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Macropolyhedral boron-containing cluster chemistry. Ligand-induced two-electron variations of intercluster bonding intimacy. Structures of nineteen-vertex[(eta(5)-C5Me5) HIrB18H19(PMe2Ph)] and the related carbene complex [(eta(5)-C5Me5)HlrB18H19{C(NHMe)(2)}]
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Macropolyhedral boron-containing cluster chemistry. Ligand-induced two-electron variations of intercluster bonding intimacy. Structures of nineteen-vertex $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ and the related carbene complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}\{\text{C}(\text{NHMe})_2\}]$.*

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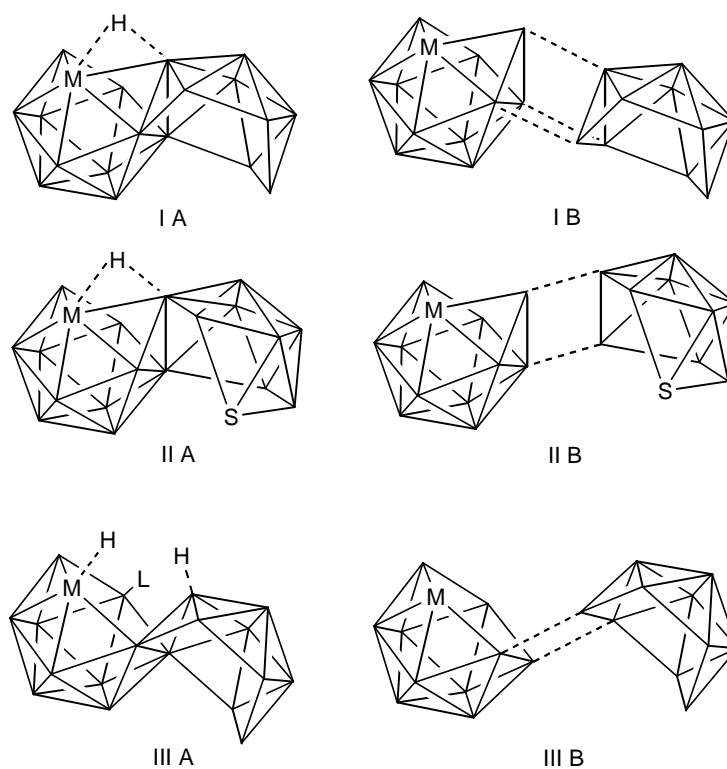
Addition of PMe_2Ph to fused-cluster *syn*- $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}]$ **1** to give $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ **3** entails a diminution in the degree of intimacy of the intercluster fusion, rather than retention of inter-subcluster binding intimacy and a *nido* \rightarrow *arachno* conversion of the character of either of the subclusters. Reaction with MeNC gives $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}\{\text{C}(\text{NHMe})_2\}]$ **4** which has a similar structure, but with the ligand now being the carbene $\{\text{:C}(\text{NHMe})_2\}$, resulting from a reductive assembly reaction involving two MeNC residues and the loss of a carbon atom.

The addition of electrons to a single-cluster compound generally results in cluster opening; conversely, removal of electrons results in cluster closure.¹ In macropolyhedral boron-containing cluster compounds, in which single clusters are fused together, the addition and removal of electrons can, alternatively, result in a respective decrease or increase in the degree of intimacy of the intercluster fusion, rather than the opening or closure of any of the subclusters.²⁻⁴ In the development of macropolyhedral boron cluster chemistry, there is merit in establishing systems in which such differential behaviour may be observed, so that the controlling factors for this differential behaviour may ultimately be defined.

The macropolyhedral metallaborane *syn*- $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}]$ **1** (Figure 1) consists of *nido* twelve-vertex $\{\text{IrB}_{11}\}$ and *nido* ten-vertex $\{\text{B}_{10}\}$ subclusters fused together, with three atoms held in common between the two subclusters (schematic skeletal structures **I**).³ In the reaction of compound **1** with elemental sulphur / sulfur, the observed reductive opening to give the $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrSB}_{18}\text{H}_{19}]^-$ anion **2** entails the addition of a sulphur / sulfur vertex to the non-metallated subcluster and the conversion of this non-metal-containing subcluster from *nido* to *arachno* (schematics **II**).⁴ The addition of a sulphur / sulfur atom effectively adds four reducing electrons to the double-cluster system, resulting in a reductive two-electron opening of the non-metallated subcluster from *nido* to *arachno*, and a reductive two-electron diminution of intercluster bonding intimacy from three-atoms-in-common to a two-atoms-in-common mode.

