The Preparation, ^{11}B, ^{1}H, and ^{31}P Nuclear Magnetic Resonance Spectra, and Properties of Alkylidenetriphenylphosphorane–Triborane(7), $P(C_6H_5)_3CHRB_3H_7$ (R = H, CH_3, or C_6H_5)

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Ylide derivatives of triborane(7) of the alkylidenetriphenylphosphorane type [$P(C_6H_5)_3CHRB_3H_7$, where R = H, CH_3, or C_6H_5] have been prepared from B_3H_7·thf (thf = tetrahydrofuran) by ligand displacement. Their structures have been established by ^{11}B, ^{1}H, and ^{31}P n.m.r. spectroscopy and thermal and electrochemical properties investigated.

Ylides of the alkylidenetriphenylphosphorane type and related compounds have been shown to react with borane to form adducts, $PR_3CH_2BH_3$ (R = alkyl or aryl), which contain P–C–B linkages.[1] Such derivatives have also been shown to undergo thermal rearrangement to monoalkyl derivatives of triphenylphosphine–borane, *e.g.* $PPh_3BH_2(CH_3)$.[2] However, reactions of methylenetriphenylphosphorane with decaborane(14), instead of forming a donor–acceptor adduct led to deprotonation and the formation of $[P(C_6H_5)_3CH_3][B_{10}H_{13}]$.[1a,1b] Similarly, reactions of methylenetriphenylphosphorane with $S(C_2H_5)_2B_9H_{13}$ led to deprotonation and formation of $[P(C_6H_5)_3CH_3][B_9H_{12}]$.[1c] We have therefore examined reactions of intermediate borane derivatives with alkylidenetriphenylphosphoranes to evaluate further the types of behaviour exhibited by the ylide and to study the properties of compounds produced.

Experimental

Preparation of $P(C_6H_5)_3CHRB_3H_7$ (R = H, CH_3, *or* C_6H_5).—$[P(C_6H_5)_3CH_2R]Br$ (12 mmol) and sodium hydride (15 mmol) were refluxed in anhydrous tetrahydrofuran (thf) (100 cm^3) under an atmosphere of nitrogen for *ca.* 16 h. The resulting solution was filtered to give a solution of $P(C_6H_5)_3CHR$ in thf, which was then slowly added to a solution of B_3H_7·thf {prepared from $[N(CH_3)_4][B_3H_8]$ and I_2 (5 mmol) in thf} under nitrogen until the colour of the ligand persisted on stirring. The solvent was removed under reduced pressure to leave a crude residue which was dissolved in dichloromethane and washed several times with distilled water. The dichloromethane solution was separated and dried over anhydrous sodium sulphate, filtered, and the solvent removed to leave a product. The product was then purified by chromatography using silica gel as the stationary phase and dichloromethane as eluant. Analytical data are presented in Table 1.

N.M.R. Spectra.—360-MHz ^{1}H and 115.5-MHz ^{11}B n.m.r. spectra were recorded on a Bruker WH-360 spectrometer. Lock was achieved by the use of a deuteriated solvent. Chemical shifts are quoted as being negative to high field of the reference standard [$BF_3·O(C_2H_5)_2$ for ^{11}B n.m.r., $Si(CH_3)_4$ for ^{1}H n.m.r.]. All spectra were recorded at ambient temperature.

Electrochemical Methods.—The electrochemical apparatus used for cyclic voltammetry has been described previously.[3] Scans were from negative to positive potential. The reference used was Ag–$AgNO_3$ (0.1 mol dm^{-3} in CH_3CN) whose potential with respect to the standard calomel electrode (s.c.e.) was 0.336 ± 0.005 V. The supporting electrolytes $[NBu^n_4][BF_4]$ and $[NBu^n_4][PF_6]$ were used as supplied (Fluka A. G). All electrochemical experiments were carried out in an atmosphere of dry nitrogen.

Apparatus used for a.c. voltammetry consisted of a variable-frequency a.c. signal generator and a phase-sensitive detector with associated reference phase shifter and amplifiers.

The controlled electrochemical oxidation of $P(C_6H_5)_3CH_2B_3H_7$ was achieved by dissolving 0.2 mmol of the compound in a solution of $[NBu^n_4][PF_6]$ (0.1 mol dm^{-3}) in acetonitrile (15 cm^3) and introducing the mixture into the anode compartment of the cell. The cathode compartment contained a solution of $[NBu^n_4][PF_6]$ (0.1 mol dm^{-3}) in acetonitrile (15 cm^3). Both working and secondary electrodes were constructed from platinum foil. Electrolysis was carried out under an atmosphere of dry nitrogen at a potential of 1.5 V and the solution was stirred during the course of the reaction.

