Synthesis and Characterization of Novel Siloxyalanes

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The siloxyalanes $[(Et_3SiOAlH_2)_2AlH_3]_n$ (**1**), $[^tBuMe_2SiOAlH_2]_2$ (**2**), $[(^tBuMe_2SiO)_2AlH]_2$ (**3**), and $[(^tBuMe_2SiO)_5Al_2H]$ (**4**) have been synthesized and characterized by IR and NMR spectroscopic means. By X-ray diffraction studies on single crystals it was established that molecule **1** is a coordination polymer in the solid state with tetrameric units $[Et_3SiOAlH_2]_4$ (almost linear Al···Al···Al···Al arrangement) interlinked by Al_2H_6 groups to form a one-dimensional chain (formal description with neutral building blocks). Compound **3** is dimeric through Al−O contacts with a cis orientation of the hydride ligands with respect to the central Al_2O_2 cycle. Compound **4** may be described as a double adduct between the two Lewis acid−base compounds $(^tBuMe_2SiO)_2AlH$ and $Al(OSiMe_2{}^tBu)_3$. The bulkiness of the substituents on the silicon atoms plays an important role in the aggregation of the compounds. Hydride bridging between molecules or within the molecular entities is only observed in compound **1**.

Introduction

Alkoxyalanes of the general formula $ROAlH_2$ and $(RO)_2AlH$ crystallize, with decreasing steric bulk of the organic groups, as dimers, oligomers, or polymers. Monomers with trigonal-planar aluminum atoms have been unknown until now but may be obtained in the case of dialkoxyalanes in adducts (now displaying almost tetrahedral coordination around the aluminum atoms) using electron pair donors bearing voluminous alkoxy substituents as, for instance, in $[(2,6\text{-}^tBu_2\text{-}4\text{-}MeC_6H_2O)_2AlH(OEt_2)]$[1] and $[(Ph_3CO)_2AlH(thf)]$.[2] In the absence of external donors monoalkoxyalanes and dialkoxyalanes associate through hydride as well as alkoxo bridges. The aggregation to higher molecular associates increases with decreasing bulk of the alkoxy ligand, as may be deduced by comparing the structures of dimeric $[(^tBu)_2MeCOAlH_2]_2$ and tetrameric $[^tBuMeHCOAlH_2]_4$.[3] Further examples of simple dimers are $[^tBuOAlH_2]_2$ and $[(^tBuO)_2AlH]_2$, which are both bridged by the oxygen atoms of the alkoxy ligands.[4,5]

A formal mixture of two monoalkoxyalanes and a dialkoxyalane is known as well: $[(^iPrO)_2AlH\{(^iPrO)AlH_2\}_2]$. This compound may crystallize as an isolated species or as a coordination polymer.[3] Apart from the above-mentioned simple hydridoalkoxyalanes, there are a number of adducts with other metal hydrides or metal alkoxides known, in which the aluminum atoms show mostly tetrahedral coordination, as in the anionic part $[AlH_x(OR)_{4-x}]^-$.[6]

Compared to this relatively large number of alkoxy compounds, only a few siloxyalanes have been described to date, of which only four have been characterized by diffraction methods. One of these is the monosiloxyalane $[Me_3SiOAlH_2]_n$. Its synthesis was reported by Robert and Toner in 1970,[7] whereas its polymeric crystal structure was established only recently by X-ray diffraction.[8] The dimeric $[(^tBuO)(Me_3SiO)AlH]_2$ is the second representative which was synthesized and structurally characterized.[8] Apart from these two compounds, two others have been structurally characterized: $[Me_3SiOAlHCl]_2$[9] and the dimeric borane adduct $[(Me_3SiOAlH_2)_2{\cdot}4BH_3]$.[10]

One reason for the far smaller number of well-characterized siloxyalanes compared to the number of known alkoxyalanes may have its origin in the lower thermal stability of siloxyalanes and in the tendency of the starting silanols to condense to disiloxanes. The difference in the composition between the alkoxy- and siloxyalanes has a direct influence on the crystal structures, as may be seen by comparing $[Me_3SiOAlH_2]_n$ and $[^tBuOAlH_2]_2$. Chart 1 shows the structures of the two compounds.

The higher polarity of the Si−O bond compared to that of the C−O bond should normally cause increased donor properties of the siloxy groups compared to alkoxy groups. However, this is counterbalanced by oxygen−silicon back-donation, an effect which has been widely discussed[11−13] and which makes alkoxy groups more basic.

Whereas in $[^tBuOAlH_2]_2$ the electron-deficient aluminum atoms (apart from the two terminal hydride ligands) are coordinated exclusively by the oxygen atoms, in $[Me_3SiOAlH_2]_n$ not only the electron-poorer oxygen atoms coordinate to aluminum but also the hydride ligands participate in bridging.

