Ten-vertex Metallaborane Chemistry: Facile, Thermally Induced, *nido* ⟶ *isocloso* Cluster-closure Oxidation Reactions in Iridadecaborane Clusters

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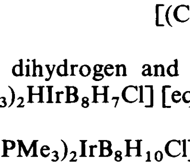
Four *nido*-iridadecaborane cluster compounds $[\text{6-H-6,6-(PR}_3)_2\text{-}nido\text{-6-IrB}_9\text{H}_{13}]$ [R = Ph, (**1**); Me, (**5**)] $[sym\text{-6-H-6-(PPh}_3)\text{-6-(PPh}_2\text{-}ortho\text{-}\overline{\text{C}_6\text{H}_4)\text{-}nido\text{-6-IrB}_9\text{H}_{12}\text{-5}}]$ (**2**), and $[\text{5-H-5-(PPh}_3)\text{-5-(PPh}_2\text{-}ortho\text{-}\overline{\text{C}_6\text{H}_4)\text{-}nido\text{-5-IrB}_9\text{H}_{12}\text{-2}}]$ (**3**) lose hydrogen on heating in dichloroethane solution at *ca.* 80 °C (bath) to give, in each case, an '*isocloso*' iridadecaborane cluster compound. These *isocloso* species have been characterised by multielement n.m.r. studies and, in the case of $[\text{1-H-1-(PPh}_3)\text{-1-(PPh}_2\text{-}ortho\text{-}\overline{\text{C}_6\text{H}_4)\text{-}isocloso\text{-1-IrB}_9\text{H}_8\text{-2}}]$ (**4**), by a single-crystal *X*-ray crystallographic study. Crystals of (**4**) are monoclinic, space group $P2_1/c$ with a = 1366.0(3), b = 1906(4), c = 1429.1(3) pm, β = 103.71(2)°, and Z = 4. The '*isocloso*' structures and a possible mechanism for the *nido* ⟶ *isocloso* cluster closure are briefly discussed.

During the course of our work on metalladecaborane and metallanonaborane clusters of iridium[1–5] we found that the *arachno*-metallanonaborane *arachno*-$[\text{(CO)(PMe}_3)_2\text{HIrB}_8\text{H}_{11}\text{Cl}]$, when heated in solution at *ca.* 100 °C, quantitatively loses dihydrogen to form *nido*-$[\text{(CO)(PMe}_3)_2\text{IrB}_8\text{H}_{10}\text{Cl}]$ [equation (1)].[3,4] With stronger heating the *nido* cluster loses further dihydrogen and carbon monoxide to give *isocloso*-$[\text{(PMe}_3)_2\text{HIrB}_8\text{H}_7\text{Cl}]$ [equation (2)].[2]

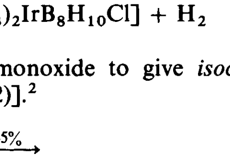
$$[\text{(CO)(PMe}_3)_2\text{HIrB}_8\text{H}_{11}\text{Cl}] \xrightarrow{100\,^\circ\text{C},\,100\%} [\text{(CO)(PMe}_3)_2\text{IrB}_8\text{H}_{10}\text{Cl}] + \text{H}_2 \quad (1)$$

$$[\text{(CO)(PMe}_3)_2\text{IrB}_8\text{H}_{10}\text{Cl}] \xrightarrow{135\,^\circ\text{C},\,45\%} [\text{(PMe}_3)_2\text{HIrB}_8\text{H}_7\text{Cl}] + \text{CO} + \text{H}_2 \quad (2)$$

Similar experiments with the isostructural and isoelectronic (but not necessarily isoelectrolobal‡)[3,6,7] platinum analogue *arachno*-$[\text{(PMe}_2\text{Ph)}_2\text{PtB}_8\text{H}_{12}]$ result in a complex mixture of compounds that have been identified as macropolyhedral polymetallaborane clusters in which the platinanonaborane cluster has undergone a number of cluster degradations and fusions.[6,8] The lack of a smooth *arachno* ⟶ *nido* cluster oxidation in the latter case prompted the thought that the terminal iridium hydride might play an important role in these types of facile oxidative cluster-closure reactions. It was therefore of interest to carry out thermolysis studies on some ten-vertex iridadecaborane clusters with this terminal iridium hydride feature. Some preliminary details of this work have already been communicated.[2,9] The numbering scheme for the clusters discussed in this paper are given in (I) (ten-vertex *nido*) and (II) (ten-vertex *isocloso*).



(I)



(II)

Results and Discussion

1. *Preparation and Identification of Compounds* (**4**)—(**6**).—The *nido*-6-iridadecaboranes $[\text{H(PPh}_3)_2\text{-6-IrB}_9\text{H}_{13}]$[1] (**1**) and $[sym\text{-6-H-6-(PPh}_3)\text{-6-(PPh}_2\text{-}ortho\text{-}\overline{\text{C}_6\text{H}_4)\text{-}nido\text{-6-IrB}_9\text{H}_{12}\text{-5}}]$ (**2**),[5,9,10] when heated in dichloroethane solution at *ca.* 80 °C, were found to evolve hydrogen, each giving the identical product (**4**) in quantitative yield [equations (3) and (4)]. A similar

$$\underset{(\mathbf{1})}{[\text{H(PPh}_3)_2\text{IrB}_9\text{H}_{13}]} \xrightarrow{80\,^\circ\text{C}} \underset{(\mathbf{4})}{[\text{H(PPh}_3)(\text{PPh}_2\overline{\text{C}_6\text{H}_4)\text{IrB}}_9\text{H}_8]} + 2\text{H}_2 \quad (3)$$

$$\underset{(\mathbf{2})\text{ or }(\mathbf{3})}{[\text{H(PPh}_3)(\text{PPh}_2\overline{\text{C}_6\text{H}_4)\text{IrB}}_9\text{H}_{12}]} \xrightarrow{80\,^\circ\text{C}} \underset{(\mathbf{4})}{[\text{H(PPh}_3)(\text{PPh}_2\overline{\text{C}_6\text{H}_4)\text{IrB}}_9\text{H}_8]} + 2\text{H}_2 \quad (4)$$

thermolysis of a 5-irida structural isomer of compound (**2**), *viz*, $[\text{5-H-5-(PPh}_3)\text{-5-(PPh}_2\text{-}ortho\text{-}\overline{\text{C}_6\text{H}_4)\text{-}nido\text{-5-IrB}_9\text{H}_{12}\text{-2}}]$ (**3**), also resulted in the same product. A solution of compound (**3**) in CDCl_3 showed a *ca.* 30% conversion into the product (**4**) at 21 °C over 5 days.

The product (**4**) has been identified by multielement n.m.r. spectroscopy and by single-crystal *X*-ray diffraction analysis to be $[\text{1-H-1-(PPh}_3)\text{-1-(PPh}_2\text{-}ortho\text{-}\overline{\text{C}_6\text{H}_4)\text{-}isocloso\text{-1-IrB}_9\text{H}_8\text{-2}}]$. Details from the structural analysis and the atomic co-ordinates are summarised in the Experimental section. Selected interatomic distances and interatomic angles are given in Tables 1 and 2 respectively. All atoms, including hydrogen atoms, were located and an ORTEP drawing of the molecule is shown in Figure 1.