Thermal Studies.—Thermogravimetric analysis (t.g.a.) was carried out on a Stanton Redcroft T.G.-150 thermal balance. Heating was carried out under an atmosphere of dry nitrogen in the temperature range 0—400 °C. Differential scanning calorimetry (d.s.c.) was performed on the Du Pont 910 Differential Scanning Calorimeter and 990 Thermal Analyzer. Thermal decompositions were carried out under vacuum in an apparatus designed to collect volatile products in a *U*-tube to which an n.m.r. sample tube was sealed. Solvent ($CDCl_3$) was condensed in, and the solution of the volatile products

Table 1. Melting points and analytical data of alkylidenetriphenylphosphorane–triborane(7) complexes, $P(C_6H_5)_3CHRB_3H_7$ (R = H, CH_3, or C_6H_5)

		C (%)		H (%)		P (%)	
	M.p./°C *	Found	Calc.	Found	Calc.	Found	Calc.
$P(C_6H_5)_3CH_2B_3H_7$	174—180	71.60	72.30	7.55	7.60	9.95	9.85
$P(C_6H_5)_3CH(CH_3)B_3H_7$	169—170	72.70	72.85	7.95	7.90	9.40	9.40
$P(C_6H_5)_3CH(C_6H_5)B_3H_7$	146—147	76.85	76.60	7.30	7.15	8.00	7.90

* Uncorrected.

Table 2. Proton, ^{11}B, and ^{31}P n.m.r. parameters of methylenetriphenylphosphorane–triborane(7) in CD_2Cl_2

Nucleus	Atom position	δ/p.p.m.	J/Hz	Comments
^{31}P	—	31.18	—	Structure not resolved
^{11}B *	2, 3	−16.8	—	Line-narrowed spectra showed fine structure
—	1	−34.5	—	possibly due to coupling with hydrogens and phosphorus
^{1}H	Aromatic	7.5—7.75	—	At least 13 lines resolvable
—	CH_2	1.97	J(H–C–P) 14.57 (14.85) J(H–C–B) *ca.* 7	See text
—	B_3H_7	0.76	J[H–B(1)] 21.73 J(H–B–C–P) 5.16 (5.6)	See text

* In CD_3CN.

was allowed to run into the n.m.r. tube, which was then sealed under vacuum. The volatile products and the solid residue were examined by ^{11}B and ^{1}H n.m.r. spectroscopy.

Results and Discussion

Alkylidenetriphenylphosphoranes, $P(C_6H_5)_3CHR$, were found to react with B_3H_7·thf to form the adducts $P(C_6H_5)_3CHRB_3H_7$ (R = H, CH_3, or C_6H_5) by a ligand displacement reaction [equation (1)]. This represents the preparation of triborane(7) derivatives with a carbon substituent and derivatives of this type are rare. The only other examples known are a cleavage product of 2,4-dimethylenetetraborane(8)[4] and $B_3H_7(CO)$.[5] The species originally reported as $[B_3H_7(CN)]^-$ has recently been shown to be $[Ag\{(CN)B_3H_7\}_2]^-$.[6] The behaviour of the ligands $P(C_6H_5)_3CHR$ towards triborane(7) is similar to that observed with borane as opposed to deprotonation which is found with the higher boranes.

$$P(C_6H_5)_3CHR + B_3H_7{\cdot}thf \longrightarrow P(C_6H_5)_3CHRB_3H_7 + thf \quad (1)$$

N.M.R. Spectra and Structure.—(*a*) $P(C_6H_5)_3CH_2B_3H_7$. The structure of $P(C_6H_5)_3CH_2B_3H_7$ was fully confirmed from its ^{1}H, ^{11}B, and ^{31}P n.m.r. spectra. The parameters are presented in Table 2.

The ^{31}P n.m.r. spectrum comprised a singlet of line width *ca.* 21 Hz from which no fine structure could be resolved on line narrowing.

The ^{11}B n.m.r. spectrum comprised two signals, a broad signal of relative area 2 at −16.8 p.p.m. and a sharper signal of relative area 1 at −34.5 p.p.m. On line narrowing these signals gave multiplets of *ca.* 12 and 16 lines respectively which were not analysed readily on a simple basis. In the light of the ^{1}H n.m.r. results (below) it is probable that this spectrum represents a second-order A_2B coupled boron system which is further coupled to a fluxional 7-proton system and further coupled to a phosphorus with additional small coupling to the methylene protons and the total pattern is complicated by partial quadrupolar relaxation.[7]

The ^{1}H n.m.r. spectra (Figure 1) were much more informative particularly with specific frequency [continuous wave (c.w.)] ^{11}B decoupling. Spectra were obtained in CD_2Cl_2, $CDCl_3$, and CD_3CN and gave essentially similar results. Resonances due to aromatic protons were observed as at least 13 lines in the range 7.5—7.75 p.p.m. of total relative intensity of 15.

The methylene protons (relative intensity 2) were observed in the ^{1}H-{^{11}B, broad band} spectra as a doublet centred at 1.97 p.p.m. resulting from coupling with ^{31}P [J(H–C–P) = 14.57 Hz]. A similar doublet (J = 14.85 Hz) was obtained by ^{1}H-{^{11}B, c.w. at B(1)}. In the absence of ^{11}B irradiation or with ^{1}H-{^{11}B, c.w. at B(2,3)} the doublet structure was not observed, but instead a broad, unresolved multiplet was obtained, whose half width of *ca.* 30 Hz implied coupling to B(1) with J(H–C–B) of *ca.* 7 Hz.

