Pergamon

Tetrahedron Vol. 50, No. 48, pp. 13829-13846, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00931-7

Hindered Organoboron Groups in Organic Chemistry. 29

The Effect of Hindered Triorganoboranes on Anionic Butadiene Polymerisations

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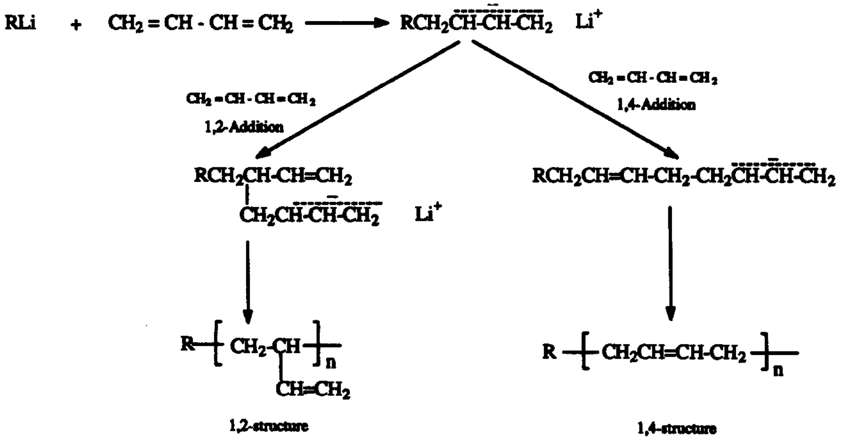
Abstract. Three new highly hindered triorganoboranes *tris*(4-*t*-butyl-2,6-dimethylphenyl)borane (BDP)$_3$B), (5) *tris*-(4-methoxy-2,6-dimethylphenyl)borane, (DMP)$_3$B (6), and *t*-butyl*bis*(2,4,6-trimethylphenyl)borane (Mes$_2$BBu^t) (7), were prepared and compared with trimesitylborane (4) for their influence on the 1,4-content of anionically produced polymers of butadiene. Each was designed to overcome known side reactions of (4). Unexpectedly, none was more effective overall than (4) in increasing the 1,4- content of the polymer. Borane (7) simply quenched LiBu^n induced polymerisations, whilst (6) and (7) somewhat enhanced the 1,4-character and sharpened the polymer profile. However, (6) and (7) quenched polymerisations by sodium bases. Studies of the reactions of bases with a variety of hindered boranes suggest reasons for the results obtained, and help with the design of other, possibly more effective, catalysts.

Introduction. The predicted desirable physical properties of 1,4-telechelic (terminally functionalised) polymers of low (~ 3000) molecular weight derived from butadiene and isoprene make them attractive synthetic targets. However, in ethereal solutions and an alkyllithium initiator, butadiene yields a high molecular weight polymer with about 90% of 1,2-structure and only 10% of 1,4-structure[1] (Scheme 1). This contrasts strongly with the polymerisation in hydrocarbon solvents, from which results high molecular weight polybutadiene which is about exclusively 1,4- in structure.[1]



Scheme 1

The growing ionic species (**1**) may exist in solution in a number of forms, some of which are represented in Figure 1.

$$\begin{array}{ccccccccc} (\mathrm{RMet})_n & \rightleftharpoons & \mathrm{RMet} & \rightleftharpoons & \mathrm{R}^-\,\mathrm{Met}^+ & \rightleftharpoons & \mathrm{R}^-\ \mathrm{S}\ \mathrm{Met}^+ & \rightleftharpoons & \mathrm{R}^- \text{----} \mathrm{Met}^+ \\ \mathbf{(1a)} & & \mathbf{(1b)} & & \mathbf{(1c)} & & \mathbf{(1d)} & & \mathbf{(1e)} \end{array}$$

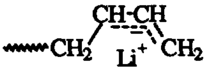
Met = metal ; R = growing organyl group ; S = solvent.

Figure 1

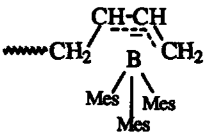
The structures range from covalent aggregates (**1a**) through to free ions (**1e**), the position of the overall equilibrium being critically dependant on the solvent. In hydrocarbons only the species (**1a**), (**1b**) and (**1c**) are significant, and of these the contact pair (**1c**) is the species by which polymerisation occurs. For butadiene systems in hydrocarbon solvent (**1c**) has been identified[2] as (**2a**) (*cis* : *trans* ~ 3 : 1). Location of the negative charge on the terminal atom ensures 1,4-addition by a further monomer, leading to high 1,4-structure in the resultant polymer.

$$\sim\!\sim\!\sim CH_2CH{=}CH{-}CH_2^-\ \ Li^+$$

(2a)



(2b)

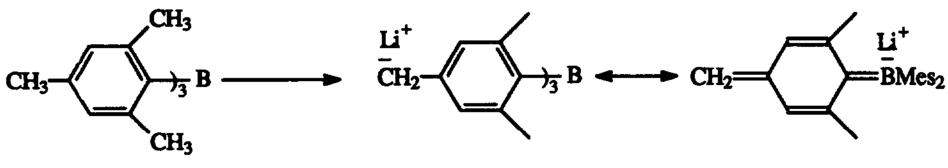


(3)

In more polar solvents, such as ether, the principal species present is the solvent separated ion pair (**1d**) and with butadiene as the monomer this can be represented as (**2b**) (solvent excluded). In (**2b**) the electron densities at C-1 and C-3 are comparable[2], leading to an increase in the 1,2-structure of the polybutadiene.

Telechelic polybutadienes could, in theory, be prepared by use of a difunctional anionic initiator. However, such initiators are only soluble in polar solvents,[3,4] which are unfavourable for the formation of 1,4-polymer. If the propagating species in ethers were transformed from (**2b**) to (**2a**), the resulting polymer would most likely have enhanced 1,4-character.[5] This might be achieved by interaction with an appropriate Lewis acid, such as a triorganylborane. It had already been shown that triphenylborane influences the tritylsodium initiated polymerisation of butadiene, but the effect is short lived due to the irreversible formation of a stable borate complex that does not undergo further polymerisation. Tritylsodium will only add to butadiene in the presence of triphenylborane[6], possibly due to initiation by tritylsodium-triphenylborane complex.

