

Accepted Manuscript

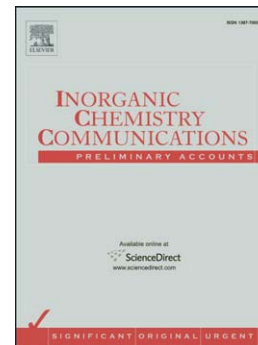
Synthesis and structure of sterically overloaded tetra-coordinated yttrium and lanthanum disiloxides

Brian McNerney, Suresh Mummadi, Fernando Hung-Low, David B. Cordes, Daniel K. Unruh, Clemens Krempner

PII: S1387-7003(16)30155-1
DOI: doi: [10.1016/j.inoche.2016.05.016](https://doi.org/10.1016/j.inoche.2016.05.016)
Reference: INOCHE 6326

To appear in: *Inorganic Chemistry Communications*

Received date: 4 January 2016
Accepted date: 16 May 2016



Please cite this article as: Brian McNerney, Suresh Mummadi, Fernando Hung-Low, David B. Cordes, Daniel K. Unruh, Clemens Krempner, Synthesis and structure of sterically overloaded tetra-coordinated yttrium and lanthanum disiloxides, *Inorganic Chemistry Communications* (2016), doi: [10.1016/j.inoche.2016.05.016](https://doi.org/10.1016/j.inoche.2016.05.016)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Synthesis and Structure of Sterically Overloaded Tetra-coordinated Yttrium and Lanthanum Disiloxides

Brian McNerney ^[a], Suresh Mummadi ^[a], Fernando Hung-Low ^[a], David B. Cordes ^[b], Daniel K. Unruh ^[a], Clemens Krempner*^[a]

^[a] Department of Chemistry & Biochemistry, Texas Tech University, Box 1061, Lubbock, Texas, 79409-1061, E-mail: clemens.krempner@ttu.edu

^[b] School of Chemistry, St. Andrew University, Purdie Building Fife KY16 9ST, St. Andrews, UK

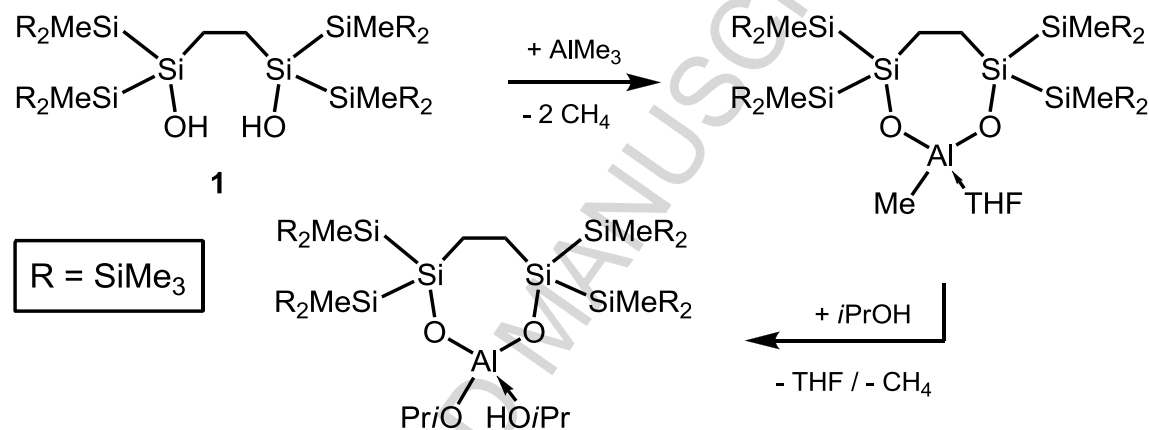
Abstract:

The synthesis, structures and reactivity of the spirocyclic yttrium and lanthanum disiloxides $\{[(\text{CH}_2\text{R}_2\text{SiO})_2]_2\text{M}\}\text{H}$ [M = Ln, Y; R = SiMe(SiMe₃)₂] **3** and **4** are reported. Compounds **3** and **4** were prepared from reactions of two equivalents of $[\text{CH}_2(\text{R})_2\text{SiOH}]_2$ [R = Si(SiMe₃)₂Me] (**1**) with one equivalent of $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$ (M = Y, La), respectively.

In the past half century, rare earth metal siloxides ^[1] have gained some popularity primarily due to their potential as homogeneous catalysts in polymerization catalysis ^[2-4], as precursors for the formation of metal oxides and silicates ^[5-7], and as models for silica-supported lanthanide metal heterogeneous catalysts. ^[8-13] In particular work by the Edlmann group has resulted in significant advancements in the synthesis of rare earth metal complexes supported by the tetraphenyldisiloxanediolate dianion, $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$. ^[12-20]

Our group recently synthesized a sterically overloaded silanediol of formula $(\text{CH}_2\text{SiR}_2\text{OH})_2$ (**1**), where R = Si(SiMe₃)₂Me, and demonstrated that its deprotonated form serves as a dianionic chelating spectator ligand for aluminum alkyls, hydroxides and alkoxides. ^[21] One of these complexes, a monomeric aluminum isopropoxide (Scheme 1) proved to be one of the most active MPV

catalyst for the reduction of ketones and aldehydes reported so far.^[22] Key to its high activity was its monomeric nature enforced by the bulkiness of the supporting disiloxide ligand. Based on these results, we reasoned that sterically overloaded disilanol **1** might be the ideal ligand for the synthesis of heteroleptic and salt- and adduct-free rare earth siloxide complexes, the latter potentially useful as Lewis acid catalysts.