There is consequent interest in the effect of a single two-electron reduction: will it result in an individual cluster-opening, or in a decrease in intercluster bonding intimacy? In this regard, we now report preliminary results on an interesting complementary behaviour. Specifically, reaction of compound **1** with the two-electron ligand PMe_2Ph results in addition of the ligand to give a compound of formulation $[(\text{C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(\text{PPh}_2)]$ **3** (equation 1 below). The ligand adds to a boron atom on the cage, and there is a transfer of a boron-bound hydrogen atom onto the iridium centre. The two-electron reduction leaves the *nido*-decaboranyl ten-vertex cage intact, with the reductive addition occurring now at the metal-containing subcluster, rather than at the metal-free subcluster. It is also apparent that there is a decrease in the intimacy of intercluster fusion, rather than an opening of either of the individual subclusters from *nido* to *arachno*. This is manifested in the conversion of the fusion mode from a three-atoms-in-common triangle to a two-atoms-in-common edge, which thereby has the effect of converting the iridium-containing subcluster from twelve-vertex *nido* (schematics **I**) to eleven-vertex *nido* (schematics **III**).

[schematics **I**, **II** and **III** near here]



Thus, PMe_2Ph (25 μl , 1.62 mmol) was added to an orange solution of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir-syn-B}_{18}\text{H}_{20}]$ **1** (44 mg, 810 μmol) in CH_2Cl_2 (*ca.* 15 ml). After 24 hours the solvent was removed from the resulting yellow solution (rotary evaporator, water pump, 30 $^\circ\text{C}$). TLC separation of the residue (silica gel G, CH_2Cl_2 /hexane 50/50 v/v) thence gave $[\text{BH}_3(\text{PMe}_2\text{Ph})]$ (R_f 0.8, 3 mg, 200 μmol , 1 %) and yellow $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIr-syn-B}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ **3** (R_f 0.5, 49 mg, 720 μmol , 89 %), the latter characterised as such by single-crystal X-ray crystal diffraction analysis⁵ and by NMR spectroscopy.⁶ The equation for its formation is stoichiometric (equation 1).



The polyhedral cluster structure of **3** (Figure 2 and schematics **III**) is seen to consist of *nido* eleven-vertex $\{IrB_{10}\}$ and *nido* ten-vertex $\{B_{10}\}$ subclusters conjoined with a common two-boron edge. Any Ir-H-B bonding to link between the subclusters, as observed in **1** and **2** (Figure 1 and schematics **I A** and **II A**) is no longer present, and so the three-atom intercluster intimacy observed for **1** (schematic **I A**) is thereby reduced to a two-atom mode. The hydride unit that is effectively displaced intramolecularly by the incoming ligand finds itself on the metal atom (schematic **III A**), and the compound thence has structural similarities to $[(PMe_2Ph)HPtB_{18}H_{19}(PMe_2Ph)]$,⁴ which is based on *nido*-type eleven-vertex $\{PtB_{10}\}$ and *nido* ten-vertex $\{B_{10}\}$ subclusters with two boron atoms held in common. In **3**, however, instead of a square-planar $\{PtH(PMe_2Ph)\}$ platinum(II) unit contributing two orbitals and one electron to a simple cluster bonding scheme, this function is fulfilled by the octahedral $\{IrH(\eta^5-C_5Me_5)\}$ iridium(III) unit. It is interesting that the iridium centre does not switch to square-planar $\{Ir(\eta^4-C_5HMe_5)\}$ iridium(I) for this purpose, in contrast to the observation of a square-planar $\{Rh(\eta^4-C_5HMe_5)\}$ feature in the single-borane-cluster rhodium species $[(\eta^4-C_5HMe_5)RhS_2B_9H_9(SMe)]$.⁷ In this last regard, and in competitive cluster-opening terms,⁷ it is pertinent to note that the $\{M(\eta^5-C_5Me_5)\}$ units are six-vertex *nido*, whereas the $\{M(\eta^4-C_5HMe_5)\}$ units, effectively containing two more electrons, are six-vertex *arachno*.

