Polyhedral Osmaborane Chemistry: the Platination of [4,4,4-(CO)$(PPh_3)_2$-*nido*-4-OsB_5H_9] and the Isolation, Nuclear Magnetic Resonance Properties, and Molecular Structures of Two Seven-vertex *nido*-type Dimetallaheptaboranes [(CO)$(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7$] and [(CO)$(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph$] *

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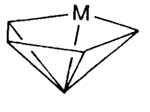
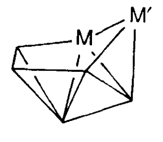
Reaction of the *nido* six-vertex osmaborane [(CO)$(PPh_3)_2OsB_5H_9$] **1** with base followed by [$PtCl_2(PMe_2Ph)_2$] yields (34%) the air-stable lemon-yellow seven-vertex osmaplatinaborane [(CO)$(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7$] **2** which retains the approximate structure of the *nido* six-vertex osmaborane **1**, but which has three basal atoms (BBOs) co-ordinated trihapto to a {PtCl(PMe_2Ph)} moiety, with the platinum and osmium atoms linked by a two-electron hydrogen bridge. The overall seven-vertex structure resembles that of a regular triangulated dodecahedron that has a five-connected vertex missing. It is geometrically and electronically *nido*. Treatment of this species with base, or thermolysis at 140 °C, gives a small yield (3%) of the related species [(CO)$(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph$] **3**. This is formally derived from **2** *via* $PPh_3 \rightleftharpoons PMe_2Ph$ ligand exchange plus the elimination of HCl, and has a similar *nido*-type seven-vertex osmaplatinaheptaborane cluster geometry. Now however there is a direct osmium–platinum bond, the metals are also linked by a four-electron {PPh_2} bridge, and a migrant phenyl group is bound to a basal boron atom on the *nido*-{OsB_5} subcluster. The compounds have been investigated by NMR spectroscopy, the results of which suggest that a number of other (minor) products from the reactions may also be interesting platinaosmaboranes. Crystals of **2** are monoclinic, space group $P2_1/n$, with a = 1.5397(3), b = 1.8489(3), c = 1.7189(3) nm, β = 92.568(13)° and Z = 4. Crystals of **3** are triclinic, space group $P\bar{1}$ (no. 2), with a = 1.4491(7), b = 1.7730(4), c = 1.0763(3) nm, α = 82.08(2), β = 102.71(3), γ = 105.42(4)° and Z = 2.

There is considerable current interest in the synthesis of compounds in which two or more transition-metal centres are bound in adjacent and potentially interactive positions on an electronically flexible substrate. Polyhedral boron-containing substrates are in principle potentially useful 'B-frame' matrices for this purpose,[1–7] since they often exhibit considerable electronic and geometric flexibility.[8] However, although the systematic chemistry of the monometallaboranes is becoming increasingly well developed,[9–11] systematic polymetallaborane chemistry is as yet rudimentary. The synthesis of the monometallic *nido* six-vertex 2-metallaboranes [(CO)$(PPh_3)_2IrB_5H_8$][12,13] and [(CO)$(PPh_3)_2OsB_5H_9$][13] (configuration **I** and Fig. 1) in reasonable yield (85 and 80% respectively) permits their ready investigation as possible substrates for the accumulation of additional metal centres about the reactive open face. In addition, since both are air-stable solids, they also in principle permit the investigation of the chemistry of *nido* six-vertex species by avoiding the tedious preparation and handling procedures associated with the use of the binary boron hydride B_6H_{10} itself. In these contexts we now report chemistry arising from the treatment of [(CO)$(PPh_3)_2OsB_5H_9$] (compound **1**, Fig. 1) with *cis*-[$PtCl_2(PMe_2Ph)_2$] in the presence of base, this reaction constituting a metallaborane analogue of the well used synthetic procedure[1,3,11,14–17] in which a discrete or incipient borane anion displaces halide from a phosphineplatinum halide complex to give a monometallaborane. This work has resulted in the isolation and identification of two heterobimetallic *nido*-type seven-vertex dimetallaboranes of schematic cluster configuration **II** which exhibit some interesting features. Some preliminary[2,9,10] and related[18] aspects of this work have been presented elsewhere.



