Ten-vertex metallaborane clusters: action as a B-frame support for heterobimetallic species: [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$\overline{C_6H_4)}$-*nido*-7,9-$PtIrB_9H_{10}$-4⌋] and related compounds

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(Received May 15, 1992; revised August 21, 1992)

Abstract

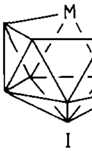
Reaction of the *nido* ten-vertex iridaborane [*sym*-6,6,6-H$(PPh_3)(PPh_2$-*ortho*-$\overline{C_6H_4)}$-*nido*-6-IrB_9H_{12}-5⌋] (**1**) or its uncyclized analogue **2** with KH followed by *cis*-$[PtCl_2(PMe_3)_2]$ yields the orange–red air-stable complex [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$\overline{C_6H_4)}$-*nido*-7,9-$PtIrB_9H_{10}$-4⌋] (**3**) or the corresponding acyclic analogue (**4**). Compound **3** has been characterized by multi-element NMR spectroscopy and by X-ray crystallography. It crystallizes in the monoclinic space group *C*2/*c* with $a = 4072.1(8)$, $b = 1509.2(4)$, $c = 1912.9(4)$ pm, $\beta = 110.63(2)°$, $Z = 8$, and the structure ($R = 0.047$ from 5641 reflections) is that of an eleven-vertex *nido*-dimetallaundecaborane with non-adjacent metal atoms in its open face, and has similarities to the structures of related *nido*-monometallaundecaboranes. During the course of the reaction the starting compounds **1** and **2** are shown to undergo a cluster rearrangement that may also play a role in many hitherto ostensibly disparate ten-vertex cluster reactions.

Introduction

We have developed an interest in the use of polyhedral borane frameworks as 'B-frame' matrices on which to bind two potentially reactive transition-metal centres in positions in which they may mutually interact and thereby generate interesting chemistry [1–9]. We have previously reported the synthesis of the *nido*-6-iridadecaboranes $[(PPh_3)_2HIrB_9H_{13}]$ and $[(PPh_3)(PPh_2\text{-}\overline{C_6H_4)HIrB}_9H_{12}]$ in reasonable yields from the easily synthesized starting materials *arachno*-$[B_9H_{14}]^-$, *nido*-$[B_9H_{12}]^-$ and $[IrCl(PPh_3)_3]$ [10–12]. These two iridaboranes are direct metallaborane analogues (schematic cluster structure I) of the binary borane *nido*-$B_{10}H_{14}$ (schematic structure II). This *nido* decaborane is known to react with bis(phosphine)platinum dihalides in the presence of base (eqn. (1)) to form *nido* eleven-vertex 7-platinaundecaboranes (schematic structure III) in good yield [13, 14]. This communication reports the results of experiments to explore the possibility that the *nido*-6-iridadecaboranes might undergo similar reactions to yield *nido* eleven-vertex platinairidaundecaboranes. Aspects of this work have already been reported in a preliminary fashion [2]. Here we present a more detailed account.

$$[PtCl_2(PR_3)_2] + B_{10}H_{14} + 2\ \text{base} \longrightarrow [(PR_3)_2PtB_{10}H_{12}] + 2\ \text{baseH}^+Cl^- \quad (1)$$

The numbering schemes for the clusters of the compounds described in this paper are represented in structures IV (ten-vertex *nido*) and structure V (eleven-vertex *nido*).



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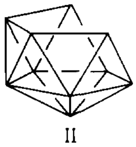

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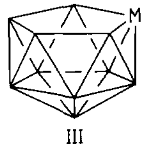

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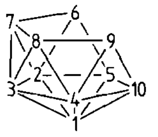

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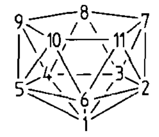

V

Results and discussion

The reaction (scale *c.* 2 mmol) of a tetrahydrofuran–CH_2Cl_2 solution of [*sym*-6,6,6-H$(PPh_3)(PPh_2$-*ortho*-$\overline{C_6H_4)}$-*nido*-6-IrB_9H_{12}-5⌋] (**1**) with KH, followed by the addition of *cis*-$[PtCl_2(PMe_3)_2]$, gave a 46% isolated yield of the orange–red air-stable complex [7,7-

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0020-1693/93/$6.00

$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$\overline{C_6H_4)}$-*nido*-7,9-$\overline{\text{Pt-IrB}_9\text{H}_{10}\text{-4}}$] (**3**). A similar reaction using the non-cyclic compound $[(PPh_3)_2HIrB_9H_{13}]$ gave a 5% yield of [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)_2$-*nido*-7,9-$PtIrB_9H_{11}$] (**4**). A simple stoichiometry may be written down for both these reactions (eqns. (2) and (3)).

$$[(PPh_3)(Ph_2P\overline{C_6H_4)HIrB}_9H_{12}] + 2KH + [PtCl_2(PMe_3)_2] \longrightarrow [(PMe_3)_2H(PPh_3)(Ph_2P\overline{C_6H_4)PtIrB}_9H_{10}] + 2KCl + H_2 \qquad (2)$$

$$[(PPh_3)_2HIrB_9H_{13}] + 2KH + [PtCl_2(PMe_3)_2] \longrightarrow [(PMe_3)_2H(PPh_3)_2PtIrB_9H_{11}] + 2KCl + H_2 \qquad (3)$$

The compounds have been identified by a combination of multi-element NMR spectroscopy and X-ray crystallography. The measured NMR data are listed in Tables 1 and 2 and the lists of interatomic distances and interatomic angles for compound **3** are given in Tables 3 and 4, respectively.

