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Synthesis and Structure of Cyclic Aluminum Disiloxides

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The synthesis and structure of cyclic five- and six-membered aluminum disiloxides containing the chelating diolate ligands $SiMe_2[(Me_3Si)_2SiO]_2^{2-}$ (**1a**)-2H, $[(Me_3Si)_2SiO]_2^{2-}$ (**1b**)-2H, and $[Me(Me_3Si)_3SiSiO]_2^{2-}$ (*rac*-**1c**)-2H are reported. The dinuclear aluminum disiloxides $[SiMe_2\{(Me_3Si)_2SiO\}_2AlMe]_2$ (**2a**) and $[(E)$-$\{Me(Me_3Si)_3SiSiO\}_2AlMe]_2$ (**2c**) were prepared in *n*-pentane by treatment of $AlMe_3$ with 1 equiv of the free ligands **1a** and **1c**, respectively. The analogous reaction of **1c** with $AlMe_3$ in THF as solvent yielded the monomeric THF adduct (E)-$[Me(Me_3Si)_3SiSiO]_2AlMe{\cdot}THF$ (**4c**). Irrespective of the molar ratio, treatment of **1b** with $AlMe_3$ in pentane gave the trinuclear complex $[\{(Me_3Si)_2SiO\}_2]_2Al_3Me_5$ (**3b**) as the major product, whereas the thermally stable $AlMe_3$ adduct (E)-$[Me(Me_3Si)_3SiSiO]_2AlMe{\cdot}AlMe_3$ (**5c**) was synthesized by employing a 2-fold excess of $AlMe_3$ in the reaction with **1c**. Treatment of **4c** with $B(C_6F_5)_3$ led to full exchange of the methyl group by C_6F_5 with quantitative formation of (E)-$[Me(Me_3Si)_3SiSiO]_2Al(C_6F_5){\cdot}THF$ (**6c**) and a mixture of $B(C_6F_5)_{3-n}Me_n$, where $n = 1, 2, 3$. The reaction of **4c** with phenol did not yield the expected complex (E)-$[Me(Me_3Si)_3SiSiO]_2AlOPh{\cdot}THF$; rather, quantitative ligand transfer to give the spirocyclic complex $\{[(E)$-$\{Me(Me_3Si)_3SiSiO\}_2]_2Al\}^-H^+$ (**7c**) occurred. The structures of the complexes **2a**, **2c**, **3b**, **4c**, and **7c** were determined by X-ray crystallography.

Introduction

Due to their electrophilic properties, aluminum-containing compounds are important reagents in both organic and inorganic synthesis.[1] The acceptor properties of aluminum reagents can be modified by addition of suitable oxygen donor (typically alkoxides, aryloxides, or siloxides) ligation into the metal coordination sphere. For example, the attachment of extremely bulky aryloxide ligands to aluminum generates monomeric Lewis acid catalysts that have been employed in a variety of organic transformations.[2]

Aluminum siloxides have found application as soluble precursors for aluminum oxides and silicates in sol−gel and related processes,[3] as homogeneous models for silica-supported heterogeneous catalysts,[4] and as active homogeneous cocatalysts in olefin polymerizations.[5] Aluminum siloxides of general formula $(R_3SiO)_{3-n}AlX_n$, where X = alkyl, hydride, halide, or alkoxide, are available from reactions of cyclic siloxanes,[6] disiloxanes,[7] and polymeric siloxanes (silicon grease)[8] and of silanols[9] with appropriate aluminum precursor compounds. Suitable starting materials for the synthesis of cyclic aluminum siloxides are $Ph_2Si(OH)_2$ and $(HO)SiPh_2OSiPh_2(OH)$, which readily react under self-condensation and/or ring expansion with aluminum alkyls and hydrides to afford mainly eight-membered spirocyclic or polycyclic compounds.[10,11] Smaller cycles such as five- and six-membered ring compounds have not been obtained in these reactions, and this is mainly due to the considerable strain energy in smaller cycles as compared to larger ones.[12] The only successful synthesis furnishing cyclic

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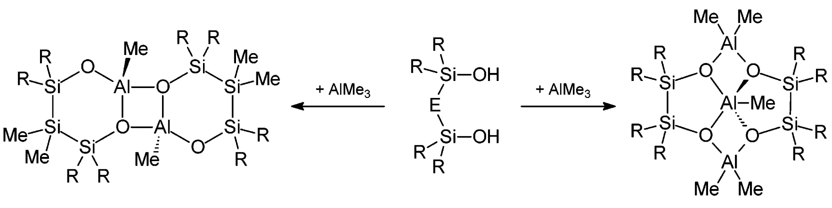
Scheme 1. Synthesis of 2a and 3b

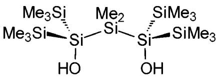


2a **1a,b** **3b**

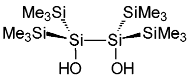
a R = $SiMe_3$; E = $SiMe_2$
b R = $SiMe_3$; E = 0

six-membered aluminum siloxides with a trinuclear Al_3O_4 core involves the cleavage of cyclotrisiloxanes with aluminum halides (Cl, Br).[13]

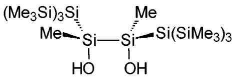
As we have shown for cyclic five- and six-membered titanium and zirconium disiloxides,[14,15] ring expansion can be avoided by use of vicinal silanediols with an "inert" Si−Si or Si−C ligand backbone. As an extension of this work, we have begun to study highly strained five- and six-membered cyclic aluminum derivatives. Herein we report the synthesis and structural characterization of a series of cyclic aluminum compounds containing the ligands trisilane-1,3-diolate (**1a**)-2H,[15] disilane-1,2-diolate (**1b**)-2H, and racemic disilane-1,2-diolate (**1c**)-2H.[14a] The reactivity of these complexes toward Lewis and Broensted acids is described.



1a



1b



***rac*-1c**

Results and Discussion

Reactions of 1a and 1b with $AlMe_3$. Methyl-substituted aluminum siloxides are readily available from Broensted acid−base reactions of trialkylaluminum compounds with silanols. As recently shown for incompletely condensed silsesquioxanes (POSS), the product distribution of such reactions strongly depends on the ligand/$AlMe_3$ ratio and on the donor properties of the solvent.[4g] In fact, treatment of the trisilane-1,3-diol **1a** with equimolar amounts of $AlMe_3$ in pentane selectively afforded the dimeric aluminum siloxide **2a** in good yields (Scheme 1). The analogous reaction of disilane-1,2-diol **1b** did not give **2b** but instead yielded the trinuclear aluminum compound **3b** as the main product irrespective of whether THF or *n*-pentane is used as solvent. Best yields, however, were obtained when 2 equiv of the ligand and 3 equiv of $AlMe_3$ in pentane are employed.