Richards and Stewart[5] chose trimesitylborane (TMB) (**4**) as their Lewis acid, as this highly hindered borane does not form complexes with methanol or sodium hydride[7,8]. Indeed, TMB did have a marked effect in enhancing the 1,4-structure of polybutadiene produced by anionic polymerisation, particularly with sodium naphthalene radical anion (NaN) or the disodium salt of α-methylstyrene tetramer (α_4Na_2). The reactions are however temperature dependant and suffer from the known reaction[5,9,10] of proton abstraction from the 4-methyl of the mesityl group (equation 1) which stops the polymerisation and leads to low molecular weight tailing in the molecular weight distribution.[5]

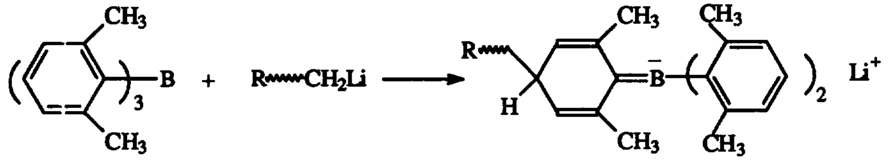

(1)

(4)

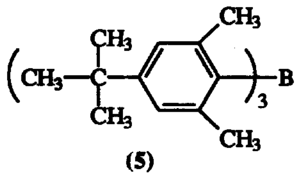
Trimesitylborane has been reported[11] to yield an anion radical with *t*-butyllithium.

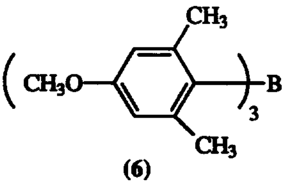
The effect of trimesitylborane on the anionic polymerisation of isoprene was far less marked than its effect on butadiene.[12] It appears that complex formation in the isoprene case is inhibited due to steric interactions with the 2-methyl groups of (4), which in turn suggests structure (3) for the complex between TMB and the growing polybutadiene anion. If so, then the influence of the trimesitylborane is more steric than ionic.

To avoid proton abstraction from the C-4 methyl group, the inclusion of tris(2,6-dimethylphenyl)borane in the polymerisations was tried.[13] However, a major side reaction, addition of the alkyllithium (equation 2), was observed. A similar reaction has previously been noted with *n*-butyllithium[9]. The same type of reaction was observed[13], when *tris*(α-naphthyl)borane was used[13].


(2)

Current Work. In order to avoid the problems associated with borate formation (Ph_3B), proton abstraction (4), and alkyl addition *tris*(2,6-dimethylphenylborane), we required *tris*(2,6-dimethylphenyl)boranes (to prevent ate complex formtion) which were substituted at the 4-positions by groups that did not undergo either proton abstraction or metal exchange (*e.g.* not Br or Cl). For those reasons we fixed on *tris*(4-*t*-butyl-2,6-dimethylphenyl)borane (5) ($(BDP)_3B$) and *tris*(2,4-dimethyl-6-methoxyphenyl)borane (6) ($(DMP)_3B$) as highly hindered Lewis acids. Additionally we were interested in *t*-butyl*bis*(2,4,6-dimethylphenylborane (7) (Mes_2BBu^t) in order to judge the effect of replacing a mesityl group by a hindered alkyl group lacking a proton α to boron. This would not allow the production of a boron stabilised α-carbanion.


(5)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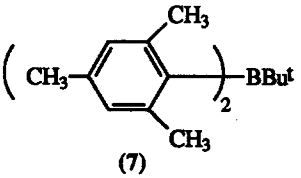
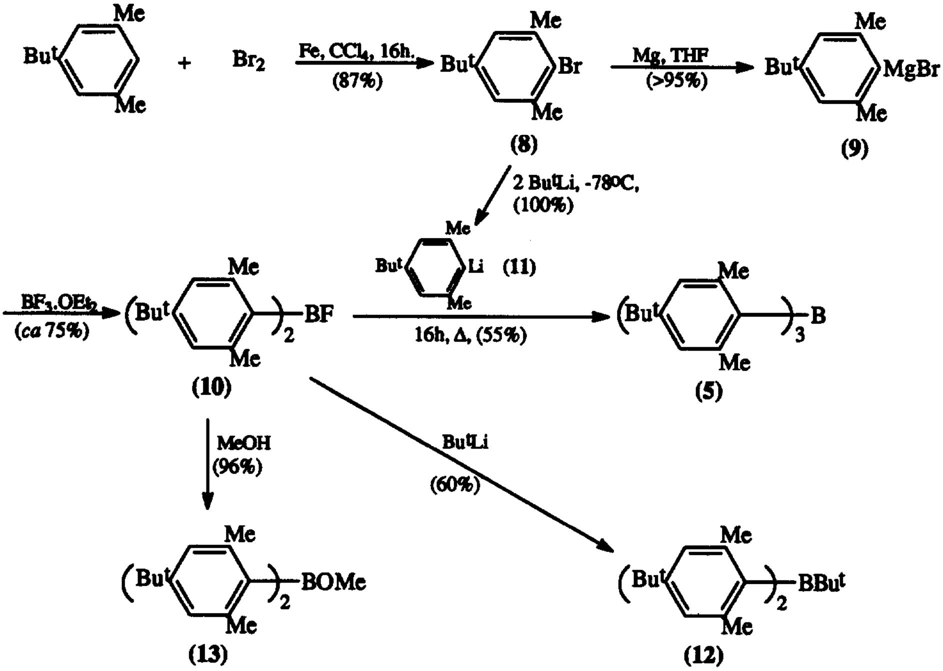

(7)

The syntheses of compounds (5)-(7)

The synthesis of compound (**5**) and related compounds was achieved as shown in Scheme 2.