An ORTEP drawing of the molecule of **3** may be seen in Fig. 1. All atomic positions including the hydrogen ones were located from the X-ray data with the exception of the terminal iridium hydride, of which the position was determined from Orpen-type potential-well calculations [15], all in accordance with the NMR data. These NMR data show signals due to nine boron atoms (Fig. 2), eight with terminal hydrogen atoms and one which gives rise to a sharp singlet ^{11}B resonance due to the presence of an *ortho*-phenylene substituent rather than a hydrogen atom. The *ortho*-phenylene ring hydrogen atoms give rise to a characteristic [12] complex pattern in the low-field aromatic region of the proton spectrum. The bridging hydrogen atoms in the open face are also apparent from selective ^1H-$\{^{11}B\}$ NMR experiments, and also from the potential-well calculations which give results in good agreement with the positions obtained from the X-ray data.

The chemical shifts of the ^{11}B, ^1H and ^{31}P resonances for the acyclic analogue, compound **4**, are very close to those of compound **3**, except for the resonance assigned to $^{11}B(4)$ which shows an upfield shift of *c.* 13 ppm compared to that for **3**, in which this position bears an *ortho*-phenylene substituent. The deshielding effect of the phenylene substituent is similar to that for a chlorine substituent in this type of molecule ($\Delta\sigma$ *c.* −10 to *c.* −15 ppm) [4, 17–19]. This $^{11}B(4)$ resonance is associated with a ^1H(*exo*) resonance, and so compound **4** is reasonably assigned as [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)_2$-*nido*-7,9-$PtIrB_9H_{11}$].

Figure 3 compares the structure of the cyclic compound **3** with that of the isoelectronic and quasi-isostructural compounds [7,7,7-$(PPh_3)_2(CO)$-*nido*-7-$IrB_{10}H_{11}$-1-(PPh_3)] [20] (**5**) and [7,7-$(PMe_2Ph)_2$-*nido*-7-$PtB_{10}H_{12}$] [13] and emphasizes the marked similarity of the three clusters although the iridium vertex in **5** is in a position more similar to that of the platinum vertex in **3** (Fig. 3(b)) and in the platinaundecaborane (Fig. 3(c)) in that it is remote from the bridging hydrogen atoms.

Metal to boron distances in the open face, of compound **3**, for both platinum and iridium, range from 228.5(11) to 226.2(12) pm and tend to be longer than distances from the metal to the inner cluster boron atoms which range from 220.6(11) to 226.2(12) pm. The Pt(7)–B(8) distance is significantly longer (6σ) than

TABLE 1. Proton and ^{11}B and NMR data for [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$\overline{C_6H_4)}$-*nido*-7,9-$\overline{\text{PtIrB}_9\text{H}_{10}\text{-4}}$] (**3**) and [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)_2$-*nido*-7,9-$PtIrB_9H_{11}$] (**4**) in CD_2Cl_2 solution at *c.* 25 °C

Tentative assignments	Compound **3**			Compound **4**		
	$\delta(^{11}B)$ (ppm)	$w_{1/2}(^{11}B)$ (Hz)	$\delta(^1H)$ (ppm)	$\delta(^{11}B)$ (ppm)	$w_{1/2}(^{11}B)$ (Hz)	$\delta(^1H)$ (ppm)
(1), (5) or (10)	+28.9	250	+3.93	+28.7	250	+3.98
(2) or (3)	+24.7[a]	250	+6.67	+18.9[a]	250	+6.65
8	+23 ± 1[a]	>370	+4.73	+24.9[a]	>370	+4.47
(1), (5) or (10)	+22.1	250	+4.63	+28.3	250	+4.30
(11), (2) or (3)	+7.8[a]	320	+1.55	+5.8[a]	320	+1.57
4	+6.4	120	[b]	−6.5	180	+1.76
(1) or (5)	−0.5	120	+2.56[c]	+0.6	150	+1.98[c]
(11), (2) or (3)	−4.0[a]	320	+1.52	−1.3[a]	320	+1.28
6	−21.6	100	+1.66	−23.9	120	+1.11
H(8, 9)			−8.43[d]			−8.44[d]
H(10, 11)			−3.18[d]			−3.20[d]
H(9)			−15.52[d]			−15.87[d]

[a] Possible satellites $^2J(^{195}Pt-^{11}B)$ *c.* 250 Hz. [b] Site of phenylene substituent. [c] $^2J(^{195}Pt-^1H)$ 70 Hz. [d] Shows coupling to other nuclei, see Table 2.

TABLE 2. (^{31}P)^{a} and (^{1}H) chemical shift and coupling constant data for compounds **3** and **4**

