Quantitative *ortho*-Cycloboronation of *P*-Phenyl Groups in Metallaborane Chemistry and the Crystal and Molecular Structure of the Novel *iso*-*closo*-Ten-vertex Metallaborane

$[1,1,1\text{-}H(PPh_3)(Ph_2P\text{-}\mathit{ortho}\text{-}\overline{C_6H_4)\text{-}\mathit{iso}\text{-}\mathit{closo}\text{-}(1\text{-}IrB_9H_8\text{-}2}\text{-})]$

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High-yield *ortho*-cycloboronation reactions of *P*-phenyl groups on phosphine ligands in iridadecaboranes accompany both *nido* cluster expansion and *nido* → *closo* cluster closing processes that are associated with changes in the formal oxidation state of the metal atom;† one of the products has a novel *iso*-*closo*-ten-vertex iridium(v) metallaborane cluster structure of idealized C_{3v} symmetry ($IrB_3B_3B_3$).

Interestingly, the *ortho*-cycloboronation of the *P*-phenyl groups of metal ligands in iridaboranes has been observed in a number of species.[1] However, it does not seem to occur in general *via* straightforward dihydrogen elimination from the acyclic analogues.[2] Its mechanistic origins therefore have been unclear. We now report results which demonstrate its occurrence in essentially quantitative yield in two related reactions in ten-vertex iridadecaborane chemistry.

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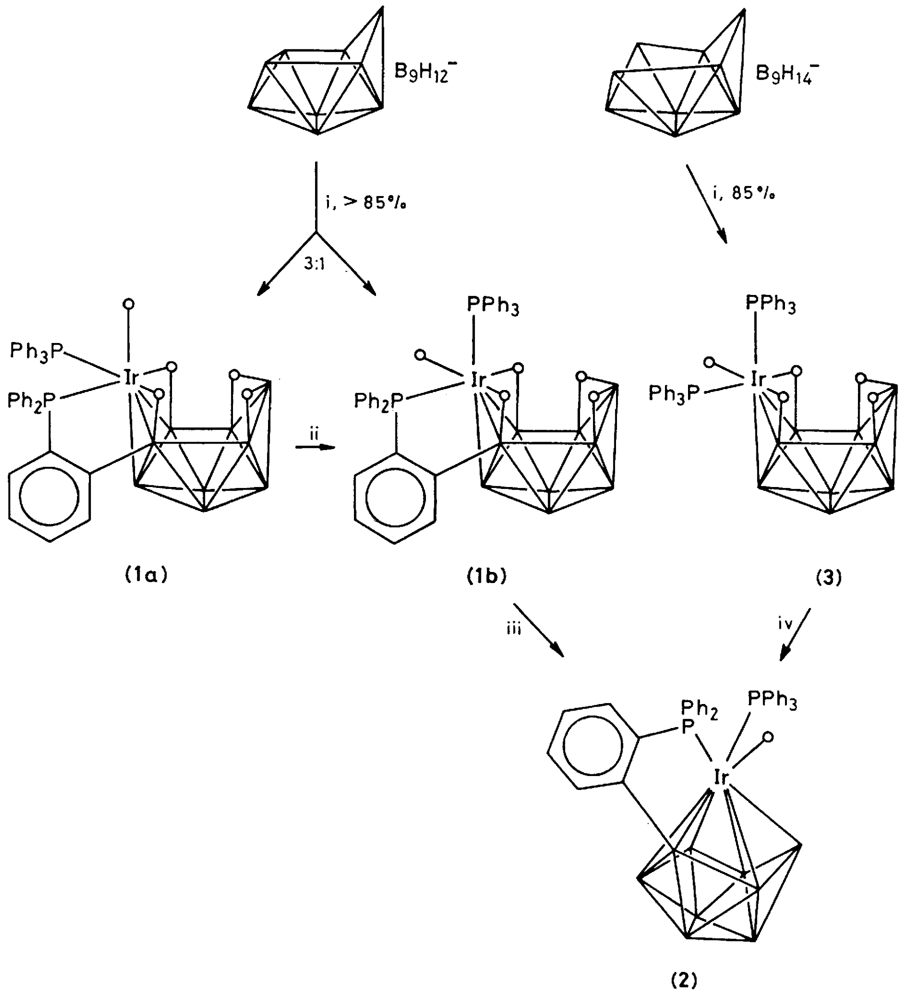
† For the definition of metal oxidation state in this context, see J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 346.



Scheme 1. *Reagents and conditions:* i, $[IrCl(PPh_3)_3]$, 20 °C; ii, 65 °C, 100%; iii, 85 °C, $-2H_2$, 100%; iv, 85 °C, $-3H_2$, 100%.

The reaction of the *nido*-anion $B_9H_{12}^-$ with the iridium(I) complex $[IrCl(PPh_3)_3]$ in CH_2Cl_2 solution at room temperature gives an 85% isolated yield of the yellow *ortho*-cycloboronated *nido*-iridium(III) compound $[6,6,6\text{-}H(PPh_3)(Ph_2PC_6H_4)(6\text{-}IrB_9H_{12}\text{-}5\text{-})]$ (**1**). The formulation was established by single and multiple resonance n.m.r. spectroscopy. Two isomers, (**1a**) and (**1b**) are formed which differ in the disposition of ligands about the Ir atom (Scheme 1). The more labile of these can be converted to the more stable form by mild thermolysis (*ca.* 65 °C). The clean reaction, its exact stoicheiometry (equation 1), and the high yield suggest that a

$$[IrCl(PPh_3)_3] + B_9H_{12}^- \longrightarrow$$

$$\underset{(\mathbf{1})}{[(Ph_3P)(Ph_2PC_6H_4)(HIrB_9H_{12})]} + PPh_3 + Cl^- \quad (1)$$

driving force for the *ortho*-cycloboronation in this case is the provision of two additional electrons required for the stable *nido*-ten-vertex structure. In this it is similar to 'oxidative addition' at transition metal centres. The additive cycloboronation involving the incipient metallaborane cluster may therefore contribute indirectly to the conversion of iridium(I) to iridium(III).