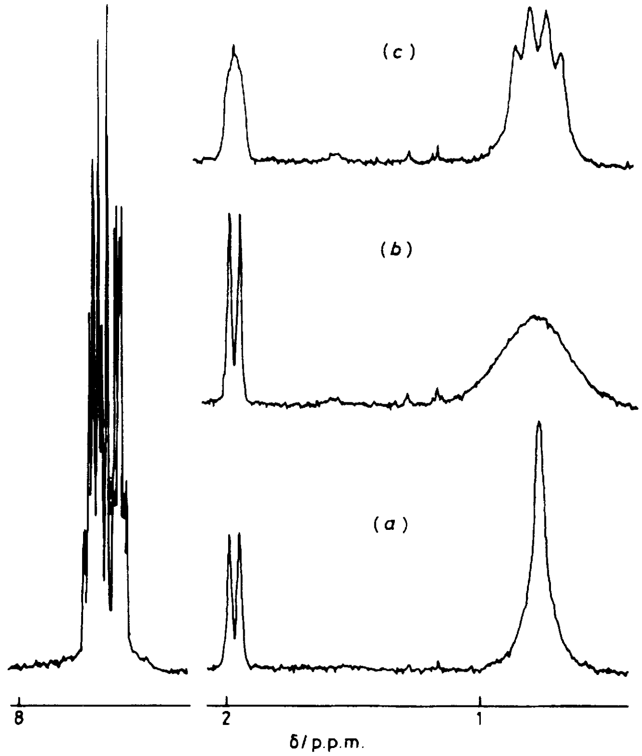


Figure 1. ^{1}H N.m.r. spectrum (360 MHz) of $P(C_6H_5)_3CH_2B_3H_7$ in CD_2Cl_2. Spectra (*a*)—(*c*) recorded with ^{11}B (broad band), ^{11}B [c.w. at B(1)], and ^{11}B [c.w. at B(2,3)] decoupling

The hydrogens on the boron cage were observed at a chemical shift of 0.76 p.p.m. (relative intensity 7). In the absence of decoupling, only a broad featureless resonance was apparent. With ^{1}H-{^{11}B, broad band}, a sharper singlet with a broad base was noted, and on line narrowing (Figure 2) this resolved to a doublet resulting from long-range coupling with phosphorus [J(H–B–C–P) = 5.16 Hz]. The broad base observed can be attributed to ^{10}B–H coupling. With ^{1}H-{^{11}B, c.w. at B(2,3)} a 1 : 1 : 1 : 1 quartet was observed whose intensities were slightly perturbed due to relaxation effects, and on line narrowing the components of the quartet further resolved into doublets. The doublet separation was again attributable to long-range coupling to the phosphorus with

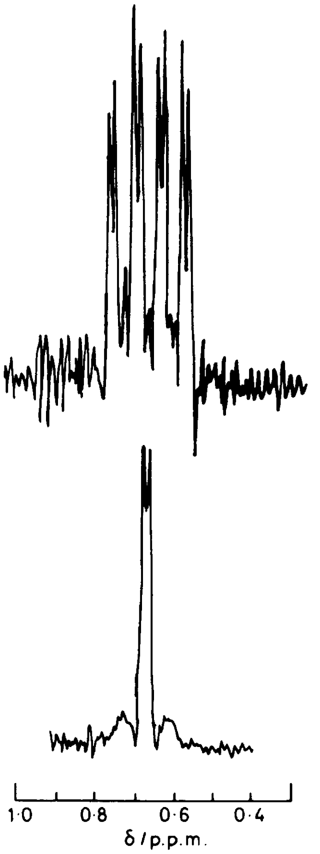
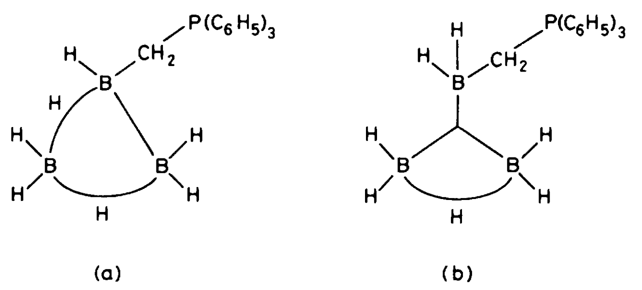


Figure 2. ^1H-{^{11}B, c.w. at B(2), B(3)} (upper) and ^1H-{^{11}B, broad band} (lower) line-narrowed n.m.r. spectra of $P(C_6H_5)_3CH_2B_3H_7$ (hydrogens on boron cage) in CD_3CN



(a) (b)

Figure 3. Topological structures for $P(C_6H_5)_3CH_2B_3H_7$ in solution

J(H–B–C–P) of 5.6 Hz. The separations of the components of the quartet which averaged 21.73 Hz were consistent with partial relaxation effects, since the separations of the inner components (21.97 Hz) was larger than those of the outer components. With ^1H-{^{11}B, c.w. at B(1)}, a featureless, broad resonance was observed and for reasons of inadequate signal strength it was not possible to apply the line-narrowing technique to attempt to resolve the coupling.

