

Facile Thermally-induced Cluster Oxidations in Metallaborane Chemistry: *arachno* → *nido* → *closo* Reaction Sequences exhibited by Iridanonaboranes and Iridadecaboranes, and the Stabilization of the Iridium(v) Oxidation State†

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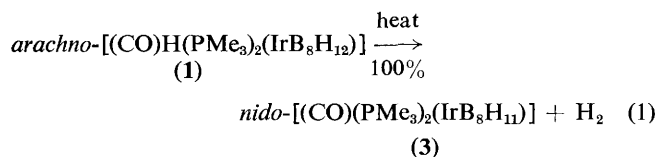
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Iridanonaboranes and iridadecaboranes which have adjacent open-face bridging H atoms and terminal Ir–H atoms readily lose H₂ in formal cluster oxidations which involve stable isolable iridium(v) species.

The reaction between *trans*-[Ir(CO)Cl(PMe₃)₂] and *nido*-B₉H₁₂⁻ gives a number of products among which is the colourless *arachno*-nine-vertex iridium(III) cluster compound [4,4,4,4-(CO)H(PMe₃)₂(4-IrB₈H₁₂)] (1) (yield *ca.* 30%) together with a chlorinated analogue [1-Cl-4,4,4,4-(CO)H(PMe₃)₂(4-IrB₈H₁₁)] (2) (yield *ca.* 7%) (Figure 1). Apart from the chlorine substituent, compounds (1) and (2) differ also in the disposition of the CO, H, and PMe₃ ligands about the

metal atom. They have similar gross *arachno*-structures to that of the previously reported¹ *arachno*-platinum(IV) compound [4,4-(PMe₂Ph)₂(4-PtB₈H₁₂)], but important differences occur in the detail of the metal–borane bonding.

When the *arachno*-iridium compound (1) is heated in hydrocarbon solution in the temperature range 50–100 °C a facile, quantitative, first order decomposition occurs (ΔH^\ddagger *ca.* 127 kJ mol⁻¹; ΔS^\ddagger *ca.* 35 J K⁻¹ mol⁻¹), to give the very pale yellow *nido*-nine-vertex iridium(III) compound [2,2,2-(CO)(PMe₃)₂(2-IrB₈H₁₁)] (3) (equation 1).



† We use the term oxidation state of an element to mean the sum of the formal number of electrons contributed to the cluster and other attached groups. In this sense the oxidation state of boron and of carbon in boranes and carboranes is +3 and +4, respectively. In assigning an oxidation state to a metal we first allocate the metallaborane to a structural class (*closo*-, *nido*-, *arachno*-, *etc.*) and then apply Wade's rules.

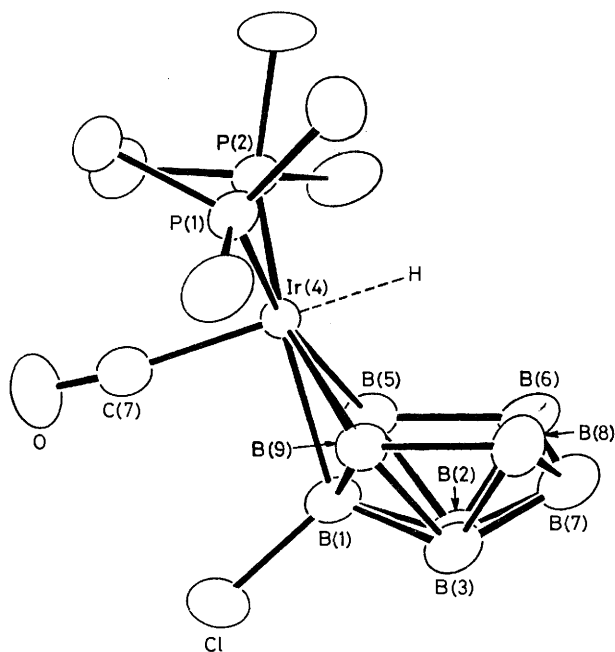
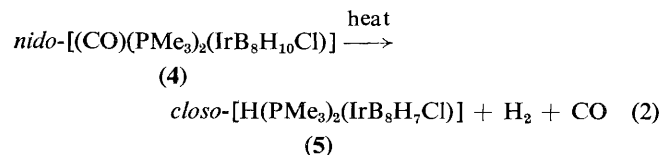


Figure 1. ORTEP drawing of the molecular structure of the colourless compound $[(\text{CO})\text{H}(\text{PMe}_3)_2(\text{IrB}_8\text{H}_{11}\text{Cl})]$ (2). $^1\text{H}\{^{11}\text{B}\}$ n.m.r. spectroscopy shows that there is an *exo*-terminal H atom on each B atom except B(1), that there are *endo*-terminal H atoms on B(6) and B(8), that there are bridging H atoms between B(5) and B(6) and between B(8) and B(9), and also that there is a terminal H atom on Ir(4), mutually *cis* to P(1) and P(2) and presumably *trans* to (CO) (broken line); peaks corresponding to all these H atom positions appeared on final difference maps. Crystal data are in Table 1. Distances from Ir(4) to B(1), B(5), and B(9) are 226.1(10), 228.4(11), and 229.1(8) pm respectively, and to C(1), P(1), and P(2), 193.4(10), 233.4(2), and 234.6(2) pm respectively. The non-chlorinated compound (1), $[(\text{CO})\text{H}(\text{PMe}_3)_2(\text{IrB}_8\text{H}_{12})]$, differs also in the disposition of the ligands about Ir(4).

