Polyhedral Metallaphosphaborane Chemistry: The Preparation, Molecular Structure, and Nuclear Magnetic Resonance Study of [2-Ph-1,1-$(PMe_2Ph)_2$-*closo*-1,2-$PtPB_{10}H_{10}$], and Some Related Chemistry *

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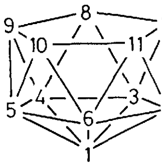
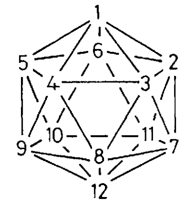
The reaction of $[B_{10}H_{11}PPh]^-$ with *cis*-$[PtCl_2(PMe_2Ph)_2]$ in CH_2Cl_2 yields the new *closo* twelve-vertex species $[(PMe_2Ph)_2PtB_{10}H_{10}PPh]$ (43% yield) and small quantities of the known nine-vertex *arachno*-$[(PMe_2Ph)_2PtB_8H_{12}]$. Crystals of the yellow, air-stable platinaphosphaborane are triclinic, space group $P\bar{1}$, with a = 961.8(1), b = 1 077.2(2), c = 1 661.4(2) pm, α = 108.67(1), β = 84.63(1), γ = 115.96(1)°, and Z = 2; the final R factor is 0.0212 for 3 702 observed reflections. Diffraction analysis shows that the cluster structure is based on a $PtB_{10}P$ icosahedron with the platinum and phosphorus atoms occupying adjacent positions. The metal-to-cluster bonding is rotationally fluxional with $\Delta G^{\ddagger}_{277}$ *ca.* 58 kJ mol^{-1}. Detailed n.m.r. data for $[(PMe_2Ph)_2PtB_{10}H_{10}PPh]$, neutral $B_{10}H_{12}PPh$, and anionic $[B_{10}H_{11}PPh]^-$ are presented, compared, and briefly discussed. In contrast to the platinum reaction, reaction of $[B_{10}H_{11}PPh]^-$ with $[\{Rh(\eta^5-C_5Me_5)Cl_2\}_2]$ gives the known *nido* ten-vertex [6-$(\eta^5-C_5Me_5)$-*nido*-6-RhB_9H_{13}] and two other products identified as the twelve-vertex *closo* dimetallaphosphaboranes [7-X-1-Ph-2,3-$(\eta^5-C_5Me_5)$-*closo*-2,3,1-$Rh_2PB_9H_8$] (X = Cl or H).

We have recently become interested in the modes of interaction of tertiary (PPh_3, PMe_3, PMe_2Ph)[1–6] and secondary (PPh_2)[7–10] phosphine units with polyhedral borane and metallaborane clusters, and their structural and mechanistic consequences. We report here the preparation, n.m.r. properties, and molecular structure of the twelve-vertex *closo*-type platinaphosphaborane [2-Ph-1,1-$(PMe_2Ph)_2$-*closo*-1,2-Pt-$PB_{10}H_{10}$] which contains the primary phosphine residue PPh. Although metallaphosphaboranes of this structural type have been known for over a decade[11–13] this species is only the second contiguous polyhedral metallaphosphaborane to be structurally characterised, the first being based on a boron-dilute seven-vertex Co_4B_2P unit.[14] The work forms part of a general survey of platinaborane chemistry using $\{Pt(PMe_2Ph)_n\}$ centres as standard environments (see also, for example, refs. 1, 10, 15—19), and the product may also be compared to recently reported[20,21] *closo* twelve-vertex platinaheteroboranes that contain sulphur, selenium, or tellurium as heteroatoms.

For comparison we also report the detailed and assigned ^1H and ^{11}B n.m.r. properties of the *nido* eleven-vertex 7-phosphaundecaborane precursors $B_{10}H_{12}PPh$ and $[B_{10}H_{11}PPh]^-$, previous n.m.r. work being limited as far as we are aware[23] to ^{11}B and non-borane ^1H spectroscopy on $B_{10}H_{12}PR$ and $[B_{10}H_{11}PR]^-$ (R = Me, Et, Pr^n, or Ph) measured at lower fields.[11,13,22,23] Numbering schemes for the eleven-vertex *nido* and twelve-vertex *closo* skeletons are displayed in structures (I) and (II) respectively, those for *nido* ten-vertex and *arachno* nine-vertex compounds in structures (III) and (IV) respectively.



(I)



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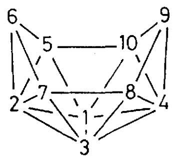

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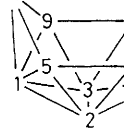

(IV)

Results and Discussion

Preparation and Molecular Structure of $[(PMe_2Ph)_2$-$PtB_{10}H_{10}PPh]$ (2).—In a procedure related to that used by Little and Wong[11] to make $[NMe_4][(CO)_3MnB_{10}H_{10}PPh]$, the reaction between $[PtCl_2(PMe_2Ph)_2]$ and $[NEt_4]$[*nido*-7-$PhPB_{10}H_{11}$] (1) in refluxing CH_2Cl_2 solution for 1 h, followed by chromatographic separation, gave [2-Ph-1,1-$(PMe_2Ph)_2$-*closo*-1,2-$PtPB_{10}H_{10}$] (2) as a yellow air-stable solid (yield 43%). The compound was characterised by n.m.r. and mass spectrometry, and by single-crystal *X*-ray diffraction analysis. A stoicheiometry for its formation is given in equation (1). The

$$\underset{}{[PtCl_2(PMe_2Ph)_2]} + \underset{(1)}{[B_{10}H_{11}PPh]^-} \longrightarrow \underset{(2)}{[(PMe_2Ph)_2PtB_{10}H_{10}PPh]} + Cl^- + HCl \quad (1)$$

only other identifiable metallaborane product, formed in small quantities, was the known[24] nine-vertex metallaborane [4,4-$(PMe_2Ph)_2$-*arachno*-4-PtB_8H_{12}] [(3), structures (IV) and (V)],

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* 1,1-Bis(dimethylphenylphosphine)-2-phenyl-1-platina-2-phospha-*closo*-dodecaborane.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

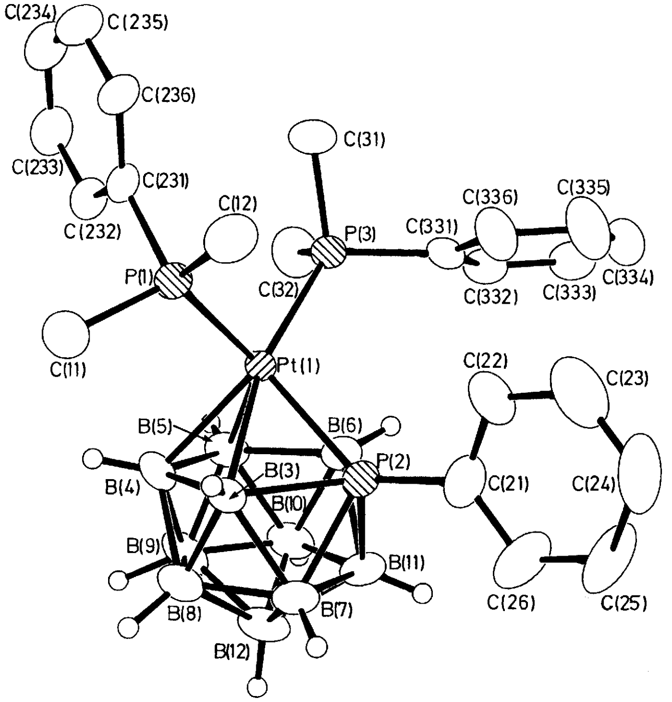


Figure 1. Crystallographically determined molecular structure of $[(PMe_2Ph)_2PtB_{10}H_{10}PPh]$, (**2**)

