Cage Expansion in Metallopentaborane Chemistry: The Preparation and Structure of 2-{Carbonylbis(triphenylphosphine)irida}-*nido*-hexaborane, $[(IrB_5H_8)(CO)(PPh_3)_2]$

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The reaction of $K[B_5H_8]$ with $[Ir(CO)Cl(PPh_3)_2]$ at low temperature yields $[(IrB_5H_8)(CO)(PPh_3)_2]$ which crystallises as yellow blocks in the monoclinic space group $P2_1/c$ with a = 10.097(2), b = 20.708(5), c = 16.493(3) Å, β = 92.85(2)°, and Z = 4. Single-crystal X-ray diffraction analysis shows that the compound has a novel structure in which the transition-metal atom has inserted into the polyhedral pentaborane cluster; the iridium and boron atoms form a pentagonal pyramid in which the metal occupies a basal position, and the structure is therefore that of a metallahexaborane. The co-ordination number of the iridium atom is seven and the geometry is a distorted, monocapped, trigonal prism which probably results from formally octahedral hybridisation about the iridium(III) atom, one of the bonds being a two-electron three-centre bond involving the apical and a basal boron atom in the metallaborane cluster. This is consistent with formal skeletal electron-counting rules.

TREATMENT of pentaborane(9) with a base such as KH results in deprotonation from a bridging position to form the octahydro-*nido*-pentaborate(1−) anion.[1] Recently, it has been found that this anion can displace halide ions from transition-metal complexes to give metallopentaboranes in which the metal occupies the available bridging position; [2-8] less commonly σ-bonded metallopentaboranes may be produced,[9] or alternatively partial degradation of the borane cage may occur to give metallaborane clusters containing four or fewer boron atoms.[10-12] We now report that, in the reaction of $K[B_5H_8]$ with $[Ir(CO)Cl(PPh_3)_2]$, a fourth type of process occurs: in this case the metal atom is assimilated into the pentaborane cluster in a cage-expansion reaction to form a compound with a metalla-*nido*-hexaborane structure, for which we present i.r. and n.m.r. data and the results of a single-crystal X-ray diffraction analysis. Only one other example of this general structural class has hitherto been reported in transition-metal chemistry,[13] although a beryllium derivative is known.[14] Few iridium derivatives of polyhedral boranes of any kind have been reported.

TABLE 1

N.m.r. data for $[(IrB_5H_8)(CO)(PPh_3)_2]$ and related compounds

(*a*) ^{11}B

	$[(IrB_5H_8)(CO)(PPh_3)_2]$ [a]				$\delta(^{11}B)$ [c]		
Assignment [b]	$\delta(^{11}B)$ [c]	$w_{\frac{1}{2}}$ [d]	Relative area	$^1J(^{11}B-^1H)$ [d]	B_5H_9	B_6H_{10}	$[(FeB_5H_9)(CO)_3]$ [e]
B(3),B(6)	$+42\pm3$	*ca.* 600	2	*f*	−13.6	+13.7	+46.1
B(4),B(5)	$+10\pm3$	*ca.* 600	2	*f*	−13.6	+13.7	+8.6
B(1)	-28 ± 3	*ca.* 300	1	140 ± 20	−53.1	−52.2	−47.2

(*b*) ^1H [a,g]

	^1H spectrum, 25 °C			$^1H-\{^{11}B\}$ spectrum, 25 °C		
Assignment [b]	$\delta(^1H)$ [h,i]	$w_{\frac{1}{2}}$ [d]	Relative area	$\delta(^1H)$ [i]	$w_{\frac{1}{2}}$ [d,j]	Relative area
B(3)–H,B(6)–H	*k*			+6.7	*l*	2
B(4)–H,B(5)–H	*k*			+4.9	20 ± 5	2
B(1)–H	*k*			−0.4	25 ± 5	1
B(3)–H–B(4),B(5)–H–B(6)	−2.6	40 ± 5	2	−2.6	25 ± 5	2
Ir(2)–H–B(3) [m]	−12.05	25 ± 5	1	−12.05	20 ± 5	1

[a] Saturated solution in CD_2Cl_2 at 25 °C unless otherwise indicated. Additional data: $\delta(^1H)$(*P*-phenyl) 6.5—7.7 p.p.m.; $\delta(^{31}P)$ (25 °C) −134.9 (s) p.p.m. [b] Numbering as in Figure 1. [c] In p.p.m. to high frequency (low field) of $OEt_2 \cdot BF_3$. [d] In Hz. [e] From ref. 13. [f] Not resolved. [g] No coupling $^1J(^{11}B-^1H)$ resolved in the ^1H spectrum [h] Boron–hydrogen assignments confirmed by selective $^1H-\{^{11}B\}$ experiments. [i] In p.p.m. to high frequency (low field) of $SiMe_4$. [j] Width quoted is the minimum observed with maximum power selective single-frequency unmodulated ^{11}B irradiation. [k] Lines too broad to be observable. [l] Partially obscured by *P*-phenyl ^1H resonances. [m] No coupling $^2J(^{31}P-Ir-^1H)$ resolved.

EXPERIMENTAL

General.—All the manipulations, apart from those involving the air-stable crystalline samples of $[(IrB_5H_8)(CO)(PPh_3)_2]$, were carried out under anaerobic conditions using standard vacuum line, Schlenk, and glove-box techniques. Pentaborane(9) was obtained by courtesy of Dr. R. E. Williams (Chemical Systems, Inc.). Commercially obtained potassium hydride was freed from mineral oil by washing with pentane.

