Preparation and Nuclear Magnetic Resonance Properties of Eleven-vertex *closo*-Type Osmaundecaboranes and the *X*-Ray Crystal Structure of the *ortho*-Cycloboronated Compound [2,5-(OEt)$_2$-1-(PPh$_3$)-1-(o-Ph$_2$P$\overline{\text{C}_6$H$_4$)-*closo*-1-OsB$_{10}$H$_7$-3}$] *

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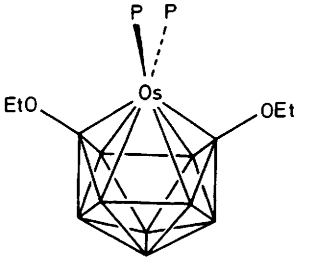
Reaction of the osmium(III) species [OsCl$_3$(PMe$_2$Ph)$_3$] with *closo*-[B$_{10}$H$_{10}$]$^{2-}$ in EtOH gives red-orange [(PMe$_2$Ph)$_2$OsB$_{10}$H$_8$(OEt)$_2$] (42%) identified by n.m.r. spectroscopy. By contrast, a similar procedure with the osmium(II) species [OsCl$_2$(PPh$_3$)$_3$] gives the P-phenylene *ortho*-cycloboronated amber-brown compound [(PPh$_3$)(Ph$_2$PC$_6$H$_4$)OsB$_{10}$H$_7$(OEt)$_2$] (39%), identified by single-crystal *X*-ray crystallography. Crystals are monoclinic, space group $P2_1/n$, with a = 1 123.7(1), b = 2 092.4(3), c = 1 750.9(2) pm, β = 92.54(1)°, and Z = 4; the final R factor is 0.0283 for 4 623 observed reflections. These new eleven-vertex osmaboranes are air-stable as solids, and have closed eleven-vertex 1-metallaundecaborane geometries for which '*isocloso*' electronic configurations have been proposed.

Osmaborane chemistry is a relatively uninvestigated area.[1,2] Although it is apparent that osmium metal centres can partake in stable borane-to-metal bonding configurations, only a few such compounds have so far been made.[2–6] Reported structural characterisation by *X*-ray diffraction analysis has so far been limited to the *nido* four-vertex trimetallaborane [(CO)$_6$H$_3$Os$_3$B(CO)],[3] the *nido*-type seven-vertex dimetallaborane [(CO)(PPh$_3$)$_2$OsHPt(Cl)(PMe$_2$Ph)B$_5$H$_7$],[4] and the *nido* ten-vertex 6-metalladecaborane [(PMe$_2$Ph)$_3$OsB$_9$H$_{13}$].[5] The recently reported carborane derivative [(CO)$_3$OsC$_2$B$_4$H$_4$(SiMe$_3$)$_2$] should also be mentioned.[6]

Here we report the preparation of two new eleven-vertex osmaboranes which have closed polyhedral structures, and which can at present be interpreted to have the so called '*isocloso*' cluster electronic configuration that is believed to arise from a metal four-orbital contribution to cluster bonding.[7–13] The work includes the characterisation, by single-crystal *X*-ray diffraction analysis, of a derivative in which a P-phenyl group on an osmium-bound triphenylphosphine ligand has been *ortho*-cycloboronated by the incipient new cluster during metallaborane formation. Although spontaneous P-phenyl ⟶ P-phenylene *ortho*-cycloboronation during metallaborane formation has been noted a number of times in the metallaborane chemistry of iridium,[7,11,14–17] this appears to be the first time that it has been observed in the metallaborane chemistry of any other metal. Some preliminary and related aspects of this work have been presented elsewhere.[18,19]

Results and Discussion

It has previously been found that the reaction between the ruthenium(II) species [RuCl$_2$(PPh$_3$)$_3$] and the *closo*-[B$_{10}$H$_{10}$]$^{2-}$ anion in ethanolic solution gives an 80% yield of the eleven-vertex '*isocloso*' species [(PPh$_3$)$_2$RuB$_{10}$H$_8$(OEt)$_2$] [idealised equation (1)].[8,9] An analogous product is obtained in 52% yield when the ruthenium(III) starting material [RuCl$_3$(PMe$_2$Ph)$_3$] is treated under the same conditions [idealised equation (2)].[20]



(I)

$$[\text{RuCl}_2(\text{PPh}_3)_3] + [\text{B}_{10}\text{H}_{10}]^{2-} + 2\text{EtOH} \longrightarrow [(\text{PPh}_3)_2\text{RuB}_{10}\text{H}_8(\text{OEt})_2] + \text{PPh}_3 + 2\text{Cl}^- + 2\text{H}_2 \quad (1)$$

$$[\text{RuCl}_3(\text{PMe}_2\text{Ph})_3] + [\text{B}_{10}\text{H}_{10}]^{2-} + 2\text{EtOH} \longrightarrow [(\text{PMe}_2\text{Ph})_2\text{RuB}_{10}\text{H}_8(\text{OEt})_2] + [\text{PHMe}_2\text{Ph}]^+ + 3\text{Cl}^- + 1.5\text{H}_2 \quad (2)$$

We have now found that the reaction summarised in equation (2) also works for the osmium(III) complex [OsCl$_3$(PMe$_2$Ph)$_3$]: heating this compound with [NEt$_3$H]$_2$[B$_{10}$H$_{10}$] in refluxing ethanol for 16 h, followed by chromatographic separation, yields [(PMe$_2$Ph)$_2$OsB$_{10}$H$_8$(OEt)$_2$] as the predominant chromatographically mobile component; it is a red-orange, air-stable, crystalline solid isolable in 42% yield [see equation (3) below].

