An Unexpected Cluster Rearrangement in the Formation of a *closo*-Carbametallaborane from an *arachno*-Carbaborane. The Crystal and Molecular Structure of [1-(PPh_3)-2-H-2,2-(PPh_3)$_2$-2,10-$IrCB_8H_8$]

Nathaniel W. Alcock, John G. Taylor, and Malcolm G. H. Wallbridge*

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL, U.K.

A novel *closo*-iridium(III) complex, [1-(PPh_3)-2-H-2,2-(PPh_3)$_2$-2,10-$IrCB_8H_8$], has been isolated as one of several products from the reaction of [$IrCl(PPh_3)_3$] with the *arachno*-[CB_8H_{13}]$^-$ anion; the position of the cluster carbon atom indicates the process by which the cage rearrangement occurs.

In spite of the many reports of insertion of metal atoms into borane/carborane cages, there is very little information available on the nature of the cage rearrangements involved.[1] We now report an example of a direct and unusual rearrangement of an *arachno*-nine vertex (CB_8) cluster during its conversion to a *closo*-ten vertex (CB_8Ir) cluster under moderate conditions; a phosphine ligand is transferred from the metal to the cage to complete the 22-electron count required for a *closo*-structure,[2] and the presence and position of a single carbon atom in the cage indicates the rearrangement pathway involved.

The reaction of Li[CB_8H_{13}] (**1**) (prepared from *arachno*-CB_8H_{14}[3]) with [$IrCl(PPh_3)_3$] in diethyl ether (20 °C, 6 days) yields several products, including the yellow title compound (**2**), which was isolated (yield *ca.* 10%) by preparative t.l.c. An *X*-ray diffraction study of (**2**) (Figure 1)[†] shows the ten-vertex cage to have bicapped Archimedean square antiprismatic geometry, with the metal in an equatorial position. The apical sites are occupied by the carbon, and a boron covalently bonded to the phosphorus of a triphenylphosphine ligand. As expected for this structure, the $^{11}B\{^1H\}$ n.m.r. spectrum shows a 1:1:2:2:2 peak intensity ratio with the low field resonance split into a doublet [$^1J(^{11}B–^{31}P)$ 173 Hz], assignable to the apical boron atom. The $^1H\{^{11}B\}$ n.m.r. spectrum indicates that a terminal hydride is associated with each of the equatorial boron atoms and integration confirms that a singlet at 5.06 p.p.m. (relative to Me_4Si) and a quartet at −4.36 p.p.m. are due to C–H and Ir–H protons respectively. Selective decoupling of the metal co-ordinated phosphorus nuclei, and the cage bonded phosphorus, reduces the Ir–H quartet to a doublet [$^3J(^1H–^{31}P)$ 25 Hz], and a triplet [$^2J(^1H–^{31}P)$ 12 Hz], respectively. Therefore, in addition to the expected coupling of the iridium hydride to equivalent *cis*-phosphorus nuclei, there is an unexpectedly large coupling to the unique phosphorus atom on the apical boron. Such couplings have also been observed in related systems containing iridium hydride fragments bonded into boron frameworks.[4] We have been unable to detect any absorption associated with the Ir–H bond in the i.r. spectrum, and at present it is not clear whether there is any substantial Ir–H–B bridge bonding involved. Preliminary results of a ^{11}B COSY (*J*-correlated spectroscopy) 2-dimensional study[5] of the anion [CB_8H_{13}]$^-$ indicate that the original *arachno*-CB_8H_{14} structure is maintained on deprotonation, and therefore cage rearrangement prior to oxidative addition to the metal can be discounted.

It is reasonable to postulate that a *nido*-iridum(III) complex [(**3**), M = $IrH(PPh_3)_2$] (see Scheme 1) is an intermediate in the reaction, in view of the isolation of a similar *nido*-platinum(II) species [(**3**), M = $Pt(PPh_3)_2$];[6] the cage rearrangement would then involve a shift of the B(10) atom to an equatorial position, and a shift of the metal atom to occupy the position vacated by B(10). Two consecutive diamond–square–diamond rearrangements,[7] involving B(1)–B(10)–M(9)–B(4) and B(1)–B(5)–B(10)–M(9), would effect these shifts.

The *closo*-cage geometry observed for (**2**) is unexpected since, in contrast to these results, reaction of [$IrCl(PPh_3)_3$] with *arachno*-$B_9H_{14}^-$ (isoelectronic with $CB_8H_{13}^-$) yields trace quantities of the *iso-nido*-[$(PPh_3)_2IrB_9H_{10}(PPh_3)$],[8] and an 85% yield of the *nido*-[6-H-6,6-(PPh_3)$_2$-6-IrB_9H_{13}].[9,10] The latter, which is isoelectronic with the proposed *nido*-iridium(III) complex (**3**), is converted into the cyclic *iso-closo*-species [$(PPh_3)(Ph_2PC_6H_4)(HIrB_9H_{13})$] on thermolysis *via* an *ortho*-cycloboronation reaction. The ten vertex cage in this case possesses idealised C_{3v} symmetry.[9] Also, the *closo*-species [2,2,2-H(Et_3P)$_2$-1,6,2-$C_2RhB_7H_9$], (**4**) {produced by reaction

