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Macropolyhedral boron-containing cluster chemistry. Isolation and characterisation of the eighteen-vertex *nido*-5′-iridaoctaborano[3′,8′:1,2]-*closo*-4-iridadodecaborane, $[(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2]$†

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The novel eighteen-vertex macropolyhedral diiridaborane $[(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2]$ has been isolated in low yield from the products of thermolysis of the nine-vertex *arachno*-monoiridaborane $[(CO)(PMe_3)_2HIrB_8H_{12}]$, and examined by single-crystal X-ray diffraction analysis, NMR spectroscopy and mass spectrometry. The macropolyhedral framework consists of a *closo*-type twelve-vertex $\{IrB_{11}\}$ subcluster and a *nido*-type eight-vertex $\{IrB_7\}$ subcluster fused with two boron atoms in common. In addition there is an iridium–boron two-electron two-centre intercluster cross-linkage that is suprafacial to the open *nido* subcluster. The results are briefly discussed in terms of bonding schemes among individual subclusters.

The extent of structure available to polyhedral boron-containing cluster compounds[1] is considerably increased by the application of the principle of cluster fusion, in which smaller single-cluster building blocks are intimately joined, with two or more atoms in common, to generate so-called 'macropolyhedral' cluster species.[2,3] Experimentally this is an oxidation, often difficult to engender. It may be performed chemically, for example by the use of oxidising agents based on transition elements. Thus $B_{12}H_{16}$ is derived from the $[nido\text{-}B_6H_9]^-$ anion by use of $FeCl_2$–$FeCl_3$,[4] and the $[anti\text{-}B_{18}H_{21}]^-$ anion or neutral *anti*-$B_{18}H_{22}$ from the $[nido\text{-}B_9H_{12}]^-$ anion *via* reaction with $[\{Os(CO)_3Cl_2\}_2]$ or $HgBr_2$ respectively.[5,6] Alternatively, an oxidative electron loss can occur by dihydrogen elimination, and/or by the elimination of electron-rich ligands.[7] So far, this has usually been induced thermally. For single-cluster boranes this is classically exemplified[8] by the thermolysis of B_2H_6 to give B_5H_9 and thence $B_{10}H_{14}$, and in macropolyhedral synthesis by the thermolysis of *nido*-B_8H_{12} to give $B_{16}H_{20}$.[7,9] Thermolysis of nine-vertex *arachno*-$B_9H_{13}(SMe)_2$ yields $B_{18}H_{22}$[7] and of nine-vertex *arachno*-SB_8H_{12} yields $S_2B_{16}H_{16}$.[10] Thermolysis of nine-vertex *arachno*-$[(PMe_2Ph)_2PtB_8H_{12}]$ gives several macropolyhedral species, *e.g.* seventeen-vertex $[(PMe_2Ph)Pt\text{-}B_{16}H_{18}(PMe_2Ph)]$ and $[(PMe_2Ph)_4Pt_3B_{14}H_{16}]$.[11] Two further nine-vertex *arachno* species that have interesting chemistries are $[(CO)(PMe_3)_2HIrB_8H_{12}]$ and $[(CO)(PMe_3)_2HIrB_8H_{11}Cl]$.[12–15] We found previously that mild thermolysis of these yields corresponding nine-vertex *nido*-$[(CO)(PMe_3)_2IrB_8H_{11}]$ and *nido*-$[(CO)(PMe_3)_2IrB_8H_{10}Cl]$. With the latter B-chlorinated compound stronger heating thence gives uniquely structured *isocloso*-$[(CO)(PMe_3)_2HIrB_8H_7Cl]$.[13] By contrast, we now report that thermolysis of the unsubstituted species $[(CO)(PMe_3)_2IrB_8H_{11}]$ gives small quantities of an eighteen-vertex macropolyhedral diiridaborane of molecular formulation $[(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2]$.

† 4,5′-Dicarbonyl-4,4,5′,5′-tetrakis(trimethylphosphine)-σ{Ir(5′)B(6)}-*nido*-5′-iridaoctaborano[3′,8′:1,2]-*closo*-4-iridadodecaborane. The compound and the crystal habit adopted ($P2_12_12_1$ symmetry) are both chiral, and this name is for the configuration as determined in the particular crystal selected (Fig. 1). The bulk compound as prepared would be racemic.