The cluster structure may be described as a ten-vertex closed deltahedron approximating to idealised C_{3v} symmetry and it is, therefore, in contrast with the more common bicapped Archimedian square-antiprismatic structure with D_{4h} symmetry[11] as typified by *closo*-$[\text{B}_{10}\text{H}_{10}]^{2-}$. It may be viewed, ideally, as a 1:3:3:3 stack comprising an iridium vertex and three layers of three equivalent boron atoms of which the upper and middle layers are within bonding distance of the iridium atom. The metal vertex is bonded to these latter six boron atoms in an η^6-

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‡ 'Electrolobal' is defined in ref. 6.

Table 1. Selected interatomic distances (pm) for [1-H-1-(PPh_3)-1-(PPh_2-*ortho*-C_6H_4)-*isocloso*-1-IrB_9H_8-2] (**4**) with estimated standard deviations (e.s.d.s) in parentheses

From the iridium atom			
Ir(1)–B(2)	216.3(9)	Ir(1)–B(6)	238.8(10)
Ir(1)–B(5)	246.0(9)	Ir(1)–B(4)	214.8(10)
Ir(1)–B(3)	218.8(10)	Ir(1)–B(7)	237.8(9)
Ir(1)–P(1)	238.6(2)	Ir(1)–P(2)	239.9(9)
Ir(1)–H(1)	157.4(77)		
Boron–boron			
B(2)–B(5)	173.1(13)	B(6)–B(4)	174.0(14)
B(2)–B(7)	172.9(13)	B(6)–B(9)	180.7(13)
B(2)–B(8)	172.4(12)	B(6)–B(10)	178.4(13)
B(5)–B(3)	173.7(13)	B(4)–B(7)	175.2(13)
B(5)–B(8)	181.4(13)	B(4)–B(10)	175.8(13)
B(5)–B(9)	179.3(14)	B(7)–B(8)	181.5(13)
B(3)–B(6)	172.9(13)	B(7)–B(10)	178.3(14)
B(3)–B(9)	172.5(12)	B(8)–B(9)	177.3(14)
B(10)–B(9)	183.0(14)	B(8)–B(10)	179.9(14)
Boron–carbon			
B(2)–C(62)	159.2(11)		
Boron–hydrogen			
B(5)–H(3)	124(7)	B(7)–H(7)	129(8)
B(3)–H(4)	109(8)	B(8)–H(8)	116(8)
B(6)–H(5)	104(8)	B(9)–H(9)	117(8)
B(4)–H(6)	120(8)	B(10)–H(10)	116(8)
Phosphorus–carbon*			
P(1)–C(11)	184.5(4)	P(2)–C(41)	181.3(4)
P(1)–C(21)	182.8(4)	P(2)–C(51)	182.6(4)
P(1)–C(31)	183.2(4)	P(2)–C(61)	179.2(4)

* The phenyl rings were constrained to C–C 139.5, C–H 108.0 pm, H–C–C 120, and C–C–C 120°.

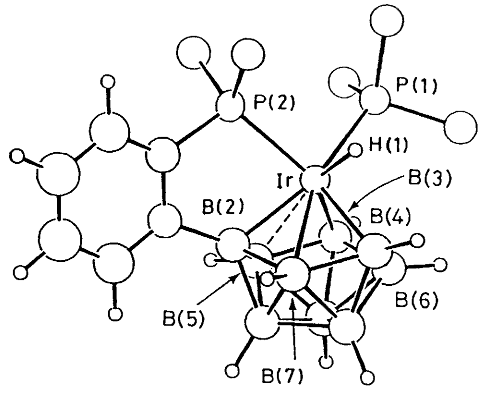


Figure 1. ORTEP drawing of [1-H-1-(PPh_3)-1-(PPh_2-*ortho*-C_6H_4)-*isocloso*-1-IrB_9H_8-2] (**4**). All atoms, including hydrogen atoms, were located in the analysis although the phenyl rings, except for the *ipso* carbon atoms, are omitted for clarity

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

At the iridium atom			
P(1)–Ir(1)–P(2)	96.3(1)	P(1)–Ir(1)–B(7)	160.8(2)
P(1)–Ir(1)–H(1)	82.1(28)	P(2)–Ir(1)–B(2)	77.2(2)
P(1)–Ir(1)–B(2)	151.1(3)	P(2)–Ir(1)–B(5)	103.8(2)
P(1)–Ir(1)–B(5)	114.2(2)	P(2)–Ir(1)–B(3)	136.2(2)
P(1)–Ir(1)–B(3)	80.3(2)	P(2)–Ir(1)–B(6)	170.1(2)
P(1)–Ir(1)–B(6)	93.5(2)	P(2)–Ir(1)–B(4)	130.7(3)
P(1)–Ir(1)–B(4)	115.9(3)	P(2)–Ir(1)–B(7)	100.3(2)
H(1)–Ir(1)–B(2)	125(3)	H(1)–Ir(1)–B(6)	98(3)
H(1)–Ir(1)–B(5)	160(3)	H(1)–Ir(1)–B(4)	65(3)
H(1)–Ir(1)–B(3)	136(3)	H(1)–Ir(1)–B(7)	90(3)
P(2)–Ir(1)–H(1)	85.1(29)		
Iridium–boron–boron			
Ir(1)–B(2)–B(8)	105.6(6)	Ir(1)–B(6)–B(10)	93.7(5)
Ir(1)–B(5)–B(8)	91.5(5)	Ir(1)–B(4)–B(10)	103.2(6)
Ir(1)–B(5)–B(9)	92.3(5)	Ir(1)–B(7)–B(8)	94.2(5)
Ir(1)–B(3)–B(9)	104.2(6)	Ir(1)–B(7)–B(10)	94.1(5)
Ir(1)–B(6)–B(9)	94.3(5)	Ir(1)–B(2)–C(62)	129.9(11)
Other selected angles			
B(2)–B(5)–B(3)	116.4(7)	Ir(1)–P(1)–C(11)	116.8(2)
B(5)–B(3)–B(6)	107.3(7)	Ir(1)–P(1)–C(21)	109.1(2)
B(3)–B(6)–B(4)	120.1(7)	Ir(1)–P(1)–C(31)	116.2(2)
B(6)–B(4)–B(7)	103.8(7)	Ir(1)–P(2)–C(41)	118.1(2)
B(4)–B(7)–B(2)	119.0(7)	Ir(1)–P(2)–C(51)	116.6(2)
B(7)–B(2)–B(5)	108.8(8)	Ir(1)–P(2)–C(61)	107.9(2)

'chair' conformation with the iridium–boron distances falling into two groups reflecting the $IrB_3B_3B_3$ idealised C_{3v} symmetry of the cluster. Thus, the distances between the iridium atom and the upper layer boron atoms B(2), B(3), and B(4) are 216.3(9), 218.8(10), and 214.8(10) pm respectively in contrast to the distances to the middle layer of atoms [B(5), B(6), and B(7)] which are 10–25 pm longer at 246.0(9), 238.8(10), and 237.8(9) pm. These are, however, still within a reasonable bonding distance (250 pm being the longest iridium–boron bonding interaction reported in the literature).[2,4,12] The upper-layer atoms have a connectivity of four whereas the middle-layer atoms have a connectivity of five and it has previously been noted that four-connected vertices tend to exhibit shorter interatomic distances than five-connected vertices.[10,11,13] The main determinant of the metal–boron distance must, however, be the unusual structure of the cluster.