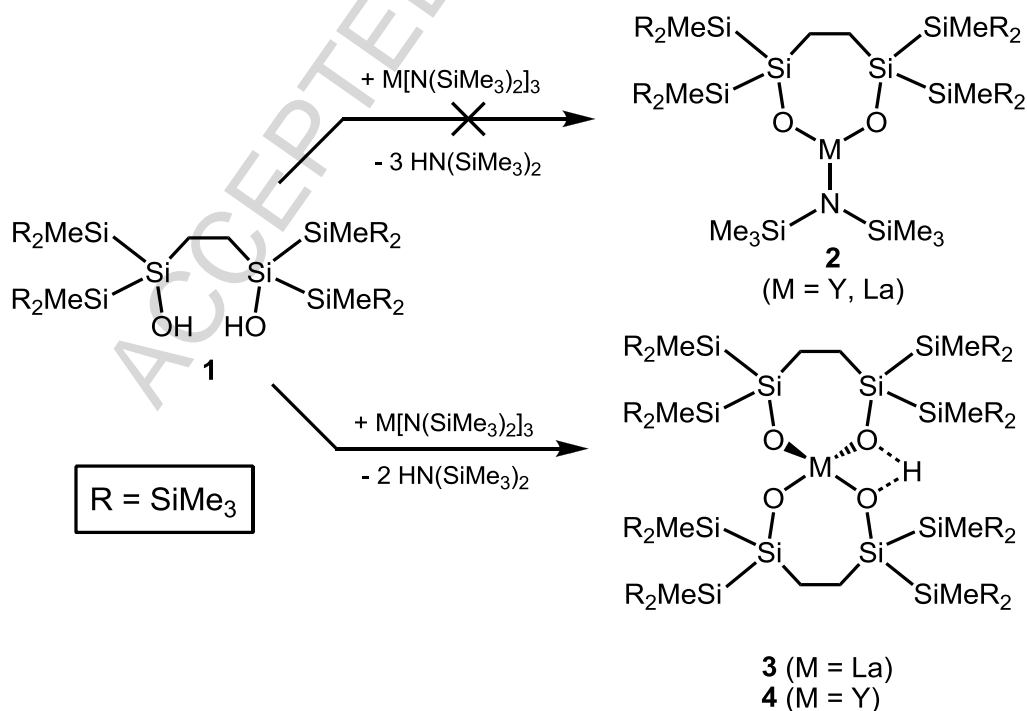


Scheme 1. Synthesis of sterically overloaded aluminum disiloxides.

We first attempted to prepare the heteroleptic yttrium and lanthanum disiloxides of formula $[(\text{CH}_2\text{R}_2\text{SiO})_2\text{MN}(\text{SiMe}_3)_2]$ ($\text{M} = \text{Ln}, \text{Y}$; $\text{R} = \text{SiMe}(\text{SiMe}_3)_2$) (**2**), respectively, as illustrated in Scheme 2. Initially, one equivalent of disilanol **1** was reacted with one equivalent of $\text{La}(\text{N}(\text{SiMe}_3)_2)_3$ in toluene as solvent. The reaction, however, did not give **2** but instead yielded the spirocyclic lanthanum disiloxide **3** as the main product irrespective whether toluene, THF or hexanes were used as solvents. Best yields were obtained when two equivalents of ligand **1** and one equivalent of $\text{La}(\text{N}(\text{SiMe}_3)_2)_3$ were employed at room temperature in toluene as solvent. After the preparation of lanthanum siloxide **3** we decided to investigate the coordination chemistry of yttrium, which is significantly smaller than lanthanum. The reaction of two equivalents of **1** with one equivalent of $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ at room temperature after 24 hours gave the spirocyclic yttrium siloxide **4** in 70% yield. Again, the formation of the heteroleptic yttrium complex **2** was

not observed regardless of the reaction conditions and the stoichiometry of the reagents employed.

Compounds **3** and **4** are thermally stable but extremely moisture sensitive colorless solids that are well soluble in donor solvents (diethyl ether, THF) and less soluble in hydrocarbons such as pentanes and hexanes. Their structures were established by means of multi-nuclear NMR spectroscopy and single-crystal X-ray crystallography. The NMR spectroscopic features of **3** and **4** are very similar to each other as the ^1H , ^{13}C and ^{29}Si NMR spectra of both compounds showed two signals for the $\text{Si}(\text{CH}_3)_3$ groups, respectively. These findings are consistent with the proposed formula, $\{[(\text{CH}_2\text{SiR}_2\text{O})_2]_2\text{M}\}\text{H}$, where $\text{R} = \text{Si}(\text{SiMe}_3)_2\text{Me}$ and $\text{M} = \text{La}$ or Y , and with two disiloxide ligands binding to each of the metal ions (Scheme 2). To balance the charge in **3** and **4**, one of the oxygen atoms must contain a proton to form a dative bond to the central yttrium and lanthanum ions, resp. In fact, both OH protons appear in the ^1H NMR spectra as sharp signals at 2.09 ppm and 2.71 ppm for **3** and **4**, resp.



Scheme 2. Synthesis of the homoleptic lanthanum and yttrium siloxides **3** and **4**.

