Metallaborane Reaction Chemistry. Part 1. Two Interesting Closed Cluster Compounds from the Reaction of Acetylene with an Open *nido*-6-Iridadecaborane *

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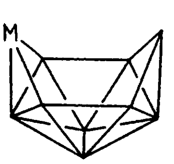
The passing of acetylene through a refluxing solution in benzene of [6,6,6-(PPh$_3$)H(Ph$_2$P-*ortho*-C$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5] results in the formation of the *closo* ten-vertex [2,2,2-(PH$_3$)$_2$(Ph$_2$P-*ortho*-C$_6$H$_4$)-*closo*-2-IrB$_9$H$_7$-10-(PPh$_3$)-1] **4** (up to 95% based on phosphine content; 47% based on iridium content) and [1,1,1-(CH=CH–CH=CH)(Ph$_2$P-*ortho*-C$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_7$-5-(PPh$_3$)-2] **5** (5%). Both compounds have been characterised by multielement NMR spectroscopy and by single-crystal X-ray diffraction studies. Compound **4** [monoclinic; a = 1334.1(2), b = 1798.9(3), c = 1646.2(2) pm, β = 97.86(1)°, and Z = 4; space group $P2_1/c$; R = 0.0337 for 5703 reflections] has a conventional ten-vertex {*closo*-2-IrB$_9$} cluster structure and has two PH$_3$ ligands on the metal atom which arise from the reductive stripping of the P-aryl groups from arylphosphine ligands. Compound **5** [monoclinic; a = 1778.9(5), b = 1368.7(3), c = 1789.9(5) pm, β = 116.69(2)°, and Z = 4; space group $P2_1/c$; R = 0.0396 for 5190 reflections] has a ten-vertex {*isocloso*-1-IrB$_9$} cluster structure and also has an unsubstituted 1-metallacyclopenta-2,4-diene system resulting from the oligomerisation of two acetylene molecules.

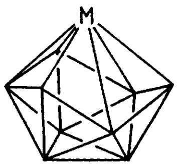
Metallaboranes that combine a redox-flexible transition-metal centre with an electronically flexible B-frame matrix will in principle exhibit interesting redox chemistry in their reactions with small unsaturated molecules. Only a few systems have been investigated for this type of behaviour: (a) the *closo* twelve-vertex 3,1,2-rhodadicarbadodecaboranes have been examined as potential alkene hydrogenation catalysts,[1] (b) the fluxional *nido*-type eleven-vertex 8,7-rhodathiaundecaborane [(PPh$_3$)$_2$RhSB$_9$H$_{10}$] readily adds S=C=S which is thereby reduced to a dithioformyl ligand,[2] and (c) the *nido* ten-vertex 6-metalladecaborane [6-(η^6-C$_6$Me$_6$)-*nido*-6-RuB$_9$H$_{13}$] (schematic structure **I**) reduces MeN≡C to Me$_2$NH and is correspondingly oxidised to [1-(η^6-C$_6$Me$_6$)-*isocloso*-1-RuB$_9$H$_9$] (schematic structure **II**) with successive dihydrogen transfer to the MeN≡C residue *via* identifiable types of intermediate.[3]

The ten-vertex compound [6,6,6-(PPh$_3$)H(Ph$_2$P-*ortho*-C$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5] **1** has a cluster that is isostructural (**I**) with [6-(η^6-C$_6$Me$_6$)-*nido*-6-RuB$_9$H$_{13}$]. Upon heating, it undergoes autooxidation *via* a double dihydrogen loss to give an *isocloso* structured product, [1,1,1-(PPh$_3$)H(Ph$_2$P-*ortho*-C$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_8$-2] **2** (structure type **II**), in a process that has been postulated to occur *via isonido* intermediates (of schematic structure type **III**),[4–7] of which some probably have co-ordinatively unsaturated iridium centres. The species [6,6,6-(PPh$_3$)$_2$H-*nido*-6-IrB$_9$H$_{13}$] **3** also yields compound **2** upon heating,[4] but undergoes an additional oxidative process during cluster closure that results in the orthocycloboronation.

These observations suggested that the successive loss of hydrogen from *nido*-6-iridadecaboranes such as these might induce interesting redox processes with electron-rich unsaturated molecules.



I



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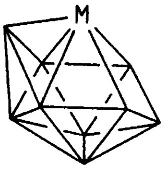

III

Somewhat in accord with this, we have recently reported a preliminary observation[8] that the reaction between [6,6,6-(PPh$_3$)H(Ph$_2$P-*ortho*-C$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5] **1** (basic cluster type **I**) and acetylene gives the *closo* ten-vertex 2-metalladecaborane [2,2,2-(PH$_3$)$_2$(Ph$_2$P-*ortho*-C$_6$H$_4$)-*closo*-2-IrB$_9$H$_7$-10-(PPh$_3$)-1] **4** as the predominant product. Remarkably, an acetylene-induced reductive stripping of the aryl groups from the iridium-bound PPh$_3$ and Ph$_2$PC$_6$H$_4$ ligands appears to occur. Herein we describe and discuss compound **4** in more detail, and also report and describe the characterisation of a second metallaborane product from this reaction, [1,1,1-(CH=CH–CH=CH)(Ph$_2$P-*ortho*-C$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_7$-5-(PPh$_3$)-2] **5** (basic cluster type **II**) which, interestingly, contains an iridacyclopentadiene moiety resulting from acetylene oligomerisation. The numbering schemes for this work are given in structures **IV** (ten-vertex *nido*), **V** (ten-vertex *isocloso*) and **VI** (ten-vertex *closo*).

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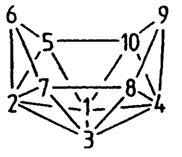
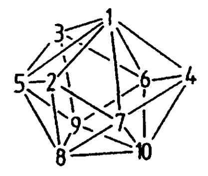
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



IV



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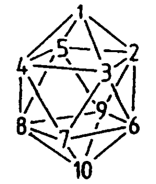

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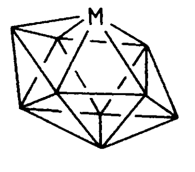

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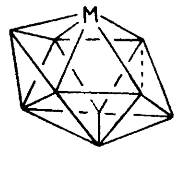
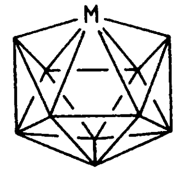
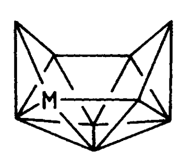


VIII



IX



X

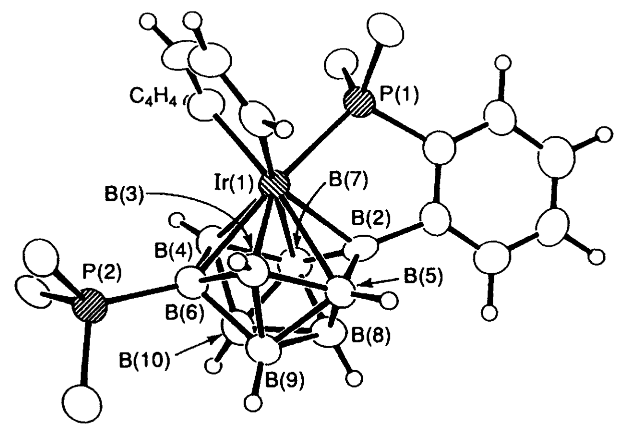


Fig. 1 Molecular structure of $[2,2,2-(PH_3)_2(Ph_2P$-*ortho*-$C_6H_4)$-*closo*-$2-IrB_9H_7-10-(PPh_3)-1]$ **4** with P-phenyl group atoms (except for *ipso* carbons) omitted for clarity. All atoms, including hydrogen atoms, were located from the X-ray data

Table 1 Selected interatomic distances (pm) for $[2,2,2-(PH_3)_2-(PPh_2$-*ortho*-$C_6H_4)$-*closo*-$2-IrB_9H_7-10-(PPh_3)-1]$ **4** with estimated standard deviations (e.s.d.s) in parentheses

