

(Ethyl-, Ethenyl- and Ethynylsilyloxy)aluminum Compounds Generated by Heterolytic Cleavage of 1,3-Disubstituted Disiloxanes

Peter Bissinger, Martin Paul, Jürgen Riede and Hubert Schmidbaur*

Anorganisch-chemisches Institut, Technische Universität München,
Lichtenbergstraße 4, D-85747 Garching

Received June 1, 1993

Key Words: Aluminosiloxanes / 1,3-Diorganodisiloxanes / Siloxane cleavage by aluminum halides

sym-Diorganodisiloxanes $\text{RH}_2\text{SiOSiH}_2\text{R}$ ($\text{R} = \text{C}_2\text{H}_5$, **7**; C_2H_3 , **8**; C_2H , **9**) are prepared by hydrolysis of organo(bromo)silanes which are available in high yields by the reaction of organo(phenyl)silanes with liquid HBr . Asymmetrical cleavage of these disiloxanes with AlCl_3 leads to the formation of organo(chloro)silanes and aluminosiloxane dimers $[\text{RH}_2\text{SiOAlCl}_2]_2$ ($\text{R} = \text{C}_2\text{H}_5$, **10**; C_2H_3 , **11**; C_2H , **12**). Crystal structure determinations of **11** and **12** reveal a planar centrosymmetrical SiOAl_2OSi skeleton with three-coordinate oxygen atoms and tetrahedral four-coordinate aluminum atoms. Treatment of

7–9 with Me_2AlCl yields volatile dimethylaluminumorganosilyl oxides $[\text{RH}_2\text{SiOAlMe}_2]_x$ ($\text{R} = \text{C}_2\text{H}_5$, **13**; C_2H_3 , **14**; C_2H , **15**; $x = 2, 3, 4$). NMR studies confirm the presence of more than one oligomer in solutions of these compounds. The asymmetrical compound $(\text{HC}\equiv\text{CSiH}_2\text{O})_2\text{Me}_3\text{Al}_2\text{Cl}$ (**16**), resulting from small amounts of MeAlCl_2 in the Me_2AlCl used, is isolated as a byproduct in the synthesis of **15**. The crystal structure of **16** shows a disorder of the molecules leading to pseudosymmetry with a center of inversion.

The catalytic activity of (alkylsilyloxy)aluminum halides and -aluminumalkyls in Ziegler-Natta polymerization and olefin metathesis is currently receiving considerable attention^[1]. Previous investigations of aluminosiloxanes ("siloxalanes"), organosiloxanes with Si—O—Al linkages in the basic skeleton, have been undertaken in attempts to design new inorganic polymers^[2–4], but there is also renewed interest in these compounds from the material science point of view. Aluminosiloxanes are expected to be promising precursors for the preparation of new aluminosilicate products via the sol-gel process or through chemical vapor deposition techniques for ceramics, glass and surface technology.

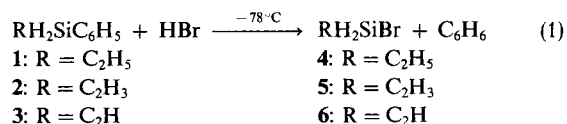
As a continuation of our own work in this field^[5] new symmetrically substituted disiloxanes have now been prepared via a general procedure that allows wide variations in R and gives high yields. By the attachment of *two hydride substituents* to the silicon atoms the corresponding siloxalanes should gain higher volatility through lower molecular mass and improved fragmentation behavior due to lower thermal stability^[6].

Following studies^[5] of the *monohydrido* species $\text{R}_2\text{HSiOSiHR}_2$ and $(\text{R}_2\text{HSiOAlX})_2$, we here report on the synthesis of the *dihydrido* compounds $\text{RH}_2\text{SiOSiH}_2\text{R}$ and the (organosilyloxy)aluminum compounds $(\text{RH}_2\text{SiOAlX})_2$ prepared by AlX_3 cleavage of these disiloxanes. NMR investigations of the aluminosiloxanes in solution and determination of the solid-state structures by single crystal X-ray diffraction have shown many interesting parallels and differences as compared to the analogous alkoxy derivatives in the association behavior^[6].

Preparation and Properties of 1,3-Diorganodisiloxanes

1,3-Diorganodisiloxanes are most readily prepared by the hydrolysis of organo(halogeno)silanes $(\text{RSiH}_2\text{X})_2$ ^[7]. Organo(halogeno)silanes have been synthesized in the past by se-

lective halogenation of organosilanes or by partial hydride reduction of organo(trihalogeno)silanes. These reactions often lead to mixtures of products and yields are rather unsatisfactory^[8]. A more sophisticated synthetic route is based on the cleavage of organo(phenyl)silanes with liquid HBr at -78°C ^[9]. In this reaction the aromatic hydrocarbon and the organo(bromo)silane are formed in virtually quantitative yield. Ethyl-, ethenyl- and ethynyl(bromo)silane have now been prepared according to this procedure.

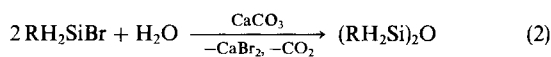


Ethyl(phenyl)silane (**1**) is the product of the reaction of phenyl(chloro)silane with ethylmagnesium bromide. *Ethenyl(phenyl)silane* **2** is obtained by the reduction of commercially available ethenyl(phenyl)dichlorosilane with lithium aluminium hydride, and *ethynyl(phenyl)silane* **3** is available from the reaction of phenyl(bromo)silane with sodium acetylide^[10]. The three compounds are colorless, air-stable liquids of distinct odor. Although the boiling points exceed 150°C , distillation under standard pressure is not accompanied by noticeable decomposition or substituent redistribution.

