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**Published paper**
Macropolyhedral boron-containing cluster chemistry. Two-electron variations in intercluster bonding intimacy. Contrasting structures of nineteen-vertex \([(\eta^5-C_5Me_5)IrB_{18}H_{19}(PHPh_2)] \) and \([(\eta^5-C_5Me_5)IrB_{18}H_{18}(PH_2Ph)].\)

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Fused double-cluster \([(\eta^5-C_5Me_5)IrB_{18}H_{18}(PH_2Ph)] \) 8, from syn-[{(\eta^5-C_5Me_5)IrB_{18}H_{20}} 1 and PH_2Ph, retains the three-atoms-in-common cluster fusion intimacy of 1, in contrast to \([(\eta^5-C_5Me_5)IrB_{18}H_{19}(PHPh_2)] \) 6, from PHPH_2 with 1, which exhibits an opening to a two atoms-in-common cluster fusion intimacy. Compound 8 forms via spontaneous dihydrogen loss from its precursor \([(\eta^5-C_5Me_5)IrB_{18}H_{18}(PH_2Ph)] \) 7, which has two-atoms-in-common cluster-fusion intimacy and is structurally analogous to 6.

keywords: Borane cluster, Macropolyhedral opening and closure, X-ray structure, NMR spectroscopy, Redox changes in intercluster intimacy, Metallaborane, Iridium-borane cluster compound.
[(CO)(PMe$_3$)$_2$IrB$_{16}$H$_{14}$Ir(CO)(PMe$_3$)$_2$] [26], [7,7,7-(CO)(PMe$_3$)$_2$-syn-7-IrB$_{17}$H$_{20}$] [27],
[(PMe$_3$)$_2$IrB$_{25}$H$_{25}$Ir(CO)(PMe$_3$)$_2$] [20,21,28], [($\eta^5$-C$_5$Me$_5$)IrB$_{18}$H$_{20}$] [6], the [($\eta^5$-C$_5$Me$_5$)IrB$_{18}$H$_{19}$S]$^-$ anion [6], and [($\eta^5$-C$_5$Me$_5$)$_2$Ir$_2$B$_{18}$H$_{15}$(OH)] [20,21,29].

The addition of electrons to the cluster in a single-cluster compound generally results in cluster opening along the *closo-nido-arachno-etc* sequence; conversely, removal of electrons generally results in cluster closure [30].

In macropolyhedral boron-containing cluster compounds, in which single clusters are fused together, the addition or removal of electrons can, alternatively, result in a decrease or an increase, respectively, in the degree of intimacy of intercluster fusion, rather than the opening or closing of individual subclusters [6,18,20,29]. For the development and understanding of intercluster fusion chemistry, there is merit in establishing systems in which such alternative behaviours can be observed and defined.

Addition of electrons to a cluster is commonly effected by the addition of a two-electron ligand [31] and, in this context, we have recently found that the addition of the two-electron ligand PMe$_2$Ph to the macropolyhedral iridaborane [($\eta^5$-C$_5$Me$_5$)Ir-syn-B$_{18}$H$_{20}$] 1 (Figure 1, upper diagram) [6] results in the adduct [($\eta^5$-C$_5$Me$_5$)HIr-syn-B$_{18}$H$_{19}$(PMe$_2$Ph)] 2 (Figure 1, lower diagram) (equation 1, where L is PMe$_2$Ph) [32]. In compound 1, the cluster structure (schematic I A) is that of a *nido* twelve-vertex {IrB$_{11}$} unit fused with a *nido* ten-vertex {B$_{10}$} unit, with three boron atoms held in common (schematic I B). By contrast, in compound 2, the cluster structure (schematic II A) is that of a *nido* eleven-vertex {IrB$_{10}$} unit fused with a *nido* ten-vertex {B$_{10}$} unit, but now with only two boron atoms held in common (schematic II B). The conversion of 1 to 2 by the addition of the two-electron ligand PMe$_2$Ph therefore results in a reduction of intimacy of cluster bonding rather than an opening of the individual subclusters along the *closo-nido-arachno-etc* sequence.
In attempts at the further investigation of this and related phenomena, we found in siting experiments that the reaction of PMe$_2$Ph with the rhodium analogue of 1, viz. [(η$^5$-C$_5$Me$_5$)-syn-Rh$_{18}$H$_{30}$] 3, results in a species reasonably formulated from NMR spectroscopy and mass spectrometry as [(η$^5$-C$_5$Me$_5$)HRh-syn-B$_{18}$H$_{19}$](PMe$_2$Ph)] 4, *i.e.* a species analogous to compound 2, with the less intimately fused two-atoms-in-common double-cluster configuration II. However, in our hands so far, compound 4 has proved to be unstable in solution, precluding purification, definitive NMR work, crystallisation and structural elucidation. It decomposes to a further compound, for which NMR spectroscopy suggests formulation as [(η$^5$-C$_5$Me$_5$)Rh-syn-B$_{18}$H$_{19}$(PMe$_2$Ph)] 5, *i.e.* a species with two hydrogen atoms fewer, and thence two cluster electrons fewer, than its precursor 4. Compound 5, in turn, has also proved to be unstable in solution, again, so far, precluding definitive NMR work, purification, crystallisation and thence structural confirmation by single-crystal X-ray diffraction analysis.