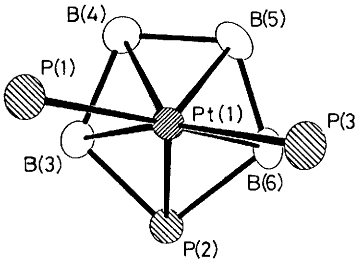
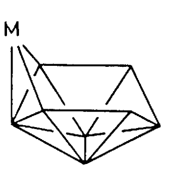


Figure 2. View approximately normal to the P(2)B(3)B(4)B(5)B(6) plane of compound (**2**) to illustrate the stereochemistry of the metal-to-phosphaborane bonding. The twist angle θ is *ca.* 83.4°. On heating in solution there is a contrarotational twist of the $Pt(PMe_2Ph)_2$ moiety relative to the PB_5 face (corresponding to θ increasing through 90 and 180 to 270°)



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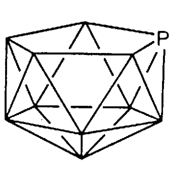

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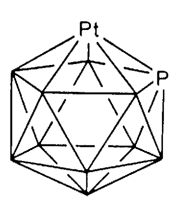

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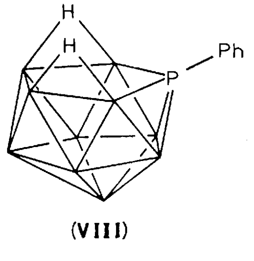

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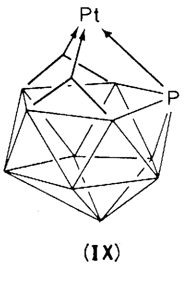


(IX)

Table 1. Selected interatomic distances (pm) for $[(PMe_2Ph)_2PtB_{10}H_{10}PPh]$ (**2**) with estimated standard deviations (e.s.d.s) in parentheses

(*i*) To the Pt atom			
Pt(1)–P(1)	230.4(3)	Pt(1)–P(3)	232.1(3)
Pt(1)–P(2)	235.8(3)		
Pt(1)–B(3)	230.1(6)	Pt(1)–B(6)	227.3(6)
Pt(1)–B(4)	225.6(6)	Pt(1)–B(5)	228.1(6)
(*ii*) Phosphorus–boron and phosphorus–carbon			
P(2)–B(3)	203.4(6)	P(2)–B(6)	207.4(7)
P(2)–B(7)	199.4(6)	P(2)–B(11)	199.2(7)
P(2)–C(21)	180.2(4)		
P(1)–C(11)	182.5(6)	P(3)–C(31)	183.8(5)
P(1)–C(12)	179.3(6)	P(3)–C(32)	182.2(6)
P(1)–C(131)	181.2(4)	P(3)–C(331)	182.0(4)
(*iii*) Boron–boron			
B(3)–B(4)	188.0(8)	B(5)–B(6)	184.3(8)
B(4)–B(5)	180.8(9)		
B(3)–B(7)	187.5(8)	B(6)–B(11)	190.4(9)
B(3)–B(8)	176.6(8)	B(6)–B(10)	176.1(8)
B(4)–B(8)	180.0(8)	B(5)–B(10)	178.8(9)
B(4)–B(9)	176.2(9)	B(5)–B(9)	176.0(8)
B(7)–B(8)	179.4(9)	B(10)–B(11)	177.6(9)
B(7)–B(11)	182.5(9)		
B(7)–B(12)	174.8(9)	B(11)–B(12)	175.0(9)
B(8)–B(9)	175.0(9)	B(10)–B(9)	175.8(9)
B(8)–B(12)	180.3(9)	B(10)–B(12)	178.2(9)
B(9)–B(12)	175.9(9)		
(*iv*) Boron–hydrogen			
B(3)–H(3)	113(2)	B(6)–H(6)	105(2)
B(4)–H(4)	101(1)	B(5)–H(5)	99(2)
B(7)–H(7)	106(2)	B(11)–H(11)	100(1)
B(8)–H(8)	108(2)	B(10)–H(10)	105(2)
B(9)–H(9)	120(1)		
B(12)–H(12)	101(2)		

identified by its ^{11}B, ^{1}H, and ^{31}P n.m.r. properties. The basic molecular cluster structure of compound (**2**) (Figure 1, and Tables 1 and 2) is that of an icosahedron with the platinum and phosphorus atoms occupying adjacent sites [structure (**VII**)], so that the compound is seen to derive *via* the capping of the five-membered open face of the eleven-vertex *nido*-7-phospha-undecaborane cluster [structure (**VI**)] with the metal centre. The intracluster interatomic distance Pt(1)–P(2) is somewhat, though not markedly, longer than the distances from Pt(1) to the *exo*-bound ligand phosphorus atoms P(1) and P(3), which, we would tentatively suggest, indicates possible substantial two-electron two-centre character in this linkage. Some support from this may derive from the high intracluster coupling constant between $^{195}Pt(1)$ and $^{31}P(2)$ (Table 3). If this was so, then contributions to the metal-to-cluster bonding description could derive by the formal replacement of the two bridging hydrogen atoms [at B(8)B(9) and B(10)B(11) in the neutral species $B_{10}H_{12}PPh$, structure (**VIII**)] by bonding vectors to platinum, together with a P(2) lone-pair donation to the platinum centre as in structure (**IX**).

