FORMATION OF HETEROBIMETALLAHEPTABORANES FROM THE *NIDO*-METALLAHEXABORANES $(PPh_3)_2(CO)OsB_5H_9$ AND $(PPh_3)_2(CO)IrB_5H_8$

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Abstract

A number of new heterobimetallaborane clusters have been synthesized from reactions of the metallahexaboranes *nido*-[$(PPh_3)_2(CO)OsB_5H_9$], **(IV)**, and *nido*-[$(PPh_3)_2(CO)IrB_5H_8$] **(V)**. Treatment of the Li salt of **(IV)** with $Ir(PPh_3)_2(CO)Cl$ affords *pileo*-[2,2,2-H(PPh_3)(CO)-3,3,3-$(PPh_3)_2$(CO)-2,3-$IrOsB_5H_5$] **(VI)**, whereas treatment with $[\{\eta^5\text{-}(C_5Me_5)Ir\}Cl_2]_2$ affords the species *closo*-[1-(C_5Me_5)-2,2,2,-(CO)$(PPh_3)_2$-1,2-(μH)-1,2-$IrOsB_4H_5$] **(VIIa)**, and *nido*-[2,2,2,-(CO)(PPh_3)-3-(C_5Me_5)-2-(μH)-2,3,-$IrOsB_3H_6$]**(VIII)**. A rhodium analogue of **VIIa** was also prepared and characterized by NMR spectroscopy as *closo*-[1-(C_5Me_5)-2,2,2,-(CO)$(PPh_3)_2$-1,2-(μH)-1,2-$RhOsB_4H_5$] **(VIIb)**. The complexes all contain seven cluster skeletal electron pairs within 7, 6 and 5 cluster vertices thus attaining an interesting *pileo - closo - nido* sequence of structures. The two standard reactions in which metal-containing moieties may be incorporated into the B_6H_{10} cage find success when applied to the iridahexaborane **(V)**. The reaction of $Fe_2(CO)_9$ with **V** in CH_2Cl_2 solution affords [1,1,1-$(CO)_3$-2,2,2-$(CO)_2$(PPh_3)-4-(PPh_3)-*closo*-1,2-$FeIrB_5H_4$] **(IX)** in 28.5% yield. **IX** is the first structurally characterized *closo*-heterobimetallaheptaborane. Treatment of a THF solution of the anion salt of **V**, Na[$(PPh_3)_2(CO)IrB_5H_7$] with $[Pt(PMe_2Ph)Cl_2]_2$ in CH_2Cl_2 affords yellow solid [2,2,2-(CO)$(PPh_3)_2$-7,7-Cl-(PMe_2Ph)-*nido*-2,7-$IrPtB_5H_7$] **(X)** in 5% yield. **X** exists as a *nido* 7-vertex cluster formally derived by removal of a vertex of connectivity 5 from a closed triangulated dodecahedral polyhedron. The species **VI**, **VIIa**, **VIII**, **IX** and **X** are all characterized fully.

Introduction.

Metallaboranes have been known for about 30 years. The discovery of the first metallacarboranes[1] played a major role in the subsequent expansion of the areas of both metallacarborane and metallaborane chemistry. However this article concerns only metallaboranes. The first metallaboranes to be discovered were borane(3)[2] and tetrahydroborate[3a] complexes and these discoveries were soon followed by the development of the chemistry of metal complexes of the tetrahydroborate[3] and octahydrotriborate[4] anions. Metallaboranes containing large cage boranes were also discovered during this era of remarkable advancement in this field. These included species containing 9, 10 and 11 boron atoms.[4b,5] This article describes heterobimetalladerivates of the mid-sized boranes. The first metallaboranes derived from such species were reported by V. T. Brice and Sheldon Shore in 1970 when they

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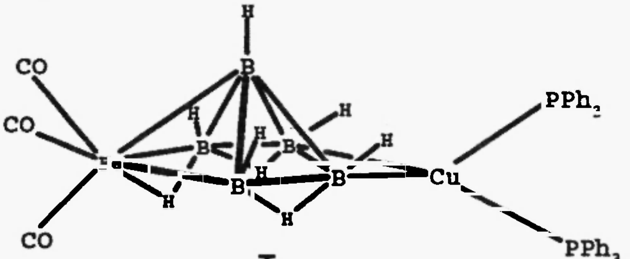
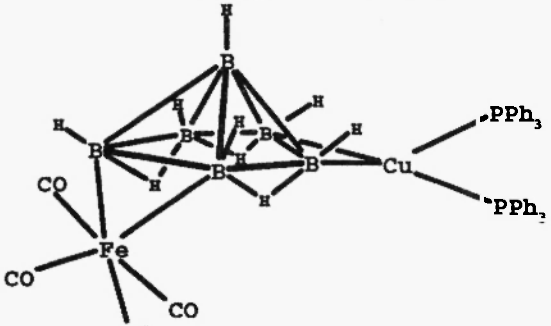
† Dedicated to Professor Sheldon G. Shore on the occasion of his 65th birthday.

described the cuprioboranes $(PPh_3)_2CuB_5H_8$ and $(PPh_3)_2CuB_6H_9$.[6] Since then the field of metallaborane chemistry has developed substantially.[7] Prior to our work there were very few examples of heteropolymetallaboranes. The first *nido* species $Cu[Ph_3P]_2B_5H_8Fe(CO)_3$,**I**, was reported by Shore et al.[9] This is a bimetallaborane in which the Fe atom is a true vertex and the Cu group may be considered as a "pseudo"-proton. The osmaplatinåheptaboranes $[(CO)(PPh_3)_2(\mu\text{-}H)Os(PMe_2Ph)ClPtB_5H_7]$ and $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$,[9] discovered a little later, may be considered to be true heterobimetallaboranes in that both metals are vertices.

