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New lanthanide(III) disiloxanediolates: Syntheses and structures

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ABSTRACT

Three new chloro-functionalized lanthanide(III) bis(disiloxanediolate) complexes, $[\{(Ph_2SiO)_2\}_2\{Li(DME)\}_2]Nd(DME)Cl$ (**3**), $[\{(Ph_2SiO)_2\}_2\{Li(THF)_2\}_2]HoCl\cdot2THF$ (**4**), and $[\{(Ph_2SiO)_2\}_2\{Li(THF)_2\}_2]ErCl\cdot2THF$ (**5**) have been prepared by the treatment of anhydrous lanthanide trichlorides, $LnCl_3$ (Ln = Nd, Ho, Er), with two equivalents of *in situ* prepared $(Ph_2SiOLi)_2O$ (**2**). In a similar manner, the treatment of $PrCl_3$ with 2 equivalents of $(Ph_2SiOLi)_2O$ (**2**) in the presence of $LiN(SiMe_3)_2$ afforded the silylamide-functionalized derivative $[\{(Ph_2SiO)_2\}_2\{Li(THF)_2\}_2]Pr[N(SiMe_3)_2]$ (**6**). All new compounds have been structurally characterized by X-ray diffraction analyses. Compounds **4** and **5** represent a new intermediate structural type of lanthanide bis(disiloxanediolates) between the "inorganic metallocenes" (Pr, Nd, Sm) and the "metallacrowns" (Sc, Y).

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1. Introduction

The investigation of metallasiloxanes derived from silanediols, disiloxanediols, silsesquioxanes and related Si-OH species continues to be an area of vigorous research activities [1–7]. This is mainly contributable to the fact that such compounds are valuable precursors for metal oxides and silicates [2,3] as well as molecular models for silica-supported heterogeneous catalysts [1,4], or are catalytically active themselves [5]. A highly useful and versatile ligand in this field is the tetraphenyldisiloxanediolate dianion, $[(Ph_2SiO)_2O]^{2-}$, which gives rise to a variety of interesting structures, especially in combination with alkali metals [6] and early transition metals [2b,6,7]. The starting material tetraphenyldisiloxanediol, $Ph_2Si(OH)O-SiPh_2(OH)$ (**1**), is easily accessible from cheap precursors [8]. Group 3 metal (Sc, Y) and lanthanide complexes containing the $[(Ph_2SiO)_2O]^{2-}$ ligand have mainly been investigated in our laboratory [9]. It was found that the small Sc^{3+} and Y^{3+} ions form heterobimetallic complexes in which the Group 3 metal fits into the center of a 12-membered $Si_4O_6Li_2$ inorganic ring system formed by two lithium disiloxanediolate units. Additional chloro functionalities and solvent molecules are arranged in the *trans*-positions. Accordingly these complexes have been termed "metallacrown" derivatives of scandium and yttrium (Scheme 1).

In contrast, large Ln^{3+} ions such as Pr^{3+} or Sm^{3+} do not fit into the center of the 12-membered $Si_4O_6Li_2$ inorganic ring system, but are significantly displaced, leading to a series of bis(disiloxanediolate) complexes, which have been termed "inorganic lanthanide metallocenes" [9]. It was shown that this new class of heterobimetallic lanthanide disiloxanediolates (Scheme 2a) shares structural similarities with the well-known bent metallocenes containing pentamethylcyclopentadienyl (= C_5Me_5) ligands (Scheme 2b). The latter form a large and well-investigated class of organolanthanides with many of them displaying high catalytic activities in various olefin transformations [10]. In both cases two bulky ligands are coordinated to the central lanthanide ion in a bent geometry, leaving room for functional groups X (X = Cl, $N(SiMe_3)_2$, alkyl, H, etc.) as well as additional solvent molecules S (S = Et_2O, THF, etc.).

Thus far, isolated examples of the "inorganic metallocene" form of lanthanide bis(disiloxanediolates) have been restricted to the elements praseodymium, samarium, and gadolinium [9]. In this contribution, we report a significant extension of the series by including new representatives

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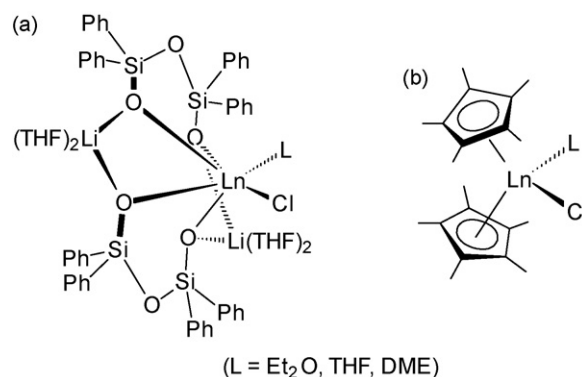*E-mail address:* frank.edelmann@ovgu.de (F.T. Edelmann).
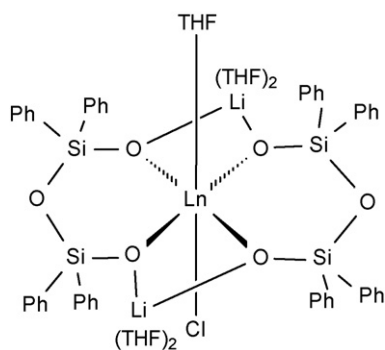
Scheme 1. The "metallacrown form" of lanthanide bis(disiloxanediolates) [9].

