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Hindered Organoboron Groups in Organic Chemistry. 19. Synthesis of Heteroatom Substituted Dimesitylborylmethanes

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Abstract. Syntheses are described of a series of bifunctional heteroatom substituted dimesitylborylmethanes, $Mes_2BCH_2MetR_x$ (Met = Si, S, Sn, Pb) and also $Hg(CH_2BMes_2)_2$. Some properties of these compounds have been investigated. These include their stability to protic reagents, the production of carbanions, with and without cleavage of the metal carbon bond, and the nature of the stabilisation in two of the derived, uncleaved carbanions.

In the preceding paper[1], details were given for the preparation of alkyldimesitylboranes as starting materials for the production of boron stabilised carbanions. The carbanions were produced using either lithium dicyclohexylamide ($LiNChx_2$) or 2,4,6-trimethylphenyllithium (mesityllithium, MesLi) as hindered bases for proton abstraction without ate complex formation. The boron-stabilised carbanions are valuable intermediates that take part in numerous reactions[2-7] that will be detailed in the following papers.

Similarly, the bifunctional compounds $Mes_2BCH_2MetR_x$ might also be valuable starting materials for the production of stabilised carbanions that could also give rise to interesting and synthetically valuable processes.[8,9]

We envisaged that such compounds might be made by either of the sequences outlined in equations (1) and (2).

$$\underset{(1)}{Mes_2BCH_3} \xrightarrow[LiNChx_2]{MesLi\ or} \underset{(2)}{Mes_2BCH_2Li} \xrightarrow{R_xMetX} Mes_2BCH_2MetR_x \qquad (1)$$

$$\underset{(3)}{Mes_2BF} + \underset{(4)}{LiCH_2MetR_x} \longrightarrow Mes_2BCH_2MetR_x \qquad (2)$$

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We have previously described the conversion of the readily available and stable compound (1) to its anionic derivative (2), and therefore (1) seemed an ideal intermediate for the production of $Mes_2BCH_2MetR_x$, as shown in equation (1). Fluorodimesitylborane (3) is readily produced[1], but in general the lithio derivatives (4) are not so easily available for use in the conversions shown in equation (2).

We have used the process given in equation (1) to produce $Mes_2BCH_2SiMe_3$ (5), m.p. 72°C; Mes_2BCH_2SPh (6), m.p. 113°C; $Mes_2BCH_2SnMe_3$ (7); $Mes_2BCH_2SnBu^n_3$ (8); $Mes_2BCH_2SnPh_3$ (9), m.p. 124°C and $Mes_2BCH_2PbPh_3$ (10), m.p. 122°C. We have also made $(Mes_2BCH_2)_2Hg$ (11), m.p. 180°C, as shown in equation (3).

$$\underset{(2)}{2Mes_2BCH_2Li} + HgCl_2 \longrightarrow \underset{(11)}{(Mes_2BCH_2)_2Hg} + 2LiCl \qquad (3)$$

For compounds (5), (7), (8), (9) and (10), the component R_xMetX was the corresponding triorganylmetal chloride. However, attempts to make (6) by use of PhSCl failed completely, as did use of $(PhS)_2$. The former reagent gave a plethora of products whilst the latter seemed reluctant to react. Use of $PhSSO_2Ph$ however did eventually lead to a reproducible synthesis of (6) *via* equation (1). Production of (2) could be accomplished either with $LiNChx_2$ or MesLi, although in the former case the amine had to be removed prior to reaction with the metal halide used.

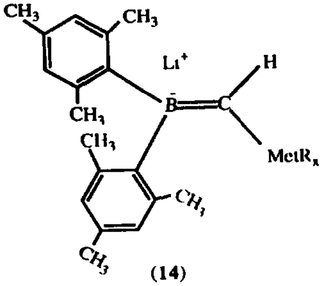
Because of the problems we encountered in the synthesis of (6) using equation (1), we turned to equation (2), particularly because $PhSCH_2Li$ is a readily available carbanion.[10] Reaction was slow but reproducible to give an isolated yield of *ca.* 60% of pure (6).

