DALTON

Reactions of carbon disulfide with open *nido*-6-iridadecaboranes. The formation of closed ten-vertex cluster compounds with boron-to-metal dithioformate bridges and a novel *isocloso* ⟶ *closo* cluster conversion

Richard S. Coldicott, John D. Kennedy and Mark Thornton-Pett

School of Chemistry, University of Leeds, Leeds LS2 9JT, UK

The compounds [6-H-6,6-(PPh$_3$)$_2$-*nido*-6-IrB$_9$H$_{13}$] **1** or [6-H-6-(PPh$_3$)-6-(*o*-Ph$_2$PC$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5] **2** reacted with refluxing CS$_2$ to form respectively [2,10-(PPh$_3$)$_2$-2,6;2,9-(μ-S$_2$CH)$_2$-*closo*-2-IrB$_9$H$_6$] **4** (14%) or [10-(PPh$_3$)-2,6;2,9-(μ-S$_2$CH)$_2$-2-(*o*-Ph$_2$PC$_6$H$_4$)-*closo*-2-IrB$_9$H$_5$-1] **5** (17%). Compound **5** (37%) was also obtained from CS$_2$ and [1-H-1-(PPh$_3$)-1-(*o*-Ph$_2$PC$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_8$-2] **3** in an unprecedented *isocloso* ⟶ *closo* conversion. The new compounds **4** and **5** are characterised by NMR spectroscopy, mass spectrometry and a single-crystal X-ray diffraction analysis on **4**. Compound **4** has a conventional *closo* ten-vertex {2-IrB$_9$} cluster structure with two SCHS units that bridge symmetrically from the iridium atom to the boron cluster at B(6) and B(9). Compound **5** has the same cluster structure, but now the metal-bound triarylphosphine is *ortho*-cycloboronated to B(1).

We have developed an interest in the interaction of small unsaturated and/or electron-rich molecules with polyhedral metallaboranes. This arises because metallaboranes that combine a redox-flexible transition-element centre with an electronically flexible boron 'B-frame' matrix should in principle permit interesting chemical manipulation of the unsaturated species. Conversely, the smaller reacting species could induce interesting changes in the metallaborane matrices.

Previous work in this area has been confined to few systems: for example, (*a*) the *closo* twelve-vertex 3,1,2-rhodadicarbadodecaboranes have been examined for alkene-hydrogenation catalysis;[2] (*b*) the *nido* ten-vertex 6-metalladecarboranes [6-(η^5-C$_5$Me$_5$)-6-RhB$_9$H$_{13}$][3] and [6-(η^5-C$_5$Me$_5$)-6-IrB$_9$H$_{13}$][4] react with MeNC to give [6-(η^5-C$_5$Me$_5$)-6,9-(MeNC)$_2$-*arachno*-6-MB$_9$H$_{13}$] (M = Rh or Ir) and [4-(η^5-C$_5$Me$_5$)-4-(MeNC)-*arachno*-4-IrB$_8$H$_{12}$], and (*c*) [6-(η^6-C$_6$Me$_6$)-*nido*-6-RuB$_9$H$_{13}$][5] reacts with MeNC to give NHMe$_2$ and [1-(η^6-C$_6$Me$_6$)-*isocloso*-1-RuB$_9$H$_9$] in a defined multistep redox process. In addition to these, (*d*) there is a series of reactions of CS$_2$ with a small selection of metallaheteroboranes:[6–9] these are particularly relevant to the present paper and are summarised separately below.

In terms of flexible metallaborane substrates with which to explore these types of reaction, we have previously found that the ten-vertex iridadecaboranes [6-H-6,6-(PPh$_3$)$_2$-*nido*-6-IrB$_9$H$_{13}$] **1** and [6-H-6-(PPh$_3$)-6-(*o*-Ph$_2$P-C$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5] **2** exhibit potentially appropriate redox behaviour. For example, both **1** and **2** readily undergo formal oxidation to the structurally interesting *isocloso*-type ten-vertex species [1-H-1-(PPh$_3$)-1-(*o*-Ph$_2$-PC$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_8$-2] **3** by simple dihydrogen-loss processes [equations (1) and (2)],[10] and the occurrence of P-aryl *ortho*-cycloboronation [equation (1)] suggests that a

$$\underset{\mathbf{1}}{[\mathrm{H(PPh_3)_2IrB_9H_{13}}]} \longrightarrow \underset{\mathbf{3}}{[\mathrm{H(PPh_3)(Ph_2PC_6H_4)IrB_9H_8}]} + 3\mathrm{H_2} \quad (1)$$

$$\underset{\mathbf{2}}{[\mathrm{H(PPh_3)(Ph_2PC_6H_4)IrB_9H_{12}}]} \longrightarrow \mathbf{3} + 2\mathrm{H_2} \quad (2)$$

$$\mathbf{1} \longrightarrow \mathbf{2} + \mathrm{H_2} \quad (3)$$

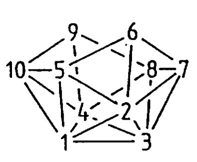
1 ⟶ **2** conversion [equation (3)] may readily occur as part of the **1** ⟶ **3** process. Further, the formation of these three compounds and their interconversions have been postulated to occur *via* open *isonido* intermediates, of which models have been isolated, and of which some may have co-ordinatively unsaturated iridium centres.[10–12] These processes occur readily, and therefore suggested to us that compounds such as **1**–**3** might undergo interesting redox processes with unsaturated molecules. In accord with this we have previously reported that **2** reacts with acetylene to give ten-vertex [2,2-(PH$_3$)$_2$-10-(PPh$_3$)-2-(*o*-Ph$_2$ PC$_6$H$_4$)-*closo*-2-IrB$_9$H$_7$-1], in which a unique reductive P-aryl stripping reaction has occurred, and ten-vertex [1,1-(η^2-1,4-C$_4$H$_4$)-5-(PPh$_3$)-1-(*o*-Ph$_2$PC$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_7$-2], in which acetylene oligomerisation has occurred.[1,13]