Spectra.—28.9-MHz ^{11}B and $^{11}B-\{^1H\}$, and 36.4-MHz $^{31}P-\{^1H\}$ n.m.r. spectra were obtained for a saturated solution in CD_2Cl_2 using a Bruker HFX4 spectrometer modified for Fourier transform with a Bruker BNC12 Datasystem. 100-MHz $^1H-\{^{11}B\}$ work was carried out on a JEOL FX-100 spectrometer with the co-operation of Dr. P. Beynon. Chemical shifts (δ) are quoted to high frequency (low field) of the reference standards which were $SiMe_4$ for ^1H, $P(OMe)_3$ for ^{31}P, and $OEt_2 \cdot BF_3$ for ^{11}B. It should be noted that, with this sign convention,[15] the nuclear shielding and chemical shifts are of opposite sign.[16] Infrared spectra were recorded using a Perkin-Elmer 457 grating spectrometer; errors in the quoted band maxima are ±5 cm^{-1}.

Preparation of 2-{*Carbonylbis*(*triphenylphosphine*)*irida*}-nido-*hexaborane.*—Pentaborane(9) (*ca.* 4.0 mmol) and tetrahydrofuran (*ca.* 10 cm^3) were condensed at −196 °C on to potassium hydride (75% active, 0.21 g, corresponding to 3.95 mmol KH) and the mixture was stirred at −60 °C for 1 h to produce potassium octahydropentaborate, K[B_5H_8].[1] Dichloromethane (*ca.* 20 cm^3) was then condensed in at −196 °C, and *trans*-[Ir(CO)Cl(PPh_3)$_2$] (3.11 g, 3.96 mmol) was added. The mixture was warmed to −70 °C with stirring, which produced an immediate colour change from yellow to red, and it was then allowed to warm slowly (*ca.* 3 h) to −20 °C, at which temperature the red colour started to diminish in intensity. The mixture was then maintained at *ca.* −25 °C for *ca.* 3 h, during which time it slowly became yellow, and it was then stored at −80 °C overnight. The cold solution was filtered rapidly and the filtrate reduced in volume to *ca.* 5 cm^3 at −60 °C under reduced pressure. The solution was stirred vigorously at this temperature and diethyl ether (40 cm^3) was distilled on to precipitate the crude product as a yellow *powder* (0.6 g, 0.69 mmol; 17.5% yield). Purification was effected by dissolution in dichloromethane (*ca.* 5 cm^3) and reprecipitation by diethyl ether (*ca.* 40 cm^3) at −70 °C, followed by recrystallisation from dichloromethane at $-10 < \theta_c < 25$ °C to yield air-stable pale yellow crystals, m.p. (decomp.) *ca.* 180 °C [Found: C, 54.2; H, 4.85; B, 6.55; P, 7.5; Ir + O (by difference) 26.9. Calc. for $C_{37}H_{38}B_5IrOP_2$: C, 55.0; H, 4.75; B, 6.7; P, 7.7; Ir + O 25.9%]; $\nu_{max.}$ at 2 540m, 2 520s, 2 500s, 2 480m [ν(BH)], *ca.* 2 340vw [ν(BHB)], 2 030s [ν(CO)], and 1 930vw cm^{-1} [ν(IrHB)] (Nujol mull and KCl disc). N.m.r. data are summarised in Table 1.

X-*Ray Diffraction Experiments*.—(*a*) *Crystal data*. $C_{37}H_{38}B_5IrOP_2$, M = 806.89, Monoclinic, a = 10.097(2), b = 20.708(5), c = 16.493(3) Å, β = 92.85(2)°, U = 3 444.2(9) Å^3, Z = 4, D_c = 1.167 g cm^{-3}, $F(000)$ = 1 600, space group $P2_1/c$ (no. 14), Mo-K_α graphite-monochromatised radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 39.8 cm^{-1}.

(*b*) *Structure determination*. The compound was recrystallised from dichloromethane as pale yellow blocks. The crystal used was regular and of dimensions *ca.* 0.6 × 0.4 × 0.4 mm. Preliminary photographs yielded approximate cell dimensions and indicated the centrosymmetric, monoclinic, space group $P2_1/c$. Subsequent measurements were made on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 reflections having $35 < 2\theta < 40°$. Intensities of all the independent reflections having $5 < 2\theta < 50°$ were measured in the θ—2θ scan mode using scans from 1.0° below K_{α_1} to 1.0° above K_{α_2}. The structure analysis used the 4 782 independent reflections having $I > 3\sigma(I)$ where $\sigma(I)$ is the standard deviation derived from counting statistics; another 967 reflections having $I < 3\sigma(I)$ were excluded as 'unobserved'.

Non-hydrogen atoms were located from Patterson and electron-density syntheses. Block-diagonal least-squares refinement of co-ordinates for all the non-hydrogen atoms, anisotropic thermal parameters for iridium and phosphorus atoms, and isotropic thermal parameters for all the remaining non-hydrogen atoms led to convergence with R 0.054 and R' 0.063. The data were then corrected for the effects of absorption, and continued refinement (as above) converged at R 0.036 and R' 0.041.