The extreme similarity between the ^{31}P, ^{11}B, and ^{1}H n.m.r. parameters of this compound and those of the similarly prepared ruthenium analogue (Table 1) readily establishes the identity of the new osmaborane as [2,5-(OEt)$_2$-1,1-(PMe$_2$Ph)$_2$-*isocloso*-1-OsB$_{10}$H$_8$]. This has an eleven-vertex closed 1-metallaundecaborane cluster of idealised C_{2v} symmetry [structure (I)], in which the borane-to-metal bonding mode is boat-hexahapto; the two alkoxy substituents are on the two prow boron atoms B(2) and B(5), and the two *exo*-polyhedral

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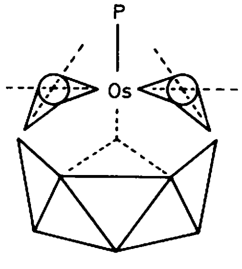
* 1,3-μ-[*o*-Diphenylphosphinophenyl-*P*(Os), *C*^{1}(B^3)]-2,5-bis(ethoxy)-1-(triphenylphosphine)-*closo*-1-osmaundecaborane.

Supplementary data available (No. SUP 56607, 4 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii– xx. Structure factors are available from the editorial office.

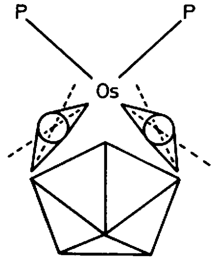
Table 1. Measured n.m.r. parameters for $[(PMe_2Ph)_2MB_{10}H_8(OEt)_2]$ (M = Os or Ru) in CD_2Cl_2 solution at +21 °C unless otherwise indicated[a]

	M = Os		M = Ru	
Tentative assignment[b]	$\delta(^{11}B)$/p.p.m.	$\delta(^{1}H)$/p.p.m.	$\delta(^{11}B)$/p.p.m.	$\delta(^{1}H)$/p.p.m.
(2,5)	+85.5(2 B)	*c*	+88.3(2 B)	*c*
(8,10)	+10.8(2 B)	+4.04(2 H)	+7.8(2 B)	+3.63(2 H)
(9,11)	+5.5(2 B)	+2.55(2 H)	+3.0(2 B)	+2.37(2 H)
(3,4,6,7)	+4.8(4 B)	+1.96(4 H)	+6.8(4 B)	+2.24(4 H)
$\delta(^{1}H)(PMe)$/p.p.m.	+1.28		+1.16	
$N(^{31}P-^{1}H)$/Hz	*ca.* 9.5		8.6 ± 0.5	
$\delta(^{31}P)$/p.p.m.[a]	−6.4[d]		−4.2	
$\delta(^{1}H)(OEt)$/p.p.m.	+1.57(6 H), +4.54(4 H)		+1.58(6 H), +4.59(4 H)	

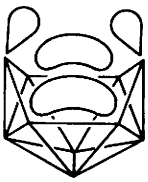
[a] ^{31}P data measured at −50 °C in $CDCl_3$ solution. [b] By two-dimensional $^{11}B-^{11}B$ COSY n.m.r. on $[(PMe_2Ph)_2RuB_{10}H_8(OMe)_2]$, and by comparison with $[(PMe_2Ph)_2HRhB_{10}H_8(OMe)_2]$ which has time-averaged C_s rather than C_{2v} symmetry (refs. 12 and 20). [c] Site occupied by OEt. [d] Possible ^{183}Os satellites corresponding to $^{1}J(^{183}Os-^{31}P)$ *ca.* 210 Hz.



(II)



(III)



(IV)

osmium-bound ligand phosphorus atoms are in the plane which bisects the two B(3)–B(4) and B(6)–B(7) vectors (for numbering scheme see Figure 1 below).

