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# Nine-vertex metallaborane chemistry. Preparation and characterisation of $[1,1,1\text{-}(PMe_3)_2H\text{-}\mathit{isocloso}\text{-}IrB_8H_7\text{-}8\text{-}X]$, where X = H or Cl

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It is a pleasure to be able to contribute to this Edition celebrating the 75th Birthday of Tom Fehlner. Happy Birthday Tom!

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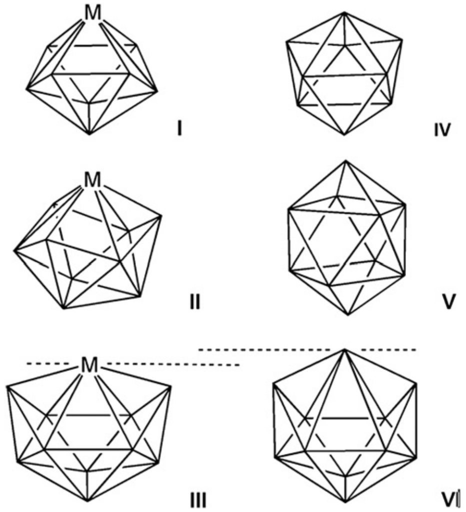
## ABSTRACT

The heating of solutions of $[(CO)(PMe_3)_2H\text{-}\mathit{arachno}\text{-}IrB_8H_{11}Cl]$ **1a** or $[(CO)(PMe_3)_2\text{-}\mathit{nido}\text{-}IrB_8H_{10}Cl]$ **2** in xylene results in the iridanonaborane cluster compound $[1,1,1\text{-}(PMe_3)_2H\text{-}\mathit{isocloso}\text{-}IrB_8H_7\text{-}8\text{-}Cl]$ **3a** in yields of up to 42%. Significantly less stable is the non-chlorinated analogue $[1,1,1\text{-}(PMe_3)_2H\text{-}\mathit{isocloso}\text{-}IrB_8H_8]$ **3b**, prepared *via* solutions of $[(CO)(PMe_3)_2H\text{-}\mathit{arachno}\text{-}IrB_8H_{12}]$ **1b** and excess *nido*-$B_{10}H_{14}$ in refluxing xylene. The structures of the $\{IrB_8\}$ units of **3a** and **3b**, characterised by multielement NMR spectroscopy and by single-crystal X-ray diffraction analyses, both approximate closely to an idealised $C_{2v}$ symmetry with the $\{IrH(PMe_3)_2\}$ moiety capping the six-membered open faces of *arachno*/*nido*-shaped $\{B_8\}$ units. This structural geometry differs significantly from the classical nine-vertex *closo* $D_{3h}$ tricapped trigonal prismatic (*ttp*) structure of the $[\mathit{closo}\text{-}B_9H_9]^{2-}$ anion. NMR spectroscopy shows that both **3a** and **3b** are fluxional with regard to the orientation of the $\{Ir(H(PMe_3)\}$ ligand set relative to the $\{IrB_8\}$ unit. Density functional theory (DFT) calculations have been carried out to help rationalise and extend the conclusions from the experimental observations. The calculations suggest that the *isocloso* cluster structure for chloro-substituted **3a** may be both the kinetically and the thermodynamically favoured one, whereas for unsubstituted **3b** a *ttp* structure would be thermodynamically the more stable and so the observed *isocloso* structure may well be the favoured kinetic product. However, the differences in these relative stabilities are marginal, and both compounds are unstable in solution relative to a general decomposition, **3b** much more so than **3a**, so there may be little significance in the relative stabilities of the *ttp* structures: the calculations suggest that the energy barrier to an *isocloso*-to-*ttp* conversion would preclude a decomposition pathway for **3a** or **3b** via a *ttp* structure at room temperature.

## 1. Introduction

It was recognised some time ago [1,2] that certain closed deltahedral metallaborane cluster structures of high symmetry deviated fundamentally from the classical Wade/Williams [3–6] electron-counting/geometrical-structure paradigms. These deviant '*isocloso*' geometries were categorised for nine-, ten- and eleven-vertex monometallaborane compounds, respectively with $C_{2v}$, $C_{3v}$ and $C_{2v}$ symmetries (schematic geometries **I**, **II** and **III**).