The nature of this further structural type is, however, clarified from the results of the investigation of the reaction of the iridium species [(C$_5$Me$_5$)Ir-syn-B$_{18}$H$_{30}$] 1 with the phosphines PHPh$_2$ and PH$_2$Ph. Reaction overnight at room temperature between excess PHPh$_2$ (0.3 ml, 1400 μmol) and 1 (38 mg, 700 μmol) in CH$_2$Cl$_2$ (ca. 15 ml), followed by removal of solvent (rotary evaporator, water pump, 30 °C) and separation of the yellow residue by TLC (silica-gel G, CH$_2$Cl$_2$/C$_6$H$_5$ 60/40 v/v), gave air-stable orange crystals of [(η$^5$-C$_5$Me$_5$)HIr-syn-B$_{18}$H$_{19}$(PHPh$_2$)] 6 (R$_f$ 0.7, 26 mg, 370 μmol, 53 %) after recrystallisation from a solution in CH$_2$Cl$_2$ that was overlaid with C$_6$H$_5$-2. Compound 6 was characterised by NMR spectroscopy and single-crystal X-ray diffraction analysis (Figure 2), and thereby shown to have the more-open two-atoms-in-common cluster structure of its PMe$_2$Ph analogue 2 [32]. By contrast, the analogous product from the reaction of PH$_2$Ph with 1 was not so robust. Overnight reaction (ca. 18 hours) of PH$_2$Ph (9 μl, 820 μmol) with 1 (40 mg, 740 μmol) in CH$_2$Cl$_2$ (ca. 15 ml) gave a yellow solution. Filtration through silica-gel G, followed by removal of solvent as above gave an impure orange powder, formulated, on the basis of NMR spectroscopic similarities to the PMe$_2$Ph and PHPh$_2$ species 2 and 6, *i.e.* as principally [(η$^5$-C$_5$Me$_5$)HIr-syn-B$_{18}$H$_{19}$(PH$_2$Ph)] 7 (21 mg, 320 μmol, 43 %) of two-atoms-in-common configuration II. Attempted purification by TLC on silica-gel G using a variety of solvent systems resulted in decomposition of 7, although a small quantity of a yellow component 8, not present in the crude product 7, was isolatable, and was purified by crystallisation. NMR spectroscopy on 8 thence suggested a formulation [(η$^5$-C$_5$Me$_5$)Ir-syn-B$_{18}$H$_{19}$(PH$_2$Ph)], which was confirmed by the results of single-crystal X-ray diffraction analysis (Figure 3). The molecular structure of compound 8 thence in turn clearly shows that the three-atoms-in-common intercluster intimacy of the starting species 1 (schematic I and Figure 1, upper diagram) is conserved, in contrast to the structure of the [(C$_5$Me$_5$)HIrB$_{18}$H$_{19}$(PHPh$_2$)] 7, in which an opening to the two-atoms-in-common fusion mode is noted.