(L = Et$_2$O, THF, DME)

Scheme 2. The "inorganic metallocene form" of lanthanide bis(disiloxanediolates) [9].

for neodymium, holmium, and erbium in addition to a new silylamide-functionalized praseodymium derivative.

2. Results and discussion

The established synthetic route leading to chloro-functionalized lanthanide(III) bis(disiloxanediolates) [9] was successfully employed to extend the series to the rare earth elements neodymium, holmium, and erbium. It starts with the in situ preparation of (Ph$_2$SiOLi)$_2$O (2) through treatment of tetraphenyldisiloxanediol, Ph$_2$Si(O-H)OSiPh$_2$(OH) (1) [8] with two equivalents of LiN(SiMe$_3$)$_2$ (obtained by deprotonation of HN(SiMe$_3$)$_2$ with n-butyl-lithium in a THF/hexane mixture). To the resulting solution of (Ph$_2$SiOLi)$_2$O (2) anhydrous lanthanide trichlorides, LnCl$_3$ (Ln = Nd, Ho, Er), were added in a ligand:Ln molar ratio of 2:1. The product from the neodymium reaction was worked up by crystallization from DME resulting in the formation of pale pink crystal blocks, which were isolated in 75% yield. A single-crystal X-ray diffraction analysis revealed the presence of the DME-solvated heterobime-tallic neodymium bis(disiloxanediolate) derivative [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Nd(DME)Cl (3), the formation of which can be illustrated according to Scheme 3.

In the ^{1}H NMR spectrum of 3, two resonances at δ 3.50 (s) and 3.31 (s) ppm could be clearly assigned to the coordinated DME ligands, while the phenyl resonances were broad and uninformative due to the paramagnetic nature of the central Nd^{3+} ion. In the ^{29}Si NMR spectrum a single peak at δ −60.1 ppm was observed. No meaningful comparison with literature data could be made as compound 3 is the first disiloxanediolate derivative of neodymium isolated thus far. The molecular structure of 3

was authenticated by X-ray diffraction. Crystal data and structure refinement details for all new compounds reported here are listed in Table 1. Fig. 1 depicts the molecular structure of 3.

The X-ray analysis clearly revealed that the compound is isostructural with the previously reported praseody-mium(III) complex [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Pr(DME)Cl. Thus it also belongs to the group of "inorganic metallo-cenes" [9c]. Here again the neodymium is coordinated to the [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]$^{2−}$ ligand system in an out-of-plane arrangement. A terminal chloride ligand and a chelating DME complete the coordination sphere around neodymium. The overall coordination geometry can be best described as monocapped trigonal-prismatic. Struc-turally related lanthanide metallocenes of the type (C$_5$Me$_5$)$_2$LnCl(THF) are well established [11]. The Nd-O distances to the disiloxanediolate ligands in 3 are in the range of 2.335(3)–2.375(4) Å, and the Nd-Cl bond length is 2.737(1) Å. The corresponding values in the Pr analogue are Pr-O$_{silox}$ (av.) 2.370(2) Å and the Pr-Cl 2.768(1) Å [9c].

In the case of holmium and erbium, the THF-adducts [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]HoCl·2THF (4, pale pink rods, 70% yield) and [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]ErCl·2THF (5, pale pink needles, 72% yield) were obtained according to Scheme 4.

In both cases no meaningful NMR spectra could be obtained due to the strongly paramagnetic nature of the Ho^{3+} and Er^{3+} ions, respectively. However, both com-pounds could be structurally characterized by X-ray diffraction (Table 1). The structural analyses revealed that, despite the smaller ionic radii of Ho^{3+} and Er^{3+} as compared to Pr^{3+} and Nd^{3+} both complexes adopt the "inorganic metallocene" structural type. This means that the lantha-
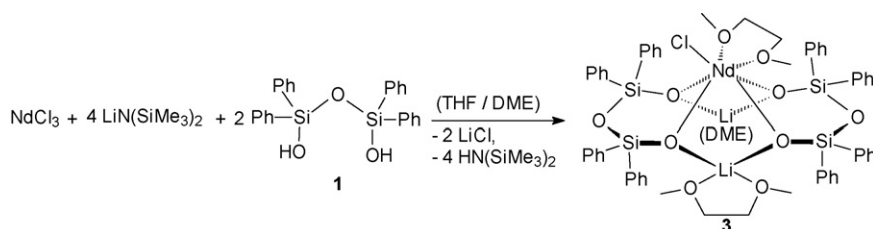
Scheme 3. Formation of [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Nd(DME)Cl (3).