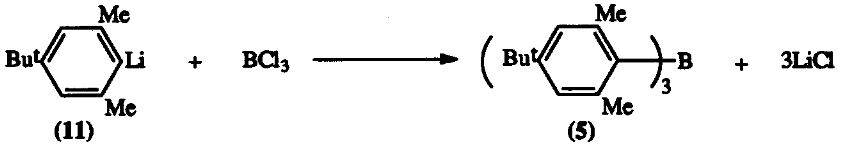


Scheme 2

Bromination of cheap, commercially available 1-*t*-butyl-3,5-dimethylbenzene to give (**8**) proceeded in good yield. The Grignard reagent (**9**) was readily made and from that we attempted to make (**5**) directly by reaction with trifluoroborane. However, only 5% of (**5**) was isolated when three equivalents of (**9**) was heated in THF under reflux with trifluoroborane for 24h, and only 10% of (**5**) was produced after 2h irradiation of the reaction with ultrasound. Use of five equivalents of (**9**) and 4h reflux gave only 24% of (**5**). In each case the major product of work up was $(BDP)_2BOH$. Direct reaction of the bromide (**8**) with trifluoroborane in the presence of magnesium[14], either in the presence or absence of ultrasound irradiation gave no (**5**). We therefore made the lithio-derivative (**11**) and reacted it with trifluoroborane in various solvents (THF/hexane, glyme/hexane, ether/hexane) but failed to produce more than 5% of (**5**) even after prolonged heating under reflux. The replace-ment of the THF/hexane mix by *m*-xylene followed by 16h reflux, successful for the preparation of trimesitylborane[7], was not successful in this case.

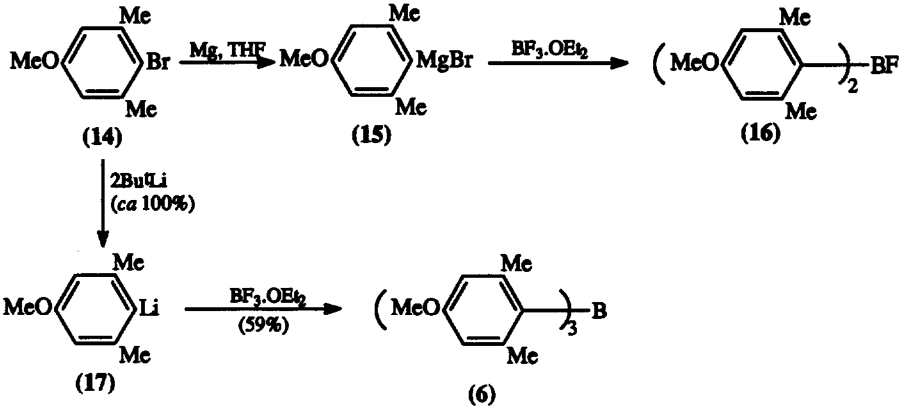
We therefore isolated the diarylfluoroborane (**10**) and found that it reacted well with *t*-butyllithium to yield the corresponding derivative (**12**) and with methanol to give (**13**). We then reacted (**11**) (50% excess) and (**10**) in a THF/hexane mixture and, after 16h under reflux, were able to isolate (**5**) in 55% yield from (**10**) (41% from (**8**). When the reaction was carried out without isolation of the intermediate fluoroborane (**10**), the yield dropped to 11%, perhaps due to interaction of the aryllithium with the magnesium salts present.

Although the process shown in Scheme 2 to obtain (5) was viable, it was rather tedious and we sought a more direct method. We found this in the reaction of (11) with trichloroborane in THF/hexane at ambient temperature (equation 3). The solvent mix was critical for good yields. Thus in hexane alone the yield was only 26% and in a 3 : 1 mixture of hexane and ether 35% was obtained. If the ratio of hexane to ether dropped to 0.5 : 1, on the other hand, the yield decreased to 17%. A 1 : 1 mixture of ether and hexane gave reproducible yields of >70%, and this is the method of choice to prepare (5).



(3)

The preparation of *tris*(2,6-dimethyl-4-methoxyphenyl)borane (6) was also not straight forward (Scheme 3).



Scheme 3

We have previously[15] described the preparations of (14), (15) and (16) but attempts to convert either (15) or (16) to the triarylborane (6) met with little success. Thus reaction of seven equivalents of (15) with trifluoroborane etherate in THF under reflux for 4h gave only 7% of (6), a yield not increased by replacement of THF by toluene and treating under reflux for 4h. Reaction of (15) with trichloroborane in ether was also unsuccessful, even after prolonged reflux. We therefore made the lithio derivative (17) by our usual method.[16] However, (17) gave the desired product (6) in only 15% yield on reaction with trichloroborane and in 10% yield on reaction with tribromoborane. The reaction of (17) and (16) gave no triarylborane in a THF/hexane mixture. Therefore a thorough study of the reaction of (16) with trifluoroborane etherate was carried out. No triarylborane was produced in THF/hexane mixtures but a solvent mixture consisting of ether and hexane in a 1.7 : 1 mixture gave a 59% isolated yield of the desired (6). Variations in the solvent mix were deleterious (*e.g.* Et_2O : hexane = 2.0 : 1 (33%); 0.7 : 1 (19%)).

We have previously described the preparation of compound (7).[17]

Polymerisation studies

Living polybutadiene was prepared by collecting a known volume of dry butadiene as a liquid at -78°C. The butadiene was allowed to warm and bubbled into THF at room temperature. Polymerisation was initiated about 10 min after the start of the addition of butadiene by addition of Bu^{n}Li, disodium α-methylstyrene tetramer or sodium naphthalide. The amount of initiator was calculated to give an average degree of polymerisation of *ca.* 75. Polymerisation was allowed to proceed for 5 min and a solution of the borane in THF added. The resulting polymer was analysed for 1,2- and 1,4-structures by ^{1}H nmr, and its molecular weight distribution was determined by gel permeation chromatography.

Structure Analysis

Table 1. Chemical shift values for protons in polybutadienes

Structure	**Proton Location**	**Chemical shift (δ)**
$-CH_2\overset{\alpha}{C}H=\overset{\alpha}{C}H-\overset{\gamma}{C}H_2-$	α	5.3
	γ	2.0
$-\overset{\delta}{C}H_2-\overset{\gamma}{C}H-$	α	5.3
$\vert$	β	5.0
$CH=CH_2$	γ	2.0
α β	δ	1.3

The structure analysis depended on the difference in chemical shift between the α- and β-protons. The % 1,4 content is given by equation 4, in which A and B are the total integrated areas of the bands at 5.3 and 5.0.

$$\%\ 1,4\text{-content} = \frac{(A - 0.5B) \times 100}{(A + 0.5B)} \qquad (4)$$

The results of our experiments are presented in Table 2.