Slightly stronger thermolysis (*ca.* 85 °C) of the cyclic *nido*-species (**1b**) [and also (**1a**) as this converts to (**1b**) at *ca.* 65 °C] results in the loss of dihydrogen to give quantitatively the novel bright orange-yellow cyclic *iso-closo*-compound $[1,1,1\text{-}H(PPh_3)(Ph_2PC_6H_4)(1\text{-}IrB_9H_8\text{-}2\text{-})]$ (**2**). The structure of this was established by single crystal *X*-ray diffraction analysis (Figure 1). Crystals are monoclinic, space group $P2_1/c$, with $a = 1366.0(3)$, $b = 1906.2(4)$, $c = 1429.1(3)$ pm, $\beta = 103.71(2)°$. The final R for 3728 independent F_o was 0.037.‡ In this compound the $\{IrB_9\}$ cluster is a ten-vertex closed deltahedron having the previously unobserved idealized C_{3v} symmetry. A formal *closo*-cluster electron count then requires that the Ir centre contribute 4 electrons to the cluster bonding. This together with the Ir–H terminal bond indicates that the compound can be regarded as an iridium(V) species.

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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.

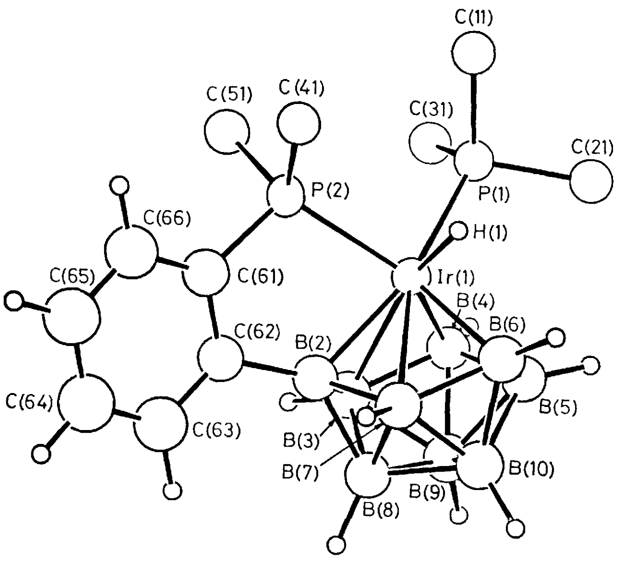

Figure 1. ORTEP drawing of the molecular structure of $[(PPh_3)(Ph_2PC_6H_4)(HIrB_9H_8)]$ **(2)** with *P*-phenyl groups omitted for clarity. All H atoms were located. Selected distances are Ir(1) to B(2), B(4), and B(6) of 216.3(9), 218.8(9), and 214.8(9) pm respectively, and Ir(1) to B(3), B(5), and B(7) of 246.0(9), 238.8(10), and 237.8(9) pm, respectively. In addition Ir(1) to P(1), P(2), and H(1) are 238.6(2), 239.9(2), and 157(8) pm, and B(2)–C(62) is 159.2(11) pm. (The distances B(2)–B(4), B(4)–B(6), and B(6)–B(2) of 295—301 pm are all clearly non-bonding.) Note that the P(1), P(2), and H(1) ligands eclipse the nearer B atoms B(2), B(4), and B(6), presumably owing to the rotational constraint arising from the fixed position of the *ortho*-cycloboronated *P*-phenylene link. The acyclic trimethylphosphine analogue $[(PMe_3)_2(HIrB_9H_9)]$ is fluxional with a very low activation energy. The novel *iso-closo*-cluster clearly differs in the distribution of connectivities from that normally found in *closo*-ten-vertex systems (exemplar $B_{10}H_{10}{}^{2-}$).

Interestingly, the *acyclic* analogue of the cyclic *nido*-compound **(1)**, *viz.* $[6,6,6\text{-}H(PPh_3)_2(6\text{-}IrB_9H_{13})]$ **(3)**[3] also gives the cyclic *iso-closo*-species **(2)** quantitatively upon mild thermolysis (*ca.* 85 °C) (equation 2). In this instance it is not

$$[(PPh_3)_2(HIrB_9H_{13})] \longrightarrow$$

$$\textbf{(3)} \qquad [(Ph_3P)(Ph_2PC_6H_4)(HIrB_9H_8)] + 3H_2 \qquad (2)$$

$$\textbf{(2)}$$

possible to distinguish whether an initial cyclisation to give **(1)** precedes the cluster closure, or whether the cyclisation and cluster closure are concerted. However, it is of interest that the overall cyclisation of equation (2) is associated with a *nido*→*closo* cluster *closure*. This contrasts with that of equation (1) in which it is associated with a *nido*-nine-vertex→*nido*-ten-vertex cluster expansion. It may be significant however that the cyclisation is again associated with the formal oxidation of the iridium centre, this time from iridium(III) to iridium(V).

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References

1 J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1981, 933; and 1982, 383.

2 J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, unpublished observations; paper in preparation for submission to *J. Chem. Soc., Dalton Trans.*

3 S. K. Boocock, J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 1982, in the press.