The nine- and ten-vertex *isocloso* examples have markedly different symmetries from the $D_{3h}$ and $D_{4d}$ nine- and ten-vertex classical *closo* geometries (schematics **IV** and **V**). For the eleven-vertex systems, the differences between *isocloso* (Schematic **III**)



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and classical *closo* (Schematic **VI**) are more subtle. Both are of $C_{2v}$ symmetry: however, for the *isocloso* structure, the metal atom is held more intimately (dashed lines in **III** and **VI**), and, compared to classical *closo*, the rest of the cluster flexes outwards to accommodate it (see, for example, Refs. [7,8]). Since the recognition of these alterative closed geometries, theoretical aspects of the bonding in compounds with clusters with these *isocloso* geometries, which have been described either as having *n*-electron-pair '*hypercloso*' cluster electron-counts with a classical three-orbital involvement of the metal atom with the cluster, or as $(n + 1)$-electron-pair species with a four-orbital involvement of the metal atom with the cluster, have received sustained interest in the literature [9–16].

Although several ten- and eleven-vertex cluster compounds that merit the *isocloso* structural cluster descriptor are known [17–19], the title compound, [1,1,1-$(PMe_3)_2$H-*isocloso*-$IrB_8H_7$-8-Cl] **3a**, first reported in a preliminary communication some thirty years ago [20], is currently the only nine-vertex example, and has therefore received particular attention [9,13–15]. However, a full account of its preparation and structure is hitherto lacking and, in view of the continual theoretical interest in these types of species, there is merit in more definitive work. The original room-temperature single-crystal X-ray diffraction work suffered from disorder problems such that only non-hydrogen atoms could be located. The disorder was presumed to arise from the presence of two isomers that differed in that there are two symmetric dispositions of the $\{IrH(PMe_3)_2\}$ moiety relative to the $\{B_8H_7Cl\}$ unit. No definitive NMR data were reported with respect to the compound, or with respect to its supposed fluxionality. Now, the readier availability of low-temperature single-crystal X-ray data collection and higher-field NMR facilities has enabled the collection of a higher quality dataset for diffraction analysis, a definitive measurement of relevant NMR parameters, and an assessment of the fluxionality, as well as the gleaning of additional results to describe the non-chlorinated analogue [1,1,1-$(PMe_3)_2$H-*isocloso*-$IrB_8H_8$] **3b**. These new experimental findings, together with XHYDEX potential-well [21] and density functional theory (DFT) calculations of energies, structures and NMR parameters [22], make possible the resolution of several of the uncertainties regarding this key compound type.

## 2. Results and discussion

### 2.1. Synthesis and experimental characterisation

The *arachno*-iridanonaborane cluster compound [(CO)$(PMe_3)_2$-$HIrB_8H_{11}Cl$] **1a** [23] (schematic **VII**) loses dihydrogen when heated in xylene solution at *ca.* 350 K to give the *nido* cluster compound [(CO)$(PMe_3)_2IrB_8H_{10}$-3-Cl] (**2**, schematic **VIII**) in high yield (Equation (1) and Scheme 1, **VII** → **VII**) [24]. A stronger heating at *ca.* 400 K results in a loss of a second molecule of dihydrogen, together with a molecule of carbon monoxide, to give the poppy-red compound [1,1,1-$(PMe_3)_2$H-*isocloso*-$IrB_8H_7$-8-Cl] **3a** (schematic **IX**) in yields of up to 42% (Equation (2) and Scheme 1, **VIII** → **IX**). Compound **3a** was isolated as dark red crystals from the reaction mixture by thin-layer chromatography, followed by crystallisation from $CH_2Cl_2$/pentane solution, and identified by multielement NMR spectroscopy, mass spectrometry and by a single-crystal X-ray diffraction analysis. The basic data for the X-ray diffraction analysis of **3a** have been reported previously in an overview article [25], but a discussion of the derived parameters has hitherto been lacking.