Table 2. % 1,4-Structure of polybutadienes with added organoboranes

Exp.	**Initiation**	**Borane : Living Ends (molar ratio)**	**% 1,4-Polybutadienes with Boranes (4)-(7)[1]** (4)	(5)	(6)	(7)
1	Bu^{n}Li	1 : 1	20	14.5	17.1	killed[2]
2	Bu^{n}Li	2 : 1	25	18.3	23.3	-
3	Bu^{n}Li	3 : 1	29	17.1	20.1	-
4	α_4Na_2[3]	1 : 1	25	killed[2]	killed[2]	-
5	NapNa[4]	1 : 1	29	killed[2]	killed[2]	-

[1] With no borane present, *n*-BuLi initiated polymer had 9% of 1,4-structure in the same conditions.

[2] Immediate decolourisation and stopping of polymerisation. [3] Disodium salt of α-methylstyrene tetramer.

[4] Sodium naphthalide radical anion.

Our first surprise was the instant and irreversible quenching of polymerisation by one equivalent of Mes_2BBu^t (7), in strong contrast with trimesitylborane (4). Secondly, both (5) and (6) increase the 1,4-content of Bu^{n}Li initiated polymerisation, though neither is quite as effective as (4). It is noteworthy that with (5), *no low molecular weight tailing was observed.* However, due to the low solubility of (5) in THF, dilute solutions had to be used which in turn led to an increase in trace impurities and to some quenching of the reaction. This may account also for the lack of increase in 1,4-structure when three equivalents of (5) were used (exp. 3). When one or two equivalents of (6) were added, no low molecular weight tailing was observed in the Bu^nLi initiated polymerisation. When three equivalents of (6) were used, the solution became dark blue and polymerisation was slowly quenched.

With sodium as the counter ion, addition of one equivalent of (5)and (6) immediately killed the polymerisation! In experiment 4, use of (5) led to immediate decoloursation, and addition of α_4Na_2 then gave a dark green solution, *but no further polymerisation*. Addition of methanol to the solution allowed the quantitative recovery of (5). Reaction of (5) with sodium metal gave a dark green solution of the radical anion[7,18], and it appears likely that it was this that was formed on addition of α_2Na_4. In a similar fashion, a brown solution resulted when (6) was utilised with sodium as the counter ion. Reaction of (6) with sodium gave a dark blue solution initially and, on standing, this became brown, as in the polymerisation experiment.

We had expected that compounds (5) and (4) would behave similarly in the polymerisations as they are electronically similar and differ only in that (5) has a 4-*t*-alkyl group that cannot ionise. This should lead to a lack of low molecular weight tailing, as was indeed observed, but does not explain the results with organylsodium initiated polymerisations. Borane (6) differs electronically from (4) and (5) and some differences in behaviour are therefore not unexpected. Some further studies to gain more insight into the reactions of (5), (6) and (7) with bases were undertaken.

Model reactions of Mes_2BBu^t (7), $(BDP)_2BBu^t$ (12), and $(DMP)_2BBu^t$ (18).[15]

It was decided to react compounds (7), (12), and (18) with a variety of bases, so that their behaviour could be compared with each other and with the triarylboranes (5) and (6). Our results are given in Table 3.

Table 3. ^{11}B Chemical shifts on reaction of (7), (12) and (18) with bases

Exp.	Base	Products	δ_B (peak height)		
			7	*12*	*18*
6	None	-	86.5	79.3	73.3
7	Bu^nLi	Borate Hydroborate	-4.74 [100] -9.00 [65] (J_{B-H}, 78.4Hz)	-6.56 [100] -10.68 [75] (78.3Hz)	-8.21 [100] -11.32 [79] (78.6Hz)
8	LiBD[2]	Borate	-4.41	-5.39	-
9	Bu^nNa	Borate	-4.71 [100] -4.10 [50]	-6.49[100]	-
		Hydroborate	-8.52 [44] (J_{B-H}, 79.2Hz)	-9.36 [18] (J_{B-H}, 76.9Hz)	
10	Bu^tLi	Hydroborate	-8.97 (J_{B-H}, 78.4Hz)	-	-11.30 (J_{B-H}, 78.5)

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1) Figures in square brackets are the proportions of the mixture of the species obtained.

2) Lithium polybutadiene.

The reaction of Bu^{t}Li (exp. 10) on **(7)** and **(18)** gave, as expected[16] solely the hydroborates by β-hydrogen transfer. However, both Bu^{n}Li and Bu^{n}Na gave mixtures of organoborates and hydroborates and *lithium polybutadiene gave only organoborate.* All peaks are sharp and show that clean compounds are formed rather than molecular associations. It is clear therefore that despite inferences drawn from molecular models, **the triarylboranes used are more hindered than the corresponding diaryl-*t*-butylboranes.** There is an indication of this in the literature already as trimesitylborane (4) does not form a complex with ammonia, in contrast to tri-*t*-butylborane, which does.[19] *The explanation for the inhibition of polymerisation by (7) is therefore that rapid and irreversible borate formation occurs.*

The reactions of hindered triarylboranes and bases.

The three hindered triarylboranes, Mes$_3$B (4), (BDP)$_3$B (5) and (DMP)$_3$B, (6) were reacted with a range of bases, and changes in the electron densities at boron were monitored by ^{11}B nmr. Living sodium and lithium polybutadienes were prepared with a degree of polymerisation of about ten, (equation 5) the polymerisations being allowed to go to completion before the solutions were examined.

$$\mathrm{Bu^nLi} + 10\,\mathrm{CH_2=CH\text{-}CH=CH_2} \longrightarrow \mathrm{Bu^n(C_4H_6)_{10}Li} \qquad (5)$$

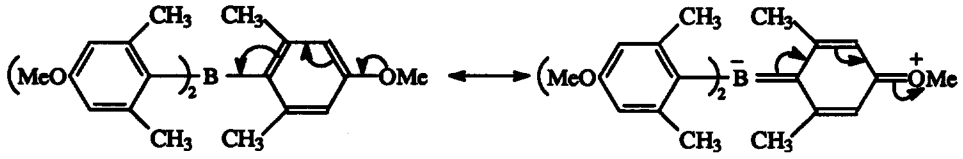
The results are given in Table 4. *In all cases, except when hydroborates were formed (experiment 17), the peaks were very broad, showing associations rather than compound formation.*

Table 4. ^{11}B Shifts for the reactions of triarylboranes with bases

Exp.	Base	δ_B		
		Mes$_3$B (4)	(BDP)$_3$B (5)	(DMP)$_3$B (6)
11	None	79.0	71.7	60.1
12	Bu^{n}Li (1 equiv.)	31.3	22.9	43.0
13	Bu^{n}Li (2 equiv.)	-	7.2	36.6
14	Bu^{t}Li	34.3	-13.6	-6.1
15	LiBD	-8.8	13.6	40.7
16	NaBD^1	-17.1	-57.1	-5.6
17	Bu^{n}Na	-	-7.6 -13.6 (4%)	-5.3
18	LiAl(OMe)$_3$H	-14.3 ($J_{B\text{-}H}$, 77.14Hz)	-14.4 ($J_{B\text{-}H}$, 76.7Hz)	-14.8 ($J_{B\text{-}H}$, 77.54Hz)
19	NaOMe	74.3	7.4	66.1
20	Na Metal	-	8.8	-5.6

1) Sodium polybutadiene.