Compounds **1**, **2** and **3** react with excess liquid HBr within a few hours at -78°C to give almost quantitative yields of ethyl- (**4**), ethenyl- (**5**) and ethynyl(bromo)silane (**6**). No solvent is needed for the reaction. The reaction mixtures are colorless solutions of the corresponding organo(bromo)silanes in benzene, which can be used for the preparation of 1,3-diorganodisiloxanes without any further purification. The solutions are stable at room temperature, but fume vig-

ously in humid air. It is important to note that the reactions of ethenyl- (**2**) and ethynyl(phenyl)silane (**3**) with liquid HBr are completely regioselective. No phenyl(bromo)silane is formed.

Organo(bromo)silanes readily react with water to give 1,3-diorganodisiloxanes and HBr. In small-scale preparations the products are unaffected by the presence of the acid generated in the process^[7]. For larger quantities the addition of calcium carbonate as an acid scavenger helps to improve the overall yield.

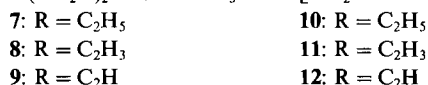


Dry calcium carbonate is inert to solutions of organo(bromo)silanes in benzene, but reacts with the HBr evolved in the reaction to give calcium dibromide and carbon dioxide. The calcium bromide is hygroscopic and absorbs any excess of water present after completion of the reaction.

1,3-Diethyl- (**7**), 1,3-diethenyl- (**8**) and 1,3-diethynyl-disiloxane (**9**) are volatile, colorless liquids (**7**: b.p. 89 °C, **8**: b.p. 84 °C, **9**: b.p. 80 °C) with an aromatic odor. They are perfectly stable in air and can be separated from benzene by cryofiltration and high-efficiency column distillation.

Preparation and Properties of (Monoorganosilyloxy)aluminum Dichlorides **10–12**

Hexamethyldisiloxane (Me₃SiOSiMe₃)^[11], 1,1,3,3-tetramethyldisiloxane (Me₂HSiOSiHMe₂)^[5] and disiloxane (H₃SiOSiH₃)^[12] are known to react smoothly with a slurry of anhydrous aluminum chloride in inert solvents to give silyloxyaluminum dichlorides. As byproducts of the heterolytic cleavage reactions of the siloxanes the corresponding organo(chloro)silanes are generated. Molecular mass studies by cryoscopy, crystal structure determination and NMR investigations have shown that di- and (triorganosilyloxy)aluminum dichlorides (Me_xH_{3-x}SiOAlCl₂, x = 2, 3) are dimeric in solution and in the solid state^[1,5,11,13], while the involatile and thermally unstable H₃SiOAlCl₂^[12] appears to be polymeric. It has now been shown that 1,3-diorganodisiloxanes are also readily cleaved by aluminum trichloride to give the analogous (monoorganylsilyloxy)aluminum dichlorides.

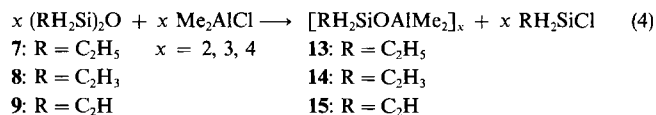


Already after very short reaction times (several minutes at 0 °C) the products can be isolated by fractional distillation or recrystallization from hydrocarbon solvents. They are very sensitive to moisture but can be stored under nitrogen in the refrigerator. While (ethylsilyloxy)aluminum dichloride **10** (m.p. 15 °C, b.p. 35 °C/0.1 mbar) has a lower melting point

and is considerably more volatile than the isomeric (dimethylsilyloxy)aluminum dichloride (m.p. 32 °C, b.p. 84 °C/1 mbar), the corresponding ethenyl derivative **11** melts well above room temperature (m.p. 35 °C) and can be distilled only with decomposition. The ethynyl derivative **12** finally is totally involatile (m.p. 102 °C, dec.). NMR studies of solutions in [D₆]benzene have shown that the three compounds are present as only one oligomer identified as the dimers for **11** and **12** by crystal structure determination. In the CI mass spectra of **10** and **12** peaks that can be assigned to higher oligomers have been discovered, but these may arise from rearrangements occurring under the high-energy conditions of the experiment.

Preparation and Properties of Dimethylaluminum Monoorganosilyl Oxides **13–15**

Heterolytic cleavage of the 1,3-diorganodisiloxanes **7**, **8** and **9** by chlorodimethylaluminum leads to the corresponding dimethylaluminum organosilyl oxides **13**, **14**, and **15** in good yields.



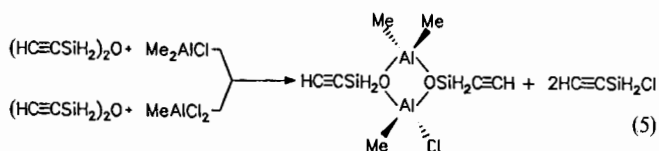
The products **13–15** are colorless liquids which are much more volatile than the corresponding chloro compounds (**10–12**), and can be distilled in a vacuum at room temperature. Compounds **13** to **15** are extremely air- and moisture-sensitive, thermolabile substances which should be handled with care. According to NMR spectroscopic data two (**13**, **15**) or three (**14**) oligomers are present in benzene solutions. ¹H-, ¹³C- and ²⁹Si-NMR spectra consistently show two or three distinguishable sets of resonances which can be assigned to di-, tri- and tetrameric species, respectively. Recent investigations of the homologous dimethylaluminum alkoxides have shown close analogies^[13]. Primary alkoxy compounds (which are valence-isoelectronic to monoorganosilyloxy species) have been found to exist as more highly aggregated oligomers, while secondary and tertiary alkoxides (valence-isoelectronic to di- and triorganosilyloxy species) appear solely as dimers.

Structure determinations have confirmed the presence of a planar Al₂O₂ ring for all dimethylaluminum silyl oxide and alkoxide dimers investigated to date^[1,5,13,14]. Electron diffraction on dimethylaluminum methoxide in the gas phase revealed the existence of trimers with a six-membered, chair-shaped Al₃O₃ ring^[15]. The ¹³C-NMR chemical shifts of the AlMe groups (which are virtually independent of the nature of the substituents at oxygen, but sensitive to the angle O¹-Al-O) seem to be the most reliable probe for the ring size of this type of compound^[6]. Taking these results as reference data, we can assign a tetrameric structure to compound **14**.

