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Article

Structural Varieties in Heterobimetallic Lanthanide Disiloxanediolates: "Inorganic Metallocenes" versus In-Plane Metallacrowns

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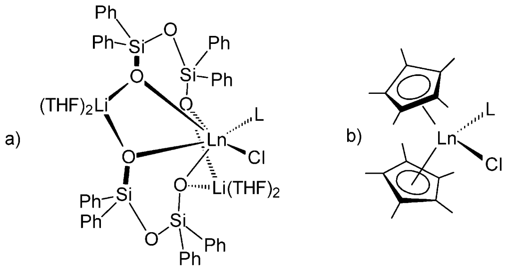
The previously proposed concept of "inorganic metallocenes" of group 3 and rare-earth elements has been tested by preparing a series of novel disiloxanediolates with metals displaying different ionic radii. For the smaller scandium and yttrium, approximately planar arrangements of the disiloxanediolate frameworks with solvent and chloride ligands in trans positions were found. Thus, the compounds $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]ScCl(THF/DME)$ (**2**; DME = 1,2-dimethoxyethane and THF = tetrahydrofuran) and $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]YCl(THF)$ (**3**) can be described as heterobimetallic inorganic ring systems or metallacrown complexes with "in-plane" coordination of the metal. In contrast, "out-of-plane" geometries with cis coordination of additional ligands were identified in the praseodymium derivatives $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}\{Li(THF)\}]Pr(\mu\text{-}Cl)_2Li(THF)_2$ (**4**) and $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]PrCl(DME)$ (**5**). These compounds can be viewed as analogues of the known metallocene derivatives $(C_5Me_5)_2Pr(\mu\text{-}Cl)_2Li(THF)_2$ and $(C_5Me_5)_2PrCl(THF)$. The molecular structures of **2**–**5** have been determined by X-ray diffraction.

Introduction

The organometallic chemistry of the rare-earth elements continues to be a highly attractive field of research, in particular because of the numerous applications of organolanthanides in catalysis[1] and organic synthesis.[2] An increasingly important area focuses on the development of noncyclopentadienyl organolanthanide complexes.[3] In the first papers of this series, we proposed the novel concept of "inorganic lanthanide metallocenes".[4] It was based on the experimental finding that a new class of heterobimetallic lanthanide disiloxanediolates (Scheme 1a) share structural similarities with the well-known metallocenes containing pentamethylcyclopentadienyl (= C_5Me_5) ligands (Scheme 1b). The latter form a large and well-investigated class of organolanthanides, with many of them displaying high catalytic activities in various olefin transformations.[1] In both cases, bulky ligands effectively block one side of the central lanthanide ion, leaving room for functional groups X (X = Cl, $N(SiMe_3)_2$, alkyl, H, etc.) as well as additional solvent molecules L [L = Et_2O, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), etc.] in cis positions.

Scheme 1



(L = Et_2O, THF, DME)

Structurally characterized examples of the new lanthanide disiloxanediolates included the gadolinium bis(trimethylsi-

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lyl)amide $[\{(Ph_2SiO)_2O\}Li(THF)_2]_2GdN(SiMe_3)_2$, which can be regarded as an disiloxanediolate analogue of the known compounds $(C_5Me_5)_2LnN(SiMe_3)_2$.[5] The inorganic variety is based on the bidentate disiloxanediolate ligand $[(Ph_2SiO)_2O]^{2-}$. This particularly useful ligand gives rise to a variety of unusual and unexpected structures especially when combined with alkali metals[6] and early transition metals.[7,8] Most previously reported disiloxanediolate complexes contain the $[(Ph_2SiO)_2O]^{2-}$ *di*anion coordinated to *one* metal atom in a chelating fashion. In all of these cases, a comparison with metallocene derivatives bearing the *mono*anionic $C_5Me_5^-$ ligand would be meaningless. What makes the heterobimetallic lanthanide disiloxanediolates shown in Scheme 1a special is the fact that in these compounds one negative charge of each $[(Ph_2SiO)_2O]^{2-}$ ligand is compensated for by a Li^+ ion. The resulting formally *mono*anionic lithium disiloxanediolate moieties seen as a whole can now take the role of the $C_5Me_5^-$ ligands in regular metallocene derivatives. A structural analogy between the two classes of compounds is reached when the lithium disiloxanediolate units are coordinated to the central lanthanide ion in a bent geometry, as is the case in the previously reported complex $[\{(Ph_2SiO)_2O\}Li(THF)_2]_2GdN(SiMe_3)_2$.[4] It should, however, be made clear that the term "inorganic metallocenes" should not be stressed to the limit. It should mainly be understood in terms of a steric similarity, i.e., the blocking of one side of a lanthanide ion leaving room for functional groups and solvent molecules arranged in the cis position. This can be effected by two bulky $C_5Me_5^-$ ligands or, as in our case, by two lithium disiloxanediolate moieties connected to each other. However, the metallocene analogy by no means implies an electronic analogy because $C_5Me_5^-$ is a six-electron donor whereas our ligand system donates a total of eight electrons.