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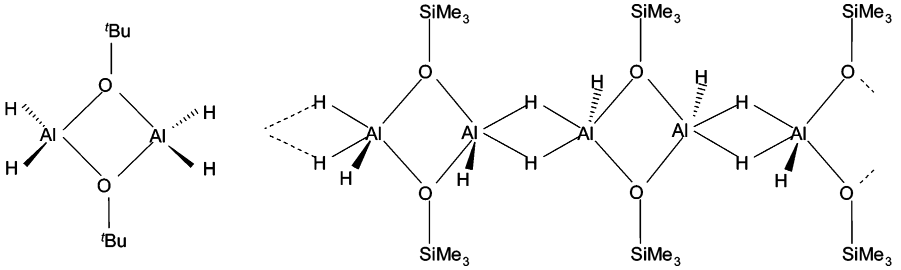
Chart 1. Two-Dimensional Representation of the Molecular Structures of $[{}^t\mathrm{BuOAlH_2}]_2$ and $[\mathrm{Me_3SiOAlH_2}]_n$



The formation of multicenter hydride bridges between the aluminum atoms increases their electron density and thus leads to a stabilization of the whole molecule ($^{\delta+}\mathrm{Al}\leftarrow\mathrm{H}^{\delta-}-\mathrm{Al}^{\delta+}$). On the other hand, the Si−O bond is approximately longer by 0.23 Å than the C−O bond,[11,12] which opens the coordination sphere of the aluminum atoms, allowing higher coordination numbers.

Here, we report the synthesis and structural characterization of further siloxyalanes, one of which is a compound possessing tetrahedrally, trigonal bipyramidally, and octahedrally coordinated aluminum atoms in the same molecule.

Results and Discussion

Syntheses and Spectroscopic Properties. Alkoxyalanes as well as siloxyalanes can be synthesized by hydrogen elimination between an aluminum hydride and an alcohol, or a silanol in diethyl ether solution at temperatures below 0 °C. In these reactions diethyl ether serves as a donor to aluminum hydride as well as a solvent.[4]

$$x\mathrm{R_3SiOH} + \mathrm{AlH_3{\cdot}}m\mathrm{Et_2O} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} (1/y)[(\mathrm{R_3SiO})_x\mathrm{AlH}_{3-x}]_y + x\mathrm{H_2}\uparrow \quad (1)$$

$$x = 1-3$$

The aluminum hydride etherate is obtained in situ by the 3/1 molar ratio reaction of lithium aluminum hydride and aluminum trichloride. As this etherate can either lose the ether, forming the polymeric and insoluble $(\mathrm{AlH_3})_\infty$, or add further donor molecules to the aluminum centers, the nature of the reacting silanol (reactivity and bulk of the substituents on silicon) has an important impact on the products formed in the reaction.[14−16]

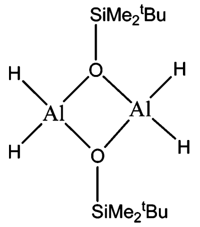
In the case of triethylsilanol, the product of its reaction with the diethyl ether−alane adduct is the complex hydride $[(\mathrm{Et_3SiOAlH_2})_2{\cdot}\mathrm{AlH_3}]_n$ (**1**), obtained in 50% yield at 0 °C (eq 1; $x = 2$). Formally, in compound **1** 2 molar equiv of $\mathrm{Et_3SiOAlH_2}$ are combined with 1 molar equiv of $\mathrm{AlH_3}$, and a product of definite structure crystallizes (see below).

When triethylsilanol is replaced by the more bulky *tert*-butyldimethylsilanol the reaction with alane proceeds differently (eq 2).

$$x{}^t\mathrm{BuMe_2SiOH} + \mathrm{AlH_3{\cdot}}m\mathrm{Et_2O} \xrightarrow[0\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} \underset{\mathbf{2-4}}{(1/2)\ [({}^t\mathrm{BuMe_2SiO})_x\mathrm{AlH}_{3-x}]_2} + x\mathrm{H_2}\uparrow + m\mathrm{Et_2O} \quad (2)$$

$$x = 1\ (\mathbf{2}),\ 2\ (\mathbf{3}),\ 2.5\ (\mathbf{4})$$

Now, the product does not contain an $\mathrm{AlH_3}$ molecule and, depending on the stoichiometry of the reactants, the monosubstituted alane $[{}^t\mathrm{BuMe_2SiOAlH_2}]_2$ (**2**), the disubstituted alane $[({}^t\mathrm{BuMe_2SiO})_2\mathrm{AlH}]_2$ (**3**), or the mixed compound $[({}^t\mathrm{BuMe_2SiO})_5\mathrm{Al_2H}]$ (**4**) is isolated. Even when an excess of the starting silanol is used, complete substitution of all hydrogen atoms in the alane molecule (with formation of $[({}^t\mathrm{BuMe_2SiO})_3\mathrm{Al}]$) is not observed; compound **4** still is the only isolable product. This very likely is a result of steric factors: i.e., the voluminous *tert*-butyl substituent on silicon.



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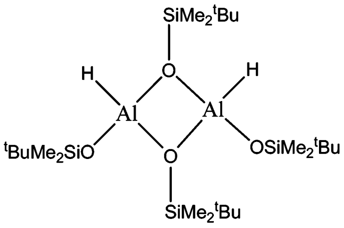

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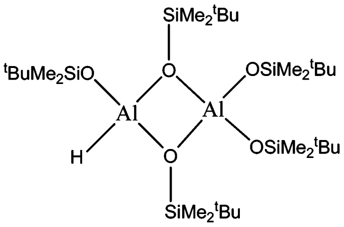

4

Note that the analogous reactions of trimethylsilanol with the diethyl ether adduct of $\mathrm{AlH_3}$ using different molar ratios of reactants leads either to the monosiloxyalane $[\mathrm{Me_3SiOAlH_2}]_n$ or to the completely substituted product $[(\mathrm{Me_3SiO})_3\mathrm{Al}]_2$.[8] The molecule $[(\mathrm{Me_3SiO})_2\mathrm{AlH}]_2$, which is analogous to **3**, cannot be obtained by this procedure. We assume that the disiloxyalane is only a transient intermediate and quickly disproportionates to the thermodynamically more stable products $[\mathrm{Me_3SiOAlH_2}]_n$ and $[(\mathrm{Me_3SiO})_3\mathrm{Al}]_2$. This instability is attributed to the low donor property of the oxygen in the trimethylsiloxy group and to steric requirements which apparently are different in the *tert*-butyldimethylsilyl derivatives.[8]