Experimental

Synthesis of $[(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2]$

In an evacuated flask, *arachno*-$[(CO)(PMe_3)_2HIrB_8H_{12}]$ (650 mg, 1.4 mmol; prepared as in ref. 12) was heated for 2 min in an oil-bath maintained at 180 °C, during which time the solid melted, bubbled and turned red. The ^{11}B NMR spectrum of the product showed that it was essentially all *nido*-$[(CO)(PMe_3)_2IrB_8H_{11}]$, as expected,[12–15] although the red colour indicated the trace presence of other species. The NMR solvent was removed, and the solid then heated again at 180 °C for 15 min, after which time the resulting mixture was dissolved in CH_2Cl_2, applied to a preparative TLC plate (silica gel, Aldrich TLC grade, with gypsum binder and fluorescent indicator; 1 × 200 × 200 mm), and developed using dichloromethane–pentane (70:30) as the liquid phase. Several coloured bands were evident between R_f *ca.* 0.55 and *ca.* 0.15 (*ca.* 0.5, red; *ca.* 0.45, red; *ca.* 0.4, brown; *ca.* 0.2, yellow). Each of the bands was removed from the plate, extracted with CH_2Cl_2, the filtrate reduced to dryness, and then redissolved in $CDCl_3$ for NMR analysis. Each component appeared to be a mixture of compounds. Further repeated attempts at chromatographic differentiation have so far proved ineffective, although ultimately, for the strongest band (yellow, R_f 0.2), a slow diffusion of hexane at 5 °C into a $CDCl_3$ solution produced small orange crystals which, after recrystallisation, were fully characterised by NMR, mass spectrometry, and single-crystal X-ray diffraction analysis, as the compound $[(CO)(PMe_3)_2Ir\text{-}B_{16}H_{14}Ir(CO)(PMe_3)_2]$ **1** (1 mg, 1.1 μmol, 0.1% yield). A second component, at R_f *ca.* 0.18, was partially characterisable as a sixteen-boron iridaborane species, **2**, and gave yellow needle crystals (< 1 mg) which were not suitable for single-crystal X-ray analysis. Compound **2** was insufficiently robust to survive repeated recrystallisation attempts. The remaining bands have not so far been at all amenable to full characterisation on the scale of the experiments conducted, although some appear to contain macropolyhedral cluster compounds similar to **1**. A subsequent preparation using 100 mg (*ca.* 200 μmol) of the *arachno*-iridanonaborane, and heating at *ca.* 175 °C for 4 min, resulted in a yield of *ca.* 1 mg (0.5% yield) of compound **1**. The mass spectrum (FAB mode; 3-nitrobenzyl alcohol matrix) of **1** was as follows, ordered as *m*/*z* (observed) [observed relative intensity (calculated relative intensity for $C_{14}H_{50}B_{16}Ir_2O_2P_4$ isotopomers in natural abundance)]: 927 [13(13)], 928 [25(28)], 929 [52(50)], 930 [78(76)], 931 [100(95)], 932 [87(100)], 933 [82(86)], 934 [62(58)], 935 [33(29)], 936 [6(10)].

Nuclear magnetic resonance spectroscopy

This was carried out[16] at *ca.* 9.35 and *ca.* 11.69 T on commercially available instruments. Chemical shifts, δ, are given in ppm to low field (high frequency) of Ξ = 32.083 971 MHz (nominally $Et_2O \cdot BF_3$) for ^{11}B, of 100 MHz ($SiMe_4$) for ^1H and of 40.480 730 MHz (nominally 85% H_3PO_4) for ^{31}P, Ξ being defined as in ref. 17. The data for compound **1** (CD_2Cl_2 at 294–297 K) are given as, $\delta(^{11}B)$ (relative intensities greater than unity, tentative assignment where possible) {$\delta(^1H)$ of directly attached hydrogen atom}: +63.0 {+7.70 (br, partially resolved d structure due to unassigned coupling)}, +26.9 {+5.94}, +22.3 {+5.16}, +15.7 [2B, B(6′) or B(7′)] {+4.78, +3.11}, +5.4 {+3.50}, *ca.* +0.6 (2B) {+2.34, +2.60}, −0.6 {+2.96}, −6.9 {+2.67}, −9.9 [B(2), B(6) or B(1)] {*conjuncto* linkage}, −10.3 [B(2), B(6) or B(1)] {*conjuncto* linkage}, −12.9 {+1.87}, −17.0 {+2.32}, −21.3 [B(2), B(6) or B(1)] {*conjuncto* linkage}, −28.2 {−1.29, d, splitting 25}. Additional $\delta(^1H)$: +0.91 [H(6′), H(7′)] +1.93 (18 H, d of d, splitting 9.4 and 2.4, PMe_3), +1.73 (9 H, d, splitting 9.5) and +1.56 (d, splitting 8.9 Hz). $\delta(^{31}P)$ (230 K, $CDCl_3$–CH_2Cl_2 solution): −40.9 [d, P(1), P(2)], −41.9 {d, $^2J[^{31}P(1/2)-^{31}P(2/1)]$ 27, P(2), P(1)}, −49.7 {d, $^2J[^{31}P(3)-^{31}P(4)]$ 24 Hz, P(3)} and *ca.* −55 [vbr, P(4)]. For compound **2**, $\delta(^{11}B)$ ($CDCl_3$ at 297 K, intensity 1B unless otherwise indicated) +53.5, +18.7, *ca.* +14.2 (2B), +5.3, +3.5, *ca.* −5.3 (2B), −11.2, −11.7, −13.9, −18.5, −21.5, −24.5, −26.8 and −27.9.

