Macropolyhedral boron-containing cluster chemistry. Triple cluster fusion and the molecular structure of [$(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$]. A 28-vertex metallaborane cluster with a polyboron core†

Jonathan Bould,[a,b] **John D. Kennedy,***[a] **Lawrence Barton**[b] **and Nigam P. Rath**[b]

[a] *The School of Chemistry of the University of Leeds, Leeds, UK LS2 9JT*
[b] *The Department of Chemistry of the University of Missouri St. Louis, St. Louis, Missouri 63121, USA*

[$(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$], from the thermolysis of [$(CO)(PMe_3)_2HIrB_8H_{12}$] in molten $B_{10}H_{14}$, is a triple-cluster species that consists of *closo* twelve-vertex {IrB_{11}} and *closo* ten-vertex {IrB_9} units fused by (*a*) a common {IrB_2} triangular face and (*b*) by an adjacent 'wedge' interboron linkage that also binds a *nido* nine-vertex {IrB_8} subcluster; the resulting {Ir_2B_{26}} cluster has a novel five-boron core.

The extension of contiguous polyhedral boron-containing cluster chemistry beyond the constraints of single clusters of up to fourteen vertices is engendered by cluster fusion to generate so-called macropolyhedral species. Several compounds of up to about twenty vertices have been synthesized by the fusion of two clusters, but triple fusion to generate larger macropolyhedral assemblies has so far proved elusive. The *arachno* nine-vertex system appears to be particularly suitable for cluster-fusion chemistry, for example in the synthesis of $B_{18}H_{22}$ and its derivatives,[1] and in macropolyhedral platinaborane,[2] thiaborane,[3] and iridaborane formation.[4] These processes all appear to occur *via* reactive nine-vertex intermediates. We surmised that, if these intermediates are generated in the presence of suitable substrates of intermediate reactivity, then the possibility of mixed or multiple fusion to generate larger macropolyhedral assemblies arises. In this regard the *arachno*/*nido* {IrB_8} system has interesting reactivity,[5] and we have recently reported preliminary results on the autofusion of the *arachno* nine-vertex compound [$(CO)(PMe_3)_2HIrB_8H_{12}$] to give double-cluster [$(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2$][4] and the mixed cluster fusion of molten *nido*-$B_{10}H_{14}$ with [$(CO)(PMe_3)_2HIrB_8H_{12}$] to give double-cluster [$(PMe_3)_2(CO)IrB_{17}H_{20}$] **1**.[6] We now report preliminary findings on the principle of multiple cluster fusion, as manifested in the isolation and characterization of a triple-cluster species of formulation [$(PMe_3)_2HIrB_{26}H_{24}(CO)(PMe_3)_2$] **2** from the latter molten $B_{10}H_{14}$ system.

The sample of compound **2** was prepared by reaction of [$(CO)(PMe_3)_2HIrB_8H_{12}$] (25 mg, 610 μmol) with $B_{10}H_{14}$ (134 mg; 1100 mmol; mp *ca.* 99 °C) under N_2 at 134 °C for 25 min. The excess of molten $B_{10}H_{14}$ was used to engender solubility of [$(CO)(PMe_3)_2HIrB_8H_{12}$] and also to minimise the double-cluster autofusion[4] that would give [$(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2$]. The excess $B_{10}H_{14}$ was then removed by vacuum sublimation (bath *ca.* 80 °C). Extraction with CH_2Cl_2, filtration through silica gel, followed by repeated TLC (95:5 CH_2Cl_2–MeCN) on silica gel G revealed many coloured products, and ultimately gave an orange band [R_F 0.7 using CH_2Cl_2–hexane (1:1)] as a predominant component. HPLC separation (silica, Lichrosorb Si60 7 μm; 260 × 16 mm column; rapid initial gradient 25% CH_2Cl_2 in hexane to 100% CH_2Cl_2, flow rate 4 ml min^{-1}) gave one impure major component of R_T *ca.* 32 min, and several minor components, of which one has been identified as [7,7-$(PMe_3)_2$-7-(CO)-*syn*-7-$IrB_{17}H_{20}$] **1** (R_T *ca.* 30 min).[6] Repeated fractional crystallisation of the principal component of the mixture with R_T *ca.* 32 min gave a small sample (< *ca.* 500 μg) of orange–yellow crystals of a CH_2Cl_2 solvate of [$(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$] **2** (Fig. 1). They were identified by single crystal X-ray diffraction analysis‡ and NMR spectroscopy.§ Although the very small quantities and complex nature of the compound have precluded chemical shift assignments by homonuclear ^1H or ^{11}B NMR COSY techniques, the NMR data on the bulk material are otherwise consistent with the structure of Fig. 1. Separation of the many reaction products is difficult; NMR spectroscopy suggests the presence of a number of other large iridaborane cluster compounds.