(*i*) To the iridium atom			
P(1)–Ir(2)	231.6(3)		
P(2)–Ir(2)	227.5(4)	P(3)–Ir(2)	231.8(4)
B(1)–Ir(2)	211.6(8)		
B(3)–Ir(2)	228.9(8)	B(5)–Ir(2)	234.7(7)
B(6)–Ir(2)	227.3(8)	B(9)–Ir(2)	188.7(8)
(*ii*) Boron–boron			
B(3)–B(1)	177.6(11)	B(5)–B(1)	178.2(10)
B(4)–B(1)	168.8(10)		
B(4)–B(3)	186.2(11)	B(5)–B(4)	183.4(10)
B(6)–B(3)	184.8(11)	B(9)–B(5)	181.1(11)
B(7)–B(3)	183.0(11)	B(8)–B(5)	180.6(10)
B(7)–B(4)	182.8(11)	B(8)–B(4)	180.8(10)
B(7)–B(6)	185.5(11)	B(9)–B(8)	182.5(10)
B(9)–B(6)	205.0(11)	B(8)–B(7)	184.0(11)
B(10)–B(6)	169.6(11)	B(10)–B(8)	168.8(11)
B(10)–B(7)	171.1(11)	B(10)–B(9)	168.9(10)
(*iii*) Boron–hydrogen			
H(3)–B(3)	126(5)	H(5)–B(5)	116(5)
H(4)–B(4)	130(5)		
H(6)–B(6)	125(5)	H(9)–B(9)	117(6)
H(7)–B(7)	109(5)	H(8)–B(8)	104(5)
(*iv*) Other			
C(122)–B(1)	160.6(8)	B(10)–P(4)	188.7(8)

Results and Discussion

Acetylene gas at atmospheric pressure was passed through a refluxing solution in benzene of $[6,6,6-(PPh_3)H(Ph_2P$-*ortho*-$C_6H_4)$(*nido*-$6-IrB_9H_{12}-5]$ **1** (basic cluster type **I**)* for 16 h. Preparative thin-layer chromatography (TLC) of the resultant solution gave two major products of which both have been fully identified and characterised.

The predominant of these two products, isolated in a yield of up to 95% based on the phosphorus content of the material consumed, was a pale yellow air-stable compound, identified as $[2,2,2-(PH_3)_2(Ph_2P$-*ortho*-$C_6H_4)$-*closo*-$2-IrB_9H_7-10-(PPh_3)-1]$ **4** (basic cluster type **VII**) by multielement NMR spectroscopy and by a single-crystal X-ray diffraction analysis. The molecular structure is shown in Fig. 1, with Tables 1 and 2 listing selected interatomic distances and angles respectively.

The compound is seen to be based upon a closed deltahedral cluster of one iridium and nine boron atoms, with one triphenylphosphine ligand on a boron atom and three phosphine ligands on the iridium atom. Of these latter, two are PH_3 ligands, and the third an *ortho*-diphenylphosphinophenyl ligand with the phenylene group bound to a cluster boron atom adjacent to iridium. All atoms, including hydrogen atoms, were located, which in particular confirmed the presence of two metal-bound PH_3 ligands that had been suggested from ^{31}P and ^{1}H NMR spectroscopy (Table 3). These PH_3 groups were unexpected and are of particular interest. There are few examples of structurally characterised compounds with unsubstituted phosphine ligands,[11–13] and of these only one example contains an iridium atom, *viz.* *trans,trans*-$[IrHCl_2(PH_3)(PPr^i{}_3)_2]$.[14]

In contrast to compound **5** (see below), the $\{IrB_9\}$ unit of **4** adopts the conventional[15] bicapped Archimedean antiprismatic structure of *closo*-$[B_{10}H_{10}]^{2-}$ (*i.e.* basic cluster type **VII**). As such it is a conventional Wadian[16] compound, with an 'octahedral' iridium(III) centre in the 2 position contributing three orbitals and three electrons to the cluster bonding formulation. Structurally characterised *closo* metalladecaborane clusters that have the metal in the 2 position are rare, the only other examples being the rhodaborane $[2-(\eta^5-C_5Me_5)$-*closo*-$2-RhB_9H_7-3,10-(PMe_2Ph)_2]$ **6**[10] and the monorhodaborane subcluster of $[(\eta^5-C_5Me_5)RhB_9(SMe_2)H_{10}RhB_9H_7-(SMe_2)_2]$ **7**[17] (although *closo*-2-metallaheterodecaboranes are known).[18] The two rhodaborane compounds **6** and **7** have long interboron distances of 199.8(8) and 202.8(12) pm between B(6)

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* The actual material used consisted of a mixture of two isomers, with symmetric and asymmetric arrangements of the phosphine ligands about the iridium atom. There is however a rapid *sym* ⟶ *asym* conversion at *ca.* 65 °C and therefore the symmetric isomer would not be present after the first few minutes.[9]

Table 2 Selected angles between interatomic vectors (°) for $[2,2,2\text{-}(PH_3)_2\text{-}(PPh_2\text{-}\textit{ortho}\text{-}C_6H_4)\text{-}\textit{closo}\text{-}2\text{-}IrB_9H_7\text{-}10\text{-}(PPh_3)\text{-}1]$ **4** with e.s.d.s in parentheses

(*i*) About the iridium atom			
P(2)–Ir(2)–P(1)	93.1(2)	P(3)–Ir(2)–P(1)	97.0(2)
P(3)–Ir(2)–P(2)	90.1(2)	B(1)–Ir(2)–P(1)	79.2(3)
B(1)–Ir(2)–P(2)	110.1(3)	B(1)–Ir(2)–P(3)	159.5(2)
B(3)–Ir(2)–P(1)	120.3(3)	B(3)–Ir(2)–P(2)	84.6(3)
B(3)–Ir(2)–P(3)	142.4(2)	B(3)–Ir(2)–B(1)	47.3(2)
B(5)–Ir(2)–P(1)	92.9(3)	B(5)–Ir(2)–P(2)	154.1(2)
B(5)–Ir(2)–P(3)	114.1(3)	B(5)–Ir(2)–B(1)	46.7(2)
B(5)–Ir(2)–B(3)	70.7(3)	B(6)–Ir(2)–P(1)	167.7(2)
B(6)–Ir(2)–P(2)	89.1(3)	B(6)–Ir(2)–P(3)	95.1(3)
B(6)–Ir(2)–B(1)	88.7(3)	B(6)–Ir(2)–B(3)	47.8(2)
B(6)–Ir(2)–B(5)	80.1(3)	B(9)–Ir(2)–P(1)	127.4(3)
B(9)–Ir(2)–P(2)	139.0(2)	B(9)–Ir(2)–P(3)	79.3(3)
B(9)–Ir(2)–B(1)	87.0(3)	B(9)–Ir(2)–B(3)	80.6(3)
B(9)–Ir(2)–B(5)	45.8(2)	B(9)–Ir(2)–B(6)	53.1(3)
(*ii*) Boron–boron–iridium			
B(3)–B(1)–Ir(2)	71.5(4)	B(5)–B(1)–Ir(2)	73.5(4)
B(4)–B(1)–Ir(2)	111.6(5)		
B(1)–B(3)–Ir(2)	61.2(4)	B(1)–B(5)–Ir(2)	59.8(3)
B(4)–B(3)–Ir(2)	98.4(4)	B(4)–B(5)–Ir(2)	97.2(4)
B(6)–B(3)–Ir(2)	65.6(4)	B(9)–B(5)–Ir(2)	66.1(4)
B(7)–B(3)–Ir(2)	112.2(5)	B(8)–B(5)–Ir(2)	111.1(4)
B(3)–B(6)–Ir(2)	66.6(4)	B(5)–B(9)–Ir(2)	68.2(4)
B(7)–B(6)–Ir(2)	111.9(5)	B(8)–B(9)–Ir(2)	111.9(4)
B(9)–B(6)–Ir(2)	64.4(3)	B(6)–B(9)–Ir(2)	62.5(3)
B(10)–B(6)–Ir(2)	115.8(5)	B(10)–B(9)–Ir(2)	114.2(5)
(*iii*) Boron–boron–boron			
B(4)–B(1)–B(3)	65.0(5)	B(5)–B(1)–B(4)	63.7(4)
B(5)–B(1)–B(3)	97.8(5)		
B(7)–B(10)–B(6)	66.0(5)	B(9)–B(10)–B(8)	65.4(5)
B(8)–B(10)–B(6)	104.2(5)	B(9)–B(10)–B(7)	104.0(5)
B(8)–B(10)–B(7)	65.5(5)	B(9)–B(10)–B(6)	74.5(5)
B(5)–B(4)–B(3)	93.0(5)		
B(9)–B(6)–B(7)	86.5(5)	B(8)–B(9)–B(6)	86.9(5)
B(8)–B(7)–B(6)	92.6(5)	B(9)–B(8)–B(7)	94.0(5)
All B–B–B acute angles	52.6(4)–60.6(4)		
B_{apical}–$B_{tropical}$–$B_{tropical}$	110.1(5)–116.2(5)		
$B_{tropical}$–$B_{tropical}$–$B_{tropical}$	99.3(5)–104.1(5)		
(*iv*) Other			
Ir(2)–B(1)–C(122)	120.1(4)	B(4)–B(1)–C(122)	128.0(5)
B(3)–B(1)–C(122)	136.2(5)	B(5)–B(1)–C(122)	125.9(5)
B(6)–B(10)–P(4)	121.9(5)	B(9)–B(10)–P(4)	122.3(5)
B(7)–B(10)–P(4)	133.6(4)	B(8)–B(10)–P(4)	133.9(4)