There is obvious interest in the further examination of the behaviour of unsaturated and/or electron-rich species with these types of metallaborane system. As mentioned above, there is some current interest in the reactions of CS$_2$ with metallated boron-containing cluster compounds. For example (*a*) the fluxional eleven-vertex *nido*-type 8,7-rhodathiaundecaborane [(PPh$_3$)$_2$RhSB$_9$H$_{10}$], together with the fluxional twelve-vertex *closo*-type rhodaheteroboranes [(PPh$_3$)$_2$HRhC$_2$B$_9$H$_{11}$] and [(PPh$_3$)$_2$HRhTeB$_{10}$H$_{10}$], each add CS$_2$ which thence becomes a dithioformyl ligand.[6,7] However, (*b*) under different conditions [(PPh$_3$)$_2$HRhTeB$_{10}$H$_{10}$] with CS$_2$ can give phosphonium betaine ligands that engender dimers of general formulation [Rh$_2$(TeB$_{10}$H$_{12}$)$_2${S$_2$CH(PPh$_3$)}$_2$],[8] and (*c*) conditions have also been found for the reaction of CS$_2$ with rhodadicarbaborane isomers of general formulation [(PPh$_3$)$_2$-HRhC$_2$B$_9$H$_{11}$] to give other types of phosphonium betaine ligands, SCH(PPh$_3$)$^-$ and SCH=C(PPh$_3$)S$^-$, bound to rhodium on the RhC$_2$B$_9$H$_{11}$ cluster.[9]

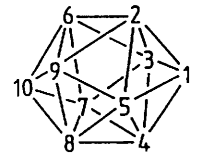
We now report the results of the reactions of CS$_2$ with the *nido* and *isocloso* ten-vertex iridaboranes **1**–**3**. The numbering systems for the clusters discussed are given in **I** (ten-vertex *nido*), **II** (ten-vertex *closo*) and **III** (ten-vertex *isocloso*); note that because of numbering conventions, the interconversions dealt with will generally change the formal numbering of a particular site.

---

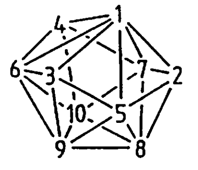
* Metallaborane reaction chemistry. Part 2.[1]



I



II



III

Results and Discussion

A solution of [6-H-6,6-$(PPh_3)_2$-*nido*-6-IrB_9H_{13}] **1** in CS_2 was heated at reflux for 2 h, and the resulting mixture separated chromatographically, to yield two metallaborane components. One was identified as unreacted bright yellow **1**, and the second, a black air-stable crystalline solid, as [2,10-$(PPh_3)_2$-2,6;2,9-(μ-$S_2CH)_2$-*closo*-2-IrB_9H_6] **4**, characterised as such by single-crystal X-ray diffraction analysis (Tables 1 and 2) and NMR spectroscopy (Table 3). The yield was 14%, corresponding to *ca.* 16% conversion of unrecovered compound **1**.

Crystals suitable for X-ray diffraction analysis were obtained from pentane–benzene–dichloromethane. Diffraction data were gathered at 120 K, and the analysis, apart from some solvent disorder, was straightforward. The structure is shown in Fig. 1, and selected interatomic distances are in Table 1, selected angles in Table 2. The $\{IrB_9\}$ cluster structure of compound **4** is seen to be a straightforward Williamsian[15] *closo*-type ten-vertex bicapped square antiprism with the metal atom in the 'tropical' 2 position. There is a PPh_3 ligand on the axial boron atom distant from iridium, B(10), and one on the metal atom, Ir(2), itself. The most interesting feature consists of the two SCHS dithioformato bridges linking Ir(2) to the B(6) and B(9) positions that are adjacent to Ir(2), but in the other tropical belt: these give a doubly bridged feature of pleasing symmetry (structure **IV**). Related dithioformato links have precedent in metallaheteroborane chemistry, for example (*a*) in [μ-8,8′-$(S_2CH)M(x,y\text{-}C_2B_9H_{10})_2$] (*x*,*y* = 1,2 or 1,7 for M = Co and 1,2 for M = Fe), in which the {SCHS} unit bridges between boron atoms on the two different clusters in a *commo*-metal *conjuncto* species[16–18] and (*b*) in [8,8-$(PPh_3)_2$-μ-8,9-(S_2CH)-*nido*-8,7-$RhSB_9H_9$][6] which exhibits a metal-to-boron {SCHS} linkage. As mentioned above, interesting reduction/degradation reactions of CS_2 with metal-bound PPh_3 centres in the 3,1,2 and 2,1,7 isomers of [$(PPh_3)_2HRhC_2B_9H_{11}$] have also recently been reported,[9] but now to give phosphonium betaine ligands $SCH(PPh_3)^-$ and $SCH{=}C(PPh_3)S^-$, a phenomenon related to a variety of other reductive additions of phosphine residues to CS_2 that have been observed in non-boron-containing transition-metal complexes.[19] However, these phosphonium betaine ligands have remained exclusively bound to the metal centre, and do not bridge from metal to boron as observed for the dithioformyl unit here in compound **4**, and also in [8,8-$(PPh_3)_2$-μ-8,9-(S_2CH)-*nido*-8,7-$RhSB_9H_9$].[6]

In terms of electronic bookkeeping, each {SCHS} moiety in compound **4** can be considered as a conventional two-electron donor to Ir(2) and as a straightforward one-electron substituent on boron. The compound is thence a conventional Wadian[20] ten-vertex *closo* cluster species with an 'octahedral' iridium(III) centre (*a*) that has three *exo*-polyhedral two-electron ligands, and (*b*) that contributes three orbitals and three electrons to the cluster bonding. Only three other *closo*-2-metalladecaborane clusters have been previously characterised: [2,2-$(PH_3)_2$-10-(PPh_3)-2-(*o*-$Ph_2PC_6H_4$)-*closo*-2-IrB_9H_7-1],[13] [2-(η^5-C_5Me_5)-3,10-$(PMe_2Ph)_2$-*closo*-2-RhB_9H_7][21] and the ten-vertex monorhodadecaborane subcluster of [(η^5-C_5Me_5)RhB_9-$(SMe_2)H_{10}RhB_9H_7(SMe_2)$].[22] All of these *closo*-type ten-vertex 2-metalladecaboranes have long B(6)–B(9) distances of *ca.* 200 pm, as also seen for compound **4** [199.0(12) pm], which characterise a tendency towards an '*isonido*' geometry (structure **V**) that has a four-membered open face (as depicted by the heavier lines). This tendency is also a common feature of many heteroboranes and metallaheteroboranes of the *closo* ten-vertex family, and is adequately discussed elsewhere.[12,23,24] The shorter distance from the Ir(2) atom to B(1) of 211.2(10) pm, compared to the distances to B(3) and to B(5) [230.3(10) and 229.6(10) respectively] is in accord with the shorter interatomic distances generally observed to the axial atoms in *closo* ten-vertex species. In addition the NMR $\delta(^{11}B)$ value for this B(1) position is at characteristically low field (+42.3) as often observed for a vertex of low cluster connectivity, particularly when adjacent to a metal atom.