I



II

Results and Discussion

Preparation and Structure of [(CO)$(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7$] **2**.—Reaction of [(CO)$(PPh_3)_2OsB_5H_9$] **1** with methyllithium, followed by addition of *cis*-[$PtCl_2(PMe_2Ph)_2$] and chromatographic separation, gave a lemon-yellow air-stable, crystalline, dimetallaborane product in a yield of 34%. It was identified by single-crystal X-ray diffraction analysis and NMR spectroscopy (see below) as [2-(CO)-2,2-$(PPh_3)_2$-7-(PMe_2Ph)-7-Cl-2,7-μ-H-*nido*-2,7-Os-PtB_5H_7] [**2**, schematic cluster structure **V**, equation (3)

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

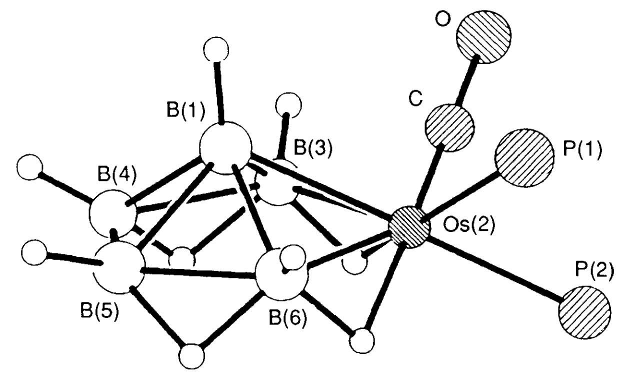


Fig. 1 Representation of the molecular structure of [4-(CO)-4,4-$(PPh_3)_2$-*nido*-4-OsB_5H_9] **1**.[13] Note that, for ease of comparison with compounds **2** and **3** the IUPAC-recommended numbering Os(4), B(2), B(3), B(5) and B(6) of ref. 13 is changed here to Os(2), B(4), B(3), B(6) and B(5) respectively; see also NMR data in Table 5 and the anionic structure **VIII** in the text.

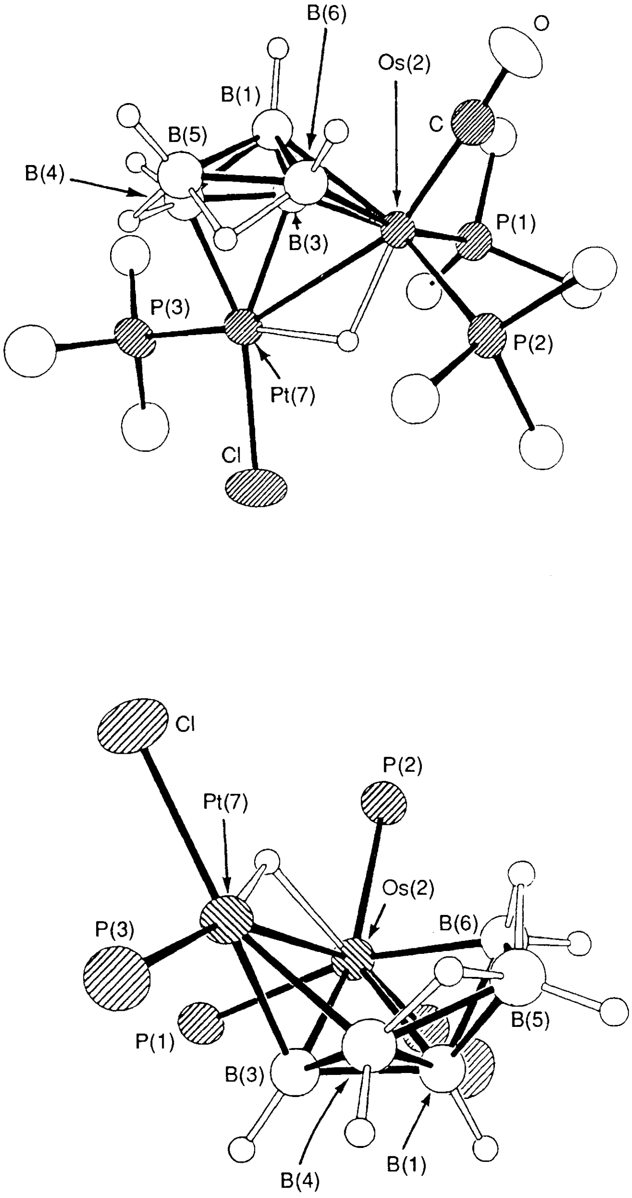
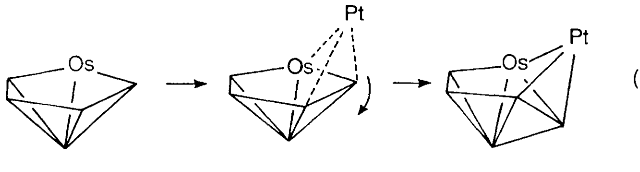