The study presented here was carried out in order to find out how the structures of heterobimetallic group 3 and lanthanide disiloxanediolates vary with the ionic radius of the metal ion employed. We report here the preparation and characterization of new heterobimetallic disiloxanediolates of scandium, yttrium, and praseodymium. The results clearly show that "inorganic metallocenes" are formed mainly with the early and middle lanthanide elements (praseodymium and gadolinium) and that the ionic radii of of the group 3 metal ions Sc^{3+} and Y^{3+} are apparently small enough to fit into the cavity of the surrounding metallacrowns.

Experimental Section

General Methods. All reactions were carried out in an atmosphere of dry nitrogen either in a drybox (M. Braun Labmaster 130 and 150B-G) or with the use of standard Schlenk techniques. Solvents were dried over sodium benzophenone and freshly distilled under nitrogen prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer system 2000. NMR spectra were recorded on a Bruker DPX FT-NMR spectrometer (^1H NMR, 400 MHz; ^{13}C NMR, 101 MHz; ^{29}Si NMR, 79.5 MHz). Chemical shifts are reported in ppm and referenced to residual solvent resonances (^1H and ^{13}C NMR) or an external standard [^{29}Si NMR (TMS) = 0 ppm]. 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 an Electrothermal IA 9100 apparatus. The starting materials 1,1,3,3-tetraphenyl-1,3-disiloxanediol (**1**),[9] $ScCl_3(THF)_3$,[10] anhydrous $LnCl_3$ (Ln = Y, Pr),[11] and $LiN(SiMe_3)_2$[12] were prepared according to published procedures.

$[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]ScCl(THF/DME)$ (2). At room temperature, 3.35 g (20.0 mmol) of $LiN(SiMe_3)_2$ was added to a suspension of 1.80 g (4.9 mmol) of $ScCl_3(THF)_3$ in 100 mL of DME. The mixture was stirred for 12 h and treated with 4.10 g (9.9 mmol) of solid **1**. The final reaction mixture was heated under reflux for 1 h. A white precipitate (LiCl) was filtered off. The solution was concentrated to a volume of about 60 mL and stored for 1 week at 2 °C. This afforded the formation of thick needle-shaped crystals (4.70 g, 81%). Anal. Calcd for $C_{60}H_{69.29}ClLi_2O_{11.64}ScSi_4$ (taken into account the disordered THF and DME according to the X-ray analysis; $M_r = 1183.38$): C, 60.90; H, 5.90. Found: C, 60.04; H, 5.59. ^1H NMR (400.1 MHz, THF-d_8, 20 °C): δ 7.80−7.70 (m, 16 H, *o*-Ph), 7.25−7.11 (m, 24 H, *m*-Ph + *p*-Ph), 3.42 (s, 12 H, OCH_2), 3.24 (s, 18 H, OCH_3). ^{13}C NMR (100.6 MHz, THF-d_8, 20 °C): δ 139.7−125.7 (Ph), 70.9 (CH_2O, DME), 57.1 (CH_3O, DME). ^{29}Si NMR (79.5 MHz, THF-d_8, 20 °C): δ −52.8. IR (KBr): 3438, 3068, 3046, 3000, 2937, 1591, 1568, 1451, 1428, 1367, 1244, 1193, 1120, 1081, 955, 872, 825, 743, 701, 531, 440, 410 cm^{-1}. Mp: 245−255 °C (dec).

$[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]YCl(THF)$ (3). A mixture of 0.98 g (5.0 mmol) of YCl_3 and 2.51 g (15.0 mmol) of $LiN(SiMe_3)_2$ was dissolved in 200 mL of THF and stirred for 24 h at room temperature. A total of 4.15 g (10.0 mmol) of **1** was added. The reaction solution was kept under reflux for 3 h and after cooling to room temperature was filtered over a P4 glass frit to separate a white precipitate from the clear, slightly yellowish solution. After the volume of the solution was reduced in vacuum to 20 mL, the product crystallized in the cold (2 °C) in the form of colorless blocks. Yield: 5.08 g (77%). Anal. Calcd for $C_{72}H_{83}ClLi_2O_{12}Si_4Y$ ($M_r = 1390.98$): C, 62.17; H, 6.01. Found: C, 61.59; H, 5.88. ^1H NMR (400.1 MHz, THF-d_8, 20 °C): δ 7.75−6.90 (m, br, Ph), 3.62, 1.76 (THF). ^{13}C NMR (100.6 MHz, THF-d_8, 20 °C): δ 142.0 (*ipso*-C), 135.9, 135.1, 128.4, 127.3 (Ph), 67.44, 25.26 (THF). ^{29}Si NMR (79.5 MHz, THF-d_8): not detected due to low solubility. IR (KBr): 3068, 3047, 3000, 2978, 2879, 1591, 1568, 1486, 1460,

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Table 1. Crystallographic Data of **2**−**5**

