A Novel *exo*-Bicyclic *closo*-Six-vertex Dimetalla-hexaborane: $[1,1,2\text{-}(CO)_3\text{-}1\text{-}(PPh_3)\text{-}2,2\text{-}(Ph_2PC_6H_4)_2\text{-}\mathit{closo}\text{-}(1,2\text{-}Ir_2B_4H_2\text{-}3,5\text{-})].CH_2Cl_2$

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The molecular structure of the novel compound $[1,1,2\text{-}(CO)_3\text{-}1\text{-}(PPh_3)\text{-}2,2\text{-}(Ph_2P\text{-}\mathit{ortho}\text{-}C_6H_4)_2\text{-}\mathit{closo}\text{-}(1,2\text{-}Ir_2B_4H_2)]$, isolated as an advanced degradation product from the reaction of *closo*-$B_{10}H_{10}^{2-}$ with *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in methanolic solution, is based on a closed $\{Ir_2B_4\}$ octahedral cluster with the metal atoms occupying adjacent vertices.

We report here the molecular structure of the previously unknown compound $[1,1,2\text{-}(CO)_3\text{-}1\text{-}(PPh_3)\text{-}2,2\text{-}(Ph_2P\text{-}\mathit{ortho}\text{-}C_6H_4)_2\text{-}\mathit{closo}\text{-}(1,2\text{-}Ir_2B_4H_2)]$ isolated as yellow crystals which contain an equimolar amount of CH_2Cl_2. The compound exhibits a novel bis(*ortho*-cycloboronation) of two of the metal ligand *P*-phenyl groups associated with an unusual *closo*-six-vertex dimetallahexaborane cluster. Crystals were monoclinic, space group $P2_1/c$, with a = 1609.5(2), b = 2022.0(4), and c = 1712.6(3) pm, β = 105.83(1)°, Z = 4, and the structure (based on 6194 independent F_0 having $I > 2\sigma_I$, out of a total of 7176), was refined to R = 0.040. A drawing of the essential features of the molecular structure is in Figure 1.†

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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.

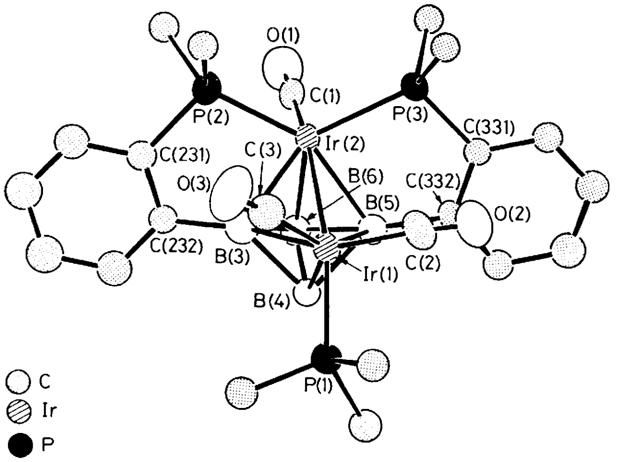

Figure 1. ORTEP drawing of the molecular structure of $[(CO)_3(PPh_3)(Ph_2P\overline{C_6H_4)_2(Ir_2B}_4H_2)]$ with the solvent of crystallization (CH_2Cl_2) and the *P*-phenyl groups (apart from their *ipso* C atoms) omitted, but with the *ortho*-cycloboronated *P*-phenylene groups retained. Cluster H atoms were not refined, but ^1H-$\{^{11}B\}$ n.m.r. spectroscopy (CD_2Cl_2 solution, + 21 °C) showed that there was an *exo*-terminal H atom associated with B(4) and one with B(6) $\{\delta(^1H)$ +8.13, $J[^{31}P(1)-^1H]$ 33 Hz and $\delta(^1H)$ +8.56, no apparent coupling [*i.e.* any $J(^{31}P-^1H) \leqslant$ *ca.* 5 Hz]$\}$ but no others. Peaks corresponding to these two H atom positions appeared on final difference maps. Selected interatomic distances are as follows: from Ir(1) to Ir(2) 279.9(1), B(3) 230.4(11), B(4) 219.7(10), and B(5) 223.7(11); from Ir(2) to B(3) 218.3(11), B(5) 218.7(10), and B(6) 219.0(10); from B(3) to C(232) 157.8(12), and from B(5) to C(332) 160.3(11) pm.

The structure is seen to be based on an idealized octahedral arrangement of the *closo*-$\{Ir_2B_4\}$ cluster. The two metal atoms occupy adjacent sites, and the disposition of the ligands shows that the idealized molecular symmetry is C_s. The *closo*-structure (*cf.* $B_6H_6^{2-}$) implies that each Ir atom contributes 3 electrons to the $\{Ir_2B_4\}$ cluster bonding and may therefore be regarded as an iridium(III) centre. The compound has important differences from the related cobalt(III) compound $[1,2\text{-}(\eta^5\text{-}C_5H_5)_2\text{-}(1,2\text{-}Co_2B_4H_6)]$:[1] this also has an octahedral *cis*-dimetalla disposition of atoms in the cluster, but each Co atom must, in addition, contribute one electron to $(\eta^5\text{-}C_5H_5)$–Co bonding. The additional two electrons therefore required for complete *closo*-cluster bonding are supplied by two additional H atoms. These are believed to take up face-bridging positions on the two deltahedral faces with the common Co–Co edge.

The iridium compound (Figure 1) exhibits an interesting double incidence of an *ortho*-cycloboronation of metal ligand *P*-phenyl groups. It was isolated ($\leqslant$ *ca.* 1% yield) as one of the numerous products of the reaction of the *closo*-$B_{10}H_{10}^{2-}$ anion with *trans*-$[Ir(CO)Cl(PPh_3)_2]$ in methanolic solution. An example of single *ortho*-cycloboronation has been observed previously in another product from this reaction.[2] Its repeated incidence now suggests that it may be of fundamental significance in this particular system, and also in others. Preliminary experiments suggest that this cycloboronation does not generally occur *via* straightforward elimination of dihydrogen from acyclic precursors. This leads to the idea that it may arise in the initial stages of the reaction. One important possibility is that such an initial interaction with the phenyl *ortho*-C–H might provide an additional cluster electron pair to facilitate opening of the *closo*-$B_{10}H_{10}^{2-}$ anion prior to its partial degradation. Currently experiments in our laboratories are being carried out in an attempt to test this hypothesis.

The overall reaction is known to give a variety of products which may be classified by n.m.r. spectroscopy into a number of structural families.[2] The reaction appears to proceed *via* the initial formation of more than one *nido*-ten-boron eleven-vertex metallaundecaborane species which may or may not exhibit *ortho*-cycloboronation. This is then followed by methanolic degradation to form initially *nido*-metallaboranes containing nine and then eight boron atoms in the clusters. From comparative n.m.r. spectroscopy further degradation products appear to include families of smaller *closo*-metallaborane cluster compounds (some containing more than one Ir atom). These smaller *closo* species together constitute about 12% of the reaction yield. The compound reported here is the first to be structurally defined. Its *immediately* related co-products (total yield *ca.* 7%) appear, from n.m.r. spectroscopy, to differ principally in the nature and disposition of ligands about the Ir–Ir feature in the $\{Ir_2B_4\}$ clusters, and in the extent and stereochemistry of *ortho*-cycloboronation of the ligand *P*-phenyl groups.

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