Fig. 2 Two views of the crystallographically determined molecular structure of $[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]$ **2** with selected P-organyl carbon and hydrogen atoms omitted for clarity. The Os(2)–H(2,7)–Pt(7) bridging hydrogen atom was not detected crystallographically by diffraction analysis, but was located by potential-well calculations.[19,20] The lower diagram illustrates the essential *nido* character of the seven-vertex cluster (compare structures **V** and **VI**, and also refs. 18 and 22).

below]. A straightforward stoichiometry may be written for the reaction process [equations (1) and (2)], one possibility for the mechanism being *via* initial nucleophilic displacement of Cl^- at platinum by the osmaborane anion [**III**, equation (2)] resulting in the addition of the second metal centre to the cluster as depicted schematically in equation (3). The initial *nido* six-

$$[(CO)(PPh_3)_2OsB_5H_9] + LiMe \longrightarrow \quad (\mathbf{1}) \quad MeH + Li^+[(CO)(PPh_3)_2OsB_5H_8]^- \quad (1)$$

$$[(CO)(PPh_3)_2OsB_5H_8]^- + [PtCl_2(PMe_2Ph)_2] \longrightarrow [(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7] \; (\mathbf{2}) + Cl^- + PMe_2Ph \quad (2)$$

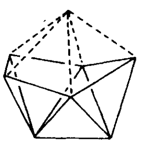


(3)

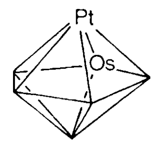
III **IV** **V**

vertex cluster (structure **III**, and Fig. 1) would thereby flex (structure **IV**) to accommodate the second metal centre during the course of its transition to *nido* seven-vertex character, **V**, and the process is accompanied by a bridging hydrogen-atom rearrangement about the open face.

Crystals suitable for single-crystal X-ray diffraction analysis were grown by diffusion of pentane into a CH_2Cl_2 solution. A drawing of the main part of the molecular structure is in Fig. 2 and selected interatomic distances and angles are in Tables 1 and 2, respectively. The Os(2)–H–Pt(7) bridging hydrogen atom was not located in the X-ray analysis but its presence was apparent from NMR spectroscopy (see below, also Table 6), and its position as drawn in Fig. 2 was established by potential-well calculations.[19,20]



VI



VII

The cluster structure is clearly seen to be geometrically of the *nido* seven-vertex variety (see also schematic structures **II** and **V** above), derived by the formal removal of a five-connected vertex from the dodecahedral structure **VI** that is exemplified by the solid-state structure[21] of the *closo*-$[B_8H_8]^{2-}$ anion in $[Zn(NH_3)_4][B_8H_8]$. As such it constitutes the first *nido* seven-vertex boron-containing cluster to have been structurally characterized,[2] although a second example has been recently reported[22] for the *nido*-$[Me_2C_2B_5H_6]^-$ anion in $[NMe_4][Me_2C_2B_5H_6]$. Although the authors of ref. 22 propose that our platinaosmaborane **2** is of *closo* constitution, this is clearly not the case.[18,23] There is an unambiguous open face, with the Pt(7)–B(5) and Pt(7)–B(6) distances clearly non-bonding at 332.6 and 362.8 pm respectively. Furthermore, there is a fold of 152° in the Os(2)B(3)B(4)B(5)B(6) surface (in a *closo* structure **VII** the atoms 2–6 would be coplanar), and there are three bridging hydrogen atoms about the open face, patently not a *closo* feature (compare Williams' VN7 configuration for *nido*-$[B_7H_{10}]^-$).[24]

The geometry about the osmium centre is pseudo-octahedral

Table 1 Selected interatomic distances (pm) for [(CO)(PPh$_3$)$_2$HOs(PMe$_2$Ph)ClPtB$_5$H$_7$] **2** with estimated standard deviations (e.s.d.s) in parentheses

