# *closo–nido*-Cluster Isomerism in Metallacarbaboranes *via* a Change of Metal Valency State: Molecular Structure of μ-1,2-Acetato-2-hydrido-2,10-bis(triphenylphosphine)-*closo*-1,2-carbairidadecaborane

**Janet E. Crook, Norman N. Greenwood,* John D. Kennedy, and Walter S. McDonald**

*Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, U.K.*

The iridium(III) *closo*-cluster structure of $[\mu\text{-}1,2\text{-}(MeCO{\cdot}O)\text{-}2\text{-}H\text{-}2,10\text{-}(PPh_3)_2\text{-}closo\text{-}1,2\text{-}ClrB_8H_7]$, which also contains a novel acetate bridge, contrasts with the otherwise ostensibly isoelectronic iridium(V) *iso-nido*-cluster structure of $[(PPh_3)(Ph_2P\overline{C_6H_4)\{Ir}B_8H_6(OMe)C(OH)\}]$

---

Polyhedral boron-containing clusters should in principle be able to act as two-electron sinks or donors *via arachno*$\rightleftharpoons$*nido* and *nido*$\rightleftharpoons$*closo* processes. If the cluster also contains a transition element, then any flexibility of co-ordination mode and

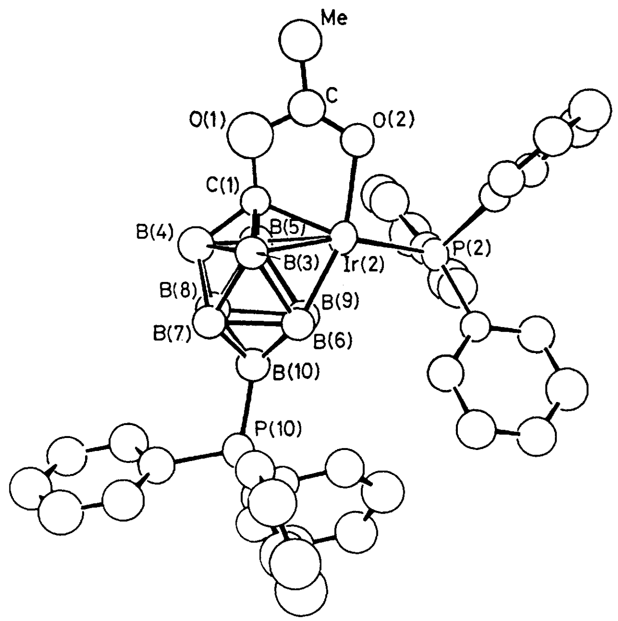
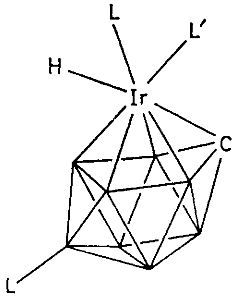


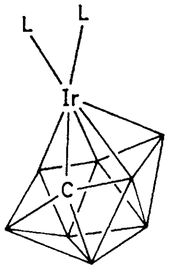
**Figure 1.** ORTEP drawing of [(MeCO·O)(Ph$_3$P){HIrCB$_8$H$_7$-(PPh$_3$)}]. Distances from Ir(2) are as follows: to C(1) 204.0(15), to B(3) 233.2(22), to B(5) 240.4(23), to B(6) 222.0(24), to B(9) 219.6(22) pm. Distances within the exocyclic IrOCOC ring are Ir(2) to O(2) 215.5(15), O(2) to C(carbonyl) 128.8(22), C(carbonyl) to O(1) 137.0(25), and O(1) to C(1) 144.1(22) pm. C(carbonyl) to C(Me) is 149.8(31) pm and angles about C(carbonyl) are 128(2) and 111(2)°. H atoms were not located, but selective $^1$H-{$^{11}$B} n.m.r. spectroscopy showed an *exo*-terminal H atom associated with each of the seven boron atoms B(3)—B(9) inclusive, and also a terminal H atom on the metal centre [$\delta$($^1$H)(CD$_2$Cl$_2$) −11.92].

