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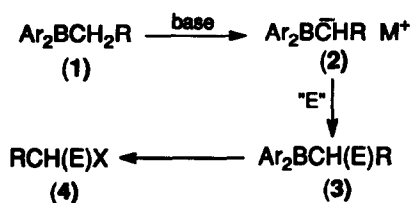
## Hindered Organoboron Groups in Organic Chemistry. 27. Preparations and Some Properties of Alkylbis(2,6-dimethyl-4- methoxyphenyl)boranes ((DMP)<sub>2</sub>BR)

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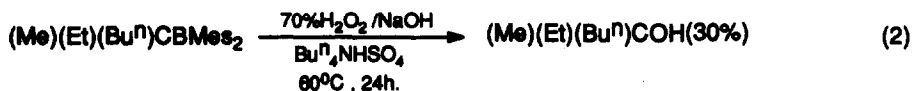
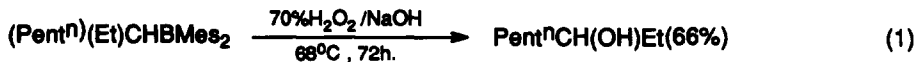
**Abstract.** Alkylbis(2,6-dimethyl-4-methoxyphenyl)boranes ((DMP)<sub>2</sub>BR) have been synthesised in an attempt to overcome the limitations of the steric hindrance approach to the production of boron stabilised carbanions. Anion production from (DMP)<sub>2</sub>BR, followed by alkylations and condensations with aldehydes are reported. Reduction of (DMP)<sub>2</sub>F with potassium hydride yields the corresponding hydroborate. Attempts to isolate (DMP)<sub>2</sub>BH were unsuccessful but the borane was readily trapped with alkynes, yielding alkenylboranes. The allyl derivative, (DMP)<sub>2</sub>BAllyl, was made and some of its reactions were investigated.

**Introduction.** We have previously used a steric control approach in order to produce boron stabilised carbanions<sup>1,2,3,4,5,6,7,8,9,10</sup>, and in particular have investigated alkylbis(2,4,6-trimethylphenyl)boranes, (alkyldimesitylboranes, Mes<sub>2</sub>BR)<sup>1-7</sup> and alkylbis(2,4,6-triisopropylphenyl)boranes, (alkylditriptylboranes, Trip<sub>2</sub>BR)<sup>8-10</sup>. This approach leads to a logical problem that is illustrated in Scheme 1.



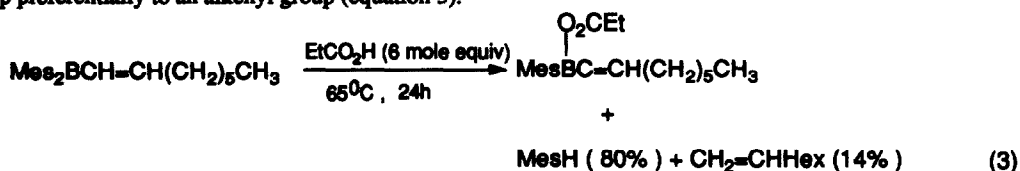
Scheme 1

By definition, in order to prevent borate production, the aromatic groups in (1) are hindered so as to allow proton abstraction from (1) to give (2). However, when (2) reacts with an electrophile, the product (3) (E ≠ H) is inevitably more hindered than (1), and reactions at boron to release the organyl group are therefore greatly slowed down or rendered non viable. Even using a small electrophile such as the hydroperoxide anion this effect is readily demonstrated as in equations (1) and (2).



To overcome this limitation in the methodology used, it was decided to introduce arylboranes that would undergo reaction at the aryl groups rather than on boron so that increasing hindrance at the boron would not inhibit reaction. Once one aromatic group was removed, the decrease in bulk around the boron atom would be such that conventional methods of releasing the organyl group could be used.

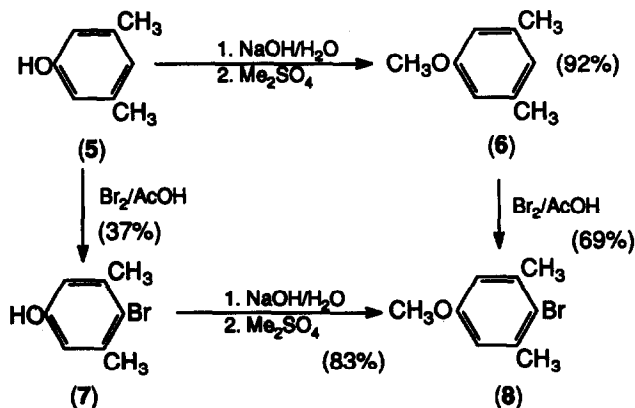
It has been shown that brominolysis<sup>11</sup> and protodeboronation<sup>12</sup> of dihydroxyphenylboranes occurs through initial attack on the aromatic ring. We have also shown<sup>13</sup> that propionic acid slowly releases a mesityl group preferentially to an alkenyl group (equation 3).



It seemed to us that the 2,6-dimethyl-4-methoxyphenyl (DMP) group was worthy of investigation<sup>14</sup>, as it retains the steric hindrance of the mesityl group but might allow enhanced protonation of the aromatic ring. Thus dihydroxy(4-methoxyphenyl)borane undergoes protonolysis<sup>12</sup> and brominolysis<sup>11</sup> more readily than dihydroxy(4-methylphenylborane). Anisole is more susceptible to electrophilic attack than is toluene<sup>15</sup> and trimethoxyborane is much more readily hydrolysed than trimethylborane<sup>16</sup>. This paper deals with the preparations and some properties of representative (DMP)<sub>2</sub>BR. Protonolysis studies follow in the next paper.

#### Preparation of (DMP)<sub>2</sub>BR (13)

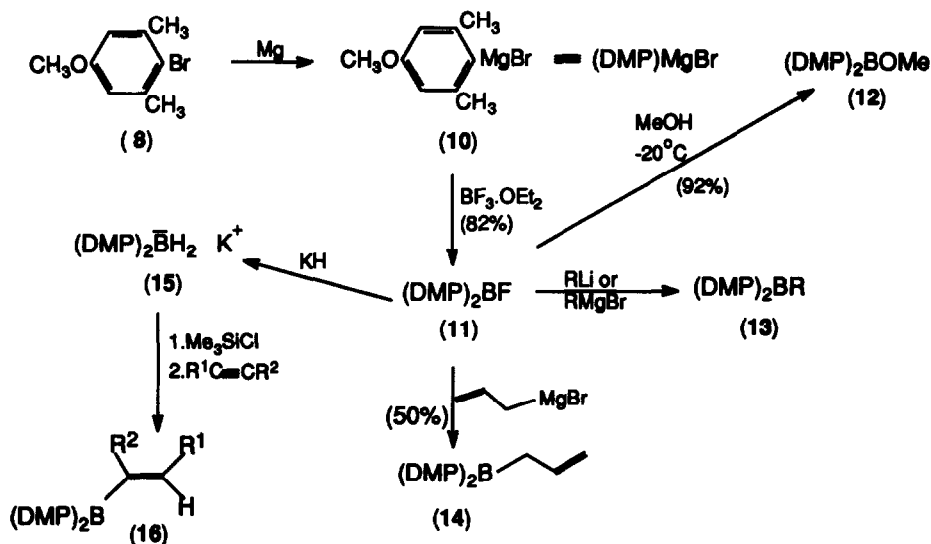
2,6-Dimethyl-4-methoxy-1-bromobenzene (8) was prepared from cheap, readily available 3,5-dimethylphenol (5) by the two routes shown in Scheme 2, the route by initial methylation being preferable.



Scheme 2

The methylation of (5) to (6) was routinely carried out on a 4-mole scale with consistently high yields. This was followed by bromination in acetic acid in 69% yield. The direct bromination of (5)<sup>17</sup> is very solvent dependant. In acetic acid some 50% of the crude product was (7). In carbon tetrachloride the main product was 2-bromo-3,5-dimethylphenol, (9), whilst in carbon disulphide, mixtures of (7), (9) and dibrominated material were formed. Bromination of the anion of (5) in a two phase water/CCl<sub>4</sub> system, gave 42% of 3,5-dimethyl-2,4,6-tribromophenol as the only isolable product.

The Grignard reagent (10) was readily prepared from (8) in THF and the lithium derivative was available by reaction of two equivalents of *tert*-butyllithium with (8) in a variety of solvent mixes (Scheme 3).

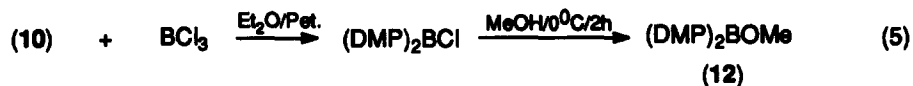


Scheme 3

The Grignard reagent (10) readily reacted with BF<sub>3</sub>·OEt<sub>2</sub> in THF to give (11) m.p. 72°-74°C. The yield is sensitive to the number of equivalents of (10) used and 2.2 equivalents were optimal to give 82% of (11). Yields of 58% and 56% were obtained with 2.03 and 2.27 equivalents respectively. Reaction of (10) with trimethoxyborane gave 73% of (DMP)B(OMe)<sub>2</sub>, (17), whilst reaction of (11) with methanol at -20°C gave (DMP)<sub>2</sub>BOMe (12) in 92% isolated yield. Compound (12) represents an alternative source of compounds (DMP)<sub>2</sub>BR. Of interest was that reaction of (11) with warm methanol containing a catalytic quantity of sulphuric acid led to complete methanolysis (equation 4), a very hopeful result for our stated objectives.



Another method of obtaining (12) in 53% yield was to react (10) with trichloroborane followed by *in situ* addition of methanol (equation 5).



Compound (11) readily reacted with *prim*-RMgBr (Table 1, exp. 1-4) but the reaction failed for *sec*-RMgBr (Table 1, exp. 5).

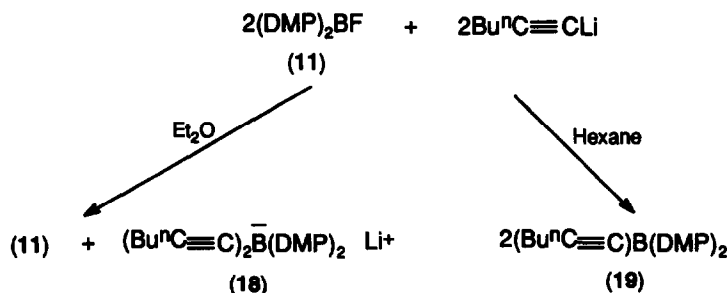
Table 1. Yields of  $(\text{DMP})_2\text{BR}$ , (13) from (11) and RMgX

Experiment	R	Yield (%) <sup>a</sup>
1	Me	30
2	Et	52
3	Ocr <sup>a</sup>	63
4	Allyl	50
5	Pr <sup>i</sup>	0

<sup>a</sup>Isolated, purified product.

The experiments were carried out in ether at 25°C and followed by <sup>11</sup>B nmr. When R = Me (exp. 1) reaction was over in <10 min., and even with R = Ocr<sup>a</sup> (exp. 3), reaction was complete in 4h. The allyl derivative (14) was easily obtained (exp. 4). However, even when a solution of Pr<sup>i</sup>MgBr was heated under reflux for 4h. with (11) there was still no sign of reaction. The modest yields in experiments 1-4 were mainly due to experimental difficulties associated with separations of the somewhat insoluble products from salts. Use of THF as a solvent led to borate formation even when one equivalent only of Grignard reagent was used. Alkyl Grignard reagents failed entirely to react with  $(\text{DMP})_2\text{BOMe}$ , (12), in either boiling ether or THF.