Compound (6), due to electron donation from the three *p*-methoxy groups (equation 5), would be expected to have a lower electron deficiency at boron, and hence not to associate with electron rich species as strongly as (4) or (5).


(6)

This is shown in the far smaller upfield ^{11}B shifts seen when (6) reacts with Bu^nLi and LiBD, (exp. 12, 13, 15). On the other hand (6) readily forms a radical anion (exp. 20) with sodium metal, and also with Bu^nNa (exp. 17) and with NaBD (exp. 16). *The formation of the radical anion of (6) with sodium polybutadiene but not with lithium polybutadiene, explains the contrasts seen (Table 2, exp. 1-3, and exp. 4,5) between the behaviours of lithium and sodium polybutadienes with borane (6).*

It is rather difficult to compare (4) and (5) due to the intervention of the anion derived from the 4-methyl group (equation 1) in the reactions of (4) (experiment 15). The enormous shift (129 ppm) in the ^{11}B signal of (5) when added to NaBD shows a very strong interaction indeed. The nature of that interaction is unknown. The solution is colourless and so a radical anion is not involved, and the peak is so broad that simple borate formation is excluded. Possibly there is the formation of a complex similar to that between triphenylborane and tritylsodium.[3,4] In any case, the reaction with LiDB is nothing like so strong (experiment 15) and (4) does not exhibit a similar large shift (experiment 16), *in line with both observed differences on the course of polymerisation.*

It was noteworthy that none of these hindered triarylboranes reacted with *t*-butyllithium in the usual way[11] to give hydroborates. The peaks observed were broad and completely differentiated from the sharp doublets expected of the hydroborates. It would seem (Figure 2) that the boranes are so bulky that it is impossible for the β-hydrogen to approach the boron atom, to undergo cyclic β-hydride transfer.

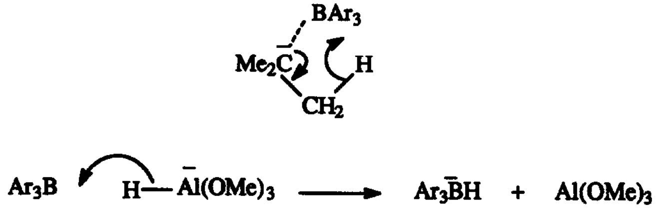


Figure 2

It was therefore surprising and synthetically significant that lithium trimethoxyaluminium hydride cleanly gave the requisite hydroborates (experiment 18), presumably through a *linear* transition state (Figure 2). *The resultant hydroborates are amongst the most hindered ever made and could well be synthetically useful as selective reductants.*

Conclusion.

None of the three new arylboranes (5), (6) and (7) are as effective as trimesitylborane (4) in enhancing the proportion of 1,4-structure in polybutadiene produced anionically. These studies, together with others[5,12,13] have delineated some of the reactions that must be avoided, *i.e.*hydroborate formation, carbanion formation, anion radical formation, organometallic addition. It would seem that to favourably influence the polymerisation six *ortho*-methyl groups are required together with a *para*-substituent which is not ionisable but not too bulky. *Tris*[4-fluoro-2,6-dimethylphenyl)borane could be a candidate for this purpose.

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^{-1} and 1495 cm^{-1} 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 (^{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 (not borosilicate glass) nmr tubes. Signals downfield from boron trifluoride (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 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 10.0mm 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 a fluorescent indicator (254 nm). Preparative chromatographic separations were achieved using silica (Merck) as absorbent in a glass column, using uv detection.

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' x $^1/_8$" stainless steel column packed with 5% SE30 on Chromsorb G packing except where stated. The basic temperature program used for the analysis of product mixtures was, 120°C for two minutes, ramp to 240°C at 30°C per minute then hold for one minute. This program 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.

Gel permeation chromatography was performed using an LDC/Milton Roy constametric pump and refractive index and uv detectors. Four styragel columns (Polymer Laboratories) of porosities 10^5, 10^4, 10^3

and 10^2 Å were used, and the molecular weights were determined from the retention times as polystyrene equivalents.

Microanalyses, where given, were determined using a Carlo Erba Strumentazione Elemental Analyser.

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 recently reviewed.[20] Solvents were treated as follows. 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.[21] Methanol was dried and purified by distillation from magnesium methoxide. Mesityl bromide and 4-bromo-3,5-dimethylmethoxybenzene were distilled under nitrogen, at reduced pressure prior to use. 1-Bromo-4-*t*-butyl-2,6-dimethylbenzene was dried in a vacuum oven at 30°C at 1 mmHg pressure for 24 hours before use. Boron trifluoride etherate was distilled at reduced pressure from 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°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 Company 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.[22]

Butadiene was dried by passing over molecular sieves, calcium chloride and calcium hydride and collected in a graduated vessel at -78°C (density 0.74 g/ml). The required volume was then bubbled into the reaction.

Experimental Procedures

The equipment and techniques involved in laboratory operations with air sensitive substances have been surveyed.[20] In particular, all glassware was dried at 120°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.