The nine-vertex *nido*-geometry of (3) (Figure 2) results from the formal removal of a five-connected vertex from a bi-capped square antiprism (as in $\text{B}_{10}\text{H}_{10}^{2-}$, and may well derive from (1) via elimination of the *endo*-terminal H(6) and (H8) atoms and a closure from Ir(4) to B(8), together with a facial shift of H[4(Ir)]. Reaction 1 also occurs quantitatively and at similar temperatures for the 1-chloro-derivative (2) to give the very pale yellow *nido*-[2,2,2-(CO)(PMe₃)₂-3-Cl-(2-IrB₈H₁₀)] (4) (ΔH^\ddagger ca. 122 kJ mol⁻¹; ΔS^\ddagger ca. 13 J K⁻¹ mol⁻¹).

When this *nido*-compound (4) is heated more strongly (*e.g.* at 135 °C) further decomposition occurs (equation 2) to give the structurally novel poppy-red iridium(v) *closo*-compound [1,1,1-H(PMe₃)₂-8-Cl(1-IrB₈H₇)] (5) (Figure 3). Clearly, the cage closure is not a simple H₂-elimination in this case, which may indicate that facile elimination of H₂ in



However, the reaction is not now clean (yield ca. 45%), CO as well as H₂ is eliminated and, also, when the non-chlorinated *nido*-compound (3) is used only traces (< ca. 1%) of the presumed corresponding red product [1,1,1-H(PMe₃)₂(1-IrB₈H₉)] (6) are formed. Additionally, the location of the 8-Cl substituent in (5) (Figure 3) implies that the cluster closure may also involve a diamond-square-diamond skeletal rearrangement.

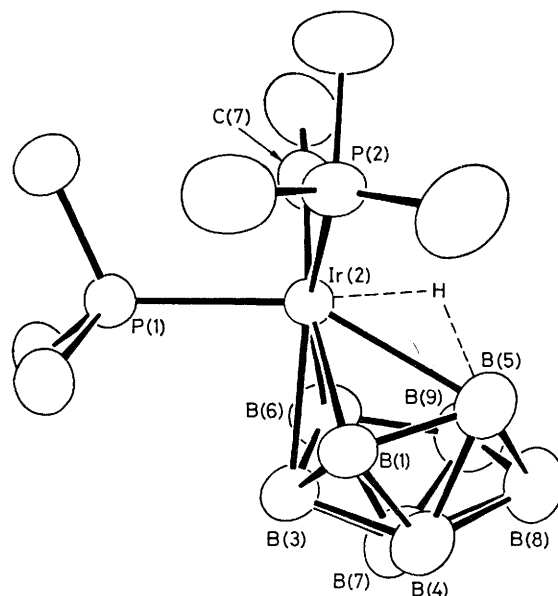


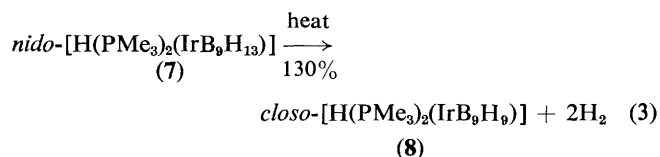
Figure 2. ORTEP drawing of the molecular structure of the pale yellow compound $[(\text{CO})(\text{PMe}_3)_2(\text{IrB}_8\text{H}_{11})]$ (3). $^1\text{H}\{^{11}\text{B}\}$ n.m.r. spectroscopy shows that there is an *exo*-terminal H atom on each B atom, and that there are bridging H atoms between B(6) and B(9) and between B(8) and B(9). There is also a bridging H atom Ir(2)-H-B(5) *trans* to P(1) as indicated by the broken lines. Peaks corresponding to all these positions except Ir(2)-H-B(5) were in the final difference map. Crystal data are given in Table 1, and distances from Ir(2) to B(1), B(3), B(5), and B(6) are 218.5(8), 230.4(7), 250.0(8), and 233.0(10) pm respectively, and to C(7), P(1), and P(2) 191.2(8), 232.0(2), and 235.9(2) pm respectively.

Table 1. Crystal data for *arachno*- $[(\text{CO})(\text{H})(\text{PMe}_3)_2(\text{IrB}_8\text{H}_{11}\text{Cl})]$ (2), *nido*- $[(\text{CO})(\text{PMe}_3)_2(\text{IrB}_8\text{H}_{11})]$ (3), and *closo*- $[\text{H}(\text{PMe}_3)_2(\text{IrB}_8\text{H}_7\text{Cl})]$ (5).