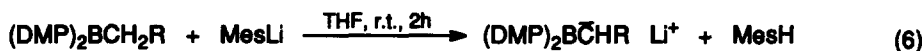
By contrast, alkyllithium reagents, RLi, reacted with (11) to give (13) in moderate to good yields *even when a tertiary alkyllithium was used* (R = Me, 68%; R = *n*-Bu, 45%; R = *tert*-Bu, 70%). If excess alkyllithium in ether were used then the corresponding ate complex resulted. With 1-hexynyllithium in ether only the ate complex (18) was formed but when hexane was used as solvent then the desired hexynyl derivative (19) was obtained (Scheme 4).



Scheme 4

*Chemical Properties of (DMP)<sub>2</sub>BR, (13)*

The  $\alpha$ -carbanions of (13) were readily obtained by treating the solid boranes with an equivalent of mesityllithium in THF at 0°C<sup>1</sup> (equation 6). The reactions were then stirred at room temperature for 2h to give red solutions of the required anions, as shown by deuteration experiments.



The anions were alkylated and the products were either isolated or oxidised. The results are given in Table 2.

Table 2.  $(\text{DMP})_2\text{BCHLiR}^1\text{R}^2 + \text{R}^3\text{X} \rightarrow (\text{DMP})_2\text{BR}^1\text{R}^2\text{R}^3 + \text{LiX}$

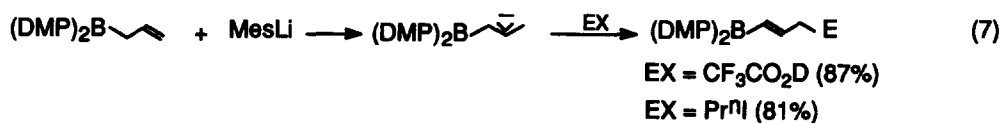
Exp.	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup> X	Product	Yield (%) <sup>a</sup>
6	H	H	DO <sub>2</sub> CCF <sub>3</sub>	(DMP) <sub>2</sub> BCH <sub>2</sub> D	84
7	H	H	MeI	(DMP) <sub>2</sub> BEt	60
8	H	H	HeptI	OctOH <sup>b</sup>	67
9	H	H	Me <sub>3</sub> SiCl	(DMP) <sub>2</sub> BCH <sub>2</sub> SiMe <sub>3</sub>	59
10	Me	H	HeptI	HeptCHOHMe <sup>b</sup>	76
11	Bu	H	MeI	(DMP) <sub>2</sub> BCH(Me)(Pr)	73
12	Bu	H	EtI	(DMP) <sub>2</sub> BCH(Et)(Pr)	76
13	Oct	H	EtBr	(DMP) <sub>2</sub> BCH(Et)(Hept)	67
14	Me	Pr	EtBr	(DMP) <sub>2</sub> BC(Me)(Et)(Pr)	69
15	Et	Pr <sup>c</sup>	MeI	(DMP) <sub>2</sub> BC(Me)(Et)(Pr)	0

<sup>a</sup>Yield of isolated, purified product. <sup>b</sup>Produced by oxidation of the product.

<sup>c</sup>Made *in situ*, without isolation, by the reaction of (DMP)<sub>2</sub>BCHLiPr with EtBr.

The 4-methoxy substituent of the DMP group was expected to lower the electron deficiency at boron and hence lower its ability to stabilise an adjacent carbanion as compared with the corresponding mesityl series.<sup>1</sup> Nevertheless, substantial *isolated* yields of deuteriated (exp. 6) and alkylated (exp. 7-14) products can be obtained *via* the carbanions. Primary (exp. 6-9), secondary (exp. 10-13) and tertiary (exp. 14) alkyl groups can be attached to the boron atom in this way. However, the contrast between experiments 14 and 15 shows that, at that extreme of bulk, the alkylations are very sensitive to the hindrance around the boron atom. It is noteworthy that (DMP)<sub>2</sub>BCH<sub>2</sub>Li yields a silyl derivative (exp. 9) in a manner similar to Mes<sub>2</sub>BCH<sub>2</sub>Li.

The carbanion derived from (DMP)<sub>2</sub>BAllyl (14) is readily produced and reacts with electrophiles exclusively at the  $\gamma$ -position to give *E*-alkenylboranes in the same fashion as does the anion from Mes<sub>2</sub>BAllyl (equation 7).<sup>20</sup>



*Condensations of carbanions (DMP)<sub>2</sub>BCHLiR with carbonyl compounds*

These experiments were carried out to see whether there were any significant differences between the condensations with aldehydes of (DMP)<sub>2</sub>BCHLiHept (as a representative carbanion) as compared with the analogous condensations of Mes<sub>2</sub>BCHLiHept<sup>5-7</sup>. The results are presented in Table 3. No attempt was made to optimise yields or to investigate the reactions in depth.

Table 3. Reactions of Ar<sub>2</sub>BCHLiHept with RCHO

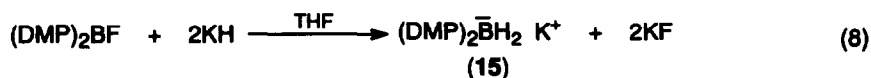
Exp.	R	Conditions	Products <sup>a</sup>	
			Ar = DMP	Ar = Mes
16	Ph	i) -110°C, 2h.	PhCH:CHHept (67%)	PhCH:CHHept (77%)
		ii) TFAA, -110°C, 1h.	<i>E:Z</i> = 28:72	<i>E:Z</i> = 10:90
17	Et	i) -127°C, 1h	EtCOCH <sub>2</sub> Hept (63%)	EtCOCH <sub>2</sub> Hept (72%)
		ii) TFAA, -127°C, 0.5h.	EtCH:CHHept (6%)	
18	Et	-127°C	EtCH:CHHept (47%)	EtCH:CHHept (75%)
			<i>E:Z</i> = 80:20 (DMP) <sub>2</sub> BOct (39%)	<i>E:Z</i> = 49:51

<sup>a</sup>All yields are of isolated, purified material.

In general, the reactions of the two series of anions proceed in a similar fashion. However, there were differences in the *E:Z* ratios of the alkenes produced, with (DMP)<sub>2</sub>BCHLiHept favouring the production of *E*-alkenes. Additionally, the change in product from ketone to alkene in experiments 17 and 18 is paralleled in both series. The yields of products seem lower in the DMP series, but allowing for recovered borane the actual yield in experiment 18 is 80% although the conditions used were not optimised for the DMP series. Clearly the condensations for the two series are similar but with interesting and potentially useful differences in the stereochemistry of the alkene products.

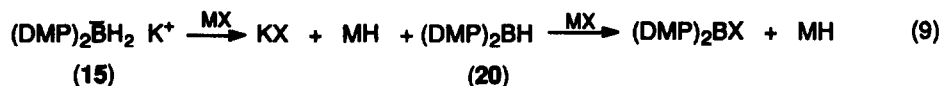
*Hydrido derivatives containing the DMP group*

Reaction of (DMP)<sub>2</sub>BF, (11), with LAH in THF, ether or glyme led to reduction and redistribution so that mixtures of (11), (DMP)<sub>3</sub>B, (DMP)<sub>2</sub>BH, and (DMP)BH<sub>2</sub> were obtained. This is different from similar reactions with Mes<sub>2</sub>BF<sup>21</sup> and Trip<sub>2</sub>BF<sup>22</sup>. Even a large excess of activated NaH<sup>18,19</sup> did not react with either (11) or (12) in THF. However, two equivalents of activated KH<sup>18,19</sup> reacted with (11) in THF (though not in ether) to give the hydroborate (15) in essentially quantitative yield (equation 8). After filtration, the clear solution may be estimated and used directly for further reactions.

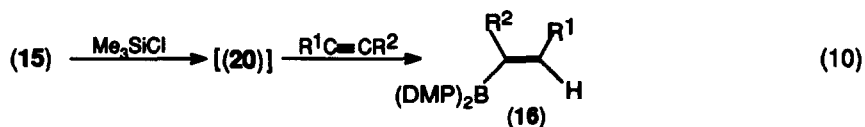


Addition of an equal volume of light petroleum to the hydroborate solution led to quantitative precipitation of (15) as an air-sensitive solid m.p. >250°C with a BH<sub>2</sub> stretching band at  $\nu_{\text{max}}$  2180 cm<sup>-1</sup>, in close agreement with that reported for lithium dimesitylhydroborate.<sup>23</sup>

Attempts to produce (DMP)<sub>2</sub>BH, (20), from (15) using either iodomethane<sup>24</sup> or chlorotrimethylsilane<sup>25</sup> gave a product that was always contaminated with haloborane (equation 9). This is unusual as dialkylboranes do not react with either of the reagents used.



However, if an equivalent of an alkyne is present during the addition of Me<sub>3</sub>SiCl then an alkenylborane (16) results due to efficient trapping of (20) prior to its further reaction with the chlorosilane (equation 10). After sublimation or distillation yields were 72% (16, R<sup>1</sup> = H, R<sup>2</sup> = Bu<sup>n</sup>), and 65% (16, R<sup>1</sup> = R<sup>2</sup> = Et).



#### Physical properties of bis(2,6-dimethyl-4-methoxyphenyl)boron derivatives

Virtually all of compounds (DMP)<sub>2</sub>BX are white crystalline solids that can be sublimed in high vacuum. They are readily handled by glove box techniques but are somewhat sensitive to moisture, particularly in the presence of acid.

#### U.V. Spectra of (DMP)<sub>2</sub>BX

The absorption spectra and photochemistry of Mes<sub>2</sub>BAR and Mes<sub>2</sub>BAR<sub>2</sub><sup>-</sup> M<sup>+</sup> have been the subject of wide ranging investigations.<sup>24-29</sup> The Mes<sub>2</sub>B group has been proposed<sup>24</sup> as a dye auxochrome with electron-withdrawing properties similar to those of the nitro group but not subject to photochemical reduction. The  $\sigma_{\text{UV,H}}$  value for the Mes<sub>2</sub>B group is 0.65, that for the NO<sub>2</sub> is 0.78.

We report here, in Table 4, for the first time, the UV spectra of (DMP)<sub>2</sub>BX.

Table 4. U.V. Spectra of (DMP)<sub>2</sub>BX<sup>a</sup>

X	$\lambda^b(\epsilon)$			
F	227(30,980),	271(20,160)		
OMe	223(22,860),	262(16,630)		
OH	223(22,400),	266(14,330)		
Me	213(14,800),	229(11,700),	292(7,100),	313(7,400)
Et	215(24,210),	235(14,300),	296(8,410),	316(10,490)
Bu	232(8,800),	296(5,267),	316(6,620)	
Oct	211(26,040),	241(10,260),	290(5,160),	315(6,300)

Table 4. (Continued)

X	$\lambda^b(\epsilon)$				
(Pr)(Me)CH	210(29,880),	230(17,020),	297(8,630),	314(9,790)	
(Pr)(Et)CH	213(24,350),	233(14,336),	241(11,500),	315(8,010)	
Bu <sup>t</sup>	223(17,730),	233(15,615),	246(8,946),	291(6,181)	310(7,525)
(Bu)(Et) <sub>2</sub> C	216(19,310),	235(12,080),	289(4,380),	315(6,510)	
(Me)(Et)(Pr)C	209(54670),				314(8,800)
DCH <sub>2</sub> CH=CH	209(36,720),	235(15,600),	327(11,830),		
BuCH=CH	209(39,970),	232(18,250),	249(14,210),	328(11,270)	
EtCH=C(Et)	210(43,680),	235(16,626),	252(13,500),	326(12,390)	
DMP <sup>c</sup>	215(30,570),	234(26,640),	255(19,210),	347(24,020)	
BuC≡C	210(30,570),	242(12,920),	325(11,660),	344(9,280)	
CH <sub>2</sub> =CH-CH <sub>2</sub>	221(12,450),	240(10,670),	300(6,880),	320(8,180)	
Me <sub>3</sub> SiCH <sub>2</sub>	210(31,960),	232(16,350),	300(10,330),	307(10,770)	

a) Recorded on a Perkin-Elmer 402 spectrophotometer as solutions in hexane using 10mm cells. b)  $\lambda$  in nm.

c) Compound will be reported in detail in a separate paper - put in here for comparison.

