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A Novel Oxidative Insertion of a Metal Centre into a Degraded *closo*-borane cluster; Crystal and Molecular Structure of the Ten-vertex *iso-nido* Cluster $[\{IrC(OH)B_8H_6(OMe)\}(C_6H_4PPh_2)(PPh_3)]$

By Janet E. Crook, Norman N. Greenwood, John D. Kennedy, and Walter S. McDonald
(*Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds* LS2 9JT)

Summary The reaction of *trans*-$[Ir(CO)Cl(PPh_3)_2]$ with *closo*-$[B_{10}H_{10}]^{2-}$ in MeOH solution has been found to yield a number of novel structural types; one of these has been identified by single-crystal *X*-ray diffraction analysis as the ten-vertex *iso-nido*-iridacarbadecaborane $[\{IrC(OH)B_8H_6(OMe)\}(C_6H_4PPh_2)(PPh_3)]$.

It is known that the reaction of *closo*-$[B_{10}H_{10}]^{2-}$ with platinum complexes such as *cis*-$[Pt(PMe_2Ph)_2Cl_2]$ in the presence of EtOH–$CHCl_3$ proceeds stoicheiometrically and quantitatively to yield isomers of the ethoxy-*nido*-platinaundecaborane $[\{PtB_{10}H_{11})(OEt)\}(PMe_2Ph)_2]$.[1] We now report that reaction with the formally isoelectronic complex *trans*-$[Ir(CO)Cl(PPh_3)_2]$ yields a variety of novel species in addition to compounds tentatively identified as the analogous methoxy-*nido*-iridaundecaborane complexes.

When $[Ir(CO)Cl(PPh_3)_2]$ and $[NEt_3H]_2[B_{10}H_{10}]$ were heated in methanol solution under reflux for a few hours, several air-stable metallaborane products in individual isolable yields of up to *ca.* 8% were obtained. Those species which are covalent were separable by chromatography, and ^{31}P, ^{11}B, and ^{1}H n.m.r. spectroscopy indicate that they may be categorised into a number of structurally novel families. Of particular interest is a dark purple, thermally stable product (**1**), the detailed structure of which indicates a reaction sequence of intriguing complexity.

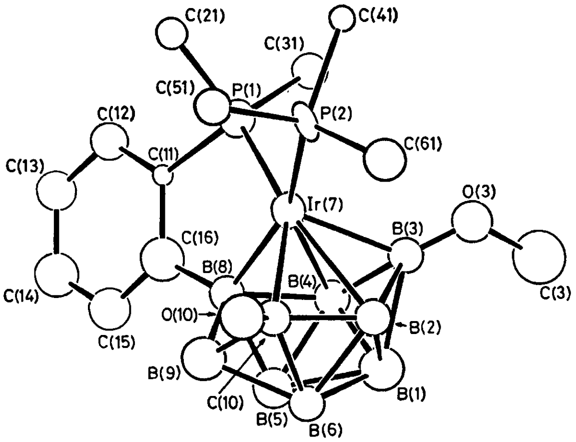

Figure 1. ORTEP drawing of $[\{IrC(OH)B_8H_6(OMe)\}(C_6H_4\text{-}PPh_2)(PPh_3)]$ (**1**) with *P*-phenyl carbon atoms other than the *ipso* ones omitted for clarity. Selected molecular dimensions are: from Ir(7) to B(2) 241(3), to B(3) 213(4), to B(4) 231(3), to B(8) 215(3), to B(9) 282(4), to C(10) 215(3), to P(1) 235·2(7), and to P(2) 236·4(6); from C(10) to B(2) 167(4), to B(6) 171(4), and to B(9) 170(5); from B(8) to B(4) 176(5), to B(5) 173(5), to B(9) 185(5), and to C(16) 160(4) pm.

