Tris(trimethylsilyl)methyl and Tris(dimethylphenylsilyl)methyl Derivatives of Boron. Crystal Structures of Dihydroxy[tris(trimethylsilyl)methyl]borane and of the Lithium–Boron Complex $[(MeOH)_2Li(\mu\text{-}OMe)_2B(OMe)_2]$†

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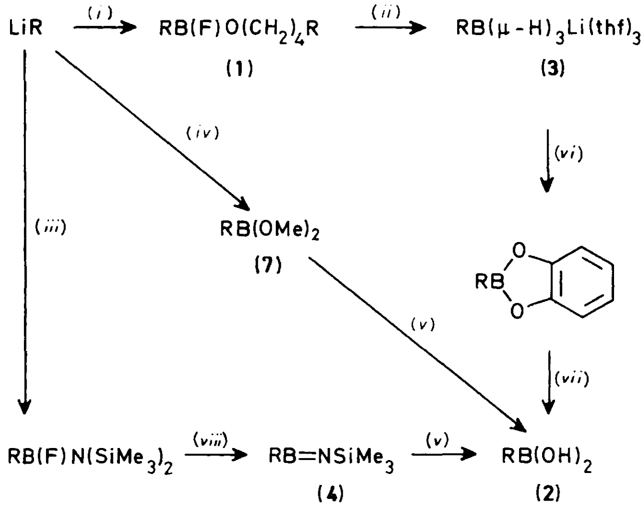
Tris(trimethylsilyl)methyl-lithium, $LiC(SiMe_3)_3$, reacts with trimethoxyborane to give the compound $(Me_3Si)_3CB(OMe)_2$ (**7**) and the lithium–boron complex $LiB(OMe)_4$ (**8**). The latter is converted on crystallisation from methanol into the solvate $[(MeOH)_2Li(\mu\text{-}OMe)_2B(OMe)_2]$ (**11**), which has been characterised by *X*-ray diffraction. The hydrolysis of (**7**) gives the dihydroxyborane $(Me_3Si)_3CB(OH)_2$ (**2**), which may be converted into the dichloride $(Me_3Si)_3CBCl_2$ (**12**), the difluoride $(Me_3Si)_3CBF_2$ (**14**), the fluoride hydroxide $(Me_3Si)_3CB(F)OH$ (**15**), the boranes $(Me_3Si)_3CBR_2$ [R = Ph (**16**) or Me (**17**)], and the hydride $[(thf)_3Li(\mu\text{-}H)_3BC(SiMe_3)_3]$ (**3**) (thf = tetrahydrofuran). An *X*-ray study shows that crystals of (**2**) consist of hydrogen-bonded dimers. Tris(dimethylphenylsilyl)methyl-lithium, $LiC(SiMe_2Ph)_3$, reacts with boron trifluoride–diethyl ether to give $(PhMe_2Si)_3CBF_2$ (**5**), which may be hydrolysed to the dihydroxyborane $(PhMe_2Si)_3CB(OH)_2$ (**6**).

Tris(trimethylsilyl)methyl boron derivatives were first isolated from the reaction between tris(trimethylsilyl)methyl-lithium LiR [R = $C(SiMe_3)_3$] and $BF_3{\cdot}OEt_2$ in tetrahydrofuran (thf)–diethyl ether.[1] However, in this procedure the solvent was attacked, and thf was incorporated into the product $RB(F)O(CH_2)_4R$ (**1**). Several further steps (Scheme 1) were then necessary to obtain the dihydroxyborane (boronic acid) $RB(OH)_2$ (**2**), and it was particularly difficult to separate the very moisture-sensitive hydride (**3**) from traces of the alcohol $R(CH_2)_4OH$.[2] The dihydroxyborane (**2**) was made independently by hydrolysis of the iminoborane (**4**), but again several steps were involved.[3,4] In this paper we report a much simpler synthesis of (**2**), its crystal structure, and some of its reactions. [The oxidation of (**2**) to give the alcohol ROH has been described.[5]] For comparison, we have made the tris(dimethylphenylsilyl)methyl compounds $R'BX_2$ [R' = $C(SiMe_2Ph)_3$; X = F (**5**) or OH (**6**)]; the crystal structure of the unusual fluoride hydroxide $(PhMe_2Si)_3CB(F)OH$ has already been published.[6]



Scheme 1. R = $(Me_3Si)_3C$. (*i*) $BF_3{\cdot}OEt_2$, thf; (*ii*) $LiAlH_4$; (*iii*) $(Me_3Si)_2NBF_2$; (*iv*) $B(OMe)_3$; (*v*) H_2O; (*vi*) catechol; (*vii*) (*a*) NaOH, (*b*) HCl; (*viii*) $-SiMe_3F$, 60 °C

Experimental

Schlenk-tube techniques were used for the manipulation of air- and moisture-sensitive compounds. Solvents were dried by standard procedures. The compounds $LiC(SiMe_3)_3$ and $LiC(SiMe_2Ph)_3$ were made as described earlier.[7,8] Proton n.m.r. spectra were recorded at 90 or 360 MHz; chemical shifts are relative to internal $SiMe_4$ (^1H, ^{13}C, and ^{29}Si), external $BF_3{\cdot}OEt_2$ (^{11}B), $CFCl_3$ (^{19}F), or $LiNO_3$ in D_2O (^7Li). It was usually difficult to observe the signal from the quaternary carbon in ^{13}C spectra. Unless otherwise indicated, mass spectra were obtained by electron impact (e.i.) at 70 eV ($\approx 1.1 \times 10^{-17}$ J), where relevant the *m/z* values refer to ions containing ^{11}B, ^{28}Si, or ^{35}Cl, and relative intensities refer to the strongest peak.