In accord with the parallels with ruthenium,[8,9] and also with rhodium,[12] chemistry, the osmium valence-bonding configuration can be regarded as formally six-orbital octahedral 16-electron d^4 osmium(IV), with predominant contributions to the borane-to-metal bonding occurring *via* two two-electron two-centre bonds [to B(2) and B(5)] and two two-electron three-centre bonds [Os(1)B(3)B(4) and Os(1)B(6)B(7)]. The site of maximum overlap of these polyhedral bonds will be in tangential positions *exo* to the polyhedral faces and edges as indicated in structures **(II)** and **(III)**. The neutral metal centre $Os(PMe_2Ph)_2$ can therefore be regarded as contributing four electrons to the bonding in the OsB_{10} cluster, which thereby achieves a 24-electron eleven-vertex *closo* count. Since the osmium centre thereby contributes *four* orbitals to the cluster-bonding scheme, rather than the three implied by classical electron-counting rules, the descriptor '*isocloso*' may be invoked to define the metallaborane electronic configuration.[7–13,*]

In terms of a metal complex of a polydentate borane ligand,[1,24–26] the (as yet unsynthesised) unsubstituted parent compound $[(PMe_2Ph)_2OsB_{10}H_{10}]$ would be a notional complex between the eight-electron d^4 osmium(IV) centre $[Os(PMe_2Ph)_2]^{4+}$ and the tetradentate hexahapto ligand $[B_{10}H_{10}]^{4-}$ [structure **(IV)**]. This last would formally be derived from the quadruple open-face deprotonation of a *nido*-$B_{10}H_{14}$ configuration of *styx* 2802 topology,[8,12] rather than one of *styx* 4620 topology as exhibited by ground-state neutral molecular $B_{10}H_{14}$ itself.

The osmaborane product $[(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]$ described above is obtained by the reaction of the osmium(III) complex $[OsCl_3(PMe_2Ph)_3]$ [idealised equation (3)]. By contrast, when the triphenylphosphine osmium(II) complex $[OsCl_2(PPh_3)_3]$ is used instead [idealised equation (4)], the product that is formed, although still an eleven-vertex *isocloso*-1-osmaundecaborane, now also exhibits *ortho*-cycloboronation of one of the osmium-bound phosphine aromatic groups to the cluster boron atom in the off-mirror-plane 3-position. Interestingly, this apparently does *not* occur in the precisely analogous ruthenium reaction [equation (2) above].[20]

$$[OsCl_3(PMe_2Ph)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow [(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]\ (42\%) + [PHMe_2Ph]^+ + 3Cl^- + 1.5H_2 \quad (3)$$

$$[OsCl_2(PPh_3)_3] + [B_{10}H_{10}]^{2-} + 2EtOH \longrightarrow [(PPh_3)(Ph_2PC_6H_4)OsB_{10}H_7(OEt)_2]\ (39\%) + PPh_3 + 2Cl^- + 3H_2 \quad (4)$$

We have determined the molecular structure of this new *ortho*-cycloboronated osmoborane, [2,5-$(OEt)_2$-1-(PPh_3)-1-(*o*-$Ph_2PC_6H_4$)-*closo*-1-$OsB_{10}H_7$-3], by single-crystal *X*-ray diffraction analysis. A drawing of the molecular structure is given in Figure 1, selected interatomic distances are in Table 2, and interatomic angles in Table 3. N.m.r. spectra (Figure 2 and Table 4) are consistent with the molecular structure established by the *X*-ray work, thus confirming that the crystal selected represents the bulk sample.

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[*] An alternative description has been proposed that would regard the metal as a conventional three-orbital cluster contributor,[21] in which case clusters such as these would have formal 22-electron *pileo* eleven-vertex counts.[22] That there is no apparent distortion to a less symmetrical capped *closo* eleven-vertex geometry would then be explained by the ability of the C_{2v} eleven-vertex closed polyhedron in principle to accommodate a 22-electron configuration without being subject to Jahn–Teller-type cluster-geometry adjustment.[23]

Table 2. Interatomic distances (pm) for $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$ with estimated standard deviations in parentheses

(*i*) To the osmium atom			
Os(1)–P(1)	245.1(3)	Os(1)–P(2)	242.1(3)*
Os(1)–B(2)	204.6(8)	Os(1)–B(5)	206.0(8)
Os(1)–B(3)	231.3(7)*	Os(1)–B(6)	239.4(8)
Os(1)–B(4)	234.9(7)	Os(1)–B(7)	235.3(9)
(*ii*) Interboron			
B(2)–B(3)	182.1(10)	B(2)–B(7)	180.1(11)
B(2)–B(8)	175.5(11)	B(5)–B(10)	171.4(11)
B(3)–B(4)	173.0(11)	B(6)–B(7)	172.8(12)
B(3)–B(8)	181.2(11)	B(7)–B(8)	182.6(11)
B(3)–B(9)	177.4(10)	B(7)–B(11)	179.0(10)
B(4)–B(5)	174.4(10)	B(5)–B(6)	176.8(12)
B(4)–B(9)	178.8(12)	B(6)–B(11)	174.1(11)
B(4)–B(10)	181.6(11)	B(6)–B(10)	182.0(11)
B(8)–B(9)	175.6(12)	B(8)–B(11)	174.3(12)
B(9)–B(10)	178.1(12)	B(10)–B(11)	177.4(12)
B(9)–B(11)	177.9(11)		
(*iii*) Boron–hydrogen			
B(4)–H(4)	126.1(30)	B(6)–H(6)	112.3(28)
B(8)–H(8)	123.1(32)	B(10)–H(10)	109.4(27)
B(9)–H(9)	106.7(23)	B(11)–H(11)	104.4(27)
B(7)–H(7)	115.4(23)		
(*iv*) Others			
B(3)–C(216)	158.8(9)*		
B(2)–O(2)	136.3(8)	B(5)–O(5)	137.8(9)
P(1)–C(111)	182.6(5)	P(2)–C(211)	182.7(7)*
P(1)–C(121)	182.3(5)	P(2)–C(221)	182.4(5)
P(1)–C(131)	182.1(5)	P(2)–C(231)	182.3(5)
C(211)–C(216)	139.5(8)*		

* Distance involved in *ortho*-cycloboronated ring.

