)^\circ$ to $122.2(2)^\circ$ and average Li–O and Li–B bond lengths of 1.936 Å and 2.510 Å , respectively. Selected bond lengths and angles of **4** and **5** are listed and compared in Table 4.

Table 4. Selected bond lengths [Å] and angles [°] for **4** and **5**.

	4	5
Distances		
Nd–N1	2.370(2)	2.297(2)
Nd–N2	2.350(2)	2.311(2)
Nd–B1	2.631(2)	2.720(2)
Nd–B2	2.631(3)	2.693(2)
Nd–C1	3.394(2)	2.847(2)
Nd–C16	3.387(2)	3.229(2)
Li–O1		1.944(3)
Li–O2		1.928(3)
Li–B1		2.600(4)
Li–B2		2.420(3)
Angles		
N1–Nd–B1	108.39(7)	98.88(5)
N2–Nd–B2	108.22(7)	99.25(5)
Nd–N1–C1	124.9(2)	97.03(9)
B2–Li–B1		107.6(2)
O2–Li–O1		105.5(2)

Since the choice of the alkali metal markedly affected the reaction outcome for the amido–chloro derivatives (vide supra), $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ was next treated with 2 equiv. of $\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_{2-2,6})]$ in thf or hexane at ambient temperature (**c** and **d**, Scheme 4). Both reactions produced pale purple suspensions, which turned green within a few

seconds indicating an immediate reaction. The green solid, which was obtained from the “thf reaction” showed several resonances for the trimethylsilyl groups in the ^1H NMR spectrum, clearly indicating a product mixture. However, after dissolving the crude product mixture in a small amount of thf and storing it at -35°C for six weeks a few blue single crystals formed. An X-ray structure analysis unequivocally proved the formation of the envisaged product $\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2(\text{BH}_4)(\text{thf})$ (**6**). In contrast, the “hexane reaction” (**d**, Scheme 4) afforded blue crystals within one day at -35°C in 64% crystallized yield. An X-ray crystallographic study proved that complex **6** can be reproducibly synthesized via this approach, however, under these reaction conditions as the main product. The ^1H NMR spectrum revealed well separated peaks in a signal range from 25 ppm to -8 ppm with a similar pattern as observed for **5**. Using the same reaction protocol (**d**, Scheme 4), the lanthanum analog $\text{La}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2(\text{BH}_4)(\text{thf})$ (**7**) was synthesized. In comparison to the potassium amide precursor the ^1H and ^{13}C NMR spectra of diamagnetic **7** show two distinct features: a) two sets of signals for the methyl groups of the isopropyl substituents due to the hindered rotation around the C–N axis of the 2,6-diisopropylphenyl moiety; b) a broad quartet ($w_{1/2} \approx 208$ Hz) for the borohydrido ligand, showing H–B coupling [$I(^1\text{H}) = 3/2$].

Complexes **6** (Nd) and **7** (La) are isostructural, constituting monomeric species in the solid state (Figure 6), quite different from ate complex **4** (Nd) and polymeric complex **5** (Nd). The overall structural features are closely related to those of **B** and **C** (Figure 1). A comparison of important bond lengths and angles of all four complexes **6**, **7**, **B**, and **C** is presented in Table 5.

The geometry around the four coordinate neodymium and lanthanum metal centers is again distorted tetrahedral with bond angles ranging from $96.35(5)^\circ$ to $121.84(4)^\circ$ in **6** and $99.1(2)^\circ$ to $122.03(4)^\circ$ in **7**, respectively. While this distortion from ideal symmetry is more pronounced than in complex $\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2\text{Cl}(\text{thf})$ (**C**),^[7] the bond lengths match well for isostructural complexes **B**, **C**, **6**, and **7**, considering the difference in ion size.^[22] The coordination mode of the BH_4 moieties to the respective neo-

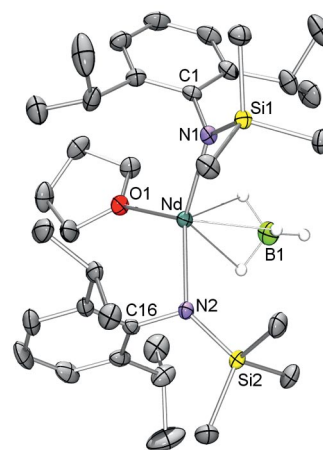


Figure 6. Molecular structure of $\text{Ln}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2(\text{BH}_4)(\text{thf})$ ($\text{Ln} = \text{Nd}$ (**6**), La (**7**)) represented by complex $\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2(\text{BH}_4)(\text{thf})$. Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms except for the BH_4 moiety are omitted for clarity.

dymium or lanthanum metal center could be assigned by FTIR spectroscopy and verified through the crystal structure. The terminal hydrogen–boron stretching mode was found at 2454 cm^{-1} for the neodymium complex and at 2448 cm^{-1} for the lanthanum complex. Bands at $2204/2144\text{ cm}^{-1}$ (**6**) as well as at $2201/2143\text{ cm}^{-1}$ (**7**) could be assigned to the two bridging hydrogen–boron stretching modes. Using the criteria published by Marks et al.^[21] a tridentate coordination of the tetrahydroborate is suggested.

Interactions between the lanthanide centers and the *ipso*-carbon atoms of the phenyl ring in the ligand backbone were reported for chloro derivative **C** and are also observable for borohydride complexes **6** and **7**. This is documented by close $\text{Ln}\cdots\text{C}_{\text{ipso}}$ contacts and acute angles $\text{Ln1-N-C}_{\text{ipso}}$ (Table 5).

Attempted Synthesis of Heteroleptic Complexes with Amido and Triflate Ligands

Lanthanide triflates have been exploited for the synthesis of various organolanthanide compounds.^[23] Belot et al.

Table 5. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for **6**, **7**, **B**, and **C**.

	6 ($\text{Ln} = \text{Nd}$, $\text{X} = \text{B}$)	7 ($\text{Ln} = \text{La}$, $\text{X} = \text{B}$)	B ($\text{Ln} = \text{La}$, $\text{X} = \text{Br}$)	C ($\text{Ln} = \text{Nd}$, $\text{X} = \text{Cl}$)
Ln-N1	2.303(2)	2.358(2)	2.335(3)	2.276(2)
Ln-N2	2.282(2)	2.345(2)	2.332(3)	2.264(2)
Ln-O1	2.450(2)	2.510(2)	2.508(3)	2.445(1)
Ln-X1	2.603(2)	2.675(2)	2.8664(7)	2.617(1)
Ln-C1	2.927(2)	2.959(2)	3.181(3)	3.129(2)
Ln-C16	2.853(2)	2.883(2)	2.876(5)	2.814(2)
N1-Ln-N2	121.83(4)	122.03(4)	115.1(2)	116.60(7)
N1-Ln-X1	100.63(5)	99.22(6)	109.62(8)	103.98(5)
N1-Ln-O1	114.78(4)	115.83(4)	97.5(2)	102.12(7)
N2-Ln-X1	96.35(5)	95.40(6)	102.14(9)	103.24(6)
N2-Ln-O1	116.39(4)	116.59(4)	117.5(2)	121.03(6)
O1-Ln-X1	99.66(5)	99.10(6)	115.5(2)	108.61(5)
Ln-N1-C1	100.94(8)	100.18(9)	113.3(2)	113.4(1)
Ln-N2-C16	98.10(8)	97.104(9)	97.0(3)	96.7(1)