In the elemental analyses of compounds **2**−**4** the carbon values tend to be less than those calculated; this seems to come from the ratios Al/C and Si/C which are higher in these compounds and which may indicate carbide formation during analysis, even using $\mathrm{V_2O_5}$ as a combustion aid.[29]

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Compound **1** is crystalline and was characterized by solid-state MAS NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si, and ^{27}Al). In the aluminum NMR spectrum, three different resonances were observed. The signal at 6.4 ppm may be attributed to the octahedrally coordinated aluminum, the shoulder at 33.4 ppm to a 5-fold coordinated aluminum, and the resonance around 120 ppm (hampered by the spinning sidebands of the main signal) to the tetrahedrally coordinated aluminum atoms. In any case, the spectrum is in accord with the crystal structure of **1** (see below). In the ^{29}Si NMR spectrum only one signal at 26.01 ppm was observed. The resonance of the ethyl groups in the ^{13}C spectrum at 7.0 ppm is broad and is not resolved. Finally the organic groups in the ^{1}H NMR spectrum are indicated by a number of overlapping signals between 0.6 and 1.3 ppm. In addition to these resonances broad signals of relatively low intensity were observed between 3.5 and 3.9 ppm and around 4.5 ppm, which may be assigned to different hydrides (see also Supporting Information).

The infrared spectrum of **1** indicates the presence of Al−H bonds. Several Al−H vibration bands between 1550 and 1900 cm^{-1} were observed, indicating different coordination modes of the hydride ligands (terminal at high wavenumbers, bridging at the lower end) and reflecting different coordination numbers of the aluminum atoms to which they are bound. As is well-known, an increase of the coordination number of aluminum is accompanied by a shift of the wavenumber of the Al−H vibration toward lower values.[4,17−19]

Using this argument, we assign within the three bands observed between 1800 and 1900 cm^{-1} the lowest value to the six-coordinate, the middle to the five-coordinate, and the highest to the four-coordinate aluminum atom (see also the crystal structure). The Al−H−Al bridges are characterized by a broad band ranging from 1550 to 1750 cm^{-1}.[3,4,8,20]

We were not able to obtain single crystals of compound **2** for an X-ray crystal structure analysis, but the molar mass determination in benzene showed the molecule to be dimeric. The crystals of **4** were not of good quality, and the refinement of the X-ray structure was problematic (vide infra).

Compounds **2**−**4** were characterized using IR and NMR spectroscopy. The wavenumbers of the Al−H valence vibration (1850−1900 cm^{-1}), typical for μ-bonded hydrogen atoms, were shifted to higher values when passing from **2** to **3** and **4**. This shift is in accord with a strengthening of the Al−H bond, when further siloxy substituents are bonded to aluminum. The Al−H deformation vibrations could not be assigned with certainty, but bands at 764 and 773 cm^{-1}, respectively, were possibilities.[4]

The increase of the number of $R'R_2SiO$ groups with concomitant decrease of the Al−H substituents in **2**−**4** can be followed by an increase in the intensity of the band at approximately 1256 cm^{-1}, which is characteristic of the deformation vibration of the CH_3 groups on silicon ($\delta((CH_3)Si)$).[21−23] While the intensity of the Al−H absorption decreased within molecules **2**−**4**, this band steeply increased (the gain of relative intensity between the $H_3C-Si/H-Al$ signals on passing from **2** to **4** was measured to be 1.0/4.1/10.0 compared to calculated 1.0/4.0/10.0).

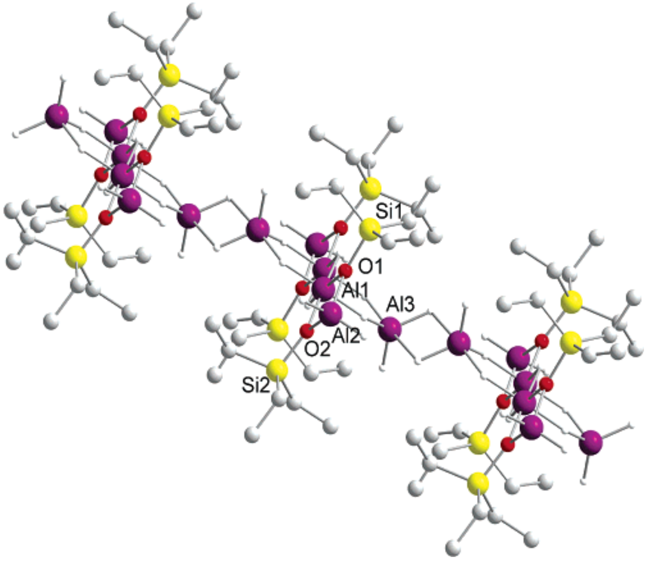

Figure 1. Two-dimensional hydride-connected polymer as part of the crystal structure of compound **1**. Only some atoms are designated, and carbon atoms (smaller balls) and hydride atoms (very small balls) are not addressed; hydrogen atoms on the carbon atoms have been omitted for clarity.

