

*f*-Element Disiloxanediolates: Novel Si–O-based Inorganic HeterocyclesVolker Lorenz,<sup>[a]</sup> Axel Fischer,<sup>[a]</sup> Klaus Jacob,<sup>[b]</sup> Wolfgang Brüser,<sup>[a]</sup> and Frank T. Edelmann\*<sup>[a]</sup>

Dedicated to Professor Herbert W. Roesky on the occasion of his 65th birthday

**Abstract:** The preparation and structural characterization of scandium and *f*-element complexes derived from the disiloxanediolate dianion,  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ , are reported. Reactions of in situ prepared  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  ( $\text{Ln} = \text{Eu}, \text{Sm}, \text{Gd}$ ) with  $(\text{Ph}_2\text{SiOH})_2\text{O}$  in different stoichiometries afforded the lanthanide disiloxanediolates  $[\text{Eu}\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Li}(\text{Et}_2\text{O})\}_3]$  (**1**),  $[\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Li}(\text{dme})\}_2\text{SmCl}(\text{dme})]$  (**2**), and  $[\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Li}(\text{thf})\}_2\text{GdN}(\text{SiMe}_3)_2]$  (**3**). In situ formed  $(\text{Ph}_2\text{SiOLi})_2\text{O}$  reacted with anhydrous  $\text{NdBr}_3$  (molar ratio 3:1) to give polymeric  $[\{\text{Nd}\{[(\text{Ph}_2\text{SiO})_2\text{O}]\}_3\{\mu\text{-Li}(\text{thf})\}_2\{\mu_2\text{-}$

$\text{LiBrLi}(\text{thf})(\text{Et}_2\text{O})\}_n]$  (**4**). Treatment of **3** with  $\text{Ph}_2\text{Si}(\text{OH})_2$  in the presence of acetonitrile yielded the dilithium trisiloxanediolate derivative  $[\{\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2\}\{\text{Li}(\text{MeCN})\}_2]$  (**5**), which according to an X-ray analysis displays an  $\text{Li}_4\text{O}_4$  heterocubane structure. The trinuclear scandium complex  $[\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Sc}(\text{acac})_2\}_2\text{Sc}(\text{acac})]$  (**6**) was obtained by reaction of  $[\{(\text{C}_5\text{Me}_5)\text{Sc}(\text{acac})_2\}$  ( $\text{C}_5\text{-}$

$\text{Me}_5 = \eta^5\text{-pentamethylcyclopentadienyl}$ ) with  $(\text{Ph}_2\text{SiOH})_2\text{O}$  in a 3:2 molar ratio. Selective formation of the colorless uranium(vi) derivative  $[\text{U}\{\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2\}\{[(\text{Ph}_2\text{SiO})_2\text{O}]\}]$  (**7**) was observed when uranocene,  $\text{U}(\eta^8\text{-C}_8\text{H}_8)_2$ , was allowed to react with  $(\text{Ph}_2\text{SiOH})_2\text{O}$ . An X-ray diffraction study of the solvated derivative  $[\text{U}\{\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2\}\{[(\text{Ph}_2\text{SiO})_2\text{O}]\} \cdot \text{Et}_2\text{O} \cdot \text{TMEDA}$  (TMEDA = *N,N,N',N'*-tetramethyl-ethylenediamine) (**7a**) revealed the presence of both the original  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$  dianion as well as the ring-enlarged  $[\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2]^{2-}$  ligand in the same molecule.

**Keywords:** disiloxanediolates • scandium • silicon • lanthanides • uranium

## Introduction

The chemistry of metallasiloxanes derived from silanediols, disiloxanediols, and related Si–OH species is an area of vigorous research activities<sup>[1]</sup> because such compounds are valuable precursors for metal oxides and silicates<sup>[2, 3]</sup> as well as models for silica-supported heterogeneous catalysts.<sup>[1, 4, 5]</sup> A particularly useful ligand is the readily available tetraphenyl-disiloxanediolate dianion,  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ , which gives rise to a variety of unusual and unexpected structures especially when combined with alkali metals<sup>[6]</sup> and early transition metals.<sup>[2b, 6, 7]</sup> The starting material tetraphenyl-disiloxanediol,  $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2(\text{OH})$ , is readily accessible from cheap starting materials.<sup>[8]</sup> Hydrolysis of  $\text{Ph}_2\text{SiCl}_2$  in the presence

of ammoniumcarbonate afforded tetraphenyl-disiloxanediol in yields up to 51%. Minor by-products in this synthesis are diphenylsilanediol,  $\text{Ph}_2\text{Si}(\text{OH})_2$  (6%) and hexaphenyltrisiloxanediol,  $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2\text{OSiPh}_2(\text{OH})$  (18%). The dilithium derivative of tetraphenyl-disiloxanediol,  $\text{Ph}_2\text{Si}(\text{OLi})\text{OSiPh}_2(\text{OLi})$ , can be prepared and isolated in the presence of various Lewis bases such as THF, pyridine, or 1,4-dioxane. Interesting supramolecular structures have been found in the crystalline adducts  $\text{Ph}_2\text{Si}(\text{OLi})\text{OSiPh}_2(\text{OLi}) \cdot 2\text{py}$ <sup>[9]</sup> and  $\text{Ph}_2\text{Si}(\text{OLi})\text{OSiPh}_2(\text{OLi}) \cdot 3\text{dioxane}$ .<sup>[10]</sup> In the former, dimeric self-assembly leads to the formation of a ladder-structure comprising three four-membered  $\text{Li}_2\text{O}_2$  rings, while the latter is polymeric in the solid state. Such well-defined Lewis base adducts of  $\text{Ph}_2\text{Si}(\text{OLi})\text{OSiPh}_2(\text{OLi})$  can be used as precursors for the preparation of transition metal derivatives of tetraphenyl-disiloxanediol. However, a more convenient preparative route involves in situ formation of  $\text{Ph}_2\text{Si}(\text{OLi})\text{OSiPh}_2(\text{OLi})$  by treatment of tetraphenyl-disiloxanediol with two equivalents of *n*-butyllithium in THF followed by reaction with the appropriate main group or transition metal halides. Various metallasiloxanes containing six-membered  $\text{MSi}_2\text{O}_3$  rings ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{V}, \text{Cr}, \text{Mn}, \text{Co}, \text{Cu}, \text{Mg}, \text{B}, \text{Sn}$ ) have been synthesized using this method. In these complexes the

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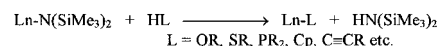
disiloxanediolate ligand can either be chelating,<sup>[11–13]</sup> bridging,<sup>[14–21]</sup> or chelate-bridging,<sup>[22, 23]</sup> with the latter two coordination modes being generally preferred over simple chelation. The coordination chemistry of silanediolate,  $[\text{R}_2\text{SiO}_2]^{2-}$ , and  $\alpha,\omega$ -siloxanediolate,  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ , ligands has been summarized in a most recent review article by Sullivan et al.<sup>[24]</sup> Apparently the  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$  ligand has not yet been employed in *f*-element chemistry.<sup>[25]</sup> To our knowledge,  $(\mu\text{-OSiMe}_2\text{OSiMe}_2\text{O})[(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{thf})_2]^{[26]}$  is the only closely related rare earth siloxane derivative reported in the literature. This compound was first obtained from a reaction of the highly reactive organosamarium hydride  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-H})_2]$  with dimethylsilicone joint grease. A more straightforward preparation involves treatment of  $[(\text{C}_5\text{Me}_5)_2\text{Sm}(\mu\text{-H})_2]$  with hexamethylcyclotrisiloxane in THF solution.<sup>[26]</sup> Somewhat related are a series of highly interesting lanthanide complexes containing *cyclo*(poly)siloxanolate ligands which were reported by Zhdanov et al.<sup>[27]</sup> We describe here the synthesis of novel lanthanide complexes derived from  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$  as well as the first scandium and uranium derivatives.

## Results and Discussion

Our initial investigations in this field were focussed on the preparation of lanthanide complexes containing the tetraphenyldisiloxanediolate ligand. It was soon discovered that a “silylamide route”<sup>[28a]</sup> was the method of choice for preparing such species. This synthetic method involves the reaction of lanthanide bis(trimethylsilylamides) with acidic substrate