stated explicitly the high yield synthesis of archetypal silylamide complexes $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Er}$) employing $\text{Ln}(\text{OTf})_3$.^[24] Our comprehensive studies on bis(dimethylsilyl)amide complexes $\text{Ln}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})_2$ revealed that the synthesis of pure compounds is extremely dependent on the solvent, the nature of the alkali metal salt, and choice of the rare-earth metal precursor.^[25,26] For example, use of $\text{La}(\text{OTf})_3$ and $\text{LiN}(\text{SiHMe}_2)_2$ gave complicated product mixtures, while the corresponding reaction with $\text{Y}(\text{OTf})_3$ yielded the tris(amido) derivative $\text{Y}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})_2$ only contaminated with LiOTf ^[25] and the donor solvent-free ate complex $\{\text{Y}[\text{N}(\text{SiHMe}_2)_2]_4\text{Li}\}_2$.^[26] Use of the bulkier $[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ ligand might counteract ligand scrambling and allow the isolation of putative complexes $\text{Ln}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_2(\text{OTf})(\text{thf})$. However, ^1H NMR spectroscopic investigations of the crude products obtained from the reactions of $\text{Ln}(\text{OTf})_3$ ($\text{Ln} = \text{Y}, \text{Nd}$) with 2 equiv. of $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ in thf showed mixtures of several species, which could not be unambiguously identified. The chemical shift of the SiMe_3 moiety of the neodymium congener ($\delta = -2.13$ ppm) was found to be almost identical to that of $\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]_3(\text{thf})$ ($\delta = -2.14$ ppm) and gave an indication of the formation of a neodymium amide species (for comparable compound **C**, Figure 1, no NMR spectroscopic data were given).^[7] Fractionate crystallization from thf solutions yielded only colorless crystals of side product $\text{Li}_4(\text{OTf})_4(\text{thf})_6$ (**8**), allowing for a partial enrichment of the rare-earth metal containing complexes. The putative yttrium or neodymium derivatives were nevertheless not accessible in pure form and unfortunately did so far not crystallize.

The high-yield formation of compound **8** is reproducible. Tetrameric **8** crystallizes in the monoclinic space group $P2_1/n$ (see Figures 7 and 8), with four $\text{Li}(\text{OTf})$ moieties assembled to three annelated eight-membered rings. For comparison, from the salt metathesis reaction of $\text{CpLu}(\text{OTf})_2(\text{thf})_3$ with $\text{LiCH}_2\text{SiMe}_3$ a polymeric side product, $[\text{Li}(\text{OTf})(\text{thf})]_n$, could be isolated.^[27] Crystals of the latter compound were grown from toluene solutions at ambient temperature (cf., **8**; thf, -35°C) and an X-ray structure analysis showed an oligomeric two-dimensional network, in which the individual oligomers are further arranged in layers. Again are eight-membered rings the prevailing structural motif, four of which are connected via $\text{Li}\cdots\text{O}=\text{S}$ bonds to form a 16-membered ring (Figure 7). Apparently, the different structural motifs of $\text{Li}_4(\text{OTf})_4(\text{thf})_6$ (**8**) and $[\text{Li}(\text{OTf})(\text{thf})]_n$ originate from the different number of coordinating thf molecules. In $[\text{Li}(\text{OTf})(\text{thf})]_n$ each of the lithium atoms carries one thf molecule, whereas in **8** two molecules thf are coordinated to the lithium cations in the outer eight-membered rings and only one to the lithium atoms in the inner ring. The formation of two different thf adducts of $[\text{Li}(\text{OTf})]$ is most likely caused by a solvent effect, i.e., toluene vs. thf. All bonds in **8** compare relatively well to those in $[\text{Li}(\text{OTf})(\text{thf})]_n$ and trifluoromethanesulfonic acid HOTf .^[27,28] The average S–O, C–F, and C–S distances are 1.430 Å, 1.321 Å, and 1.808 Å in **8**, 1.430 Å, 1.313 Å, and 1.821 Å in $[\text{Li}(\text{OTf})(\text{thf})]_n$, and 1.449 Å, 1.329 Å, and 1.833 Å for the free acid, respectively. Also the average O–S–C angles of 103.25° (**8**), 103.3° ($[\text{Li}(\text{OTf})(\text{thf})]_n$), and 104.0° (HOTf) are similar.

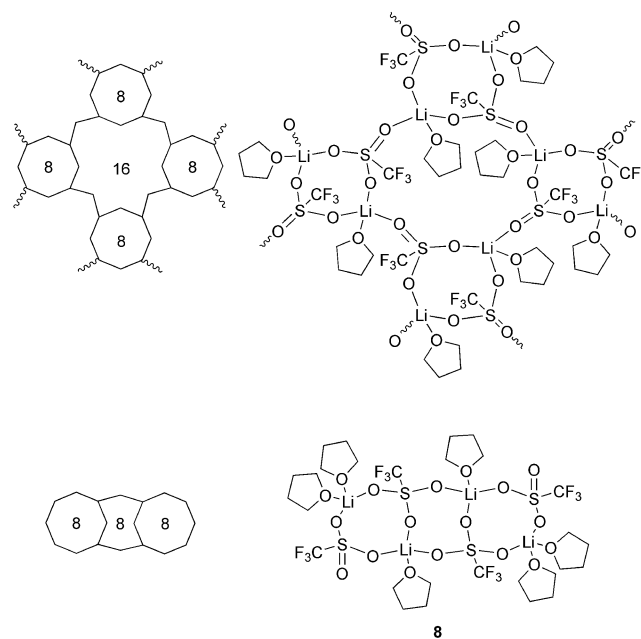


Figure 7. Structural motifs in lithium trifluoromethanesulfonates: $[\text{Li}(\text{OTf})(\text{thf})]_n$ ^[27] and $\text{Li}_4(\text{OTf})_4(\text{thf})_6$ (**8**).