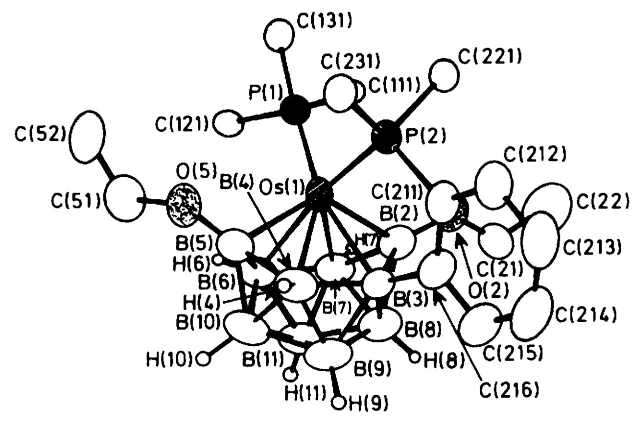

Figure 1. ORTEP drawing of the molecular structure of $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$ with selected organyl group atoms omitted for clarity

Table 3. Selected angles (°) between interatomic vectors for $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$ with estimated standard deviations in parentheses

(*i*) About the osmium atom			
P(1)–Os(1)–P(2)	101.8(1)		
P(1)–Os(1)–B(2)	110.5(3)	P(2)–Os(1)–B(2)	91.6(3)
P(1)–Os(1)–B(3)	159.3(2)	P(2)–Os(1)–B(3)	78.9(2)*
P(1)–Os(1)–B(4)	155.6(2)	P(2)–Os(1)–B(4)	90.9(3)
P(1)–Os(1)–B(5)	109.9(3)	P(2)–Os(1)–B(5)	120.7(3)
P(1)–Os(1)–B(6)	95.7(2)	P(2)–Os(1)–B(6)	161.5(1)
P(1)–Os(1)–B(7)	95.3(2)	P(2)–Os(1)–B(7)	139.3(2)
B(2)–Os(1)–B(3)	48.9(2)	B(2)–Os(1)–B(7)	47.7(2)
B(2)–Os(1)–B(4)	89.6(3)	B(2)–Os(1)–B(6)	87.6(3)
B(2)–Os(1)–B(5)	119.9(3)		
B(3)–Os(1)–B(4)	43.5(2)	B(6)–Os(1)–B(7)	42.7(2)
B(3)–Os(1)–B(5)	86.5(3)	B(5)–Os(1)–B(7)	86.3(3)
B(3)–Os(1)–B(6)	86.7(3)	B(4)–Os(1)–B(7)	88.0(3)
B(3)–Os(1)–B(7)	72.6(3)	B(4)–Os(1)–B(6)	70.6(3)
B(4)–Os(1)–B(5)	46.0(2)	B(5)–Os(1)–B(6)	46.0(2)
(*ii*) Boron–boron–boron			
B(3)–B(2)–B(7)	99.3(5)	B(4)–B(5)–B(6)	102.6(6)
B(2)–B(3)–B(4)	121.9(5)	B(2)–B(7)–B(6)	121.7(6)
B(3)–B(4)–B(5)	119.6(5)	B(5)–B(6)–B(7)	119.8(6)
(*iii*) Others			
O(2)–B(2)–Os(1)	122.9(5)	O(5)–B(5)–Os(1)	112.8(5)
O(2)–B(2)–B(3)	128.4(6)	O(5)–B(5)–B(4)	124.0(6)
O(2)–B(2)–B(7)	131.3(5)	O(5)–B(5)–B(6)	133.3(5)
O(2)–B(2)–B(8)	129.8(6)	O(5)–B(5)–B(10)	135.2(5)
B(2)–O(2)–C(21)	124.4(6)	B(5)–O(5)–C(51)	122.7(5)
O(2)–C(21)–C(22)	120.2(9)	O(5)–C(51)–C(52)	108.2(6)
Os(1)–B(3)–C(216)	73.2(4)*	B(3)–C(216)–C(211)	118.6(5)*
C(216)–C(211)–P(2)	121.9(5)*	C(211)–P(2)–Os(1)	107.0(3)*

* Angle involved in *ortho*-cycloboronated ring.

