

Synthesis and Derivatization of Homoleptic Dinuclear Lanthanide Siloxide Complexes

Andreas Fischbach^a, Georg Eickerling^b, Wolfgang Scherer^b, Eberhardt Herdtweck^a, and Reiner Anwander^a

^a Department Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany

^b Institut für Physik, Universität Augsburg, Universitätsstraße 1, D-86159 Augsburg, Germany

Reprint requests to Dr. R. Anwander. Fax: +49 (0)89 289 13473. E-mail: reiner.anwander@ch.tum.de

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

Homoleptic dinuclear lanthanide siloxide complexes $[\text{Ln}(\text{OSi}^i\text{BuPh}_2)_2(\mu\text{-OSi}^i\text{BuPh}_2)]_2$ ($\text{Ln} = \text{Y}$ (**1a**), La (**1b**)), $[\text{Ln}(\text{OSi}^i\text{HrBu}_2)_2(\mu\text{-OSi}^i\text{HrBu}_2)]_2$ ($\text{Ln} = \text{Y}$ (**2a**), La (**2b**), Nd (**2c**), Lu (**2d**)), and $\{\text{Ln}[\text{OSi}(\text{OrBu})_3]_2[\mu\text{-OSi}(\text{OrBu})_3]\}_2$ ($\text{Ln} = \text{Y}$ (**3a**), La (**3b**)) were synthesized according to the silylamide route in yields between 67 and 92%. Their bis(siloxide)-bridged molecular arrangement was proven by variable temperature ^1H NMR spectroscopy as well as by an X-ray structure analysis of **2c**. The IR spectra of complexes **2** feature low-energy Si–H stretching vibrations ($1965\text{--}1915\text{ cm}^{-1}$) indicative of $\beta(\text{Si-H})\cdots\text{Ln}$ agostic interactions. Complexes **2** and **3** readily form monomeric bis(donor) adducts with tetrahydrofuran, triphenylphosphine oxide, and *N*-methylimidazol as shown for fully characterized $\text{Ln}(\text{OSi}^i\text{HrBu}_2)_3(\text{thf})_2$ ($\text{Ln} = \text{Y}$ (**4a**), La (**4b**)), $\text{Y}(\text{OSi}^i\text{HrBu}_2)_3(\text{OPPh}_3)_2$ (**5**), $\text{Ln}(\text{OSi}^i\text{HrBu}_2)_3(\text{N-MeIm})_2$ ($\text{Ln} = \text{Y}$ (**6a**), La (**6b**)), and $\text{Y}[\text{OSi}(\text{OrBu})_3]_3(\text{thf})_2$ (**7**). Treatment of complexes **1–3** with excess of trimethylaluminum (TMA) generated several alkylated rare-earth metal species including homoleptic $\text{Ln}(\text{AlMe}_4)_3$ as indicated by ^1H NMR spectroscopy. $\text{La}[\text{OSi}(\text{OrBu})_3](\text{AlMe}_4)_2(\text{AlMe}_3)$ (**8b**) was isolated by crystallization and analyzed by X-ray diffraction.

Key words: Lanthanides, Siloxide Ligands, Metallosiloxanes, Adduct Formation, Tetramethylaluminate

Introduction

M–O–Si metallasiloxane linkages are a prevailing structural motif and building unit in naturally abundant silicates. For example, silicates such as thortveitite, $(\text{Y,Sc})_2[\text{Si}_2\text{O}_7]$, gadolinite, $\text{Be}_2\text{Y}_2\text{Fe}[\text{Si}_2\text{O}_8]\text{O}_2$, and monazite, $(\text{Ce,Th})[(\text{P,Si})\text{O}_4]$, are important minerals in rare-earth metal chemistry [1]. Today, the chemical and thermal stability of silicates are routinely exploited in material science and heterogeneous catalysis as shown for the application of rare-earth metal-exchanged aluminosilicates in fluid catalytic cracking (FCC) [2]. Organically functionalized variants as represented by siloxide (silanolate) complexes have been identified in the late 1950s as well-defined hydrocarbon soluble counterparts for fundamental studies of main group- and transition metal-based M–O–Si linkages [3]. Siloxide ligands allow an efficient fine-tuning of the reactivity of the metal center *via* distinct ste-

reoelectronic properties of the substituents at the silicon atom [4]. Additionally, the ^{29}Si NMR spectroscopic probe as well as strong(er) Si–O bonds often make siloxide ligands superior to the more common alkoxide derivatives [5]. Hence, transition metal siloxide complexes have attracted considerable interest in homogeneous catalysis and material science [6]. Metal siloxide complexes are also classified as *realistic* molecular models of (functionalized) metal sites of silica supported (immobilized) complexes and of catalytically active silicates [7]. Such model complexes can reveal not only details of the surface attachment (connectivity) of organometallic catalyst precursors but also unravel multifunctional surface reactions [8]. Moreover, the application of tailor-made molecular oxo surfaces imparts a deeper insight into structure-reactivity relationships of the active surface species. Up to now, several different types of lanthanide complexes with mono- (**A**) [9–18], di- (**B**) [19–21],

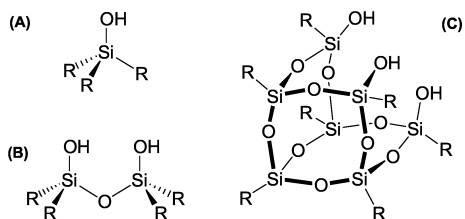


Fig. 1. Mono- (A), di- (B), and trifunctional silanols (C).

and trifunctional siloxide ligands (C) [21–23] have been structurally characterized (Fig. 1). Recently, we have discussed the use of lanthanide siloxide complexes as catalyst precursors for the polymerization of isoprene [24]. In this paper, we wish to report the synthesis and characterization of several new homoleptic lanthanide complexes derived from type-A silanols. Furthermore, donor adduct formation and trimethylaluminum (TMA)-based alkylation reactions have been performed in order to examine the strength of terminal and μ_2 -bridging M–O–SiR₃ linkages.

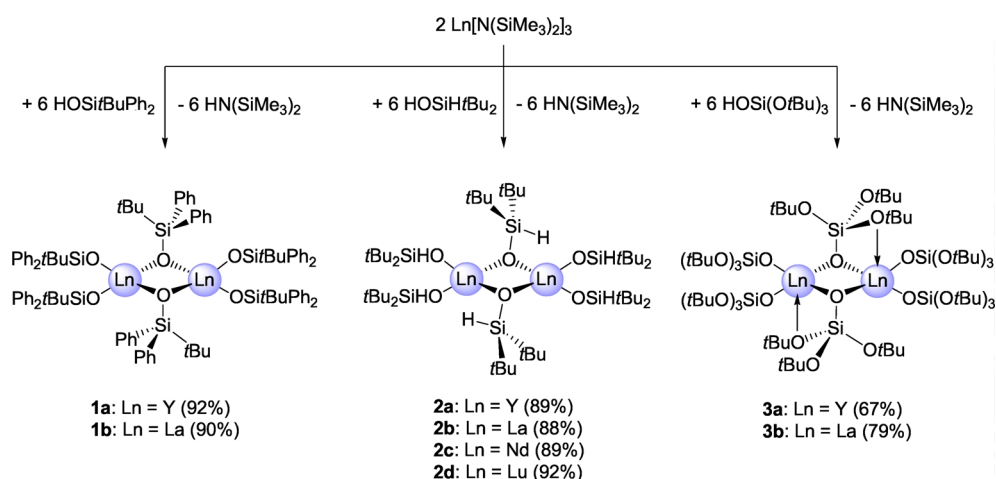
Results and Discussion

Synthesis of dinuclear lanthanide siloxide complexes

Homoleptic lanthanide siloxide complexes **1–3** were obtained by the established silylamide elimination route [25]. Accordingly, addition of three equivalents of a silanol precursor, HOSi^{*t*}BuPh₂, HOSi^{*t*}Bu₂, or HOSi(O^{*t*}Bu)₃, to a hexane solution of the homoleptic bis(trimethylsilyl)amide complexes Ln[N(SiMe₃)₂]₃ at ambient temperature gave the dinuclear complexes **1–3** in high yields (Scheme 1). Siloxide complexes **1** and **2** were isolated either as colorless (Ln = Y, La, Lu) or as bluish purple solids (Ln = Nd)

by evaporation of the solvent *in vacuo*. Further purification of the crude reaction products was achieved by several hexane washings or by crystallization from saturated hexane solutions at –45 °C. On the other hand, addition of three equivalents of silanol HOSi(O^{*t*}Bu)₃ to a hexane solution of Ln[N(SiMe₃)₂]₃ (Ln = Y, La) immediately formed hexane-insoluble siloxide complexes **3** as white precipitates which were separated by centrifugation and subjected to several hexane washings for purification.

Complete silylamide/siloxide ligand exchange for complexes **1–3** was evidenced by the microanalytical data (< 0.1% N) and by IR spectroscopy (absence of any [NSi₂]-characteristic vibration bands). The NMR spectra of complexes **1** are in agreement with siloxide-bridged dinuclear molecules as drawn in Scheme 1. The formation of such dinuclear species has been confirmed in the late 1980s and early 1990s by X-ray structural investigations of the triphenyl substituted derivatives [Ln(OSiPh₃)₂(μ -OSiPh₃)]₂ (*e. g.*, Ln = Y [10c], Ce [26]). Complexes **1** show two sets of signals with a relative integral ratio of 2:1 in the ¹H, ¹³C, and ²⁹Si NMR spectra which can be explained by a 2:1-ratio of terminal and bridging Ph₂^{*t*}BuSiO ligands. A dinuclear arrangement of readily hexane soluble complexes **2** (Ln = Y (**2a**), La (**2b**), Nd (**2c**), Lu (**2d**)) featuring the siloxide ligand OSi^{*t*}Bu₂ [27] could be anticipated on the basis of the molecular structure of the corresponding cerium(III) alkoxide complex [Ce(OCH^{*t*}Bu₂)₂(μ -OCH₂^{*t*}Bu₂)]₂ [28]. At ambient temperature, two sets of NMR signals with a relative integral ratio of 2:1 were observed for the smallest lanthanide center only (Ln = Lu (**2d**)): the Si^{*H*} functionalities of the bridging and terminal sil-



Scheme 1.