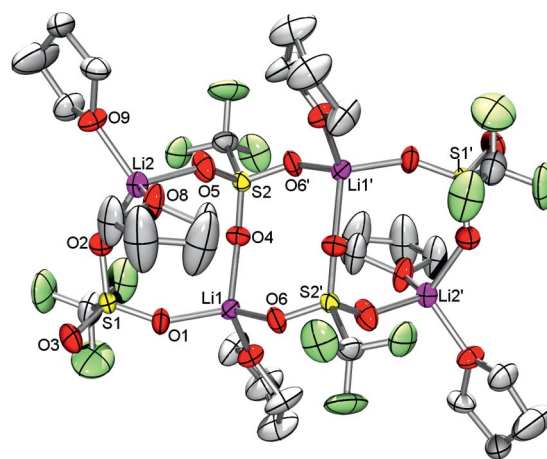


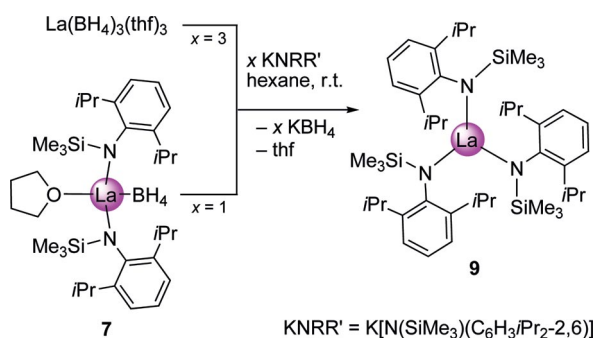
Figure 8. Solid-state structure of complex $\text{Li}_4(\text{OTf})_4(\text{thf})_6$ (**8**). Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

A Homoleptic Lanthanum Amide

Homoleptic amide complexes of the rare-earth metals are considered valuable synthesis precursors and the synthesis and characterization of such species is pursued for amides of the entire lanthanide series.^[4] Within the class of Ln^{III} tris(amide) complexes, donor-solvent free derivatives are of particular interest.^[29] Schumann et al.^[7] reported that homoleptic amide complexes of neodymium and lutetium bearing the bulky amido ligand $[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ were not accessible by reacting three equivalents of $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2-2,6)]$ with rare-earth metal trifluoromethanesulfonates.

(SiMe₃)(C₆H₃iPr₂-2,6)] with the respective lanthanide chlorides LnCl₃ (Ln = Nd, Lu). Instead the bis(amido) derivatives Ln[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂Cl(thf) [Ln = Lu, Nd (C: Figure 1)] were isolated. So far homoleptic species Ln[N(SiMe₃)(C₆H₃R₂-2,6)]₃ (Ln = Y, La, Nd, Sm, Eu, Tb, Dy, Er, Yb, Lu) were isolable for the less sterically demanding amido ligand where R = H. Herein the first successful synthesis of homoleptic La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₃ is presented.

Contrary to Schumanns reaction protocol based on LnCl₃ (Ln = Nd, Lu)^[7] and lithium amide in thf, we initially utilized the heteroleptic complex La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂(BH₄)(thf) (**7**) in a consecutive ligand exchange reaction with another equiv. of K[N(SiMe₃)(C₆H₃iPr₂-2,6)] in hexane (Scheme 5). After stirring at ambient temperature for 24 h the cloudy suspension was filtered, the solvent reduced, and the remaining solution stored at –35 °C. Colorless crystals formed within another 24 h and were examined by IR and NMR spectroscopy, elemental analysis, and X-ray crystallography. Both ¹H and ¹³C NMR spectroscopy as well as elemental analysis pointed toward the successful synthesis of putative La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₃ (**9**). The proton resonances are in the expected regions similar to those of the potassium amide K[N(SiMe₃)(C₆H₃iPr₂-2,6)]. As in the spectrum of La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂(BH₄)(thf) (**7**) two sets of signals are observed for the methyl groups of the isopropyl substituents indicating a rigid structure even in solution due to a hindered rotation around the C–N axis of the 2,6-diisopropylphenyl moieties. Compound **9** could be also obtained from the reaction of La(BH₄)₃·(thf)₃ with 3 equiv. of K[N(SiMe₃)(C₆H₃iPr₂-2,6)] in hexane (Scheme 5).



Scheme 5. Synthesis of the homoleptic lanthanum amide **9**.

The solid-state structure of **9** was determined by X-ray crystallography (Figure 9, Table 6), albeit twinned, twofold around direct axis 1 0 1 in a ratio 2:1. Refinement was performed on the main component only. A hoax electron density in close proximity to the metal center (4.26 e/Å³) reflects the anomalous effects of the twinning. The lanthanum metal center in **9** is coordinated by three amido ligands in a distorted trigonal planar fashion. All three amido ligands are tilted in such a way that the trimethylsilyl groups are located above and the 2,6-diisopropylphenyl moieties beneath the N1N2N3 plane. Two of the isopropyl carbon atoms of each phenyl ring, namely C10/C11, C22/C23, C37/

C38, lie as well in the N1N2N3 plane, while the lanthanum metal center is displaced from this plane by 0.665 Å towards the phenyl rings. This results in N–La–N bond angles ranging from 111.86(9)° to 113.10(9)°. The average La–N bond length of 2.373 Å is marginally elongated compared to those in **7** (2.351 Å) and **B** (2.334 Å). However, the interatomic La1...C_{ipso} distances 3.130(3) Å (C1), 3.110(3) Å (C16), and 3.129(3) Å (C31) appear in average elongated compared to those observed in **B**^[6] [3.181(3)/2.876(5) Å], in **C**^[7] [3.129(2)/2.814(2) Å] as well as in complex **7** (2.959(2)/2.883(2) Å). These pronounced secondary interactions are also indicated by more obtuse bond angles La–N–C_{ipso}.

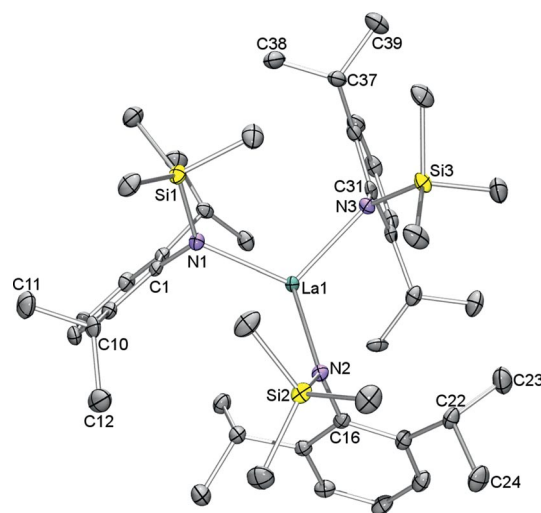


Figure 9. Molecular structure of complex La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₃ (**9**). Non-H atoms are represented by atomic displacement ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity.

Table 6. Selected bond lengths [Å] and angles [°] for **9**.