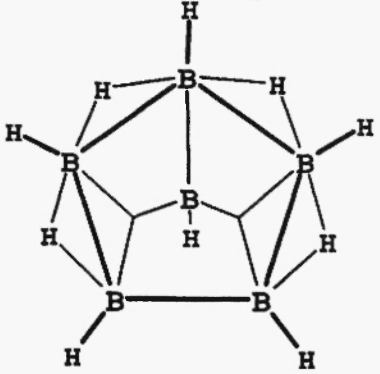


I

Finally there is $[Cu(Ph_3P)_2B_6H_9Fe(CO)_4]$,[10] **II**, in which both metals are "pseudo-protons" in that they occupy positions which may be replaced by protons. Grimes and coworkers described the first example of a *closo*-heteropolymetallaborane in this context, *closo*-$[\{\eta^5\text{-}(C_5H_5)Co\}_2(CO)_4Fe\text{-}B_3H_3]$,[11] which contains a trimetal triangle, and recently the novel species, *pileo*-$[\{\eta^5\text{-}(C_5H_5)Fe\}\text{-}(ML_3H)B_5H_7]$ where M = Mo and L = PMe_2Ph and M = W, L = PMe_3,[12] were reported from use of a similar synthetic approach to that we describe herein. Our approach was to use hexaborane(10) and its metallahexaborane analogues which provide several possibilities for the preparation of heterobimetallaboranes. Hexaborane(10),[13] (Illustration **III**) contains two types of bridging hydrogen atoms, each of which may, in principle, be removed and replaced by metal moieties. The basal B-B bond in B_6H_{10} is basic and reacts with electrophiles.[14] Thus possible routes to hetero-bimetallaboranes involve addition of metal moieties to the iron hexaborane complex $[\mu\text{-}\{(CO)_4Fe\}B_6H_{10}]$ in which an iron tetracarbonyl moiety coordinates to the basal B-B pseudo-single bond in B_6H_{10}.[14] Reaction of the anion $[\mu\text{-}\{(CO)_4Fe\}\text{-}B_6H_9]^-$ with borane(3) affords a cluster expansion products[4c,d] whereas reaction with $[(PPh_3)_2CuBr]^+$ affords the heterobimetallaborane $[Cu(PPh)_3B_6H_9\{Fe(CO)_4\}]$ (**II**) described above. Hexaborane(10), in principle, can coordinate to metals through the open face in reactions analogous to those the cyclopentadienly system and although this has not been directly observed, there are many examples for the related carborane species $C_2B_4H_8$ and its derivatives.[15] Also oxidative addition of a BX bond to coordinatively unsaturated complexes, such as $Ir(PPh_3)_2(CO)Cl$, should afford σ-bonded derivatives as they do B_5H_9.[16]



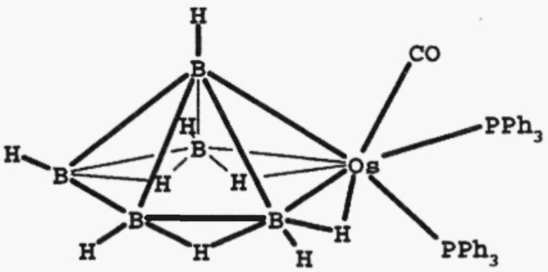
II



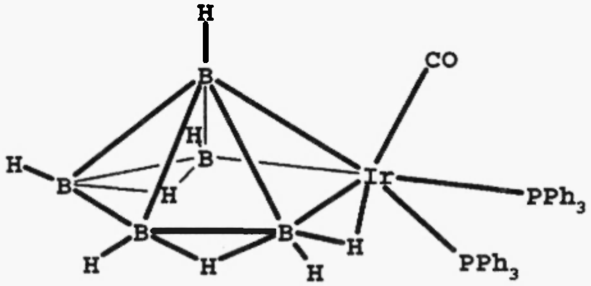
III

Recent reports of the formation of polymetallaboranes involve building the cluster from a metal complex and a tetrahydroborate or monoborane adduct. The latter methods have seen much success recently in the laboratories of Leach, Housecroft and Fehlner and their respective coworkers[17] but they are not ideally suited to the formation of heterobimetallaboranes. Perhaps the most promising approach to the formation of heterobimetallaboranes is to use a metallahexaborane, $L_nMB_5H_{(9-x)}$ for example, where ML_n replaces a BH vertex and x depends on the number of skeletal electrons supplied by ML_n, as starting material, and to add metal-containing moieties to it. This was the way in which species **I** was prepared, that is, the replacement of a bridging H atom in the ferrahexaborane $B_5H_9Fe(CO)_3$[18] by a metal-containing group.[8] There are now known *nido*-metallahexaboranes containing Mn, Re,[19] Fe,[18-22] Ru,[23] Os,[24] Co,[25] and Ir[26] and some of them have been used to prepare bimetallaboranes.

We were encouraged to use the metallahexaboranes $[(PPh_3)_2(CO)OsB_5H_9]$,[24] **IV** and $[(PPh_3)_2(CO)IrB_5H_8]$,[26] **V** on the basis of a statement by Kennedy[7a] which suggested that **IV** and **V** "are air-stable and more conveniently prepared in high yield from B_5H_9 than B_6H_{10} itself. Their use as starting materials offers an interesting convenient alternative means of examining the higher metallaborane chemistry that derives from a nido six-vertex cluster as a starting substrate, and further developments in this area will be of interest". Species **IV** had been used in the preparation of $[(CO)(PPh_3)_2(\mu\text{-}H)Os(PMe_2Ph)ClPtB_5H_7]$.[9] This article summarizes our recent work in the preparation of heterobimetallaboranes from **IV** and **V**.



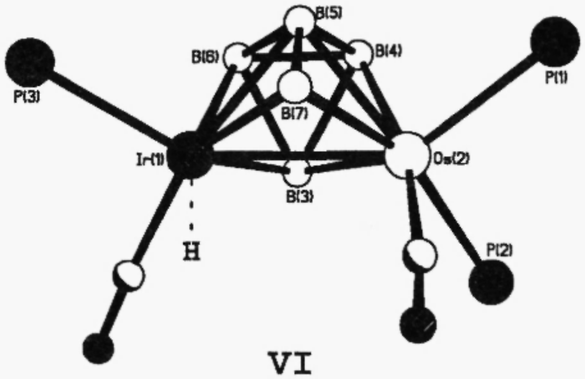
IV



V

Formation of heterobimetallaboranes from IV.