Table 1
Crystallographic Data for **3–6**.

	3	4	5	6a
Empirical formula	$C_{60}H_{70}ClLi_2NdO_{12}Si_4$	$C_{72}H_{88}ClHoLi_2O_{12}Si_4$	$C_{72}H_{88}ClErLi_2O_{12}Si_4$	$C_{70}H_{90}Li_2NO_{10}PrSi_6$
a (Å)	17.268(4)	10.745(2)	21.667(4)	22.415(5)
b (Å)	17.242(3)	16.283(3)	16.332(3)	14.574(3)
c (Å)	21.199(4)	21.164(4)	10.737(2)	23.749(5)
α (°)	90	90	90	90
β (°)	97.88(3)	102.71(3)	106.75(3)	106.69(3)
γ (°)	90	90	90	90
V (Å^3)	6252(2)	3612.1(13)	3638.4(13)	7431(3)
Z	4	2	2	4
Formula weight	1289.09	1472.09	1474.37	1428.76
Space group	$P2_1/c$	Pn	Cm	$C2/c$
T (°C)	−123	−140	−93	−60
λ (Å)	0.71073	0.71073	0.71073	0.71073
D_{calcd} (g cm^{-3})	1.370	1.221	1.214	1.277
μ (mm^{-1})	1.007	1.247	1.304	0.806
R (Fo or Fo^2)	0.0409	0.0428	0.0317	0.0280
R_w (Fo or Fo^2)	0.0777	0.1061	0.0819	0.0653

nide metal is significantly displaced from the center of the 12-membered $Si_4O_6Li_2$ inorganic ring system formed by two lithium disiloxanediolate units. However, the use of these intermediate size lanthanide ions leads to formation of a new structural variety in that the molecules are "unsolvated", *i.e.* no solvent molecules are coordinated to the lanthanides. This is in contrast not only to the related Pr [9c] and Nd (this work) derivatives, but also to the previously reported samarium(III) bis(disiloxanediolate) complex [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Sm(DME)Cl [9a]. In all these three cases, the central lanthanide ion is large enough to leave room for an additional chelating DME ligand. Thus the new holmium and erbium derivatives represent an intermediate structural type of lanthanide bis(disiloxanediolates) between the "inorganic metallocenes" (Pr, Nd, Sm) and the "metallacrowns" (Sc, Y). At present, however, we cannot offer a plausible explanation for the differences in the solid-state structures of the Ho/Er complexes, on one hand, and the related yttrium complex [9], on the other, especially as there are no significant

Fig. 1. Molecular structure of [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Nd(DME)Cl (**3**). Selected bond lengths [Å] and angles [°]: Nd – O$_{silox}$ 2.335(3) – 2.375(4), Nd – Cl 2.737(1), Nd – O$_{DME}$ 2.627(3), 2.663(4), Li – O$_{silox}$ 1.899(11) – 1.974(9), O$_{silox}$ – Nd – O$_{silox}$ 83.42(12) – 84.62(11), Cl – Nd – O$_{silox}$ 86.97(7), 110.12(7), 155.51(9), 103.01(7).

differences in the ionic radii between these metals. As depicted in Figs. 2 and 3, the two compounds **4** and **5** are isomorphous. Two lithium disiloxanediolate units are connected to form a 12-membered $Si_4O_6Li_2$ metallacycle to which the lanthanide ion is coordinated in an out-of-plane fashion. The coordination sphere around the lanthanide is completed by a single chloro-functionality with no room left for additional solvent molecule coordination. The main structural details of **4** and **5** are unexceptional with Ho – O$_{silox}$ distances of 2.224(4) and 2.205(4) Å (**4**) and Er – O$_{silox}$ bond lengths of 2.183(2) and 2.196(2) Å (**5**). Apart from various lanthanide silicates only very few examples for molecular compounds comprising Ho-O-Si and Er-O-Si moieties can be found in the literature for comparison. A notable example for an organometallic holmium siloxide complex is [CpHo(PzMe$_2$)(OSi-Me$_2$PzMe$_2$)]$_2$ (Cp = η^5-cyclopentadienyl, Pz = pyrazolyl), although the siloxide ligands are bridging in this dimeric compound. Here the Ho – O$_{silox}$ distances are 2.270(4) and 2.290(4) Å, respectively [12]. The Ho – Cl bond length in the holmium derivative **4** is 2.535(2) Å. There are several organoholmium chlorides reported in the literature to compare with [13]. Typical literature values for Ho – Cl bonds are *e.g.* 2.618(3) and 2.623(3) Å in CpHoCl$_2$(THF)$_3$ [13a], 2.573(2) in a 1,1′-(3-oxapentamethylene)-bridged bis(indenyl) *ansa*-lanthanocene chloride complex of holmium [13b], 2.611(3) in (C$_9$H$_7$)HoCl$_2$(THF)$_3$ (C$_9$H$_7$ = η^5-indenyl) [13c], and 2.578(1) Å in bis(tetrahydrofurfur-ylindenyl)holmium chloride [13d]. The Er-Cl distance in **5** is 2.523(2) Å. This value agrees favorably with the Er-Cl bond length of 2.616(2) Å found in the mono(cyclopenta-dienyl)erbium dichloride complex CpErCl$_2$(THF)$_3$ [14].

