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Dimethylsiloxy-aluminiumdihalide dimers. Molecular structures of $[Me_2HSiOAlX_2]_2$ (X = Cl, I) and $[Me_3SiOAl(BH_4)_2]_2$

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Abstract

sym-Tetramethyldisiloxane $Me_2HSiOSiHMe_2$ is cleaved by aluminium trihalides AlX_3 (X = Cl, Br, I) to give dimethylhalosilanes Me_2HSiX and alumosiloxane dimers $[Me_2HSiOAlX_2]_2$ (x = (Cl, **1**; Br, **2**; I, **3**). Treatment of **1** with four equivalents of methyllithium yields the dimeric tetramethylsiloxalane $[Me_2HSiOAlMe]_2$, **4**, which is also available from $Me_2HSiO–SiHMe_2$ and Me_2AlCl. Compounds **1–4** have been identified and characterized by their physical data, analytical data, NMR and mass spectra. The crystal structures of the dichloride and the diiodide dimers have been determined by single crystal X-ray diffraction studies. The molecules have a planar, centrosymmetrical $SiOAl_2OSi$ skeleton with three-coordinate oxygen atoms and pseudo-tetrahedral four-coordinate aluminium atoms. Gallium trichloride cleaves methyl groups from *sym*-tetramethyldisiloxane to give methylgallium dichloride and polymeric by-products.

Dimeric trimethylsiloxyaluminium-bis(tetrahydridoborate), **5**, prepared in previous studies, has also been investigated by an X-ray diffraction study. The $SiOAl_2OSi$ skeleton of the dimer $[Me_3SiOAl(BH_4)_2]_2$ resembles that of **1** and **3**, but the aluminium atoms are hexacoordinated by two bidentate BH_4 groups and the two siloxy oxygen atoms.

1. Introduction

There is considerable interest in alkylsiloxyaluminiumalkyls and -aluminium halides because of the catalytic activity of such species in processes such as Ziegler–Natta polymerisation and olefin metathesis [1]. Previous work on alumosiloxanes (“siloxalanes”) having Si–O–Al linkages in the basic skeleton was undertaken in a search for new inorganic polymers [2–4]. This area of research is receiving renewed attention from the material science point of view. Sol-gel processes or chemical vapour deposition techniques can be expected to give new alumosiloxane or alumosilicate products with properties tailored for special applications, *e.g.* in surface technology.

We have resumed our earlier studies in this field [2,5–8] with siloxane precursors having hydride ligands on the silicon atoms. This should give the corresponding siloxalanes different solubility characteristics, higher volatility through lower molecular masses, and improved fragmentation behaviour through lower thermal stability. In contrast to the rather inert Si–Me bonds, the Si–H bond could also enter into hydrolysis or hydrosilylation reactions of primary products having siloxalane components integrated into oligomers or polymers.

In this first part we report on the compounds prepared from *sym*-tetramethyldisiloxane $Me_2HSiO-SiHMe_2$, a stable, colourless, not spontaneously inflammable, distillable liquid that is readily available by hydrolysis of chlorodimethylsilane formed in the Rochow–Müller process.

2. Results

2.1. *Preparation and properties of the compounds*

Like hexamethyldisiloxane ($Me_3SiOSiMe_3$) [2,4,8,10,11], 1,1,3,3-tetramethyldisiloxane ($HMe_2SiOSiMe_2$-H) was found to react smoothly with a slurry of one equivalent of anhydrous aluminium tri-chloride, -bromide or -iodide in toluene at room temperature to give high yields of the corresponding dimethylhalosi-

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* Dedicated to Professor M.G. Voronkov in recognition of his contributions to organosilicon chemistry.

lanes and dimethylsiloxyaluminium dihalides (**1**–**3**). The products can be isolated by fractional distillation and vacuum sublimation, respectively [eqn. (1)]. The chloro- and bromo-alumosiloxanes obtained are colourless, strongly hygroscopic compounds with melting points just above room temperature (**1**: m.p. 32°C, **2**: m.p. 45°C), while the iodo-analogue is much less volatile and has a much higher melting point (**3**: m.p. 140°C). Compounds **1**–**3** fume strongly in air, **3** rapidly turning brown owing to decomposition of the HI formed in the hydrolysis.