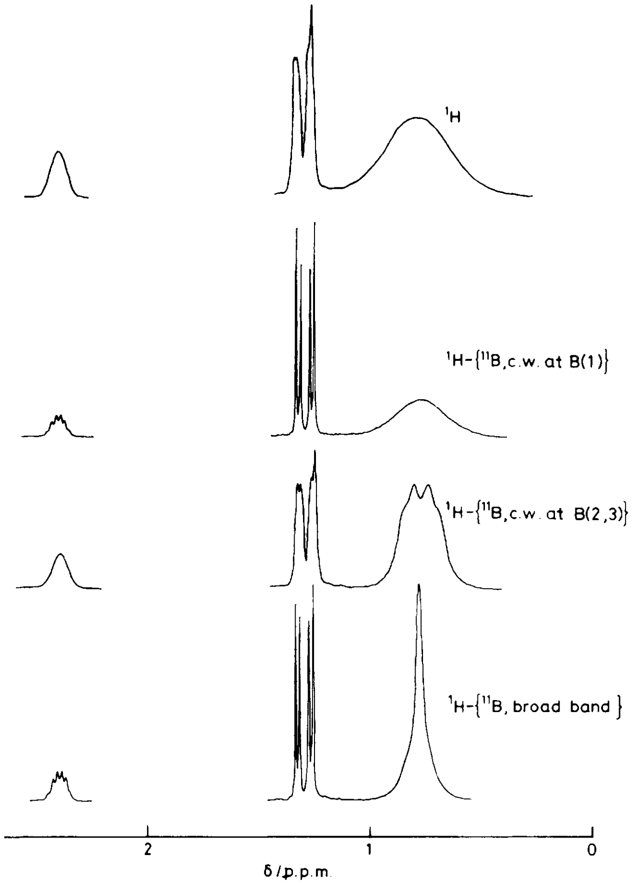


Figure 4. Partial ^1H and ^1H-{^{11}B} n.m.r. spectra of $P(C_6H_5)_3CH(CH_3)B_3H_7$ in $CDCl_3$

The n.m.r. spectra of $P(C_6H_5)_3CH_2B_3H_7$ in solution were fully consistent with the structures shown in Figure 3 in which all seven of the hydrogens on the B_3H_7 cage are fluxional. The magnitude of the B(1)–H coupling constant is considerably smaller than those observed in the $B_3H_8^-$ ion and its neutral and ionic derivatives where it has been resolved. In the solid state, preliminary crystallographic data [8] indicated $P(C_6H_5)_3CH_2B_3H_7$ to adopt the structure shown in Figure 3(*b*) similar to that of $B_3H_7(CO)$.[5]

(*b*) $P(C_6H_5)_3CH(CH_3)B_3H_7$. The ^{11}B n.m.r. spectrum of $P(C_6H_5)_3CH(CH_3)B_3H_7$ recorded in CD_3CN comprised two signals, similar to the unsubstituted complex, a broad signal of relative area 2 at −19.5 p.p.m. and a sharper signal of relative area 1 at −31.5 p.p.m. (Table 3). The latter showed fine structure which on line narrowing gave multiplets of 6 lines which are not analysed readily on a simple basis.

The proton spectra were obtained in $CDCl_3$ (Figure 4). The spectrum showed resonances due to aromatic hydrogens of the phenyl group in the region 7.5—7.75 p.p.m., with relative intensity 15. The unique methylene proton of relative intensity 1 was observed in all the spectra near 2.38 p.p.m. In the ^1H-{^{11}B, broad band} and ^1H-{^{11}B, c.w. at B(1)} spectra the signal was found to be a multiplet of 6 lines. This is due to a combination of coupling with the hydrogens of the methyl group and phosphorus. In the normal ^1H spectrum and ^1H-{^{11}B, c.w. at B(2,3)} a medium broad resonance {half width 30 Hz} with unresolved structure was observed which can be attributed to coupling between the unique hydrogen and the unique boron.

The hydrogens on the methyl group appeared as 4 lines with relative intensity 3, centred at *ca.* 1.29 p.p.m. The appearance of the 4 lines is due to coupling of the methyl hydrogens with phosphorus [J(H–C–C–P) = 21.6 Hz] to give doublets which are then further split by coupling with the unique hydrogen [J(H–C–C–H) = 7.1 Hz]. In the normal ^1H spectrum and the ^1H-{^{11}B, c.w. at B(2,3)} spectrum, a doublet with some structure was observed. The broad nature

Table 3. Proton and ^{11}B n.m.r. parameters of ethylidenetriphenylphosphorane–triborane(7) in $CDCl_3$

Nucleus	Atom position	δ/p.p.m.	*J*/Hz	Comments
^{11}B *	2, 3	−19.5	—	Line narrowed spectra showed fine structure due to partial relaxed coupling
	1	−31.5	—	
^1H	Aromatic	7.5—7.75	—	Aromatic due to $P(C_6H_5)_3$ (16 lines)
—	C–H	2.38	*J*(H–C–P) *J*(H–C–B)	Unresolved, occurs as 16 lines
—	$C-CH_3$	1.29	*J*(H–C–C–P) 21.6 *J*(H–C–C–H) 7.1	See text
—	B_3H_7	0.78	*J*[(H–B(1)] 21.5 *J*(H–B–C–P) 4.5	See text

* In CD_3CN.