Previously reported praseodymium bis(disiloxanedio-late) complexes include the "inorganic metallocenes" [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}{Li(THF)}]Pr(μ-Cl)$_2$Li(THF)$_2$ and [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]PrCl(DME) [9c]. These compounds can be viewed as analogues of the known metallocene derivatives (C$_5$Me$_5$)$_2$Pr(μ-Cl)$_2$Li(THF)$_2$ and (C$_5$Me$_5$)$_2$PrCl(THF) [11]. We now found that by slightly changing the reaction conditions the reaction of anhydrous PrCl$_3$ with two equivalents of (Ph$_2$SiOLi)$_2$O (**2**) (made *in situ* by treatment of tetraphenyldisiloxanediol, Ph$_2$Si(OH)OSi-
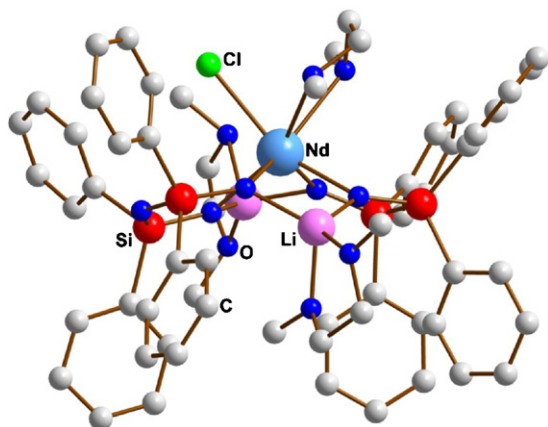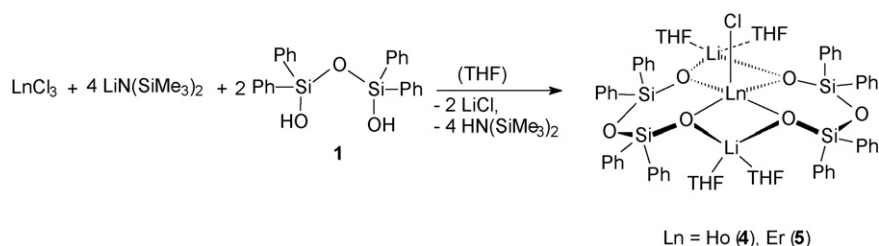
Scheme 4. Synthesis of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]HoCl·2THF (**4**) and [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]ErCl·2THF (**5**).

Ph$_2$(OH) (**1**) [8] with two equivalents of LiN(SiMe$_3$)$_2$ according to Scheme 5 a new silylamide-functionalized complex, [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]Pr[N(SiMe$_3$)$_2$] (**6**), becomes available.

The formation of **6** can be explained by the fact that an excess of LiN(SiMe$_3$)$_2$ (five equivalents) was used for the preparation of **2** instead of four equivalents as would be required. Thus it is likely that the silylamide **6** was formed by a metathetical reaction of an intermediate chloro derivative with the remaining equivalent of LiN(SiMe$_3$)$_2$. Thus far, more deliberate preparations of **6** by treatment of the chloro precursors [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)}{Li(THF)}]Pr(μ-Cl)$_2$Li(THF)$_2$ or [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]PrCl(DME) [9c] with LiN(SiMe$_3$)$_2$ failed due to the formation of complex product mixtures. Crystallization of **6** from a concentrated solution in THF yielded pale green crystals in 65% yield. An indication for the formation of a silylamide-functionalized species came already from the NMR data. The ^{1}H NMR spectrum displayed a singlet at δ 0.03 ppm, while in the ^{29}Si NMR spectrum two signals at δ 10.4 ppm (SiMe$_3$) and δ −50.1 (Ph$_2$SiO) with an intensity ratio of 1:4 were observed. This was verified by a single crystal X-ray structure determination (Table 1). Fig. 4 shows the molecular structure of **6**.