Table 3 Boron-11, ^1H and ^{31}P[a] NMR data for $[2,2,2\text{-}(PH_3)_2(Ph_2P\text{-}\textit{ortho}\text{-}C_6H_4)\text{-}\textit{closo}\text{-}2\text{-}IrB_9H_7\text{-}10\text{-}(PPh_3)\text{-}1]$ **4** recorded in $CDCl_3$ solution at *ca.* 278 K

Tentative assignments	$\delta(^{11}B)$	Relative intensity	$\delta(^1H)$[b]	$[^1H\text{–}^1H]$-COSY correlations
1	+53.8[c]	1	—	—
4	−6.0	1	+3.17	7,8 [s]
6,9[d]	−10.5[e]	2	+2.16[f]	[H(P)] [s], 7,8 [w]
10	−12.5[g]	1	—	—
7,8	−26.2	2	−0.13	4 [s]
3,5[d]	−27.2	2	−0.47[h]	[H(P)] [s], 7,8 [w]
H(P)	—	6	+3.08[i]	6,9 [s], 3,5 [s]

[a] $\delta(^{31}P)$: P(1) +23.1 {t, $^2J[^{31}P(2/3)\text{–}^{31}P(1)]$ *ca.* 29 Hz}, P(2,3) −143.7 [d, *J ca.* 29 Hz due to coupling to P(2,3) plus other unresolved coupling possibly to P(4) and ^{11}B] and P(4) +17.1 (vbr). [b] Aromatic region exhibits features characteristic of orthocycloboronation,[8] *viz.* doublet at δ +8.37, splitting *ca.* 9 Hz. [c] Shows coupling to proton at $\delta(^1H)$ +8.37 on *ortho*-phenylene ring. [d] Assigned by comparison with the assigned (two-dimensional COSY) chemical shifts in $[2\text{-}(\eta^5\text{-}C_5Me_5)\text{-}\textit{closo}\text{-}2\text{-}RhB_9H_7(PMe_2Ph)_2]$[10] where $\delta[^{11}B(6,9)]$ +0.1 and +1.5 and $\delta[^{11}B(5,3)]$ −21.5 and −30.1. [e] Doublet structure splitting *ca.* 19 Hz. [f] Some doublet structure splitting *ca.* 12 Hz. [g] Doublet, $^2J[^{31}P(4)\text{–}^{11}B]$ *ca.* 200 Hz. [h] Some doublet splitting of *ca.* 12.4 Hz; possible coupling to ^{31}P in addition to coupling to protons of PH_3 groups. [i] $[AX_3]_2$ pattern centred at δ +3.08. $N[^{31}P(Ir)\text{–}^1H]$ 372.2 Hz ($N = {}^1J + {}^3J$), with additional splitting $^4J[^{31}P(4)\text{–}^1H]$ 9.6 Hz, and with contributions from couplings to cluster ^{11}B and ^1H nuclei in subsidiary lines centred at $\nu(^1H)$ ± *ca.* 353 Hz.

and B(9) respectively, a characteristic also of the present compound **4**, where the distance is 205.0(11) pm. This longer distance (hatched lines in schematic structure **VIII**) characterises a tendency towards *isonido* cluster geometry (structure **III** above), as enunciated and discussed elsewhere.[6,7] The relatively short distance from the iridium atom to B(1) [211.6(8) pm], compared to those to B(3) and to B(5) [228.9(8) and 234.7(7) pm respectively], is a reflection of the generally shorter interatomic distances for axial four-connected boron atoms in *closo* ten-vertex species [the phenomenon is similarly apparent for the interboron distances to the other axial vertex B(10)].[18] It is of interest that this type of four-connected boron position adjacent to a metal atom appears in general to give characteristic boron NMR signals at very low field [$\delta(^{11}B)$ *ca.* +60 to +100] in ten-vertex *closo*, *isonido*[6] and *isocloso* clusters such as those in compounds **2**, **4** and **5**. A similar low-field behaviour is apparent in related ten-vertex ruthenacarbaboranes,[19] and also, for example, in eleven-vertex *isocloso*-type $\{MB_{10}H_{10}\}$ cluster compounds where M = Ru or Os (schematic structure type **IX**).[20]

Another aspect of the NMR behaviour is that, although the solid-state structure of compound **4** is asymmetric, with the phosphine atoms P(2) and P(3) in a twisted disposition with respect to the Ir(2)–B(1)–B(4)–B(10) pseudo-plane, the room-temperature ^{11}B NMR spectrum shows the 1:1:2:1:2:2 relative-intensity pattern expected for a more symmetrical species with a mirror plane through Ir(2), P(1), P(4), B(1), B(4) and B(10). Concomitantly, the low-temperature ^{31}P NMR spectrum (233 K) shows a 2:1 pattern. These factors suggest that the observed solid-state asymmetry (Fig. 3 below) arises from crystal-packing forces, and that there is a rocking in the solution phase between an enantiomer similar to that depicted in Fig. 1 and its mirror image. The enantiomer of that shown in Fig. 1 is of course also contained in the crystalline solid (space group $P2_1/c$, $Z = 4$).

The second product, isolated in a *ca.* 5–10% yield (based on the amount of compound **1** consumed) is the red, air-stable compound $[1,1,1\text{-}(CH{=}CH\text{–}CH{=}CH)(Ph_2P\text{-}\textit{ortho}\text{-}C_6H_4)\text{-}\textit{isocloso}\text{-}1\text{-}IrB_9H_7\text{-}5\text{-}(PPh_3)\text{-}2]$ **5**, characterised as such by single-crystal X-ray diffraction analysis and NMR spectroscopy.

The NMR studies (Table 4) revealed nine ^{11}B resonances grouped in an approximately 3:3:3 arrangement with one low-field group centred around $\delta(^{11}B)$ *ca.* +90, a characteristic of all *isocloso*-type 1-metalladecaboranes (cluster type **II**) so far investigated.[19–24] The proton spectrum features an $[AX]_2$ pattern centred at $\delta(^1H)$ +5.68 (2 H) and +6.61 (2 H), with additional small splitting due to ^{31}P coupling, suggesting either a C_6H_4 benzyne-type or a C_4H_4 butadiene-type ligand on the iridium atom. The second of these two possibilities is preferred on the basis of mass spectrometric data. These features are confirmed by the results of a single-crystal X-ray diffraction study. The molecular structure is shown in Fig. 2, with the interatomic distances and angles listed in Tables 5 and 6 respectively.