$$2\ \mathrm{Me_2HSi{-}O{-}SiHMe_2} + (\mathrm{AlX_3})_2 \longrightarrow$$

$$2\ \mathrm{Me_2HSiX} + [\mathrm{Me_2HSiO{-}AlX_2}]_2 \qquad (1)$$

1: X = Cl
2: X = Br
3: X = I

The compounds are soluble in inert polar solvents, such as di- or tri-chloromethane, and diethyl ether, but also in benzene or toluene. According to NMR spectroscopic data, solutions in benzene contain a single type of oligomer, which can be identified as the dimer by EI mass spectrometry. Solutions of **1** in chloroform appear to contain more than one oligomer, however, as shown by the presence of several NMR signals and higher m/z values in the CI mass spectra. However, the solids crystallized from solution, as well as the sublimates, consist solely of dimers, as shown by crystal structure determination (see below).

It should be noted that disiloxane ($H_3SiOSiH_3$) on reaction with aluminium halides gives only insoluble and involatile, probably polymeric siloxy-aluminium dihalides. Halosilanes and monosilane are identified as cleavage products. However, with dimethylaluminium bromide ($(Me_2AlBr)_2$), a sublimable product $[H_3SiOAlMe_2]_2$ could be isolated [12].

The chloro-compound **1** is easily converted into dimeric dimethylsiloxy-dimethylaluminium, **4**, by treatment with four equivalents of methyllithium in diethyl ether [eqn. (2)]. The same product is generated in the reaction of chlorodimethylaluminium with *sym*-tetramethyldisiloxane in hexane solvent [eqn. (3)], and from trimethylaluminium and oligomeric methylsiloxanes [13]. Compound **4** is obtained as a colourless, air-sensitive, distillable liquid in good yields:

$$\mathbf{1} + 4\ \mathrm{MeLi} \longrightarrow 4\mathrm{LiCl} + [\mathrm{Me_2HSi{-}O{-}AlMe_2}]_2 \qquad (2)$$

$$2\ \mathrm{Me_2HSi{-}O{-}SiHMe_2} + (\mathrm{Me_2AlCl})_2 \longrightarrow$$

$$2\ \mathrm{Me_2HSiCl} + [\mathrm{Me_2HSi{-}O{-}AlMe_2}]_2 \qquad (3)$$

4

The reaction of *sym*-tetramethyldisiloxane with anhydrous *gallium* trichloride does not afford the analogous dimethylsiloxy-galliumdichloride, but instead results in methylation of $GaCl_3$ to give $MeGaCl_2$, as observed previously for the reaction of $GaCl_3$ with hexamethyldisiloxane [9].

Treatment of **1** with four equivalents of lithium tetrahydridoborate did not give a stable borohydride complex, but instead mixed products that were difficult to characterize. In an attempt to clarify this point, the reaction of the analogous trimethylsiloxy compound with $LiBH_4$ was repeated [7]. The product (**5**) was obtained in good yield as described previously [7], and its structure determined by single crystal X-ray diffraction study (below). This confirmed the dimeric structure with hexacoordinate aluminium atoms (two bidentate borohydride ligands, two siloxide oxygen atoms) that was predicted from analytical and spectroscopic data [7].

$$\mathbf{1} + 4\ \mathrm{LiBH_4} \xrightarrow{/\!/} 4\ \mathrm{LiCl} + [\mathrm{Me_2HSiO{-}Al(BH_4)_2}]_2 \qquad (4)$$

$$[\mathrm{Me_3SiO{-}AlCl_2}]_2 + 4\ \mathrm{LiBH_4} \longrightarrow$$

$$4\ \mathrm{LiCl} + [\mathrm{Me_3SiO{-}Al(BH_4)_2}]_2 \qquad (5)$$

5

The ^1H, ^{13}C, and ^{29}Si NMR data for compounds **1**–**5** are summarized in the Experimental part. No major deviations from standard values for related reference compounds were observed.