The Reaction between $LiC(SiMe_3)_3$ *and* $B(OMe)_3$.—This was monitored carefully by ^1H and ^{11}B n.m.r. spectroscopy. When $B(OMe)_3$ (2.23 g, 21.5 mmol) was added to a stirred solution of $LiC(SiMe_3)_3$ (21.5 mmol) in thf (50 cm^3) the solution remained brown and no precipitate formed. Both ^1H and ^{11}B n.m.r. spectra showed the presence of one main species, with δ_B 2.8 p.p.m., indicating that it was from four-co-ordinate boron, together with a small amount of $(Me_3Si)_3CB(OMe)_2$ (**7**) (see below). When a second equivalent of $B(OMe)_3$ was added the spectra showed that it disappeared only slowly during 4 h with formation of (**7**). It was necessary to add a third equivalent of $B(OMe)_3$ before the brown colour was discharged and a white

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† 2,2-Bis(methanol)-di-μ-methoxo-1,1-dimethoxoboronlithium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: Torr ≈ 133 Pa.

precipitate formed. The reaction had thus proceeded according to equation (1).

$$\mathrm{LiC(SiMe_3)_3 + B(OMe)_3 \xrightarrow{fast} \underset{(\mathbf{9})}{LiB\{C(SiMe_3)_3\}(OMe)_3}}$$

$$\xrightarrow[\mathrm{B(OMe)_3}]{\mathrm{slow}} \underset{(\mathbf{7})}{\mathrm{(Me_3Si)_3CB(OMe)_2}} + \underset{(\mathbf{8})}{\mathrm{LiB(OMe)_4}} \qquad (1)$$

The reaction mixture was worked up in two ways. In the first, the mixture of (**7**) and (**8**), after removal of solvent, was washed with water (200 cm^3) and then shaken with light petroleum (300 cm^3, b.p. 60—80 °C). The ^{1}H n.m.r. spectrum (CCl$_4$–CH$_2$Cl$_2$, 95:5) of the solid obtained by removing the solvent from the organic layer showed peaks at: (*a*) δ 0.18 and 4.32, attributable to (Me$_3$Si)$_3$CB(OH)$_2$ (**2**);[4] (*b*) 0.09, 3.52, and 4.19, attributable to (Me$_3$Si)$_3$CB(OH)(OMe) (**10**); and (*c*) 0.15 and 3.77, attributable to (Me$_3$Si)$_3$CB(OMe)$_2$ (**7**).[2] When this solid was heated under reflux with batches of thf–water (4:1), with removal of volatile material after each heating period, the peaks due to (**7**) and (**10**) successively disappeared, leaving only those due to (**2**). The solvent was then evaporated and the solid residue was sublimed at 70 °C (0.1 Torr). The sublimate, after recrystallisation from pentane, was *dihydroxy*[*tris*(*trimethylsilyl*)*methyl*]*borane* (35%), m.p. 204 °C (lit.,[4] 201 °C) (Found: C, 44.2; H, 9.8. C$_{10}$H$_{29}$BO$_2$Si$_3$ requires C, 43.4; H, 10.5%); ^{1}H and ^{11}B spectra were identical to those in ref. 4; δ_{C}(CDCl$_3$) 5.7 (SiMe$_3$); δ_{Si}(CDCl$_3$) −0.46 p.p.m. The lower and clearly incorrect m.p. found earlier[2] can be attributed to the presence of some (Me$_3$Si)$_3$C(CH$_2$)$_4$OH impurity.

Alternatively, the solvent was removed from the mixture of (**7**) and (**8**) obtained as above, and the residue was extracted with heptane. Evaporation of the heptane from the extract yielded the previously described (Me$_3$Si)$_3$CB(OMe)$_2$ (**7**). The solid residue from the extraction (Found: C, 31.9; H, 8.9. C$_4$H$_{12}$BLiO$_4$ requires C, 33.8; H, 8.5%) was only slightly soluble in hydrocarbons and ethers. It dissolved in methanol [δ_{H}(CH$_3$OD) 3.48, δ_{B} 2.9, δ_{Li} −1.0 p.p.m.] and the solid obtained on recrystallisation from that solvent was shown by an *X*-ray structure determination to be the solvate [(MeOH)$_2$Li-(μ-OMe)$_2$B(OMe)$_2$] (**11**).

The dihydroxyborane (boronic acid) (**2**) did not react with HO(CH$_2$)$_3$OH in pentane at 20 °C, with *o*-phenylenediamine in MeOH at 60 °C, with SiMe$_3$Cl in CCl$_4$ at 20 °C, or with SiMe$_3$Cl–NEt$_3$ in CH$_2$Cl$_2$ at 20 °C. With *o*-phenylenediamine in MeOH at 60 °C some (Me$_3$Si)$_3$CB(OH)(OMe) was formed, but no B–N heterocycle was detected.

When KOH (0.18 mmol) in ethanol–water (1:1) (1.0 cm^3) was added to compound (**2**) (0.07 mmol) the ^{11}B n.m.r. spectrum of the resulting solution showed a peak at δ_{B} 7.9 p.p.m. ($\Delta w_{\frac{1}{2}}$ = 2 Hz); for a similar solution but without KOH, δ_{B} was 31.5 p.p.m. ($\Delta w_{\frac{1}{2}}$ = 300 Hz). Compound (**2**) was recovered when the alkaline solution was neutralised with 1 mol dm^{-3} HCl, the solution shaken with pentane, and solvent removed from the organic layer. In a similar experiment with dimethyl sulphoxide as solvent (**2**) was again recovered.

Dichloro[*tris*(*trimethylsilyl*)*methyl*]*borane*, (**12**).—A mixture of compound (**2**) (3.0 g, 10 mmol) and PCl$_5$ (3.0 g, 14 mmol) in CCl$_4$ (30 cm^3) was heated under reflux. After 30 min the ^{11}B n.m.r. spectrum of the mixture showed a new peak at 40.3 p.p.m. attributable to (Me$_3$Si)$_3$CB(OH)Cl (**13**) (δ_{H} 0.22 p.p.m.). On further heating this peak was replaced by another at lower field. After 9 h the solvent was evaporated off and the residue was extracted with pentane. After removal of pentane from the extract, the white solid residue was heated at 70 °C (0.1 Torr) to remove traces of (**2**) and then recrystallised from pentane to give the *dichloride* (Me$_3$Si)$_3$CBCl$_2$ (3.0 g, 88%; m.p. 192—193 °C) (Found: C, 41.9; H, 8.7. C$_{10}$H$_{27}$BCl$_2$Si$_3$ requires C, 38.5; H, 8.7%); δ_{H}(CCl$_4$–CH$_2$Cl$_2$) 0.27; δ_{B} 56.0; δ_{C}(CDCl$_3$) 5.01 (SiMe$_3$) and 4.11 (*C*SiMe$_3$); δ_{Si} −1.27 p.p.m.; ν(B–Cl)[9] 1 030 and 1 070 cm^{-1}; *m/z* 297 ([*M* − Me]$^+$).