Compounds **2a** and **3b** are thermally stable and soluble in most organic solvents (pentane, ether, toluene, THF). Their structures were established by means of NMR and MS data, elemental analyses, and X-ray crystallography. The mass spectrum of compound **2a** is consistent with the formulated dimeric structure. Through ^1H, ^{13}C, and ^{29}Si NMR spectroscopic studies in benzene-d_6, the structure of **2a** in solution has been assigned unambiguously to be dimeric. The ^1H and ^{13}C NMR spectra show two signals for the $SiMe_3$ and $SiMe_2$ groups, respectively, and the aluminum methyl group leads to one signal, which is consistent with the presence of tetrahedral aluminum centers. In contrast, compound **3b** exhibits in the ^1H and ^{13}C NMR spectra two distinct signals for the $SiMe_3$ groups and three for the aluminum methyl groups in 2:2:1 ratio, indicative of the presence of three aluminum centers, two of which are equivalent. Also the mass spectrum is consistent with a trinuclear aluminum siloxide.

The solid-state structures of both compounds along with selected distances and bond angles are seen in Figures 1 and 2. The dimeric structure **2a** consists of two six-membered ring systems each with envelope conformation, which are fused by a planar Al_2O_2 core. The aluminum centers have a slightly distorted tetrahedral coordination environment with C−Al−O angles in the range of ca. 114−117°. It is worth noting that the dative Al1−O1 distance [1.823(2) Å] is somewhat shorter than the Al1−O1A distance within the six-membered ring of 1.851(2) Å. This strong dative Al−O interaction significantly

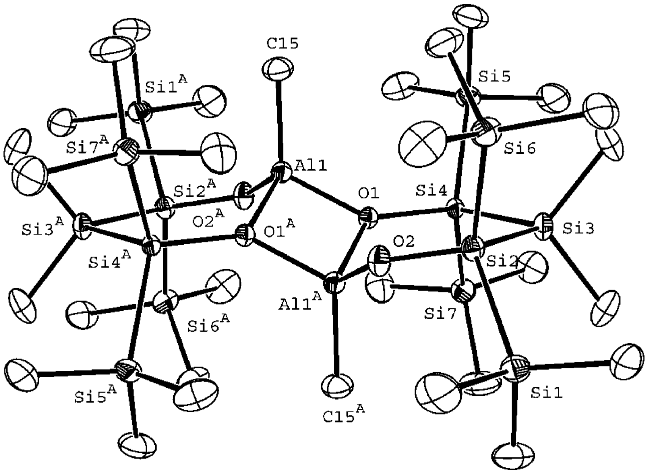


Figure 1. Molecular structure of **2a** in the crystal. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−O1 1.823(2), Al1−O1A 1.851(2), Al1−O2 1.709(2), Al1−C15 1.941(3), Si2−O2 1.647(2) Si4−O1 1.717(2), Si1−Si2 2.353(1), Si2−Si6 2.354(1), Si2−Si3 2.388(1), Si3−Si4 2.388(1), Si4−Si5 2.3644(8), Si4−Si7 2.375(1), O2−Al1A−O1A 112.73(10), O2−Al1A−O1 107.54(9), O1−Al1A−O1 85.28(9), Al1−O1−Al1A 94.72(9), O2A−Al1−C15 117.06(14), O1−Al1−C15 115.95(13), O1A−Al1−C15 113.73(12), Si4−O1−Al1 138.05(10), Si4−O1−Al1A 126.79(11), Si2−O2−Al1A 135.70(14).

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[12] For example, the strain energy of cyclotrisiloxanes is 16−21 kJ mol^{-1}, while cyclotetrasiloxanes and larger ring systems have almost no strain energy. See also: (a) Hossain, M. A.; Hursthouse, M. B.; Mazid, M. A.; Sullivan, A. C. *J. Chem. Soc., Chem. Commun.* **1988**, 1305. (b) Hossain, M. A.; Hursthouse, M. B.; Ibrahim, A.; Mazid, M. A.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1989**, 2347.

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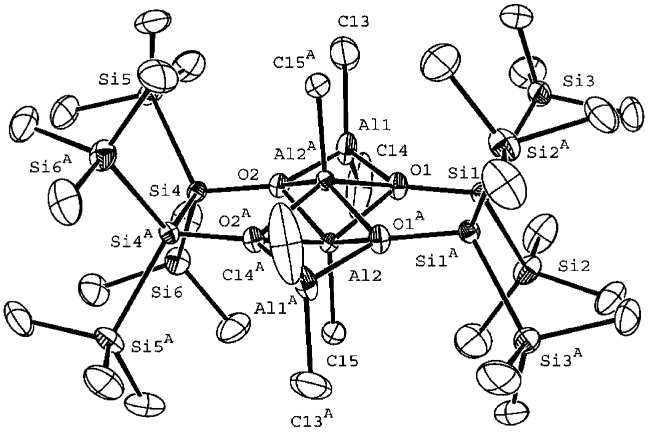


Figure 2. Molecular structure of **3b** in the crystal. The thermal ellipsoids correspond to 30% probability. A disorder is shown for the central aluminum methyl moiety (Al2−C15, relative occupancy 50%). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−O1 1.814(2), Al1−O2 1.807(2), Al2−O1 1.949(3), Al2−O1A 1.905(3), Al2−O2 1.950(2), Al2−O2A 1.895(2), Al1−C13 1.989(9), Al1−C14 1.943(7), Al2−C15 1.943(7), Si1−O1 1.704(2), Si4−O2 1.697(2), Si1−Si1A 2.392(2), Si4−Si4A 2.396(1), Si1−Si3 2.363(1), Si1−Si2 2.382(1), Si4−Si5 2.365(1), Si4−Si6 2.383(1), C14−Al1−C13 125.3(5), O2−Al1−O1 84.29(9), O1−Al2−O2 77.09(10), O2−Al2−O1 140.64(14), O1−Al2−O1A 88.38(13), O2−Al2−O2A 88.32(12), C15−Al2−O2 111.4(2), C15−Al2−O1 112.1(2), C15−Al2−O2A 107.3(2), C15−Al2−O1A 108.9(2), Si1−O1−Al1 137.96(12), Si1−O1−Al2 122.57(12), Si4−O2−Al2 123.02(12), Si4−O2−Al1 137.29(12), Al1−O2−Al2 98.60(10), Al1−O1−Al2 98.42(11).

