

Note

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

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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 *syn*- $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}]$  (**1**) and  $\text{PH}_2\text{Ph}$ , retains the three-atoms-in-common cluster fusion intimacy of **1**, in contrast to  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(\text{PPh}_2)]$  (**6**), from  $\text{PPh}_2$  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  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(\text{PH}_2\text{Ph})]$  (**7**), which has two-atoms-in-common cluster-fusion intimacy and is structurally analogous to **6**. © 2004 Elsevier B.V. All rights reserved.

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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 ex-

ample 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  $[(\text{CO})(\text{PPh}_3)\text{Rh}_2\text{-}$

<sup>☆</sup> IUPAC nomenclature for the new species **6** would be 11-diphenylphosphine-9-pentahapto-pentamethylcyclopentadienyl-9-hydrido-*nido*-9-iridaundecaborano-<7,8: 5', 6' >-*nido*-decaborane, CCDC 165855, and, for compound **3**, 11-monphenylphosphine-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.

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$B_{18}H_{20}]^-$  anion [24],  $[(C_5Me_5)_2RhB_{18}H_{20}]$  [3],  $[(C_5Me_5)_2RhB_{17}H_{21}]$  [23],  $[(C_5Me_5)_2Rh_2B_{17}H_{19}]$  [23,25],  $[(C_5Me_5)_2Rh_2S_2B_{15}H_{14}(OH)]$  [26],  $[(CO)(PMe_3)_2IrB_{16}H_{14}Ir(CO)(PMe_3)_2]$  [27],  $[7,7,7-(CO)(PMe_3)_2-syn-7-IrB_{17}H_{20}]$  [28],  $[(PMe_3)_2IrB_{26}H_{24}Ir(CO)(PMe_3)_2]$  [21, 22,29],  $[(\eta^5-C_5Me_5)IrB_{18}H_{20}]$  [7], the  $[(\eta^5-C_5Me_5)IrB_{18}H_{19}S]^-$  anion [7], and  $[(\eta^5-C_5Me_5)_3Ir_3B_{18}H_{15}(OH)]$  [21,22,30].

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,

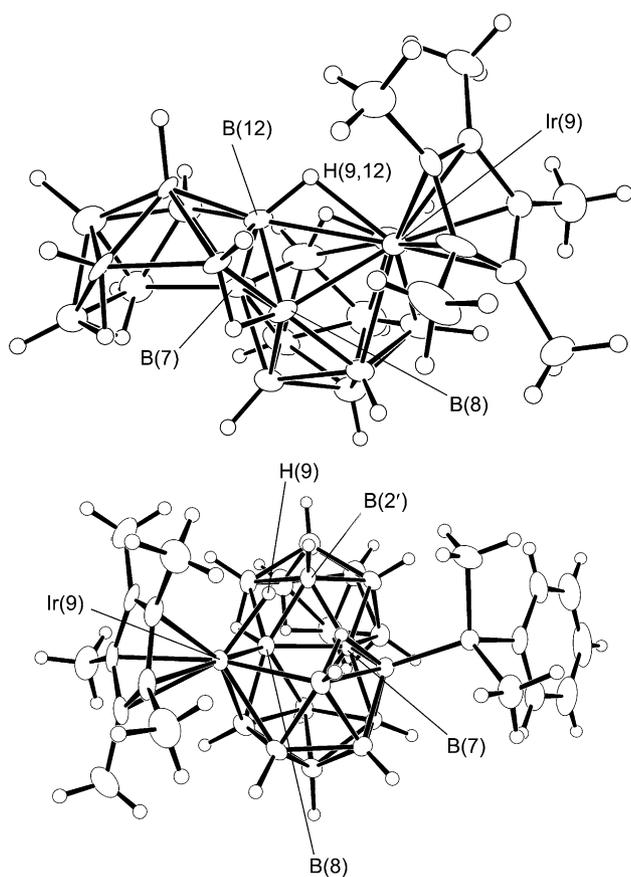
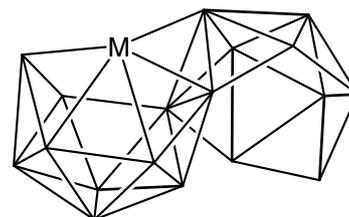


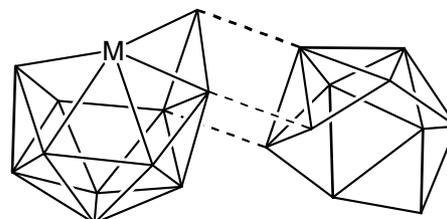
Fig. 1. ORTEP-type [37] drawings of (upper diagram)  $[(\eta^5-C_5Me_5)IrB_{18}H_{20}]$  (**1**, data from reference [7], CCDC 101291) and (lower diagram)  $[(\eta^5-C_5Me_5)HIrB_{18}H_{19}(PHPh_2)]$  (**2**, data from reference [36], CCDC 233343). In the more condensed structure **1**, the hydride unit 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)°.