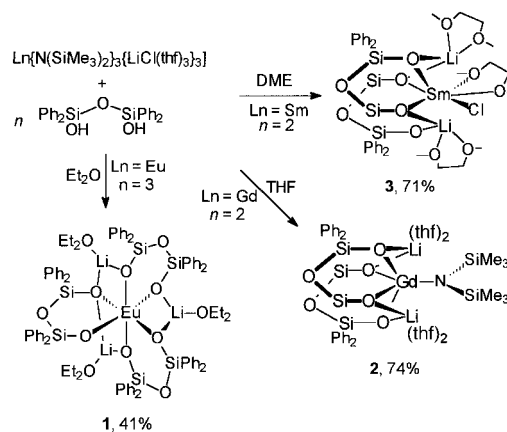
**Abstract in German:** *Es wird über die Darstellung und strukturelle Charakterisierung von Scandium- und f-Element-Komplexen des  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ -Dianions berichtet. Reaktionen von in situ hergestelltem  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  ( $\text{Ln} = \text{Eu}, \text{Sm}, \text{Gd}$ ) mit  $(\text{Ph}_2\text{SiOH})_2\text{O}$  in unterschiedlichen Stöchiometrien liefern die Lanthanoiddisiloxandiolate  $\text{Eu}\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Li}(\text{Et}_2\text{O})\}_3$  (**1**),  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Li}(\text{dme})\}_2\text{SmCl}(\text{dme})$  (**2**), und  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Li}(\text{thf})_2\}_2\text{GdN}(\text{SiMe}_3)_2$  (**3**). In situ gebildetes  $(\text{Ph}_2\text{SiOLi})_2\text{O}$  reagiert mit wasserfreiem  $\text{NdBr}_3$  (Molverhältnis 3:1) zum polymeren  $\{\mu\text{-LiBrLi}(\text{thf})(\text{Et}_2\text{O})\}[\text{Nd}\{(\text{Ph}_2\text{SiO})_2\text{O}\}_3\{\text{Li}(\text{thf})\}_2]_n$  (**4**). Die Umsetzung von **3** mit  $\text{Ph}_2\text{Si}(\text{OH})_2$  in Gegenwart von Acetonitril führt zum Dilithiumtrisiloxandiolat-Derivat  $\{[(\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2)\{\text{Li}(\text{MeCN})\}_2]_2$  (**5**), welches nach der Röntgenstrukturanalyse eine  $\text{Li}_4\text{O}_4$ -Heterokubanstruktur besitzt. Der dreikernige Scandiumkomplex  $\{[(\text{Ph}_2\text{SiO})_2\text{O}]\text{Sc}(\text{acac})_2\}_2\text{Sc}(\text{acac})$  (**6**) ist durch Reaktion von  $[(\text{C}_5\text{Me}_5)\text{Sc}(\text{acac})_2]$  ( $\text{C}_5\text{Me}_5 = \eta^5\text{-Pentamethylcyclopentadienyl}$ ) mit  $(\text{Ph}_2\text{SiOH})_2\text{O}$  im Molverhältnis 3:2 zugänglich. Bei der Reaktion von  $\text{U}(\eta^8\text{-C}_8\text{H}_8)_2$  mit  $(\text{Ph}_2\text{SiOH})_2\text{O}$  erfolgt selektiv die Bildung des farblosen Uran(VI)-Derivats  $[\text{U}\{(\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2\}_2\{(\text{Ph}_2\text{SiO})_2\text{O}\}]$  (**7**). Eine Röntgenstrukturanalyse des Solvats  $[\text{U}\{(\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2\}_2\{(\text{Ph}_2\text{SiO})_2\text{O}\}] \cdot \text{Et}_2\text{O} \cdot \text{TMEDA}$  ( $\text{TMEDA} = \text{N,N,N',N'-Tetramethyl-ethylenediamin}$ ) (**7a**) zeigt das Vorliegen sowohl des ursprünglichen  $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$ -Dianions als auch des ringerweiterten  $[(\text{Ph}_2\text{Si}(\text{OSiPh}_2\text{O})_2)]^{2-}$ -Liganden im selben Molekül.*

molecules such as alcohols, phenols, thiols, phosphines, cyclopentadienes, or alkynes in a general Scheme (1).<sup>[28b–p]</sup> The silylamide route offers several preparative advantages over classical salt metathesis routes: The reactions can be carried out in non-coordinating solvents at ambient temperature and the volatile by-product  $\text{HN}(\text{SiMe}_3)_2$  is easily removed together with the solvent. Most important, however, is the fact that it is a salt-free route which allows the preparation of base-free products without retention of, for example, alkali metal halide by-products. The latter would lead to the formation of ate complexes, a phenomenon which is quite common in organo-lanthanide chemistry.<sup>[29]</sup>



Scheme 1. The silylamide route in organo-lanthanide chemistry.

According to Bradley et al. the silylamide precursors  $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3\{\text{LiCl}(\text{thf})_3\}_3]$  ( $\text{Ln} = \text{Eu}, \text{Gd}, \text{Sm}$ ) are readily accessible by treating anhydrous lanthanide trichlorides with three equivalents of  $\text{LiN}(\text{SiMe}_3)_2$  in THF.<sup>[30]</sup> Salt-free complexes of the type  $\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3$  can be obtained by sublimation of the crude products. For our purposes, however, these silylamides were prepared in situ and subsequently treated with  $\text{Ph}_2\text{Si}(\text{OH})\text{OSiPh}_2(\text{OH})$  in different stoichiometries according to Scheme 2.



Scheme 2. Synthesis of the lanthanide disiloxanediolates **1–3** (in the formulas of **2** and **3** four phenyl substituents are omitted for clarity).

It was found that in all cases novel heterobimetallic lanthanide complexes are formed which formally contain lithium disiloxanediolate ligands acting as mono-anionic ligands. Thus it is important to employ the silylamide precursors prepared in situ which still contain a large amount of lithium chloride. This is in marked contrast to all previous cases in which the silylamide route was employed to prepare salt-free lanthanide complexes.<sup>[27]</sup> In our hands, control experiments using sublimed  $\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3$  precursors thus far did not produce any characterizable lanthanide disiloxanediolates. Another interesting result of the present study is the finding that the nature of the products strongly depends on both the stoichiometry of the precursors and the size of the  $\text{Ln}^{3+}$  ion. The three complexes **1–3** have been isolated in the

form of colorless crystalline solids which are moderately moisture-sensitive and dissolve freely in various organic solvent including diethyl ether, THF, DME, or toluene. They were fully characterized by elemental analyses, spectroscopic data, and X-ray-crystallography. In the case of trivalent europium as central ion a homoleptic complex was obtained. The X-ray structural analysis of **1** (Figure 1) revealed the

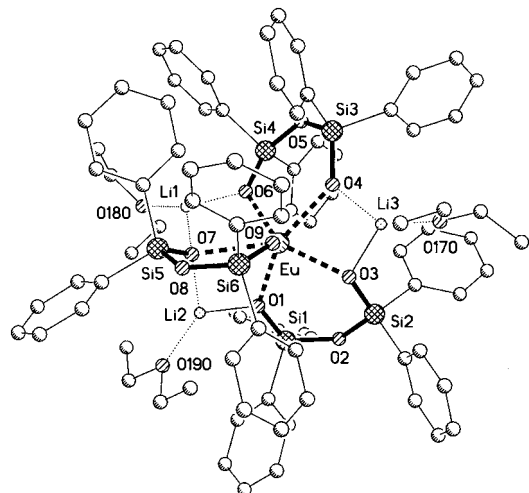
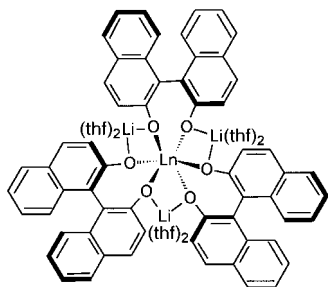


Figure 1. X-ray structure of **1** in the crystal. Selected interatomic distances [pm] and bond angles [°]: Eu–O1 234.9(2), Eu–O3 229.3(2), Eu–O4 233.0(2), Eu–O6 234.1(2), Eu–O7 255.3(2), Eu–O9 219.3(2), Li1–O6 186.8(5), Li1–O7 193.8(5), Li2–O1 186.5(5), Li2–O7 192.0(5), Li3–O3 186.5(6), Li3–O4 184.8(6), O1–Eu–O3 83.2(1), O4–Eu–O6 82.1(1), O7–Eu–O9 81.2(1), O6–Li1–O7 101.1(2), O1–Li2–O7 98.7(2), O3–Li3–O4 97.1(3).

presence of a heterobimetallic metallasiloxane, in which the  $\text{Eu}^{3+}$  ion is surrounded by three mono-anionic chelating  $(\text{Et}_2\text{O})\text{Li}[(\text{Ph}_2\text{SiO})_2\text{O}]^-$  units. Thus, the molecule comprises three inorganic  $\text{EuSi}_2\text{O}_3$  heterocyclic ring systems. The lithium ions are only tricoordinate with one diethyl ether ligand completing the coordination sphere around each Li. The molecular structure of this  $\text{EuLi}_3$  heteronuclear species bears some close structural resemblance to Shibasaki's well-known and widely used heterobimetallic binaphthol complexes of the type  $\text{M}_3[\text{Ln}(\text{H}_2\text{O})(\text{binol})_3]$  [31] or the related THF adducts  $\text{Li}_3[\text{Ln}(\text{R}-\text{binol})_3] \cdot 6\text{THF}$  as reported by Aspinall et al. (Scheme 3). [32] However, differences in the connectivity between lithium and the siloxanediolate oxygen atoms make the overall molecular structure of **1** less symmetrical than the



Scheme 3. Schematic representation of the heterobimetallic binaphthol reagents  $\text{Li}_3[\text{Ln}(\text{R}-\text{binol})_3] \cdot 6\text{THF}$  ( $\text{M}$  = alkali metal;  $\text{Ln}$  = lanthanide,  $\text{R}-\text{H}_2\text{binol} = \text{R}-\text{binaphthol}$ ). [32]

binaphthol complexes. Four oxygen atoms are coordinated to one Li (tricoordination around O) while one oxygen is engaged in two Li–O bonds (tetracoordination around O). The remaining oxygen is not bonded to lithium at all and is thus dicoordinate. This situation is reflected in the different Li–O distances which are 232.8(3) pm (av) for the tricoordinate oxygens and 255.3(2) pm in the case of the tetracoordinate oxygen atom O7. The shortest Li–O distance is found for the dicoordinate oxygen atom O9 with 219.3(2) pm.

