Polyhedral Iridathiaborane Chemistry. Reactions of *nido*-6-SB_9H_{11} and of [*arachno*-6-SB_9H_{12}]$^-$ with [{Ir(η^5-C_5Me_5)Cl_2}$_2$] to give *nido*-8,7-Iridathiaundecaboranes. A Nuclear Magnetic Resonance and Structural Study*

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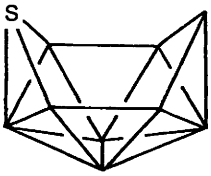
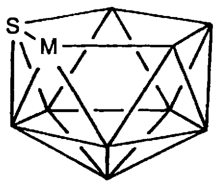
The reaction of [{Ir(η^5-C_5Me_5)Cl_2}$_2$] with *nido*-6-SB_9H_{11} and a non-nucleophilic base yields [8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{11}$] **1**, whereas with the [*arachno*-6-SB_9H_{12}]$^-$ anion it yields [8-(η^5-C_5Me_5)-9-Cl-*nido*-8,7-$IrSB_9H_{10}$] **2**, [8-(η^5-C_5Me_5)-10-Cl-*nido*-8,7-$IrSB_9H_{10}$] **3** and [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$] **4**. With [Ir(CO)Cl(PPh_3)$_2$], Cs[B_9H_{12}] yields a compound formulated as [*exo*-9-{Cl-*trans*-(PPh_3)$_2$-*cis*-H_2Ir}-*arachno*-6-SB_9H_{11}] which, on thermolysis, yields 9-(PPh_3)-*arachno*-6-SB_9H_{11}. The crystal and molecular structures of Cs[*arachno*-6-SB_9H_{12}] and compound **2** have been established by single-crystal X-ray diffraction analysis, and all the iridathiaboranes have been examined in detail by ^1H and ^{11}B single and multiple magnetic resonance spectroscopy.

We have recently developed an interest in the chemistry of the *nido* and *arachno* ten-vertex species 6-SB_9H_{11} and [6-SB_9H_{12}]$^-$ (both of schematic structure **I**),[1–5] and here report the isolation and characterization, by NMR spectroscopy and single-crystal X-ray diffraction analysis, of some *nido* eleven-vertex iridathiaboranes of schematic structure **II** arising from the reactions of [{Ir(η^5-C_5Me_5)Cl_2}$_2$] with *nido*-6-SB_9H_{11} and [*arachno*-6-SB_9H_{12}]$^-$. We also report the tentative identification of an unstable *closo*-type eleven-vertex species of cluster configuration **III**. As background to this work it is also convenient to report here work we have done on the crystal and molecular structure of Cs[*arachno*-6-SB_9H_{12}]. Other recent background work on the incorporation of the M(η^5-C_5Me_5) moiety (M = Rh or Ir) into boron-containing polyhedral clusters is in refs. 1, 3 and 6–15.



I



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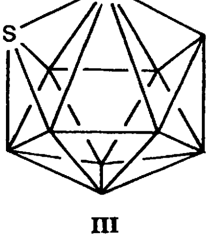
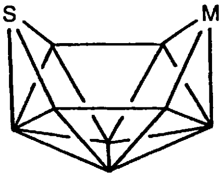
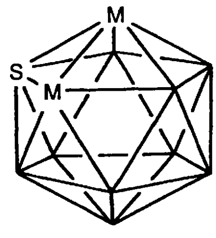


III

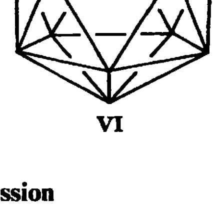
Surprisingly, contiguous metallaheteroborane chemistry where the heteroatom is sulphur has previously been but sparsely investigated; so far as we are aware well characterized compounds are limited to the *arachno* ten-vertex species [9,9-(PPh_3)$_2$-*arachno*-9,6-$PtSB_8H_{10}$] of schematic structure **IV**,[16,17] the *nido* eleven-vertex species [8-H-8,8-(PPh_3)$_2$-*nido*-8,7-$PtSB_9H_{10}$] (of schematic structure **II**)[18] and the *closo* twelve-vertex species [2,3-(η^5-C_5Me_5)$_2$-7-Cl-*closo*-2,3,1-$Rh_2SB_9H_8$] (of schematic cluster structure **V**).[19] Additional species reasonably identified are a twelve-vertex *closo* compound [2-H-2,2-(PPh_3)$_2$-*closo*-2,1-$RhSB_{10}H_{10}$] (of schematic configuration **VI**)[20] and several eleven-vertex *nido* compounds of nickel and palladium[21] (of schematic configuration **II**). Some platinum and palladium complexes of the eleven-vertex *closo*-type configuration **III** have also been proposed,[21] although it has been claimed[16] that these are more likely to be *arachno* ten-vertex species of configuration **IV**. Two iron species of schematic configurations **II** and **VI** have also been reported,[22a] and very recently rhodium species of schematic structures **II** and **V** have been characterized.[22b]



IV



V



VI

Results and Discussion

(1) *Preparation and Isolation of Three* nido-8,7-*Iridathiaundecaboranes* **1–3**.—The reaction of [{Ir(η^5-C_5Me_5)Cl_2}$_2$]

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Crystallographic data for Cs[SB_9H_{12}] and compound **2***

Formula	$H_{12}B_9CsS$	$C_{10}H_{25}B_9ClIrS$
M	274.37	502.35
a/pm	839.2(1)	988.0(2)
b/pm	1079.0(1)	1480.0(3)
c/pm	1134.2(1)	1497.8(3)
α/°	—	113.02(2)
β/°	93.16(1)	93.93(2)
γ/°	—	107.68(2)
U/nm^3	1.0254(2)	1.8762(6)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
D_c/g cm^{-3}	1.78	1.78
Z	4	4
F(000)	508	960
μ/cm^{-1}	36.29	73.27
No. of data collected	1965	5045
No. observed [$I > 2\sigma(I)$]	1660	4692
R	0.0516	0.0413
R′	0.0531	0.0446
Weighting factor *g*	0.0008	0.0003
No. of variables	148	429

* For both compounds: scan widths 2.0° + α-doublet splitting; scan speeds 2.0–29.3° min^{-1}; $4.0 < 2\theta < 50.0°$.

with *nido*-6-SB_9H_{11} in the presence of the non-nucleophilic base *N,N,N′,N′*-tetramethylnaphthalene-1,8-diamine (tmnd) in dichloromethane solution, followed by chromatographic separation, resulted in the isolation of the new iridathiaborane [8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{11}$] **1** in a yield of 47% as a pale orange-yellow solid, reasonably stable in air in the solid state, but not indefinitely so. The compound was identified by mass spectrometry and NMR spectroscopy (section 3 below) in conjunction with a single-crystal X-ray diffraction analysis (section 2 below) on the 9-chlorinated derivative **2**. Compound **2** itself was isolated from the reaction of [{Ir(η^5-C_5Me_5)Cl_2}$_2$] with the Cs[*arachno*-6-SB_9H_{12}] in dichloromethane solution. In this latter reaction chromatographic separation of the products also yielded a third *nido*-8,7-iridathiaundecaborane, the 10-chlorinated derivative **3**. Compounds **2** and **3** were obtained in yields of 9 and 11% respectively and, like **1**, were reasonably air-stable pale orange-yellow solids. The identification of compound **2** by single-crystal X-ray diffraction analysis (section 2 below) was supported by NMR spectroscopy which also identified compound **3** by comparison (section 3 below).

A reasonable stoichiometry may be written for the formation of compounds **2** and **3** from their precursors [equation (1)], the

$$\tfrac{1}{2}[\{Ir(C_5Me_5)Cl_2\}_2] + [SB_9H_{12}]^- \longrightarrow [(C_5Me_5)IrSB_9H_{10}Cl] + Cl^- + H_2 \quad (1)$$

$$\textbf{2 and 3}$$

incorporation of the chlorine into the products having precedent in what appears to be a related formation of [11-Cl-8-(PMe_2Ph)-7-(η^5-C_5Me_5)-*nido*-7-$RhB_{10}H_{11}$] from [{Rh(η^5-C_5Me_5)Cl_2}$_2$] and *arachno*-$B_{10}H_{12}(PMe_2Ph)_2$ [equation (2)],[23]

$$\tfrac{1}{2}[\{Rh(C_5Me_5)Cl_2\}_2] + B_{10}H_{12}(PMe_2Ph)_2 \longrightarrow [\{C_5Me_5)RhB_{10}H_{11}Cl(PMe_2Ph)] + [PHMe_2Ph]Cl \quad (2)$$

the reaction presumably proceeding initially *via* the opening of the iridium halide dimer and the complexation of the [SB_9H_{12}]$^-$ moiety to the metal centre. The formation of the unchlorinated species **1** cannot be accounted for on such a simple stoichiometric basis, however, but the observation that [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$] **4** (section 4 below) appears to form compound **1** on extensive handling in air suggests that the formation of **1** may perhaps involve compound **4** as an intermediate. A reasonable stoichiometry can be proposed for the formation of compound **4** in the *nido*-6-SB_9H_{11} reaction [equation (3)], and the examination of the initial *nido*-SB_9H_{11} reaction product mixture by NMR spectroscopy does, in fact, reveal resonance lines corresponding to compound **4**.

