Heterobimetallic B-Frame Compounds: Systematic Synthesis and Molecular Structure of the Seven-vertex μ-$H_{Os,Pt}$-*nido*-osmaplatinaborane $[(Ph_3P)_2(CO)\overline{Os(PhMe_2P)ClHPt}B_5H_7]$†

Jonathan Bould, Janet E. Crook, Norman N. Greenwood, and John D. Kennedy
Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

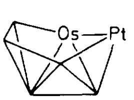
The first structurally characterized polyhedral metallaborane osmium compound has a seven-vertex *nido*-osmaplatinaborane cluster structure based on the dodecahedron with one five-connected vertex missing, the metal atoms being located on adjacent (2,7) positions in the five-membered open face and linked *via* an Os–H–Pt bridging bond; important wider implications of the mechanism of formation are indicated.

The interesting and theoretically important area of seven-vertex polyhedral borane and metallaborane clusters is little examined, mainly because the obvious six-vertex starting substrate *nido*-B_6H_{10} is generally held to be difficult to make and handle. However, the facile high-yield syntheses (80—90%) of air-stable *nido* six-vertex metallaborane analogues of B_6H_{10}, such as $[(Ph_3P)_2(CO)IrB_5H_8]$[1,2] and $[(Ph_3P)_2(CO)OsB_5H_9]$,[2] in principle permits their convenient use firstly as starting substrates from which to examine seven-vertex cluster chemistry, and secondly as B-frame matrices† on which to build up selected heterobimetallic systems,[3] an area in which there is much current interest. We now exemplify these principles by the preparation and structural characterisation of the novel seven-vertex *nido*-bimetallaborane $[(Ph_3P)_2(CO)Os(PhMe_2P)ClHPtB_5H_7]$.

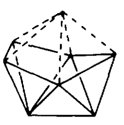
Treatment of *nido*-$[4,4,4\text{-}(Ph_3P)_2(CO)\text{-}4\text{-}OsB_5H_9]$[2] with NaH followed by addition of *cis*-$[PtCl_2(PMe_2Ph)_2]$ led to the isolation of the osmaplatinaheptaborane as a lemon-yellow crystalline compound in a yield (as yet unoptimized) of *ca.* 35% [equation (1)].

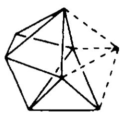
$$Na[(Ph_3P)_2(CO)OsB_5H_8] + [PtCl_2(PMe_2Ph)_2] \rightarrow [(Ph_3P)_2(CO)Os(PhMe_2P)ClHPtB_5H_7] + PMe_2Ph + NaCl \quad (1)$$

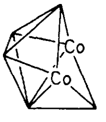
Crystals of $C_{45}H_{49}B_5ClOsOP_3Pt$ were monoclinic, space group $P2_1/n$, with $a = 1539.7(3)$, $b = 1848.9(3)$, $c = 1718.9(3)$ pm; $\beta = 92.57(2)°$; $Z = 4$. The data were corrected for absorption and the structure (Figure 1), based on 5349 independent F_0 with $I > 2\sigma(I)$, was refined to $R = 0.043$.‡ All atoms except the metal–metal bridging hydrogen atom were located and refined in the diffraction analysis; the presence and location of this bridging H atom can be reasonably inferred as indicated in the caption to Figure 1. The overall molecular structure is seen to be that of a *nido* seven-vertex cluster (I) notionally derived from a *closo* eight-vertex dodecahedron (II) by the elimination of a five-connected vertex. This is in interesting contrast to the alternative notional elimination of a four-connected vertex (III) to give the structure (IV) as proposed for *nido*-$[(C_5Me_5)_2Co_2B_5H_9]$[4] (though this last has not yet been confirmed by definitive structural methods).



(I)


(II)

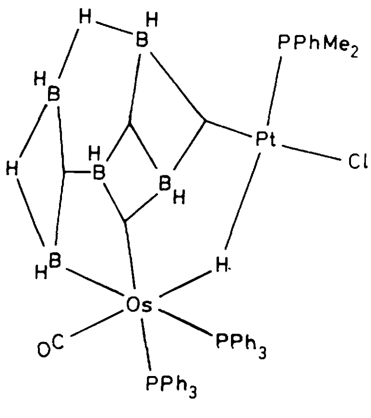

(III)



(IV)

Simple valence-bond structures such as (V) may be readily written for the compound. This involves straightforward octahedral osmium(II)- and square planar platinum(II)-type centres, although the metal-to-borane bonding probably also has some similarities to that in other dimetallic species such as $[(PhMe_2P)_2Pt_2B_{12}H_{18}]$[5] and $[(PhMe_2P)_2Pt_2B_8H_{14}]$[6] in which contributions from higher formal metal valence states may be present. In simple electron-counting terms, structure (V) represents a sixteen-electron cluster configuration. As such, however, it is two electrons short for a *nido* seven-vertex cluster.[7] This interpretative conflict arises because cluster rules implicitly count orbitals as well as electrons, and the platinum vertex in (V) has a non-conical two-orbital contribution, rather than the three-orbital conical contribution of the boron vertex that it notionally subrogates. The significance of any bonding participation from the higher formal valence state of platinum(IV), which by contrast would in fact involve a *quasi*-conical three orbital contribution and also supply an additional two electrons as required for a full *nido* count, is difficult to assess in this species.

