

THE FIRST OSMABORANES AND A NEW IRIDATETRABORANE *

JONATHAN BOULD, NORMAN N. GREENWOOD,* and JOHN D. KENNEDY

Department of Inorganic and Structural Chemistry, University of Leeds, Leeds LS2 9JT (Great Britain)

(Received February 2nd, 1983)

Summary

The reactions of $[\text{Os}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ under mild conditions with the anions *arachno*- $[\text{B}_3\text{H}_8]^-$ and *nido*- $[\text{B}_5\text{H}_8]^-$ yield the first air-stable polyhedral osmaborane species *arachno*- $[(\text{HOsB}_3\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (65%) and *nido*- $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ (80%) respectively. The ^{11}B and ^1H NMR properties of these osmaboranes are similar to those of their iridium analogues *arachno*- $[(\text{H}_2\text{IrB}_3\text{H}_8)(\text{PPh}_3)_2]$ (also previously unreported) and *nido*- $[(\text{IrB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$. Mild thermolysis of *nido*- $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ yields *nido*- $[(\text{OsB}_4\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (40%) for which there is, as yet, no iridium analogue.

Introduction

A consideration of borane-to-metal bonding modes, ligand *trans* effects, etc., within the metallaborane derivatives of the heavier transition elements indicates that the electronic requirements of borane ligands in many cases are similar to those of organic and hydridic ligands [1–5]. In accord with this, it is apparent from surveys of known compounds [6] that those types of metal centre that readily form hydrocarbon complexes or polyhydride species with high formal metal valency states also form particularly stable metallaborane cluster compounds. In particular, iridium, which readily forms a variety of organic and hydridic complexes with formal valency states as high as iridium(V) [7,8], has a very rich polyhedral metallaborane chemistry which also exhibits these formally high valency states [1,2,5,6,9–25]. This may imply that other mid-to-late 5d transition metal centres which form high valency polyhydridic species, such as tungsten, rhenium, and osmium, may similarly exhibit a rich polyhedral metallaborane chemistry. Of these, however, only limited investigations have been reported in wolfraborane [26,27] and rhenaborane [27–29] chemistry, and no osmaboranes appear to have been previously investigated. We now report that stable osmaboranes can be readily prepared, and that some of these have remarkably

* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983.

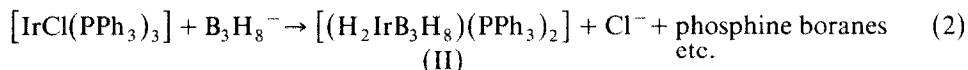
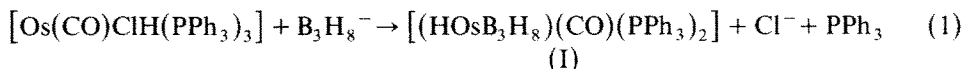
similar properties to previously reported iridium analogues. We also take this opportunity to describe a new iridatetaborane, synthesized in this laboratory but previously unreported.

The preparation and identification of the new compounds follow below, but in addition to these, which were readily identifiable due to their structural similarities to known species, there were a number of additional products which appear to exhibit new structural features and which we hope to be able to describe in future communications.

Results and discussion

2,2,2,2-Carbonylhydridobis(triphenylphosphine)-arachno-2-osmatetaborane, [(HOsB₃H₈)(CO)(PPh₃)₂] (I) and *2,2,2,2-dihydridobis(triphenylphosphine)-arachno-2-iridatetaborane*, [(H₂IrB₃H₈)(PPh₃)₂] (II)

The reactions between TiB₃H₈ and [(Os(CO)ClH)(PPh₃)₃] or [IrCl(PPh₃)₃] in dichloromethane solution at ambient temperature over 4 days yield the colourless, air-stable, crystalline solids [(HOsB₃H₈)(CO)(PPh₃)₂] (I) and [(H₂IrB₃H₈)(PPh₃)₂] (II), identified as such by analytical data and spectroscopy. Isolated yields were 65 and 30% respectively. The reaction of the osmium compound may be represented as a straightforward metathesis accompanied by the elimination of the two-electron donor PPh₃ (eq. 1), whereas in the iridium reaction a hydrogenation of the metal centre also occurs with a concomitant increase in the formal metal valency state (eq. 2):



The NMR properties of I and II are summarised in Tables 1 and 2 with those of

TABLE 1

¹¹B AND ¹H NMR DATA ^a FOR *arachno*-[(HOsB₃H₈)(CO)(PPh₃)₂] (I), *arachno*-[(H₂IrB₃H₈)(PPh₃)₂] (II) AND *arachno*-[(ReB₃H₈)(CO)₄]

Assignment	[(HOsB ₃ H ₈)(CO)(PPh ₃) ₂] ^b		[(H ₂ IrB ₃ H ₈)(PPh ₃) ₂] ^b		[(ReB ₃ H ₈)(CO) ₄] ^c	
	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H) ^e	δ(¹¹ B)	δ(¹ H) ^e
4	1.0	4.34, 2.20	1.2	4.81, 2.32	0.3	4.60, 2.86
(1,3) ^d	{ -40.5 -39.5	0.56, -0.21 -0.83	-39.4	{ 0.04 (2) -0.74 (2)	-43.2	{ 1.17 (2) -0.17 (2)
H(1,2)		-9.07				
H(2,3)		-10.20		-9.48 (2)		-8.97 (2)
M-H _i		-10.10 ^f		-13.30 (2) ^g		