Parameter^{b}	Compound **3**	Compound **4**
At the platinum		
$\delta[(^{31}P)(A/B)]$ (ppm)	-14.1, -16.6	-13.5, -15.4
$^{2}J[(^{31}P)(A)-^{31}P(B)]$*cis* (Hz)	27.0 ± 0.2	27.0 ± 0.2
$^{1}J[^{195}Pt-P(A/B)]$ (Hz)	2492.7, 2573.3	2390.1, 2462.2
$\delta[(^{1}H)(Me)]$ (ppm)	$+1.39$, $+1.23$	$+1.53$, $+1.41$
$^{2}J[^{31}P-^{1}H(Me)]$ (Hz)	9 ± 0.5, 8 ± 0.5	^{c}
$^{2}J[^{195}Pt-^{1}H(Me)]$ (Hz)	23.9, 24.0	^{c}
At the iridium		
$\delta[(^{31}P)(C/D)]$ (ppm)	$+26.4$, $+21.2$	$+21.5$, $+18.8$
$^{2}J[^{31}P(C)-^{31}P(D)]$*cis* (Hz)	12 ± 1	16 ± 1
$^{3}J[^{195}Pt-^{31}P(C/D)]$ (Hz)	21 ± 2, 12 ± 2	14 ± 2, 18 ± 2
$\delta[(^{1}H)(9)]$ (ppm)	-15.52	-15.87
$^{2}J[^{31}P(C/D)-^{1}H(9)]$cis (Hz)	19 ± 1	20 ± 1
$^{2}J[^{1}H(8,9)-^{1}H(9)]$*trans* (Hz)	8.0 ± 0.5	8.0 ± 0.5
$^{3}J[^{195}Pt-^{1}H(9)]$ (Hz)	21 ± 2	^{c}
$\delta[^{1}H(8,9)]$ (ppm)	-8.43	-8.44
$^{2}J[^{195}Pt-^{1}H(8,9)]$ (Hz)	54 ± 1	40 ± 1
$\delta[(^{1}H)(10,11)]$ (ppm)	-3.18	-3.20
$^{2}J[^{195}Pt-^{1}H(10,11)]$ (Hz)	36 ± 1	38 ± 1

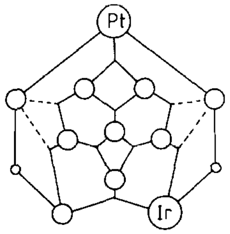
^{a}Recorded in CD_2Cl_2 solution at -60 °C and 40 MHz. ^{b}A and B refer to chemically distinct phosphorous atoms on the platinum, C and D refer to those on the iridium atom. ^{c}Not measured.

the Pt(7)–B(11) distance: a tendency which may also be noted for the Ir(9)–B(8) versus the Ir(9)–B(10) vector although here the difference is below the level of significance. The B(11)–Pt(7)–B(8) and B(8)–Ir(9)–B(10) angles of 90.4(5) and 90.2(4)°, respectively, are not significantly different and are similar to those in $[(PMe_2Ph)_2PtB_{10}H_{12}]$ (90.1(2)°) [13] and $[\{P(OMe)_3\}_2PtB_{10}H_{12}]$ (90.5(4)°) [14]. The equivalent angle in the iridaundecaborane **5** is slightly smaller at 85.1(8)°. Other angles about the iridium in compound **3** are reasonable for an octahedral iridium(III) centre bound to a borane cluster.

The main-group-metal *nido*-metallaundecaborane clusters have sometimes been regarded as metal complexes of an effective η^4-*nido*-$[B_{10}H_{12}]^{2-}$ ligand rather than as integral *nido* eleven-vertex clusters [21, 22]. In this type of approach the metal-atom centres are regarded as replacing the two bridging hydrogen atoms of the neutral *nido*-$[B_{10}H_{14}]$ and thereby as binding to the cluster via two two-electron three-centre bonds. Thus the interboron distances corresponding to the long B(5)–B(10) linkage in *nido*-$[B_{10}H_{14}]$ (197.3(4) pm) [23, 24] remain largely unperturbed at 197(3) pm in the $[Me_2TlB_{10}H_{12}]^-$ anion [25] and at 194(1) pm in the $[Zn(B_{10}H_{12})_2]^{2-}$ anion [26]. In compound **3**, however, the structurally equivalent distance, viz. B(2)–B(3) (185.6(17) pm), is more akin to the normal intracluster interboron range of *c*. 170–190 pm, suggesting that the bonding may have changed from that of the ten-vertex *nido*-decaborane face-edge type of bonding to the more fully intracluster multicentre type of interboron bonding of an integral *nido* eleven-vertex undecaborane cluster. This effect has also been considered in $[7,7-(PMe_2Ph)_2$-*nido*-$7-PtB_{10}H_{12}]$ [13, 14, 21, 27], where contributions to the bonding have been described in terms of a platinum(IV) $\{Pt(PMe_2Ph)\}^{4+}$ moiety binding with an *arachno*-type $\{B_{10}H_{12}\}^{4-}$ ligand, thus generating a formalism for the resultant cluster in which the neutral $\{Pt(PMe_2Ph)_2\}$ centre acts as a four-electron, three-orbital cluster contributor. The similarity of the bonding geometry about platinum in $[(PMe_2Ph)_2PtB_{10}H_{12}]$ [13] with that of **3** suggests that a similar interpretation may also be a valid description for this compound. The fact that the 3-orbital, 3-electron $\{(CO)(PPh_3)Ir\}$ moiety in **5** occupies an equivalent position to that of the platinum vertex in **3** illustrates that the site is suitable for a variety of bonding possibilities. The bonding around the iridium centre Ir(9) can in a straightforward manner be reasonably interpreted as pseudo-octahedral and the iridium vertex thereby regarded [9] now as an 18-electron $\{IrH(PPh_3)_2\}$ iridium(III) centre, contributing three orbitals and two electrons to combine in a classical Wadian [28] manner with an *arachno*-type $\{(PMe_2Ph)_2PtB_9H_{11}\}$ unit. As such the overall eleven-vertex cluster bonding might be regarded as being based upon a 2740 *styx* topological description of *nido*-$[B_{11}H_{13}]^{2-}$ as in structure VI (*styx* being defined as in ref. 29).