The location of the hydrogen atoms was attempted by running three difference-Fourier syntheses based on different (sinθ)/λ cut-offs of data,[17] respectively those 2 301 data having (sinθ)/λ ⩽ 0.45, those 1 648 data having (sinθ)/λ ⩽ 0.4, and those 717 data having (sinθ)/λ ⩽ 0.3. The hydrogen atoms in the structure appeared at their expected positions in each of the difference maps and the

TABLE 2

Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
B(1)	0.397 8(6)	0.124 9(3)	0.180 7(3)
Ir(2)	0.230 0(1)	0.060 8(1)	0.221 3(1)
B(3)	0.434 7(6)	0.085 1(3)	0.272 5(4)
B(4)	0.486 8(7)	0.163 3(4)	0.263 3(4)
B(5)	0.373 7(7)	0.206 7(3)	0.212 5(4)
B(6)	0.239 0(6)	0.161 3(3)	0.181 9(4)
P(1)	0.273 8(1)	−0.052 0(1)	0.242 3(1)
P(2)	0.019 8(1)	0.079 8(1)	0.271 5(1)
C(1)	0.343 1(4)	−0.077 8(2)	0.343 2(2)
C(2)	0.407 7(5)	−0.137 4(2)	0.353 1(3)
C(3)	0.452 7(5)	−0.157 6(2)	0.430 0(3)
C(4)	0.432 2(5)	−0.120 0(3)	0.496 0(3)
C(5)	0.371 5(5)	−0.060 8(3)	0.487 2(3)
C(6)	0.326 2(5)	−0.039 7(2)	0.410 9(3)
C(7)	0.127 6(4)	−0.103 3(2)	0.225 1(2)
C(8)	0.072 1(5)	−0.138 7(2)	0.285 7(3)
C(9)	−0.045 5(5)	−0.172 6(2)	0.271 0(3)
C(10)	−0.108 5(5)	−0.171 2(3)	0.194 2(3)
C(11)	−0.053 4(6)	−0.137 2(3)	0.133 2(3)
C(12)	0.064 9(5)	−0.103 0(2)	0.148 8(3)
C(13)	0.389 5(5)	−0.086 9(2)	0.171 3(3)
C(14)	0.479 4(5)	−0.047 5(2)	0.135 8(3)
C(15)	0.572 9(6)	−0.074 6(3)	0.084 2(3)
C(16)	0.572 0(6)	−0.139 3(3)	0.070 7(3)
C(17)	0.484 6(5)	−0.178 6(3)	0.104 3(3)
C(18)	0.388 6(5)	−0.152 5(2)	0.154 9(3)
C(19)	−0.092 9(4)	0.115 2(2)	0.194 3(2)
C(20)	−0.130 7(5)	0.179 4(2)	0.197 1(3)
C(21)	−0.215 5(5)	0.205 4(3)	0.136 6(3)
C(22)	−0.261 1(6)	0.167 2(3)	0.073 7(3)
C(23)	−0.221 9(6)	0.104 2(3)	0.067 7(3)
C(24)	−0.136 4(5)	0.077 6(2)	0.127 9(3)
C(25)	0.018 0(4)	0.137 3(2)	0.356 8(2)
C(26)	−0.104 8(5)	0.151 2(2)	0.390 0(3)
C(27)	−0.108 8(6)	0.194 0(3)	0.455 3(3)
C(28)	0.005 4(6)	0.221 4(3)	0.488 7(3)
C(29)	0.124 3(5)	0.207 3(2)	0.457 8(3)
C(30)	0.132 2(5)	0.165 3(2)	0.391 5(3)
C(31)	−0.079 2(4)	0.015 1(2)	0.315 3(2)
C(32)	−0.027 0(5)	−0.012 8(2)	0.386 5(3)
C(33)	−0.098 0(5)	−0.059 6(3)	0.426 9(3)
C(34)	−0.221 0(6)	−0.078 7(2)	0.369 1(3)
C(35)	−0.273 6(6)	−0.051 5(3)	0.326 0(3)
C(36)	−0.202 8(5)	−0.004 4(2)	0.285 0(3)
C(37)	0.173 8(5)	0.047 3(2)	0.112 7(3)
O(1)	0.146 9(4)	0.042 0(2)	0.044 4(2)

Borane hydrogens

	x	*y*	*z*		*x*	*y*	*z*
H(1)	0.444	0.108	0.127	H(6)	0.167	0.185	0.138
H(3)	0.497	0.044	0.305	H(23)	0.314	0.080	0.312
H(4)	0.604	0.169	0.272	H(34)	0.443	0.135	0.328
H(5)	0.387	0.256	0.177	H(56)	0.252	0.205	0.238

Phenyl hydrogens

H(2)	0.427	−0.164	0.305	H(20)	−0.107	0.208	0.248
H(3)	0.494	−0.205	0.422	H(21)	−0.242	0.256	0.149
H(4)	0.451	−0.138	0.563	H(22)	−0.331	0.190	0.024
H(5)	0.355	−0.031	0.540	H(23)	−0.244	0.067	0.024
H(6)	0.292	0.008	0.403	H(24)	−0.117	0.028	0.124
H(8)	0.115	−0.142	0.344	H(26)	−0.192	0.132	0.364
H(9)	−0.081	−0.187	0.320	H(27)	−0.204	0.203	0.479
H(10)	−0.214	−0.189	0.192	H(28)	0.001	0.261	0.538
H(11)	−0.119	−0.129	0.072	H(29)	0.217	0.225	0.479
H(12)	0.109	−0.079	0.102	H(30)	0.216	0.156	0.367
H(14)	0.486	−0.002	0.147	H(32)	0.075	−0.001	0.411
H(15)	0.622	−0.036	0.060	H(33)	−0.055	−0.079	0.482
H(16)	0.649	−0.153	0.025	H(34)	−0.270	−0.121	0.425
H(17)	0.455	−0.222	0.111	H(35)	−0.361	−0.066	0.289
H(18)	0.318	−0.181	0.171	H(36)	−0.250	0.021	0.228

co-ordinates from each differed only slightly. Preliminary bond-length calculations showed that the hydrogen positions from the $(\sin\theta)/\lambda \leqslant 0.45$ map gave the smallest scatter of C–H distances (0.93—1.18 Å). The 38 hydrogen atoms appeared in this difference map among a total of 58 peaks of height >0.3 e Å^{-3}. Peak heights were in the range 0.59—0.30 e Å^{-3}, the peak of lowest height being that due to the Ir–H–B hydrogen. The majority of the remaining peaks of height $\geqslant 0.3$ e Å^{-3} were in the close vicinity of carbon atoms. In addition, a peak of height comparable with those of true hydrogen atoms appeared in all the three difference maps at a chemically implausible position *ca.* 0.9 Å from the iridium atom.