This assignment is confirmed by the results of CI mass spectral studies which show peaks for tri- and tetrameric species. It should be noted that the fragmentation pat-

terns of dimethylaluminum *monoorganosilyl* oxides e.g. $[\text{RH}_2\text{SiOAlMe}_2]_x$ show interesting differences as compared to the recently investigated dimethylaluminum *diorganosilyl* oxides $[\text{Me}_2\text{HSiOAlMe}_2]_2$.^[5] While the desintegration of the latter proceeds mainly via elimination of monomeric formula units, the former decompose mainly by losing organyl and organosilyl residues. This may have important consequences for the prospective use of these substances for depositing refractory materials.

Commercially available chlorodimethylaluminum Me_2AlCl contains impurities of dichloromethylaluminum MeAlCl_2 . This reagent cleaves disiloxanes to give (organosilyloxy)methylaluminum chlorides $\text{RH}_2\text{SiOAlMeCl}$, which react with the main product $(\text{RH}_2\text{SiOAlMe}_2)_2$ to give unsymmetrically substituted dimers (5).



Usually, these compounds cannot be separated due to their minute concentrations (< 1%). During the preparation of **15** the precipitation of a very small amount of a crystalline sample is detected which can be isolated. Single-crystal X-ray diffraction confirms the compound to be the unsymmetrically substituted dimer $(\text{HC}\equiv\text{CSiH}_2\text{O})_2(\text{Me}_3\text{Al}_2\text{Cl})$ **16**.

Crystal and Molecular Structures

Compounds **11**, **12** and **16** crystallize in the triclinic space group $P\bar{1}$ (No. 2) with two (**11**) or one (**12**, **16**) dimeric formula units in the unit cell. For **11** the two molecules found are crystallographically independent, but structurally virtually indistinguishable except for a minor disorder of the ethenyl group of one of the dimers. The dimers found in **11**,

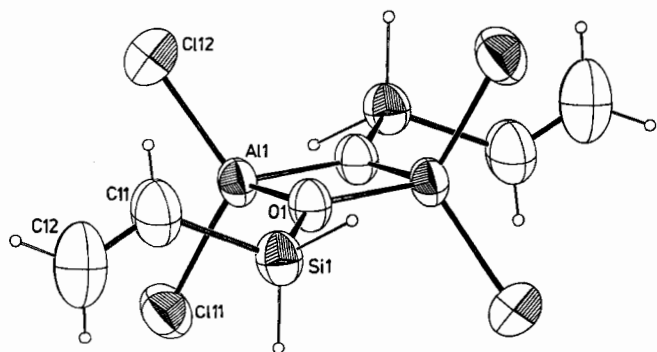


Figure 1. Molecular structure of dimeric ethynylsilyloxyaluminum dichloride **11**. Only one of two crystallographically independent molecules is shown. The molecule has a center of inversion (ORTEP, 50% probability level). Selected distances [\AA] and angles [$^\circ$]; *Molecule 1*: Al1—O1 1.805(4), Al1—O1' 1.814(4), Al1—Cl11 2.082(2), Al1—Cl12 2.082(2), Al1...Al1' 2.686(3), Si1—O1 1.698(4), Si1—C11 1.831(7), C11—C12 1.232(9); Al1—O1—Al1' 95.8(3), O1—Al1—O1' 84.2(2), Al1—O1—Si1 131.3(2), Al1'—O1—Si1 131.5(2), O1—Si1—C11 106.9(3); *Molecule 2*: Al2—O2 1.807(4), Al2—O2' 1.803(4), Al2—Cl21 2.075(3), Al2—Cl22 2.086(2), Al2...Al2' 2.684(3), Si2—O2 1.697(4); Al2—O2—Al2' 96.0(3), O2—Al2—O2' 84.0(2), Al2—O2—Si2 132.2(2), Al2'—O2—Si2 131.4(2)

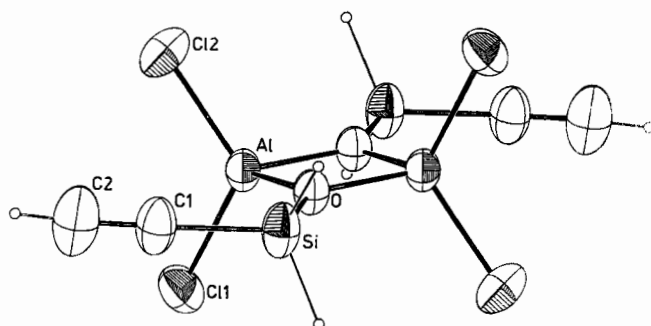


Figure 2. Molecular structure of dimeric ethynylsilyloxyaluminum dichloride **12**. The molecule has a center of inversion (ORTEP, 50% probability level). Selected distances [\AA] and angles [$^\circ$]: Al—O 1.815(1), Al—O' 1.819(1), Al—Cl1 2.083(1), Al—Cl2 2.076(1), Al...Al' 2.707(1), Si—O 1.682(1), Si—C1 1.819(2), C1—C2 1.159(3); Al—O—Al' 96.3(1), O—Al—O' 83.7(1), Al—O—Si 130.7(1), Al—O'—Si 132.7(1), O—Si—C1 104.7(1), Si—C1—C2 177.6(2)