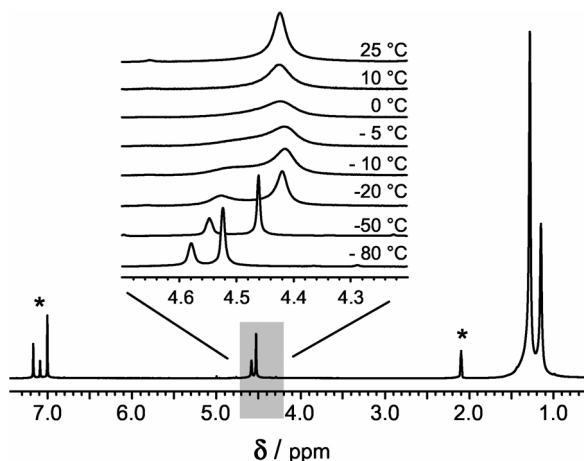


Fig. 2. ^1H -NMR spectrum of **2a** measured in toluene- d_8 at $-80\text{ }^\circ\text{C}$. The temperature dependence of the SiH signal(s) between -80 and $25\text{ }^\circ\text{C}$ is presented in the enlarged region; solvent signals are indicated by an asterisk.

oxide ligands show two slightly broadened ^1H resonances at 4.75 and 4.51 ppm. However, a variable temperature study in toluene- d_8 revealed decoalescence of the SiH resonances even for the “larger” metal centers [29]. The SiH decoalescence temperatures of $T_c \approx 55$ (Ln = Lu (**2d**)), -5 (Ln = Y (**2a**)), and -85 $^\circ\text{C}$ (Ln = La (**2b**)) are in accordance with sterically less saturated metal centers in the order $\text{Lu}^{3+} < \text{Y}^{3+} < \text{La}^{3+}$ [30]. The ^1H NMR spectrum of yttrium derivative **2a** is presented in Figure 2. The region of the SiH resonances is shown in the temperature range from $-80\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$ featuring either two separated SiH singlets for the bridging and terminal siloxide ligands or one broadened resonance. A similar coalescence behavior was observed for the *tert*-butyl resonances.

$^1J_{\text{HSi}}$ coupling constants which are usually applied for clarifying the extent of (SiH)–M bonding were assigned for complexes **2a** (Ln = Y) and **2d** (Ln = Lu) by means of the ^{29}Si satellites in the proton NMR spectra at $-80\text{ }^\circ\text{C}$ (Fig. 3). Whereas the $^1J_{\text{HSi}}$ coupling constants of the terminal ligands (188–189 Hz) are similar to those of the silanol precursor (194 Hz), the bridging moieties show coupling constants in the range 168–171 Hz clearly indicating a significant weakening of the Si–H bonds.

These findings were supported by the “SiH” IR spectroscopic features of complexes **2**. The Si–H stretch vibrations appear as a strong band in the region between 2059 and 2066 cm^{-1} and a second weaker and significantly broadened band at lower energies ($\tilde{\nu}_2 = 1963\text{--}1915\text{ cm}^{-1}$), the latter being indicative of

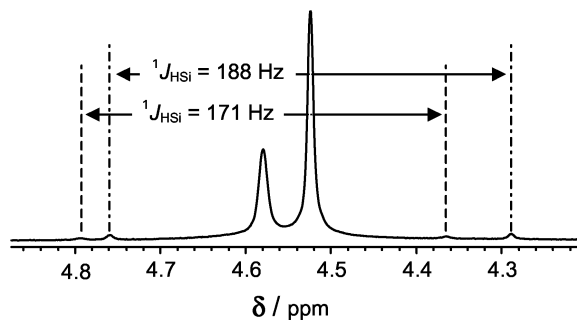


Fig. 3. ^{29}Si satellites in the proton NMR spectrum of complex **2a** (at $-80\text{ }^\circ\text{C}$): $^1J_{\text{HSi}}$ coupling constants.

$\beta(\text{Si-H})\cdots\text{M}$ agostic interactions [31]. Furthermore, the increasing discrepancy $\Delta\tilde{\nu}$ between the peak maxima with decreasing metal size ($\Delta\tilde{\nu} = 151\text{ cm}^{-1}$ (**2d**), 133 cm^{-1} (**2a**), 123 cm^{-1} (**2c**), 96 cm^{-1} (**2b**)) can be attributed to a stronger (Si–H)···M interaction associated with a more Lewis acidic metal center. This is in good agreement with the concept of $\beta(\text{Si-H})\cdots\text{M}$ agostic interactions as a consequence of an electrostatic attraction between the “negative” hydrogen atom and the positive charge of the metal cation [32].

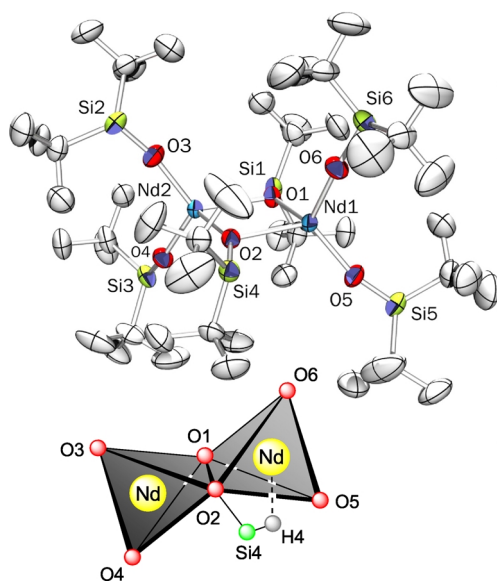
Finally, dinuclear structures were also observed for the tris(*tert*-butoxy)siloxide complexes **3a** (Ln = Y) and **3b** (Ln = La). The synthesis of the corresponding samarium and gadolinium derivatives has been reported recently and the solid state structure confirmed for the samarium complex by X-ray structure analysis [18d]. The ^1H NMR spectra of the diamagnetic derivatives **3** show three broadened singlets. An integral ratio of 12:4:2 is in agreement with a dinuclear complex with four terminal (= 12 terminal *tert*-butoxy groups) and two bridging η^2 -coordinating siloxide ligands (= 6 bridging *tert*-butoxy groups). Each of the two lanthanide centers is coordinated by four siloxide ligands and one *Ot*Bu group of the bridging siloxide ligand (Scheme 1).

Molecular structure of [Nd(OSiHtBu₂)₂(μ -OSiHtBu₂)₂] (**2c**)

Single crystals suitable for an X-ray structure determination were obtained by repeated crystallization of saturated hexane solutions of complex **2c** at $-45\text{ }^\circ\text{C}$. The molecular structure in the solid state shown in Figure 4 is similar to those of previously reported [Ce₂(OSiPh₃)₆] and [Ce₂(OCHtBu)₆] [26, 28]. Selected intramolecular bond distances and angles are presented in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] for [Nd(OSiHtBu₂)₂(μ-OSiHtBu₂)₂] (2c).

Nd1 – O1	2.340(2)	Nd1 ... Si4	3.264(2)
Nd1 – O2	2.423(3)	Nd2 ... Si1	3.271(2)
Nd1 – O5	2.158(3)	O1 – Si1	1.656(2)
Nd1 – O6	2.141(3)	O2 – Si4	1.646(2)
Nd2 – O1	2.440(2)	O3 – Si2	1.635(3)
Nd2 – O2	2.334(2)	O4 – Si3	1.631(3)
Nd2 – O3	2.144 (3)	O5 – Si5	1.632(3)
Nd2 – O4	2.161(2)	O6 – Si6	1.638(3)
O1 – Nd1 – O2	75.07(7)	Nd1 – O2 – Si4	105.1(2)
O1 – Nd1 – O5	111.70(8)	Nd1 – O5 – Si5	164.5(2)
O1 – Nd1 – O6	110.94(8)	Nd1 – O6 – Si6	166.5(2)
O2 – Nd1 – O5	120.17(8)	Nd2 – O1 – Si1	104.4(2)
O2 – Nd1 – O6	113.68(8)	Nd2 – O2 – Si4	149.1(2)
Nd1 – O1 – Nd2	104.59(8)	Nd2 – O3 – Si2	167.2(2)
Nd1 – O1 – Si1	147.3(2)	Nd2 – O4 – Si3	152.0(2)

Fig. 4. Molecular structure and [Nd₂O₆] coordination polyhedron of complex [Nd(OSiHtBu₂)₂(μ-OSiHtBu₂)₂] (2c). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level.