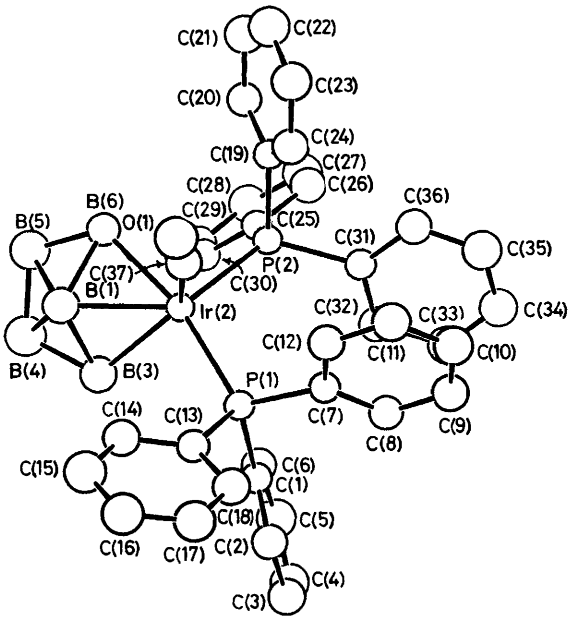

FIGURE 1 ORTEP drawing of the molecular structure of $[(IrB_5H_8)(CO)(PPh_3)_2]$ (hydrogen atoms omitted) showing the numbering system

These hydrogen atoms were included as fixed contributions with isotropic temperature factors of 0.06 Å^2. Further refinement of the non-hydrogen atoms led to final convergence at R 0.030 and R' 0.031. Atomic scattering factors were calculated using the analytical approximation and coefficients tabulated in ref. 18.

Final atomic co-ordinates and estimated standard deviations are listed in Table 2.* The molecular structure and atom numbering of the non-hydrogen atoms are shown in Figure 1. Hydrogen atoms are numbered according to the carbon atom or boron atom(s) to which they are bound.

RESULTS AND DISCUSSION

The reaction of $K[B_5H_8]$ with the d^8 iridium(I) complex *trans*-$[Ir(CO)Cl(PPh_3)_2]$ at low temperature yields an air-stable crystalline product; analytical data are

$$K[B_5H_8] + [Ir(CO)Cl(PPh_3)_2] \longrightarrow KCl + [Ir(B_5H_8)(CO)(PPh_3)_2] \quad (1)$$

consistent with the formation of a straightforward substitution product [equation (1)]. We have already established[8] that under similar conditions the iso-electronic d^8 platinum(II) compounds $[PtX_2(PPh_3)_2]$ gave straightforward metathesis products $[Pt(B_5H_8)X(PPh_3)_2]$ in which both the stereochemistry about the metal atom and the geometry of the *nido*-pentaborane skeleton are maintained: the $PtX(PPh_3)_2$ moiety remains *exo*-polyhedral and may formally be regarded as replacing a bridging hydrogen atom in pentaborane(9). However, although the 2 : 2 : 1 intensity ratio of the resonances in the ^{11}B n.m.r. spectrum of the iridium compound (Table 1) at first sight suggests a similar structure in which the metal atom is between two basal boron atoms, the extreme low-field shifts argue against its formulation as a direct structural analogue. This conclusion is supported by the ^1H and ^1H-$\{^{11}B\}$ n.m.r. spectra (Table 1), which in addition to the B–H–B proton resonance at $\delta = -2.5$ p.p.m. show both a resonance at 12.05 p.p.m. ascribable to a proton associated with the iridium atom and also basal-terminal boron hydride resonances at substantially lower field than those normally encountered[2-8] in substituted *nido*-pentaborane(9) species. Some of these data are similar to those recently reported for the compound $[(FeB_5H_9)(CO)_3]$,[13] a product of the co-thermolysis of $[Fe(CO)_5]$ with B_5H_9, which has a pentagonal-pyramidal *nido*-metallahexaborane structure with the metal atom in a basal position. That the compound $[(IrB_5H_8)(CO)(PPh_3)_2]$ reported here also falls into this new structural category was confirmed by the results of a single-crystal *X*-ray diffraction analysis (Tables 2—4 and Figures 1 and 2).

Figure 2 shows the structure about the iridium atom and of the metallahexaborane fragment; *P*-phenyl groups have been omitted for clarity. In the metal–boron cluster the iridium and the five boron atoms form a pentagonal pyramid in which the iridium atom is in a basal position. The metal atom and the basal boron

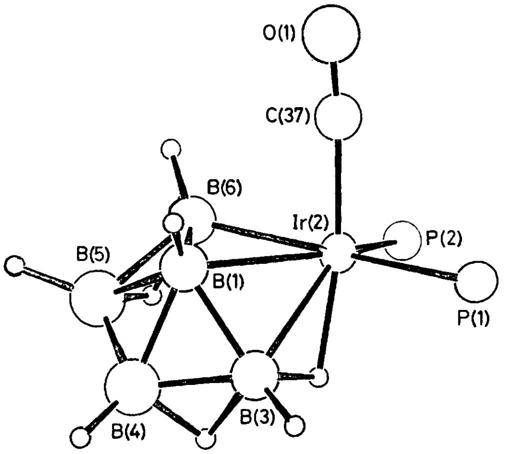

FIGURE 2 ORTEP drawing of $[(IrB_5H_8)(CO)(PPh_3)_2]$ with the phenyl groups omitted in order to show the structure about the iridium atom and of the metallaborane cluster. Hydrogen atoms have been given artificial temperature factors of B = 0.5 Å^2. Terminal hydrogen atoms are numbered according to the boron atom to which they are attached, and bridging hydrogen atoms according to the two boron atoms to which they are attached (Tables 1—4)