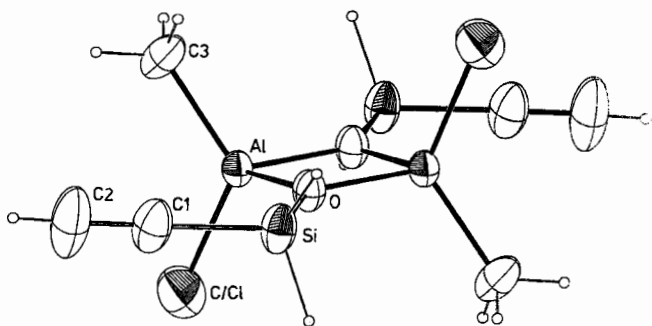


Figure 3. Molecular structure of bis(ethynylsilyloxy)trimethyl(chloro)dialuminum **16**. The disordered molecule has a pseudo-inversion symmetry (ORTEP, 50% probability level). Selected distances [\AA] and angles [$^\circ$]: Al—O 1.850(2), Al—O' 1.852(2), Al—Cl/C 2.085(2), Al—C3 1.931(3), Al...Al' 2.776(2), Si—O 1.651(2), Si—C1 1.817(3), C1—C2 1.169(6); Al—O—Al' 97.2(1), O—Al—O' 82.8(1), Al—O—Si 130.3(1), Al—O'—Si 132.2(1), Cl/C—Al—C3 121.0(1), O—Si—C1 106.3(2), Si—C1—C2 177.6(4)

12 and **16** feature planar Al_2O_2 four-membered rings at a center of inversion.

For all structures the silicon atoms are found to lie approximately in the plane of the central ring to give a trigonal planar coordination geometry at the oxygen atoms. The quality of all structures is high enough to allow detection of the positions of the hydrogen atoms at the silicon atoms. The carbon—carbon distances in the organic ligands are in accordance with standard data for double and triple bonds, respectively [**11**: 1.232(9); **12**: 1.159(3), **16**: 1.169(3) \AA].

Experimental

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 $^\circ\text{C}$, TMS as a reference). — MS: Varian MAT 311A (EI at 70 eV); Finnigan MAT 90 (CI with isobutane). Gaschromatographic analyses: Hewlett-Packard Mod. 5890, Series II with integrated mass detector (EI at 70 eV) and capillary column (HP1, cross-linked methylsilicon gum 12 m). — Microanalyses were performed at the local laboratory. — Phenyl(chloro)-, phenyl(bromo)silane^[16] and ethynyl(phenyl)silane^[10] **3** were ob-

tained by standard procedures. All other starting compounds were purchased (Aldrich, Fluka, ABCR).

Caution: Compounds **10–15** are extremely sensitive to moisture and highly corrosive. Grease is readily attacked^(1b). They are thermolabile and should be stored at temperatures below 0°C to avoid pressure build-up with inflammable gases due to decomposition. Samples of **13–15** explode on contact with water.

Preparation of Organo(phenyl)silanes 1, 2. — **1:** A Grignard solution is prepared from magnesium (25.3 g, 1.04 mol) and bromoethane (108.8 g, 1.00 mol) in 150 ml of diethyl ether. The Grignard reagent is added dropwise at 0°C to a stirred solution of phenyl(chloro)silane (141.9 g, 1.00 mol) in 200 ml of diethyl ether. After filtration from precipitated magnesium salts and removal of the solvent in vacuo the product is separated by distillation. Yield of **1** 103.7 g (77%), colorless liquid, b.p. 150°C/1 bar, purity 98% (GC-MS). — ¹H NMR (C₆D₆): δ = 0.60–1.15 (m, 5H, CH₂ and CH₃), 4.38 [t, 2H, SiH₂, ³J(HH) = 3.4 Hz], 7.02–7.18 (m, 3H, C_{ar}H), 7.31–7.51 (m, 2H, C_{ar}H). — ¹³C NMR (C₆D₆): δ = 2.6 [t, CH₂, ¹J(CH) = 121.3 Hz], 9.0 [q, CH₃, ¹J(CH) = 125.9 Hz], 128.2 [d, C_{3/5}, ¹J(CH) = 157.2 Hz], 129.8 [d · t, C₄, ¹J(CH) = 155.6, ²J(CH) = 7.0 Hz], 132.6 (s, C₁), 135.5 [d, C_{2/6}, ¹J(CH) = 157.9]. — ²⁹Si NMR (INEPT, C₆D₆): δ = -27.9 [t · m, ¹J(SiH) = 187.3 Hz]. — MS (GC-coupled), *m/z* (%): 136 [C₈H₁₂Si], 121 [C₇H₉Si], 105–109 (100) [C₆H₇Si].

2: A solution of ethenyl(phenyl)dichlorosilane (90.9 g, 0.45 mol) in 300 ml of diethyl ether is added dropwise to an ice-cooled suspension of lithium aluminum hydride (9.0 g, 0.24 mol) in 200 ml of diethyl ether. After filtration from precipitated salts and removal of the solvent in vacuo, the product is purified by distillation. Yield of **2** 52.2 g (87%), colorless liquid, b.p. 155°C/1 bar, purity >99% (GC-MS). — ¹H NMR (C₇D₈): δ = 4.58 [d, 2H, SiH₂, ³J(SiH) = 2.9 Hz], 5.77 [d · d, 1H, CH_{cis}, ³J(HH) = 19.0, ²J(HH) = 9.0 Hz], 5.91 [d · d, 1H, CH_{trans}, ³J(HH) = 14.7 Hz], 6.02 [d · d · t, 1H, CH_{gem}], 7.03–7.08 (m, 3H, C_{ar}H); 7.35–7.39 (m, 2H, C_{ar}H). — ¹³C NMR (C₇D₈): δ = 128.2 (m, C_{3/5}), 129.9 (m, C₄), 130.9 (m, CH₂), 131.2 (s, C₁), 135.6 [d, C_{2/6}, ¹J(CH) = 158.1 Hz], 136.9 [d, CH, ¹J(CH) = 153.7 Hz]. — ²⁹Si NMR (INEPT, C₇D₈): δ = -37.0 [t · m, ¹J(SiH) = 197.9 Hz]. — MS (CI), *m/z* (%): 131–135 (57) [C₈H₉Si], 104–108 (100) [C₆H₇Si], 53–59 (48) [C₂H₅Si]. — C₈H₁₀Si (134.25): calcd. C 70.40, H 7.27, Si 19.56; found C 71.57, H 7.51, Si 20.92.