	2	**3**	**4**	**5**
formula	$C_{60}H_{69.29}ClLi_2O_{11.64}Si_4$	$C_{72}H_{83}ClLi_2O_{12}Si_4Y$	$C_{70}H_{84}Cl_2Li_3O_{11.50}PrSi_4$	$C_{60}H_{70}ClLi_2O_{12}PrSi_4$
fw	1183.38	1390.98	1454.36	1285.76
T (K)	210(2)	210(2)	200(2)	210(2)
cryst syst, space group	orthorhombic, *Pbca*	mononclinic, *P*2(1)/*m*	monoclinic, *P*2(1)/*n*	monoclinic, *P*2(1)/*c*
unit cell dimens (Å, deg)	$a = 17.034(2)$	$a = 13.0818(6)$	$a = 14.0067(2)$	$a = 17.5599(12)$
	$b = 20.649(2)$	$b = 17.1151(8)$	$b = 22.8399(4)$	$b = 17.3036(11)$
	$c = 35.785(4)$	$c = 17.1817(8)$	$c = 23.0701(4)$	$c = 21.4873(14)$
	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$	$\alpha = 90$
	$\beta = 90$	$\beta = 92.599(1)$	$\beta = 90.64$	$\beta = 99.681(2)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$	$\gamma = 90$
V (Å^3)	12586(2)	3843.0(3)	7379.9(2)	6435.9(7)
Z, calcd density (g·cm^{-3})	8, 1.249	2, 1.202	4, 1.309	4, 1.327
abs coeff (mm^{-1})	0.292	0.910	0.853	0.929
F(000)	4979	1458	3016	2656
θ range for data collection (deg)	2.28−29.60	2.00−26.07	1.71−28.29	2.25−29.54
limiting indices	$-20 \le h \le 23$,	$-16 \le h \le 16$,	$-17 \le h \le 17$,	$-20 \le h \le 23$,
	$-8 \le k \le 28$,	$-21 \le k \le 21$,	$-29 \le k \le 30$,	$-22 \le k \le 22$,
	$-44 \le l \le 48$	$-21 \le l \le 21$	$-29 \le l \le 15$	$-26 \le l \le 29$
reflns collected/unique	38 949/15 373 [*R*(int) = 0.0270]	55 738/7598 [*R*(int) = 0.10510]	55 545/16 954 [*R*(int) = 0.0319]	34 460/13 946 [*R*(int) = 0.0192]
completeness to	$\theta = 29$, 60 86.8%	$\theta = 26.07$, 96.4%	$\theta = 28.29$, 92.5%	$\theta = 29.54$, 77.5%
abs corr	*SADABS*	*SADABS*	multiscan	*SADABS*
max and min transmn	0.8921 and 0.8443	0.8389 and 0.6589	0.7266 and 0.6751	0.8360 and 0.6538
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
data/restraints/param	15 373/0/1003	7598/0/486	16 954/0/847	13 946/0/721
GOF on F^2	1.009	1.057	1.036	0.995
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0528$, $wR_2 = 0.1263$	$R_1 = 0.0584$, $wR_2 = 0.1802$	$R_1 = 0.0415$, $wR_2 = 0.1151$	$R_1 = 0.0352$, $wR_2 = 0.0901$
R indices (all data)	$R_1 = 0.0775$, $wR_2 = 0.1400$	$R_1 = 0.0743$, $wR_2 = 0.1877$	$R_1 = 0.0535$, $wR_2 = 0.1231$	$R_1 = 0.0434$, $wR_2 = 0.0978$
largest diff peak and hole, e·Å^{-3}	0.450 and −0.400	1.085 and −0.338	1.267 and −0.724	0.860 and −0.769

1429, 1373, 1307, 1252, 1186, 1120, 1036, 1019, 996, 962, 861, 843, 743, 714, 701, 684, 620, 529, 418 cm^{-1}. Mp: 125−145 °C (dec).

$[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}\{Li(THF)\}]Pr(\mu\text{-}Cl)_2Li(THF)_2$ (4). A mixture of 1.24 g (5.01 mmol) of $PrCl_3$ and 2.51 g (15.0 mmol) of $LiN(SiMe_3)_2$ was dissolved in 200 mL of THF, and the resulting solution was stirred for 24 h at room temperature. A total of 4.15 g (10.0 mmol) of **1** was added to the clear, yellowish solution. The reaction solution was kept under reflux for 3 h and after cooling to room temperature was filtered over a P4 glass frit to separate a white precipitate from the clear, slightly yellowish solution. After the volume of the solution was reduced in vacuum to 100 mL, the product crystallized in the cold in the form of colorless platelets. Yield: 4.69 g (68%). Anal. Calcd for $C_{68}H_{80}Cl_2Li_3O_{11}PrSi_4$ (M_r = 1418.35): C, 57.58; H, 5.69. Found: C, 57,28; H, 5,57. ^{1}H NMR (400.1 MHz, THF-d_8, 20 °C): δ 7.71−7.63 (m, br, Ph), 3.47, 1.72 (THF). ^{13}C NMR (100.6 MHz, THF-d_8, 20 °C): δ 139.1 (*ipso*-C), 135.3, 129.1, 128.6, 128.3 (Ph), 68.1, 26.3 (THF). ^{29}Si NMR (79.5 MHz, THF-d_8, 20 °C): δ −46.6. IR (KBr): 3069, 3048, 3001, 2957, 2878, 2376, 2347, 2342, 1620, 1591, 1569, 1487, 1457, 1429, 1374, 1307, 1252, 1186, 1122, 1043, 996, 954, 843, 742, 715, 700, 662, 619, 527, 498 cm^{-1}. Mp: 119−130 °C (dec).