Difluoro[*tris*(*trimethylsilyl*)*methyl*]*borane*, (**14**).—A mixture of compound (**12**) (0.7 g, 2.2 mmol) and SbF$_3$ (4.0 g, 22 mmol) in benzene (30 cm^3) was heated under reflux for 8 h. The solvent was removed and the residue was extracted with pentane. The extract was filtered, the filtrate evaporated, and the white solid residue sublimed (45 °C, 0.1 Torr) and identified as (Me$_3$Si)$_3$CBF$_2$ (0.30 g, 48%), m.p. 165—168 °C (Found: C, 42.3; H, 8.2. C$_{10}$H$_{27}$BF$_2$Si$_3$ requires C, 42.9; H, 9.6%); δ_{H}(CDCl$_3$) 0.22 [t, SiMe$_3$, ^5J(FH) = 0.77]; δ_{B}(CDCl$_3$) 27.1 [t, ^1J(BF) = *ca.* 75]; δ_{F}(CDCl$_3$) −63.8 (q); δ_{C}(CDCl$_3$) 3.60; δ_{Si}(CDCl$_3$) −0.55 p.p.m. [t, ^3J(SiF) = 6 Hz]; *m/z* 263 ([*M* − Me]$^+$).

The Reaction between (Me$_3$Si)$_3$CBCl$_2$ *and* LiPh.—A solution of LiPh (1.47 mmol) in ether (2 cm^3) was added to one of compound (**12**) (0.46 g, 1.47 mmol) in ether (25 cm^3) and the mixture stirred for 2 h at 20 °C. The ^{1}H n.m.r. spectrum showed the formation of both mono- and di-phenylboranes. A further 1.47 mmol of LiPh were then added: after 3 d the solvent was removed and the residue extracted with pentane. Evaporation of the pentane extract followed by recrystallisation from CH$_2$Cl$_2$–MeOH (1:9) gave (Me$_3$Si)$_3$CBPh$_2$ (17%) (**16**), which was made previously from BPh$_2$Br and LiC(SiMe$_3$)$_3$.[10]

Dimethyl[*tris*(*trimethylsilyl*)*methyl*]*borane*, (**17**).—A solution of compound (**12**) (0.52 g, 1.6 mmol) in thf (25 cm^3) was added dropwise to LiMe (4.8 mmol) in ether (10 cm^3) and the mixture was stirred at 20 °C for 3 d. The solvent was removed and the residue was extracted with pentane (60 cm^3). Evaporation of the pentane from the extract left a white solid, which was recrystallised from pentane and shown to be [Li(OEt$_2$)$_2${(Me$_3$Si)$_3$CBMe$_3$}] (**18**) (0.6 g, 82%), m.p. 40 °C (decomp.); δ_{H}(C$_6$D$_5$CD$_3$) −0.5 (9 H, s, BMe$_3$), 0.29 (27 H, s, SiMe$_3$), 0.77 (12 H, t, CH$_3$), and 2.97 (8 H, q, CH$_2$); δ_{B} −21.3 p.p.m.

Chlorotrimethylsilane (2.0 cm^3, 15.7 mmol) was added to a solution of compound (**18**) (0.30 g, 0.67 mmol) in pentane (10 cm^3) and the mixture stirred for 2 d. The residue was extracted with toluene (20 cm^3) and the extract filtered. The solvent was removed from the extract and the residue sublimed at 50 °C (0.05 Torr). The sublimate was recrystallised from pentane and shown to be (Me$_3$Si)$_3$CBMe$_2$ (**17**) (0.13 g, 70%), m.p. 210—213 °C (Found: C, 53.7; H, 13.1. Calc. for C$_{12}$H$_{33}$BSi$_3$: C, 52.9; H, 12.1%); δ_{H}(CCl$_4$–CH$_2$Cl$_2$, 95:5) 0.21 (6 H, s, BMe$_2$) and 0.26 (27 H, s, SiMe$_3$); δ_{B}(CDCl$_3$) 81.5; δ_{C}(C$_6$D$_5$CD$_3$) 5.4 (SiMe$_3$) and 1.05 (BMe$_2$) p.p.m. [The m.p. and n.m.r. spectra of (**17**) were incorrectly reported earlier.[2]] Solid (Me$_3$Si)$_3$CBMe$_2$ could be handled quickly in air without decomposition, but when a solution in CCl$_4$ was left in an open n.m.r. tube about half of the (**17**) in it had decomposed after 16 h.

Tri-μ-hydrido-2,2,2-tris(*tetrahydrofuran*)*-1-*[*tris*(*trimethylsilyl*)*methyl*]*boronlithium* (**3**).—A mixture of compound (**12**) (0.31 g, 0.99 mmol) and LiAlH$_4$ (0.11 g, 3.0 mmol) in thf (25 cm^3) was heated under reflux for 4 h. The solvent was removed and the residue extracted with pentane. The extract was filtered, concentrated, and then kept at −10 °C to give white needles of [(thf)$_3$Li(μ-H)$_3$BC(SiMe$_3$)$_3$] (**3**) (0.44 g, 94%) (*cf.* lit.,[2] yield 40%). The ^{1}H and ^{11}B n.m.r. data have been reported.[2,11] The signal from the B–H protons was found at δ_{H} 0.46 [q, *J*(B–H) = 80 Hz]; δ_{Li}(C$_6$D$_6$) −1.6; δ_{C}(C$_6$D$_6$) 3.5 (Me$_3$Si), 25.3 and 68.6 (thf); δ_{Si}(C$_6$D$_6$) −1.18 p.p.m.

Tris(*dimethylphenylsilyl*)*methyl Boron Compounds.*—The compound LiC(SiMe$_2$Ph)$_3$ reacted only very slowly with

$B(OMe)_3$ under the conditions used for the reaction between $LiC(SiMe_3)_3$ and $B(OMe)_3$.