Preparation of Organo(bromo)silanes 4–6. — **General Procedure:** To a weighed amount of the corresponding organo(phenyl)silane, twice the volume of liquid HBr is condensed at -196°C. After stirring the solution for several hours at -78°C excess HBr is removed by warming the flask to room temperature. The remaining mixture of the organo(bromo)silane in benzene is recondensed in vacuo and used without further purification.

4: **1** (98.4 g, 0.72 mol), reaction time: 16 h. Yield 90.6 g (90.2%), colorless solution, 58% **4** in benzene (GC-MS). — ¹H NMR (C₆D₆): δ = 0.62–0.92 (m, 5H, CH₂ and CH₃), 4.29 [t, 2H, SiH₂, ³J(HH) = 2.2 Hz]. — ¹³C NMR (C₆D₆): δ = 6.1 [t · m, CH₂, ¹J(CH) = 121.1 Hz], 7.6 [q · m, CH₃, ¹J(CH) = 127.8 Hz]. — ²⁹Si NMR (C₆D₆): δ = -14.8 [t · m, ¹J(SiH) = 222.7 Hz]. — MS (GC-coupled), *m/z* (%): 136–141 [C₂H_xBrSi], 107–112 (100) [H_xBrSi], 79–82 [Br, HBr], 53–59 [C₂H_xSi].

5: **2** (24.8 g, 0.19 mol), reaction time: 19 h. Yield 38.7 g (97.1%), colorless solution, 64% **5** in benzene (GC-MS). — ¹H NMR (C₆D₆): δ = 4.59 [d, 2H, SiH₂, ³J(HH) = 2.4 Hz], 5.87 [d · d, 1H, CH_{cis}, ³J(HH) = 17.7, ²J(HH) = 5.5 Hz], 5.9 (m, 1H, CH_{trans}), 6.0 (m, 1H, CH_{gem}). — ¹³C{¹H} NMR (C₆D₆): δ = 128.7 (CH), 138.7 (CH₂). — ²⁹Si NMR (DEPT, C₆D₆): δ = -29.1 [t · d · m, ¹J(SiH) = 238.0, ²J(SiH) = 21.3 Hz]. — MS (GC-coupled), *m/z* (%): 134–139

[C₂H_xBrSi], 107–111 (100) [H_xBrSi], 79–82 [Br, HBr], 52–57 [C₂H_xSi].

6: **3** (59.0 g, 0.45 mol), reaction time: 18 h. Yield 88.5 g (93.0%), colorless solution, 63% **6** in benzene (GC-MS). — ¹H NMR (C₆D₆): δ = 2.10 (s, 1H, CH), 4.30 (s, 2H, SiH₂). — ¹³C NMR (C₆D₆): δ = 78.5 [d · t, C_{ipso}, ²J(CH) = 43.7, ²J(CH) = 11.0 Hz], 99.7 [d · t, CH, ¹J(CH) = 244.0, ³J(CH) = 4.1 Hz]. — ²⁹Si NMR (DEPT, C₆D₆): δ = -56.1 [t · d, ¹J(SiH) = 263.7, ³J(SiH) = 5.2 Hz]. — MS (GC-coupled), *m/z* (%): 132–137 [C₂H_xBrSi], 107–110 (100) [H_xBrSi], 79–82 [Br, HBr], 52–56 [C₂H_xSi].

Preparation of 1,3-Diorganodisiloxanes 7–9. — **General Procedure:** A slurry of calcium carbonate in a solution of the corresponding organo(bromo)silane in benzene is cooled to 0°C. Water is added dropwise until the evolution of gas ceases. After filtration of the calcium bromide precipitate the major part of benzene is removed by cryofiltration at -50°C. The disiloxanes are purified by spaltrohr distillation.

7: Calcium carbonate (32.5 g, 0.33 mol), **4** (141.5 g, 0.59 mol, 58% in benzene), water (10 g, 0.56 mol). Yield 27.1 g (68%), colorless liquid, b.p. 89°C/1 bar, 98% **7** (GC-MS). — ¹H NMR (C₆D₆): δ = 0.60 [q · t, 2H, CH₂, ³J(HH) = 7.9, ³J(HH) = 2.5 Hz], 0.93 (t, 3H, CH₃), 4.68 (t, 2H, SiH₂). — ¹³C NMR (C₆D₆): δ = 6.4 [q · t · t, CH₃, ¹J(CH) = 126.9, ²J(CH) = 9.7, ³J(CH) = 3.7 Hz], 6.9 [t · m, CH₂, ¹J(CH) = 119.5 Hz]. — ²⁹Si NMR (DEPT, C₆D₆): δ = -15.2 [t · q · t · t, ¹J(SiH) = 187.3, ²J(SiH) = 8.8, ³J(SiH) = 7.5, ³J(SiH) = 1.5 Hz]. — MS (GC-coupled), *m/z* (%): 132–135 [C₄H₈OSi₂], 103–107 (100) [C₂H_xOSi₂], 72–79 [C₂H_xOSi]. — C₄H₁₄O₂Si₂ (134.33): calcd. C 35.77, H 10.50, Si 41.82; found C 33.39, H 10.36, Si 40.76.