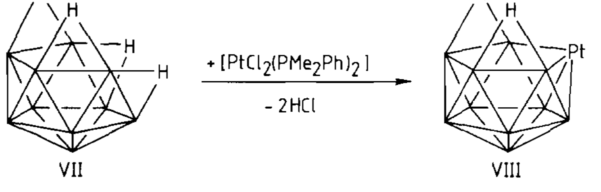
TABLE 3. Interatomic distances (pm) for compound **3**

To the platinum atom			
P(1)–Pt(7)	233.4(5)	P(2)–Pt(7)	233.4(4)
B(2)–Pt(7)	221.6(11)	B(3)–Pt(7)	224.3(13)
B(8)–Pt(7)	235.7(11)	B(11)–Pt(7)	228.5(12)
To the iridium atom			
P(3)–Ir(9)	230.8(4)	P(4)–Ir(9)	230.3(4)
B(4)–Ir(9)	226.2(12)	B(5)–Ir(9)	220.6(11)
B(8)–Ir(9)	231.2(10)	B(10)–Ir(9)	228.6(13)
H(8,9)–Ir(9)	175(7)		
Phosphorus–carbon			
C(11)–P(1)	181.1(13)	C(12)–P(1)	179.0(17)
C(13)–P(1)	181.0(15)	C(21)–P(2)	181.3(14)
C(22)–P(2)	181.2(12)	C(23)–P(2)	182.3(14)
C(311)–P(3)	183.2(6)	C(321)–P(3)	181.3(8)
C(331)–P(3)	182.6(7)	C(411)–P(4)	182.1(7)
C(421)–P(4)	183.4(7)	C(431)–P(4)	182.5(8)
Boron–boron and boron–carbon			
B(2)–B(1)	177.6(17)	B(3)–B(1)	176.4(16)
B(4)–B(1)	175.6(15)	B(5)–B(1)	177.4(16)
B(6)–B(1)	174.1(20)	B(3)–B(2)	185.6(17)
B(6)–B(2)	175.2(16)	B(11)–B(2)	173.1(19)
B(4)–B(3)	177.0(14)	B(8)–B(3)	178.9(15)
B(5)–B(4)	182.3(17)	B(8)–B(4)	183.3(15)
C(322)–B(4)	162.3(15)	B(6)–B(5)	179.8(16)
B(10)–B(5)	182.2(19)	B(10)–B(6)	177.2(17)
B(11)–B(6)	176.2(18)	B(11)–B(10)	186.3(15)
Boron–hydrogen			
H(1)–B(1)	114(10)	H(2)–B(2)	121(6)
H(3)–B(3)	112(7)	H(5)–B(5)	121(5)
H(6)–B(6)	124(7)	H(8)–B(8)	112(6)
H(10)–B(10)	109(9)	H(8,9)-B(8)	135(8)
H(10,11)–B(10)	111(9)	H(11)–B(11)	106(9)
H(10,11)–B(11)	137(8)		



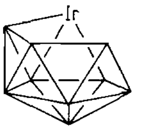
VI

Aspects of the mechanism of formation of compounds **3** and **4** merit brief discussion. The reaction of *cis*-[PtCl$_2$(PR$_3$)$_2$] with *nido* decaborane and base is reasonably regarded as proceeding according to eqn. (4) (structures VII→VIII) (see also eqn. (1) above).



(4)

An analogous reaction (eqns. (2) and (3) above) with the *nido*-iridadecaboranes **1** and **2** (schematic structures I and IX) would be expected to give an eleven-vertex *nido*-platinairidaundecaborane cluster with the platinum and iridium atoms in adjacent positions (structure X). In the event the two metal atoms are separated by a boron atom (structure XI) showing that a rearrangement has occurred either in the iridadecaborane cluster before or during the insertion of platinum or in the platinairidaundecaborane cluster after insertion. At present we believe that the observation can be better rationalized in terms of an initial 'vertex-swing' type of rearrangement of the *nido*-iridadecaborane cluster possibly via an *isonido* intermediate type [30] (Scheme 1, schematic structures XII and XIII) as has been more fully described in a previous paper of ours [12] and, furthermore, that this rearrangement is common to many *nido* ten-vertex cluster reactions although not necessarily via *isonido* intermediates, as has become more apparent [8, 19, 30–36] since our preliminary communication [2].



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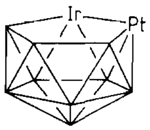

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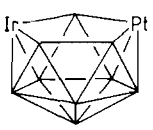


XI

Attempts were made to add a third metal centre, via an initial deprotonation of the platinairidaborane compounds **3** and **4** with KH or MeLi, followed by the addition of low-valent transition-metal halide complexes such as [Rh(cod)Cl]$_2$ (cod = 1,5-cyclooctadiene), [Os(CO)$_3$Cl$_2$]$_2$ and [Fe(CO)$_4$Br$_2$]. In each case a reaction occurred but the yields of any metallaborane products were too low to enable their proper characterization. Also, the overall pattern and colour of the bands on the t.l.c. plates appeared to be the same regardless of the metal halide complex used, suggesting that the metal complexes initiate a decomposition or modification of the basic {PtIrB$_9$} cluster and that the products do not therefore have a third metal incorporated.

Experimental

General

The *nido*-metallaboranes [*sym*-6,6,6-H(PPh$_3$)-(PPh$_2$-*ortho*-$\overline{\mathrm{C_6H_4)\text{-}}\mathit{nido}\mathrm{\text{-}6\text{-}Ir\text{-}B_9H_{12}\text{-}5}}$] (**1**) and [(PPh$_3$)$_2$-HIrB$_9H_{13}$] (**2**) were synthesized as described elsewhere [9–12], and *cis*-[PtCl$_2$(PMe$_3$)$_2$] was prepared by literature methods [37]. Reactions were carried out, and solutions and solids kept, under dry nitrogen although separatory procedures were carried out in air. Preparative and analytical thin-layer chromatography (t.l.c.) were performed using silica gel (Fluka type GF 254) with a fluorescent indicator as the stationary phase [1, 35]. IR spectra were recorded from KBr discs using a Perkin-Elmer 457 grating infrared spectrometer.