Bond lengths		Bond angles	
La–N1	2.379(3)	N1–La1–N2	111.86(9)
La–N2	2.369(3)	N2–La1–N3	112.43(9)
La–N3	2.372(3)	N3–La1–N1	113.10(9)
La–C1	3.130(3)	La1–N1–C1	108.2(2)
La–C16	3.110(3)	La1–N2–C16	107.4(2)
La–C31	3.129(3)	Si3–N3–C31	120.7(2)
		La1–N1–Si1	128.5(1)
		La1–N2–Si2	129.5(1)
		La1–N3–Si3	129.5(1)

Conclusions

Heteroleptic rare-earth metal complexes bearing the bulky amido ligand [N(SiMe₃)(C₆H₃iPr₂-2,6)] and the anionic coligands [Cl] or [BH₄] are readily accessible via salt metathesis reactions, employing LnCl₃(thf)_x or Ln(BH₄)₃·(thf)₃ as precursors. The product composition, be it the envisaged monomeric alkali metal-free complexes or any undesired ate derivatives, crucially depends on the solvent and choice of alkali metal amide precursor. For the larger rare-earth metal centers, use of Li[N(SiMe₃)(C₆H₃iPr₂-2,6)] in

thf as a solvent clearly favors the formation of ate complexes and polymeric coligand-bridged compounds. The combination $\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]/\text{hexane}$ gives access to alkali metal-free monolanthanide complexes $\text{Ln}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})_2(\text{BH}_4)(\text{thf})]$ and $\text{Ln}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})_3]$ while conducting the reaction in thf cannot impede salt contamination. Using lanthanide triflates as rare-earth metal precursors yielded mixtures of products from which only the side product $\text{Li}_4(\text{OTf})_4(\text{thf})_6$ could be isolated and characterized. The large lanthanum centers can accommodate three bulky amido ligands accomplishing the homoleptic complex $\text{La}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})_3]$. Current studies address the reactivity of such heteroleptic amide complex toward alkylating reagents such as trimethylaluminum and the potential of the activated species in polymerization reactions, according to Scheme 1.

Experimental Section

General Information and Material: All of the manipulations of metal complexes were performed under rigorous exclusion of air and moisture in an argon-filled glovebox (MB Braun MB150B-G-II; <1 ppm O_2 , <1 ppm H_2O). Solvent pretreatment/purification was performed with Grubbs columns (MBraun SPS, solvent purification system). $[\text{D}_6]\text{benzene}$ was obtained from Aldrich, degassed, dried with Na for 24 h, filtered, and stored in a glovebox. $\text{Y}(\text{OTf})_3$ and $\text{Nd}(\text{OTf})_3$ were ordered from Aldrich and dried at 180 °C under high vacuum for 24 h before use. $\text{Nd}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})_2\text{Cl}]_2$, $[\text{HN}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]^{[30]}$ and $\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})^{[30]}$ were synthesized according to literature procedures. $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ was synthesized by treating $\text{NdCl}_3(\text{thf})_{1.75}$ with NaBH_4 in thf at ambient temperature for 48 h; similar procedures have been presented previously.^[31] NMR spectroscopic data were obtained in $[\text{D}_6]\text{benzene}$ solution at 25 °C on a Bruker DMX-400 Avance (^1H : 400.13 MHz; ^{13}C : 100.61 MHz) and a Bruker-BIO-SPIN-AV600 (5 mm cryo probe, ^1H : 600.13 MHz; ^{13}C : 150.91 MHz). ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using Nujol mulls sandwiched between CsI plates. Elemental analyses were performed on an Elementar Vario EL III.

$\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]$: To a solution of $\text{HN}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})$ (125 mg, 0.50 mmol) in 10 mL hexane a suspension of potassium bis(trimethylsilyl)amide (100 mg, 0.50 mmol) in hexane was added and the reaction mixture stirred at ambient temperature overnight. Then the solvent was decanted off and the remaining white solid was washed 3 times with equal amounts of hexane (5 mL). $\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]$ (115 mg, 0.40 mmol) formed with 81 % yield. ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 6.99 (d, $^3J_{\text{H,H}} = 7.3$ Hz, 2 H, C_6H_3), 6.51 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 1 H, C_6H_3), 3.81 (sept, $^3J_{\text{H,H}} = 6.9$ Hz, 2 H, CHMe_2), 1.24 (d, $^3J_{\text{H,H}} = 6.7$ Hz, 12 H, CHMe_2), 0.36 (s, 9 H, SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, $[\text{D}_6]\text{benzene}$): δ = 141.7 (*ortho*-C C_6H_3), 122.9 (*meta*-C C_6H_3), 111.8 (*para*-C C_6H_3), 27.0 (CHMe_2), 23.8 (CHMe_2), 5.2 (SiC) ppm. IR (Nujol): $\tilde{\nu}$ = 1880 (w), 1842 (w), 1801 (w), 1578 (m), 1417 (s), 1344 (s), 1295 (m), 1260 (m), 1227 (m), 1153 (w), 1132 (w), 1118 (w), 1102 (w), 1045 (m), 980 (s), 939 (w), 925 (w), 838 (s), 805 (s), 756 (s), 745 (m), 647 (m), 609 (w), 468 (w) cm^{-1} .

$\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})(\text{thf})_3$ (1): Compound **1** could be obtained by dissolving the donor-free species $\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})$

in thf or as a side product in the synthesis of **2**. Colorless crystals were grown from saturated thf solutions. ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 7.21 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 2 H, C_6H_3), 6.94 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 1 H, C_6H_3), 4.19 (br. s, 2 H, CH), 3.35 (m, 12 H, thf), 1.35 (s, 12 H, iPr), 1.31 (m, 12 H, thf), 0.40 (s, 9 H, SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, $[\text{D}_6]\text{benzene}$): δ = 143.1, 124.2, 123.4, 68.0 (thf), 28.5, 27.4, 25.5, 25.0, 23.8, 0.8 (SiMe_3) ppm. $\text{C}_{27}\text{H}_{50}\text{LiNO}_3\text{Si}$ (471.72 g mol^{-1}): calcd. C 68.75, H 10.68, N 2.97; found C 67.57, H 11.21, N 3.43.

$\text{Y}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]\text{Cl}_2(\text{thf})_3$ (2): To a suspension of $\text{YCl}_3(\text{thf})_{3.5}$ (147 mg, 0.33 mmol) in thf, $\text{LiN}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})$ (168 mg, 0.66 mmol) dissolved in thf was slowly added. After having been stirred for several minutes a colorless solution formed which was further reacted at ambient temperature overnight. The solvent was removed in vacuo and the remaining solid extracted with hexane. The crude product (164 mg, 0.26 mmol, 80%) was re-dissolved in a hexane/thf mixture. Colorless crystals formed under slow evaporation of the solvents and were identified as **2** (the crystallized yield was not determined). The reaction was rerun with equimolar amounts of $\text{YCl}_3(\text{thf})_{3.5}$ (212 mg, 0.47 mmol) and $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]$ (121 mg, 0.47 mmol) yielding 52% of **2** (154 mg, 0.25 mmol) after extraction with hexane. ^1H NMR (500.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 7.17 (d, $^3J_{\text{H,H}} = 7.2$ Hz, 2 H, C_6H_3), 7.02 (t, $^3J_{\text{H,H}} = 7.6$ Hz, 1 H, C_6H_3), 4.31 (br. s, 2 H, iPr), 3.67 (s, thf), 1.54 (d, $^3J_{\text{H,H}} = 6.4$ Hz, 6 H, iPr), 1.41 (s, thf), 1.37 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 6 H, iPr), 0.56 (s, 9 H, SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.77 MHz, $[\text{D}_6]\text{benzene}$): δ = 146.5, 144.6, 124.2, 123.3, 72.2 (thf), 27.5, 26.6 (thf), 25.9, 23.8, 4.1 ppm. IR (Nujol): $\tilde{\nu}$ = 1422 (s), 1311 (m), 1244 (m), 1230 (m), 1179 (m), 1105 (w), 1040 (w), 1008 (w), 895 (s), 874 (s), 844 (s), 780 (s), 747 (w), 671 (w), 623 (vw), 526 (w), 439 (w), 405 (w) cm^{-1} . $\text{C}_{27}\text{H}_{50}\text{Cl}_2\text{NO}_3\text{SiY}$ (624.59 g mol^{-1}): calcd. C 51.92, H 8.07, N 2.24; found C 49.74, H 8.56, N 1.83.