We have also found that an additional interesting reductive feature in this new type of system occurs when the two-electron ligand used is MeNC. Thus, MeNC (23 μ l, 4.0 mmol) was added to a solution of $[(\eta^5-C_5Me_5)Ir\text{-}syn\text{-}B_{18}H_{20}]$ **1** (59 mg, 1.09 mmol) in CH_2Cl_2 (*ca.* 15 ml). The resulting orange solution was heated at reflux for 3.5 hours, allowed to cool, and stirred overnight. Following removal of the solvent (rotary evaporator, water pump, 30 °C), TLC separation of the product mixture (silica gel G, CH_2Cl_2 /hexane 60/40 v/v) thence gave yellow $[(\eta^5-C_5Me_5)IrH\text{-}syn\text{-}B_{18}H_{19}(C(NHMe)_2)]$ **4** (R_F 0.2, 11 mg, 0.18 mmols, 16 %) as a principal product, characterised as such by single-crystal X-ray crystal diffraction analysis⁵ and by NMR spectroscopy.⁶ Although the basic, more open, two-atoms in common, metallaborane structural type of **3** above is again formed (Figure 3), compound **4** now exhibits an unusual reductive and degradative combination of two MeNC moieties: it has the carbene ligand, $\{C(NHMe)_2\}$, rather than a simple MeNC moiety, in the 11-position. The carbene fragment is derived from two MeNC residues with the loss of one carbon atom. The nitrogen-bound hydrogen atoms in the carbene presumably derive from the oxidation of other borane residues, the < 50 % yield of **4** of being consistent with this. A related reductive / degradative oligomerisation with loss of carbon has been observed in the reaction of MeNC with the non-metallated macropolyhedral $B_{18}H_{22}$: this last reaction results in a formation of a species $[B_{18}H_{20}\{CN_2Me_2CHC(NHMe)\}]$, which contains an imidazole-like carbene ligand, now formed from the assembly of three, rather than two, MeNC residues, but again with the loss of one carbon atom.⁸ In this context also the bis(carbene) species $[B_{12}H_{10}\{C(OH)_2\}_2]$ may also be noted.⁹ Complexes of elements of Main-Group III (*i.e.* Group 13) with carbenes are rare,¹⁰ as is loss of carbon from isocyanides upon reaction with boron-containing clusters.¹¹

Acknowledgements

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Crystallographic data

Crystallographic data are deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition nos. 233343 and 165856 for compounds **3** and **4** respectively.

Index words

Macropolyhedral opening, carbene formation, X-ray structure, cluster fusion intimacy, metallaborane, iridium-boron cluster compound

Footnotes

*** Footnote for title if required**

A IUPAC nomenclature for the new species **3** would be 11-(dimethylphenylphosphine)-9-*pentahapto*-pentamethylcyclopentadienyl-9-hydrido-*nido*-9-iridaundecaborano- < 7,8 : 5',6' > -*nido*-decaborane, CCDC 233343, and, for compound **4**, 11-{bis(methylamino)carbene}-9-*pentahapto*-pentamethylcyclopentadienyl-9-hydrido-*nido*-9-iridaundecaborano- < 7,8 : 5',6' > -*nido*-decaborane, CCDC 165856. 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.

Captions for Figures

Figure 1. ORTEP-type¹² drawing of $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}]$ (compound **1**).³ 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 the angle Ir(9)B(8)B(12), corresponding to Ir(9)B(8)B(2') in compounds **3** and **4**, is acute at 75.0(6)°