$[((Ph_2SiO)_2O)_2(Li(DME))_2]PrCl(DME)$ (5). This compound was obtained by recrystallization of **4** from DME. Anal. Calcd for $C_{60}H_{70}ClLi_2O_{12}PrSi_4$ (M_r = 1285.76): C, 56.05; H, 5.49. Found: C, 54.35; H, 5.36. ^{1}H NMR (400.1 MHz, THF-d_8, 20 °C): δ 7.07−5.42 (br), 3.57, 3.37 (br, DME). ^{13}C NMR (100.6 MHz, THF-d_8, 20 °C): δ 138.7 (*ipso*-C), 133.0, 128.0, 126.0 (Ph), 72.7, 59.0 (DME). ^{29}Si NMR (79.5 MHz, THF-d_8, 20 °C): δ −57.8. IR (KBr): 3068, 3048, 3000, 2929, 2853, 1631, 1591, 1568, 1485, 1453, 1428, 1385, 1307, 1247, 1189, 1120, 1084, 1033, 967, 858, 843, 743, 713, 701, 683, 620, 530, 493, 415 cm^{-1}. Mp: 310−335 °C (dec).

X-ray Crystallographic Studies of 2−5. The intensity data of **2**−**5** were collected on a Stoe IPDS 2T diffractometer with Mo Kα radiation. The data were collected with the Stoe XAREA program using ω scans. Numeric absorption correction was applied. The space groups were determined with the *XPREP* program, and the structures were solved by direct methods (*SHELXS-97*) and refined with all data by full-matrix least-squares methods on F^2 using *SHELXL-97*.[13] CCDC-651314 (**2**), CCDC-651316 (**3**), CCDC-651313 (**4**), and CCDC-651315 (**5**) contain the detailed crystallographic data for the compounds reported here. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. Data collection parameters are given in Table 1.

Results and Discussion

The starting material 1,1,3,3-tetraphenyl-1,3-disiloxanediol, $Ph_2Si(OH)OSiPh_2(OH)$ (**1**), is readily accessible from cheap precursors. Hydrolysis of Ph_2SiCl_2 in the presence of ammonium carbonate affords **1** in yields up to 51%. Minor byproducts in this synthesis are diphenylsilanediol, $Ph_2Si(OH)_2$ (6%), and hexaphenyltrisiloxanediol, $Ph_2Si(OH)OSiPh_2OSiPh_2(OH)$ (18%).[9] The preparation of heterobimetallic disiloxanediolates of scandium and yttrium was performed as illustrated in Schemes 2 and 3 in analogy with the previously developed method.[4] In the first step, $ScCl_3(THF)_3$ or anhydrous YCl_3 was allowed to react with $LiN(SiMe_3)_2$ in order to produce in situ the "ate" complexes

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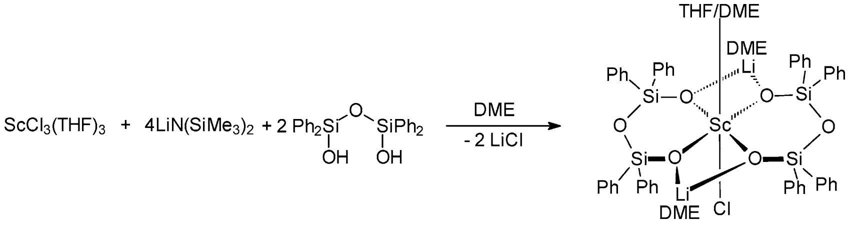
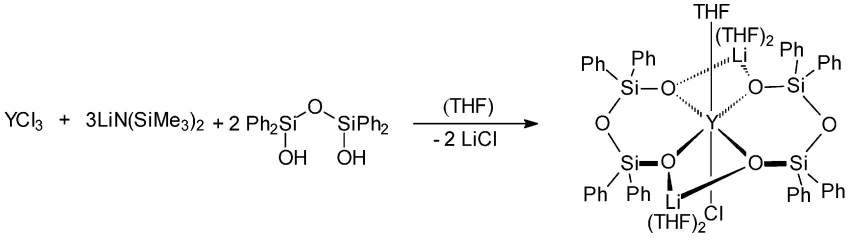
Scheme 2



2

Scheme 3



3

$[(Me_3Si)_2N]_3M(\mu\text{-}Cl)Li(THF)_3$.[14] The addition of 2 equiv of **1** to the resulting reaction mixtures produced colorless or slightly yellowish solutions from which the new heterobimetallc disiloxanediolates $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]ScCl(THF/DME)$ (**2**) and $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}_2]YCl(THF)$ (**3**) could be isolated in high yields (**2**, 81%; **3**, 77%). The scandium derivative **2** was isolated in the form of colorless, needlelike crystals, while the yttrium complex **3** forms colorless blocks. Both are soluble in THF and DME but virtually insoluble in aliphatic hydrocarbon.