The absorption bands around 795 cm^{-1} may be attributed to the Si−O vibrations (ν(Si−O)) when the silyl group is bonded to an oxygen atom of the Al_2O_2 ring. The corresponding absorption of terminal Si−O groups should appear at ∼1060 cm^{-1},[24] and such bands are observed in the IR spectra of compounds **3** and **4** (a band at ∼1078 cm^{-1} may be due to contamination by hydrolysis products[22]). The bands at 844 and 675 cm^{-1} may be due to the asymmetric and symmetric Al_2O_2 ring vibrations (see also the Supporting Information).[4]

NMR spectra (^{1}H, ^{13}C, and ^{29}Si) of compounds **2**−**4** were obtained in benzene or in THF solution. The number of peaks in the NMR spectra of benzene solutions of **2** and **3** indicate that they are present as dimers. Resonances for bridging and for terminal siloxy groups can be distinguished (see Experimental Section).[25,26] The NMR spectra of **2** and **3** change, when benzene is replaced by THF as a solvent, showing only a single set of resonances. This indicates that the dimers have dissociated into THF-solvated monomers. Compound **3** shows two resonances in its ^{29}Si NMR spectrum in benzene. In agreement with the NMR results, there is only one resonance in THF, with a considerable chemical shift due to the adduct formation.

The NMR spectra of compound **4** in benzene are in agreement with the structure found by X-ray diffraction (see below). As there is a mirror plane in the molecule (perpendicular to the four-membered ring), there are four signals in the ^{29}Si NMR spectrum. The ^{1}H and ^{13}C NMR spectra of **4** indicate that the molecule does not dissociate in benzene solution, as the dimethysilyl group of the siloxy bridges is diastereotopic and shows two resonances.

Structural Investigations. Figures 1 and 2 show representative parts of the crystal structure of compound **1**, which crystallizes in the monocline crystal system (space group

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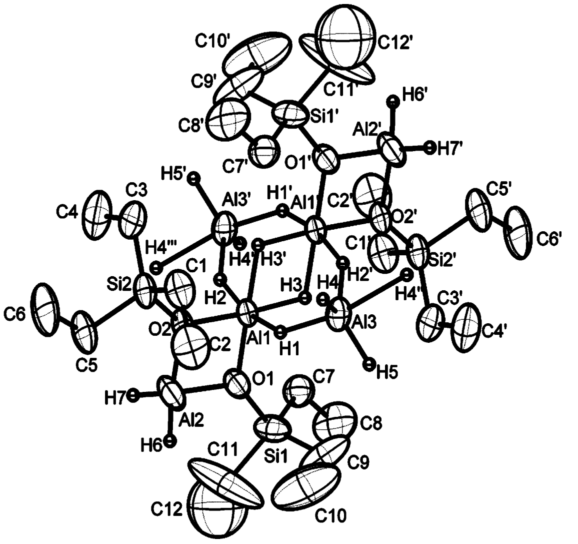

Figure 2. Part of the crystal structure of compound **1** (thermal ellipsoids with 50% probability). Hydrogen atoms on the carbon atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Al(1)−H(1) = 1.70(3), Al(1)−H(2) = 1.80(3), Al(1)−H(3) = 1.69(3), Al(1)−H(3′) = 1.73(3), Al(1)−O(1) = 1.872(2), Al(1)−O(2) = 1.852(2), Al(2)−H(6) = 1.55(5), Al(2)−H(7) = 1.51(5), Al(2)−O(1) = 1.837(2), Al(2)−O(2) = 1.849(2), Al(3)−H(1) = 1.73(3), Al(3)−H(2′) = 1.55(3), Al(3)−H(4) = 1.57(3), Al(3)−H(4″) = 2.17(3), Al(3)−H(5) = 1.48(4), Si(1)−O(1) = 1.694(2), Si(2)−O(2) = 1.685(2); H(3)−Al(1)−H(3′) = 76(2), Al(1)−H(3)−Al(1′) = 104(2), H(1)−Al(1)−H(2) = 168(1), O(1)−Al(1)−H(2) = 93(1), O(2)−Al(1)−H(2) = 92(1), H(3′)−Al(1)−H(2) = 81(2), H(3)−Al(1)−H(2) = 85(1), H(3)−Al(1)−H(1) = 88(1), H(3′)−Al(1)−H(1) = 88(1), O(1)−Al(1)−O(2) = 83.0(1), O(1)−Al(1)−H(3) = 99.7(9), O(2)−Al(1)−H(3) = 176(1), O(1)−Al(1)−H(1) = 97(1), O(2)−Al(1)−H(1) = 95(1), O(1)−Al(1)−H(3) = 173.3(9), O(2)−Al(1)−H(3′) = 100.8(9), Al(2)−O(1)−Al(1) = 96.3(1), Al(2)−O(2)−Al(1) = 96.6(1), O(1)−Al(2)−O(2) = 84.0(1), Si(1)−O(1)−Al(1) = 135.4(1), Si(1)−O(1)−Al(2) = 128.2(1), Si(2)−O(2)−Al(1) = 134.9(1), Si(2)−O(2)−Al(2) = 128.4(1), H(6)−Al(2)−H(7) = 117(3), O(2)−Al(2)−H(7) = 116(2), H(6)−Al(2)−O(1) = 111(2), H(7)−Al(2)−O(1) = 110(1), H(6)−Al(2)−O(2) = 113(1), H(4)−Al(3)−H(5) = 120(4), H(2′)−Al(3)−H(5) = 120(3), H(1)−Al(3)−H(5) = 100(3), H(4″)−Al(3)−H(5) = 90(3), H(2′)−Al(3)−H(4) = 113(3), H(1)−Al(3)−H(2′) = 91(3), H(2′)−Al(3)−H(4″) = 79(3), H(1)−Al(3)−H(4) = 104(3), H(4)−Al(3)−H(4″) = 76(3), H(1)−Al(3)−H(4″) = 168(3).