Figure 2. ORTEP-type¹² drawing of $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ (compound **3**). There are two independent molecules in the unit cell, differing principally in phosphine-ligand rotamer disposition. Cluster dimensions for both are very similar. Dimensions here are for 'molecule 1'. Selected interatomic distances (Å) are Ir(9)-B(4) 2.176(7), Ir(9)-B(5) 2.200(7), Ir(9)-B(8) 2.209(7), Ir(9)-B(10) 2.331(7), Ir(9)-H(9) 1.7155(3), Ir(9)-C(C₅Me₅) 2.215(6)-2.331(7), B(7)-B(8) 1.876(10), B(7)-B(11) 1.892(8), B(7)-B(2') 1.810(10), B(7)-B(10') 2.063(10), B(8)-B(2') 1.804(9), B(8)-B(7') 1.910(9), B(10)-B(11) 1.897(10), B(7')-B(8') 1.940(11), B(8')-B(9') 1.806(14), and B(9')-B(10') 1.768(12), with other interboron distances between 1.754(10) and 1.892(8) Å for the {IrB₁₀} subcluster and between 1.721(11) and 1.824(12) Å for the {B₁₀} subcluster; B(11)-P(11) is 1.913(6) Å, and angles at P(11) are 105.6(3)-113.2(3)°. In this less intimately conjoined double-cluster structure (contrast with compound **1**, Figure 1), 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 3.274(7) Å; only two atoms, B(7) and B(8), are held in common between the two sub-clusters, and the angle Ir(9)B(8)B(2') is much more obtuse at 109.1(4)° than the otherwise corresponding acute Ir(9)B(8)B(12) angle in compound **1**.

Figure 3. ORTEP-type¹² drawing of $[(\eta^5\text{-C}_5\text{Me}_5)\text{HIrB}_{18}\text{H}_{19}\{\text{C}(\text{NHMe})_2\}]$ (compound **4**). Selected interatomic distances (Å) are Ir(9)-B(4) 2.170(4), Ir(9)-B(5) 2.178(5), Ir(9)-B(8) 2.203(4), Ir(9)-B(10) 2.234(4), Ir(9)-H(9) 1.6097, Ir(9)-C(C₅Me₅) 2.214(4)-2.254(4), B(7)-B(8) 1.890(5), B(7)-B(11) 1.885(5), B(7)-B(2') 1.823(5), B(7)-B(10') 2.038(6), B(8)-B(2') 1.776(5), B(8)-B(7') 1.871(6), B(10)-B(11) 1.917(6), B(7')-B(8') 1.934(6), B(8')-B(9') 1.797(7), and B(9')-B(10') 1.787(6), with other interboron distances between 1.726(6) and 1.823(6) Å for the {IrB₁₀} subcluster and between 1.706(6) and 1.809(6) Å for the {B₁₀} subcluster. As with compound **3** (Figure 2 above), the hydride unit on Ir(9) is *endo*-terminal, B(2')-H(2') is *exo*-terminal, and Ir(9)-B(2') is non-bonding, now at 3.189(4) Å; again, only two atoms, B(7) and B(8), are held in common between the two sub-clusters, and the angle Ir(9)B(8)B(2') is again obtuse, at 106.1(2)°. Within the carbene ligand, B(11)-C(111) is 1.583(5), C(111)-N(111) is 1.326(4) and C(111)-N(112) is 1.311(5), with N(111)-C(112) 1.455(5) and N(112)-C(113) 1.445(5) Å, with angles B(11)C(111)N(111) 123.2(3), B(11)C(111)N(112) 118.5(3) and N(111)C(111)N(112) 118.3(3)°.