The X-ray analysis confirmed the presence of the silylamide-functionalized praseodymium bis(disiloxane-diolate) complex [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]PrN(SiMe$_3$)$_2$ (**6**). As expected, this compound too belongs to the class

of "inorganic metallocene"-type lanthanide bis(disiloxane-diolates) comprising an out-of-plane coordination of the Ln^{3+} ion to the 12-membered Si$_4$O$_6$Li$_2$ inorganic ring system formed by two lithium disiloxanediolate units. Only one closely related compound, the gadolinium(III) complex [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]GdN(SiMe$_3$)$_2$, had been reported earlier in the literature [9a]. Both compounds, which are isostructural, can be seen as "inorganic metallocenes" analogues of the well-known lanthanide(III) metallocene silylamides (C$_5$Me$_5$)$_2$LnN(SiMe$_3$)$_2$ [15]. With 2.350(1) Å the average Pr – O$_{silox}$ distance compares favorably with those found for [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)}{Li(THF)}]Pr(μ-Cl)$_2$Li(THF)$_2$ (2.301(2)–2.346(2) Å) and [{(Ph$_2$SiO)$_2$O}$_2${Li(D-ME)}$_2$]PrCl(DME) (ave. 2.370(2) Å) [9c]. Further comparison with literature values is difficult as apparently only one other praseodymium siloxide has been structurally charac-terized in the past. In the recently reported heterobimetallic siloxide complex [Pr{OSi(O^{t}Bu)$_3$}(AlMe)(AlMe)] [16] the Pr – O distances are 2.357(2) and 2.714(2) Å. The compound Pr(OSiPh$_3$)$_3$(THF)$_3$·THF [17] has been reported, but its structure has not been determined by X-ray methods. The Pr – N bond length to the silylamide functionality in **6** is 2.411(2) Å. Literature values for Pr – N distances in a PrN(SiMe$_3$)$_2$ derivative are e.g. 2.292(3) and 2.303(3) Å in [{(Me$_3$Si)$_2$N}$_2$Pr(μ-S^{t}Bu)]$_2$ [18].

In previous studies on this subject, we have shown that the structural chemistry of heterobimetallic Group 3 metal and lanthanide(III) bis(disiloxanediolates) is quite diverse
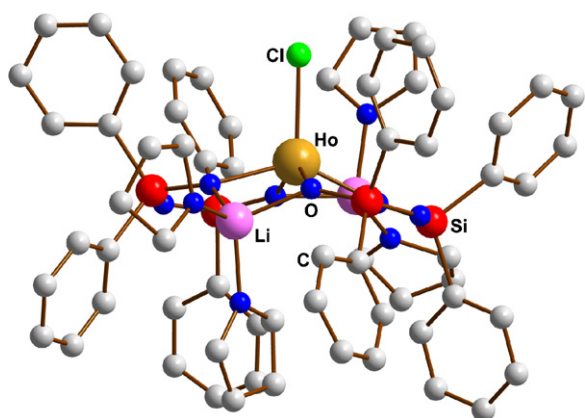

Fig. 2. Molecular structure of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]HoCl·2THF (**4**). Selected bond lengths [Å] and angles [°]: Ho – O$_{silox}$ 2.224(4), 2.205(4), Ho – Cl 2.535(2), Li – O$_{silox}$ 1.908(15) – 1.996(11), O$_{silox}$ – Ho – O$_{silox}$ 88.11(15), Cl – Ho – O$_{silox}$ 101.95(13) – 116.04(12).
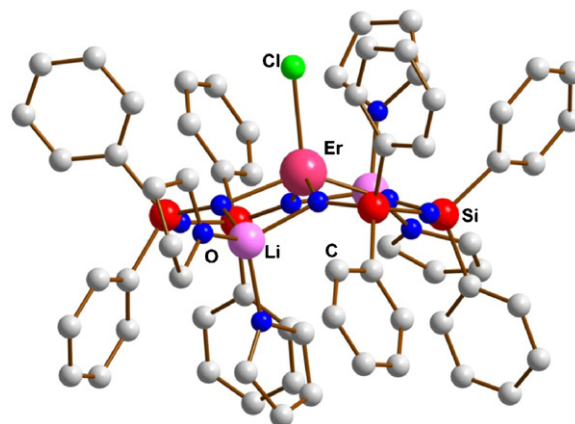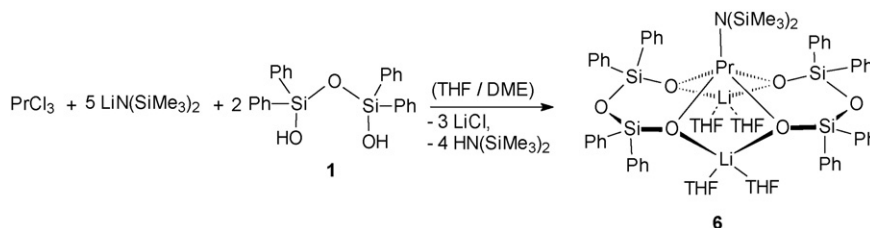

Fig. 3. Molecular structure of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]ErCl·2THF (**5**). Selected bond lengths [Å] and angles [°]: Er – O$_{silox}$ 2.183(2), 2.196(2), Er – Cl 2.523(2), Li – O$_{silox}$ 1.948(5), 1.960(6), O$_{silox}$ – Er – O$_{silox}$ 88.58(8), Cl – Er – O$_{silox}$ 104.37(8), 114.01(8).