Compound (**4**) can be usefully compared to two previously reported[14,15] structurally analogous metalladicarbaborane cluster compounds, [2,3-Me_2-1-(CH_2=$CHCH_2C_6H_4PPh_2$)-1,2,3-Ru-$C_2B_7H_7$][15] and [1,6-(η^5-C_5H_5)$_2$-1,6,2,3-$Fe_2C_2B_6H_8$],[14] and to the metallaborane [1-H-1-Cl-1-(PPh_3)-1-RuB_9H_7-3,5-(PPh_3)$_2$].[16] These three compounds are here numbered as in (**II**). Of these the first two cluster species have two of the upper-row boron atoms replaced either by carbon atoms (in the first compound) or by a (C_5H_5)Fe group and a carbon atom (in the second). This causes some distortion but, in both cases, the upper-layer metal–boron distances are 202 and 209 pm respectively compared to the second-layer distances of *ca.* 217 pm (average) in the ferradicarbaborane and 247, 234, and 249 pm, to B(5), B(6), and B(7) respectively, in the ruthenadicarbaborane. The relative shortening in the Ru–B(6) distance has been attributed [15] to the influence of the phosphine ligand *trans* to B(9). Similarly, the lengthening of the Ir(1)–B(5) distance of 246.0 pm in compound (**4**), which is *ca.* 8 pm longer than the equivalent distances to B(6) and B(7), may be attributed to the *trans* effect of the metal hydride [the angle H(1)–Ir(1)–B(5) is 160° compared to 98° for H(1)–Ir(1)–B(6) and 90° for H(1)–Ir(1)–B(7)]. The ruthenaborane, likewise, exhibits a shortening of 10—15 pm,[16] although *ca.* 5 pm of this may be due to the effect of the phosphine ligand on B(5). Interestingly, the three ligands in both compounds have an eclipsed conformation with respect to atoms B(2), B(3), and B(4).

The multielement n.m.r. data (which are consistent with the

Table 3. Boron-11, proton, and phosphorus-31 n.m.r. data for [1-H-1-(PPh_3)-1-(PPh_2-*ortho*-C_6H_4)-*isocloso*-1-IrB_9H_8-2] (**4**), [1-H-1,1-(PMe_3)$_2$-1-*isocloso*-IrB_9H_9] (**6**), and [1-X-1, 1-(η^2:η^2-C_8H_{12})-*isocloso*-1-IrB_9H_9] (**7**)

	Compound (**4**)[a]		Compound (**6**)[b,c]		Compound (**7**)[b,d]	
Assignment	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{1}H)$
(2)	+99.7	*e*				
(3), (4)	+92.5	+10.39	+94.1	+10.99	+88.2	+9.93
	+86.9	+10.04				
(8), (9), (10)	+29.8	+5.39	+22.4	+4.60	+29.3	+6.33
	+25.6	+5.34				
	+22.0	+5.15				
(5), (6), (7)	−9.6	+1.63	−18.0	−0.54	−14.7	+0.74
	−13.9	+0.09				
	−16.0	−1.63				
(1)	—	−11.79[f]	—	−13.43[g]		

[a] All resonances have relative intensity of one; ^{31}P n.m.r. spectrum shows two doublets $\delta(^{31}P)$ +23.9 and +18.4 p.p.m., $^{2}J(^{31}P-^{31}P)$(*cis*) 20 Hz. [b] All resonances have a relative intensity of three compared to compound (**4**) except for the signal at $\delta(^{1}H)$ -13.43 which has unit intensity. [c] ^{31}P n.m.r. spectrum shows peak at $\delta(^{31}P)$ −37.7 p.p.m. [d] $CDCl_3$–CD_3CN solution. Also $\delta(^{1}H)$(cod) at +4.47, +3.34, +1.61, +1.38, and +1.12 [e] Absent due to *o*-phenylene substituent. [f] Coupled to two ^{31}P nuclei giving two doublets, $^{2}J(^{31}P-^{1}H)$ (*cis*) 25.0 and 16.0 Hz. [g] Triplet $^{2}J(^{31}P-^{1}H)$ (*cis*) 24.5 Hz.

Table 4. Rate data for the *nido* ⟶ *isocloso* conversion of compound (**5**) into (**6**)

Rate constant, 10^4k (s^{-1})	ln *k*	$10^3\ T^{-1}/K^{-1}$
4.63	−7.678	2.857
0.628	−9.675	2.976
0.544	−9.819	2.959
0.136	−11.21	3.090
0.148	−11.12	3.115

By least-squares manipulation the data fit the rate expression

$$k_{5\rightarrow6}/s^{-1} = [(1.07 \pm 0.25) \times 10^{13}] \exp[(1.11 \pm 0.13) \times 10^5/RT]$$

where the error figure represents one standard deviation, and the numerator in the exponent has the same units as *RT*.

structure) are listed in Table 3. The ^{11}B n.m.r. spectrum shows three groups of three inequivalent resonances one of which, at $\delta(^{11}B)$ + 99.7 p.p.m., is a singlet due to the absence of $^{1}J(^{11}B-^{1}H)$, and is therefore assigned to the B(2) position, enabling all three low-field resonances to be assigned to B(2), B(3), and B(4). This contrasts to the assignments made for the ruthenadicarbaboranes in which the lower-field resonances are assigned to the middle belt of atoms.[17] Based upon assignments made for the ruthenaborane,[16] the middle-row atoms in compound (**4**), B(5), B(6), and B(7), are thereby associated with the resonances centred at $\delta(^{11}B)$ *ca.* −13 p.p.m., $\delta(^{1}H)$ *ca.* 0.0, and the lower row, B(8), B(9), and B(10), with the resonances centred at $\delta(^{11}B)$ *ca.* + 25 p.p.m., $\delta(^{1}H)$ *ca.* + 5.3. (It is of interest that the latter two sets of assignments contrast to those made for [(1,3,5-$C_6H_3Me_3$)FeB_9H_9], where they are reversed).[18] The extreme low-field resonances exhibited by the top row of boron atoms compared to the high-field resonances for the middle row atoms, which are also within metal bonding distance, suggest that the cluster-bonding environment is very different for the two sets of boron atoms. In both metallaboranes the boron atoms directly *trans* to the metal ligands are located in the middle row so that it is toward these middle-row atoms that the formal iridium bonding vectors would be directed in a formal 'octahedral' iridium(III) complex.