TABLE 4. Selected angles (°) between interatomic vectors for compound **3**

About the platinum atom			
P(2)–Pt(7)–P(1)	100.7(2)	B(2)–Pt(7)–P(1)	99.2(4)
B(2)–Pt(7)–P(2)	148.6(3)	B(3)–Pt(7)–P(1)	143.4(2)
B(3)–Pt(7)–P(2)	102.6(4)	B(3)–Pt(7)–B(2)	49.2(4)
B(8)–Pt(7)–P(1)	167.9(3)	B(8)–Pt(7)–P(2)	81.0(3)
B(8)–Pt(7)–B(2)	84.5(4)	B(8)–Pt(7)–B(3)	45.7(3)
B(11)–Pt(7)–P(1)	84.3(4)	B(11)–Pt(7)–P(2)	161.2(2)
B(11)–Pt(7)–B(2)	45.2(4)	B(11)–Pt(7)–B(3)	82.7(5)
B(11)–Pt(7)–B(8)	90.4(5)		
About the iridium atom			
P(4)–Ir(9)–P(3)	107.2(2)	B(4)–Ir(9)–P(3)	82.5(4)
B(4)–Ir(9)–P(4)	169.3(3)	B(5)–Ir(9)–P(3)	117.7(4)
B(5)–Ir(9)–P(4)	127.0(4)	B(5)–Ir(9)–B(4)	48.1(4)
B(8)–Ir(9)–P(3)	84.2(4)	B(8)–Ir(9)–P(4)	127.7(4)
B(8)–Ir(9)–B(4)	47.2(3)	B(8)–Ir(9)–B(5)	85.2(4)
B(10)–Ir(9)–P(3)	165.0(3)	B(10)–Ir(9)–P(4)	87.2(4)
B(10)–Ir(9)–B(4)	83.6(5)	B(10)–Ir(9)–B(5)	47.8(4)
B(10)–Ir(9)–B(8)	90.2(4)	H(8,9)–Ir(9)–P(3)	96(3)
H(8,9)–Ir(9)–P(4)	92.4(27)	H(8,9)–Ir(9)–B(4)	82(3)
H(8,9)–Ir(9)–B(5)	109(2)	H(8,9)–Ir(9)–B(8)	35(3)
H(8,9)–Ir(9)–B(10)	87(3)		
About the open face			
H(8,9)–B(8)–Pt(7)	89(3)	H(8,9)–B(8)–Ir(9)	49(3)
Ir(9)–B(8)–Pt(7)	117.6(6)	B(11)–B(10)–Ir(9)	118.9(7)
B(10)–B(11)–Pt(7)	116.6(7)	H(10,11)–B(11)–Pt(7)	95(4)
Others			
B(8)–H(8,9)–Ir(9)	96(5)	B(11)–H(10,11)–B(10)	97(6)
B–B–B(acute)	57.9(7)–63.6(7)	B–B–B(obtuse)	106.3(8)–115.2(9)

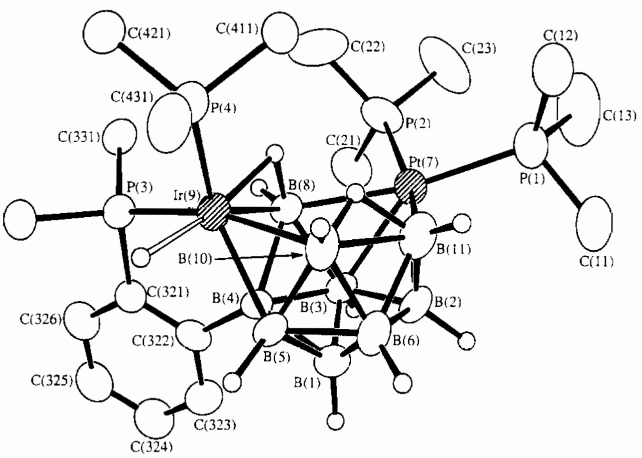


Fig. 1. ORTEP diagram of [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$C_6H_4)$-*nido*-7,9-$PtIrB_9H_{10}$-4] (**3**). The terminal iridium hydride atom was not located from the X-ray analysis but its position was determined from Orpen-type [15] potential-well calculations. Phenyl carbon and hydrogen atoms, except for the *ipso*-carbon ones, are omitted for clarity.

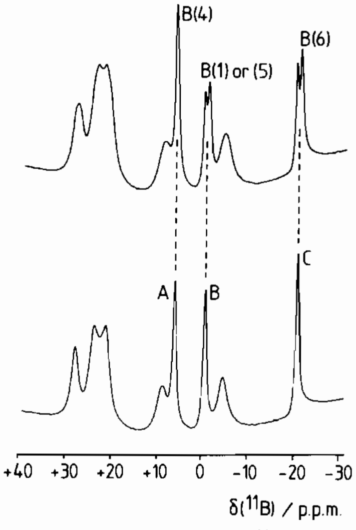


Fig. 2. 128 MHz ^{11}B and ^{11}B-{^{1}H} NMR spectra of [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$C_6H_4)$-*nido*-7,9-$PtIrB_9H_{10}$-4] (**3**) at *c.* 25 °C. Under these conditions [^{11}B–^{11}B]-COSY correlations were observed among the sharper lines A, B and C as follows: A–B(m) and B–C(m) (see Figure 8.8 in ref. 17).