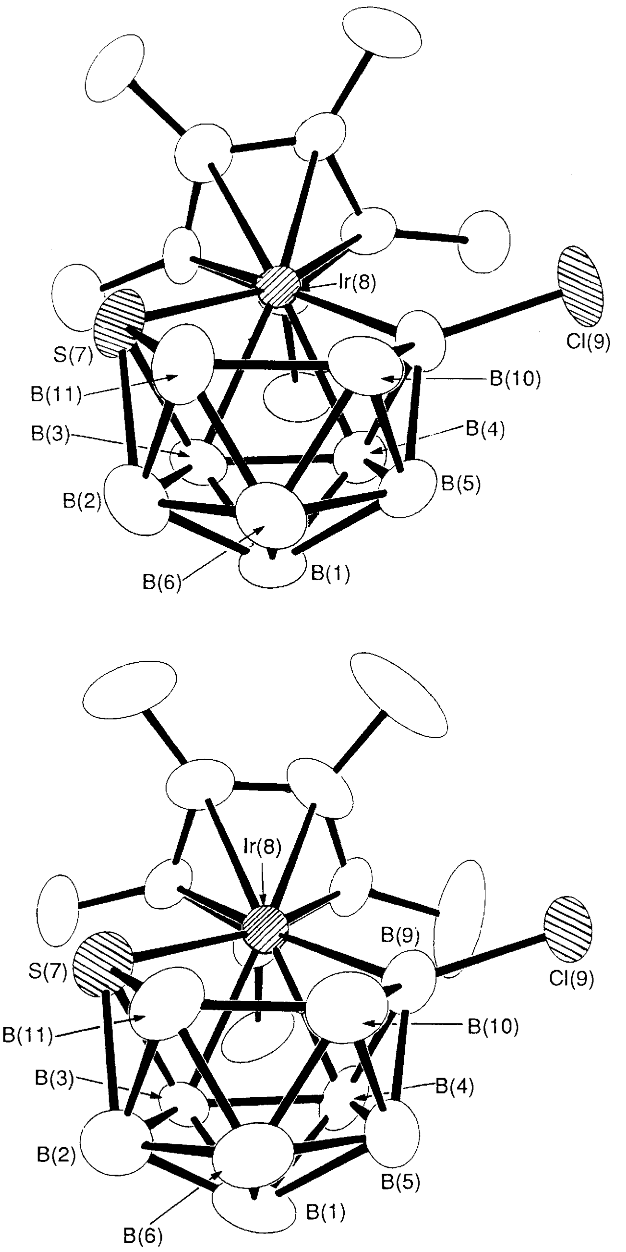


Fig. 1 Crystallographically determined molecular structure of [8-(η^5-C_5Me_5)-9-Cl-*nido*-8,7-$IrSB_9H_{10}$] **2**. Hydrogen atoms were not located from the diffraction analysis, but NMR spectroscopy reveals B–H(*exo*-terminal) units for all boron atoms except B(9) and bridging hydrogen atoms at Ir(8)–B(9) and B(10)–B(11). The molecules shown are the two independent ones in the asymmetric part of the unit cell; they differ principally in a slight difference of twist of the {η^5-C_5} unit relative to the {SB_9} cluster. The other two molecules in the centrosymmetric unit cell are the enantiomers of the two molecules shown

$$\tfrac{1}{2}[\{Ir(C_5Me_5)Cl_2\}_2] + SB_9H_{11} + 2\text{tmnd} \longrightarrow [(C_5Me_5)IrSB_9H_9] + 2(\text{Htmnd})Cl \quad (3)$$

$$\textbf{4}$$

(2) *Crystal and Molecular Structure of* [8-(η^5-C_5Me_5)-9-Cl-*nido*-8,7-$IrSB_9H_{10}$] **2**.—The structure type of compounds **1**–**3**

Table 2 Selected interatomic distances (pm) for [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{10}$] **2** with estimated standard deviations (e.s.d.s) in parentheses

	Molecule 1	Molecule 2
(*i*) To the iridium atom		
Ir(8)–C(1)	217.6(10)	219.8(10)
Ir(8)–C(2)	221.1(10)	218.7(11)
Ir(8)–C(3)	223.0(10)	217.6(12)
Ir(8)–C(4)	220.6(10)	220.7(11)
Ir(8)–C(5)	218.1(10)	223.0(10)
Ir(8)–B(3)	224.2(11)	226.0(11)
Ir(8)–B(4)	221.9(12)	219.5(12)
Ir(8)–S(7)	235.4(4)	235.9(4)
Ir(8)–B(8)	228.1(12)	228.5(12)
(*ii*) To the sulphur atom		
S(7)–B(2)	199.0(13)	201.4(13)
S(7)–B(3)	207.9(12)	209.3(13)
S(7)–B(11)	197.7(12)	193.3(13)
(*iii*) Boron–boron		
B(2)–B(3)	185(2)	189(2)
B(3)–B(4)	184(2)	183(2)
B(9)–B(10)	190(2)	191(2)
B(10)–B(11)	183(2)	184(2)
Other B–B	169(2)–181(2)	170(2)–185(2)
(*iv*) Carbon–carbon		
C–C(cyclic)	142.0(12)–144.5(15)	139.5(15)–145.6(16)
C–C(terminal)	145.5(13)–151.9(14)	145.3(15)–151.3(16)
(*v*) Others		
B(9)–Cl(9)	188.9(12)	186.6(13)

Table 3 Selected angles (°) between interatomic vectors for [9-Cl-8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{10}$] **2** with e.s.d.s in parentheses

	Molecule 1	Molecule 2
(*i*) About the iridium atom		
S(7)–Ir(8)–B(3)	53.7(4)	53.9(4)
S(7)–Ir(8)–B(4)	89.7(3)	90.0(4)
S(7)–Ir(8)–B(9)	90.6(3)	92.4(4)
B(3)–Ir(8)–B(4)	48.2(3)	48.6(4)
B(3)–Ir(8)–B(9)	83.5(5)	85.3(5)
(*ii*) About the sulphur atom		
Ir(8)–S(7)–B(2)	107.2(4)	107.4(5)
Ir(8)–S(7)–B(3)	60.4(4)	60.7(4)
Ir(8)–S(7)–B(11)	108.9(4)	107.5(5)
B(2)–S(7)–B(3)	54.2(5)	54.8(5)
B(2)–S(7)–B(11)	56.2(6)	57.2(6)
B(3)–S(7)–B(11)	98.1(5)	97.4(5)
(*iii*) Boron–boron–iridium		
B(1)–B(3)–Ir(8)	117.9(7)	116.6(7)
B(2)–B(3)–Ir(8)	117.2(7)	116.3(7)
B(4)–B(3)–Ir(8)	65.2(5)	63.8(5)
B(1)–B(4)–Ir(8)	115.9(7)	115.8(7)
B(3)–B(4)–Ir(8)	66.6(5)	67.6(5)
B(5)–B(4)–Ir(8)	115.7(7)	116.9(7)
B(9)–B(4)–Ir(8)	68.4(6)	68.9(6)
B(4)–B(9)–Ir(8)	64.7(5)	63.6(5)
B(5)–B(9)–Ir(8)	116.0(7)	114.4(7)
B(10)–B(9)–Ir(8)	115.0(7)	112.8(8)
(*iv*) Boron–boron–sulphur		
B(1)–B(2)–S(7)	113.0(7)	112.2(8)
B(3)–B(2)–S(7)	65.4(6)	64.7(5)
B(6)–B(2)–S(7)	109.1(7)	108.9(8)
B(1)–B(3)–S(7)	107.8(7)	106.0(7)
B(2)–B(3)–S(7)	60.5(6)	60.5(6)
B(4)–B(3)–S(7)	111.5(7)	110.1(7)
B(2)–B(11)–S(7)	61.8(6)	64.1(6)
B(6)–B(11)–S(7)	110.5(8)	114.6(8)
B(10B(11)–S(7)	114.2(7)	116.0(8)
(*v*) Boron–boron–boron		
B–B–B(acute)	54.6(6)–66.5(7)	55.3(7)–66.1(8)
B–B–B(obtuse)	104.6(8)–116.0(8)	105.3(9)–115.6(8)
(*vi*) Boron–boron–chlorine		
B(4)–B(9)–Cl(9)	122.2(8)	121.8(8)
B(5)–B(9)–Cl(9)	115.2(7)	117.1(8)
B(10)–B(9)–Cl(9)	115.5(7)	119.7(8)
(*vii*) Other		
Ir(8)–B(9)–Cl(9)	120.9(6)	119.8(6)

was established by a single-crystal X-ray diffraction analysis on the chlorinated species **2**. Straw-yellow platelets of compound **2** suitable for this work were obtained from cyclohexane–dichloromethane. Crystals were triclinic, space group $P\bar{1}$ (see Table 1 for crystallographic data). The unit-cell volume and the calculated density indicated that there were two crystallographically independent molecules in the asymmetric unit and the structure solution showed this to be the case. The two molecules have very similar molecular dimensions (see Tables 2 and 3) and differ only by a slight rotation about a vector from the iridium atom to the C_5Me_5 centroid.

The data were not good enough for us to obtain reliable borane-cluster hydrogen-atom positions. However, NMR spectroscopy (see section 3) showed that all boron atoms except B(9) had *exo*-terminal hydrogen atoms associated with them, and that there were additionally two bridging hydrogen atoms, one at Ir(8)–B(9) and one at B(10)–B(11). Peaks corresponding to all these positions in fact appeared on difference maps, but did not refine satisfactorily.

Drawings of the molecular structure of the two independent molecules are given in Fig. 1, with selected interatomic distances and angles in Tables 2 and 3 respectively. The structure is seen to be of the eleven-vertex *nido* type, formally derived from the icosahedron by the removal of one vertex, with the iridium and sulphur atoms occupying adjacent positions (designated the 8 and 7 positions respectively) on the open face (schematic structure **II** above). The boron atom on the open face and adjacent to the iridium atom [*i.e.* B(9)] has an *exo*-terminal chlorine atom bound to it rather than the *exo*-hydrogen that each of the other boron atoms has. The C_5Me_5 group is bound to the iridium atom in a straightforward pentahapto fashion, with the five iridium–carbon distances all being essentially identical. The compound has sandwich character in that the cyclopentadienyl η^5-C_5 plane and the B(9)B(3)B(4)S(7) plane are essentially parallel [dihedral angles 7.9(4) and 6.4(3)° for molecules 1 and 2 respectively]. The methyl groups of the C_5Me_5 groups are bent slightly away from the iridium atom [mean angle of deviation from the η^5-C_5 plane 3.2(6) and 3.7(6)° for molecules 1 and 2 respectively], a phenomenon also observed[9,11,23–25] with a variety of pentamethylcyclopentadienylrhodoboranes.