In these terms the metal centre in the platinaphosphaborane would be 18-electron platinum(II) with five principal bonding orbitals, three to the cluster and two to the phosphine ligands. The angle of tilt of the Pt(1)P(1)P(3) plane to the P(2)B(3)—(6) plane is 93.7° [*i.e.* slightly away from the cluster phosphorus atom P(2)] whereas the angle of twist of the projection Pt(1)P(1)P(3) with respect to the vector joining P(2) and the midpoint of B(4)B(5) in this particular solid-state configuration is 83.4° (Figure 2). However, in view of the rotational

Table 2. Selected interatomic angles (°) for $[(PMe_2Ph)_2PtB_{10}H_{10}PPh]$ (**2**) with e.s.d.s in parentheses

(*i*) About the Pt atom			
P(1)-Pt(1)-P(3)	97.2		
P(1)-Pt(1)-P(2)	122.3	P(3)-Pt(1)-P(2)	114.3
P(1)-Pt(1)-B(3)	89.8(2)	P(3)-Pt(1)-B(6)	87.1(2)
P(1)-Pt(1)-B(4)	95.3(2)	P(3)-Pt(1)-B(5)	100.9(2)
P(1)-Pt(1)-B(5)	133.5(1)	P(3)-Pt(1)-B(4)	142.0(1)
P(1)-Pt(1)-B(6)	175.0(1)	P(3)-Pt(1)-B(3)	165.7(1)
P(2)-Pt(1)-B(3)	51.7(2)	P(2)-Pt(1)-B(6)	53.2(2)
P(2)-Pt(1)-B(4)	88.2(2)	P(2)-Pt(1)-B(5)	88.3(2)
B(3)-Pt(1)-B(4)	48.7(2)	B(6)-Pt(1)-B(5)	47.8(2)
B(3)-Pt(1)-B(5)	82.9(3)	B(6)-Pt(1)-B(4)	82.6(3)
B(3)-Pt(1)-B(6)	85.4(3)		
B(4)-Pt(1)-B(5)	47.0(2)		
(*ii*) About atom P(2)			
Pt(1)-P(2)-B(3)	62.7(2)	Pt(1)-P(2)-B(6)	61.3(2)
Pt(1)-P(2)-B(7)	109.9(2)	Pt(1)-P(2)-B(11)	109.4(2)
B(3)-P(2)-B(6)	98.0(3)		
B(3)-P(2)-B(7)	55.5(3)	B(6)-P(2)-B(11)	55.8(3)
B(3)-P(2)-B(11)	97.3(3)	B(6)-P(2)-B(7)	97.3(3)
C(21)-P(2)-Pt(1)	133.1(1)		
C(21)-P(2)-B(3)	129.9(3)	C(21)-P(2)-B(6)	131.9(2)
C(21)-P(2)-B(7)	111.4(3)	C(21)-P(2)-B(11)	112.2(3)
(*iii*) Phosphorus-boron-boron			
P(2)-B(3)-B(4)	110.2(4)	P(2)-B(6)-B(5)	111.0(4)
P(2)-B(3)-B(7)	61.2(3)	P(2)-B(6)-B(11)	59.9(3)
P(2)-B(3)-B(8)	110.2(4)	P(2)-B(6)-B(10)	108.3(4)
P(2)-B(7)-B(11)	62.7(3)	P(2)-B(11)-B(7)	62.8(3)
(*iv*) Others			
B(3)-B(4)-B(5)	110.7(4)	B(6)-B(5)-B(4)	110.0(4)

B-B-B(acute) 57.3(3)—65.1(4) B-B-B(obtuse) 105.2(4)—113.8(4)

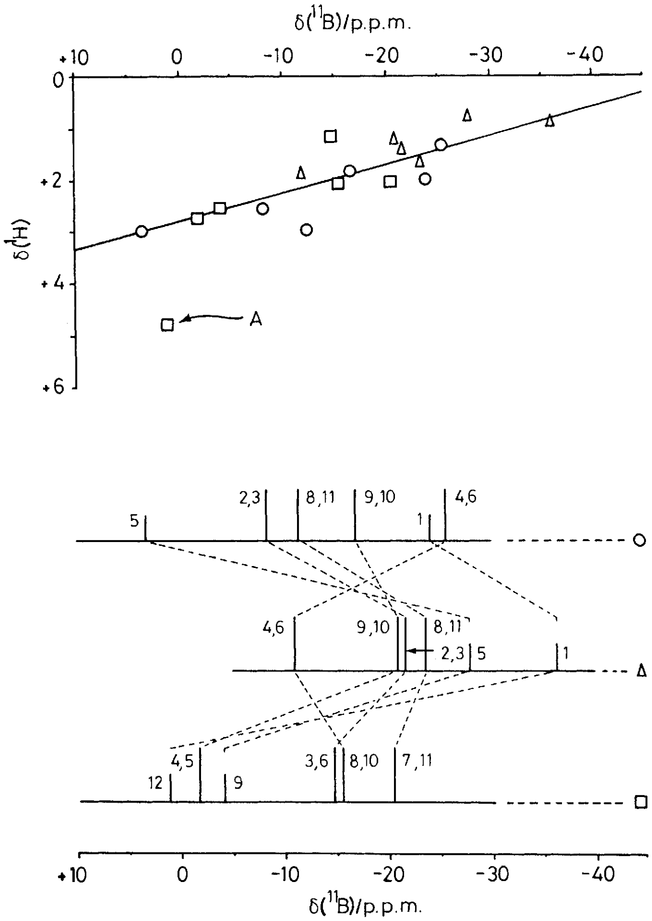


Figure 3. Representation of n.m.r. data for $[NEt_4][B_{10}H_{11}PPh]$ (**1**) (△), [2-Ph-1,1-$(PMe_2Ph)_2$-*closo*-1,2-$PtPB_{10}H_{10}$] (**2**) (□), and $B_9H_{12}PPh$ (**4**) (○). The uppermost diagram is a plot of $\delta(^{11}B)$ *versus* $\delta(^{1}H)$ for directly bound B–H(*exo*) groups in the three species; the line drawn has slope $\delta(^{11}B)$:$\delta(^{1}H)$ 18 : 1, intercept $\delta(^{1}H)$ + 2.8, and the datum A is that for $^{11}B^{1}H(12)$ in compound (**2**) (see text). The lower diagrams are stick representations of the relative intensities and chemical shifts of the ^{11}B n.m.r. spectra of the three species, with the hatched lines connecting resonance positions for equivalent sites in the three molecules. Note that particular sites will have different numbering in the *nido* eleven-vertex and *closo* twelve-vertex cluster types [structures (**I**) and (**II**)]

fluxionality of the platinum-to-cluster bonding (see below) these probably do not represent a minimum energy conformation for the isolated molecule.

Consistent with the 18-electron formulation, and in contrast to the 16-electron species $[(PMe_2Ph)_2PtB_{10}H_{12}]$,[25] ^{31}P n.m.r. spectroscopy at low temperatures showed no interaction of excess of phosphine with the metal centre.

The boron–phosphorus distances to P(2) *within* the cluster, which are in the range 199.2(7)—207.4(7) pm, average over 10 pm longer than those usually found for two-electron two-centre boron–phosphorus σ bonds *exo* to the cluster in polyhedral boron-containing cluster compounds[1,2,4,6,8,9,26] which reflects the multicentre bonding and/or increased *p* character in the intracluster linkages. The interboron distances between adjacent pairs of atoms that flank the phosphorus atom are somewhat longer than the others in the cluster, which presumably reflects diversion of electron density towards bonds with the more electronegative phosphorus centre at the expense of interboron bonding. This also to some extent applies to the platinum–boron distances, though these are all well within established metallaborane ranges.