Even more remarkable are the molecular structures of the gadolinium and samarium derivatives **2** and **3**. According to the X-ray analyses, both compounds are disubstituted lanthanide metallasiloxanes containing two lithium disiloxanediolate units while retaining one functional ligand [Cl or  $\text{N}(\text{SiMe}_3)_2$ , respectively] (Figures 2 and 3). The Sm–Cl

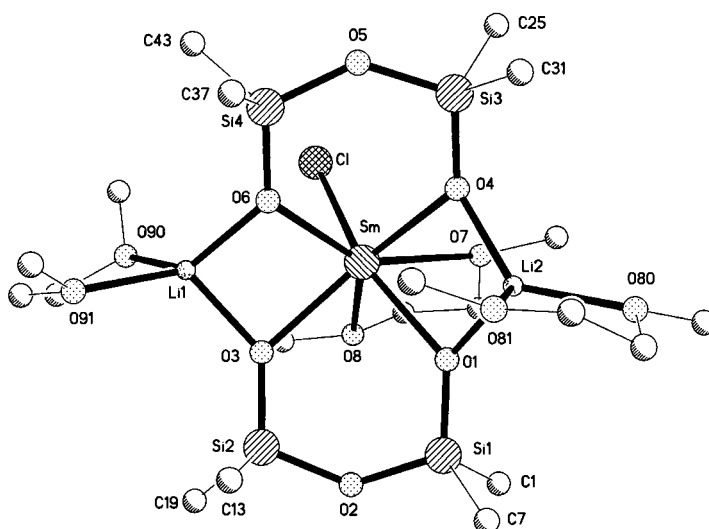


Figure 2. X-ray structure **2**. Only the *ipso*-carbon atoms of the phenyl substituents are shown. Selected interatomic distances [pm] and bond angles [°]: Sm–Cl 271.7(1), Sm–O1 232.2(2), Sm–O3 231.9(2), Sm–O4 231.3(3), Sm–O6 235.1(2), Sm–O7 266.5(3), Sm–O8 261.8(3), O1–Sm–O4 76.2(1), O1–Sm–O3 85.2(1), O3–Sm–O6 72.1(1), O4–Sm–O6 83.6(1), O7–Sm–O8 63.3(1), Sm–O1–Li2 94.4(2), Sm–O4–Li2 93.8(2), O1–Li2–O4 94.8(3), O80–Li–O81 81.0(3), Sm–O3–Li1 91.9(2), Sm–O6–Li1 91.2(2), O3–Li1–O6 92.0(3), O90–Li–O91 82.4(3).

distance in **2** is 271.1(1) pm while the Sm–O(Si) distances are in the range of 231.3(3)–335.1(2) pm. Average Sm–Cl distances in structurally characterized bis(cyclopentadienyl)-samarium chlorides are 276.9 pm in  $[(t\text{BuC}_5\text{H}_4)_2\text{Sm}(\mu\text{-Cl})_2]$  [33] and 273.7 pm in  $[(\text{C}_5\text{Me}_5)_2\text{SmCl}(\text{thf})]$ . [34] The Sm–O bond lengths to the coordinated dimethoxyethane ligand are 262.8(3) and 266.5(3) pm, respectively.

For **3**, a Gd–N distance of 234.1(3) pm has been determined, while the average Gd–O bond length is 237.2(3) pm. For structurally characterized gadolinium oxo-alkoxides Gd–O distances ranging from 208(2) to 267.4(8) pm have been reported in the literature, the order of variation being  $\text{Gd}-\text{OR} \ll \text{Gd}-\mu_4-\text{O} \ll \text{Gd}-\mu-\text{OR} \ll \text{Gd}-\mu_3-\text{OR} \ll \text{Gd}-\text{O}(\text{Et}_2\text{O})$ . [35, 36]

The value found for **2** can be favorably compared with the Gd– $\mu_3$ -ORtBu distance of 235(1) pm reported for  $\text{Na}_2-[(t\text{BuOGd})_4(\mu_3-\text{O}t\text{Bu})_8(\mu_6-\text{O})]$ . [36] The remaining functional

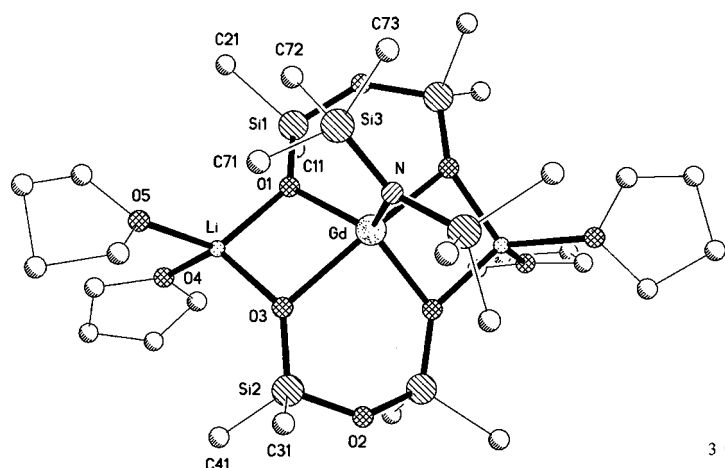
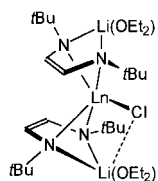


Figure 3. X-ray structure **3**. Only the *ipso*-carbon atoms of the phenyl substituents are shown. Selected interatomic distances [pm] and bond angles [°]: Gd–O1 226.5(2), Gd–O3 228.7(2), Gd–N 234.1(3), N–Si3 170.8(2), Li–O1 199.4(5), Li–O3 196.7(5), Li–O4 196.0(6), Li–O5 2.011(6), O1–Gd–O3 77.9(1), Gd–O1–Li 93.8(2), Gd–O3–Li 93.8(2), O1–Li–O3 92.5(2), O4–Li–O5 99.5(2).

ligands in the new disiloxanediole complexes **2** and **3** should make these compounds suitable candidates for carrying out derivative chemistry. The most striking structural feature of the species, however, is their similarity with certain lanthanide metallocenes such as  $[(C_5Me_5)_2LnN(SiMe_3)_2]$  (cf. **2**) or  $[(C_5Me_5)_2LnCl(thf)]$  (cf. **3**).<sup>[29]</sup> Such organolanthanide complexes are important as catalyst precursors or highly active catalysts in a variety of organic transformations.<sup>[37]</sup> It can be anticipated that the lithium disiloxanediole units in the “inorganic metallocenes” **2** and **3** are quite robust “spectator” ligands as they involve only lanthanide–oxygen coordination. Thus there might be a chance of using these materials to prepare organolanthanide catalysts which are less sensitive to air and moisture than the catalytically active lanthanide metallocenes. In the literature there is only one previous report on Li-containing anionic ligands formally replacing the  $C_5Me_5$  ligands in lanthanide metallocenes, that is the  $[Li(DAD)]^-$  units ( $DAD = tBuNCH=CHNtBu^-$ ).<sup>[38]</sup> There



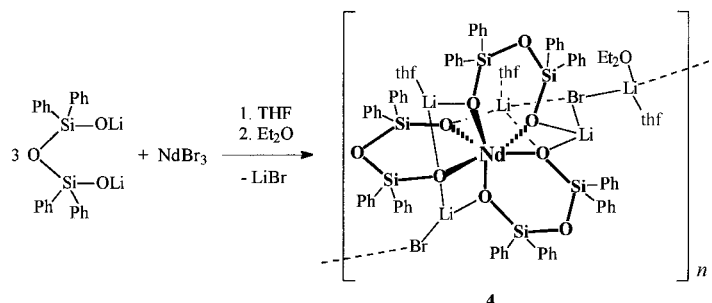
Scheme 4. Disubstituted lanthanide complexes containing  $[(DAD)Li(OEt_2)]^-$  ligands ( $Ln = Y, Lu$ ).

are interesting structural parallels between the “inorganic metallocenes” reported here and diazadiene complexes such as  $[(dad)Li(OEt_2)_2]LnCl$  ( $Ln = Y, Lu$ ) as shown in Scheme 4. The latter were prepared by treating anhydrous lanthanide trichlorides with two equivalents of the DAD dianions. They also comprise

two Li-containing anionic chelate ligands while retaining a reactive chloro function.

While the reactions of tetraphenyldisiloxanediol with the lanthanide silylamide reagents as described above proceed in a clear and straightforward manner, a completely different picture is observed when anhydrous lanthanide trihalides are treated with  $Ph_2Si(OLi)OSiPh_2(OLi)$ . Some products resulting from these reactions still remain to be fully characterized,

but it appears that they are all different from those shown in Scheme 2. An interesting example in which retention of lithium halide leads to a self-assembled polymeric structure is the product obtained from the reaction of anhydrous  $NdBr_3$  with three equivalents of  $Ph_2Si(OLi)OSiPh_2(OLi)$  in THF solution according to Scheme 5. Extraction of the crude product with diethyl ether afforded the heterobimetallic neodymium disiloxanediole **4** as a blue crystalline solid.



Scheme 5. Preparation of the polymeric neodymium disiloxanediole **4**.