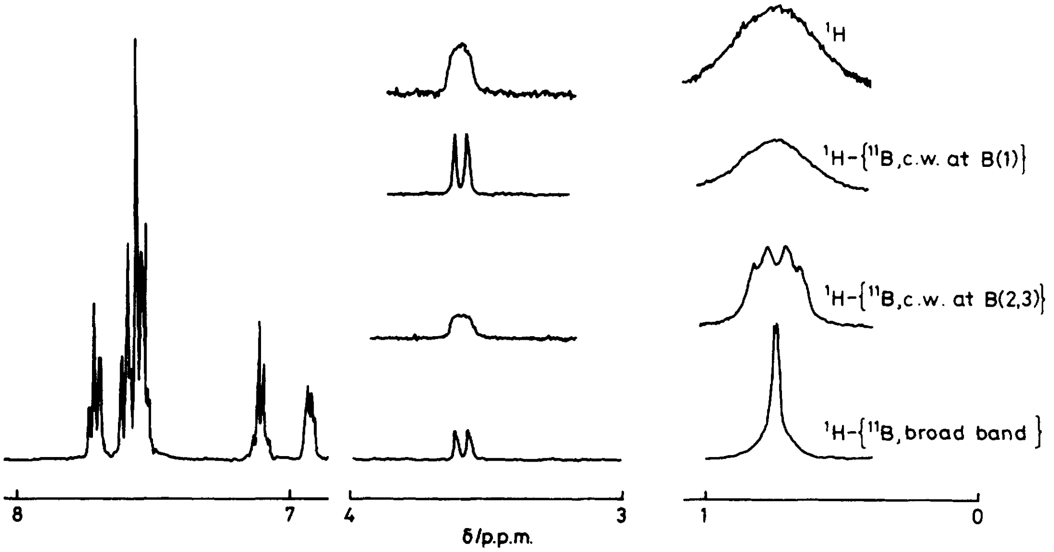


Figure 5. Partial ^1H and ^1H-{^{11}B} n.m.r. spectra of $P(C_6H_5)_3CH(C_6H_5)B_3H_7$ in CD_3CN

of the doublet can be attributed to coupling with the unique boron, since in the ^1H-{^{11}B, c.w. at B(1)} or ^1H-{^{11}B, broad band} spectrum the doublet resolved to reveal 4 lines.

Hydrogens of the boron cage were observed as a sharp singlet of relative intensity 7 with a broad base at 0.78 p.p.m. in the ^1H-{^{11}B, broad band} spectra. The broad base is due to ^{10}B–H coupling being incompletely resolved. In the absence of ^{11}B decoupling or by irradiating the unique boron, a broad unresolved signal was observed. The singlet resolved into a doublet upon line narrowing with a coupling constant of *J*(H–B–C–P) = 4.5 Hz due to coupling with phosphorus. In the ^1H-{^{11}B, c.w. at B(2,3)} spectrum, a signal which appeared to be a quartet was observed. On line narrowing a 1 : 1 : 1 : 1 quartet with further fine structure, whose intensities were slightly perturbed due to relaxation effects, was observed. The appearance of the 'quartet' may be attributed to coupling of the 7 hydrogens {*J*[H–B(1)] = 21.5 Hz} with the unique boron and the unresolved details on these multiplets to long-range coupling between the hydrogens and the phosphorus.

(*c*) $P(C_6H_5)_3CH(C_6H_5)B_3H_7$. The ^{11}B n.m.r. spectrum of $P(C_6H_5)_3CH(C_6H_5)B_3H_7$ was also similar to the unsubstituted and methyl-substituted complexes, and consisted of two signals: a broad signal with relative intensity 2 at low field (−15.5 p.p.m.) and a single resonance of relative intensity 1 at high field (−31.4 p.p.m.) (Table 4). Detailed examination of the two resonances showed them to be more complex. The broad resonance may have some fine structure which cannot be resolved even on line narrowing. The sharp signal resolved into 6 lines upon line narrowing. The structures observed may be attributed to long-range coupling with phosphorus.

Proton spectra recorded in CD_3CN (Figure 5) showed the presence of two groups of aromatic protons. The first group appears in the region 7.5—7.75 p.p.m. with relative intensity 15 and the second in the region 6.9—7.13 p.p.m. with relative intensity 5. The former group can be assigned to hydrogens of the phenyl groups of the triphenylphosphine while the latter can be assigned to hydrogens on the phenyl group bonded to the unique carbon.

The unique hydrogen bonded to the carbon was found at 3.58 p.p.m. with relative intensity 1 in all the spectra. In the ^1H-{^{11}B, broad band} and ^1H-{^{11}B, c.w. at B(1)} spectra the signal appears as a doublet due to coupling with phosphorus [*J*(H–C–P) = 16.5 Hz]. In the ^1H{^{11}B, c.w. at B(2,3)} and normal ^1H spectra, the signal was found to be a broad singlet with unresolved structures.