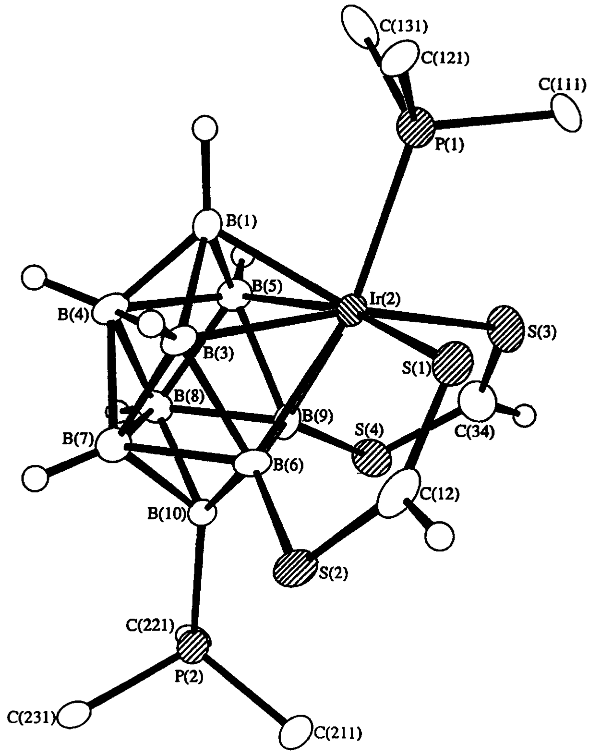
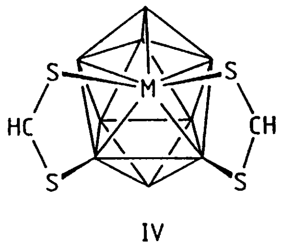
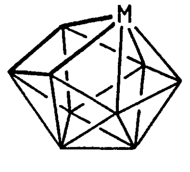


Fig. 1 An ORTEP[14] type diagram of the molecular structure of [2,10-$(PPh_3)_2$-2,6;2,9-(μ-$S_2CH)_2$-*closo*-2-IrB_9H_6] **4**. For clarity phenyl groups, with the exception of *ipso*-carbon atoms, have been omitted. Thermal ellipsoids for non-hydrogen atoms are drawn at the 50% probability level and hydrogen atoms are drawn with a small arbitrary radius



IV



V

The general NMR properties (Table 3) of compound **4** are generally consistent with the molecular structure (see also discussion below, near Fig. 2), confirming that the crystal selected for the X-ray work was representative of the bulk sample. The ^{11}B NMR spectrum has a 1:2:1:1:2:2 relative-intensity pattern, as expected from the C_s symmetry. Similarly, the ^1H NMR spectrum displayed the expected cluster BH relative-intensity pattern of 1:2:1:1:2. It also exhibited a characteristically low-field dithioformate proton signal at $\delta(^1H)$ +10.96.

The reaction of the P-aryl 5-*ortho*-cycloboronated derivative of compound **1**, *viz.* [6-H-6-(PPh_3)-6-(*o*-Ph_2P-

C_6H_4)-*nido*-6-IrB_9H_{12}-5] **2**,* is similar to that with **1**, but occurs somewhat more slowly, perhaps because the constraints of the *ortho*-cycloboronated link inhibit the flexibility of transition states. The reaction with CS_2 at reflux for 24 h gave the black air-stable solid [10-(PPh_3)-2,6;2,9-(μ-S_2CH)$_2$-2-(*o*-$Ph_2PC_6H_4$)-*closo*-2-IrB_9H_5-1] **5** as the only isolatable product in characterisable quantities. Starting material **2** was also recovered; the yield of **5** was 17% overall (54% based on **2** consumed). Compound **5** is the 1-*ortho*-cycloboronated analogue of **4**, readily characterised as such by an NMR comparison (Table 3 and Fig. 2). Thus, it has a similar ^{11}B chemical shift and 1:2:1:1:1:2 relative-intensity pattern to that for non-*ortho*-cycloboronated **4**, indicating a similar formulation with the same symmetry. The principal difference is that the lowest-field ^{11}B resonance, due to B(1), is some 10 ppm to lower field for compound **5**. Selective ^1H-{^{11}B} experiments show that this position is not associated with an *exo* ^1H resonance and it is therefore reasonably assigned to the point of *ortho*-cycloboronation. The lower shielding is also consistent with organic-for-hydrogen substitution,[25] all being consistent with the general formulation for compound **5**, as represented schematically in structure **VI**.

In Fig. 2 the ^{11}B and ^1H NMR cluster chemical shifts of compounds **4** and **5** are compared with those of the previously reported *closo*-2-metalladecaboranes[13,21] for which assignments exist. There are clear ^{11}B and ^1H parallels with the closely related species [2,2-(PH_3)$_2$-10-(PPh_3)-2-(*o*-Ph_2P-C_6H_4)-*closo*-2-IrB_9H_7-1] **6**,[13] and also with the less closely related rhodaborane [2-(η^5-C_5Me_5)-3,10-(PMe_2Ph)$_2$-*closo*-2-RhB_9H_7] **7**.[21] Relative intensities, identification of the substituted positions by lack of associated ^1H(*exo*) resonances, and in particular, comparison with the phosphine species **6**, permits assignment of the spectra of compounds **4** and **5**. Salient features include a downfield shift of the (6,9) positions upon substitution of S for H, and a downfield shift of the (1) position on *ortho*-cyclophenylation as mentioned above. Assignment between the (3,5) and (7,8) resonances is perhaps less unequivocal, but for both **4** and **5** the lower-field resonance of the two is ascribed to ^{11}B(3,5) on the basis that the site nearer the iridium atom is more likely to be susceptible to transoid effects due to the change between phosphine ligands on **6** and sulfur-based ligands in **4** and **5**.