Crystallography

Orange irregularly shaped crystals were obtained by slow diffusion at 5 °C of pentane into a solution of compound **1** in CH_2Cl_2. Data were collected on a Siemens P4 (sealed tube) apparatus using Mo-Kα irradiation at 0.710 73 Å. Crystal data, intensity-data collection parameters and structure-refinement parameters are in Table 1. Reduction and decay correction were carried out using XSCANS,[18] solution and refinement using SHELXTL PLUS (5.03)[19] and absorption using XEMP.[19] Full-matrix least-squares refinement was carried out by minimising $\Sigma w(F_o^2 - F_c^2)^2$. The non-hydrogen atoms were refined anisotropically to convergence. The hydrogen atoms on the borane cage were located from Fourier-difference syntheses and H(4′), H(6′), H(7′) and H(6,7′) were refined freely with an isotropic thermal parameter equal to 1.2 times that of the boron atom to which they are attached. The hydrogen atoms on the rest of the cage, together with those of the methyl groups, were refined using the riding models[19] AFIX 153 and AFIX 33, respectively. The absolute configuration was determined using the Flack parameter [$x = -0.02(1)$]. A drawing is in Fig. 1.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/80.

Results and Discussion

Thermolysis of *arachno*-[(CO)(PMe_3)$_2$HIrB$_8$H$_{12}$] under vacuum at *ca.* 180 °C for 4–15 min yielded, after repeated chromatographic separation and recrystallisation, the *nido*-5′-iridaoctaborano[3′,8′:1,2]-*closo*-4-iridadodecaborane, [(CO)-(PMe_3)$_2$IrB$_{16}$H$_{14}$Ir(CO)(PMe_3)$_2$] **1** in 0.1–0.5% yield. Boron-11 NMR spectroscopy suggested that other macropolyhedral products were also formed in low yield, of which only one

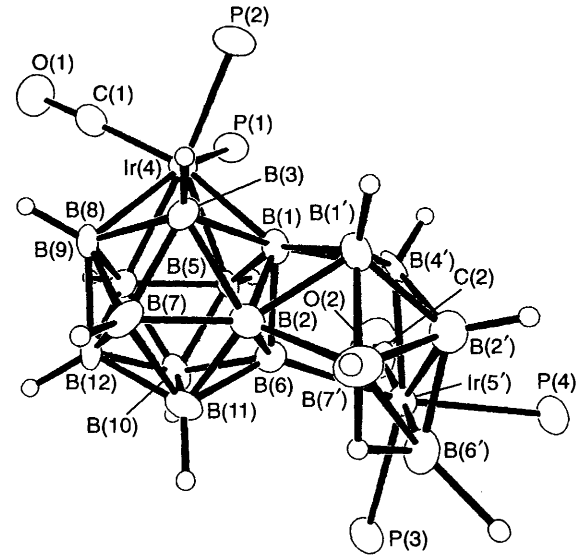
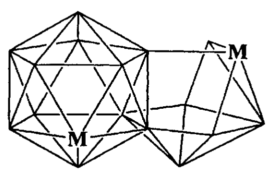


Fig. 1 Molecular structure of [(CO)(PMe_3)$_2$IrB$_{16}$H$_{14}$Ir(CO)(PMe_3)$_2$] **1**, with non-hydrogen atoms as 50% probability thermal ellipsoids and methyl group atoms omitted for clarity