The observed *nido* structure for the [(C_5Me_5)$IrSB_9H_{10}Cl$] formulation is entirely in accord with the Williams–Wade[26,27] cluster-geometry and electron-counting rules. It is a formal *nido*-$\{B_{11}H_{13}\}^{2-}$ analogue in which a neutral {BH(*exo*)} unit has been replaced by a neutral {Ir(C_5Me_5)} unit that also contributes three orbitals and two electrons to the cluster bonding scheme, and a $\{BH(exo)\}^{2-}$ unit has been replaced by an 'isoelectronic' neutral sulphur atom which contributes three orbitals and four electrons to the cluster bonding scheme. In

Table 4 Measured NMR data for a series of *nido*-iridathiaundecaboranes: [8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{11}$] **1**, [8-(η^5-C_5Me_5)-10-Cl-*nido*-8,7-$IrSB_9H_{10}$] **3** and [8-(η^5-C_5Me_5)-9-Cl-*nido*-8,7-$IrSB_9H_{10}$] **2** in $CDCl_3$ solution at 291–294 K

	Compound **1**			Compound **3**			Compound **2**		
Position[a]	$\delta(^{11}B)$[b]	$^1J(^{11}B-^1H)$[c]/Hz	$\delta(^1H)$[d]	$\delta(^{11}B)$[b]	$^1J(^{11}B-^1H)$[c]/Hz	$\delta(^1H)$[d]	$\delta(^{11}B)$[b]	$^1J(^{11}B-^1H)$[c]/Hz	$\delta(^1H)$[d]
1	−22.1	*e*	+1.46	−22.8	146.5	+1.44	−23.3	147	+1.55
2	−17.0	*e*	+2.61	−18.7	172	+2.51	−20.6	*e*	+2.17
3	+1.1	161	+2.52	−2.3	159	+2.25	−0.4	158	+2.47
4	−13.8	*e*	+1.20	−15.6	*e*	+1.24	−15.4	146	+1.42
5	+7.7	142	+4.80	+8.8	145	+5.28	+10.1	152	+4.84
6	−18.2	*e*	+3.91	−15.9	*e*	+3.93	−19.5	*e*	+3.73
7(S)	—	—	—	—	—	—	—	—	—
8(Ir)	—	—	+2.11 (C_5Me_5)	—	—	+2.11 (C_5Me_5)	—	—	+2.13 (C_5Me_5)
9	−2.6	145[f]	+2.90	+0.2	155[f]	+3.10	+7.0	50[g]	—
10	−23.0	*e*	+1.64	−10.7	58[g]	—	−19.9	*e*	+1.92
11	−12.9	*e*	+2.57	−12.5	163[f]	+3.02	−13.0	157[f]	+2.64
8,9 bridging	—	—	−11.4	—	—	+11.25	—	—	−9.86
10,11 bridging	—	—	−4.52	—	—	−2.27	—	—	−4.00

[a] Assignments by [$^{11}B-^{11}B$] COSY, [$^1H-^1H$] COSY (Table 5) and ^1H-{^{11}B(selective)} experiments; numbering as in Fig. 1. [b] ±0.5 ppm to high field of $BF_3(OEt_2)$ in $CDCl_3$. [c] ±8 Hz, measured from ^{11}B-{^1H} spectrum with resolution enhancement to achieve baseline separation of doublet components. [d] ±0.05 ppm to frequency of $SiMe_4$; ^1H resonances assigned to directly bound boron positions by ^1H-{^{11}B(selective)} spectroscopy. [e] Not measured because of overlap of resonances. [f] Coupling to bridging hydrogen atom not resolved. [g] Coupling to bridging hydrogen on the Cl-substituted boron atom.

Table 5 Observed two-dimensional COSY NMR data for compounds **1**–**3**

	[$^{11}B-^{11}B$] COSY[a]			[$^1H-^1H$] COSY[b]
Position	Compound **1**	Compound **3**	Compound **2**	Compound **2**
1	2m, 3m, 4m, 6w	2m, 3m, 4m,[c] 5m, 6w[c]	2m,[c] 3w, 4m, 5s, 6w[c]	2w, 3m, 5m, 6m, $10m_4$?, μ(8/9)w_4, μ(10/11)w_4
2	1m	1m	1m[c]	1m, $5m_4$, 6s, μ(8/9)?, μ(10/11)s
3	1m, 4m	1m, 4m[c]	1w, 5w?	1m, 2?, 4m
4	1m, 3m, 5m, 9m	[1m, 3m, 5m, 9m][c]	1m, 5m, 9s	$2w_4$, 3m, 5m, μ(8/9)?
5	1m, 4m, 6w, 9m, 10m	1m, 4m,[c] 9m, 10s	1s, 3w?, 4m, 6w,[c] 9s, 10m[c]	1m, $2m_4$, 4m, 6m, 10m, μ(10/11)m
6	1w, 5w, 11m	[1w, 5m, 11m][c]	[1w, 5w, 11m][c]	1m, 2m, 5m, 10s, 11m, μ(8/9)m, μ(10/11)m
7(S)	—	—	—	—
8(Ir)	—	—	—	—
9	4m, 5m, 10m	4m,[c] 5m, 10m	4s, 5s, 10s[c]	—
10	5m, 6m, 9m	5s, 6m,[c] 9m	[5m, 9s][c]	$1m_4$?, 5m, 6s, μ(10/11)s
11	6m	6m[c]	6m[c]	2m, 6m, μ(10/11)s_2
μ(8/9)				$1w_4$, $2m_4$, 6m, μ(10/11)m
μ(10/11)				$1w_4$, 2m, 5m, 6m, $10s_2$, $11s_2$, μ(8/9)m

[a] Measured with {^1H(broad-band noise)} decoupling; note that the observed intensities depend on *both* $^1J(^{11}B-^{11}B)$ and T_2^* and therefore on solution conditions; s = stronger, m = intermediate, w = weaker. [b] Measured with (gated) [^{11}B(broad-band noise)] decoupling; subscripts refer to n in $^nJ(^1H-^1H)$ coupling path when $n \neq 3$. [c] Some uncertainty due to overlap of resonances.

these terms the S(7) atom is formally 'tetrahedral' sulphur(IV) with the remaining valence-shell lone pair being equivalent to the pair of electrons in the BH(*exo*) bond of the $\{BH\}^{2-}$ unit that it has formally replaced. In terms of a metal–ligand co-ordination approach, the compound may be viewed as a complex between the d^6 $\{Ir(C_5Me_5)\}^{2+}$ moiety and the tridentate {*arachno*-$SB_9H_{10}Cl$}$^{2-}$ ligand, the iridium centre thus being formally eighteen-electron 'octahedral' iridium(III). The *arachno* character of the notional thiaborane ligand is supported to some extent by its NMR properties (see section 3 below).

The interboron distances are all within normal ranges for Wadian species,[28] as are the iridium–boron distances.[29] The interboron distances flanking the sulphur atom are somewhat longer perhaps than the others, as noted for other chalcogena- and metallachalcogena-boranes,[15,22,30–33] including the $[SB_9H_{12}]^-$ anion discussed in section 5 below. There are only a handful of reports in the literature of crystallographically determined iridium–sulphur distances for compounds in which the sulphur atom is not also bound to oxygen, the reported range for alkyl sulphide, dialkyl sulphide and mercapto species being 230.0–251.2 pm.[34–38] The iridium–sulphur distances found for compound **2**, which average *ca.* 235.7 pm, are within this range and similar to values for dialkyl sulphide[34] or alkyl sulphide[36] groups that bridge two iridium centres. Comparison data are, however, limited.

(3) *NMR Properties of Compounds* **1**–**3**.—The measured NMR properties of compounds **1**–**3** are given in Table 4 (see also Table 5 and Fig. 2). The assignments were made by a combination of (*a*) [$^{11}B-^{11}B$] correlation spectroscopy (COSY) (Table 5), (*b*) 'singlet' resonances in the ^{11}B spectrum arising from the Cl-substituted positions together with (*c*) the incidence of lower values of $^1J(^{11}B-^1H)$, corresponding to $^1J(^{11}B-^1H)_\mu$, for these positions, (*d*) selective ^1H-{^{11}B} experiments, and finally (*e*) [$^1H-^1H$]-{^{11}B} COSY (the correlations given for compound **3** in Table 5 are typical) to confirm the assignments and remove remaining minor uncertainties.

These results show that the ^{11}B shielding patterns for the three compounds **1**–**3** are very similar, the only significant difference among the three being the α-substituent effect due to the chlorine substituents in compounds **2** and **3**, which give deshielding effects of 12.3 and 9.6 ppm respectively. These are within ranges typical[39,40] for chlorine substituent effects in metallaboranes. The longer-range substituent effects are much smaller than this, generally less than *ca.* ±3 ppm, the exception

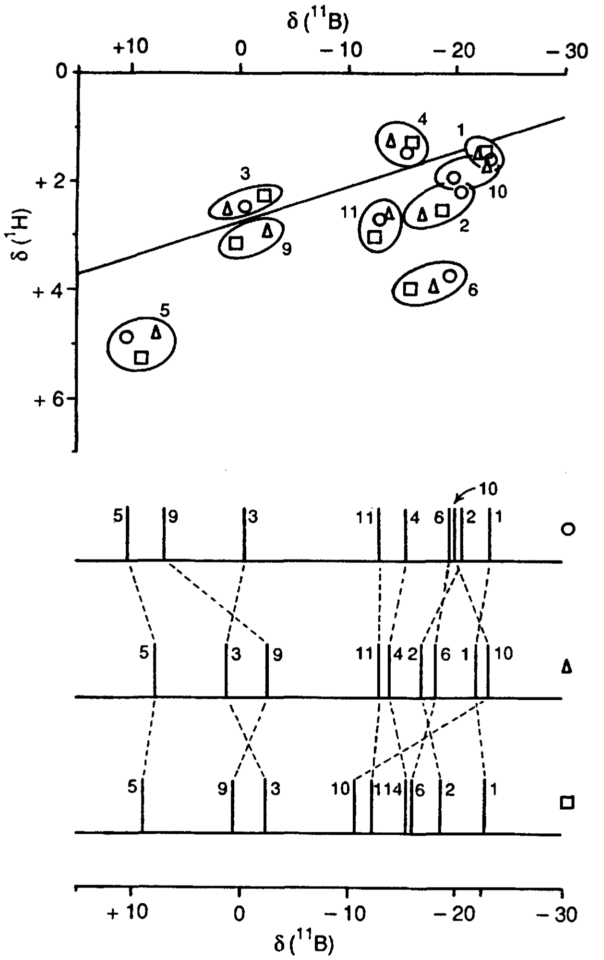


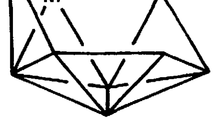
Fig. 2 Stick representations (lower) of the ^{11}B NMR peak positions for (○) [8-(η^5-C_5Me_5)-9-Cl-*nido*-8,7-$IrSB_9H_{10}$] **2**, (△) [8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{11}$] **1** and (□) [8-(η^5-C_5Me_5)-10-Cl-*nido*-8,7-$IrSB_9H_{10}$] **3** with dashed lines connecting equivalent site positions in the three species. The upper diagram is a plot of δ(^{11}B) *versus* δ(^{1}H) for the BH(*exo*) units of the three compounds. The line drawn has slope δ(^{11}B):δ(^{1}H) 15:1, intercept δ(^{1}H) +2.75, and the cartouches contain data for equivalent sites in the three compounds.