Scheme 5. Synthesis of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]Pr[N(SiMe$_3$)$_2$] (**6**).

and that the structures of the products strongly depend on the ionic radius of the Group 3 or lanthanide metal. In the case of the small scandium and yttrium ions, octahedral complexes were obtained, which according to X-ray diffraction studies can be best described as novel metallacrown complexes with the lithium disiloxanediolate ligand systems arranged in the equatorial plane and additional ligands in *trans*-positions. In contrast, the larger Pr^{3+} ion afforded heterobimetallic disiloxanediolates, which could be regarded as "inorganic metallocenes" or out-of-plane metallacrown complexes. Thus the lithium disiloxanediolate ligand system provides a rational way to block one side of a larger lanthanide ion and, presumably, control the reactivity of the lanthanide. In summarizing the results reported here, we were able to extend the series of "inorganic metallocenes" to Nd, Ho, and Er through isolation and structural characterization of [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Nd(DME)Cl (**3**), [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]HoCl·2THF (**4**), and [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]ErCl·2THF (**5**). The latter two represent a new intermediate structural type of lanthanide bis(disiloxanediolates) between the "inorganic metallocenes" (Pr, Nd, Sm) and the "metallacrowns" (Sc, Y). In these compounds, the central Ln^{3+} ions are still too large to fit into the center of the 12-membered Si$_4$O$_6$Li$_2$ inorganic ring system formed by two lithium disiloxanediolate units. However, their

reduced ionic radii as compared to Pr^{3+}, Nd^{3+}, and Sm^{3+} do not leave room for additional solvent molecule coordination so that **4** and **5** are unsolvated at the lanthanides. Finally, the successful preparation of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]Pr[N(SiMe$_3$)$_2$] (**6**) shows that silylamide-functionalized lanthanide bis(disiloxanediolate) complexes are deliberately accessible in a one-pot reaction by treatment of LnCl$_3$ with two equivalents of (Ph$_2$SiOLi)$_2$O (**2**) plus LiN(SiMe$_3$)$_2$. The derivative chemistry of the silylamide complexes will be the subject of future investigations in this field.

3. Experimental section

3.1. General procedures

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 using KBr pellets on a Perkin-Elmer FT-IR spectrometer system 2000 between 4000 and 400 cm^{-1}. ^{1}H (400.1 MHz), ^{13}C (100.6 MHz), ^{29}Si NMR (79.5 MHz) spectra were recorded in THF-d_8, C$_6$D$_6$ or d_8-toluene solutions on a Bruker DPX 400 spectrometer at 25 °C. ^{1}H, ^{13}C and ^{29}Si chemical shifts are referenced to TMS. Microanalyses of the compounds were performed using a Leco CHNS 923 or a vario EL cube (Elementar Analysensysteme GmbH) apparatus. The starting materials 1,1,3,3-tetraphenyl-1,3-disiloxanediol [8] and anhydrous LnCl$_3$ (Ln = Er, Ho, Nd, Pr) [19] were prepared according to published procedures. HN(SiMe$_3$)$_2$ and *n*-butyllithium in *n*-hexane solution were obtained from commercial sources and used as received. Intensity data were collected on a Stoe IPDS 2T diffractometer with MoK$_\alpha$ radiation. The data were collected with the Stoe XAREA [20] program using ω-scans. Numeric absorption corrections were applied using XRED32 [20]. The space group was determined with XRED32 program [20]. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97 [21]. Data collection parameters are given in Table 1.