$\{\text{La}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})_2(\text{thf})(\mu\text{-Cl})\text{K}(\text{thf})_2(\mu\text{-Cl})\}_n$ (3): $\text{LaCl}_3(\text{thf})_{1.25}$ (50 mg, 0.15 mmol) and 2 equiv. of $\text{K}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]$ (86 mg, 0.30 mmol) were suspended in thf and stirred at ambient temperature overnight. Upon filtration the slightly yellow solution was reduced in volume by evaporation of the solvent under vacuum and stored at −35 °C. Colorless crystals of **3** formed in 60% yield (87 mg, 0.09 mmol). ^1H NMR (400.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 7.09 (br., 4 H, C_6H_3), 6.86 (br., 2 H, C_6H_3), 3.81 (br., CHMe_2), 3.49 (br., thf), 1.37 (br., CHMe_2), 1.20 (br., thf), 1.18 (br., CHMe_2), 0.49 (br., SiMe_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.61 MHz, $[\text{D}_6]\text{benzene}$): δ = 124.7 (*ortho*-C C_6H_3), 123.3 (*para*-C C_6H_3), 68.1 (thf), 28.5 (CHMe_2), 25.7 (thf), 23.8 (CHMe_2), 4.1 (SiC) ppm. IR (Nujol): $\tilde{\nu}$ = 1308 (w), 1243 (m), 1197 (w), 1110 (w), 1042 (w), 922 (m), 876 (w), 840 (m), 783 (m), 721 (m), 654 (w), 612 (w), 574 (w) cm^{-1} . $\text{C}_{42}\text{H}_{76}\text{Cl}_2\text{KLaN}_2\text{O}_3\text{Si}_2$ (962.14 g mol^{-1}): calcd. C 52.43, H 7.96, N 2.91; found C 52.14, H 7.94, N 3.06.

$[\text{Nd}\{\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})_2(\text{BH}_4)_2\}]\text{Li}(\text{thf})_4$ (4): $\text{Nd}(\text{BH}_4)_3(\text{thf})_3$ (91 mg, 0.22 mmol) was dissolved in thf and a solution of $\text{Li}[\text{N}(\text{SiMe}_3)(\text{C}_6\text{H}_3\text{iPr}_2\text{-2,6})]$ (115 mg, 0.45 mmol) in thf added. The blue solution was stirred at ambient temperature for 48 h. Then the volume was reduced by evaporation of the solvent and the reaction mixture stored at −35 °C. Blue crystals formed which were identified as **4** by X-ray structure analysis (193 mg, 0.20 mmol, 91%). ^1H NMR (600.13 MHz, $[\text{D}_6]\text{benzene}$): δ = 34.44 (BH_4), 22.82, 16.37, 13.54, 12.89, 11.87, 10.49, 5.23, 4.68, 4.54, 4.31, 3.60, −4.44, −5.82 br., −20.28 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150.91 MHz, $[\text{D}_6]\text{benzene}$): δ = 145.5, 144.6, 143.0, 124.2, 123.3, 65.7, 60.4, 29.7, 28.4, 27.5, 25.2, 24.2, 23.9, 18.8, 3.4, 0.8 ppm. IR (Nujol): $\tilde{\nu}$ = 2432 (vs) cm^{-1} (BH_4), 2213 (vs), br. (BH_4), 1900 (vw), 1845 (vw), 1585 (m), 1421 (s), 1359 (m), 1309 (s), 1251 (vs), 1178 (vs), 1104 (s), 1043 (vs), 892

(vs), 838 (vs), 774 (s), 741 (m), 667 (m), 615 (m), 569 (w), 522 (m), 426 cm⁻¹ (m). C₄₆H₃₂B₂LiN₂NdO₄Si₂ (966.21 g mol⁻¹): calcd. C 57.18, H 9.60, N 2.90; found C 57.11, H 10.73, N 2.78.

{Nd[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂(μ-BH₄)Li(thf)₂(μ-BH₄)}_n (5**): Solid Nd(BH₄)₃(thf)₃ (81 mg, 0.2 mmol) and Li[N(SiMe₃)(C₆H₃iPr₂-2,6)] (102 mg, 0.40 mmol) were mixed and suspended in 10 mL hexane. The slurry turned blue after a few minutes and was stirred overnight at ambient temperature. After filtration, the remaining blue solution was reduced in volume by evaporation of the solvent. Storage at -35 °C produced crystals which were identified as **5** by X-ray crystallography (100 mg, 0.12 mmol, 61%). ¹H NMR (400.13 MHz, [D₆]benzene): δ = 21.85, 20.03, 18.73, 16.17 (br), 12.56, 9.49, 9.02, 7.88, 7.13, 7.02, 4.80, 1.94, 0.07, -0.59, 0.88, -2.20, -8.63 ppm. ¹³C{¹H} NMR (100.61 MHz, [D₆]benzene): δ = 216.4, 145.5, 123.3, 114.6 (vbr), 63.9, 40.3, 28.4, 22.2, 19.2, 2.0 ppm. IR (Nujol): ν̄ = 2430 (w, BH₄), 2360 (m, BH₄), 2338 (m, BH₄), 1423 (m), 1360 (m), 1238 (m), 1175 (m), 1102 (m), 1047 (m), 922 (m), 890 (w), 835 (m), 778 (m), 656 (w), 618 (w), 566 (w), 514 (w) cm⁻¹. C₃₈H₇₆B₂LiN₂NdO₂Si₂ (821.97 g mol⁻¹): calcd. C 55.53, H 9.32, N 3.41; found C 55.56, H 8.81, N 3.28.**

Nd[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂(BH₄)(thf) (6**): Solid Nd(BH₄)₃(thf)₃ (162 mg, 0.40 mmol) and K[N(SiMe₃)(C₆H₃iPr₂-2,6)] (230 mg, 0.80 mmol) were combined and suspended in 10 mL of hexane. The green suspension was stirred at ambient temperature for 24 h in order to drive the reaction to completion. After filtration the green solution was concentrated by evaporation of the solvent and subsequently stored at -35 °C yielding blue crystals of **6** in 64% yield (186 mg, 0.26 mmol). ¹H NMR (400.13 MHz, [D₆]benzene): δ = 20.88, 17.64, 8.73, 7.15, 4.67, 1.23, 0.88, 0.10, -1.92 ppm. ¹³C{¹H} NMR (100.61 MHz, [D₆]benzene): δ = 152.8, 123.3, 31.9, 28.5, 23.9, 23.0, 15.9, 14.3, 0.8 ppm. IR (Nujol): ν̄ = 3044 (m), 2454 (m, BH₄), 2343 (w), 2204 (m, BH₄), 2144 (m, BH₄), 1915 (w), 1856 (w), 1586 (w), 1415 (s), 1308 (m), 1246 (s), 1230 (s), 1189 (s), 1110 (m), 1097 (m), 1044 (m), 1012 (m), 909 (s), 884 (s), 833 (s), 775 (s), 746 (s), 675 (w), 653 (m), 615 (w), 585 (w), 569 (w), 503 (s), 429 (m) cm⁻¹. C₃₄H₆₄BN₂NdOSi₂ (728.08 g mol⁻¹): calcd. C 56.09, H 8.86, N 3.85; found C 56.33, H 9.26, N 3.87.**