The parent compounds DMPH and 1-Br-DMP have  $\lambda_{\max}$  at 226(5590), 274(1510) and 282(1720)nm and 230(5590), 270(1380) and 278(1380)nm respectively whilst (DMP)B(OMe)<sub>2</sub> has  $\lambda_{\max}$  at 225(7350), 228(7405), 275(1330) and 283(1460)nm.

The enhanced intensity of the absorptions of (DMP)<sub>2</sub>BX compared with DMPH, 1-Br-DMP and (DMP)B(OMe)<sub>2</sub>, shows clearly that extended  $\Pi$  systems are present in all the (DMP)<sub>2</sub>BX compounds. All (DMP)<sub>2</sub>R compounds have an absorption at >310nm, and despite expected conformational changes, this is the same whether R=*prim*-R, *sec*-R or *tert*-R. When X is an alkenyl, alkynyl or aryl group this band moves to longer wavelength and is increased in intensity, showing further extensions of the  $\Pi$ -systems. This is particularly noteworthy in (DMP)<sub>3</sub>B and in (DMP)<sub>2</sub>BC≡CBu.

#### The <sup>11</sup>B nmr of (DMP)<sub>2</sub>BX

If back donation from the 4-OMe group were an important factor then it would be expected that the electron density at boron would be less for (DMP)<sub>2</sub>BR than for Mes<sub>2</sub>BR. This effect for Ar<sub>2</sub>BF, Ar<sub>2</sub>BOMe and Ar<sub>2</sub>BOH would be less, due to the overwhelming influence of the heteroatoms directly attached to the boron atom. Some comparisons are given in Table 5.



Table 5<sup>1</sup>. Comparisons of <sup>11</sup>B nmr of (DMP)<sub>2</sub>BX and Mes<sub>2</sub>BX

X =	F	OMe	OH	Me	Et	Bu <sup>a</sup>	Oct <sup>a</sup>
(DMP) <sub>2</sub> BX	50.7	50.0	48.2	80.2	72.6	73.3	72.6
Mes <sub>2</sub> BX	53.0	51.0	50.5	82.0	84.9	83.7	85.2
X =	3-Hexyl	3-Decyl	Bu <sup>t</sup>	2-M-3-Hexyl	1-Hexenyl		
(DMP) <sub>2</sub> BX	75.5	75.5	73.3	66.9	64.4		
Mes <sub>2</sub> BX	81.3	87.8	91.6	87.8	70.0 <sup>2</sup>		
X =	Mes	DMP	CH <sub>2</sub> SiMe <sub>3</sub>	Allyl			
(DMP) <sub>2</sub> BX	-	60.1	78.4	70.0			
Mes <sub>2</sub> BX	79.2	-	80.3	87.5			

<sup>1</sup>) All values relative to BF<sub>3</sub>·OEt<sub>2</sub>. <sup>2</sup>) Mes<sub>2</sub>BCH=CH<sub>2</sub>.

Analyses have been made<sup>30-33</sup> of the <sup>11</sup>B, <sup>13</sup>C and <sup>1</sup>H nmr of Mes<sub>2</sub>BR<sup>30,31</sup>, Mes<sub>2</sub>BOR<sup>32</sup> and Mes<sub>2</sub>BNR<sub>2</sub><sup>33</sup>. These analyses highlighted the problems of the difficulties of chemical shift theory for nuclei other than hydrogen. Thus for R<sub>2</sub>BX, the chemical shifts of the compounds are in the order N > O > F. This is reversed in RBX<sub>2</sub>, in which the order is F=O > N and in BX<sub>3</sub> it is F > O > N.<sup>34</sup> Again the <sup>11</sup>B chemical shift values for R<sub>2</sub>BX for X=S, Se, Cl, Br or I<sup>34</sup> are virtually constant at 79 ± 5, despite the different π electron donating abilities of these atoms.

This effect is clearly seen in the first three entries of Table 5. The Table also shows however, that two DMP groups attached to boron in (DMP)<sub>2</sub>BR have a strong effect on chemical shifts as compared with two mesityl groups in Mes<sub>2</sub>BR.<sup>35</sup> In general there is an upfield shift of 5-15 ppm in the (DMP)<sub>2</sub>BR series compared with Mes<sub>2</sub>BR<sup>35</sup> which would be compatible with a strong π back-donation from the methoxy groups to the boron, *via* the aromatic ring. However, it has been stated<sup>36</sup> that B-aryl π-bonding is of only minor importance in some very hindered Ar<sub>2</sub>BOR systems and this generalisation has been tentatively proposed as being general for all Ar<sub>2</sub>BX systems, including Ar<sub>2</sub>BR and Ar<sub>2</sub>BAr<sup>1,32</sup>. Another factor of importance is the bond angles at boron, in turn influenced by the nature and size of X in Ar<sub>2</sub>BX.<sup>37,38</sup> Our <sup>13</sup>C nmr (Table 6) indicates that the electron density at boron varies little between (DMP)<sub>2</sub>BX and Mes<sub>2</sub>BX.

Table 6. <sup>13</sup>C Chemical Shift Values for (DMP)<sub>2</sub>BX<sup>1,2</sup>

X	C-1	C-2	C-3	C-4	ArCH <sub>3</sub>	ArOCH <sub>3</sub>	Other Carbons
F	~130	144.8 <sup>3</sup>	113.3	161.3	22.71 <sup>4</sup>	54.73	
OCH <sub>3</sub>	131.5	143.0	112.9	160.0	22.51	54.62	
OH 132.7	43.1	113.0	160.0	22.71	54.73		

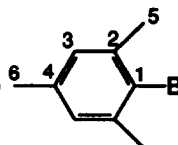
Table 6.  $^{13}\text{C}$  Chemical Shift Values for  $(\text{DMP})_2\text{BX}^{1,2}$ 

X	C-1	C-2	C-3	C-4	ArCH <sub>3</sub>	ArOCH <sub>3</sub>	Other Carbons
<sup>a</sup> CH <sub>3</sub>	139.2	141.3	113.2	160.1	23.28	54.56	a,19.38
<sup>a</sup> <sup>b</sup> CH <sub>2</sub> CH <sub>3</sub>	138.2	141.1	113.1	159.9	23.01	54.68	a,26.10; b,9.24
<sup>a</sup> <sup>b</sup> <sup>c</sup> <sup>d</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	138.3	141.0	113.1	159.9	23.03	54.64	a,34.45; b,27.85; c,25.93; d,13.93
<sup>a</sup> <sup>b</sup> <sup>c</sup> CH <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	~138	141.0	113.0	159.7	23.05	54.77	a,~33; b,32.35, 31.96, 29.50, 29.31, 23.38, 22.73; c,14.12
<sup>a</sup> <sup>e</sup> <sup>b</sup> <sup>c</sup> <sup>d</sup> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	137.9	140.6	112.9	159.4	23.61	54.61	a,36.06; b,35.60; c,22.61; d,14.20; e,15.88
<sup>a</sup> <sup>e</sup> <sup>f</sup> <sup>b</sup> <sup>c</sup> <sup>d</sup> CH(CH <sub>2</sub> CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	138.2	140.6	113.0	159.4	23.67	54.73	a,44.34; b,33.85; c,23.76; d,14.40; e,24.62; f,15.44
<sup>a</sup> <sup>d</sup> <sup>e</sup> <sup>b</sup> <sup>c</sup> CH(CH <sub>2</sub> CH <sub>3</sub> )(CH <sub>2</sub> )CH <sub>3</sub>	138.1	140.6	113.0	159.4	23.67	54.70	a,44.55; b,d 31.79, 31.34, 30.67, 29.73, 29.05, 24.75, 22.65, c,e 15.47, 14.90
<sup>a</sup> <sup>b</sup> C(CH <sub>3</sub> ) <sub>3</sub>	137.3	140.4	113.4	158.9	25.77	54.52	a,31.97; b,30.23
<sup>g</sup> CH <sub>3</sub>							
<sup>l</sup> <sup>a</sup> <sup>b</sup> <sup>c</sup> <sup>d</sup> C-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	137.8	140.6	113.5	158.8	25.90	54.67	a,39.47; b,38.49; c,18.20 <sup>5</sup> ; d,f, 15.22, 9.06; e,28.84
<sup>l</sup> <sup>e</sup> <sup>f</sup> CH <sub>2</sub> CH <sub>3</sub>							f,18.20; g,23.20 <sup>6</sup>
<sup>a</sup> <sup>b</sup> <sup>c</sup> <sup>d</sup> <sup>e</sup> <sup>f</sup> CH=CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	137.9	142.5	112.8	159.9	23.63	54.64	a,141.0; b,158.7; c,35.91; d,30.32; e,22.49, f,13.91

Table 6.  $^{13}\text{C}$  Chemical Shift Values for  $(\text{DMP})_2\text{BX}^{1,2}$ 

X	C-1	C-2	C-3	C-4	ArCH <sub>3</sub>	ArOCH <sub>3</sub>	Other Carbons
$\begin{array}{c} \text{a} \quad \text{b} \quad \text{c} \quad \text{d} \\ \text{C}=\text{CHCH}_2\text{CH}_3 \\ \text{e} \quad \text{f} \\ \text{CH}_2-\text{CH}_3 \end{array}$	137.8	142.2	112.7	159.7	23.26	54.76	a,154.1; b,151.7; c,e, 23.62, 22.54; d,f,15.65, 13.12
$\begin{array}{c} \text{a} \quad \text{b} \quad \text{c} \\ \text{CH}=\text{CHCH}_2\text{D} \end{array}$	137.8	142.39	112.81	159.5	23.59	54.68	a, 142.4; b,158.5; c,26.23
$\begin{array}{c} \text{a} \quad \text{b} \quad \text{c} \quad \text{d} \quad \text{e} \quad \text{f} \\ \text{C}=\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$	~141	142.2	113.2	159.7	23.5	54.87	a <sup>7</sup> ,b, 68.02; c,30.29; d,22.23; e,21.08; f,13.59
$\begin{array}{c} \text{a} \quad \text{b} \quad \text{c} \\ \text{CH}_2\text{CH}=\text{CCH}_2 \end{array}$	137.7	141.3	113.1	160.1	23.23	54.69	a,40.3; b,136.1; c,113.9
$\begin{array}{c} \text{a} \quad \text{b} \\ \text{CH}_2\text{Si}(\text{CH}_3)_3 \end{array}$	139.6	140.7	113.1	159.5	23.51	54.64	a,26.75; b,1.38

<sup>1</sup>)Run in  $\text{CDCl}_3$ , relative to TMS. <sup>2</sup>)Designation of carbons according to



<sup>3</sup>)Doublet  $J_{\text{C,F}} = 4.0\text{Hz}$ ; <sup>4</sup>) Doublet  $J_{\text{C,F}} = 1.4\text{Hz}$ . <sup>5</sup>)Coupled to protons of  $\text{CH}_2$  at  $\delta 1.1$ .

<sup>6</sup>)Coupled to protons of  $\text{CH}_3$  singlet at  $\delta 1.34$ . <sup>7</sup>)Carbon atom a, not observable.

Table 6 contains much of interest. Firstly, despite the large changes in the  $^{11}\text{B}$  chemical shifts as between  $(\text{DMP})_2\text{BR}$  and  $\text{Mes}_2\text{BR}$ , the  $^{13}\text{C}$  chemical shifts of  $\alpha$ -carbon atoms (and even  $\beta$ -carbon atoms, where appropriate) remain little changed between the series<sup>1</sup>. Some representative results are given in Table 7.