We have also isolated and identified by multielement n.m.r. spectroscopy (data in Table 3) a further two *isocloso* iridadecaborane cluster compounds. The first was isolated in quantitative yield from the thermolysis of a solution of [6-H-6,6-(PR_3)$_2$-*nido*-6-IrB_9H_{13}] (**5**; R = Me) in dichloroethane solution at *ca.* 80 °C and identified as [1-H-1,1-(PMe_3)$_2$-*isocloso*-1-IrB_9H_9] (**6**). The second was isolated in *ca.* 5% yield from the reaction of [{IrCl(cod)}$_2$] (cod = cyclo-octa-1,5-diene) with the *nido*-[B_9H_{12}]$^-$ anion in dichloromethane solution at ambient temperature. The reaction proceeds rapidly with evolution of hydrogen to give a species identified as [1-X-1,1-(η^2:η^2-C_8H_{12})-*isocloso*-1-IrB_9H_9] (**7**), where X is probably Cl.

Compounds (**6**) and (**7**) both feature three groups of three equivalent resonances in their ^{11}B and ^{1}H n.m.r. spectra with no apparent separation or broadening of the ^{31}P or ^{1}H n.m.r. peaks down to −88 °C. With regard to the disposition of the ligands about the iridium centre, the molecules would be expected to feature non-equivalent resonances in 2:1 relative intensity patterns due to the asymmetry of the $IrH(PMe_3)_2$ and $IrCl(\eta^2$:η^2-$C_8H_{12})$ moieties with respect to the three-fold symmetry of the borane fragment. The absence of this at −88 °C suggests a trigonal-twist pseudo-rotational process with a very low activation energy (<*ca.* 40 kJ mol^{-1}). The minimum-energy rotamer is probably that in which the nearer boron atoms are eclipsed, basing it on the preferred conformation observed for the *isocloso*-ruthenadecaborane.[16] If the eclipsed conformation is indeed preferred then it must imply that the disposition of the metal-bonding orbitals within the clusters is of importance and it would therefore be of interest to see how this fits in with a minimum-presumption molecular-orbital treatment for this type of cluster. In this context it is of interest that the (heavily substituted) ruthenaborane is not fluxional,[16] in contrast to the iridaboranes (**6**) and (**7**) reported here.

The thermolysis of compound (**5**) was followed by ^{11}B-{^{1}H} n.m.r. spectroscopy and found to obey pseudo-first-order rate expressions. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from the rate of fall of the intensity of the boron resonance at $\delta(^{11}B)$ − 31.5 p.p.m. of the parent compound (**5**; R = Me) at various temperatures (see, for example, Figure 2). The derived data for these are given in Table 4. From these, using the Arrhenius equation, the obtained activation parameters are $\Delta H^{\ddagger} = 108 \pm 13$ kJ mol^{-1} and $\Delta S^{\ddagger} = 28 \pm 7$ J K^{-1} mol^{-1} (error figures represent one standard deviation). The limited amount of the *nido* starting compound (**5**) conveniently available restricted the number of data sets that were obtainable, giving, therefore, only an imprecise estimation of the activation parameters. However, they may be compared to similar values of $\Delta H^{\ddagger}$ of *ca.* 125 kJ mol^{-1} and $\Delta S^{\ddagger}$ 29 J K^{-1} mol^{-1} obtained from a similar study[4] of the thermolysis of *arachno*-

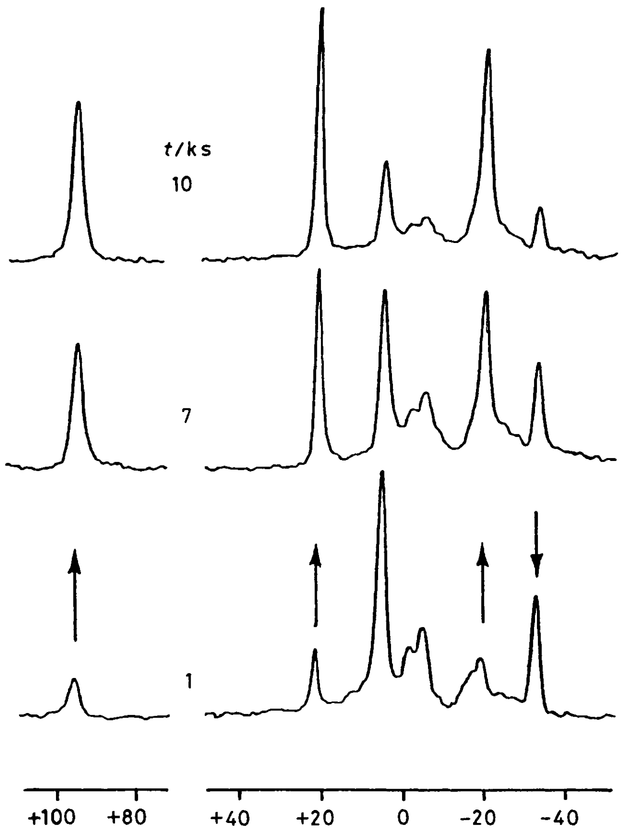


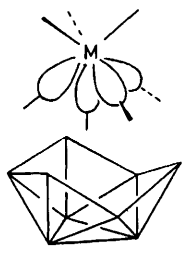
Figure 2. ^{11}B-{^1H} N.m.r. spectrum of $[H(PMe_3)_2IrB_9H_{13}]$ (5) at 48 °C after 1, 7, and 10 ks. Activation parameters were calculated from the rate of fall of the resonance at $\delta(^{11}B)$ -31.5 p.p.m.

$[H(PMe_3)_2(CO)IrB_8H_{12}]$ and *arachno*-$[H(PMe_3)_2(CO)IrB_8H_{11}Cl]$.

Compound (7) was identified by n.m.r. spectroscopy which showed no metal–hydride resonance in the proton spectrum. The compound was too unstable in solution for the isolation of a sample suitable for chlorine analysis but it is reasonable to assume that the necessary univalent ligand on the iridium is a chlorine atom. That the initial reaction, during its formation, was so rapid tends to belie the initial working hypothesis stated earlier, in the Introduction, that a terminal metal hydride might be of general importance in these facile *nido* ⟶ *closo* cluster oxidation processes. Indeed $[(1,3,5\text{-}C_6H_3Me_3)FeB_9H_{13}]$ has also been observed to thermolyse to $[(1,3,5\text{-}C_6H_3Me_3)FeB_9H_9]$, although in very low yield, and at higher temperatures.[18]

2. *The Nature of the Metallaborane Clusters in Compounds* (4)—(6).—Since the initial preliminary publication of our results,[9] some discussion has arisen about a suitable scheme for electron bookkeeping for the experimentally observed structure of compound (4) and whether (*a*) a '*hypocloso*' descriptor based on a *pileo* 2*n* electron count for a unique *hypercloso* cluster structure (as distinct from a normal *closo*-$[B_{10}H_{10}]^{2-}$ type cluster) is suitable,[17,19] or (*b*) whether an '*isocloso*' descriptor based on a normal *closo* $2n + 2$ electron count, but in which the hyperWadian electronic and atomic orbital contribution to the cluster bonding by the metal vertex alters the shape of the cluster, is preferred.[6] The former view derives from a straightforward application of simple electron-counting rules. The latter view derives from the approach that the orbital *and* electronic contribution of each vertex, whether transition element or boron, should be considered more specifically before a final cluster electron bookkeeping scheme is proposed. The latter approach has in fact been formally recognised for some time[20] although it has not been fully described and, hence, perhaps not fully appreciated by all electron-counting chemists. It takes account of the perception that the formal Wadian cluster electron count and the actual bonding electron count for a cluster are not always the same since Wade's rules do not explicitly (rather than implicitly) take into account the *lobal* contribution of a particular cluster vertex. In view of the slight confusion and consequent contention about these points in the *hypercloso*/*isocloso* ten-vertex area, it is convenient here to develop the matter in a little more detail in the context of experimental observations.