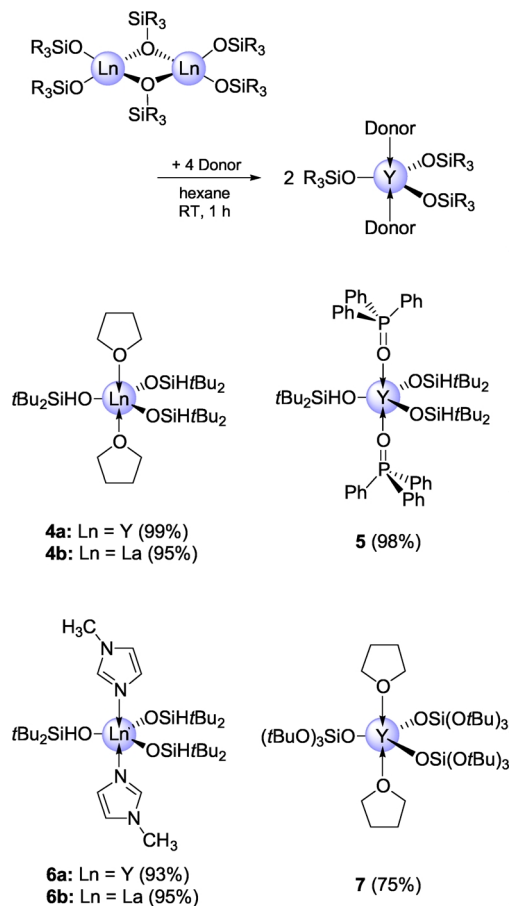
Complex **2c** crystallizes as a dimer with two bridging and four terminal siloxide ligands. Each neodymium(III) is coordinated by four oxygen atoms in a distorted tetrahedral fashion resulting in two *edge-sharing* [NdO₄]-tetrahedrons. As a consequence, the asymmetrically coordinated metal centers form two shorter (Nd–O_{terminal}, 2.141(3)–2.161(2) Å) and two longer Nd–O distances (Nd–O_{bridging}, 2.334(2)–2.440(2) Å). The O–Nd–O bond angles of the central four-membered Nd₂O₂ ring are in good agreement with the corresponding val-

ues of the structurally related neodymium alkoxide [Nd₂(OCHtBu)₆(CH₃CN)] [33]. Probably for reasons of minimum steric hindrance the Nd–O–Si angles of the bridging units (105.1(2) and 104.4(2)°) are significantly smaller than those of the terminal ligands (147.3(2)–167.2(2)°). Such small Nd–O–Si angles would also be in accordance with the presence of β(Si–H)···Nd agostic interactions in complex **2c**.

Monomeric bis(donor) adduct complexes

Although relatively bulky siloxide ligands have been employed for the synthesis of homoleptic complexes **1–3**, siloxide-bridged dinuclear molecules with four-coordinated metal centers were generated in non-coordinating solvents. Donor molecules such as tetrahydrofuran (thf), triphenylphosphine oxide (Ph₃PO), and *N*-methylimidazole (*N*-MeIm) are known to disrupt bridging ligands, affording mononuclear complexes on the expense of higher coordination numbers [31]. We examined this donor adduct formation in detail for complexes **2** featuring the sterically least demanding siloxide ligands. According to Scheme 2, addition of four equivalents of the donor molecule to a hexane solution of the homoleptic (dimeric) siloxide complex quantitatively gave the monomeric bis(donor) adduct complexes **4–6**. It can be assumed that such bis(donor) adduct complexes adopt a trigonal bipyramidal geometry with the donor ligands occupying the apical positions [31e]. Complexes **4–6** were characterized by elemental analysis, NMR and IR spectroscopy. Although an additional purification of the crude reaction products seems to be unnecessary, the bis(donor) adducts complexes can be easily recrystallized from hexane or hexane/toluene mixtures.

The ¹H NMR signals of the Si–H groups of OSiHtBu₂-siloxide complexes **4** do not show any pronounced shift compared to the dinuclear educt complexes **2**. It is only *N*-methylimidazol, the strongest donor molecule in this study, which caused a significant shift of Δδ = 0.15 (**6a**, Ln = Y) and 0.17 ppm (**6b**, Ln = La) to lower field. On the other hand, the resonances of the donor molecules themselves are shifted considerably. For example, the multiplets of the coordinated thf molecules in complex **4a** are observed at 4.08 and 1.40 ppm. The IR spectra of complexes **4–6** confirm donor adduct formation *via* disappearance of any lower-energy Si–H stretch vibrations. Correspondingly, a single Si–H absorption band



Scheme 2.

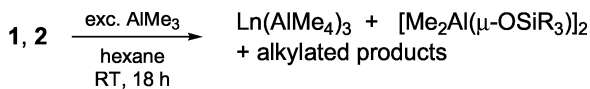
was found. The decrease of the wave numbers in the order **4a** (2030 cm⁻¹, THF) < **5** (2023 cm⁻¹, Ph₃PO) < **6a** (2013 cm⁻¹, *N*-MeIm) is in good agreement with increasing donor capability and hence stronger donor-metal interactions. Similar effects have been discussed for heteroleptic ytrocene(III) silylamide complexes of the type *rac*-[Me₂Si(2-MeBenzInd)₂][Y[N(SiHMe₂)](Donor)] (THF: $\tilde{\nu}_{SiH}$ = 1982 cm⁻¹, Ph₃PO: $\tilde{\nu}_{SiH}$ = 1895 cm⁻¹) [34]. A strong Y←O=PPh₃ interaction in complex **5** is also indicated by a lower-energy $\tilde{\nu}$ (P=O) band at 1170 cm⁻¹ compared to free Ph₃PO (1193 cm⁻¹) [35] and a deshielded ³¹P NMR resonance. The ²J_{PY} coupling constant of 10.9 Hz compares well to those found for triphenylphosphine oxide adduct complexes Y[N(SiMe₃)₂]₃(OPPh₃) (12.0 Hz) [36], Y[N(SiMe₃)₂]₂(PPh₂)(OPPh₃) (12.4 Hz) [36], and Y(C₅H₄PPh₂)₃(OPPh₃) (10.7 Hz) [37].

Interestingly, also the μ_2 : η^2 -bridging siloxide lig-

ands OSi(*Or*Bu)₃ of complex **3a** could be disrupted in the presence of the weakest donor molecule THF (Scheme 2). Thus obtained bis(donor) adduct **7** is soluble in warm hexane.

Reactivity towards trimethylaluminum (TMA)

In the course of our investigations of the reactivity of lanthanide complexes toward alkylaluminum reagents [38], we have also studied the alkylation behavior of some of the siloxide complexes presented in this work. Unfortunately, the reaction of homoleptic complexes **1** and **2** with an excess of TMA gave complex mixtures of differently alkylated rare-earth metal species. Several attempts to isolate one of the products by crystallization from saturated hexane or toluene solutions failed due to the extremely high solubility of the complexes or the formation of amorphous solids. However, several details of the alkylation sequence could be obtained from the proton NMR spectra of the crude reaction mixtures. As shown in Scheme 3, treatment of complexes **1** and **2** with an excess of TMA in hexane produced peralkylated species Ln(AlMe₄)₃ in varying amounts, independent of the type of siloxide ligand. Additionally, the NMR signals of dimethylaluminum siloxide complexes [Me₂Al(μ-OSiR₃)]₂ as the major cleavage products were detected [39]. In the presence of only a slight excess of TMA (3–6 equivalents), formation of the homoleptic tetramethylaluminates does not seem to be a dominant reaction pathway.

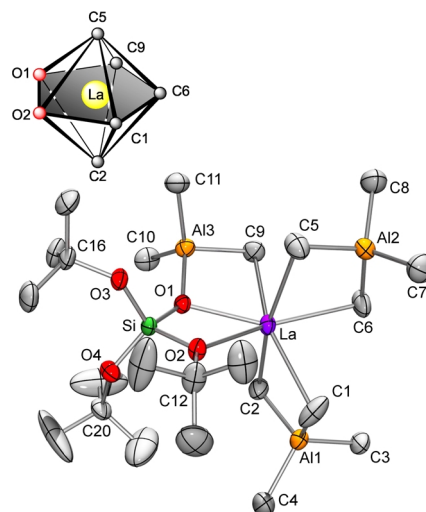


Scheme 3.

Recently, we have been able to synthesize the first structurally authenticated alkylated rare-earth metal siloxide derivatives, Ln[OSi(*Or*Bu)₃](AlMe₄)₂ (AlMe₃) (**8**), from the reaction of one equivalent HOSi(*Or*Bu)₃ with homoleptic lanthanide tetramethylaluminates Ln(AlMe₄)₃ (Ln = La, Nd) [24]. Now, we also found that complexes **8** are formed by the reaction of **3** with six equivalents of TMA along with other alkylated products (Scheme 4). For the large lanthanum atom, complex **8b** was not only identified by NMR spectroscopy as the major product but could be also crystallized from the reaction mixture in moderate yields. The ¹H NMR spectrum of complexes **8** revealed three signals with relative integral ratio of 27:24:9 assignable to *Or*Bu, AlMe₄, and AlMe₃ groups, re-

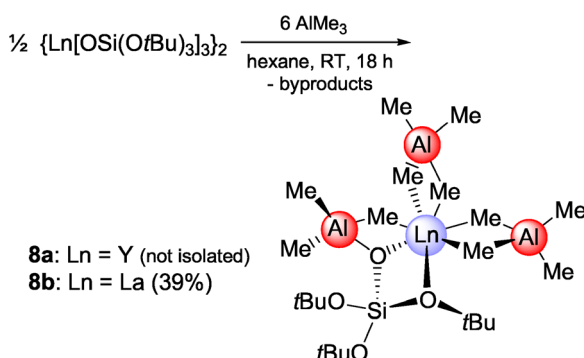
Table 2. Selected bond lengths [Å] and angles [°] for La[OSi(OrBu)₃](AlMe₄)₂(AlMe₃) (**8b**).