(*a*) *Difluoro[tris(dimethylphenylsilyl)methyl]borane*, (**5**). A solution of $BF_3{\cdot}OEt_2$ (1.42 g, 0.01 mol) in ether (25 cm^3) was added dropwise to a solution of $LiC(SiMe_2Ph)_3$ (0.01 mol) in thf–OEt_2 (2.5:1) (10 cm^3) at 20 °C. The mixture was heated under reflux for 4 h, and the solvent was then removed. The residue was extracted three times with boiling heptane and the extracts were combined, filtered, and concentrated to give *crystals* of $(PhMe_2Si)_3CBF_2$, m.p. 168—170 °C (5.8 g, 85%) (Found: C, 64.3; H, 7.1. $C_{25}H_{33}BF_2Si_3$ requires C, 64.4; H, 7.1%); $\delta_H(CDCl_3)$ 0.26 (18 H, s, Me) and 7.2—7.6 (15 H, m, Ph); $\delta_B(C_6D_6)$ 29.4; $\delta_F(C_6D_6)$ −57.5 p.p.m. The mass spectrum showed weak peaks at *m/z* 466 ($[M]^+$) and 451 ($[M - Me]^+$); the strongest peak was at *m/z* 297 $\{[(PhMe_2Si)_2C{=}BF - Me]^+\}$, showing the ready elimination of $SiFMe_2Ph$ in the spectrometer.

In an attempt to study this elimination more carefully a sample of compound (**5**) was melted in a Schlenk tube under nitrogen and stirred at 180 °C. It was apparent from the ^{19}F n.m.r. spectrum that all the starting difluoride had disappeared after 24 h, but a complex mixture was obtained. Only $SiFMe_2Ph$ and biphenyl were identified by gas chromatography–mass spectroscopy.

(*b*) *Fluoro(methoxy)[tris(dimethylphenyl)methyl]borane*, (**19**). A mixture of compound (**5**), CH_2Cl_2 (10 cm^3), and MeOH (3 cm^3) was stirred at 20 °C for 0.5 h. The solvent was evaporated off and the residue sublimed at 175 °C (0.05 Torr), recrystallised from heptane, and shown to be $(PhMe_2Si)_3CB(F)OMe$ (0.87 g, 85%), m.p. 142—144 °C (Found: C, 64.5; H, 7.6. $C_{26}H_{36}BFOSi_3$ requires C, 64.1; H, 7.5%); $\delta_H(CCl_4)$ 0.18 (18 H, s, Me), 3.70 (3 H, s, OMe), and 7.5—7.7 (15 H, m, Ph); $\delta_B(CDCl_3)$ 28.5; $\delta_F(CDCl_3)$ −70.0 p.p.m. The mass spectrum showed a weak peak at *m/z* 478 (M^+), and much stronger ones at 463 ($[M - Me]^+$), 401 ($[M - Ph]^+$), and 385 ($[M - Ph - CH_4]^+$). The last three peaks were much stronger in the positive chemical ionization (NH_3) spectrum.

(*c*) *Tri-μ-hydrido-2,2,2-tris(tetrahydrofuran)-1-[tris(dimethylphenylsilyl)methyl]boronlithium*, (**20**). A solution of compound (**5**) (0.5 g, 1 mmol) in thf (15 cm^3) was added dropwise to one of $LiAlH_4$ (0.05 g, 1.3 mmol) in thf (15 cm^3). The mixture was stirred for 1.5 h, the solvent removed, and the residue extracted with boiling toluene. The extract was filtered, concentrated, and kept at 20 °C overnight. The white crystals which separated were too sensitive for C and H microanalysis but were shown to be (**20**) by an *X*-ray diffraction study.[12] A similar compound, m.p. 142—144 °C, with ether in place of thf was isolated and characterised by n.m.r. spectroscopy: $\delta_H(C_6D_5CD_3)$ 0.45 (s, 18 H, $SiMe_2$), 1.1 (18 H, t, CH_3), 3.3 (12 H, q, CH_2), and 6.9—8.0 (15 H, m, Ph); $\delta_{Li}(C_6D_6)$ −3.54; δ_B −30.7 p.p.m. [q, *J*(BH) 81 Hz]. The weak quartet from the B–H protons was partly obscured by the Me_3Si signal.

(*d*) *Dihydroxy[tris(dimethylphenylsilyl)methyl]borane*, (**6**). A solution of $BF_3{\cdot}OEt_2$ (0.88 cm^3, 7.1 mmol) in ether (10 cm^3) was added dropwise to $LiC(SiMe_2Ph)_3$ (7.1 mmol) in thf (25 cm^3). The mixture was heated under reflux for 4 h, then water (20 cm^3) was added and the mixture heated for a further 8 h. After removal of volatile material the organic layer was separated, dried ($MgSO_4$), and filtered. The crystals that separated from the concentrated extract were of $(PhMe_2Si)_3CB(OH)_2$, m.p. 162—164 °C (2.5 g, 75%) (Found: C, 65.2; H, 7.6. $C_{25}H_{35}BO_2Si_3$ requires C, 64.9; H, 7.6%); $\delta_H(CDCl_3)$ 0.24 (18 H, s, $SiMe_3$), 4.69 (2 H, s, OH, disappeared on shaking with D_2O), and 7.2—7.6 (15 H, m, Ph); $\delta_B(C_6D_6)$ 31.5; $\delta_C(CDCl_3)$ 2.3 (Me), 127.7, 129.0, 135.1, and 141.3 (Ph); $\delta_{Si}(CDCl_3)$ −5.5 p.p.m.; ν(OH) 3 600 and 3 380 cm^{-1}; *m/z* 447 (7% $[M - Me]^+$), 369 (40, $[M - Me - C_6H_6]^+$), and 309 $\{40, [(PhMe_2Si)_2CBO]^+\}$. There were several strong peaks from fragments of the $(PhMe_2Si)_3C$ group. The ^{11}B peak was shifted to 15.7 p.p.m. in alkaline solution but (**6**) was recovered on acidification.

Compound (**6**) could also be made by hydrolysis of (**20**). A mixture of compound (**20**) (0.5 g, 0.9 mmol), thf (25 cm^3), and water (3 cm^3) was stirred for 1 h, then extracted with light petroleum (20 cm^3, b.p. 30—40 °C). The organic layer was separated, dried ($MgSO_4$), and concentrated to give (**6**) (51%).