^a δ(¹¹B) in ppm to high frequency of BF₃OEt₂ and δ(¹H) in ppm to high frequency of TMS. ^b CDCl₃ solution at 21°C. ^c CD₂Cl₂ solution at ambient temperature, ref. 29. ^d Absolute assignments for protons uncertain. ^e Values in parentheses indicate number of hydrogens. ^f Triplet ²J(³¹P-¹H_i) 20 ± 1 Hz. ^g Triplet of doublets ²J(³¹P-¹H_i) 18.0 ± 0.5 Hz, ²J(¹H_{bridge}-¹H_i) 7.0 ± 0.5 Hz.

TABLE 2

^{31}P NMR DATA ^a FOR $[(\text{HOsB}_3\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (I), $[(\text{H}_2\text{IrB}_3\text{H}_8)(\text{PPh}_3)_2]$ (II), $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ (III) AND $[(\text{OsB}_4\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (IV)

Compound	$\delta(^{31}\text{P})^a$	$^2J(^{31}\text{P}-^{31}\text{P})$ (Hz)
I	21.5, 13.7	230 $\pm$ 2
II	19.0, 10.1	333 $\pm$ 2
III	13.5, 5.6	19.5 $\pm$ 0.2
IV	14.1, 7.0	12.2 $\pm$ 0.5

^a CDCl_3 solution at -50°C ; $\delta(^{31}\text{P})$ in ppm to high frequency of $\delta(^{31}\text{P})$ (85% H_3PO_4) = zero.

the well-characterized rhenaborane [27] analogue $[(\text{ReB}_3\text{H}_8)(\text{CO})_4]$.

The similarity of the ^{11}B and ^1H NMR chemical shifts of the borane ligand in all three compounds confirms the similarity of bonding in the three species as does the interesting selective decoupling of the $^1\text{H}(4\text{-exo})$ and the $^1\text{H}(4\text{-endo})$ resonances *only* in selective $^1\text{H}\{-^{11}\text{B}(4)\}$ experiments [27], together with the selective decoupling of $^1\text{H}(1)$, $^1\text{H}(3)$, $^1\text{H}(1,4)$, $^1\text{H}(3,4)$, $^1\text{H}(2,3)$ and $^1\text{H}(1,3)$ in $^1\text{H}\{-^{11}\text{B}(1), ^{11}\text{B}(3)\}$ experiments. It is well known that the protons in the bridging H atoms in B_4H_{10} itself similarly exhibit strong coupling to $^{11}\text{B}(1,3)$, but not to $^{11}\text{B}(2,4)$. That separate resonances are observed for all protons in the osmatetaborane indicates that there is asymmetry at the metal centre, as is also observed [27] for the iron analogue $[(\text{HFeB}_3\text{H}_8)(\text{CO})_3]$, whereas the iridatetaborane shows the same pattern as the symmetrical rhenaborane. The ^1H NMR signals for the terminal hydrides on osmium (relative intensity 1) and iridium (relative intensity 2) are triplets due to *cisoid* coupling to two ^{31}P nuclei with very similar couplings: $^2J(^{31}\text{P}\text{--Os--}^1\text{H})_{\text{cis}}$ ca. 20 Hz and $^2J(^{31}\text{P}\text{--Ir--}^1\text{H})_{\text{cis}}$ ca. 18 Hz. The large couplings $^2J(^{31}\text{P}\text{--M--}^{31}\text{P})$ of 230 and 333 Hz indicate a mutually *trans*-disposition of the two phosphorus atoms in both cases. The presence of a further small coupling $^2J(^1\text{H}_{\text{br}}\text{--}^1\text{H}_{\text{t}}(\text{M}))$ in the iridium compound of 7 Hz (confirmed by $^1\text{H}\{-^1\text{H}\}$ selective decoupling experiments) has been observed before [17] where the Ir–H–B bridging H atom is *trans* to a terminal Ir–H hydrogen atom. The absence of this coupling in the osmium compound is interesting and may imply that the borane ligand is twisted slightly with respect to the idealized octahedral coordination, or that other differential CO vs. H *trans*-effects apply. This is consistent with the general asymmetry of the molecule. The alternative coordination stereochemistry involving mutually *cis* phosphine ligands is excluded by the magnitude of $^2J(^{31}\text{P}\text{--}^{31}\text{P})$ and the absence of any *trans* couplings $^2J(^{31}\text{P}\text{--}^1\text{H}_{\text{br}})$ to the nuclei of the bridging H atoms. The diamagnetism of the complex, together with the intermediate position of osmium between rhenium and iridium in the periodic table, implies that there is an additional neutral 2-electron donor ligand to the metal in the osmium compound. That this is a carbonyl ligand follows readily from the infrared spectrum which has $\nu_{\text{max}}(\text{CO})$ at 1970 cm^{-1} . The presumed structures are therefore as represented in Fig. 1.