Table 1 Selected interatomic distances (pm) for [2,10-(PPh_3)$_2$-2,6;2,9-(μ-S_2CH)$_2$-*closo*-2-IrB_9H_6] **4**, with estimated standard deviations (e.s.d.s) in parentheses

P(1)–Ir(2)	237.3(4)	B(1)–Ir(2)	211.2(10)
S(1)–Ir(2)	236.2(4)	S(3)–Ir(2)	239.2(4)
B(3)–Ir(2)	230.3(10)	B(5)–Ir(2)	229.6(10)
B(6)–Ir(2)	225.9(9)	B(9)–Ir(2)	227.4(9)
B(10)–P(2)	190.2(9)		
C(12)–S(1)	164.8(9)	C(34)–S(3)	163.7(9)
C(12)–S(2)	167.3(9)	C(34)–S(4)	168.0(9)
B(6)–S(2)	187.7(9)	B(9)–S(4)	188.8(9)
B(3)–B(1)	177.9(12)	B(5)–B(1)	175.4(13)
B(4)–B(1)	169.1(12)		
B(6)–B(3)	181.1(12)	B(9)–B(5)	180.6(12)
B(7)–B(3)	183.4(12)	B(8)–B(5)	182.8(12)
B(4)–B(3)	183.9(13)	B(5)–B(4)	187.5(13)
B(7)–B(4)	178.8(12)	B(8)–B(4)	179.9(12)
B(7)–B(6)	182.1(12)	B(9)–B(8)	180.7(12)
B(9)–B(6)	199.0(12)	B(8)–B(7)	181.3(13)
B(10)–B(6)	170.3(12)	B(10)–B(9)	168.1(12)
B(10)–B(7)	169.4(13)	B(10)–B(8)	169.3(12)

Table 2 Selected angles (°) between interatomic vectors for compound **4**, with e.s.d.s in parentheses

S(1)–Ir(2)–P(1)	86.0(2)	S(3)–Ir(2)–P(1)	85.2(2)
S(3)–Ir(2)–S(1)	90.7(2)	B(1)–Ir(2)–P(1)	80.4(3)
B(1)–Ir(2)–S(1)	127.6(3)	B(1)–Ir(2)–S(3)	137.4(2)
B(3)–Ir(2)–P(1)	111.7(3)	B(5)–Ir(2)–P(1)	105.8(3)
B(3)–Ir(2)–S(1)	94.3(3)	B(5)–Ir(2)–S(3)	101.1(3)
B(3)–Ir(2)–S(3)	162.7(2)	B(5)–Ir(2)–S(1)	163.9(2)
B(3)–Ir(2)–B(1)	47.3(3)	B(5)–Ir(2)–B(1)	46.7(3)
B(5)–Ir(2)–B(3)	71.2(4)		
B(6)–Ir(2)–P(1)	155.5(2)	B(9)–Ir(2)–P(1)	146.7(2)
B(6)–Ir(2)–S(1)	84.8(3)	B(9)–Ir(2)–S(3)	83.7(3)
B(6)–Ir(2)–S(3)	117.5(3)	B(9)–Ir(2)–S(1)	125.4(3)
B(6)–Ir(2)–B(1)	87.4(4)	B(9)–Ir(2)–B(1)	86.8(4)
B(6)–Ir(2)–B(3)	46.8(3)	B(9)–Ir(2)–B(5)	46.6(3)
B(6)–Ir(2)–B(5)	80.1(4)	B(9)–Ir(2)–B(3)	79.8(4)
B(9)–Ir(2)–B(6)	52.1(4)		
C(12)–S(1)–Ir(2)	108.7(3)	C(34)–S(3)–Ir(2)	109.5(4)
B(6)–S(2)–C(12)	102.5(4)	B(9)–S(4)–C(34)	102.5(4)
S(2)–C(12)–S(1)	126.7(5)	S(4)–C(34)–S(3)	126.8(6)
B(3)–B(1)–Ir(2)	72.0(5)	B(5)–B(1)–Ir(2)	72.2(5)
B(4)–B(1)–Ir(2)	111.3(5)		
B(1)–B(3)–Ir(2)	60.7(4)	B(1)–B(5)–Ir(2)	61.2(4)
B(4)–B(3)–Ir(2)	98.4(5)	B(4)–B(5)–Ir(2)	97.6(5)
B(6)–B(3)–Ir(2)	65.3(4)	B(9)–B(5)–Ir(2)	66.1(4)
B(7)–B(3)–Ir(2)	111.0(5)	B(8)–B(5)–Ir(2)	111.3(5)
B(3)–B(6)–Ir(2)	67.9(4)	B(5)–B(9)–Ir(2)	67.4(4)
B(7)–B(6)–Ir(2)	113.5(5)	B(8)–B(9)–Ir(2)	113.1(5)
B(10)–B(6)–Ir(2)	116.9(5)	B(10)–B(9)–Ir(2)	117.2(5)
B(9)–B(6)–Ir(2)	64.3(4)	B(6)–B(9)–Ir(2)	63.6(4)
S(2)–B(6)–Ir(2)	116.5(4)	S(4)–B(9)–Ir(2)	117.4(4)
B(3)–B(6)–S(2)	114.8(6)	B(5)–B(9)–S(4)	118.0(6)
B(7)–B(6)–S(2)	121.6(6)	B(8)–B(9)–S(4)	122.8(6)
B(9)–B(6)–S(2)	141.8(5)	B(6)–B(9)–S(4)	138.5(5)
B(10)–B(6)–S(2)	118.0(5)	B(10)–B(9)–S(4)	115.1(6)
B(6)–B(10)–P(2)	131.2(5)	B(9)–B(10)–P(2)	129.0(6)
B(7)–B(10)–P(2)	128.6(6)	B(8)–B(10)–P(2)	127.0(6)
B–B–B(acute)	53.5(5)–64.8(5)	B–B–B (intermediate)	86.8(5)–104.0(6)
B–B–B(obtuse)	110.2(6)–116.5(7)		

Table 3 Selected ^{11}B, ^1H and ^{31}P NMR data for compound **4** and [10-(PPh_3)-2,6;2,9-(μ-S_2CH)$_2$-2-(*o*-$Ph_2PC_6H_4$)-*closo*-2-IrB_9H_5-1] **5** in CD_2Cl_2 solution at 294–297 K

	4[a]		**5**[b]	
Assignment	δ(^{11}B)	δ(^1H)	δ(^{11}B)	δ(^1H)
1	+42.3	+6.89	+52.6	[C substituted]
6,9	+3.7	[S substituted]	+3.7	[S substituted]
4	+0.3	+3.52	−2.9	+3.91
10	−11.2[c]	[P substituted]	−12.7[d]	[P substituted]
3,5	−16.3	+0.56	−17.0	+0.73
7,8	−27.8	−1.19	−27.1	−0.53
S_2CH	—	+10.96	—	−10.79

[a] δ(^{31}P) −2.8 (sharper) (iridium substituent) and +11.3 (broader) (boron substituent). [b] δ(^{31}P) +33.7 (sharper) (iridium substituent) and +14.8 (broader) (boron substituent). [c] $^1J(^{31}P-^{11}B)$ *ca.* 190 Hz. [d] $^1J(^{31}P-^{11}B)$ *ca.* 185 Hz.