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5. Single-crystal X-ray data: compound **3**, $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ $\text{C}_{18}\text{H}_{46}\text{B}_{18}\text{IrP}$: $M = 680.30$, triclinic (yellow block, $0.52 \times 0.35 \times 0.32$ mm, from $\text{CH}_2\text{Cl}_2 / \text{C}_6\text{H}_{14}$), Space Group $\bar{P}1$, $a = 10.2788(9)$, $b = 17.251(2)$, $c = 18.126(2)$ Å, $\alpha = 99.201(8)^\circ$, $\beta = 98.006(9)^\circ$, $\gamma = 90.678(8)^\circ$, $U = 3140.0(5)$ Å³, $D_{\text{calc}} = 1.439$ Mg m⁻³, $Z = 4$, Mo- K_α , $\lambda = 0.71073$ Å, $\mu = 4.314$ mm⁻¹, $T = 160(2)$ K, $R_1\{I > 2\sigma(I)\} = 0.0318$ and $wR_2 = 0.0692$ for all 10075 reflections collected, CCDC 233343; compound **4**, *syn*- $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}\{\text{C}(\text{NHMe})_2\}]$, $\text{C}_{13}\text{H}_{43}\text{B}_{18}\text{IrN}_2$: $M = 614.27$, monoclinic (yellow prism, $0.52 \times 0.38 \times 0.22$ mm, from $\text{CH}_2\text{Cl}_2 / \text{C}_6\text{H}_{14}$), Space Group $P2_1/n$, $a = 12.6547(2)$, $b = 11.4546(2)$, $c = 21.2777(4)$ Å, $\beta = 104.5570(11)^\circ$, $U = 2985.29(9)$ Å³, $D_{\text{calc}} = 1.367$ Mg m⁻³, $Z = 4$, Mo- K_α , $\lambda = 0.71073$ Å, $\mu = 4.480$ mm⁻¹, $T = 160(2)$ K, $R_1\{I > 2\sigma(I)\} = 0.0390$ and $wR_2 = 0.1132$ for all 27971 collected reflections, CCDC 165856. For both **3** and **4**, methods and programs were standard (G. M. Sheldrick, SHELXS86, Program for crystal structure solution, University of Göttingen, 1986; and SHELXL93, Program for crystal structure refinement, University of Göttingen, 1993).
6. Criteria of bulk purity and identity were clean NMR spectra consistent with the results of the X-ray diffraction analysis. In each case positive-ion mass spectrometry (EI, 70 eV) gave highest mass isotopomer envelopes corresponding to a mixture of M^+ and $(M - 2H)^+$, with principal fragmentations involving loss of PMe_2Ph (compound **3**) and loss of $\{\text{Me}\}$ and $\{\text{C}(\text{NHMe})_2\}$ (compound **4**). NMR data at 297-300K (CDCl_3), ordered as $\delta(^{11}\text{B})/\text{ppm}$ [$\delta(^1\text{H})/\text{ppm}$ of directly bound hydrogen atoms] (relative intensity): for $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ (compound **3**) - *ca.* +17.0 [+3.86] (1BH), +16.5 [+3.95] (1BH), +5.0 [no *exo* H] (1B), +2.9 [+3.25] (1BH), *ca.* +1.5 [+4.79] (1BH), *ca.* +0.7 [+3.01] (1BH), *ca.* -1.0 [+2.30] (1BH), -2.0 [+2.14] (1BH), -8.7 [+1.98] (1BH), *ca.* -10.8 [no *exo* H] (1B), *ca.* -11.7 [+1.97] (1BH), *ca.* -16.2 [+2.03] (1BH), *ca.* -16.8 [+2.11] (1BH), *ca.* -20.4 [no *exo* H, unresolved coupling $^1J(^{31}\text{P}\text{-}^{11}\text{B})$ *ca.* 150 Hz] (1B), *ca.* -21.7 [+0.15] (1BH), -25.3 [+1.74] (1BH), -29.4 [-1.24] (1BH), -40.0 [+0.07]

(1BH); additionally $\delta(^1\text{H})$ at +1.12, -1.02, -2.63 [unresolved doublet splitting $^2J(^{31}\text{P}-^1\text{H})$] and -2.89 ($4 \times \text{H}\mu$), at +2.06 (15H, C_5Me_5), at +1.98 (3H, PMe) and +1.94 (3H, PMe), and at -14.89 (1H, IrH), with $\delta(^{31}\text{P})$ -2.6 ppm [unresolved coupling $^1J(^{31}\text{P}-^{11}\text{B})$ ca. 150 Hz]; for $[(\eta^5\text{-C}_5\text{Me}_5)\text{HfIrB}_{18}\text{H}_{19}\{\text{C}(\text{NHMe})_2\}]$ (compound **4**) – ca. +6.0 [+3.81] (1BH), ca. +16.7 [+3.98] (1BH), +5.0 [no *exo* H] (1B), +2.0 [+3.22] (1BH), ca. +0.5 [+4.83] (1BH), ca. +0.1 [+3.01] (1BH), -2.2 [+2.31] (1BH), ca. -2.0 [+1.95] (1BH), -10.9 [+1.58] (1BH), -10.2 [no *exo* H] (1B), ca. -9.1 [+1.99] (1BH), ca. -17.5 [+2.00] (1BH), ca. -17.0 [+2.38] (1BH), -16.4 [no *exo* H] (1B), ca. -22.1 [+0.13] (1BH), -25.8 [+1.70] (1BH), -28.9 [-1.17] (1BH), -40.3 [+0.08] (1BH); additionally $\delta(^1\text{H})$ at +1.12, -1.04, -2.57 and -2.84 ($4 \times \text{H}\mu$), at +2.07 (15H, C_5Me_5), at +3.20 (3H, NMe) and +2.92 (3H, NMe), at +0.96 (1NH) and +0.88 (1NH) and at -14.93 (1H, IrH).