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.

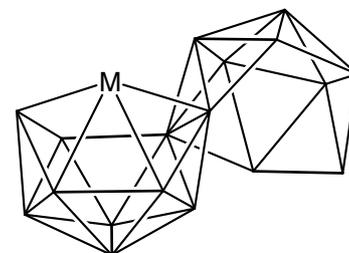
Addition of electrons to a cluster is commonly effected by the addition of a two-electron ligand [35] and, in this context, we have recently found that the addition of the two-electron ligand  $PMe_2Ph$  to the macropolyhedral iridaborane  $[(\eta^5-C_5Me_5)Ir-syn-B_{18}H_{20}]$  (**1**) (Fig. 1, upper diagram) [7] results in the adduct  $[(\eta^5-C_5Me_5)HIr-syn-B_{18}H_{19}(PMe_2Ph)]$  (**2**) (Fig. 1, lower diagram) (Eq. (1), where L is  $PMe_2Ph$ ) [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



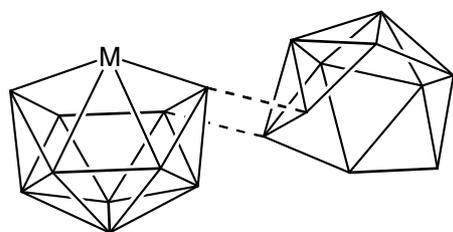
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

{IrB<sub>10</sub>} unit fused with a *nido* 10-vertex {B<sub>10</sub>} unit, but now with only two boron atoms held in common (Schematic 4). The conversion of **1** to **2** by the addition of the two-electron ligand PMe<sub>2</sub>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<sub>2</sub>Ph with the rhodium analogue of **1**, viz. [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)-*syn*-RhB<sub>18</sub>H<sub>20</sub>] (**3**), results in a species reasonably formulated from NMR spectroscopy and mass spectrometry as [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)HRh-*syn*-

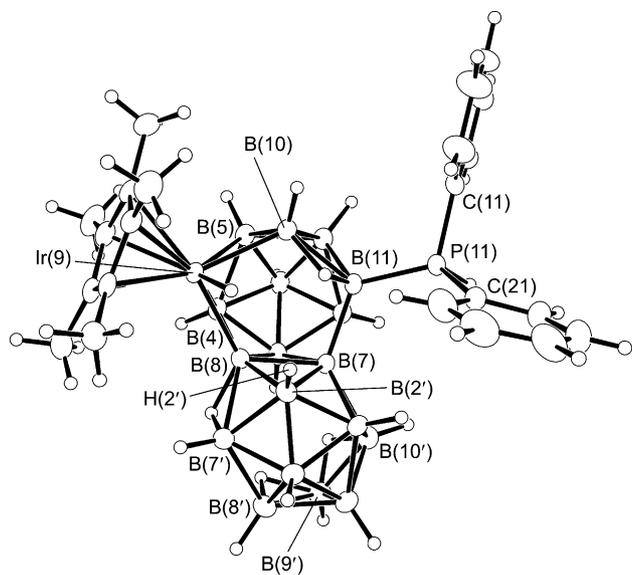


Fig. 2. ORTEP-type [37] drawing of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)H]IrB<sub>18</sub>H<sub>19</sub>(PHPh<sub>2</sub>) (**6**). Selected interatomic distances (Å) are Ir(9)–B(4) 2.164(4), Ir(9)–B(5) 2.175(4), Ir(9)–B(8) 2.214(4), Ir(9)–B(10) 2.215(4), Ir(9)–H(9) 1.43(4), Ir(9)–C(C<sub>5</sub>Me<sub>5</sub>) 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 {IrB<sub>10</sub>} subcluster and between 1.704(7) and 1.820(6) Å for the {B<sub>10</sub>} 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)<sup>o</sup> (compare **2** in Fig. 1, lower).