La – C1	2.668(5)	Si – O1	1.627(2)
La – C2	2.714(3)	Si – O2	1.670(2)
La – C5	2.680(4)	Si – O3	1.602(2)
La – C6	2.800(4)	Si – O4	1.600(2)
La – C9	2.798(3)	Al1 – C1	2.074(4)
La ... Al1	3.288(1)	Al1 – C2	2.054(4)
La ... Al2	3.311(1)	Al2 – C5	2.080(4)
La ... Al3	3.347(1)	Al2 – C6	2.063(4)
La ... Si	3.343(97)	Al3 – C9	2.045(4)
La – O1	2.409(2)	Al3 – O1	1.854(2)
La – O2	2.727(2)		
O1 – La – O2	56.83(5)	C5 – La – C6	77.2(1)
O1 – La – C1	131.2(1)	C5 – La – C9	87.7(1)
O1 – La – C2	89.50(8)	C6 – La – C9	77.3(1)
O1 – La – C5	99.56(9)	Al1 – La – Al2	112.52(2)
O1 – La – C6	146.8(1)	Al1 – La – Si	109.73(2)
O1 – La – C9	69.56(8)	Al2 – La – Si	132.93(2)
O2 – La – C1	83.5(1)	C1 – Al1 – C2	109.4(2)
O2 – La – C2	109.63(8)	C5 – Al2 – C6	111.3(2)
O2 – La – C5	84.9(1)	La – C1 – Al1	86.9(1)
O2 – La – C6	152.16(8)	La – C2 – Al1	86.0(1)
O2 – La – C9	123.50(8)	La – C5 – Al2	87.2(1)
C1 – La – C2	77.5(1)	La – C6 – Al2	84.3(1)
C1 – La – C5	104.2(1)	La – C9 – Al3	85.9(1)
C1 – La – C6	80.6(1)	La – O1 – Al3	102.69(8)
C1 – La – C9	151.8(1)	O1 – Al3 – C9	100.0(1)
C2 – La – C5	165.5(1)	La – O1 – Si	110.40(9)
C2 – La – C6	89.0(1)	La – O2 – Si	96.02(8)
C2 – La – C9	84.8(1)		

Fig. 5. Molecular structure of and [LaO₂C₅] core atoms of complex La[OSi(OrBu)₃](AlMe₄)₂(AlMe₃) (**8b**). Heavy atoms are represented by atomic displacement ellipsoids at the 50% level.

analysis. There is only one structurally authenticated example of a rare-earth metal complex with combined AlMe₄[−] monoanionic and AlMe₃ donor ligands, Nd(NiPr₂)(AlMe₃)(AlMe₄) [40]. Figure 5 shows the previously communicated molecular structure of complex **8b** [24], the structural features of which we would like to discuss in more detail in the following.

The lanthanum center is 7-coordinated by five “AlMe” carbon atoms and two oxygen atoms of an asymmetrically η²-coordinating siloxide ligand. Overall, a distorted pentagonal bipyramidal coordination geometry is realized, with one methyl carbon atom of each of the η²-coordinating tetramethylaluminate ligands in the apical positions (La–C2 2.714(3) Å, La–C5 2.680(4) Å, ∠C2–La–C5 165.5(1)°). In contrast to structurally related mono(pentamethylcyclopentadienyl) bis(tetramethylaluminate) complexes Cp^{*}Ln(AlMe₄)₂ [41], one of the [AlMe₄] units in **8b** is asymmetrically η²-coordinated: The La–C bond length involving carbon atom C6 which is in pseudo-trans position to the oxygen atoms of the η²-coordinated siloxide ligand appears with 2.800(4) Å significantly elongated compared to the La–C5 distance (2.680(4) Å) and is equal to that of La–C9 (AlMe₃ donor). For further comparison, the La–C1 and La–C2 distances of the less distorted second AlMe₄[−] ligand are 2.668(5) and 2.714(3), respectively, and those of the η²-coordinated AlMe₄[−] in Cp^{*}La(AlMe₄)₂ are 2.694(3) and 2.707(3) Å, [41].



Scheme 4.

spectively. This is in accordance with the molecular composition given in Scheme 4. A variable temperature NMR study of the lanthanum derivative **8b** did not show any decoalescence of the “AlMe” signals. Even at −90 °C a marginal resonance broadening indicates rapid exchange of the bridging and terminal methyl groups of each AlMe₃ donor and AlMe₄[−] monoanionic ligand.

The solid state structure of complex **8b** could be unambiguously established by an X-ray structure

The bond lengths and angles involving the TMA adduct are in good agreement with similar adduct complexes such as $\text{La}(\text{OC}_6\text{H}_3i\text{Pr}_2\text{-2,6})_3(\text{AlMe}_3)_2$ (La–C 2.800(5) Å) [42]. The La–O distances of **8b** clearly show an elongated La–O(donor) contact of 2.727(2) Å and a shorter La–O(siloxide) bond length of 2.409(2) Å. For comparison, the corresponding Sm–O distances in $\{\text{Sm}[\text{OSi}(\text{OtBu})_3]_2[\mu\text{-OSi}(\text{OtBu})_3]_2\}$ range from 2.257(6) Å (terminal) to 2.701(6) Å (bridging). Finally, the O1–La–O2 bite angle of $56.83(5)^\circ$ is significantly smaller than those in structurally related neodymium(III) complexes $\text{Nd}(\text{OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2(\text{THF})_2(\mu\text{-OC}_6\text{H}_3\text{Me}_2\text{-2,6})_2(\text{AlEt}_2)$ ($61.5(3)^\circ$) [43] and $\text{Nd}[(\mu\text{-OC}_6\text{H}_4\text{Me-4})_2\text{AlMe}_2]_3$ ($63.7(2)^\circ$) [44].

Conclusions

A dinuclear molecular arrangement seems to be a favored structural motif in homoleptic lanthanide complexes derived from sterically bulky siloxide ligands. The bis(siloxide)-bridged composition $[\text{Ln}(\text{OSiR}_3)_2(\mu\text{-OSiR}_3)]_2$ tolerates a wide range of siloxide substituents including $\text{SiR}_3 = \text{Si}^t\text{BuPh}_2$, $\text{Si}^i\text{H}^t\text{Bu}_2$, $\text{Si}(\text{OtBu})_3$ (this work) and SiPh_3 , and Si^tBuMe_2 [10,26]. The $\text{OSi}^i\text{H}^t\text{Bu}_2$ siloxide ligand features the “SiH” moiety as an efficient spectroscopic probe for the elucidation of secondary Si–H···Ln interactions. Donor molecules Do such as tetrahydrofurane, triphenylphosphine oxide, and *N*-methylimidazol readily cleave μ_2 -bridging OSiR_3 ligands, even the $\mu_2 : \eta^2$ -bonded $\text{OSi}(\text{OtBu})_3$ ligands, to afford bis(donor) adducts of type $\text{Ln}(\text{OSiR}_3)_3(\text{Do})_2$. Rare-earth metal-bonded terminal and bridging siloxide ligands can be completely separated off by treatment with excess of organoaluminum reagents such as trimethylaluminum (TMA) as shown for the formation of homoleptic $\text{Ln}(\text{AlMe}_4)_3$ and co-product $[\text{Me}_2\text{Al}(\mu\text{-OSiR}_3)]_2$. Interestingly, partly alkylated complex $\text{La}[\text{OSi}(\text{OtBu})_3](\text{AlMe}_4)_2(\text{AlMe}_3)$ revealed a markedly asymmetric η^2 -coordination mode of one of the AlMe_4^- ligands.

Experimental Section

General considerations

All operations were performed with rigorous exclusion of air and water, using high-vacuum and glove-box techniques (MB Braun MB150B-G-II; < 1 ppm O_2 , < 1 ppm H_2O). Solvents were predried and distilled from Na/K alloy (benzophenone ketyl) under argon. Deuterated solvents were

obtained from Deutero GmbH and degassed and dried over Na/K alloy. $(t\text{BuO})_3\text{SiOH}$ was purchased from Aldrich and sublimed before use. *Tert*-butyldiphenylsilanol and *Di-tert*-butylsilanol were synthesized according to slightly modified literature procedures [45,46]. NMR spectra were recorded either on a JEOL-GX-400 (FT, 399.78 MHz ^1H ; 100.5 MHz ^{13}C) or on a JEOL JNM-GX-270 (FT, 270.16 MHz ^1H ; 67.93 MHz ^{13}C) spectrometer in C_6D_6 at 25 °C unless otherwise noted. ^1H and ^{13}C shifts are referenced to internal solvent resonances and reported relative to TMS. IR spectra were recorded on a Perkin-Elmer 1650-FTIR spectrometer as Nujol mulls. Elemental analyses were performed in the microanalytical laboratory of the institute.

General procedure for the synthesis of homoleptic lanthanide siloxide complexes **1** and **2**

To a solution of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ in hexane was slowly added a hexane or toluene solution of three equivalents of the silanol. The mixture was stirred at ambient temperature overnight. Then, the solvent was removed *in vacuo*. The remaining solid was washed several times with small amounts of cold hexane or crystallized from hexane at -45°C to give the lanthanide siloxide complexes in good yields.