being for ^{11}B(2) antipodal to the chlorinated site in compound **2**, and for ^{11}B(3) antipodal to the chlorinated site in compound **3**, which have δ effects Δσ of *ca.* +3.6 and −3.4 ppm respectively. It is of interest that a number of the features of the ^{11}B shielding patterns are shared by the [*arachno*-6-SB_9H_{12}]$^-$ anion,[2] tending to support the supposition of *arachno* ten-vertex character for the {SB_9} unit discussed in the structural section 2 above. Thus the ^{11}B{(1), (6), (4) and (10)} resonances are towards the higher-field end of the spectrum, and ^{11}B(5) at the lower end, a feature that tends to be diagnostic of *arachno* ten-vertex character, and which is thereby also a characteristic of [SB_2H_{12}]$^-$ (in which the equivalent positions are conventionally numbered 1, 3, 10, 8 and 4 respectively).

The overall shielding pattern of the unsubstituted compound **1** has strong similarities to the assigned pattern recently reported for [8-(η^6-MeC_6H_5)-*nido*-8,7-$FeSB_9H_{11}$],[22] the principal difference being a decrease in shielding for the ^{11}B nuclei in the B(1)B(4)B(5) triangle, of between 5 and 8 ppm, with the other shielding differences being less than ±4 ppm. The [^{11}B–^{11}B] COSY behaviour is also generally similar between the iron[22] and iridium species, with the reduced intensity of correlations between B–H–B bridged ^{11}B positions, and between ^{11}B positions that flank the chalcogen atom, being noteworthy (and diagnostic of these types of structural feature).[2,15,32,33,39,41]

The upper diagram in Fig. 2 is a plot of δ(^{1}H) *versus* δ(^{11}B) for the BH(*exo*) units in the three iridathiaborane compounds **1**–**3**. It can be seen that the (^{11}B,^{1}H) data for equivalent sites are closely grouped, which tends to strengthen the assignments. There is also a reasonable grouping about a correlation line δ(^{11}B):δ(^{1}H) of *ca.* 15:1, as found for a variety of metallaborane species,[39,42,43] the exception being for the ^{11}B^{1}H(6) position antipodal to the Ir(8) position, which is some 2 ppm less shielded in δ(^{1}H) than the general trend, a feature becoming diagnostic of positions antipodal to heavier atoms in polyhedral heteroborane clusters.[15,32,33,44,45] The BH(5) proton antipodal to the S(7) position also appears to be deshielded somewhat in these terms. A final point to be noted about the ^{1}H shielding behaviour is the reduction in shielding of about 2 ppm for B–H–B and M–H–B bridging protons when they are bound to the boron sites that have the electronegative chlorine substituents [*i.e.* B(9) in compound **2** and B(10) in compound **3**]. Again, this is becoming a diagnostic feature in the general case.[40,46]

(4) *Isolation and Identification of* [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$] **4**.—Apart from the *nido*-8,7-iridathiaundecaboranes described above, the reactions yielded other coloured (yellow, orange, red) products, of which some are iridathiaboranes. One of these was tentatively identified as an *arachno*-5,4-$IrSB_7$ cluster species of schematic structure **VII** (see Experimental section), whereas others have been reasonably identified as air-stable *closo*-type twelve-vertex 2,3,1-diiridathiadodecaboranes (schematic structure **V** above) that are related to the reported[19] rhodium analogue [11-Cl-2,3,1-*closo*-$Rh_2SB_9H_8$], and it is



VII

hoped to be able to report on these more definitively at a later date.[5] Another product, obtained in the [*arachno*-SB_9H_{12}]$^-$ reaction and isolated in about 20% yield, was less stable in solution in air, but is reasonably identified from NMR spectroscopy as the *closo*-type eleven-vertex iridathiaborane [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$] **4** (schematic structure **III** above).

Measured NMR data for compound **4** are in Table 6, which also contains equivalent data for the recently reported[47] 2,1-azaruthenaborane analogue [1-(η^6-$MeC_6H_4Pr^i$-4)-*closo*-1,2-$RuNB_9H_{10}$] for comparison. Compound **4** has six different BH environments, in relative proportions 1:1:2:1:2:2, this pattern being consistent with the mirror-plane symmetry of the proposed structure, and it can be seen that the overall cluster ^{11}B and ^{1}H shielding pattern has very close parallels with the azaruthenaborane, the only substantial difference in this overall behaviour being in the low nuclear shielding for ^{1}H(9) in compound **4**, this being the position antipodal to the sulphur atom that is in the 2 position (compare shielding effects for ^{1}H in positions antipodal to chalcogen atoms in refs. 15 and 45; see also Fig. 2 above). A single unperturbed η^5-C_5Me_5 group is also apparent from the ^{1}H NMR spectrum (footnote *f* in Table 6) and so compound **4** is reasonably formulated as [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$], of gross structure as illustrated in Fig. 3.

The closed eleven-vertex cluster is in accord with the Williams–Wade cluster-geometry and electron-counting rules,[26,27] in that the formally 'octahedral' iridium(III) {Ir(C_5Me_5)} moiety can be regarded as contributing three orbitals and two electrons to the cluster bonding scheme, and the sulphur vertex [formally 'tetrahedral' sulphur(IV)] three orbitals and four electrons, with a lone pair in an *exo*-terminal position corresponding to the pair of electrons in the

Table 6 Measured NMR parameters for [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$] **4**, together with those of [1-(η^6-$MeC_6H_4Pr^i$-4)-*closo*-1,2-$RuNB_9H_{10}$][a] for comparison

		{$IrSB_9$} compound **4**[b]			{$RuNB_9$} compound[a]	
Assignment	Relative intensity	$\delta(^{11}B)$[c]	$^1J(^{11}B-^1H)$[d]/Hz	$\delta(^1H)$[e,f]	$\delta(^{11}B)$[b,c]	$\delta(^1H)$[e]
3	1BH	+50.1	161	+7.68	+53.2	+7.68
9	1BH	+21.6	144	+6.22	+19.6	+3.92
4,5	2BH	+5.8	168	+2.68	+0.6	+2.54
8	1BH	−18.2	*ca.* 170[g]	+2.05	−13.8	+2.50
6,7	2BH	−19.5	*ca.* 145[g]	−0.54	−22.5	+0.15
10,11	2BH	−23.7	147	−0.80	−25.7	+0.09

[a] Data from ref. 47. [b] In $CDCl_3$ solution at 294–297 K. [c] ±0.5 ppm to low frequency (high field) of $BF_3(OEt_2)$. [d] ±8 Hz; measured from ^{11}B NMR spectrum with resolution enhancement. [e] ±0.05 ppm to low frequency (high field) of $SiMe_4$; ^1H resonances related to directly bound B atom positions by ^1H-{^{11}B(selective)} spectroscopy. [f] Also $\delta(^1H)(C_5Me_5)$ at +2.00 (15 H) in CD_2Cl_2 solution at 297 K. [g] Resonance overlap may distort measured values.

Table 7 Interatomic distances (in pm) for the [*arachno*-6-SB_9H_{12}]$^-$ anion in Cs[SB_9H_{12}] with e.s.d.s in parentheses

S(6)–B(2)	193.6(9)	—	
S(6)–B(5)	194.1(9)	S(6)–B(7)	194.4(10)
B(1)–B(2)	174.5(12)	B(3)–B(2)	175.4(11)
B(1)–B(3)	179.1(11)	—	
B(1)–B(4)	178.5(10)	B(3)–B(4)	180.0(11)
B(1)–B(5)	176.5(11)	B(3)–B(7)	176.0(11)
B(1)–B(10)	178.0(11)	B(3)–B(8)	177.1(11)
B(2)–B(5)	190.3(12)	B(2)–B(7)	191.1(12)
B(4)–B(8)	173.4(11)	B(4)–B(10)	171.1(11)
B(4)–B(9)	172.0(12)	—	
B(5)–B(10)	183.4(11)	B(7)–B(8)	183.4(12)
B(9)–B(10)	189.3(11)	B(9)–B(8)	191.2(12)
B(1)–H(1)	111.7(28)	B(3)–H(3)	110.0(28)
B(2)–H(2)	113.3(23)	B(4)–H(4)	104.2(27)
B(5)–H(5)	116.2(28)	B(7)–H(7)	114.2(26)
B(10)–H(10)	106.9(27)	B(8)–H(8)	108.4(30)
B(9)–H(9)(*endo*)	111.0(29)	B(9)–H(9)(*exo*)	123.0(23)
B(5)–H(5,10)	111.2(28)	B(7)–H(7,8)	126.4(24)
B(10)–H(5,10)	136.4(23)	B(8)–H(7,8)	125.0(28)

