Tetrasupersilyldialuminum $[(t\text{-Bu})_3Si]_2Al-Al[Si(t\text{-Bu})_3]_2$: The Dialane(4) with the Longest Al−Al Bond to Date[†,§]

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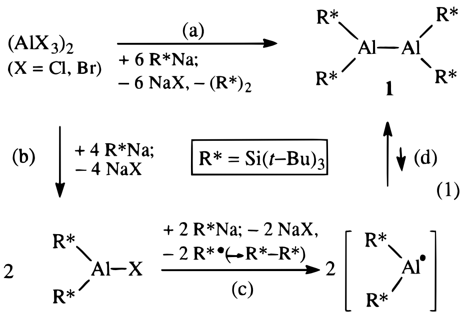
*Summary: Reaction of AlX_3 (X = Cl, Br) with R*Na (R* = supersilyl, $Si(t\text{-Bu})_3$) in heptane at room temperature gave the ruby dialane $R^*_2Al-AlR^*_2$ (**1**). X-ray structure analysis showed it to contain a $Si_2Al-AlSi_2$ skeleton with D_{2d} symmetry and the longest Al−Al bond to date (2.751(2) Å). Water- and air-sensitive **1** reacts with iodine or hydrogen to form R^*_2AlI or R^*_2AlH, respectively. Thermolysis and photolysis transform **1,** via $[R^*_2Al-AlR^*]^\bullet$, into the tetraalatetrahedrane $Al_4R^*_4$.*

Introduction

Unlike aluminum triorganyls AlR_3, which were first synthesized in the middle of the 19th century,[1] aluminum organyls Al_mR_n ($n/m < 3$) with aluminum in the oxidation state <III were unknown for a long time because of their high tendency for disproportionation into AlR_3 und Al. As was shown afterward,[2,3] the tendency for decomposition of Al_mR_n is lowered by bulky substituents R. Thus, in 1988 a dialane(4), $Al_2[CH(SiMe_3)_2]_4$,[4] with aluminum in oxidation state +II, and in 1991 *tetrahedro*tetraalanes(4), $Al_4[Si(t\text{-Bu})_3]_4$[5,6] as well as $Al_4(C_5Me_5)_4$,[7] with aluminum in oxidation state +I were synthesized for the first time. In continuation of that we discuss here the preparation, structure, and reactions of the dialane $Al_2R^*_4$ (**1**) with bulky tri-*tert*-butylsilyl groups ("*supersilyl*" groups), R* = $Si(t\text{-Bu})_3$. Its properties differ markedly from those of other hitherto structurally characterized dialanes Al_2R_4 (R = $CH(SiMe_3)_2$ = "*Disyl*"[2,4] and 2,4,6-$(i\text{-Pr})_3C_6H_2$ = "*Tip*"[8]).

Scheme 1. Preparation of 1



Results and Discussion

Scheme 1 describes the *preparation* of dialane **1**: The starting materials, R^*_2AlX, are prepared by reaction of AlX_3 with supersilylsodium R*Na (molar ratio 1:2) for 2 h (X = Cl) or 1 h (X = Br) in pentane at room temperature [cf. Scheme 1, eq 1b]. Subsequent treatment with R*Na provides tetrasupersilyldialane **1** in quantitative yields. The latter reactions probably give—besides NaX—at first disupersilylalanyl radicals $R^*_2Al^\bullet$ and supersilyl radicals $R^{*\bullet}$, which on sterical grounds could not combine to form AlR^*_3 but instead dimerized to **1** and to superdisilane R*−R*, respectively [cf. Scheme 1, eqs 1c and 1d]. **1** may also be prepared directly from AlX_3 and R*Na (molar ratio 1:3) in alkanes at room temperature [cf. Scheme 1, eq 1a].

The dialane is isolable from a solution in pentane at −23 °C in the form of ruby moisture- and air-sensitive crystals that decompose at 50 °C. Thus, **1** is more thermolabile than the colorless dialane Al_2Disyl_4 or the yellow-green dialane Al_2Tip_4, which are stable to 200 °C and 171 °C, respectively. In alkanes, **1** is stable only when light is excluded; in benzene, on the other hand, **1** decomposes also in the dark.