The molecules may be regarded as eighteen-electron six-coordinate octahedral d^6 osmium(II) and iridium(III) complexes, with the *arachno*- B_3H_8^- moiety acting as a bidentate η^2 -ligand via two B–H–M bridge bonds. Alternatively, if I and II are considered as *arachno* four-vertex clusters, the $\{\text{Os}(\text{CO})\text{H}(\text{PPh}_3)_2\}$ and $\{\text{IrH}_2(\text{PPh}_3)_2\}$

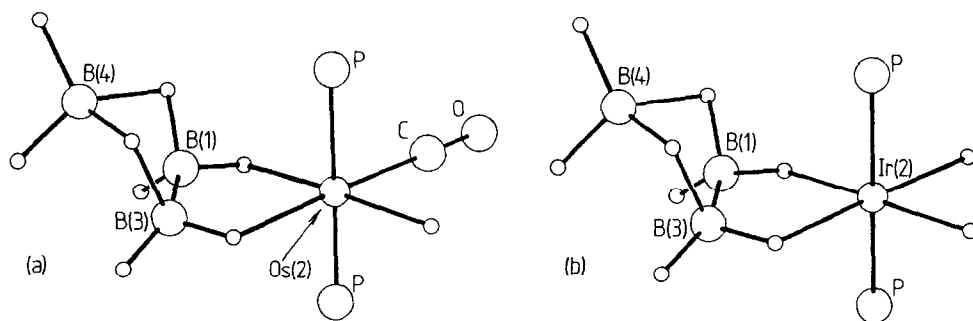


Fig. 1. Proposed structures and numbering scheme for (a) 2,2,2,2-carbonylhydridobis(triphenylphosphine)-*arachno*-2-osmatetaborane, $[(\text{HOSB}_3\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (I), and its iridium analogue (b) 2,2,2,2-dihydridobis(triphenylphosphine)-*arachno*-2-iridatetaborane, $[(\text{H}_2\text{IrB}_3\text{H}_8)(\text{PPh}_3)_2]$ (II).

moieties are equivalent to the $\{\text{BH}_2\}$ moiety in the 2-position of the parent *arachno*- B_4H_{10} cluster, and there probably will be significant cluster interaction in addition to the two $\text{M}-\text{H}-\text{B}$ linkages.

The iridium compound (a) in Fig. 2 has important differences to the other known *arachno*-iridatetaborane $[1,1,1,1-(\text{CO})(\text{H})(\text{PPh}_3)_2-1-\text{IrB}_3\text{H}_7]$ (Fig. 2b). This was previously thought also to be an 18-electron d^6 6-bonding-orbital octahedral iridium(III) complex [13], but recent structural evidence [22] suggests that it is better considered as an 18-electron d^4 7-orbital capped octahedral iridium(V) complex as in schematic structure b. The electronic equivalence $\{\text{Ir(III)} + 2\text{H}\} \equiv \{\text{Ir(V)}\}$ is of interest here.

4,4,4-Carbonylbis(triphenylphosphine)-*nido*-4-osmahexaborane, $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ (III)

The reaction between *nido*- B_5H_8^- and the iridium(I) complex *trans*- $[\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2]$ in $\text{CH}_2\text{Cl}_2/\text{THF}$ solution at low temperatures has been previously reported to give an 18% yield of the *nido*-iridahexaborane species $[(\text{IrB}_5\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ [5]. We have subsequently repeated this synthesis and can now isolate the iridaborane in ca. 85% yield on a scale of 2 mmol under very similar conditions. We have found that the osmium(II) complex $[\text{Os}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ also reacts under these conditions with the *nido*- B_5H_8^- anion to give a high isolated yield (ca. 80% on a scale of 0.4 mmol) of the pale-yellow, air-stable crystalline solid

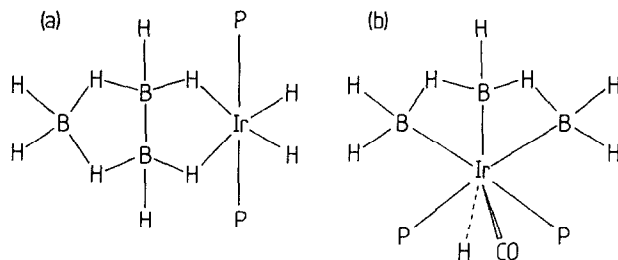
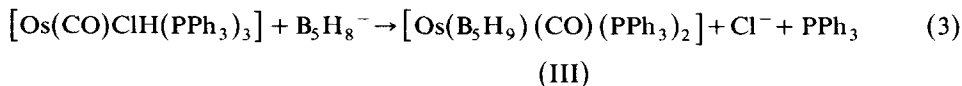


Fig. 2. Representations of localized valence bond structures for (a) the *arachno*-2-iridatetaborane $[(\text{H}_2\text{IrB}_3\text{H}_8)(\text{PPh}_3)_2]$ (II) and (b) the iridium(V) *arachno*-1-metallatetaborane $[(\text{H}\text{IrB}_3\text{H}_7)(\text{CO})(\text{PPh}_3)_2]$ (from ref. 22).

compound $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$, identified as such by analytical data and NMR spectroscopy. Mass spectrometry gives only trace quantities of the parent ion at m/e 807, the fragmentation pattern being otherwise very similar to the osmapentaborane described below. The reaction may again be represented by a straightforward stoichiometry (eq. 3):