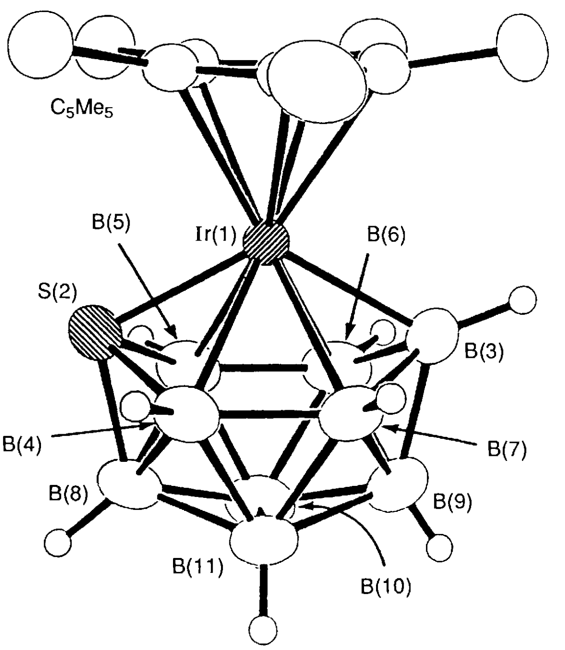


Fig. 3 Proposed molecular structure of [1-(η^5-C_5Me_5)-*closo*-1,2-$IrSB_9H_9$] **4**

BH(2)(*exo*) linkage in the formal binary borane analogue *closo*-[$B_{11}H_{11}$]$^{2-}$. However, in view of the 'slippage' towards *nido* often observed experimentally in formally *closo* eleven-vertex clusters with a Wadian[27] *closo* 24-electron count,[1,7,47–50] it may well be that compound **4** exhibits a tendency towards a more open aspect, with a 'long' Ir–S linkage (compare refs. 15 and 47). The instability of compound **4** has so far precluded the growing of crystals suitable for a single-crystal X-ray diffraction analysis that would enable this consideration to be experimentally assessed. Attempts to grow crystals of **4** using CH_2Cl_2–hexane and $CHCl_3$–hexane in air resulted in the reasonably clean formation of the unsubstituted *nido* species [8-(η^5-C_5Me_5)-*nido*-8,7-$IrSB_9H_{11}$] **1** discussed above, identified as such by NMR spectroscopy (Table 3 above). This apparent *closo* $\longrightarrow$ *nido* conversion of compound **4** to **1** is remarkable because it is one of effective cluster reduction by the net addition of two hydrogen atoms under conditions that would be expected either to be oxidizing, or to result in cluster chlorination by the solvent[51–53] under the solution conditions obtaining.

The only previously claimed examples of this eleven-vertex *closo*-1,2-metallathiadecaborane structural type are the compounds formulated as [$(PPh_3)_2PdSB_9H_9$], [$(C_{10}H_8N_2)PdSB_9H_9$], [$AsPh_4$][{$C_2S_2(CN)_2$}$PdSB_9H_9$] and [$(PPh_3)_2PtSB_9H_9$].[21] For these species the unassigned overall ^{11}B shielding patterns have some similarities to that of the {$Ir(C_5Me_5)$} species **4** reported here. However, the different nature of the iridium *versus* the palladium and platinum metal centres (ref. 15 *versus* ref. 32 for an analogous twelve-vertex comparison) would induce substantial cluster-shielding differences that would preclude any meaningful comparisons at present, and in any event the shielding patterns of the palladium compounds are much more similar to those of the ten-vertex *arachno*-9,6-metallachalcogenaboranes (of schematic structure **IV** above)[16,45] which suggests that the palladium compounds also have this *arachno* ten-vertex structure. Compound **4** is, therefore, the first reasonably established eleven-vertex metallathiaborane of the *closo* structural type.

(5) *Crystal and Molecular Structure of* Cs[SB_9H_{12}].—As part of our work on the chemistry of the ten-vertex thiaboranes we have examined a sample of Cs[SB_9H_{12}] by single-crystal X-ray diffraction analysis, for which it is convenient to summarize the results here. A picture of the [SB_9H_{12}]$^-$ anion is in Fig. 4. Although this anion has previously been investigated crystallographically in [$Au(PPh_3)_3$][SB_9H_{12}],[31] the molecular dimensions obtained were of limited accuracy and, in view of the increasing interest in Group 6 heteroborane chemistry,[1–5,15,19,22,30–33,45,54–60] we thought an alternative

Table 8 Angles (°) between interatomic vectors for the [*arachno*-6-SB_9H_{12}]$^-$ anion in Cs[SB_9H_{12}] with e.s.d.s in parentheses

B(7)–S(6)–B(5)	99.5(4)		
S(6)–B(5)–B(10)	118.5(5)		
B(5)–B(10)–B(9)	112.5(17)		
B(10)–B(9)–B(8)	102.1(5)		
B(9)–B(8)–B(7)	112.6(6)		
B(8)–B(7)–S(6)	118.6(5)		
B(5)–S(6)–B(2)	58.8(4)	B(10)–B(9)–B(4)	57.0(4)
S(6)–B(5)–B(2)	60.5(4)	B(9)–B(10)–B(4)	56.5(4)
S(6)–B(2)–B(5)	60.7(4)	B(9)–B(4)–B(10)	66.5(5)
B(7)–S(6)–B(2)	59.0(4)	B(8)–B(9)–B(4)	56.7(4)
S(6)–B(7)–B(2)	60.3(4)	B(9)–B(8)–B(4)	56.1(5)
S(6)–B(2)–B(7)	60.7(4)	B(9)–B(4)–B(8)	67.2(5)
B(5)–H(5,10)–B(10)	95.0(19)	B(7)–H(7,8)–B(8)	93.6(19)
H(5,10)–B(5)–B(10)	37.2(12)	H(7,8)–B(7)–B(8)	42.9(12)
H(5,10)–B(10)–B(5)	47.8(12)	H(7,8)–B(8)–B(7)	43.5(11)
B(4)–B(9)–H(9)(*exo*)	110.1(15)	H(9)(*endo*)–B(9)–H(9)(*exo*)	108.9(19)
B(4)–B(9)–H(9)(*endo*)	140.6(13)		
B(8)–B(9)–H(9)(*endo*)	104.5(15)	B(10)–B(9)–H(9)(*endo*)	101.5(15)
B(8)–B(9)–H(9)(*exo*)	123.7(15)	B(10)–B(9)–H(9)–(*exo*)	113.6(14)

Table 9 Measured NMR parameters for [$Cl(PPh_3)_2H_2IrB_9H_{11}S$] **5** in $CDCl_3$ at room temperature[a]

Assignment	$\delta(^{11}B)$	Observed [^{11}B–^{11}B] COSY correlations[b]	$^1J(^{11}B$–$^1H)$/Hz	$\delta(^1H)$[c]	Observed [^1H–^1H] COSY correlations[d]
4	+5.4	[(1,3)m, (8,10)m]	133	+2.51	
5,7	−8.2	—	*e*	+2.49	[(1,3)m, (8,10)m, 9m?, (μ)s]
2	−11.7	—	*e*	+2.49	
9				+0.71	[(1,3)w?, (8,10)w?, (μ)w]
8,10	−31.3	[(1,3)m, 4m]	140	+0.48[f]	[{2,4(5,7)}m, 9w?, (μ)s]
1,3	−37.2	[4m, (8,10)m]	145	+0.81	[{2,4(5,7)}m, 9w?, (μ)w]
μ(5,10)μ(7,8)	—	—	*e*	−2.05[g]	[(1,3)m, {2,4(5,7)}m, (8,10)s, 9w]

[a] $\delta(^{31}P)$ +11.06. [b] Measured with {^1H(broad-band noise)} decoupling. [c] Ir–H at $\delta(^1H)$ −9.13 [triplet (splitting *ca.* 4 Hz) of doublets (splitting *ca.* 17 Hz)] and −14.98 [triplet (splitting of *ca.* 3 Hz) of doublets (splitting *ca.* 15 Hz) with further, unresolved, fine structure]. [d] Measured with {^{11}B(broad-band noise)} decoupling. [e] Peaks too broad for *J* measurement. [f] In boron-decoupled spectra this resonance is a *ca.* 1:3:3:1 quartet, splitting *ca.* 20 Hz. [g] Coupling to B(8,10) is substantially greater than to B(5,7) (compare calculations on {PtB_8Se} analogue in ref. 45).

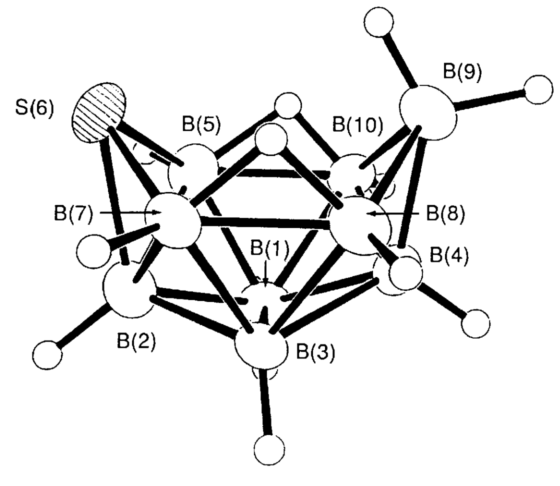


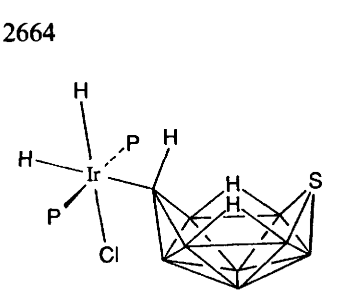
Fig. 4 Crystallographically determined structure of the [*arachno*-6-SB_9H_{12}]$^-$ anion in Cs[SB_9H_{12}]

data set and more accurate parameters would be useful. Interatomic distances and selected interatomic angles are listed in Tables 7 and 8 respectively.

The structure is characterized by more consistent B–H(*exo*) distances than those previously reported,[54] and there is much greater consistency between those pairs of distances that would be expected to be equal if the molecule had the mirror-plane symmetry [through S(6)B(2)B(4)B(9)] that the lattice constraints remove.