Nuclear Magnetic Resonance Properties.—The measured n.m.r. parameters for the platinaphosphaborane (**2**) are in Table 3 (see also Figure 3 below). They were assigned, as described and exemplified elsewhere[21] for other *closo* platinaheteroboranes recently examined by n.m.r. spectroscopy in our laboratories. Noteworthy in the ^{1}H shielding behaviour (Figure 3), is the BH(3, 6) position, which has $\sigma(^{1}H)$ higher than the general trend, as also observed for twelve-vertex platina-selena- and -tellura-boranes,[20,21] and may arise from steric effects. By contrast, $\sigma(^{1}H)$ for BH(12) is markedly lower, by some 2 p.p.m., than the general trend. This proton is however antipodal to the heavy transition metal atom Pt(1), and a similar antipodal deshielding of the *exo*-terminal proton when antipodal to an atom of a third-row transition element has been observed in other metallaboranes.[21,27–30] Also noteworthy is the incidence of couplings *via* ^{3}J(*ortho*) and ^{4}J(*para*, or antipodal) paths from ^{195}Pt(1) and ^{31}P(2) to the ^{1}H(9) and ^{1}H(12) cluster protons (*c.f.* ref. 21).

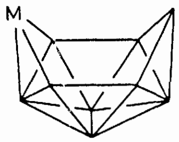
Variable temperature ^{1}H n.m.r. spectroscopy (footnote *n* in Table 3) revealed a fluxionality arising from a contrarotation of the phosphine *versus* the η^5-phosphaborane ligands about an approximate Pt(1)–B(12) axis (*cf.* ref. 21). The activation energy $\Delta G^{\ddagger}_{277}$ of *ca.* 58 kJ mol^{-1} is some 20 kJ less than that for a similar rotational fluxionality of $\{Pt(PMe_2Ph)_2\}$ in the η^4-borane complex $[(PMe_2Ph)_2PtB_{10}H_{12}]$,[19,31,32] the lower value possibly arising from a more 'conical' contribution of the platinum valence orbitals to the cluster bonding than occurs in the eleven-vertex species.

As part of this work we have also measured and assigned the ^{11}B and ^{1}H n.m.r. spectra of the phosphaborane precursor

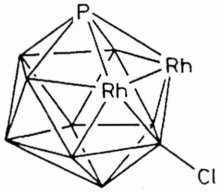
Table 3. Measured n.m.r. parameters for [$(PMe_2Ph)_2PtB_{10}H_{10}PPh$] (**2**) in $CDCl_3$ solution at 294 K

Assignment	Relative intensity	$\delta(^{11}B)^a$/p.p.m.	Observed [$^{11}B-^{11}B$]-COSY correlations^b	$^1J(^{11}B-^1H)^c$/Hz	$\delta(^1H)^d$/p.p.m.
(9)	1BH	−6.3 (−4.0)	(12)w (4, 5)w (8, 10)s	140	+2.52^e
(4, 5)	1BH	−3.6 (−1.8^f)	(9)w	127	+2.72^g
(12)	1BH	−1.5 (+1.2)	(9)w (7, 11)m (8, 10)w	145	+4.80^h
(3, 6)	2BH	−16.0 (−14.7)	*i*	*j*	+1.16
(7, 11)	2BH	−21.6 (−20.4)	(12)w (8, 10)m	150	+2.02
(8, 10)	2BH	−17.1 (−15.5)	(9)s (12)m (7, 11)m^i	141	+2.05
(1)		*k*, *l*	{2}^{m} {4, 5}^{f}		
(2)		*l*, *m*	{1}^{m}		{+1.66, +1.92}^{n}

[a] ±0.5 p.p.m. to high frequency (low field) of $BF_3(OEt_2)$; values in parentheses refer to $CD_3C_6D_5$ solution at 358 K. [b] Measured under conditions of {^1H(broad-band noise)} decoupling; s = stronger, w = weaker, m = intermediate. [c] Measured from resolution-enhanced ^{11}B n.m.r. spectrum. [d] ±0.5 p.p.m. to high frequency (low field) of $SiMe_4$; ^1H resonances related to directly bound B positions by ^1H-{^{11}B(selective)} experiments. [e] $^4J(^{31}P-^1H)$ *ca.* 21.5; $^3J(^{195}Pt-^1H)$ *ca.* 70 Hz. [f] $^1J[^{195}Pt(1)-^{11}B(4, 5)]$ *ca.* 215 Hz. [g] $^3J(^{31}P-^1H)$ *ca.* 16, $^2J(^{195}Pt-^1H)$ *ca.* 35 Hz. [h] $^3J(^{31}P-^1H)$ *ca.* 13.5, $^4J(^{195}Pt-^1H)$ *ca.* 42 Hz. [i] Any cross-correlations between the (3, 6) and (8, 10) positions not observable due to partial overlap of resonances. [j] Not resolved (broad ^{11}B resonance). [k] $\delta[^{31}P(\text{Pt-bound})] = -19.5$ p.p.m.; $^1J(^{195}Pt-^{31}P) = 3\,130$ Hz; $\Xi[^{195}Pt(1)] = 21.380\,09 \pm 0.000\,02$ MHz. [l] $^2J[^{31}P-Pt-^{31}P(2)] = 17$ Hz. [m] $\delta[^{31}P(2)] = -73.2$ p.p.m., $^1J(^{195}Pt-^{31}P) = 259$ Hz. [n] Refers to P-methyl protons at 243 K; $^3J(^{195}Pt-^1H)$ *ca.* 27 and 23 Hz respectively. On heating, these two resonances coalesce [T_c 277 ± 2 K in ^1H-{^{31}P(broad band)} spectrum at 100 MHz; 2.35 T]; at 323 K $\delta(^1H) = 1.78$ p.p.m., $^1J(^{195}Pt-^1H)$ *ca.* 26 Hz. The derived value of $\Delta G^{\ddagger}_{277}$ is 58 ± 1 kJ mol^{-1}.



(**X**)



(**XI**)

species 7-Ph-*nido*-7-$PB_{10}H_{12}$ (**5**) and its monoanion [7-Ph-*nido*-7-$PB_{10}H_{11}$]$^-$ (**1**) in order to compare them with the platinated species (**2**). The neutral species (**5**) has bridging hydrogen atoms at B(8)B(9) and B(10)B(11) [structures (**I**) and (**VIII**)], whereas the anion (**1**) has a bridging hydrogen atom at B(9)B(10) only. The measured parameters are in Table 4, assignments being made on the basis of [$^{11}B-^{11}B$]-COSY correlations and Heřmánek's rules,[33–35] any remaining ambiguities being resolved by [$^1H-^1H$]-COSY-{^{11}B} work. For compound (**5**) the ^{11}B assignments agree with those previously published.[22] It was noted in the [$^{11}B-^{11}B$]-COSY experiments that correlations among atoms in the open faces, whether hydrogen-bridged or not, and correlation between atom pairs flanking the electronegative heteroatom P(7), are all generally weaker than those between all other pairs (*cf.* ref. 20). As for the platinaphosphaborane (**2**), and a variety of other species,[4,15,17,21,36,37] there is a general parallel between $\delta(^{11}B)$ and $\delta(^1H)$ for directly bound atoms in compounds (**1**) and (**5**) (Figure 3).