The NMR properties of the osmahexaborane product are summarized in Tables 2 and 3 together with those of the well-characterized iridaborane [5], manganaborane [30], and ferraborane [31] analogues $[(\text{IrB}_5\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (V), $[(\text{MnB}_5\text{H}_9)(\text{CO})_3]^-$ (VI) and $[(\text{FeB}_5\text{H}_9)(\text{CO})_3]$ (VII). The similarities of the ^{11}B and ^1H chemical shifts clearly characterise the osmium species as an analogue of these iridium, manganese, and iron compounds, viz. as a *nido*-metalla-hexaborane with the metal atom in a basal position. The bridging proton shieldings indicate that there are two B–H–B and two M–H–B bridging H atoms, and that separate resonances for all the (B and) H positions are observed indicates that the metal centre is asymmetric with respect to the idealized C_s mirror plane of the metalla-hexaborane cluster. The small coupling constant $^2J(^{31}\text{P}-^{31}\text{P})$ of 18 Hz indicates two mutually *cis* phosphine ligands and the analytical, mass-spectrometric, and infrared data point to the remaining Os coordination site being occupied by a carbonyl ligand, $\nu_{\text{max}}(\text{CO})$ 1980 cm^{-1} .

The geometry thus established is represented in Fig. 3, which also contains the structure of the known [5] iridium species $[(\text{IrB}_5\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ for comparison. It may be noted here incidentally that we have now examined this iridium compound (which is asymmetric in the solid state) more thoroughly than we were previously able, for any asymmetry in solution by NMR spectroscopy: we conclude that there is in fact very rapid exchange even at -80°C of the Ir–H–B bridging H atom between the Ir(2)–B(3) and Ir(2)–B(6) positions, as previously postulated [5], and as is also found for the ferra-hexaborane analogue $[(\text{FeB}_5\text{H}_9)(\text{CO})_3]$ [31,32].

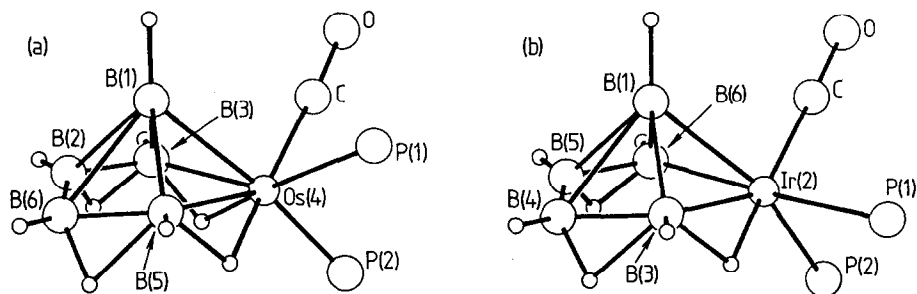


Fig. 3. (a) Proposed structure of 4,4,4-carbonylbis(triphenylphosphine)-*nido*-4-osmahexaborane, $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ (III) and (b) a representation of the known structure [5] of its iridium analogue 2,2,2-carbonylbis(triphenylphosphine)-*nido*-2-iridahexaborane, $[(\text{IrB}_5\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (V). In the osmium compound (a) the atom P(1) is *trans* to the Os–H–B(3) bridging H atom, P(2) is *trans* to the B(1) atom, and the carbonyl group is *trans* to the Os–H–B(5) bridging H atom. In the iridium compound (b) the atom P(1) is *trans* to the B(6) atom, the carbonyl group is *trans* to the Ir–H–B(3) bridging H atom, and the atom P(2) is *trans* to a three-centre bond involving the B(1) and B(3) centres.

TABLE 3

¹¹B AND ¹H NMR DATA ^a FOR *nido*-[(OsB₃H₉)(CO)(PPh₃)₂]⁺ (III), *nido*-[(IrB₃H₉)(CO)(PPh₃)₂]⁺ (V), *nido*-[2.2.2-(CO)₃-2-MnB₃H₉]⁺ (VI) AND *nido*-[2.2.2-(CO)₃-2-FeB₃H₉]⁺ (VII)

Assignment ^f	III	V ^h		VI ^c		VII ^d	
	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹¹ H)	δ(¹ H)
3 }	32.2	6.62	42	6.7	32.0	5.42	6.40
5 }	30.0	5.85	42	6.7	32.0	5.42	6.40
2 }	18.0	5.18	10	4.9	17.6	4.00	4.19
6 }	16.4	4.96	10	4.9	17.6	4.00	4.19
1	-39.2	-1.49	-28	-0.4	-43.9	-2.08	-1.19
B-H-B		-2.24		-2.6		-3.00	0.10
		-2.59		-2.6		-3.00	0.10
M(4)-H-B		-10.59 ^e		-12.05		-12.06	-16.82
		-9.03 ^g		-		-12.06	-

^a δ(¹¹B) in ppm to high frequency of BF₃·OEt₂; δ(¹H) in ppm to high frequency of TMS. ^b Ref. 5, CD₂Cl₂ solution. ^c Ref. 30, (C₂D₅)₂O solution. ^d Ref. 31, CD₂Cl₂ solution. ^e ²J(³¹P-¹H) (*trans*) 40 Hz, ²J(³¹P-¹H) (*cis*) 11 Hz. ^f Numbering for compounds V, VI and VII based on that for compound III. ^g Any coupling ²J(³¹P-¹H) (*cis*) not resolved, i.e. ≤ ca. 5 Hz.

