B-Frame Supported Heterobimetallic Species; Molecular Structure of $[(Me_3P)_2Pt(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_{10}]$†

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The new heterobimetallic 'B-frame' compound $[(Me_3P)_2Pt(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_{10}]$† has been prepared in a systematic synthesis in an overall yield of 40% from *nido*-decaborane, and has been structurally characterised by single-crystal *X*-ray diffraction analysis.

There is great current interest in both strongly and weakly coupled bimetallic and polymetallic systems supported on a variety of molecular matrices. We now draw attention to the fact that high-yield routes to *nido*-monometallapolyborane species from easily attainable starting materials permit in turn their ready use as substrates for the addition of further metals in *planned syntheses* to form compounds which have different types of metal centres supported on a borane-cluster, or B-frame matrix. This is exemplified by the synthesis in encouraging yield (50%, as yet unoptimised) of the platina-iridaundecaborane $[7,7\text{-}(Me_3P)_2\text{-}9\text{-}(Ph_3P)\text{-}9\text{-}(Ph_2P\text{-}2'\text{-}C_6H_4)\text{-}9\text{-}H\text{-}nido\text{-}7,9\text{-}PtIrB_9H_{10}\text{-}4]$, compound (**1**), for which we report the molecular structure obtained by single-crystal *X*-ray diffraction analysis (Figure 1 and Table 1).

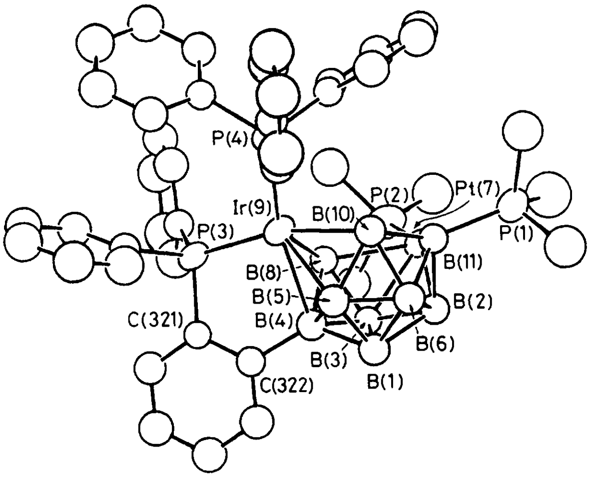

Figure 1. ORTEP drawing of the molecular structure of the compound *nido*-$[(Me_3P)_2Pt(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_{10}]$ (**1**). Hydrogen atoms were not located by *X*-ray diffraction, but n.m.r. spectroscopy shows that (a) each boron atom except B(4) has one *exo*-terminal H atom bound to it, (b) there is a bridging H atom in each of the Ir(9)B(8) and B(10)B(11) positions, and (c) there is an *exo*-terminal H atom on iridium approximately *trans* to the Ir(9)–H–B(8) hydrogen atom and *cis* to P(3) and P(4). Distances from Ir(9) to B(4), B(5), B(8), and B(10) are 232.1(15), 223.4(16), 232.5(15), and 233.8(17) pm respectively, to P(3) 230.9(3), and to P(4) 230.7(3) pm. Distances from Pt(7) to B(2), B(3), B(8), and B(11) are 223.0(16), 223.5(16), 234.5(15), and 231.5(16) pm respectively, and to P(1) and P(2), 232.8(4) and 233.4(4) respectively. From B(4) to C(322) is 162.8(18) pm.

The starting iridadecaborane $[6\text{-}(Ph_3P)\text{-}6\text{-}(Ph_2P\text{-}2'\text{-}C_6H_4)\text{-}6\text{-}H\text{-}nido\text{-}6\text{-}IrB_9H_{12}\text{-}5]$ (**2**) may be prepared in almost quantitative yield from the reaction of $[IrCl(PPh_3)_3]$ with *nido*-$B_9H_{12}^-$ followed by isomerisation at 65 °C.[1] Treatment of this with KH as base followed by addition of *cis*-$[PtCl_2(PMe_3)_2]$ leads to the isolation of the orange-red, air-stable platinairidaundecaborane species (**1**) (equation 1). The reaction is very similar to that undergone by *nido*-decaborane itself, compound (**3**), to give the corresponding *nido*-7-platinaundecaborane, compound (**4**), in the similar yield of 57% (equation 2).[2]

The structure of compound (**1**) is seen to be that of a *nido* eleven-vertex cluster with metal atoms in non-adjacent positions on the open face; as such it is the first *nido* eleven-vertex dimetallaborane cluster to be characterized. Other particularly interesting features include the similarity of the two metal-to-borane bonding environments, indicating similar iridium(III)- and platinum(IV)-type three-orbital contributions to cluster bonding, and the effective isomerization of the starting ten-vertex 6-iridadecaboranyl cluster to the 5-iridadecaboranyl configuration during the course of the reaction.

This last type of cluster rearrangement is now emerging as an apparently general feature of ten- and eleven-vertex boron cluster chemistry.[3] In the present example, the *ortho*-phenylene link plays an important role as a 'marker' in this system since it effectively links together two vertices of the cluster and thereby limits (and identifies) the routes by which the cluster may isomerise, thereby providing mechanistic information. The

Table 1. Crystal data for *nido*-$[(Me_3P)_2Pt(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_{10}]$ compound (**1**) and *nido*-$[(Ph_3P)(Ph_2PC_6H_4)HIrB_9H_{12}]$ compound (**5**).[a,b]

	(1)	(5)
a/pm	4072.1(8)	1254.4(3)
b/pm	1509.2(4)	1524.6(4)
c/pm	1912.9(4)	1091.7(2)
α/°	90.0	97.69(2)
β/°	110.63(2)	115.09(2)
γ/°	90.0	88.80(2)
Space group	$C2/c$	$P\bar{1}$
Z	8	2
No. of F_o [with $I > 2\sigma(I)$]	5641	4638
$\mu(\text{Mo-}K_\alpha)$/mm^{-1}	5.314	3.660
Final R	0.047	0.037

[a] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. [b] The data were collected in the range 4° < 2θ <45°.