Figure 3 also shows stick diagrams of the ^{11}B n.m.r. spectra for the platinaphosphaborane (**2**) and the neutral and anionic phosphaborane precursors [(**5**) and (**1**) respectively]. These show the shielding changes at particular boron nuclei as the cluster changes in the three species (**2**), (**1**), and (**5**). From neutral $B_{10}H_{12}PPh$ (**5**) to the anion (**1**) $\delta[^{11}B(5)]$ shifts from extreme low to extreme high field, and conversely $\delta[^{11}B(4, 6)]$ shifts from extreme high to extreme low field. These changes follow Heřmánek's Rules,[33–35] but the inversion of the two positions also indicates a change in character of the ten-boron fragment from *nido* to *arachno*,[3,4,7,27,28,37] particularly on the side of the molecule distant from P(7). This inversion is effectively reversed from the anionic species (**1**) to the platinaphosphaborane (**2**), tending to support the supposition that the phosphaborane cluster fragment in (**2**) is much more akin to that in neutral (**5**) than anionic (**1**). Boron-11 shielding is in fact quite similar for (**5**) and (**2**), the differences $\Delta\sigma$ (of the order 5—10 p.p.m.) being small, except for the positions adjacent and antipodal to platinum ($\Delta\sigma \approx -15$ and -25 p.p.m. respectively).

Reactions of [NEt_4][$B_{10}H_{11}PPh$] *with other Metal Halide Complexes.*—In view of the reaction between [$B_{10}H_{11}PPh$]$^-$ and [$PtCl_2(PMe_2Ph)_2$] under mild conditions, a preliminary study was undertaken for other metal halide complexes that have readily generated polyhedral metallaboranes.[2,4,6,29,37–48] Of the reagents investigated *viz.* [$Rh(CO)Cl(PPh_3)_2$], [$RhCl_3(PMe_2Ph)_3$], [$IrCl_3(PMe_2Ph)_3$], [{$Rh(C_5Me_5)Cl_2$}$_2$] and [{$Ru(C_6Me_6)Cl_2$}$_2$], only [{$Rh(C_5Me_5)Cl_2$}$_2$] gave viable quantities of metallaboranes. The others, together with the added [NEt_4][$B_{10}H_{11}PPh$], were apparently unchanged after several hours in refluxing dichloromethane or refluxing toluene solution although more forcing conditions may induce productive reactions.

With [{$Rh(\eta^5-C_5Me_5)Cl_2$}$_2$] two metallaboranes were formed, one being readily identified by n.m.r. work as the known species [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}] (**6**), [configuration (**III**) and (**X**)].[38] The second, an orange crystalline solid, was reasonably identified by ^1H and ^{11}B n.m.r. work (Table 5) as a {$(C_5Me_5)_2Rh_2/PPh$} analogue of the {R_2M_2/S} *closo* twelve-vertex dirhodium,[49] di-iridium,[50] and diruthenium[40,51] thiaborane compounds [2,3-R_2-2,3,1-$M_2SB_9H_8$-X-7], where RM = (C_6Me_6)Ru, (*p*-$MeC_6H_4Pr^i$)Ru, (C_5Me_5)Ir, or (C_5Me_5)Rh, and X = Cl or H, *viz.* as previously unreported [1-Ph-2,3-(η^5-C_5Me_5)$_2$-*closo*-2,3,1-$Rh_2PB_9H_9$] [compound (**7**), schematic configuration (**XI**)]. A third product, in much lower yield (**8**), is probably a 7-substituted analogue of compound (**7**). The ^{11}B n.m.r. pattern of this structural type, as discussed elsewhere,[50,52] has most resonances centrally around $\delta(^{11}B) = 0$, but with $\delta[^{11}B(5)]$ and $\delta[^{11}B(7)]$ at somewhat higher and lower fields respectively, and with broader peaks for $^{11}B(4, 6)$ and $^{11}B(5)$ (Table 5). The formation of nine-boron ten-vertex and twelve-vertex clusters is in obvious contrast to the formation of the eight-boron nine-vertex and ten-boron twelve-vertex clusters in the platinum reaction (*cf.* Scheme 1 in ref. 53).

Experimental

General.—Reactions were carried out under an atmosphere of dry nitrogen using dry degassed solvents, subsequent manipulations and separations being carried out in air. The

Table 4. Measured n.m.r. parameters for $[NEt_4][B_{10}H_{11}PPh]$ (**1**) and $[B_{10}H_{12}PPh]$ (**5**) at 294 K

	(**1**) $[(CD_3)_2CO$ solution][a]				(**5**) $[CDCl_3$ solution][b]			
Assignment[c]	$\delta(^{11}B)$[d]/p.p.m.	Observed $[^{11}B-^{11}B]$ COSY correlations[e]	$^1J(^{11}B-^1H)$[f]/Hz	$\delta(^1H)$[g]/p.p.m.	$\delta(^{11}B)$[d]/p.p.m.	Observed $[^{11}B-^{11}B]$-COSY correlations[e]	$^1J(^{11}B-^1H)$[f]/Hz	$\delta(^1H)$[g]/p.p.m.
(1)	−36.2[h]	(2, 3)s (4, 6)s (5)m	137	+0.90	−23.9	(2, 3)m (4, 6)w (5)w	*i*	+1.99[j]
(2), (3)	−21.4[h]	(1)s (4, 6)s	*i*	+1.38	−8.1	(1)m (4, 6)m	163	+2.54
(4), (6)	−11.9	(1)s (2, 3)s (5)s (8, 11)m (9, 10)m	137	+1.85[k]	−25.4	(1)w (2, 3)m (5)m (8, 11)s (9, 10)m	*i*	+1.32[l]
(5)	−28.0[h]	(1)m (4, 6)s (9, 10)m	140	+0.79	+3.6	(1)w (4, 6)m (9, 10)m	149	+2.97
(8), (11)	−23.3	(4, 6)m (9, 10)m	150	+1.64	−12.3	(4, 6)s	157	+2.94[m]
(9), (10)	−20.9[h]	(4, 6)m (5)m (8, 11)m	*i*	+1.19	−16.8	(4, 6)m (5)m	150	+1.82[j]
Bridge (8, 9; 10, 11)							*n*	−3.92[o]
Bridge (9, 10)			*n*	−4.63[p]				