2.2. *Crystal and molecular structures*

Compound **1** crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14), with two formula units (dimers) in the unit cell. The individual molecules have a crystallographic centre of inversion. Atomic coordinates are presented in Tables 1 and 2, and selected bond distances and angles are listed in the caption to Fig. 1.

TABLE 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1**. ($U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix. E.s.d.'s in parentheses)

Atom	x	y	z	U_{eq}
Al	0.15404(8)	0.01420(9)	0.46175(3)	0.036
Cl1	0.33381(8)	0.2146(1)	0.45905(4)	0.059
Cl2	0.22183(9)	0.2646(1)	0.39700(4)	0.056
Si	0.15456(7)	0.14328(9)	0.66093(3)	0.038
O	0.0729(2)	0.0609(2)	0.56504(8)	0.038
C1	0.3272(4)	−0.0260(4)	0.7004(2)	0.058
C2	0.2312(4)	0.3923(4)	0.6472(2)	0.058

TABLE 2. H Atom parameters for 1

Atom	*x*	*y*	*z*	U_{iso}
H	−0.002(3)	0.148(4)	0.715(1)	0.054(7)
H11	0.37814	0.02188	0.75517	0.05000
H12	0.42061	−0.03458	0.66012	0.05000
H13	0.27614	−0.15397	0.70756	0.05000
H21	0.31863	0.39613	0.61072	0.05000
H22	0.27551	0.44341	0.70144	0.05000
H23	0.13242	0.47151	0.62525	0.05000

Compound **3** crystallizes in the triclinic system, space group $P\bar{1}$ (No. 2), with two crystallographically independent formula units (dimers) in the unit cell. The two individual molecules each have a crystallographic centre of inversion. The structures of the two forms in the crystals of the tetraiodide **3** are very similar. Atomic coordinates and vibrational parameters are presented in Table 3, and selected bond distances and angles are given in the caption to Fig. 2.

Unexpectedly in view of the very different physical properties of the compounds (melting points, volatility, unit cell parameters *etc.*), the molecular structures of **1** and **3** are very similar. The molecular skeletons contain planar four-membered rings $(AlO)_2$ with the two silicon atoms also coplanar (not by crystallographical symmetry), as derived from sums of the valence angles at oxygen very close to 360°. Except for the AlX_2 part (X = Cl, I), the individual distances and angles are only marginally different for **1** and **3**, and also close to values for reference compounds [1,2,10].

Compound **5** crystallizes in the monoclinic system, space group $P2_1/n$ with two formula units in the unit cell. The individual molecules have a crystallographic centre of inversion. The $SiOAl_2OSi$ skeleton is again planar. Atomic coordinates are presented in Table 4, and selected bond distances and angles in the caption to Fig. 3.

The quality of the structural data allowed the localization of all hydrogen atoms of the molecule **5**. Thus the coordination environment of the aluminium atom,