Single crystals of **3** and **4** were grown from toluene and analyzed by X-ray crystallography; the structures are shown in Figures 1 and 2. Two independent molecules were found in the unit cell of lanthanum siloxide **3**; for clarity only one is shown in Figure 1. The results of the X-ray analysis of **3** and **4** clearly confirm homoleptic, tetra-coordinated lanthanum and yttrium complexes each with distorted tetrahedral geometry. Note that this is an uncommon structural motif for rare-earth metal siloxides, as previous work using the sterically less demanding bidentate disiloxides, $[(\text{Ph}_2\text{SiO})_2\text{O}]^{2-}$, have displayed “ate” complexes or salt adducts with distorted octahedral or distorted bipyramidal coordination environments.^[11-19] As expected, it was not possible to locate the OH protons necessary for balancing the overall zero charge. Inspection of the La-O distances in one of the two independent molecules of **3** (not shown in Figure 1) did not reveal significant differences between individual La-O distances, as they were ranging unremarkably from 2.25 to 2.34 Å. The second molecule of **3** shown Figure 1, however, shows one short La1-O1 distance (2.210 Å) and a relatively long La1-O4 distance (2.505 Å), indicating the proton to be bound to O4. In contrast, two short Y-O distances (both at ca. 2.08 Å) and two relatively long ones (2.17 and 2.25 Å) were observed for yttrium complex **4**. The short Y-O distances are in the expected range for Y-O bonds of sterically less hindered yttrium siloxides (Table 1). The longer Y-O distances are clearly out of range, which can be attributed to the dative bond formed between the hydroxyl group and the metal center. That both elongated Y-O bonds in **4** are in proximity to each other suggests the proton to be bound to both oxygens via hydrogen bond interactions as illustrated in Scheme 2.

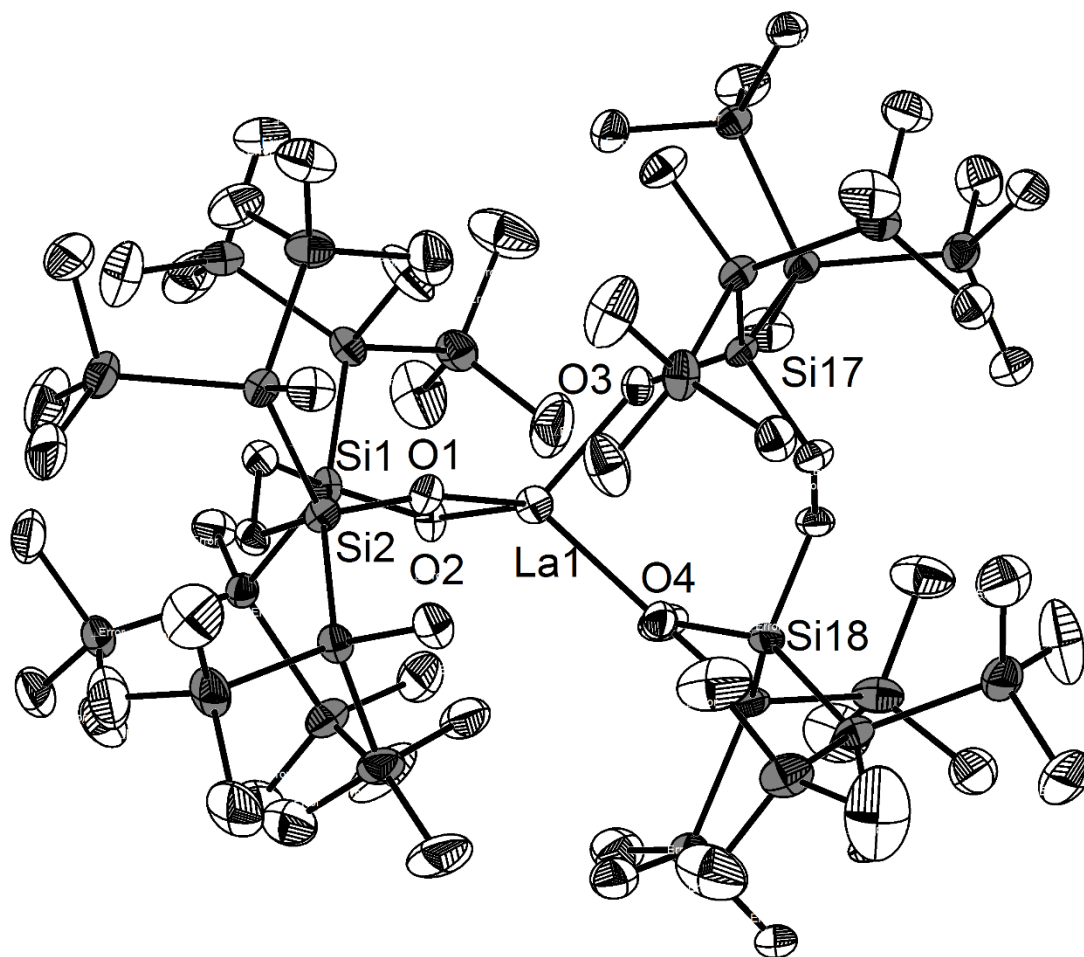


Figure 1. Solid-state structure of **3** (only one molecule of the unit cell is shown and all hydrogen atoms omitted for clarity). Selected bond lengths [\AA] and angles [$^\circ$]: La1-O1 2.210(2), La1-O2 2.299(2), La1-O3 2.315(2), La1-O4 2.505(2), Si1-O1 1.626(3), Si2-O2 1.653(3), Si18-O4 1.691(3), Si17-O3 1.659(2), O1-La1-O2 92.54(8), O1-La1-O3 115.09(9), O2-La1-O3 120.19(9), O1-La1-O4 120.71(8), O2-La1-O4 119.02(9), O3-La1-O4 91.78(8), Si1-O1-La1 149.58(14), Si2-O2-La1 141.78(15), Si17-O3-La1 146.84(14), Si18-O4-La1 139.82(14).