Compounds (5) to (11) deteriorate only very slowly on standing in air, indeed some have been kept for up to 10 years in this way. When stoichimetric amounts of neat (5) - (11) were mixed with equimolar amounts of protic reagents H_2O, MeOH, EtOH, PhOH, Bu^nNH_2, PhSH, Pr^nSH as 0.01M solutions in THF for 24h. at room temperature, they were recovered unchanged with one exception. The reactions of the thiols with compound (11) were quantitative and complete in 2h, as shown in equation (4).

$$\underset{(11)}{Hg(CH_2BMes_2)_2} + 2RSH \longrightarrow Hg(SR)_2 + \underset{(1)}{2Mes_2BCH_3} \qquad (4)$$

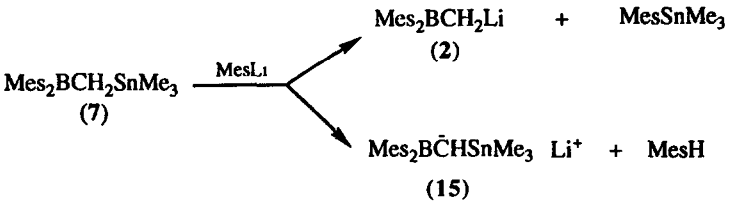
Moreover, we did find it difficult to carry out chromatography of (7) on silica, due to cleavage of the tin-carbon bond by the acidic substrate. The lack of reactivity of compounds (5) - (11) to air and protic reagents emphasises that they are convenient and readily handled laboratory reagents.

Anion formation was next examined. Compound (5) reacts with either MesLi or $LiNChx_2$ to give (12), $Mes_2BCHLiSiMe_3$, (δ_B 41.7 (THF)) in quantitative yield, as shown by methylation and deuteration studies. Compound (6) also reacts with MesLi to give a quantitative yield of the corresponding carbanionic species $Mes_2BCHLiSPh$ (13), (δ_B39.2 (THF)). Both (12) and (13) were taken into diglyme and investigated by variable temperature ^{13}C nmr. If most of the stabilisation of these anions is due to the adjacent boron atom they can be described as shown in structure (14), and the *ortho*-methyl groups should be differentiated, as they are in $Mes_2BCHLiPh$[1] (15). In practise, at room temperature, the *o*-methyl groups of both (12) and (13) give two sharp singlets of equal intensity which do not coalesce even up to 140°C, above which observation was not possible due to thermal degradation. This gives a rotational barrier of >98kJ mol^{-1} for anions (12) and (13), similar to that for $Mes_2BCHLiPh$ and the isoelectronic compounds Mes_2BNHR[11]. We conclude that the major part of the stabilisation of (12) and (13) is due to the α-boron atom.



(14)

Compounds (7) and (8) undergo C-Sn cleavage with methyllithium, as demonstrated by alkylation experiments. Detailed studies of the reaction of (7) with MesLi showed that in THF, the production of (2) and (15) (Scheme 1) proceeded in a ratio of 1:1. In the presence of one equivalent of HMPA the ratio of (2):(15) was 1:4, and we did not succeed in finding conditions that led exclusively to (15). The situation with compound (8) was similar.



Scheme 1

From compound (9) the anionic compound $Mes_2BCHLiSnPh_3$ (16) could be produced using mesityllithium in THF and benzylated to yield 1-benzyl-1-dimesitylboryl-1-triphenylstannane (17). It was of interest to see whether C-Sn cleavage of (9) could be effected. Compound (9) was therefore treated with an equivalent of PhSLi in THF for 24h at r.t., in the expectation of attack on the thiophilic tin atom. In fact, only 20% of (2) was produced, showing that (9) is particularly resistant to C-Sn cleavage.

The preparation of bifunctional compounds (5) to (11), together with their stability and the production of carbanions from some of them, opens the way to the exploitation of a wide variety of reactions of potential synthetic. Some of these reactions have been reported in preliminary form[8,9].