Table 4. Measured n.m.r. parameters for $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$ in CD_2Cl_2 solution at +21 °C unless otherwise indicated[a]

δ(^{11}B)	δ(^{1}H)	Tentative assignment[b]
+84.5	*c*	2,5
+78.9	*c*	
+14.1	*d*	3
+7.9	+3.99	8,10
+6.1	+3.92	
+5.1	+1.69	One of 4,6,7; probably 4
+2.9	+2.33	9,11
+1.7	+2.42	
−0.7	+1.53	Two of 4,6,7; probably 6,7
−1.1	+1.20	

[a] ^{31}P data at −50 °C in $CDCl_3$: δ(^{31}P) +18.9 and +4.9 p.p.m.; ^2J(^{31}P–Os–^{31}P)(*cis*) 11 ± 2 Hz. [b] By similarity of intercorrelated ^{11}B and ^{1}H shielding patterns to other species of this structural type (refs. 9, 12, and Table 1). [c] δ(^{1}H) for four chemically distinct ethoxy methylene groups are centred at *ca.* 4.27, 4.29, 3.98, and 4.03 p.p.m. [d] Large spread of aromatic δ(^{1}H) 6.70—7.75 indicative of *ortho*-cycloboronated P–phenylene link (*cf.* refs. 7 and J. E. Crook, Ph.D. Thesis, University of Leeds, 1982).

The overall structural behaviour is very similar to that of the other reported *closo*-type 1-metallaboranes that have been structurally investigated.[9,12,18,20] The similarity of the metallaborane cluster dimensions with those of the ruthenium (non-*ortho*-cycloboronated) analogue $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$[9] is particularly marked. The general similarity of osmium *versus* ruthenium bonding dimensions has been noted elsewhere (see, for example, refs. 27 and 28). In the present comparison (Table 5) it is apparent that, although the ruthenium–phosphorus distances average some 9 pm longer than the osmium–phosphorus ones, the metal–boron distances are very similar for both compounds. The ruthenium–boron distances appear to be marginally the longer, but this may not be statistically significant [although a shortening of the distance from Os(1) to the *ortho*-cycloboronated position B(3) in the exocyclic osmaborane does appear to be reasonably well

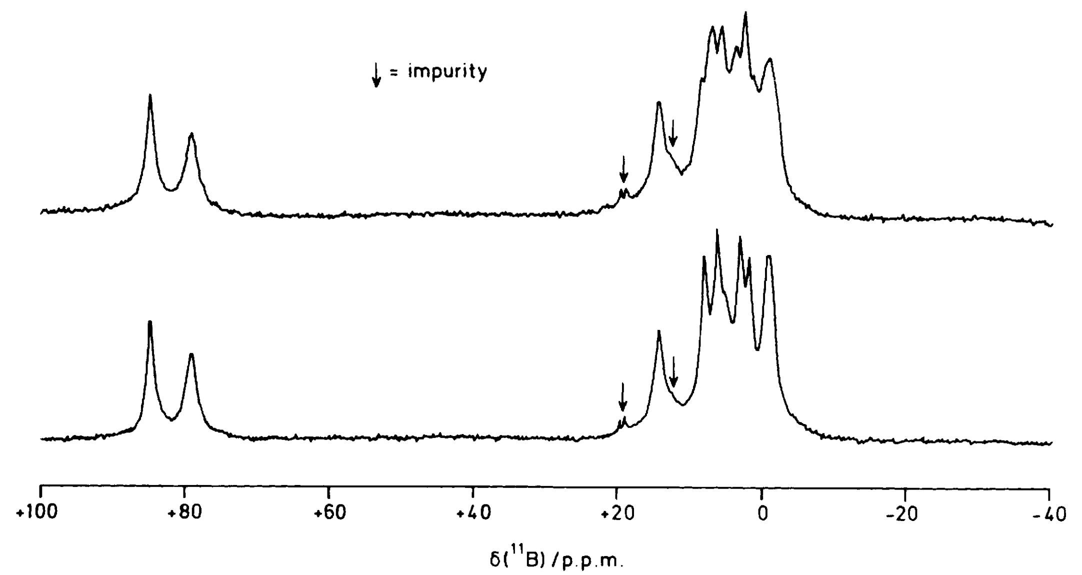

Figure 2. 115.5-MHz ^{11}B (upper trace) and ^{11}B-{^{1}H(broad-band noise)} (lower trace) n.m.r. spectra of $[(PPh_3)(Ph_2PC_6H_4)OsB_{10}H_7(OEt)_2]$. The overall pattern, of two isolated resonances at extreme low field [corresponding to B(2) and B(5)] together with the close grouping of the remaining eight resonance lines around δ(^{11}B) *ca.* zero, is characteristic of this structural type (refs. 9, 12, and 29)

Table 5. Comparative interatomic distances (pm) for $[(PPh_3)(Ph_2PC_6H_4)OsB_{10}H_7(OEt)_2]$ (this work) and $[(PPh_3)_2RuB_{10}H_8(OEt)_2]$ (data from ref. 9)