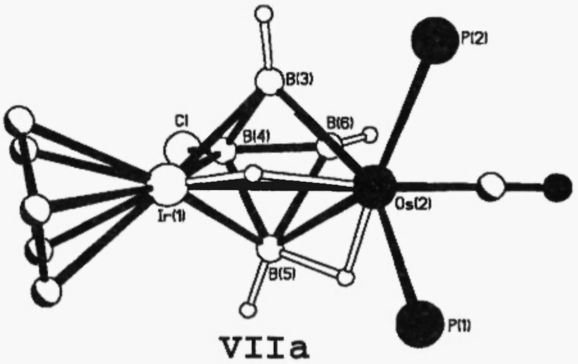
The osmaborane $[(PPh_3)_2(CO)OsB_5H_9]$ **IV**, is readily prepared in yields of up to 80 % by the reaction: $[B_5H_8]^- + Os(CO)ClH(PPh_3)_3 \rightarrow [(PPh_3)_2(CO)OsB_5H_9]$ (**IV**)+ Cl^- + PPh_3. Treatment of **IV** with $LiCH_3$ in THF at -35°C followed by addition of $[trans\text{-}(PPh_3)_2(CO)IrCl]$ and slow warming to room temperature gives, after chromatographic separation, the hetero-bimetallaheptaborane *pileo*-$[1,1,1\text{-}H(PPh_3)(CO)\text{-}2,2,2\text{-}(PPh_3)_2(CO)\text{-}1,2\text{-}IrOsB_5H_5]$ (**VI**)[27] in up to 33% yield according to the equation: $[(PPh_3)_2(CO)OsB_5H_8]^- + [(PPh_3)_2(CO)IrCl] \rightarrow [(PPh_3)H(CO)IrB_5H_5Os(PPh_3)_2(CO)]$ (**VI**) + PPh_3 + Cl^- + H_2. The known osmaborane $[2\text{-}2\text{-}2\text{-}(PPh_3)_2(CO)OsB_4H_8]$[24] is also formed in small quantities. The use of n-butyllithium affords the alkyl substituted species $[2\text{-}2\text{-}2\text{-}(PPh_3)_2(CO)OsB_4H_7(n\text{-}Bu)]$.[27] The species **VI** is easily identified by NMR spectroscopy, IR, mass spectrometry and single crystal X-ray diffraction study. A representation of the structure of **VI** is given below. It exists as a slightly distorted octahedral bimetallic subunit with a BH moiety capping a Ir-Os-B face. The structure, thus conforms to a *pileo*-cluster[28] description and contains 2n skeletal electrons and n vertices. Such species are quite rare in metallaborane chemistry although there are several examples in metal cluster chemistry.[29] We recently published details on the isoelectronic isostructural analogue $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2B_5H_5]$[30] and the first row analogue $[\{\eta^5\text{-}(C_5Me_5)Co\}_2B_5H_5]$[25b] was prepared some time ago and identified from NMR and mass spectroscopic data together with the trimetalla analogues $[1,2,3\text{-}\{\eta^5\text{-}(C_5H_5)Co\}_3B_4H_4]$,[31] and $[1,2,3\text{-}\eta^5\text{-}(C_5Me_5)Co\}_3B_4H_4]$,[25b,32] in which the boron vertex caps the triangular $[\{\eta^5\text{-}(C_5Me_5)\text{-}Co\}_3]$ face. Recently a *pileo* species has been characterized in which a BH_2 group caps an M_2B face in $[1\text{-}\{\eta^5\text{-}(C_5Me_5)Fe\}\text{-}2\text{-}Mo\text{-}(PMe_2Ph)_3\text{-}B_5H_7)]$.[12] Another system, a 2*n* + 2 skeletal electron, bicapped molybdenaborane species $[\{\eta^5\text{-}(C_5H_4Me)\text{-}Mo\}_2\text{-}B_5H_9]$,[17a] in which the 'capping' BH moieties are joined to the cluster *via* two bridging hydrogen atoms, thereby constituting what are essentially capping BH_3 groups, has been structurally characterized.[17a]



VI

The identity of **VI** was clearly confirmed by the crystal structure determination and NMR data but there was some uncertainty about the positions of the metals since X-ray diffraction cannot distinguish between Ir and Os. The assignment of the H atom on Ir was based on the observation of the chemical shift of the metal hydride at δ (^{1}H) -8.29ppm. This resonance did not couple to boron and coupled to one cis-^{31}P resonance suggesting a terminal rather than a M-H-B or Os-H-Ir bridging position. Hydrides on Os atoms tend to fall at lower field than those for Ir[33] and iridaboranes with triphenylphosphine ligands tend to exhibit phosphine loss from the metal or migration of the phosphine to the borane cluster.[34,35] Although the identification of the metal atom positions is not absolutely definite, their combined contribution to the cluster is clear. They represent two effectively octahedral 18-electron metal centers providing a total of 4-electrons and 6-orbitals to cluster bonding. Thus they replace two BH vertices which, together with the 10-electron $\{B_5H_5\}$ unit, provide 14 skeletal bonding electrons; correct for a 7-vertex pileo cluster.[28,36] The notable feature of the boron-11 NMR spectrum is that the capping B atom falls at very low field (δ = 94ppm) and this conforms to spectra for a series of systems in which the boron atom is bonded to more than one metal atom. Examples range all the way to encapsulated borons in metal clusters and the greater the number of metal atoms bonded to the boron atom, the greater the deshielding and the lower the ^{11}B chemical shift.[37]