Experimental

Technical Information

Proton nmr were recorded on a Hitachi Perkin-Elmer R-24B spectrometer at 60 MHz, a Varian HA-100 spectrometer at 100 MHz and a Bruker WM-250 spectrometer at 250 MHz using $CDCl_3$ as solvent and Me_4Si as reference except where stated. Boron (^{11}B) nmr were recorded on a Varian XL-100 Fourier transform nmr spectrometer, using boron trifluoride etherate in a co-axial cell as external standard and quartz nmr tubes. Signals downfield from the BF_3 (i.e. deshielded) were recorded as positive and the chemical shifts are in ppm. Carbon (^{13}C) nmr were recorded on a Varian XL-100 or a Bruker WM-250 Fourier transform nmr spectrometer, using $CDCl_3$ as a solvent and Me_4Si as an internal standard, except where stated. Low resolution c.i. and e.i. mass spectra were recorded on an AEI MS9 mass spectrometer or a GC12-253 mass spectrometer. High resolution c.i., e.i. and FAB mass spectra were recorded on a VG ZAB-E mass spectrometer. Ultra violet spectra were recorded on a Perkin-Elmer 402 spectrophotometer as solutions in cyclohexane, using 10.0 mm cells.

Melting points were recorded on a Gallenkamp Hot Stage apparatus and were uncorrected. Boiling points were determined by Kugelrohr distillation and the temperature given is that of the Kugelrohr oven. Thin layer chromatography was performed on silica gel (Merck) mounted on aluminium cards with fluorescent indicator (254 nm). Preparative chromatographic separations were achieved using silica (Merck) as absorbent in a glass column, using uv detection. Microanalyses, where given, were determined using a Carlo Erba Strumentazione Elemental Analyser.

All reactions involving organoboranes were carried out using purified anhydrous reagents, unless otherwise stated. Reactions involving the use of production of air and water sensitive compounds were carried out under a static pressure of argon or nitrogen using directly from the cylinder through a glass line directly connected *via* a three-way tap to a vacuum pump. The preparation and purification of reagents for use in reactions of organoboron compounds have been reviewed[12]. Solvents were treated as follows[13]. THF was purified first by passing through dry, neutral alumina under nitrogen or argon. Sodium (2g per litre) and benzophenone (8g per litre) were then added to the THF in a still and the mix stirred under argon to give a purple solution of the sodium benzophenone ketyl. The THF was then distilled from the ketyl, under argon, as required. Glyme, diethyl ether, petroleum ether and cyclohexane were passed through an alumina column, stirred for 16 hours with calcium hydride and distilled from calcium hydride under nitrogen or argon. Carbon tetrachloride and ethyl acetate were purified by distillation from phosphorus pentoxide. Methanol was dried and purified by distillation from magnesium methoxide.

Mesityl bromide was distilled under nitrogen, at reduced pressure, prior to use. Boron trifluoride etherate was distilled at reduced pressure from CaH_2. All other reagents were distilled under nitrogen prior to use. Solutions of *n* and *t*-butyllithium in hexanes and methyllithium in ether were obtained from Aldrich and standardised every three to four weeks by direct titration of the carbon-lithium bond with butan-2-ol using 1,10-phenanthroline as indicator[14].

Purified solvents and reagents were stored under standard conditions for use in reactions involving air-sensitive compounds, and these conditions have been extensively described.[12]

Experimental Procedures

The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed[12]. All glassware was oven dried (typically >4 hours at 120°C), assembled hot, and allowed to cool under a stream of nitrogen or argon introduced *via* hypodermic needles inserted through serum capped inlets with outlets protected by inert oil bubble. Manipulation of liquids was carried out under an inert atmosphere, using syringes and double-ended needle techniques. Syringes and double-ended needles were flushed with nitrogen as they cooled. Solids were transferred either in air without delay and flushed with nitrogen prior to reaction, or stored in Schlenk vessels and transferred to tared reaction vessels in a dry nitrogen filled glove box.[15]

Unless otherwise stated, the apparatus for reactions at below room temperature consisted of a septum capped flask equipped with a spiral inlet arm which is wholly immersed in the cooling bath[16]. The flask contains a coated magnetic follower to enable stirring of the reaction mixture *via* an external magnetic stirrer. A bleed needle to the argon line was inserted through the cap to allow for any changes in the pressure within the vessel during reaction. Apparatus for reactions at elevated temperatures consisted of a two-necked round-bottomed flask; one neck equipped with a septum capped tap adaptor, the other with a septum capped reflux condenser carrying a nitrogen bleed.