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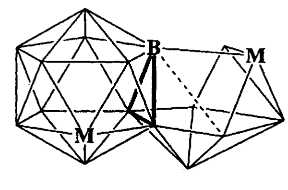
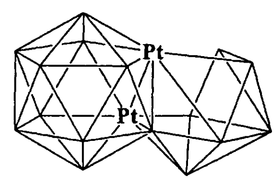


IIa



IIb

(compound **2**) was isolatable in a pure state as yellow crystals, and partially characterisable by NMR spectroscopy as a sixteen-boron species (see Experimental section). However, **2** decomposed during repeated attempts to obtain single crystals suitable for an X-ray diffraction study. Only compound **1** was amenable to full characterisation. It was characterised by single-crystal X-ray diffraction analysis (Fig. 1 and Tables 1 and 2), and by NMR and mass spectrometry (see Experimental section). The NMR spectra were consistent with the results of the X-ray work. In particular, they confirmed the hydrogen-atom count and disposition. The structure is based on an eighteen-vertex cluster with two iridium and sixteen boron atoms. These are represented in **I**, in which M is {Ir(CO)(PMe_3)$_2$}. Structure **I** has a different perspective from that of Fig. 1 to facilitate discussion. The architecture consists of a closed twelve-vertex {IrB_{11}} unit fused, with two boron atoms in common, to an open eight-vertex {IrB_7} unit. The {IrB_{11}} unit has classical *closo* icosahedral geometry.[1] The {IrB_7} unit has eight-vertex *nido* or *arachno* geometry, as typified by *nido*-B_8H_{12}[20] and *arachno*-B_8H_{14}[21] respectively. The similarity of *nido* or *arachno* octaborane shapes[15,16] prevents distinction based on geometry. However the presence of just one bridging hydrogen atom and electron-counting considerations (see below) suggest *nido*. In addition to the two-boron fusion, the subclusters are linked by a suprafacial two-centre, two-electron bond. This is *endo* to the iridium atom [Ir(5′)] of the eight-boron subcluster and *exo* to a boron atom

[B(6)] of the *closo*-{IrB_{11}} subcluster. There is a somewhat related linkage in the nineteen-vertex platinaborane [$(PMe_2Ph)_2Pt$-(η^1,η^2)-*anti*-$B_{18}H_{20}$].[22] The Ir(5′)–B(6) distance of 2.24(2) Å is within established ranges for iridaborane clusters.[23] It is somewhat longer than a σ-bonded distance, as in [2-{$(CO)(PMe_3)_2HBr_2Ir$}-*nido*-B_5H_8] (2.07 Å).[24] Such intercluster linkages presumably arise from the proximity of reactive transition-element centres to *exo*-BH units of an opposing subcluster. They may mimic intermediate stages in fusions that produce more condensed species.[25] Here, for example, compound **1** has an open four-membered ring, Ir(5′)–B(6)–B(1)–B(4′). Simple closure across B(6)–B(4′) (observed distance 2.45 Å) would then result in a more intimate fusion involving a common triangular face (heavier lines in **IIa**): this would give a nine-vertex *nido*-shaped subcluster, as observed in the eighteen-vertex diplatinaborane [$(PMe_2Ph)_2$-$Pt_2B_{16}H_{15}(C_6H_4Me$-4)$(PMe_2Ph)$][26] **IIb**. Other intercluster dimensions are in normal ranges. Compound **1** is the first macropolyhedral metallaborane to have a two-boron edge fusion between *closo* and *nido* subclusters. The platinaborane **IIb** has a two-metal one-boron triangular-face *closo to nido* fusion. The thermolysis of [$(CO)(PMe_3)_2HIrB_8H_{12}$] therefore results in a *conjuncto* linkage of shared boron atoms only. This is in contrast to the ostensibly similar [$(PMe_2Ph)_2Pt$-B_8H_{12}][11,26] which generates several macropolyhedrals that all have fusions involving shared platinum as well as shared boron atoms.

Table 1 Crystal data and structure refinement for compound **1**

Empirical formula	$C_{14}H_{50}B_{16}Ir_2O_2P_4$
M	931.78
T/K	295(2)
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	10.150(2)
b/Å	14.839(3)
c/Å	22.970(5)
U/Å^3	3459.7(11)
Z	4
D_c/Mg m^{-3}	1.789
μ/mm^{-1}	7.885
Crystal size/mm	0.1 × 0.1 × 0.1
F(000)	1776
θ range for data collection/°	1.63–27.50
hkl Ranges	−1 to 13, −15 to 19, −29 to 1
Reflections collected	8079
Independent reflections	6668 (R_{int} = 0.0379)
Maximum, minimum transmission	0.9666, 0.6480
Absorption correction	Semiempirical from ψ-scans
Data, restraints, parameters	6646, 0, 335
Goodness of fit on F^2	1.072
Final *R* indices [$I > 2\sigma(I)$] R_1	0.0436
$wR_2(F^2)$	0.0990
Largest difference peak and hole/e Å^{-3}	1.251 to −1.664