In the overall formation of 8 from 1, the two-electron gain associated with the incorporation of the PH$_2$Ph ligand is cancelled by the two-electron loss associated with the elimination of dihydrogen (equation 2, where L is PH$_2$Ph); overall, the three-atoms-in-common configuration is thence retained, and the individual subclusters retain their individual *nido* characters. The observations involving the conversion of rhodium compound 4 to
give 5, and of the iridium compound 7 to give 8, indicate that the stepwise process reasonably involves an initial stoichiometric adduct with a comparatively simple adduct reaction stoichiometry (equation 1), to give the more open two-atoms-in-common configuration, followed by dihydrogen elimination (equation 3) to give the more condensed three-atoms-in-common product species 5 and 8.

\[
\text{[(C}_5\text{Me}_5)\text{Ir-syn-B}_{18}\text{H}_{20}] + L \rightarrow [(\text{C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(L)] \quad (1)
\]

\[
\text{[(C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}] + L \rightarrow [(\text{C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{18}(L)] + \text{H}_2 \quad (2)
\]

\[
[(\text{C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(L)] \rightarrow [(\text{C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{18}(L)] + \text{H}_2 \quad (3)
\]

We currently examine reactions of other two-electron ligands with compound 1 and related species, and examine for other products from the systems reported in this present note.

Acknowledgements

Contribution no. 95 from the Řež -Leeds Anglo-Czech Polyhedral Collaboration (ACPC). We thank Mr. Simon Barrett for assistance with NMR spectroscopy. The support of the UK EPSRC (Grants nos. F/78323, J/56929, K/05818, L/49505 and M/83360), the Grant Agency of the Academy of Sciences of the Czech Republic (Grant no. A 403 2701), and the Grant Agency of the Czech Republic (Grant no. 203 00 1042) is greatly appreciated, and we thank The Royal Society (London) and the Academy of Sciences of the Czech Republic, together with the Royal Society of Chemistry Scheme for Journals Grants for International Authors, for assistance with reciprocal visits.

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Crystallographic data

Crystallographic data are deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition nos. 165855 and 233342 for compounds 6 and 8 respectively.

References.


Captions for Figures

Figure 1. ORTEP-type [33] drawings of (upper diagram) [(η^5-C5Me5)IrB18H20] (1, data from reference [6], CCDC 101291, and (lower diagram) [(η^5-C5Me5)HlIrB18H19(PPh2)] (2, data from reference [32], CCDC 233343). In the more condensed structure 1, the hydride unit on Ir(9) bridges to B(12), and the distance Ir(9)-B(12) is bonding at 2.387(11) Å; the three atoms B(7), B(8) and B(12) are held in common between the two subclusters, and Ir(9)B(8)B(12) is acute at 75.0(6)°. In less intimately conjoined 2, the hydride unit on Ir(9) is endo-terminal, there is an exo-terminal hydrogen unit on B(2'), and Ir(9)-B(2') is non-bonding at 3.279(7) Å; only two atoms, B(7) and B(8), are held in common between the two sub-clusters, and the corresponding angle Ir(9)B(8)B(2') is now more obtuse at 109.1(4)°.

Figure 2. ORTEP-type [33] drawing of [(η^5-C5Me5)HlIrB18H19(PPh2)] 6. Selected interatomic distances (Å) are Ir(9)-B(4) 2.164(4), Ir(9)-B(5) 2.175(4), Ir(9)-B(8) 2.214(4), Ir(9)-B(10) 2.215(4), Ir(9)-H(9) 1.43(4), Ir(9)-C(C5Me5) 2.215(4)-2.271(3), B(7)-B(8) 1.905(5), B(7)-B(11) 1.892(5), B(7)-B(2') 1.828(5), B(7)-B(10') 2.050(6), B(8)-B(2') 1.810(6), B(8)-B(7') 1.900(6), B(10)-B(11) 1.914(5), B(7')-B(8') 1.945(6), B(8')-B(9') 1.816(6), and B(9')-B(10') 1.776(7), with other interboron distances between 1.756(6) and 1.831(6) Å for the {IrB10} subcluster and between 1.704(7) and 1.820(6) Å for the {B10} subcluster. Ir(9)-H(9) is endo-terminal, B(2')-H(2') is exo-terminal, Ir(9)-B(2') is non-bonding at 3.307(4) Å, and Ir(9)B(8)B(2') is 110.1(2)° (compare 2 in Figure 1, lower).