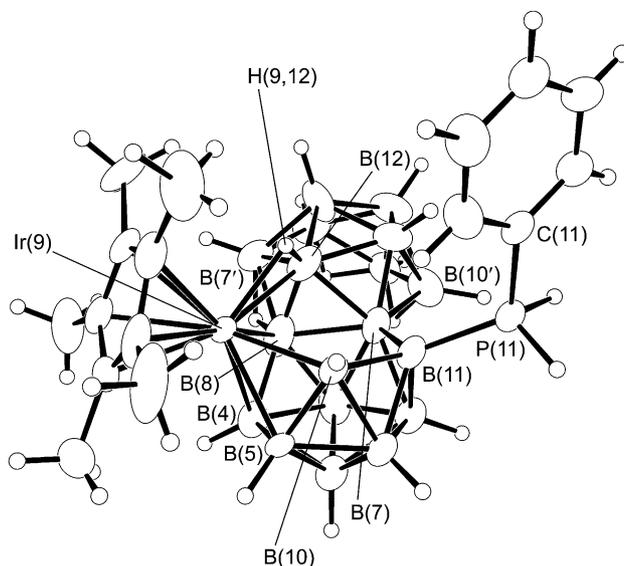


Fig. 3. ORTEP-type [37] drawing of [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Ir]B<sub>18</sub>H<sub>18</sub>(PH<sub>2</sub>Ph) (**8**). Selected interatomic distances (Å) are Ir(9)–B(4) 2.272(7), Ir(9)–B(5) 2.257(6), Ir(9)–B(8) 2.227(7), Ir(9)–B(10) 2.255(6), Ir(9)–B(12) 2.316(8), Ir(9)–H(9,12) 1.845(8), Ir(9)–C(C<sub>5</sub>Me<sub>5</sub>) 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<sub>11</sub>} subcluster and between 1.688(11) and 1.872(11) Å for the {B<sub>10</sub>} subcluster. In contrast to **6** (Fig. 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)<sup>o</sup> (compare **1** in Fig. 1, upper).

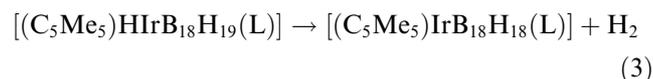
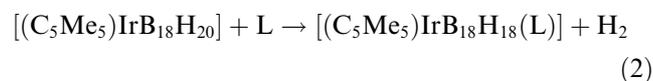
B<sub>18</sub>H<sub>19</sub>(PMe<sub>2</sub>Ph)] (**4**), i.e. a species analogous to compound **2**, with the less intimately fused two-atoms-in-common double-cluster configuration of schematic 3. However, in our hands so far, compound **4** has proved to be unstable in solution, precluding purification, definitive NMR work, crystallisation and structural elucidation. It decomposes to a further compound, for which NMR spectroscopy suggests formulation as [(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)Rh-*syn*-B<sub>18</sub>H<sub>18</sub>(PMe<sub>2</sub>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<sub>5</sub>Me<sub>5</sub>)Ir-*syn*-B<sub>18</sub>H<sub>20</sub>] (**1**) with the phosphines PPh<sub>2</sub> and PH<sub>2</sub>Ph. Reaction overnight at room temperature between excess PPh<sub>2</sub> (0.3 ml, 1400 μmol) and **1** (38 mg, 700 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (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<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>12</sub> 60/

40 v/v), gave air-stable orange crystals of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIr-syn-B}_{18}\text{H}_{19}(\text{PPh}_2)]$  (**6**) ( $R_F$  0.7, 26 mg, 370  $\mu\text{mol}$ , 53%) after recrystallisation from a solution in  $\text{CH}_2\text{Cl}_2$  that was overlaid with  $\text{C}_6\text{H}_{12}$ . Compound **6** was characterised by NMR spectroscopy<sup>1</sup> and single-crystal X-ray diffraction analysis (Fig. 2),<sup>2</sup> and thereby shown to have the more-open two-atoms-in-common cluster structure of its  $\text{PMe}_2\text{Ph}$  analogue **2** [36]. By contrast, the analogous product from the reaction of  $\text{PH}_2\text{Ph}$  with **1** was not so robust. Overnight reaction (ca. 18 h) of  $\text{PH}_2\text{Ph}$  (9  $\mu\text{l}$ , 820  $\mu\text{mol}$ ) with **1** (40 mg, 740

$\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (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  $\text{PMe}_2\text{Ph}$  and  $\text{PPh}_2$  species **2** and **6**,<sup>1</sup> as principally  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIr-syn-B}_{18}\text{H}_{19}(\text{PH}_2\text{Ph})]$  **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<sup>1</sup> on **8** thence suggested a formulation  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir-syn-B}_{18}\text{H}_{18}(\text{PH}_2\text{Ph})]$ , which was confirmed by the results of single-crystal X-ray diffraction analysis (Fig. 3).<sup>2</sup> 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  $[(\text{C}_5\text{Me}_5)\text{-HfIrB}_{18}\text{H}_{19}(\text{PPh}_2)]$  (**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  $\text{PH}_2\text{Ph}$  ligand is cancelled by the two-electron loss associated with the elimination of dihydrogen (Eq. (2), where L is  $\text{PH}_2\text{Ph}$ ); 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 (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**.



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.