The compound is seen to be based on a closed deltahedral $\{IrB_9\}$ cluster unit. There is a triphenylphosphine ligand on one of the boron atoms, and a diphenylphosphinophenyl ligand

Table 4 Boron-11, ^1H and $^{31}P^a$ NMR data for [1,1,1-(CH=CH–CH=CH)(Ph$_2$P-*ortho*-C_6H_4)-*isocloso*-1-IrB$_9$H$_7$-5-(PPh$_3$)-2] **5**, together with those of [1,1,1-(PPh$_3$)(Ph$_2$P-*ortho*-C_6H_4)H-*isocloso*-1-IrB$_9$H$_8$-2] **2** (data from ref. 4) for comparison, recorded in CD_2Cl_2 solution at *ca.* 298 K

Tentative assignments	**2**[a] δ(^{11}B)	**2**[a] δ(^{1}H)	**5**[b] δ(^{11}B)	**5**[b] δ(^{1}H)[c]
2	+99.7	—	+97.5	—
3	+92.5	+10.39	+84.7(2)	+9.95(2)
4	+86.9	+10.04		
8	+29.8	+5.39	+20.2	+5.28
9	+25.6	+5.34	+21.7(2)	+4.78(2)
10	+22.0	+5.15		
6	−9.6	+1.63	−20.6	—
5	−13.9	+0.09	−13.4(2)	+0.62(2)
7	−16.0	−1.63		
Ir–H		−11.79		—

[a] ^{31}P NMR data recorded at −51 °C for compound **2**: δ[^{31}P(1)] +34.7, doublet splitting ^nJ[^{31}P(1)–^{31}P(2)] *ca.* 6 Hz; δ[^{31}P(2)] +3.3 (vbr). [b] Relative intensities in parentheses. [c] Spectrum for the IrC$_4$H$_4$ moiety shows an [AX]$_2$ pattern centred at δ(^{1}H) +5.68 (2 H) and +6.61 (2 H) with additional splitting due to couplings *J*[P(1)–H] *ca.* 4 and *J*[P(2)–H] *ca.* 1.5 Hz. The aromatic region shows features diagnostic of ortho-cycloboronation at δ(^{1}H) +7.08 (2 H) {basic triplet, ^nJ = 7.5 Hz with doublet splitting ^nJ[^{31}P(1)–^{1}H] 1.6 Hz, plus additional unresolved coupling} and +8.00 (1 H) [doublet, ^nJ = 7.4 Hz with additional fine doublet splitting from coupling to P(1), *J* = 0.8 Hz].

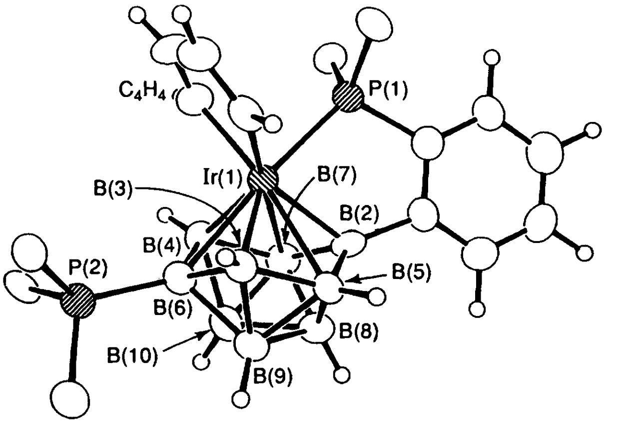


Fig. 2 Molecular structure of [1,1,1-(CH=CH–CH=CH)(Ph$_2$P-*ortho*-C_6H_4)-*isocloso*-1-IrB$_9$H$_7$-5-(PPh$_3$)-2] **5** with P-phenyl group atoms (except for *ipso* carbons) omitted for clarity. All atoms, including hydrogen atoms, were located from the X-ray data

Table 5 Selected interatomic distances (pm) for [1,1,1-(CH=CH–CH=CH)(PPh$_2$-*ortho*-C_6H_4)-*isocloso*-1-IrB$_9$H$_7$-5-(PPh$_3$)-2] **5** with e.s.d.s in parentheses

(*i*) To the iridium atom			
P(1)–Ir(1)	236.8(4)		
C(1)–Ir(1)	211.2(8)	C(4)–Ir(1)	210.4(9)
B(2)–Ir(1)	215.8(9)		
B(3)–Ir(1)	217.5(10)	B(4)–Ir(1)	216.4(9)
B(5)–Ir(1)	248.1(9)	B(7)–Ir(1)	246.5(10)
B(6)–Ir(1)	241.2(9)		
(*ii*) Carbon–carbon			
C(2)–C(1)	134.4(11)	C(4)–C(3)	133.1(11)
C(3)–C(2)	145.3(12)		
(*iii*) Boron–boron			
B(5)–B(2)	173.2(13)	B(7)–B(2)	176.0(14)
B(8)–B(2)	174.4(13)		
B(5)–B(3)	174.4(12)	B(7)–B(4)	172.5(13)
B(6)–B(3)	173.8(12)	B(6)–B(4)	175.1(12)
B(9)–B(3)	177.7(12)	B(10)–B(4)	175.7(13)
B(8)–B(5)	181.0(13)	B(8)–B(7)	179.9(13)
B(9)–B(5)	180.2(13)	B(10)–B(7)	178.8(14)
B(9)–B(6)	181.4(12)	B(10)–B(6)	181.3(12)
B(9)–B(8)	177.7(13)	B(10)–B(8)	179.1(14)
B(10)–B(9)	180.1(14)		
(*iv*) Carbon–hydrogen and boron–hydrogen			
H(1)–C(1)	107(6)	H(4)–C(4)	98(7)
H(2)–C(2)	106(6)	H(3)–C(3)	93(7)
H(3)–B(3)	124(6)	H(4)–B(4)	108(5)
H(5)–B(5)	113(6)	H(7)–B(7)	105(5)
H(8)–B(8)	106(7)		
H(9)–B(9)	109(6)	H(10)–B(10)	113(6)
(*v*) Others			
B(2)–C(116)	157.4(11)	B(6)–P(2)	194.5(9)

P-bound to the iridium and *C*-*ortho*-linked to a boron atom adjacent to the metal centre. In addition there is a butadiendiyl residue bound α,ω to the metal atom to generate a metallacyclopentadiene ring, a feature of some interest. Although metallacyclopentadiene moieties have been invoked in many transition-metal catalysed reactions of acetylene,[25] few unsubstituted metallacyclopentadiene compounds have in fact been both isolated and structurally characterised. The only other examples in the cobalt triad are, as far as we are aware, the two cobalt compounds [Co(CH=CH–CH=CH)(η^5-C$_5$H$_4$R)(PPh$_3$)] **8** (R = H or CO$_2$Me).[26] A number of iridacyclopentadiene species, for example Ir{C$_4$(CF$_3$)$_4$}(η^5-C$_5$Me$_5$)(CO)$_2$][27] **9** and some compounds[28] based upon [Ir(CR=CR–CR=CR)(PPh$_3$)$_2$(CO){=C(CH$_2$)$_3$O}][BF$_4$] **10** (R = CO$_2$Me) have been structurally characterised, but these are all heavily substituted with electron-withdrawing substituents. Of all these, compound **5** more closely resembles the cobalt compounds **8** and the tetraacetoxy compound **10** in the geometry of the metallacyclopentadiene moiety. An examination of the intrametallacycle bond distances in **5** shows little evidence of electron delocalisation within the metallacyclopentadiene unit. Thus the C(1)–C(2) and C(3)–C(4) distances of 134.4(11) and 131.1(11) pm in **5** are close to the values expected for an intercarbon sp^2–sp^2 double-bond distance, and are significantly shorter than the C(2)–C(3) distance of 143.3(12) pm which is similar to that expected for an intercarbon sp^2–sp^2 single bond [*cf.* 133(1) *versus* 148(1) pm in the tetraacetoxy compound **10** and *ca.* 134 *versus ca.* 144 pm in the cobaltacyclopentadiene species **8**]. In contrast, for the C$_4$-perfluorinated iridacyclopentadiene species **9**, in which π-electron delocalisation is claimed, all intercarbon distances are experimentally equal at *ca.* 145(2) pm. Additionally, the Ir(1)–C(1) and Ir(1)–C(4) distances in **5** at *ca.* 211(1) pm are significantly longer than those in delocalised **9** [*ca.* 202(2) pm], being more similar to those in the non-π-delocalised compound **10** [*ca.* 210(1) pm]. The butadienediyl fragment is planar within experimental error, with the dihedral angle between this four-carbon plane and the C(1)–Ir–C(4) plane also being almost flat at 2.5(4)°. The metallacycle bonding about the iridium atom deviates somewhat from orthogonality, with the C(1)–Ir(1)–C(4) angle being 76.6(4)°, presumably due to the constraints of the five-membered ring. However, the Ir–P(1) vector is angled at 85.5(1)° to the ring plane, more consistent with a formally 'octahedral' iridium bonding geometry for the *exo*-polyhedral ligand sphere.