Lithium dicyclohexylamide.

Lithium dicyclohexylamide was made in bulk by treating equimolar quantities of dry dicyclohexylamine and *n*-butyllithium in 40-60°C petroleum. The product immediately precipitated and, by removal of the solvent, a free flowing, pyrophoric powder was obtained. The product was assayed by titration against standard 0.1M HCl to a methyl red end point. The product, always better than 99% pure, was stored in a nitrogen filled dry glove box, in which all subsequent weighings and manipulations took place.

Preparation of lithio(dimesitylboryl)methane (2)

(i) Dimesitylmethylborane[1] (1) (1.57g, 6mmol) was dissolved in THF (30ml) and lithium dicyclohexylamide (1.117g, 6mmol) was added. The solution was stirred at room temperature for 2h, by which time it was deep red. The volatiles were taken into a cooled trap under high vacuum and the solid residue washed with pentane (3 x 5 ml), pumped dry and dissolved in THF (20ml) to give a 0.3M solution of (2) in THF.

(ii) Bromomesitylene (1g, 5mmol) was made up to a 1M solution in THF (5ml) in an argon flushed flask containing a magnetic follower and sealed with a septum cap. The solution was stirred at -78°C whilst *t*-butyllithium (4.76ml of 2.1M in hexane, 10mmol) was added dropwise, after which the reaction was stirred at -78°C for 15 min, then allowed to warm to room temperature and stirred for a further 15min. A solution of (1) (1.23g, 5mmol) in THF (10ml) at 23°C was added *via* a double-ended needle and the mixture stirred for 1h to give a deep red solution, (*ca.* 0.25M).

Synthesis of compounds (5) - (11)

1-Dimesitylboryl-1-trimethylsilylmethane (5)

(a) Compound (1) (7.0g, 26mmol) was converted to anion (2) by procedure (i), and chlorotrimethylsilane (6ml, 47mmol) was injected into the stirred solution held at 0°C. The red colour was immediately discharged to leave a pale yellow solution from which volatiles were removed under high vacuum. The semi-solid residue was repeatedly extracted with 40°-60°C light petroleum, and the light petroleum extracts removed and combined. Solvent was removed to give a viscous oil which on treatment with ethanol (10ml) gave almost pure (5) (6.76g, 77%). Recrystallisation from 40°-60°C light petroleum gave (5), (5.45g, 61%) m.p. 72°C.

(b) To a mechanically stirred solution of mesityllithium (from 1.68M Bu^tLi, (80 mmol), MesBr (7.96g, 6.1ml, 40mmol) in THF (71ml) at -78°C) was added a 1M solution of (1) (9.6g, 36.4 mmol) in THF). The resulting mixture was allowed to warm to room temperature and then stirred for 1h. Chlorotrimethylsilane (23.1ml, 182mmol) in THF (22.4ml) was then added in a dropwise fashion to the well stirred solution at room temperature, and the reaction then allowed to stir for a further 12h. Solvent was removed under vacuum, and the residue was extracted with 40°-60°C petroleum. The mixture was then filtered through a sintered tube under nitrogen pressure and the filtrate evaporated in vacuum. The product (9.18g, 74%) was almost pure (5) by g.c. Recrystallisation from 40°-60°C petroleum* gave (5) (6.4g, 52%), m.p. 71-72°C, identical in all respects with the sample prepared as in (a).*

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* We thank Mr. Stifun Mittoo for details of this procedure.

δ_H -0.9(9H, s, Si(CH_3)$_3$, 1.74(2H, s, H-1), 2.28(12H, s, H-2"), 2.30(6H, s, H-4"), 6.79 (4H, s, H-3′). δc 0.93(SiCH_3)$_3$, 19.57(C-4"), 21.71(C-2"), 25.36(C-1), 127.06(C-3′), 136.36(C-4′), 137.08(C-2′), 142.48(C-1′). δ_B 82.8. m.s[*] 335($M^{\cdot+}$, 46), 321(27, M-14), 249(53, Mes_2B), 217 (100, M-Mes), 201(49).