La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₂(BH₄)(thf) (7**): Solid La(BH₄)₃(thf)₃ (136 mg, 0.34 mmol) and 2 equiv. of K[N(SiMe₃)(C₆H₃iPr₂-2,6)] (195 mg, 0.68 mmol) were mixed and suspended in hexane. The slightly yellow suspension was stirred at ambient temperature overnight. The solution was then filtered, reduced in volume, and stored at -35 °C. Colorless crystals formed which were identified as **7** (crystallized yield 129 mg, 0.18 mmol 52%). ¹H NMR (400.13 MHz, [D₆]benzene): δ = 7.02 (d, ³J_{H,H} = 7.5 Hz, 4 H, C₆H₃), 6.84 (t, ³J_{H,H} = 7.5 Hz, 2 H, C₆H₃), 3.77 (br., 4 H, CHMe₂), 2.63 (br., 4 H, thf), 1.82 (br. q, ¹J_{B,H} = 80.3 Hz, 4 H, BH₄) 1.22 (br., 12 H, CHMe₂), 1.20 (br., 4 H, thf), 1.18 (d, ³J_{H,H} = 6.5 Hz, 12 H, CHMe₂), 0.50 (s, 18 H, SiMe₃) ppm. ¹³C{¹H} NMR (100.61 MHz, [D₆]benzene): δ = 147.2 (*ipso*-C C₆H₃), 143.9 (*ortho*-C C₆H₃), 125.0 (*meta*-C C₆H₃), 123.1 (*para*-C C₆H₃), 70.4 (thf), 27.6 (CHMe₂), 25.7 (thf), 23.0 (CHMe₂), 4.1 (SiC) ppm. IR (Nujol): ν̄ = 2448 (w, BH₄), 2201 (w, BH₄), 2143 (w, BH₄), 1415 (m), 1312 (w), 1243 (m), 1197 (w), 1170 (w), 1110 (w), 1091 (w), 1042 (w), 1012 (w), 925 (m), 838 (m), 776 (m), 656 (w), 620 (w), 501 (w) cm⁻¹. C₃₄H₆₄BLaN₂OSi₂ (722.77 g mol⁻¹): calcd. C 56.50, H 8.93, N 3.88; found C 56.55, H 9.20, N 3.88.**

Li₄(OTf)₄(thf)₆ (8**):** Colorless crystals of **8** were obtained from the reaction of Ln(OTf)₃ (Ln = Y, Nd) with 2 equiv. of Li[N(SiMe₃)(C₆H₃iPr₂-2,6)] in thf.

Route I: To Y(OTf)₃ (123 mg, 0.23 mmol) in thf Li[N(SiMe₃)(C₆H₃iPr₂-2,6)] (117 mg, 0.46 mmol) dissolved in thf was added and the

suspension stirred at ambient temperature until a clear solution developed. The solvent was evaporated and the product mixture repeatedly extracted with hexane. The remaining white solid (90 mg, 0.09 mmol, 72%) was dissolved in a hexane/thf mixture, affording **8** as colorless crystals.

Route II: Nd(OTf)₃ (159 mg, 0.27 mmol) was suspended in thf and Li[N(SiMe₃)(C₆H₃iPr₂-2,6)] (137 mg, 0.46 mmol) dissolved in thf added, resulting in a green solution with a fine precipitate. The reaction mixture was stirred overnight and the solvent removed under vacuum giving a green oil. Extraction with 2 × 5 mL hexane gave **8** as white hexane insoluble powder (99 mg, 0.09 mmol, 70%).

Route III: Upon stirring at ambient temperature, the reaction mixtures of route I/II were reduced in volume and stored at -35 °C, giving colorless crystals of **8** exclusively. ¹H NMR (400.13 MHz, [D₆]benzene): δ = 3.53 (thf), 1.32 (thf) ppm. C₂₈H₄₈F₁₂Li₄O₁₈S₄·C₄H₈O (1128.78 g mol⁻¹): calcd. C 34.05, H 5.00; found C 34.6, H 4.6.

La[N(SiMe₃)(C₆H₃iPr₂-2,6)]₃ (9**):** Route I: Compound **7** (78 mg, 0.11 mmol) and K[N(SiMe₃)(C₆H₃iPr₂-2,6)] (31 mg, 0.11 mmol) were stirred in hexane at ambient temperature for 24 h. Any insoluble parts of the slightly green, cloudy solution were filtered off. The volume was reduced by evaporation of the solvent and the solution stored at -35 °C to yield colorless crystals (41 mg, 0.05 mmol, 43%).

Route II: To a suspension of La(BH₄)₃(thf)₃ (80 mg, 0.2 mmol) in 10 mL hexane was slowly added a suspension of K[N(SiMe₃)(C₆H₃iPr₂-2,6)] (172.5 mg, 0.6 mmol) in 5 mL hexane. The reaction mixture was stirred at ambient temperature for 24 h, then reduced in volume, and finally the insoluble parts filtered off. Colorless crystals of **9** were obtained at -35 °C (97 mg, 0.11 mmol, 55%). ¹H NMR (400.13 MHz, [D₆]benzene): δ = 7.00 (d, ³J_{H,H} = 7.1 Hz, 6 H, C₆H₃), 6.91 (t, ³J_{H,H} = 7.5 Hz, 3 H, C₆H₃), 3.44 (sept, ³J_{H,H} = 6.9 Hz, 3 H, CHMe₂), 3.36 (br., 3 H, CHMe₂) 1.23 (br., 36 H, CHMe₂), 0.39 (s, 27 H, SiMe₃) ppm. ¹³C{¹H} NMR (100.61 MHz, [D₆]benzene): δ = 125.5 (*ipso*-C C₆H₃), 124.2 (*ortho*-C C₆H₃), 123.3 (*meta*-C C₆H₃), 123.0 (*para*-C C₆H₃), 27.5 (CHMe₂), 23.0 (CHMe₂), 3.9 (SiC) ppm. IR (Nujol): ν̄ = 1583 (w), 1420 (m), 1333 (w), 1303 (m), 1246 (m), 1227 (m), 1181 (s), 1148 (w), 1104 (m), 1050 (w), 1037 (w), 914 (s), 876 (m), 840 (s), 772 (s), 745 (m), 731 (m), 659 (m), 617 (w), 568 (w), 508 (m), 443 (w), 424 (m) cm⁻¹. C₄₅H₇₈LaN₃Si₃ (884.3 g mol⁻¹): calcd. C 61.12, H 8.89, N 4.75; found C 60.98, H 7.96, N 4.68.