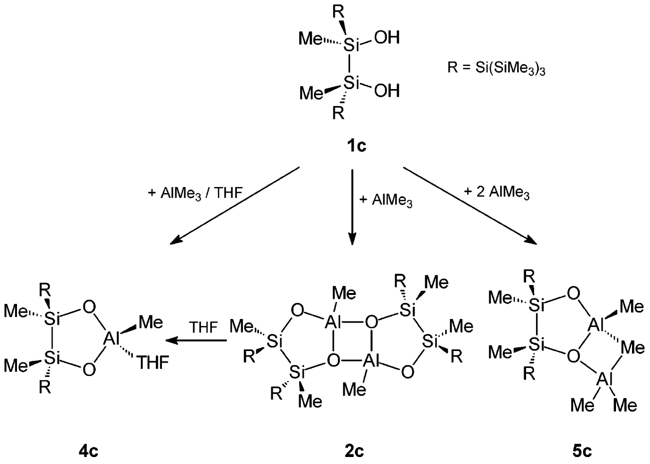
elongates the Si4−O1 bond [1.717(2) Å] as compared to the Si2−O2 distance of 1.647(2) Å.

Structure **3b** consists of a trinuclear spirocyclic Al_3O_4 core in which the central aluminum Al2 is disordered (the possible positions of Al2 are shown in Figure 2). Whereas the outer aluminums Al1 are tetrahedrally surrounded by two methyl groups and two siloxy moieties, the central disordered aluminum Al2 has a square pyramidal coordination environment with C−Al−O angles in the range of ca. 107−112°. The central Al2 is coordinated by one methyl group [Al2−C15 1.943(7) Å] and two disiloxides moieties, forming a five-membered ring, each with an envelope conformation. Interestingly, the Al−O distances of the central aluminum (Al2), being in the range 1.90−1.96 Å, are considerably longer than those of the outer aluminums (Al1) with Al1−O1 and Al1−O2 distances of 1.814(2) and 1.807(2) Å, respectively. Structurally similar trinuclear aluminum siloxide complexes of formula $[Al_3X_5(OSiMe_2OSiMe_2O)_2]$ (X = Cl, Br) have been observed in the reaction of AlX_3 with $[SiMe_2O]_4$.[14]

Reactions of *rac*-1c with $AlMe_3$. In analogy with the reaction of **1a** noted above, treatment of *rac*-**1c** with equimolar amounts of $AlMe_3$ in *n*-pentane selectively affords the dimeric aluminum siloxide **2c** as a mixture of two diastereomers (ca. 1:1 ratio) in good yields. In contrast, the analogous reaction with THF as solvent does not give **2c**, but instead yields the monomeric aluminum siloxide **4c**, which is coordinated by one molecule of THF (Scheme 2).

The structures of **2c** and **4c** were established by means of NMR and MS data, elemental analyses, and X-ray crystallography. As expected, owing to the tetrahedral coordination environment of the aluminum caused by THF coordination, the ^1H and ^{13}C NMR spectra of **4c** exhibit two signals for the $Si(SiMe_3)_3$ and SiMe groups, respectively, whereas the Me−Al groups showed only one signal. As for **2a**, the structure of **2c** in solution has been assigned unambiguously to be dimeric through NMR spectroscopy in benzene-d_6. The ^1H and ^{13}C NMR spectra show four signals for the $Si(SiMe_3)_3$ and the methyl group, respectively, and two distinct signals for the aluminum methyl groups, indicating the presence of a mixture of two diasteromers. Clearly this arises from the racemic ligand that can adopt two different orientations, giving two structures in total considering that the aluminum methyl groups are orientated trans to each other. In fact, at least one of both diasteromers present in solution has been found to be trans orientated by X-ray crystallography. Dissolving the dimeric aluminum complex **2c** in THF-d_8 reduces the number of signals that appear in the ^1H and ^{13}C NMR spectra to a total of five, three for the aluminum- and silicon-bonded methyl groups and two for the $Si(SiMe_3)_3$ moieties. Clearly, this is consistent with the quantitative formation of the monomeric THF adduct **4c** and indicates the dimeric complex **2c** to be easily cleaved even by the relatively weak donor THF (Scheme 1). However, attempts by thermal elimination of THF to drive the reaction back to the dimer **2c** failed. No reaction occurred under the conditions applied.

Scheme 2. Reactions of 1c with $AlMe_3$



The molecular structures of **2c** and **4c** were confirmed by X-ray crystallography; suitable single crystals were grown from *n*-pentane solutions (Figures 3 and 4). As expected, compound **2c** is dimeric in the solid state with the aluminum centers tetrahedrally surrounded by a methyl group and three oxygen atoms. Like many other aluminum alkoxides[16] and siloxides, the bridging siloxy functionalities form a planar four-membered ring system [O2−Al1−O2A 85.59(5)°, Al1−O2−Al1A 94.41(5)°]. Similar to **2a**, the dative Al1−O2A distance [1.818(1) Å] in **2c** is considerably shorter than the Al1−O2 distance [1.880(1) Å] within the planar five-membered ring. As a consequence of this dative interaction, also the Si4−O1 [1.651(1) Å] and Si3−O2 [1.726(1) Å] distances differ markedly from each other. The results for **4c** clearly reveal the compound to be monomeric in the solid state; one molecule of THF weakly coordinates [Al1−O3 1.875(2) Å] to the Lewis acidic aluminum center, resulting in a tetrahedral coordination environment of the aluminum. The central Si3−Si4 ring distances in both compounds are significantly widened to values of 2.404(1) Å (**2c**) and 2.409(1) Å (**4c**).

When *rac*-**1c** was reacted with 2 equiv of $AlMe_3$ in pentane at −78 °C, a new product was formed that was identified by multinuclear NMR spectroscopy and X-ray crystallography as

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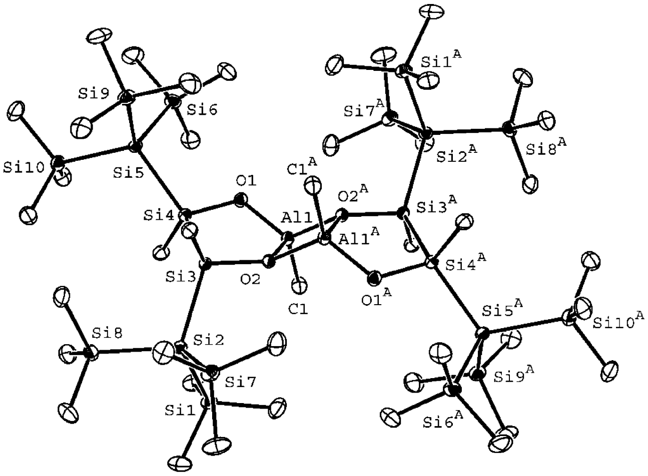

Figure 3. Molecular structure of **2c** in the crystal. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−O1 1.730(1), Al1−O2A 1.818(1), Al1−O2 1.880(1), Al1−C1 1.939(2), Si4−O1 1.651(1), Si3−O2 1.726(1), Si3−Si4 2.404(1), Al1−O2−Al1A 94.41(5), O1−Al1−O2A 118.42(6), O1−Al1−O2 99.46(5), O2−Al1−O2A 85.59(5), O1−Al1−C1 116.12(7), O2−Al1−C1A 115.53(7), O2−Al1−C1 116.41(7), Si4−O1−Al1 119.56(7), Si3−O2−Al1A 136.93(7), Si3−O2−Al1 116.15(6), O2−Si3−Si4−O1 8.03(6), Al1−O1−Si4−Si3 30.95(8), O2−Al1−O1−Si4 40.39(9), O1−Al1−O2−Si3 30.57(8) Si2 Si3 Si4 Si5 115.04(3), O2−Al1−O2A−Al1A 0.0.

