



Short communication

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



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ABSTRACT

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

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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 Edelmann 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 $\text{R} = \text{Si}(\text{SiMe}_3)_2\text{Me}$, 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.

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

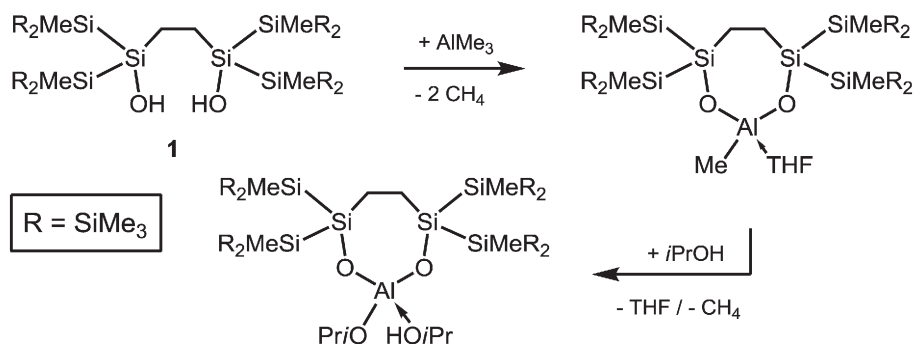
$\text{La}(\text{N}(\text{SiMe}_3)_2)_3$ in toluene as solvent. The reaction, however, did not give **2** but instead yielded the spirocyclic lanthanum disiloxide **3** as the main product irrespective whether toluene, THF or hexanes were used as solvents. Best yields were obtained when two equivalents 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 h 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.

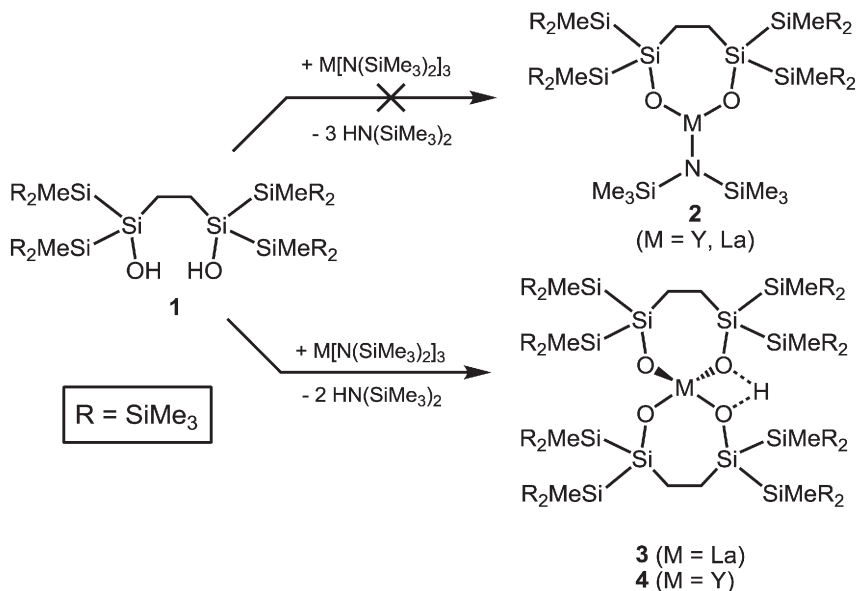
Compounds **3** and **4** are thermally stable but extremely moisture sensitive colorless solids that are well soluble in donor solvents (diethyl ether, THF) and less soluble in hydrocarbons such as pentanes and hexanes. Their structures were established by means of multi-nuclear NMR spectroscopy and 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, $\{[(\text{CH}_2\text{SiR}_2\text{O})_2\text{M}]\text{H}$, 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.

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Scheme 1. Synthesis of sterically overloaded aluminum disiloxides.



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

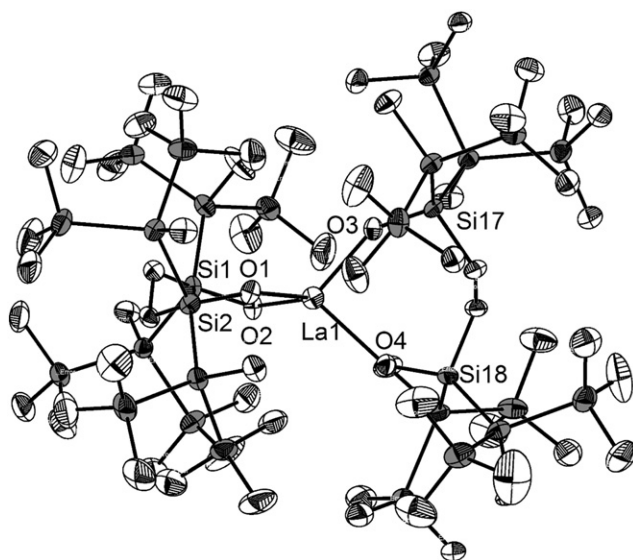


Fig. 1. Solid-state structure of **3** (only one molecule of the unit cell is shown and all hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: La1–O1 2.210(2), La1–O2 2.299(2), La1–O3 2.315(2), La1–O4 2.505(2), Si1–O1 1.626(3), Si2–O2 1.653(3), Si18–O4 1.691(3), Si17–O3 1.659(2), 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).

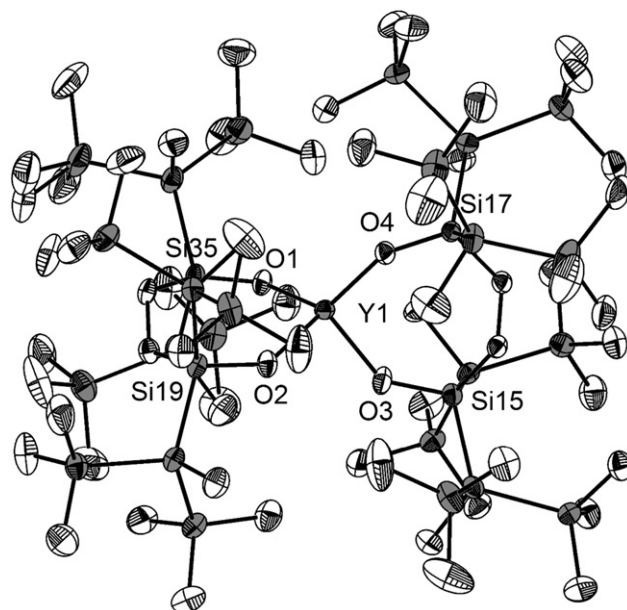


Fig. 2. Solid-state structure of **4** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Y1–O4 2.079(2), Y1–O1 2.0873(19), Y1–O3 2.175(2), Y1–O2 2.253(2), Si19–O2 1.706(2), Si17–O4 1.636(2), Si15–O3 1.679(2), Si35–O1 1.637(2), O4–Y1–O1 120.70(8), O4–Y1–O3 98.02(8), O1–Y1–O3 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).

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