NMR data of **2** and **3** were only slightly informative and showed resonances due to the phenyl substituents as well as coordinated solvent molecules (THF and DME). It should be pointed out that this chemistry strongly relies on the results of X-ray diffraction studies when it comes to definite statements about the structures of new compounds. The molecular and crystal structures of both **2** and **3** were determined by X-ray diffraction. Suitable single crystals of the scandium complex were obtained from DME, while the yttrium compound was recrystallized from THF. The structures are depicted in Figures 1 and 2, respectively, and Table 1 summarizes the crystal data of all new compounds reported here.

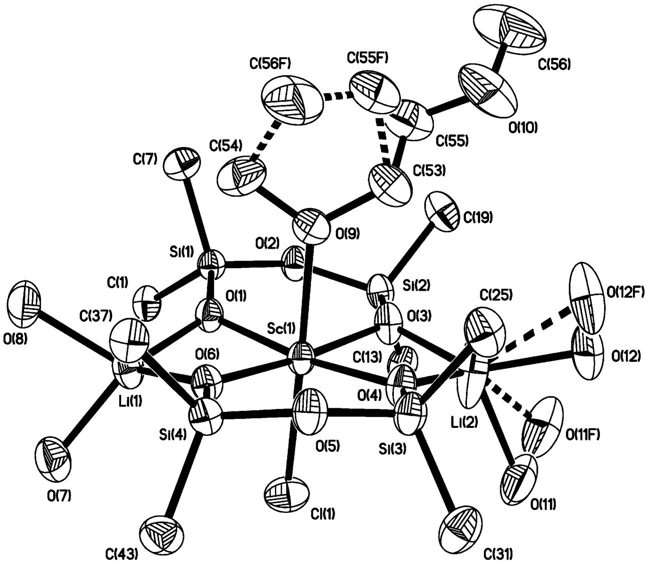


Figure 1. Molecular structure of **2**. For clarity, only the *ipso*-carbon atoms of the phenyl substituents and the oxygen atoms of the DME ligands at lithium are shown. Selected bond lengths [Å] and angles [deg]: Sc(1)−Cl(1) 2.4920(7), Sc(1)−O(1) 2.0600(14), Sc(1)−O(3) 2.0729(16), Sc(1)−O(4) 2.0622(14), Sc(1)−O(6) 2.0715(15), Sc(1)−O(9) 2.2917(16), O(1)−Sc(1)−O(3) 95.61(6), Cl(1)−Sc(1)−O(1) 92.58(4), O(1)−Sc(1)−O(6) 83.88(6), Cl(1)−Sc(1)−O(3) 95.35(5), O(3)−Sc(1)−O(4) 83.81(6), Cl(1)−Sc(1)−O(4) 96.25(5), O(4)−Sc(1)−O(6) 95.61(6), Cl(1)−Sc(1)−O(6) 90.63(6), O(1)−Sc(1)−O(9) 86.83(6), O(3)−Sc(1)−O(9) 86.30(7), Cl(1)−Sc(1)−O(9) 178.30(5), O(4)−Sc(1)−O(9) 84.34(6), O(6)−Sc(1)−O(9) 87.72(6).

In the solid-state structure of **2**, the central scandium adopts a distorted octahedral coordination geometry (Figure 1). Because of the use of $ScCl_3(THF)_3$ as the starting material and carrying out the reaction in DME, both solvent molecules are coordinated to scandium with a statistical disorder of ca. 40/60 (THF/DME). The coordinated DME ligand is bonded in a monodentate fashion. One of the DME ligands coordinated to lithium is also disordered. One oxygen of the coordinated solvent and a chloride ligand occupy the trans positions. With 178.30(5)°, the Cl(1)−Sc(1)−O(9) unit is almost linear. An inorganic $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]^{2-}$ ring system is wrapped around the Sc^{3+} ion in the equatorial plane like a metallacrown ether ligand.[15] The Sc−O distances within this ring system are in the range of 2.0600(14)−