---

* The actual starting material **2** consisted of a mixture of two isomers, with what have been described[1,10] as 'symmetric' (*sym*) and 'asymmetric' (*asym*) arrangements of the phosphine ligands about the iridium atom. At higher temperatures there is a rapid *sym* ⟶ *asym* conversion,[10] and in reactions conducted at higher temperatures than in this work[1] the *sym* isomer **2a** would not be present after the first few minutes. In the experiments reported here a little *sym* isomer is recovered in the unreacted material (*sym*:*asym* ratios *ca.* 1:4), but, since the reaction takes some time and only one product is obtained, we think it unlikely that the starting ratio of isomers influences the course of the reaction.

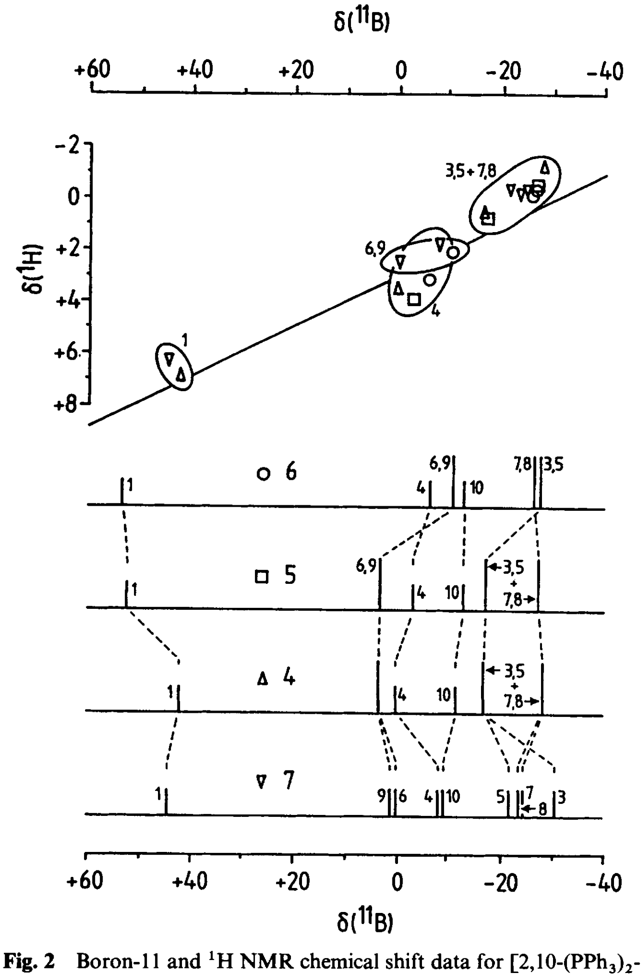
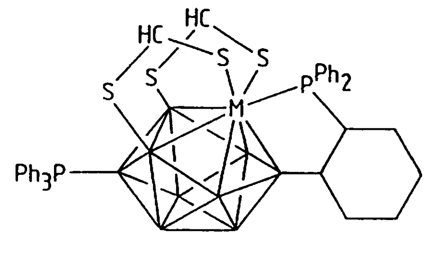


Fig. 2 Boron-11 and ^{1}H NMR chemical shift data for $[2,10\text{-}(PPh_3)_2\text{-}2,6;2,9\text{-}(\mu\text{-}S_2CH)_2\text{-}\mathit{closo}\text{-}2\text{-}IrB_9H_6]$ **4** (△), $[10\text{-}(PPh_3)\text{-}2,6;2,9\text{-}(\mu\text{-}S_2CH)_2\text{-}2\text{-}(o\text{-}Ph_2PC_6H_4)\text{-}\mathit{closo}\text{-}2\text{-}IrB_9H_5\text{-}1]$ **5** (□), $[2,2\text{-}(PH_3)_2\text{-}10\text{-}(PPh_3)\text{-}2\text{-}(o\text{-}Ph_2PC_6H_4)\text{-}\mathit{closo}\text{-}2\text{-}IrB_9H_7\text{-}1]$ **6** (○)[13] and $[2\text{-}(\eta^5\text{-}C_5Me_5)\text{-}3,10\text{-}(PMe_2Ph)_2\text{-}\mathit{closo}\text{-}2\text{-}RhB_9H_7]$ **7** (▽).[21] The uppermost diagram plots δ(^{1}H) *versus* δ(^{11}B) for BH(*exo*) units for compounds **4**–**7**; the slope, δ(^{1}H) : δ(^{11}B), is 1 : 10.5, intercept +3.0 in δ(^{1}H) (compare ref. 21). The bottom diagrams are stick representations of the chemical shifts and relative intensities in the ^{11}B NMR spectra of the four compounds, with lines joining resonances for equivalent sites in the four species

The **1** ⟶ **4** and **2** ⟶ **5** *nido* ⟶ *closo* ten-vertex cluster-closure processes contrast to the reported reaction[6] of CS_2 with eleven-vertex $[8,8\text{-}(PPh_3)_2\text{-}8,7\text{-}RhSB_9H_{10}]$ **8** to give $[8,8\text{-}(PPh_3)_2\text{-}8,9\text{-}(\mu\text{-}S_2CH)_2\text{-}\mathit{nido}\text{-}8,7\text{-}RhSB_9H_9]$ **9**, in which the open *nido* geometry is retained. Here the starting metallathiaborane **8** has eleven-vertex *nido* geometry but, because of the sixteen-electron nature of the transition-element centre,[26] it has a formally *closo* electron count, the two-electron 'electron deficiency' decrement being localised on the transition-element centre. The formation of its *nido* product **9** entails a formal cluster two-electron gain associated with the assimilation of the CS_2, so that **9** now has an eighteen-electron transition-element centre and is thereby of less ambiguous eleven-vertex all-round *nido* character. With each of the conversions **1** ⟶ **4** and **2** ⟶ **5**, by contrast, the assimilation of two CS_2 units is accompanied by a triple dihydrogen loss, resulting in a net two-electron cluster loss [equations (4) and (5) below].