The observed structure of these ten-vertex *isocloso*-type cluster compounds is that of a convex hexadecahedron which is an isogonal permutation of the D_{4d} bicapped-Archimedian antiprism that requires, according to basic borane electron-counting rules, $2n + 2$ skeletal bonding electrons.[21,22] The assumption that the *closo* nature of the cluster would require a normal Wadian quota of $2n + 2$ cluster electrons would then in turn imply an iridium(v) vertex supplying four electrons to the cluster. This would require a seven-orbital iridium bonding configuration such as capped octahedral. A similar seven-orbital iridium configuration has been invoked in two other iridium(v) metallaborane clusters, *viz.* $[(CO)(PPh_3)_2HIrB_3H_7]$[23] and $[H(PMe_3)_2$-*isocloso*-$IrB_8H_7Cl]$,[2,5,24] and also in the iridacarbaborane $[(PPh_3)(PPh_2$-*ortho*-$C_6H_4)$-*isonido*-$IrC(OH)B_8H_6(OMe)]$.[25] In these terms the cluster structure could therefore be rationalised *via* a four-orbital involvement of the iridium with the cluster where the fourth orbital is an Ir-octahedral capping position directed into the centre of the cluster along the formal three-fold axes of both the iridium octahedron and the cluster [structure (III)]. This orbital may be regarded as



(III)

corresponding to the inward-pointing radial *sp* hybrid atomic orbital required in molecular-orbital approaches to straightforward *closo*-boron hydrides,[22] the difference now being that there are now three 'tangential' iridium-centred orbitals rather than the two usually associated with a BH fragment. In this approach, the cluster could therefore be thought of in terms of an $\{HL_2Ir\}^{4+}$ vertex capping a $\{B_9H_9\}^{4-}$ fragment that has an *arachno* geometry in spite of its formal *nido* electron count. Elements of the preference for the C_{3v}-based convex-hexadecahedral structure over that of the bicapped-Archimedian antiprism could also derive from the longer bonding distances and greater co-ordination numbers available to the *d*-block transition elements relative to those of boron. Examples of seven-co-ordinate boron are rare though it may be found in the (probably unstable)[26] proposed structure of *closo*-$[B_{11}H_{11}]^{2-}$, and the structurally characterised dicarboborane analogue *closo*-$[2,3\text{-}Me_2\text{-}2,3\text{-}C_2B_9H_9]$.[27] The latter compound features extremely long bonds from boron to the six-connected boron vertex of *ca.* 206 pm and the former compound a facile fluxionality which may be interpreted in terms of an open, C_{5v}, *nido*-11-vertex icosahedron,[28] or in terms of an open '*isonido*' eleven-vertex cluster.[26,29] Thus a *closo*-borane with a six-connected boron vertex would probably be less stable than one with four- and five-connected vertices whereas a transition metal, with its greater electrolobal expansion power, may accomodate all these connectivities. The complete capping of an *arachno* type *geometrical* structure is required to generate the high connectivities observed in the *isocloso* clusters: an *arachno*-type fragment will have more orbitals available in the metal–borane overlap region than a *nido* one, and so in this approach would be better able to accommodate the four-orbital overlap that would be required for this '*isocloso*' hypothesis.

In the *hypercloso* hypothesis[19] the preference for the convex hexadecahedron is regarded as being a consequence of distortion by the cluster in order to accommodate the *pileo* count of $2n$ skeletal electrons rather than the *closo* count of $2n + 2$ skeletal electrons required for the Archimedian antiprism. This *hypercloso* approach has been applied[19] to the $[H(PR_3)_2IrB_9H_9]$ (R = alkyl or aryl) type compounds, and in the treatment three suggestions were made.

(*a*) That four hydrogen atoms are lost from the *nido* cluster during the *reaction* [equation (4)], implying a transition from $2n + 2$ to $2n$ skeletal electrons in the cluster. This, however, assumes that the electrolobal contribution of the metal vertex *is not changed* by the reaction process, and, additionally, that the metal vertex always contributes only three orbitals to the formal cluster bonding, that the transition-element 18-electron rule holds in all cases, and that the metal retains six non-bonding electron pairs.

(*b*) That the hypothesis, in which the observed η^6 hapticity of the metal could be the result of a four-orbital contribution, does not hold because the compound $[1\text{-}H\text{-}1,1\text{-}(PPh_3)_2\text{-}1,2,4\text{-}IrC_2B_8H_{10}]$ is of *closo* structure and can therefore be accommodated by Wade's rules, implying three metal skeletal bonding orbitals interacting with an η^6-carbaborane ligand. However, recent experimental structural evidence[26] has shown that this cluster does in fact have a well defined open face and is not *closo* at all (see also ref. 29): therefore, although η^6 bonding between borane and three-orbital iridium(III) centres may well be feasible, this evidence does not support it.

(*c*) That the formal oxidation state [iridium(V) in this case] does not necessarily change the number of skeletal electrons contributed by the vertex. However, although this is of course true, the statement is confusing because in this particular case an iridium(V) description *would* necessarily dictate that the iridium centre contributes two extra electrons to the cluster bonding proper.

The *hypercloso* hypothesis has also been applied in the literature to the compound $[(PEt_3)_2RuC_2B_7H_9]$, in which an assumption of a bis(phosphine)ruthenium(0) metal vertex was deduced from a combination of a number of factors.[19] First, the addition of excess of ligand to $[(PEt_3)_2RuC_2B_7H_9]$ caused an equilibrium between the *hypercloso* species and a supposed *closo* species $[(PEt_3)_3RuC_2B_7H_9]$ (although neither compound was structurally characterised). Secondly, the *closo* nature of the latter compound was adduced to the *hypercloso* hypothesis *via* an assumption that the addition of a two-electron ligand to an 18-electron co-ordinatively saturated metal vertex would result in two electrons being transferred to cluster bonding giving the cluster a *closo* count. This would imply a formal oxidation from ruthenium(0) to ruthenium(II) [contrast (*c*) above]. The *isocloso* approach, on the other hand, would regard the bis(phosphine) compound as having a 16-electron ruthenium(II) vertex from which the extra phosphine ligand generates an 'octahedral' 18-electron ruthenium(II) vertex by removing one metal orbital (but no electrons) from cluster bonding which would also result in a straightforward Williams–Wade *closo* cluster. Alternatively, if the extra electrons from the phosphine are regarded as entering the cluster proper they would probably generate an *isonido*-type structure[5,30–32] which would be indistinguishable from a *closo* structure on available ^{11}B n.m.r. evidence; certainly the recently established[33] ready fluxionality of *closo*-2-ruthena- and *closo*-2-rhoda-dicarbadecaboranes indicates that the ten-vertex *closo* and *isonido* structures must be energetically very similar. It will be useful to have more structural work in this dicarbaborane area.