Distance	M = Os	M = Ru
M(1)–P(1)	245.1(3)	253.3(4)
M(1)–P(2)	242.1(3)*	251.1(4)
M(1)–B(2)	204.6(8)	205.4(8)
M(1)–B(5)	206.0(8)	203.6(8)
M(1)–B(3)	231.3(7)*	235.5(8)
M(1)–B(4)	234.9(7)	239.9(8)
M(1)–B(6)	239.4(8)	235.9(8)
M(1)–B(7)	235.3(9)	238.2(8)

* Indicates distances in *ortho*-cycloboronated ring.

defined . There is little apparent other distortion of the cluster geometry, indicating that the accommodation of the *exo*-polyhedral five-membered ring does not introduce any 'strain' into the molecule. This conclusion is supported by the results of n.m.r. spectroscopy (Figure 2 and Table 4); in particular, apart from the loss of symmetry, the only marked difference when compared to acyclic species (*e.g.* Table 1) is the deshielding of some 10—15 p.p.m. noted for the ^{11}B(3) position that has the aromatic substituent. This, however, is within the range expected for the replacement of an *exo*-terminal hydrogen by organic carbon.[29] Any residual 'strain' appears to be incorporated in the slight twist of the Os(1)P(1)P(2) plane relative to that of Os(1)B(9)B(11), the dihedral angle being *ca.* 15.7°.

Experimental

General and N.M.R. Spectroscopy.—The starting compounds $[NEt_3H]_2[B_{10}H_{10}]$,[30,31] $[RuCl_3(PMe_2Ph)_3]$,[32,33] $[OsCl_3(PMe_2Ph)_3]$,[33] and $[OsCl_2(PPh_3)_3]$[34] were prepared by previously published methods. Reactions were carried out under dry nitrogen in oxygen-free solvents, but subsequent manipulations and separations were generally carried out in air. Preparative t.l.c. was carried out using silica gel G (Fluka, type GF254) plates of dimensions 200 × 200 × 1 mm made in these laboratories from an acetone slurry on glass followed by drying in air at *ca.* 373 K.

N.m.r. spectroscopy at 2.35 and 8.46 T was carried out on JEOL FX-100 (in these laboratories) and Bruker WH-360 (S.E.R.C. Service, University of Edinburgh) instruments respectively. The ^{1}H-{^{11}B(selective)} experimental technique, used to relate ^{1}H resonances to their directly bound boron positions, has been described elsewhere, [35,36] and ^{31}P-{^{1}H (broad-band noise)} spectra were recorded at low temperatures to maximise 'thermal decoupling' of the boron nuclei.[37] The n.m.r. spectroscopy was otherwise straightforward. Chemical shifts δ(^{1}H), δ(^{31}P), and δ(^{11}B) are given in p.p.m., positive to high frequency (low field) of Ξ 100, Ξ 40.480 730 (nominally 85% H_3PO_4), and Ξ 32.083 971 MHz [nominally $BF_3(OEt_2)$ in $CDCl_3$],[29] respectively.

Preparation of $[(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]$.—A solution of $[OsCl_3(PMe_2Ph)_3]$ (150 mg, 0.21 mmol) in ethanol (*ca.* 80 cm^3) was added to a solution/suspension of $[NEt_3H]_2[$*closo*-$B_{10}H_{10}]$ in refluxing ethanol (20 cm^3). The resulting deep red reaction mixture was then heated under reflux for 16 h, after which time all the solids had dissolved. The solution was reduced in volume under reduced pressure (40—80 °C, rotary evaporator, water-pump pressure), and the solid residues dissolved in a small volume of CH_2Cl_2 for application to t.l.c. plates. Chromatographic separation using CH_2Cl_2–hexane (80:20) as eluting medium then yielded $[(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]$ (R_f 0.85; 59 mg, 42%) as an orange-red air-stable solid, identified by ^{31}P, ^{11}B, and ^{1}H n.m.r. spectroscopy as described in the text.

Preparation of $[(PMe_2Ph)_2RuB_{10}H_8(OEt)_2]$.—$[NEt_3H]_2[$*closo*-$B_{10}H_{10}]$ (200 mg, 0.62 mmol) was added to a refluxing solution of $[RuCl_3(PMe_2Ph)_3]$ (387 mg, 0.62 mmol) in ethanol (*ca.* 80 cm^3). Refluxing was continued until the reaction mixture, which was initially brown, had turned orange (*ca.* 3 h). After removal of the solvent under reduced pressure (40—80 °C, rotary evaporator, water-pump pressure), the solid residues were taken up in a small volume of CH_2Cl_2 and applied to