The closed deltahedral metallaborane cluster has an '*isocloso*' ten-vertex structure approximating to the idealised 'polar' C_{3v} symmetry as represented in schematic structure **II** above. This geometry is not of the conventional Williamsian[15] closed cluster sequence, and it is at present uncertain[4] whether this is

Table 6 Selected angles between interatomic vectors (°) for [1,1,1-(CH=CH–CH=CH)(PPh$_2$-*ortho*-C$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_7$-5-(PPh$_3$)-2] **5** with e.s.d.s in parentheses

(*i*) About the iridium atom			
C(1)–Ir(1)–P(1)	86.2(3)	C(4)–Ir(1)–P(1)	80.4(3)
C(4)–Ir(1)–C(1)	76.6(4)		
B(2)–Ir(1)–P(1)	78.0(3)		
B(2)–Ir(1)–C(1)	131.5(3)	B(2)–Ir(1)–C(4)	142.4(3)
B(3)–Ir(1)–P(1)	141.7(2)	B(4)–Ir(1)–P(1)	125.0(3)
B(3)–Ir(1)–C(1)	79.6(4)	B(4)–Ir(1)–C(4)	81.7(4)
B(3)–Ir(1)–C(4)	129.1(4)	B(4)–Ir(1)–C(1)	138.2(3)
B(3)–Ir(1)–B(2)	85.2(4)	B(4)–Ir(1)–B(2)	85.9(4)
B(4)–Ir(1)–B(3)	87.3(4)	B(7)–Ir(1)–B(5)	69.9(4)
B(5)–Ir(1)–P(1)	107.8(3)	B(7)–Ir(1)–P(1)	97.7(3)
B(5)–Ir(1)–C(1)	102.9(4)	B(7)–Ir(1)–C(4)	110.3(4)
B(5)–Ir(1)–C(4)	171.8(3)	B(7)–Ir(1)–C(1)	172.5(3)
B(5)–Ir(1)–B(2)	43.1(3)	B(7)–Ir(1)–B(2)	44.1(3)
B(5)–Ir(1)–B(3)	43.4(3)	B(7)–Ir(1)–B(4)	43.1(3)
B(5)–Ir(1)–B(4)	93.7(4)	B(7)–Ir(1)–B(3)	93.5(4)
B(6)–Ir(1)–P(1)	167.3(2)		
B(6)–Ir(1)–C(1)	106.5(3)	B(6)–Ir(1)–C(4)	102.5(4)
B(6)–Ir(1)–B(2)	92.8(4)		
B(6)–Ir(1)–B(3)	44.2(3)	B(6)–Ir(1)–B(4)	44.6(3)
B(6)–Ir(1)–B(5)	69.6(3)	B(7)–Ir(1)–B(6)	69.6(4)
(*ii*) Boron–boron–iridium			
B(5)–B(2)–Ir(1)	78.4(5)	B(7)–B(2)–Ir(1)	77.2(5)
B(8)–B(2)–Ir(1)	106.1(6)		
B(5)–B(3)–Ir(1)	77.7(5)	B(7)–B(4)–Ir(1)	77.7(5)
B(6)–B(3)–Ir(1)	75.2(5)	B(6)–B(4)–Ir(1)	75.2(5)
B(9)–B(3)–Ir(1)	104.7(5)	B(10)–B(4)–Ir(1)	105.4(5)
B(2)–B(5)–Ir(1)	58.5(4)	B(2)–B(7)–Ir(1)	58.6(4)
B(3)–B(5)–Ir(1)	58.9(4)	B(4)–B(7)–Ir(1)	59.1(4)
B(8)–B(5)–Ir(1)	92.3(5)	B(8)–B(7)–Ir(1)	93.1(5)
B(9)–B(5)–Ir(1)	92.8(5)	B(10)–B(7)–Ir(1)	93.4(5)
B(3)–B(6)–Ir(1)	60.7(4)	B(4)–B(6)–Ir(1)	60.2(4)
B(9)–B(6)–Ir(1)	94.8(5)	B(10)–B(6)–Ir(1)	94.5(5)
(*iii*) Boron–boron–boron			
B(3)–B(5)–B(2)	115.1(6)	B(4)–B(7)–B(2)	115.4(6)
B(6)–B(3)–B(5)	106.7(6)	B(7)–B(4)–B(6)	106.4(6)
B(4)–B(6)–B(3)	118.2(6)	B(7)–B(2)–B(5)	108.4(7)
Other B–B–B (acute)	58.3(5)–62.8(6)		
Other B–B–B (obtuse)	101.3(6)–110.7(6)		
(*iv*) Boron–boron–phosphorus and boron–boron–carbon			
B(3)–B(6)–P(2)	117.0(6)	B(4)–B(6)–P(2)	119.0(6)
B(9)–B(6)–P(2)	118.9(6)	B(10)–B(6)–P(2)	119.8(6)
B(5)–B(2)–C(116)	123.0(7)	B(7)–B(2)–C(116)	127.2(7)
B(8)–B(2)–C(116)	132.2(5)		
(*iv*) Others			
C(2)–C(1)–Ir(1)	115.5(7)	C(3)–C(4)–Ir(1)	116.3(7)
C(3)–C(2)–C(1)	115.7(7)	C(4)–C(3)–C(2)	115.7(8)
B(2)–C(116)–C(111)	116.2(4)	B(2)–C(116)–C(115)	123.8(4)
C(116)–B(2)–Ir(1)	121.7(5)	P(2)–B(6)–Ir(1)	140.2(3)

better regarded as a consequence of a metal four-orbital contribution to the cluster bonding scheme,[20] which in this case would imply an iridium(v) metal centre, or whether it derives from a cluster bonding scheme involving ten[21] rather than eleven occupied cluster bonding orbitals within the constraints of a metal three-orbital contribution, which would imply 'octahedral' iridium(III). The detailed geometry is very similar to that of the only other structurally characterised *isocloso* iridadecaborane, *viz.* [1,1,1-(PPh$_3$)H(Ph$_2$P-*ortho*-C$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_8$-2][4] **2**, which also exhibits orthocycloboronation. Thus in compound **5** the distances from the iridium atom to the top layer of three boron atoms range from 215(1) to 218(1) pm [*cf.* 215(1)–219(1) pm in **2**] and to the middle layer from 241(1) to 248(1) pm [*cf.* 238(1)–246(1) pm in **2**]. Interboron distances between the top two layers of boron atoms range from 172.5(13) to 176.0(14) pm, whereas interboron distances between these atoms and B(8), B(9) and B(10) range from 174.4(13) to 181.4(12) pm, trends again noticeable in compound **2**. This contrasts to the pattern of interboron separations in the conventionally *closo* species **4** (structures **VII** and **VIII**) described above. In this latter species the interboron separations of 184.8(11) and 181.1(11) pm for B(3)–B(6) and B(5)–B(9), *i.e.* for the boron atom pairs that flank the iridium atom, are not particularly shorter than other interboron distances within the cluster and are significantly longer than the average of the equivalent distances in the *isocloso* cluster compound **2** (174.0 pm for six values).