Additional confusion in the application of the *hypercloso* approach arises from conflict between (*a*) the assertion[19] that 'the combination of electron-deficient metallaborane ligands with heavy transition-metal vertices capable of existing in high formal oxidation states is favourable for the formation of stable *hypercloso* structures,' and (*b*) that the reasonable interpretation of the *hypercloso* approach is that the clusters are hyperelectron deficient *because* the metal does not choose to adopt its higher formal oxidation states.

The interpretative confusion is compounded somewhat by an approach using the sums of calculated one-electron energies of hypothetical $[(CO)_3RhB_9H_9]^+$ and $[(CO)_3Rh_9H_9]^-$ clusters, which show a small difference of 31 kJ mol^{-1} in favour of the convex hexadecahedron over the Archimedian antiprism.[34] This, however, amounts to only 0.025% of the total energy, and, from a one-electron energy sum on extended-Hückel calculations on (hypothetical) molecules of such complexity, it is not clear what valid conclusions the approach engenders. This is particularly so in view of the π acidity of the CO ligand invoked for the model calculation, because, experimentally, only phosphine, hydride, and C_5Me_5-type ligands have been observed in *isocloso* rhodium and iridium ten-vertex species.

This emphasises that it will be useful to have additional experimental and theoretical work in this interesting area.

3. *The Mechanism of Formation of the* isocloso *Compounds* **(4)**—**(6)**.—The loss of two or three molecules of dihydrogen during the cluster closure must, of course, involve a number of intermediate steps. The pseudo-first-order nature of this cluster closure of $[H(PMe_3)_2IrB_9H_{13}]$ suggests that it proceeds *via* intramolecular rather than intermolecular steps. In this case the loss of the first molecule of H_2 would give a cluster with a formal *closo* count but one that would still retain two extra bridging hydrogen atoms. Closed metallaborane clusters with face-capping[12,35–37] or edge-bridging[38] hydrogen atoms are known but they are not common, and are more usually associated with polymetallic systems.[12,29,37,39] It is of interest that the formula for the intermediate after the loss of H_2 [equation (5)] coincides with that suggested[10] for the initial reaction of $[B_9H_{12}]^-$ and $[IrCl(PPh_3)_3]$ [equation (6)], implying that they may proceed *via* a common intermediate **(8)** which, as illustrated in Figure 3, may be an *isonido* type cluster.

$$[H(PMe_3)_2IrB_9H_{13}] \xrightarrow{\text{Heat}} \underset{\textbf{(8)}}{\{H(PMe_3)_2IrB_9H_{11}\}} + H_2 \quad (5)$$

$$[B_9H_{12}]^- + [IrCl(PPh_3)_3] \longrightarrow \underset{\textbf{(8)}}{\{H(PPh_3)_2IrB_9H_{11}\}} + Cl^- + PPh_3 \quad (6)$$

Thus the initial two extra hydrogen atoms (over those contained in the ultimate *isocloso* product) may be accommodated in an *isonido*-type[5,30–32,40] geometry in which the metal atom would possibly increase its oxidation state from iridium(III) to iridium(V). The most reasonable path for a cluster closure for **(1)**, as shown in Figure 3(i), is *via* a movement of the 6 vertex toward the B(5,10,9) corner of the cluster, together with a rearrangement of the bridging hydrogen atoms. This could be followed by an *ortho*-cycloboronation reaction in the open face thus supplying a further two electrons sufficient to attain the stable *nido*-decaborane structure [(ii)] as in the conversion of