The general ten-vertex *arachno*-type features[2,31,61] are of course confirmed, and the structure has many similarities to that[62] of the [$B_{10}H_{14}$]$^{2-}$ anion. The distances B(2)–B(5) and B(2)–B(7) flanking the Group 6 heteroatom are longer than the corresponding distances B(4)–B(7) and B(4)–B(10) at the other end of the molecule, this weaker bonding being manifested in weaker [^{11}B–^{11}B] COSY NMR correlations as noted elsewhere,[2] and it is of interest in this context that the other interboron distances to these atoms [B(2), B(5) and B(7)] seem to be correspondingly shorter. The distance from the S(6) atom to the open-face boron atoms B(5) and B(7) is only marginally longer than the distance to the apical atom B(2), in contrast to the corresponding distances involving B(9) which differ by nearly 20 pm, B(8)–B(9) and B(9)–B(10) thereby being quite long at *ca.* 190 pm. This may be a consequence of greater contributions from a sulphur three-orbital bonding involvement with B(2), B(5) and B(7),[45] whereas the B(9) bonding involvement with B(4), B(8) and B(10) is limited to two orbitals because of the two BH(terminal) bonds for the 9 position. Because of this asymmetry, there is interest in assessing the asymmetry in the B–H–B bridge bonding, but data were insufficiently accurate for a comparison.

Reaction of [*arachno*-6-SB_9H_{12}]$^-$ *with* ($Ir(CO)Cl(PPh_3)_2$).—As part of this work we have also briefly assessed the reaction of the [*arachno*-6-SB_9H_{12}]$^-$ anion with [$Ir(CO)Cl(PPh_3)_2$] in chloroform solution at room temperature. The reaction



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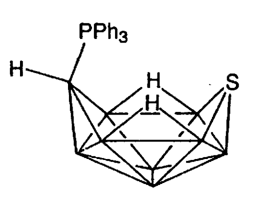

IX

Table 10 Measured NMR parameters of the product tentatively identified as 9-(PPh_3)-*arachno*-6-SB_9H_{11} **6**, in $CDCl_3$ solution at 294 K

Assignment	$\delta(^{11}B)$	$^1J(^{11}B-^1H)^b$/Hz	$\delta(^1H)^c$
4	+8.3	142	+3.38[d]
2	−3.3	—[e]	+3.61
5,7	−6.9	147	+3.25
9	−23.4[f]	—[g]	+1.18
8,10	−34.3	152	+1.40
1,3	−36.6	149	+1.88
μ(5,10;7,8)	—	*ca.* 40[h]	−1.21[h]

[a] ±0.5 ppm to high frequency (low field) of $BF_3(OEt_2)$. [b] ±8 Hz; measured from ^{11}B NMR spectrum with resolution enhancement. [c] ±0.05 ppm to high frequency (low field) of $SiMe_4$; ^1H resonances related to directly bound ^{11}B atoms by $^1H-\{^{11}B(selective)\}$ spectroscopy. [d] Coupling $^3J(^{31}P-^1H)$ 17 Hz. [e] Boron-11 resonance too broad for accurate $^1J(^{11}B-^1H)$ estimation. [f] $^1J(^{31}P-^{11}B)$ 110 Hz. [g] Accurate estimate not possible because $^1J(^{31}P-^{11}B)$ splitting also present (footnote *f*). [h] $^1J(^{11}B-^1H)$ for this position is to the $^{11}B(8,10)$ nuclei; $\delta(^1H)$ at −1.21 selectively sharpened only by $\nu[^{11}B(8,10)]$ and not by $\nu[^{11}B(5,7)]$ in $^1H-\{^{11}B(selective)\}$ experiments.

proceeded less readily than that with $[\{Ir(C_5Me_5)Cl_2\}_2]$ and the only metallaborane product that we were able to isolate in sufficient yield for reasonable investigation (10%, reaction scale 640 μmol) was tentatively identified by NMR spectroscopy as the *arachno*-6-thiadecaborane species [*exo*-9-{Cl-*trans*-$(PPh_3)_2$-*cis*-H_2Ir}-*arachno*-6-SB_9H_{11}] **5**. The overall cluster ^{11}B and ^1H NMR shielding properties (Table 9) were very similar indeed to those[2] of the $[SB_9H_{12}]^-$ anion, except that the B(9) position had only one ^1H resonance associated with it, the higher shielding of this proton[2,63] suggesting it was *endo* and the substituent thereby *exo*. The ^1H NMR spectrum showed two different, although mutually *cis*, hydrogen atoms on the metal centre, of which each exhibited *cis* couplings $^2J(^{31}P-^1H)$ to two equivalent, and therefore mutually *trans*, triphenylphosphine ligands. Mass spectroscopy using electron-impact ionization gave only a weak spectrum and did not give a sufficiently strong molecular ion at *m*/*z ca.* 890 to distinguish between $\{(PPh_3)_2(CO)IrSB_9H_{12}\}$ or $\{(PPh_3)_2ClIrSB_9H_{11}\}$ formulations, but the absence of ν(CO) in the infrared spectrum at *ca.* 2000 cm^{-1}, together with the covalent, rather than ionic, nature of the compound suggested by ready chromatographic mobility on silica using mixtures of MeCN–CH_2Cl_2–C_6H_{14} as eluent, suggests a neutral formulation with a chloro rather than a carbonyl substituent on the sixth octahedral iridium(III) co-ordination site, resulting in the [*exo*-9-{Cl-*trans*-$(PPh_3)_2$-*cis*-H_2Ir}-*arachno*-6-SB_9H_{11}] formulation represented schematically in **VIII**; this will presumably have some zwitterionic character. Iridium(III) σ-bound to boron in polyhedral boron-containing compounds is well documented, for example in [2-{BrH(CO)-*trans*-$(PMe_3)_2Ir$}-*nido*-B_5H_8],[64–66] and in thiaborane chemistry it has been proposed in the complexes $[(PPh_3)_2HIrSB_nH_{n-1}]$, where n = 9 or 11.[20]

The hydridic nature of the metal residue in compound **5** suggested[43,67,68] that mild thermolysis may result in condensed contiguous metallaborane formation. However, although mild thermolysis (100 °C, 30 min, $CD_3C_6D_5$ solution) did result in reasonably clean thermolysis (≥ *ca.* 80% yield based on integrated ^{11}B NMR spectroscopy) it gave a non-metal product provisionally formulated, from its NMR properties, as 9-(PPh_3)-*arachno*-6-SB_9H_{11} **6**, with the PPh_3 substituent probably in the *endo* position as indicated in structure **IX**. Thus the cluster ^{11}B and ^1H NMR shielding properties of compound **6** (Table 10) were again very similar to those of the $[SB_9H_{12}]^-$ anion, and to those of compound **5**, except that the ^{11}B lines were somewhat sharper than those of compound **5**, suggesting a smaller molecule. There was only one ^1H resonance associated with $^{11}B(9)$, with a normal *exo* shielding,[39] suggesting that the substituent, reasonably identified as PPh_3 from $^1J(^{31}P-^{11}B)$ of *ca.* 110 Hz to $^{11}B(9)$ and from ^{31}P NMR spectroscopy, was thereby *endo* (compare refs. 2, 63, 69 and 70). The formation of *endo*-$(PPh_3)B_9H_{11}S$ is probably related to the formation of *exo*-$(PPh_3)B_9H_{13}$ which is often observed as a by-product[24] in reactions of non-heteroatom-containing nine- and ten-boron substrates with metal phosphine complexes. It is interesting that in the heteroatom system the *endo* configuration seems preferred.

Experimental

General.—Reactions were carried out in dry solvents under dry nitrogen, but subsequent manipulatory and separatory procedures were carried out in air. The compounds SB_9H_{11} and $Cs[SB_9H_{12}]$,[71] and the organometallic halide $[\{Ir(\eta^5-C_5Me_5)Cl_2\}_2]$,[72] were made by the published procedures. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions 20 × 20 cm, followed by drying in air at 100 °C for >2 d. Preparative high-pressure liquid chromatography (HPLC) was carried out using a Lichrosorb Si60 (mesh 7 μm) column (Knauer) of dimensions 25 cm × 16 mm, retention times R_t being given for a flow-rate of 10 cm^3 min^{-1} (unless otherwise specified), with detection by ultraviolet absorption at 254 or 260 nm. Mass spectrometry was done on an AEI (now Kratos) MS30 instrument using 70 eV (*ca.* 1.12 × 10^{-17} J) electron impact (EI) ionization and the solid-sample introduction probe.

Reaction between $[\{Ir(\eta^5-C_5Me_5)Cl_2\}_2]$ *and nido*-6-SB_9H_{11}.—A solution of *nido*-6-SB_9H_{11} (35 mg, 250 μmol) and 1,8-bis(dimethylamino)naphthalene (108 mg, 500 μmol) in CH_2Cl_2 (*ca.* 10 cm^3) was stirred at ambient temperature for 10 min, during which time the colour of the solution changed from very pale yellow to orange. To this was added a solution of $[\{Ir(\eta^5-C_5Me_5)Cl_2\}_2]$ (100 mg, 130 μmol) in CH_2Cl_2 (*ca.* 20 cm^3). A deep orange-red colouration occurred almost immediately. Stirring was continued for 10 min, whereupon analytical TLC indicated one major orange product. The mixture was filtered, the filtrate reduced in volume (rotary evaporator, water-pump pressure, ambient temperature) to *ca.* 5 cm^3 and applied to a series of preparative TLC plates. Elution with hexane–CH_2Cl_2 (30:70) yielded one major orange band (R_f 0.80) and several minor components. The major orange component was purified by repeated TLC, the final pure compound [R_f 0.73 with hexane–CH_2Cl_2 (50:50) as the liquid phase] being identified as [8-$(\eta^5-C_5Me_5)$-*nido*-8,7-$IrSB_9H_{11}$] **1** as described in the text. The yield of the orange microcrystalline solid was 55 mg, 47% [mass spectrum: *m*/*z* (max.) 470; $^{12}C_{10}{}^1H_{26}{}^{11}B_9{}^{193}Ir^{32}S$ requires 470. Interestingly, the principal fragmentation involved the loss of *ca.* 47 mass units from the molecular ion; there was also a significant incidence of doubly charged ions corresponding to *ca.* M^{2+} and $(M - 47)^{2+}$].