(*e*) 2-[*Tris(dimethylphenylsilyl)methyl*]-1,3,2-*benzodioxaborole*, (**21**). Catechol (0.16 g, 1.5 mmol) in thf (10 cm^3) was added to a solution of compound (**20**) (0.5 g, 0.93 mmol) in thf (10 cm^3) and the mixture was stirred for 3 h at 20 °C. The solvent was removed and the residue boiled with heptane; the heptane solution was filtered, then concentrated and kept at 0 °C to give white crystals of $(PhMe_2Si)_3CBO_2C_6H_4$, m.p. 145—146 °C (0.23 g, 56%) (Found: C, 69.3; H, 7.1. $C_{31}H_{37}BO_2Si_3$ requires C, 69.4; H, 6.9%); $\delta_H(CCl_4)$ 0.25 (18 H, s, $SiMe_2$) and 7.1—7.5 (19 H, m, Ph, C_6H_4); δ_B 35.0 p.p.m.; *m/z* 536 ($[M]^+$) and 521 ($[M - Me]^+$).

Crystal Structure Determinations.—(*a*) *Crystal data for* $(Me_3Si)_3CB(OH)_2$ (**2**). $C_{10}H_{29}BO_2Si_3$, $M = 276.4$, orthorhombic, space group $Pna2_1$, $a = 15.675(2)$, $b = 16.121(2)$, $c = 14.662(2)$ Å, $U = 3\,694.9$ Å^3, $Z = 8$, $D_c = 0.99$ g cm^{-3}, $F(000) = 1\,216$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 2.39$ cm^{-1}.

Several crystals, from batches crystallised under various conditions and from various solvents, were examined but all gave only limited diffraction data. The crystal selected for data collection on an Enraf–Nonius CAD4 diffractometer had dimensions of *ca.* 0.20 × 0.25 × 0.15 mm and was sealed in a capillary. Intensities were measured for reflections with $+h$, $+k$, $+l$ and $2 < \theta < 20°$ using the θ—2θ mode and a maximum scan time of 1 min. After correction for Lorentz polarisation effects but not for absorption there were only 600 reflections with $|F^2| > \sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.21I)^2]^{\frac{1}{2}}/\mathrm{Lp}$. These were used in the refinement.

The systematic absences of $0kl$ for $(h + l)$ odd and $h01$ for h odd indicated either space group *Pnam* or $Pna2_1$. The structure was initially solved by direct methods (MULTAN)[13] in *Pnam* to reveal two independent molecules both lying across the mirror plane, but it was impossible to locate all the carbon atoms and the molecular geometry was peculiar. The structure solution was continued in $Pna2_1$, which allowed the location of all the C atoms with an improved, although still distorted, geometry. In both space groups it proved necessary to include two orientations at equal occupancy for both $B(OH)_2$ groups. Final refinement in $Pna2_1$, with the Si atoms anisotropic, gave $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.163$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w{\cdot}|F_o|^2]^{\frac{1}{2}} = 0.165$ with a weighting scheme of $w = 1/\sigma^2(F)$. A final difference map showed no feature >0.5 e Å^{-3}. Computer programs used were from the Enraf-Nonius SDP-Plus package. Scattering factors were from ref. 14. Fractional atomic coordinates are given in Table 1 and principal bond lengths and angles in Table 2.

(*b*) *Crystal data for* $[(MeOH)_2Li(\mu\text{-}OMe)_2B(OMe)_2]$ (**11**). $C_6H_{20}BLiO_6$, $M = 206.0$, monoclinic, space group $C2/c$, $a = 16.421(2)$, $b = 7.186(2)$, $c = 11.352(2)$ Å, $\beta = 110.76(1)°$, $U = 1\,252.3$ Å^3, $Z = 4$, $D_c = 1.09$ g cm^{-3}, $F(000) = 448$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 0.9$ cm^{-1}.

The general procedure was as described for (**2**). Data for h, k, $\pm l$ reflections with $2 < \theta < 25°$ were collected from a crystal of size 0.4 × 0.4 × 0.4 mm, and 569 reflections with $|F^2| > \sigma(F^2)$ were used for the structure analysis. The positions of the Li, C, O, and B atoms were found by direct methods. Full-matrix least-squares refinement, with anisotropic thermal parameters, converged at $R = 0.117$, $R' = 0.132$. Hydrogen atoms were not included. The final difference map showed no feature >0.7 e Å^{-3}.

Table 1. Fractional atomic co-ordinates ($\times 10^4$ for Si atoms, $\times 10^3$ for other atoms) for compound (**2**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Si(1)	3 884(13)	8 666(18)	6 517(0)	C(5)	360(5)	745(4)	866(4)
Si(2)	3 826(15)	8 684(10)	8 665(11)	C(6)	449(6)	868(5)	986(6)
Si(3)	5 563(28)	8 542(13)	7 480(9)	C(7)	281(5)	925(4)	876(4)
Si(4)	6 278(25)	6 249(18)	3 619(13)	C(8)	571(5)	749(3)	732(3)
Si(5)	6 301(21)	6 232(18)	1 662(22)	C(9)	619(3)	899(3)	644(2)
Si(6)	4 516(27)	5 919(14)	2 461(12)	C(10)	633(7)	935(6)	833(5)
O(1)	389(6)	1 055(6)	803(5)	C(11)	568(4)	652(2)	248(2)
O(1′)	380(4)	1 023(5)	657(4)	C(12)	550(5)	652(5)	484(5)
O(2′)	463(4)	1 038(3)	839(3)	C(13)	658(5)	510(3)	391(3)
O(2)	517(4)	1 030(3)	707(3)	C(14)	731(9)	699(8)	387(7)
O(3′)	480(3)	785(3)	275(2)	C(15)	626(5)	673(5)	41(4)
O(3)	497(4)	786(3)	167(3)	C(16)	605(5)	500(7)	125(6)
O(4)	618(4)	792(4)	307(4)	C(17)	751(5)	616(4)	223(4)
O(4′)	588(5)	781(4)	153(4)	C(18)	350(4)	633(4)	273(4)
C(1)	445(4)	890(2)	756(2)	C(19)	456(5)	497(4)	265(3)
C(2)	444(6)	878(6)	531(6)	C(20)	442(5)	630(5)	117(5)
C(3)	261(6)	894(5)	686(5)	B(1)	453(5)	995(3)	750(2)
C(4)	354(5)	750(4)	688(5)	B(2)	542(5)	768(4)	230(4)