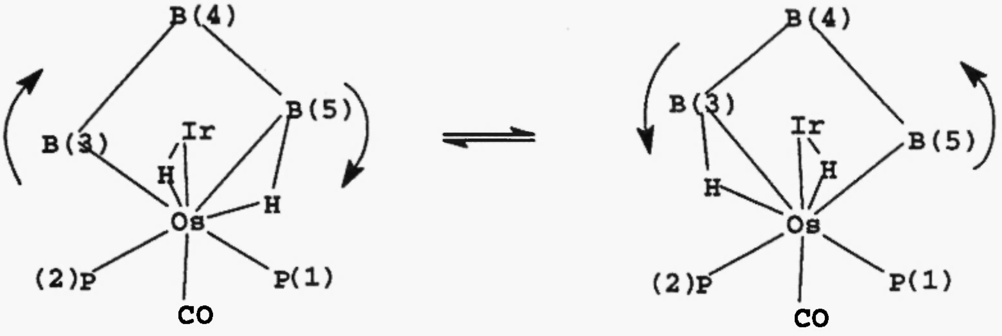
In order to provide further information about the metal locations, the ligands on the starting metal complex were changed. The use of $[(PMe_3)_2(CO)IrCl]$ for the preparation of an analogue of **VII** proved to be unsuccessful so we chose to use $[\{\eta^5\text{-}(C_5Me_5)Ir\}Cl_2]_2$. Deprotonation of **IV** using n-BuLi in THF at -35 ºC, addition of $[\{\eta^5\text{-}(C_5Me_5)Ir\}Cl_2]_2$ and slow warming to room temperature followed by chromatographic separation resulted in the isolation of several products. Two of these were characterized by NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. The first, a yellow, air-stable crystalline solid obtained in yields of up to 21%, was *closo*-$[1\text{-}(C_5Me_5)\text{-}2,2,2,\text{-}(CO)(PPh_3)_2\text{-}1,2\text{-}(\mu H)\text{-}1,2\text{-}IrOsB_4H_5]$ (**VIIa**). The second, also a yellow air-stable crystalline solid and isolated in ca. 5% yields was *nido*-$[2,2,2,\text{-}(CO)(PPh_3)_2\text{-}3\text{-}(C_5Me_5)\text{-}2\text{-}(\mu H)\text{-}2,3\text{-}IrOsB_3H_6]$(**VIII**). FAB mass spectra confirmed the formulation of **VIIa** as a B_4H_6 cluster containing the metal groups $\{\eta^5\text{-}(C_5Me_5)Ir\}$ and $\{(CO)(PPh_3)_2Os\}$. As indicated in the representation of the 4-Cl derivative of **VIIa** below, each boron atom contains a terminal H atom. In addition, the $^1H\{^{11}B\}$ NMR spectrum identifies bridging H atoms associated with the Os(2)-B(5) and Os(2)-Ir(1) edges. By analogy with related systems, the two bridging hydrogen resonances, observed at -11.65 and -19.20 ppm, are assigned to occupancy of the two aforementioned edges respectively. The angle that P(1) makes with the cage [P(1)-Os-B(5)] is 24º greater than the corresponding angle P(2) makes with the cage [106.3(2) º vs. 84.4(2) respectively], probably due to the steric influence of the bridging H atom. The final electron density maps showed no significant residual electron density about the Os-B(6)-B(3) or the Os-B(5)-B(6) faces other than that attributed to $H\mu_{2.5}$ thus supporting the assignment of this H atom.



VIIa

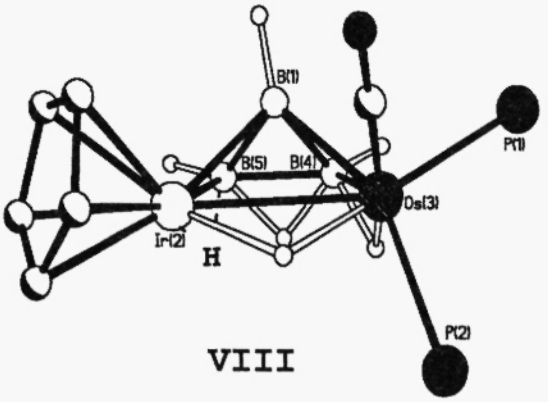
The electron density map also indicated the presence of $H\mu_{1\ 2}$. This assignment was confirmed by the preparation of *closo*-$[1\text{-}(C_5Me_5)\text{-}2,2,2,\text{-}(CO)(PPh_3)_2\text{-}1,2\text{-}(\mu H)\text{-}1,2\text{-}RhOsB_4H_5]$ (**VIIb**) in which the low temperature proton-NMR spectrum clearly shows coupling to ^{103}Rh for $H\mu_{1\ 2}$ in addition to coupling to one ^{31}P on the osmium and no coupling to boron, suggesting that the H atom is also not in the face capping position. The two bridging H atoms lie on the face of the cluster that would hold the capping vertex in a pileo cluster such as **VI** and this may be used as supporting evidence for the placement of the bridging H atoms in edge-bridging positions. The related dicobalt analogue $[\eta^5\text{-}(C_5Me_5)Co\}_2B_4H_6]$,[38] is considered to contain face-capping H atoms rather than edge bridging positions but the assignments are based primarily on the refinement of X-ray data. Although face capping H atoms are more common than edge-bridging ones in *closo* clusters, there are other examples with this latter feature. $[1,1\text{-}(PMe_2Ph)_2\text{-}1,2\text{-}\mu\text{-}H\text{-}2,5\text{-}(OMe)_2\text{-}$*isocloso*-$1\text{-}RhB_{10}H_8]$,[39] for example, contains one bridging H atom and the *pileo* systems reported by Leach et al. including $[\{\eta^5\text{-}(C_5H_4Me)Mo\}_2B_5H_9]$[17a] and $[\{\eta^5\text{-}(C_5H_5)Fe\}(MoL_3H)B_5H_7]$[12] contain capping BH_3 and BH_2 groups respectively involving two and one bridging H atoms.

Variable temperature NMR spectra of **VIIa** indicate a fluxional process which renders the two boron atoms B(3) and B(5), their associated terminal H atoms and the two bridging hydrogens, respectively as equivalent on the NMR time scale at ambient temperature. On cooling to 179 K separate resonances are observed for the two boron atoms and the four H atoms. The free energy barrier for the process is $\Delta G^{\#}_{230\ K} = 38$ kJ mol^{-1} and we suggest an effective rocking motion as indicated by **A** and **B** below wherein the Os-H-Ir bridging hydrogen atom moves to an Os-H-B(3) bridging position and the Os-H-B(5) atom moves to a metal-metal bridging position. The motion would render B(3) and B(5) equivalent as the angles P(2)-Os-B(5) and P(1)-Os-B(5) undergo concurrent increase and decrease. The NMR spectra of **VIIb** suggest similar behavior.