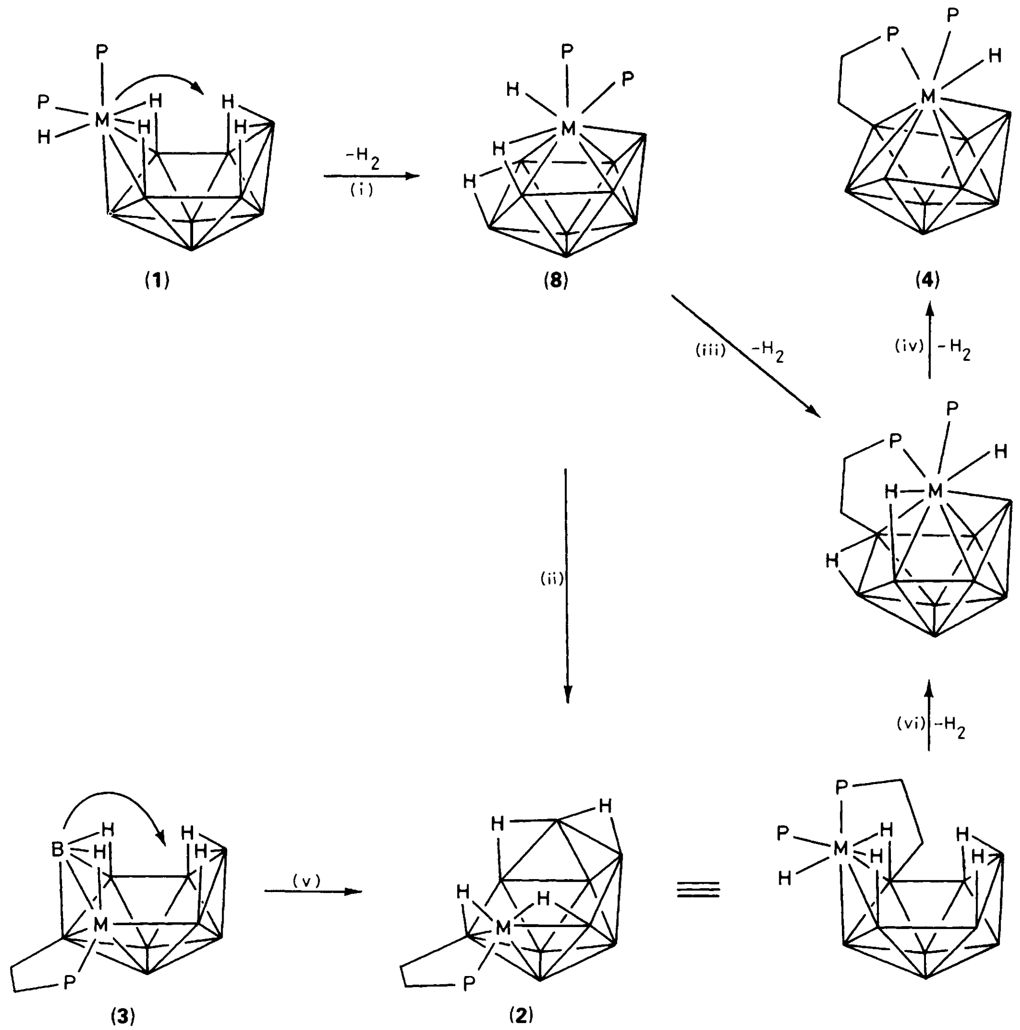


Figure 3. An illustration of the possible mechanism of the formation of [1-H-1-(PPh$_3$)-1-(PPh$_2$-*ortho*-C$_6$H$_4$)-*isocloso*-1-IrB$_9$H$_8$-2] (4) from compounds (1)—(3): (i) loss of H$_2$ from [6-H-6,6-(PR$_3$)$_2$-*nido*-6-IrB$_9$H$_{13}$] (1) to give an *isonido* type intermediate (8) which can then undergo (ii) an *ortho*-cycloboronation reaction to revert to a *nido*-decaborane cluster [*sym*-6-H-6-(PPh$_3$)-6-(PPh$_2$-*ortho*-C$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5] (2), or, (iii) and (iv), loses a further two molecules of dihydrogen to give compound (4). Compound (3), [5-H-5-(PPh$_3$)-5-(PPh$_2$-*ortho*-C$_6$H$_4$)-*nido*-5-IrB$_9$H$_{12}$-2], undergoes a clockwise vertex swing,[10] (v), to give compound (2) which then proceeds to product (4), (vi) and (iv). Note that for clarity, terminal H and P ligands on M are omitted from (2) and (3).

nido compound (1) to *nido* compound (2) described in ref. 10. Alternatively, it would then proceed to lose two further pairs of hydrogen atoms, continuing *via* the *isonido* intermediate (8) to the *isocloso* product described in this paper *via* elimination of H$_2$ and the formation of an *o*-phenylene linkage to B(2) as shown in Figure 3(iii) and (iv). The *o*-phenylene substituent would appear on the upper-row boron atoms in this scheme. An analogous cluster-closure sequence to this ten-vertex one has been proposed for the iridanonaborane system mentioned in the Introduction.[2,4,5] Whether the dihydrogen is eliminated *via* dinuolear elimination from the iridium atom or from the boron cage itself is not yet clear.

In the case of the 5-iridadecaborane cluster (3), the initial position of the metal atom precludes such a simple closure reaction, but a 'clockwise' vertex swing of the B(6) vertex [Figure 3(v)], as discussed in the preceding paper, would in fact produce the same structure as that obtained from (2), the process then proceeding as for compound (2) [Figure 3(vi) and (iv)]. As just mentioned, a more complete rationalisation of the vertex-swing mechanism for the 5-metalladecaborane formation is described in the preceding paper.[10]

The mechanism for the reaction between [{IrCl(cod)}$_2$] and the *nido*-[B$_9$H$_{12}$]$^-$ anion must be more complex because of the dimeric nature of the iridium halide starting complex, and because three hydrogen atoms are eliminated per {B$_9$H$_{12}$}$^-$ unit. With *arachno*-[B$_9$H$_{14}$]$^-$ as the starting borane anion, however, the major stable product (5%) is the *nido* species [Cl(cod)IrB$_9$H$_{13}$] which suggests that with two fewer hydrogen atoms in [B$_9$H$_{12}$]$^-$, and with no possibility of stabilisation *via* an *ortho*-cycloboronation reaction, the intermediate [similar to (8)] proceeds immediately to the thermodynamically stable *isocloso* product.

Experimental

General.—The starting materials [6-H-6,6-(PR$_3$)$_2$-*nido*-6-IrB$_9$H$_{13}$] (R = PPh$_3$ or PMe$_3$), [*sym*-6-H-6-(PPh$_3$)-6-(PPh$_2$-*ortho*-C$_6$H$_4$)-*nido*-6-IrB$_9$H$_{12}$-5], and [5-H-5-(PPh$_3$)-5-(PPh$_2$-*ortho*-C$_6$H$_4$)-*nido*-5-IrB$_9$H$_{12}$-2] were prepared as described before.[1,5,10] The borane anion *nido*-[B$_9$H$_{12}$]$^-$ was prepared as [NEt$_4$][B$_9$H$_{12}$] according to literature methods[41] as was [{IrCl(cod)}$_2$].[42] Dichloroethane solvent was used after drying over 3A molecular sieve. The reactions were carried out under an atmosphere of dry nitrogen, although subsequent

Table 5. Fractional atomic co-ordinates for compound (**4**) with e.s.d.s in parentheses