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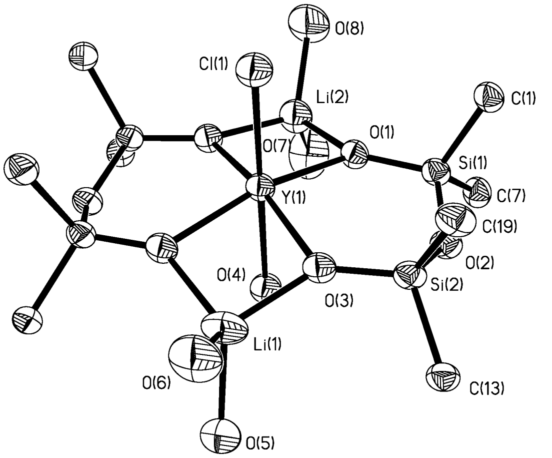


Figure 2. Molecular structure of **3**. For clarity, only the *ipso*-carbon atoms of the phenyl substituents and the oxygen atoms of the THF ligands are shown. Selected bond lengths [Å] and angles [deg]: Y(1)−Cl(1) 2.591(2), Y(1)−O(1) 2.219(2), Y(1)−O(3) 2.222(2), Y(1)−O(4) 2.492(4), O(1)−Y(1)−O(3) 95.79(9), C(l)−Y(1)−O(4) 179.5(1), O(1)−Y(1)−O(1′) 82.2(1), O(1)−Y(1)−Cl(1) 95.90(7), O(3)−Y(1)−O(3′) 82.2(1), O(3)−Y(1)−Cl(1) 99.20(7), O(1)−Y(1)−O(4) 81.2(1), O(3)−Y(1)−O(4) 81.2(1).

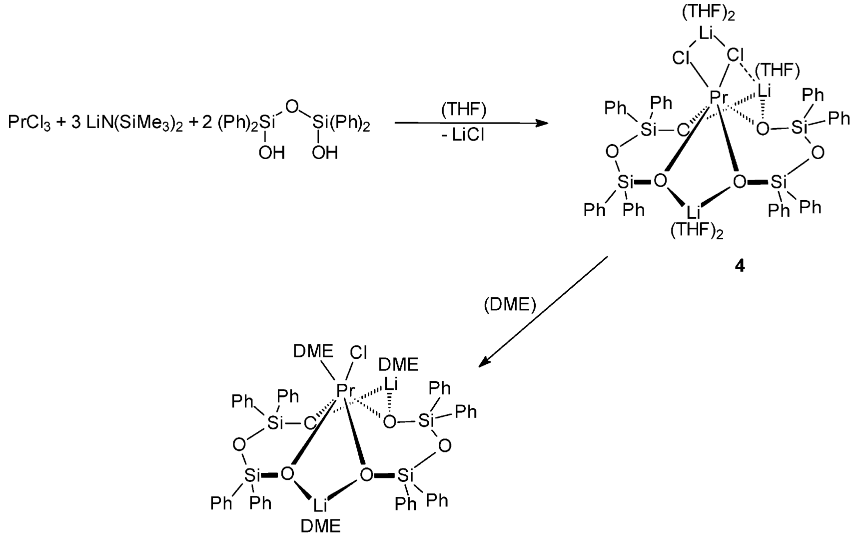
2.0729(16) Å. This can be favorably compared with the Sc−O distances in previously reported molecular species comprising Sc−O−Si units.[4,16] As expected, the Sc−O distance to the coordinated solvent is significantly longer [2.2917(16) Å]. The most important result of this structural study is the finding that the scandium derivative **2** does *not* fit into the concept of "inorganic metallocenes". Obviously, the ionic radius of Sc^{3+} (0.885 Å for coordination number 6) is a small enough to fit into the cavity of the $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]^{2-}$ ligand system so that in this case the in-plane metallacrown form is clearly favored.

An X-ray crystal structure determination of the yttrium complex **3** revealed a similar result for Y^{3+} (ionic radius of 1.040 Å for coordination number 6). As shown in Figure 2, this compound too adopts the metallacrown type structure with nearly octahedral coordination, although the larger Y^{3+} ion is not contained as perfectly in the metallacrown as the smaller Sc^{3+}. Again the oxygen of the coordinated THF ligand and a chloride ligand occupy the trans positions. The Cl(1)−Y(1)−O(4) angle is 159.5(1)°. A symmetry plane running through Li(1), Y(1), Cl(1), O(4), and Li(2) bisects the molecule. The average Y−O distance within the metallacrown system is 2.221(2) Å. A number of structurally characterized molecular yttrium siloxide species have been described in the literature. Typical Y−O distances in the Y−O−Si units are, e.g., 2.13(2) Å in $Y(OSiPh_3)_3(THF)_3\cdot THF$[17a] and 2.248(4) in $[(C_5H_5)Y(NPPh_2)(\mu\text{-}OSiMe_2NPPh_3)]_2\cdot 4toluene$.[17g]

Praseodymium was then employed as a representative of the larger early lanthanide elements. The ionic radius of Pr^{3+} in hexacoordinate complexes is 1.13 Å. The reactions leading to the first praseodymium disiloxanediolates are summarized in Scheme 4. At first, anhydrous $PrCl_3$ was allowed to react with 3 equiv of $LiN(SiMe_3)_2$ in order to produce in situ the "ate" complex $[(Me_3Si)_2N]_3Pr(\mu\text{-}Cl)Li(THF)_3$.[14] Subsequent treatment of the resulting solution with 2 equiv of **1** afforded a clear yellowish solution from which the new compound $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}\{Li(THF)\}]Pr(\mu\text{-}Cl)_2Li(THF)_2$ (**4**) was isolated in 68% yield in the form of colorless platelets.