1-Dimesitylboryl-1-phenylthiomethane (6).

(a) A slight excess (1.1 equiv) of $PhSCH_2Li$, prepared from thioanisole and phenyllithium by the published method[10] was added at room temperature to a stirred solution of dimesitylfluoroborane (3.0g, 11mmol) in THF (25ml). The reaction was then stirred for 1h, after which solvent was removed at high vacuum to give a semi-solid residue that was repeatedly extracted with 40°-60°C petroleum. The combined extracts were concentrated and stored at -25°C to give slightly impure (6) (^1H nmr) (2.45g, 60%). Repeated recrystallisation from hot petrol gave a pure sample of (6), m.p. 113-114°C.

(b) A solution of anion (2) (from Mes_2BCH_3 (1.32g, 5mmol) in THF (20ml) was made by procedure (ii) and added *via* double-ended needle to a stirred solution of $PhS.SO_2Ph$ (1.82g, 7.3mmol) in THF (10ml) held at -20°C. The red anion colour was rapidly discharged and the reaction was stirred for 2h at -20°C, allowed to warm to room temperature and left for 14h. The solvents were removed under vacuum and the resultant yellow slurry extracted with pentane (4 x 25 ml). The pentane extracts were filtered and the pentane removed to yield a white semi-solid (2.93g) which contained (6) but no (1) by ^1H nmr. This residue was taken into chloroform and pentane added. The mixture was left at room temperature for 30 min. then filtered to give (11) (1.0g, 54%), m.p. 106°C. The ^1H and ^{13}C nmr spectra of this sample were identical with that of the purest sample obtained, and this material may be used for further experiments. δ_H 2.22(12H, s, H-2"), 2.20(6H, s, H-4"), 3.44(2H, s, H-1), 6.74(H, s, H-3′), 6.8-7.4(5H, m, SC_6H_5). δ_C 21.1(C-4"), 22.6(C-2"), 34.4(C-1), 141.2(C-1′). Other aromatic carbon signals are at 124.7, 126.8, 128.3, 128.6, 137.5, 139.3, 139.6, 139.7. δ_B 82.3 m.s. 372(20, $M^{\cdot+}$), 265 (12), 264(5Mes_2BCH_3), 263(29, Mes_2BCH_2), 250(100), 249(100, Mes_2B), 248(100), 123(37, $PhSCH_2$), 120(30, MesH), 119(90, Mes), 109(17, SPh).

1-Dimesitylboryl-1-trimethylstannylmethane (7).

(a) Compound (1) (3.6g, 13.6mmol) was converted into anion (2) according to procedure (i), chlorotrimethylstannane (2.66g, 13.3mmol) was injected at room temperature and the solution stirred for 2h. The solvents were removed at high vacuum and the resulting semi-solid repeatedly extracted with 40°-60°C petroleum. The combined extracts were concentrated and stored at -25°C to give crystalline (7), (3.36g, 58%), m.p. 52°C.

(b) Carbanion (2) was prepared from (1) (1,32g,5mmol) as in procedure (ii) using MesBr (0.82ml 5.5mmol) in THF (10ml) and Bu^tLi (6.65ml of 1.66M, 11.0mmol). The carbanion solution was added dropwise *via* a double-ended needle to a stirred solution of chlorotrimethylstannane (1.5g, 7.5mmol) in THF (8 ml) at -10°C, and the pale yellow solution was stirred for 3h at 0°C and then for 12h at room temperature. The solvents were removed at 0.1mm Hg and then the total crude product was distilled. Mesitylene and other volatile impurities were removed at 60°C/0.1mm Hg and then pure (7) (1.76g, 82.4%) distilled over at 166°C/0.2mm Hg as a colourless oil that crystallised, m.p. 51°C, on standing. The sample was identical in all respects with that prepared in (a). δ_H 0.0(9H, s, Sn(CH_3)$_3$, 1.88(2H, s, H-1), 2.16(12H, s, H-2"), 2.20(6H, s, H-4"). δ_C -5.2(Sn(CH_3)$_3$), 21.08(C-4"), 23.53(C-2"), 128.7(C-3"), 137.4(C-4"), 138.8(C-2′), 143.5(C-1′). δ_B 78 m.s. 413(100, $M^{\cdot+}$ - 14), 373(100, $M^{\cdot+}$ - 14 - 2 x CH_3), 269(80), 249(46, Mes_2B), 178(Me_3SnCH_2), 164(11, Me_3Sn).