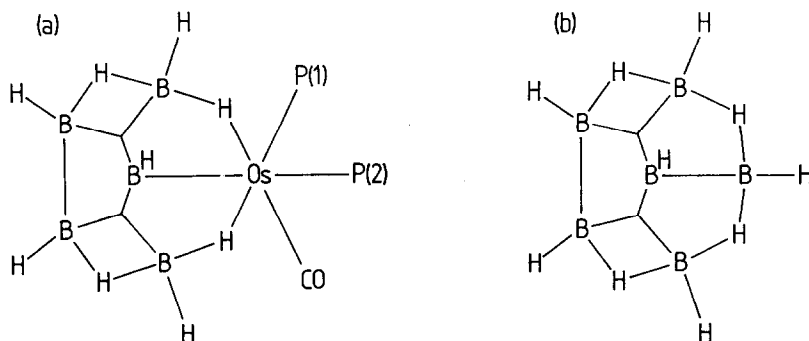


Fig. 4. Representations of localized valence bond structures for (a) the *nido*-4-osmahexaborane $[(OsB_5H_9)(CO)(PPh_3)_2]$ (III) and (b) *nido*-hexaborane itself (B_6H_{10}), to illustrate the essential similarities of the cluster bonding schemes. In each case a number of additional contributory canonical forms may be written down.

The osmaborane may be regarded as an eighteen-electron six-coordinated d^6 octahedral osmium(II) complex, with an effective *arachno*- $B_5H_9^{2-}$ ligand acting as a tridentate η^3 -ligand formally bonding to the metal centre via two B–H–Os bridge bonds and one direct Os–B(1) two-electron two-centre bond. A valence-bond structure may be written down for this as in Fig. 4a, although it must be emphasized that this will represent only one canonical form and that there will be significant cluster delocalisation. The similarity to a localized valence-bond scheme for *nido*-hexaborane, B_6H_{10} , itself (Fig. 4b) is readily apparent, and in cluster terms the $\{Os(CO)(PPh_3)_2\}$ moiety is equivalent to the $\{BH\}$ group in the 4-position of the parent binary hexaborane cluster.

It may finally be noted that there is no formal increase in the valency state of osmium(II) during the course of formation of the compound (eq. 2). This contrasts with the increase in valency state from iridium(I) to iridium(III) in the formation of the analogous iridium species [5]. In each case however an additional two electrons are supplied from the metal centre to the cluster during the course of the reaction. In the osmium reaction these are supplied by the bonding pair of electrons which are associated with the Os–H bond in the starting complex $[Os(CO)ClH(PPh_3)_3]$; these are transferred to the cluster by the formation of an Os–H–B bridging bond. There is no disruption of the d^6 core and there is consequently no formal increase in the metal valency state. In the iridium reaction, by contrast, these two electrons are supplied from the formally non-bonding d^8 core of the starting complex $[Ir(CO)Cl(PPh_3)_2]$ and so there is an increase in the formal valency state of the metal atom.

2,2,2-Carbonylbis(triphenylphosphine)-nido-2-osmapentaborane $[(OsB_4H_8)(CO)(PPh_3)_2]$ (IV)

The thermolysis of a sample of $[(OsB_5H_9)(CO)(PPh_3)_2]$ in tetrachloroethane solution at 100°C for 1 h produces the air-stable, colourless compound $[(OsB_4H_8)(CO)(PPh_3)_2]$ in an isolated yield of ca. 40% (on a scale of 0.1 mmol), the product being identified by NMR spectroscopy, mass spectrometry, and analytical data. The NMR properties of the osmapentaborane are summarized in Tables 2 and

TABLE 4

¹¹B AND ¹H NMR DATA FOR *nido*-[(OsB₄H₈)(CO)(PPh₃)₂] (IV) AND *nido*-[2-(η^5 -C₅H₅)-2-CoB₄H₈] (VIII)

Assignment	IV ^a		VIII ^b	
	$\delta(^{11}\text{B})^c$	$\delta(^1\text{H})^{d,e}$	$\delta(^{11}\text{B})^{c,f}$	$\delta(^1\text{H})^{d,f}$
1	8.9	0.25	6.2(1)	3.64(1)
(3,5)	{ -7.5 -14.2 -34.4	3.32	-15.9(3)	2.79(1)
		1.41		1.70(2)
4		6.04		
(2,5) bridge		-9.75 ^g	{	-15.28(2) ^h
(2,3) bridge		-10.34		
(3,4)(4,5) bridge		-1.68, -2.03		

^a Dilute CDCl₃ solution at 21°C. ^b From ref. 35, CDCl₃ solution. ^c $\delta(^{11}\text{B})$ in ppm to high frequency of BF₃·OEt₂. ^d $\delta(^1\text{H})$ in ppm to high frequency of TMS. ^e ¹H resonances related to ¹¹B resonances by selective ¹H-¹¹B experiments. ^f Figures in parentheses indicate relative intensities of resonance signals. Selective ¹H-¹¹B experiments were not performed in ref. 35 and the assignments are those tentatively made by us by comparison with compound II; they have not been experimentally confirmed. ^g Doublet ²J(³¹P-¹H) 37 Hz, confirmed by ¹H-(³¹P) decoupling experiments. ^h ²J(H_{br}-H_t) 72 Hz; in view of this strong coupling it is interesting that no analogous coupling was observed in compound IV.