Figure 3. ORTEP-type [33] drawing of [(η^5-C5Me5)IrB18H18(Ph2)] 8. Selected interatomic distances (Å) are Ir(9)-B(4) 2.272(7), Ir(9)-B(5) 2.257(6), Ir(9)-B(8) 2.227(7), Ir(9)-B(10) 2.255(6), Ir(9)-B(12) 2.316(8), Ir(9)-H(9,12) 1.845(8), Ir(9)-C(C5Me5) 2.199(6)-2.261(6), B(7)-B(8) 1.864(10), B(7)-B(11) 1.822(9), B(7)-B(12) 1.801(10), B(7)-B(10') 1.881(10), B(8)-B(12) 1.567(12), B(8)-B(7) 1.892(11), B(10)-B(11) 1.728(9), B(12)-B(3') 1.684(11), B(7')-B(8') 1.810(13), B(8')-B(9') 1.799(12), and B(9')-B(10')
1.799(11), with other interboron distances between 1.700(10) and 1.842(11) Å for the \{IrB_{11}\} subcluster and between 1.688(11) and 1.872(11) Å for the \{B_{10}\} subcluster. In contrast to 6 (Figure 2), the hydride unit on Ir(9) bridges to B(12), and the distance Ir(9)-B(12) is bonding; three atoms, B(7), B(8) and B(12), are held in common between the two subclusters, and Ir(9)B(8)B(12) is acute at 72.9(4)° (compare unit on Ir(9) bridges to B(12), and the distance Ir(9)-B(12) is bonding; three atoms, B(7), B(8) and B(12), are held in common between the two subclusters, and Ir(9)B(8)B(12) is acute at 72.9(4)° (compare 1 in Figure 1, upper).

**Footnotes**

*Footnote for title if required*

IUPAC nomenclatures for the new species 6 would be 11-diphenylphosphine-9-pentahapto-pentamethylcyclopentadienyl-9-hydrido-nido-9-iridaundecaborano-<7,8:5',6'>-nido-decaborane, CCDC 165856, and, for compound 3, 11-monophenylphosphine-9-pentahapto-pentamethylcyclopentadienyl-nido-9-iridadodecaborano-<7,8,12:5',6',7'>-nido-decaborane, CCDC 233342. This article was freely submitted for publication without royalty. By acceptance of this paper, the publisher and/or recipient acknowledges the right of the authors to retain non-exclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce all or part of the copyrighted paper.

**NMR footnote**

1 Footnote for NMR data.

Cluster NMR data at 297-300K (CDCl₃), ordered as δ₁¹B [δ₁‘H] of directly bound hydrogen atoms (relative intensity); [₁¹B-₁¹H] correlations for solution-unstable 7 and 8 are tentative (impure and decomposing solutions): for [(η⁵-C₅Me₅)HIrBr₃H₁₉(PHPh₂)] 6 - ca. +17.0 [+3.73] (1BH), +16.2 [+4.02] (1BH), +5.7 [no exo H] (1B), +3.6 [+3.34] (1BH), ca. +1.5 [+4.58] (1BH), ca. +0.5 [+2.97] (1BH), ca. −1.5 [+2.27] (1BH), −2.0 [+2.28] (1BH), −8.8 [+1.99] (1BH), ca. −10.7 [no exo H] (1B), ca. −11.5 [+2.13] (1BH), −16.3 [+2.06], −17.0 [+2.30] (1BH), ca. −25.5 [+0.12] (1BH), ca. −22.7 [no exo H, unresolved coupling ¹J(³¹P-¹¹B) ca. 150 Hz] (1B), −25.3 [+1.78] (1BH), −28.9 [−1.46] (1BH), −40.1 [+ 0.12] (1BH); additionally δ₁(H) at +1.08, −1.00, −2.39 [unresolved doublet splitting ²J(³¹P-¹H) ] and −2.86 (4 × H₄), at +2.07(15H, C₅Me₅), at +1.43 (1H, PHPh₂, ¹J(³¹P-¹H) ca. 80 Hz) and at −14.78 (1H, IrH), with δ(³¹P) +0.8 ppm [unresolved coupling ¹J(³¹P-¹¹B) ca. 150 Hz];