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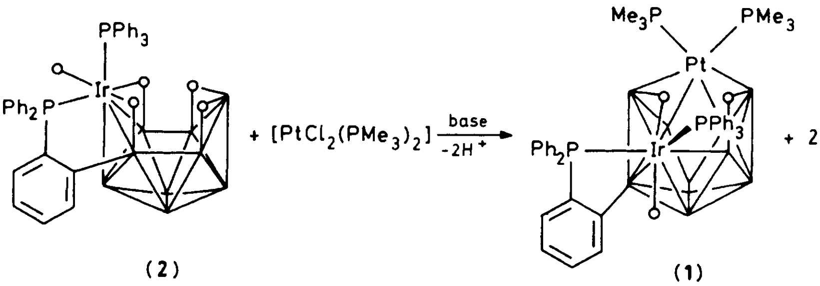
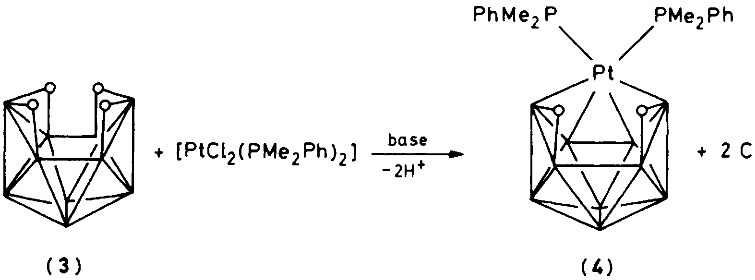
† 7,7-Bistrimethylphosphine-4-[2-(diphenylphosphino)phenyl(*P*–*Ir*)]-9,9-hydrido-triphenylphosphine-*nido*-7-platina-9-iridaundecaborane.



(1)



(2)

o = H

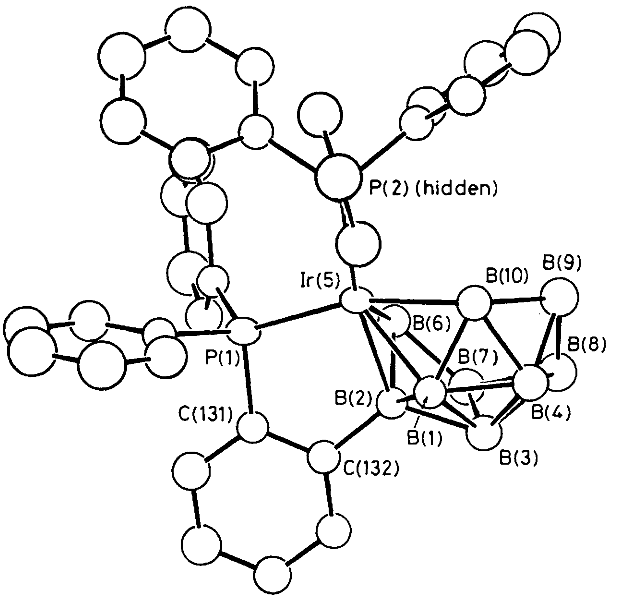


Figure 2. ORTEP drawing of the molecular structure of the compound *nido*-[(Ph_3P)($Ph_2PC_6H_4$)$HIrB_9H_{12}$] (**5**). Hydrogen atoms were not located by *X*-ray diffraction, but n.m.r. spectroscopy shows that (a) each boron atom except B(2) has one *exo*-terminal H atom bound to it, (b) there is a bridging H atom in each of the Ir(5)B(6), B(6)B(7), B(8)B(9), and B(9)B(10) positions, and (c) there is an *exo*-terminal H atom on iridium approximately *trans* to the Ir(5)–B(6) bridging H atom, and *cis* to both P(1) and P(2). The projection is chosen to emphasize the similarity to compound (**1**) (Figure 1) and P(2) is thereby fortuitously hidden behind the *ipso* and *para* C atoms of one of the P(2) phenyl groups. Selected distances are: from Ir(5) to B(1) 222.7(9), to B(2) 225.0(9), to B(6) 224.5(9), to B(10) 234.0(10), to P(1) 231.6(2), and to P(2) 230.8(2) pm. B(2) to C(132) is 161.4(10) pm. The B(7)–B(8) distance of 198.7(14) pm is longer than the corresponding bond B(2)–B(3) of 186.1(22) pm in the {$PtIrB_9$} compound (**1**).

parent 5-iridadecaborane [5-(Ph_3P)-5-(Ph_2P-2′-C_6H_4)-5-H-*nido*-5-IrB_9H_{12}-2] (**5**) which is often present as a by-product in the initial synthesis of compound (**1**), has an almost identical overall gross molecular configuration to that of the platinated species (Figure 2 and Table 1), although there are important differences in detailed dimensions.

The systematic stepwise synthesis of the dimetallaundecaborane in an overall yield of *ca.* 40% from the readily available $B_{10}H_{14}$ contrasts with the isolation of most polymetallaborane clusters which are usually obtained randomly in excruciatingly small yields in somewhat serendipitous circumstances.[4] Specific planned syntheses of compounds such as the one described here, which have two or more adjacent, or otherwise close, metal centres on the reactive metallaborane open face, have important chemical potentialities in a number of areas, particularly when associated with the *arachno* ⟷ *nido* ⟷ *closo* two-electron redox capabilities of the clusters themselves.[5]

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