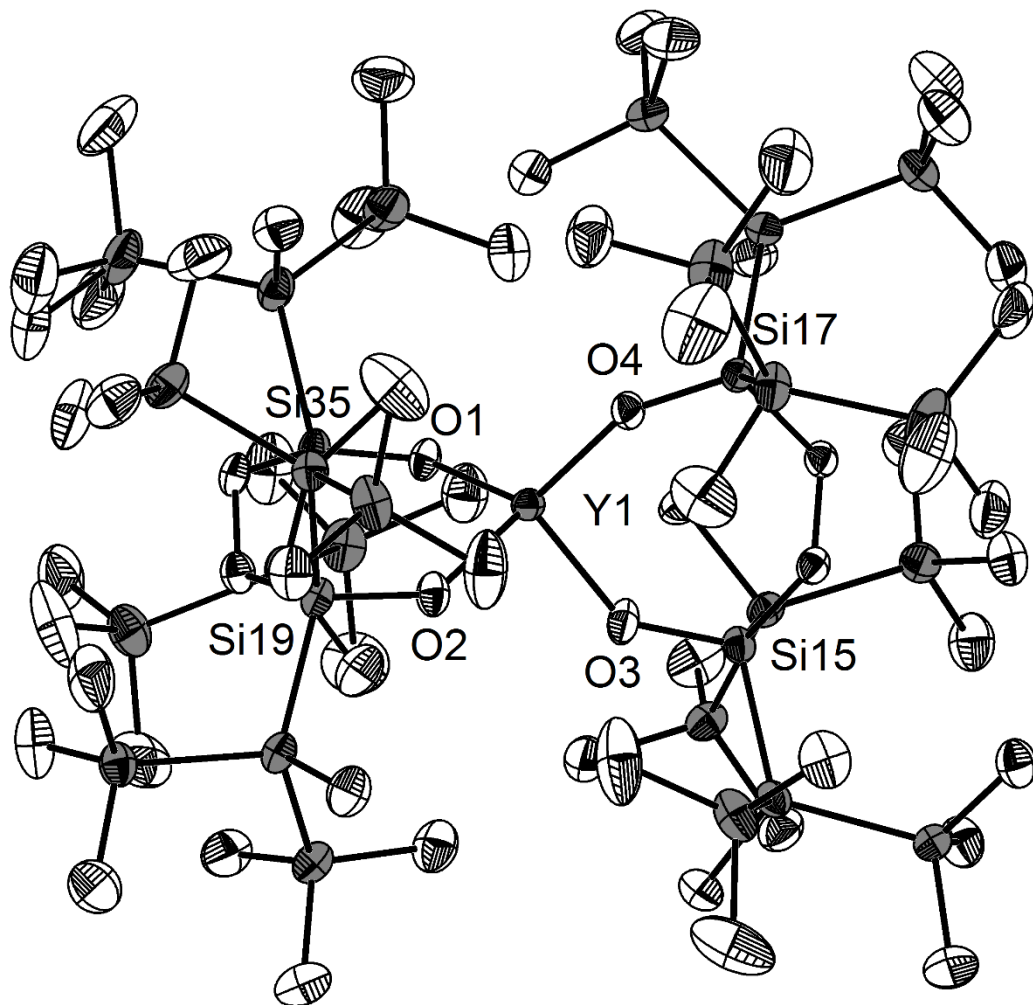
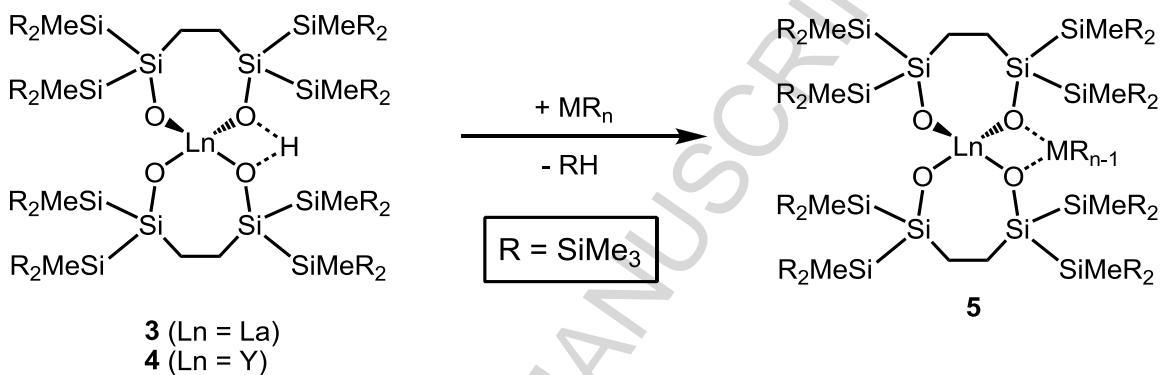


Figure 2. Solid-state structure of **4** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Y1-O4 2.079(2), Y1-O1 2.0873(19), Y1-O3 2.175(2), Y1-O2 2.253(2), Si19-O2 1.706(2), Si17-O4 1.636(2), Si15-O3 1.679(2) Si35-O1 1.637(2), O4-Y1-O1 120.70(8), O4-Y1-O3 98.02(8), O1-Y1-O3 122.23(8), O4-Y1-O2 123.97(8), O1-Y1-O2 97.21(8), O3-Y1-O2 93.38(8), Si19-O2-Y1 138.89(11), Si17-O4-Y1 152.21(11), Si35-O1-Y1 151.17(12), Si15-O3-Y1 140.93(12).

