A Unique Acetylene-induced Reductive $PPh_3 \rightarrow PH_3$ Stripping of Phenyl Groups from Triphenylphosphine Ligands Bound to a Metallaborane 'B-Frame' Matrix

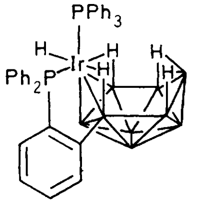
Jonathan Bould,[a,b] Paul Brint,[a] Xavier L. R. Fontaine,[b] John D. Kennedy,[b] and Mark Thornton-Pett[b]

[a] *Department of Chemistry, University College, Cork, Eire*
[b] *School of Chemistry, University of Leeds, Leeds LS2 9JT, U.K.*

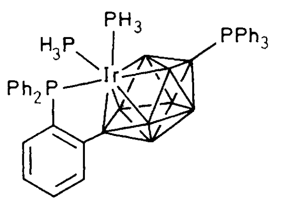
Passage of acetylene through a refluxing solution of [6,6,6-$(PPh_3)(Ph_2P$-*o*-$C_6H_4)H$-*nido*-6-IrB_9H_{12}-5] in benzene results in cluster condensation to yield air-stable pale yellow [10-(PPh_3)-2,2,2-$(PH_3)_2(Ph_2P$-*o*-$C_6H_4)$-*closo*-2-IrB_9H_7-1] (yield 47% based on Ir; 95% based on P) which exhibits two Ir-bound PH_3 ligands arising from the reductive $PPh_3 \rightarrow PH_3$ stripping of phenyl groups from the Ir-bound PPh_3 ligands of the starting complex.

We report preliminary findings on a reaction that occurs when acetylene is passed through a boiling solution of [6,6,6-$(PPh_3)(Ph_2P$-*o*-$C_6H_4)H$-*nido*-6-IrB_9H_{12}-5][1,2] [compound (**1**); schematic structure (**I**)] in benzene for 20 h. Chromatography of the product mixture in air (reaction scale 50 μmol) resulted in the recovery of unreacted (**1**) (12%) and the isolation of the principal metallaborane product as air-stable pale yellow [10-(PPh_3)-2,2,2-$(PH_3)_2(Ph_2P$-*o*-$C_6H_4)$-*closo*-2-IrB_9H_7-1], compound (**2**). The yield was 47% based on iridium content of unrecovered compound (**1**) [94% based on phosphorus content since compound (**1**) has two phosphine ligands, whereas compound (**2**) has four phosphine ligands]. Compound (**2**) was identified by single-crystal *X*-ray diffraction analysis† and NMR spectroscopy.‡

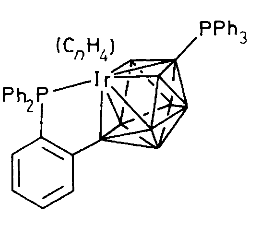
Compound (**2**) has a straightforward Williams–Wade[4] ten-vertex *closo*-2-metalladecaborane cluster structure [Figure 1 and schematic structure (**II**)]. The noteworthy feature is the incidence of two equivalent unsubstituted (PH_3) phosphine ligands, instead of two triphenylphosphine ligands, on the metal atom, a remarkable occurrence in view of the high yield [94% based on the phosphorus content of starting compound (**1**)] and mild conditions of the reaction. Examples of structurally characterised compounds with metal-bound PH_3 ligands are rare in themselves, being limited, as far as we are aware, to four chromium complexes $[Cr(CO)_n(PH_3)_{6-n}]$ (where $n = 2,3,4,5$),[5] one niobium complex,[6] one manganese complex,[7] and the iridium complex[8] *mer*-[(PH_3)-*trans*-(PPr^i_3)$_2$IrH-*trans*-Cl_2].