8: Calcium carbonate (18.0 g, 0.18 mol), **5** (67.9 g, 0.15 mol, 20% in toluene), water (5.9 g, 0.33 mol). Yield 6.2 g (65%), colorless liquid, b.p. 84°C/1 bar, >99% **7** (GC-MS). — ¹H NMR (C₆D₆): δ = 4.84 [d, 2H, SiH₂, ³J(HH) = 2.0 Hz], 5.78 [d · d, 1H, CH_{cis}, ²J(HH) = 4.9, ³J(HH) = 19.0 Hz], 5.91 [d · d, 1H, CH_{trans}, ³J(HH) = 14.7 Hz], 6.03 [d · d · t, 1H, CH_{gem}]. — ¹³C NMR (C₆D₆): δ = 133.8 (m, CH₂), 136.3 [d · m, CH, ¹J(CH) = 157.2 Hz]. — ²⁹Si NMR (DEPT, C₆D₆): δ = -27.4 [t · d · d · d · t, ¹J(SiH) = 219.2, ²J(SiH) = 19.3, ²J(SiH) = 11.7, ³J(SiH) = 9.7, ³J(SiH) = 1.7 Hz]. — MS (GC-coupled), *m/z* (%): 129 [C₄H₉OSi₂], 100–104 (100) [C₂H_xOSi₂], 72–77 [C₂H_xOSi], 53–57 [C₂H_xSi]. — C₄H₁₀O₂Si₂ (130.28): calcd. C 36.81, H 8.15; found C 36.87, H 7.74.

9⁽¹⁷⁾: Calcium carbonate (40.0 g, 0.40 mol), **6** (84.6 g, 0.40 mol, 64% in benzene), water (15 g, 0.83 mol). Yield 22.5 g (88%), colorless liquid, b.p. 80°C/1 bar, 86% **9** (GC-MS, not to be separated from residual benzene). — ¹H NMR (C₆D₆): δ = 2.16 [t, 1H, CH, ⁴J(HH) = 1.2 Hz], 4.61 (d, 2H, SiH₂). — ¹³C NMR (C₆D₆): δ = 84.2 [d · t, C_{ipso}, ²J(CH) = 42.7, ²J(CH) = 13.0 Hz], 97.0 [d · t, CH, ¹J(CH) = 241.1, ³J(CH) = 4.2 Hz]. — ²⁹Si NMR (DEPT, C₆D₆): δ = -51.2 [t · d · t, ¹J(SiH) = 245.6, ³J(SiH) = 14.8, ³J(SiH) = 2.1 Hz]. — MS (GC-coupled), *m/z* (%): 125–127 (100) [C₄H_xOSi₂], 97–101 [C₂H_xOSi₂], 72–74 [C₂H_xOSi], 53–57 [C₂H_xSi].

Preparation of (Organosilyloxy)aluminum Dichlorides 10–12. — **General Procedure:** To a stirred slurry of crystalline anhydrous aluminum trichloride in pentane at 0°C equimolar quantities of the corresponding 1,3-diorganodisiloxane are added by means of a syringe. After 15 minutes the reaction mixture is filtered from solid residue. After removal of the solvent from the filtrate the product is purified by distillation in vacuo.

10: AlCl₃ (4.8 g, 36.2 mmol), **7** (4.9 g, 36.1 mmol). Yield 4.0 g (65%), colorless liquid, m.p. 15°C, b.p. 35°C/0.1 mbar. — ¹H NMR (C₆D₆): δ = 0.59 (m, 2H, CH₂), 0.81 [t, 3H, CH₃, ³J(HH) = 7.9 Hz], 4.50 [t, 2H, SiH₂, ³J(HH) = 2.7 Hz]. — ¹³C NMR (C₆D₆): δ = 5.3 [t · m, CH₂, ¹J(CH) = 120 Hz], 5.9 [q · m, ¹J(CH) = 126.9 Hz]. —

^{29}Si NMR (C_6D_6): $\delta = 4.7$ [t · q · t, $^1J(\text{SiH}) = 225.8$, $^3J(\text{SiH}) = 9.3$, $^2J(\text{SiH}) = 7.6$ Hz]. — MS (CI), m/z (%): 361 (9) [$\text{C}_3\text{H}_{17}\text{Al}_2\text{Cl}_4\text{Si}_2\text{O}_2$], 321 (100) [$\text{C}_2\text{H}_8\text{Al}_2\text{Cl}_4\text{SiO}_2$].

11: AlCl_3 (1.3 g, 9.8 mmol), **8** (1.2 g, 9.4 mmol). Yield 1.3 g (81%), ice-like, colorless, deliquescent crystals, m.p. 35°C , b.p. $55^\circ\text{C}/0.1$ mbar. — ^1H NMR (C_6D_6): $\delta = 4.55$ (s, 2H, SiH_2), 5.56–5.95 (m, 3H, CH and CH_2). — ^{13}C NMR (C_6D_6): $\delta = 127.7$ [d · m, CH, $^1J(\text{CH}) = 152$ Hz], 143.3 (m, CH_2). — ^{29}Si NMR (C_6D_6): $\delta = -13.5$ [t · m, $^1J(\text{SiH}) = 235.8$ Hz]. — MS (CI), m/z (%): 435 (10) [$\text{C}_4\text{H}_{10}\text{Al}_3\text{Cl}_6\text{O}_3\text{Si}_2$], 351 (63) [$\text{C}_5\text{H}_{13}\text{Al}_2\text{Cl}_4\text{O}_2\text{Si}_2$], 279 (60) [$\text{C}_2\text{HAl}_2\text{Cl}_4\text{O}_2\text{Si}$].

12: AlCl_3 (3.8 g, 28.2 mmol), **9** (3.6 g, 28.2 mmol). Purification by recrystallization from *n*-hexane. Yield 4.6 g (97%), colorless crystals, m.p. 102°C (dec.). — ^1H NMR (C_6D_6): $\delta = 1.90$ (s, 1H, CH), 4.31 (s, 2H, SiH_2). — ^{13}C NMR (C_6D_6): $\delta = 78.4$ [d · t, C_{ipso} , $^2J(\text{CH}) = 43.7$, $^2J(\text{CH}) = 12.4$ Hz], 103.3 [d · t, CH, $^1J(\text{CH}) = 246.3$, $^3J(\text{CH}) = 4.1$ Hz]. — ^{29}Si NMR (C_6D_6 , DEPT): -39.7 [t · d, $^1J(\text{SiH}) = 262.0$, $^3J(\text{SiH}) = 5.2$ Hz]. — MS (CI), m/z (%): 619 (61) [$\text{C}_6\text{H}_{11}\text{Al}_4\text{Cl}_8\text{O}_4\text{Si}_3$], 585 (30) [$\text{C}_6\text{H}_{12}\text{Al}_4\text{Cl}_8\text{O}_4\text{Si}_3$], 367 (54) [$\text{C}_4\text{H}_9\text{Al}_2\text{Cl}_4\text{O}_2\text{Si}_3$], 311 (31) [$\text{C}_2\text{H}_5\text{Al}_2\text{Cl}_4\text{O}_2\text{Si}_2$], 133 (100) [$\text{C}_2\text{H}_4\text{AlClOSi}$].

