Macropolyhedral boron-containing cluster chemistry: two-electron variations in intercluster bonding intimacy. Contrasting structures of 19-vertex \((\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{19}(\text{PHPh}_2)\) and \((\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{18}(\text{PH}_2\text{Ph})\)

Suzanne L. Shea \(^a\), Tomáš Jelínek \(^b\), Sarath D. Perera \(^a,c\), Bohumil Šťibr \(^b\), Mark Thornton-Pett \(^a\), John D. Kennedy \(^a,*\)

\(^a\) The School of Chemistry of the University of Leeds, Woodhouse Lane, Leeds LS2 9JT, UK
\(^b\) Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, 25068 Rež u Prahy, Czech Republic
\(^c\) The Department of Chemistry of the Open University, Nawala, Nugegoda, Sri Lanka

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Abstract

Fused double-cluster \((\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{18}(\text{PH}_2\text{Ph})\) \((8)\), from \(3\text{yn}-[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}]\) \((1)\) and \(\text{PH}_2\text{Ph}\), retains the three-atoms-in-common cluster fusion intimacy of \(1\), in contrast to \([((\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}(\text{PHPh}_2)]\) \((6)\), from \(\text{PHPh}_2\) 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 \([((\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{19}(\text{PH}_2\text{Ph})]\) \((7)\), 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

The redox flexibility of transition-element centres allied with the closo-nido-arachno-etc redox flexibility of boron-containing cluster structures engenders much interesting metallaborane structural, behavioural, and reaction chemistry [1–3]. Rhodium and iridium metallaboranes have figured significantly in this regard, for example in terms of reactions, both catalytic and non-catalytic [4–10], in phenomena such as fluxionalities [11,12], and in the establishment of interesting cluster types, such as those of ‘isocloso’ and ‘isonido’ geometries [13–16]. Single-cluster borane, heteroborane and metallaborane chemistry is governed at present by an uppermost limit to cluster size of about 14 vertices [17,18]: to extend beyond this horizon the clusters need to be linked or fused together to make bigger cluster assemblies. Intimate intercluster fusions, with two or more atoms held in common between the constituent subclusters, result in so-called ‘macropolyhedral’ species [19–22], in which the multicentre bonding characteristics of boron extend across the nexus between the constituent subclusters. The structural flexibility resulting from the incorporation of rhodium and iridium centres in macropolyhedral metallaborane assemblies has been most useful in the development of this macropolyhedral area [23–30], and milestone compounds include the \([(\text{CO})(\text{PPh}_3)\text{Rh}_2]\)
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 [31–34]. 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 [7,19,21,30]. 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 [35] and, in this context, we have recently found that the addition of the two-electron ligand PMe2Ph to the macropolyhedral iridaborane \([\eta^5\text{-C}_5\text{Me}_5]\text{Ir-syn-B}_{18}\text{H}_{20}\) (1) (Fig. 1, upper diagram) [7] results in the adduct \([\eta^5\text{-C}_5\text{Me}_5]\text{Ir-syn-B}_{18}\text{H}_{19}\text{(PMe}_2\text{Ph)}\) (2) (Fig. 1, lower diagram) (Eq. (1), where L is PMe2Ph) [36]. In compound 1, the cluster structure (Schematic 1) is that of a nido 12-vertex \{IrB_{11}\} unit fused with a nido 10-vertex \{B_{10}\} unit, with three boron atoms held in common (Schematic 2). By contrast, in compound 2, the cluster structure (Schematic 3) is that of a nido 11-vertex unit fused with an exo-10-vertex \{B_{10}\} unit, with three boron atoms held in common (Schematic 2).
The conversion of 1 to 2 by the addition of the two-electron ligand PMe₂Ph 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 sited experiments that the reaction of PMe₂Ph with the rhodium analogue of 1, viz. [(η⁵-C₅Me₅)IRB₁₁H₁₀(PH₂Ph)] (3), results in a species reasonably formulated from NMR spectroscopy and mass spectrometry as [(η⁵-C₅Me₅)HRh-syn-B₁₈H₁₉(PMe₂Ph)] (4), i.e. a species analogous to compound 2, with the less intimately fused two-atoms-in-common double-cluster configuration of schematic 3. 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 [(η⁵-C₅Me₅)Rh-syn-B₁₈H₁₈(PMe₂Ph)] (5), i.e. a species with two hydrogen atoms 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 [(η⁵-C₅Me₅)IR-syn-B₁₈H₂₀] (1) with the phosphines PHPh₂ and PH₂Ph. Reaction overnight at room temperature between excess PHPh₂ (0.3 ml, 1400 μmol) and 1 (38 mg, 700 μmol) in CH₂Cl₂ (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, CH₂Cl₂/C₆H₁₂ 60/
40 v/v), gave air-stable orange crystals of \( \left[ \eta^3\text{-}C_5\text{Me}_5\right]\text{Ir}r\text{-syn-}B_{18}H_{19}(\text{PHPh}_2) \) (6) \((R_F\ 0.7, 26\ mg, 370 \mu\text{mol}, 53\%)\) after recrystallisation from a solution in CH2Cl2 that was overlayed with CaH2. Compound 6 was characterised by NMR spectroscopy \(^1\) and single-crystal X-ray diffraction analysis (Fig. 2), \(^2\) and thereby shown to have the more-open two-atoms-in-common cluster structure of its PMe2Ph analogue 2 \([36]\). By contrast, the analogous product from the reaction of PH2Ph with 1 was not so robust. Overnight reaction (ca. 18 h) of PH2Ph (9 \(\mu\)l, 820 \mu\text{mol}) with 1 (40 mg, 740 \mu\text{mol}) in CH2Cl2 (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 PMe2Ph and PHPh2 species 2 and 6, \(^3\) as principally \( \left[ \eta^3\text{-}C_5\text{Me}_5\right]\text{Ir}r\text{-syn-}B_{18}H_{19}(\text{PHPh}_2) \) 7 (21 mg, 320 \mu\text{mol}, 43\%), of two-atoms-in-common configuration of schematic 3. 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 \(^1\) on 8 thence suggested a formulation \( \left[ \eta^3\text{-}C_5\text{Me}_5\right]r\text{-syn-}B_{18}H_{19}(\text{PH2Ph}) \), which was confirmed by the results of single-crystal X-ray diffraction analysis (Fig. 3). \(^2\) 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 1 and 2 and Fig. 1, upper diagram) is conserved, in contrast to the structure of \( \left[ \eta^3\text{-}C_5\text{Me}_5\right]r\text{Ir}rB_{18}H_{20}(\text{PHPh}_2) \) (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 PH2Ph ligand is cancelled by the two-electron loss associated with the elimination of dihydrogen (Eq. (2), where L is PH2Ph); 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 (Eq. (1)), to give the more open two-atoms-in-common configuration, followed by dihydrogen elimination (Eq. (3)) to give the more condensed three-atoms-in-common product species 5 and 8.

\[
\left[ \left( \eta^3\text{-}C_5\text{Me}_5\right)\text{Ir}rB_{18}H_{20}\right] + L \rightarrow \left[ \left( \eta^3\text{-}C_5\text{Me}_5\right)\text{Ir}rB_{18}H_{19}(L)\right]
\]

\( \left( \eta^3\text{-}C_5\text{Me}_5\right)\text{Ir}rB_{18}H_{19}(L) \rightarrow \left[ \left( \eta^3\text{-}C_5\text{Me}_5\right)\text{Ir}rB_{18}H_{18}(L)\right] + H_2
\]

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.

1. Crystallographic data

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