NMR spectroscopy

The 2.35 T ^{1}H (*c.* 100 MHz), ^{31}P (*c.* 40 MHz) and ^{11}B (*c.* 32 MHz) NMR spectra were obtained using a JEOL FX100 instrument [17, 38]. the ^{31}P {^{1}H(broadband noise)} spectra were recorded at lower temperature to maximize line-sharpening arising from the 'thermal decoupling' of the effects of boron nuclear spins [39]. High-field (*c.* 9.35 T; 128 MHz) ^{11}B and ^{11}B-{^{1}H} experiments were performed on a Bruker WH-400 pulse (FT) spectrometer as part of the S.E.R.C. service at Sheffield University. Some selective ^{1}H-{^{11}B} experi-

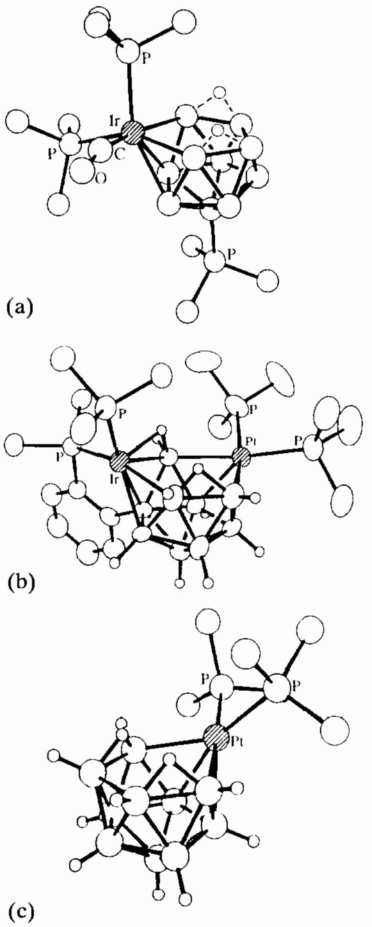
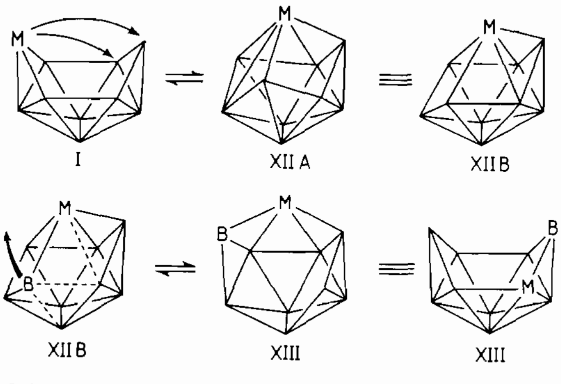


Fig. 3. ORTEP diagrams of [7,7,7-$(PPh_3)_2(CO)$-*nido*-7-$IrB_{10}H_{11}$-1-(PPh_3)] (**5**) (a) (the bridging hydrogens were not located but are probably in the positions indicated by the dashed lines [20]), [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-*ortho*-$C_6H_4)$-*nido*-7,9-$PtIrB_9H_{10}$-4-] (**3**) (b) and [7,7-$(PMe_2Ph)_2$-*nido*-7-$PtB_{10}H_{12}$] (c), illustrating the structural similarities between the mono- and di-metallaborane clusters.



Scheme 1.

ments were carried out at *c.* 8.41 T (360 MHz for ^1H) on a Bruker WH-360 instrument as part of the S.E.R.C. service at the University of Edinburgh, based on approaches as described elsewhere [10, 16, 38]. Chemical shifts δ are given in parts per million (ppm) to high frequency (low field) of $[SiMe_4]$ (Ξ 100 MHz) for ^1H, of $[BF_3(OEt_2)]$ (Ξ 32 083 971 Hz) for ^{11}B, and of 85% H_3PO_4 (Ξ 40 480 730 Hz) for ^{31}P, Ξ being defined as in ref. 40. Spectra were calibrated in δ using solvent deuteron or residual proton resonances as internal secondary standards.

Synthesis of [7,7-$(PMe_3)_2$-9,9,9-H$(PPh_3)(Ph_2P$-ortho-$C_6H_4)$-nido-7,9-$PtIrB_9H_{10}$-4-] (3)

To a solution of [*sym*-6,6,6-H$(PPh_3)(PPh_2$-*ortho*-$C_6H_4)$-*nido*-6-IrB_9H_{12}-5-] (**1**; 2.0 g, 2.5 mmol) in tetrahydrofuran (thf) (100 ml), potassium hydride (0.4 g, 2.5 mmol based on 50% activity) was added and the mixture stirred for 2.5 h, after which time dichloromethane (60 ml) was added, followed by a sample of *cis*-$[PtCl_2(PMe_3)_2]$ (1.0 g, 2.5 mmol). The stirred solution turned from yellow–orange to a dark red–brown colour. After 30 min the solution was filtered in air and reduced in volume to *c.* 10 ml, at which point *c.* 0.8 g of the title compound **3** had precipitated out. This was filtered off, washed with thf, the combined filtrate reduced to dryness, redissolved in dichloromethane, and applied to a preparative t.l.c. plate. The plate was developed with dichloromethane/pentane (80:20) as mobile phase, giving two bands. The first band (R_f 0.8) was identified as unreacted starting iridadecaborane complex (**1**; 0.6 g, 0.75 mmol) and the second (R_f 0.3) as the title compound **3**. The latter was combined with the filtered sample, dissolved in dichloromethane, and purified by slow precipitation with pentane to give pure **3** (0.95 g, 0.81 mmol; 46% yield based upon unrecovered compound **1**) (ν_{max}(Ir–H) 2185 cm^{-1}).