[a] $\delta(^{31}P)$ −63.7 p.p.m.; $w_{\frac{1}{2}}$ *ca.* 195 Hz. [b] $\delta(^{31}P)$ = 81.8 p.p.m.; $w_{\frac{1}{2}}$ *ca.* 125 Hz. [c] See text and footnote *h*. [d] ±0.5 p.p.m. to low field (high frequency) of $BF_3(OEt_2)$. [e] Measured under conditions of $\{^1H$(broad band noise)$\}$ decoupling; s = stronger, w = weaker, m = intermediate. [f] Measured from 'resolution-enhanced' ^{11}B spectrum; ±8 Hz. [g] ±0.05 p.p.m. to high frequency (low field) of $SiMe_4$. ^1H Resonances related to directly bound B positions by $^1H-\{^{11}B$(selective)$\}$ spectroscopy. [h] Ambiguous assignment between (1) and (5) positions, and between (2, 3) and (9, 10) positions resolved by $[^1H-^1H]$-COSY work (see text and footnote *p*). [i] Accurate estimate precluded because of peak overlap. [j] Possible unresolved doublet structure arising from $^3J(^{31}P-^1H)$. [k] Doublet structure, $^2J(^{31}P-^1H)$ *ca.* 25 Hz. [l] Doublet structure, $^2J(^{31}P-^1H)$ *ca.* 15 Hz. [m] Possible unresolved doublet structure arising from $^2J(^{31}P-^1H)$. [n] Not measured. [o] Doublet structure, $^2J(^{31}P-^1H)$ *ca.* 18 Hz; resonance selectively sharpened by $\nu(^{11}B)$ corresponding to $\delta(^{11}B)$ −16.8 in $^1H-\{^{11}B\}$ experiments; strong correlation with $\delta(^1H)$ +1.82 in $[^1H-^1H]$-COSY experiments. [p] Doublet structure, $^3J(^{31}P-^1H)$ *ca.* 50 Hz; resonance apparently sharpened more by irradiation at $\nu(^{11}B)$ corresponding to $\delta(^{11}B)$ −20.9 rather than that corresponding to $\delta(^{11}B)$ −21.4; strong correlation with $\delta(^1H)$ +1.19 in $[^1H-^1H]$-COSY experiments.

Table 5. Measured n.m.r. properties for compounds (**7**) {tentatively identified as $[1\text{-Ph-}2,3\text{-}(\eta^5\text{-}C_5Me_5)_2\text{-}closo\text{-}2,3,1\text{-}Rh_2PB_9H_9]$} and (**8**), together with those of $[7\text{-Cl-}2,3\text{-}(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)_2\text{-}closo\text{-}2,3,1\text{-}Ru_2SB_9H_8]$ (**9**) (refs. 40 and 52) for comparison

	(**7**)[a,b]		(**8**)[a]		(**9**)[c]	
Assignment	$\delta(^{11}B)$[d]/p.p.m.	$\delta(^1H)$[e]	$\delta(^{11}B)$[d]/p.p.m.	$\delta(^1H)$[e]	$\delta(^{11}B)$[d]/p.p.m.	$\delta(^1H)$[e]
(7)	+41.4[f]	+4.66	+42.9[f]		+45.0	
(8, 11)	+8.7	+2.87	*ca.* +7.6	*ca.* +2.83	−1.1	+3.05
(9, 10)	+1.8	+3.65[g]	+0.2	+3.50[h]	−2.3	+3.17
(4, 6)	−6.5[i]	+2.11	*ca.* −9.7[i]	+2.07	−10.2[i]	+2.27
(12)	−10.9	+2.13	−8.4	+2.12	−6.0	+2.59
(5)	−29.5[i]	+1.55	*ca.* −30.1[i]	+1.33	−35.4[i]	+0.43
(2, 3)		(+1.78)[j]		(+1.73)[j]		

[a] $CDCl_3$ solution at 294 K. [b] $\delta(^{31}P)$ *ca.* +57 p.p.m.; $^1J(^{103}Rh-^{21}P)$ *ca.* 90 Hz. [c] CD_2Cl_2 solution at 294 K. [d] ±0.5 p.p.m. to low field (high frequency) of $BF_3(OEt_2)$. [e] ±0.05 p.p.m. to low field (high frequency) of $SiMe_4$; ^1H resonances related to directly bound ^{11}B positions by $^1H-\{^{11}B$(selective)$\}$ spectroscopy. [f] $T_1[^{11}B(7)]$ for compounds (**7**) and (**8**) differ by at least an order of magnitude (**8**) ≫ (**7**) (*cf.* W. L. Smith, B. J. Meneghelli, N. McClure, and R. W. Rudolph, *J. Am. Chem. Soc.*, 1976, **98**, 624). [g] Doublet structure, $^3J(^{31}P-^1H)$ = 17.8 Hz. [h] Doublet structure, $^3J(^{31}P-^1H)$ = 16.6 Hz. [i] These resonances adjacent to heteroatom much broader than the others in the ^{11}B spectra. [j] Refers to C_5Me_5 group, doublet splitting of *ca.* 1 Hz arising from $^4J(^{31}P-^1H)$ or $^3J(^{103}Rh-^1H)$.

compounds $B_{10}H_{12}PPh$ (**5**) and $[NEt_4][B_{10}H_{11}PPh]$ (**1**) were prepared by established methods,[13] as were the metal halide complexes *cis*-$[PtCl_2(PMe_2Ph)_2]$[15] and $[\{Rh(\eta^5\text{-}C_5Me_5)_2Cl_2\}_2]$.[54] Preparative thin layer chromatography (t.l.c.) was carried out using 1-mm layers of silica (Kieselgel GF 54, Fluka) on glass plates of dimensions 200 x 200 mm; these were prepared as required from an acetone slurry, followed by drying in air at *ca.* 80 °C.

Nuclear Magnetic Resonance Spectroscopy.—N.m.r. spectroscopy was carried out at 2.35 and/or 9.4 T using JEOL FX100 and Bruker AM400 instrumentation, with the general techniques, and also the techniques of the $^1H-\{^{11}B\}$,[3] the $^1H-\{^{31}P\}$,[31,32] the $[^{11}B-^{11}B]$-COSY[55,56] and the $[^1H-^1H]$-COSY[57] experiments being essentially as described in other recent papers from our laboratories.[2–6,9,10,39,42,53] In the $^1H-\{^{11}B\}$ experiments use was made of the technique[51] in which a $^1H-\{^{11}B$(40 kHz off-resonance)$\}$ spectrum was subtracted from a $^1H-\{^{11}B$(on-resonance)$\}$ spectrum in order to remove ^1H lines not associated with the ^{11}B nucleus/nuclei of interest. Chemical shifts δ are given in p.p.m. to high frequency (low field) of Ξ 100 ($SiMe_4$) for ^1H, 40.480 730 (nominally 85% H_3PO_4) for ^{31}P, and 32.083 971 MHz {nominally $[BF_3(OEt_2)]$ in $CDCl_3$}[37] for ^{11}B, Ξ being defined as in ref. 58. The chemical shifts were measured relative to solvent deuteron or residual proton resonances as internal secondary standards.