Preparation of *Bis*(4-t-butyl-2,6-dimethylphenyl)boranes

1-Bromo-4-t-butyl-2,6-dimethylbenzene (8)

A two-necked round-bottomed flask fitted with a dropping funnel, a mechanical stirrer and a gas absorption device, was covered with aluminium foil and charged with 1-*t*-butyl-3,5-dimethylbenzene (200g, 1.24mol) in dry carbon tetrachloride (150 ml) and iron filings (6g). A solution of bromine (198.2g, 1.24mol) in carbon tetrachloride (50 ml) was then added slowly *via* the dropping funnel with constant stirring, which was continued overnight. The reaction was then washed with water (3 x 100 ml), 5M NaOH solution (3 x 50 ml) and water (3 x 50 ml). The organic layer was dried ($MgSO_4$), filtered and evaporated to give crude product (275g) that was recrystallised from 95% ethanol to give (8) (260g, 1.08mol, 87% yield) as a white solid, m.p. 49°C (lit.[23], m.p. 47-48°C).

δ_H, 1.26(9H, s, C(CH_3)$_3$), 2.38(6H, s, ArCH_3), 7.04(2H, s, Ar*H*). δ_C, 24.02(q, ArCH_3), 31.29(q, C(CH_3)$_3$), 34.23 (s, Ar*C*(CH_3)), 124.42(s, Ar-*C*-Br), 125.41(d, Ar-*C*-H), 137.57(s, Ar-*C*-Me), 149.62(s, Ar-*C*-^{t}Bu). The low resolution e.i. mass spectrum gave peaks at m/z 242 (23.6), 240 (23.0), 227 (99.8), 225 (100), 199 (6.6), 197 (8.9), 187 (1.6), 185 (2.4), 146 (41.9), 131 (15.5), 115 (10.9). ν_{max} (CCl_4), (cm^{-1}) 2975, 1482, 1367, 1236, 1148 and 1034.

4-t-Butyl-2,6-dimethylphenylmagnesium bromide (9)

A dry 250 ml three-necked round-bottomed flask equipped with a pressure equalising dropping funnel, reflux condenser and magnetic follower was flushed with dry nitrogen and maintained under positive nitrogen pressure. The flask was charged with magnesium turnings (3.5g, 0.145mol) and the dropping funnel charged with a solution of (8) (35g, 0.145mol) in THF (70 ml). The magnesium turnings were heated (~ 70°C) with a hot air gun, after which dropwise addition of (8) led to immediate reaction and the addition rate was adjusted to maintain a constant reflux. After the addition, the reaction mixture was heated under reflux for 2h and the resulting dark brown solution was then allowed to cool slightly.

Bis(4-t-butyl-2,6-dimethylphenyl)fluoroborane (10)

A dry 250 ml two-necked round-bottomed flask was equipped with a mechanical stirrer and flushed with dry nitrogen. The flask was charged with a solution of boron trifluoride etherate (8.03 ml, 0.072mol) in dry ether (50 ml) and cooled in ice water and the warm Grignard solution was then added slowly to the well stirred solution *via* a double ended needle. After some time magnesium fluoride precipitated out of solution. The reaction mixture was brought to room temperature, stirred for two hours then left overnight at 0°C. The supernatent liquid was transferred by double ended needle into a second flask and the solvent removed by applying vacuum (12 mmHg) to give a yellow solid. The magnesium fluoride precipitate was washed with 40°-60° petrol (2 x 40 ml) and the petrol extracts added to the yellow solid in the second flask to precipitate magnesium salts. The salts were allowed to settle, the supernatent transferred to a third flask and the salts washed with 40°-60° petrol (2 x 40 ml). The washings were added to the third flask and the solvent evaporated until a solid started to precipitate. The flask was warmed to redissolve the solid then left at -20°C overnight to give a *bis(4-t-*butyl-2,6-dimethylphenyl)fluoroborane (17.6g, 69%) as a white solid, m.p. 72°-75°C.

δ_H,* 1.30(18H, s, H-7), 2.29(9H, d, $J_{(H\text{-}F)}$ = 2.4 Hz, H-5), 7.01(4H, s, H-3). δ_C, 22.67 (q, d(proton decoupled) $J_{(C\text{-}F)}$ = 1.32 Hz, C-5) 31.19(q, C-7), 34.49 (s, C-6), 124.68(d, C-3), 142.05(s, d(proton decoupled) $J_{(C\text{-}F)}$ = 4.05 Hz, C-2), 153.61 (s, C-4). δ_B, 48.9.

Bis(4-t-butyl-2,6-dimethylphenyl)methoxyborane (13)

A dry 50ml round-bottomed flask was equipped with a reflux condenser and flushed with dry nitrogen. The flask was charged with bis(4-*t*-butyl-2,6-dimethylphenyl)fluoroborane (12) (1g. 2.9 mmol) and dry methanol (10 ml). The mixture was heated under reflux for 30 min. then kept at -20°C overnight. *Bis*(4-*t*-butyl-2,6-dimethylphenyl)methoxyborane (13) (1.01g, 96%) came out as white crystals, m.p. 92°-94°C.

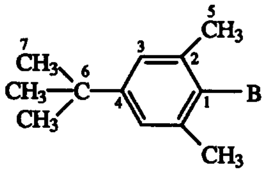
$C_{25}H_{37}BO$ requires C, 82.42%; H, 10.16%; found, C,82.70%; H 10.25%. δ_H, 1.29(18H, s, H-7), 2.24(12H, s, H-5), 3.73(3H, s, BOCH_3), 6.95(4H, s, H-3). δ_C, 22.59(q, C-5), 31.29(q, C-7), 34.19(s, C-6), 53.96(q, BOCH_3), 124.25(d, C-3), 136.19(s, C-1), 140.57(s, C-2), 151.38(s, C-4). δ_B, 45.5. m.s. (e.i.), 364(0.6), 349(4.6), 203(23.2), 202(100), 201(24.5), 187(24.8).

Bis(4-t-butyl-2,6-dimethylphenyl)-t-butylborane (12)

A dry 100 ml two-necked flask was equipped with a reflux condenser and a magnetic follower and flushed with nitrogen. The flask was charged with a solution of (10), 60°-80°C petrol (60 ml) and then a solution of *t*-butyllithium in hexanes (6.7 ml, 1.8M, 12.1mmol) was added slowly with good stirring. The resulting yellow solution was stirred for 2 hours at room temperature, followed by two hours heating under reflux. The resulting dark red suspension was poured onto crushed ice, the organic layer was separated and the aqueous layer extracted with 60°-80°C petrol (2 x 20 ml). The organic extracts were combined, washed with water (2 x 20 ml), dried ($MgSO_4$), filtered and the solvent removed to give crude product. Recrystallisation from ethyl acetate gave (12) (6.02g, 60%) as white crystals, m.p. 110°C.