$P2_1/n$; see Table 1). Using a simple covalent model, compound **1** may be regarded as an adduct between tetramers of the monosiloxyalane, $[H_2Al(OSiEt_3)]_4$, and dimers of alane, $(AlH_3)_2$ (Figure 1). These two units are connected by hydride bridges to a one-dimensional, polymeric strand. In the middle of the Al_2H_6 unit and the $[H_2Al(OSiEt_3)]_4$ tetramer, both of which contain a Al_2H_2 cycle, there are crystallographic inversion centers.

The tetrameric building block in **1** can be formally separated into $[R_3SiOAlH_2]_2$ dimers (see above), which are held together by Al−O−Al bridges. The oxygen atoms in these bridges are in a trigonal-planar coordination site of two aluminum atoms and a silicon atom. The sum of the angles within the Al_2O_2 rings is near 360° (found 359.9(1)°). The four aluminum atoms in the tetrameric block are arranged in an almost linear row (angle Al(2)⋯Al(1)⋯Al(1′) = 172.9(1)°) and, as may be concluded from inspection of Figures 1 and 2, a quasi-planar sheet is formed which includes all oxygen, all silicon, all aluminum, and parts of the hydrogen atoms. Six of the hydrogen atoms within $[H_2Al(OSiEt_3)]_4$ do not participate in the bonding within the sheet part of the structure and are oriented perpendicular to it (one hydrogen atom at Al(1) and two at Al(2); Figures 1 and 2). Interestingly, two other hydrogen atoms add to this perpendicular arrangement, formally belonging to the Al_2H_6 linkers, which are below and above the sheet structure subunit. Thus, on both sides of the molecular sheet two hydride bridges to a common aluminum atom (Al(3)) are present, as well as four terminal ones at Al(2) and Al(2′).

Table 1. Crystal Data and Structure Solution Parameters of Compounds 1 and 3

	1	3
empirical formula	$C_{24}H_{74}Al_6O_4Si_4$	$C_{24}H_{62}Al_2O_4Si_4$
formula mass	701.07	581.06
temp (K)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	*Pbcn*
unit cell dimens		
a (Å)	8.081(2)	10.480(2)
b (Å)	19.357(4)	16.344(3)
c (Å)	14.929(3)	22.310(4)
β (deg)	101.82(3)	
V (Å^3)	2285.7(9)	3821.4(12)
Z	2	4
density (Mg/m^3)	1.019	1.010
abs coeff (mm^{-1})	0.268	0.224
$F(000)$	768	1280
cryst size (mm^3)	0.6 × 0.5 × 0.3	0.5 × 0.5 × 0.3
θ range for data collecn (deg)	2.52−24.10	2.31−24.08
index ranges	$-8 \le h \le 8$, $-21 \le k \le 21$, $-17 \le l \le 17$	$-11 \le h \le 11$, $-18 \le k \le 18$, $-25 \le l \le 25$
no. of rflns collected	13 983	22 383
no. of indep rflns	3343 (R(int) = 0.0411)	2979 (R(int) = 0.0775)
completeness to θ = 24.10° (%)	92.0	98.2
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	3343/0/195	2979/0/158
goodness of fit on F^2	1.069	1.084
final R indices ($I > 2\sigma(I)$)		
R1	0.0535	0.0661
wR2	0.1511	0.1510
R indices (all data)		
R1	0.0670	0.0802
wR2	0.1615	0.1621
largest diff peak and hole (e Å^{-3})	1.023 and −0.566	0.388 and −0.258

A consequence of the different interactions between the aluminum and the hydrogen and oxygen atoms in compound **1** is the existence of three different coordination polyhedra around aluminum. While Al(1) is octahedrally surrounded by four hydrides and two oxygen atoms, Al(2) is tetrahedrally coordinated by two hydrides and two oxygen atoms and Al(3) has five hydrides as neighbors in a trigonal-bipyramidal site. The different coordination numbers of the three aluminum atoms are reflected by their distances to the atoms bonded to them, the aluminum atom with the highest number displaying the largest distances.

The Al−H bond lengths can be roughly divided into two groups: short Al−H bond lengths are found for terminal ligands (H(5), H(6), and H(7)) with values up to a maximum of 1.55 Å, and longer bond lengths are found for the bridging hydrides with values between 1.57 and 2.17 Å.

Compound **1** has been described so far as a polymeric adduct of $[H_2Al(OSiEt_3)]_4$ with Al_2H_6, the connection between the units occurring through hydride bridges. There are, of course, also other ways to view the structure: for example, by assigning charges to the two interacting structure blocks leading to the