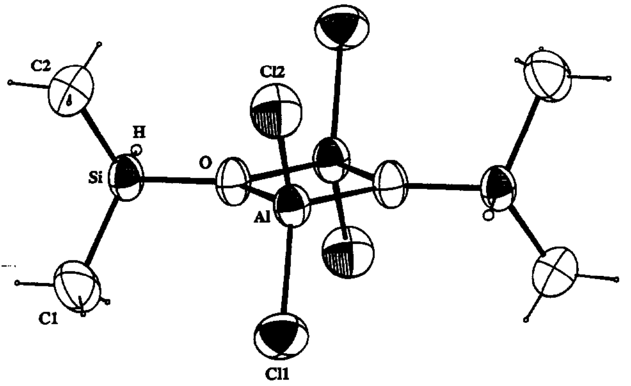

Fig. 1. Molecular structure of $[Me_2HSiO{-}AlCl_2]_2$, **1**, with atomic numbering scheme (ORTEP, 50% probability level; hydrogen atoms with arbitary radii). Selected distances and angles: Al–Cl1 2.080(1), Al–Cl2 2.084(1), Al–O 1.803(1), Al–Al 2.678(1), Si–O 1.703(1), Si–C1 1.831(3), Si–C2 1.828(3), Al′–O 1.813(1) Å. Cl1–Al–Cl2 116.2(1), Cl1–Al–O 114.0(1), Cl2–Al–O 113.6(1), Al–O–Al′ 95.6(1), O–Si–C1 107.8(1), O–Si–C2 108.0(1), C1–Si–C2 114.6(1), Al–O–Si 138.0(1), O–Al–O′ 84.4(1), Al′–O–Si 126.4(1)°.

TABLE 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for **3**. ($U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix. E.s.d.'s in parentheses)

Atom	*x*	*y*	*z*	U_{eq}
I1	0.25294(7)	0.67614(7)	0.09759(4)	0.043
I2	0.49841(8)	0.83486(8)	−0.19091(4)	0.049
Al1	0.4387(3)	0.8755(3)	−0.0245(2)	0.030
Si1	0.7971(3)	0.8142(3)	0.0271(2)	0.030
O1	0.6190(6)	0.9148(6)	0.0112(3)	0.027
C11	0.737(1)	0.6231(9)	0.1109(6)	0.043
C12	0.927(1)	0.786(1)	−0.0904(6)	0.041
I3	0.12621(9)	0.66777(7)	0.65743(4)	0.049
I4	0.38330(8)	0.62642(9)	0.37722(5)	0.056
Al2	0.1313(3)	0.5725(3)	0.5089(2)	0.033
Si2	−0.1180(3)	0.8258(3)	0.4313(2)	0.036
O2	−0.0552(6)	0.6321(6)	0.4702(3)	0.030
C21	−0.303(1)	0.875(1)	0.5227(6)	0.044
C22	−0.151(1)	0.839(1)	0.3135(6)	0.047

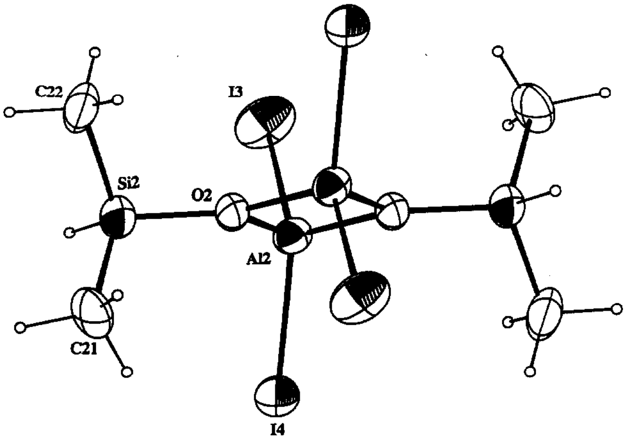

Fig. 2. Structure of one of the two crystallographically independent, but very similar molecules $[Me_2HSiO{-}AlI_2]_2$, **3**, with atomic numbering scheme (ORTEP, 50% probability level, hydrogen atoms with arbitrary radii). Selected distances and angles: *Molecule 1*: Al1–I1 2.477(2), Al1–I2 2.469(2), Al1–O1 1.802(5), Al1′–O1 1.830(8), Al1–Al1′ 2.699(5), Si1–O1 1.711(5), Si1–C11 1.827(8), Si1–C12 1.838(8). I1–Al1–I2 116.2(1), I1–Al1–O1 112.7(2), I2–Al1–O1 114.1(2), Al1–O1–Al1′ 96.2(3), Al1–O1–Si1 137.8(3), Al1′–O1–Si1 126.0(4), O1–Al1–O1′ 83.8(3). *Molecule II*: Al2–I3 2.478(2), Al2–I4 2.459(2), Al2–O2 1.811(5), Al2′–O2′ 1.817(5), Al2–Al2′ 2.691(5), Si2–O2 1.706(5), Si2–C21 1.849(8), Si2–C22 1.819(8) Å. I3–Al2–I4 116.7(1), I3–Al2–O2 111.9(2), I4–Al2–O2 112.4(2), Al2–O2–Al2′ 95.9(4), O2–Al2–O2′ 84.1(3), Al2′–O2–Si2 137.0(5). Al2–O2–Si2 126.5(3).