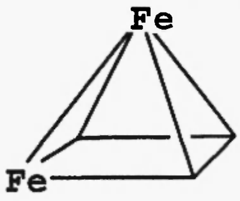
A **B**

Ignoring the ligands on Os and Ir, the structures of **VIIa/b** are related to that of **VI** by the simple removal of the capping BH vertex. The two bridging H atoms in **VII** replace the two skeletal electrons lost with the BH moiety, thus the octahedral cluster conforms structurally to a *closo*.system and has the required skeletal electron count.[40] Formal removal of a second BH vertex from **VI** affords a structure consistent with that deduced from analytical and spectroscopic data for **VIII**, that is a *nido*-five vertex cluster resembling that of *nido*-B_5H_9 with the two metal atoms in adjacent basal positions. Although the H atom bridging the 2-5 edge was not located in the X-ray structure determination, it was clearly identified by NMR measurements. There are several examples of structurally characterized bimetallapentaboranes in which two metal moieties replace BH vertices in various positions but **VIII** is the first example of a heterobimetallapentaborane to be structurally characterized and also the first 2,3-bimetallapentaborane. The other members of of this class are $[1,2\text{-}\{Fe(CO)_3\}_2\text{-}B_3H_7]$[41], $[1\text{-}\{\eta^5\text{-}(C_5Me_5)Co\}\text{-}2\text{-}(\eta^5\text{-}C_5Me_5H)CoB_3H_8]$,[42,17c] $[2,4\text{-}\{\eta^5\text{-}(C_5Me_5)Co\}_2B_3H_7]$[42,17c] and the unique capped *nido*-system $[2,3\text{-}\{Fe(PMe_3)_2\}_2(\mu\text{-}H)B_4H_9]$.[43] These are shown as **C** - **F** below.

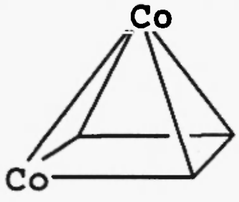


VIII

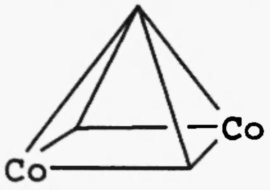
The nido-pentaborane cluster, **VIII**, clearly adds to the series **C** - **F**, but it also is related to the *closo* species **VIIa** by the loss of one BH vertex and to the *pileo* species **VI** by the loss of two BH vertices. The four bridging H atoms point towards the location of the missing vertex in **VIIa** and effectively supply the electrons and orbitals of the two missing BH moieties. Another way of representing the relationship between the three species **VI**, **VII** and **VIII** is given in **Scheme I**; that is they represent a series of metallaboranes essentially differing only in the number of BH vertices. They all conform to the polyhedral skeletal electron pair theory (PSEPT) and thus represent a unique series of homologous cluster types.[27a] All three contain 14 skeletal electrons or seven skeletal pairs of electrons. **VI** has seven vertices and thus meets the criteria for a capped octahedral cluster.[36] Removal of the capping BH vertex gives **VII**, a conventional six-vertex *closo* cluster and removal of a second BH vertex gives **VIII**, a classical *nido* five-vertex cluster. Formation of **VI** was unexpected and it is not easy to visualize a rational reaction pathway for the insertion of $[(PPh_3)_2(CO)Ir]^+$ into the $[OsB_5]^-$ cluster such that a *pileo* system is formed but it is interesting to note that the addition of metal reagents to a *nido*-FeB_5 cluster forms products which are also capped octahedral clusters.[12] On the basis of our results, these latter observations and our previous preparation of $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2B_5H_5]$,[30] perhaps *pileo* species may be the preferred closed structures in 7-vertex bimetallaborane clusters.



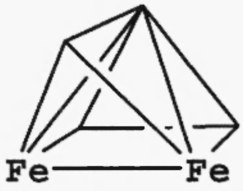
C



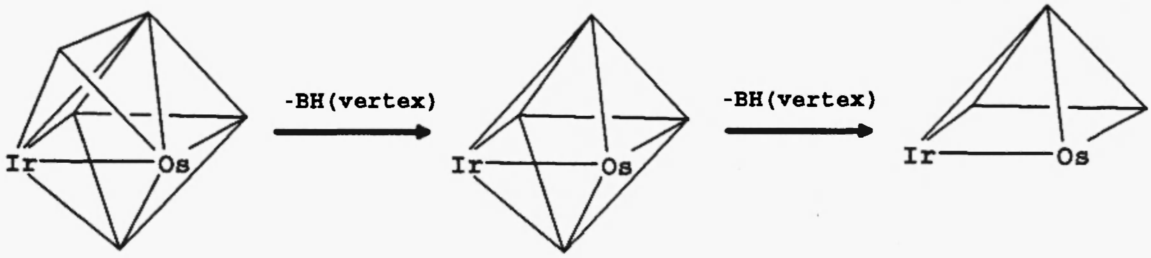
D



E



F



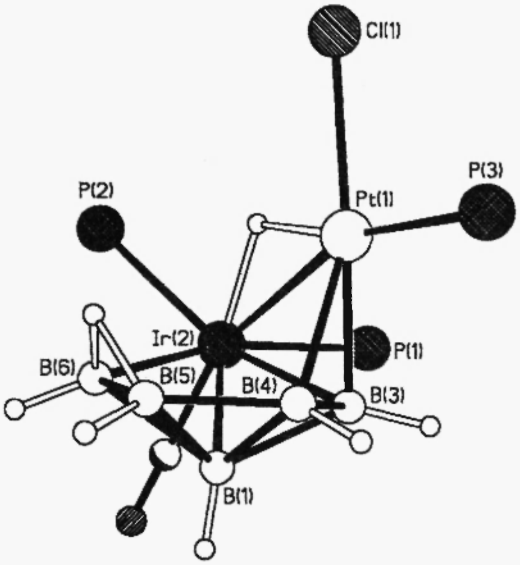
Scheme I

Formation of heterobimetallaboranes from V.