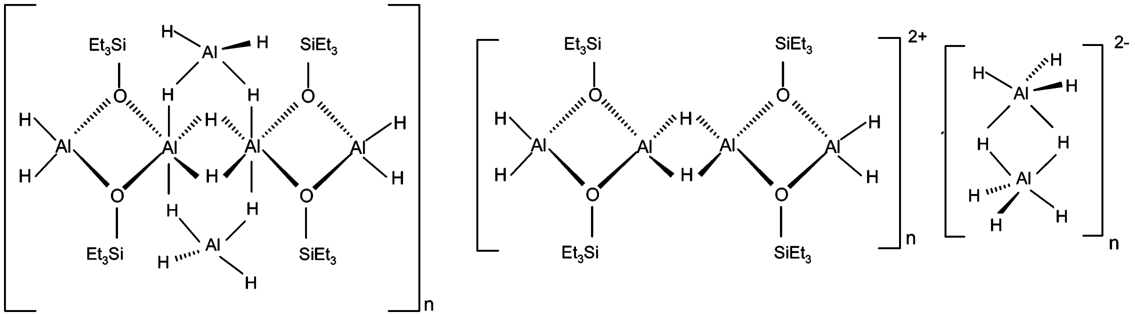

Figure 3. Two different formal descriptions of structure **1**.

formula $[Al_4(OSiEt_3)_4H_6]^{2+}[Al_2H_8]^{2-}$. A counterargument against such an ionic description of the compound may be derived by closer inspection of the Al−H bond lengths around the five-coordinate Al(3) atom. The axial bond lengths Al(3)−H(1) = 1.73 Å and Al(3)−H(4) = 2.17 Å are approximately 0.19−0.63 Å longer than the average value for the equatorial hydrides. These considerably different bond lengths are more compatible with adduct formation than with a more symmetric ionic model (see Figure 3).

The linear structure block of compound **1** resembles structural details of the polymer $(Me_3SiOAlH_2)_\infty$, which we have mentioned before.[8] This trimethylsilyl derivative forms alternate Al_2O_2 and Al_2H_2 cycles which are spirocyclically connected at the aluminum atoms. For crystal symmetry reasons the Al_2O_2 rings are planar, while the angle sum in the Al_2H_2 rings amounts to 358.9°. As every aluminum atom has a further hydrogen atom bonded to it, the chain of the four-membered cycles deviates considerably from linearity (Al···Al···Al angle 139.57°), in contrast to the similar structure element $(Et_3SiOAlH_2)_4$ in **1** (see above).[8]

Single crystals of $[(^tBuMe_2SiO)_2AlH]_2$ (**3**) can be obtained within a few minutes from saturated benzene solutions at room temperature. Compound **3** crystallizes in the orthorhombic crystal system in space group *Pbcn*, displaying a C_2 crystal point symmetry (Table 1). The compound is dimeric, with oxygen atoms serving as bridges between the aluminum atoms and with the peculiarity that the terminal hydrogen and siloxy ligands are in *syn and cis* orientations, respectively. Furthermore, the Al_2O_2 ring (angle sum 359.6(1)°) is almost planar (Figure 4).

As expected, the larger angles in the ring are found at the oxygen atoms, 95.3(1)°, while the angle at the softer aluminum atoms is 84.6°. The sum of the angles at the bridging oxygen atoms amounts to 359.4(1)°, consistent with the usual almost trigonal planarity.

The aluminum−μ_3-oxygen bond lengths of the bridging siloxy group are approximately 0.15 Å longer than the Al−μ_2-O bond lengths of the terminal siloxy ligands, reflecting the different coordination numbers. The different Si−O bond lengths can be explained in a similar way. Compound **3** shows, unlike the case for the bis(alkoxo)alane $[(^tBuO)_2AlH]_2$, a *syn* (*cis*) position of the siloxy ligands with respect to each other, which we ascribe to the steric requirements and not to the different atoms bonded to oxygen.

Single crystals of $[(^tBuMe_2SiO)_5Al_2H]$ (**4**) were obtained from a benzene solution at room temperature within a few days. Unfortunately, all crystals were of bad quality, excluding an exact crystal structure determination. Even using split positions in the siloxy groups we obtained only an *R* value of 0.22. In Figure 5 a model of the structure of **4** is given without further details. However, the NMR spectra of the compound confirm the overall principle of the structure.

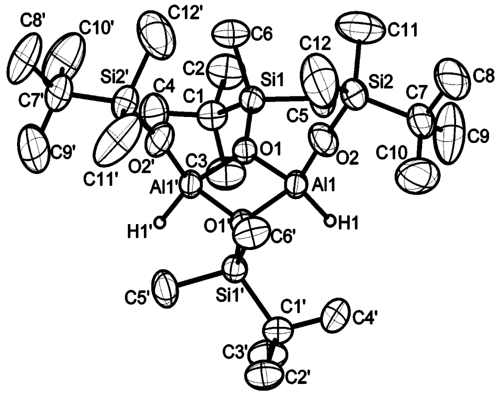

Figure 4. Molecular structure of $[(^tBuMe_2SiO)_2AlH]_2$ (**3**) (thermal ellipsoids with 50% probability). Hydrogen atoms on the carbon atoms have been omitted for clarity. Selected distances (Å) and angles (deg): Al(1)···Al(1′) = 2.721(2), Al(1)−O(1′) = 1.832(2), Al(1)−O(1) = 1.850(2), Al(1)−O(2) = 1.691(3), Si(1)−O(1) = 1.692(2), Si(2)−O(2) = 1.626(3), O(1)···O(1) = 2.477(4), Al(1)−H(1) = 1.51(4); O(1′)−Al(1)−O(1) = 84.6(1), H(1)−Al(1)−O(1) = 111.1(9), H(1)−Al(1)−O(1′) = 113.0(9), O(1′)−Al(1)−O(2) = 111.3(1), O(1)−Al(1)−O(2) = 111.3(1), H(1)−Al(1)−O(2) = 120.1(9), O(1)···O(1′)−Si(1′) = 174.3(1), Al(1′)−O(1)−Al(1) = 95.3(1), Si(1)−O(1)−Al(1) = 127.4(1), Si(1)−O(1)−Al(1′) = 136.7(1).