Table 2. Intramolecular distances (Å) and angles (°) for compound (**2**) with e.s.d.s in parentheses

Si(1)–C(1)	1.80(4)	Si(1)–C(2)	1.98(9)	Si(6)–C(11)	2.07(7)	Si(6)–C(18)	1.77(7)
Si(1)–C(3)	2.11(9)	Si(1)–C(4)	2.03(3)	Si(6)–C(19)	1.56(6)	Si(6)–C(20)	1.99(8)
Si(2)–C(1)	1.92(4)	Si(2)–C(5)	2.01(7)	O(2)–B(1)	1.31(8)	O(1)–B(1)	1.59(6)
Si(2)–C(6)	2.04(9)	Si(2)–C(7)	1.83(8)	O(1′)–B(1)	1.83(5)	O(2′)–B(1)	1.47(6)
Si(3)–C(1)	1.84(7)	Si(3)–C(8)	1.73(6)	O(3′)–B(2)	1.21(9)	O(3)–B(2)	1.21(4)
Si(3)–C(9)	1.95(5)	Si(3)–C(10)	2.17(5)	O(4′)–B(2)	1.36(9)	O(4)–B(2)	1.69(9)
Si(4)–C(11)	1.96(5)	Si(4)–C(12)	2.21(8)	C(11)–B(2)	1.93(8)	C(1)–B(1)	1.70(6)
Si(4)–C(13)	1.95(6)	Si(4)–C(14)	2.04(7)	O(1) · · · O(4)$^{\mathrm{I}}$	2.48	O(2) · · · O(3)$^{\mathrm{I}}$	3.03
Si(5)–C(11)	1.62(5)	Si(5)–C(15)	2.00(7)	O(1′) · · · O(4′)$^{\mathrm{I}}$	3.18	O(2′) · · · O(3′)$^{\mathrm{I}}$	3.13
Si(5)–C(16)	2.11(3)	Si(5)–C(17)	2.07(8)				

C(1)–Si(1)–C(2)	121(3)	C(1)–Si(1)–C(3)	103(3)	C(11)–Si(6)–C(18)	128(3)	C(11)–Si(6)–C(19)	115(4)
C(1)–Si(1)–C(4)	96(1)	C(2)–Si(1)–C(3)	128(3)	C(11)–Si(6)–C(20)	86(3)	C(18)–Si(6)–C(19)	112(4)
C(2)–Si(1)–C(4)	116(3)	C(3)–Si(1)–C(4)	83(2)	C(18)–Si(6)–C(20)	92(3)	C(19)–Si(6)–C(20)	118(3)
C(1)–Si(2)–C(5)	105(2)	C(1)–Si(2)–C(6)	118(3)	Si(6)–C(11)–B(2)	105(4)	Si(1)–C(1)–Si(2)	115(3)
C(1)–Si(2)–C(7)	115(2)	C(5)–Si(2)–C(6)	95(3)	Si(1)–C(1)–Si(3)	110(2)	Si(1)–C(1)–B(1)	102(3)
C(5)–Si(2)–C(7)	109(3)	C(6)–Si(2)–C(7)	112(3)	Si(2)–C(1)–Si(3)	119(2)	Si(2)–C(1)–B(1)	105(3)
C(1)–Si(3)–C(8)	116(3)	C(1)–Si(3)–C(9)	114(2)	Si(3)–C(1)–B(1)	103(4)	Si(4)–C(11)–Si(5)	106(3)
C(1)–Si(3)–C(10)	108(3)	C(8)–Si(3)–C(9)	101(3)	Si(4)–C(11)–Si(6)	109(2)	Si(4)–C(11)–B(2)	116(3)
C(8)–Si(3)–C(10)	127(4)	C(9)–Si(3)–C(10)	87(3)	Si(5)–C(11)–Si(6)	112(2)	Si(5)–C(11)–B(2)	108(3)
C(11)–Si(4)–C(12)	112(3)	C(11)–Si(4)–C(13)	121(2)	O(1′)–B(1)–O(2′)	126(4)	O(1)–B(1)–O(2)	117(5)
C(11)–Si(4)–C(14)	113(4)	C(12)–Si(4)–C(13)	98(3)	O(1)–B(1)–C(1)	122(5)	O(1′)–B(1)–C(1)	104(3)
C(12)–Si(4)–C(14)	100(4)	C(13)–Si(4)–C(14)	109(4)	C(1)–B(1)–O(2)	121(5)	O(2′)–B(1)–C(1)	116(3)
C(11)–Si(5)–C(15)	123(3)	C(11)–Si(5)–C(16)	112(2)	C(11)–B(2)–O(3′)	108(5)	O(3′)–B(2)–O(4′)	148(7)
C(11)–Si(5)–C(17)	106(3)	C(15)–Si(5)–C(16)	96(3)	O(3)–B(2)–C(11)	118(5)	O(3)–B(2)–O(4)	152(7)
C(15)–Si(5)–C(17)	115(3)	C(16)–Si(5)–C(17)	103(2)	C(11)–B(2)–O(4′)	99(5)	O(4)–B(2)–C(11)	88(4)

Transformation I $1 - x, 2 - y, \frac{1}{2} + z$.

Fractional atomic co-ordinates are given in Table 3 and bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters.