We next attempted to deprotonate **4** with ZnMe_2 and AlMe_3 , but in both cases no reaction was observed even at elevated temperatures and with ten-fold excess of the respective organometallic reagent employed. We attribute the poor reactivity of **4** to the steric bulk of the two disiloxy ligands inhibiting deprotonation. Treatment with the considerably more basic LiBu^n led to rapid

decomposition of **4**. Adding one equivalent of MgMe_2 to a THF solution of **4** resulted in the formation of a mixture of crystalline products that could not be separated from each other. Crystallization experiments in C_6D_6 yielded, however, a few single crystals suitable for single crystal X-analysis analysis.



Scheme 3. Attempted formation of **5**.

The results are shown in Figure 3 and reveal that one of the components of this crystalline mixture is the magnesium salt of formula $\{[(\text{CH}_2\text{SiR}_2\text{O})_2\text{Y}]\text{[MeMg(THF)}_4]\}$ (**5**), which is derived from deprotonation of **4** with Me_2Mg . The Y-O distances of **5** are within the narrow range of 2.12 to 2.14 Å indicating that both siloxide ligands bind to yttrium to the same extent. Note, that the average Y-O distances (ca. 2.13 Å) are slightly longer than those of yttrium siloxide **4** (ca. 2.15 Å), which perhaps is the result of the anionic charge of the yttrium disiloxide unit leading to weaker Y-O bond interactions than in the neutral complex **4**. Furthermore, the O-Y-O bond angles showed that despite deprotonation the structure still retains its distorted tetrahedral geometry. The solvated methyl magnesium cation displays a distorted trigonal-bipyramidal geometry as it is coordinated by four molecules of THF.