$C_{25}H_{43}B$ requires C, 86.15%; H, 11.03%; found C, 86.22%; H, 11.06%. δ_H, 1.17(9H, s, BC(CH_3)$_3$), 1.26(18H, s, H-7), 2.35(12H, s, H-5), 6.92(4H, s, H-3). δ_C, 25.94(q, C-5), 30.27(q, BC(CH_3)$_3$), 31.20(q, C-7), 32.10(s, B*C*(CH_3)$_3$), 33.88(s, C-6), 124.87(d, C-3), 137.82(s, C-2), 141.77(s, C-1), 149.84(s, C-4). δ_B, 79.7. m.s. (e.i.), 334(26), 333(100), 57(22).

*The numbering of *bis*(4-*t*-butyl-2,6-dimethylphenyl)boranes is as follows.



4-t-Butyl-2,6-dimethylphenyllithium (11)

A round-bottomed 500ml flask was equipped with a magnetic follower and a septum cap and flushed with argon. The flask was charged with a solution of (8) (28.86g 120mmol) in dry diethyl ether (150ml) and cooled to -78°C (Cardice/acetone). A solution of *t*-butyllithium (100ml, 2.46M, 246mmol) in hexane was then added over *ca.* 30 min. by syringe. The reaction was stirred for 15 min. at -78°C and then allowed to warm to room temperature to give a pale yellow solution of (11).

Tris(4-t-butyl-2,6-dimethylphenyl)borane(5)

A solution of trichloroborane (48ml, 0.76M, 36.5mmol) in hexanes was added by syringe to the previously prepared, well stirred solution of (11). The reaction was stirred overnight during which time the solution became deep red in colour and salts precipitated. Saturated aq. NH_4Cl solution (100ml) and water (100ml) were then added, the organic layer separated, and the aqueous layer extracted with CH_2Cl_2 (2 x 50ml), dried ($MgSO_4$), filtered and concentrated on a rotary evaporator to give the crude product. Recrystallisation from ethyl acetate gave *tris*(4-*t*-butyl-2,6-dimethylphenyl)borane (5) (13.9g, 77%) as a white solid, m.p. 278°-280°C.

$C_{36}H_{51}B$ requires C, 87.45%; H, 10.32%; found C, 87.43%; H, 10.34%.
δ_H 1.24(27H, s, H-7), 1.97(18H, s, H-5), 6.84(6H, s, H-3). δ_C, 23.17(q, C-5), 31.32(q, C-7), 34.33(s, C-6), 124.61(d, C-3), 140.10(s, C-2), 144.3(s, C-1), 152.29(s, C-4). δ_B, 71.7. m.s. (e.i.) 479(0.4), 333(30.3), 332(100), 331(24.4), 317(6.0), 232(6.5), 57(21.3). υ_{max} (cm^{-1}), 2970, 1601, 1420, 1230, 1125, 934, 866, 850, 724. λ_{max} (nm), (ϵ_{max}), 222(24700), 334(14600).

The reaction of 4-t-butyl-2,6-dimethylphenyllithium (11) with bis(4-t-butyl-2,6-dimethylphenyl)fluoroborane (10).

A solution of (8) (3.0g, 12.4mmol) in THF (20ml) was reacted with a solution of *t*-butyllithium (14ml, 1.77M, 24.8mmol) in hexane as above. A solution of (10) (3.04g, 9.6mmol) in dry THF (20ml) was prepared and added to the solution of (11) by double-ended needle. The reaction was heated under reflux overnight during which time the solution became dark orange and salts precipitated. Saturated aq. NH_4Cl solution (20ml) and water (20ml) were then added, the organic layer separated and the aqueous layer was then extracted with CH_2Cl_2 (2 x 20ml). The combined organic extracts were washed with water (2 x 20ml), dried ($MgSO_4$), filtered and concentrated on a rotary evaporator. The crude product was recrystallised from ethyl acetate to give (5) (2.34g, 55%) as a white solid, m.p. 278°-280°C, with ^1H, ^{13}C and ^{11}B nmr spectra identical to those obtained previously.

Tris(2,6-dimethyl-4-methoxyphenyl)borane (6).

A round-bottomed 500ml flask was equipped with a magnetic stirrer and a septum cap and flushed with argon. The flask was charged with 1-bromo-2,6-dimethyl-4-methoxybenzene (17.62g, 82.0mmol) and dry ether (160ml). The contents of the flask were cooled to -78°C (Cardice/acetone) and stirring commenced. A solution of *t*-butyllithium (95ml, 1.73M, 164.4mmol) in hexane was then added by syringe over *ca.* 30 min. The reaction was stirred at -78°C for 1h. and then allowed to warm to 0°C.

Trifluoroborane etherate (3.4ml, 27.1mmol) was added to the stirred solution of 2,6-dimethyl-4-methoxyphenyllithium by syringe over 5 min. The reaction was allowed to warm to room temperature and stirred overnight, during which time the solution became orange in colour and salts precipitated. Saturated aq. NH_4Cl solution (100ml) and water (100ml) were then added and the aqueous layer was extracted with ether (2 x 50ml). The organic extracts were combined, washed with water (2 x 50ml), dried ($MgSO_4$), filtered and concentrated on a rotary evaporator. The crude product was recrystallised from methanol to give (6) (6.65g, 59%) as a white solid, m.p. 177°-179°C. The product could be further purified by sublimation at 150°C/0.001mmHg to give (6) as a white powder, m.p. 178°-179°C.

$C_{27}H_{33}BO_3$ requires C, 77.9%; H, 7.9%, found C, 78.3%; H, 8.2%. M + H, $C_{27}H_{34}BO_3$, calculated 417.2601, found 417.2605. υ_{max} (cm^{-1}) 3050, 2975, 2940, 2845, 1600, 1560, 1467, 1443, 1414, 1306, 1296, 1231, 1190, 1148, 1067, 1030, 995, 952, 834, 714. λ_{max} nm (ε), 215(30570), 234(26640), 255(19210), 347(24020).