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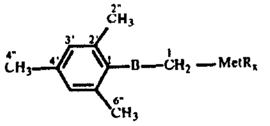
[*] Only one peak from each of the four peak clusters given.

[*] All compounds are numbered as shown.



*1-Dimesitylboryl-1-tri-*n*-butylstannylmethane (8).*

Carbanion (2) was prepared from (1) (1.32g, 5mmol) as in procedure (ii) using MesBr (0.82ml,5.5mmol) in THF (10ml) and Bu^{t}Li (6.65ml of 1.66M, 11mmol). Chlorotri-*n*-butylstannane (2.4g, 2.0ml, 7.5mmol) in THF (5ml) was added as for (7) and the reaction worked up in the same fashion. Compound (8) (2.1g,76%) was obtained as a pale yellow oil, b.p. 177-181°C./0.1mm Hg, running as a single peak by hplc (light petrol 99.5%, CH_3CN 0.5%). δ_H 0.4-1.0(5H, m, $Sn(CH_2)_3CH_3$ plus $SnCH_2(CH_2)_2CH_3$, 1.0 – 1.6(4H, m,$SnCH_2(CH_2)_2CH_3$), 1.86(2H, s, H-1), 2.16(12H, s, H-2"), 2.20(6H, s, H-4"), 6.72(4H, s, H-3'). δ_C 11.7 ($SnCH_2(CH_2)_2CH_3$), 13.6($Sn(CH_2)_3CH_3$), 21.01(C-4"), 23.58(C-2"), 27.4($SnCH_2CH_2CH_2CH_3$), 29.98($SnCH_2CH_2CH_2CH_3$), 128.6(C-3'), 137.4(C-4'), 138.8(C-2'), 144.2(C-1').

1-Dimesitylboryl-1-triphenylstannylmethane (9)

(a) Compound (1) (4.10g,15.5mmol) was converted into (2) by procedure (i) and chlorotriphenylstannane (5.67g,14.7mmol) in THF (50ml) was injected with stirring at room temperature. After 2h the solvent was removed under vacuum and the residue repeatedly extracted with 40°-60°C petroleum. Solvent was removed from the combined extracts to give (9) contaminated with a small quantity of Ph_3SnCl. Recrystallisation from hexane/MeOH (1:1, v/v) gave pure (9) (6.6g, 70%) m.p. 124°C.

(b) Compound (1) (5.28g, 20mmol) was converted to (2) by procedure (ii) using MesBr, (3.3ml, 22mmol) in THF (41ml) and ^{t}BuLi (24.5ml of 1.8M, 44mmol). To this solution at 0°C was added over 10 min, with stirring, a solution of chlorotriphenylstannane (7.71g, 20mmol) in THF (20ml) also at 0°. The mixture was stirred for 16h at room temperature, then the volatiles removed at 0.5mm/Hg and the residue extracted with hot 40°-60°C petroleum (3 x 50 ml). Removal of the solvent gave crude product (14g). Although a small sample could be crystallised directly, the bulk product was separated on a Chromatotron (silica plate) in 1.5g batches. Elution with petrol (500ml) gave (1) (0.8g, 15%), and with petrol-chloroform (9:1, v.v) gave (9), m.p.117°C (6.75g, 55%). Found C, 72.56; H, 6.35%. $C_{37}H_{39}BSn$ requires C, 72.43; H, 6.36%. δ_H 1.96(12H, s, H-2"), 2.19(6H, s, H-4"), 2.46(2H, s, H-1), 6.64(2H, s, H-3'), 7.24(15H, m, $Sn(C_6H_5)_3$). δ_C 21.03(C-4"), 23.47(C-2"), 143.7(C-1'). Other aromatic carbons are at 128.3, 128.6, 136.9, 137.9, 139.1, 139.5. δ_B 80. m.s. (FAB)* 613(8, $M^{\cdot+}$), 537(62, $M^{\cdot+}$ + H - C_6H_5), 393(62), 351(100, $M^{\cdot+}$ – $BMes_2$), 263(13, CH_2BMes_2), 239(12, $BMes_2$) 195(31, SnPh).