(*i*) From the metal atoms

Os(2)–Pt(7)	295.9(1)	P(2)–Os(2)	240.5(4)
P(3)–Pt(7)	226.1(4)	C–Os(2)	189.3(19)
Cl–Pt(7)	237.8(5)	B(1)–Os(2)	228.4(18)
B(3)–Pt(7)	213.6(19)	B(3)–Os(2)	218.3(18)
B(4)–Pt(7)	214.5(20)	B(6)–Os(2)	214.7(19)
P(1)–Os(2)	243.0(4)		

(*ii*) Phosphorus–carbon

C(111)–P(1)	181.6(9)	C(231)–P(2)	184.9(9)
C(121)–P(1)	184.0(9)	C(31)–P(3)	181.7(19)
C(131)–P(1)	181.1(9)	C(32)–P(3)	178.6(18)
C(211)–P(2)	182.9(9)	C(331)–P(3)	178.9(10)
C(221)–P(2)	180.4(9)	C–O	113.1(19)

(*iii*) Boron–boron

B(3)–B(1)	173.9(25)	B(4)–B(3)	174.7(26)
B(4)–B(1)	179.2(28)	B(5)–B(4)	187.4(28)
B(5)–B(1)	178.8(27)	B(6)–B(5)	176.3(28)
B(6)–B(1)	181.5(26)		

(*iv*) Boron–hydrogen

H(1)–B(1)	121(16)	H(4,5)–B(5)	93(17)
H(3)–B(3)	150(15)	H(5,6)–B(5)	150(15)
H(4)–B(4)	81(16)	H(6)–B(6)	117(15)
H(4,5)–B(4)	144(16)	H(5,6)–B(6)	138(15)
H(5)–B(5)	120(15)		

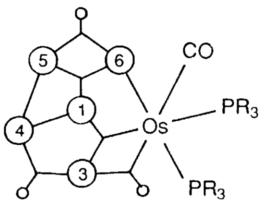
Table 2 Selected interatomic angles (°) for [(CO)(PPh$_3$)$_2$-HOs(PMe$_2$Ph)ClPtB$_5$H$_7$] **2** with e.s.d.s. in parentheses

(*i*) At the metal atoms

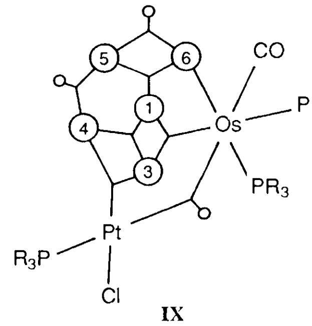
P(1)–Os(2)–Pt(7)	91.6(1)	B(6)–Os(2)–P(1)	165.8(5)
P(2)–Os(2)–Pt(7)	110.4(1)	B(6)–Os(2)–P(2)	88.2(5)
P(2)–Os(2)–P(1)	104.9(1)	B(6)–Os(2)–C	85.8(7)
C–Os(2)–Pt(7)	157.4(5)	B(6)–Os(2)–B(1)	48.2(7)
C–Os(2)–P(1)	88.2(5)	B(6)–Os(2)–B(3)	89.5(7)
C–Os(2)–P(2)	91.5(5)	P(3)–Pt(7)–Os(2)	155.4(1)
B(1)–Os(2)–Pt(7)	73.1(5)	Cl–Pt(7)–Os(2)	112.3(1)
B(1)–Os(2)–P(1)	118.7(5)	Cl–Pt(7)–P(3)	91.3(2)
B(1)–Os(2)–P(2)	136.4(5)	B(3)–Pt(7)–Os(2)	47.4(5)
B(1)–Os(2)–C	87.2(7)	B(3)–Pt(7)–P(3)	108.0(5)
B(3)–Os(2)–Pt(7)	46.1(5)	B(3)–Pt(7)–Cl	155.4(5)
B(3)–Os(2)–P(1)	80.8(5)	B(4)–Pt(7)–Os(2)	76.3(5)
B(3)–Os(2)–P(2)	156.4(5)	B(4)–Pt(7)–P(3)	86.0(5)
B(3)–Os(2)–C	111.7(7)	B(4)–Pt(7)–Cl	151.9(6)
B(3)–Os(2)–B(1)	45.8(6)	B(4)–Pt(7)–B(3)	48.2(7)
B(6)–Os(2)–Pt(7)	89.1(5)		