Results and Discussion

The initial product of the reaction between $LiC(SiMe_3)_3$ and $B(OMe)_3$ seems to be an alkyltrimethoxyborane $Li(Me_3Si)_3CB(OMe)_3$ (**9**). This reaction is followed in a slow step by transfer of an OMe group from (**9**) to $B(OMe)_3$, with relief of steric strain as the boron atom attached to the $C(SiMe_3)_3$ group changes from four- to three-co-ordinate [equation (1)]. Methyltrialkoxyborates analogous to (**9**) have been identified in reactions between methyl-lithium and various trialkoxyboranes, but these much less sterically hindered species are rapidly attacked by methyl-lithium to give di- or tri-methyl(alkoxy)-boranes.[15]

The compound $(Me_3Si)_3CB(OMe)_2$ (**7**) or $(Me_3Si)_3CB(OH)_2$ (**2**) may be isolated from the reaction mixture (Scheme 1). The boronic acid (**2**) melts at >200 °C without elimination of Me_3SiOH or formation of a boroxin $(RBO)_n$ where R = $C(SiMe_3)_3$ (though the ion $[RBO]^+$ was detected in the mass spectrum).[2] Attempts to form the boroxin on a preparative scale have so far been unsuccessful. Thus (**2**) appears not to lose water in contact with 4 Å molecular sieve or calcium hydride; it reacts with phosphorus(V) oxide and with the Martin dehydrating agent $Ph_2S\{OC(CF_3)_2Ph\}_2$,[16] but pure boron-containing products have not been isolated. It therefore differs from boronic acids with smaller organic groups and seems to be even

Table 3. Fractional atomic co-ordinates ($\times 10^4$) for compound (**11**) with e.s.d.s in parentheses

Atom	x	y	z
O(1)	−680(3)	819(8)	1 749(5)
O(2)	308(3)	3 381(7)	1 742(5)
O(3)	−930(4)	7 229(9)	2 162(7)
C(1)	−1 448(5)	1 637(15)	836(9)
C(2)	630(6)	2 618(14)	824(8)
C(3)	−1 770(5)	7 058(16)	2 109(10)
B	0	2 130(17)	2 500
Li	0	5 606(33)	2 500

Table 4. Intramolecular distances (Å) and angles (°) for compound (**11**) with e.s.d.s in parentheses

O(1)–C(1)	1.444(9)	O(1)–B	1.478(9)
O(2)–C(2)	1.434(12)	O(2)–B	1.454(10)
O(2)–Li	1.96(2)	O(3)–C(3)	1.365(11)
O(3)–Li	1.85(2)		
B–O(1)–C(1)	116.3(7)	B–O(2)–C(2)	119.3(7)
B–O(2)–Li	92.7(6)	C(2)–O(2)–Li	148.0(7)
O(1)–B–O(1$^{\text{I}}$)	100.8(8)	O(1)–B–O(2)	113.8(3)
O(2)–B–O(2$^{\text{I}}$)	103.6(8)	O(1)–B–O(2$^{\text{I}}$)	112.7(3)
C(3)–O(3)–Li	134.4(8)	O(2)–Li–O(2$^{\text{I}}$)	71.1(8)
O(2)–Li–O(3)	138.0(4)	O(2)–Li–O(3$^{\text{I}}$)	106.4(3)
O(3)–Li–O(3$^{\text{I}}$)	102(1)		

Symmetry element I is $\bar{x}, y, \frac{1}{2} - z$.

less reactive than the sterically hindered arylboronic acids $B(C_6H_2R_3\text{-}2,4,6)(OH)_2$ (R = Me[17] or Bu^t[18]) both of which can be dehydrated, though with difficulty, on heating.

In order to gain further insight into this finding and because no structure of an alkylboronic acid has been described, we have determined the crystal and molecular structure of (**2**) (Figure 1). Owing to the poor quality of the crystal and the extremely limited diffraction data the observed bond lengths and angles in the molecules are too imprecise to permit meaningful comparison with the structures of the arylboronic acids $4\text{-BrC}_6H_4B(OH)_2$[19] and $PhB(OH)_2$.[20] However, we believe the molecular structure of (**2**) is correctly identified.

The two independent molecules are linked by hydrogen bonds; the apparent O ⋯ O distances vary between 2.4 and 3.2 Å. Each BO_2 group is arranged in two alternative orientations related by a rotation about the C–B bond of 98° for B(1) and 95° for B(2). In all four cases the CBO_2 group appears to be planar. There is no hydrogen bonding between the dimers. In the case of phenylboronic acid[20] pairs of hydrogen bonds link the molecules into dimers and weaker hydrogen bonds link the dimers into an extended framework. In $(Me_3Si)_3CB(OH)_2$, however, the weaker hydrogen bonds are apparently precluded by intermolecular repulsion between alkyl groups. In the absence of an extended framework the planar CBO_2 groups are free to adopt two possible orientations, so that the precise details of the hydrogen bonds within the dimers are obscured. For the compounds (**2**) and (**6**) the condensation of pairs of $RB(OH)_2$ molecules to form boroxin dimers is probably prevented by steric hindrance.

The ^{11}B n.m.r. spectra show that the species formed on addition of alkali to a solution of (**2**) in ethanol–water (1 : 1) is $[BR(OH)_3]^-$ [R = $C(SiMe_3)_3$] rather than $[RBO_2H]^+$ indicating that (**2**), like $PhB(OH)_2$,[21] behaves as a Lewis rather than a protic acid. It is possible to recover (**2**) by acidification and there is thus no evidence for migration of Me_3Si from C to O such as might be expected (by analogy with the behaviour of silanolate anions[22]) if an anion $RB(OH)O^-$ were formed.