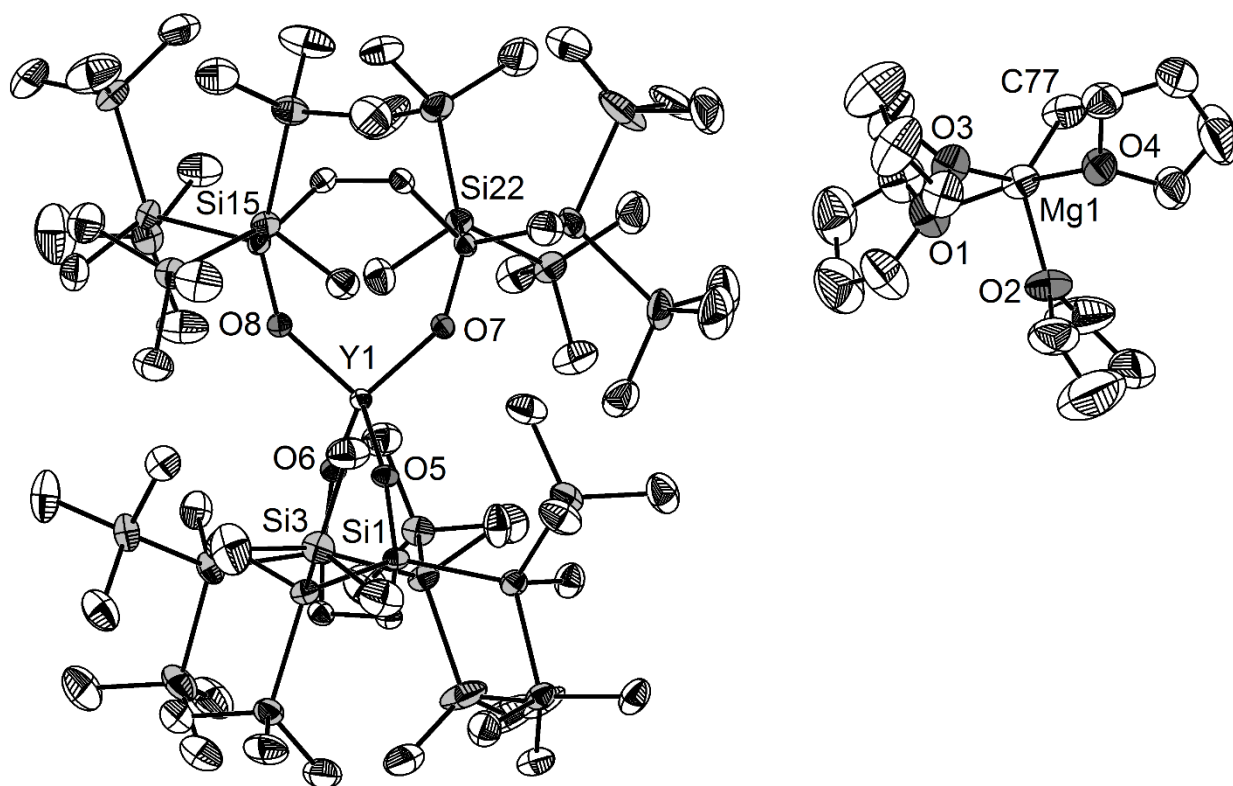


Figure 3. Solid-state structure of **5** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Y1-O6 2.121(2), Y1-O8 2.121(2), Y1-O7 2.131(2), Y1-O5 2.142(2), Si1-O5 1.616(2), Si8-O6 1.617(2), Si15-O8 1.615(2), Si22-O7 1.615(2), Mg1-O3 2.010(3), Mg1-O2 2.028(3), Mg1-C77 2.105(5), Mg1-O1 2.142(4), Mg1-O4 2.165(3), O6-Y1-O8 111.67(9), O6-Y1-O7 115.22(9), O8-Y1-O7 97.62(9), O6-Y1-O5 98.73(9), O8-Y1-O5 118.81(9), O7-Y1-O5 115.79(9), Si1-O5-Y1 147.27(14), Si8-O6-Y1 145.77(14), Si22-O7-Y1 147.16(14), Si15-O8-Y1 146.89(14).

Table 1 shows the average M-O(Si) and Si-O bond lengths as well as the M-O-Si bond angles of the newly prepared complexes **3** - **5** along with those of other yttrium and lanthanum siloxides reported in the literature. As expected the M-O(Si) distances follow the size-dependent trend as the Y-O(Si) distances were shorter than the La-O(Si) distances. A slight increase in the average Y-O(Si) bond length from compounds **4** to **5** was observed, which can be attributed to the anionic charge of **5**. The same trend is seen for the hexa-coordinated complexes

$[(\text{Ph}_3\text{SiO})_4\text{Y}(\text{DME})][\text{K}(\text{DME})_4]$ and $(\text{Ph}_3\text{SiO})_3\text{Y}(\text{THF})_3$, the latter having the shorter Y-O_(Si) distances. Furthermore, tetra-coordinated anionic yttrium siloxide **5** has shorter Y-O_(Si) distances than the anionic siloxides $[(\text{Ph}_3\text{SiO})_4\text{Y}(\text{DME})][\text{K}(\text{DME})_4]$ and $\{[\text{Ph}_2\text{SiO})_2\text{O}]_2\text{YCl}(\text{THF})\}[\text{Li}(\text{THF})_2]_2$ both representing hexa-coordinated yttrium species. This is consistent with the general assumption that the M-O distance in a metal complex increases as the coordination number of the metal increases, provided the overall charge of the metal complex remains unchanged. A similar conclusion can be drawn for the “neutral” yttrium siloxide **4**, which displays slightly shorter average M-O(Si) distances than those of hexa-coordinated $(\text{Ph}_3\text{SiO})_3\text{Y}(\text{THF})_3$ and penta-coordinated $(\text{Ph}_3\text{SiO})_3\text{Y}(\text{O}=\text{P}^n\text{Bu})_2$. Lanthanum siloxide **3** may be an exception as its La-O(Si) distance is longer than that of hexa-coordinated $(\text{Ph}_3\text{SiO})_3\text{La}(\text{THF})_3$ despite its lower coordination number.

In conclusion, we have successfully prepared the first homoleptic, spirocyclic yttrium and lanthanum disiloxides $\{[(\text{CH}_2\text{R}_2\text{SiO})_2]_2\text{M}\}\text{H}$ [**3**; M = La, **4**; M = Y; R = SiMe(SiMe₃)₂]. These tetra-coordinated rare earth metal species are bound to three anionic oxygens and form a dative bond with an oxygen atom of a hydroxyl group.

Table 1. Selected average atom distances [pm] and angles [°] of various yttrium and lanthanum siloxides.

Compound	CN ^a	M-O(Si)	Si-O	M-O-Si	Reference
$[(\text{Ph}_3\text{SiO})_3\text{Y}]_2$	4	206	161	178	[23]
$\{[(\text{CH}_2\text{SiR}_2\text{O})_2]_2\text{Y}\}\text{H}$ (4)	4	211	165	146	this work
$(\text{Ph}_3\text{SiO})_3\text{Y}(\text{O}=\text{P}^n\text{Bu})_2$	5	212	159	163	[24]
$(\text{Ph}_3\text{SiO})_3\text{Y}(\text{THF})_3$	6	213	158	172	[25]
$\{[(\text{CH}_2\text{SiR}_2\text{O})_2]_2\text{Y}\}[\text{MeMg}(\text{THF})_4]$ (5)	4	213	162	147	this work
$[(\text{Ph}_3\text{SiO})_4\text{Y}(\text{DME})][\text{K}(\text{DME})_4]$	6	217	158	169	[23]
$\{[\text{Ph}_2\text{SiO})_2\text{O}]_2\text{YCl}(\text{THF})\}[\text{Li}(\text{THF})_2]_2$	6	222	159	127	[18]
$\{[(\text{CH}_2\text{SiR}_2\text{O})_2]_2\text{La}\}\text{H}$ (3)	4	229	166	143	this work
$(\text{Ph}_3\text{SiO})_3\text{La}(\text{THF})_3$	6	223	160	173	[24]

^a CN = coordination number of M (M = Y or La)

Acknowledgement

The NSF is thanked for purchase of a JEOL ECS-400 NMR Spectrometer (CRIF-MU CHE-1048553).