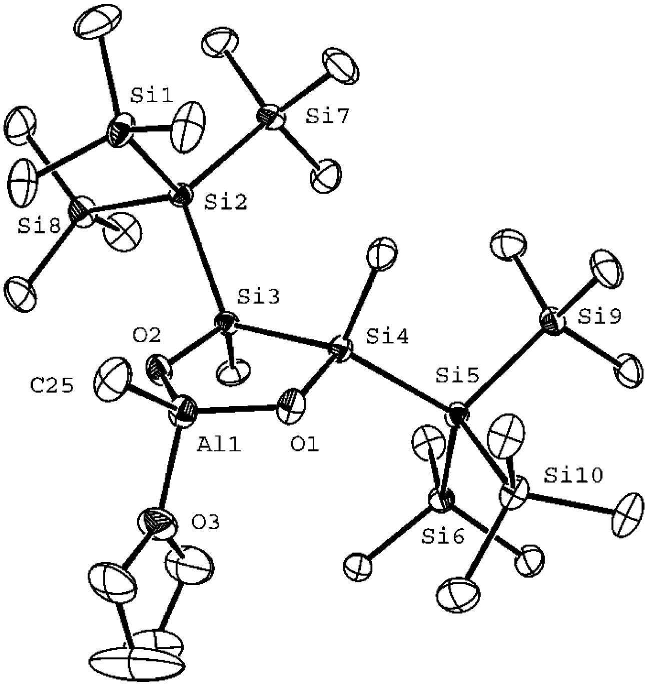

Figure 4. Molecular structure of **4c** in the crystal. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−O1 1.746(1), Al1−O2 1.736 (1), Al1−O3 1.875(2), Al1−C25 1.951(2), Si4−O1 1.655(1), Si3−O2 1.649(1), Si3−Si4 2.409(1), Si2−Si3 2.367(1), Si4−Si5 2.381(1), Si5−Si6 2.357(1); O1−Al1−O2 104.96(6), O1−Al1−O3 103.10(8), O1−Al1−C25 119.93(10), O3−Al1−C25 103.20(10), Si4−O1−Al1 120.48(7), Si3−O2−Al1 120.73(7), Al1−O1−Si4−Si3 10.65(9), O1−Si4−Si3−O2 3.18(7), Si3−O2−Al1−O1 11.22(11), Si2−Si3−Si4−Si5 121.29(3).

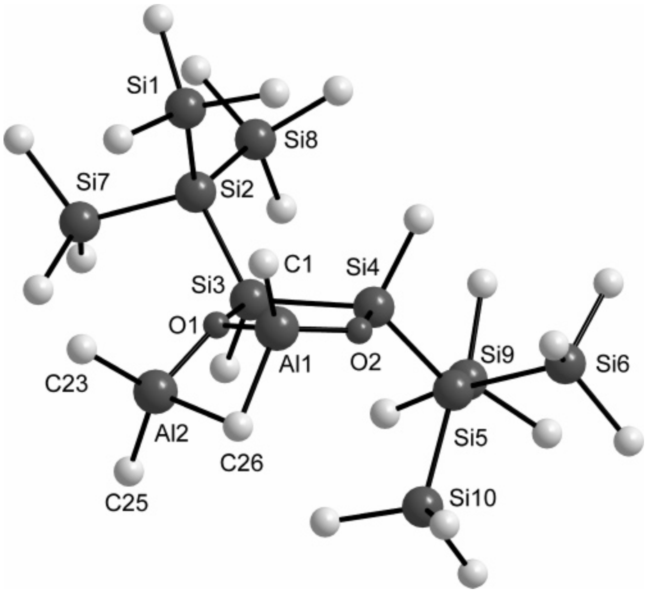

Figure 5. Structural model of compound **5c**.

the dinuclear aluminum complex **5c** (Scheme 1). As expected, in the ^{1}H and ^{13}C NMR spectra the signals of the ligand backbone show roughly the same features as in the methyl aluminum complexes **2c** and **4c**. In the ^{29}Si NMR spectrum, however, the central silicon atoms of the SiO bond sequence display two distinct signals appearing at 28.3 and 9.7 ppm, respectively. This implies an asymmetric species rather than a symmetrical one to be present and indicates that the AlMe$_3$ is strongly coordinated by one of the ring oxygen atoms, resulting in a significant low-field shift of the respective silicon signal in the ^{29}Si NMR spectrum. Further evidence for the formation of the AlMe$_3$ adduct **5c** is given by the fact that all four methyl aluminum groups display distinct signals in the ^{1}H NMR (signal ratio 1:1:1:1) and in the ^{13}C NMR spectra. One of the aluminum methyl groups is significantly downfield shifted in the ^{1}H NMR ($\delta = 0.19$ ppm), which suggests that this methyl group bridges between both aluminum centers, as observed in dimeric Al$_2$Me$_6$. This view is supported by the results of an X-ray structure analysis of **5c** (Figure 5). Although the quality of the data (R value ca. 0.17) was insufficient to make any commentary on structural parameters in detail, the orientation and connectivity of the located aluminum and carbon atoms reveal, however, the presence of an edge-shared, four-membered ring structure similar to that of Al$_2$Me$_6$.

The AlMe$_3$ adduct **5c** is soluble in most organic solvents (pentane, ether, toluene, THF) and is surprisingly thermally stable. According to variable-temperature ^{1}H NMR measurements, no spectral change occurred upon increasing the temperature to 60 °C. To the best of our knowledge, there is only one structurally related aluminum siloxide of formula [Mes$_3$SiOAlMe$_2$·AlMe$_3$] with a bridging methyl group reported in the literature, and in this case no X-ray data are available.[17] However, two structurally related aluminum alkoxides were reported by Scott et al.[18] and Rothwell et al.,[19] the solid-state structures of which have been determined by X-ray crystallography. In these complexes the AlMe$_3$ is only loosely bonded to the alkoxide moiety, as shown by the presence of only one distinct signal for all the aluminum methyl groups in the ^{1}H and ^{13}C NMR spectra. The equivalence of the methyl signals

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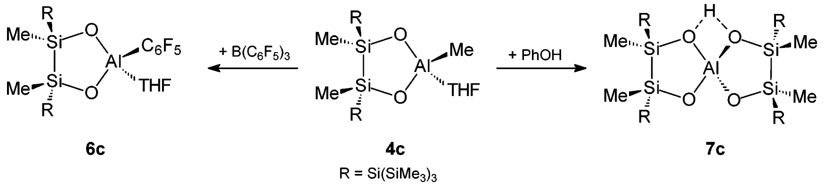
(17) Wrobel, O.; Schaper, F.; Brintzinger, H. H. *Organometallics* **2004**, *23*, 900.