4, together with those of the only other [35] well-characterized analogue, the cobaltapentaborane [2-(η -C₅H₅)-*nido*-2-CoB₄H₈].

The mass spectrum shows a fragmentation pattern characteristic of a metal-laborane, with the parent ion at *m/e* 796 (¹²C₃₇¹H₃₈¹¹B₄¹⁶O³¹P₂¹⁹²Os requires 796.2) but also with a peak at 797 of variable intensity with respect to the parent ion from sample to sample. This is believed to be due to an impurity.

The structure may be deduced from the NMR data in a similar manner to that for the preceding compound. The presence of four separate ¹¹B resonances indicates that the ligands on the metal centre are asymmetric with respect to the borane ligand.

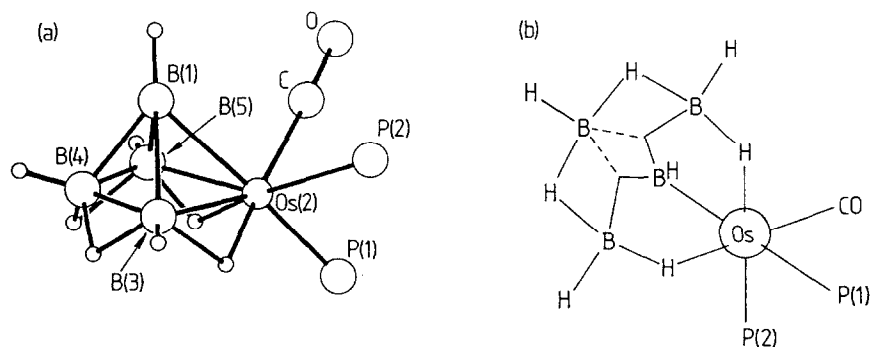


Fig. 5. (a) Proposed structure and numbering scheme for the *nido*-2-osmapentaborane [(OsB₄H₈)(CO)(PPh₃)₂] (IV), and (b) a representation of a localized valence bond structure for this compound. A number of additional contributory canonical forms may be written down, and there will be considerable cluster bonding delocalization. The phosphorus atom P(1) is believed to be approximately *trans* to the apical boron atom B(1), with P(2) and the carbonyl group being approximately *trans* to the Os-H-B bridging H atoms.

The proton resonances at $\delta(^1\text{H})$ -9.75 and -10.34 ppm are characteristic of M–H–B bridging H atoms with the former again exhibiting coupling ascribable to an approximately *trans* phosphorus atom [$^2J(^{31}\text{P}-^1\text{H})$ 37 Hz; cf. $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ 40 Hz]. This is similar to the range of such couplings previously found for iridaboranes [17,24]. ^{31}P NMR spectroscopy shows two *cis*-phosphines (J 12.2 ± 0.5 Hz) and infrared spectroscopy a carbonyl ligand ($\nu(\text{CO})_{\text{max}}$ 1955 cm^{-1}). Thus, as only one M–H–B hydrogen atom is *trans* to a phosphorus atom, the other (assuming a quasi-octahedral environment) must be *trans* to the carbonyl group. The bonding about the osmium is therefore essentially identical to that for $[(\text{OsB}_5\text{H}_9)(\text{CO})(\text{PPh}_3)_2]$ and the presumed structure is shown in Fig. 5 together with one of its resonance topological descriptions which in this case is equivalent to that for *nido*- B_5H_9 of 4120 *styx* topology. The compound may be regarded in the same way as the osmahexaborane (III) i.e. as an 18-electron octahedral d^6 osmium(II) complex.

The formation of $[(\text{OsB}_4\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ has obvious parallels to the thermolytic formation of $[1,1,1-(\text{CO})_3\text{-nido-1-FeB}_4\text{H}_8]$ from $[2,2,2-(\text{CO})_3\text{-nido-2-FeB}_5\text{H}_9]$, a reaction which has been studied in some detail [32]. However, the ferraborane product has the metal atom in the apical 1-position whereas in the osmium reaction it remains in a basal position. It is possible that the iron reaction proceeds via the basal ferrapentaborane, since it is also known [35] that the 2-cobaltapentaborane rearranges to the 1-cobalta isomer in ca. 10% yield on heating to 200°C for 30 min. By contrast, it is of interest to note that heating the iridium metallahexaborane analogue $[(\text{IrB}_5\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ causes extensive decomposition to many very low-yield unidentified compounds, and thus far there are no known five vertex *nido*-iridapentaboranes, although *arachno* derivatives have been described [15,16], and recently the *nido*-2-rhodapentaborane $[(\text{HRhB}_4\text{H}_8)(\text{PPh}_3)_2]$ has been reported [16].