(**I**) (**1**)



(**II**) (**2**)



(**III**) (**3**)

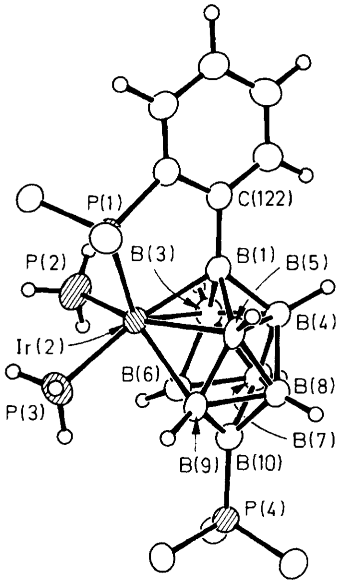


Figure 1. Drawing of the molecular structure of [10-(PPh_3)-2,2,2-(PH_3)$_2$(Ph_2P-*o*-C_6H_4)-*closo*-2-IrB_9H_7-1], compound (**2**), with P-phenyl group atoms [except for the *ipso* carbon ones, on P(1) and P(4)] omitted for clarity. P(2) and P(3) are the phosphorus atoms of the PH_3 ligands, P(4) is that of the PPh_3 ligand, and P(1) is that of the {Ph_2P-*o*-C_6H_4} moiety. Distances (pm): Ir(2) to P(1) 231.5(3), P(2) 227.6(4), P(3) 231.9(4), B(1) 211.6(8), B(3) 229.1(8), B(5) 234.7(7), B(6) 227.3(8), and B(9) 231.2(8). B(10)–P(4) 188.7(8) and B(1)–C(122) 160.7(9). Nearest neighbour interboron distances are in the range 168.7(10)—186.4(11) pm, except B(6)–B(9) at 204.9(11), which suggests some *isonido* cluster character. Bond angles (°) P(1)–Ir(2)–P(3) 97.0(2), P(1)–Ir(2)–P(2) 93.1(2), and P(2)–Ir(2)–P(3) 90.2(2).

The role of the acetylene, and the fate of the phenyl entities together with that of the residual [IrB_9] unit, are not yet known. However, NMR spectroscopy and mass spectrometry‡ indicate that a bright red metallaborane by-product (*ca.* 5% yield) may well be a benzyne- or butadiene-type complex of formulation [1,1-(C_nH_4)($Ph_2PC_6H_4$)-*isocloso*-1-IrB_9H_7-6-(PPh_3)-2] [n = 4 or 6, compound (**3**); schematic structure(**III**)]. The precise nature of the C_nH_4 unit, the nature of binding to the metal atom in compound (**3**), and whether its origin is in a cleaved phenyl group, in acetylene oligomerisation, or in benzene solvent, are not yet established. Compound (**3**) is somewhat less air-stable than compound (**2**).§

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† *Crystal data* for $C_{36}H_{42}B_9IrP_4$: M = 888.14, monoclinic, a = 1334.1(2), b = 1798.9(3), c = 1646.2(2) pm, β = 97.86(1)°, U = 3.9136(10) nm^3, Z = 4, space group $P2_1/c$, D_c = 1.51 Mg m^{-3}, μ = 50.77 cm^{-1}, $F(000)$ = 1913.71, $R(R_W)$ = 0.0337(0.0342) for refinement of 5703 unique absorption corrected reflections with $I > 2.0\sigma(I)$ and $4.0 < 2\theta < 50.0°$.