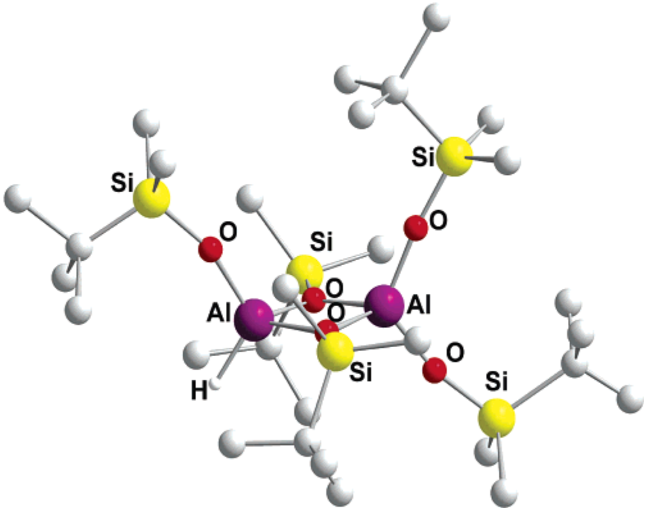

Figure 5. Structural model from a preliminary structure determination of compound **4**. Hydrogen atoms on the carbon atoms have been omitted for clarity.

Experimental Section

General Considerations. All compounds were synthesized under dry nitrogen using standard Schlenk techniques. The solvents were dried with appropriate agents and were distilled before use. The elemental analyses of the compounds were carried out using a CHN analyzer from LECO Corp., St. Joseph, MI. The NMR spectra were obtained using Bruker 200 MHz spectrometers, Models AC 200 F (^{1}H and ^{13}C spectra) and AC 200 P (^{29}Si spectra), using d_6-benzene, toluene, or tetrahydrofuran (thf) as solvent; MAS NMR were obtained on a Bruker MSL-200 instrument.

Crystal Structure Determinations. For single-crystal X-ray diffraction analyses an Image Plate (IPDS I, Stoe, Darmstadt, Germany) was used. The structure calculations were performed with SHELXS97[27] and the graphical representation with Diamond 3.[28]

$[(Et_3SiOAlH_2)_2 \cdot AlH_3]_n$ (1). During 5 min a solution of 2.84 g (21.26 mmol) of anhydrous aluminum trichloride in 30 mL of diethyl ether was added to an ice-cooled suspension of 2.42 g (63.79 mmol) of lithium aluminum hydride in 45 mL of diethyl ether. After the mixture had been stirred for another 5 min, a solution of 15.0 g (113.4 mmol) of triethylsilanol in 10 mL of diethyl ether was added dropwise during 20 min. A strong evolution of hydrogen ensued. The mixture was stirred for 3 h, and subsequently the precipitated lithium chloride was removed by filtration. After the removal of the solvent under vacuum, a white solid was obtained, which was purified by washing several times with *n*-hexane, affording transparent, colorless crystals (yield 50%) by cooling a saturated hexane solution to 0 °C. Compound **1**, just as the other compounds described in this paper, is *very pyrophoric and must be handled under a protective gas*.

Anal. Found for $C_{12}H_{37}Al_3O_2Si_2$ (mol wt 350.54): C, 40.36; H, 10.82; Al, 23.17. Calcd: C, 41.12; H, 10.64; Al, 23.09. ^{1}H MAS NMR: δ 0.59−1.27 (broad, C_2H_5), = 3.54−3.92, 4.50 (broad, several signals Al−H). ^{13}C NMR: δ 7.02 (broad, C_2H_5). ^{29}Si NMR: δ 26.01 (s, $OSiEt_3$). ^{27}Al NMR: δ 6.44 (s, octahedrally coordinated), 33.37 (s, trigonal bipyramidally coordinated), 120 (s, tetrahedrally coordinated). IR (Nujol, 2000−1500 cm^{-1}): 1840, 1861, 1888 (ν(Al−H), terminal), 1550−1750 cm^{-1} (ν(Al−H), bridging).

$[^tBuMe_2SiOAlH_2]_2$ (2), $[(^tBuMe_2SiO)_2AlH]_2$ (3), and $[(^tBuMe_2SiO)_5Al_2H]$ (4). The syntheses of compounds **2**−**4** were performed in an analogous manner using *tert*-butyldimethylsilanol instead of triethylsilanol. The molar ratios of the reactants ($LiAlH_4/AlCl_7$ (0.75/0.25) with respect to silanol) were chosen as 1 (**2**), 2 (**3**) and 2.5 (**4**).