Synthesis of [7,7-$(PMe_3)2$-9,9,9-H$(PPh_3)_2$-nido-7,9-$PtIrB_9H_{11}$] (4)

To a solution of $[(PPh_3)_2HIrB_9H_{13}]$ (**2**; 300 mg, 360 μmol) in dry dichloromethane–thf (15:10; 25 ml) was added KH (60 mg, 720 μmol based on 50% activity) and *cis*-$[PtCl_2(PMe_3)_2$ (150 mg, 360 μmol). The mixture was stirred for 2 days during which time it changed from a yellow to a reddish colour. Some KH remained unreacted at the end of this time. The mixture was filtered through silica gel (Fluka type GF254), reduced to dryness, redissolved in dichloromethane and applied to a preparative t.l.c. plate which was then developed using 100% dichloromethane as liquid phase. Two main bands resulted: one (R_f 0.9) was identified as the unreacted iridadecaborane **2** (130 mg, 43% recovery) and the second, a reddish-orange band (R_f 0.3), as compound **4**. The latter was repeatedly chromatographed until pure and was obtained as a non-crystalline solid (20 mg, *c.* 5% yield).

X-ray crystallography

All crystallographic measurements were carried out on a Syntex $P2_1$ diffractometer operating in the $\omega/2\theta$ scan mode and with graphite monochromatized Mo Kα

TABLE 5. Atom coordinates ($\times 10^4$) for compound **3**

	x	y	z
Pt(7)	2717.9(1)	1858.5(2)	1611.4(2)
Ir(9)	3618.5(1)	2374.8(2)	3273.8(2)
P(1)	2115(1)	1932(2)	1369(1)
P(2)	2775(1)	385(2)	1302(1)
P(3)	4103(1)	1627(1)	3216(1)
P(4)	3563(1)	2014(1)	4397(1)
C(11)	1921(3)	2980(7)	971(6)
C(12)	1971(3)	1814(10)	2147(7)
C(13)	1815(3)	1201(10)	691(8)
C(21)	2999(3)	273(7)	639(5)
C(22)	3015(4)	−315(6)	2085(6)
C(23)	2391(3)	−303(8)	837(8)
B(1)	3263(3)	3624(7)	1692(6)
B(2)	2821(3)	3279(6)	1479(6)
B(3)	3162(3)	2523(6)	1380(5)
B(4)	3564(3)	2775(6)	2098(5)
B(5)	3482(3)	3648(6)	2674(6)
B(6)	3028(3)	3959(7)	2251(6)
B(8)	3334(3)	1737(6)	2119(5)
B(10)	3158(3)	3326(7)	3085(6)
B(11)	2740(3)	3111(7)	2298(5)
C(311)	4531(1)	1767(4)	3958(3)
C(312)	4763(1)	1066(4)	4241(3)
C(313)	5085(1)	1219(4)	4808(3)
C(314)	5174(1)	2072(4)	5093(3)
C(315)	4942(1)	2772(4)	4809(3)
C(316)	4620(1)	2620(4)	4242(3)
C(321)	4188(1)	2087(4)	2421(2)
C(322)	3926(1)	2623(4)	1939(2)
C(323)	3974(1)	3004(4)	1317(2)
C(324)	4283(1)	2848(4)	1177(2)
C(325)	4544(1)	2312(4)	1659(2)
C(326)	4496(1)	1932(4)	2281(2)
C(331)	4070(2)	429(3)	3071(3)
C(332)	4019(2)	−99(3)	3623(3)
C(333)	3987(2)	−1016(3)	3528(3)
C(334)	4006(2)	−1403(3)	2881(3)
C(335)	4056(2)	−875(3)	2329(3)
C(336)	4088(2)	42(3)	2424(3)
C(411)	3122(1)	1601(4)	4233(3)
C(412)	2878(1)	2070(4)	4447(3)
C(413)	2540(1)	1734(4)	4285(3)
C(414)	2446(1)	930(4)	3909(3)
C(415)	2690(1)	460(4)	3694(3)
C(416)	3028(1)	796(4)	3856(3)
C(421)	3855(1)	1186(4)	5007(3)
C(422)	4206(1)	1439(4)	5332(3)
C(423)	4454(1)	837(4)	5766(3)
C(424)	4352(1)	−19(4)	5875(3)
C(425)	4001(1)	−272(4)	5550(3)
C(426)	3753(1)	330(4)	5116(3)
C(431)	3608(2)	2883(4)	5088(3)
C(432)	3681(2)	3758(4)	4959(3)
C(433)	3712(2)	4404(4)	5500(3)
C(434)	3670(2)	4175(4)	6170(3)
C(435)	3597(2)	3299(4)	6299(3)
C(436)	3566(2)	2653(4)	5758(3)
H(1)	3318(24)	4070(62)	1265(49)
H(2)	2622(17)	3604(42)	909(34)
H(3)	3136(17)	2410(39)	787(36)
H(5)	3677(14)	4258(32)	2954(29)
H(6)	2947(17)	4733(43)	2332(33)
H(8)	3460(15)	1131(38)	1992(30)
H(10)	3134(21)	3555(53)	3606(45)
H(11)	2542(21)	3375(51)	2477(42)
H(8,9)	3310(19)	1575(46)	2791(39)
H(10,11)	2968(24)	2771(57)	2952(48)

radiation ($\lambda = 71.069$ pm) following a standard procedure [41]. The data set was corrected for absorption numerically using the SHELX program system [42]. The structure was solved by standard heavy-atom methods and was refined by blocked full-matrix least-squares using SHELX. All non-hydrogen atoms were assigned anisotropic thermal parameters except for the atoms of two disordered CH_2Cl_2 molecules which were assigned isotropic thermal parameters. Phenyl groups were treated as rigid bodies with idealized hexagonal symmetry (C–H = 139.5 pm). All phenyl and methyl hydrogen atoms were included in calculated positions (C–H = 108 pm) and were refined with an overall isotropic thermal parameter. All cluster-associated hydrogen atoms were located in Fourier difference maps (apart from the terminal hydride associated with the iridium atom which was not located) and were freely refined with isotropic thermal parameters. Final atomic coordinates (other than methyl and phenyl hydrogens) are listed in Table 5.