All crystallographic measurements were made on a Nicolet P3/F diffractometer operating in the ω scan mode using graphite monochromated *X*-ray radiation. The structure was determined *via* standard heavy-atom methods and refined by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl and PH_3 hydrogen atoms were included in calculated positions and assigned to an overall isotropic thermal parameter. The borane hydrogen atoms were located in a Fourier difference synthesis and were refined with isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + 0.0004\,(F_o)^2]^{-1}$ was used at the end of refinement. Atomic co-ordinates, interatomic distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ *NMR data* for compound (**2**):. (CD_2Cl_2, 294—297 K): BX and BH groups {ordered as: tentative assignment $\delta(^{11}B)$/p.p.m. [$\delta(^1H)$/p.p.m.]}: B(1) +53.8 (*ortho*-cyclophenylated position), BH(4) −6.0 [+3.17], BH(6,9) −10.2 [+2.16, some doublet structure, splitting (?^{31}P) 19 Hz], B(10) −11.6 [PPh_3-bound position, doublet $^1J(^{31}P{-}^{11}B)$ *ca.* 200 Hz], BH(7,8) −26.2 [−0.13], and BH(3,5) −27.2 [−0.47, some doublet structure, splitting (?^{31}P) 12 Hz]; $\delta(^{31}P_{Ir})_x$ −143.7 (2P), $\delta(^{31}P_{Ir})_y$ +23.1 (1P) [$^2J(^{31}P{-}^{31}P)_{xy}$ 29 Hz], and $\delta(^{31}P_B)$ *ca.* +17 (broad); aromatics exhibit *ortho*-cycloboronation feature[2] at $\delta(^1H)$ +8.37 (apparent doublet splitting *ca.* 8 Hz); $\delta(^1H)(PH_3)$ +3.08, basic $[AX_3]_2$ (A = ^{31}P, X = ^1H) pattern, $N(= {}^1J + {}^3J)(^{31}P_{Ir}{-}^1H)_x$ 372.2 Hz, with additional splitting $^3J(^{31}P_{Ir}{-}^1H)_y$ 9.6 Hz and with additional contributions from couplings to cluster ^{11}B and ^1H nuclei in some of the subsidiary lines centred at $\nu(^1H) \pm$ *ca.* 353 Hz.

For compound (**3**) (CD_2Cl_2, 294—297 K except for ^{31}P data, measured at 222 K) BX and BH groups {ordered as: assignment $\delta(^{11}B)$/p.p.m. [$\delta(^1H)$/p.p.m.]}: BH(3,4) +84.7 [+9.95], BH(5,7) −13.4 [+0.62], B(6) −20.6 [PPh_3-bound position, doublet structure $^1J(^{31}P{-}^{11}B)$ 134 Hz], BH(8) +20.2 [+5.28], and BH(9,10) +21.7 [+4.78]; $\delta(^{31}P_{Ir})$ +34.7 {2P, doublet structure, splitting *ca.* 6 Hz [?$^4J(^{31}P_{Ir}{-}^{31}P_B)$]} and $\delta(^{31}P_B)$ +3.3 (1P, broad); aromatics at $\delta(^1H)$ +7.25—7.60 with additional *ortho*-cycloboronation features[2] at +7.08 (2H) {apparent triplet splitting *ca.* 7.5 Hz, with doublet splitting [$J(^{31}P_{Ir}{-}^1H)$ 1.6 Hz] plus additional very fine structure}, and at +8.00 (1H) {apparent doublet splitting *ca.* 7.4 Hz with additional fine doublet splitting [$J(^{31}P_{Ir}{-}^1H)$ 0.8 Hz]}; $\delta(^1H)(IrC_nH_4)$ an $[AX]_2$ pattern centred at +5.68 (2H) and +6.61 (2H) p.p.m., each with superposed doublet splitting, arising from $J(^{31}P_{Ir}{-}^1H)$ 1.5 and 4.0 Hz, respectively. Mass spectrometry (70 eV, EI) gave m/z (max) 898 which would correspond to $[(C_4H_4)^{193}Ir(Ph_2PC_6H_4){-}\,^{11}B_9H_7(PPh_3)]$.

§ *Note added in proof* (October 1989): preliminary results from a single-crystal *X*-ray diffraction analysis now indicate that n = 4 in compound (**3**), and that the C_4H_4 moiety is bound to the iridium atom in a manner that results in a five-membered iridacyclopentadiene (IrC_4H_4) ring.

The reductive cleavage of the six phenyl groups from the two triphenylphosphine ligands under the conditions of the reaction is remarkable, and does not occur when a benzene solution of the *nido* starting material (**1**) is boiled on its own,[1,3] or when ethylene or carbon monoxide is passed instead of acetylene. We are currently devising experiments to explore further the potentialities that these results suggest, and to determine the fate of the hydrocarbon residues that are eliminated in the formation of compound (**2**).

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