These contrasting electronic implications are compounded in the reaction of CS_2 with the closed cluster compound $[1\text{-}H\text{-}1\text{-}(PPh_3)\text{-}1\text{-}(o\text{-}Ph_2PC_6H_4)\text{-}\mathit{isocloso}\text{-}1\text{-}IrB_9H_8\text{-}2]$ **3**. Compound **3**, which has a three-fold *isocloso* geometry (structure **III**) rather than a more conventional four-fold *closo* shape (**II**), readily derives from the mild thermolysis in neutral solvents of the *nido* starting compounds **1** and **2** [equations (1) and (2) above],[10] and it was of interest to see if and how it too would react with CS_2. A parallel to the reactions of CS_2 with the *closo* twelve-vertex species $[(PPh_3)_2HRhTeB_{10}H_{10}]$ and $[(PPh_3)_2HRhC_2B_9H_9]$,[7] in both of which the *exo*-polyhedral $\{RhH(PPh_3)_2\}$ grouping is converted into an effectively isolobal $\{Rh(\eta^2\text{-}S_2CH)(PPh_3)\}$ moiety, with the basic cluster skeletons unperturbed, might suggest an analogous formation of $[1,1\text{-}\eta^2\text{-}(S_2CH)\text{-}1\text{-}(o\text{-}Ph_2PC_6H_4)\text{-}\mathit{isocloso}\text{-}IrB_9H_8\text{-}2]$ from **3**. This, however, proves not to be so. In fact, the reaction of compound **3** with refluxing CS_2 for 5 h, gave, surprisingly, black air-stable **5** with a conventional *closo* cluster structure. The only other metallaborane component in the reaction mixture in significant quantity was the bright yellow starting material **3**. The isolated yield of **5** was 37% overall (73% based on **3** consumed). An *isocloso* ⟶ *closo* conversion, or its converse, has not previously been observed, although the structures are related by a diamond–square–diamond (d.s.d.) process across a pair of adjacent triangular faces (see, for example, hatched lines in **IX** below). The d.s.d. process would go *via* an *isonido*-structured intermediate of schematic structure type **V**. This structure type has reasonably been invoked for ten-vertex *closo* ⟶ *closo* interconversions[27] and also for a variety of other ten-vertex reaction processes that are related to the *nido* ⟶ *closo* processes described here.[1,10,12,27–29]



VI

In this context the mechanisms of the reactions described above are of interest, because the products are formed relatively cleanly, and simple stoichiometries may be written [equations (4)–(6)]. As far as the CS_2 ⟶ {SCHS} reductions in the

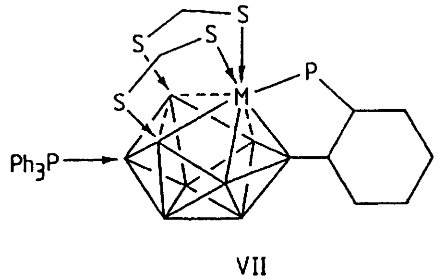
$$\underset{\mathbf{1}}{[H(PPh_3)_2IrB_9H_{13}]} + 2CS_2 \longrightarrow \underset{\mathbf{4}}{[(PPh_3)(S_2CH)_2IrB_9H_6(PPh_3)]} + 3H_2 \quad (4)$$

$$\underset{\mathbf{2}}{[H(PPh_3)(Ph_2PC_6H_4)IrB_9H_{12}]} + 2CS_2 \longrightarrow \underset{\mathbf{5}}{[(S_2CH)_2(Ph_2PC_6H_4)IrB_9H_5(PPh_3)]} + 3H_2 \quad (5)$$

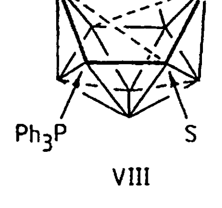
$$\underset{\mathbf{3}}{[H(PPh_3)(Ph_2PC_6H_4)IrB_9H_8]} + 2CS_2 \longrightarrow \mathbf{5} + H_2 \quad (6)$$

conversions **1** ⟶ **4** and **2** ⟶ **5** are concerned [equations (4) and (5)], there is probably a high mobility of hydrogen atoms associated with the open-face cluster atoms of iridaboranes of this type, so the precise pathway must remain speculative.[10,12,28] It is possible to be a little more specific for the concomitant cluster-closure process. In the **2** ⟶ **5** conversion the *ortho*-cycloboronated link effectively labels the cluster and suggests that cluster closure is a classical *nido* ⟶ *closo* process (hatched lines in **VII** and **VIII**). The addition of two CS_2 units and the loss of three dihydrogens must involve a multistep process, and it is likely that this goes *via* an *isonido* intermediate of which the four-membered open face is defined by the heavier lines in structure **VIII**. *A priori*, in the **2** ⟶ **5** conversion it is not clear which of the two possible four-membered open faces will be favoured, *syn* or *anti* to the $C_6H_4PPh_2$-*o* group, but the formation of the same product **5** from the *isocloso* starting compound **3** (schematic structure **IX**) suggests that it is the one *anti* to the *ortho*-cyclophenylation site (the nearer face in structure **VIII**). A reasonable interpretation is therefore attack by CS_2 at the *nido*-6-metalladecaboranyl (5) and (9) positions (**VIII**), for which there is precedent,[21,30] although it is not possible to decide whether this precedes or follows attack at the metal centre. Additionally, the timing of the attack of PPh_3 at the *nido*-6-metalladecaboranyl (10) position is not known, although the resulting incidence of a two-electron ligand in this position in ten-vertex *closo*-2-metalladecaboranes and *closo*-2-metallaheteroboranes is not uncommon.[21,22,31]

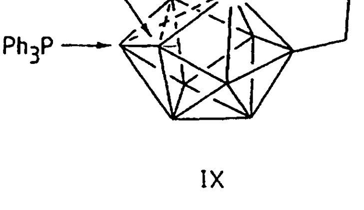
An *isocloso* to *closo* conversion, as exemplified by the reaction of compound **3** to give **5** [equation (6)] is of interest because it is previously unobserved, and because the precise relationship between *isocloso* and *closo* structures is not unequivocally established.[10,12,32–35] Here it seems reasonable to propose a d.s.d. mechanism (hatched lines in structure **IX**) associated with the addition of the sulfur and phosphorus ligands about the periphery of the faces involved in the d.s.d. process. This could imply a common *isonido* intermediate (compare structures **VII–IX**) in the latter stages of the formation of compound **5** from either *isocloso* **3** or *nido* **2**. The lack of an open face in the *isocloso* starting compound **3** could imply an initial oxidative addition of IrH to CS_2; the addition of PPh_3 at what becomes B(10) would thence constitute a two-electron addition to the cluster. Here it may be noted that there is some question as to whether (*a*) *n*-vertex *isocloso* cluster structures may involve $(2n + 2)$ electrons in the cluster bonding scheme and thereby require a four-orbital involvement of the metal centre in the cluster bonding or (*b*) they involve $2n$ electrons and thereby have a hypo-*closo* electronic structure.[32–34] In the $3 \longrightarrow 5$ conversion, therefore, it remains a moot point[10,11,23,32–37] whether this two-electron addition to the cluster engenders (*a*) a reduction from iridium(V) to iridium(III), with a concomitant reduction in the iridium orbital contribution and a corresponding *isocloso* ⟶ *closo* change with a formal *closo* $(2n + 2)$ electron count in both **3** and **5**, or (*b*) converts a bonding scheme involving only $2n$ electrons into the conventional *closo* $(2n + 2)$ one, with an iridium(III) valence scheme in both **3** and **5**.