According to the X-ray analysis, the neodymium complex **4** contains a central core which is closely related but not identical with that of the monomeric europium derivative **1** (Figure 4). Three formally mono-anionic lithium disiloxane-

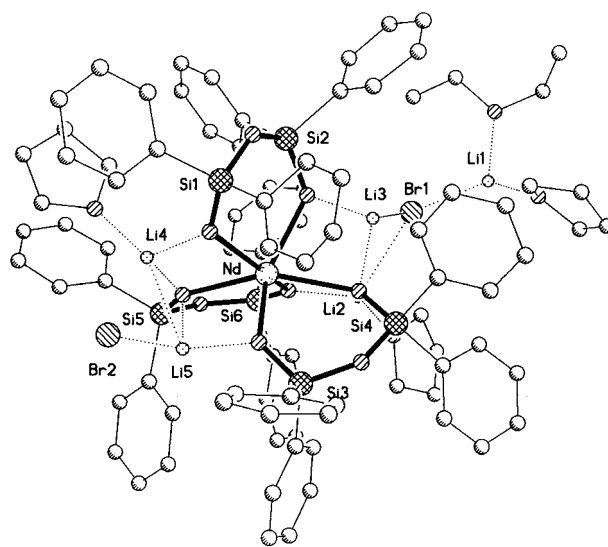


Figure 4. X-ray structure **4**. Selected interatomic distances [pm] and bond angles [°]: Nd–O1 242.1(3), Nd–O3 232.3(3), Nd–O4 231.6(3), Nd–O6 246.7(3), Nd–O7 237.1(3), Nd–O9 233.9(3), Li1–Br1 247.9(13), Li1–O12 193.7(15), Li1–O13 194.5(16), Li2–Br1 277.8(9), Li2–O6 201.5(9), Li2–O9 194.0(9), Li2–O11 192.2(10), Li3–Br1 241.8(9), Li3–O3 186.2(19), Li3–O6 197.1(9), Li4–O1 191.2(9), Li4–O7 195.5(9), Li4–O10 189.8(10), Li5–Br2 237(2), Li5–O4 202.5(19), Li5–O7 212(2), O1–Nd–O3 80.9(1), O4–Nd–O6 86.2(1), O7–Nd–O9 87.7(1).

diole ligands are coordinated to Nd and the coordination sphere of two lithium ions is completed by an additional THF ligand. In contrast to the molecular structure of **1** there are four three-coordinated disiloxanediole oxygen atoms while two are four-coordinate. The Nd–O distances fall in the range between 231.4(3)–242.1(3) pm for the tricoordinate oxygen

atoms. In the case of the tetracoordinate oxygens the Nd–O distances are 246.7(3) pm for O6 and 237.1(3) for O7. A fairly large number of structurally characterized neodymium(III) alkoxides<sup>[39]</sup> and aryloxides<sup>[40]</sup> has been reported in the literature. Nd–O distances comparable to those in **4** are 236(4) pm (Nd– $\mu$ -OR) and 245(5) (Nd– $\mu_3$ -OR) in [Nd<sub>6</sub>(O*i*Pr)<sub>17</sub>]Cl<sup>[39a]</sup> as well as 238.9(4) and 235.9(4) in [Nd<sub>2</sub>(OCH*t*Bu)<sub>6</sub>(MeCN)]<sup>[39f]</sup>. In **4** a polymeric superstructure results from retention of lithium bromide, which connects these monomeric units to give a linear chain polymer (Figure 5). Clearly more structural investigations are needed to

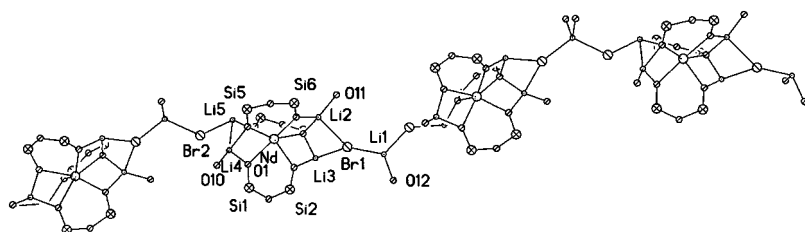


Figure 5. Polymeric structure of **4**.

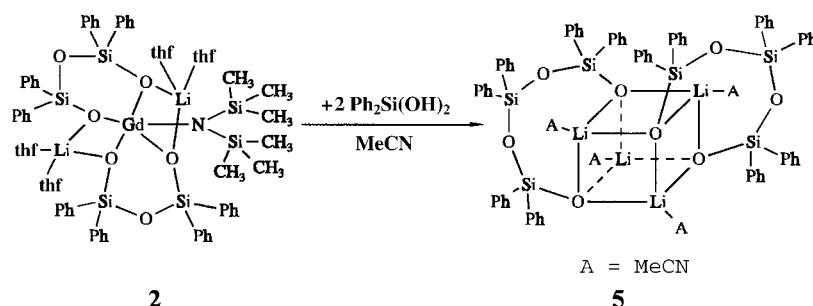
corroborate the nature of lanthanide disiloxanediolates resulting from reactions of anhydrous lanthanide trihalides with the lithium reagent **7**. A further structural variety can be expected when other alkali metal derivatives of tetraphenyldisiloxanediol are employed.

The remaining functional groups in the “inorganic metallocenes” **1–3** [Cl or N(SiMe<sub>3</sub>)<sub>2</sub>, respectively] should lead to some interesting derivative chemistry. The replacement of these ligands by other reactive groups such as alkyl, alkynyl, or hydride functions is currently under intense investigation in our lab. Especially the preparation of related  $\sigma$ -alkyl and hydride derivatives are of interest as they could lead to potential catalytically active species. As an initial reactivity study we report here on an attempted ring enlargement reaction involving the gadolinium derivative **2**. The formation of ring-enlarged products containing the hexaphenyltrisiloxanediolate ligand [Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> is a particularly interesting phenomenon frequently encountered in the chemistry of metal disiloxanediolates, especially in the case of early transition metals.<sup>[6a,c,7c]</sup> This anion can be coordinated to the metal either as a simple chelating ligand or in a chelate-bridging coordination mode, that is, in certain heterobimetallic complexes. For example, Sullivan et al. reported that the ring-expanded bis-chelate hafnium complex [Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>]Hf(py)<sub>2</sub> was the only product when HfCl<sub>4</sub> was treated with three equivalents of Ph<sub>2</sub>Si(ONa)OSiPh<sub>2</sub>(ONa) followed by addition of pyridine.<sup>[7c]</sup> In order to achieve a ring-enlargement reaction with a lanthanide derivative we studied the reaction of **2** with diphenylsilanediol, Ph<sub>2</sub>Si(OH)<sub>2</sub>. In fact, ring-enlargement did occur, but in a rather unexpected way. Treatment of **2** with two equivalents of Ph<sub>2</sub>Si(OH)<sub>2</sub> resulted in the formation of a colorless crystalline solid after recrystal-

lization from acetonitrile. Spectroscopic data and X-ray diffraction analysis revealed that the complex is the acetonitrile solvate of the dilithium derivative of hexaphenyltrisiloxanediol, [(Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>Li<sub>2</sub>(MeCN)<sub>2</sub> (**5**, Scheme 6).

As shown in Figure 6, the product [(Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>Li<sub>2</sub>(MeCN)<sub>2</sub> (**5**) is self-assembled in the solid state in the form of a heterocubane-type dimer. The molecular structure consists of a Li<sub>4</sub>O<sub>4</sub> heterocubane in which one acetonitrile ligand is coordinated to each lithium ion. The two hexaphenyltrisiloxanediolate ligands are arranged in a perpendicular fashion with respect to each other. The reaction leading to **5** is

of interest as a deliberate way of achieving the ring-enlargement [(Ph<sub>2</sub>SiO)<sub>2</sub>O]<sup>2-</sup> → [Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> starting from a tetraphenyldisiloxanediolate and a monosilicon building block. In addition, the dilithium derivative **5** may well serve as a useful reagent for the prepara-



Scheme 6. Ring-enlargement reaction leading to compound **5**.

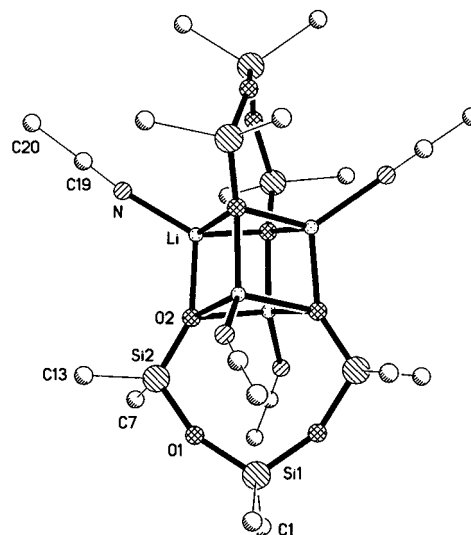
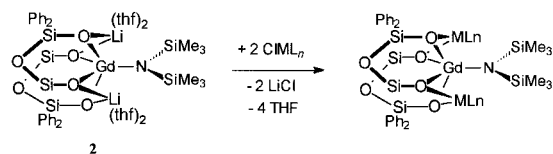


Figure 6. X-ray structure **5**. Only the *ipso*-carbon atoms of the phenyl substituents are shown. Selected interatomic distances [pm] and bond angles [°]: Li–O2 191.3(3), Si1–O1 162.2(1), Si2–O1 164.2(1), Si2–O2 158.8(1), Li–N 203.8(3), N–C19 113.7(2), C19–C20 145.2(3), O2–Li–N 119.7(2), Li–N–C19 157.7(2), N–C19–C20 179.0(2).

tion of other metal hexaphenyltrisiloxanediolates. This option is under current investigation in our laboratory.

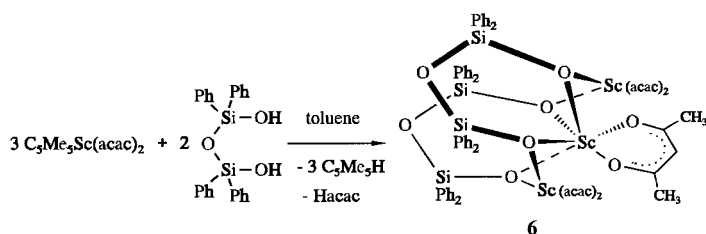
Another promising reaction pathway involving the “inorganic metallocenes” such as **2** and **3** would be the replacement

of the lithium ions by other metal centers leading to interesting novel trinuclear or heterotrinnuclear metallasiloxanes. This preparative concept as exemplified with the gadolinium derivative **2** is outlined in Scheme 7.