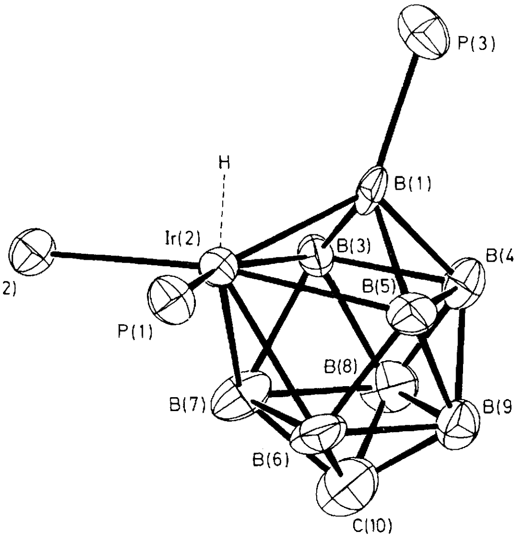
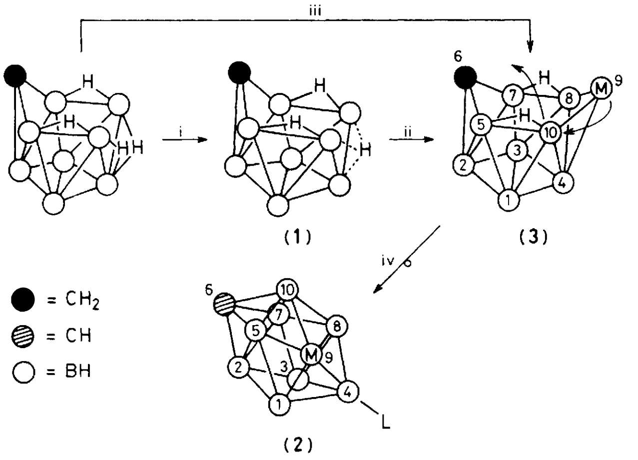


Figure 1. View of *closo*-[1-(PPh_3)-2,2,2-H(PPh_3)$_2$-2,10-$IrCB_8H_8$] (**2**). The phenyl groups are omitted for clarity. Selected distances: Ir(2) to B(1), B(3), B(5), B(6), and (B7) are 2.075(19), 2.318(18), 2.335(18), 2.262(20), and 2.279(19) Å respectively; C(10) to B(6), B(7), B(8), and B(9) are 1.642(28), 1.652(27), 1.572(30), and 1.630(29) Å respectively; B–B distances are in the range 1.712—1.985 Å. The angle between the planes Ir(2)–P(2)–P(1) and Ir(2)–B(6)–B(7) is 116° and the angle between the plane Ir(2)–P(2)–P(1) and the bond Ir(2)–B(1) is 158°. The Ir–H hydrogen was not detected.

[†] *Crystal data* for (**2**): $C_{55}H_{54}B_8IrP_3$, orthorhombic, space group $P2_12_12_1$, a = 12.728(3), b = 19.487(4), c = 20.274(3) Å, U = 5028.72 Å^3, Z = 4, D_c = 1.44 g cm^{-3}, μ(Mo-K_α) = 27.74 cm^{-1}, F(000) = 2184. Data were collected with a Syntex $P2_1$ four circle diffractometer. The final R value for 3998 independent reflections was 0.057. 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.



Scheme 1. i, BuLi (1 mol) in diethyl ether, 20 °C; ii, [IrCl-$(PPh_3)_3$] (1 mol) in diethyl ether, 20 °C, 6 days, M = $IrH(PPh_3)_2$; iii, [$Pt(PPh_3)_4$] (1 mol) in refluxing benzene, M = $Pt(PPh_3)_2$ (ref. 6); iv, 20 °C, $-2H_2$, +L = PPh_3, M = $IrH(PPh_3)_2$. The numbering of atoms in (**2**) is not systematic and corresponds to the numbering in (**3**) for simplicity.

of *arachno*-1,3-$C_2B_7H_{13}$ with [Rh(η-C_3H_5)$(PEt_3)_2$]} has bicapped square antiprismatic geometry, as in (**2**), but with the two carbon atoms separated by the metal.[11] The cage closing mechanisms must therefore be different in these cases, since for example the mechanism indicated for (**2**) would lead to adjacent carbon atoms in (**4**). Conversely, related cage rearrangements that yield (**4**), such as the addition of the rhodium moiety to an edge or the open face of 1,3-$C_2B_7H_{13}$, followed by collapse of the *nido*-cage, when applied to (**1**) would lead *not* to (**2**) but to a structure having the carbon and metal atoms adjacent.

[2,2,2-$H(Et_3P)_2$-1,6,2-$C_2RhB_7H_9$]

(**4**)

These results indicate that several pathways are available for cage closure reactions, and also that the presence of a varying number of cage carbon atoms is valuable in delineating such processes.

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