Table 7. Comparison of  $^{13}\text{C}$  chemical shifts of  $\alpha$ - and  $\beta$ - carbon atoms of  $\text{Mes}_2\text{BR}$  and  $(\text{DMP})_2\text{BR}$ 

R	$\text{CH}_3$	$\text{CH}_2\text{CH}_3$	$\text{CH}(\text{CH}_3)_2$	$\text{CH}(\text{CH}_3)(\text{Pr})$	$\text{C}(\text{CH}_3)_3$
$\text{Mes}_2\text{BR}$	19.4	26.3, 9.2	31.0		32.0, 30.2 <sup>1</sup>
$(\text{DMP})_2\text{BR}$	19.38	26.1, 9.2		36.06	31.97, 30.23

<sup>1</sup>) Based on heteronuclear decouplings we have reversed the original assignments<sup>30</sup> as between Ar- $\text{CH}_3$  and  $\text{C}(\text{CH}_3)_3$ .

Although the absolute values of the  $^{13}\text{C}$  chemical shifts vary, the changes in shift of the carbon-atoms and of the aromatic rings made by varying the substituent X of  $\text{Ar}_2\text{BX}$ , is similar for both  $(\text{DMP})_2\text{BX}$  and  $\text{Mes}_2\text{BX}$  (Table 8). The shifts in the  $\alpha$ -carbon in particular indicate no, or little, difference in electron density at boron brought about by the substitution of a 4-OMe group by a 4-Me group, and hence little  $\Pi$ -aryl effects.

Table 8. Changes<sup>1</sup> in  $\delta_{\text{C}}$  between  $(\text{DMP})_2\text{BX}$  compared with  $\text{Mes}_2\text{BX}$

	X =	F	OMe	Et	Bu <sup>1</sup>	Ar <sup>2</sup>
C-1	$(\text{DMP})_2\text{BX}$	-9.2	-7.7	-1.0	-1.9	1.0
	$\text{Mes}_2\text{BX}$	-9.2	-7.3	-0.9	-1.8	0.8
C-2	$(\text{DMP})_2\text{BX}$	3.51	1.74	-0.22	-0.90	1.39
	$\text{Mes}_2\text{BX}$	3.35	2.05	-0.15	-0.72	1.43
C-3	$(\text{DMP})_2\text{BX}$	0.10	-0.36	-0.16	0.18	-0.04
	$\text{Mes}_2\text{BX}$	0.70	-0.033	-0.13	0.36	0.04
C-4	$(\text{DMP})_2\text{BX}$	1.23	-0.12	-0.25	-1.19	0.31
	$\text{Mes}_2\text{BX}$	2.13	-0.07	-0.27	-1.47	0.62
Ar-CH <sub>3</sub> <sup>3</sup>	$(\text{DMP})_2\text{BX}$	-0.57	-0.77	-0.27	2.49	-0.10
	$\text{Mes}_2\text{BX}$	-0.58	-0.48	-0.28	2.70	-0.10

<sup>1</sup>) All changes (ppm) relative to  $\text{Ar}_2\text{BCH}_3$ . Positive changes indicate downfield shifts.

<sup>2</sup>) This refers to  $(\text{MDP})_3\text{B}$  and  $\text{Mes}_3\text{B}$ . <sup>3</sup>) *ortho*-methyl groups.

The trends are the same for each of the carbon atoms in each of the series, and the absolute values of the changes are extremely similar. The similarity in the changes brought about at C-1, in particular, strengthen the case against fundamental changes in electron density at boron between the two series of compounds. The rather large differences in both series in  $\delta_{\text{C}}$  of Ar-CH<sub>3</sub> on going from  $\text{Ar}_2\text{BCH}_3$  to  $\text{Ar}_3\text{B}$  may indicate a conformational change.

The  $^1\text{H}$  nmr data for  $(\text{DMP})_2\text{BX}$  are given in Table 9.

Table 9.  $^1\text{H}$  nmr data for  $(\text{DMP})_2\text{BX}$ <sup>1</sup>

X	H-3	ArCH <sub>3</sub>	Ar-OCH <sub>3</sub>	Other protons
F	6.63	2.35 <sup>2</sup>	3.86 <sup>2</sup>	
OCH <sub>3</sub> <sup>a</sup>	6.52	2.24	3.76	a,3.73s
OH <sup>a</sup>	6.52	2.26	3.76	a,6.06

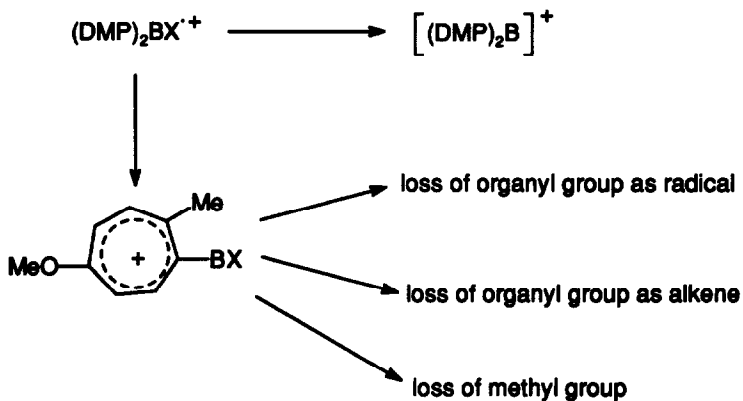
Table 9. (Continued)

X	H-3	ArCH <sub>3</sub>	Ar-OCH <sub>3</sub>	Other protons
$\overset{\text{a}}{\text{CH}_3}$	6.53	2.20	3.73	a,1.46s
$\overset{\text{a}}{\text{CH}_2}\overset{\text{b}}{\text{CH}_3}$	6.52	2.21	3.75	a,1.85q; b,1.04t
$\overset{\text{a}}{\text{CH}_2}\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_3}$	6.52	2.21	3.69	a,1.85t; b,c,1.2-1.6m; d,0.84t
$\overset{\text{a}}{\text{CH}_2}(\overset{\text{b}}{\text{CH}_2})_6\overset{\text{c}}{\text{CH}_3}$	6.52	2.21	3.75	a,1.85t; b,1.2-1.5m; c,0.89t
$\overset{\text{a}}{\text{CH}}(\overset{\text{c}}{\text{CH}_3})\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_3}$	6.50	2.22	3.74	a,1.5t; b,c,1.1-1.4m; d,0.81t; e,1.07t
$\overset{\text{a}}{\text{CH}}(\overset{\text{e}}{\text{CH}_2}\overset{\text{f}}{\text{CH}_3})\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_3}$	6.49	2.22	3.77	a,1.98m; b,c,e,1.1-1.7m; d,f,0.81t, 0.76t
$\overset{\text{a}}{\text{CH}}(\overset{\text{d}}{\text{CH}_2}\overset{\text{e}}{\text{CH}_3})(\overset{\text{b}}{\text{CH}_2})_6\overset{\text{c}}{\text{CH}_3}$	6.49	2.23	3.75	a,1.95m; b,d,1.1-1.7m; c,e,0.75t, 0.9t.
$\text{C}(\overset{\text{a}}{\text{CH}_3})_3$	6.56	2.36	3.74	1.17s
$\text{C}(\overset{\text{f}}{\text{CH}_3})\overset{\text{a}}{\text{CH}_2}\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CH}_3}$   $\overset{\text{d}}{\text{CH}_2}\overset{\text{e}}{\text{CH}_3}$	6.50	2.31	3.74	a,b,d,1.1-1.7m; e,0.82t; f,1.13s
$\overset{\text{a}}{\text{CH}}=\overset{\text{b}}{\text{CH}}\overset{\text{c}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_2}\overset{\text{e}}{\text{CH}_2}\overset{\text{f}}{\text{CH}_3}$	6.53	2.18	3.73	a,6.68d, J=18Hz; b,6.38-6.56m; c,2.24m; d,e,1.5-1.2m; f,0.89t
$\text{C}(\overset{\text{d}}{\text{CH}_2}\overset{\text{e}}{\text{CH}_3)=\overset{\text{a}}{\text{CH}}\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CH}_3}$	6.53	2.14	3.76	a,6.12t; b,d,2.35-2.1m; c,e,0.97t, 0.91t
$\overset{\text{a}}{\text{C}}\text{H}=\overset{\text{b}}{\text{CH}}\overset{\text{c}}{\text{CH}_2}\text{D}$	6.53	2.17	3.73	a,6.60d, J=17Hz; b,6.1m; c,1.89d
$\text{C}=\overset{\text{a}}{\text{C}}\overset{\text{b}}{\text{CH}_2}\overset{\text{c}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_2}\overset{\text{d}}{\text{CH}_3}$	6.53	2.30	3.78	a,2.2t; b,c,1.4-1.6m; d,0.9t
$\overset{\text{a}}{\text{CH}_2}\overset{\text{b}}{\text{CH}}=\overset{\text{c}}{\text{CH}_2}$	6.52	3.72	2.22	a,2.81d; b,5.99-5.83m; c,5.00-4.81m
$\overset{\text{a}}{\text{CH}_2}\text{Si}(\overset{\text{b}}{\text{CH}_3})_3$	6.34	3.58	2.06	a,1.47s, b,-0.24s

1) Solution in CDCl<sub>3</sub> relative to TMS=O. 2) Doublet, J<sub>C,F</sub> = 2.5Hz.

#### E.I. Mass Spectra of (DMP)<sub>2</sub>BX

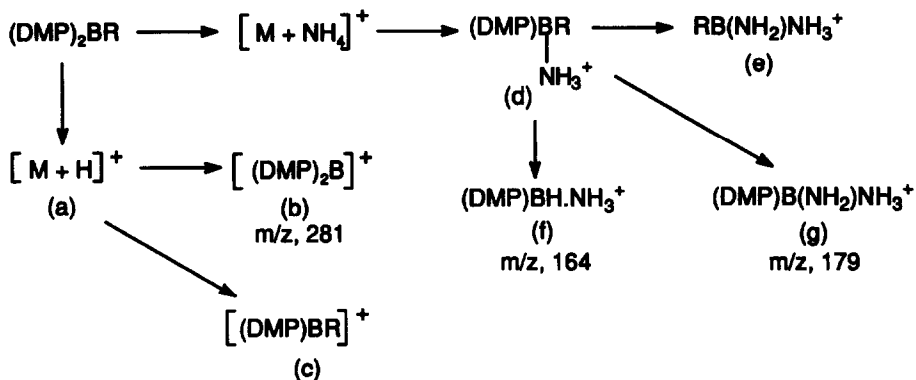
The e.i. mass spectra of Mes<sub>2</sub>BX derivatives have been analysed<sup>39</sup> and similar patterns to those reported are found for (DMP)<sub>2</sub>BX. These are summarised in Scheme 5. In general the molecular ions are weak, except for (DMP)<sub>2</sub>BOMe and (DMP)<sub>2</sub>BC≡CBu. The detailed data are given in the experimental section.



Scheme 5

### *C.I. Mass Spectra of $(DMP)_2BX$*

The c.i. mass spectra of  $(DMP)_2BX$  were studied using ammonia as the ionising gas. Once more  $[(DMP)_2B]^+$  formed a major peak, but so also did  $[(DMP)BR]^+$  and  $(DMPH(NH_2))^+$ . Addition of  $NH_4^+$  to the molecular ion followed by loss of DMPH was confirmed by high resolution studies. The data are given in Table 10 and rationalised in Scheme 6. The ion (h), due to  $DMPH_2^+$ , which could arise in a variety of ways, is also important in all cases.