Table 6. Non-hydrogen atom co-ordinates (× 10^4) for $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	6 488	3 659	7 207	C(221)	4 531(2)	3 710(1)	8 816(2)
P(1)	4 571(1)	3 615(1)	6 485(1)	C(222)	4 544(2)	4 307(1)	9 171(2)
P(2)	5 919(1)	3 381(1)	8 483(1)	C(223)	3 475(2)	4 599(1)	9 350(2)
C(111)	3 601(2)	4 315(1)	6 485(2)	C(224)	2 394(2)	4 294(1)	9 174(2)
C(112)	2 926(2)	4 491(1)	5 831(2)	C(225)	2 381(2)	3 697(1)	8 819(2)
C(113)	2 107(2)	4 990(1)	5 863(2)	C(226)	3 450(2)	3 405(1)	8 640(2)
C(114)	1 962(2)	5 314(1)	6 550(2)	C(231)	5 878(2)	2 536(1)	8 734(2)
C(115)	2 637(2)	5 138(1)	7 204(2)	C(232)	6 592(2)	2 111(1)	8 344(2)
C(116)	3 457(2)	4 638(1)	7 172(2)	C(233)	6 624(2)	1 467(1)	8 547(2)
C(121)	4 675(3)	3 434(2)	5 472(1)	C(234)	5 943(2)	1 246(1)	9 140(2)
C(122)	4 285(3)	2 847(2)	5 176(1)	C(235)	5 229(2)	1 671(1)	9 530(2)
C(123)	4 392(3)	2 712(2)	4 402(1)	C(236)	5 196(2)	2 315(1)	9 327(2)
C(124)	4 890(3)	3 163(2)	3 924(1)	B(2)	6 873(5)	4 578(3)	7 535(2)
C(125)	5 280(3)	3 749(2)	4 219(1)	B(3)	8 067(5)	4 077(3)	7 937(2)
C(126)	5 173(3)	3 885(2)	4 993(1)	B(4)	8 473(5)	3 368(3)	7 509(4)
C(131)	3 639(2)	2 969(1)	6 817(2)	B(5)	7 737(5)	3 126(3)	6 661(3)
C(132)	4 226(2)	2 418(1)	7 080(2)	B(6)	7 666(5)	3 840(4)	6 124(4)
C(133)	3 576(2)	1 914(1)	7 374(2)	B(7)	7 226(5)	4 536(3)	6 545(4)
C(134)	2 341(2)	1 959(1)	7 405(2)	B(8)	8 342(5)	4 732(4)	7 295(4)
C(135)	1 755(2)	2 510(1)	7 141(2)	B(9)	9 319(5)	4 078(4)	7 355(4)
C(136)	2 404(2)	3 014(1)	6 847(2)	B(10)	9 039(5)	3 538(3)	6 576(4)
C(211)	7 060(2)	3 698(1)	9 145(1)	B(11)	8 770(5)	4 367(3)	6 452(4)
C(212)	7 026(2)	3 601(1)	9 932(1)	O(2)	6 097(3)	4 952(2)	7 912(2)
C(213)	7 922(2)	3 852(1)	10 421(1)	C(21)	6 210(8)	5 599(4)	8 002(6)
C(214)	8 852(2)	4 201(1)	10 122(1)	C(22)	5 381(6)	5 943(4)	8 382(5)
C(215)	8 886(2)	4 298(1)	9 336(1)	O(5)	7 366(3)	2 510(2)	6 515(2)
C(216)	7 990(2)	4 046(1)	8 847(1)	C(51)	7 249(5)	2 247(3)	5 751(3)
				C(52)	6 488(7)	1 657(4)	5 778(4)

Table 7. Hydrogen atom co-ordinates (× 10^4) for $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
H(112)	3 038(2)	4 241(1)	5 299(2)	H(226)	3 440(2)	2 943(1)	8 364(2)
H(113)	1 584(2)	5 127(1)	5 357(2)	H(232)	7 120(2)	2 282(1)	7 886(2)
H(114)	1 328(2)	5 700(1)	6 575(2)	H(233)	7 177(2)	1 138(1)	8 246(2)
H(115)	2 526(2)	5 388(1)	7 735(2)	H(234)	5 968(2)	747(1)	9 297(2)
H(116)	3 979(2)	4 502(1)	7 678(2)	H(235)	4 701(2)	1 500(1)	9 988(2)
H(122)	3 900(3)	2 498(2)	5 546(1)	H(236)	4 643(2)	2 644(1)	9 628(2)
H(123)	4 091(3)	2 258(2)	4 173(1)	H(4)	8 835(17)	2 928(15)	7 945(15)
H(124)	4 973(3)	3 058(2)	3 324(1)	H(6)	7 428(17)	3 730(13)	5 521(7)
H(125)	5 665(3)	4 099(2)	3 849(1)	H(7)	6 474(17)	5 067(14)	6 134(15)
H(126)	5 475(3)	4 339(2)	5 222(1)	H(8)	8 724(17)	5 270(15)	7 441(15)
H(132)	5 182(2)	2 383(1)	7 056(2)	H(9)	10 193(18)	4 128(15)	7 597(16)
H(133)	4 030(2)	1 487(1)	7 577(2)	H(10)	9 739(17)	3 290(15)	6 291(16)
H(134)	1 838(2)	1 568(1)	7 632(2)	H(11)	9 297(17)	4 599(14)	6 062(15)
H(135)	798(2)	2 545(1)	7 165(2)	H(21A)	6 232(8)	5 800(4)	7 434(6)
H(136)	1 950(2)	3 441(1)	6 644(2)	H(21B)	7 055(8)	5 681(4)	8 304(6)
H(212)	6 306(2)	3 331(1)	10 163(1)	H(22A)	5 626(6)	6 442(4)	8 391(5)
H(213)	7 895(2)	3 777(1)	11 030(1)	H(22B)	5 342(6)	5 768(4)	8 961(5)
H(214)	9 545(2)	4 395(1)	10 501(1)	H(22C)	4 519(6)	5 887(4)	8 091(5)
H(215)	9 606(2)	4 568(1)	9 105(1)	H(51A)	6 829(5)	2 594(3)	5 369(3)
H(222)	5 381(2)	4 543(1)	9 308(2)	H(51B)	8 118(5)	2 128(3)	5 554(3)
H(223)	3 485(2)	5 061(1)	9 625(2)	H(52A)	6 389(7)	1 454(4)	5 212(4)
H(224)	1 567(2)	4 520(1)	9 312(2)	H(52B)	5 621(7)	1 780(4)	5 977(4)
H(225)	1 544(2)	3 461(1)	8 682(2)	H(52C)	6 910(7)	1 314(4)	6 162(4)

