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THE DIMESITYLBORON GROUP IN ORGANIC SYNTHESIS. 5.
HETERO-ATOM SUBSTITUTED DIMESITYLBORYLMETHANES.

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The synthesis of the title compounds where the heteroatoms are silicon, tin, lead and sulphur and mercury is demonstrated. Some of these derivatives readily form anions of structural and chemical interest.

We have shown that carbanions stabilised by an α boron atom can be readily synthesised and are of considerable synthetic utility.[1] The effects of a second heteroatom on the α carbon are also of significance since such novel compounds should lend themselves to a variety of synthetic uses. The synthesis and physical properties of the simplest derivative, bis(dimesitylboryl)methane have already been reported.[2] We now report the synthesis of those heteroatom derivatives that are likely to be of the greatest synthetic use[3] viz.:

$Mes_2BCH_2MR_n$

Mes = 2,4,6 trimethylphenyl

1	M = Si	R = Me	n = 3	m.p 72°-73°C
2a	M = Sn	R = Me	n = 3	
2b	M = Sn	R = Ph	n = 3	m.p 124°C
3	M = Pb	R = Ph	n = 3	m.p 122°C
4	M = S	R = Ph	n = 1	m.p 113-114°C
5	M = Hg	R = Mes_2BCH_2	n = 1	m.p 180°C

Of particular interest is the possibility that these compounds may provide methods of transferring the Mes_2BCH_2 functionality, under non basic conditions, by reaction with suitable substrates.

Compounds **1**, **2a**, **2b**, **3** and **5** were synthesised in isolated yields of 60% or better by the reaction of Mes_2BCH_2Li with the appropriate chloro substrate in tetrahydrofuran. The synthesis of **4** by this method was inefficient (yield of 15% based on Mes_2BCH_2Li) and the alternative but slower method (eq. 1) was used. This gave an isolated yield of ca.60%.

$$Mes_2BF \;+\; PhSCH_2Li \longrightarrow Mes_2BCH_2SPh \;+\; LiF \qquad (1)$$

The compounds were characterised by ^{1}H, ^{13}C and ^{11}B n.m.r. spectroscopy and mass spectrometry. They are crystalline with the exception of **2a** which is a waxy solid at room temperature and they deteriorate very slowly on standing in air. Compounds 1-4 are soluble in most organic solvents and do not react at room temperature with water, alcohols, phenols, primary amines or thiols with the exception of **5** which reacts quantitatively and quickly with thiols according to eq.2.

$$\mathrm{Hg(CH_2BMes_2)_2 \;+\; 2RSH \longrightarrow Hg(SR)_2 \;+\; 2Mes_2BCH_3} \qquad (2)$$

Silicon and sulphur are known to promote carbanion formation.[4] It was found that **1**, **2a** and **4** are readily deprotonated by mesityl lithium in tetrahydrofuran, whilst it is known[2] that **5** readily forms an anion. The resulting carbanions are deuterated and methylated with ease (alkylation studies on these compounds will be presented separately).

Dynamic n.m.r. studies on the anions generated from **1** and **4** show that it is the boron atom that provides most of the carbanion stabilisation in that the anions behave like $\mathrm{Mes_2B\bar{C}HPh}$[5] and thermally decompose in diglyme at 140°C before rotation effects about the $\mathrm{B\text{-}\bar{C}HMR_n}$ bond are observed. The $^{11}\mathrm{B}$ chemical shift behaviour of these systems is consistent with these observations in that $\delta\ ^{11}\mathrm{B}$ (relative to $\mathrm{BF_3OEt_2}$) for **1**, **4** and $\mathrm{Mes_2BCH_2Ph}$ are 83±2 ppm whilst those for the corresponding carbanions are 41±2 ppm. The figures for $\mathrm{(Mes_2B)_2CH_2}$ and its anion are 80.0 and 52.0 ppm respectively.

We have initiated studies on the Wittig type reaction of these hetero-substituted derivatives. Thus the carbanion, **6** derived from **1** condenses with benzaldehyde to give an intermediate X, presumably an alkenylborane, which on oxidation gives phenylacetaldehyde in 95% yield (eq. 3). This process represents an efficient new formyl homolgation sequence which is not a boron-Wittig reaction but is more like the Peterson reaction[6] as it is the silicon group that is eliminated.

$$\mathrm{PhCHO \;+\; \underset{\mathbf{6}}{Mes_2B\bar{C}HSiMe_3\ Li^+} \longrightarrow X \xrightarrow{H_2O_2/NaOH} PhCH_2CHO} \qquad (3)$$

Anion **6** readily condenses with benzophenone but oxidation gives a mixture of the homologated aldehyde (45%) and the vinyl silane (55%) (eq. 4). In this case the transition states are becoming so crowded that elimination of the bulky dimesitylboryl group competes successfully with elimination of the trimethylsilyl group.

$$\mathrm{Ph_2CO \;+\; Mes_2B\bar{C}HSiMe_3\ Li^+ \longrightarrow Ph_2C{:}CHSiMe_3 \;+\; \begin{array}{c} Ph_2C{:}CHBMes_2 \\ \big\downarrow [O] \\ Ph_2CHCHO \end{array}} \qquad (4)$$

Heteroatom derivatives of dimesitylmethylborane have been synthesised and characterised. Their scope and application in chemical synthesis are being explored.

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References

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