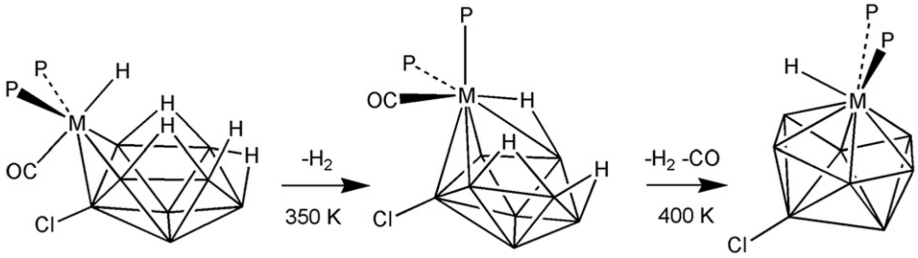
$$[(CO)(PMe_3)_2HIrB_8H_{11}Cl]\ \mathbf{1a} \rightarrow [(CO)(PMe_3)_2IrB_8H_{10}Cl]\ \mathbf{2} + H_2 \quad (1)$$

$$[(CO)(PMe_3)_2HIrB_8H_{10}Cl]\ \mathbf{2} \rightarrow [(PMe_3)_2HIrB_8H_7Cl]\mathbf{3a} + CO + H_2 (2)$$

In gross mechanistic terms the two successive closure steps can be visualised simplistically as successively more intimate involvements of the metal atom with the $\{B_8\}$ unit, although the change in location of the chloro substituent in **1a** and **2** (schematics **VII** and **VIII**), from sites adjacent to the metal to a more distal position in **3a** (schematic **IX**), implies that the final closure step is not so straightforward and involves a cluster rearrangement. It may be noted that chlorine substituent migration in the thermolysis of [(CO)$(PMe_3)_2IrB_8H_{10}$-3-Cl] (**2**) to form [(CO)$(PMe_3)_2IrB_8H_{10}$-4-Cl] has been observed previously [26], and thus the stage at which the migration occurs is not yet resolved.

An ORTEP3 [27] diagram of the crystallographically determined molecular structure of **3a** is shown in Fig. 1, and Table 1 lists selected interatomic distances and angles. The *isocloso* nine-vertex $\{IrB_8\}$ geometry is clearly confirmed, with the $\{IrB_8\}$ unit approximating closely to an ideal $C_{2v}$ symmetry, and there is one chloro substituent on one of the two boron atoms, B(8) and B(9), that are not connected directly to the iridium atom. There is crystallographic disorder with respect to the location of the chloro substituent on the B(8)/B(9) positions; the crystallographic solution refined with a 59:41% ClB(8)–B(9)H:ClB(9)–B(8)H occupancy ratio, implying a similar disorder for the terminal hydride position on the iridium atom (see below).

The position of the *exo*-polyhedral phosphine and hydride ligands on the iridium centre is of interest. In the crystallographic solution, the two phosphorus atoms lie approximately in the Ir(1)B(3)B(6) plane, and approximately perpendicular to the B(2)B(4)B(5)B(7) plane [the angle between the {P(1)Ir(1)P(2)} and {B(2)B(4)B(5)B(7)} planes is 93.8(2)°] thus conforming with the approximate $C_{2v}$ symmetry of the $\{IrB_8\}$ unit. However, DFT calculations (section 2.2) predict a greater tilt of 107.5°, and also a slight displacement of the iridium atom away from the approximate $C_2$ axis. Here it seems reasonable to infer that the crystallographic disorder is manifest in an effective averaging of the phosphorus positions across the pseudo-mirror plane to result in the {P(1)Ir(1)P(2)} plane appearing approximately perpendicular to B(2)B(4)B(5)B(7).



**VII** **VIII** **IX**

**Scheme 1.** Illustration of the reaction sequence affording [$(PMe_3)_2$H-*isocloso*-$IrB_8H_7Cl$] **IX** (compound **3a**) from [(CO)$(PMe_3)_2$H-*arachno*-$IrB_8H_{11}Cl$] **VII** (compound **1a**).