Structurally the compound is seen to be based on the conceptual fusion, with a common {IrB_2} triangular face, of a *closo* twelve-vertex {IrB_{11}} unit **IA** and a *closo* ten-vertex {IrB_9} unit **IB**. The clusters are additionally linked by an interboron 'wedge' linkage that is also involved in multicentre bonding to the third subcluster, a *nido* nine-vertex {IrB_8} unit **IC**. This latter linkage is reminiscent of the intercluster linkages in the simpler macropolyhedrals $B_{14}H_{22}$ and $B_{15}H_{23}$.[9] Mechanistically, *arachno* [$(CO)(PMe_3)_2HIrB_8H_{12}$] will readily dehydrogenate to give *nido* [$(CO)(PMe_3)_2IrB_8H_{11}$] under the

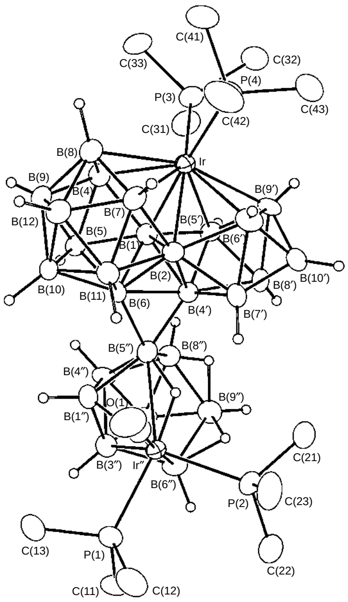
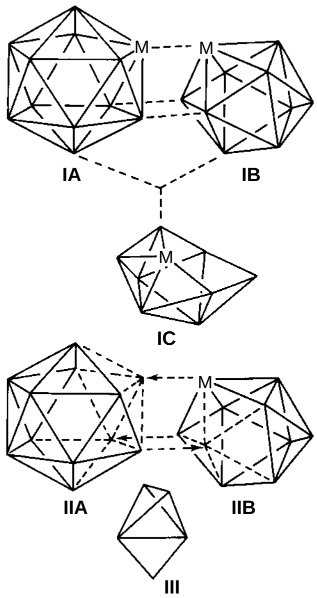


Fig. 1 Representation of the crystallographically determined molecular structure of [$(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2$] with non-hydrogen atoms as thermal ellipsoids of 50% probability, and with the methyl hydrogen atoms omitted for clarity. Selected interatomic distances (Å): to Ir: B(1) 2.149(8), B(2) 2.248(8), B(4) 2.296(9), B(7) 2.330(9), B(8) 2.329(9), B(5′) 2.416(8), B(6′) 2.273(10), B(9′) 2.351(9); to Ir″: B(1″) 2.161(8), B(3″) 2.263(9), B(5″) 2.533(8), B(6″) 2.287(9). Selected interboron distances: to B(6): B(1) 1.786(11), B(2) 1.874(12), B(5) 1.814(12), B(10) 1.776(11), B(11) 1.797(12), B(4′) 1.822(11), B(5″) 1.854(12); to B(7′): B(4′) 1.848(12), B(8′) 1.859(12), B(6′) 1.832(12), B(10′) 1.688(12), B(2) 1.803(12). Angles (°) between interatomic vectors at B(2) are in the ranges 53.4(4)–69.0(4), 98.9(4)–113.8(8), 121.4(5)–124.8(7) and 143.7(6)–155.4(7).



reaction conditions.[4,10] A *nido* $\{IrB_8\}$ unit **IIB** will supply two vertices to the *nido* decaboranyl skeleton **IIA** to generate the $\{IrB_{11}\}$ unit **IA**, with a reciprocal supply of one vertex to the *nido* unit **IIB** to generate the $\{IrB_9\}$ unit **IB**. The fusion mechanism is thereby seen to be the successive addition of two *nido*-type $\{IrB_8\}$ units **IC** and **IIB** to the *nido*-decaboranyl substrate **IIA**. Although a very minor product of a reaction system that yields several complex iridaboranes, a simple stoichiometry can be written as in eqn. (1).

$$2[(CO)(PMe_3)_2HIrB_8H_{12}] + B_{10}H_{14} \rightarrow [(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2] + CO + 8H_2 \quad (1)$$

Compound **2** has several noteworthy features. (*a*) It nicely demonstrates the principle of triple cluster fusion and (*b*) with 28 vertices it one of the biggest contiguous boron-cluster compounds yet synthesized. (*c*) There are two vertices, one boron and one iridium, that have the high cluster connectivity number eight. The iridium atom has the high overall coordination number ten. If multicentre bonding of boron is limited to participation in two- and three-centre bonding only, eight-connectivity represents the maximum for boron with its four valence orbitals. (*d*) The $\{IrB_8\}$ subcluster still retains *nido* nine-vertex character, and is therefore in principle available for further cluster incorporation, either for increased condensation within the 28-vertex system, or for fusion with a further substrate to generate quadruple cluster character. (*e*) At the region of conjunction of the three subclusters there is a central five-boron unit **III** without *exo* substituents.