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* Observed and calculated structure-factor amplitudes and thermal parameters are listed in Supplementary Publication No. SUP 22349 (28 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

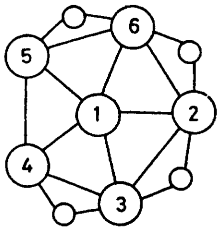
atoms are essentially coplanar, the deviation of the metal from the mean B(3)B(4)B(5)B(6) plane being 0.12 Å. This structure is similar to that of the ferrahexaborane mentioned above,[13] and is in contrast to the metallopentaborane structures exhibited by copper [2,4] and other late transition [6-8] and *p*-block [5,19,20] metal–pentaborane derivatives in which the metal is below the plane of the square base and is essentially coplanar with a triangular B–B–B *nido*-pentaboranyl face. The metallahexaborane formulation is therefore confirmed, and the atomic dispositions [schematic structure (2)] resemble those [21] of *nido*-hexaborane(10), B_6H_{10} (1), distorted to accommodate the larger iridium atom and with the omission of a bridging hydrogen atom between the basal 2 and 6 positions. The interboron bond lengths (Table 3) are within the normal ranges,[22] and as in hexaborane(10) [21] the direct boron–boron bond [B(4)–B(5)] is shorter than those between two hydrogen-bridged boron atoms [B(3)–B(4) and B(5)–B(6)] which in turn are shorter than those between the apical boron atom B(1) and the four basal boron atoms. This sequence is repeated for the lengths of the iridium–boron bonds Ir(2)–B(6), Ir(2)–B(3), and Ir(2)–B(1) which are 2.18, 2.25, and 2.38 Å respectively. The direct Ir–B bond length of 2.18 Å is somewhat longer than that of 2.07 Å found [23,24] for the direct iridium(III)–boron two-centre two-electron σ bond in the pentaboran-2-yl compound $[Ir(B_5H_8)Br_2(CO)(PMe_3)_2]$; this may be a consequence of partial three-centre bonding (see below) or a result of interbond-angle 'strain' arising from the geometric constraints of the cluster. The hydrogen-atom positions are subject to the usual uncertainties inherent in the *X*-ray method but each of the B–H–B bridging groups appears to have the longer arm of the bridge directed towards the side of the molecule containing the metal atom. In addition to this, it may be noted that the B–H terminal hydrogen atoms nearer the

TABLE 3

Interatomic distances (Å) with estimated standard deviations in parentheses

(*i*) From the iridium atom			
Ir(2)–P(1)	2.400(1)	Ir(2)–B(1)	2.278(6)
Ir(2)–P(2)	2.349(1)	Ir(2)–B(3)	2.250(6)
Ir(2)–C(37)	1.873(5)	Ir(2)–B(6)	2.183(6)
Ir(2)–H(23)	1.73 *		
(*ii*) Boron–boron			
B(1)–B(3)	1.747(9)	B(3)–B(4)	1.711(10)
B(1)–B(4)	1.781(9)	B(4)–B(5)	1.649(10)
B(1)–B(5)	1.793(10)	B(5)–B(6)	1.708(10)
B(1)–B(6)	1.772(9)		
(*iii*) Boron–hydrogen(terminal) *			
B(1)–H(1)	1.07	B(5)–H(5)	1.20
B(3)–H(3)	1.18	B(6)–H(6)	1.11
B(4)–H(4)	1.20		
(*iv*) Boron–hydrogen(bridging) *			
B(3)–H(23)	1.41	B(5)–H(56)	1.31
B(3)–H(34)	1.39	B(6)–H(56)	1.29
B(4)–H(34)	1.28		
(*v*) Phosphorus–carbon			
P(1)–C(1)	1.851(4)	P(2)–C(19)	1.820(4)
P(1)–C(7)	1.829(5)	P(2)–C(25)	1.843(5)
P(1)–C(13)	1.842(5)	P(2)–C(31)	1.841(5)
(*vi*) Other			
C(37)–O(1)	1.150(6)		
C–C(Ph)	1.358(8)—1.418(8);	mean C–C(Ph)	1.385(8)
C–H(Ph) *	0.95—1.20;	mean C–H(Ph) *	1.07

* The hydrogen atoms were taken as fixed contributions in the refinement and therefore estimated standard deviations are not available. Dimensions involving them are subject to the usual uncertainties evident in the variation of the C–H(Ph) interatomic distances.


(1)

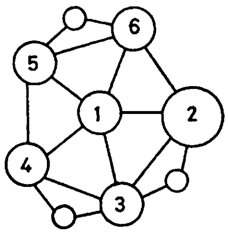

(2)

TABLE 4

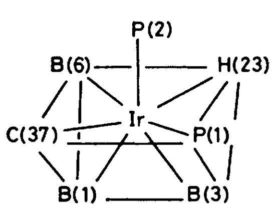
Angles (°) between interatomic vectors with estimated standard deviations in parentheses