Table 2 Selected interatomic distances (Å) and angles (°) for compound **1**

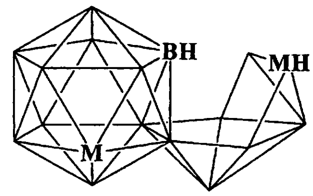
Ir(4)–C(1)	1.88(2)	Ir(4)–B(8)	2.278(14)	Ir(5′)–C(2)	1.909(13)	Ir(5′)–B(2′)	2.25(2)
Ir(4)–B(1)	2.197(14)	Ir(4)–B(9)	2.328(13)	Ir(5′)–B(6′)	2.14(2)	Ir(5′)–P(3)	2.329(3)
Ir(4)–B(3)	2.22(2)	Ir(4)–P(2)	2.360(3)	Ir(5′)–B(4′)	2.22(2)	Ir(5′)–P(4)	2.375(4)
Ir(4)–B(5)	2.27(2)	Ir(4)–P(1)	2.367(4)	Ir(5′)–B(6)	2.24(2)		
O(1)–C(1)	1.17(2)	B(2)–B(6)	1.80(2)	B(6)–B(10)	1.75(2)	B(10)–B(12)	1.78(2)
O(2)–C(2)	1.125(14)	B(2)–B(3)	1.81(2)	B(6)–B(11)	1.81(2)	B(11)–B(12)	1.75(2)
B(1)–B(2)	1.76(2)	B(2)–B(1′)	1.86(2)	B(7)–B(12)	1.73(2)	B(1′)–B(4′)	1.70(2)
B(1)–B(5)	1.79(2)	B(2)–B(7′)	1.89(2)	B(7)–B(8)	1.77(2)	B(1′)–B(2′)	1.73(2)
B(1)–B(6)	1.81(2)	B(3)–B(7)	1.77(2)	B(7)–B(11)	1.80(2)	B(1′)–B(7′)	1.78(2)
B(1)–B(1′)	1.82(2)	B(3)–B(8)	1.78(2)	B(8)–B(12)	1.78(2)	B(2′)–B(6′)	1.72(2)
B(1)–B(4′)	1.89(2)	B(5)–B(6)	1.76(2)	B(8)–B(9)	1.86(2)	B(2′)–B(4′)	1.73(2)
B(1)–B(3)	1.92(2)	B(5)–B(10)	1.77(2)	B(9)–B(12)	1.77(2)	B(2′)–B(7′)	1.81(2)
B(2)–B(11)	1.72(2)	B(5)–B(9)	1.82(2)	B(9)–B(10)	1.77(2)	B(6′)–B(7′)	1.76(2)
B(2)–B(7)	1.77(2)			B(10)–B(11)	1.77(2)		
C(1)–Ir(4)–B(1)	163.7(6)	B(5)–Ir(4)–B(9)	46.5(4)	B(8)–Ir(4)–P(1)	146.5(4)	B(6)–Ir(5′)–B(2′)	84.5(5)
C(1)–Ir(4)–B(3)	115.4(6)	B(8)–Ir(4)–B(9)	47.7(5)	B(9)–Ir(4)–P(1)	100.3(4)	C(2)–Ir(5′)–P(3)	94.3(4)
B(1)–Ir(4)–B(3)	51.7(5)	C(1)–Ir(4)–P(2)	92.4(5)	P(2)–Ir(4)–P(1)	93.67(13)	B(6′)–Ir(5′)–P(3)	88.2(4)
C(1)–Ir(4)–B(5)	128.7(6)	B(1)–Ir(4)–P(2)	96.1(4)	C(2)–Ir(5′)–B(6′)	174.2(5)	B(4′)–Ir(5′)–P(3)	161.0(4)
B(1)–Ir(4)–B(5)	47.1(5)	B(3)–Ir(4)–P(2)	86.1(4)	C(2)–Ir(5′)–B(4′)	88.1(6)	B(6)–Ir(5′)–P(3)	94.7(3)
B(3)–Ir(4)–B(5)	83.8(5)	B(5)–Ir(4)–P(2)	137.9(3)	B(6′)–Ir(5′)–B(4′)	87.8(6)	B(2′)–Ir(5′)–P(3)	134.2(4)
C(1)–Ir(4)–B(8)	80.6(6)	B(8)–Ir(4)–P(2)	118.6(4)	C(2)–Ir(5′)–B(6)	88.9(5)	C(2)–Ir(5′)–P(4)	90.6(4)