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Figure 1

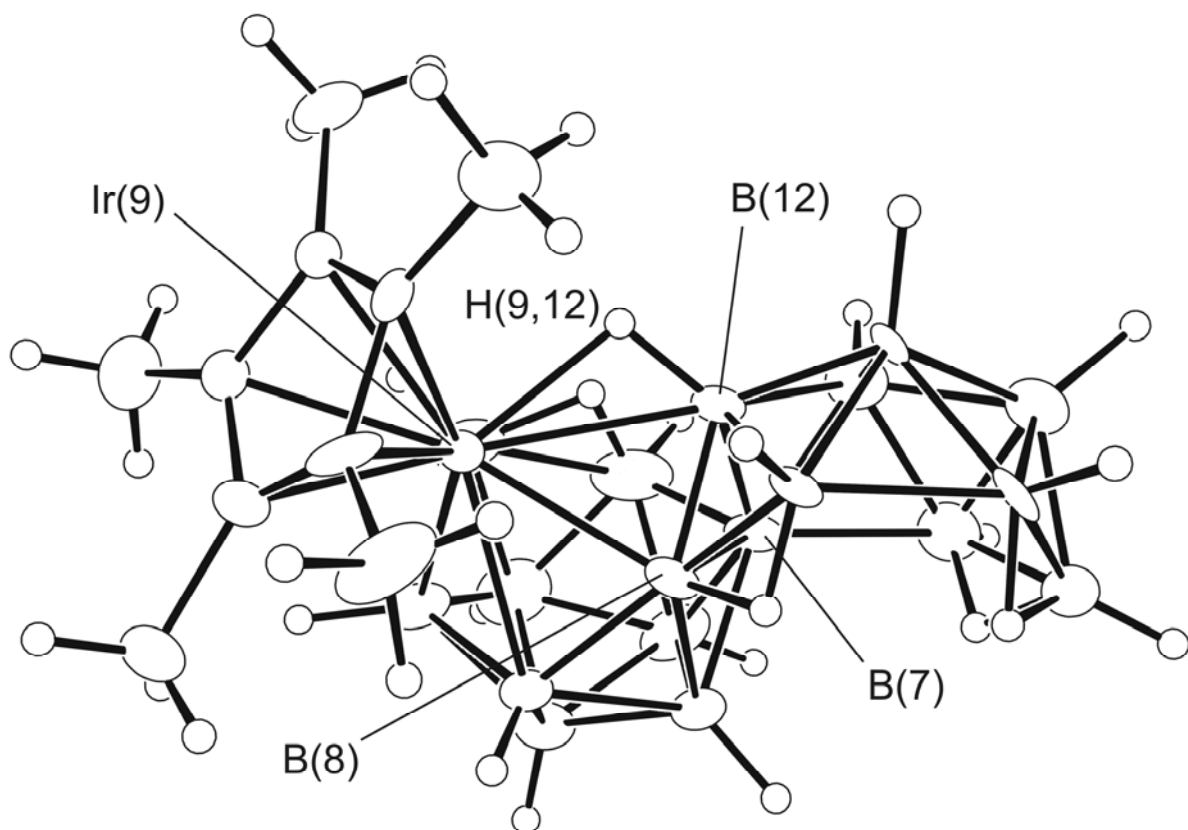


Figure 2

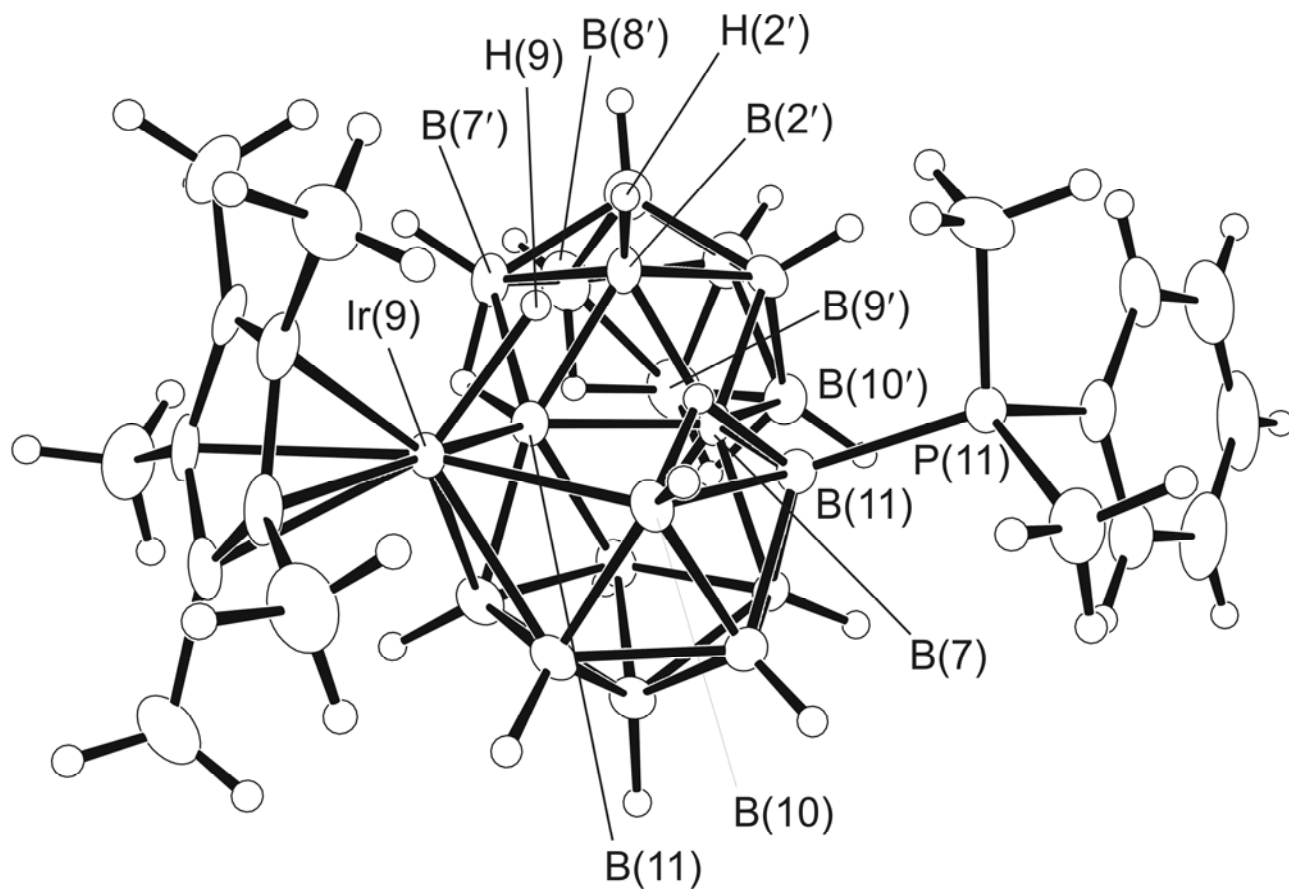
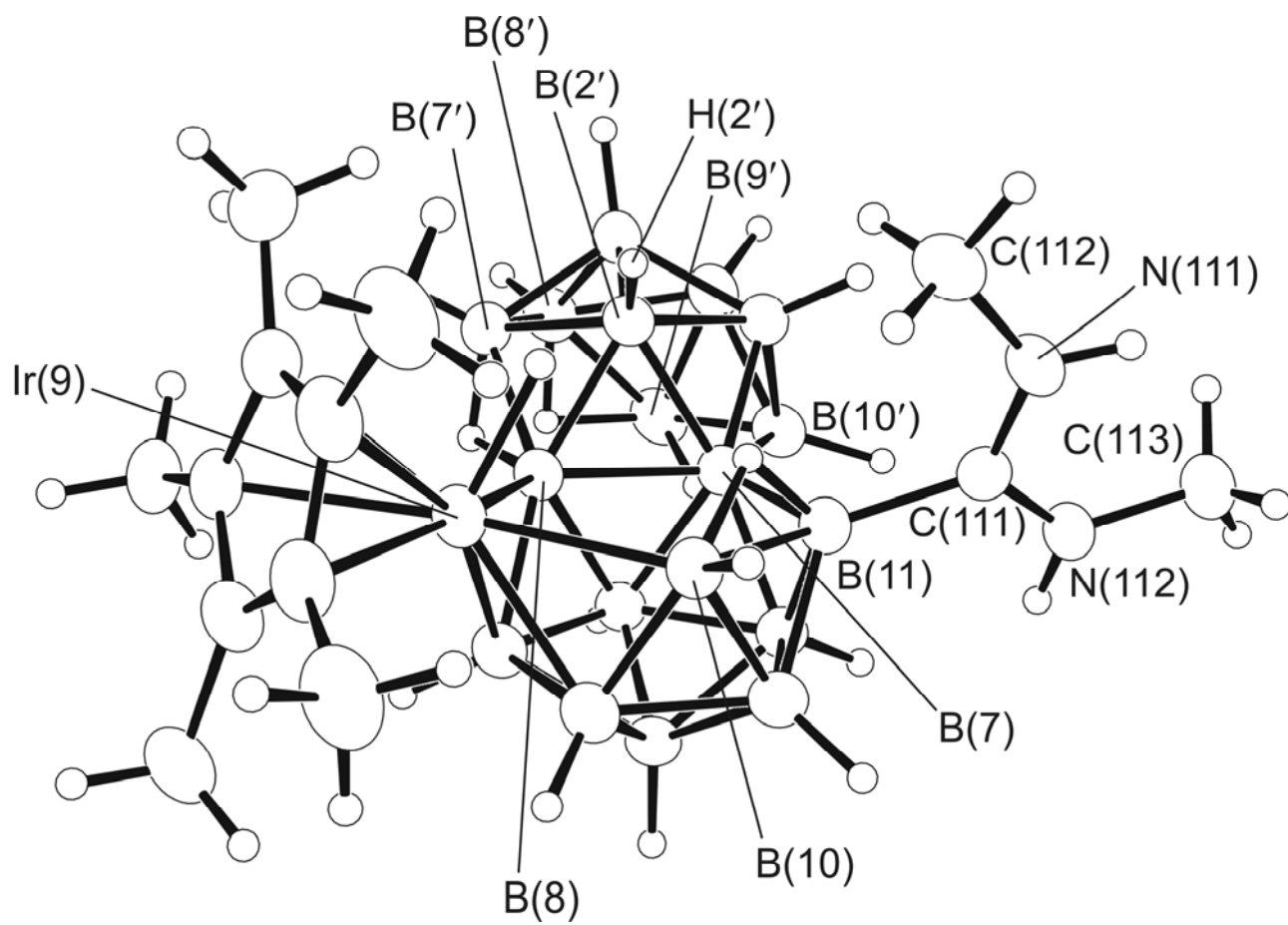


Figure 3



Suggestion for graphical abstract

Addition of PMe_2Ph to *nido-nido* fused-cluster *syn*- $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrB}_{18}\text{H}_{20}]$ gives $[(\eta^5\text{-C}_5\text{Me}_5)\text{H}\text{IrB}_{18}\text{H}_{19}(\text{PMe}_2\text{Ph})]$ with a diminution in the degree of intimacy of the intercluster fusion, rather than a retention of inter-subcluster binding intimacy and a *nido* \rightarrow *arachno* conversion of the character of either of the two subclusters.