(*i*) At the iridium atom			
P(1)–Ir(2)–P(2)	106.0(1)	C(37)–Ir(2)–B(1)	90.0(2)
P(1)–Ir(2)–C(37)	92.1(1)	C(37)–Ir(2)–B(3)	128.4(2)
P(2)–Ir(2)–C(37)	97.3(1)	C(37)–Ir(2)–B(6)	82.7(2)
		C(37)–Ir(2)–H(23) *	167
P(1)–Ir(2)–B(1)	118.4(1)		
P(1)–Ir(2)–B(3)	90.2(1)	B(1)–Ir(2)–B(3)	45.4(2)
P(1)–Ir(2)–B(6)	163.9(1)	B(1)–Ir(2)–B(6)	46.8(2)
P(1)–Ir(2)–H(23) *	91	B(1)–Ir(2)–H(23) *	77
P(2)–Ir(2)–B(1)	134.8(1)	B(3)–Ir(2)–B(6)	81.2(2)
P(2)–Ir(2)–B(3)	131.2(2)	B(3)–Ir(2)–H(23) *	39
P(2)–Ir(2)–B(6)	89.9(1)	B(6)–Ir(2)–H(23) *	91
P(2)–Ir(2)–H(23) *	94		
(*ii*) Iridium–boron–boron			
Ir(2)–B(1)–B(3)	66.5(3)	Ir(2)–B(3)–B(1)	68.1(3)
Ir(2)–B(1)–B(4)	112.9(3)	Ir(2)–B(3)–B(4)	117.3(3)
Ir(2)–B(1)–B(5)	110.5(3)	Ir(2)–B(6)–B(1)	69.5(3)
Ir(2)–B(1)–B(6)	63.8(3)	Ir(2)–B(6)–B(5)	118.7(3)
(*iii*) Iridium–hydrogen–boron bridge *			
Ir(2)–H(23)–B(3)	91	Ir(2)–B(3)–H(23)	50
(*iv*) Boron–boron–boron			
B(1)–B(3)–B(4)	62.0(4)	B(3)–B(1)–B(4)	58.0(4)
B(1)–B(4)–B(3)	60.0(4)	B(3)–B(1)–B(5)	102.7(4)
B(1)–B(4)–B(5)	62.9(5)	B(3)–B(1)–B(6)	110.2(4)
B(1)–B(5)–B(4)	62.2(5)	B(3)–B(4)–B(5)	110.7(5)
B(1)–B(5)–B(6)	60.8(4)		
B(1)–B(6)–B(5)	62.0(4)	B(4)–B(1)–B(5)	55.0(4)
		B(4)–B(1)–B(6)	103.0(4)
B(5)–B(1)–B(6)	57.2(4)	B(4)–B(5)–B(6)	111.8(5)
(*v*) Boron–boron–hydrogen and boron–hydrogen–boron *			
B(1)–B(3)–H(3)	146	B(3)–H(34)–B(4)	78
B(1)–B(4)–H(4)	127	B(5)–H(56)–B(6)	82
B(1)–B(5)–H(5)	130		
B(1)–B(6)–H(6)	138		
(*vi*) Iridium–carbon–oxygen			
Ir(2)–C(37)–O(1)	174.9(3)		
(*vii*) Iridium–phosphorus–carbon			
Ir(2)–P(1)–C(1)	118.0(1)	Ir(2)–P(2)–C(19)	111.4(1)
Ir(2)–P(1)–C(7)	113.6(1)	Ir(2)–P(2)–C(25)	114.9(1)
Ir(2)–P(1)–C(13)	114.1(1)	Ir(2)–P(2)–C(31)	122.3(1)

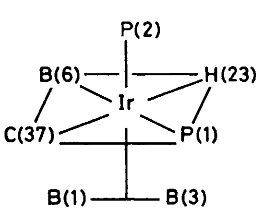
* The hydrogen atoms were taken as fixed contributions in the refinement and therefore dimensions involving them are subject to the usual uncertainties.

metal appear to have more equatorial character [B(1)–B(3)–H(3) > B(1)–B(4)–H(4) and B(1)–B(6)–H(6) > B(1)–B(5)–H(5); Table 4], again presumably arising from the distortion due to the incorporation of a large metal atom in the cluster. As expected, the Ir(2)–H(23) arm of the Ir(2)–H(23)–B(3) bridging bond is longer (Table 3), although there is probably more uncertainty in the position of this hydrogen atom.

The number of atoms in the iridium nearest-neighbour co-ordination sphere is seven, and their disposition suggests the monocapped trigonal-prismatic stereochemistry typified by $[NbF_7]^{2-}$ and related species,[25] somewhat distorted by the constraints of the IrB_5 cage [structure (3)]. However, this analogy would require seven two-electron two-centre bonds about the metal atom with typical interbond angles [26] of *ca.* 80°. A more realistic representation of the bonding about the metal is therefore that of essentially octahedral stereochemistry typical of $\mathrm{Ir^{III}}$ [structure (4)], again distorted by the constraints of the metallaborane cluster, with one of the iridium d^2sp^3 hybrid orbitals directed towards a three-centre two-electron bond with the boron atoms B(1) and B(3). The *fac* disposition of the neutral ligands is rare in octahedral iridium(III) chemistry, but this is dictated by the *fac*-tridentate nature of the effective $[B_5H_8]^{3-}$ ligand; in fact, the pioneering work [27] in tris(ligand)iridium(III) chemistry suggests that this stereochemistry may well be the thermodynamically most favoured. The Ir–CO distance Ir(2)–C(37) (Table 3) is at the high end of the range of the few values of this bond length which have been measured for neutral carbonylbis(triphenylphosphine)iridium complexes,[28,29] but the two iridium–phosphorus bond lengths fall in the middle of typical ranges.[30] There is, however, a significant difference between these last two. The bond Ir(2)–P(1) which is *trans* to the direct Ir(2)–B(6) bond is 0.05 Å longer than the bond Ir(2)–P(2) which is *trans* to the three-centre Ir(2)–B(1)–B(3) bond. This suggests that the *trans* lengthening effect [31] of a direct boron–metal bond (σ-B) is greater than that of a three-centre bond involving two boron atoms and the metal atom (μ-BB).