B(1)–Ir(4)–B(8)	83.1(5)	B(9)–Ir(4)–P(2)	166.1(4)	B(6′)–Ir(5′)–B(6)	85.7(6)	B(6′)–Ir(5′)–P(4)	94.2(4)
B(3)–Ir(4)–B(8)	46.5(5)	C(1)–Ir(4)–P(1)	89.7(6)	B(4′)–Ir(5′)–B(6)	66.4(4)	B(4′)–Ir(5′)–P(4)	100.1(4)
B(5)–Ir(4)–B(8)	81.6(5)	B(1)–Ir(4)–P(1)	103.6(4)	C(2)–Ir(5′)–B(2′)	131.4(6)	B(6)–Ir(5′)–P(4)	166.5(3)
C(1)–Ir(4)–B(9)	87.7(6)	B(3)–Ir(4)–P(1)	154.9(4)	B(6′)–Ir(5′)–B(2′)	46.0(5)	B(2′)–Ir(5′)–P(4)	85.7(4)
B(1)–Ir(4)–B(9)	80.8(5)	B(5)–Ir(4)–P(1)	79.6(4)	B(4′)–Ir(5′)–B(2′)	45.4(6)	P(3)–Ir(5′)–P(4)	98.72(13)
B(3)–Ir(4)–B(9)	81.3(6)						
B(2)–B(1)–B(5)	105.4(10)	B(4′)–B(1)–B(3)	140.3(10)	B(3)–B(1)–Ir(4)	64.7(6)	B(2)–B(6)–B(11)	57.1(8)
B(2)–B(1)–B(6)	60.6(8)	B(2)–B(1)–Ir(4)	117.8(8)	B(10)–B(6)–Ir(5′)	138.6(10)	B(1)–B(6)–B(11)	105.9(11)
B(5)–B(1)–B(6)	58.5(7)	B(5)–B(1)–Ir(4)	68.6(7)	B(5)–B(6)–Ir(5′)	121.9(10)	B(10)–B(6)–Ir(5′)	138.6(10)
B(2)–B(1)–B(1′)	62.7(8)	B(6)–B(1)–Ir(4)	121.6(8)	B(2)–B(6)–Ir(5′)	113.3(7)	B(5)–B(6)–Ir(5′)	121.9(10)
B(5)–B(1)–B(1′)	154.4(11)	B(1′)–B(1)–Ir(4)	136.6(8)	B(1)–B(6)–Ir(5′)	106.6(7)	B(2)–B(6)–Ir(5′)	113.3(7)
B(6)–B(1)–B(1′)	97.0(10)	B(4′)–B(1)–Ir(4)	141.3(9)	B(11)–B(6)–Ir(5′)	129.3(9)	B(1)–B(6)–Ir(5′)	106.6(7)
B(2)–B(1)–B(4′)	100.1(10)	B(11)–B(2)–B(1′)	154.5(11)	B(10)–B(6)–B(5)	60.8(7)	B(11)–B(6)–Ir(5′)	129.3(9)
B(5)–B(1)–B(4′)	110.4(9)	B(1)–B(2)–B(1′)	60.3(8)	B(10)–B(6)–B(2)	104.0(11)	B(7)–B(2)–B(7′)	131.1(11)
B(6)–B(1)–B(4′)	82.7(8)	B(7)–B(2)–B(1′)	143.0(11)	B(5)–B(6)–B(2)	105.0(11)	B(6)–B(2)–B(7′)	104.9(10)
B(1′)–B(1)–B(4′)	54.6(7)	B(6)–B(2)–B(1′)	95.8(9)	B(10)–B(6)–B(1)	108.0(10)	B(3)–B(2)–B(7′)	129.7(10)
B(2)–B(1)–B(3)	58.8(8)	B(3)–B(2)–B(1′)	88.1(9)	B(5)–B(6)–B(1)	60.3(8)	B(1′)–B(2)–B(7′)	56.9(8)
B(5)–B(1)–B(3)	107.7(10)	B(11)–B(2)–B(7′)	114.4(10)	B(2)–B(6)–B(1)	58.3(8)	O(1)–C(1)–Ir(4)	177(2)
B(6)–B(1)–B(3)	108.8(10)	B(1)–B(2)–B(7′)	113.2(10)	B(10)–B(6)–B(11)	59.7(8)	O(2)–C(2)–Ir(5′)	177.2(12)
B(1′)–B(1)–B(3)	86.0(8)			B(5)–B(6)–B(11)	107.8(11)		