Scheme 6

Table 10. C.I. mass spectral data for (DMP)<sub>2</sub>BX

X	Peak intensity (m/z) <sup>1</sup>								Other peaks
	a	b (281)	c	d	e	f (164)	g	h (137)	
F	29(301)	-	-	100(182)	-	-	-	98	-
OMe	79(313)	11	21(177)	49(194)	-	-	-	100	-
OH	-	-	-	9(180)	-	-	-	100	-
Me	62(297)	35	47(161)	100(178)	42(59)	-	39(179)	63	46(296), 38(160)
Et	79(311)	19	19(175)	75(192)	77(73)	-	19(178)	100	-
Bu <sup>a</sup>	11(339)	16	25(203)	77(220)	77(101)	-	-	100	-
Oct <sup>a</sup>	100(395)	36	4(259)	97(276)	65(157)	-	-	69	-
2-Pent	15(353)	29	27(217)	100(234)	24(115)	18	-	34	-
3-Hex	15(367)	8	13(231)	96(248)	20(129)	9	-	100	9(165)
3-Dec	11(423)	59	23(287)	100(304)	21(185)	33	-	64	47(270)
Bu <sup>t</sup>	14(339)	30	57(203)	100(220)	6(101)	-	-	-	-
C(Me)(Et)(Pr)	3(381)	43	22(248)	28(262)	-	-	37(178)	100	-
CH=CHCH <sub>2</sub> D	57(324)	-	16(188)	89(205)	-	-	-	100	55(204)
CH=CHBu	49(365)	4	33(229)	100(246)	40(127)	-	-	57	-
C(Et)=CHEt	34(365)	4	66(229)	100(246)	16(127)	-	-	90	7(256)
C=Cu	21(363)	4	13(227)	100(244)	42(125)	-	-	81	-
CH <sub>2</sub> -CH=CH <sub>2</sub>	85(323)	100	23(187)	20(204)	-	-	8(179)	27	12(162)
CH <sub>2</sub> SiMe <sub>3</sub>	8(369)	7	65(233)	100(250)	17(131)	-	-	88	-

<sup>1</sup>) Peak designation according to Scheme 6.

## EXPERIMENTAL

### Instrumentation

Infra-red spectra were recorded on a Pye Unicam SP1050 infra-red spectrometer using NaCl cells with neat liquids or solutions and KBr disks with solids. The polystyrene absorbances at 1603 cm<sup>-1</sup> and 1495 cm<sup>-1</sup> were used as references.

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 deuteriochloroform as solvent and tetramethylsilane as reference except where stated.

Boron (<sup>11</sup>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 (not borosilicate glass) nmr tubes. Chemical shifts are in p.p.m. and signals downfield from boron trifluoride (i.e., deshielded) were recorded as positive.

Carbon ( $^{13}\text{C}$ ) nmr were recorded on a Varian XL-100 or a Bruker WM-250 Fourier transform nmr spectrometer, using deuteriochloroform as a solvent and tetramethylsilane 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 VG12-253 mass spectrometer. High resolution c.i. and e.i. 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.

Gas liquid chromatography was performed on a Varian Vista series 6000 chromatograph with a Varian CDS-401 data system as integrator and plotter. All mixtures were analysed on a  $10' \times \frac{1}{8}"$  stainless steel column packed with 5% SE30 on Chromosorb G packing, except where stated. The basic temperature program used for the analysis of product mixtures was,  $120^\circ\text{C}$  for two minutes, ramp to  $240^\circ\text{C}$  at  $30^\circ\text{C}$  per minute then held for one minute. This programme was modified as required, such changes being noted in the relevant section. Glc estimations of reaction yields were made by adding a known weight of a standard to the reaction mixture and determining the detector response factor for each component to be examined. Typical internal standards were straight chain hydrocarbons such as dodecane and hexadecane. Where possible, products were identified by coinjection of an authentic sample.

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 were determined using a Carlo Erba Strumentazione Elemental Analyser. Many labile products proved difficult to analyse. In all cases the molecular formula was determined by high resolution mass spectrometry on a sample which was pure by tlc, hplc and nmr.

### *Reagents*

All reactions involving organoboranes were carried out using purified anhydrous reagents, unless otherwise stated. Reactions involving the use or production of air and water sensitive compounds were carried out under a static pressure of argon used 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.<sup>40</sup>

*Solvents* were treated as follows. THF was first purified 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.<sup>41</sup> Methanol was dried and purified by distillation from magnesium methoxide.



Bromomesitylene and 1-bromo-2,6-dimethyl-4-methoxybenzene were distilled under nitrogen, at reduced pressure prior to use. Boron trifluoride etherate was distilled from  $\text{CaH}_2$ . Magnesium turnings used in the preparation of Grignard reagents were treated prior to use with dilute hydrochloric acid for an hour, then acetone and dried for over three hours at  $120^\circ\text{C}$  under vacuum. 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 Chemical Co. 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.<sup>43</sup>

Purified solvents and reagents were stored under standard conditions<sup>40</sup> for use in reactions involving air-sensitive compounds.

#### *Experimental Procedures*

The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.<sup>40</sup> In particular, all glassware was dried at  $120^\circ\text{C}$  for at least four hours, assembled hot and cooled under a stream of argon introduced and expelled *via* septum capped inlets and outlets, using hypodermic needles. Manipulation of liquids under argon was achieved using oven-dried syringes and double-ended needles which had been cooled by flushing with argon. All operations involving solid bis(2,6-dimethyl-4-methoxyphenyl)boranes were carried out in an argon flushed glove box. Sublimations were performed using a cold finger apparatus, that fitted inside the oven of a Kugelrohr, and was directly connected to a mercury diffusion pump *via* wide bore glass tubing.

For some of the reactions only one example will be described in detail and then the data for the products of different examples will be presented afterwards. The yields given will be the best obtained and any non-standard reaction conditions will be described.

#### *Preparation of 1-bromo-2,6-dimethyl-4-methoxybenzene (8)*

##### *(a) Preparation of 3,5-Dimethylmethoxybenzene (6)*

A 15 litre flask was equipped with a mechanical stirrer and a dropping funnel. The flask was charged with 3,5-dimethylphenol (500g, 4.10mol), aqueous sodium hydroxide solution (5M, 900ml, 4.50mol) and water (9 litres) to give an orange solution. The funnel was charged with dimethyl sulphate (430ml, 4.55mol) which was added to the stirred phenoxide solution over 1h. Stirring was continued for 3h after the addition, during which time 3,5-dimethylmethoxybenzene separated out. The mechanical stirrer was then replaced with a double sided condenser and the solution heated under reflux for an hour to destroy excess dimethyl sulphate. The organic layer was separated and the aqueous layer extracted with diethyl ether (2 x 500ml). The organic extracts were combined, washed with water (2 x 100ml), saturated aqueous sodium bicarbonate solution (3 x 100ml) and water (3 x 100ml), dried ( $\text{MgSO}_4$ ), filtered and concentrated on a rotary evaporator. The crude product was distilled at  $60.5^\circ\text{C}$  at 4.5mmHg, (lit.<sup>43</sup>,  $193^\circ\text{C}$ ) to give (6) (457g, 82%).

$\delta_{\text{H}}$ , 2.27(6H, s, Ar- $\text{CH}_3$ ), 3.73(3H, s,  $\text{OCH}_3$ ), 6.52(2H, s, H-2), 6.58(1H, s, H-4),  
 $\delta_{\text{C}}$  21.38(q, Ar- $\text{CH}_3$ ), 54.82(q,  $\text{OCH}_3$ ), 111.8(d, C-2), 122.5(d, C-4), 139.1(s, C-3), 159.93(s, C-1).  $m/z$  (intensity) 136(100), 135(10.6), 121(35.9), 105(13.5), 93(14.3), 91(65.2), 77(30.4).  
 $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ), 3010, 2960, 2930, 2850, 1619, 1609, 1474(b), 1327, 1298, 1196, 1170, 1153, 1073, 828, 684.  $\lambda_{\text{max}}$ , 226(5590), 274(1510), 282(1720)nm.

(b) *1-Bromo-2,6-dimethyl-4-methoxybenzene* (8)

A 5 litre flask was equipped with a mechanical stirrer and a 2 litre dropping funnel. The flask was charged with (6) (450g, 3.31mol) and glacial acetic acid (1.6 litres), and the contents of the flask cooled to 5°C. The funnel was charged with a solution of bromine (529.0g, 3.31mol) in acetic acid (1 litre). The bromine solution was added slowly (*ca.* 4h) to the well stirred mixture, stirring being continued for 30 min. after the addition was complete. The reaction was neutralised with saturated aqueous NaHCO<sub>3</sub> and the organic product extracted into dichloromethane (2 x 500ml). The organic layer was washed with water (2 x 100ml), dried and concentrated on a rotary evaporator. The crude product was distilled at 83°-85°C at 1mmHg (lit.<sup>44</sup>, 137°-138°C at 20mmHg) to give (8) (491g, 69%) that crystallised on standing to a colourless solid, m.p. 24°C, (lit.<sup>44</sup>, 24-25°C).

$\delta_{\text{H}}$  2.37(6H, s, Ar-CH<sub>3</sub>), 3.73(3H, s, OCH<sub>3</sub>), 3.73(3H, s, OCH<sub>3</sub>), 6.64(2H, s, H-2).  
 $\delta_{\text{C}}$  23.96(q, Ar-CH<sub>3</sub>), 55.10(q, OCH<sub>3</sub>), 113.9(d, C-2), 118.2(s, C-4), 140.0(s, C-3), 158.2(s, C-1).  
 m/z (intensity) (e.i.), 216(100), 214(99.1), 173(31.6), 171(33.7), 135(45.1), 105(36.9), 92(37.1), 91(78.9).  $\nu_{\text{max}}$  (cm<sup>-1</sup>), 2965, 2935, 2869, 1580, 1472, 1431, 1322, 1197, 1164, 1078, 1032, 1018, 852, 830.  $\lambda_{\text{max}}$ , 230(5590), 270(1380), 278(1380)nm.

Recrystallisation of the pot residue from dichloromethane gave a 12% yield of *2,4-dibromo-3,5-dimethylmethoxybenzene* as a white solid m.p. 110°-112°C (lit.<sup>44</sup>, 108-109°C).

$\delta_{\text{H}}$ , 2.35, 2.58(6H, s, Ar-CH<sub>3</sub>), 3.81(3H, s, OCH<sub>3</sub>), 6.61(1H, s, H-6).  $\delta_{\text{C}}$  24.45, 24.58(q, Ar-CH<sub>3</sub>), 56.28(q, C-9), 111.3(d, C-5), 111.8(s, C-2), 118.5(s, C-2), 137.7(s, C-5), 138.4(s, C-3), 158.6(s, C-1). m/z (intensity), 296(47.1), 294(100), 292(49.0), 281(12.2), 279(24.9), 277(13.1), 172(16.7), 170(17.6).  $\nu_{\text{max}}$  (cm<sup>-1</sup>), 3110, 2970, 2940, 2850, 1578, 1570, 1466, 1376, 1327, 1214, 1095, 1039, 1002, 928, 827, 644.

**Preparation of alkyl(2,6-dimethyl-4-methoxyphenyl)boranes (13)\****Bis(2,6-dimethyl-4-methoxyphenyl)fluoroborane* (11).

A three-necked 1 litre round-bottomed flask was equipped with a reflux condenser, a pressure equalising funnel, a magnetic follower and a septum cap. The flask was charged with magnesium turnings (9.80g, 0.408mol) and the dropping funnel was charged with (8) (86.81g, 0.404mol) and dry THF (200 ml). The magnesium was heated with a hot air gun (~70°-80°C) and a portion (*ca.* 10ml), of the solution of (8) run into the flask. Reaction started immediately and the rate of addition was adjusted so as to maintain reflux. The reaction was heated under reflux for 2 hours after completion of the addition. The resulting solution of the Grignard reagent was then allowed to cool to room temperature.