Scheme 7. Proposed synthesis of heterotrinnuclear metallasiloxanes through lithium/metal exchange reactions,  $ML_n = Mn(CO)_5$ ,  $Ir(COD)$ ,  $Rh(CO)_2$ ,  $Ti(C_5Me_5)_2$ ,  $Ln(C_5H_5)_2$  etc.

While a metathetical synthesis using suitable metal exchange reactions as outlined in Scheme 7 has not yet been achieved, a trimetallic disiloxanediolate complex has been prepared in the case of scandium via a rather unexpected synthetic route. (Pentamethylcyclopentadienyl)scandium-bis(acetylacetonate),  $[(C_5Me_5)Sc(acac)_2]$ ,<sup>[41]</sup> was treated with **1** (molar ratio 3:2) in refluxing toluene according to Scheme 8.



Scheme 8. Synthesis of the trinuclear scandium disiloxanediolate complex **6**.

Recrystallization of the crude product from diethyl ether afforded the trinuclear scandium disiloxanediolate  $\{[(Ph_2Si-O)_2O]_2Sc_3(acac)_5\}$  (**6**) in 72% yield. Apparently, no related group 3 metal disiloxanediolate complex has been reported in the literature.<sup>[6a,c,7c]</sup>

During the course of this reaction the pentamethylcyclopentadienyl ligand in the starting material was completely replaced upon protonation by tetraphenyldisiloxanediol. An X-ray structure analysis of **6** (Figure 7) confirmed the presence of a trinuclear scandium complex containing the tetraphenyldisiloxanediolate ligand in a novel chelate-bridging coordination mode involving three scandium ions.

Finally, another surprising result was achieved when the study of metal disiloxanediolates was extended to uranium as a representative element of the actinide series. Just like the rare earth elements, actinides were virtually nonexistent in metallasiloxane chemistry until recently. In this context it is interesting to note that even the chemistry of simple uranium trialkylsilanolates is very little developed and no structural information is available. The few existing reports in the literature are mainly concerned with uranium(v) and uranium(vi) siloxides such as  $U(OSiR_3)_5$  ( $R = Me, Et$ ) or  $U(OSiR_3)_6$  ( $R = Me, Et$ ).<sup>[42–45]</sup> It was found that reactions of  $UCl_4$  with two or three equivalents of  $(Ph_2SiOH)_2O$  were always accompanied by complete decolorization of the reaction mixtures, indicating oxidation to uranium(vi) species.

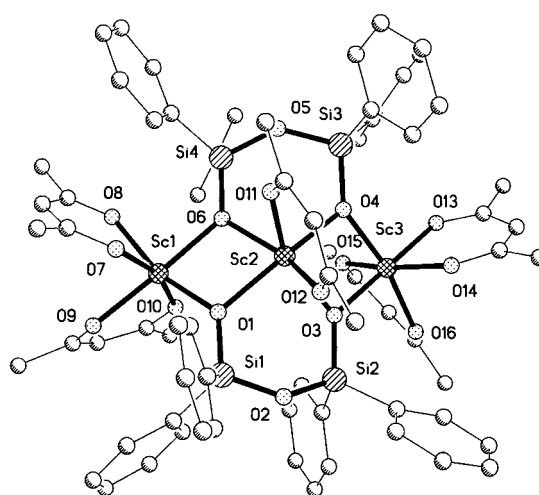
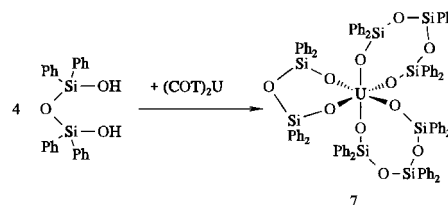


Figure 7. X-ray structure of **6**. Selected interatomic distances [pm] and bond angles [°]: Sc–O(acac) 209.5(2) (av), Sc–O( $\mu$ -OSi) 213.0(2) (av), Si–O( $\mu$ -OSi) 164.9(2) (av), O–Sc–O(acac) 81.3(1) (av), O1–Sc1–O6 77.2(1), Sc1–O1–Sc2 104.2(1), Sc1–O6–Sc2 102.9(1), O1–Sc2–O6 75.7(1), O1–Sc2–O3 90.6(1), O4–Sc2–O6 90.2(1), O3–Sc2–O4 77.0(1), Sc2–O3–Sc3 102.1(1), Sc2–O4–Sc3 102.2(1), O3–Sc3–O4 78.6(1).

However, it proved difficult to isolate pure compounds from these mixtures. Finally this became possible by employing a salt-free synthetic route starting with the long-known uranium sandwich complex uranocene,  $(COT)_2U$  ( $COT = \eta^8-C_8H_8$ ).<sup>[46]</sup> Treatment of uranocene with an excess of tetraphenyldisiloxanediol in toluene solution resulted in clean formation of the colorless uranium(vi) complex  $[U\{Ph_2Si(OSiPh_2O)_2\}_2\{(Ph_2SiO)_2O\}]$  (**7**) according to Scheme 9.



Scheme 9. Synthesis of the uranium(vi) complex **7**.

This reaction and the nature of the product are quite remarkable in several ways. First of all, the replacement of both cyclooctatetraenyl ligands upon treatment with the disiloxane reagent is an unprecedented reaction pathway for uranocene. Secondly, clean oxidation to uranium(vi) readily takes place in the presence of  $(Ph_2SiOH)_2O$  and not even traces of uranium(iv) disiloxanediolate species have been detected. Finally, an X-ray structure analysis revealed that **7** represents the first example of a mixed-ligand metallasiloxane containing both the original tetraphenyldisiloxanediolate dianion and the ring-expanded hexaphenyltrisiloxanediolate chelating ligand (Figure 8). Thus, the monomeric molecule contains one six-membered and two eight-membered metallasiloxane ring systems. The mean U–O distance in **7** is 214.0(5) pm.

In summarizing these results it becomes clear that the chemistry of *f*-element complexes containing disiloxanediolates is quite diverse and gives rise to a variety of interesting

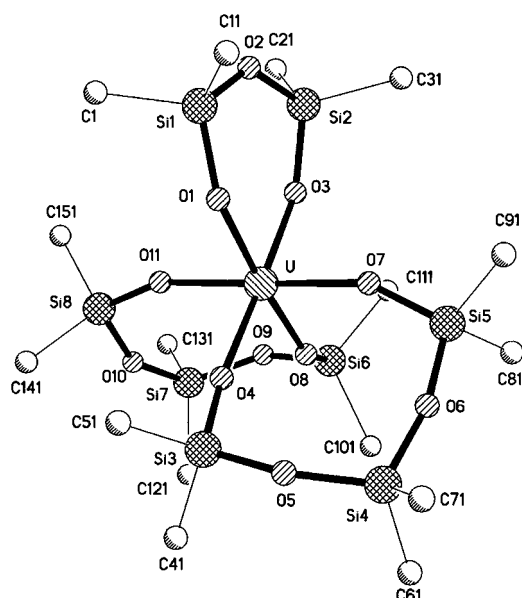


Figure 8. X-ray structure of **7a**. Hydrogen atoms and solvent molecules have been omitted for clarity. Only the *ipso*-carbon atoms of the phenyl substituents are shown. Selected interatomic distances [pm] and bond angles [°]: U–O1 216.3(4), U–O3 212.2(4), U–O4 213.9(3), U–O7 214.5(5), U–O8 213.1(4), U–O11 213.7(5), Si–O–U 1.615(5), O1–U–O3 84.9(1), O4–U–O7 89.8(2), O8–U–O11 90.9(2).

and novel structures. Especially noteworthy is the finding that, given the right choice of rare earth metal and metal-to-ligand ratio, heterobimetallic lanthanide complexes are accessible which exhibit a structural resemblance to certain catalytically active lanthanide metallocenes. Future investigations will show if such “inorganic metallocenes” of the rare earth elements are valuable precursors to new types of organo-lanthanide catalysts. This work also shows that not all seemingly simple reactions in this field are easily predictable. The unexpected high-yield formation of the mixed-ligand uranium(vi) derivative **7** is a good example of the surprises which this area of metallasiloxane chemistry offers.