	(2)	(3)	(5)
<i>a</i> /pm	971.9(2)	916.0(3)	916.5(2)
<i>b</i> /pm	2423.9(4)	1179.2(3)	1603.5(3)
<i>c</i> /pm	955.0(2)	1695.5(3)	1263.6(3)
β /°	117.80(2)	93.81(2)	99.83(2)
Space group	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>1</i> / <i>n</i>	<i>P</i> ₂ / <i>c</i>
No. of <i>F</i> ₀	2430	2162	2168
Final <i>R</i> ^a	0.034	0.032	0.033

^a The structures were refined with anisotropic temperature factors for non-hydrogen atoms. Methyl hydrogen atoms were included as part of rigid-groups with C-H 108 pm and *U*_{iso} 700 pm². 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.

these systems may require an Ir-H terminal H atom as well as an adjacent bridging H atom. This would be consistent with the quantitative first-order decomposition (ΔH^\ddagger ca. 108 kJ mol⁻¹, ΔS^\ddagger ca. 6 J K⁻¹ mol⁻¹) of the previously reported² bright yellow ten-vertex *nido*-iridium(III) species [6,6,6-H(PMe₃)₂(6-IrB₉H₁₃)] (7) to give the bright orange-yellow *closo*-iridium(v) compound [1,1,1-H(PMe₃)₂(1-IrB₉H₉)] (8) (equation 3).



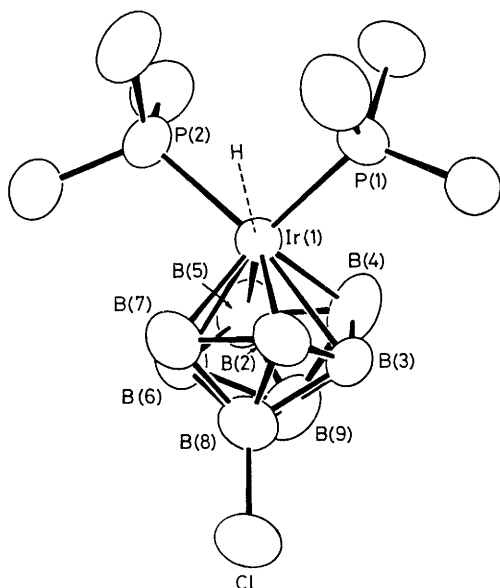


Figure 3. ORTEP drawing of the molecular structure of the poppy-red compound $[\text{H}(\text{PMe}_3)_2(\text{IrB}_8\text{H}_7\text{Cl})]$ (5). H atoms were not located but selective ^1H (^{11}B) n.m.r. spectroscopy showed that each B atom except B(8) has one terminal H atom and that, additionally, there is a terminal H atom on Ir(1) symmetrically *cis* to both P(1) and P(2), presumably in a position such as indicated by the broken lines. The crystal was disordered with respect to the 8-Cl (ca. 67%) and 9-Cl (ca. 33%) positions. Further, the thermal anisotropy of Ir(1) suggests that there may also be disorder with respect to the position of H[Ir(1)] *cis* and *trans* to the 8- and/or 9-Cl positions. Crystal data are summarized in Table 1. The IrB_8 cluster is a closed deltahedron with idealized C_{2v} symmetry and with an η^6 borane-to-metal co-ordination mode, in which the Ir–B(2,4,5,7) distances are in the range 217.7(10)–219.4(9) pm and Ir–B(3,6) are 231.5(8) and 230.7(9) pm; the Ir–B(8) and Ir–B(9) distances are also rather short [282.5(10) and 285.2(10) pm respectively]. There is no significant bonding between B(2)–B(4) (307 pm) or between B(5)–B(7) (304 pm).

Preliminary evidence suggests that the rigid IrB_9 cluster structure of (8) has idealized C_{3v} symmetry with a 'chair'- η^6 borane-to-metal co-ordination mode which has similarities to the 'inverted boat'- η^6 co-ordination in (5) and (6). Compounds (5), (6), and (8) are all closed deltahedral species, which implies that the Ir centre contributes 4 electrons to the cluster bonding in each case: these compounds may therefore be regarded as 9-co-ordinate 18-electron iridium(v) species.

The extremely ready formal cluster oxidations *arachno* \rightarrow *nido* and *nido* \rightarrow *closo* which occur by elimination of dihydrogen in these compounds are accompanied by, and presumably assisted by, a flexibility of co-ordination mode and oxidation state about the iridium atom. In particular the metal atom can act as an odd or even electron sink either by donating electrons to the cluster bonding or withholding them; this can be done in the form of lone pairs or by switching between Ir–H–B bridging and Ir–H terminal bonding pairs, or by both processes in concert. The results are clearly relevant to attempts to devise metalloborane or metallocarborane cluster systems which show useful catalytic activity, and in this context the incidence in these and related systems³ of the high formal oxidation state of iridium(v), generally regarded as rare,⁴ is also of interest.

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