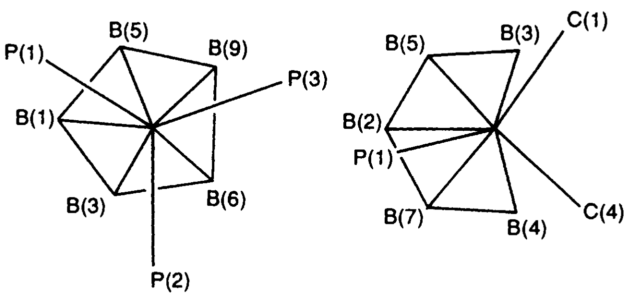
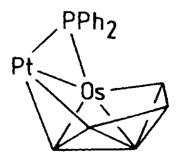


Fig. 3 Diagrams of selected interatomic links in compounds **4** (left) and **5** (right) viewed perpendicular to the B(3)B(5)B(6)B(9) and B(3)B(4)B(5)B(7) planes

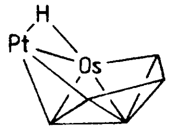
Although comparative evidence is somewhat limited, the data for compounds **2** and **5** suggest that the PPh$_3$ substituents introduce no significant disturbance to the *isocloso* intracluster dimensions. This contrasts to observations for phosphine substituents on the open face of conventional *nido*-iridadecaborane clusters of structure types **I** and **X**, which are associated with shorter facial B–B(PPh$_3$) distances,[9] and to similar shortenings observed for B-phosphine substituted *isonido* ten-vertex iridaborane clusters of structure type **III**.[6] However, in both of these latter instances the phosphine ligand is notionally replacing terminal *and* bridging hydrogen atoms in the comparison species. An alternative contrasting comparison is afforded by the amido-substituted *isocloso* ruthenaborane [1-(η^6-C$_6$Me$_6$)-1-RuB$_9$H$_8$-2-(NEt$_2$)] (structure type **II**), in which now a substituent-induced iridium–boron *lengthening* is in fact observed, although in this case ligand-to-cluster π donation is invoked to account for the lengthening.[29]

For compound **5** it may be noted that a two-fold symmetry through the Ir(1)B(2)B(5)B(8) plane is more nearly maintained in the solid-state structures (Figs. 2 and 3) than it is for the *closo* compound **4** above (Fig. 1). This is presumably a consequence of relative crystal-packing phenomena; as for compound **4** the solution NMR behaviour is consistent with mirror-plane symmetry. It is interesting to speculate whether the greater distortion for **4** reflects a greater bonding sphere flexibility, but more comparison data would be needed to substantiate this.

It is interesting that compounds **4** and **5** adopt markedly different cluster geometries. This is because they differ in the nature of the ligands on the metal vertex [one 'two-electron' and (effectively) two 'one-electron' ligands in **5** compared to three 'two-electron' ligands in **4**]. There has been some discussion[4,30–33] on the nature of the comparative bonding in such ten-vertex closed clusters, which has often centred around a comparison[32,33] of hypothetical *closo* species on one hand, and hypothetical *isocloso*[4,31] (or *hypercloso*)[30] species on the other. The hypothetical species invoked, while being held to be structurally analogous to real *closo* and *isocloso* species, have nevertheless so far generally been constitutionally rather different. Perhaps this pair of more closely related compounds



XI



XII

will now provide interesting and more realistic models for theoretical calculations.

Each of the two products has an interesting feature, *viz*. the incidence of two PH_3 groupings in compound **4**, and the incidence of a metallacyclopentadiene ring in compound **5**. These merit some discussion as to their origins.

The derivation of a metallacyclopentadiene unit from acetylene is as far as we are aware unique in metallaborane and metallaheteroborane chemistry, although there is ample precedent in non-boron systems.[25,26] It may be that the mechanism is closely related to those typically proposed in mainstream non-boron transition-metal chemistry, perhaps occurring *via* a co-ordinatively unsaturated metal centre arising from initial phosphine dissociation (see also following paragraph), with the borane residue perhaps playing a more subtle role, although other possibilities cannot be excluded on present limited evidence. Nevertheless, it is important that this type of oligomerisation has now been recognised in metal B-frame chemistry because it now re-emphasises the potentialities[1] of tailoring suitable metallaborane substrates for stoichiometric or catalytic hydrocarbon manipulation.

The high-yield formation of PH_3 (compound **4**), *via* the reductive stripping of the aryl groups from arylphosphine ligands, has less precedent. As far as we are aware it is unique, and it is remarkable that it is induced by acetylene under such mild conditions. There seems to be only one example of a metallaborane reaction giving cleavage of aryl groups from a triarylphosphine. This is in the formation of the Ph_2P-bridged species $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$[34] **11** (schematic structure **XI**) from H-bridged $[(CO)(PPh_3)_2OsH(PMe_2Ph)PtB_5H_8]$ **12** (schematic structure **XII**), where the diphenylphosphido group and the phenyl substituent on the boron cage in compound **11** are thought to derive from a PPh_3 group originally bound to osmium in **12**. The high yields of compound **4** (up to 47% based on iridium content, 95% on phosphorus content) suggest that the two extra phosphine ligands in **4** arise from an initial comproportionation process as in equation (1).

$$\underset{2\times\mathbf{1}}{2\{P_2IrB_9\}} \longrightarrow \underset{\mathbf{4}}{\{P_4IrB_9\}} + \{\text{unknown IrB}_9\} \qquad (1)$$

This would imply the formation of non-phosphine-containing iridaboranes, which could perhaps contain co-ordinated acetylenic or oligomerised organic ligands, in yields of up to *ca*. 50%, but none have so far been isolatable from the product mixture using our present methods. In this context it may be pertinent that the diene complex $[1\text{-Cl-}1,1\text{-}(\eta^2{:}\eta^2\text{-}C_8H_{12})\text{-}isocloso\text{-}1\text{-}IrB_9H_9]$ (structure type **II**), and related diene *nido*-iridadecaborane complexes of structure type **I**, are much less stable in solution than their triphenylphosphine analogues.[35] Whether the phosphines are first dissociated from their parent cluster, or whether they are transferred *via* a bimolecular intermediate cannot be determined at present, but it is of interest that the platinaosmaheptaborane **11** (schematic cluster structure **XI**), mentioned above, contains features that might be present in a bimolecular intermediate. For example, in **11** it is apparent that one of the phosphorus–phenyl linkages of an osmium-bound PPh_3 ligand of the precursor **12** has been cleaved, with the resulting $\{PPh_2\}$ moiety taking up a metal–metal bridging position whence it could, in principle, transfer to the platinum atom.

Table 7 Crystallographic data for compounds **4** and **5**[a]

	5	**4**
Formula	$C_{40}H_{40}B_9IrP_2$	$C_{36}H_{42}B_9IrP_4$
M	872.21	888.14
a/pm	1778.9(5)	1334.1(2)
b/pm	1368.7(3)	1798.9(3)
c/pm	1789.9(5)	1646.2(2)
α/°	—	—
β/°	116.69(2)	97.86(1)
γ/°	—	—
U/nm^3	3.894(2)	3.914(1)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
D_c/g cm^{-3}	1.49	1.51
Approximate crystal dimensions/mm	0.6 × 0.5 × 0.2	0.7 × 0.4 × 0.2
Z	4	4
F(000)	1727.8	1913.7
μ/cm^{-1}	33.87	50.77
No. of data collected	7562	7285
No. observed[b]	5190 [$I > 2\sigma(I)$]	5703 [$I > 2\sigma(I)$]
R[c]	0.0396	0.0337
R'[d]	0.0369	0.0342
Weighting factor g[e]	0.0004	0.0004
No. of variables	442	414

[a] For both compounds: scan width, 2.0° + α-doublet splitting; scan speed, 2.0–29.3° min^{-1}; and $4.0 < 2\theta < 45.0°$. [b] Criterion for observed reflections $|F_o| > 4.0\sigma(|F_o|)$. [c] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [d] $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$. [e] $w = [\sigma^2(|F_o|) + g(|F_o|)^2]^{-1}$.