A single-crystal X-ray diffraction study of **4** revealed the presence of a heterobimetallic praseodymium disiloxanediolate, which fits into the concept of "inorganic metallocenes" (Figure 3). This result clearly demonstrates the dependence of the molecular structures of these compounds on the ionic radius of the central Ln^{3+} ion. In **4**, the $[\{(Ph_2SiO)_2O\}_2\{Li(THF)_2\}\{Li(THF)\}]^{2-}$ ligand system is coordinated to praseodymium in a slightly bent arrangement, because the Pr^{3+} ion is too large to fit into the cavity of the metallacrown. As a consequence, the additional ligands are now forced into the cis positions. Retention of LiCl leads to the formation of a typical "ate" complex in which praseodymium and lithium are connected via two bridging chloride ligands. As depicted in Scheme 5, this type of complex is quite common in the chemistry of bis(pentamethylcyclopen-

Scheme 4



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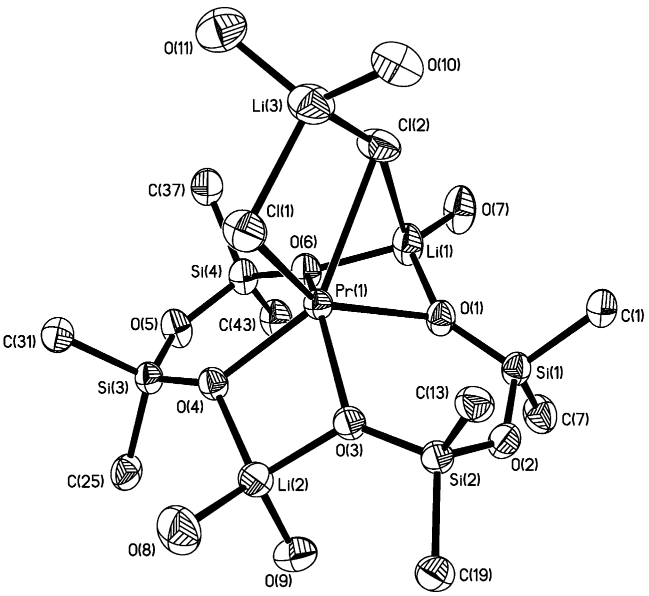
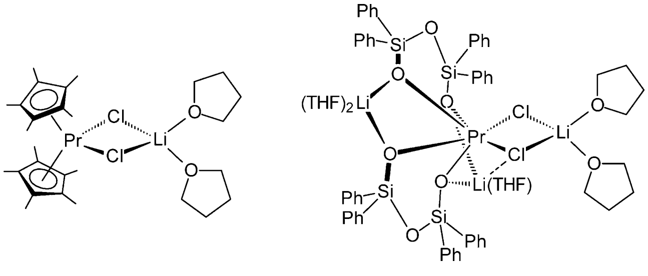


Figure 3. Molecular structure of **4**. For clarity, only the *ipso*-carbon atoms of the phenyl substituents and the oxygen atoms of coordinated THF are shown. Selected bond lengths [Å] and angles [deg]: Pr(1)−O(1) 2.346(2), Pr(1)−O(3) 2.301(2), Pr(1)−O(4) 2.310(2), Pr(1)−O(6) 2.341(2), Pr(1)−Cl(1) 2.791(1), Pr(1)−Cl(2) 2.909(1), Li(3)−Cl(1) 2.349(6), Li(3)−Cl(2) 2.336(6), Li(1)−Cl(2) 2.667(6), O(1)−Pr(1)−O(3) 83.90(7), O(4)−Pr(1)−O(6) 84.40(7), O(3)−Pr(1)−O(6) 134.24(7), O(3)−Pr(1)−O(4) 76.01(7), O(1)−Pr(1)−O(6) 74.91(7), Cl(1)−Pr(1)−Cl(2) 78.87(2).

Scheme 5



tadienyl)lanthanide complexes.[18] The molecular structure of **4** nicely demonstrates the structural relationship between the “inorganic metallocenes” or out-of-plane metallacrowns with their well-known C_5Me_5 counterparts.

