

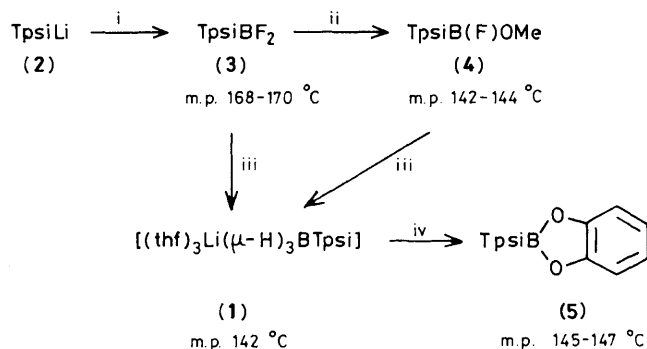
The Crystal Structure of the Alkyltrihydroborate $[(\text{thf})_3\text{Li}(\mu\text{-H})_3\text{BC}(\text{SiMe}_2\text{Ph})_3]$, (thf = tetrahydrofuran)

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Molecules of the compound $[(\text{thf})_3\text{Li}(\mu\text{-H})_3\text{BC}(\text{SiMe}_2\text{Ph})_3]$, (thf = tetrahydrofuran) made by reduction of difluoro-tris(dimethylphenylsilyl)methyl boron with LiAlH_4 , have been shown by X-ray crystallography to have almost C_3 symmetry, with tridentate bridges between alkyltrihydroborate and lithium.

Alkyltrihydroborates are attracting increasing interest as selective reducing agents in organic synthesis.¹ Most such compounds have been obtained only in solution;²⁻⁴ some have been isolated as solids,^{5,6} but none has been structurally characterized, and little information is available about the nature of the interaction between the alkyltrihydroborate anion and the counter ion, either in the solid state or in the ether solvents in which the compounds are normally used.



Scheme 1. Reagents and conditions: i, $\text{BF}_3\text{-Et}_2\text{O}$, Et_2O , reflux; ii, $\text{MeOH-CH}_2\text{Cl}_2$, $\frac{1}{2}$ h, 20°C ; iii, $\text{LiAlH}_4\text{-thf}$, 1.5 h, reflux; iv, catechol-thf, 2 h, 20°C . Compounds (3)–(5) gave satisfactory elemental analyses and n.m.r. and mass spectra.

Following our work on tris(trimethylsilyl)methyl (Tsi) derivatives of boron⁶⁻⁸ we have now made several tris(dimethylphenylsilyl)methyl (Tpsi) derivatives, and have determined the structure of the lithium alkyltrihydroborate $[(\text{thf})_3\text{Li}(\mu\text{-H})_3\text{BC}(\text{SiMe}_2\text{Ph})_3]$, (1) (thf = tetrahydrofuran) by X-ray diffraction.

Tris(dimethylphenylsilyl)methyl-lithium (2)⁹ reacts with $\text{BF}_3\text{-Et}_2\text{O}$ to give the white crystalline difluoride, (3) (see Scheme 1). [In contrast, the reaction between TsiLi and $\text{BF}_3\text{-Et}_2\text{O}$ in thf gives $\text{TsiB(F)O(CH}_2)_4\text{Tsi}$, as a result of cleavage of the thf.⁷ The lower reactivity of TpsiLi than of TsiLi, both as an alkylating agent⁹ and towards BF_3 -catalysed ether cleavage, may be associated with the fact that TpsiLi has a molecular structure¹⁰ whereas TsiLi is an ionic species.¹¹] The difluoride (3) reacts readily with MeOH to give the methoxyfluoride (4). Both (3) and (4) are reduced by LiAlH_4 in thf to the alkyltrihydroborate, (1). Compound (1) reacts with catechol to give compound (5). Crystals of (1) suitable for the diffraction study were obtained by recrystallization from toluene; they are moisture sensitive.

Crystal data: $\text{C}_{37}\text{H}_{60}\text{O}_3\text{Si}_3\text{BLi}$ $M = 654.9$, triclinic, space group $P\bar{1}$, $a = 12.162(3)$, $b = 13.335(3)$, $c = 15.263(1)$ Å, $\alpha = 79.91(1)$, $\beta = 78.45(1)$, $\gamma = 63.82(2)^\circ$, $U = 2165.8$ Å³, $Z = 2$, $D_c = 1.00$ g cm⁻³, Monochromated Mo- K_α radiation, $\lambda = 0.71069$ Å, $\mu = 1.34$ cm⁻¹, $R = 0.13$, $R' = 0.17$ for 2718 reflections with $|F^2| > \sigma(F^2)$ measured on an Enraf-Nonius