In any event, that both compounds **4** and **5** feature phosphine ligands that have transferred from a metal atom to a boron cage indicates that the ligands are quite mobile. An analogous ligand transfer has very recently been also noted during the reactions of compounds **1** and **2** with CS_2 to give $[(Ph_2PC_6H_4)(SCHS)_2IrB_9H_5(PPh_3)]$ of *isocloso* structure type **II**.[36]

The unrecovered borane fragments from the reaction could be the source of the six hydrogen atoms on the PH_3 ligands. Alternatively, because six hydrogen atoms are lost from the cluster of **1** during the *nido* ⟶ *closo* cluster closure, a mechanism involving intramolecular polyhydrogen reduction is also a possibility. As alluded to in the Introduction, the related compound $[6\text{-}(\eta^6\text{-}C_6Me_6)\text{-}nido\text{-}6\text{-}RuB_9H_{13}]$ (structure type **I**) acts as a four-hydrogen reducing agent in the reduction of $MeN{\equiv}C$ to Me_2NH in an intramolecular process *via* unstable $[(\eta^6\text{-}C_6Me_6)RuB_9H_{11}(CH_2NMe)]$ which decomposes to $[1\text{-}(\eta^6\text{-}C_6Me_6)\text{-}isocloso\text{-}1\text{-}RuB_9H_9]$ (structure type **II**) and Me_2NH.[3] These two types of reduction may be related; certainly they presage other interesting reductive possibilities for B-frame species that involve intimate co-operation between borane ligands and the metal centres. The two iridaborane and ruthenaborane systems are non-catalytic, but it may be possible to devise systems that permit a reversal of the *nido* ⟶ *isocloso* and/or *nido* ⟶ *closo* cluster oxidations and thus engender catalytic processes; in this context it is of interest that recent work in metallaheteroborane chemistry has revealed *closo* ⇌ *closo* interconversions that proceed *via* *nido*-type intermediates,[37] and *nido* ⇌ *nido* interconversions that proceed *via* closed intermediates.[2,38,39] Other important experiments on the iridaborane system reported here will include attempts to ascertain the fate of the extraneous phenyl and iridaborane residues, and to assess for any other acetylene-derived products.

Experimental

General.—All reactions were carried out under an atmosphere of acetylene gas. Subsequent manipulations were carried out

Table 8 Non-hydrogen (× 10^4) and cluster hydrogen (× 10^3) atomic coordinates for compound **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ir(2)	3212.6(1)	2105.7(1)	2059.0(1)
P(1)	1534(1)	1779(1)	1682(1)
P(2)	3647(1)	1800(1)	812(1)
P(3)	3773(1)	956(1)	2570(1)
P(4)	6252(1)	2808(1)	3997(1)
C(111)	1302(3)	1091(2)	863(2)
C(112)	1386(3)	339(2)	1064(2)
C(113)	1403(3)	−192(2)	447(2)
C(114)	1335(3)	31(2)	−370(2)
C(115)	1251(3)	784(2)	−571(2)
C(116)	1234(3)	1314(2)	45(2)
C(121)	858(2)	2613(1)	1312(2)
C(122)	1393(2)	3268(1)	1517(2)
C(123)	939(2)	3955(1)	1318(2)
C(124)	−50(2)	3987(1)	914(2)
C(125)	−585(2)	3332(1)	708(2)
C(126)	−131(2)	2645(1)	907(2)
C(131)	830(2)	1409(2)	2477(2)
C(132)	1274(2)	1413(2)	3295(2)
C(133)	730(2)	1160(2)	3906(2)
C(134)	−259(2)	902(2)	3699(2)
C(135)	−703(2)	898(2)	2881(2)
C(136)	−158(2)	1152(2)	2270(2)
C(411)	7353(2)	2991(2)	3483(2)
C(412)	8304(2)	2729(2)	3819(2)
C(413)	9157(2)	2919(2)	3460(2)
C(414)	9059(2)	3373(2)	2766(2)
C(415)	8108(2)	3635(2)	2431(2)
C(416)	7255(2)	3444(2)	2789(2)
C(421)	6329(3)	1829(2)	4289(2)
C(422)	6756(3)	1314(2)	3803(2)
C(423)	6770(3)	561(2)	4007(2)
C(424)	6356(3)	323(2)	4696(2)
C(425)	5930(3)	838(2)	5182(2)
C(426)	5916(3)	1591(2)	4978(2)
C(431)	6470(3)	3336(2)	4947(2)
C(432)	7007(3)	3047(2)	5665(2)
C(433)	7121(3)	3467(2)	6383(2)
C(434)	6699(3)	4177(2)	6385(2)
C(435)	6162(3)	4466(2)	5668(2)
C(436)	6047(3)	4045(2)	4949(2)
B(1)	2513(5)	3163(3)	2003(4)
B(3)	3768(5)	3269(4)	1774(4)
B(4)	3223(5)	3792(3)	2586(4)
B(5)	2818(5)	2942(3)	3063(4)
B(6)	4735(5)	2679(4)	2374(4)
B(7)	4591(5)	3671(4)	2643(4)
B(8)	3931(5)	3438(3)	3521(4)
B(9)	3988(5)	2437(3)	3350(4)
B(10)	5002(5)	3000(4)	3348(4)
H(3)	389(4)	346(3)	106(3)
H(4)	285(4)	446(3)	258(3)
H(5)	212(4)	293(3)	341(3)
H(6)	536(4)	240(3)	196(3)
H(7)	502(4)	414(3)	246(3)
H(8)	391(3)	368(2)	409(3)
H(9)	402(4)	191(3)	376(4)

in air. Commercial-grade acetylene was used and passed through two traps at *ca.* 195 K to remove acetone. Benzene was stored over sodium wire and distilled into the reaction mixture under a flow of nitrogen immediately prior to use. Dichloromethane was distilled over phosphorus pentaoxide, and light petroleum over calcium hydride. Preparative and analytical thin-layer chromatography (TLC) were performed using silica gel with a fluorescent indicator (Fluka type GF-254), with general chromatographic techniques as described in other recent papers from our laboratories.[4,6,9] The starting iridaborane [$(PPh_3)H(Ph_2P$-*ortho*-$C_6H_4)$-*nido*-6-IrB_9H_{12}-5] **1** was prepared as described previously,[9] and the samples used consisted of approximately 75:25 mixtures of the 'symmetric' and 'asymmetric' isomers. Boron-11, ^{11}B-{^1H}, ^1H-{^{11}B}, [^1H-^1H]-COSY and ^{31}P-{^1H} NMR spectra were obtained on a Bruker AM400 instrument. Chemical shifts (δ) are given in ppm positive to high-frequency (low-field) of Ξ 100 MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), of Ξ 32.083 971 MHz (nominally $BF_3{\cdot}OEt_2$) for ^{11}B (quoted ±0.5 ppm), and of Ξ 40.480 730 MHz (nominally 85% H_3PO_4) for ^{31}P (quoted ±0.5 ppm), Ξ being defined as in ref. 40. Mass spectra were obtained using an AEI/Kratos MS30 instrument and electron-impact ionisation at 70 eV. Infrared spectra were recorded on a Polaris Fourier-transform IR machine using KBr discs and values quoted are ± 5 cm^{-1}.