(18) (a) Cottone A., III; Scott, M. J. *Organometallics* **2000**, *19*, 5254. (b) Cottone A., III; Scott, M. J. *Organometallics* **2002**, *21*, 3610.

(19) Son, A. J. R.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2003**, *22*, 2318.

Scheme 3. Reaction of 4c with $B(C_6F_5)_3$ and Phenol



even at −60 °C was thought to be due to a fast bridge/terminal exchange on the NMR time scale. We note that mixed alkoxide methyl-bridged aluminum compounds have been proposed to be important intermediates in the methylation of tertiary and secondary alcohols to hydrocarbon by trimethylaluminum.[20]

Reactions of 2a, 2c, 3b, and 4c with $B(C_6F_5)_3$ and Phenol. With the synthesized aluminum complexes in hand we investigated their reactivity toward the Lewis acid $B(C_6F_5)_3$, which is known to abstract alkyl groups from metal centers to form cationic species, which are active in olefin polymerization. The reactions initially were performed at room temperature in a J-Young NMR tube using benzene-d_6 as solvent, and the course of the reactions was monitored by ^1H NMR spectroscopy. Unexpectedly, solutions of the dinuclear and trinuclear aluminum siloxides **2a**, **2c**, and **3b** in C_6D_6 are inert toward $B(C_6F_5)_3$ at ambient conditions over a prolonged period of time, and even at higher temperature no substantial conversion occurred. In contrast, the THF adduct **4c** reacted cleanly with $B(C_6F_5)_3$ (molar ratio 1:1) within minutes, resulting in quantitative formation of a new complex, which, however, was not the expected zwitterionic complex $[(E)\text{-}\{Me(Me_3Si)_3SiSiO\}_2Al\cdot THF]^+[MeB(C_6F_5)_3]^-$. Rather, the product of quantitative C_6F_5 group transfer, **6c**, was formed together with BMe_3, $Me_2BC_6F_5$, and $MeB(C_6F_5)_2$, as evidenced by multinuclear NMR spectral data. Compound **6c** could be isolated in a larger scale experiment, and the spectroscopic data obtained were identical to those from the NMR tube experiments (Scheme 3). The reason that only in **4c** the methyl group has been replaced smoothly by a C_6F_5 group is clearly steric in nature, i.e., as a consequence of less steric protection of the aluminum center in mononuclear complexes as compared to the di- and trinuclear complexes. Although not isolated from the reaction mixture, a similar product resulting from a C_6F_5 transfer reaction after 24 h at 80 °C, the dendritic aluminum siloxide of formula $[(Ph_2MeSiCH_2CH_2)_3SiOAl]_2Me_3(C_6F_5)$, has been previously detected by NMR spectroscopy.[21]

The reaction behavior of the aluminum siloxides toward phenol is closely related to that observed with $B(C_6F_5)_3$. The dinuclear complexes **2a** and **2c** did not react with phenol (molar ratio 1:1) under ambient conditions. In fact, when a solution was heated at 70 °C for several hours in C_6D_6, almost no change (as determined by ^1H NMR) was observed. After prolonged periods of time only signals arising from the free ligand were detected. In striking contrast, **4c** reacted cleanly with phenol (molar ratio 1:1) within minutes, resulting in quantitative formation of $MeAl(OPh)_2$ and the new complex **7c**, rather than the expected $(E)\text{-}[Me(Me_3Si)_3SiSiO]_2AlOPh\cdot THF$ (as evidenced by multinuclear NMR spectral data).

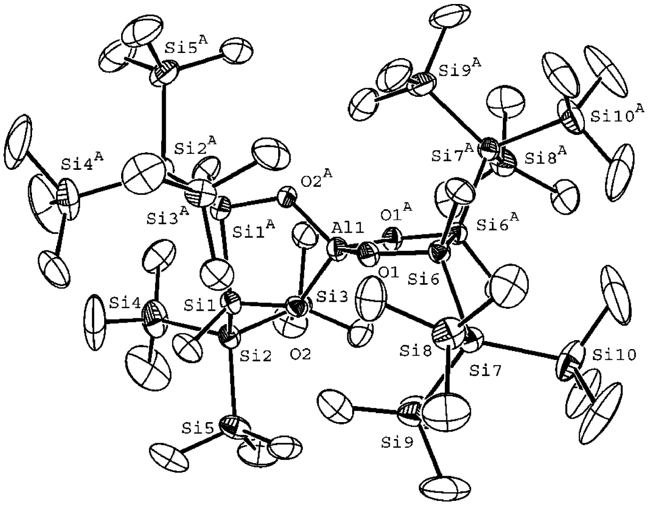


Figure 6. Molecular structure of **7c** in the crystal. The thermal ellipsoids correspond to 30% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Al1−O1 1.745(4), Al1−O2 1.781(4), Si1−O2 1.694(4), Si6−O1 1.674(4), Si1−Si1A 2.393(4), Si6−Si6A 2.390(4), Si1−Si2 2.366(3), Si6−Si7 2.375(3), O1−Al1−O1A 103.4(3), O2−Al1−O2A 99.8(3), O1−Al1−O2 112.9(2), O1−Al1−O2A 114.2(2).

Compound **7c**, whose structure was determined by X-ray crystallography, is a spirocyclic compound in which two siloxide ligands are attached to the aluminum center, resulting in a negatively charged complex (Figure 6). However, a counter cation could not be found in the difference map. Therefore, we propose compound **7c** to be an acid of formula $\{[(E)\text{-}\{Me(Me_3Si)_3SiSiO\}_2]_2Al\}^-H^+$ in which the proton might be bonded weakly to the oxygen atoms.[22,23]

Although the mechanism of formation of **7c** is still unclear, we propose that the first step of the reaction involves a slow nucleophilic exchange of the methyl group attached to the aluminum center in **4c** by a phenoxide group (Scheme 4). The formed phenoxide complex **8c** may react rapidly with another molecule of **4c** under elimination of $MeAl(OPh)_2$ to yield the final product **7c**. Similar behavior has been observed for $Me_2Al(OCPh_3)(THF)$, which rapidly undergoes ligand redistribution, resulting in the formation of $AlMe(OCPh_3)_2(THF)$ and $AlMe_3(THF)$.[24] This view is supported by the fact that the reaction of **4c** with the free ligand **1c** does not give the expected product **7c**. Thus, a pathway involving a ligand dissociation of **4c** resulting in the formation of the free ligand and $MeAl(OPh)_2$ can be excluded.