Reaction between $[\{Ir(\eta^5-C_5Me_5)Cl_2\}_2]$ *and* Cs[*arachno*-6-SB_9H_{12}].—A suspension of Cs[*arachno*-6-SB_9H_{12}] (280 mg,

Table 11 Non-hydrogen atom coordinates (× 10^4) for compound **2**

Atom	x	y	z
Ir(18)	2451.8(3)	2551.8(3)	7567.6(2)
Ir(28)	3413.4(4)	7712.3(3)	7557.0(2)
Cl(19)	1570(3)	2539(2)	5167(2)
Cl(29)	4146(3)	6089(2)	8650(2)
S(17)	4927(2)	3414(2)	8360(2)
S(27)	2998(3)	9227(2)	8611(2)
C(11)	693(8)	1406(6)	7788(6)
C(12)	1556(8)	2162(8)	8739(6)
C(13)	1433(9)	3147(8)	8853(7)
C(14)	572(8)	3001(7)	7984(6)
C(15)	86(8)	1900(7)	7307(6)
C(16)	380(10)	222(7)	7374(8)
C(17)	2305(10)	1974(9)	9485(7)
C(18)	2102(11)	4162(8)	9780(7)
C(19)	176(10)	3836(8)	7824(9)
C(110)	−999(9)	1374(8)	6322(7)
C(21)	3554(9)	8070(7)	6266(6)
C(22)	2886(10)	6962(7)	5933(6)
C(23)	3861(12)	6592(7)	6267(7)
C(24)	5191(10)	7466(9)	6791(7)
C(25)	5026(10)	8422(8)	6823(7)
C(26)	2934(12)	8764(8)	6039(7)
C(27)	1410(11)	6281(9)	5270(8)
C(28)	3611(18)	5451(10)	6010(10)
C(29)	6553(13)	7389(13)	7217(10)
C(210)	6149(11)	9463(9)	7240(8)
B(11)	4926(11)	1584(8)	6428(8)
B(12)	6014(10)	2607(10)	7516(8)
B(13)	4132(10)	1803(8)	7460(7)
B(14)	3039(10)	1479(8)	6273(7)
B(15)	4235(11)	2094(8)	5684(7)
B(16)	6012(10)	2789(9)	6425(8)
B(19)	2993(10)	2620(9)	6134(7)
B(110)	4926(11)	3490(8)	6258(8)
B(111)	6031(11)	3872(9)	7465(8)
B(21)	508(11)	7416(12)	8689(9)
B(22)	1183(12)	8742(10)	9094(9)
B(23)	1226(10)	7822(8)	7805(7)
B(24)	1596(10)	6727(8)	7922(8)
B(25)	1723(12)	6979(10)	9197(8)
B(26)	1555(12)	8219(10)	9928(8)
B(29)	3301(11)	7079(8)	7829(7)
B(210)	3269(12)	8079(10)	9997(8)
B(211)	3007(13)	9216(9)	9897(8)

Table 12 Atom coordinates (× 10^4) for Cs[SB_9H_{12}]

Atom	x	y	z
Cs	2 533.0(4)	2 186.3(4)	−136.2(4)
B(1)	7 783(8)	5 228(6)	2 455(6)
B(2)	9 349(8)	4 161(7)	2 499(7)
B(3)	8 061(7)	4 169(6)	3 665(6)
B(4)	6 082(8)	4 576(6)	3 103(6)
B(5)	8 013(8)	4 435(6)	1 113(6)
S(6)	8 846(2)	2 786(2)	1 446(2)
B(7)	8 462(8)	2 681(6)	3 117(7)
B(8)	6 477(8)	3 082(6)	3 598(7)
B(9)	5 005(8)	3 474(7)	2 305(6)
B(10)	6 023(8)	4 825(6)	1 593(6)
H(1)	8 111(25)	6 231(25)	2 506(24)
H(2)	10 648(25)	4 410(25)	2 697(24)
H(3)	8 437(25)	4 495(24)	4 556(24)
H(4)	5 384(25)	5 163(24)	3 591(24)
H(5)	8 532(25)	4 824(24)	259(25)
H(7)	9 346(25)	2 056(24)	3 637(25)
H(8)	6 290(25)	2 769(24)	4 488(25)
H(9a)	5 171(25)	2 725(24)	1 653(25)
H(9b)	3 568(25)	3 634(25)	2 407(24)
H(10)	5 554(25)	5 656(25)	1 195(24)
H(5,10)	6 424(25)	4 255(24)	849(24)
H(7,8)	7 062(25)	2 252(24)	2 985(25)

1020 μmol) in a solution of [{Ir(η^5-C_5Me_5)Cl_2}$_2$] (200 mg, 250 μmol) in CH_2Cl_2 (*ca.* 40 cm^3) was stirred for 1 h at ambient temperature, during which time the orange colour of the reaction mixture darkened. The reaction mixture was then filtered, the filtrate reduced in volume (rotary evaporator, ambient temperature, water-pump pressure) to *ca.* 10 cm^3 and applied to a series of preparative TLC plates. Use of hexane–CH_2Cl_2 (20:80) as the liquid phase resulted in the separation of a series of overlapping orange and yellow components (R_f 0.51–0.99). These were washed from the silica using CH_2Cl_2–MeCN (80:20), the filtrate evaporated to dryness (reduced pressure at ambient temperature), the solid residue taken up in hexane–CH_2Cl_2 (30:70) and subjected to HPLC separation, using the same solvent mixture as the liquid phase. The fractions with R_t 8.8–14.8 min were collected, and further separated by repeated HPLC and TLC using various mixtures of hexane, CH_2Cl_2, and MeCN as liquid phases. This resulted in a pure sample of compound **3** [28 mg, 56 μmol, 11%; R_t *ca.* 33.1 min, hexane–CH_2Cl_2 (50:50)] and a mixture of compounds **2** and **4** [R_t 19.5–22.3 min, hexane–CH_2Cl_2(50:50)]. Further HPLC on this last mixture [hexane–CH_2Cl_2 (60:40), flow-rate 8 cm^3 min^{-1}] resulted in pure compound **2** (*ca.* 22 mg, 44 μmol, 9%; R_t *ca.* 31–33 min), and compound **4** contaminated with other unidentified species (R_t *ca.* 27–29 min). Compound **4** was thence isolated from this mixture by repeated TLC as the most mobile component when hexane–CH_2Cl_2–MeCN (80:10:10) was used as eluting medium (yield: 45 mg, 97 μmol, 19.2%). Compounds **2**–**4** were pale orange-yellow microcrystalline solids, reasonably stable in air in the solid state. They were identified as described in the text. Solutions of compound **4** developed significant quantities of **1** upon extensive handling in air. An unstable {SB_8} cluster species, possibly an [$IrSB_8$} one, or an [SB_8H_{11}]$^-$ salt, with δ(^{11}B) values as follows (relative intensities in parentheses) +15.0(1B), −3.2(2B), −12.2(1B), −41.5(4B = 2B + 2B?) was also isolatable from this system, as was a yellow unstable metallathiaborane less tentatively identified as a nine-vertex *arachno*-5,4-$IrSB_7$ compound, *viz.* [8-Cl-5-(η^5-C_5Me_5)-*arachno*-5,4-$IrSB_7H_{10}$] (12 mg, 4.8%) R_t 14.3 min, hexane–CH_2Cl_2 (50:50)]. This latter compound had measured NMR properties (CD_2Cl_2 solution at 294–297 K) as follows {ordered as: tentative assignment, δ(^{11}B), δ(^{1}H) [^1J(^{11}B–^{1}H)/Hz]}: BH(1), −1.6, +2.66[165]; BH(2), −18.3, + 1.20[144]; BH(3), −42.5, −0.59[145]; BH(6), −30.4, + 1.81(*exo*), + 0.62(μ), −12.45(μ, splitting 12 Hz) [^1J obscured]; BH(7), + 21.3, + 5.92[153]; BH(8), −28.4, +2.60, −1.43(μ) [^1J obscured]; and BH(9), −5.6, +3.68[152]; δ(^{1}H)(C_5Me_5) + 1.99; observed [^{11}B–^{11}B] COSY correlations were (1–2)s, (1–3)s, (2–3)m, (2–6)s, (2–7)m, (3–7)m, (3–8)m and (3–9)s.

Reaction between [IrCl(CO)(PPh_3)$_2$] *and* Cs[*arachno*-6-SB_9H_{12}].—A solution/suspension of [IrCl(CO)(PPh_3)$_2$] (0.50 g, 0.65 mmol) and Cs[SB_9H_{12}] (0.35 g, 1.28 mmol) in $CHCl_3$ (40 cm^3) was stirred for 12 d, during which time the original yellow solution with a white suspension gave way to a dark orange solution containing a grey suspension. This mixture was filtered, the orange filtrate reduced in volume (room temperature, rotary evaporator, water-pump pressure), and subjected to repeated TLC followed by HPLC separation. Of many coloured bands ultimately separated, only one was found to contain a single component in reasonably viable quantities. This was isolated as an orange-yellow moderately air-stable solid, identified as [$ClH_2(PPh_3)_2IrB_9H_{11}S$] **5** (schematic structure **VII**) [56 mg, 9.9% based on Ir; R_t *ca.* 13 min in CH_2Cl_2–hexane (40:60) as eluting medium] as described in the text.

NMR Spectroscopy.—NMR spectroscopy was performed at 2.35 and/or 9.35 T on commercially available instrumentation, with the general techniques, and also the techniques of ^{1}H-{^{11}B},[63] [^{11}B–^{11}B] COSY[41] and [^{11}H–^{11}H] COSY[73] being essentially as detailed in other recent papers from our laboratories.[2,32,43,74] In the ^{1}H-{^{11}B} experiments use was made of the technique in which a ^{1}H-{^{11}B(40 kHz off-resonance)} spectrum is subtracted from a ^{1}H-{^{11}B(on-resonance)} spectrum in order to remove resonance lines from protons not coupled to the ^{11}B nuclei of interest.[75,76] Chemical shifts δ are given to high frequency (low field) of Ξ 100 ($SiMe_4$) for ^{1}H and Ξ 32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$],[39] Ξ being defined as in ref. 77. The chemical shifts were calibrated using solvent deuteron or residual proton resonances as internal secondary standards.