Boron trifluoride etherate (23.1ml, 0.184mol) was added by syringe over 10 minutes to the stirred Grignard solution prepared previously and the reaction was stirred overnight at room temperature during which time salts precipitated. The solvent was then distilled from the reaction into a trap under vacuum (1mmHg). Dry cyclohexane (200ml) was then added to the flask which was heated on an oil bath at 55°C. The flask was stirred for 30 minutes and the contents allowed to settle whilst the flask was maintained at 55°C. The supernatant was then decanted into a second flask and the contents of the first flask extracted twice more with cyclohexane by the same method. The combined clear yellow organic extract was concentrated under vacuum and cooled (1-2°C) to give (11) (45.3g, 82%) as a white solid, m.p. 74°-74°C.

\*For *all* compounds (DMP)<sub>2</sub>BX data for u.v. spectra are in Table 4, most <sup>11</sup>B nmr spectra are in Table 5,

<sup>13</sup>C nmr spectra are in Table 6, <sup>1</sup>H nmr spectra are in Table 9, and c.i. mass spectra are in Table 10.

Unless otherwise stated, the mass spectra given below are electron impact mass spectra.

Further purification was achieved by sublimation at 100°C at 0.001 mmHg to give a white powder, m.p. 73°-74°C. M + H, C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>BF; calc., 301.17751, found 301.17769 and M + NH<sub>4</sub>-DMPH, C<sub>9</sub>H<sub>14</sub>BNOF; calc., 182.1153, found, 182.1180. m/z (intensity), 300(10.8), 285(12.9), 164(35.0), 163(24.4), 136(100), 91(45.4).  $\nu_{\max}$  (cm<sup>-1</sup>), 2950, 2860, 1600, 1450 (b), 1304, 1240, 1220, 1188, 1150, 1092, 1061, 947, 929, 849, 834, 652.

Treatment of the concentrated supernatant from the cyclohexane recrystallisation with methanol (100 ml) and cooling to -20°C gave *bis*(2,6-dimethyl-4-methoxyphenyl)methoxyborane (12) (4.0g, 7%) as a white solid, m.p. 80°-81°C, (lit.<sup>45</sup> 76-77°C). Sublimation at 110°C at 0.001mmHg gave (12) as a white powder, m.p. 80°-81°C.

C<sub>15</sub>H<sub>25</sub>BO<sub>3</sub> requires C 73.08%, H 8.01%; found, C 73.15%, H 8.06%. M + H, C<sub>15</sub>H<sub>25</sub>BO<sub>3</sub>; calc., 313.1975, observed, 313.1995. m/z (intensity), 312(93.0), 281(75.6), 177(37.8), 176(100), 161(44.8).  $\nu_{\max}$  (cm<sup>-1</sup>), 3090, 2960, 2865, 1600, 1570, 1460, 1308, 1294, 1249, 1191, 1150, 1065, 972, 860, 840, 822, 664.

*Bis*(2,6-dimethyl-4-methoxyphenyl)hydroxyborane

Compound (11) (1g, 3.3mmol) was dissolved in ether (10 ml) and shaken with saturated aqueous NH<sub>4</sub>Cl solution (10ml) and water (10ml) for 10 min. The organic layer was separated and the aqueous layer was extracted with ether (2 x 5ml). The organic extracts were combined, washed with water (2 x 5ml), dried (MgSO<sub>4</sub>) filtered and concentrated on a rotary evaporator. The crude product was recrystallised from 60°-80° petrol to give product (0.86g, 87%) as a white solid, m.p. 119°-121°C, (lit.<sup>45</sup> 121°-123°C).

C<sub>18</sub>H<sub>23</sub>BO<sub>3</sub>; calc., 298.1740, found 298.1717. m/z (intensity), 298(1.6), 162(9.2), 137(100), 91(13.9).  $\nu_{\max}$  (cm<sup>-1</sup>), 3520, 3005, 2970, 2840, 1600, 1462, 1441, 1305, 1290, 1220, 1190, 1153, 1100, 1057, 948, 928, 851, 832, 819, 692.

*Bis*(2,6-dimethyl-4-methoxyphenyl)methoxyborane (12)

A 250ml three-necked round-bottomed flask was equipped with a pressure equalising dropping funnel, a reflux condenser, a septum cap and a magnetic follower. The flask was charged with magnesium (1.03g, 42.9mmol) and a crystal of iodine, the dropping funnel was charged with (8) (8.63g, 40.1mmol) and dry diethyl ether (40ml). The magnesium was heated to 70°-80°C with a hot air gun and 5ml of the solution of (8) run in. Reaction started immediately and the rate of addition was adjusted to maintain constant reflux. Reflux was continued for two hours after completion of the addition to give a dark brown solution of the Grignard reagent, which was cooled to 0°C and then a solution of boron trichloride (25ml, 0.76, 19mmol) in hexanes was added by syringe. The reaction was allowed to warm to room temperature and stirred overnight, during which time salts precipitated. The reaction was then recooled to 0°C, dry methanol (5ml) added by syringe and the reaction was stirred at 0°C for 2 hours and then allowed to settle at 0°C. The supernatant liquid was decanted to a second flask by double-ended needle and the salts washed twice with dry diethyl ether (40ml) at room temperature. The organic extracts were combined and concentrated *in vacuo*. The resulting solid (4.5g) was dissolved in methanol (50ml) at room temperature and kept at -20°C overnight. This gave (13) (3.44g, 58%) as white crystals, m.p. 80°-82°C, identical in all respects with the sample prepared as above.

*Preparation of (12) by the reaction of (11) with methanol*

A 50ml flask was fitted with a septum cap, flushed with nitrogen and cooled to 0°C. The flask was charged with (11) (1.53g, 5.1mmol) and dry methanol (10ml) that had been precooled to 0°C. The flask was immediately placed in a deep freeze at -20°C and left overnight, during which time a solid precipitated. This

was collected to give (12) (1.46g, 92%), m.p. 80°-81°, identical in all respects with the samples previously prepared.

*(2,6-Dimethyl-4-methoxyphenyl)dimethoxyborane*

A 100ml round-bottomed flask was equipped with a septum cap and a magnetic follower. The flask was charged with trimethoxyborane (5.2ml, 45.8mmol) and THF (30 ml) and a THF solution of (10) (23ml, 1.73M, 39.9mmol) was added by syringe to the flask at room temperature. The reaction was stirred overnight at room temperature during which time salts precipitated. The salts were filtered off under nitrogen, and the solvent removed *in vacuo* to give a yellow oil, which was distilled at 80°C/0.03mmHg to give the *product* (6.06g, 73%) as a clear liquid.

M + H, C<sub>11</sub>H<sub>18</sub>BO<sub>3</sub>; observed, 209.1345, calc., 209.1349.  $\delta_B$ , 31.6;  $\delta_H$ , 6.53(2H, s, Ar-H), 3.72(3H, Ar-OCH<sub>3</sub>), 3.55(6H, B-OCH<sub>3</sub>), 2.25(12H, s, Ar-CH<sub>3</sub>);  $\delta_C$ , 160.1(C-4), 140.8(C-2), 139.2(C-1), 111.9(C-3), 54.81(Ar-OCH<sub>3</sub>), 52.03(B-OCH<sub>3</sub>), 21.94(Ar-CH<sub>3</sub>). m/z (c.i.), 209(96), 137(39). m/z (e.i.) 208(13.5), 193(23.2), 161(40.0), 135(34.1), 91(48.7), 73(100).  $\nu_{max}$  (cm<sup>-1</sup>), 2960, 2865, 1601, 1473, 1320 b, 1193, 1151, 1062, 1010, 850, 832.  $\lambda_{max}$ , 224.5 (7350), 227.9(7405), 274.5(1330), 282.9(1460)nm.

**Preparation of bis(2,6-dimethyl-4-methoxyphenyl)alkylboranes**

*Bis(2,6-dimethyl-4-methoxyphenyl)methylborane (13, R=Me, (DMP)<sub>2</sub>BMe)*

A 250ml round-bottomed flask was equipped with a septum cap and a magnetic follower and purged with argon. The flask was charged with (11) (10.50g, 35mmol) and diethyl ether (100ml) and cooled in an ice water bath. A solution of methyllithium (27ml, 1.3M, 35.1mmol) was then added by syringe over 15 min. and the mixture allowed to warm to room temperature and stirred overnight. The salts were filtered off under nitrogen and washed with ether (20ml). The organic extracts were combined and concentrated *in vacuo* too give a pale yellow solid (9.1g), which was sublimed at 70°C (0.001mm Hg to give *product* (7.04g, 68%) as a white powder, m.p. 79°C.

M + H, C<sub>19</sub>H<sub>26</sub>BO<sub>2</sub>; calc., 297.2026, found, 297.2027 and M + NH<sub>4</sub>-DMPH, C<sub>10</sub>H<sub>17</sub>BNO; calc., 178.1403, found 178.1400. m/z (intensity), 296(4.6), 281(20.2), 160(100), 136(18.2), 91(22.6).  $\nu_{max}$  (cm<sup>-1</sup>), 2970, 2845, 1600, 1566, 1470, 1449, 1305, 1296, 1227, 1193, 1146, 1068, 968, 862, 851, 709.

*Bis(2,6-dimethyl-4-methoxyphenyl)-n-butylborane (13, R=Bu<sup>n</sup>)*

The reaction was carried out by the method used for the preparation of (DMP)<sub>2</sub>BMe except that (i) one equivalent of a 2.5M solution of *n*-butyllithium in hexanes was used, (ii) the addition was carried out at room temperature and (iii) the mix was only stirred for two hours. The work up was identical and gave a yellow solid that was sublimed at 90°C/0.001mmHg to give *product* (5.32g, 45%) as a white solid, m.p. 74.5°-76°C. M + H, C<sub>22</sub>H<sub>32</sub>BO<sub>2</sub> calc., 220.1873, found, 220.1876 and M + NH<sub>4</sub> + NH<sub>3</sub>-2DMP, C<sub>4</sub>H<sub>14</sub>BN<sub>2</sub>; calc., 101.1250, found, 101.1251. m/z (intensity), 338(3.3), 281(100), 202(16.8), 163(29.3), 147(24.4).  $\nu_{max}$  (cm<sup>-1</sup>), 2970, 2940, 2870, 1600, 1475, 1305, 1197, 1150, 1136, 1066, 851, 834, 663.

*Bis(2,6-dimethyl-4-methoxyphenyl)-t-butylborane (13, R=Bu<sup>t</sup>)*

The title compound was prepared by the same method as for (DMP)<sub>2</sub>BMe, except that one equivalent of a 1.7M solution of *t*-butyllithium in hexanes was used. The work up was identical and gave a yellow solid that was sublimed at 100°C/0.001mmHg to give *product* (8.3g, 70%) as a white solid, m.p. 110°-111.5°C. M + H, C<sub>22</sub>H<sub>32</sub>BO<sub>2</sub>; calc., 339.2495, found 339.2480. m/z (intensity), 282(21.1), 281(100), 280(28), 203(9.4).  $\nu_{max}$  (cm<sup>-1</sup>), 3005, 2950, 2870, 2840, 1600, 1567, 1470, 1305, 1295, 1195, 1143, 1118, 1068, 952, 941, 892, 853, 842, 835, 819, 709, 687.