Conclusion

Protolysis of $AlMe_3$ by the chelating diols $SiMe_2[(Me_3Si)_2SiO]_2H_2$ (**1a**), $[(Me_3Si)_2SiO]_2H_2$ (**1b**), and [Me(Me$_3$-

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(20) (a) Harney, D. W.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, *27*, 1639. (b) Obrey S. J.; Bott S. G.; Barron A. R. *Organometallics* **2001**, *20*, 5162.

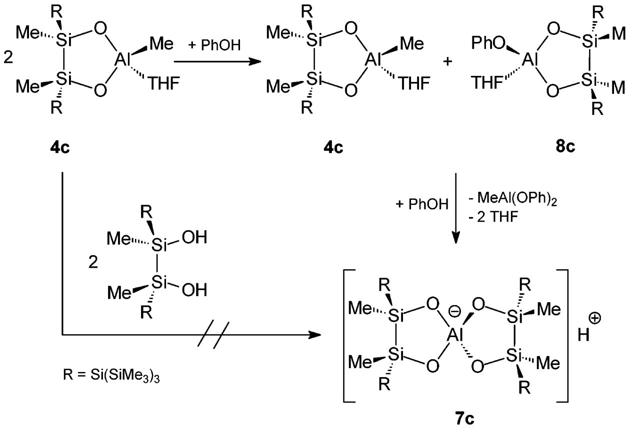
(21) Amo, V.; Andres, R.; De Jesus, E.; De la Mata, F. J.; Flores, J. C.; Gomez, R.; Gomez-Sal, M. P.; Turner, J. F. C. *Organometallics* **2005**, *24*, 2331.

(22) There are only four examples of spirocyclic aluminum siloxides being characterized by X-ray crystallography, namely, $[HNEt_3][Al\{(c\text{-}C_6H_{11})_7Si_7O_{12}(OSiMe_3)\}_2]$,[23] $[HNEt_3][Al\{(c\text{-}C_5H_9)_7Si_7O_{12}(OSiMe_3)\}_2]$,[4g] $[HPy][Al\{(OSiPh_2O)_2SiPh_2\}_2]$,[11] and $[HNEt_3][Al\{(c\text{-}C_5H_9)_7Si_7O_{12}(OSiMePh_2)\}_2]$.[4e] All these anionic complexes have an ammonium counter cation.

(23) Edelmann, F. T.; Gun'ko, Y. K.; Gissmann, S.; Olbrich, F.; Jacob, K. *Inorg. Chem.* **1999**, *38*, 210.

(24) Obrey, S. J.; Bott, S. G.; Barron, A. R. *Organometallics* **2001**, *20*, 5119.

Scheme 4. Proposed Formation of 4c



$Si)_3SiSiO]_2H_2$ (*rac*-**1c**) is an efficient procedure for the synthesis of a series of strained cyclic five- and six-membered aluminum disiloxides. The selectivity of protolysis strongly depends on several factors such as choice of the ligand, temperature, solvents, and the ligand to $AlMe_3$ ratio. The aluminum centers in these complexes proved to be highly electrophilic, as reflected in the rapid formation of the thermally stable THF and $AlMe_3$ adducts **4c** and **5c**, respectively.

Experimental Section

General Procedure. All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk and glovebox techniques. THF, diethyl ether, *n*-heptane, and *n*-pentane were distilled under argon from alkali metals prior to use. Benzene-d_6 was dried over activated molecular sieves and stored in the glovebox. $B(C_6F_5)_3$[25] and $Ph(Me_3Si)_2Si-Si(SiMe_3)_2Ph$[26] were prepared as previously described. The silanols **1a**[15] and **1c**[14a] were prepared according to the literature procedures. NMR: Bruker AC 250, Bruker ARX 300, Bruker ARX 500. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas.

2,3-Dihydroxy-1,1,1,4,4,4-hexamethyl-2,3-bis(trimethylsilyl)-tetrasilane (1b). Freshly distilled TfOH (0.97 mL, 0.011 mol) was added to a stirred solution of $Ph(Me_3Si)_2Si-Si(SiMe_3)_2Ph$ (2.51 g, 0.005 mol) in CH_2Cl_2 (25 mL) at −40 °C. The stirred mixture was allowed to warm to room temperature within 2 h. The solvent was replaced by diethyl ether, an aqueous solution of NH_4COONH_2 (10 mL, 1 M) was added dropwise, and stirring was continued for 30 min. The organic phase was separated and dried over $MgSO_4$, and the solvent was evaporated under vacuum. Drying under high vacuum afforded 1.76 g (92%) of the title compound, which was kept in a freezer. ^1H NMR (C_6D_6, 250 MHz): δ 0.72 (br s, OH, 2 H), 0.29 (s, $Si(CH_3)_3$, 36 H) ppm. ^{13}C NMR (C_6D_6, 62.9 MHz): δ 0.1 ($Si(CH_3)_3$) ppm. ^{29}Si-INEPT (C_6D_6, 59.6 MHz): δ 8.1 (SiOH), −15.0 ($Si(CH_3)_3$) ppm. MS (70 eV): *m/z* (%): 383 (8) [M^+], 279 (8) [$M^+ - 2Me - SiMe_3$], 205 (20) [$M^+ - Me - 2SiMe_3 - OH$], 131 (42) [$M^+ - Me - 3SiMe_3 - OH$]. Anal. Calcd for $C_{12}H_{38}O_2Si_6$ (382.94): C, 37.64; H, 10.00. Found: C, 37.49; H, 9.98. IR (Nujol): $\nu_{OH} = 3394.4$ cm^{-1} (assoc), 3641.6 cm^{-1} (nonassoc).