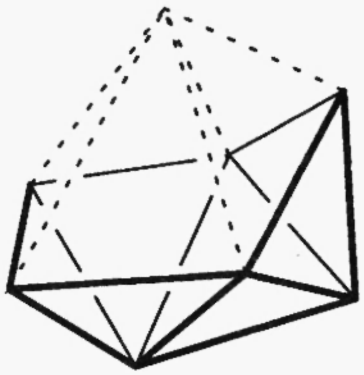
The iridahexaborane (**V**), is similarly prepared by the oxidative insertion of $[(CO)(PPh_3)_2Ir(I)]$ into the $[B_5H_8]^-$ anion[26] however formation of derivatives of **V** using similar procedures to those described above for **IV** proved to be much more difficult. **IV** contains one more bridging H atom than **V** and is consequently easier to deprotonate. In fact our lack of success in this effort led us to attempt to prepare the species $[\{(\eta^5\text{-}C_5Me_5)Ir\}B_5H_9]$ from $Na_2[B_5H_9]$ which resulted in the formation of $[\{(\eta^5\text{-}C_5Me_5)Ir\}_2B_5H_5]$.[30] However we were successful in preparing an iridium analogue of the Os compound, $[(CO)(PPh_3)_2(\mu\text{-}H)Os(PMe_2Ph)ClPtB_5H_7]$, reported previously by Bould et al.[9]

Treatment of **V** with NaH in THF followed by addition of $[(PMe_2Ph)PtCl_2]_2$ results in the formation of yellow solid $[2,2,2\text{-}(CO)(PPh_3)_2\text{-}7,7\text{-}Cl\text{-}(PMe_2Ph)\text{-}$*nido*$\text{-}2,7\text{-}IrPtB_5H_7]$, **IX**, in 5% yield. NMR spectra for **IX** were very similar to those for of $[(CO)(PPh_3)_2(\mu\text{-}H)Os(PMe_2Ph)ClPtB_5H_7]$ suggesting that the structures of the two species were very similar. This was confirmed by an X-ray structure determination which is shown below. The structure of **IX** resembles a classical seven vertex polyhedron from which a five-connectivity vertex has been removed (**X**). A projection of **IX** and a representation of **X** are given below. There are significant differences between the idealized structure and **IX**. In the latter the original IrB_4 plane (of **V**), Ir-B(3)B(4)B(5)B(6), remains relatively flat with a fold between the two subplanes IrB(4)B(5)B(6) and IrB(3)B(4) of only 22°. For an idealized eight vertex triangulated dodecahedral cluster, the value should be 39.9°. This latter value was observed for the structurally determined system $[Zn(NH_3)_4][B_8H_8]$.[44] Other features of the structure of **IX** are quite similar to those of **X** , without the 4-connected vertex, thus supporting the assignment of **IX** as a seven-vertex *nido* cluster.

The skeletal electron count for **IX** gives eight skeletal electron pairs: 14 electrons from the $[B_5H_7]^{2-}$ moiety, 2 electrons from the $[(PPh_3)_2(CO)Ir]^+$ moiety and no electrons from the

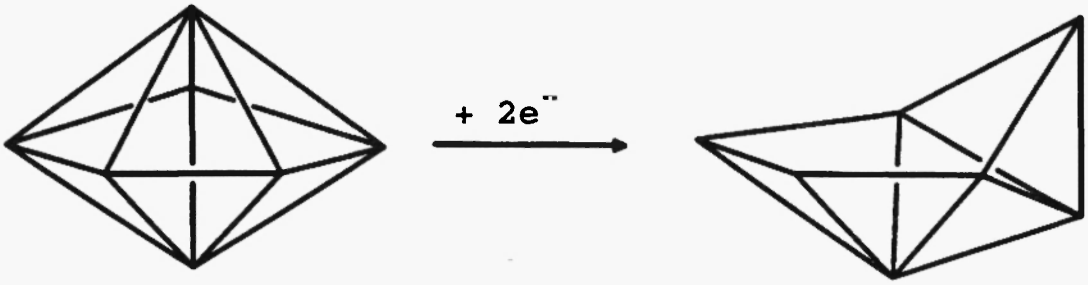


IX



X

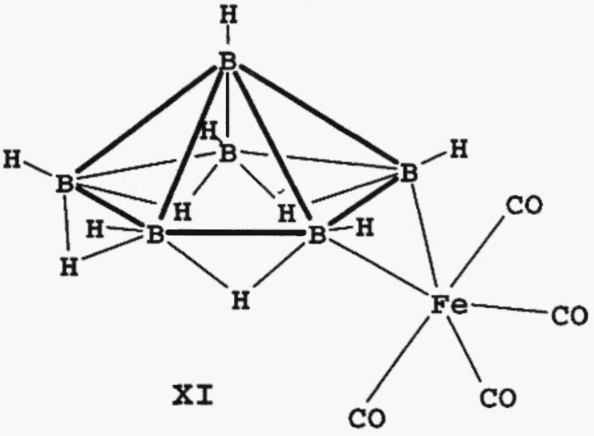
$[(PMe_2Ph)PtCl]^+$ moiety. For a seven-vertex cluster, *closo* geometry would be expected,[40b,c,d] thus **IX** is two electrons short for a *nido*-seven vertex system. The same result was observed for the related $OsPtB_5$ cluster $[(CO)(PPh_3)_2(\mu\text{-}H)Os(PMe_2Ph)ClPtB_5H_7]$.[9] The rationale suggested by the authors to explain the structure of the latter noted that the Pt center is not a conventional three orbital two electron conical vertex because the square planar Pt^{2+} moiety contributes only two orbitals and one electron to the skeletal electron count.[9] A more complete discussion of this and related points are found in ref 9c and 45. A comparison of the structures of **IX** and **V** allows an examination of the differences between *nido* 6-vertex and *nido* 7-vertex clusters. A *nido* 6-vertex cluster is a regular pentagonal pyramid whereas a nido 7-vertex cluster is one based on the loss of a four-connected vertex from a triangulated dodecahedron. Thus addition of a vertex to the former to give the seven vertex nido-system occurs with a concomitant folding of the original basal five membered plane. The difference between the conventional 7-vertex *nido* and *closo*-clusters is seen in **Scheme II**. Addition of a pair of electrons to the *closo*-cluster would be normally be required to form the *nido* system but in this case the presence of the Pt moiety changes the situation. Clearly, as indicted by the projection of **IX** and illustration **X**, the former is structurally, a *nido*-cluster.