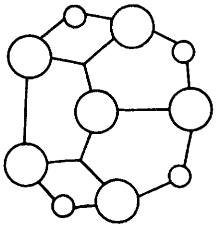


(3)

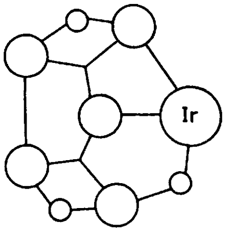


(4)

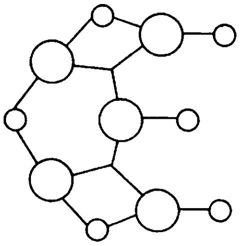
It has previously been shown [23,24] that the *trans* lengthening effect of a σ-bonded boron atom is somewhat greater than that of a σ-bonded alkyl group (σ-C) and n.m.r. measurements indicate [8] that the *trans* effect of a boron–boron–metal three-centre bond lies in the sequence σ-C ⩽ μ-BB < I < Br < Cl. These results together with the present work suggest that this series may now be extended to give the sequence σ-B ⩽ σ-C < μ-BB < I < Br < Cl, and may be taken to indicate that, where the alternatives exist,[8,9] an increase in *s*-electron availability in the metal orbitals used for bonding is an additional factor that will favour a direct metal–boron σ bond rather than a three-centre bond involving two boron atoms with the metal.



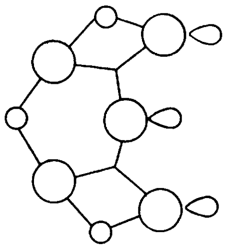
(5)



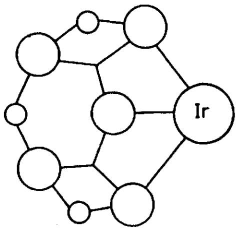
(6)



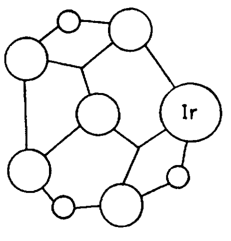
(7)



(8)



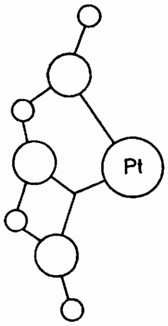
(9)



(10)

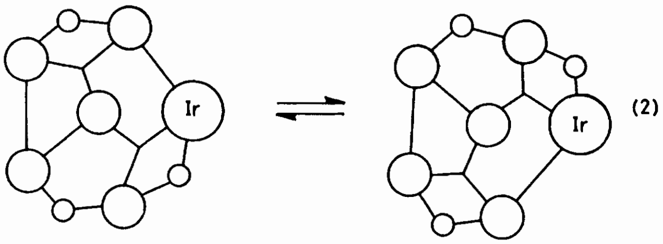
As an approach to the description of the electronic structure within the metallaborane cluster, $[(IrB_5H_8)(CO)(PPh_3)_2]$ may be regarded as being formally derived from *nido*-hexaborane(10) [structure (5)] by the replacement of a neutral bridging hydrogen atom and a neutral BH unit, which together supply three skeletal electrons,[32] by a neutral d^9 $Ir(CO)(PPh_3)_2$ fragment [structure (6)]. Since the *nido*-hexaborane structure is retained in the product, the iridium moiety supplies three electrons to the polyhedral skeleton and the compound may be regarded as a d^6 iridium(III) species, consistent with the octahedral stereochemistry about the metal atom. An alternative formal approach suggested by the disposition of the five boron atoms in the molecule, and which has potential synthetic implications, is to regard (6) as a derivative of *arachno*-pentaborane(11). Removal of three protons from *arachno*-pentaborane(11) [structure (7)] yields the *arachno*-anion $[B_5H_8]^{3-}$ (8) which acts as a six-electron donor ligand to the d^6 cation $[Ir(CO)(PPh_3)_2]^{3+}$. This cation contributes an additional apex but no additional bonding electrons to the cluster and therefore converts the *arachno*-pentaborane species into a *nido*-hexaborane derivative (9). A formal proton shift converts (9) into (6).

A number of canonical forms can be written down based on structure (6), and, of these, the observed molecular structure suggests that structures such as (10) which contain a three-centre Ir(2)–B(1)–B(3) bond make the dominant contributions to the resonance hybrid. The Ir–B(3)–B(1)–B(6) system therefore has similarities with the 'borallyl' compounds such as $[Pt(B_3H_7)(PMe_2Ph)_2]$, which are also thought to involve significant contributions from a σ,η^2 type structure (11).[33]



(11)

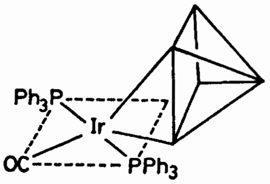
The final structural implication that merits comment is that the solid-state molecular structure (Figure 2) requires that the five boron atoms and eight hydrogen atoms in the metal–borane cluster be all chemically distinct and therefore they should exhibit separate ^{11}B or ^1H n.m.r. signals. In common with many other iridium–borane species,[34,35] the ^{11}B n.m.r. peaks (Table 1) are too broad for small differences in chemical shift between B(3) and B(6), and between B(4) and B(5), to be apparent. That separate resonances in the ^1H n.m.r. spectrum are not observed for H(3) and H(6), for H(4) and H(5), and for H(34) and H(35), however, suggests either that accidental equivalence of chemical shift occurs, or that the structure is in dynamic equilibrium in solution [equation (2)]; *i.e.* the Ir–H–B hydride alternates between the Ir(2)–B(3) [structure (10a)] and Ir(2)–B(6) positions [structure (10b)] thus rendering the pairs of boron and hydrogen atoms B(3)B(6), B(4)B(5), H(34)H(56), H(3)H(6), and H(4)H(5) on a time-average chemically equivalent. This latter behaviour is observed for the other transition-metal metallahexaborane reported, $[(FeB_5H_8)(CO)_3]$,[13] but we have not yet been able to detect it in $[(IrB_5H_8)(CO)(PPh_3)_2]$. A sample cooled to −70 °C in CD_2Cl_2 solution showed only slight further broadening but no further multiplicity in the ^1H-$\{^{11}B\}$ n.m.r. spectrum.