Synthesis of [$SiMe_2\{(Me_3Si)_2SiO\}_2AlMe]_2$ (2a). A heptane solution of $AlMe_3$ (1.2 mL, 2.40 mmol, 2 M) was slowly added to a solution of **1a** (1 g, 2.27 mmol) in *n*-pentane (20 mL) −78 °C. The resulting reaction mixture was stirred for 10 min and allowed to warm to room temperature. Stirring was continued for an additional 2 h. Crystallization of a concentrated solution in a freezer at −40 °C afforded the title compound as colorless crystals. Yield: 0.42 g (44%). Mp: 193−195 °C. ^1H NMR (C_6D_6, 500 MHz): δ 0.53, 0.40 (2s, $Si(CH_3)_2$, 2 × 6 H), 0.41, 0.41 0.30, 0.39 (4s, $Si(CH_3)_3$, 4 × 18 H), −0.33 (s, $AlCH_3$, 6 H) ppm. ^{13}C NMR (C_6D_6, 125.8 MHz): δ 1.6, 1.2, 1.1, 1.0 ($Si(CH_3)_3$), 0.5, −0.2 ($Si(CH_3)_2$), −6.6 ($AlCH_3$) ppm. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 16.8, −3.0 (SiOAl), −14.1, −14.2, −15.5, −16.5 ($Si(CH_3)_3$), −39.3 ($Si(CH_3)_2$) ppm. MS (CI, *m/z* in %): 962 (30) [M^+], 945 (100) [$M^+ - Me$], 889 (88) [$M^+ - SiMe_3$]. Anal. Calcd for $C_{15}H_{45}O_2Si_7Al$ (418.12): C, 37.45; H, 9.43. Found: C, 36.70; H, 9.39.

Synthesis of [(*E*)-$\{Me(Me_3Si)_3SiSiO\}_2AlMe]_2$ (2c). The same procedure was used as for compound **2a**; *rac*-**1c** (1 g, 1.63 mmol) and $AlMe_3$ (0.85 mL, 1.70 mmol). Yield: 0.56 g (52%). Mp: 134−136 °C. ^1H NMR (C_6D_6, 250 MHz): δ 1.05, 0.97, 0.96, 0.93 (4s, $SiCH_3$, 4 × 3 H), 0.45, 0.44, 0.42, 0.40 (4s, $Si(CH_3)_3$, 4 × 27 H), −0.18, −0.19 (2s, $AlCH_3$, 2 × 3 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 9.2, 10.2, 10.5, 11.0 ($SiCH_3$), 3.8, 3.9, 4.0, 4.5 ($Si(CH_3)_3$), −5.8, −7.1 ($AlCH_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ 27.6, 25.9, 10.1 (SiOAl), −9.3, −9.9 ($Si(CH_3)_3$), −125.1, −125.6, −126.2 (*Si*($SiMe_3$)) ppm. MS (EI, *m/z* in %): 1312 (29) [M^+], 1297 (15) [$M^+ - CH_3$], 1239 (7) [$M^+ - Si(CH_3)_3$], 1065 (100) [$M^+ - Si(SiMe_3)_3$]. Anal. Calcd for $C_{21}H_{63}O_2Si_{10}Al$ (655.60): C, 38.48; H, 9.96. Found: C, 37.67; H, 9.69.

NMR data in THF-d_8: ^1H (250 MHz): δ 0.63 (s, SiMe, 6 H), 0.25 (s, $SiMe_3$, 54 H), −0.93 (s, AlMe, 3 H) ppm. ^{13}C NMR (75.5 MHz): δ 10.5 ($SiMe_2$), 3.6 ($SiMe_3$) ppm. ^{29}Si NMR (59.6 MHz): δ 7.5 (SiOAl), −10.0 ($SiMe_3$), −128.5 (*Si*Si_4) ppm.

Synthesis of [$\{(Me_3Si)_2SiO\}_2]_2Al_3Me_5$ (3b). The same procedure was used as for compound **2a**; **1b** (0.44 g, 1.15 mmol) and $AlMe_3$ (0.6 mL, 0.12 mmol, 2 M). Yield: 0.26 g (49%). Mp: 93−94 °C. ^1H NMR (C_6D_6, 250 MHz): δ 0.38, 0.36 (2s, $Si(CH_3)_3$, 2 × 36 H), −0.29, −0.32 (2s, $Al(CH_3)_2$, 2 × 6 H), −0.42 (s, $AlCH_3$, 3 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 1.8, 1.6 ($Si(CH_3)_3$), −4.7, −6.7 ($AlCH_3$), −15.1 ($Al(CH_3)_2$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ −6.5 (SiOAl), −14.6, −15.3 ($Si(CH_3)_3$) ppm. MS (EI, *m/z* in %): 918 (21) [$M^+ - Me$], 912 (68) [$M^+ - 4H$], 844 (100) [$M^+ - SiMe_3$], 756 (5) [$M^+ - 2SiMe_3 - Me$]. Anal. Calcd for $C_{29}H_{87}O_4Si_{12}Al_3$ (917.97): C, 37.94; H 9.55. Found: C, 37.13; H 9.56.

Synthesis of (*E*)-[$Me(Me_3Si)_3SiSiO]_2AlMe\cdot THF$ (4c). The same procedure was used as for compound **2a**; *rac*-**1c** (1 g, 1.63 mmol), THF (20 mL), and $AlMe_3$ (0.85 mL, 1.70 mmol, 2 M). Yield: 0.48 g (41%). Mp: 181−183 °C. ^1H NMR (C_6D_6, 250 MHz): δ 3.55 (m, THF CH_2CH_2O, 4 H), 1.08 (m, THF CH_2CH_2O, 4 H), 0.96 (s, $SiCH_3$, 6 H), 0.46 (s, $Si(CH_3)_3$, 54 H), −0.58 (s, $AlCH_3$, 3 H) ppm. NMR (THF-d_8, 250 MHz): δ 0.63 (s, $SiCH_3$, 6 H), 0.25 (s, $Si(CH_3)_3$, 54 H), −0.93 (s, $AlCH_3$, 3 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 69.7 (THF CH_2CH_2O), 25.1 (THF CH_2CH_2O), 10.6 ($SiCH_3$), 3.7 ($Si(CH_3)_3$), −13.8 ($AlCH_3$) ppm. ^{29}Si-INEPT (C_6D_6, 59.6 MHz): δ 8.4 (SiOAl), −9.7 ($Si(CH_3)_3$), −128.2 (*Si*($SiMe_3$)) ppm. MS (FAB, *m/z* in %): 655 (6) [$M^+ - THF$], 639 (9) [$M^+ - THF - Me$], 582 (31) [$M^+ - THF - SiMe_3$], 598 (10) [$M^+ - THF - AlMe - Me$] 351 (100) [$M^+ - THF - AlMe - Me - SiMe_3$]. Anal. Calcd for $C_{21}H_{63}O_2Si_{10}Al\cdot C_4H_8O$ (727.37): C, 41.28; H, 9.84. Found: C, 40.90; H, 10.04.