Hydrogens on the boron cage were observed at 0.75 p.p.m. with relative intensity 7. In the ^1H-{^{11}B, broad band} spectrum a sharp resonance with a broad base was observed. The broad base was due to ^{10}B–H coupling being incompletely resolved. Closer examination reveals the signal to be split due to coupling with phosphorus [*J*(H–B–C–P) = 4 Hz]. In the ^1H-{^{11}B c.w. at B(2,3)} spectrum a 1 : 1 : 1 : 1 quartet was observed, whose intensities were slightly perturbed due to

Table 4. Proton and ^{11}B n.m.r. parameters of benzylidenetriphenylphosphorane–triborane(7) in CD_3CN

Nucleus	Atom position	δ/p.p.m.	J/Hz	Comments
^{11}B	2, 3	−15.5	—	Line-narrowed spectra showed fine structure
	1	−31.4	—	due to partial relaxed coupling
^{1}H	Aromatic	7.5—7.75	—	Aromatic due to $P(C_6H_5)_3$
—	Aromatic	6.9—7.13	—	Aromatic due to $(C_6H_5)C$
—	C–H	3.58	J(H–C–P) 16.5	
			J(H–C–B) unresolved	See text
—	B_3H_7	0.75	J[H–B(1)] 21.9	
			J(H–B–C–P) 4	Fine unresolved structure

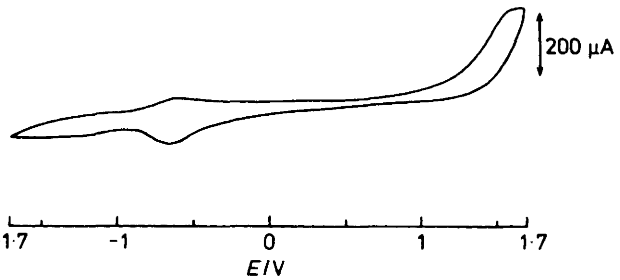


Figure 6. Cyclic voltammogram of $P(C_6H_5)_3CH_2B_3H_7$ in CH_3CN at Pt (0.5 V s^{-1})

relaxation effects. No further structure was resolved upon line narrowing. The coupling constant of the quartet was found to be 21.9 Hz which is likely to be due to coupling between the hydrogens and the unique boron {J[H–B(1)] = 21.9 Hz}. In both the ^{1}H-{^{11}B, c.w. at B(1)} and undecoupled spectra, only a broad single resonance was observed. No structure was found on line narrowing.

The observation of extensive long-range coupling, particularly in the ^{1}H spectra, is rare in polyborane derivatives. In these compounds it leads to unambiguous structural assignments: the parameters are listed in Tables 2—4.

Electrochemistry.—The cyclic voltammograms of $P(C_6H_5)_3CHRB_3H_7$ (R = H, CH_3, or C_6H_5) in acetonitrile containing the supporting electrolyte $[NBu^n{}_4][BF_4]$ (0.1 mol dm^{-3}) are all very similar (Figure 6). They showed irreversible oxidation waves near +1.6 V and reductions at −0.65 V. The reduction wave was only observed on scans more positive than *ca.* +1.0 V and this together with its potential and previous observations on triborane derivatives[9] suggested that this resulted from reduction of H^+ produced in an oxidation process. After the first scan a weak oxidation wave was observed in the unsubstituted and methyl substituted compounds near −0.5 V which may indicate the oxidation of some reduced species. When the cathodic limit was decreased to −1.99 V no distinct reduction wave was found except for the methyl derivative which showed a reduction wave at −1.7 V accompanied by the appearance of an oxidation wave at −0.95 V. Increasing the cathodic limit to −1.2 V resulted in the elimination of the reduction at −1.7 V as well as the oxidation wave at −0.95 V, indicating that the oxidation involves the reduction product formed at −1.7 V.

Overall, the cyclic voltammograms of these compounds showed that their electrochemical behaviours are complex and may involve the oxidation and reduction of products formed in the initial oxidation. The series of compounds $P(C_6H_5)_3CHRB_3H_7$ are found to be more stable to electrochemical oxidation than the parent anion $B_3H_8^-$.