Crystal data for (3)

$C_{42}H_{58}B_9IrP_4Pt.2CH_2Cl_2$, $M = 1424.20$ (includes solvent molecules), monoclinic, space group $C2/c$, $a = 4072.1(8)$, $b = 1509.2(4)$, $c = 1912.9(2)$ pm, $\beta = 110.63(2)°$, $U = 11.002(4)$ nm^3, $Z = 8$, $D_x = 1.71$ Mg m^{-3}, $\mu = 50.77$ cm^{-1}, $F(000) = 5223.25$.

Data collection and structure refinement

Scan widths $1.8° + \alpha$-doublet splitting, scan speeds 2.0–29.3° min^{-1}, $4.0 < 2\theta < 45.0°$. Total data collected 6349, no. observed 5637 ($F > 4.0\sigma(F)$). No. of parameters = 547, $R = 0.0331$, $R_w = 0.0325$ ($w = [\sigma^2(F_o) + 0.0002(F_o)^2]^{-1}$).

Acknowledgements

We wish to thank the SERC for support, Drs B. E. Mann, O. Howarth and D. Reed for services in NMR spectroscopy, and Dr P. Brint, the University of Cork, and Eolas (Ireland) for support (to J.B.) during the preparation of this paper. We also thank Professor N.

N. Greenwood for facilities and encouragement during the initial stages of the work reported here.

References

1 J. Bould, *Metallaborane clusters of some platinum metals, Ph.D. Thesis,* University of Leeds, 1983.

2 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Chem. Commun.,* (1983) 949.

3 J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.,* (1983) 951.

4 J. Bould, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.,* (1984) 2477.

5 M. Elrington, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.,* (1984) 1398.

6 Y. M. Cheek, J. D. Kennedy and M. Thornton-Pett, *Inorg. Chim. Acta, 99* (1985) L43.

7 X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, M. Thornton-Pett and Zheng Peiju, *J. Chem. Soc., Chem. Commun.,* (1987) 1717.

8 K. Nestor, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.,* (1989) 455.

9 J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.,* (1991) 185.

10 S. K. Boocock, J. Bould, N. N. Greenwood, J. D. Kennedy and W. S. McDonald, *J. Chem. Soc., Dalton Trans.,* (1982) 713.

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

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

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

14 M. Kirk, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, to be published.

15 A. G. Orpen, *HYDEX and XHYDEX,* programs for the indirect location of hydrogen atoms using potential well calculations; M. Thornton-Pett, A. G. Orpen and J. D. Kennedy, unpublished findings.

16 J. D. Kennedy and B. Wrackmeyer, *J. Magn. Reson., 38* (1980) 529.

17 J. D. Kennedy, in J. Mason (ed.), *Multinuclear N.M.R.,* Plenum, London, 1987, Ch. 8, pp. 221–258, and refs. therein.

18 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.

19 R. Ahmed, *Reactions of substituted decaboranes and nonaboranes with platinum(II) complexes, Ph.D. Thesis,* University of Leeds, 1982; R. Ahmed, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.,* to be submitted for publication.

20 J. E. Crook, *Synthetic and structural studies on some novel metallaboranes, Ph.D. Thesis,* University of Leeds, 1982, as cited, for example, in ref. 21.

21 J. D. Kennedy, *Prog. Inorg. Chem., 34* (1986) 211–434.

22 N. N. Greenwood and I. M. Ward, *Chem. Soc. Rev., 3* (1974) 23–123.

23 A. Tippe and W. C. Hamilton, *Inorg. Chem., 8* (1969) 464.

24 *Gmelin Handbuch der Anorganischen Chemie,* Vol. 54, Borverbindungen, Part 20, Springer, Berlin.

25 N. N. Greenwood, and J. A. Howard, *J. Chem. Soc., Dalton Trans.,* (1976) 177.

26 N. N. Greenwood, J. A. McGinnety and J. D. Owen, *J. Chem. Soc. A,* (1971) 809.

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

28 K. Wade, *Adv. Inorg. Chem. Radiochem., 18* (1976) 1.

29 W. N. Lipscomb, *Boron Hydrides,* W. A. Benjamin, New York, 1963.

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

31 B. Štíbr, J. Plešek and A. Zobačová, *Polyhedron, 11–12* (1982) 826.

32 D. F. Gaines, J. W. Lott and J. C. Calabrese, *Inorg. Chem., 13* (1974) 2419.

33 E. J. Ditzel and Zhu Sisan, Leeds University, 1988–89, unpublished observations; E. J. Ditzel, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy, Zhu Sisan and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.,* (1989) 1762.

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

35 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.

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

37 G. W. Parshall, *Inorg. Synth., 12* (1970) 27.

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

39 J. D. Kennedy and J. Staves, *Z. Naturforsch., Teil B, 34* (1979) 808.

40 W. McFarlane, *Proc. R. Soc.* London, *Ser. A, 360* (1968) 185.

41 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.,* (1974) 2065.

42 G. M. Sheldrick, *SHELX 76,* program system for X-ray structure determinations, University of Cambridge, UK, 1976.