Reaction of [$(PPh_3)H(Ph_2P$-*ortho*-$C_6H_4)$-*nido*-6-IrB_9H_{12}-5] **1** *with* C_2H_2.—In a typical reaction benzene (20 cm^3) was distilled into a two-necked round-bottomed flask containing [$(PPh_3)H(Ph_2P$-*ortho*-$C_6H_4)$-*nido*-6-IrB_9H_{12}-5] (40 mg, 50 μmol). Acetylene was bubbled through the mixture for *ca.* 15 min before the mixture was heated to reflux. After 5 min refluxing all the solid had dissolved giving a yellow solution. Acetylene was passed continuously, and heating under reflux was continued for *ca.* 16 h. After this time the solution had turned a slightly paler colour and showed little sign of decomposition, although in one experiment a black metallic ring formed above the liquid. After cooling, the mixture was reduced to dryness at room temperature under reduced pressure, redissolved in dichloromethane (2 cm^3), and applied to a preparative TLC plate. TLC was carried out using CH_2Cl_2–light petroleum (b.p. 40–60 °C) (1:1) as the mobile phase. A number of bands were produced. Band A [R_f 0.50; 1.8 mg, 2.1 μmol, 4.9% (maximum yield obtained in any experiment 3.4 mg, 3.8 μmol, 9.5%) was isolated as a red crystalline material and identified as [1,1,1-(CH=CH–CH=CH)(Ph_2P-*ortho*-C_6H_4)-*isocloso*-1-IrB_9H_7-5-(PPh_3)-2] **5** [mass spectrum: *m*/*z*(max.) 874 (corresponding to $^{12}C_{40}{}^1H_{40}{}^{11}B_9{}^{31}P_4{}^{193}Ir$); IR: ν(BH) 2540s, 2520 (sh), 2500s cm^{-1}]. Band B (R_f 0.45; 5.6 mg, 6.8 μmol) was identified as the starting material **1** (100% of the asymmetric[8] isomer). Band C [R_f 0.25; 17.5 mg, 19.7 μmol, and 10.2 mg, 11.5 μmol (respectively maximum and minimum yields of 97 and 55% based on material consumed)], was located on the plate under UV light, appearing as a very pale yellow band under ambient light. It was identified as [2,2,2-$(PH_3)_2(Ph_2P$-*ortho*-$C_6H_4)$-*closo*-2-IrB_9H_7-10-(PPh_3)-1] **4**. No electron-impact mass spectrum was obtained (Found: C, 47.8; H, 4.65. $C_{36}H_{42}B_9P_4Ir$ requires C, 48.6; H, 4.75%); IR: ν(BH) 2480s, ν(PH) 2365m, 2350 (sh), 2340 (sh) cm^{-1}. A fourth chromatographic band (D) containing 2–5 mg of material would sometimes be apparent. On rechromatographing using 100% CH_2Cl_2 as the eluting medium, band D would split into a number of other bands, of which none has been characterised as yet, although the IR spectrum of one minor component suggests that it contains PH_3 ligands and that it may be an isomer of compound **4**. Crystals of compounds **4** and **5** were obtained in each case by diffusion of hexane into a solution of the compound in CH_2Cl_2.

X-Ray Diffraction Analyses.—Crystallographic measurements for compounds **4** and **5** were made on a Syntex *P*2_1 diffractometer operating in the ω–2θ scan mode using graphite-monochromated Mo-Kα radiation (λ = 71.069 pm) following a procedure described elsewhere in detail.[41]

The structures were solved *via* standard heavy-atom procedures and were refined by full-matrix least squares using

Table 9 Non-hydrogen (× 10^4) and cluster hydrogen (× 10^3) atomic coordinates for compound **5** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ir(1)	2418.2(2)	1294.1(2)	1539.6(1)
P(1)	1980(1)	2896(1)	1657(1)
P(2)	3004(1)	−1620(1)	1683(1)
C(111)	1603(3)	3477(3)	651(2)
C(112)	1367(3)	4456(3)	486(2)
C(113)	1108(3)	4831(3)	−317(2)
C(114)	1085(3)	4227(3)	−955(2)
C(115)	1320(3)	3249(3)	−790(2)
C(116)	1579(3)	2873(3)	13(2)
C(121)	2793(3)	3711(3)	2390(2)
C(122)	2964(3)	3790(3)	3228(2)
C(123)	3645(3)	4348(3)	3777(2)
C(124)	4156(3)	4826(3)	3487(2)
C(125)	3985(3)	4747(3)	2649(2)
C(126)	3303(3)	4190(3)	2100(2)
C(131)	1049(2)	2993(3)	1851(3)
C(132)	414(2)	2295(3)	1501(3)
C(133)	−329(2)	2395(3)	1578(3)
C(134)	−436(2)	3194(3)	2005(3)
C(135)	199(2)	3892(3)	2355(3)
C(136)	942(2)	3791(3)	2278(3)
C(211)	3266(3)	−2333(4)	976(3)
C(212)	3932(3)	−2013(4)	828(3)
C(213)	4129(3)	−2509(4)	258(3)
C(214)	3661(3)	−3325(4)	−164(3)
C(215)	2995(3)	−3645(4)	−16(3)
C(216)	2798(3)	−3149(4)	554(3)
C(221)	3969(3)	−1559(3)	2643(2)
C(222)	4514(3)	−2358(3)	2907(2)
C(223)	5260(3)	−2303(3)	3649(2)
C(224)	5460(3)	−1450(3)	4126(2)
C(225)	4915(3)	−652(3)	3862(2)
C(226)	4169(3)	−706(3)	3120(2)
C(231)	2266(3)	−2353(3)	1887(3)
C(232)	2525(3)	−2891(3)	2623(3)
C(233)	1960(3)	−3513(3)	2731(3)
C(234)	1136(3)	−3596(3)	2103(3)
C(235)	876(3)	−3057(3)	1367(3)
C(236)	1441(3)	−2436(3)	1259(3)
C(1)	3579(4)	1668(5)	2556(4)
C(2)	3613(5)	1573(5)	3318(4)
C(3)	2840(6)	1252(6)	3331(4)
C(4)	2190(5)	1103(5)	2586(4)
B(2)	1831(5)	1774(6)	254(4)
B(3)	3283(5)	509(5)	1200(4)
B(4)	1596(5)	37(6)	1099(5)
B(5)	2761(5)	1274(6)	340(4)
B(6)	2558(5)	−364(5)	1163(4)
B(7)	1170(5)	816(6)	252(5)
B(8)	1753(5)	741(6)	−347(5)
B(9)	2631(5)	−32(6)	217(5)
B(10)	1622(5)	−321(6)	168(5)
H(1)	412(4)	192(5)	249(4)
H(2)	415(4)	174(5)	389(4)
H(3)	279(4)	115(5)	382(4)
H(4)	165(5)	85(5)	252(4)
H(3)	406(4)	47(4)	160(4)
H(4)	129(3)	−26(4)	145(3)
H(5)	316(4)	177(4)	17(3)
H(7)	52(3)	94(4)	0(3)
H(8)	152(5)	70(5)	−100(4)
H(9)	291(4)	−49(5)	−9(4)
H(10)	128(4)	−100(4)	−18(4)

the SHELX program system.[42] Both data sets were corrected for absorption empirically once their structures had been determined.[43]

Refinement of the two structures was basically the same with all non-hydrogen atoms assigned anisotropic thermal parameters. All phenyl groups were included in the refinement as rigid bodies with hexagonal symmetry (C–C 139.5 pm). The phenyl and PH_3 hydrogen atoms were included in calculated positions (C–H 96 pm, P–H 96 pm) and assigned an overall isotropic thermal parameter. All the borane hydrogen atoms in compounds **4** and **5** and the C_4H_4 hydrogen atoms in **5** were located in the Fourier-difference syntheses and were refined freely with individual isotropic thermal parameters.

Details of crystal data, data collection and structure refinement parameters are given in Table 7 and atomic coordinates for **4** and **5** are listed in Tables 8 and 9 respectively.

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

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