A simplistic application of electron counting[27] to the whole compound indicates a $\{B_{18}H_{16}\}^{2-}$ equivalent, formally an eighteen-vertex *pileo* species. However, overall *pileo*, *closo*, *nido*, *arachno*, *etc.* descriptors have limited meanings in macropolyhedral compounds: the character of each individual subcluster and the nature of the intercluster linkages separately affect the overall electron count. They have to be assessed separately. The analysis of compound **1** is complicated by the Ir(5′)–B(6) two-electron, two-centre suprafacial linkage. For easier analysis, this can can be replaced by a BH(6) and an IrH(5′) unit (**III**, vertices BH and MH respectively), as it is extraneous to the fundamental cluster fusion that involves the common atoms B(1) and B(2). The $\{Ir_2B_{16}\}$ cluster thence becomes a $\{B_{18}H_{18}\}^{2-}$ equivalent. This is two electrons short of the electron count for the formulation $B_{18}H_{22}$, of which both known isomers have a *nido*:*nido* constitution with two boron atoms in common.[28–30] Formal removal of two electrons from the *nido*:*nido* $B_{18}H_{22}$ formulation plus retention of the same type of two-boron cluster linkage would result in a *closo*:*nido* constitution as observed for compound **1**. Compound **1** and $B_{18}H_{22}$ also of course differ in that the $B_{18}H_{22}$ isomers are ten vertex:ten vertex species, whereas **1** is twelve vertex:eight vertex. In general, removal of an electron pair from a fused cluster compound can result either in (*a*) an increase in the intimacy of the fusion or (*b*) a two-electron condensation of either individual subcluster along the *hypho*-*arachno*-*nido*-*closo*-*pileo* sequence.

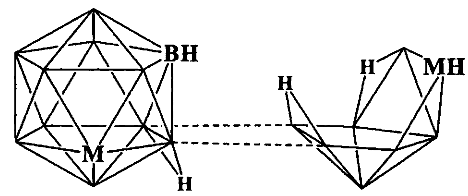
The cluster structure of compound **1** is therefore based on a *nido* eight-vertex subcluster fused with a *closo* twelve-vertex subcluster. It is useful to consider the fusion modes of macropolyhedral species in terms of the neutral constituent subcluster molecules. Thus $B_{18}H_{22}$, consisting of two *nido* ten-vertex units,[28–30] notionally derives from two *nido*-$B_{10}H_{14}$ molecules fused with two boron vertices in common, and $B_{12}H_{16}$,[4] consisting of a *nido* eight-vertex unit and a *nido* six-vertex unit, derives similarly from *nido*-B_8H_{12} and *nido*-B_6H_{10}. Likewise, **1**, after again converting the B(6)–Ir(5′) link into BH(*exo*) and IrH(*endo*) as in **III**, derives from a *nido*-type eight-vertex species $[(CO)(PMe_3)_2HIrB_7H_9]$ **IVb** and a *closo*-type twelve-vertex species $[(CO)(PMe_3)_2IrB_{11}H_{12}]$ **IVa**. The eight-vertex species would correspond to a $\{$*nido*-$B_8H_{11}\}^-$ unit of *styx* 2521 topology. The twelve-vertex species would correspond to a *closo*-type $\{B_{12}H_{13}\}^-$ unit, and protonation of the B(1)–B(2) edge of a so-far hypothetical conventionally *closo* $[4,4,4\text{-}(CO)(PMe_3)_2\text{-}closo\text{-}4\text{-}IrB_{11}H_{11}]^-$ anion (numbering as in Fig. 1) would be required to generate the neutral $[(CO)(PMe_3)_2IrB_{11}H_{12}]$ entity. These neutral species would notionally come together (**V**), with one three-centre boron–hydrogen–boron and two direct boron–hydrogen bonds in the BH(1)–μ-H–BH(2) unit of the twelve-vertex subcluster being replaced by one three-centre and two direct interboron bonds involving B(1′), B(4′) and B(7′) in the eight-vertex subcluster (other canonical forms can be drawn).[31]