Preparation of Dimethylaluminum Organosilyl Oxides 13–16. — *General Procedure:* To an ice-cooled solution of the corresponding 1,3-diorganodisiloxane in pentane, equimolar quantities of a 1 molar solution of Me_2AlCl in hexane are added dropwise within 15 min. The solvent is distilled from the clear solution and the product is distilled in vacuo.

The spectroscopic data are given separately for the detected dimers (*Di*), trimers (*Tr*) and tetramers (*Te*).

13: **7** (2.7 g, 19.7 mmol), Me_2AlCl (19.7 ml). Yield 2.6 g (86%), colorless liquid, b.p. $0^\circ\text{C}/0.1$ mbar. — ^1H NMR (C_6D_6), *Di*: $\delta = -0.60$ (s, 6H, MeAl), 0.51–0.67 (m, CH_2 , for *Di* and *Tr*), 0.80 [t, 3H, CH_3 , $^3J(\text{HH}) = 7.9$ Hz], 4.46 (s, 2H, SiH_2); *Tr*: -0.46 (s, 6H, MeAl), 0.87 [t, 3H, CH_3 , $^3J(\text{HH}) = 7.9$ Hz], 4.55 (s, 2H, SiH_2). — ^{13}C NMR (C_6D_6), *Di*: $\delta = -9.8$ (s, MeAl), 6.2 [t · m, CH_2 , $^1J(\text{CH}) = 120.4$ Hz], 6.2 [q · m, CH_3 , $^1J(\text{CH}) = 127.5$ Hz]; *Tr*: -8.0 (s, MeAl), 6.0 [t · m, CH_2 , $^1J(\text{CH}) = 120$ Hz], 6.1 [q · m, CH_3 , $^1J(\text{CH}) = 128.2$ Hz]. — ^{29}Si NMR (DEPT, C_6D_6), *Di*: $\delta = -10.1$ [t · q · t, $^1J(\text{SiH}) = 213.5$, $^3J(\text{SiH}) = 9.0$, $^2J(\text{SiH}) = 7.6$ Hz]; *Tr*: -7.7 [t · q · t, $^1J(\text{SiH}) = 216.5$, $^3J(\text{SiH}) = 9.0$, $^2J(\text{SiH}) = 7.6$ Hz]. Relative intensities are 100:70 for *Di*: *Tr*. — MS (CI), m/z (%): 573 (7) [$\text{C}_{16}\text{H}_{53}\text{Al}_4\text{O}_5\text{Si}_5$], 513 (22) [$\text{C}_{15}\text{H}_{49}\text{Al}_4\text{O}_4\text{Si}_4$], 397 (20) [$\text{C}_{12}\text{H}_{40}\text{Al}_3\text{O}_3\text{Si}_3$], 381 (43) [$\text{C}_{11}\text{H}_{36}\text{Al}_3\text{O}_3\text{Si}_3$], 367 (56) [$\text{C}_{10}\text{H}_{34}\text{Al}_3\text{O}_3\text{Si}_3$], 263 (26) [$\text{C}_8\text{H}_{25}\text{Al}_2\text{O}_2\text{Si}_2$], 249 (100) [$\text{C}_7\text{H}_{23}\text{Al}_2\text{O}_2\text{Si}_2$], 235 (16) [$\text{C}_6\text{H}_{21}\text{Al}_2\text{O}_2\text{Si}_2$].

14: **8** (2.2 g, 17.0 mmol), Me_2AlCl (17.0 ml). Yield 1.9 g (86%), colorless liquid, b.p. $30^\circ\text{C}/0.1$ mbar. — ^1H NMR (C_6D_6), $\delta = \text{Di}$: -0.61 (s, 6H, MeAl), 4.67–4.76 (m, SiH_2 , for *Di*, *Tr* and *Te*), 5.75–6.04 (m, CH and CH_2 , for *Di*, *Tr* and *Te*); *Tr*: -0.48 (s, 6H, MeAl); *Te*: -0.48 (m, 6H, MeAl). — ^{13}C NMR (C_6D_6), *Di*: $\delta = -8.7$ (s, MeAl), 131.5 [d · m, CH, $^1J(\text{CH}) = 152.0$ Hz], 139.0 (m, CH_2); *Tr*: -6.8 (s, MeAl), 130.6 [d · m, CH, $^1J(\text{CH}) = 153.1$ Hz], 140.1 (m, CH_2); *Te*: -10.1 (s, MeAl), 130.0 [d · m, CH, $^1J(\text{CH}) = 152.0$ Hz], 138.3 (m, CH_2). — ^{29}Si NMR (C_6D_6), *Di*: $\delta = -35.3$ [t · m, $^1J(\text{SiH}) = 222.2$ Hz]; *Tr*: -33.3 [t · m, $^1J(\text{SiH}) = 226.4$ Hz]; *Te*: -31.0 (m). Relative intensities are 70:100:30 for *Di*: *Tr*: *Te*. — MS (CI), m/z (%): 294–297 (100) [$\text{C}_{10}\text{H}_x\text{Al}_3\text{O}_3\text{Si}_3$], 279–284 (66) [$\text{C}_{10}\text{H}_x\text{Al}_3\text{O}_3\text{Si}_3$].