## Experimental Section

**General methods:** All reactions were carried out in an atmosphere of dry nitrogen either in a dry box (M. Braun, Labmaster 130 and MB 150B-G) or with the use of standard Schlenk techniques. Solvents were dried over Na/benzophenone and freshly distilled under nitrogen prior to use. IR spectra were recorded on a Perkin–Elmer FTIR Spectrometer System 2000. NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer ( $^1\text{H}$  400 MHz,  $^{13}\text{C}$  101 MHz,  $^{29}\text{Si}$  79.5 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or an external standard ( $^{29}\text{Si}$ , TMS  $\delta = 0$ ). Elemental analyses were performed at the Chemistry Department of the Otto-von-Guericke-Universität using a Leco CHNS 932 apparatus. Melting and decomposition points were measured on a Electrothermal IA 9100 apparatus. The following starting materials were prepared according to literature procedures: Anhydrous  $\text{LnCl}_3$  (Ln = Eu, Sm, Gd),<sup>[47]</sup>  $\text{NdBr}_3$ ,<sup>[48]</sup>  $\text{LiN}(\text{SiMe}_3)_2$ ,<sup>[49]</sup>  $(\text{Ph}_2\text{SiOH})_2\text{O}$ ,<sup>[8]</sup>  $\text{Ph}_2\text{Si}(\text{OH})_2$ ,<sup>[8]</sup>  $[(\text{C}_5\text{Me}_5\text{Sc}(\text{acac})_2)]$ ,<sup>[41]</sup> and  $(\text{COT})_2\text{U}$ .<sup>[46]</sup>

**[Eu{((Ph<sub>2</sub>SiO)<sub>2</sub>O)Li(Et<sub>2</sub>O)}<sub>3</sub>] (1):** At room temperature,  $\text{LiN}(\text{SiMe}_3)_2$  (2.50 g, 15 mmol) was added as a solid to a suspension of anhydrous  $\text{EuCl}_3$  (1.30 g, 5 mmol) in diethyl ether (200 mL) and the mixture was stirred for 24 h. During this time the solution turned bright orange, indicating the formation of  $\text{Eu}[\text{N}(\text{SiMe}_3)_2]_3$ . Addition of solid  $(\text{Ph}_2\text{SiOH})_2\text{O}$  (6.22 g,

15 mmol) resulted in complete decolorization. After stirring for another 24 h the solvent was removed in vacuo and the white residue was washed with hexane (20 mL). The crude product was placed on a filter frit and continuously extracted with diethyl ether (80 mL). Cooling of the extract to  $-20^\circ\text{C}$  afforded **1** as colorless crystals (3.35 g, 41 %). M.p.  $116^\circ\text{C}$  (dec.); IR (Nujol):  $\tilde{\nu} = 3134\text{w}$ ,  $3087\text{w}$ ,  $3067\text{m}$ ,  $3047\text{m}$ ,  $3020\text{m}$ ,  $3006(\text{sh})\text{m}$ ,  $2999\text{m}$ ,  $2976\text{m}$ ,  $2965(\text{sh})\text{m}$ ,  $2930\text{m}$ ,  $2904(\text{sh})\text{m}$ ,  $2878(\text{sh})\text{m}$ ,  $2856\text{m}$ ,  $1962\text{w}$ ,  $1891\text{w}$ ,  $1832\text{w}$ ,  $1734\text{w}$ ,  $1655\text{w}$ ,  $1611\text{w}$ ,  $1590\text{m}$ ,  $1566\text{w}$ ,  $1546\text{w}$ ,  $1484\text{w}$ ,  $1448\text{w}$ ,  $1428\text{s}$ ,  $1389\text{w}$ ,  $1306\text{m}$ ,  $1261\text{m}$ ,  $1244(\text{sh})\text{m}$ ,  $1183\text{m}$ ,  $1153\text{m}$ ,  $1120\text{vs}$ ,  $1095\text{s}$ ,  $1065\text{s}$ ,  $1038\text{vs}$ ,  $1022\text{vs}$ ,  $991\text{vs}$ ,  $963\text{vs}$ ,  $917\text{s}$ ,  $800\text{m}$ ,  $742\text{s}$ ,  $713\text{vs}$ ,  $701\text{vs}$ ,  $684\text{m}$ ,  $670\text{w}$ ,  $664\text{w}$ ,  $620\text{w}$ ,  $558(\text{sh})\text{m}$ ,  $531\text{vs}$ ,  $495\text{s}$ ,  $466\text{m}$ ,  $452\text{m}$ ,  $433\text{m}$ ,  $401\text{s}$ ,  $377\text{m}$ ,  $297\text{m}$ ,  $284\text{m}$ ,  $245\text{w cm}^{-1}$ ;  $^1\text{H NMR}$  ( $[\text{D}_8]\text{THF}$ , 400 MHz):  $\delta = 8.82$  (brs, 24 H, *o*-Ph), 7.53 (t, 12 H, *p*-Ph), 7.39 (t, 24 H, *m*-Ph), 3.40 (q, 12 H,  $\text{OCH}_2$ ), 1.13 (t, 18 H,  $\text{CH}_3$ ); elemental analysis calcd (%) for  $\text{C}_{68}\text{H}_{90}\text{EuLi}_3\text{O}_{12}\text{Si}_6$  (1632.88): C 61.79, H 5.55; found C 60.32, H 5.89.

**[{((Ph<sub>2</sub>SiO)<sub>2</sub>O)Li(dme)}<sub>2</sub>SmCl(dme)] (2):** In a similar manner as described for **1**,  $\text{Sm}[\text{N}(\text{SiMe}_3)_2]_3$  was prepared in situ from anhydrous  $\text{SmCl}_3$  (1.28 g, 5 mmol) and  $\text{LiN}(\text{SiMe}_3)_2$  (2.50 g, 15 mmol) and treated with  $(\text{Ph}_2\text{SiOH})_2\text{O}$  (4.15 g, 10 mmol). The final reaction mixture was heated under reflux for 3 h and the extraction was carried out with DME (80 mL) to afford **2** as colorless crystals (4.60 g, 71 %). M.p.  $135^\circ\text{C}$  (dec.); IR (Nujol):  $\tilde{\nu} = 3061\text{m}$ ,  $3050\text{m}$ ,  $3017\text{w}$ ,  $3005\text{w}$ ,  $2998\text{w}$ ,  $2962\text{m}$ ,  $2948(\text{sh})\text{m}$ ,  $2928\text{m}$ ,  $2883(\text{sh})\text{m}$ ,  $2853\text{w}$ ,  $2838(\text{sh})\text{w}$ ,  $1963\text{w}$ ,  $1896\text{w}$ ,  $1831\text{w}$ ,  $1735\text{w}$ ,  $1636\text{w}$ ,  $1607\text{w}$ ,  $1590\text{w}$ ,  $1560\text{w}$ ,  $1541\text{w}$ ,  $1457\text{w}$ ,  $1428\text{m}$ ,  $1367\text{w}$ ,  $1261\text{m}$ ,  $1193\text{w}$ ,  $1172\text{w}$ ,  $1150(\text{sh})\text{m}$ ,  $1121\text{vs}$ ,  $1084\text{s}$ ,  $1056\text{s}$ ,  $1033(\text{sh})\text{s}$ ,  $1028(\text{sh})\text{s}$ ,  $1019\text{s}$ ,  $996\text{m}$ ,  $970\text{s}$ ,  $859\text{w}$ ,  $831\text{w}$ ,  $818\text{w}$ ,  $802\text{w}$ ,  $745\text{m}$ ,  $715\text{m}$ ,  $701\text{s}$ ,  $633\text{m}$ ,  $668\text{m}$ ,  $526\text{s}$ ,  $493\text{m}$ ,  $485\text{m}$ ,  $388\text{m}$ ,  $332\text{w}$ ,  $317\text{m}$ ,  $302\text{m}$ ,  $277\text{w}$ ,  $257\text{w}$ ,  $243\text{w}$ ,  $224\text{m}$ ,  $145\text{m cm}^{-1}$ ;  $^1\text{H NMR}$  ( $[\text{D}_8]\text{THF}$ , 400 MHz):  $\delta = 7.62$  (brs, 16 H, *o*-Ph), 7.17 (t, 8 H, *p*-Ph), 7.09 (t, 16 H, *m*-Ph), 3.48 (s, 12 H,  $\text{OCH}_2$ ), 3.31 (s, 18 H,  $\text{OCH}_3$ ); elemental analysis calcd (%) for  $\text{C}_{60}\text{H}_{70}\text{LiLi}_2\text{O}_{12}\text{Si}_4\text{Sm}$  (1295.20): C 55.64, H 5.45; found C 55.32, H 6.04.

**[{((Ph<sub>2</sub>SiO)<sub>2</sub>O)Li(thf)}<sub>2</sub>GdN(SiMe<sub>3</sub>)<sub>2</sub>] (3):** Following the procedure outlined for **2**, anhydrous  $\text{GdCl}_3$  (1.30 g, 4.9 mmol) was treated with  $\text{LiN}(\text{SiMe}_3)_2$  (2.50 g, 15 mmol) and subsequently treated with  $(\text{Ph}_2\text{SiOH})_2\text{O}$  (4.15 g, 10 mmol). Extraction with THF yielded **3** as colorless crystals (5.20 g, 74 %). M.p.  $102^\circ\text{C}$  (dec.); IR (Nujol):  $\tilde{\nu} = 3134\text{w}$ ,  $3086\text{w}$ ,  $3067\text{m}$ ,  $3047\text{m}$ ,  $3018(\text{sh})\text{m}$ ,  $3009(\text{sh})\text{m}$ ,  $3000\text{m}$ ,  $2974(\text{sh})\text{m}$ ,  $2956\text{m}$ ,  $2932(\text{sh})\text{m}$ ,  $2891\text{m}$ ,  $2877(\text{sh})\text{w}$ ,  $2854\text{w}$ ,  $1960\text{w}$ ,  $1892\text{w}$ ,  $1832\text{w}$ ,  $1736\text{w}$ ,  $1655\text{w}$ ,  $1612\text{w}$ ,  $1590\text{m}$ ,  $1567\text{w}$ ,  $1546\text{w}$ ,  $1484\text{w}$ ,  $1459\text{w}$ ,  $1428\text{s}$ ,  $1383\text{w}$ ,  $1306\text{w}$ ,  $1257\text{m}$ ,  $1184\text{m}$ ,  $1156\text{w}$ ,  $1120\text{vs}$ ,  $1035\text{vs}$ ,  $1018\text{vs}$ ,  $961\text{vs}$ ,  $935(\text{sh})\text{s}$ ,  $893\text{m}$ ,  $840\text{m}$ ,  $804(\text{sh})\text{w}$ ,  $743\text{s}$ ,  $713\text{vs}$ ,  $701\text{vs}$ ,  $684\text{s}$ ,  $668\text{s}$ ,  $654\text{m}$ ,  $607\text{w}$ ,  $579\text{w}$ ,  $530\text{vs}$ ,  $510(\text{sh})\text{s}$ ,  $492\text{s}$ ,  $466(\text{sh})\text{m}$ ,  $442\text{s}$ ,  $406\text{s}$ ,  $393\text{s}$ ,  $382(\text{sh})\text{m}$ ,  $368\text{m}$ ,  $347\text{m}$ ,  $318\text{m}$ ,  $307\text{m}$ ,  $238\text{w cm}^{-1}$ ; no interpretable  $^1\text{H NMR}$  data could be obtained due to the presence of the paramagnetic  $\text{Gd}^{3+}$  ion; elemental analysis calcd (%) for  $\text{C}_{70}\text{H}_{90}\text{GdLi}_2\text{NO}_{10}\text{Si}_6$  (1445.10): C 58.18, H 6.28, N 0.97; found C 56.65, H 6.43, N 0.43.