The crystals of (**1**) are hexagonal, space group $P6_1$, with $a = 11{\cdot}145(2)$ and $c = 51{\cdot}944(12)$ Å. The structure, based on 4040 independent F_0 and refined to $R = 0{\cdot}077$, is shown in Figure 1.† H atoms were not locatable, but ^{11}B, $^{11}B\{^{1}H\}$, ^{1}H, and $^{1}H\{^{11}B\}$ n.m.r. spectroscopy showed that the

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

molecule contains eight unique boron environments, of which only six are bound to terminal H atoms, and that there are no iridium hydride or bridging H atoms in the molecule. The compound is diamagnetic, and this together with the shorter interatomic distances involving the cluster atom in the 10 position suggests that this 10 atom is carbon, reasonably derived from insertion of Ir-carbonyl into the cluster to form the *C*-hydroxy group [ν(OH) 3515 cm⁻¹], consistent with the formulation $[\{\mathrm{IrC(OH)}\overline{\mathrm{B_8H_6(OMe)\}(C}}\mathrm{{}_6H_4PPh_2)(PPh_3)}]$. Analytical data and high resolution mass spectrometry on the molecular ion are also consistent with this.

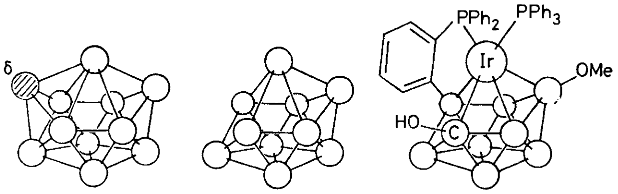

FIGURE 2. Structural relations of the *iso-nido* product to *closo*-B_{11}; alternative removal of the 6-connected vertex yields the more usual *nido*-B_{10} cluster as found, for example, in $B_{10}H_{14}$.

The compound (Figure 1) has a number of interesting features. Firstly, it has the unusual *iso-nido* ten-vertex cluster geometry derived formally from an eleven-vertex *closo* geometry by the removal of a 4-connected rather than the 6-connected vertex as indicated in Figure 2. Secondly, a novel *ortho*-cycloboronation of one of the P-phenyl groups to form an $\overline{\mathrm{IrPCCB}}$ ring has occurred. Thirdly, it is apparent that the moiety has undergone a rare *clusto*-boronation of the Ir-carbonyl ligand to form the hydroxycarba C(10) cluster vertex, the only precedent for which appears to be the formation of *closo*-$[\mathrm{Mo(B_{10}H_{10}COH)_2(CO)_4}]^-$ from $B_{10}H_{13}^-$ and $\mathrm{Mo(CO)_6}$ under ultraviolet irradiation.[2] Fourthly, the *nido* ten-1-vertex electron count requires the $\{\mathrm{Ir(PR_3)_2}\}$ vertex to contribute five electrons to the cluster bonding which implies a formal oxidation from iridium(I) to iridium(V) during the sequence of reactions: in accord with this, the cluster structure may also be regarded as a derivative of 7,8,9-trisubstituted *iso-arachno*-7-$\mathrm{CB_8H_{14}}$: *formal* removal of bridging and *endo*-terminal protons from *iso-arachno*-7-$\mathrm{CB_8H_{14}}$ results in the nine-vertex $\{7,4,8,5,9\text{-}\eta^5\text{-}arachno\text{-}7\text{-}\mathrm{CB_8H_9}\}^{5-}$ ligand and coordination of this to $\{\mathrm{Ir(PR_3)_2}\}^{5+}$ then gives the observed *iso-nido* ten-vertex geometry. The overall stoicheiometry of the preparative reaction can be represented as in equation (1). The mode of formation of the compound is also of interest, and present evidence indicates that it probably derives *via* methanolic deboronation of an initially formed methoxy-*nido*-iridaundecaborane cluster species, with the *ortho*-cycloboronation and *clusto*-boronation reactions occurring independently. Identification of the other species formed should give valuable information as to the precise ordering of these reactions.

$$\begin{aligned} &trans\text{-}[\mathrm{Ir(CO)Cl(PPh_3)_2}] + \mathrm{B_{10}H_{10}}^{2-} + 8\mathrm{MeOH} \rightarrow \\ &[\{\mathrm{IrC(OH)}\overline{\mathrm{B_8H_6(OMe)\}(C}}\mathrm{{}_6H_4PPh_2)(PPh_3)}] \\ &+ \mathrm{B(OMe)_3} + [\mathrm{B(OMe)_4}]^- + \mathrm{Cl}^- + 6\mathrm{H_2} \end{aligned} \tag{1}$$

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[2] P. A. Wegner, L. J. Guggenberger, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1970, **92**, 3473.