$[\text{Y}(\text{OSi}^t\text{BuPh}_2)_2(\mu\text{-OSi}^t\text{BuPh}_2)]_2$ (**1a**)

Following the procedure described above, $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (0.570 g, 1.00 mmol) and $\text{HOSi}^t\text{BuPh}_2$ (0.769 g, 3.00 mmol) yielded **1a** as a white solid (0.790 g, 0.46 mmol, 92%). ^1H NMR: $\delta = 0.95$ (s, 36 H, CMe_3), 1.12 (s, 18 H, $\mu\text{-CMe}_3$), 6.81 (t, $^3J = 6.9$ Hz, 12 H, $\mu\text{-Ph-H}_{\text{para}}$, $\text{Ph-H}_{\text{para}}$), 7.13 (m, 16 H, $\text{Ph-H}_{\text{meta}}$), 7.19 (m, 8 H, $\mu\text{-Ph-H}_{\text{meta}}$), 7.65 (d, $^3J = 6.7$ Hz, 16 H, $\text{Ph-H}_{\text{ortho}}$), 7.75 (d, $^3J = 6.4$ Hz, 8 H, $\mu\text{-Ph-H}_{\text{ortho}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.5$ ($\mu\text{-CMe}_3$), 19.7 (CMe_3), 28.1 ($\mu\text{-CMe}_3$), 28.5 (CMe_3), 127.5, 128.8 (μ), 129.7, 131.1 (μ), 133.2 (μ), 135.6, 136.2, 138.8 (μ). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -15.7$, -4.5 (μ). Analysis for $\text{C}_{96}\text{H}_{114}\text{O}_6\text{Si}_6\text{Y}_2$: calcd. C 67.42, H 6.72; found C 67.47, H 6.75.

$[\text{La}(\text{OSi}^t\text{BuPh}_2)_2(\mu\text{-OSi}^t\text{BuPh}_2)]_2$ (**1b**)

Following the procedure described above, $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ (0.620 g, 1.00 mmol) and $\text{HOSi}^t\text{BuPh}_2$ (0.769 g, 3.00 mmol) yielded **1b** as a white solid (0.816 g, 0.45 mmol, 90%). IR: $\tilde{\nu} = 1586$ w, 1426 s, 1360 m, 1305 w, 1261 w, 1185 w, 1155 w, 1104 s, 1029 w, 998 w, 940 s, 894 s, 851 s, 822 m, 742 m, 702 s, 685 m, 622 m, 607 m, 510 s, 491 cm^{-1} . ^1H NMR: $\delta = 1.00$ (s, 36 H, CMe_3), 1.16 (s, 18 H, $\mu\text{-CMe}_3$), 6.73 (t, $^3J = 7.0$ Hz, 4 H, $\mu\text{-Ph-H}_{\text{para}}$), 6.82 (t, $^3J = 7.0$ Hz, 8 H, $\text{Ph-H}_{\text{para}}$), 7.15 (m, $^3J = 7.0$ Hz, 16 H, $\text{Ph-H}_{\text{meta}}$), 7.21 (t, $^3J = 7.0$ Hz, 8 H, $\mu\text{-Ph-H}_{\text{meta}}$), 7.73 (m, 24 H, $\mu\text{-Ph-H}_{\text{ortho}}$, $\text{Ph-H}_{\text{ortho}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 19.8$ (CMe_3), 20.1 ($\mu\text{-CMe}_3$), 28.2 (CMe_3 , $\mu\text{-CMe}_3$),

127.6, 128.8 (μ), 130.3, 131.6 (μ), 134.2 (μ), 135.3, 135.8, 139.4 (μ). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -17.5$, -9.5 (μ). Analysis for $\text{C}_{96}\text{H}_{114}\text{La}_2\text{O}_6\text{Si}_6$: calcd. C 63.69, H 6.35; found C 62.97, H 6.02.

$[\text{Y}(\text{OSiHtBu}_2)_2(\mu\text{-OSiHtBu}_2)]_2$ (**2a**)

Following the procedure described above, $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (0.570 g, 1.00 mmol) and HOSiHtBu_2 (0.481 g, 3.00 mmol) yielded **2a** as a white crystalline solid (0.503 g, 0.44 mmol, 89%). IR: $\tilde{\nu} = 2061$ m, 1928 w, br, 1365 m, 1010 w, 969 m, 925 s, 870 s, 823 s, 722 w, 621 w, 582 w, 484 m cm^{-1} . ^1H NMR: $\delta = 1.19$ (s, 108 H, CMe_3), 4.47 (s, 6 H, SiH). ^1H NMR (toluene- d_8 , -80°C): $\delta = 1.14$ (s, 36 H, $\mu\text{-CMe}_3$), 1.28 (s, 72 H, CMe_3), 4.52 (s, 4 H, SiH), 4.58 (s, 2 H, $\mu\text{-SiH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.1$ (CMe_3), 28.2 (CMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (toluene- d_8 , -80°C): $\delta = 19.9$ (CMe_3), 26.9 ($\mu\text{-CMe}_3$), 28.0 (CMe_3), $\mu\text{-CMe}_3$ -peak below solvent signal. $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = 3.3$ (very broad). Analysis for $\text{C}_{48}\text{H}_{114}\text{O}_6\text{Si}_6\text{Y}_2$: calcd. C 50.85, H 10.14; found C 49.47, H 10.25.

$[\text{La}(\text{OSiHtBu}_2)_2(\mu\text{-OSiHtBu}_2)]_2$ (**2b**)

Following the procedure described above, $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ (0.620 g, 1.00 mmol) and HOSiHtBu_2 (0.481 g, 3.00 mmol) yielded **2b** as a white solid (0.543 g, 0.44 mmol, 88%). IR: $\tilde{\nu} = 2059$ m, 1963 w, br, 1366 m, 1010 w, 998 w, 949 m, 901 s, 868 m, 841 m, 823 s, 722 w, 620 w, 576 w, 478 m cm^{-1} . ^1H NMR: $\delta = 1.16$ (s, 108 H, CMe_3), 4.49 (s, 6 H, SiH). ^1H NMR (toluene- d_8 , -90°C): $\delta = 1.10$ (s, 36 H, $\mu\text{-CMe}_3$), 1.30 (s, 72 H, CMe_3), 4.42 (s, br, 2 H, $\mu\text{-SiH}$), 4.60 (s, 4 H, SiH). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.1$ (CMe_3), 28.0 (CMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = 2.4$. ^{29}Si NMR: $\delta = 2.4$ (ddez, $^1J = 177$ Hz, $^3J = 6$ Hz, SiHtBu₂). Analysis for $\text{C}_{48}\text{H}_{114}\text{La}_2\text{O}_6\text{Si}_6$: calcd. C 46.73, H 9.31; found C 47.03, H 9.61.

$[\text{Nd}(\text{OSiHtBu}_2)_2(\mu\text{-OSiHtBu}_2)]_2$ (**2c**)

Following the procedure described above, $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$ (0.625 g, 1.00 mmol) and HOSiHtBu_2 (0.481 g, 3.00 mmol) yielded **2c** as a pale blue solid (0.550 g, 0.44 mmol, 89%). IR: $\tilde{\nu} = 2062$ m, 1939 w, br, 1362 m, 1305 w, 1246 w, 1207 w, 1170 w, 998 m, 952 s, 903 s, 843 s, 825 s, 765 m, 722 m, 622 m, 598 w, 578 w, 477 m cm^{-1} . Analysis for $\text{C}_{48}\text{H}_{114}\text{Nd}_2\text{O}_6\text{Si}_6$: calcd. C 46.33, H 9.23; found C 46.42, H 9.20.

$[\text{Lu}(\text{OSiHtBu}_2)_2(\mu\text{-OSiHtBu}_2)]_2$ (**2d**)

Following the procedure described above, $\text{Lu}[\text{N}(\text{SiMe}_3)_2]_3$ (0.656 g, 1.00 mmol) and HOSiHtBu_2 (0.481 g, 3.00 mmol) yielded **2d** as a white solid (0.603 g, 0.46 mmol, 92%). IR: $\tilde{\nu} = 2066$ s, 1915 w, sh, 1206 w, 977 m, 932 s,

849 s, 824 s, 722 w, 618 w, 528 w, 485 m cm^{-1} . ^1H NMR: $\delta = 1.21$ (s, 108 H, CMe_3), 4.51 (s, br, 4 H, SiH), 4.75 (s, br, 2 H, $\mu\text{-SiH}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.2$ (CMe_3 , $\mu\text{-CMe}_3$), 27.8 ($\mu\text{-CMe}_3$), 28.4 (CMe_3). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = 4.1$ (Si), 12.4 ($\mu\text{-Si}$). Analysis for $\text{C}_{48}\text{H}_{114}\text{Lu}_2\text{O}_6\text{Si}_6$: calcd. C 44.15, H 8.80; found C 44.43, H 8.93.

General procedure for the synthesis of homoleptic lanthanide siloxide complexes 3

To a solution of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ in hexane was slowly added a hexane solution of three equivalents of silanol $\text{HOSi}(\text{OtBu})_3$. Instantly, a white precipitate formed. To complete the reaction the mixture was stirred at ambient temperature for another 16 h. Then, the white solid was isolated by centrifugation, washed three times with small amounts of hexane and dried under reduced pressure until constant weight. Due to the extremely low solubility of yttrium complex **3a** in toluene and benzene carbon NMR spectra were not recorded.