(2)

(10a) (10b)

The formation of an iridahexaborane structure from the starting materials used [equation (1)] is interesting, and we believe that the reaction could proceed *via* an initially formed *trans*-carbonylbis(triphenylphosphine)-iridium(I) μ-2,3-*nido*-pentaborate intermediate, which probably has the geometric structure (12) [8] in which the iridium atom is coplanar with the B(1)B(2)B(3) face of the *nido*-pentaborane square pyramid and in which the B(2)–B(3) interatomic vector is perpendicular to the square plane required by the formal dsp^2 hybridisation. The iridahexaborane structure is readily formed from this by an internal oxidative rearrangement in which two non-bonding electrons on the iridium atom are made available for cluster expansion and polyhedral bonding.* The colour changes observed in the preparative reaction (see Experimental section) suggest that the red intermediate (12) forms immediately at −70 °C, and that the subsequent rearrangement takes place at *ca.* −25 °C. It is worth noting that the reaction with the isoelectronic bis(phosphine)platinum(II) dihalides stops at the stage of structure (12). This difference is presumably a consequence of the well known greater tendency of Ir^I to partake in oxidative-addition processes.



(12)

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REFERENCES

[1] H. D. Johnson, R. A. Geanangel, and S. G. Shore, *Inorg. Chem.*, 1970, **9**, 908.
[2] V. T. Brice and S. G. Shore, *Chem. Comm.*, 1970, 1312.
[3] V. T. Brice and S. G. Shore, *J.C.S. Dalton*, 1975, 335.
[4] N. N. Greenwood, J. A. Howard, and W. S. McDonald, *J.C.S. Dalton*, 1976, 1977.
[5] N. N. Greenwood and J. Staves, *J.C.S. Dalton*, 1977, 1786.
[6] N. N. Greenwood and J. Staves, *J.C.S. Dalton*, 1977, 1788.
[7] N. N. Greenwood and J. Staves, *J.C.S. Dalton*, 1978, 1144.
[8] N. N. Greenwood, J. D. Kennedy, and J. Staves, *J.C.S. Dalton*, 1978, 1146.
[9] N. N. Greenwood, J. D. Kennedy, C. G. Savory, J. Staves, and K. R. Trigwell, *J.C.S. Dalton*, 1978, 237.
[10] V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1973, **95**, 5078.
[11] V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 1976, **98**, 1600.
[12] V. R. Miller, R. Weiss, and R. N. Grimes, *J. Amer. Chem. Soc.*, 1977, **99**, 5646.
[13] T. P. Fehlner, J. Ragaini, M. Mangion, and S. G. Shore, *J. Amer. Chem. Soc.*, 1976, **98**, 7085.

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* *Note added in proof.* The metal-hydride bridge structure as described by S. G. Shore (*Proc.* 19*th Internat. Conf. Co-ord. Chem.*, Prague, September 1978, vol. 1, p. 86) for $[Cu(B_6H_9)(PPh_3)_2]$ and for $[Cu\{B_5H_8Fe(CO)_3\}(PPh_3)_2]$ could represent the intermediate in the conversion of (12) to the iridahexaborane.

[14] D. F. Gaines and J. L. Walsh, *J.C.S. Chem. Comm.*, 1976, 482.

[15] *Pure Appl. Chem.*, 1972, **29**, 627.

[16] W. T. Raynes, ' Nuclear Magnetic Resonance,' *Specialist Periodical Reports*, The Chemical Society, London, 1972, vol. 1, pp. 2—5.

[17] S. J. LaPlaca and J. A. Ibers, *Acta Cryst.*, 1965, **18**, 511.

[18] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[19] D. F. Gaines and T. V. Iorns, *J. Amer. Chem. Soc.*, 1968, **90**, 6617.

[20] J. C. Calabrese and L. F. Dahl, *J. Amer. Chem. Soc.*, 1971, **93**, 6042.

[21] F. L. Hirschfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, and W. N. Lipscomb, *J. Chem. Phys.*, 1958, **28**, 56.

[22] W. N. Lipscomb, ' Boron Hydrides,' W. A. Benjamin, New York, 1963, pp. 227—257.

[23] M. R. Churchill, J. J. Hackbarth, A. Davison, D. D. Traficante, and S. S. Wreford, *J. Amer. Chem. Soc.*, 1974, **96**, 4041.

[24] M. R. Churchill and J. J. Hackbarth, *Inorg. Chem.*, 1975, **14**, 2047.

[25] J. L. Hoard, *J. Amer. Chem. Soc.*, 1939, **61**, 1252.

[26] G. M. Brown and L. A. Walker, *Acta Cryst.*, 1966, **20**, 220, 921.

[27] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 1625.

[28] J. A. Ibers, D. S. Hamilton, and W. H. Baddley, *Inorg. Chem.*, 1973, **12**, 229.

[29] C. P. Brock and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 1282.

[30] M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1974, **13**, 1418 and refs. therein.

[31] M. R. Churchill, *Perspectives in Structural Chem.*, 1971, **3**, 91.

[32] K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

[33] L. J. Guggenberger, A. R. Kane, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 5665.

[34] E. L. Hoel and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1975, **97**, 6388.

[35] N. N. Greenwood, J. D. Kennedy, and D. Reed, unpublished work on a number of borane derivatives of Ir^{I} and Ir^{III}.