TABLE 4. Fractional atomic coordinates and equivalent isotropic displacement parameters for **5**. ($U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix. E.s.d.'s in parentheses)

Atom	x	y	z	U_{eq}
Si1	0.0206(2)	−0.00217(7)	0.23805(8)	0.044
Al1	−0.0770(1)	−0.09587(7)	0.49245(8)	0.037
O1	0.0082(3)	−0.0007(1)	0.3911(2)	0.036
C1	0.2095(7)	0.0901(3)	0.2074(3)	0.063
C2	−0.2211(7)	0.0325(3)	0.1587(3)	0.067
C3	0.0897(6)	−0.1336(3)	0.2011(3)	0.059
B1	−0.3760(7)	−0.1295(4)	0.4234(5)	0.049
B2	0.0836(8)	−0.2309(3)	0.5517(5)	0.048
H11	−0.453(8)	−0.086(3)	0.362(5)	0.11(2)
H12	−0.433(7)	−0.192(4)	0.452(4)	0.12(2)
H13	−0.331(6)	−0.084(3)	0.483(3)	0.06(1)
H14	−0.247(6)	−0.160(3)	0.389(4)	0.08(1)
H21	0.174(7)	−0.219(3)	0.616(4)	0.10(2)
H22	0.050(7)	−0.299(4)	0.515(4)	0.11(2)
H23	−0.039(6)	−0.200(3)	0.588(3)	0.08(1)
H24	0.107(5)	−0.183(3)	0.486(4)	0.08(1)

i.e. the hapticity of the borohydride ligands at the metal atoms, could be unambiguously determined. The BH_4 groups function as chelating η^2-ligands, with two hydrogen atoms in terminal and two hydrogen atoms in bridging positions (B–H–Al). The environment of the aluminium atoms is therefore distorted octahedral.

In summary, the present work has shown that the new dimethylsiloxy aluminium halides and alkyls have properties expected in the light of those of the trimethylsiloxy aluminium analogues prepared previously [1,2,4,8,10,11]. With essentially the same $SiOAl_2OSi$ skeleton, the compounds have lower melting points, higher volatility, and enhanced chemical reactivity, owing to lower molecular mass and reduced steric hindrance. The structure proposed in previous studies [7] for the trimethylsiloxy aluminium-bis(tetrahydroborate) **5** was confirmed, but its dimethylsiloxy analogue could not be isolated. It is assumed that the SiH function shows affinity for the neighbouring borohydride groups and thus induces decomposition through a redistribution of substituents.

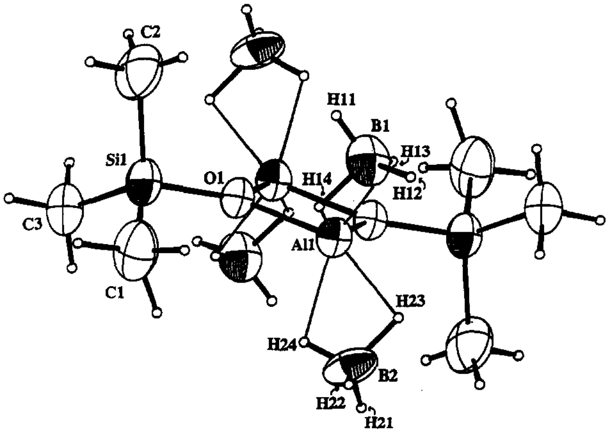

Fig. 3. Molecular structure of $[Me_3SiO{-}Al(BH_4)_2]_2$, **5**, with atomic numbering (ORTEP, 50% probability level, hydrogen atoms with arbitrary radii). Selected distances and angles: Si–O 1.707(2), Si–C1 1.844(4), Si–C2 1.842(4), Si–C3 1.844(4), Al–O 1.823(2), Al–B1 2.156(5), Al–B2 2.143(4), Al–Al' 2.720(2) Å. O–Si–C1 107.8(1), O–Si–C2 108.0(2), O–Si–C3 106.2(1), O–Al–B1 107.2(2), O–Al–B2 123.6(2), Al–O–Al' 96.5(1), O–Al–O' 83.5(1), Si–O–Al 131.7(1), Si–O–Al' 126.06(1)°.