$\{\text{Y}[\text{OSi}(\text{OtBu})_3]_2[\mu\text{-OSi}(\text{OtBu})_3]\}_2$ (**3a**)

Following the procedure described above, $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (0.570 g, 1.00 mmol) and $\text{HOSi}(\text{OtBu})_3$ (0.793 g, 3.00 mmol) yielded **3a** as a white solid (0.585 g, 0.33 mmol, 67%). IR: $\tilde{\nu} = 1364$ s, 1301 w, 1240 m, 1218 w, 1193 s, 1074 s, sh, 1046 vs, 1022 s, 1002 m, 954 s, 901 m, 822 m, 721 w, 697 m, 634 w, 616 w, 500 m, 440 m. ^1H NMR: $\delta = 1.52$ (s, 18 H, $\mu\text{-CMe}_3$), 1.58 (s, 108 H, CMe_3), 1.74 (s, 36 H, $\mu\text{-CMe}_3$). Analysis for $\text{C}_{72}\text{H}_{162}\text{O}_{24}\text{Si}_6\text{Y}_2$: calcd. C 49.18, H 9.29; found C 49.16, H 9.29.

$\{\text{La}[\text{OSi}(\text{OtBu})_3]_2[\mu\text{-OSi}(\text{OtBu})_3]\}_2$ (**3b**)

Following the procedure described above, $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ (0.620 g, 1.00 mmol) and $\text{HOSi}(\text{OtBu})_3$ (0.793 g, 3.00 mmol) yielded **3b** as a white solid (0.729 g, 0.39 mmol, 79%). IR: $\tilde{\nu} = 1364$ s, 1298 w, 1242 m, 1218 w, 1194 m, 1071 s, 1044 s, 1021 s, 992 m, 940 s, 928 s, 910 s, 822 m, 720 w, 699 m, 518 w, 494 w cm^{-1} . ^1H NMR: $\delta = 1.47$ (s, 18 H, $\mu\text{-CMe}_3$), 1.57 (s, 108 H, CMe_3), 1.72 (s, 36 H, $\mu\text{-CMe}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 31.9$ ($\mu\text{-CMe}_3$), 32.4 ($\mu\text{-CMe}_3$), 32.6 (CMe_3), 71.6 (CMe_3), 73.0 ($\mu\text{-CMe}_3$), 76.1 ($\mu\text{-CMe}_3$). Analysis for $\text{C}_{72}\text{H}_{162}\text{La}_2\text{O}_{24}\text{Si}_6$: calcd. C 46.53, H 8.79; found C 46.55, H 8.73.

General procedure for the synthesis of monomeric donor adducts

To a solution or suspension of the dinuclear lanthanide siloxide complex in hexane was added a hexane solution of two equivalents of the donor molecule (tetrahydrofuran, triphenylphosphine oxide, N-methylimidazole). The mixture was stirred at ambient temperature for 1 h. Then, the solvent

was removed *in vacuo*. The remaining solid was washed with small amounts of cold hexane or crystallized from hexane at -45°C to give the bis(donor) adduct complexes in excellent yields. Due to the “low” boiling point of THF and ease of separation the bis(THF) adduct complexes can be generated by addition of larger excess of THF.

$Y(\text{OSiHtBu}_2)_3(\text{THF})_2$ (**4a**)

Following the procedure described above, **2a** (0.113 g, 0.10 mmol) and THF (~ 0.5 ml) yielded **4a** as a white crystalline solid (0.139 g, 0.20 mmol, 99%). IR: $\tilde{\nu} = 2030$ s, 1360 m, sh, 1297 w, 1260 w, 1205 w, 1172 w, 1029 m, 1009 m, 1000 w, 956 s, 874 m, 845 s, 822 s, 722 w, 620 w, 577 w, 487 m, 441 w. ^1H NMR: $\delta = 1.21$ (s, 54 H, CMe_3), 1.40 (m, 8 H, THF), 4.08 (m, 8 H, THF), 4.43 (s, 3 H, SiH). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.3$ (CMe_3), 25.3 (THF), 28.2 (CMe_3), 71.0 (THF). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -1.5$ (broad signal). Analysis for $\text{C}_{32}\text{H}_{73}\text{O}_5\text{Si}_3\text{Y}$: calcd. C 54.05, H 10.35; found C 54.33, H 10.52.

$\text{La}(\text{OSiHtBu}_2)_3(\text{THF})_2$ (**4b**)

Following the procedure described above, **2b** (0.123 g, 0.10 mmol) and THF (~ 0.5 ml) yielded **4b** as a white crystalline solid (0.145 g, 0.19 mmol, 95%). IR: $\tilde{\nu} = 2028$ s, 1358 m, 1294 w, 1205 w, 1176 w, 1034 s, 1009 m, 998 m, 932 vs, 907 s, 874 s, 820 s, 666 w, 618 m, 576 w, 475 m. ^1H NMR: $\delta = 1.21$ (s, 54 H, CMe_3), 1.41 (m, 8 H, THF), 3.83 (m, 8 H, THF), 4.45 (s, 3 H, SiH). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.3$ (CMe_3), 25.5 (THF), 28.2 (CMe_3), 69.4 (THF). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -2.1$ (broad signal). Analysis for $\text{C}_{32}\text{H}_{73}\text{LaO}_5\text{Si}_3$: calcd. C 50.50, H 9.67; found C 51.23, H 10.11.

$Y(\text{OSiHtBu}_2)_3(\text{O=PPh}_3)_2$ (**5**)

Following the procedure described above, **2a** (0.113 g, 0.10 mmol) and Ph_3PO (0.111 mg, 0.40 mmol) yielded **5** as a white crystalline solid (0.221 g, 0.20 mmol, 98%). IR: $\tilde{\nu} = 2014$ s, 1591 w, 1437 s, 1356 w, 1308 w, 1170 s, 1123 s, 1098 w, 1070 w, 1009 w, 988 w, 969 s, 836 m, 819 s, 745 m, 725 s, 692 s, 617 w, 541 s. ^1H NMR: $\delta = 1.13$ (s, 54 H, CMe_3), 4.42 (s, 3 H, SiH), 7.12 (t, $^3J = 7.6$ Hz, 12 H, $\text{Ph-H}_{\text{para}}$), 7.19 (t, $^3J = 7.6$ Hz, 12 H, $\text{Ph-H}_{\text{meta}}$), 7.89 (m, 12 H, $\text{Ph-H}_{\text{ortho}}$). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.5$ (CMe_3), 28.7 (CMe_3), 128.8 (d, $^2J_{\text{CP}} = 13.1$ Hz, $\text{Ph-H}_{\text{ortho}}$), 130.5 (d, $^1J_{\text{CP}} = 109.2$ Hz, $\text{Ph-H}_{\text{ipso}}$), 132.6 (s, $\text{Ph-H}_{\text{para}}$), 133.3 (d, $^3J_{\text{CP}} = 10.8$ Hz, $\text{Ph-H}_{\text{meta}}$). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -3.7$ (d, $^2J_{\text{SiY}} = 5.8$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 35.0$ (d, $^2J_{\text{PY}} = 10.9$ Hz). Analysis for $\text{C}_{60}\text{H}_{87}\text{O}_5\text{P}_2\text{Si}_3\text{Y}$: calcd. C 64.15, H 7.81; found C 63.98, H 7.89.

$Y(\text{OSiHtBu}_2)_3(\text{N-MeIm})_2$ (**6a**)

Following the procedure described above, **2a** (0.113 g, 0.10 mmol) and *N*-MeIm (0.033 g, 0.40 mmol) yielded **6a**

as a white crystalline solid (0.136 g, 0.19 mmol, 93%). IR: $\tilde{\nu} = 2023$ m, 1590 w, 1529 m, 1517 m, 1420 w, 1285 m, 1230 m, 1155 w, 1110 m, 1089 m, 968 s, 934 s, 841 s, 820 s, 741 m, 660 m, 617 m, 577 w, 484 m. ^1H NMR: $\delta = 1.25$ (s, 54 H, CMe_3), 2.38 (s, 6 H, $^{\text{Im}}\text{Me}$), 4.63 (s, 3 H, SiH), 5.99 (s, 2 H, Im), 7.48 (s, 2 H, Im), 7.92 (s, 2 H, Im). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.5$ (CMe_3), 28.3 (CMe_3), 32.4 ($^{\text{Im}}\text{Me}$), 120.0 (Im), 129.3 (Im), 139.6 (Im). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -2.4$. Analysis for $\text{C}_{32}\text{H}_{69}\text{N}_4\text{O}_3\text{Si}_3\text{Y}$: calcd. C 52.57, H 9.51, N 7.66; found C 52.60, H 9.46, N 8.08.

$\text{La}(\text{OSiHtBu}_2)_3(\text{N-MeIm})_2$ (**6b**)

Following the procedure described above, **2b** (0.123 g, 0.10 mmol) and *N*-MeIm (0.033 g, 0.40 mmol) yielded **6b** as a white crystalline solid (0.148 g, 0.19 mmol, 95%). IR: $\tilde{\nu} = 2062$ w, sh, 1983 m, 1593 w, 1523 m, 1512 w, 1418 w, 1284 w, 1231 w, 1108 w, 1083 m, 1002 m, 959 s, 922 s, 875 m, 844 m, 818 s, 736 m, 660 m, 615 m, 476 m. ^1H NMR: $\delta = 1.27$ (s, 54 H, CMe_3), 2.43 (s, 6 H, $^{\text{Im}}\text{Me}$), 4.66 (s, 3 H, SiH), 6.03 (s, 2 H, Im), 7.31 (s, 2 H, Im), 7.91 (s, 2 H, Im). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 20.6$ (CMe_3), 28.4 (CMe_3), 32.3 ($^{\text{Im}}\text{Me}$), 120.1 (Im), 129.0 (Im), 139.6 (Im). $^{29}\text{Si}\{^1\text{H}\}$ NMR: $\delta = -3.2$. Analysis for $\text{C}_{32}\text{H}_{69}\text{LaN}_4\text{O}_3\text{Si}_3$: calcd. C 49.21, H 8.90, N 7.17; found C 49.02, H 9.01, N 7.25.