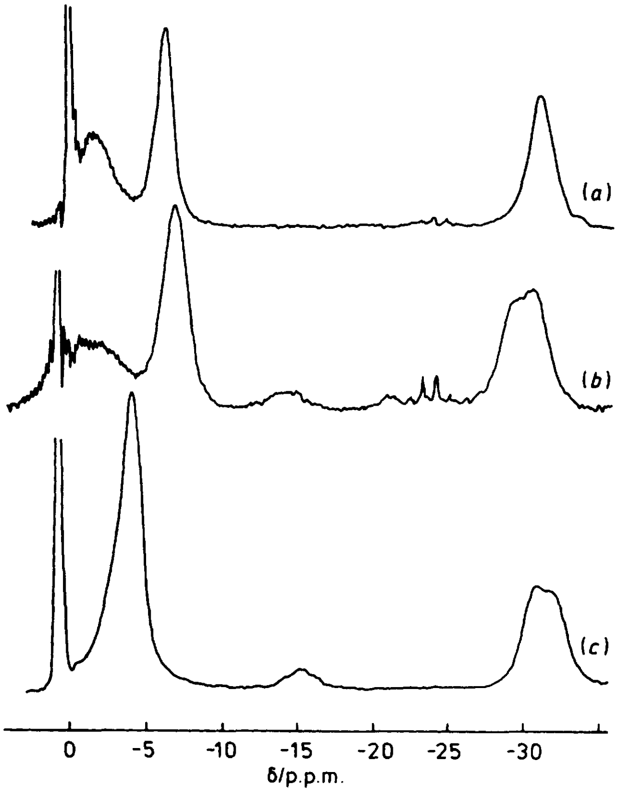


Figure 7. ^{11}B N.m.r. spectra (CH_3CN) of the electrochemical oxidation products of (*a*) $P(C_6H_5)_3CH_2B_3H_7$, (*b*) $P(C_6H_5)_3CH(C_6H_5)B_3H_7$, and (*c*) $P(C_6H_5)_3CH(CH_3)B_3H_7$

A.c. voltammograms of $P(C_6H_5)_3CHRB_3H_7$ (R = H, CH_3, or C_6H_5) in acetonitrile containing $[NBu^n{}_4][BF_4]$ (0.1 mol dm^{-3}) all showed a single peak near +1.5 V which is consistent with the irreversible oxidation wave found at +1.6 V in the cyclic voltammograms. No other peaks were observed indicating that other oxidation and reduction waves in the cyclic voltammograms are due to further oxidation and reduction of species formed in the initial oxidation.

Controlled potential electrolyses were carried out on all three derivatives at +1.5 V in acetonitrile containing $[NBu^n{}_4][BF_4]$ (0.1 mol dm^{-3}) between platinum electrodes in a divided cell. $P(C_6H_5)_3CH_2B_3H_7$ underwent a clean, one-electron oxidation, whereas $P(C_6H_5)_3CH(CH_3)B_3H_7$ and $P(C_6H_5)_3CH(C_6H_5)B_3H_7$ each required slightly more than one electron. During electrolysis gas evolution was observed at the cathode (probably hydrogen). The ^{11}B n.m.r. spectra of the product solutions (Figure 7) showed the starting compounds to be completely consumed. The spectra could be assigned to a disubstituted triborane, since three resonances of relative intensity 1 : 1 : 1 were observed for the products of $P(C_6H_5)_3CH_2B_3H_7$ and $P(C_6H_5)_3CH(C_6H_5)B_3H_7$, and two resonances of relative intensity 2 : 1 with similar shifts was seen for the product from $P(C_6H_5)_3CH(CH_3)B_3H_7$. The low-field resonance of the latter product was asymmetric and had the appearance of accidental overlap of one broad and one sharper signal. In addition, each spectrum contained a resonance originally from the BF_4^- supporting electrolyte, which was absent when the supporting electrolyte was $[NBu^n{}_4][PF_6]$, although the final product contained the three major resonances at the same chemical shifts.

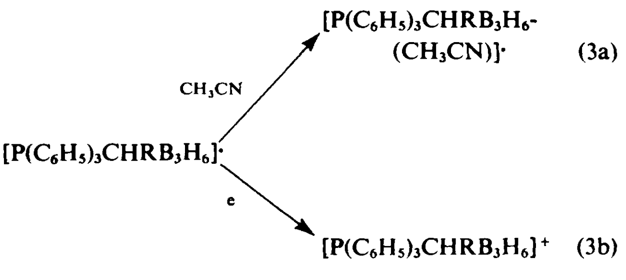
The electrochemical oxidation products were unstable in the absence of solvent, and ^{11}B n.m.r. spectra observed after the solvent was removed were different and consistent with degradation.

The mechanism and the final products of the electrochemical oxidations of the derivatives $P(C_6H_5)_3CHRB_3H_7$ are suggested to be as follows. It may be reasonable to assume that the initial step of the oxidation mechanism of $P(C_6H_5)_3CHRB_3H_7$ is the formation of the radical cation [equation (2)].

$$P(C_6H_5)_3CHRB_3H_7 \xrightarrow{-e^-} [P(C_6H_5)_3CHRB_3H_7]^{\cdot +} \quad (2)$$

This cation is unlikely to be stable and hence decomposes either to give the radical $[P(C_6H_5)_3CHRB_3H_6]^\cdot$ and H^+ or the cation $[P(C_6H_5)_3CHRB_3H_6]^+$ and $H^\cdot$.

The presence of an irreversible reduction at -0.65 V in the cyclic voltammograms may suggest the reduction of H^+ as found in the electrochemical oxidation of $B_3H_8^-$ and its derivatives,[9] hence favouring the formation of $[P(C_6H_5)_3CHRB_3H_6]^\cdot$ and H^+. The liberation of a gas at the secondary electrode is consistent with the reduction of H^+ to H_2 as indicated. The radical $[P(C_6H_5)_3CHRB_3H_6]^\cdot$ formed either underwent chemical reaction [equation (3a)] by reacting with a molecule of acetonitrile, or further electrochemical oxidation [equation (3b)] as indicated by the oxidation wave at -0.5 V.