3.2. Preparation of [{(Ph$_2$SiO)$_2$O}$_2${Li(DME)}$_2$]Nd(DME)Cl (3)

(Ph$_2$SiOH)$_2$O (6.3 mmol, 2.6 g) were added to a solution of LiN(SiMe$_3$)$_2$ prepared *in situ* by reaction of *n*-butyllithium (7.9 ml of a 1.6 M solution in *n*-hexane) with HN(SiMe$_3$)$_2$ (2.6 ml, 2.03 g, 12.6 mmol) in THF (100 ml) at
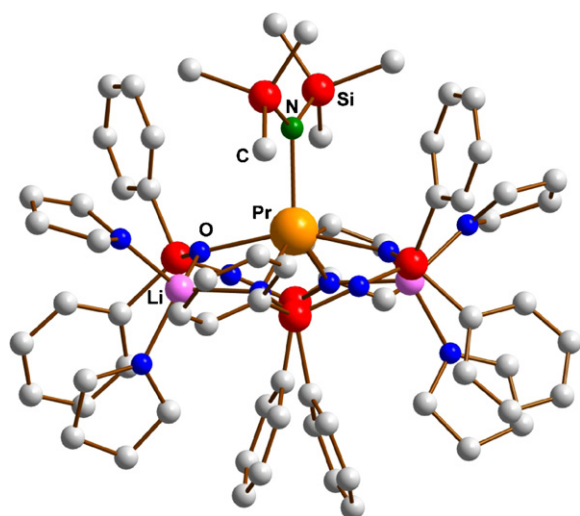

Fig. 4. Molecular structure of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]PrN(SiMe$_3$)$_2$ (**6**). Selected bond lengths [Å] and angles [°]: Pr – N 2.411(2), Pr – O 2.350(1), Si – O 1.610(1) – 1.612(1), Li – O$_{silox}$ 1.981(4), 1.994(4), N – Pr – O$_{silox}$ 101.87(3), 123.99(4), O$_{silox}$ – Pr – O$_{silox}$ 90.15(5), 76.55(5).

room temperature. The reaction mixture was stirred overnight. Then anhydrous $NdCl_3$ (0.78 g, 3.1 mmol) was added, followed by stirring for another 24 h. The reaction solution was filtered through a P4 glass-frit to separate a white precipitate from the clear, slightly brown solution. After reducing the volume of the solution in vacuum to 15 ml and adding 10 ml DME the product crystallized in form of pale pink blocks. Yield: 3.1 g (75%). Anal. Calcd for $C_{60}H_{70}ClLi_2NdO_{12}Si_4$ (M_r = 1289.12): C 55.90%; H 5.47%; Cl 2.75%. Found: C 54.95%; H 5.61%; Cl 2.23%. ^{1}H NMR (400.1 MHz, THF-d_8, 20 °C): δ = 6.96 (s, br; Ph), 6.68 (s, br; Ph), 6.43 (s, br; Ph), 6.03 (s, br; Ph), the intensities of the phenyl proton signals do not fit to the numbers of hydrogen atoms due to the paramagnetic properties of the Nd^{3+} ion, 3.50 (s, 12H, CH_2O) 3.31 (s, 18H, CH_3O). ^{13}C NMR (100.6 MHz, THF-d_8, 20 °C): δ = 150.0, 145.4, 136.6, 134.1, 128.7, 127.8, 127.5, 126.8 (Ph); 72.6, 58.9 (THF). ^{29}Si NMR (THF-d_8, 79.5 MHz): δ = −60.1 ppm. IR (KBr): 3067m, 3048m, 2999m, 2932m, 2830w, 1961w, 1893w, 1832w, 1774w, 1635w, 1590m, 1568w, 1452m, 1428s, 1368w, 1305w, 1246m, 1192m, 1156m, 1118vs, 1084s, 1059s, 1009vs, 965vs, 862m, 742s, 701vs, 683w, 530vs, 497s, 415m cm^{-1}. Mp: 145–160 °C (dec).

3.3. Preparation of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]HoCl·2THF (4)

$(Ph_2SiOH)_2O$ (6.3 mmol, 2.6 g) were added to a solution of LiN(SiMe$_3$)$_2$ prepared *in situ* by reaction of *n*-butyllithium (7.9 ml of a 1.6 M solution in *n*-hexane) with HN(SiMe$_3$)$_2$ (2.6 ml, 2.03 g, 12.6 mmol) in THF (100 ml) at room temperature. The reaction mixture was stirred overnight. Then anhydrous $HoCl_3$ (0.84 g, 3.1 mmol) was added, followed by stirring for another 24 h. The reaction solution was filtered through a P4 glass-frit to separate a white precipitate from the clear, slightly orange solution. After reducing the volume of the solution in vacuum to 25 ml the product crystallized in form of yellowish or pale pink needles depending on the light source. Yield: 3.4 g (72%). Anal. Calcd. for $C_{72}H_{88}ClHoLi_2O_{12}Si_4$ (M_r = 1472.09): C 58.75%; H 6.03%; Cl 2.41%. Found: C 58.34%; H 5.86%; Cl 1.96%. Because of the strong paramagnetic properties of the Ho^{3+} ion and low solubility of the crystalline solid, it was impossible to obtain evaluable ^{1}H, ^{13}C and ^{29}Si NMR data. IR (KBr): 3068m, 3048m, 3001m, 2978w, 2878w, 1965w, 1894w, 1829w, 1774w, 1619w, 1591m, 1568w, 1486w, 1429s, 1385w, 1307w, 1264w, 1186w, 1120vs, 1035sh vs., 1016vs, 996sh vs., 967vs, 835w, 742s, 714vs, 701vs, 684m, 663w, 620w, 528vs, 491s, 412w cm^{-1}. Mp: 120–130 °C (dec).