**[{Nd{((Ph<sub>2</sub>SiO)<sub>2</sub>O)}<sub>3</sub>{ $\mu$ -Li(thf)}<sub>2</sub>{ $\mu$ -LiBrLi(thf)(Et<sub>2</sub>O)}<sub>n</sub>}] (4):**  $\text{LiN}(\text{SiMe}_3)_2$  (1.61 g, 9.6 mmol) was added as a solid to a solution of  $(\text{Ph}_2\text{SiOH})_2\text{O}$  (2.0 g, 4.8 mmol) in THF (50 mL) and the mixture was stirred for 1 h at  $20^\circ\text{C}$ . Solid  $\text{NdBr}_3$  (0.62 g, 1.6 mmol) was added, and stirring was continued for 12 h. After evaporation to dryness the residue was washed with pentane ( $2 \times 10$  mL) and redissolved in diethyl ether (ca. 50 mL). The solution was filtered and concentrated to a total volume of about 25 mL. Upon storage at  $2^\circ\text{C}$  over a period of 14 d pale blue-violet crystals of **4** formed, which were collected by filtration (1.30 g, 43 %). M.p.  $105^\circ\text{C}$  (dec.); IR (Nujol):  $\tilde{\nu} = 3135\text{w}$ ,  $3068\text{m}$ ,  $3047\text{m}$ ,  $3017(\text{sh})\text{m}$ ,  $3000\text{m}$ ,  $2978\text{m}$ ,  $2881\text{m}$ ,  $1961\text{w}$ ,  $1892\text{w}$ ,  $1831$ ,  $1774\text{w}$ ,  $1618\text{w}$ ,  $1591\text{m}$ ,  $1568\text{w}$ ,  $1486\text{w}$ ,  $1459\text{w}$ ,  $1428\text{s}$ ,  $1376\text{w}$ ,  $1306\text{w}$ ,  $1263\text{m}$ ,  $1186\text{m}$ ,  $1119\text{vs}$ ,  $1039\text{vs}$ ,  $1018\text{vs}$ ,  $995\text{vs}$ ,  $954\text{vs}$ ,  $743\text{s}$ ,  $714\text{vs}$ ,  $701\text{vs}$ ,  $684\text{s}$ ,  $620\text{m}$ ,  $534\text{vs}$ ,  $492\text{vs cm}^{-1}$ ;  $^1\text{H NMR}$  ( $[\text{D}_8]\text{THF}$ , 400 MHz):  $\delta = 7.85$ – $7.00$  (m, Ph), other resonances could not be assigned due to strong broadening as an effect of the paramagnetic  $\text{Nd}^{3+}$  ion;  $^{13}\text{C NMR}$  ( $[\text{D}_8]\text{THF}$ , 101 MHz):  $\delta = 138.0$ – $126.0$  (Ph), 67.3 ( $\text{OCH}_2$ , THF), 65.8 ( $\text{OCH}_2$ ,  $\text{Et}_2\text{O}$ ), 24.5 ( $\text{CH}_2$ , THF), 15.2 ( $\text{CH}_3$ ,  $\text{Et}_2\text{O}$ ); elemental analysis calcd (%) for  $\text{C}_{88}\text{H}_{94}\text{Br}_2\text{Li}_5\text{NdO}_{13}\text{Si}_6$  (1866.97): C 56.61, H 5.07; found C 55.97, H 5.11.

**[{Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)}<sub>2</sub>{Li(MeCN)}<sub>2</sub>]} (5):**  $\text{Ph}_2\text{Si}(\text{OH})_2$  (0.22 g, 1.0 mmol) was added in small portions over a period of 30 min to a stirred solution of **3** (0.7 g, 0.5 mmol) in THF (40 mL). After about one-half of silanediol had been added, a gelatinous white precipitate started to form. THF (10 mL) and acetonitrile (5 mL) were added to the mixture, which was then allowed to stand undisturbedly at room temperature. During this time large colorless crystals grew on the walls of the Schlenk tube, which were isolated by decanting the supernatant solution together with the gelatinous parts. The crystals were washed with diethyl ether (20 mL), dried, and scraped off

Table 1. Summary of crystal structure determination data.

	1	2	3	4
formula	C <sub>84</sub> H <sub>90</sub> EuLi <sub>5</sub> O <sub>12</sub> Si <sub>6</sub>	C <sub>60</sub> H <sub>70</sub> ClLi <sub>2</sub> O <sub>12</sub> Si <sub>4</sub> Sm	C <sub>70</sub> H <sub>90</sub> GdLi <sub>2</sub> NO <sub>10</sub> Si <sub>6</sub>	(C <sub>88</sub> H <sub>94</sub> N <sub>3</sub> Br <sub>2</sub> Li <sub>5</sub> NdO <sub>13</sub> Si) <sub>n</sub> × 0.5 nC <sub>4</sub> H <sub>10</sub> O
<i>M<sub>r</sub></i>	1632.88	1295.20	1445.10	1303.99
habitus, color	colorless plate	colorless prism	colorless column	blue-violet prism
crystal dim. [mm <sup>3</sup> ]	0.40 × 0.30 × 0.10	0.55 × 0.40 × 0.30	0.80 × 0.30 × 0.25	0.59 × 0.52 × 0.48
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> <i>c</i>
unit cell constants				
<i>a</i> [Å]	13.6639(2)	17.349(1)	22.258(1)	14.7655(6)
<i>b</i> [Å]	14.5015(2)	17.3002(2)	14.4469(8)	23.9431(3)
<i>c</i> [Å]	24.2934(2)	21.2440(3)	23.486(2)	27.275(1)
$\alpha$ [°]	83.541(2)	90	90	90
$\beta$ [°]	86.713(2)	98.133(1)	106.427(6)	97.803(3)
$\gamma$ [°]	61.980(2)	90	90	90
<i>V</i> [Å <sup>3</sup> ]	4222.3	6312.3	7244.0	9553.4
<i>Z</i>	2	4	4	4
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.284	1.363	1.325	1.324
$\mu$ [mm <sup>-1</sup> ]	0.89	1.11	1.07	1.51
<i>F</i> (000)	1692	2668	3004	3904
<i>T</i> [°C]	–100	–100	–100	–75
2 $\theta_{\text{max}}$	56.6	52.9	50	56.6
number of reflexes				
measured	51 321	36 094	13 420	31 437
independent	20 536	12 814	6377	21 040
<i>R</i> <sub>int</sub>	0.039	0.040	0.035	0.020
refined parameters	961	727	407	1032
<i>wR</i> ( <i>F</i> <sup>2</sup> , all data)	0.094	0.145	0.073	0.112
<i>R</i> ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	0.039	0.056	0.030	0.046
<i>S</i>	1.07	1.12	0.98	1.10
max. $\Delta/\sigma$	–0.003	–0.001	–0.001	–0.003
max. $\Delta\rho$ [Å <sup>-3</sup> ]	1.48	2.77	0.64	1.18
	5	6	7	
formula	C <sub>80</sub> H <sub>72</sub> Li <sub>4</sub> N <sub>4</sub> O <sub>8</sub> Si <sub>6</sub>	C <sub>73</sub> H <sub>75</sub> O <sub>16</sub> Sc <sub>3</sub> Si <sub>4</sub> × C <sub>4</sub> H <sub>10</sub> O × C <sub>6</sub> H <sub>16</sub> N <sub>2</sub>	C <sub>96</sub> H <sub>80</sub> O <sub>11</sub> Si <sub>8</sub> U	
<i>M<sub>r</sub></i>	1413.72	1455.57	2062.68	
habitus, color	colorless prism	colorless prism	colorless prism	
crystal dim. [mm <sup>3</sup> ]	0.50 × 0.40 × 0.25	0.38 × 0.32 × 0.16	0.46 × 0.38 × 0.23	
crystal system	tetragonal	monoclinic	monoclinic	
space group	<i>I</i> 4 <sub>1</sub> / <i>a</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>C</i> <i>c</i>	
unit cell constants				
<i>a</i> [Å]	21.9947(3)	14.7916(4)	25.0349(5)	
<i>b</i> [Å]	21.9947(3)	21.3585(5)	14.6569(2)	
<i>c</i> [Å]	15.6767(2)	23.5117(5)	29.4351(5)	
$\alpha$ [°]	90	90	90	
$\beta$ [°]	90	95.311(1)	109.869(1)	
$\gamma$ [°]	90	90	90	
<i>V</i> [Å <sup>3</sup> ]	7583.9	7396.1	10 158	
<i>Z</i>	4	4	4	
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.238	1.307	1.349	
$\mu$ [mm <sup>-1</sup> ]	0.17	0.40	1.75	
<i>F</i> (000)	2960	3040	4224	
<i>T</i> [°C]	–120	–130	–100	
2 $\theta_{\text{max}}$	56.6	56.4	56.6	
number of reflexes				
measured	30 932	48 659	34 298	
independent	4700	18 019	16 973	
<i>R</i> <sub>int</sub>	0.062	0.074	0.023	
refined parameters	232	875	1118	
<i>wR</i> ( <i>F</i> <sup>2</sup> , all data)	0.103	0.122	0.060	
<i>R</i> ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ))	0.044	0.062	0.026	
<i>S</i>	1.05	1.03	1.07	
max. $\Delta/\sigma$	–0.001	–0.001	–0.001	
max. $\Delta\rho$ [Å <sup>-3</sup> ]	0.335	0.522	0.762	