Reaction between $[PtCl_2(PMe_2Ph)_2]$ *and* $[NEt_4][B_{10}H_{11}PPh]$.—A suspension of $[NEt_4][B_{10}H_{11}PPh]$ (110 mg, 0.31 mmol) in CH_2Cl_2 (*ca.* 10 cm^3) was added to a solution of $[PtCl_2(PMe_2Ph)_2]$ (150 mg, 0.28 mmol) in CH_2Cl_2 (25 cm^3). The resulting mixture was heated under reflux for 1 h, yielding a yellow solution. After cooling, the solution was filtered, reduced in volume (rotary evaporator, *ca.* 40 °C, water-pump pressure), and applied to preparative t.l.c. plates. Development of the plates [hexane–CH_2Cl_2 (1:1)] revealed a major yellow and a minor orange component with some brown material remaining unmoved. N.m.r. spectroscopy (^1H, ^{11}B, and ^{31}P) on the orange component revealed identical n.m.r. behaviour to the previously characterised[24] colourless species $[4,4\text{-}(PMe_2Ph)_2\text{-}arachno\text{-}4\text{-}PtB_8H_{12}]$, thereby identifying it as such [compound (**3**)], the orange colour presumably arising from small amounts of highly coloured impurities (integrated ^{31}P n.m.r. spectro-

Table 6. Atomic co-ordinates (× 10^4) for compound (**2**)

Atom	*x*	*y*	*z*
Pt(1)	8 906.0(1)	−118.7(1)	7 505.3(1)
P(1)	8 219(1)	1 229(1)	6 930(1)
P(2)	8 545(1)	−2 507(1)	6 740(1)
P(3)	7 480(1)	58(1)	8 709(1)
C(11)	9 529(5)	2 049(5)	6 186(3)
C(12)	6 401(5)	254(5)	6 324(3)
C(131)	8 192(2)	2 856(2)	7 691(1)
C(132)	9 421(2)	3 701(2)	8 302(1)
C(133)	9 470(2)	4 967(2)	8 906(1)
C(134)	8 292(2)	5 388(2)	8 900(1)
C(135)	7 064(2)	4 543(2)	8 289(1)
C(136)	7 014(2)	3 277(2)	7 684(1)
C(21)	6 856(3)	−4 167(2)	6 272(1)
C(22)	5 442(3)	−4 087(2)	6 305(1)
C(23)	4 083(3)	−5 344(2)	5 983(1)
C(24)	4 138(3)	−6 683(2)	5 629(1)
C(25)	5 552(3)	−6 764(2)	5 596(1)
C(26)	6 911(3)	−5 506(2)	5 918(1)
C(31)	6 192(5)	964(5)	8 887(3)
C(32)	8 757(5)	1 065(5)	9 668(3)
C(331)	6 132(2)	−1 641(2)	8 886(1)
C(332)	6 331(2)	−2 043(2)	9 571(1)
C(333)	5 209(2)	−3 311(2)	9 708(1)
C(334)	3 888(2)	−4 177(2)	9 162(1)
C(335)	3 688(2)	−3 775(2)	8 477(1)
C(336)	4 810(2)	−2 507(2)	8 340(1)
B(3)	9 929(5)	−904(5)	6 242(3)
B(4)	11 358(5)	675(5)	7 086(3)
B(5)	11 181(5)	263(5)	8 074(3)
B(6)	9 604(5)	−1 561(5)	7 954(3)
B(7)	10 421(5)	−2 460(5)	6 103(3)
B(8)	11 873(5)	−626(5)	6 296(3)
B(9)	12 572(5)	13(6)	7 356(3)
B(10)	11 545(5)	−1 300(5)	7 868(3)
B(11)	10 210(5)	−2 872(5)	7 103(3)
B(12)	12 024(5)	−1 833(6)	6 789(3)
H(3)	9 349(12)	−954(12)	5 661(11)
H(4)	11 928(12)	1 668(12)	7 015(11)
H(5)	11 583(12)	975(12)	8 642(11)
H(6)	9 015(12)	−1 955(12)	8 450(11)
H(7)	10 218(12)	−3 264(12)	5 501(11)
H(8)	12 648(12)	−335(12)	5 808(11)
H(9)	13 879(12)	885(12)	7 306(12)
H(10)	12 066(12)	−1 455(12)	8 331(11)
H(11)	9 802(12)	−3 898(12)	7 103(11)
H(12)	12 876(12)	−2 153(12)	6 589(11)

scopy showed the presence of other phosphorus-containing species at the 2—3 mole % level). The yellow component was purified by repeated t.l.c., and characterised by n.m.r. spectroscopy and single crystal *X*-ray diffraction analysis as [2-Ph-1,1-$(PMe_2Ph)_2$-*closo*-1,2-$PtPB_{10}H_{10}$] [compound (**2**); 93 mg, 0.13 mmol, 43%]. It was an air-stable crystalline solid, crystals suitable for *X*-ray analysis being obtained by diffusion of hexane into a solution in CH_2Cl_2.

Reaction between [{Rh(η^5-C_5Me_5)Cl_2}$_2$] *and* [NEt_4][$B_{10}H_{11}$PPh].—A procedure exactly analogous to that described for the [$PtCl_2(PMe_2Ph)_2$] reaction was followed, except that [{Rh(η^5-C_5Me_5)Cl_2}$_2$] (180 mg, 0.29 mmol) was used instead. Preparative t.l.c. using hexane–CH_2Cl_2 (1:1) as liquid phase revealed a yellow and an orange component, which were purified further by repeated t.l.c. experiments. The more mobile yellow component [compound (**6**)] revealed identical n.m.r. behaviour to that of previously characterised [6-(η^5-C_5Me_5)-*nido*-6-RhB_9H_{13}], and was thereby identified as such. The orange product was tentatively identified as a mixture of [1-Ph-2,3-(η^5-C_5Me_5)$_2$-*closo*-2,3,1-$Rh_2PB_9H_9$] (**7**) and a 7-substituted derivative of (**7**) [compound (**8**)].

Reactions with the metal halide complexes [Rh(CO)Cl-$(PPh_3)_2$], [$RhCl_3(PMe_2Ph)_3$], [$IrCl_3(PMe_2Ph)_3$], and [{Ru-(η^6-C_6Me_6)Cl_2}$_2$] were also surveyed under these and other conditions (refluxing CH_2Cl_2 and refluxing toluene) but in each case monitoring the mixtures by ^{11}B n.m.r. spectroscopy indicated that the starting borane moiety [$B_{10}H_{11}PPh$]$^-$ was unchanged after several hours.

Single-crystal X-*Ray Diffraction Analysis.*—All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω—2θ scan mode using graphite monochromatised Mo-K_α radiation (λ = 71.069 pm) following a standard procedure described in detail elsewhere.[59] The data set was corrected for absorption empirically once the structure had been determined.[60] The structure was solved *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[61] All non-hydrogen atoms were refined with anisotropic thermal parameters with the phenyl groups treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). The phenyl and methyl hydrogen atoms were included in calculated positions (C–H 108 pm) and were assigned with one overall isotropic thermal parameter. The borane hydrogen atoms were located in a Fourier difference map and were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in which the parameter *g* was included in refinement in order to obtain satisfactory agreement analyses.