3.4. Preparation of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]ErCl·2THF (5)

$(Ph_2SiOH)_2O$ (6.3 mmol, 2.6 g) were added to a solution of LiN(SiMe$_3$)$_2$ prepared *in situ* by reaction of *n*-butyllithium (7.9 ml of a 1.6 M solution in *n*-hexane) with HN(SiMe$_3$)$_2$ (2.6 ml, 2.03 g, 12.6 mmol) in THF (100 ml) at room temperature. The reaction mixture was stirred overnight, then anhydrous $ErCl_3$ (0.85 g, 3.1 mmol) was added, followed by stirring for another 24 h. The reaction solution was filtered through a P4 glass-frit to separate a white precipitate from the clear, slightly orange solution.

After reducing the volume of the solution in vacuum to 25 ml the product crystallized in the shape of pale pink rods. Yield: 2.9 g (70%). Anal. Calcd. for $C_{72}H_{88}ClErLi_2O_{12}Si_4$ (M_r = 1474.42): C 58.65%; H 6.02%; Cl 2.40%. Found: C 57.95%; H 5.85%; Cl 2.07%. Because of the strong paramagnetic properties of the Er^{3+} ion and low solubility of the crystalline solid it was impossible to obtain evaluable ^{1}H, ^{13}C and ^{29}Si NMR data. IR (KBr): 3068m, 3047m, 3021m, 3001m, 2879w, 1964w, 1893w, 1832w, 1774w, 1626w, 1591m, 1568w, 1486w, 1429s, 1385w, 1307w, 1264w, 1176w, 1120vs, 1095m, 1035vs, 1019vs, 996vs, 961vs, 835m, 743s, 714vs, 702vs, 684m, 663w, 620w, 527vs, 499s, 412m cm^{-1}. Mp: 126–135 °C (dec).

3.5. Preparation of [{(Ph$_2$SiO)$_2$O}$_2${Li(THF)$_2$}$_2$]PrN(SiMe$_3$)$_2$ (6)

$(Ph_2SiOH)_2O$ (6.3 mmol, 2.6 g) were added to a solution of LiN(SiMe$_3$)$_2$ prepared *in situ* by reaction of *n*-butyllithium (9.8 ml of a 1.6 M solution in *n*-hexane) with HN(SiMe$_3$)$_2$ (3.24 ml, 2.53 g, 15.7 mmol) in THF (100 ml) at room temperature. The reaction mixture was stirred overnight. Then anhydrous $PrCl_3$ (0.76 g, 3.1 mmol) was added, followed by stirring for another 24 h. The reaction solution was filtered through a P4 glass-frit to separate a white precipitate from the clear, slightly brown solution. After reducing the volume of the solution in vacuum to 20 ml the product crystallized in form of pale green almost colourless prisms. Yield: 2.9 g (65%). Anal. Calcd for $C_{70}H_{90}Li_2NO_{10}PrSi_6$ (M_r = 1428.76): C 58.84%; H 6.35%, N 0.98%; Found: C 58.42%, H 5.97%, N 1.43%. ^{1}H NMR (400.1 MHz, THF-d_8, 20 °C): δ = 6.79 (s, br, Ph), 6.60 (s, br, Ph), 6.18 (s, br, Ph), 3.55 (s, CH_2O), 1.67 (s, CH_2), 0.03 (Si(CH_3)$_3$), the intensities of the phenyl proton signals do not fit to the numbers of hydrogen atoms due to the paramagnetic properties of the Pr^{3+} ion. ^{13}C NMR (100.6 MHz, THF-d_8, 20 °C): δ = 149.9 (Ph), 134.3 (Ph), 127.9 (Ph), 127.2 (Ph), 68.1 (THF), 26.3 (THF), 2.6 (SiCH$_3$). ^{29}Si NMR (THF-d_8, 79.5 MHz): δ = 10.3 (Si(CH$_3$)$_3$), −50.1 (Ph$_2$Si-O) (1:4) ppm. IR (KBr): 3067m, 3048m, 3000m, 2955m, 2927m, 1961w, 1899w, 1832w, 1635w, 1591m, 1484m, 1428s, 1385m, 1252m, 1185m, 1118vs, 986vs, 844m, 743s, 708vs, 663w, 619w, 525vs, 492s, 407w cm^{-1}. Mp: 127–140 °C (dec).

4. Supplementary material

Crystallographic data for the crystal structures reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/) by referring to the CIF deposition codes CCDC 757880 (**3**), 757883 (**4**), 757881 (**5**), and 758467 (**6**).

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