In the case of chemical reaction the product $[P(C_6H_5)_3CHRB_3H_6(CH_3CN)]^\cdot$ then underwent electrochemical oxidation, as indicated by the oxidation wave at -0.5 V, to give $[P(C_6H_5)_3CHRB_3H_6(CH_3CN)]^+$. Alternatively, the cation $[P(C_6H_5)_3CHRB_3H_6]^+$ underwent solvation to give the same product, $[P(C_6H_5)_3CHRB_3H_6(CH_3CN)]^+$. Presumably the counter ion was BF_4^- or PF_6^- from the supporting electrolyte. The ^{11}B n.m.r. spectra (Figure 7) were consistent with the cation $[P(C_6H_5)_3CHRB_3H_6(CH_3CN)]^+$ in which there were three non-equivalent boron atoms, and was similar to those of disubstituted triborane anions $[B_3H_6Cl(NCS)]^-$ and related systems.[6a]

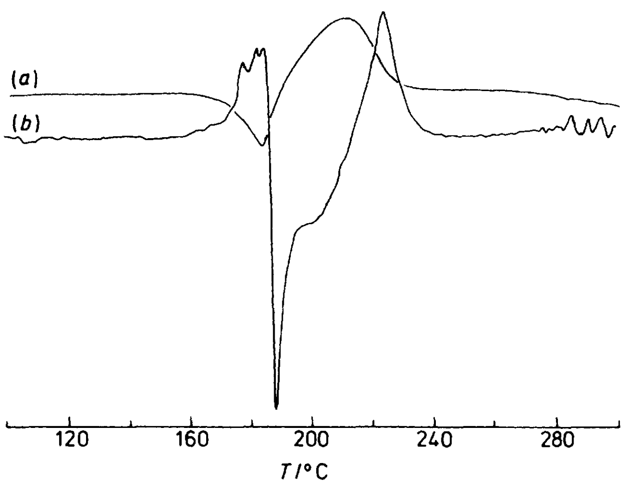


Figure 8. (*a*) D.s.c. and (*b*) differential trace of $P(C_6H_5)_3CH_2B_3H_7$

Thermal Studies.—Differential scanning calorimetry of $P(C_6H_5)_3CH_2B_3H_7$ (Figure 8) showed no thermal transition until 170—190 °C when an endothermic change occurred; the differential trace suggested that there were several processes within this endotherm. The thermal transition between 170 and 190 °C is consistent with the observed melting point of 174—180 °C for $P(C_6H_5)_3CH_2B_3H_7$. An exothermic change occurred between 190 and 230 °C with a maximum near 210 °C. The thermogravimetric result showed no weight change until 237 °C, but a weight loss of 37% occurred between 237 and 338 °C. It is apparent from these results that any thermal changes which might be associated with a rearrangement process must occur over a narrow temperature range if thermal decomposition (resulting in exothermic combustion, and weight loss) is to be avoided. It is also possible that any alkyl-substituted triphenylphosphorane–triborane(7), resulting from a rearrangement analogous to that in methylenetriphenylphosphorane–borane, decomposes to give $B(CH_3)_3$, $P(C_6H_5)_3BH_3$, and other degradation products. However, the 37% weight loss must correspond to even more drastic thermal decomposition or loss of triphenylphosphine by evaporation. A sample of $P(C_6H_5)_3CH_2B_3H_7$ was pyrolysed at 180 °C in a vessel under vacuum. Volatile components and a white sublimate were obtained. A sample of the sublimate was collected and was identified as $P(C_6H_5)_3BH_3$ by its ^{11}B n.m.r. spectrum. The volatile components liberated were collected in a trap and the ^{11}B n.m.r. recorded in $CDCl_3$ showed singlets at 33.5 and 2.5 p.p.m. and doublets at -12.5 and -18.5 p.p.m. The ^{11}B-$\{^1H\}$ spectrum showed singlets centred at these shifts with the exception of the resonance at -12.5 p.p.m. which appeared as a multiplet of 4 lines and with a distinct shoulder on the high-field side. The observed multiplets were attributed to boron–boron couplings, with an average coupling constant, $J(^{11}B-^{11}B)$, of 19.2 Hz. This corresponds to $J(^{11}B-^{11}B)$ of 19.2 Hz found in pentaborane and its derivatives.[10] The coupling constant $J(^{11}B-^1H)$ in the ^{11}B spectrum was 161.7 Hz. The formation of pentaborane(9) derivatives from the pyrolysis of $P(C_6H_5)_3CH_2B_3H_7$ is possible since pentaborane(9) has previously been obtained by the pyrolysis of $[N(C_4H_9)_4][B_3H_7Br]$.[11] These results suggest that in contrast to the rearrangement which takes place with $P(C_6H_5)_3CH_2BH_3$, the derivatives $P(C_6H_5)_3CH_2B_3H_7$ do not undergo a simple rearrangement, but rather undergo more drastic thermal decomposition yielding $P(C_6H_5)_3BH_3$, a derivative of B_5H_9, and other uncharacterized products.

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