This last feature suggests new types of families of large borane-based species based on globular structures that have condensed inner borons-only cores surrounded by outer spheres based on boron hydride cluster features, as distinct from the rope-like structures envisaged by extension of classical two-borons-in-common macropolyhedral fusion modes.[11] The known species $B_{20}H_{16}$, with a four-boron core,[12] is a simpler example of this. At the other extreme, a boron ball surrounded by a boron–hydride skin could be envisaged. In principle a continuum of behaviour between the ropes and the globules is available. These globular-core configurations for large borane clusters contrast to (hypothetical) hollow fullerene-based boron structures upon which speculation has recently centred.[13] Metal cluster compounds can be regarded as domains of metal lattice with peripheral valencies occupied by ligands, and hydrocarbons can be regarded as based on fragments of diamond or graphite with peripheral valencies bound to hydrogen. In this context it may be noted that there is a tetrahedral $\{B_4\}$ unit in β-rhombohedral boron itself,[14] at the point of fusion of three icosahedral units with a common vertex.

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Footnotes and References

* E-mail: johnk@chem.leeds.ac.uk

† A complete nomenclature would be: 3,3,2″,2″-tetrakis(trimethylphosphine)-3,2″-(dicarbonyl)-μ-6,4′-(*nido*-2″-iridanonaborane-5″-yl)-3(=2′)-irida-*closo*-decaborano-[1′,3′,2′:1,2,3][μ-4,6′]-*closo*-dodecaborane.

‡ *Crystallography*: All measurements were made at 193 K on a Siemens SMART CCD detector system with a sealed-tube X-ray source (50 kV × 40 mA) using Mo-Kα radiation (λ = 0.710 73 Å). Data reduced using SAINT,[6] structure solution and refinement carried out using SHELXTL-PLUS (5.03)[7] by minimization of $\Sigma w(F_o^2 - F_c^2)^2$. All non-hydrogen atoms refined with anisotropic displacement parameters. All of the hydrogen atoms on the cage were located from Fourier difference maps and refined using a riding model. *Crystal data*: $C_{15}H_{62}B_{26}Cl_6Ir_2OP_4$, M = 1260.69, monoclinic, space group $P2_1/n$, a = 10.4293(1), b = 24.1999(2), c = 19.8959(2) Å, β = 90.041(1)°, U = 5021.49(8) Å^3, Z = 4, D_c = 1.668 Mg m^{-3}, μ = 5.761 mm^{-1}, $F(000)$ = 2424. R_1 = 0.0476 for 8198 observed reflections with $F > 4\sigma(F)$, $R_w(F^2)$ = 0.1212 for 11 478 reflections and S = 1.142 for all data. CCDC 182/631.

§ Selected ^{11}B and ^1H NMR data, CD_2Cl_2 at 300 K, ordered as $\delta(^{11}B)$ (rel. Et_2OBF_3) [$\delta(^1H)$ of directly bound H(*exo*) in square brackets]: +38.0 [+6.84], +23.2 [+6.49], +19.0 [*conjuncto* site], +10.0 [+4.77], +8.8 [+3.84, doublet structure, splitting 28 Hz], *ca.* +5.4 [+4.53], *ca.* +5.4 [+1.76], *ca.* +5.4 [+1.21], *ca.* +3.4 [*ca.* + 2.80], *ca.* +3.4 [*ca.* +2.80], −1.5 [*conjuncto* site], −2.5 [+2.44], −3.5 [+1.79], *ca.* −7.0 [*conjuncto* site], *ca.* −7.2 [*ca.* +2.66], *ca.* −7.2 [*ca.* +2.66], −8.9 [+2.40], −12.0 [+3.04], −15.4 [*conjuncto* site], *ca.* −19.6 [+1.21], *ca.* −19.6 [+1.48], *ca.* −19.6 [+0.36] −23.6 [−0.43], − 28.0 [−1.21], −45.0 [−1.00], and −49.6 [*conjuncto* site]. Additional data are: $\delta(^1H)$ (bridge) at −17.78 [d, $^2J(^{31}P–^1H)$ 44 Hz], −2.40 and −1.82; and, at 213 K, $\delta(^{31}P)$ −33.0 and −56.0 [$^2J(^{31}P–^{31}P)$ *ca.* 15 Hz]; −38.0 and −39.7 [$^2J(^{31}P–^{31}P)$ *ca.* 4 Hz].

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