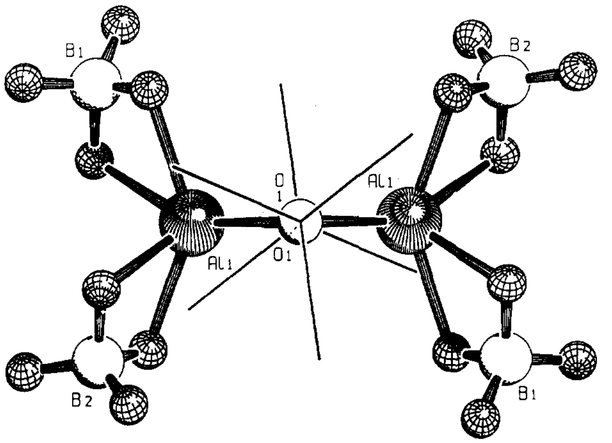

Fig. 4. Projection of the molecular structure of compound **5** down the Si–O axes, showing the staggered conformation of the trimethylsilyl groups and details of the aluminium coordination (SCHAKAL).

Work on *mono*methylsiloxides is in progress.

3. Experimental details

3.1. General

The experiments were routinely carried out under pure, dry nitrogen. Solvents were dried, and then saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. NMR: Spectrometer Jeol JMX-GX-400 (25°C, TMS as a reference). MS: Varian MAT 311A (EI at 70 eV); Finnigan MAT 90 (CI with isobutane). Microanalyses were performed at the local laboratory. Tetramethyldisiloxane was kindly provided by Wacker-Chemie GmbH, Burghausen. Anhydrous aluminium trihalides and dimethylaluminium chloride were purchased (Merck, Aldrich).

Caution: Compounds **1–5** are extremely sensitive to moisture and highly corrosive. Grease is readily attacked. Pressure build-up with inflammable gases has been observed even in tightly-closed vessels. Samples of compound **4** explode on contact with water. Powdered **5** ignites in the air.

3.2. Preparation of bis(dimethylsiloxy-aluminiumdihalides), 1–3

Finely-ground aluminium trihalide is dispersed in toluene at 0°C and equimolar quantities of tetramethyldisiloxane are added during 1 h with stirring. The mixture is stirred for a further 12 h at ambient temperature to give an almost clear and colourless solution. Precipitates, which originate in oxide contamination of the AlX_3 precursor, are removed by filtration. The solvent is removed from the filtrate and the residue purified by distillation, in a vacuum.

1: $AlCl_3$ (40.0 g, 0.30 mol); $(HMe_2Si)_2O$ (40.3 g, 0.30 mol). Yield 41.0 g (79%), ice-like colourless, deliquescent crystals, m.p. 32°C, b.p. 83–84°C/1 Torr. ^1H NMR (C_6D_6): $\delta = 0.18$ ppm (d, 6H, $J(HH) = 3.05$, $J(CH) = 121.5$ Hz, Me); 4.74 (sept, 1H, $J(SiH) = 220.3$ Hz, SiH). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = -0.74$ (s, $J(SiC) = 59.3$ Hz). ^{29}Si NMR (DEPT, C_6D_6): $\delta = 17.34$ (d · sept, $^2J(SiH) = 7.36$ Hz). MS (EI): $m/z = 329$ (73%, M − Me). Higher oligomers (tetramers and trimers) are observed in CI spectra. Anal. Found: C 13.64, H 4.00, Al 15.8, Cl 40.38. $C_4H_{14}Al_2Cl_4O_2Si_2$ (346.099) calc.: C 13.88, H 4.08, Al 15.6, Cl 40.07%.