Supporting information

^1H , ^{13}C and ^{29}Si NMR spectra of compounds **3** and **4**.

Experimental section

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere drybox containing an atmosphere of purified nitrogen. THF, toluene and hexanes and were distilled under nitrogen from alkali metals and stored over 4 Å molecular sieves prior to use. C_6D_6 was purchased from Cambridge Isotopes, and dried and stored over 4 Å molecular sieves prior to use. $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ and $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ were purchased from Aldrich and used without further purification. Disilanol **1** was synthesized according to the literature procedure.^[21] Drying of **1** in a Kugelrohrfen under vacuum (ca. 0.1 mbar) at 120°C for ca. 4 hours was necessary to remove residual amounts water. The ^1H , ^{13}C and ^{29}Si NMR spectra were obtained from a Varian Unity Inova 500 and JOEL ECS 400. The NMR chemical shifts were given in ppm. The $^{29}\text{Si}\{\text{H}\}$ NMR spectra were referenced to TMS ($\delta = 0$ ppm). The ^1H -NMR spectra were referenced to the residual protonated solvent for ^1H and the $^{13}\text{C}\{\text{H}\}$ NMR spectra were referenced to the deuterated solvent peaks. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Note: The carbon values of **3** and **4** were reproducibly low due to the formation of silicon carbide.

3. In the glove box a 20 mL Schlenk flask equipped with a magnetic stir bar was charged with **1** (0.22 g, 0.25 mmol) and 10 mL of toluene. Then $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ (0.07 g, 0.11 mmol) was added and the resulting solution was allowed to stir for 24 hours at room temperature. The solution was concentrated under vacuum and placed in a freezer at ca. -20°C overnight, upon which colorless

crystals of analytically pure **3** precipitated. Yield – 55% (0.12 g). ^1H NMR (C_6D_6 , 298 K, 400 MHz): δ 2.09 (s, OH, 1 H), 1.56 (br, CH_2CH_2 , 4 H), 0.52 (s, SiCH_3 , 24 H), 0.44, 0.39 (2s, $\text{Si}(\text{CH}_3)_3$, 2×72 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 298 K, 125.7 MHz): δ 20.7 (CH_2), 2.3, 1.7 ($\text{Si}(\text{CH}_3)_3$), -8.2 (SiCH_3) ppm. $^{29}\text{Si}\{\text{H}\}$ NMR (C_6D_6 , 338 K, 99.3 MHz): δ 19.6 (SiO), -12.1, -12.3 ($\text{Si}(\text{CH}_3)_3$), -84.9 (SiCH_3) ppm. Anal. Calc. for $\text{C}_{60}\text{H}_{177}\text{O}_4\text{Si}_{28}\text{La}$ (1888.344): C 38.16, H 9.45. Found C 36.88, H 9.43.

4. In the glove box a 20 mL Schlenk flask equipped with a magnetic stir bar was charged with **1** (1.53 g, 1.7 mmol) and 15 mL of toluene. Then $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ (0.5 g, 0.08 mmol) was added and the resulting solution was allowed to stir for 24 hours at room temperature. The solution was concentrated under vacuum and placed in a freezer at ca. -20°C overnight, upon which colorless crystals of analytically pure **4** precipitated. Yield – 70% (1.21 g). ^1H NMR (C_6D_6 , 298 K, 500 MHz): δ 2.71 (s, OH, 1 H), 1.56 (br, CH_2CH_2 , 8 H), 0.53 (s, SiCH_3 , 24 H), 0.42 (s, $\text{Si}(\text{CH}_3)_3$, 72 H), 0.37 (s, $\text{Si}(\text{CH}_3)_3$, 72 H) ppm; ^1H NMR (C_6D_6 , 338 K, 500 MHz): δ 2.65 (s, OH, 1 H), 1.56 (s, CH_2CH_2 , 8 H), 0.52 (s, SiCH_3 , 24 H), 0.40, 0.36 (2s, $\text{Si}(\text{CH}_3)_3$, 2×72 H) ppm. $^{13}\text{C}\{\text{H}\}$ NMR (C_6D_6 , 338 K, 125.7 MHz): δ 22.0 (CH_2), 2.5, 1.9 ($\text{Si}(\text{CH}_3)_3$), -7.7 (SiCH_3) ppm. $^{29}\text{Si}\{\text{H}\}$ NMR (C_6D_6 , 338 K, 99.3 MHz): δ 21.1 (SiO), -12.0, -12.4 ($\text{Si}(\text{CH}_3)_3$), -84.8 (SiCH_3) ppm. Anal. Calc. for $\text{C}_{60}\text{H}_{177}\text{O}_4\text{Si}_{28}\text{Y}$ (1838.345): C 39.20, H 9.70. Found C 37.31, H 9.79.

X-ray diffraction data for all compounds were obtained on a Bruker Smart Apex II CCD diffractometer, using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at either 100 or 296 K. Intensity data were collected using ω -steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All the data were corrected for Lorentz polarization effects. A multi-scan absorption correction was applied using SADABS.^[26] Structures were solved by direct methods and refined by full-matrix least-squares against F^2 (SHELXTL^[27]). All C-H hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. CCDC 1408454 (**3**) 1408455 (**4**) and 1408456 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (12 Union Road, Cambridge CB2 1EZ, UK, www.ccdc.cam.ac.uk/data_request/cif).

Table 2. Crystallographic data for complexes **3** – **5**.