VII



VIII



IX

Experimental

General

The starting materials [6-H-6,6-$(PPh_3)_2$-*nido*-6-IrB_9H_{13}] **1**, [6-H-6-(PPh_3)-6-(*o*-$Ph_2PC_6H_4$)-*nido*-6-IrB_9H_{12}-5] **2** and [1-H-(1-PPh_3)-1-(*o*-$Ph_2PC_6H_4$)-*isocloso*-1-IrB_9H_8-2] **3** were prepared as described elsewhere.[10,29] All solvents were dried and degassed before use, and all reactions were carried out under an atmosphere of dry dinitrogen, although subsequent manipulations were carried out in air. Preparative and analytical thin-layer chromatography (TLC) were carried out using silica gel G (with a fluorescent indicator) as stationary phase, 1 mm thick (Fluka type GF-254) on glass plates (preparative) and 250 μm foil-backed plates (Whatman type AL SIL G/UV_{254}) (analytical).

NMR spectroscopy

Boron-11, phosphorus-31 and proton spectra were obtained at *ca.* 2.35 and/or 9.4 T using JEOL FX 100 or Bruker AM 400 instrumentation, with the ^1H-{^{11}B} experiments as described previously.[35–38] Chemical shifts δ are given in ppm to high frequency (low field) of Ξ 100 ($SiMe_4$) for ^1H (± 0.05 ppm), Ξ 40.480 730 (nominally 85% H_3PO_4) for ^{31}P (± 0.5 ppm) and Ξ 32.083 971 MHz (nominally $BF_3{\cdot}OEt_2$ in $CDCl_3$)[25] for ^{11}B (± 0.5 ppm), Ξ being defined as in ref. 39.

Reactions with CS_2

Compound 1. In a typical procedure a solution of [6-H-6,6-$(PPh_3)_2$-*nido*-6-IrB_9H_{13}] **1** (80 mg, 97 μmol) in CS_2 (20 cm^3) was heated at reflux for 2 h, during which time the initially yellow solution turned purple-black. The solution was then concentrated on a rotary evaporator, and separated using TLC with CH_2Cl_2–hexane (1 : 1) as liquid phase. Two main components were apparent. Extraction of these from the silica with CH_2Cl_2 yielded unreacted yellow starting material **1** (R_f 0.40; 7 mg, 8 μmol) and a dark purple-black material identified as [2,10-$(PPh_3)_2$-2,6;2,9-$(\mu\text{-}S_2CH)_2$-*closo*-2-IrB_9H_6] **4** (R_f 0.40; 13 mg, 13 μmol, 14%), identified by X-ray crystallography and NMR spectroscopy as described. Crystals suitable for single-crystal X-ray diffraction analysis were grown by slow diffusion of pentane through a layer of benzene into a concentrated solution of **4** in CH_2Cl_2. Mass spectrometry [70 eV (*ca.* 1.12×10^{-17} J) electron-impact ionisation] gave m/z_{max} 712, corresponding to $\{M^+ - PPh_3\}$. In addition to the two main components, other darkly coloured materials were present but in quantities too small for characterisation. There was also intractable material.

Compound 2. A solution of [6-H-6-(PPh_3)-6-(*o*-Ph_2P-C_6H_4)-*nido*-6-IrB_9H_{12}-5] **2** (isomer proportions *ca.* 75% *sym* **2a** : 25% *asym* **2b**) (40 mg, 48 μmol) in CS_2 (20 cm^3) was heated at reflux for 24 h, during which time the initially yellow solution turned black. It was then concentrated on a rotary evaporator, and separated using TLC with CH_2Cl_2–hexane (1 : 1) as liquid phase. Three main components were apparent. Extraction of these from the silica with CH_2Cl_2 yielded unreacted yellow starting-material isomers **2a** (R_f 0.45; 5 mg) and **2b** (R_f 0.35; 20 mg), and a dark purple-black material identified as [10-(PPh_3)-2,6;2,9-$(\mu\text{-}S_2CH)_2$-2-(*o*-$Ph_2PC_6H_4$)-*closo*-2-IrB_9H_5-1] **5** (R_f 0.20; 8 mg, 8 μmol, 17%), identified principally by NMR spectroscopy as described. As above, there were additional low-yield molecular polyboron species present, and a quantity of intractable material.

Compound 3. A solution of [1-H-1-(PPh_3)-1-(*o*-Ph_2P-C_6H_4)-*isocloso*-1-IrB_9H_8-2] **3** (55 mg, 67 μmol) in CS_2 (20 cm^3) was heated at reflux for 5 h, during which time the initially yellow solution turned purple-black. It was then concentrated on a rotary evaporator, and separated using TLC with CH_2Cl_2–hexane (1:1) as liquid phase. Two main components were apparent. Extraction of these from the silica with CH_2Cl_2 yielded unreacted yellow starting material **1** (R_f 0.40; 17 mg, 21 μmol) and a dark purple-black material identified as compound **5** (R_f 0.20; 24 mg, 25 μmol, 37%) as described above. Mass spectrometry (70 eV electron-impact ionisation) gave m/z_{max} 972, corresponding to M^+. A third black band (R_f 0.12) contained a mixture of uncharacterised metallapolyboranes in very small yield. There was also intractable material present.

Crystallography

All crystallographic measurements on compound **4** were carried out on a Stoe STADI4 X-ray diffractometer operating in the ω–θ scan mode using an on-line profile-fitting method[40] and graphite-monochromated copper Kα X-radiation (λ = 154.184 pm). The data set was corrected for absorption semiempirically using azimuthal ψ scans (minimum and maximum transmission factors 0.5095 and 0.7432 respectively).