In conclusion it may be said that the behaviour of osmium in the clusters reported here is very similar to that of iridium and it is hoped that it may therefore be possible to duplicate and extend the interesting metallaborane cluster chemistry of the iridaboranes [9–24].

Experimental

The initial reactions were carried out under nitrogen or using standard vacuum line techniques; subsequent manipulations were carried out in air. Preparative thin layer chromatography was carried out using $20 \times 20 \times 0.1\text{ cm}^3$ plates coated with Kieselgel [60 G (Merck) or Fluka GF 254] containing a fluorescent indicator. The compounds $[\text{IrCl}(\text{PPh}_3)_3]$, $[\text{Os}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ and TiB_3H_8 were made according to the literature [22,36,37].

Proton (100 MHz) and ^{31}P (40 MHz) NMR spectra were obtained on a JEOL FX100 instrument. ^{11}B NMR spectra (128 MHz) were recorded on a Bruker WH400 instrument at the University of Sheffield. $\delta(^{31}\text{P})$ and $\delta(^{11}\text{B})$ are given to high frequency (low field) of 85% H_3PO_4 (Ξ 40 480 730 Hz) and $\text{BF}_3 \cdot \text{OEt}_2/\text{CDCl}_3$ (Ξ 32 083 971 Hz) respectively. Mass spectrometry was performed on an AEI MS30 double-beam instrument and infrared spectra were recorded on a PE457 spectrophotometer.

$[(\text{HOsB}_3\text{H}_8)(\text{CO})(\text{PPh}_3)_2]$ (I)

A dichloromethane (100 ml) solution of $[\text{Os}(\text{CO})\text{ClH}(\text{PPh}_3)_3]$ (500 mg, 0.5 mmol) and TiB_3H_8 (117 mg, 0.5 mmol) was stirred at room temperature for 4 days after

which time the mixture was filtered, reduced in volume (ca. 2 ml) and applied to 4 preparative TLC plates. After development in Et₂O/pentane (50/50) two bands were visible under UV illumination: the first, R_f 0.9, was identified as BH₃ · PPh₃ and the second (R_f 0.5), as described in the text, as the title compound I, a colourless solid (226 mg, 65% yield). Infrared: $\nu_{\max}(\text{CO})$ 1970 cm⁻¹, $\nu_{\max}(\text{OsH})$ 2040 cm⁻¹. Analysis: Found: C, 57.0; H, 5.08. C₃₇H₃₉B₃OP₂Os calcd.: C, 56.5; H, 4.96%. A mass spectrum was not obtainable.

[(H₂IrB₃H₈)(PPh₃)₂] (II)

The procedure was the same as that just described, using [IrCl(PPh₃)₃] (200 mg, 0.2 mmol) and TiB₃H₈ (50 mg, 0.2 mmol). The TLC plate was developed using CH₂Cl₂/pentane 40/60 and gave a band of the product at R_f 0.7 (50 mg, 30% yield). No mass spectrum was obtainable.

[(OsB₅H₉)(CO)(PPh₃)₂] (III)

Tetrahydrofuran was condensed into a 3-necked 250 ml flask of which one arm carried a tipper tube containing 2.0 g (2 mmol) of [OsHCl(CO)(PPh₃)₃] and the other a rubber septum. The flask was cooled to -196°C and 2.1 mmol of B₅H₉ condensed in and then the solution was warmed to -79°C whereupon an ether solution of methyllithium (1.6 mol l⁻³; 1.4 ml corresponding to 2.1 mmol MeLi) was injected through the septum with stirring. After 15 min 100 ml of CH₂Cl₂ was condensed in at -79°C and the osmium complex added. The mixture was kept at -20 to -25°C for one day and then allowed to warm slowly to room temperature over 16 h. This resulted in a clear, pale yellow solution, of which the ³¹P NMR spectrum showed no starting osmium compound. Chromatography of the mixture (50/50 CH₂Cl₂/pentane) afforded the title compound (1.36 g, 80% yield). Infrared: $\nu_{\max}(\text{CO})$ 1980 cm⁻¹; Analysis: Found: C, 54.0; H, 5.0. C₃₇H₃₉B₅OP₂Os calcd.: C, 55.1; H, 4.9%. Mass spectrum: Found: m/e 807; ¹²C₃₇¹H₃₉¹¹B₅¹⁶O³¹P₂¹⁹²Os requires 807.

[(OsB₄H₈)(CO)(PPh₃)₂] (IV)

A sample of [(OsB₅H₉)(CO)(PPh₃)₂] (100 mg, 0.1 mmol) was dissolved in dry deoxygenated tetrachloroethane (ca. 5 ml) and heated in a stoppered tube at 100°C for 1 h. The solvent was then evaporated off, the residue dissolved in CH₂Cl₂, applied to a preparative TLC plate and developed using CH₂Cl₂/pentane (50/50). A band, visible under UV light at R_f 0.7, was identified as described above as the title compound. Infrared $\nu_{\max}(\text{CO})$ 1955 cm⁻¹ Analysis: Found: C, 54.1; H, 4.8. C₃₇H₃₈B₄OP₂Os calcd.: C, 55.8; H, 4.8%. Mass spectrum: Found: m/e 796. ¹²C₃₇¹H₃₈¹¹B₄¹⁶O³¹P₂¹⁹²Os requires 796.