**Bis(2,6-dimethyl-4-methoxyphenyl)ethylborane (13, R=Et, (DMP)<sub>2</sub>BEt)**

A 250ml round-bottomed flask was equipped with a septum cap and a magnetic follower. The flask was charged with (11) (11.37g, 37.9mmol) and dry diethyl ether (80ml). A solution of ethylmagnesium bromide (28ml, 1.38M, 38.6mmol) in ether was then added by syringe over 15 min., and the reaction was stirred overnight during which time salts precipitated. The salts were filtered off under nitrogen and washed with ether (30ml). The organic filtrates were combined and concentrated *in vacuo* to give a viscous oil, which was extracted with cyclohexane (3 x 50ml). The cyclohexane extracts were combined and concentrated *in vacuo* to give an off white solid which was sublimed at 80°C/0.002mmHg to give (13, R=Et) (6.1g, 52%) as a white powder, m.p. 59°-60°C. M + H, C<sub>20</sub>H<sub>28</sub>BO<sub>2</sub>; calc., 311.21824, found, 311.21824. m/z (intensity), 310(3.0), 281(100), 174(23.2), 91(13.7), 77(13.2).  $\nu_{\max}$  (cm<sup>-1</sup>), 3000, 2950, 2870, 2835, 1600, 1565, 1460(b), 1305, 1294, 1195, 1148, 1070, 1032, 860, 830, 700.

**Bis(2,6-dimethyl-4-methoxyphenyl)allylborane (14)**

Compound (14) was prepared by the method used for (DMP)<sub>2</sub>BEt, except that one equivalent of a 0.84M solution of allylmagnesium bromide in ether was added at 0°C and the reaction only stirred for two hours at room temperature. Sublimation of the cyclohexane extract at 100°C/0.001mmHg gave (14) (6.1g, 50%) as a white powder, m.p. 69.5°-70.5°C. M + H, C<sub>21</sub>H<sub>28</sub>BO<sub>2</sub>; calc., 323.2182, found, 323.2220. m/z (intensity), 282(19.5), 281(100), 280(23.2).  $\nu_{\max}$  (cm<sup>-1</sup>), 3010, 2860, 2840, 1630, 1600, 1460, 1305, 1250, 1161, 1147, 1130, 1063, 989, 949, 891, 842, 831, 702.

**Bis(2,6-dimethyl-4-methoxyphenyl)-*n*-octylborane (13, R=Oct<sup>n</sup>)**

The method of preparation of (13, R=Oct<sup>n</sup>) was the same as that used for (DMP)<sub>2</sub>BEt. Concentration of the cyclohexane extracts gave a viscous oil, which on bulb to bulb distillation at 160°C/0.001mmHg gave *product* (8.2g, 69%) as a colourless liquid. M<sup>+</sup>, C<sub>22</sub>H<sub>30</sub>BO<sub>2</sub>; calc., 394.3043, found, 394.3035. m/z (intensity), 394(9.3), 281(100), 162(44.2), 137(32.6), 136(34.3).  $\nu_{\max}$  (cm<sup>-1</sup>), 2965, 2935, 2865, 1600, 1470, 1305, 1192, 1148, 1068, 851, 832, 661.

**Bis(2,6-dimethyl-4-methoxyphenyl)-1-hexynylborane (13, R = C≡CBu<sup>n</sup>)**

A 250ml round-bottomed flask was equipped with a septum cap and a magnetic follower. The flask was charged with (11) (7.09g, 23.5mmol) and dry 40°-60° petroleum ether (100ml). A suspension of hexynyllithium, prepared by reaction of 1-hexyne (2.8ml, 24.4mmol) and *n*-butyllithium (12.4ml, 1.97M, 24.4mmol) in 40°-60° petroleum ether (25ml) at 0°C, was then added by double-ended needle. The reaction was stirred overnight during which time salts precipitated. The salts were filtered off under nitrogen and washed with 40°-60° petroleum ether (30ml). The organic extracts were combined and concentrated *in vacuo* to give a yellow oil which was distilled at 200°C/0.01mmHg to give *product* (3.5g, 41%) as a colourless oil that on cooling became a solid, m.p. 31°C.

M<sup>+</sup>, C<sub>24</sub>H<sub>31</sub>BO<sub>2</sub>; calc., 362.2417, found, 362.2379. m/z (intensity), 362(71.3), 305(54.8), 281(42.2), 280(39.2), 227(54.3), 226(100), 136(32.2).  $\nu_{\max}$  (cm<sup>-1</sup>), 2960, 2875, 2150, 1600, 1466, 1305, 1238, 1192, 1150, 1069, 950, 849, 831, 710, 657.

**Preparation of bis(2,6-dimethyl-4-methoxyphenyl)alkylboranes via deprotonation/alkylation****Bis(2,6-dimethyl-4-methoxyphenyl)-((1-methyl)butyl)borane (13, R=CH(Me)Pr<sup>n</sup>)**

A 100ml round-bottomed flask was equipped with a septum cap and a magnetic follower. The flask was charged with mesityl bromide (1.4ml, 9.1mmol) and THF (20ml). The flask was cooled in a Cardice/acetone bath and a solution of *t*-butyllithium (13.1ml, 1.40M, 18.3mmol) in hexanes was added over 20 minutes by

syringe. The flask was stirred for half an hour at  $-78^{\circ}\text{C}$  and for one hour at room temperature to give a solution of mesityllithium. A second 100ml flask was equipped with a septum cap and a magnetic follower, charged with bis(2,6-dimethyl-4-methoxyphenyl)-*n*-butylborane (2.81g, 8.3mmol) and cooled in an ice water bath. The contents of the first flask were then added slowly by double-ended needle. The reaction mixture rapidly became dark red in colour and was stirred for four hours at room temperature. Methyl iodide (1ml, 16.1mmol) was then added at room temperature by syringe, on which an exothermic reaction ensued and the anion colour was discharged. The reaction was stirred overnight at room temperature, the solvent removed *in vacuo* and replaced by methanol (30ml). Cooling at  $-20^{\circ}\text{C}$  then gave a white solid which was sublimed at  $110^{\circ}\text{C}/0.001\text{mmHg}$  to give *product* (2.13g, 73%) as a white solid, m.p.  $84^{\circ}\text{--}86^{\circ}\text{C}$ .  $\text{M} + \text{H}$ ,  $\text{C}_{23}\text{H}_{34}\text{BO}_2$ ; calc., 353.2652, found, 353.2652.  $m/z$  (intensity), 282(43.1), 281(100).  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ), 2965, 2875, 1600, 1470, 1375, 1305, 1294, 1195, 1148, 1123, 1064, 949, 845, 830, 711, 681.

*Bis(2,6-dimethyl-4-methoxyphenyl)-((1-ethyl)butyl)borane (13, R=CH(Et)Pr<sup>n</sup>)*

The title compound was prepared by the same method as used for  $(\text{DMP})_2\text{BCH}(\text{Me})\text{Pr}^n$ , except that ethyl bromide (0.5ml, 6.7mmol) was added to the anion from bis(2,6-dimethyl-4-methoxyphenyl)-*n*-butylborane (1.878g, 5.56mmol). Sublimation at  $120^{\circ}\text{C}/0.001\text{mmHg}$  gave *product* (1.55g, 76%) as a white powder, m.p.  $123^{\circ}\text{--}125^{\circ}\text{C}$ .  $\text{M} + \text{H}$ ,  $\text{C}_{24}\text{H}_{36}\text{BO}_2$ ; calc., 367.2808, found, 367.2816;  $\text{M} + \text{NH}_4\text{-DMPH}$ ,  $\text{C}_{13}\text{H}_{27}\text{BNO}$  calc., 248.2186, found, 248.2193.  $m/z$  (intensity), 282(19.8), 281(100), 43(20.6).  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ), 2965, 2875, 1600, 1471, 1379, 1305, 1296, 1196, 1147, 1123, 1067, 851, 834, 666.

*Bis(2,6-dimethyl-4-methoxyphenyl)-3-((1-ethyl)octyl)borane (13, R=CH(Et)Hept<sup>n</sup>)*

The title compound was prepared in a fashion identical to  $(\text{DMP})_2\text{BCH}(\text{Me})\text{Pr}^n$  by reaction of the anion derived from bis(2,6-dimethyl-4-methoxyphenyl)-3-octylborane (3.705g, 9.40mmol) and ethyl bromide (1ml, 13.4mmol). The product mixture was washed rapidly with saturated aqueous  $\text{NH}_4\text{Cl}$  solution and the organic layer separated. The aqueous layer was extracted with diethyl ether (2 x 30ml) and the combined organic extracts were dried ( $\text{MgSO}_4$ ), filtered and concentrated on a rotary evaporator. The resulting oil was chromatographed on neutral silica (~40g) to give *product* (2.66g, 67%) as a colourless oil, on elution with 5%  $\text{CH}_2\text{Cl}_2$  in  $30^{\circ}\text{--}40^{\circ}$  petroleum ether.  $\text{M} + \text{H}$ ,  $\text{C}_{28}\text{H}_{44}\text{BO}_2$ ; calc. 423.3434, found 423.3432  $m/z$  (intensity), 282(20.8), 281(100), 163(22.4).  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ), 2960, 2935, 2860, 1600, 1468, 1305, 1193, 1146, 1127, 1067, 850, 829.

*Bis(2,6-dimethyl-4-methoxyphenyl)-((1-methyl)-(1-ethyl)butyl)borane, (13, R=C(Me)(Et)Pr<sup>n</sup>)*

The title compound was prepared by the same method as for  $(\text{DMP})_2\text{BCH}(\text{Me})\text{Pr}^n$ , by reaction of the anion derived from  $(\text{DMP})_2\text{BCH}(\text{Me})\text{Pr}^n$  (1.63g, 4.63mmol) and ethyl bromide (1ml, 13.4mmol). Sublimation of the product at  $120^{\circ}\text{C}/0.001\text{mmHg}$  gave *product* (1.21g, 69%) as a white powder, m.p.  $104^{\circ}\text{--}106^{\circ}\text{C}$ .  $\text{M} + \text{H}$ ,  $\text{C}_{25}\text{H}_{38}\text{BO}_2$ ; calc., 381.2987, found 381.2965.  $m/z$  (intensity), 282(42.7), 281(100), 161(14.5).  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ), 2970, 2880, 1600, 1564, 1469, 1305, 1292, 1193, 1141, 1112, 1064, 950, 934, 846, 830, 819, 709, 678.

*Bis(2,6-dimethyl-4-methoxyphenyl)ethylborane*

The title compound was prepared by the same method as for  $(\text{DMP})_2\text{BCH}(\text{Me})\text{Pr}^n$ , by reaction of the anion derived from  $(\text{DMP})_2\text{BMe}$  (3.29g, 11.1mmol) with methyl iodide (0.8ml, 12.9mmol). After 1h. at room temperature the solvent was removed *in vacuo* to give an oily solid which on sublimation at  $90^{\circ}\text{C}/0.001\text{mmHg}$  gave *product* (2.08g, 60%), m.p.  $58^{\circ}\text{--}60^{\circ}\text{C}$ ., identical with the sample previously prepared.

**Bis(2,6-dimethyl-4-methoxyphenyl)trimethylsilylmethylborane (13, R=CH<sub>2</sub>SiMe<sub>3</sub>)**

The title compound was prepared by the same method as for (DMP)<sub>2</sub>BCH(Me)Pr<sup>n</sup>, by reaction of the anion derived from (DMP)<sub>2</sub>BMe (2.46g, 8.3mmol) and chlorotrimethylsilane (1.1ml, 8.7mmol). The product was recrystallised from methanol then sublimed at 100°C/0.001mmHg to give *product* (1.80g, 59%) as a white solid, m.p. 63°-64°C. M + H, C<sub>22</sub>H<sub>34</sub>BO<sub>2</sub>; calc., 369.2421, found, 369.2437. m/z (intensity), 368(5.6), 281(32.0), 232(94.0), 217(100), 73(29.9). ν<sub>max</sub> (cm<sup>-1</sup>), 3010, 2965, 2845, 1600, 1470, 1447, 1305, 1191, 1146, 1068, 1000, 851, 831.