$[^tBuMe_2SiOAlH_2]_2$ (2). The crude product of **2** was purified by sublimation at 50°C/0.05 mbar. Yield: 64%. Anal. Found for $C_{12}H_{34}Al_2O_2Si_2$ (mol wt 320.54): C, 43.57; H, 10.64; Al, 16.41. Calcd: C, 44.97; H, 10.69; Al, 16.84. ^{1}H NMR (benzene): δ 0.19 (s, 12 H, $-SiCH_3$), 0.91 (s, 18 H, $-C(CH_3)_3$), 4.45 (broad, 4 H, AlH_2). ^{13}C NMR (benzene): δ −4.5 ($-Si\mathit{C}H_3$), 17.9 ($-\mathit{C}(CH_3)_3$), 24.9 ($-C(\mathit{C}H_3)_3$). ^{29}Si NMR (benzene): δ 27.3 (bridging siloxy group). ^{1}H NMR (thf): δ 0.02 (s, 6 H, $-SiCH_3$), 0.94 (s, 9 H, $-C(CH_3)_3$). ^{13}C NMR (thf): δ −2.1 ($-Si\mathit{C}H_3$), 18.7 ($-\mathit{C}(CH_3)_3$), 26.4 ($-C(\mathit{C}H_3)_3$). ^{29}Si NMR (thf): δ 3.1 (terminal siloxy group). IR (Nujol): 1857 (ν(Al−H)), 844 (Al_2O_2 ring-mode$_{as}$), 795 (ν(Si−O), bridging groups), 764 (δ(Al−H)), 675 cm^{-1} (Al_2O_2 ring-mode).

$[(^tBuMe_2SiO)_2AlH]_2$ (3). The solid crude product of **3** was sublimed at 130 °C/0.05 mbar in an ice-cooled glass tube. Yield: 82%. Mp: 113−118 °C. Single crystals were grown from toluene solutions at room temperature. Anal. Found for $C_{24}H_{62}Al_2O_4Si_4$ (mol wt 581.06): C, 48.33; H, 10.61; Al, 9.18. Calcd: C, 49.61; H, 10.76; Al, 9.29. ^{1}H NMR (benzene): δ 0.22 (s, 12 H, $-SiCH_3$, terminal), 0.28 (s, 12 H, $-SiCH_3$, bridging), 0.95 (s, 18 H, $-C(CH_3)_3$, bridging), 1.09 (s, 18 H, $-C(CH_3)_3$, terminal). ^{13}C NMR (benzene): δ −3.2 ($-Si\mathit{C}H_3$, bridging), −2.0 ($-Si\mathit{C}H_3$, terminal), 17.9 ($-\mathit{C}(CH_3)_3$, bridging), 18.3 ($-\mathit{C}(CH_3)_3$, terminal), 25.3 ($-C(\mathit{C}H_3)_3$, bridging), 26.0 ($-C(\mathit{C}H_3)_3$, terminal). ^{29}Si NMR (benzene): δ 6.4 (terminal), 26.8 (bridging). ^{1}H NMR (thf): δ 0.08 (s, 12 H, $-SiCH_3$), 0.99 (s, 18 H, $-C(CH_3)_3$). ^{13}C NMR (thf): −2.0 ($-Si\mathit{C}H_3$), 18.8 ($-\mathit{C}(CH_3)_3$), 26.4 ($-C(\mathit{C}H_3)_3$). ^{29}Si NMR (thf): δ 3.2 (terminal siloxy groups). IR (Nujol): 1892 (ν(Al−H)), 1063 (ν(Si−O), terminal groups), 845 (Al_2O_2 ring-mode$_{as}$), 796 (ν(Si−O), bridging groups), 773 (δ(Al−H)), 674 (Al_2O_2 ring-mode$_s$).

$[(^tBuMe_2SiO)_5Al_2H]$ (4). Compound **4** was purified by recrystallization from diethyl ether. Yield: 52%. Mp: 148 °C. Anal. Found for $C_{30}H_{76}Al_2O_5Si_5$ (mol wt 711.33): C, 48.99; H, 10.80; Al, 7.70. Calcd: C, 50.66; H, 10.77; Al, 7.59. ^{1}H NMR (benzene): δ 0.18, 0.19, 0.22 (3s, 18 H, $-SiCH_3$, terminal), 0.33, 0.35 (2s, 12 H, $-SiCH_3$, bridging), 0.99 (s, 18 H, $-C(CH_3)_3$, bridging), 1.04, 1.05, 1.07 (3s, 27 H, $-C(CH_3)_3$, terminal). ^{13}C NMR (benzene): δ −2.0, −1.9 ($-Si\mathit{C}H_3$, bridging), −0.9, −1.1, −1.1 ($-Si\mathit{C}H_3$, terminal), 18.8 ($-\mathit{C}(CH_3)_3$, bridging), 19.0, 19.1, 19.2 ($-\mathit{C}(CH_3)_3$, terminal), 26.4 ($-\mathit{C}(CH_3)_3$, bridging), 26.9, 26.9, 27.0 ($-C(\mathit{C}H_3)_3$, terminal). ^{29}Si NMR (benzene): δ 5.8, 6.4, 7.3 (terminal), 26.8 (bridging). IR (Nujol): 1892 (ν(Al−H)), 1063 (ν(Si−O), terminal groups), 844 (Al_2O_2 ring-mode$_{as}$), 794 (ν(Si−O), bridging groups), 773 (δ(Al−H)), 676 cm^{-1} (Al_2O_2 ring-mode$_s$). Crystal data: monoclinic, space group $P2_1/m$, a = 16.918(3) Å, b = 14.393(3) Å, c = 19.129(4) Å, β = 99.12(3)°; V = 4599.0 Å^3, Z = 4.

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Supporting Information Available: Figures giving ^{1}H, ^{13}C, ^{29}Si MAS NMR spectra of compound **1** and IR spectra of compounds **1**−**4** and CIF files giving further details of the crystal structure determination (compounds **1** and **3**), including bond lengths, bond angles, and anisotropic and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) This seems to be a general effect when both aluminum and silicon are present in the molecule, even using different catalysts. This was found to be the case for almost 50 different compounds (LECO-900 instrument).