δ_H, 6.49(Ar-*H*, H-3), 3.74(OC*H*$_3$), 2.00(Ar-C*H*$_3$). δ_C, 160.42(C-4), 142.68(C-2), 140.17(C-1), 113.17(C-3), 54.61(OCH$_3$), 23.18(*C*H$_3$). δ_B, 60.1. m.s.(e.i.) 417(100), 298(8), 281(31), 280(100), 137(99); m.s. (e.i.) 417(9), 281(31), 280(100), 265(18).

Preparation of Trimesitylborane

A round-bottomed 500ml flask was equipped with a magnetic follower and a septum cap. The flask was charged with 2-bromomesitylene (15.91g, 79.9mmol) and dry diethyl ether (100ml) and cooled to -78°C (Cardice/acetone). A solution of *t*-butyllithium (89ml, 1.79M, 160mmol) in hexane was then added by syringe over 25 minutes. The reaction was stirred at -78°C for 15 minutes and then allowed to warm to room temperature. At this stage the reaction had gone to completion giving a pale yellow solution of mesityllithium.

The mesityllithium solution was cooled to 0°C and a solution of boron trichloride (27ml, 0.76M, 20.5mmol) in hexane added by syringe. The reaction was stirred overnight at room temperature during which time it became dark orange and salts precipitated. Saturated NH_4Cl solution (50ml) and water (50ml) were then added, the organic layer separated and the aqueous layer extracted with Et_2O (2 x 30ml). The combined organic extracts were washed with water (2 x 30ml), dried ($MgSO_4$), filtered and concentrated on a rotary evaporator. The crude product was recrystallised from ethyl acetate to give trimesitylborane (4.07g, 54%) as a white solid, m.p. 193°C, (lit.[24,25], 195°-197°C). ^{1}H, ^{13}C and ^{11}B nmr and mass spectral data all agreed closely with those reported previously[24,25,26].

Polymerisation Reactions.

Initiators.

Disodium salt of α-methylstyrene tetramer.

A dry 250ml two-necked flask was equipped with a magnetic follower and a septum cap and flushed with nitrogen. The flask was charged with α-methylstyrene (11.8g, 0.1mol, freshly distilled from calcium hydride), and dry THF (150ml) and cooled to 0°C. Sodium metal (2.3g, 0.1mol) was pressed into the flask and the contents stirred rapidly until a red colouration spread throughout the solution. The rate of stirring was then reduced to about 100 r.p.m. and stirring was continued for 2h. The solution was then estimated by quenching known volumes in standardised hydrochloric acid solutions and back titrating with standardised sodium hydroxide solution.

Sodium naphthalene.

A dry round-bottomed 250ml flask equipped with a magnetic follower and a septum cap was flushed with nitrogen. The flask was charged with naphthalene (12.83g, 100.2mmol), sodium (4.5G, 196mmol) and

dry THF (135ml). The flask was stirred for forty minutes to give a dark green solution of sodium naphthalene, estimated as above.

Polymerisation Reactions

Polymerisations in the presence of boranes.

A typical polymerisation experiment was as follows. A round-bottomed three-necked 500ml flask, equipped with a magnetic follower, septum cap and an inlet for butadiene was flushed with nitrogen. The flask was charged with THF (200ml) and then with dry butadiene (10ml out of the ~80ml, 1.12mol collected, see 'reagents' section). The appropriate amount of initiator solution was then injected (~15mmol) to give a Dp of 75. The solution was allowed to polymerise for about five minutes, at which point a reference sample was removed and quenched with methanol. A solution of the borane in THF was added to the remaining solution to achieve the calculated molar ratio of borane to initiator. The remaining butadiene was then added and the solution left to polymerise for a further
30 min. before termination by decanting into methanol (~1 litre).

The polymers were allowed to settle out overnight, collected and vacuum dried. They were then analysed by nmr and gpc.

Preparation of polymer solutions for nmr estimation.

These were prepared by the method used above except that 0.11mol of initiator was used to give a polymer of Dp 10. No borane was added and the polymerisation was allowed to go to completion by stirring for 2h after the end of the addition. The resulting polymer solution was estimated as detailed above, and used as quickly as possible.

^{11}B nmr Studies

Preparation of Bases

Butyllithium solutions in hexane were used as supplied, after standardisation.

Preparation of n-butylsodium.[27]

n-Butylsodium was prepared under argon in a closed filtration vessel with a glass frit. To a suspension of NaOBu^t (3.84gm 40mmol), obtained from refluxing HOBu^t and sodium in hexane; the
resulting crystalline NaOBu^t was used after washing (without further purification) in hexane (20ml),
n-BuLi (40ml of 1.6M, 64mmol) in hexane was added with stirring at 0°C. The powdery Bu^{n}Na (1.9g, 24mmol) precipitate was washed thoroughly several times with hexane, and then suspended in 30ml of the same solvent and cooled to -78°C. Slow addition of THF (13ml) gave a clear yellow solution that was kept at -78°C until required. The solution was estimated and found to be 0.53M.

Preparation of lithium trimethoxyaluminium hydride.

Methanol (1.322g, 41.26mmol) was added dropwise to a well stirred solution of lithium aluminium

hydride (50ml of a 0.275M solution in THF, 13.75mmole) to give a 0.275M solution of $LiAl(OMe)_3H$, the concentration being confirmed by hydride analysis.[20]

Preparation of Sodium Methoxide

A round-bottomed flask (100ml) was equipped with a reflux condenser and a magnetic follower and flushed with argon. The flask was charged with sodium (0.5g, 22mmol), dry methanol (0.62g, 19.8mmol) and THF (50ml), then stirred for 1h. at room temperature and then under reflux for 2h. The resulting solution of sodium methoxide was decanted from the sodium residue, estimated and found to be 0.35M.

Reactions of Organoboranes and Bases.

A dry 10ml round-bottomed flask was equipped with a magnetic follower and a septum cap and flushed with argon. The flask was charged with the solid borane (~0.5mmol) and cooled to 0°C. An equivalent of base was then added and the reaction stirred for five minutes, after which a portion of the solution was transferred to a septum-capped nmr tube and the ^{11}B nmr spectrum obtained as rapidly as possible, within 1h. For reactions involving *n*-butylsodium essentially the same method was used except that the borane was dissolved in THF (~2ml) to give a 0.5M solution prior to the addition of the base. In the case of reactions of boranes with sodium, the flask was charged with both solid reactants and THF was then added.

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(*Received in UK* 27 *June* 1994; *revised* 14 *October* 1994; *accepted* 21 *October* 1994)