Scheme II

Another method of incorporating a new metal vertex into a hexaborane(10) analogue would be to add a 16-electron metal-containing moiety to a basal B-B or B-metal bond in a hexaborane(10). B_6H_{10} (illustration **III**) contains a basal B-B bond with a high degree of basic character.[46,] This is a feature which has been exploited in the formation of a number of compounds with iron, iridium, rhodium and platinum.[14] The basal bond donates two electrons to the metal.[14] Thus in the case of the iron, [μ-$Fe(CO)_4$]B_6H_{10} (illustration **XI**) is formed from the reaction between B_6H_{10} with $Fe_2(CO)_9$. It was therefore of interest to see if the iridahexaborane analogue **V**, which has a similar basal B-B bond (1.65 Å vs. 1.63 Å in B_6H_{10}),[26,13b] would exhibit similar chemistry.

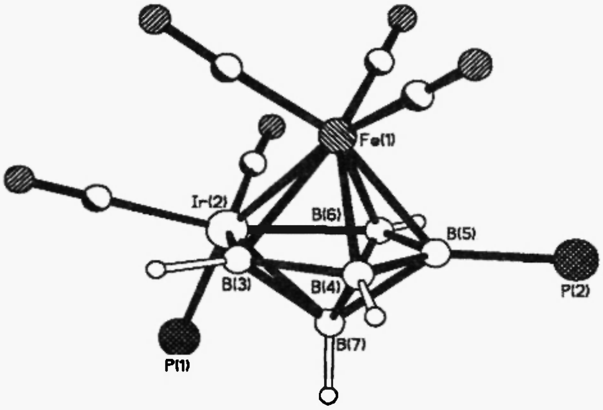
Reaction between **V** and [$Fe_2(CO)_9$] in stirring C_6H_6 for 24 h, followed by thin-layer chromatography of the resultant mixture, affords [1,1,1-$(CO)_3$-2,2,2,5-$(CO)_2(PPh_3)_2$-*closo*-1,2-$FeIrB_5H_4$], **XII,** in *ca.* 30% yield.[47] NMR spectra suggested a *closo*-cluster and this was confirmed by a single crystal X-ray diffraction study. The structure, shown below, is a *closo*-bimetallaheptaborane cluster with a $Fe(CO)_3$ moiety in an axial position and a $Ir(CO)_2PPh_3$ moiety in an equatorial position. Excluding



XI

the carboranes, there are very few known pentagonal bipyramidal metallaboranes and even fewer such systems containing two metals. The species $[\{Mo(\eta^5\text{-}C_5H_4Me)\}_2B_5H_9]$, prepared by Leach and coworkers[17] resembles a pentagonal bipyramid although the alternative description as a bicapped trigonal bipyramid is preferred by the authors. Two other pentagonal bipyramidal systems have been identified from NMR data. They are $[\{\eta^5\text{-}C_5Me_5)Ni\}B_6H_6]^{2-}$[48] and $[\{\eta^5\text{-}C_5Me_5)Co\}_2B_5H_7]$[25b] but we believe that **XII** is the only structurally characterized example and the only example of a heterobimetallaheptaborane.

Compound **XII** conforms to the PSEPT in that the seven-vertex cluster contains eight skeletal electron pairs. The geometry of **XII** is very close to that for an idealized *closo*-7-vertex cluster. The equatorial IrB_5 ring is essentially planar and in fact the $[(PPh_3)_2(CO)IrB_5H_4(PPh_3)]$ moiety retains much of the geometry of **V** with the $Fe(CO)_3$ unit capping the IrB_4 face. Interestingly, although the iron/borane analogy is a much discussed phenomenon,[49] as far as we are aware, there are no examples of borane clusters in which a $Fe(CO)_3$ group is η^5-bonded in a borane cluster and thus caps a B_5 face. There are, however, examples in metallacarborane chemistry of systems in which a $Fe(CO)_3$ caps a C_2B_3 face. These include the small *nido*-system $1,2,3\text{-}(CO)_3FeC_2B_3H_7$[50] and the recently described icosahedral species *closo*-$[(CO)_3FeC_2B_9H_{11}]$.[51]