	3	4	5
Formula	$C_{120}H_{354}La_2O_8Si_{56}$	$C_{63}H_{176}D_3O_4Si_{28}Y$	$C_{77}H_{211}MgO_8Si_{28}Y$
Molecular weight	3774.86	1879.50	2165.19
Crystal size (mm ³)	$0.57 \times 0.39 \times 0.36$	$0.36 \times 0.31 \times 0.27$	$0.27 \times 0.22 \times 0.19$
Crystal appearance	Colorless	Colorless	Colorless
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	17.4314(16)	17.038(8)	18.653(2)
b (Å)	26.184(2)	17.340(8)	15.7381(17)
c (Å)	26.452(2)	21.840(10)	45.548(5)
α (°)	73.9880(10)	90.272(4)	90.0
β (°)	79.7050(10)	94.172(4)	93.4980(10)
γ (°)	88.1980(10)	114.879(4)	90.0
Volume (Å ³)	11416.1(18)	5834(4)	13346(2)
Z	2	2	4
r_{calcd} (g cm ⁻³)	1.098	1.064	1.078
Temperature (K)	100(2)	296(2)	296(2)
μ (mm ⁻¹)	0.701	0.821	0.732
θ range (°)	0.809 to 27.127	1.56 to 25.68	1.574 to 25.682
Reflections collected	135247	57507	129553
Unique reflections (R_{int})	50102	22068	25351
R_1 [$I > 2\sigma(I)$]	0.0510	0.0459	0.0531
wR_2 (all data)	0.1384	0.1236	0.1249
GooF	1.025	1.006	1.011
Data/restraints/parameters	50102 / 1920 / 1885	22068 / 870 / 893	25351 / 1077 / 1091

References

1. McNerney, B.; Krempner, C. "Rare Earth Siloxides" Rare Earth Elements **2012**, 205.
2. Lorenz, V.; Fischer, A.; Giessmann, S.; Gilje, J. W.; Gun'ko, Y.; Jacob, K.; Edelmann, F. T., *Coord. Chem. Rev.* **2000**, 206-207, 321.
3. Lorenz, V.; Edelmann, F. T., *Adv. Organomet. Chem.* **2005**, 53, 101.
4. Lorenz, V.; Edelmann, A.; Giessmann, S.; Hrib, C.G.; Blaurock, S.; Edelmann, F. T., *Z. Anorg. Allg. Chem.* **2010**, 636, 2172.
5. Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W., *Chem. Rev.* **1996**, 96, 2205.
6. Chaput, F.; Lecomte, A.; Dauger, A.; Boilot, J. P., *J. Mater. Chem.* **1989**, 8, 1001.
7. Lazell, M.; Motevalli, M.; Shah, S. A. A.; Sullivan, A. C., *J. Chem. Soc., Dalton Trans.* **1997**, 3363.
8. Yermakov, Y. I.; Kuznetsov, B. N.; Zakharov, V. A., *Catalysis by Supported Complexes*, Elsevier, New York, **1981**.
9. Hartley, F. R., *Supported Metal Complexes*, Reidel, Boston, **1985**.
10. *Tailored Metal Catalysts*, ed. Y. Iwasawa, Reidel, Boston, **1986**.
11. Feher, F. J.; Budzichowski, T. A., *Polyhedron* **1995**, 14, 3239.
12. Edelmann, F. T., *Angew. Chem.* **1992**, 104, 600.
13. Edelmann, F. T., *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 586.
14. Lorenz, V.; Fischer, A.; Jacob, K.; Bruser, W.; Gelbrich, T.; Jones, P. G.; Edelmann, F. T., *Chem. Commun.* **1998**, 2217.
15. Geissmann, S.; Blaurock, S.; Edelmann, F. T., *Z. Anorg. Allg. Chem.* **2008**, 634, 186.
16. Geissmann, S.; Blaurock, S.; Lorenz, V.; Edelmann, F. T., *Inorg. Chem.* **2007**, 46, 10956.

17. Edelmann, A.; Blaurock, S.; Hrib, C.; Edelmann, F. T., *J. Organomet. Chem.* **2010**, *695*, 1026.
18. Giessmann, S.; Blaurock, S.; Lorenz, V.; Edelmann, F. T., *Inorg. Chem.* **2007**, *46*, 10383.
19. Lorenz, V.; Edelmann, A.; Blaurock, S.; Hrib, C.; Edelmann, F. T., *C. R. Chimie* **2010**, *13*, 577.
20. Lorenz, V.; Fischer, A.; Jacob, K.; Bruser, W.; Edelmann, F. T., *Chem. Eur. J.* **2001**, *7*, 848.
21. Weichert, K.; Carlson, B.; Reinke, H.; Krempner, C., *Dalton Trans.* **2010**, *39*, 11513.
22. McNerney, B.; Whittlesey, B.; Cordes, D. B.; Krempner, C., *Chem. Eur. J.* **2014**, *20*, 14959.
23. Coan, P. S.; McGeary, M. J.; Lobkovsky, E. B.; Caulton, K. G., *Inorg. Chem.* **1991**, *30*, 3570.
24. McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G., *Inorg. Chem.* **1991**, *30*, 1723.
25. McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G., *Inorg. Chem.* **1989**, *28*, 3283.
26. Sheldrick, G. M., *SADABS v2012/1*, **2012**.
27. Sheldrick, G. M., *Acta Crystallogr. Sect. A* **2008**, *64*, 112.