According to *X-ray structure analysis* (Figure 1), the dialane **1** shows a $Si_2AlAlSi_2$ skeleton with D_{2d} symmetry. The Al atoms are trigonal planar bonded to two Si atoms and one Al atom, whereby the $AlAlSi_2$ planes are orthogonal to each other (dihedral angle SiAlAlSi 90°). Interestingly, in dialanes Al_2R_4 with less bulky substituents the angles between the $AlAlC_2$ planes are significantly smaller (Al_2Disyl_4 8°;[4] Al_2Tip_4 44.8°[8]). The space-filling properties of the supersilyl groups lead to an unusually long Al−Al distance of 2.751(2) Å; **1**

[†] Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday.

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[‡] X-ray structure analysis.

[§] Silicon Compounds, 120; Supersilyl Compounds of Boron and Homologues, 6. Part 119 and 5: ref 6. Part 118: Wiberg, N.; Wörner, A.; Lerner, H.-W.; Karaghiosoff, K.; Fenske, D.; Baum, G.; Dransfeld, A.; Schleyer, P. v. R. *Eur. J. Inorg. Chem.* **1998**, *1*, 833. Part 4: ref 9.

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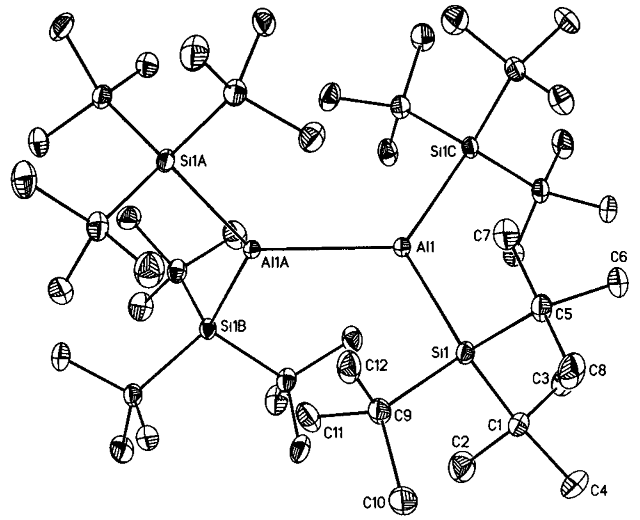


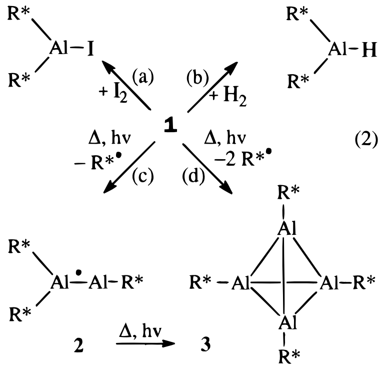
Figure 1. ORTEP drawing of **1**, showing 25% probability ellipsoids (H atoms have been omitted for clarity). Selected bond lengths [Å] and angles [deg]: Al1−Al1A 2.751(2), Al1−Si1/Al1−Si1C/Al1A−Si1A/Al1A−Si1B 2.717(1), Si1−C1 1.971(5), Si1−C5 1.962(4), Si1−C9 1.970(3) [mean value of Si−C−bonds 1.97], C1−C2 1.530(6), C1−C3 1.534(6), C1−C4 1.555(7); Si1−Al1−Si1C/Si1A−Al1A−Si1B 128.26(5), Si1−Al1−Al1A/Si1C−Al1−Al1A/Si1A−Al1A−Al1/Si1B−Al1A−Al1 115.87(2), Al1−Si1−C1 109.3(1), Al1−Si1−C5 111.5(1), Al1−Si1−C9 108.7(1), C1−Si1−C5 110.0(2), C1−Si1−C9 108.6(2), C5−Si1−C9 108.7(2) [mean value of C−Si−C angles 109.1], Si−Al−Al−Si 90.0.

contains the longest Al−Al bond of a dialane(4) to date (Al_2Disyl_4 2.660 Å;[4] Al_2Tip_4 2.647 Å[8]). Nevertheless, at room temperature a solution of **1** in alkanes gives no evidence for disupersilylalanyl, $R^*_2Al^\bullet$, by ESR. Thus, the equilibrium 1d in Scheme 1, under normal conditions, strongly favors **1** over the radical. Obviously, the R^*_2Al halves in **1** are bonded not only by a chemical Al−Al bond, which in fact is very weak, but by additional van der Waals attractions of the peripheral methyl groups also (cf. the situation with R*−R* [10,11]).