<sup>1</sup> Cluster NMR data at 297–300 K ( $\text{CDCl}_3$ ), ordered as  $\delta$  ( $^{11}\text{B}$ ) [ $\delta$  ( $^1\text{H}$ ) of directly bound hydrogen atoms] (relative intensity); [ $^{11}\text{B}$ – $^1\text{H}$ ] correlations for solution-unstable **7** and **8** are tentative (impure and decomposing solutions): for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}(\text{PPh}_2)]$  (**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  $^1J(^{31}\text{P}$ – $^{11}\text{B})$  ca. 150 Hz] (1B), –25.3 [+1.78] (1BH), –28.9 [+1.46] (1BH), –40.1 [+0.12] (1BH); additionally  $\delta$  ( $^1\text{H}$ ) at +1.08, –1.00, –2.39 [unresolved doublet splitting  $^2J(^{31}\text{P}$ – $^1\text{H})$ ] and –2.86 ( $4 \times \text{H}\mu$ ), at +2.07 (15H,  $\text{C}_5\text{Me}_5$ ), at +1.43 (1H,  $\text{PPh}_2$ ),  $^1J(^{31}\text{P}$ – $^1\text{H})$  ca. 80 Hz) and at –14.78 (1H, IrH), with  $\delta$  ( $^{31}\text{P}$ ) +0.8 ppm [unresolved coupling  $^1J(^{31}\text{P}$ – $^{11}\text{B})$  ca. 150 Hz]; for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}(\text{PH}_2\text{Ph})]$  (**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  $^1J(^{31}\text{P}$ – $^{11}\text{B})$  ca. 135 Hz] (1B), –24.6 [+1.70] (1BH), –28.7 [+1.45] (1BH), –40.0 [+0.15] (1BH); additionally  $\delta$  ( $^1\text{H}$ ) at +1.13, –1.01, –2.47 [unresolved doublet splitting  $^2J(^{31}\text{P}$ – $^1\text{H})$ ] and –2.84 ( $4 \times \text{H}\mu$ ), at +2.24 (15H,  $\text{C}_5\text{Me}_5$ ), at +1.43 (1H,  $\text{PHMe}_2$ ),  $^1J(^{31}\text{P}$ – $^1\text{H})$  ca. 80 Hz), at +2.41 and +1.28 (2H,  $\text{PPh}_2$ ), and at –14.78 (1H, IrH), with  $\delta$  ( $^{31}\text{P}$ ) –40.3 ppm [part-resolved coupling  $^1J(^{31}\text{P}$ – $^{11}\text{B})$  ca. 135 Hz]; for  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{18}(\text{PH}_2\text{Ph})]$  (**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] (1BH  $\mu\text{M}$ ), –41.8 [ca. +0.04] (1BH); additionally  $\delta$  ( $^1\text{H}$ ) at ca. +1.96 (15H,  $\text{C}_5\text{Me}_5$ ), at ca. +0.7, ca. –0.85 and ca. –2.5 ( $3 \times \text{H}\mu$ ) and two centred at ca. +1.53 (2H,  $\text{PH}_2\text{Ph}$ ), with  $\delta$  ( $^{31}\text{P}$ ) –36.6 ppm [broadened, unresolved coupling  $^1J(^{31}\text{P}$ – $^{11}\text{B})$ ].

<sup>2</sup>  $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}(\text{PPh}_2)]$  (**6**),  $\text{C}_{22}\text{H}_{46}\text{B}_{18}\text{IrP}$ :  $M = 728.34$ , monoclinic (yellow block,  $0.32 \times 0.28 \times 0.22$  mm, from  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ ), space group  $P2_1/n$ ,  $a = 10.9820(1)$ ,  $b = 26.0041(3)$ ,  $c = 12.3756(1)$  Å,  $\beta = 109.2830(6)^\circ$ ,  $U = 3335.91(6)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.450$  Mg m<sup>–3</sup>,  $Z = 4$ , Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 4.066$  mm<sup>–1</sup>,  $T = 190(2)$  K,  $R_1\{I > 2\sigma(I)\} = 0.0376$  and  $wR_2 = 0.1042$  for all 17,158 unique reflections; CCDC 165855.  $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{18}(\text{PH}_2\text{Ph})]$  (**8**),  $\text{C}_{16}\text{H}_{40}\text{B}_{18}\text{IrP}$ :  $M = 650.23$ , monoclinic (yellow prism,  $0.39 \times 0.26 \times 0.13$  mm, from  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$ ), space group  $P2_1/c$ ,  $a = 10.3712(2)$ ,  $b = 12.0290(3)$ ,  $c = 23.6126(5)$  Å,  $\beta = 99.7010(13)^\circ$ ,  $U = 2903.67(11)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.487$  Mg m<sup>–3</sup>,  $Z = 4$ , Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 4.661$  mm<sup>–1</sup>,  $T = 100(2)$  K,  $R_1\{I > 2\sigma(I)\} = 0.0352$  and  $wR_2 = 0.0902$  for all 5635 unique reflections; CCDC 233342. For both **6** and **8**, methods and programs were standard [38,39].

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