Ir(1)	0.230 47(05)	0.006 57(05)	0.164 03(05)
P(1)	0.300 65(25)	−0.093 03(15)	0.102 56(15)
P(2)	0.202 64(25)	−0.050 10(15)	0.305 36(15)
B(2)	0.241 9(7)	0.092 3(4)	0.265 1(7)
B(3)	0.357 8(7)	0.056 6(4)	0.122 0(7)
B(4)	0.132 7(8)	0.071 3(5)	0.058 8(7)
B(5)	0.353 5(7)	0.099 2(5)	0.228 4(7)
B(6)	0.251 6(7)	0.081 3(5)	0.036 1(7)
B(7)	0.142 9(7)	0.113 8(5)	0.169 4(7)
B(8)	0.256 9(7)	0.166 3(5)	0.200 5(7)
B(9)	0.327 8(8)	0.144 6(5)	0.115 4(7)
B(10)	0.190 8(8)	0.154 1(5)	0.076 8(7)
H(1)	0.128 7(58)	−0.029 2(39)	0.110 6(57)
H(3)	0.422 0(61)	0.035 6(41)	0.098 4(55)
H(4)	0.055 0(63)	0.053 9(39)	0.004 4(54)
H(5)	0.433 3(58)	0.102 4(38)	0.291 3(56)
H(6)	0.251 1(58)	0.065 5(39)	−0.033 4(59)
H(7)	0.063 6(59)	0.119 6(38)	0.202 5(56)
H(8)	0.271 5(57)	0.221 4(39)	0.236 3(56)
H(9)	0.384 6(57)	0.185 2(39)	0.096 3(55)
H(10)	0.156 8(58)	0.202 9(39)	0.033 0(57)
C(11)	0.236 9(3)	−0.177 9(2)	0.107 0(4)
C(12)	0.292 4(3)	−0.240 1(2)	0.117 8(4)
C(13)	0.243 6(3)	−0.304 4(2)	0.117 0(4)
C(14)	0.139 3(3)	−0.306 6(2)	0.105 5(4)
C(15)	0.083 9(3)	−0.244 5(2)	0.094 7(4)
C(16)	0.132 7(3)	−0.180 1(2)	0.099 5(4)
C(21)	0.285 5(4)	−0.082 6(3)	−0.027 3(3)
C(22)	0.365 2(4)	−0.061 6(3)	−0.066 4(3)
C(23)	0.348 1(4)	−0.047 1(3)	−0.164 6(3)
C(24)	0.251 4(4)	−0.053 5(3)	−0.223 7(3)
C(25)	0.171 7(4)	−0.074 5(3)	−0.184 6(3)
C(26)	0.188 7(4)	−0.089 0(3)	−0.086 3(3)
C(31)	0.434 9(3)	−0.109 6(3)	0.153 5(3)
C(32)	0.478 1(3)	−0.082 3(3)	0.244 5(3)
C(33)	0.578 9(3)	−0.096 2(3)	0.288 0(3)
C(34)	0.636 4(3)	−0.137 3(3)	0.240 5(3)
C(35)	0.593 1(3)	−0.164 6(3)	0.149 5(3)
C(36)	0.492 4(3)	−0.150 8(3)	0.106 0(3)
C(41)	0.091 3(3)	−0.104 4(2)	0.292 9(4)
C(42)	0.091 2(3)	−0.165 9(2)	0.345 8(4)
C(43)	0.003 9(3)	−0.206 4(2)	0.332 2(4)
C(44)	−0.083 3(3)	−0.185 4(2)	0.265 7(4)
C(45)	−0.083 2(3)	−0.123 9(2)	0.212 8(4)
C(46)	0.004 1(3)	−0.083 4(2)	0.226 4(4)
C(51)	0.306 6(4)	−0.102 5(2)	0.375 0(4)
C(52)	0.377 1(4)	−0.070 8(2)	0.449 7(4)
C(53)	0.461 9(4)	−0.108 1(2)	0.498 1(4)
C(54)	0.476 0(4)	−0.177 2(2)	0.471 9(4)
C(55)	0.405 4(4)	−0.208 9(2)	0.397 2(4)
C(56)	0.320 7(4)	−0.171 6(2)	0.348 8(4)
C(61)	0.185 7(4)	0.016 8(2)	0.388 3(4)
C(62)	0.217 2(4)	0.083 5(2)	0.367 9(4)
C(63)	0.211 8(4)	0.139 4(2)	0.429 5(4)
C(64)	0.175 0(4)	0.128 6(2)	0.511 4(4)
C(65)	0.143 5(4)	0.061 9(2)	0.531 8(4)
C(66)	0.148 8(4)	0.006 0(2)	0.470 2(4)

manipulations were carried out in air. Preparative thin-layer chromatography (t.l.c.) was carried out using silica gel with a fluorescent indicator (Fluka type GF254) as stationary phase.

Nuclear Magnetic Resonance Spectroscopy.—Boron-11, phosphorus-31, and proton spectra at *ca.* 32, 40, and 100 MHz respectively were obtained in these laboratories at 2.34 T on a JEOL FX-100 instrument with the multiple resonance ^{1}H-{^{11}B} experiments for the mutual assignment of ^{11}B and ^{1}H resonances (Table 3) being carried out as described elsewhere.[1,43–45] Boron-11 spectra at 128 MHz were recorded using a Bruker WH-400 instrument at the University of Sheffield. Chemical shifts $\delta(^1\mathrm{H})$, $\delta(^{31}\mathrm{P})$, and $\delta(^{11}\mathrm{B})$ are given in p.p.m. to high frequency (low field) of Ξ 100, Ξ 40.480730 (nominally 85% H_3PO_4), and Ξ 32.083971 MHz (nominally $F_3B{\cdot}OEt_2$ in $CDCl_3$) respectively, Ξ being defined as in ref. 46. Phosphorus-31 n.m.r. spectra were recorded at *ca.* −50 °C.

Synthesis of [1-H-1-(PPh_3)-1-$(PPh_2$-*ortho*-$C_6H_4)$-*isocloso*-1-IrB_9H_8-2] (**4**) *and* [1-H-1,1-$(PMe_3)_2$-*isocloso*-1-IrB_9H_9] (**6**).—These were prepared by heating (water-bath; 80—85 °C) dry deoxygenated dichloroethane solutions of the corresponding *nido*-iridadecaboranes [6-H-6,6-$(Ph_3)_2$-*nido*-6-IrB_9H_{13}] (**1**), [*sym*-6-H-6-(PPh_3)-6-$(PPh_2$-*ortho*-$C_6H_4)$-*nido*-6-IrB_9H_{12}-5] (**2**), [5-H-5-(PPh_3)-5-$(PPh_2$-*ortho*-$C_6H_4)$-*nido*-5-IrB_9H_{12}-2] (**3**), and [6-H-6,6-$(PMe_3)_2$-*nido*-6-IrB_9H_{13}] (**5**), contained in stoppered tubes. The course of the reaction was monitored by ^{11}B and ^{31}P n.m.r. spectroscopy. After most of the starting material had reacted the solvent was removed under vacuum and the solid redissolved in dichloromethane and then separated by t.l.c. (CH_2Cl_2–pentane, 60:40). Thus, for example, 200 mg (0.25 mmol) of (**1**) gave 180 mg of compound (**4**) (R_f 0.6) and *ca.* 20 mg of unreacted starting material (R_f 0.75), resulting in *ca.* 100% yield based on the amount of compound (**1**) consumed.

Synthesis of [1-X-1,1-$(\eta^2{:}\eta^2$-$C_8H_{12})$-*isocloso*-1-IrB_9H_9] (**7**).—This compound was prepared by the addition of [{IrCl(cod)}$_2$] (72 mg, 0.21 mmol) to a stirred solution of [NEt_4][*nido*-B_9H_{12}] (52 mg, 0.21 mmol) in dichloromethane (*ca.* 20 cm^3). The reaction proceeded rapidly, and the originally red solution turned black, accompanied by effervescence. The solution was reduced in volume, applied to a preparative t.l.c. plate, and developed using MeCN–CH_2Cl_2 (20:80) as mobile phase. Most of the product decomposed at this point, remaining as a brown baseline on the t.l.c. plate, leaving one yellow-orange band (R_f 0.3) to be isolated and characterised as [1-X-1,1-$(\eta^2{:}\eta^2$-$C_8H_{12})$-*isocloso*-1-IrB_9H_9] (**7**); X is probably Cl (see text) (14 mg, 16% yield). A sample suitable for elemental analysis could not be obtained as the compound decomposed over the period that would be required to obtain pure crystalline material. No reliable mass spectroscopic data were obtainable. The compound was identified by n.m.r. spectroscopy as described in the text.

X-Ray Diffraction Analysis of Compound (**4**).—This was adequately treated in a preliminary communication.[9] Crystallographic data are summarised here for convenience, and the atomic co-ordinates are published in Table 5. Crystals are monoclinic, space group $P2_1/c$ with a = 1366.0(3), b = 1906(4), c = 1429.1(3) pm, β = 103.71(2)°, and Z = 4. The final R for 3728 independent F_o was 0.037.

Acknowledgements

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