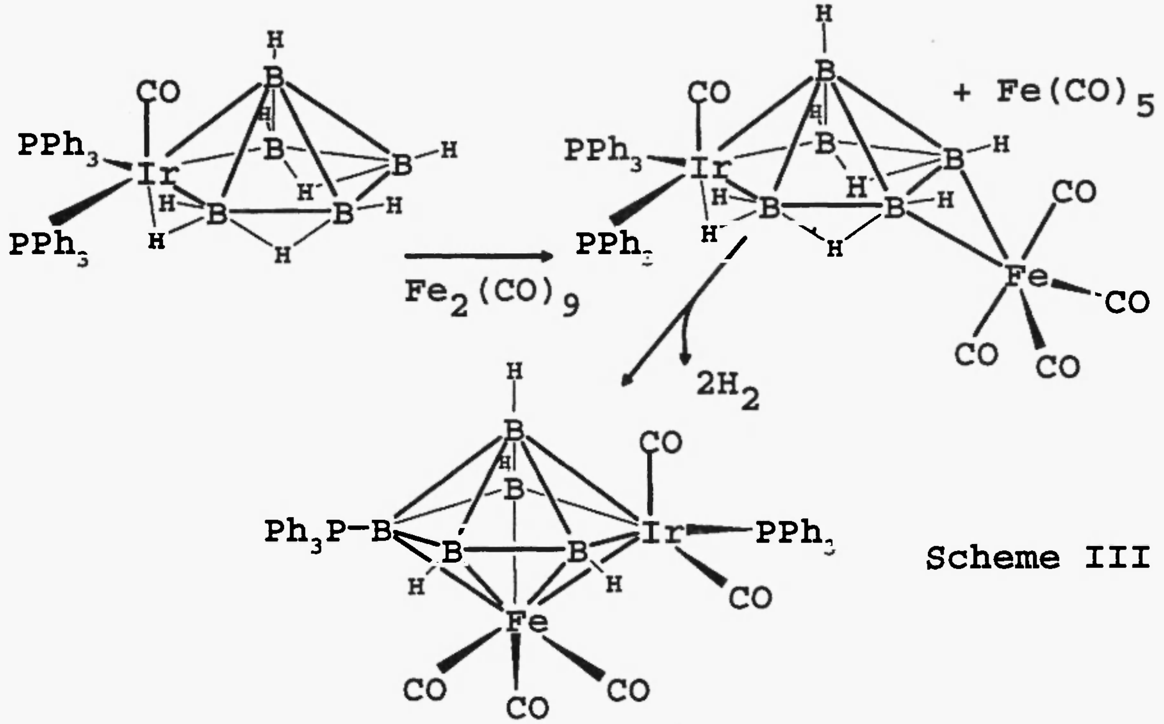


XII

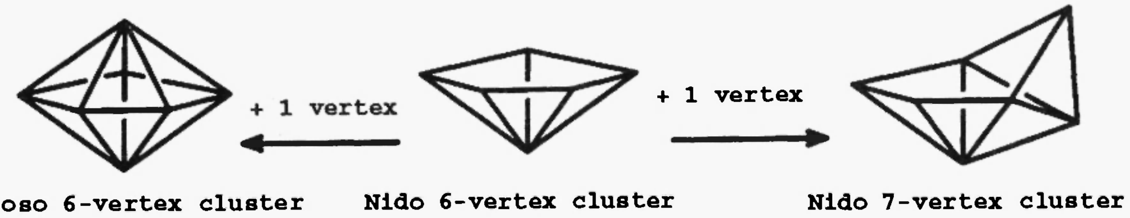
The structural features of **XII** are quite normal. The Fe-Ir distance of 2.707(2) is slightly longer than the sum of the covalent radii and also slightly longer than the Fe-Ir distance we determined in $[1,1,2,2\text{-}(CO)_4\text{-}1,2\text{-}(PPh_3)_2\text{-}1,2\text{-}FeIrB_2H_5]$ which is 2.621(1).[35] The ^{11}B NMR spectrum of **XII** exhibits two low field resonances which are assigned to two boron atoms bonded to two metals. This is typical for boron atoms bonded to metals and as mentioned earlier it has been observed that the more metal atoms bonded to the boron, the greater the deshielding and the lower the ^{11}B chemical shift.[37] The NMR spectra were not unambiguously assigned but the $B(PPh_3)$ group was easily identified as a single broad resonance. The other boron resonances were too broad to identify BH coupling. There are some metallacarborane pentagonal bipyramidal clusters with which we could compare **XII** but only one metallaboranes, $[\{\eta^5\text{-}C_5Me_5)Co\}_2B_5H_7]$,[25b] and the lack of a structure for the latter along with the influence of the $B(PPh_3)$ moiety in **XII** limit the use of such comparisons.

A reasonable reaction stoichiometry for the formation of **XII** is given in the equation below: $(CO)(PPh_3)_2IrB_5H_8 + Fe_2(CO)_9 \rightarrow 2H_2 + Fe(CO)_5 + (CO)_2(PPh_3)IrB_5H_4(PPh_3)Fe(CO)_3$. This would suggest that **XII** is formed by the initial addition of a $Fe(CO)_4$ moiety to the iridaborane followed by ligand rearrangement and hydrogen loss as indicated in **Scheme III**. This is analogous to the formation of **XI** from the reaction between **III** and $Fe_2(CO)_9$.[14] The migration of the PPh_3 group from the iridium to the boron cage has precedent[34] and we recently observed what amounted to PPh_3/CO exchange between Fe and Ir in the formation of $[1,1,2,2\text{-}(CO)_4\text{-}1,2\text{-}(PPh_3)_2\text{-}1,2\text{-}FeIrB_2H_5]$.[35]

The formation of **IX** and **XI** from **V** would appear to represent examples of standard hexaborane(10) chemistry applied to a metallahexaborane(10). However, addition of a vertex to *nido*-hexaborane(10) cluster to form a *nido* 7-vertex cluster has not been directly observed. Such a reaction involves oxidative insertion of the metal group into the cage. Addition of a metal moieties to **III** have been observed wherein the new metal is essentially a pseudo proton. This is seen in species containing Mg,[52a] Zn[52a], Cd,[52a] Cu[6], Sn[52b] and Ti[52c] moieties. The other way one would incorporate a metal moiety into **III** would add a 16-electron metal group to the basal B-B bond followed by effective oxidative insertion into the cage by loss of electrons as hydrogen and closure to afford a seven vertex closo-cluster. The two processes we observed for the incorporation of a second metal into the *nido* 6-vertex cluster are summarized schematically in **Scheme IV**.



Scheme III



Scheme IV

Conclusions

Our recent work has demonstrated that the formation of heterobimetallaheptaboranes from metallahexaboranes is a relatively straightforward process although the identity of the products, to this point, is not easily controlled. Our work complements concurrent work by Leach et al. and previous work by Bould et al. The tendency, in our work, to form *closo-* or *pileo*-boranes, or products which involve degradation of the cage suggests that there may be a rich chemistry in these systems since the precursors to these thermodynamically stable species may be isolated by adjusting the conditions. Degradation of the metallahexaborane cage was predicted from calculations[53] thus additional work may be able compare possible degradation mechanisms with those predicted by theory.

Finally we are delighted to be able to participate in this tribute to Sheldon Shore and to make contributions in a field in which he had such a major role establishing and in which he has made seminal contributions.

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