Single-crystal X-Ray Diffraction Analysis.—Crystals of $[8\text{-}(\eta^5\text{-}C_5Me_5)\text{-}9\text{-}Cl\text{-}nido\text{-}8,7\text{-}IrSB_8H_{10}]$ **2** suitable for the X-ray analysis were grown from concentrated CH_2Cl_2 solution by liquid–liquid diffusion of cyclohexane. Suitable crystals of $Cs[SB_9H_{12}]$ were obtained by recrystallization from warm (*ca.* 80 °C) water.

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω–2θ scan mode using a standard procedure described elsewhere.[78] Both sets of data were corrected for absorption empirically once their structures had been determined.[79]

The structures of both complexes were determined *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[80] For both compounds all non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms of $Cs[SB_9H_{12}]$ were located in a Fourier difference map and were freely refined with individual isotropic thermal parameters. Borane hydrogen atoms for compound **2** were also located in Fourier difference maps but because they tended to shift by large amounts to unreasonable positions during refinement they were assigned a fixed isotropic thermal parameter and their positional parameters were not refined. The methyl hydrogen atoms of this structure were included in calculated positions and were assigned an overall isotropic thermal parameter. In both cases the weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in order to obtain satisfactory agreement analyses. Crystal data, data collection and structure refinement parameters are given in Table 1 and atomic coordinates for compound **2** and $Cs[SB_9H_{12}]$ are given in Tables 11 and 12 respectively.

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

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References

1 M. Bown, Ph.D. Thesis, University of Leeds, July 1987.
2 M. Bown, X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1988, 1467.
3 K. Nestor, Ph.D. Thesis, University of Leeds, 1989.
4 M. Bown, X. L. R. Fontaine, N. N. Greenwood and J. D. Kennedy, *Z. Anorg. Allg. Chem.*, 1991, **602**, 17.
5 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, unpublished work.
6 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1986, 1113.
7 M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1987, 1650.
8 K. Nestor, 6th International Meeting on Boron Chemistry, Bechyně, June 1987, Abstracts of Proceedings no. CA14.
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 M. Bown, H. Fowkes, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon and K. Nestor, *J. Chem. Soc., Dalton Trans.*, 1988, 2597.
11 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, P. MacKinnon and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 2809.
12 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.
13 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1988, 1465.
14 K. Nestor, T. Jelínek, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett, S. Heřmánek and B. Štíbr, *J. Chem. Soc., Dalton Trans.*, 1990, 681.
15 Faridoon, M. McGrath, T. R. Spalding, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1990, 1819.
16 D. A. Thompson, T. K. Hilty and R. W. Rudolph, *J. Am. Chem. Soc.*, 1977, **99**, 6774.
17 K. Baše, B. Štíbr and I. A. Zakharova, *Synth. React. Inorg. Metal. Org. Chem.*, 1980, **10**, 509.
18 A. R. Kane, L. J. Guggenberger and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 2571.
19 G. Ferguson, M. F. Hawthorne, B. Kaitner and F. J. Lalor, *Acta Crystallogr., Sect. C*, 1984, **40**, 1707.
20 D. A. Thompson and R. W. Rudolph, *J. Chem. Soc., Chem. Commun.*, 1976, 770.
21 A. R. Siedle, D. McDowell and L. J. Todd, *Inorg. Chem.*, 1974, **13**, 2735.
22 (*a*) S. O. Kang, P. J. Carroll and L. G. Sneddon, *Organometallics*, 1988, **7**, 772; (*b*) 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, 981.
23 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1985, 1165; *J. Chem. Soc., Dalton Trans.*, 1986, 2417.
24 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 547.
25 X. L. R. Fontaine, H. Fowkes, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, 1986, 1431.
26 R. E. Williams, *Inorg. Chem.*, 1971, **10**, 210; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 67.
27 K. Wade, *Chem. Commun.*, 1971, 792; *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.
28 *Gmelin Handbook of Inorganic Chemistry*, particularly *Boron Compounds. Part 20*, New Suppl. Ser., 1979, vol. 54; and *Boron Compounds*, Third Supplement, 1987, vol. 1.
29 J. D. Kennedy, *Prog. Inorg. Chem.*, 1986, **32**, 427–428.
30 G. Ferguson, M. Parvez, J. A. MacCurtain, O. Ni Dhubhghaill, T. R. Spalding and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1987, 699.
31 L. J. Guggenberger, *J. Organomet. Chem.*, 1974, **81**, 271.
32 G. Ferguson, J. D. Kennedy, X. L. R. Fontaine, Faridoon and T. R. Spalding, *J. Chem. Soc., Dalton Trans.*, 1988, 2555.
33 Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, B. Kaitner, X. L. R. Fontaine, J. D. Kennedy and D. Reed, *J. Chem. Soc., Dalton Trans.*, 1988, 2739.
34 A. F. Williams, H. D. Flack and M. G. Vincent, *Acta Crystallogr., Sect. B*, 1980, **36**, 1206.
35 A. F. Williams, H. D. Flack and M. G. Vincent, *Acta Crystallogr., Sect. B*, 1980, **36**, 1204.
36 P. Kalck, J.-J. Bonnet and R. Poilblanc, *J. Am. Chem. Soc.*, 1982, **104**, 3069.
37 L. R. Gray, D. J. Gulliver, W. Levason and M. Webster, *Acta Crystallogr., Sect. B*, 1982, **38**, 3079.
38 D. Milstein, J. C. Calebrese and I. D. Williams, *J. Am. Chem. Soc.*, 1986, **108**, 6387.
39 J. D. Kennedy, *Multinuclear N.M.R.*, ed. J. Mason, Plenum, Oxford, 1987, ch. 8, pp. 221–254.
40 R. Ahmad, Ph.D. Thesis, University of Leeds, 1982.
41 T. L. Venable, W. C. Hutton and R. N. Grimes, *J. Am. Chem. Soc.*, 1984, **106**, 29.
42 N. N. Greenwood, M. J. Hails, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1985, 953.
43 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.
44 I. Macpherson, Ph.D. Thesis, University of Leeds, 1987.
45 Faridoon, O. Ni Dhubhghaill, T. R. Spalding, G. Ferguson, X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, 1989, 1657.
46 J. E. Crook, Ph.D. Thesis, University of Leeds, 1982.
47 K. Baše. M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, B. Štíbr and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1988, 1240.

48 M. Bown, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *Organometallics*, 1987, **6**, 2254.
49 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, J. Plešek, B. Štíbr and M. Thornton-Pett, *Inorg. Chem.*, 1989, **28**, 2219.
50 M. E. Leonowicz and F. R. Scholer, *Inorg. Chem.*, 1980, **19**, 122.
51 J. R. Pipal and R. N. Grimes, *Inorg. Chem.*, 1979, **18**, 257.
52 M. A. Beckett, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc.*, *Dalton Trans.*, 1985, 1119.
53 J. D. Kennedy, *Prog. Inorg. Chem.*, 1986, **34**, 233–235, 294, 305–306.
54 C. Viñas, W. M. Butler, F. Teixidor and R. W. Rudolph, *Inorg. Chem.*, 1986, **25**, 4369.
55 H. Binder, A. Ziegler, R. Ahlrichs and H. Schiffer, *Chem. Ber.*, 1967, **120**, 1545.
56 M. Komura, H. Nakai and M. Shiro, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1953.
57 D. Reed, G. Ferguson, B. L. Ruhl, O. Ni Dhubhghaill and T. R. Spalding, *Polyhedron*, 1988, **7**, 17.
58 G. Ferguson, B. L. Ruhl, O. Ni Dhubhghailli and T. R. Spalding, *Acta Crystallogr.*, *Sect. C*, 1987, **43**, 1250.
59 G. Ferguson, M. J. Hampden-Smith, O. Ni Dhubhghaill and T. R. Spalding, *Polyhedron*, 1988, **7**, 189.
60 J. Plešek, T. Jelínek, B. Štíbr and S. Heřmánek, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 348.
61 J. Reddy and W. N. Lipscomb, *J. Chem. Phys*, 1959, **31**, 610.
62 D. S. Kendall and W. N. Lipscomb, *Inorg. Chem.*, 1973, **12**, 546.
63 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc.*, *Dalton Trans.*, 1987, 1573.
64 M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante and S. S. Wreford, *J. Am. Chem. Soc.*, 1974, **76**, 4041.
65 M. R. Churchill and J. J. Hackbarth, *Inorg. Chem.*, 1975, **14**, 2047.
66 R. W. Marks, S. S. Wreford and D. D. Traficante, *Inorg. Chem.*, 1978, **17**, 756.
67 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 346.
68 J. Bould, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc.*, *Chem. Commun.*, 1982, 465.
69 A. R. Siedle, D. McDowell and L. J. Todd, *Inorg. Chem.*, 1977, **13**, 1756 and refs. therein.
70 K. Baše, N. W. Alcock, O. W. Howarth, H. R. Powell, A. T. Harrison and M. G. H. Wallbridge, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 341.
71 R. W. Rudolph and W. R. Pretzer, *Inorg. Synth.*, 1983, **22**, 226.
72 J. W. Kong, K. Mosely and P. M. Maitlis, *J. Am. Chem. Soc.*, 1969, **91**, 5970.
73 X. L. R. Fontaine and J. D. Kennedy, *J. Chem. Soc.*, *Chem. Commun.*, 1986, 779.
74 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and P. MacKinnon, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 1785.
75 J. D. Kennedy and J. Staves, *Z. Naturforsch.*, *Teil B*, 1979, **34**, 808.
76 S. K. Boocock, N. N. Greenwood, M. J. Hails, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 1415.
77 W. McFarlane, *Proc. R. Soc. London*, *Ser. A*, 1968, **306**, 185.
78 A. Modinos and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 1974, 2065.
79 N. Walker and D. Stuart, *Acta Crystallogr.*, *Sect. A*, 1983, **39**, 158.
80 G. M. Sheldrick, SHELX 76, Program System for X-Ray Structure Determination, University of Cambridge, 1976.

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