Another consequence of the steric hindrance of the supersilyl groups to each other is the unusually small SiAlSi angle of 128.3° (cf. R^*_2AlCl 148.3°[12]). It may be interpreted as the cone angle of the supersilyl group for a silicon element distance (here Si−Al distance) of 2.72 Å; the latter distance is unusually large (cf. R^*_2AlCl 2.53 Å[12]). As expected, **1** shows comparatively long Si−C bonds and small C−Si−C angles (mean values 1.97 Å and 109.1°; normal range 1.94−1.95 Å and 110−112°, respectively[11]).

Scheme 2 shows some *reactions* of the dialane **1**: Mild warming of **1** in alkanes obviously leads, according to eq 1d in Scheme 1, to disupersilylalanyl radicals $R^*_2Al^\bullet$ in low equilibrium concentration. This is supported by reactions of **1** with iodine as well as with hydrogen which give iododisupersilylalane ($(t\text{-}Bu_3Si)_2AlI$) and disupersilylalane ($(t\text{-}Bu_3Si)_2AlH$) at about 50 °C, according to eqs 2a and 2b in Scheme 2, respectively. Heating of **1** in alkanes up to 80 °C leads, according to eq 2c in Scheme 2, under elimination of supersilyl radicals to black-green trisupersilyldialanyl radicals **2**; the former dimerize, whereas the latter are stable even at room temperature.[13] Stronger heating of **1** in alkanes up to 135 °C leads, according to eq 2d in Scheme 1, to violet tetrasupersilyl*tetrahedro*tetraalane **3**[6,13] in low yield and to supersilyl radicals, which under the reaction conditions abstract H atoms from their chemical environment to form R*H. Photolysis transforms **1**, via **2,** into **3**, a process that also occurs thermally. Consequently the tetrahedrane **3** is available, according to eqs 1a in Scheme 1 and 2d in Scheme 2, from AlX_3 and R*Na in a one-pot process.

Scheme 2. Reactions of 1



Experimental Section

General Considerations. All experiments were carried out under dry argon with strict exclusion of air and moisture The solvents were distilled from sodium/benzophenone immediately before use. The NMR spectra (^1H, ^{13}C, ^{29}Si) were recorded on JEOL GXS-270 and EX-400. The ^{29}Si NMR spectra were recorded with the INEPT pulse sequence using empirically optimized parameters for polarization transfer from the *t*-Bu substituents. Chemical shifts are reported in δ units (ppm) referenced to internal TMS (^1H, ^{13}C) or external (^{29}Si).

Synthesis of 1. (a) A solution of 0.084 g (0.18 mmol) of R^*_2AlCl[9] and 0.041 g (0.18 mmol) of R*Na in 15 mL of pentane was stirred for 2 days at 25 °C (donor-free supersilylsodium was used[14]). The reaction mixture thus acquires a deep red color. According to ^1H NMR (C_6D_6), **1** and $(R^*)_2$ were formed in a molar ratio of about 1:1 (quantitative yield of **1**). After removal of insoluble NaCl and condensation of fractions volatile in oil pump vacuum the red residue was dissolved in 10 mL of pentane and cooled to −23 °C to get ruby crystals of **1** (0.025 g, 0.029 mmol, 35%). (b) Alternatively, 0.343 g (0.679 mmol) of R^*_2AlBr[9] and 0.151 g (0.679 mmol) of R*Na in 40 mL of pentane were stirred for 1 day at 25 °C. According to ^1H NMR (C_6D_6), **1** and $(R^*)_2$ were formed in a mol ratio of about 1:1. After removal of insoluble NaBr and condensation of fractions volatile in oil pump vacuum, the red residue was dissolved in 6 mL of pentane and cooled to −23 °C to get ruby crystals of **1** (0.18 g, 0.21 mmol, 63%). (c) A solution of 0.440 g (1.65 mmol) of $AlBr_3$ and 1.47 g (6.60 mmol) of R*Na in 45 mL of heptane was stirred for 1 h at −45 °C, then for 1 day at 25 °C. Filtration of the insoluble residue (NaBr) and concentration of the filtrate to 10 mL gave 0.650 g (0.760 mmol, 92%)

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ruby crystals of **1**. ^{1}H NMR (C_6D_6): $\delta = 1.36$ (s; 36 Me); (C_6D_{12}): $\delta = 1.29$ (s; 36 Me). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.64/35.56$ (12 *C*Me$_3$/12 C*Me*$_3$); (C_6D_{12}): $\delta = 26.08/34.88$ (12 *C*Me$_3$/12 C*Me*$_3$). ^{29}Si NMR (C_6D_6): $\delta = 44.7$ (12 *t*-Bu); (C_6D_{12}): $\delta = 44.9$ (12 *t*-Bu).