$Y[\text{OSi}(\text{OtBu})_3]_3(\text{THF})_2$ (**7**)

Following the procedure described above, **3a** (0.352 g, 0.20 mmol) and THF (~ 0.5 ml) yielded **7** as a white crystalline solid (0.307 g, 0.30 mmol, 75%). IR: $\tilde{\nu} = 1361$ s, 1301 w, 1241 m, 1195 s, 1046 s, 1022 s, 995 s, 916 w, 876 w, 822 m, 721 w, 700 m, 640 w, 632 w, 521 w, 492 m. ^1H NMR: $\delta = 1.51$ (s, 81 H, CMe_3), 1.63 (m, 8 H, THF), 4.35 (m, 8 H, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 25.4$ (THF), 32.1 (CMe_3), 70.4 (CMe_3), 71.3 (THF). Analysis for $\text{C}_{44}\text{H}_{97}\text{O}_{14}\text{Si}_3\text{Y}$: calcd. C 51.64, H 9.55; found C 51.63, H 9.59.

General alkylation procedure

To a solution or suspension of the homoleptic lanthanide siloxide complex in hexane was added a hexane solution of six equivalents of TMA. The mixture was stirred at ambient temperature overnight. Then, the solvent and the volatile components were evaporated *in vacuo* and the remaining mixture was investigated by NMR spectroscopy. Crystallization from saturated hexane or toluene solutions was attempted at -45°C .

$Y[\text{OSi}(\text{OtBu})_3](\text{AlMe}_4)_2(\text{AlMe}_3)$ (**8a**)

Following the procedure described above, **3a** (0.457 g, 0.26 mmol) and AlMe_3 (0.115 g, 1.60 mmol) yielded a white solid. According to the ^1H NMR spectrum complex **8a** was generated in $\sim 80\%$ yield, however could not be isolated

as analytically pure compound by crystallization. ^1H NMR: $\delta = -0.34$ (s, 24 H, AlMe_4), -0.14 (s, 9 H, AlMe_3), 1.26 (s, 27 H, CMe_3).

La[OSi(OtBu)₃](AlMe₄)₂(AlMe₃) (8b)

Following the procedure described above, **3b** (0.465 g, 0.25 mmol) and AlMe_3 (0.108 g, 1.50 mmol) yielded **8b** as colorless crystals (0.063 g, 0.10 mmol, 39%). IR: $\tilde{\nu} = 1305$ w, 1246 m, 1188 s, 1089 s, 1062 s, 1027 m, 941 m, sh, 923 m, 897 s, 832 w, 820 m, 802 w, 695 s, br, 573 m, 532 m, 492 m. ^1H NMR: $\delta = -0.14$ (s, 9 H, AlMe_3), 0.06 (s, 24 H, AlMe_4), 1.24 (s, 27 H, CMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 0.2$ (AlMe_3), 6.0 (AlMe_4), 31.6 (CMe_3), 78.0 (CMe_3). Analysis for $\text{C}_{23}\text{H}_{60}\text{Al}_3\text{LaO}_4\text{Si}$: calcd. C 42.59, H 9.32; found C 42.85, H 9.32.

X-ray crystallography

Crystals of **2c** were grown by repeated crystallization from saturated hexane solutions. A colorless fragment measuring $0.7 \times 0.4 \times 0.2$ mm was selected in a perfluorinated ether and transferred into a glass capillary which was mounted in a cold N_2 stream on a STOE IPDS2 two-circle diffractometer. Preliminary examination and data collection were carried out at the window of a sealed X-ray tube (50 kV, 35 mA, 1.75 kW) and graphite monochromated $\text{Ag-K}\alpha$ radiation ($\lambda = 0.56087$ Å), controlled by the STOE X-AREA software package [47a]. Collected images were processed using X-AREA, the unit cell parameters were obtained by full-matrix least-squares refinements of 57048 reflections [47a]. Data: empirical formula $\text{C}_{48}\text{H}_{114}\text{O}_6\text{Nd}_2\text{Si}_6$, $f_w = 1244.42$, monoclinic system, space group $P2_1/c$ (Int. Tables N° 14); $a = 11.919(5)$, $b = 25.717(5)$, $c = 23.403(5)$ Å, $\beta = 98.071(5)^\circ$, $V = 7102(4)$ Å³, $\rho_{\text{calcd.}} = 1.164$ g cm⁻³. The data collection was performed at 183(1) K (θ -range: $6.38^\circ <$

$\theta < 20.52^\circ$; exposure time: 180 s per image; ω scan width 1°). A total number of 58570 reflections were collected. After merging ($R_{\text{int}} = 0.0291$), 13560 reflections remained, which were used for all further calculations. Absorption was corrected empirically using SORTAV [47b], with $\mu = 0.842$ mm⁻¹. The structure was solved by direct methods and refined with standard difference Fourier techniques [47c]. All hydrogen atoms were placed in calculated positions and included in the structure factor calculations but not refined (riding model). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme [47d].

Additional data of the refinement: 559 parameters; 24.3 reflections per parameter; weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.0409P)^2 + 6.2266P]$ where $P = (F_o^2 + 2F_c^2)/3$; shift/error < 0.002 in the last cycle of refinement; residual electron density $+1.43$ e Å⁻³, -0.51 e Å⁻³; $R1 = 0.0409$, $wR2 = 0.0834$ for all data, GOF = 1.050. Neutral atom scattering factors for all atoms were taken from the International Tables for X-ray Crystallography [47e]. All calculations were performed on a PC workstation (Intel Pentium 4) with the program PLATON [47f], molecular drawings were done using the program Ortep-3 [47g] and POV-Ray [47h].

Supporting material available: Crystallographic information for complex **2c** has been deposited with the Cambridge Crystallographic Data Centre, CCDC 247448. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax. +44-1223-336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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- [1] A. F. Hollemann, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, Vol. 101, de Gruyter, Berlin (1995).
- [2] a) M. P. Rosynek, *Catal. Rev.* **16**, 111 (1977); b) G. N. Sauvion, P. Ducros, *J. Less-Common. Met.* **111**, 23 (1985); c) A. Trovarelli, *Catal. Rev.* **38**, 439 (1996).
- [3] a) H. Schmidbaur, *Angew. Chem.* **77**, 206 (1965); *Angew. Chem. Int. Ed. Engl.* **4**, 201 (1965); b) F. Schindler, H. Schmidbaur, *Angew. Chem.* **79**, 697 (1967); *Angew. Chem. Int. Ed. Engl.* **6**, 683 (1967).
- [4] P. T. Wolczanski, *Polyhedron* **14**, 3335 (1995).
- [5] C–O cleavage reactions have been observed in several early transition and rare-earth metal complexes. For examples, see a) R. E. Lapointe, P. T. Wolczanski, G. Van Duyne, *Organometallics* **4**, 1810 (1985); b) O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting, K. G. Caulton, *Inorg. Chem.* **28**, 263 (1989); c) G. Helgesson, S. Jagner, O. Poncelet, L. G. Hubert-Pfalzgraf, *Polyhedron* **10**, 1559 (1991).
- [6] For recent reviews, see a) R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev.* **96**, 2205 (1996); b) L. King, A. C. Sullivan, *Coord. Chem. Rev.* **189**, 19 (1999); c) F. J. Feher, T. A. Budzichowski, *Polyhedron* **14**, 3239 (1995); d) B. Marciniec, H. Maciejewski, *Coord. Chem. Rev.* **223**, 310 (2001).
- [7] For examples, see a) F. R. Hartley, *Supported Metal Complexes*, Reidel, Boston (1985); b) Y. Iwasawa (ed.): *Tailored Metal Catalysts*, Reidel, Boston (1986); c) F. J. Feher, *J. Am. Chem. Soc.* **108**, 3850 (1986).
- [8] a) C. Floriani, *Chem. Eur. J.* **5**, 19 (1999); b) H. C. L. Abbenhuis, *Chem. Eur. J.* **6**, 25 (2000);