preparative t.l.c. plates. Chromatographic separation using CH_2Cl_2–hexane (80:20) as eluting medium yielded an orange product, R_f 0.80, identified as $[(PMe_2Ph)_2RuB_{10}H_8(OEt)_2]$ (189 mg, 52%) by n.m.r. spectroscopy as summarised in Table 1.

Preparation of $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$.—A solution of $[NEt_3H]_2[$*closo*-$B_{10}H_{10}]$ (68 mg, 0.21 mmol) and $[OsCl_2(PPh_3)_3]$ (220 mg, 0.21 mmol) in ethanol (100 cm^3) was heated under reflux for 4 h, during which time the initially dark green solution turned red-brown. The volatile components were then removed under reduced pressure (40—80 °C, rotary evaporator, water-pump pressure), the solid residue taken up in a small volume of CH_2Cl_2, and applied to t.l.c. plates. Chromatographic separation using CH_2Cl_2–hexane (80:20) as eluting medium then yielded an amber-brown component, R_f 0.65, as the major reaction product. This was identified by single-crystal *X*-ray diffraction analysis (Tables 2, 3, and 6; and Figure 1) as $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$, yield 75 mg, 39%;

n.m.r. properties are summarised in Table 4 (see also Figure 2). In contrast to the PMe_2Ph reactions described above, this reaction yielded a number of other chromatographically mobile metallaborane products in small amounts (yields < *ca.* 2%), but we have not yet been able to characterise these.

Single-crystal X-*Ray Diffraction Analysis.*—Crystals suitable for this work were grown by diffusion of pentane into a solution of $[(PPh_3)(Ph_2P\overline{C_6H_4)OsB}_{10}H_7(OEt)_2]$ in CH_2Cl_2 at room temperature.

Crystal data. $C_{40}H_{46}B_{10}O_2OsP_2$, $M = 919.06$, monoclinic, $a = 1\,123.7(1)$, $b = 2\,092.4(3)$, $c = 1\,750.9(2)$ pm, $\beta = 92.54(1)^\circ$, $U = 4.1127$ nm^3, $Z = 4$, space group $P2_1/n$ $(= P2_1/c$, no. 14), $D_c = 1.48$ g cm^{-3}, $\mu = 30.63$ cm^{-1}, $F(000) = 1\,832$.

Data collection. Scans running from 1° below $K_{\alpha 1}$ to 1° above $K_{\alpha 2}$, scan speeds 2.0—29.3° min^{-1}, $4.0 < 2\theta < 45.0^\circ$. 5 109 Unique data, 4 623 observed $[I > 2.0\sigma(I)]$, $T = 290$ K.

Structure refinement. Number of parameters = 503, weighting factor $g = 0.0003$, $R = 0.0283$, $R' = 0.0300$.

Data collection and structure solution. Unit-cell and intensity data were recorded on a Syntex $P2_1$ diffractometer operating in the ω—2θ scan mode using graphite-monochromated Mo-K_α radiation ($\lambda = 71.069$ pm) following a procedure described elsewhere in detail.[38] The data set was corrected for absorption empirically.[39]

The structure was determined *via* standard heavy-atom methods and refined by full-matrix least squares using the SHELX program system.[40] All non-hydrogen atoms were assigned anisotropic thermal parameters with all phenyl groups (apart from the one attached to the boron cage) included in refinement as rigid bodies with hexagonal geometry (C–C = 139.5 pm). All phenyl, methyl, and methylene hydrogen atoms were included in calculated positions (C–H = 108 pm) and were assigned an overall isotropic thermal parameter for each group. The remaining hydrogen atoms were all located experimentally and these were freely refined with individual isotropic thermal parameters. The weighting scheme $w = [\sigma^2(F_o) + g(F_o)^2]^{-1}$ was used at the end of refinement in order to obtain acceptable agreement analyses. Non-hydrogen and hydrogen atom co-ordinates are given in Tables 6 and 7 respectively.

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