1-Dimesitylboryl-1-triphenylplumbylmethane (10).

Compound (1) (1.313g, 5mmol) was converted to (2) by procedure (i). Chlorotriphenylplumbane (2.34g,4.9mmol) in chloroform (15ml) was injected into the stirred solution of (2), and the reaction mixture then stirred at room temperature for 12h. Removal of the solvents at high vacuum gave a red, semi-solid residue which was repeatedly extracted with 40°-60°C petroleum. Concentration of the solution and storage overnight at -25°C gave (10) (1.53g, 45%), m.p. 122°C. δ_H 2.05(12H, s, H-2"), 2.26(6H, s, H- 4"), 2.92(2H, s, H-1), 6.74(4H, s, H-3'), 7.35 (15H, s, $Pb(C_6H_5)_3$). δ_C 21.07(C-4"), 23.67(C-2"), 31.15(C-1), 143.45(C-1'), 152.2 (quartenary carbons of $SnPh_3$). δ_B 79.3.

Bis(dimesitylborylmethyl)mercuric (II) (11).

Dimesitylmethylborane (1) (4.43g, 17mmol) was converted to (2) by procedure (i), and mercuric chloride (2.2g, 8mmol) in THF (20ml) was added. The reaction was stirred at room temperature for 15h, the solvent removed under high vacuum and the resulting pale green viscous oil was extracted with chloroform. The chloroform extracts were filtered and the chloroform removed. The residue was crystallised from ethyl acetate to give (11) (2.8g, 48%), m.p. 180°C. δ_H 2.15(24H, s, H-2"), 2.23(12H, s, H-4"), 2.47(4H, s, H-1), 6.63(8H, s, H-3'). δ_C 21.01(C-4"), 23.61(C-2"), 50.53(C-1), 128.70(C-3'), 137.41(C-4'), 138.84(C-2'). δ_B 76. m.s. (FAB) 728(2,$M^{\cdot+}$), 609(6, $M^{\cdot+}$ – Mes), 263(100, CH_2BMes_2), 249(31, Mes_2B).*

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* Only one line of the complex cluster of isotope peaks, the shape of which corresponds exactly to the theoretical, is given.

Some reactions of compounds (5 - 11).

Production of 1-dimesitylboryl-1-lithio-1-trimethylsilylmethane, $Mes_2BCHLiSiMe_3$, (12) from (5)

(a) Mesityllithium (3.06mmol) was generated as in procedure (ii) using MesBr (0.4ml, 0.61g, 3.06mmol) in THF (5.7ml) and Bu^tLi (4.0ml of 1.53M in pentane, 6.12mmol). The solution was added, with stirring, to solid (5) (1.01g, 3mmol) and the mixture stirred for 2h at room temperature. The reaction was quenched by addition of a slight excess of a 1M solution of CF_3CO_2D in THF. Work up gave monodeuterated (5) (1.0g), as shown by the integration of the ^1H nmr signal at δ 1.74 due to $BCHDSiMe_3$.

(b) Mesityllithium (2.0mmol) from MesBr (0.4g, 2.0mmol in 3.7ml THF) and Bu^tLi (2.33ml of 1.72M in hexane, 4.00mmol) was added to solid (5) (0.49g, 1.5mmol) at room temperature with stirring. After 2h the mixture was cooled to 0°C and methyl iodide (1.06g, 0.8ml, 7.45mmol) was added and the reaction stirred for 12h. Ether (10ml) was added, the solution extracted with water (2 x 5ml), dried ($MgSO_4$), filtered and evaporated to constant mass at 5mm/Hg. The product was an oil (0.45g, 88%) which was essentially one compound by g.c. (methyl silicone capillary) and contained no (5). The ^1H nmr 0.00(9H, s, $Si(CH_3)$), 1.18(3H, d, H-2), 2.1(1H, q, H-1), 2.2(18H, s, H-2",4"), 6.75(4H, s, H-3) proved that the product was $Mes_2BCH(CH_3)SiMe_3$.