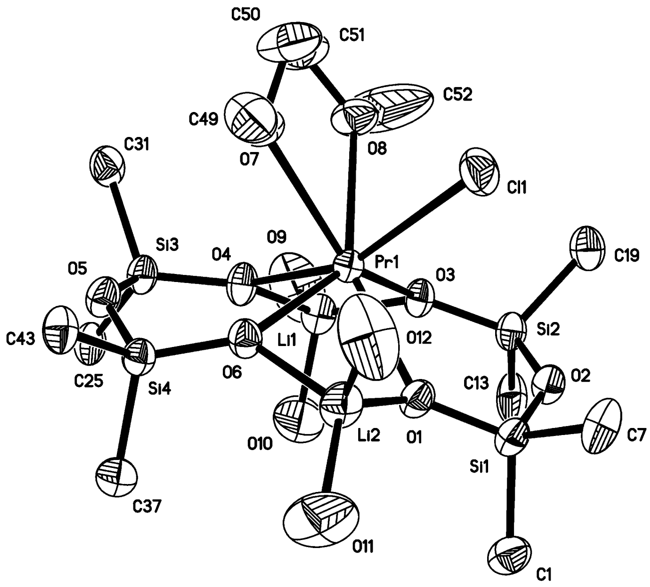


Figure 4. Molecular structure of **5**. For clarity, only the *ipso*-carbon atoms of the phenyl substituents and the oxygen atoms of coordinated DME are shown. Selected bond lengths [Å] and angles [deg]: Pr−O1 2.389(2), Pr−O7 2.658(2), Pr−O3 2.358(2), Pr−O8 2.701(2), Pr−O4 2.364(2), Pr−O6 2.367(2), Pr−Cl 2.768(1), O1−Pr−O3 84.23(6), Cl−Pr−O3 102.08(5), O1−Pr−O6 71.60(6), Cl−Pr−O1 86.41(5), O3−Pr−O4 75.56(6), Cl−Pr−O4 156.36(5), O4−Pr−O6 84.48(6), Cl−Pr−O6 110.35(5), Cl−Pr−O7 75.09(5), O7−Pr−O8 62.06(7), Cl−Pr−O8 77.87(5).

In contrast to the trans arrangement of the chloride and solvent ligands in **2** and **3**, the chloride ligands in **4** are in the cis positions. The Cl(1)−Pr(1)−Cl(2) angle is 78.87(2)°. The distances between Li(3) and the bridging chloride ligands are 2.349(6) Å [Cl(1)] and 2.336(6) Å [Cl(2)], respectively. One lithium is coordinated by two THF molecules, while the other one has only one THF ligand. In the latter case, there is an additional weaker Li(1)−Cl(2) interaction with a distance of 2.667(6) Å. Because of this weak Li−Cl bond, the overall structure of **4** approaches a trigonal-prismatic coordination geometry. The Pr−O distances to the disiloxanediolate ligands range from 2.301(2) Å [Pr(1)−O(3)] to 2.346(2) Å [Pr(1)−O(1)]. Here a comparison with literature values is difficult because apparently no praseodymium siloxides have been structurally characterized in the past. The compound $Pr(OSiPh_3)_3(THF)_3{\cdot}THF$[17b] has been reported, but its structure has not been determined by X-ray methods. In any case, the most important result of the crystal structure determination of **4** is the fact that this compound can be regarded as an “inorganic metallocene” or out-of-plane metallacrown complex.

The coordinated LiCl can be removed by recrystallization of **4** from DME as illustrated in Scheme 4. This results in the formation of the neutral heptacoordinated complex $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]PrCl(DME)$ (**5**), which was also characterized by analytical and spectroscopic methods as well as a single-crystal X-ray structure analysis. Figure 4 depicts the molecular structure of **5**. Here again the praseodymium is coordinated to the $[\{(Ph_2SiO)_2O\}_2\{Li(DME)\}_2]^{2-}$ ligand system in an out-of-plane arrangement. Thus, the compound also belongs to the group of “inorganic metallocenes” or out-of-plane metallacrowns. A terminal chloride ligand and a

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chelating DME complete the coordination sphere around the praseodymium. The overall coordination geometry can be best described as monocapped trigonal prismatic. Structurally related lanthanide metallocenes of the type $(C_5Me_5)_2LnCl(THF)$ are well established.[19] The average Pr−O distance to the disiloxanediolate ligands is 2.370(2) Å, and the Pr1−Cl1 bond length is 2.768(1) Å.

In summarizing the results reported here, we have clearly demonstrated that the structural chemistry of heterobimetallic lanthanide disiloxanediolates is more diverse than previously anticipated. The outcome of reactions between $[(Me_3Si)_2N]_3M(\mu\text{-Cl})Li(THF)_3$[14] and **1** strongly depends on the ionic radius of the group 3 or lanthanide metal. In the case of scandium and yttrium, the octahedral complexes **2** and **3** 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 the trans positions. In contrast, the larger Pr^{3+} ion affords the heterobimetallic disiloxanediolates **4** and **5**, which can be regarded as “inorganic metallocenes” or out-of-plane metallacrown complexes. Thus, the ligand system reported here provides a rational way to block one side of a larger lanthanide ion and, presumably, control the reactivity of the lanthanide.

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Supporting Information Available: CIF files giving X-ray structural data for **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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