- c) R. Duchateau, *Chem. Rev.* **102**, 3525 (2002); d) S. Scott, C. M. Crudden, C. W. Jones (eds): *Nanostructured Catalysts*, Kluwer Academic/Plenum Publishers, New York (2002); e) C. Copéret, M. Chabanas, R. P. Saint-Arroman, J.-M. Basset, *Angew. Chem.* **115**, 164 (2003); *Angew. Chem. Int. Ed.* **42**, 156 (2003).
- [9] J. M. Batwara, R. C. Mehrotra, *J. Inorg. Nucl. Chem.* **32**, 411 (1970).
- [10] a) M. J. McGearry, P. S. Coan, K. Folting, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **30**, 1723 (1991); b) M. J. McGearry, P. S. Coan, K. Folting, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **28**, 3283 (1989); c) P. S. Coan, M. J. McGearry, E. B. Lobkovsky, K. G. Caulton, *Inorg. Chem.* **30**, 3570 (1991); d) P. S. Coan, L. H. Hubert-Pfalzgraf, K. G. Caulton, *Inorg. Chem.* **31**, 1262 (1992).
- [11] a) K. J. Covert, D. R. Neithamer, M. C. Zonneville, R. E. LaPointe, C. P. Schaller, P. T. Wolczanski, *Inorg. Chem.* **30**, 2494 (1991); b) P. Shao, D. J. Berg, G. W. Bushnell, *Inorg. Chem.* **33**, 3452 (1994).
- [12] A. N. Kornev, T. A. Chesnokova, E. V. Zhezlova, L. N. Zakharov, G. K. Fukin, Y. A. Kursky, G. A. Domrachev, P. D. Lickiss, *J. Organomet. Chem.* **587**, 113 (1999).
- [13] a) P. S. Gradeff, K. Yunlu, T. J. Deming, J. M. Olofson, R. J. Doedens, W. J. Evans, *Inorg. Chem.* **29**, 420 (1990); b) P. S. Gradeff, K. Yunlu, J. Less-Common Met. **149**, 81 (1989); c) P. S. Gradeff, K. Yunlu, A. Gleizes, J. Galy, *Polyhedron* **8**, 1001 (1989).
- [14] a) R. Anwender, H. W. Görlitzer, G. Gerstberger, C. Palm, O. Runte, M. Spiegler, *J. Chem. Soc., Dalton Trans.* 3611 (1999); b) J. Arnold, C. G. Hoffman, *J. Am. Chem. Soc.* **112**, 8621 (1990); c) T. I. Gountchev, T. D. Tilley, *Organometallics* **18**, 2896 (1999); d) D. J. Berg, R. A. Andersen, A. Zalkin, *Organometallics* **7**, 1858 (1988); e) H. Schumann, J. Winterfeld, R. D. Köhn, L. Esser, J. Sun, A. Dietrich, *Chem. Ber.* **126**, 907 (1993).
- [15] M. Karl, G. Seybert, W. Massa, K. Harms, A. Agarwal, R. Maleika, W. Stelter, A. Greiner, W. Heitz, B. Neumüller, K. Dehnicke, *Z. Anorg. Allg. Chem.* **625**, 1301 (1999).
- [16] D. J. Duncalf, P. B. Hitchcock, G. A. Lawless, *J. Organomet. Chem.* **506**, 347 (1996).
- [17] A. A. Trifonov, E. N. Kirillov, A. Fischer, F. T. Edelmann, M. N. Bochkarev, *Chem. Commun.* 2203 (1999).
- [18] a) S. Kou, Y. Wakatsuki, M. Nishiura, *JP 11.255.776* (1999); b) M. Nishiura, Z. Hou, T. Imamoto, Y. Wakatsuki, *Kidorui* **32**, 294 (1998); c) Z. Hou, Y. Wakatsuki, *J. Organomet. Chem.* **647**, 61 (2002); d) M. Nishiura, Z. Hou, Y. Wakatsuki, *Organometallics* **23**, 1359 (2004).
- [19] W. E. Piers, E. E. Bunel, J. E. Bercaw, *J. Organomet. Chem.* **407**, 51 (1991).
- [20] a) W. J. Evans, T. A. Ulibari, J. W. Ziller, *Organometallics* **10**, 134 (1991); b) V. Lorenz, A. Fischer, K. Jacob, W. Brüser, T. Gelbrich, P. G. Jones, F. T. Edelmann, *Chem. Commun.* 2217 (1998); c) V. Lorenz, A. Fischer, K. Jacob, W. Brüser, F. T. Edelmann, *Chem. Eur. J.* **7**, 848 (2001).
- [21] V. Lorenz, A. Fischer, S. Gießmann, J. W. Gilje, Y. Gun'ko, K. Jacob, F. T. Edelmann, *Coord. Chem. Rev.* **206–207**, 321 (2000).
- [22] a) W. A. Herrmann, R. Anwender, V. Dufaud, W. Scherer, *Angew. Chem.* **106**, 1338 (1994); *Angew. Chem. Int. Ed. Engl.* **33**, 1285 (1994); b) V. Lorenz, A. Fischer, F. T. Edelmann, *J. Organomet. Chem.* **647**, 245 (2002); c) P. L. Arnold, A. J. Blake, S. N. Hall, B. D. Ward, C. Wilson, *J. Chem. Soc., Dalton Trans.* 488 (2001); d) J. Annand, H. C. Aspinall, *J. Chem. Soc., Dalton Trans.* 1867 (2000); e) J. Annand, H. C. Aspinall, A. Steiner, *Inorg. Chem.* **38**, 3941 (1999).
- [23] Y. Gun'ko, R. Reilly, F. T. Edelmann, H.-G. Schmidt, *Angew. Chem.* **113**, 1319 (2001); *Angew. Chem. Int. Ed.* **40**, 1279 (2001).
- [24] A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer, R. Anwender, *Angew. Chem.* **116**, 2284 (2004); *Angew. Chem. Int. Ed.* **43**, 2234 (2004).
- [25] R. Anwender, *Top. Organometal. Chem.* **2**, 1 (1999).
- [26] W. J. Evans, R. E. Golden, J. W. Ziller, *Inorg. Chem.* **30**, 4963 (1991).
- [27] M. S. Rau, C. M. Kretz, G. L. Geoffroy, *Organometallics* **13**, 1624 (1994).
- [28] H. A. Stecher, A. Sen, A. L. Rheingold, *Inorg. Chem.* **28**, 3280 (1989).
- [29] Due to the paramagnetism of neodymium no NMR spectra were measured for complex **2c**.
- [30] R. D. Shannon, *Acta Crystallogr.* **A32**, 751 (1976).
- [31] a) W. A. Herrmann, N. W. Huber, J. Behm, *Chem. Ber.* **125**, 1405 (1992); b) W. A. Herrmann, R. Anwender, F. C. Munck, W. Scherer, V. Dufaud, N. W. Huber, G. R. J. Artus, *Z. Naturforsch.* **49b**, 1789 (1994); c) L. J. Procopio, P. J. Carroll, D. H. Berry, *J. Am. Chem. Soc.* **116**, 177 (1994); d) O. Runte, T. Priermeier, R. Anwender, *Chem. Commun.* 1385 (1996); e) W. A. Herrmann, F. C. Munck, G. R. J. Artus, O. Runte, R. Anwender, *Organometallics* **16**, 682 (1997); f) W. S. Rees, O. Just, H. Schumann, R. Weimann, *Angew. Chem.* **108**, 481 (1996); *Angew. Chem. Int. Ed. Engl.* **35**, 419 (1996).
- [32] M. A. Girardello, V. P. Conticelli, L. Brard, M. Sabat, A. L. Rheingold, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **116**, 10212 (1994).
- [33] W. A. Herrmann, R. Anwender, W. Scherer, *Chem. Ber.* **126**, 1533 (1993).

- [34] J. Eppinger, Dissertation, Technische Universität München (1999).
- [35] G. B. Deacon, J. H. S. Green, *Spectrochim. Acta* **24A**, 845 (1968).
- [36] H. C. Aspinall, D. C. Bradley, K. D. Sales, *J. Chem. Soc., Dalton Trans.* 2211 (1988).
- [37] G. B. Deacon, C. M. Forsyth, B. M. Gatehouse, A. Philofof, B. W. Skelton, A. H. White, P. A. White, *Aust. J. Chem.* **50**, 959 (1997).
- [38] a) A. Fischbach, F. Perdih, P. Sirsch, W. Scherer, R. Anwender, *Organometallics* **21**, 4569 (2002); b) A. Fischbach, E. Herdtweck, R. Anwender, G. Eickering, W. Scherer, *Organometallics* **22**, 499 (2003); c) A. Fischbach, Dissertation, Technische Universität München (2003).
- [39] a) S. J. Obrey, A. R. Barron, *J. Chem. Soc., Dalton Trans.* 2456 (2001); b) K. W. Terry, P. K. Ganzel, T. D. Tilley, *Chem. Mater.* **4**, 1290 (1992).
- [40] W. J. Evans, R. Anwender, J. W. Ziller, *Inorg. Chem.* **34**, 5927 (1995).
- [41] H. M. Dietrich, E. Herdtweck, R. Anwender, unpublished results.
- [42] G. R. Giesbrecht, J. C. Gordon, J. T. Brady, D. L. Clark, D. W. Michalczyk, B. L. Scott, J. G. Watkin, *Eur. J. Inorg. Chem.* 723 (2002).
- [43] W. J. Evans, M. A. Ansari, J. W. Ziller, *Inorg. Chem.* **34**, 3079 (1995).
- [44] W. J. Evans, M. A. Ansari, J. W. Ziller, *Polyhedron* **16**, 3429 (1997).
- [45] D. G. Mullen, G. Barany, *J. Org. Chem.* **53**, 5240 (1988).
- [46] a) T. J. Barton, C. R. Tully, *J. Organomet. Chem.* **172**, 11 (1979); b) R. Goikhman, M. Aizenberg, H.-B. Kraatz, D. Milstein, *J. Am. Chem. Soc.* **117**, 5865 (1995).
- [47] a) X-Area 1.19-2003, WINEXPOSE, PEAK-SEARCH 1.05-2001, RECIPE 1.09-2001, INTEGRATE 1.19-2003, Copyright STOE & Cie GmbH; b) R. H. Blessing, *Acta Crystallogr.* **A51**, 33 (1995); c) A. Altomare, G. Casciarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **27**, 435 (1994); d) G. M. Sheldrick, *SHELXL-97*; Universität Göttingen, Germany (1998); e) A. J. C. Wilson (ed.): *International Tables for Crystallography*; Vol. C, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199), Kluwer Academic Publishers, Dordrecht (1992); f) A. L. Spek, *Acta Crystallogr.* **A46**, C34 (1990); g) Ortep-3 for Windows: L. J. Farrugia, *J. Appl. Cryst.* **30**, 565 (1997); h) Persistence of VisionTM Ray Tracer (POV-RayTM), Copyright[©], POV-TeamTM 1991–2002.