the glass walls to give colorless **5** (0.42 g, 59%). M.p. 185 °C (dec.); IR (Nujol):  $\bar{\nu}$  = 3129w, 3067m, 3047m, 3025m, 2927s, 2855m, 2263m, 1965w, 1893w, 1827w, 1590m, 1568w, 1460w, 1427s, 1380w, 1264m, 1188m, 1119vs, 1037vs, 1015vs, 994vs, 898m, 855m, 742s, 722vs, 698vs, 678m, 619w, 530vs, 487s, 457m cm<sup>-1</sup>; <sup>1</sup>H NMR ([D<sub>8</sub>]THF, 400 MHz):  $\delta$  = 7.5–7.0 (m, 60H, Ph), 1.81 (s, 12H, CH<sub>3</sub>CN); <sup>13</sup>C NMR ([D<sub>8</sub>]THF, 101 MHz):  $\delta$  = 137.2–128.3 (Ph), 118.3 (CN), 1.7 (CH<sub>3</sub>); elemental analysis calcd (%) for C<sub>80</sub>H<sub>72</sub>Li<sub>4</sub>N<sub>4</sub>O<sub>8</sub>Si<sub>6</sub> (1413.72): C 67.96, H 5.13, N 3.96; found C 67.78, H 5.03, N 4.15.

**[[{(Ph<sub>2</sub>SiO)<sub>2</sub>O]Sc(acac)<sub>2</sub>Sc(acac)] (6):** Toluene (40 mL) was added to (C<sub>5</sub>Me<sub>5</sub>)Sc(acac)<sub>2</sub> (1.20 g, 2.64 mmol) and (Ph<sub>2</sub>SiOH)<sub>2</sub>O (0.75 g, 1.80 mmol) and the mixture was stirred at reflux temperature for 24 h. All volatiles were removed in vacuo, the white residue was washed with pentane (20 mL) and recrystallized from toluene to afford **6** (0.91 g, 71%) as colorless crystals. M.p. 226 °C (dec); IR (Nujol):  $\bar{\nu}$  = 3130w, 3082w, 3069m, 3046m, 3021m, 3004(sh)m, 2994m, 2970m, 2965(sh)m, 2930m, 2921m, 1961w, 1891w, 1833w, 1732w, 1657w, 1613w, 1594m, 1567w, 1546w, 1525w, 1484w, 1447w, 1427s, 1386w, 1307m, 1265m, 1243m, 1183m, 1152m, 1119vs, 1095s, 1064s, 1039vs, 1022vs, 990vs, 963vs, 917s, 800m, 743s, 714vs, 702vs, 684m, 670w, 663w, 621w, 558(sh)m, 530vs, 496s, 466m, 452m, 433m, 402s, 375m, 297m cm<sup>-1</sup>; <sup>1</sup>H NMR ([D<sub>8</sub>]THF, 400 MHz):  $\delta$  = 7.90–7.00 (m, 40H, Ph), 4.91 (s, 5H, CH<sub>3</sub>-CO-CH-CO-CH<sub>3</sub>), 1.87 (s, 30H, CH<sub>3</sub>-CO-CH-CO-CH<sub>3</sub>); <sup>13</sup>C NMR ([D<sub>8</sub>]THF, 101 MHz):  $\delta$  = 191.91, 191.73 (CH<sub>3</sub>-CO-CH-CO-CH<sub>3</sub>), 139.18–126.85 (Ph), 105.59, 103.10 (CH<sub>3</sub>-CO-CH-CO-CH<sub>3</sub>), 26.56, 26.15 (CH<sub>3</sub>-CO-CH-CO-CH<sub>3</sub>); elemental analysis calcd (%) for C<sub>73</sub>H<sub>75</sub>O<sub>16</sub>Sc<sub>2</sub>Si<sub>4</sub> (1455.58): C 60.24, H 5.19; found C 60.24, H 5.31.

**[U(Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>)(Ph<sub>2</sub>SiO)<sub>2</sub>O] (7) and [U(Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>)(Ph<sub>2</sub>SiO)<sub>2</sub>O]·Et<sub>2</sub>O·TMEDA (7a):** Uranocene (0.45 g, 1.0 mmol) and (Ph<sub>2</sub>SiOH)<sub>2</sub>O (2.0 g, 5.0 mmol) were dissolved in toluene (25 mL) and the mixture was stirred for 12 h at 110 °C, resulting in a color change from deep green to nearly colorless. The solvent was removed in vacuo and the residue was washed with hexane (3 × 10 mL). The crude product was redissolved in toluene (about 20 mL). Cooling of the solution to 0 °C for 7 d afforded colorless microcrystalline **7** (1.40 g, 75%). M.p. 236 °C (dec.); elemental analysis calcd (%) for C<sub>96</sub>H<sub>96</sub>O<sub>11</sub>Si<sub>8</sub>U (1872.42): C 61.52, H 4.29; found C 60.73, H 4.43. Subsequent recrystallization from diethyl ether/TMEDA 9:1 gave well-formed colorless crystals of the composition [U(Ph<sub>2</sub>Si(OSiPh<sub>2</sub>O)<sub>2</sub>)(Ph<sub>2</sub>SiO)<sub>2</sub>O]·Et<sub>2</sub>O·TMEDA (**7a**). IR (Nujol):  $\bar{\nu}$  = 3131w, 3076(sh)w, 3069m, 3049m, 3023m, 3002m, 2924s, 2853m, 1964w, 1892w, 1827w, 1591m, 1568w, 1486w, 1462w, 1429s, 1377w, 1307w, 1263m, 1188m, 1119vs, 1037vs, 1015vs, 994vs, 925(sh)s, 898m, 850(sh)m, 742s, 722vs, 698vs, 678m, 619w, 527vs, 487s, 457(sh)m cm<sup>-1</sup>; <sup>1</sup>H NMR ([D<sub>8</sub>]THF, 400 MHz):  $\delta$  = 8.2–6.4 (brm, 80H, Ph), 3.37 (q, 4H, CH<sub>2</sub>-O, Et<sub>2</sub>O), 2.20 (s, 4H, CH<sub>2</sub>-N, TMEDA), 2.02 (s, 12H, CH<sub>3</sub>-N, TMEDA), 1.11 (t, 6H, CH<sub>3</sub>, Et<sub>2</sub>O); <sup>13</sup>C NMR ([D<sub>8</sub>]THF, 101 MHz):  $\delta$  = 142–125 (Ph), 66.22 (CH<sub>2</sub>-O), 54.36 (CH<sub>2</sub>-N), 44.00 (CH<sub>3</sub>-N), 15.59 (CH<sub>3</sub>); elemental analysis calcd (%) for C<sub>106</sub>H<sub>106</sub>N<sub>2</sub>O<sub>12</sub>Si<sub>8</sub>U (2062.68): C 61.74, H 5.18, N 1.36; found C 60.65, H 4.72, N 1.58.

**X-ray data collection and structure refinement:** The measurements on **1**, **2**, **4**, **5**, **6**, and **7** were performed on a Siemens SMART CCD system with MoK $\alpha$  radiation ( $\lambda$  = 0.71073 Å) and graphite monochromator. The data on **3** were collected on a Siemens P4 diffractometer (MoK $\alpha$  radiation;  $\lambda$  = 0.71073 Å). Selected crystals of **1**–**7** were coated with mineral oil, mounted on a glass fiber and transferred to the cold nitrogen stream (Siemens LT-2 attachment for both devices). In case of the CCD data collections full hemispheres of the reciprocal space were scanned by  $\omega$  in three sets of frames of 0.3°. For **1**, **2**, **4**, **5**, **6**, and **7** as an absorption correction the SADABS routine was applied. For **3** psi-scans were collected and a semiempirical absorption correction was applied. The crystal structures were solved by direct methods (**1**, **2**, **4**, **5**, **6**, and **7**) or by the heavy atom method (**3**). For structure solution and refinement of **1**, **2**, **3**, **5**, and **7** the programs SHELXS86 and SHELXL93; for **4** and **6** the programs SHELXS97 and SHELXL97<sup>[50, 51]</sup> were used. For **4** and **7**, the absolute structures could not be determined reliably (**4**:  $x = 0.243(7)$ ; **7**:  $x = 0.580(3)$ ).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141064 (**4**), -141065 (**5**), -141066 (**6**), and refiles QACZAV (**1**), QACZEZ (**2**), QACZID (**3**), QACZOJ (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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