15 (and **16**): **9** (4.7 g, 37.2 mmol), Me_2AlCl (37.2 ml). Yield 3.8 g (80%), **15**, colorless liquid, b.p. $22^\circ\text{C}/0.1$ mbar. — ^1H NMR (C_6D_6), *Di*: $\delta = -0.44$ (s, 6H, MeAl), 2.07 (s, 1H, CH), 4.48 (s, 2H, SiH_2); *Tr*: -0.36 (s, 6H, MeAl), 2.14 (s, 1H, CH), 4.56 (s, 2H, SiH_2). — ^{13}C NMR (C_6D_6), *Di*: $\delta = -8.5$ (s, MeAl), 80.5 [d · t, C_{ipso} , $^2J(\text{CH}) = 43.7$, $^2J(\text{CH}) = 12.4$ Hz], 99.3 [d · t, CH, $^1J(\text{CH}) = 243.1$,

$^3J(\text{CH}) = 4.1$ Hz]; *Tr*: -7.4 (s, MeAl), 81.5 [d · t, C_{ipso} , $^2J(\text{CH}) = 43.2$, $^2J(\text{CH}) = 12.4$ Hz], 100.7 [d · t, CH, $^1J(\text{CH}) = 244.0$, $^3J(\text{CH}) = 4.1$ Hz]. — ^{29}Si NMR (DEPT, C_6D_6), *Di*: $\delta = -43.4$ [t · d, $^1J(\text{SiH}) = 245.8$, $^3J(\text{SiH}) = 4.9$ Hz]; *Tr*: -45.6 [t · d, $^1J(\text{SiH}) = 249.3$, $^3J(\text{SiH}) = 4.9$ Hz]. Relative intensities are 100:50 for *Di*: *Tr*. On cooling **15** slowly to -25°C , **16** precipitates as white deliquescent crystals ($\approx 1\%$).

Crystal Structure Determinations: For compound **11** (crystallized by sublimation), compound **12** (crystallized from *n*-hexane) and compound **16** (crystallized from a mixture with **15**) suitable crystals were sealed at dry-ice temperature into glass capillaries under argon and investigated on the diffractometer. Reduced cell calculations did not indicate higher symmetry. The measured reflections were corrected for Lorentz and polarization effects.

The structures were solved by direct methods (SHELXS 86)^[18], completed by Fourier synthesis and refined anisotropically by full matrix techniques (SHELX 76)^[19]. For **11** two independent molecules were found in the asymmetric unit with resolved disorder of one carbon atom (CH_2) for one ethenyl group. The hydrogen atom positions were found and refined isotropically except for the carbon atoms of the disordered group in **11**. Compound **16** was found to be disordered. With the molecule possessing pseudoinversion symmetry and the given space group, the chlorine atom and one methyl group are distributed over two positions at the aluminum atom. The problem was solved by using a hybrid of scattering factors (carbon and chlorine) with positional parameters tied together. The site-occupation factor was determined to be 0.50 for both elements. For the final refinement, the “mixed atom” was treated anisotropically.

Table 1. Crystal and structure solution data

	11	12	16
Formula	$\text{C}_6\text{H}_{10}\text{Al}_2\text{Cl}_4\text{O}_2\text{Si}_2$	$\text{C}_4\text{H}_6\text{Al}_2\text{Cl}_4\text{O}_2\text{Si}_2$	$\text{C}_7\text{H}_{15}\text{Al}_2\text{ClO}_2\text{Si}_2$
M_r [g·mol ⁻¹]	342.077	338.038	276.784
Temperature [°C]	-50	-56	-74
Space group [No.]	$P\bar{1}$ [2]	$P\bar{1}$ [2]	$P\bar{1}$ [2]
<i>a</i> [Å]	6.287(1)	6.725(1)	6.880(2)
<i>b</i> [Å]	9.063(1)	7.271(1)	7.361(2)
<i>c</i> [Å]	14.420(2)	7.819(1)	7.951(2)
α [°]	82.25(1)	102.05(1)	102.66(2)
β [°]	78.12(1)	93.19(1)	94.20(2)
γ [°]	80.37(1)	100.06(1)	100.25(2)
V [Å ³]	788.4	366.5	384.0
ρ_{calc} [g·cm ⁻³]	1.441	1.532	1.197
<i>Z</i>	2	1	1
$F(000)$ [e]	344	168	144
$\mu(\text{Mo-K}\alpha)$ [cm ⁻¹]	9.9	10.7	4.9
Radiation	$\lambda = 0.71069$ Å (Mo- $K\alpha$), graphite monochromator		
Diffractometer	Syntex P2 ₁	CAD4	CAD4
Scan range (°) [°]	2–24	2–28	2–27
<i>hkl</i> range	$\pm 6, \pm 10, +16$	$\pm 8, \pm 9, +10$	$\pm 8, \pm 9, +10$
Measured refl.	2448	1760	1668
Unique refl.	2448	1759	1667
Observed refl.	1644	1543	1480
$F_o \geq$	$4\sigma(F_o)$	$3\sigma(F_o)$	$4\sigma(F_o)$
Refined param.	141	76	76
Weighting scheme	----- $w = 1/\sigma^2(F_o)$ -----		
Weighting param. <i>l</i>	2.0326	3.5728	1.0000
H atoms (f./c.)	4/3	3/-	3/3 ^[a]
<i>R</i> (R_w)	0.056 (0.045)	0.032 (0.030)	0.045 (0.052)
$\Delta\rho_{\text{fin}}(\text{max/min})$ [eÅ ⁻³]	+0.59/-0.38	+0.42/-0.32	+0.45/-0.41

[a] H-atoms at disordered carbon/chlorine hybrid atom neglected.

ically with all parameters tied together. Further information on the structure determination is given in Table 1.

Supplementary material can be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57712, the names of the authors, and the journal citation.

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