The structure was determined *via* standard heavy-atom and Fourier-difference methods and refined by full-matrix least squares using SHELX 76.[41] The asymmetric part of the unit contained two CH_2Cl_2 molecules, one of which was disordered over three positions. All non-hydrogen atoms were refined (based on F) with anisotropic thermal parameters with the exception of the carbon and partial chlorine atoms of the disordered CH_2Cl_2 molecule which were refined isotropically. The phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C 139.5 pm). The phenyl hydrogen atoms were included in calculated positions (C–H 96 pm) and refined with an overall isotropic thermal parameter; CS_2 atoms and borane-cage hydrogen atoms were located on a Fourier-difference synthesis and freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0004(F_o)^2]^{-1}$ was used.

Crystal data. $C_{38}H_{38}B_9IrP_2S_4\cdot2CH_2Cl_2$, 0.57 × 0.27 × 0.19 mm, $M = 1144.31$ (includes solvate molecules), monoclinic, space group $P2_1/n$, $a = 1566.5(1)$, $b = 1792.3(2)$, $c = 1695.0(1)$ pm, $\beta = 98.613(6)°$, $U = 4.7053(7)$ mm^3, $Z = 4$, $D_c = 1.62$ Mg m^{-3}, $\mu = 31.88$ cm^{-1}, $F(000) = 2264$.

Data collection. $4.0 < 2\theta < 50.0°$, 8590 data collected, 5608 with $I > 2.0\sigma(I)$ considered observed, $T = 120$ K.

Structure refinement. Number of parameters = 508, $R = 0.0351$, $R' = 0.0540$, maximum $\Delta/\sigma = 0.44$ [in U_{11} of H(7)], maximum and minimum residual electron density +1.08 and −0.92 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/153.

Acknowledgements

We thank the University of Leeds for the award of a Henry Ellison award (to R. S. C.), the SERC (now the EPSRC) for equipment grants, and Mr. D. Singh for mass spectrometry.

References

1 J. Bould, P. Brint, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1993, 2335.

2 M. F. Hawthorne, in *Advances in Boron and the Boranes*, eds. J. E. Liebman A. Greenberg and R. E. Williams, VCH, Weinheim, 1988, ch. 8, pp. 225–233 and refs. therein.

3 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 2809.

4 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1989, 1465.

5 E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, Z. Sisan and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1762.

6 G. Ferguson, M. C. Jennings, A. J. Lough, S. Coughlan, T. R. Spalding, J. D. Kennedy, X. L. R. Fontaine and B. Štíbr, *J. Chem. Soc., Chem. Commun.*, 1990, 891.

7 G. Ferguson, Faridoon and T. R. Spalding, *Acta Crystallogr., Sect. C*, 1988, **44**, 1360; G. Ferguson, S. Coughlan, T. R. Spalding, X. L. R. Fontaine, J. D. Kennedy and B. Štíbr, *Acta Crystallogr., Sect. C*, 1990, **46**, 1402.

8 Faridoon, T. R. Spalding, G. Ferguson, J. D. Kennedy and X. L. R. Fontaine, *J. Chem. Soc., Chem. Commun.*, 1989, 906.

9 G. Ferguson, J. F. Gallagher, M. C. Jennings, S. Coughlan, T. R. Spalding, J. D. Kennedy and X. L. R. Fontaine, *J. Chem. Soc., Chem. Commun.*, 1994, 1595.

10 J. Bould, J. D. Kennedy and N. N. Greenwood, *J. Chem. Soc., Dalton Trans.*, 1990, 1451.

11 J. Bould, P. Brint, J. D. Kennedy and M. Thornton-Pett, *Acta Crystallogr., Sect. C*, 1990, **46**, 1010.

12 J. Bould, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1992, 563.

13 J. Bould, P. Brint, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1763.

14 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

15 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210: *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 64; *Adv. Organomet. Chem.*, 1994, **36**, 1.

16 M. R. Churchill, K. Gold, J. N. Francis and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1969, **91**, 1222.

17 M. R. Churchill and K. Gold, *Inorg. Chem.*, 1971, **10**, 1928.

18 J. N. Francis and M. F. Hawthorne, *Inorg. Chem.*, 1971, **10**, 594.

19 See, for example, D. Miguel, J. A. Miguel, V. Riera and X. Solans, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1014; J. L. Moler, D. P. Eyman and L. M. Mallis, *Inorg. Chem.*, 1992, **31**, 1816.

20 K. Wade, *Chem. Commun.*, 1971, 792; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

21 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1987, 1431.

22 E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1262.

23 J. D. Kennedy and B. Štíbr, *Current Topics in the Chemistry of Boron*, ed. G. W. Kabalka, Royal Society of Chemistry, Cambridge, 1994, pp. 285–292.

24 B. Štíbr, J. D. Kennedy, E. Drdáková and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1994, 229.

25 See, for example, J. D. Kennedy, in *Multinuclear NMR*, ed. J. Mason, Plenum, London and New York, 1987, pp. 221–254 and refs. therein.

26 See, for example, J. D. Kennedy, *Main Group Metal Chem.*, 1989, **12**, 149 and refs. therein.

27 M. Bown, T. Jelínek, B. Štíbr, S. Heřmánek, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1988, 974.

28 J. Bould, J. E. Crook, J. D. Kennedy and M. Thornton-Pett, *Inorg. Chim. Acta*, 1992, **203**, 193.

29 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 1441.

30 J. W. Lott and D. F. Gaines, *Inorg. Chem.*, 1974, **13**, 2261.

31 N. W. Alcock, J. G. Taylor and M. G. H. Wallbridge, *J. Chem. Soc., Chem. Commun.*, 1983, 1168.

32 R. T. Baker, *Inorg. Chem.*, 1986, **25**, 109.

33 J. D. Kennedy, *Inorg. Chem.*, 1986, **25**, 111.

34 R. L. Johnson and D. M. P. Mingos, *Inorg. Chem.*, 1986, **25**, 3321; R. L. Johnson, D. M. P. Mingos and P. Sherwood, *New J. Chem.*, 1991, **15**, 831.

35 S. K. Boocock, J. Bould, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1982, 713.

36 J. D. Kennedy and B. Wrackmeyer, *J. Magn. Reson.*, 1980, **38**, 529.

37 J. D. Kennedy and N. N. Greenwood, *Inorg. Chim. Acta*, 1980, **38**, 93.

38 T. C. Gibb and J. D. Kennedy, *J. Chem. Soc., Faraday Trans. 2*, 1982, 525.

39 W. McFarlane, *Proc. R. Soc. London, Ser. A*, 1986, **306**, 185.

40 W. Clegg, *Acta Crystallogr., Sect. A*, 1987, **37**, 22.

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

Received 9*th January* 1996; *Paper* 6/00189K