valence state of the metal can combine with these properties to produce species that have catalytic potential, the energetic differences between appropriate redox states being suitably small in appropriate cases.[1-3] Further insight into these redox states is provided by the characterisation of the compound reported here, the air-stable, orange, neutral species [(MeCO·O)(PPh$_3$){HIrCB$_8$H$_7$(PPh$_3$)}] (**1**). The compound was isolated in low yield (<1%) from the reaction of *trans*-[Ir(CO)Cl-(PPh$_3$)$_2$] with *closo*-B$_{10}$H$_{10}$$^{2-}$ in refluxing methanol which reasonably implies that the dicarbon acetate residue arises from the combination of monocarbon units derived from carbon monoxide and/or methanol.

Crystals of (**1**) were monoclinic, space group $P2_1/n$, with $a$ = 1039.1(5), $b$ = 2825.0(9), and $c$ = 1470.1(6) pm, $\beta$ = 95.20(4)°, $Z$ = 4, and the structure (Figure 1), based on 4261 independent $F_o$ having $I > 2\sigma(I)$, was refined to $R$ = 0.095.† Integrated $^{11}$B n.m.r. spectroscopy showed that eight of the cluster atoms were boron, and the shorter intracluster distances to the atom in the 1-position, together with markedly more realistic temperature factors when it was refined as carbon rather than boron, reasonably define this as carbon. Hydrogen atoms were not located but selective $^1$H-{$^{11}$B} n.m.r. spectroscopy showed that seven boron atoms had *exo*-terminal hydrogen atoms bound to them, and that there was a hydrogen atom on the iridium atom *cis* to the phosphine.



(**1**)



(**2**)

The cluster structure is seen to be that of a *closo*-ten-vertex 'Wade's rules' cluster which has the expected bicapped Archimedean square anti-prismatic structure with the iridium(III) centre contributing three orbitals and two electrons and occupying a five-connected vertex. There are three non-borane ligands on the metal, namely hydrogen, triphenylphosphine, and a dative acetate oxygen atom. The acetate residue is additionally bonded to the cluster *via* a straightforward covalent two-electron two-centre *exo*-polyhedral bond to the capping C(1) atom, resulting in a novel exocyclic five-membered IrOCOC ring. The other capping atom, B(10), carries a pendent PPh$_3$ group rather than a terminal H atom.

The interest in this compound resides in the contrast of its straightforward *closo*-cluster structure with the unusual *iso-nido*-cluster structure of the previously reported[4] compound [(PPh$_3$)(Ph$_2$PC$_6$H$_4$){IrB$_8$H$_6$(OMe)C(OH)}] (**2**) which has a definite four-membered IrCBB concave *nido* open face. The two cluster structures (**1**) and (**2**) may be compared schematically (L = PPh$_3$ or Ph$_2$PC$_6$H$_4$, L′ = $\mu$-MeCO·O). Compared to (**2**), the pendent B-phosphine ligand in (**1**) contributes one extra electron to the cluster, but conversely the presence of a terminal Ir–H ligand removes one. The two structures are therefore ostensibly isoelectronic and should therefore be isostructural but this is not so. In compound (**1**) as mentioned above the metal atom contributes two electrons and three orbitals and is isoelectronic and 'isolobal' in gross cluster terms with boron(III) in a neutral {BH} group. In compound (**2**), by contrast, the iridium atom is regarded as contributing five electrons to the cluster and is consequently ascribed the formal valency state of iridium(V). Both compounds are stable species and so this *quasi*-isomerism of the two clusters implies that the energetic difference between the two metal valency states in these systems is very small, which is of obvious importance in understanding catalytic processes,[2] and other interesting reaction sequences[1,3,4] undergone by these and related species.

We thank the S.E.R.C. for support.

*Received, 8th October 1982; Com. 1180*

## References

1 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 346.
2 C. W. Jung, R. T. Baker, and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1981, **103**, 810.
3 J. Bould, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 465.
4 J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1981, 933.

---

† 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.