2: $AlBr_3$ (12.22 g, 45.8 mmol), $(HMe_2Si)_2O$ (6.15 g, 45.8 mmol). Yield 8.40 g (70%), ice-like colourless crystals, m.p. 45°C, b.p. 95–100°C/1 Torr. ^1H NMR (C_6D_6): $\delta = 0.20$ (d, 6H, $J(HH) = 3.05$, $J(CH) = 120.9$ Hz, Me); 4.82 (sept, 1H, $J(SiH) = 221.0$ Hz, SiH). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = -0.48$ (s, $J(SiC) = 59.5$ Hz). ^{29}Si NMR (DEPT, C_6D_6): $\delta = 17.42$ (d · sept, $^2J(SiH) = 7.12$ Hz). Anal. Found: C 9.01, H 2.65. $C_4H_{14}Al_2Br_4O_2Si_2$ (523.904) calc.: C 8.39, H 2.39%.

3: AlI_3 (14.52 g, 35.6 mmol), $(HMe_2Si)_2O$ (4.78 g, 35.6 mmol). The mixture is protected against light. Yield 2.80 g (22.1%), colourless waxy crystals, m.p. 140°C, sublimes at 140°C/0.1 Torr. ^1H NMR (C_6D_6): $\delta = 0.28$ (d, 6H, $J(HH) = 3.05$, $J(CH) = 124.5$ Hz, Me); 4.98 (sept, 1H, $J(SiH) = 223.4$ Hz, SiH). $^{13}C\{^1H\}$ NMR

TABLE 5. Crystal data and structure solution parameters

	1	**3**	**5**
Formula	$C_4H_{14}Al_2Cl_4O_2Si_2$	$C_4H_{14}Al_2I_4O_2Si_2$	$C_6H_{34}Al_2B_4O_2Si_2$
Molecular mass	346.099	711.908	291.716
Temperature (°C)	−50	−50	−50
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$ [14]	$P\bar{1}$ [2]	$P2_1/n$ [14]
a (Å)	7.522(1)	8.391(3)	6.926(1)
b (Å)	6.896(1)	8.393(2)	13.071(2)
c (Å)	15.814(2)	14.811(5)	11.062(1)
α (°)	90	78.25(2)	90
β (°)	93.07(1)	74.44(3)	97.56(1)
γ (°)	90	85.81(2)	90
V (Å^3)	819.1	983.6	992.74
$\rho_{calc.}$ (g cm^{-3})	1.403	2.403	0.976
Z	2	2	2
$F(000)$ (e)	352	668	320
μ(Mo $K\alpha$) (cm^{-1})	9.6	64.6	2.5
Radiation, ($\lambda = 0.71069$ Å, Graphite monochromator)	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Diffractometer	Syntex $P2_1$	CAD4	Syntex $P2_1$
Scan	ω	$\theta 2-\theta$	ω
Scan range (θ) (°)	2–23	2–25	2–24
hkl range	±8, +8, +19	±9, ±9, +17	±7, +14, +12
Measured reflections	1728	3432	1547
Unique reflections	1465	3426	1547
R_{int}	0.018	0.034	0.000
Observed reflections	1368	2424	1185
$F_o \geq$	$2 \cdot \sigma(F_o)$	$4 \cdot \sigma(F_o)$	$4 \cdot \sigma(F_o)$
Refined parameters	68	140	105
Weighting scheme	$w = 1/(\sigma(F_o) + k \cdot F_o^2)$		
Weighting parameter l/k	2.1808/0.000212	2.3167/0.0	1.9916/0.0
H atoms (found/calcd.)	3/4	−/14	8/9
R	0.032	0.039	0.044
R_w	0.044	0.027	0.052
(shift/error)$_{max}$	0.001	0.001	0.000
$\Delta\rho_{fin}$(max/min) (e Å^{-3})	+0.35/−0.34	+0.97/−0.83	+0.24/0.29

(C_6D_6): $\delta = -0.10$ (s, $J(SiC) = 58.6$ Hz), ^{29}Si NMR (DEPT, C_6D_6): $\delta = 17.0$ (d · sept, $^2J(SiH) = 7.35$ Hz). Anal. Found: C 6.75, H 1.98. $C_4H_{14}Al_2I_2O_2Si_2$ (815.389) Calc.: C 7.02, H 2.01%.