Acknowledgement

We thank the SERC for financial support, and for a maintenance grant (to J.B.).

References

- 1 M.R. Churchill, J.J. Hackbarth, A. Davison, D.D. Traficante and S.S. Wreford, J. Am. Chem. Soc., 96 (1974) 4041.
- 2 M.R. Churchill and J.J. Hackbarth, Inorg. Chem., 14 (1975) 2047.
- 3 N.N. Greenwood, J.D. Kennedy and J. Staves, J. Chem. Soc., Dalton Trans., (1978) 1146.
- 4 J.D. Kennedy, Proceedings XIX Internat. Conf. Coord. Chem., Prague, 1 (1978) 79.

- 5 N.N. Greenwood, J.D. Kennedy, W.S. McDonald, D. Reed and J. Staves, *J. Chem. Soc., Dalton Trans.*, (1979) 117.
- 6 N.N. Greenwood and J.D. Kennedy in R.N. Grimes (Ed.), *Metal Interactions with Borane Clusters*, Plenum, New York, 1982, Ch. 2, pp.43–118.
- 7 B.E. Mann, C. Masters and B.L. Shaw, *J. Chem. Soc., Chem. Commun.*, (1970) 703.
- 8 K. Isobe, P.M. Bailey and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1981) 808.
- 9 F. Klanberg, P.A. Wegner, A.W. Parshall and E.L. Muetterties, *Inorg. Chem.*, 7 (1968) 2072.
- 10 A. Davison, D.D. Traficante and S.S. Wreford, *J. Amer. Chem. Soc.*, 96 (1974) 2802.
- 11 A.R. Siedle and L.J. Todd, *Inorg. Chem.*, 11 (1976) 2838.
- 12 R.W. Marks, S.S. Wreford and D.D. Traficante, *Inorg. Chem.*, 17 (1978) 756.
- 13 N.N. Greenwood, J.D. Kennedy and D. Reed, *J. Chem. Soc., Dalton Trans.*, (1980) 196.
- 14 J.E. Crook, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1981) 933.
- 15 J. Bould, N.N. Greenwood and J.D. Kennedy, *J. Chem. Soc., Dalton Trans.*, (1982) 481.
- 16 S.K. Boocock, M.J. Toft and S.G. Shore, 182nd Amer. Chem. Soc. Nat. Meeting, New York, 23–28th August 1981, paper no. INOR 149, as quoted in ref. 25.
- 17 S.K. Boocock, J. Bould, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Dalton Trans.*, (1982) 713.
- 18 J. Bould, J.E. Crook, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1982) 346.
- 19 J.E. Crook, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1982) 383.
- 20 J. Bould, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1982) 465.
- 21 J.E. Crook, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Chem. Commun.*, (1983) 83.
- 22 J. Bould, N.N. Greenwood, J.D. Kennedy and W.S. McDonald, *J. Chem. Soc., Dalton Trans.*, (1983) to be submitted (structural chemistry of *arachno*-1-iridatetaboranes).
- 23 J. Bould, J.E. Crook, N.N. Greenwood and J.D. Kennedy, *J. Chem. Soc., Dalton Trans.*, (1983) to be submitted (structure and chemistry of *arachno*-iridanonaboranes).
- 24 J. Bould, N.N. Greenwood and J.D. Kennedy, *J. Chem. Soc., Dalton Trans.*, (1983) to be submitted (structural chemistry of *nido*-iridanonaboranes).
- 25 K.B. Gilbert, S.K. Boocock and S.G. Shore, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon, 1982, Volume 6, pp. 879–945.
- 26 P.A. Wegner, L.J. Guggenberger and E.L. Muetterties, *J. Amer. Chem. Soc.*, 92 (1970) 3473.
- 27 D.F. Gaines and S.J. Hildebrandt, *Inorg. Chem.*, 17 (1978) 794.
- 28 D.F. Gaines and T.V. Iorns, *Inorg. Chem.*, 7 (1968) 1041.
- 29 J.W. Lott and D.F. Gaines, *Inorg. Chem.*, 13 (1974) 2261.
- 30 M.B. Fischer and D.F. Gaines, *Inorg. Chem.*, 18 (1979) 3200.
- 31 T.P. Fehlner, J. Ragaini, M. Mangion and S.G. Shore, *J. Amer. Chem. Soc.*, 98 (1976) 7085.
- 32 S.G. Shore, J.D. Ragaini, R.L. Smith, C.E. Cottrell and T.P. Fehlner, *Inorg. Chem.*, 18 (1979) 670.
- 33 V.R. Miller and R.N. Grimes, *J. Amer. Chem. Soc.*, 95 (1973) 5078.
- 34 L.G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, (1976) 118.
- 35 V.R. Miller, R. Weiss and R.N. Grimes, *J. Amer. Chem. Soc.*, 99 (1977) 5646.
- 36 J.L. Herde, J.C. Lambert and C.V. Senoff, *Inorg. Synth.*, 15 (1974) 18.
- 37 N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, *Inorg. Synth.*, 15 (1974) 45.