Reaction of 1 with I$_2$. A solution of 0.007 g (0.03 mmol) of I_2 in 5 mL of pentane was added dropwise to a solution of 0.026 g (0.030 mmol) of **1** in 10 mL of pentane at −78 °C. The reaction mixture was warmed slowly to 40 °C and then stirred at this temperature for 3 h. In this way, the red reaction solution acquires a yellow color. According to NMR spectra, the reaction to R*$_2$AlI is quantitative (identification by comparison of the NMR spectra of the product with the spectra of R*$_2$AlCl and R*$_2$AlBr [9]). ^{1}H NMR (C_6D_6): $\delta = 1.34$ (s; 18 Me). ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 25.92/33.23$ (6 *C*Me$_3$/6 C*Me*$_3$).

Reaction of 1 with H$_2$. An evacuated NMR tube with **1** in 0.6 mL of C_6D_{12} was filled with 700 mbar of oxygen-free hydrogen and then sealed. It was heated for 15 min at 50 °C. Thereby, the solution decolorized. According to NMR spectra, the reaction to R*$_2$AlH is quantitative (identified by comparison of the NMR spectra of the product with that of a product prepared separately by the reaction of R*$_2$AlCl with $LiAlH_4$). ^{1}H NMR (C_6D_{12}): $\delta = 1.25$ (s; 18 Me). ^{13}C{^{1}H} NMR (C_6D_{12}): $\delta = 25.31/32.79$ (6 *C*Me$_3$/6 C*Me*$_3$).

Formation of 2. A sealed NMR tube, containing 0.138 g (0.163 mmol) of **1** in 1.5 mL of C_6D_{12}, was heated at 80 °C for 60 min. Thereby the color changed from red, via violet, to black-green. NMR measurements indicated the disappearance of the signals for **1** and the appearance of those for superdisilane (R*)$_2$. The formation of **2** was undoubtly confirmed by ESR measurements [$a(Al_1) = 18.9$ and $a(Al_2) = 21.8$ G; in colaboration with W. Kaim and B. Schwederski[13]]. Up to date, no crystals of **2** could be isolated that were suitable for an X-ray structure analysis (for an X-ray structure analysis of R*$_3$Ga$^\bullet{}_2$ cf. ref 15).

X-ray Structure Determination of 1. Siemens P4-Diffractometer, Mo Kα radiation, graphite monochromator, CCD area detector, crystal 0.40 × 0.40 × 0.30 mm mounted with perfluorpolyether-oil, $T = 173(2)$ K, $C_{48}H_{108}Al_2Si_4$, $M_r = 851.66$, red cubic, tetragonal, $a = b = 15.4599(1)$ Å, $c = 13.2038(1)$ Å, $V = 3155.82(3)$ Å^3, $Z = 2$, space group $I\bar{4}$, $\rho_{\mathrm{ber.}} = 0.896$ Mg m^3, $\mu = 1.349$ mm^{-1}, $F(000) = 956$. Data collection: $2\theta = 3.72$ bis 58.14°, $-19 \le h \le 20$, $-20 \le k \le 20$, $-16 \le l \le 16$, 9338 reflections collected, 3403 were independent ($R_{\mathrm{int}} = 0.0197$) and 3313 considered observed ($F > 4\sigma(F)$); absorption correction SADABS (min./max. transmission 0.9436 and 0.9573); R1 = 0.0461, wR2 = 0.1519, GOF(F^2) = 1.304; largest residual electron density 1.51 e Å^{-3}. The weighting factor $w^{-1} = \sigma^2 F_o{}^2 + (0.1055P)^2$ with $(P = F_o{}^2 + 2F_c{}^2)/3$. The structure was solved by direct methods (SHELX-97, Sheldrick, 1997). The refinement uses a twin matrix (010 100 00−1). All non-hydrogen atoms were refined anisotropically, and H atoms were included in the refinement at calculated positions with a riding model and fixed isotropic U_i-values. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101401. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Telefax: Int.+1223/336−033. E-mail: deposit@chem.crys.cam.ac.uk).

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