3.3. Dimeric tetramethylsiloxalane, [bis(dimethylsiloxy-dimethylaluminium)], 4

(a) A solution of **2** (9.60 g, 27.7 mmol) in diethyl ether (50 ml) is cooled to 0°C with ice and treated with 69.3 ml of a 1.6 M solution of methyllithium in diethyl ether (30 min). A white precipitate is formed. After a further 75 min stirring at 0°C the mixture is filtered cold, the volatiles removed in a vacuum at ambient temperature, and the residue distilled to give a yield of 4.40 g (60%) of a colourless liquid, m.p. −50°C, b.p. 39–40°C/1 Torr.

(b) A solution of $(HMe_2Si)_2O$ (5.64 g, 42.0 mmol) in pentane (30 ml) is treated at 0°C with 41.6 ml of a 0.5 M solution of $Me_4Al_2Cl_2$ in hexane (20.8 mmol). After 2 h the volatiles are removed in a vacuum and the product distilled; yield 5.00 g (90%). ^1H NMR (C_6D_6): $\delta = -0.65$ (s, 6H, AlMe); 0.14 (d, 6H, $J(HH) = 3.05$, $J(CH) = 119.6$ Hz, SiMe); 4.72 (sept, 1H, $J(SiH) = 209.4$, SiH). $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = -8.84$ (s, br, AlMe); 0.09 (s, $J(SiC) = 58.0$ Hz, SiMe). ^{29}Si NMR (C_6D_6): $\delta = 4.66$ (d · sept, $^2J(SiH) = 7.35$). MS (EI): $m/z = 263$ (10%, M − H), 249 (100%, M − Me). Anal. Found: C 36.34, H 9.91. $C_8H_{26}Al_2O_2Si_2$ (264.426) calc.: C 36.42, H 9.68%.

3.4. Bis[trimethylsiloxy-aluminium-bis(tetrahydridoborate)], 5

This was prepared by the published procedure [7]. Similar experiments with **2** gave no analogous products but only mixtures, which could not be separated.

3.5. Reactions with gallium trichloride

The procedure described for **1**, carried out with equivalent quantities of $GaCl_3$ and $(Me_2HSi)_2O$, gave $MeGaCl_2$ as the only volatile (sublimable) product isolated in appreciable yield. [^1H NMR (C_6D_6): $\delta = -0.82$ ppm]. The large amount of insoluble and involatile material, probably polymeric, was not characterized any further.

3.6. Crystal structure determination

For compounds **1** (crystallized from pentane), **3** and **5** (both crystallized by sublimation) suitable crystals were sealed in capillaries under argon at dry ice temperature and placed in the diffractometer. Reduced cell calculations did not indicate higher symmetry. The measured reflections were corrected for Lorentz and polarization effects and in the case of **3** also for decay and absorption (3.9%; empirical absorption correction: $T_{min} = 0.880$, $T_{max} = 0.999$).

The structures were solved by direct methods (SHELXS-86), completed by Fourier synthesis and refined anisotropically by full matrix methods (SHELX-76). Hydrogen atoms attached to boron were located in final difference Fourier maps and refined isotropically. The remaining hydrogen atoms were placed in calculated positions (CH_3 for **1**, **3** and **5**; SiH for **3**) and included in the structure factor calculations with fixed atomic contribution $U_{iso} = 0.05$ Å^2. Further information on the structure solution and refinement is given in Table 5.

Details of the X-ray structure determinations can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 EggensteinLeopoldshafen 2, Germany, on quoting the depository number CSD-56274, the names of the authors, and the journal citation.

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