Production of 1-dimesitylboryl-1-lithio-1-phenylthiomethane, $Mes_2BCHLiSPh$, (13) from (6).

(a) A dry 500ml round-bottomed flask was charged with THF (25ml) and dicyclohexylamine (1g, 5.5mmol) at 0°C and Bu^nLi (3.4ml of 1.6M, 5.44mmol) in hexane was added with stirring. Stirring was continued for 15min. and the solution was then transferred *via* a double-ended needle to solid (6) (1.86g, 5mmol) at 0°C. Reaction was exothermic to give a dark red-brown solution which was stirred for 2h at 0°C.[#]

(b) Mesityllithium (5.5mmol), made by procedure (i) using MesBr, (5.5mmol as a 0.5M solution in THF and Bu^tLi (5.8ml of 1.9M in heptane, 11mmol), was transferred by double-ended needle to borane (6) (1.86g, 5mmol) at 0°C. Reaction was exothermic and was completed by stirring for 2h at 0°C.

In both cases the reaction was quenched by addition at -78°C of a 1M solution CF_3CO_2H in THF. 1-Deuterio-(6) was recovered quantitatively in both cases (a) and (b). In the ^1H nmr, the signal at δ 3.44 due to $B\text{-}CH_2\text{-}SPh$ was reduced exactly by half, showing that carbanion formation was quantitative.

Cleavage of 1-dimesitylboryl-1-trimethylstannylmethane (7) by methyllithium.

A colourless solution of (7) (0.427g, 1mmol) in THF (5ml) was treated with methyllithium (0.8 ml of 1.52M, 1.2mmol) at -100°C for 1h during which the temperature was raised to -80°C. The cooling bath was replaced by an ice-bath and heptyl iodide (1.64ml of a standard solution of 1 ml $C_7H_{15}I$ in 9ml of THF, 0.226g, 1mmol) was added. The yellow green solution resulting was allowed to reach room temperature over 1h, solvents were removed under vacuum and the yellow slurry was extracted with pentane (3 x 10ml), which was filtered under nitrogen. The filtrate was concentrated under reduced pressure to give a colourless oil (350mg), which contained no $SnMe_3$ groups (^1H nmr). Quantitative g.c. and h.p.l.c. showed that the oil contained dimesityloctylborane produced quantitatively. This was confirmed by comparison of the ^1H and ^{13}C nmr of the product with an authentic sample of dimesityloctylborane.[1]

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[*] Only main peaks from the complex clusters, which correspond exactly in shape to the theoretical, are given.

[#] We thank Dr. Gina Vaughan-Williams for this procedure.

Formation of 1-dimesitylboryl-1-lithio-1-triphenylstannylmethane (16) from (9) and benzylation to give 1-benzyl-1-dimesitylboryl-1-triphenylstannylmethane (17).

Mesityllithium (1.1mmol) made by procedure (ii) was added to a stirred solution of (9) (0.613g, 1mmol) in THF (3ml) at room temperature. The solution turned orange and was left for 2h. Benzyl bromide (0.17g, 1mmol) in THF (1ml) was added at room temperature and the mixture allowed to stir for 3h. Water (1ml) was added, the mixture extracted with ether (2 x 5ml), washed with water (2 x 3ml), dried ($MgSO_4$) and concentrated to give a pale yellow semi-solid (0.72g), which contained neither (9) nor benzyl bromide. The ^1H nmr indicated the product was mainly (17), but chromatography failed to purify it. Several recrystallisations from 40°C-60°C petroleum finally gave a pure sample of (17), m.p. 146-148°C (0.148g, 22%).

δ_H 2.17(18H, 6 x CH_3), 3.17(2H q, CH_2Ph), 3.9(C-1), 6.59(4H, s, H-3'). Other Ar-H at 7.0, 7.28, 7.62 (total aromatics 2H). δ_C 21.6(C-4"), 22.6(C-2"), 36.18(CH_2Ph), 43.9(C-1), 145.9(C-1'). Other aromatic carbon atoms at 126.1, 128.5, 128.9, 139.2, 140.4.

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