Crystallographic Data Collection and Refinement: Crystals of **1–8** were grown by standard techniques from saturated solutions using thf (**1**, **3**, **4**), hexane/thf (**2**, **8**), or hexane (**5**, **6**, **7**, **9**) at -35 °C. Suitable single crystals of **1–5**, **7** and **8** were selected in a glovebox, coated with Paratone-N, fixed in a nylon loop, and measured on a Bruker SMART 2K CCD diffractometer. Compounds **6** and **9** were measured on an APEXII Ultra rotating anode diffractometer. All data were collected using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) performing ω-scans in four ϕ positions. Raw data were reduced and scaled with program SAINT.^[32] Corrections for absorption effects were applied using SADABS^[33] or SHELXTL.^[34] The structures were solved by a combination of direct methods (SHELXS-97^[34]) and difference-Fourier syntheses (SHELXL97).^[34] Final model refinement was done using SHELXL97.^[34] All plots were generated using the program ORTEP-3.^[35] Further details of the refinement and crystallographic data are listed in Tables 7 and 8 and in the CIF files.

CCDC-767394 (for **1**), -767395 (for **2**), -767396 (for **3**), -767397 (for **4**), -767398 (for **5**), -767399 (for **6**), -767400 (for **7**), -767401 (for

Table 7. Summary of crystallographic data and structure refinement for compounds 1–5.

	1	2	3	4	5
Chemical formula	C ₂₇ H ₅₀ LiNO ₃ Si	C ₂₇ H ₅₀ Cl ₂ NO ₃ SiY	C ₄₂ H ₇₆ Cl ₂ KLaN ₂ O ₃ Si ₂	C ₄₆ H ₉₂ B ₂ LiN ₂ NdO ₄ Si ₂	C ₃₈ H ₇₆ B ₂ LiN ₂ NdO ₂ Si ₂
<i>M_r</i> [g mol ^{−1}]	471.71	624.58	962.14	966.20	821.99
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 1̄	<i>Cc</i>
<i>a</i> [Å]	10.7559(4)	11.4046(4)	14.8094(4)	13.1483(5)	22.0482(8)
<i>b</i> [Å]	16.2830(6)	24.1927(9)	15.7724(5)	13.5289(5)	14.1974(5)
<i>c</i> [Å]	16.3705(6)	11.6362(4)	42.7869(13)	15.2514(5)	14.4931(5)
<i>α</i> [°]	90.00	90.00	90	85.522(1)	90
<i>β</i> [°]	92.265(1)	91.145(1)	90	80.881(1)	94.447(1)
<i>γ</i> [°]	90.00	90.00	90	83.362(1)	90
<i>V</i> [Å ³]	2864.86(18)	3209.9(2)	9994.2(5)	2655.76(17)	4523.1(3)
<i>Z</i>	4	4	8	2	4
<i>F</i> (000)	1040	1320	4032	1030	1740
<i>T</i> [K]	100(2)	123(2)	123(2)	123(2)	123(2)
<i>ρ</i> _{calcd} [g cm ^{−3}]	1.094	1.292	1.279	1.208	1.207
<i>μ</i> [mm ^{−1}]	0.108	2.047	1.128	1.061	1.231
<i>R</i> ₁ (obsd.) ^[a]	0.0636	0.0297	0.0427	0.0305	0.0169
<i>wR</i> ₂ (all) ^[b]	0.1448	0.0779	0.1069	0.0833	0.0432
<i>S</i> ^[c]	1.050	1.092	1.285	1.109	1.071

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $F_o > 4\sigma(F_o)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$.

Table 8. Summary of crystallographic data and structure refinement for compounds 6–9.

	6	7	8	9
Chemical formula	C ₃₄ H ₆₄ BN ₂ NdOSi ₂	C ₃₄ H ₆₄ BLaN ₂ OSi ₂	C ₂₈ H ₄₈ F ₁₂ Li ₄ O ₁₈ S ₄	C ₄₅ H ₇₈ LaN ₃ Si ₃
<i>M_r</i> [g mol ^{−1}]	728.10	722.77	1056.70	884.28
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 1̄	<i>P</i> 1̄	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄
<i>a</i> [Å]	9.7535(3)	9.7900(2)	9.5804(7)	13.0718(12)
<i>b</i> [Å]	12.5334(4)	12.5642(2)	19.1727(14)	13.1192(12)
<i>c</i> [Å]	17.6518(8)	17.6846(3)	13.0298(10)	15.0994(14)
<i>α</i> [°]	105.622(2)	105.83(1)	90.00	99.759(1)
<i>β</i> [°]	92.834 (1)	92.40(1)	99.640(2)	99.609(1)
<i>γ</i> [°]	109.715(1)	109.86(1)	90.00	103.273(1)
<i>V</i> [Å ³]	1932.76(12)	1946.3(2)	2359.5(3)	2425.9(4)
<i>Z</i>	2	2	2	2
<i>F</i> (000)	766	760	1088	936
<i>T</i> [K]	123(2)	123(2)	123(2)	123(2)
<i>ρ</i> _{calcd} [g cm ^{−3}]	1.251	1.233	1.487	1.211
<i>μ</i> [mm ^{−1}]	1.431	1.185	0.313	0.986
<i>R</i> ₁ (obsd.) ^[a]	0.0166	0.0252	0.0698	0.0413
<i>wR</i> ₂ (all) ^[b]	0.0438	0.0532	0.1758	0.1090
<i>S</i> ^[c]	1.062	1.055	1.096	1.035

[a] $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $F_o > 4\sigma(F_o)$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_o - n_p)]^{1/2}$.

8), -767402 (for 9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] For examples, see: a) R. A. Gendron, D. J. Berg, T. Barclay, *Can. J. Chem.* **2002**, *80*, 1285; b) M. S. Cheung, H. S. Chan, Z. Xie, *Organometallics* **2005**, *24*, 4207; c) C. Meermann, *Ph. D. Thesis*, University of Bergen **2008**.
- [2] A. Fischbach, R. Anwender, *Adv. Polym. Sci.* **2006**, *204*, 155.
- [3] C. Meermann, K. W. Törnroos, W. Nerdal, R. Anwender, *Angew. Chem. Int. Ed.* **2007**, *46*, 6508.
- [4] *Metal Amide Chemistry* (Eds.: M. F. Lappert, A. V. Protchenko, P. P. Power, A. L. Seeber), John Wiley & Sons, Hoboken **2008**.
- [5] L. Zhou, J. Wang, Y. Zhang, Y. Yao, Q. Shen, *Inorg. Chem.* **2007**, *46*, 5763.
- [6] P. B. Hitchcock, Q. G. Huang, M. F. Lappert, X. H. Wei, *J. Mater. Chem.* **2004**, *14*, 3266.
- [7] H. Schumann, J. Winterfeld, E. C. E. Rosenthal, H. Hemling, L. Esser, *Z. Anorg. Allg. Chem.* **1995**, *621*, 122.
- [8] Y. Luo, M. Nishiura, Z. Hou, *J. Organomet. Chem.* **2007**, *692*, 536.
- [9] Y. Luo, Y. Yao, W. Li, J. Chen, Z. Zhang, Y. Zhang, Q. Shen, *J. Organomet. Chem.* **2003**, *679*, 125.
- [10] S.-W. Wang, H.-M. Qian, W. Yao, L.-J. Zhang, S.-L. Zhou, G.-S. Yang, X.-C. Zhu, J.-X. Fan, Y.-Y. Liu, G.-D. Chen, H.-B. Song, *Polyhedron* **2008**, *27*, 2757.
- [11] G. B. Deacon, G. D. Fallon, C. M. Forsyth, H. Schumann, R. Weimann, *Chem. Ber./Recueil* **1997**, *130*, 409.