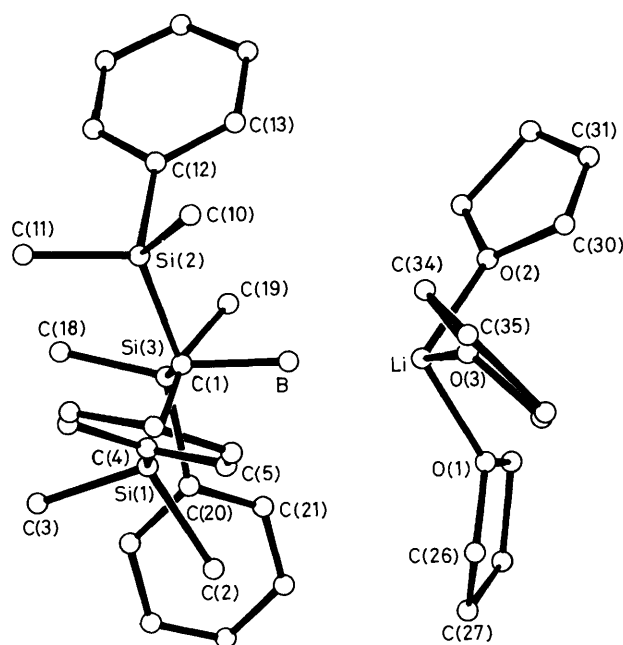


Figure 1. Molecular structure of $[(\text{thf})_3\text{Li}(\mu\text{-H})_3\text{BC}(\text{SiMe}_2\text{Ph})_3]$ (**1**) with hydrogen atoms omitted. Selected mean dimensions: C(1)–B 1.75(2), C(1)–Si 1.88(2), Si–Me 1.90(2), Si–Ph 1.91(2), Li–O 2.00(4), Li–B 2.19(4) Å, B–C–Si 106(1), Si–C–Si 113(1), Me (or Ph)–Si–Me 105(1), O–Li–O 99(2), O–Li–B 118(2), C(1)–B–Li 174(1)°.

CAD4 diffractometer in the range $2 < \theta < 20^\circ$. The quality of the data was rather poor, possibly because the crystal slowly lost thf during the diffraction study, and the hydrogen atoms could not be located. There is no doubt, however, about the nature of the heavy atom structure, which is shown in Figure 1.† The solvated lithium cations and the alkyltrihydroborate anions are linked together into molecules having approximate C_3 symmetry about a linear Li–B–C(1) axis. This implies tridentate co-ordination of lithium by trihydroborate. As in TpsIH,¹² steric hindrance leads to opening of the Si–C–Si angles [to 113(1)°] and closing of the Me–Si–Me and Me–Si–Ph angles [to 105(1)°]. The Li–B distance, 2.19(4) Å, may be used along with the usually quoted¹³ value of 1.36(6) Å for the ionic radius of tridentate BH_4^- to give a value of 0.83(7) Å for the ionic radius of lithium, which is within the range, 0.76–0.90 Å, quoted for octahedral co-ordination.¹⁴ As expected,¹³ the Li–B distance in (**1**) is ca. 0.3 Å less than that in $[(\text{MeOCH}_2\text{CH}_2\text{OMe})_3\text{Li}(\mu\text{-H})_2\text{B}(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)_2]$, which has bidentate bridges between dimesityldihydroborate and lithium.¹⁵ It is also interesting to compare the $\text{Li}(\mu\text{-H})_3\text{B}$ systems in (**1**) with $\text{Li}(\mu\text{-H})_3\text{C}$ in solid methyl-lithium¹⁶ or

lithium tetramethylborate;¹⁷ in both of these compounds $\text{Li}\cdots\text{C}$ is 2.36 Å.

Compound (**1**) is highly soluble in thf and diethyl ether and reasonably soluble in toluene and heptane. It is possible, therefore, that the species in solution and the active agent in reductions with alkyltrihydroborates may be best described as molecular rather than as ion pairs. If so, it may be possible to modify the selectivity of the reagent by changing the dielectric constant of the medium to promote dissociation or by changing the counter ion or the base co-ordinating the lithium. The spectroscopic parameters of (**1**) [i.r. $\nu(\text{BH})$ 2085, 2200 cm^{-1} ; n.m.r. ^{11}B δ (in C_6D_6 relative to $\text{BF}_3\cdot\text{OEt}_2$) -30.2 p.p.m., $J(\text{BH})$ 80 Hz; ^7Li δ -1.70 (in C_6D_6 relative to ext. LiNO_3 in H_2O)] are similar to those given for other alkyltrihydroborates.^{2,4,5} In the ^1H n.m.r. spectrum, the signal due to the BH_3 group appears as a quartet at δ 0.46 in thf; on cooling the signals broaden in the usual way by 'thermal' or 'correlation time' decoupling.¹⁸ Lithium–hydrogen spin coupling was not observed in the ^1H or ^7Li n.m.r. spectra. Further spectroscopic work has shown that the previously reported $(\text{Me}_3\text{Si})_3\text{C}$ derivative must be $[(\text{thf})_3\text{Li}(\mu\text{-H})_3\text{BTsi}]$, i.e. it has the same type of structure as (**1**), with $(\mu\text{-H})_3$ bridges between boron and lithium, not $(\mu\text{-H})_2$ bridges as originally suggested.⁶

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.