Crystal data for $C_{22}H_{37}B_{10}P_3Pt$. *M* = 697.66, triclinic, space group $P\bar{1}$, a = 961.8(1), b = 1 077.2(2), c = 1 661.4(2) pm, α = 108.67(1), β = 84.63(1), γ = 115.96(1)°, U = 1.4639(4) nm^3, Z = 2, μ = 47.55 cm^{-1}, $F(000)$ = 684.

Data collection. Scan widths 2.0° + α-doublet splitting, scan speeds 2.0—29.3° min^{-1}, and $4.0 < 2\theta < 45.0°$. Total data collected 3 929, no. observed 3 702 [$I > 2.0\sigma(I)$].

Structure refinement. Number of parameters = 344, weighting factor g = 0.0002, R = 0.0212, R' = 0.0219. Atomic co-ordinates are given in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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References

1 Y. M. Cheek, J. D. Kennedy, and M. Thornton-Pett, *Inorg. Chim. Acta*, 1985, **99**, L43.
2 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1431.
3 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1987, 1573.
4 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 2417.
5 M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *Z. Anorg. Allg. Chem.*, 1987, **553**, 24.
6 M. Elrington, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, to be submitted; M. Elrington Ph.D. Thesis, University of Leeds, 1985.

7 M. A. Beckett and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1983, 575.

8 M. A. Beckett, J. D. Kennedy, and P. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 303.

9 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 2059.

10 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, in the press.

11 J. L. Little and A. C. Wong, *J. Am. Chem. Soc.*, 1971, **93**, 522.

12 T. Yamamoto and L. J. Todd, *J. Organomet. Chem.*, 1974, **67**, 75.

13 J. L. Little, *Inorg. Chem.*, 1976, **15**, 114.

14 T. P. Fehlner, Sixth International Conference on Boron Chemistry, IMEBORON VI, Bechyně, 1987, abstract CA72; J. Ferlong, T. P. Fehlner, and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1987, 1395.

15 N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1985, 953.

16 M. A. Beckett, N. N. Greenwood, J. D. Kennedy, P. A. Salter, and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 556.

17 M. A. Beckett, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1986, 1879.

18 R. Ahmad, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1986, 2433.

19 R. Ahmad, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, to be submitted.

20 G. Ferguson, M. Parvez, J. A. MacCurtain, O. Ni Dhubhghaill, T. R. Spalding, and D. Reed. *J. Chem. Soc., Dalton Trans.*, 1987, 699.

21 G. Ferguson, J. D. Kennedy, X. L. R. Fontaine, Faridoon, and T. R. Spalding, *J. Chem. Soc., Dalton Trans.*, 1988, 2555; Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, B. Kaitner, X. L. R. Fontaine, J. D. Kennedy, and D. Reed, *ibid.*, 1989, 2739.

22 W. F. Wright, A. R. Garber, and L. J. Todd, *J. Magn. Reson.*, 1978, **30**, 595.

23 A. R. Siedle, *Annu. Rep. NMR Spectrosc.*, 1982, **12**, 177 and refs. cited therein.

24 S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1981, 1415.

25 M. Thornton-Pett and Y. M. McInnes, Sixth International Conference on Boron Chemistry, IMEBORON VI, Bechyně, 1987, abstract CA16.

26 See, for example, J. D. Kennedy, *Prog. Inorg. Chem.*, 1984, **32**, 519; 1986, **34**, 211 and refs. therein.

27 I. Macpherson, Ph.D. Thesis, University of Leeds, 1987.

28 I. Macpherson and X. L. R. Fontaine, unpublished work.

29 M. Bown, X. L. R. Fontaine, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1987, **325**, 233.

30 M. A. Beckett, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 795.

31 S. K. Boocock, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1980, 305.

32 S. K. Boocock, N. N. Greenwood, J. D. Kennedy, W. S. McDonald, and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1981, 2573.

33 S. Heřmánek, J. Plešek, and B. Štíbr, Second International Meeting on Boron Chemistry, IMEBORON II, Leeds, 1974, abstract 38.

34 S. Heřmánek and J. Plešek, *Z. Anorg. Allg. Chem.*, 1974, **409**, 115.

35 S. Heřmánek, T. Jelínek, J. Plešek, B. Štíbr, J. Fusek, and F. Mareš, 'Boron Chemistry (IMEBORON VI),' ed. S. Heřmánek, World Scientific, Singapore, 1987, pp. 26—73.

36 G. R. Eaton and W. N. Lipscomb, 'N.M.R. Studies of Boron Hydrides and Related Compounds,' Benjamin, New York and Amsterdam, 1969.

37 J. D. Kennedy, 'Multinuclear N.M.R.,' ed. J. Mason, Plenum, London and New York, 1987, ch. 8, p. 221, and refs. therein.

38 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 547.

39 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, J. Plešek, B. Štíbr, and M. Thornton-Pett, *Inorg. Chem.*, 1989, **28**, 2129.

40 M. Bown, Ph.D. Thesis, University of Leeds, 1987.

41 M. Bown, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1986, **309**, C67.

42 M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 925.

43 N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1985, 2397.

44 J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1981, 933; 1982, 383; 1983, 83.

45 J. Bould, Ph.D. Thesis, University of Leeds, 1983.

46 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 346.

47 J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 465.

48 J. Bould, J. E. Crook, N. N. Greenwood, and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1984, 1903.

49 G. Ferguson, M. F. Hawthorne, B. Kaitner, and F. J. Lator, *Acta Crystallogr., Sect. C*, 1984, **40**, 707.

50 X. L. R. Fontaine and K. Nestor, unpublished work; K. Nestor, X. L. R. Fontaine, N. N. Greenwood, and J. D. Kennedy, to be submitted.

51 J. D. Kennedy and J. Staves, *Z. Naturforsch., Teil B*, 1979, **34**, 808.

52 M. Bown, X. L. R. Fontaine, J. D. Kennedy, and N. N. Greenwood, unpublished work.

53 M. A. Beckett, M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 1969.

54 J. W. Kang, K. Mosely, and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.

55 W. C. Hutton, R. N. Grimes, and T. L. Venable, *J. Am. Chem. Soc.*, 1982, **104**, 4716; 1984, **106**, 29; D. Reed, *J. Chem. Res.*, 1984, (*S*) 198.

56 D. F. Gaines, G. M. Edvenson, T. G. Hill, and B. R. Adams, *Inorg. Chem.*, 1987, **26**, 1813.

57 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.*, 1986, 779

58 W. McFarlane, *Proc. R. Soc. London, Ser. A*, 1968, **306**, 185.

59 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2075.

60 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

61 G. M. Sheldrick, SHELX 76, Program System for *X*-Ray Structure Determination, University of Cambridge, 1976.

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