- [12] D. K. Kennepohl, S. Brooker, G. M. Sheldrick, H. W. Roesky, *Chem. Ber.* **1991**, 124, 2223.
- [13] A. J. Blake, P. Mountford, G. I. Nikonov, *Acta Crystallogr., Sect. C* **1996**, 52, 1911.
- [14] D. L. Clark, J. C. Gordon, J. C. Huffman, R. L. Vincent-Hollis, J. G. Watkin, B. D. Zwick, *Inorg. Chem.* **1994**, 33, 5903.
- [15] J. L. Atwood, W. E. Hunter, R. D. Rogers, J. A. Weeks, *J. Inclusion Phenom. Macrocyclic Chem.* **1985**, 3, 113.
- [16] a) M. Ephritikhine, *Chem. Rev.* **1997**, 97, 2193; b) S. M. Cendrowski-Guillaume, G. Le Gland, M. Lance, M. Nierlich, M. Ephritikhine, *C. R. Chim.* **2002**, 5, 73.
- [17] For recent examples in polymerization catalysis, see: a) M. Terrier, M. Visseaux, T. Chenal, A. Mortreux, *J. Polym. Sci., Part A: Polym. Chem.* **2007**, 45, 2400; b) I. Palard, M. Schappacher, B. Belloncle, A. Soum, S. M. Guillaume, *Chem. Eur. J.* **2007**, 13, 1511; c) N. Barros, P. Mountford, S. M. Guillaume, L. Maron, *Chem. Eur. J.* **2008**, 14, 5507; d) D. Robert, M. Kondracka, J. Okuda, *Dalton Trans.* **2008**, 2667; e) T. V. Mahrova, G. K. Fukin, A. V. Cherkasov, A. A. Trifonov, N. Ajellal, J.-F. Carpentier, *Inorg. Chem.* **2009**, 48, 4258.
- [18] H.-H. Giese, H. Nöth, H. Schwenk, S. Thomas, *Eur. J. Inorg. Chem.* **1998**, 941.
- [19] G. G. Skvortsov, M. V. Yakovenko, P. M. Castro, G. K. Fukin, A. V. Cherkasov, J.-F. Carpentier, A. A. Trifonov, *Eur. J. Inorg. Chem.* **2007**, 3260.
- [20] For Nd–B(borohydrido) bond lengths, see: a) A. Klein, R. W. H. Pohl, *Z. Anorg. Allg. Chem.* **2008**, 634, 1388; [Li(thf)₄]₂[Nd₂(μ-Cl)₂(BH₄)₆(thf)₂], 2.59(1)–2.78(1) Å; b) F. Bonnet, M. Visseaux, D. Barbier-Baudry, A. Hafid, E. Vigier, M. Kubicki, *Inorg. Chem.* **2004**, 43, 3682; [(C₅Me₄nPr)Nd(μ-BH₄)₂]₆, av. 2.84 Å; c) S. M. Cendrowski-Guillaume, M. Nierlich, M. Lance, M. Ephritikhine, *Organometallics* **1998**, 17, 786; [(COT)-Nd(μ-BH₄)(THF)]₂, 2.875(6) and 2.941(6) Å.
- [21] T. J. Marks, J. R. Kolb, *Chem. Rev.* **1977**, 77, 263.
- [22] For La–B(borohydrido) bond lengths, see: N. Meyer, J. Jenter, P. W. Roesky, G. Eickerling, W. Scherer, *Chem. Commun.* **2009**, 4693; DIP₂-pyrLa(BH₄)₂(thf)[DIP₂-pyrH = 2.5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole], 2.714(5), 2.711(6) Å.
- [23] a) H. Schumann, J. A. Meese-Marktscheffel, A. Dietrich, *J. Organomet. Chem.* **1989**, 377, C5; b) U. Kilimann, M. Schäfer, R. Herbst-Irmer, F. T. Edelmann, *J. Organomet. Chem.* **1994**, 469, C10; c) J. Stehr, R. D. Fischer, *J. Organomet. Chem.* **1992**, 430, C1; d) P. C. Leverd, D. Rinaldo, M. Nierlich, *Eur. J. Inorg. Chem.* **2001**, 2021.
- [24] S. A. Schuetz, V. W. Day, R. D. Sommer, A. L. Rheingold, J. A. Belot, *Inorg. Chem.* **2001**, 40, 5292.
- [25] R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck, M. Spiegler, *J. Chem. Soc., Dalton Trans.* **1998**, 847.
- [26] C. Meermann, G. Gerstberger, M. Spiegler, K. W. Törnroos, R. Anwander, *Eur. J. Inorg. Chem.* **2008**, 2014.
- [27] H. Schumann, J. A. Meese-Marktscheffel, J. Loebel, *Z. Naturforschung, Teil B* **1990**, 45, 1304.
- [28] J. B. Spencer, J.-O. Lundgren, *Acta Crystallogr., Sect. B* **1973**, 29, 1923.
- [29] a) H. C. Aspinall, D. C. Bradley, K. D. Sales, *J. Chem. Soc., Dalton Trans.* **1988**, 2211; b) W. J. Evans, R. Anwander, J. W. Ziller, *Inorg. Chem.* **1995**, 34, 5927; c) M. Zimmermann, N. Å. Frøystein, A. Fischbach, P. Sirsch, H. M. Dietrich, K. W. Törnroos, E. Herdtweck, R. Anwander, *Chem. Eur. J.* **2007**, 13, 8784.
- [30] Y. W. Chao, P. A. Wexler, D. E. Wigley, *Inorg. Chem.* **1989**, 28, 3860.
- [31] S. M. Cendrowski-Guillaume, G. Le Gland, M. Nierlich, M. Ephritikhine, *Organometallics* **2000**, 19, 5654.
- [32] Bruker, *SAINT. Area detector control and data integration and reduction software*, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, **2008**.
- [33] G. M. Sheldrick, *SADABS*, University of Göttingen, Germany, **2008**.
- [34] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112.
- [35] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, 30, 565.

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