for [(η⁵-C₅Me₅)HIrBr₃H₁₉(PH₂Ph)] 7 - ca. +17.2 [+3.89] (1BH), +16.2 [+4.03] (1BH), ca. +5.9 [no exo H] (1B), +3.4 [+3.36] (1BH), ca. +1.8 [+4.72] (1BH), ca. +0.4 [+3.04] (1BH), ca. −0.1 [+2.26] (1BH), −1.9 [+2.22] (1BH), −8.8 [+2.01] (1BH), ca. −10.5 [no exo H] (1B), ca. −11.2 [+2.12] (1BH), −15.9 [+2.12] (1BH), −16.8 [+2.23] (1BH), ca. −22.0 [+0.15] (1BH), ca. −25 [no exo H, unresolved coupling ¹J(³¹P-¹¹B) ca. 135 Hz] (1B), −24.6 [+1.70] (1BH), −28.7 [−1.45] (1BH), −40.0 [+ 0.15] (1BH); additionally δ₁(H) at +1.13, −1.01, −2.47 [unresolved doublet splitting ²J(³¹P-¹H) ] and −2.84 (4 × H₄), at +2.24 (15H, C₅Me₅), at +1.43 (1H, PHMe₂, ¹J(³¹P-¹H) ca. 80 Hz), at +2.41 and +1.28 (2H, PHPh₂), and at −14.78 (1H, IrH), with δ(³¹P) −40.3 ppm [part-resolved coupling ¹J(³¹P-¹¹B) ca. 135 Hz];
for [(η⁵-C₅Me₅)IrB₁₈H₁₈(PH₂Ph)] ⁸ - ca. +10.7 [ca. +3.7] (1BH), +5.7 [ca. +3.2] (1BH), +5.7 [ca. +2.7] (1BH), ca. +5.0 [ca. +3.9] (1BH), +3.0 [ca. +3.55] (1BH), ca. +1.0 [ca. +0.08] (1BH), −0.7 [ca. +3.9] (1BH), (1BH), −4.8 [ca. +2.3], −8.3 [ca. +1.95], ca. −10.5 [ca. +3.0] (1BH), ca. −14.0 [no exo H] (1B), ca. −14.4 [no exo H] (1B), ca. −14.4 [ca. +1.45] (1BH), ca. −16.8 [ca. +2.05] (1BH), ca. −16.8 [ca. +0.7] (1BH), −26.5 [ca. +1.75] (1BH), −29.6 [ca. +10.2] (1BHμM), −41.8 [ca. +0.04] (1BH); additionally δ¹(H) at ca. +1.96 (15H, C₅Me₅), at ca. +0.7, ca. −0.85 and ca. −2.5 (3 × Hµ) and two centred at ca. +1.53 (2H, PH₂Ph), with δ(³¹P) −36.6 ppm [broadened, unresolved coupling ¹J(³¹P-¹¹B)].

X-ray footnote

² Footnote for X-ray diffraction analyses.

[(η⁵-C₅Me₅)IrB₁₈H₁₈(PH₂Ph)] ⁶, C₂₂H₄₆B₁₈IrP: M = 728.34, monoclinic (yellow block, 0.32×0.28×0.22 mm, from CH₂Cl₂/C₆H₁₄), Space Group P2₁/n, a = 10.9820(1), b = 26.0041(3), c = 12.3756(1) Å, β = 109.2830(6)°, U = 3335.91(6) Å³, D_calc = 1.450 Mg m⁻³, Z = 4, Mo-Kα, λ = 0.71073 Å, μ = 4.066 mm⁻¹, T = 190(2) K, R₁{I > 2σ(I)} = 0.0376 and wR₂ = 0.1042 for all 17158 unique reflections; CCDC 165855. [(η⁵-C₅Me₅)IrB₁₈H₁₈(PH₂Ph)] ⁸, C₁₆H₄₀B₁₈IrP: M = 650.23, monoclinic (yellow prism, 0.39×0.26×0.13 mm, from CH₂Cl₂/C₆H₁₄), Space Group P2₁/c, a = 10.3712(2), b = 12.0290(3), c = 23.6126(5) Å, β = 99.7010(13)°, U = 2903.67(11) Å³, D_calc = 1.487 Mg m⁻³, Z = 4, Mo-Kα, λ = 0.71073 Å, μ = 4.661 mm⁻¹, T = 100(2) K, R₁{I > 2σ(I)} = 0.0352 and wR₂ = 0.0902 for all 5635 unique reflections; CCDC 233342. For both ⁶ and ⁸, methods and programs were standard [34,35].
Shorter abstract for graphical contents

\[ ((\eta^5-C_5Me_5)IrB_{18}H_{18}(PH_2Ph)) \textbf{8,} \text{ from double-cluster } \text{syn-} \[(\eta^5-C_5Me_5)IrB_{18}H_{20}] \textbf{1} \text{ and } PH_2Ph, \text{ retains the three- atoms-in-common cluster-fusion intimacy of } \textbf{1}, \text{ in contrast to } [(\eta^5-C_5Me_5)HlrB_{18}H_{19}(PHPh_2)] \textbf{6}, \text{ from PHPh}_2 \text{ with } \textbf{1}, \text{ which exhibits an opening to a two atoms-in-common cluster-fusion intimacy.} \]