Synthesis of (*E*)-[$Me(Me_3Si)_3SiSiO]_2AlMe\cdot AlMe_3$ (5c). The same procedure was used as for compound **2a**; *rac*-**1c** (1 g, 1.63 mmol) and $AlMe_3$ (1.7 mL, 3.40 mmol, 2 M). Yield: 0.58 g (49%). Mp: 191−192 °C. ^1H NMR (C_6D_6, 250 MHz): δ 1.00, 0.96 (2s, $SiCH_3$, 2 × 3 H), 0.39, 0.34 (2s, $Si(CH_3)_3$, 2 × 27 H), 0.19, −0.28, −0.29, −0.36 (4s, $AlCH_3$, 4 × 3 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 10.8, 9.5 ($SiCH_3$), 3.7, 3.6 ($Si(CH_3)_3$), −3.5, −4.8, −5.2, −8.3 ($AlCH_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ 28.3, 9.7 (SiOAl), −9.7, −10.2 ($Si(CH_3)_3$), −125.2, −125.8, (*Si*Si_4) ppm. Anal. Calcd for $C_{24}H_{72}O_2Si_{10}Al_2$ (727.65): C, 39.62; H, 9.97. Found: C, 39.35; H, 9.81.

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(26) Krempner, C.; Jäger-Fiedler, U.; Mamat, K.; Spannenberg, A.; Weichert, K. *New J. Chem.* **2005**, *29*, 1581.

Table 1. Crystal Data Collection and Refinement Details for Crystal Structures[a]

	2a	**2c**	**3b**[b]	**4c**	**7c**
formula	$C_{30}H_{90}Al_2O_4Si_{14}$	$C_{42}H_{126}Al_2O_4Si_{20}$	$C_{29}H_{87}Al_3O_4Si_{12}$	$C_{25}H_{71}AlO_3Si_{10}$	$C_{40}H_{121}AlO_4Si_{20}$
molecular weight	962.24	1311.19	918.01	727.70	1255.15
cryst size, mm^3	0.5 × 0.27 × 0.22	0.82 × 0.22 × 0.12	0.40 × 0.33 × 0.32	0.46 × 0.32 × 0.23	0.53 × 0.24 × 0.22
cryst syst	monoclinic	triclinic	tetragonal	triclinic	tetragonal
space group	$P2_1/c$	$P\bar{1}$	$P4_32_12$	$P\bar{1}$	$P4_12_12$
a, Å	13.1046(6)	9.8107(2)	13.4937(3)	9.5867(3)	17.864(3)
b, Å	12.7170(5)	14.2245(4)	13.4937(3)	13.3815(4)	17.864(3)
c, Å	19.0643(7)	16.1461(4)	35.3988(9)	18.9958(5)	26.009(5)
α, deg	90.00	73.1630(10)	90.00	106.7570(10)	90.00
β, deg	109.5620(10)	76.3740(10)	90.00	98.1520(10)	90.00
γ, deg	90.00	74.6200(10)	90.00	94.4880(10)	90.00
V, $Å^3$	2993.7(2)	2048.40(9)	6445.4(3)	2291.49(12)	8301(2)
Z	2	1	4	2	4
ρ	1.067	1.063	0.946	1.055	1.004
μ, mm^{-1}	0.356	0.359	0.306	0.328	0.342
temperature, K	193(2)	173(2)	173(2)	173(2)	293(2)
θ limit, deg	3.32−27.50	2.92−27.50	2.42−27.07	2.16−27.50	0.267−22.48
no. of measd reflns	12 686	52 257	56 902	70 845	24 332
no. of indep reflns	4248 [R(int) = 0.0362]	9206 [R(int) = 0.0322]	7039 [R(int) = 0.0376]	10 360 [R(int) = 0.0287]	5382 [R(int) = 0.0362]
no. of data, restraints, params	4248, 0, 241	9206, 0, 328	7039, 0, 226	10360, 0, 373	5382, 0, 294
final R1, wR2[c]	0.0491, 0.1190	0.0310, 0.0761	0.0563, 0.1535	0.0356, 0.1008	0.0654, 0.1400

[a] All data sets were collected on a Bruker X8Apex diffractometer system with Mo Kα radiation (λ= 0.71073 Å) [b] The solid contains a hydrocarbon solvent molecule (heptane). However, none of the atom positions could be refined properly. [c] The value of R1 is based on selected data with $F > 4\sigma(F)$; the value of wR2 is based on all data.

Synthesis of (*E*)-[Me(Me$_3$Si)$_3$SiSiO]$_2$Al(C$_6$F$_5$)·THF (6c). Ten millliliters of *n*-pentane were added to a mixture of **4c** (0.10 g, 0.14 mmol) and $B(C_6F_5)_3$ (0.05 g, 0.10 mmol) at −20 °C. The vigorously stirred mixture was allowed to warm to room temperature, and stirring was continued for an additional hour. Crystallization from concentrated solutions at −40 °C in a freezer afforded the title compound as colorless crystals. ^1H NMR (C_6D_6, 250 MHz): δ 3.62 (m, THF CH_2CH_2O, 4 H), 1.21 (m, THF CH_2CH_2O, 4 H), 0.75 (s, SiMe, 6 H), 0.30 (s, $SiMe_3$, 54 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 72.3 (THF CH_2CH_2O), 24.7 (THF CH_2-CH_2O), 10.3 ($SiMe_2$), 3.3 ($SiMe_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ 18.9 (SiOAl), −9.8 ($SiMe_3$), −125.7 (*Si*Si_4) ppm. ^{19}F NMR (C_6D_6, 235.4 MHz): δ −127.3, −151.7, −158.6 (*o*-, *p*-, *m*-F, C_6F_5) ppm. Anal. Calcd for $C_{30}H_{68}AlF_5O_3Si_{10}$ (879.69): C, 40.96; H, 7.79. Found: C, 40.43; H, 7.71.

Synthesis of {[(*E*)-{Me(Me$_3$Si)$_3$SiSiO}$_2$]$_2$Al}$^-$H$^+$ (7c). A solution of **4c** (0.15 g, 0.21 mmol) and phenol (0.02 g, 0.21 mmol) in *n*-pentane (5 mL) was stirred for 16 h. Crystallization from concentrated solutions at −40 °C in the freezer afforded the title compound as colorless crystals. Yield: 0.05 g (61%). ^1H NMR (C_6D_6, 250 MHz): δ 0.96 (s, $Si(CH_3)_3$, 108 H), 0.42 (s, $SiCH_3$, 12 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ 10.4 ($SiCH_3$), 3.6 ($Si(CH_3)_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ 12.1 (SiOAl), −9.8 ($Si(CH_3)_3$), −127.6 (*Si*Si_4) ppm. Anal. Calcd for $C_{40}H_{121}AlO_4Si_{20}$ (1255.15): C, 38.28; H 9.72. Found: C, 37.95; H 9.61.

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Supporting Information Available: Crystallographic data for **2a** (CCDC 630899), **3b** (CCDC 630901), **2c** (CCDC 630900), **4c** (CCDC 630902), and **7c** (CCDC 630903) including CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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