**Consecutive Alkylation of Boron Stabilised Carbanions****Ethylation/Methylation of Bis(2,6-dimethyl-4-methoxyphenyl)butylborane (13, R=Bu<sup>n</sup>)**

A 50ml flask equipped with a septum cap and a magnetic follower was charged with (13, R=Bu<sup>n</sup>) (1.86g, 5.50mmol). The flask was cooled in an ice water bath and a solution of mesityllithium (5.7mmol) in THF was added slowly by double-ended needle. The reaction rapidly became dark red in colour and was stirred for two hours at room temperature. Ethyl bromide (0.45ml, 6.0mmol) was then added, on which an exothermic reaction ensued and the reaction was stirred for three hours at room temperature. A second portion of mesityllithium (7.0mmol) was then added and the mix stirred for four hours at room temperature. Methyl iodide (1ml, 16.1mmol) was then added and the mix stirred overnight. The reaction was worked up as described previously. Sublimation at 120°C and 0.001mmHg gave only bis(2,6-dimethyl-4-methoxyphenyl)-((1-ethyl)butyl)borane (1.59g, 79%), m.p. 122°-124°C with nmr and mass spectra identical to those obtained previously.

**Methylation/Ethylation of (13, R=Bu<sup>n</sup>)**

This reaction was performed by the same method as used for the ethylation/methylation above. To the anion derived from (13, R=Bu<sup>n</sup>) (2.49g, 7.4mmol) was added methyl iodide (0.48ml, 7.7mmol) at 0°C. A rapid exothermic reaction ensued and the mix was stirred at room temperature for an hour. The resulting product was deprotonated with mesityllithium (8.0mmol) and reacted with ethyl bromide (1ml, 13.4mmol). Workup as described previously gave a mix of bis(2,6-dimethyl-4-methoxyphenyl)-((1-methyl)(1-ethyl)butyl)borane (57%) and bis(2,6-dimethyl-4-methoxyphenyl)-((1-methyl)butyl)borane (31%) the product yields being determined by proton nmr analysis.

**Preparation of bis(2,6-dimethyl-4-methoxyphenyl)boranes via potassium bis(2,6-dimethyl-4-methoxyphenyl)dihydroborate (15)****Potassium bis(2,6-dimethyl-4-methoxyphenyl)dihydroborate (15)**

A 250ml round-bottomed flask under argon was equipped with a septum cap and a magnetic follower and charged with a suspension of potassium hydride (6.0ml, 0.47g KH per ml, 70.3mmol). The potassium hydride was washed free of mineral oil with dry 60°-80° petroleum ether (3 x 30ml), and then activated by addition of a solution of LiAlH<sub>4</sub> (20ml, 1.1M) followed by stirring for 15 min. The supernatant was removed by double-ended needle and the potassium hydride washed with dry THF (2 x 30ml). More THF (30ml) was then added to the flask followed by a solution of (11) (7.00g, 23.3mmol) in THF (~60ml). The reaction was stirred at room temperature for an hour and filtered under dry nitrogen through a pad of Celite to give a crystal clear solution (85ml) of (15).

Hydride analysis by measurement of hydrogen evolution on quenching in MeOH:THF:2.5M H<sub>2</sub>SO<sub>4</sub> (1:1:1) showed the solution was 0.27M, giving a 98% yield. <sup>11</sup>B nmr gave a triplet at -22.73δ, J<sub>(B-H)}</sub> = 76.0 Hz that collapsed to a singlet on proton decoupling. Addition of dry 30°-40° petroleum spirit (20ml) to the potassium bis(2,6-dimethyl-4-methoxyphenyl)borohydride solution (20ml, 0.27M, 5.4mmol) gave a precipitate

of (15) (1.73g, 5.37mmol). This darkened considerably on heating but did not melt below 250°C. Its i.r. (KBr) spectrum showed a BH<sub>2</sub> stretch centred at 2180 cm<sup>-1</sup>.

*Bis(2,6-dimethyl-4-methoxyphenyl)-1-hexenylborane (16 R<sup>1</sup>=Bu<sup>n</sup>, R<sup>2</sup>=H)*

A 100ml round-bottomed flask was equipped with a septum cap and a magnetic follower. The flask was charged with a solution of (15) (30ml, 0.27M, 8.1mmol) in THF, cooled in an ice water mixture and 1-hexyne (1.1ml, 9.6mmol) was added by syringe followed by slow addition by syringe of chlorotrimethylsilane (1.05ml, 8.3mmol). Salts immediately precipitated and the reaction was stirred overnight at room temperature. The salts were filtered off under nitrogen and the solvent removed to give an oil, distillation of which at 130°C/0.001mmHg gave *product* (2.12g, 72%) as a clear viscous oil. M + H, C<sub>24</sub>H<sub>34</sub>BO<sub>2</sub>; 365.26519, found 365.26519. <sup>1</sup>H nmr (250MHz) gave a vinyl proton coupling of 18Hz demonstrating that the protons are *trans* as expected. m/z (intensity), 364(5.3), 307(8.1), 228(100), 171(29.4), 151(30.5), 136(26.6). ν<sub>max</sub> (cm<sup>-1</sup>), 2965, 2940, 2870, 1600, 1470, 1447, 1305, 1191, 1146, 1068, 1000, 851, 831.

*Bis(2,6-dimethyl-4-methoxyphenyl)-((1-ethyl)butenyl)borane (16, R<sup>1</sup>=R<sup>2</sup>=Et)*

The same method as for (DMP)<sub>2</sub>BCH=CHBu) was used except that 3-hexyne (1.1ml, 9.7mmol) was added. Removal of the solvent gave a white solid that was sublimed at 90°C/0.001mmHg to give *product* (1.92g, 65%) as a white powder, m.p. 92°-94°C. M + H, C<sub>24</sub>H<sub>34</sub>BO<sub>2</sub>; calc., 365.26519, observed 365.26520. m/z (intensity), 364(11.2), 281(50.1), 228(100), 199(28.0), 136(18.9), 91(32.9). ν<sub>max</sub> (cm<sup>-1</sup>), 2970, 2880, 1600, 1470, 1305, 1295, 1231, 1218, 1193, 1145, 1129, 1063, 1044, 950, 846, 832, 717, 681.

**Alkylation/Deuteriation of Boron Stabilised Allyl Carbanions**

*Preparation of Bis(2,6-dimethyl-4-methoxyphenyl)-1-propenyl-3-d-borane*

The anion from (14) (1.34g) (4.16mmol) was obtained as detailed above, by reaction with mesityllithium (4.3mmol). Trifluoroacetic acid-d (5ml, 1M, 5mmol) (from TFAA and H<sub>2</sub>O) in THF was then added, the red anion colouration disappeared immediately, and the mix stirred for half an hour. The solvent was then removed *in vacuo* and the resulting solid sublimed at 70°C/0.001mmHg to give bis(2,6-dimethyl-4-methoxyphenyl)-1-propenyl-3-d-borane (1.16g, 87%) as a white solid, m.p. 56°-57°C. <sup>1</sup>H nmr showed a vinylic coupling of 17Hz as expected for an *E*-alkene. δ<sub>B</sub> 68.9 m/z (intensity), 323(6.2), 307(7.3), 229(100), 228(58.4), 171(27.4), 136(38.5). ν<sub>max</sub> (cm<sup>-1</sup>), 2965, 2645, 2875, 1600, 1472, 1440, 1302, 1194, 1138, 1067, 1000, 849.

*Preparation of Bis(2,6-dimethyl-4-methoxyphenyl)-1-hexenylborane (13, R = CH=CHBu<sup>n</sup>)*

This reaction was carried out by the same method as used above, except that propyl iodide (0.5ml, 5.1mmol) was added to the anion derived from bis(2,6-dimethyl-4-methoxyphenyl)allylborane, (14), (1.30g, 4.04mmol). The reaction was stirred overnight and the solvent removed *in vacuo*. The resulting oil was distilled at 130°C/0.001mmHg to give bis(2,6-dimethyl-4-methoxyphenyl)-1-hexenylborane (1.19g, 81%) as a clear viscous oil, identical in all respects with the sample previously prepared.

**Boron Wittig Reactions**

*Deprotonation of Bis(2,6-dimethyl-4-methoxyphenyl)-octylborane (13, R=Oct<sup>n</sup>)*

A 50 ml flask equipped with a septum cap and a magnetic follower, was charged with (13, R=Oct<sup>n</sup>) (1.39g, 3.52mmol). The flask was cooled in an ice water bath and a solution of mesityllithium (3.6mmol) in THF added slowly by double-ended needle. The reaction rapidly became dark red in colour and was stirred for two hours at room temperature. The solution was then made up to 10ml with THF and 3ml (1.06mmol) aliquots used in the following reactions.



(a) *Reaction with Propanal/Acetic Acid*

The anion solution was cooled to  $-127^{\circ}\text{C}$  ( $\text{PrOH}/\text{liq N}_2$ ) and reacted with a premixed solution of  $\text{EtCHO}$  (0.55M, 1.8ml, 0.99mmol) and acetic acid (0.52M, 2.1ml, 1.09mmol) in THF at  $-127^{\circ}\text{C}$ . The reaction was stirred at  $-127^{\circ}\text{C}$  for an hour during which time the colour of the anion slowly discharged. The reaction was then allowed to warm to room temperature and stirred for half an hour. Water (10ml), was added, the organic layer was separated and the aqueous layer extracted with ether (2 x 10ml). The organic extracts were combined, washed with water (2 x 10ml), dried ( $\text{MgSO}_4$ ), filtered and concentrated on a rotary evaporator. The product mix was analysed by glc using the standard conditions (except that the temperature was ramped at  $10^{\circ}\text{C}/\text{minute}$ ) with hexadecane as an internal standard. This showed the yield of 3-decene to be 47% with a E:Z ratio of 80:20. The reaction mixture was then oxidised with alkaline hydrogen peroxide to give octanol (39%, g.c.).

(b) *Reaction with Propanal and Trifluoroacetic Anhydride*

The anion solution was cooled to  $-127^{\circ}\text{C}$  ( $\text{PrOH}/\text{liq N}_2$ ) and reacted with a solution of  $\text{EtCHO}$  (0.55M, 1.8ml, 0.99mmol) in THF that had been precooled to  $-127^{\circ}\text{C}$ . The reaction was stirred at  $-127^{\circ}\text{C}$  for an hour, during which time the solution became clear. A solution of TFAA (2.2ml, 0.496M, 1.09mmol) in THF that had been precooled to  $-127^{\circ}\text{C}$  was then added. The reaction was stirred at  $-127^{\circ}\text{C}$  for half an hour, allowed to warm and stirred at room temperature for a further half hour. The reaction was worked up by addition of water (10ml), the organic layer was separated and the aqueous layer extracted with ether (2 x 10ml). The organic extracts were combined, washed with water (2 x 10ml), dried ( $\text{MgSO}_4$ ), filtered and concentrated on a rotary evaporator. The product mix was analysed by g.l.c. using the standard conditions (except that the temperature was ramped at  $10^{\circ}\text{C}$ , using hexadecane as internal standard. This showed the yield of decan-3-one to be 63% and of 3-decene to be 6%.

(c) *Reaction with Benzaldehyde and Trifluoroacetic Anhydride.*

This reaction was performed by exactly the same method as used above, except that a solution of  $\text{PhCHO}$  (1.7ml, 0.57M, 0.97mmol) in THF was used. The reaction was carried out at  $-110^{\circ}\text{C}$  ( $\text{Et}_2\text{O}/\text{liq N}_2$ ) with all solutions being precooled before addition. Analysis by g.l.c. as above gave the yield of 1-phenyl-1-nonene as 67% with an E:Z ratio of 28:72.

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