Of additional interest is that the total synthesis of the platinaosmaborane from the *nido* five-vertex B_5H_9 molecule, through a *nido* six-vertex $\{MB_5\}$ cluster, to the final *nido* seven-vertex $\{M_2B_5\}$ product, occurs *via* the successive addition of vertices plus electrons to the original cluster. This constitutes a sequential *nido* → *nido* → *nido* cluster expansion in which reactions are chosen so that an additional vertex plus the additional bonding electrons are supplied to the cluster at each step; each successive addition then yields a *nido* cluster of higher nuclearity which permits the process to be repeated. In the general case, of course, this *aufbau* process is not limited to *nido* clusters. Energetics may sometimes be such that similar successive steps may be progressively more favoured in one reaction system, so that a cascade-type *aufbau*



(V)

---

† The term 'B-frame' refers to a polyhedral borane cluster to which one or more metal centres can be added as additional cluster vertices. The title compound is 2-carbonyl-2,2-bis(triphenylphosphine)-7-chloro-7-dimethylphenylphosphine-μ(2,7)-hydrido-*nido*-2,7-osmaplatinaheptaborane.

‡ 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.

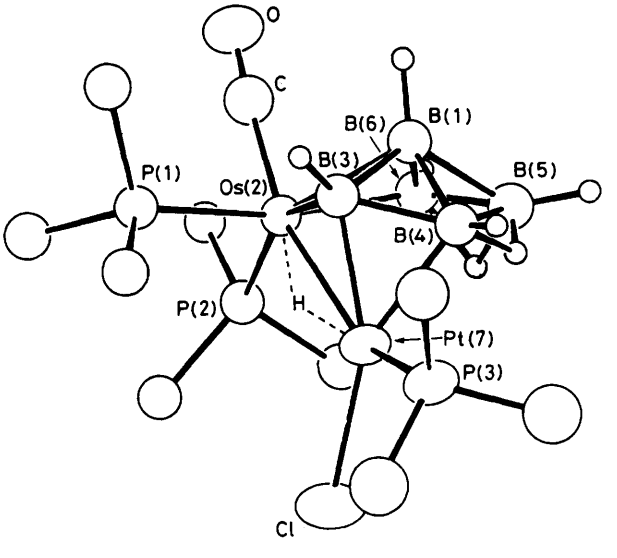


Figure 1. ORTEP drawing of the molecular structure of $[(Ph_3P)_2(CO)\overline{Os(PhMe_2P)Cl}HPtB_5H_7]$, with all except the P-carbon atoms omitted from the phosphine ligand organic groups. All atoms were located by *X*-ray diffraction except for the Os–H–Pt bridging H atom (hatched lines), of which the position *trans* to C(carbonyl) and P(3), and *cis* to P(1) and P(2), reasonably follows from n.m.r. spectroscopy [$\delta(^1H)$ −10.61, $^1J(^{195}Pt-^1H)$ 555 Hz, $^2J(^{31}P-^1H)$ 98, 19, and 5 Hz] and from stereochemical considerations about the metal atoms; although a peak corresponding to this H atom position appeared in final difference maps it did not refine. Selected distances are as follows: from Os(2) to B(1) 228(2), to B(3) 218(2), to B(6) 215(2), to Pt(7) 295.9(1), to P(1) 243.0(4), to P(2) 240.5(4), and to C(carbonyl) 189(2) pm; from Pt(7) to B(3) 214(2), to B(4) 214(2), to P(3) 226.1(4), and to Cl 237.8(5) pm. Interligand bond angles demonstrate the regular octahedral and square-planar nature of the bonding about the Os and Pt atoms: the only substantial deviations from 90° and 180° angles are P(3)–Pt(7) · · · Os(2) at 155.4(1)° and Pt(7) · · · Os(2)–C(carbonyl) at 157.4(5)° implying that the (unlocated) bridging H atom occupies the final co-ordination site at each metal.

process results.[8] This presumably accounts for the higher polymetallaborane products observed in some reactions, of which the well examined cobalt–pentaborane–cyclopentadiene-type sytems are good examples.[4,9,10] In the present system it is also apparently manifested by the formation (in a concurrent process) of what appear to be polyplatinamonosmaborane species. The precise conditions for the formation of these higher species in reasonable yields however seem quite critical, and we hope to report further on this in the future.

We thank the S.E.R.C. for support, and Dr. D. Reed (Edinburgh University) for services in high-field n.m.r. spectroscopy.

Received, 23rd May 1983; Com. 660

References

1 N. N. Greenwood, J. D. Kennedy, W. S. McDonald, D. Reed, and J. Staves, *J. Chem. Soc., Dalton Trans.*, 1979, 117.

2 J. Bould, N. N. Greenwood, and J. D. Kennedy, *J. Organomet. Chem.*, 1983, **249**, 11, and subsequent work in these laboratories to optimize the yield.

3 J. Bould, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1983, preceding communication.

4 T. L. Venable and R. N. Grimes, *Inorg. Chem.*, 1982, **21**, 887.

5 N. N. Greenwood, M. J. Hails, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1980, 36.

6 R. Ahmad, J. E. Crook, N. N. Greenwood, J. D. Kennedy, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.*, 1982, 1019.

7 K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1; M. E. O'Neill and K. Wade in, 'Metal Interactions with Boron Clusters,' ed. R. N. Grimes, ch. 1, Plenum Press, New York, 1982, p. 1.

8 G. Jaouen, A. Marinetti, B. Menteen, R. Mutin, J. Y. Saillard, B. G. Sayer, and M. J. McGlinchey, *Organometallics*, 1982, **1**, 753.

9 V. R. Miller, R. Weiss, and R. N. Grimes, *J. Am. Chem. Soc.*, 1977, **99**, 5646.

10 C. J. Zimmerman, L. W. Hall, and L. G. Sneddon, *Inorg. Chem.*, 1980, **19**, 3642.