This type of two-boron conjunction in compound **1** links *closo* with *nido* units. Most two-boron conjunctions reported are *nido* with *nido*, as in the typical series of binary boranes $B_{12}H_{16}$,[4] $B_{14}H_{18}$,[32] $B_{16}H_{20}$[7,31] and $B_{18}H_{22}$[28,29] (although the similarly linked $B_{13}H_{19}$ and the interestingly symmetrical $B_{14}H_{20}$ are formally *nido*:*arachno*).[29,31,33] This type of two-boron intercluster fusion mode is therefore general. It can thence lead to predictions of as yet unsynthesised macropolyhedral species. One of these, in view of the ready subrogation of BH groups by iridium moieties,[23,34] would be the binary boron hydride analogue of compound **1**, the *closo*:*nido* twelve vertex:eight vertex $[B_{18}H_{19}]^-$ anion.

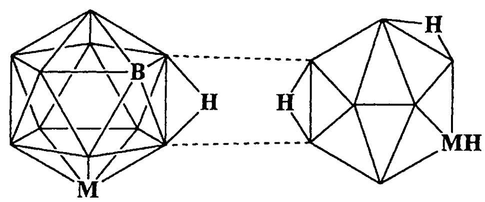
The results of ^{11}B, ^{1}H, ^{1}H-$\{^{11}$B$\}$ and ^{31}P NMR spectroscopy for compound **1** are consistent with the molecular structure in Fig. 1. The three boron resonances for the intercluster links can be pinpointed because they have no terminal hydrogen atoms (Fig. 2), and ^{1}H-$\{^{11}$B(selective)$\}$ experiments pinpoint the boron resonances associated with the bridging hydrogen atoms. The small amount (*ca.* 1 μmol) of material available precluded successful ^{11}B and ^{1}H homonuclear correlation experiments for additional assignments. The low-temperature ^{31}P-$\{^{1}$H$\}$ NMR spectrum shows sharp ^{31}P resonances due to atoms P(1), P(2) and P(3) and a broad one from P(4) which is *trans* to the boron atom B(6) involved in the suprafacial iridium–boron link.

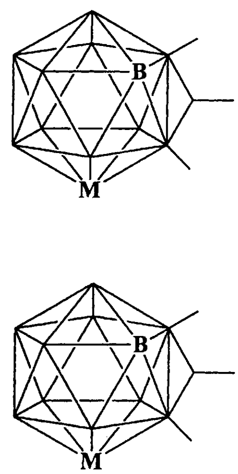


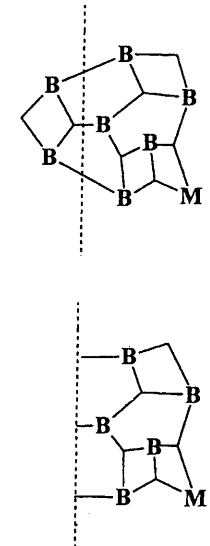
III



IVa **IVb**







Va **Vb**

Acknowledgements

We thank the Johnson-Matthey Company for a loan of $IrCl_3 \cdot 3H_2O$, the National Science Foundation (USA), the EPSRC (UK), the Missouri Research Board, and the University of Missouri-St. Louis for financial support of this work, and the National Science Foundation for a grant to purchase the X-ray diffractometer.

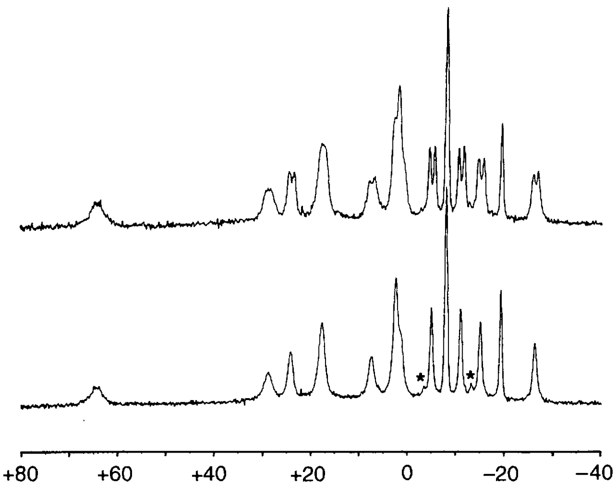


Fig. 2 The 128 MHz ^{11}B (top trace) and $^{11}B-\{^{1}H\}$ (bottom trace) NMR spectra of $[(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2]$ **1** in $CDCl_3$ solution at 294 K. The asterisks indicate impurities

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Received 4*th December* 1995; *Paper* 5/07866K