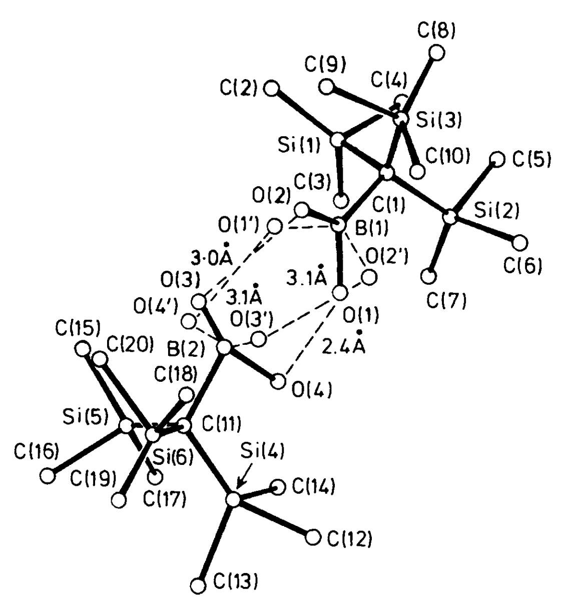
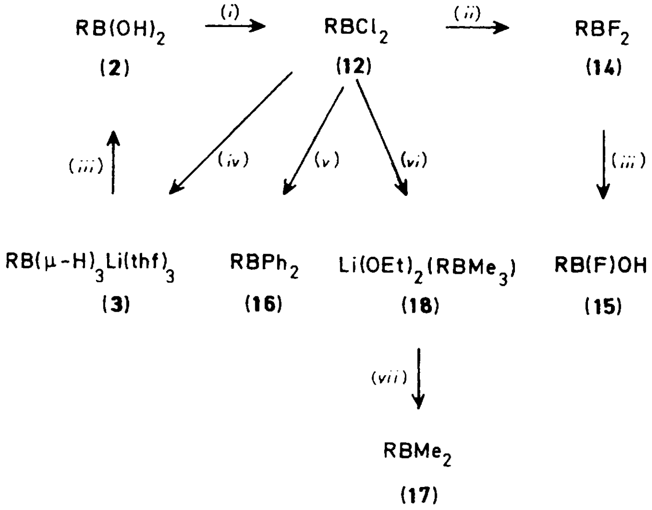


Figure 1. The molecular structure of $(Me_3Si)_3CB(OH)_2$ (**2**) showing the disorder in the positions of the atoms and hydrogen bonds between pairs of molecules. The co-ordinates of the monomer containing B(2) are obtained by the transformation $1 - x, 2 - y, \frac{1}{2} + z$ on those in Table 1



Scheme 2. R = $(Me_3Si)_3C$. (*i*) PCl_5; (*ii*) SbF_3; (*iii*) H_2O; (*iv*) $LiAlH_4$; (*v*) LiPh; (*vi*) LiMe; (*vii*) $SiMe_3Cl$

The boronic acid (**2**) is a useful starting material for the preparation of the alcohol ROH [R = $C(SiMe_3)_3$][5] and for a range of compounds RBX_2 (X = Cl, F, Ph, or Me) and $(thf)_3Li(\mu\text{-}H)_3BR$ (Scheme 2). Most of the conversions involve standard reactions in boron chemistry and require no further comment.

The borate (**8**) that separated from the reaction between $LiC(SiMe_3)_3$ and $B(OMe)_3$ is only very slightly soluble in hydrocarbon solvents, suggesting that it may have a polymeric structure in the solid. We have been unable to obtain any n.m.r. data or crystals suitable for an *X*-ray study. When (**8**) was recrystallised from methanol the product was a methanol solvate $[(MeOH)_2Li(\mu\text{-}OMe)_2B(OMe)_2]$ (**11**), which appears to

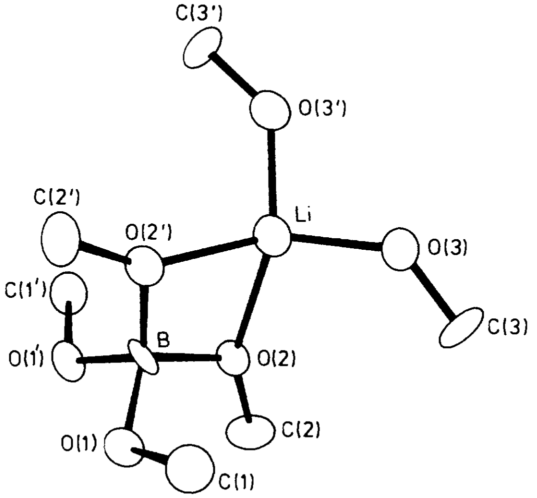


Figure 2. The molecular structure of $(MeOH)_2Li(\mu\text{-}OMe)_2B(OMe)_2$ (**11**)

have been isolated first in 1914.[23] *X*-Ray data were collected, and although these were again rather poor the molecular structure, with crystallographic two-fold rotational symmetry, was clear. There appear to be no unusual bond lengths and angles. The B–O and C–O bond lengths agree with those in piperidinium tetramethoxyborate[24] and in borates with a four-co-ordinate boron;[25] differences between B–O(2) and B–O(1) (Figure 2) are probably not significant. As in other borates the O–B–O angles deviate considerably from the tetrahedral value.

The tendency of lithium to co-ordinate directly with lone pairs from ligand atoms in metalate anions, with formation of bridged lithium–metal complexes, rather than compounds with separate fully solvated ions, has been discussed elsewhere.[26] Discrete $[B(OMe)_4]^-$ ions are found in the piperidinium salt. Methoxide bridges between sodium and boron are found in the sodium salt $Na[B(OMe)_4]{\cdot}MeOH{\cdot}1.5H_2O$,[27] which has a more complicated structure than (**11**), incorporating solvent water as well as methanol.

The boron-containing species in MeOH solutions of compound (**11**) appear from n.m.r. measurements to be the same as those in similar solutions of other tetramethoxyborates.[28,29] At 25 °C there is complete exchange between the methoxy groups of the solvent, the solvate, and the borate. It is possible that the intermediate (**9**), which is freely soluble in thf, consists of ion pairs with methoxy bridges between Li and B, as in (**11**).

Tris(dimethylphenylsilyl)methyl-lithium does not react with trimethoxyborane under the conditions used for the preparation of $(Me_3Si)_3CB(OMe)_2$. The lower reactivity of $LiC(SiMe_2Ph)_3$ than of $LiC(SiMe_3)_3$ towards silicon substrates[30] thus extends to reactions with $B(OMe)_3$. However, $LiC(SiMe_2Ph)_3$ is also less reactive than $LiC(SiMe_3)_3$ towards thf, so that $(PhMe_2Si)_3CBF_2$ (**5**) can be made directly and without difficulty from $LiC(SiMe_2Ph)_3$ and $BF_3{\cdot}OEt_2$. The boronic acid $(PhMe_2Si)_3CB(OH)_2$ (**6**) was obtained from the fluoride by hydrolysis under vigorous conditions to ensure complete removal of the fluoride hydroxide $(PhMe_2Si)_3CBF(OH)$;[6] like (**2**), (**6**) behaved as a Lewis acid in alkaline solution.

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