(*ii*) Others

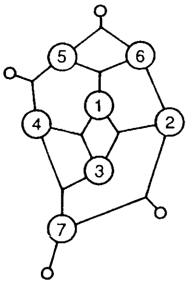
Pt(7)–B(3)–Os(2)	86.5(7)	B(5)–B(4)–B(3)	111.7(14)
B(1)–B(3)–Os(2)	70.2(9)	B(1)–B(6)–Os(2)	69.8(9)
B(1)–B(3)–Pt(7)	109.4(11)	B(5)–B(6)–Os(2)	115.2(12)
B(4)–B(3)–Os(2)	109.4(11)	B(5)–B(6)–B(1)	59.9(11)
B(3)–B(4)–Pt(7)	65.6(9)	B(4)–B(5)–B(6)	106.5(14)
B(3)–B(4)–B(1)	58.8(10)	B(3)–B(1)–Os(2)	64.1(8)
B(5)–B(4)–Pt(7)	111.5(12)		



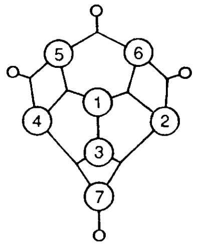
VIII



IX



X



XI

with the osmium-to-boron distances similar both to those of the platinum–boron distances and to the few examples quoted in the literature.[25–27] The Os(2)–B(1) distance at 228 pm is a notable 10–14 pm longer than Os(2)–B(3) and Os(2)–B(6), a disparity which has also been noted for the Ir(2)–B(1) distance in [(CO)(PPh$_3$)$_2$-*nido*-IrB$_5$H$_8$].[12]

The platinum atom is bonded to the cluster *via* boron atoms B(3) and B(4), where the Pt(7)–B(3) and Pt(7)–B(4) distances are the same within experimental error, *viz.* 213.6(19) and 214.5(20) pm, respectively. The angles Cl–Pt(7)–B(3) at 155.4(5)° and Cl–Pt(7)–B(4) at 151.9(6)° indicate that the platinum atomic orbital *trans* to the chlorine ligand is directed tangentially almost precisely to the midpoint of the B(3)–B(4) vector. There could therefore be a suggestion here of a η^2 (μ-bonded) unit with a two-electron three-centre bond to B(3) and B(4), similar to those found in the η^2-bonded cluster compounds [μ-4,5-{*trans*-(PEt$_3$)$_2$PtH}-*nido*-2,3-CB$_5$H$_6$][28] and [μ-2,3-{(PPh$_3$)$_2$Cu}-*nido*-B$_5$H$_8$],[29] where the metal moiety effectively subrogates a bridging hydrogen atom. However, in the last two compounds the dihedral angle between the B(basal)–B(basal)–M$_\mu$ plane and the B(basal)–B(basal)–B(apical) plane is *ca.* 180° whereas in compound **2** the plane containing the platinum vertex is tilted in toward the centre of the cluster at an angle of 132.6° as would be expected when the platinum atom is regarded as an integral vertex in a *nido*-seven-vertex cluster. From this point of view also, therefore, the compound is better regarded as a *nido* seven-vertex cluster compound.

If the osmium centre is regarded as being octahedral osmium(II), then the {Os(CO)(PPh$_3$)$_2$} unit acts as a straightforward Wadian[30] {BH} subrogator, whereas in the square-planar platinum(II) centre the {PtCl(PMe$_2$Ph)} unit would contribute two orbitals and one electron to the cluster bonding.[18] In simple electronic terms the platinaosmaborane **2** is therefore closely related to the starting osmaborane anion (structure **VIII**) by the replacement of a two-electron three-centre B–H–B link by a two-electron three-centre B–Pt–B link and the conversion of an Os–H–B two-electron three-centre bond into an Os–H–Pt one, together with an Os–H–B ⟶ B–H–B bridging hydrogen shift around the open face (structure **IX**).

This latter structure is electronically equivalent to a *nido*-B$_7$H$_{11}$ structure of *styx* 3411 topology as in **X**,* although it has been proposed[18] that the symmetrical 3411 structure **XI** may perhaps constitute the more stable configuration for B$_7$H$_{11}$ itself. Although an *endo* terminal hydrogen atom is rare in a *nido* system, the positioning of such a configuration at B(7) in a *nido* seven-vertex structure now has precedent[22] in the recently reported [Me$_2$C$_2$B$_5$H$_6$]$^-$ anion. This anion presumably would have contributions from a closely related *styx* 0441-type topology as in **XII**.

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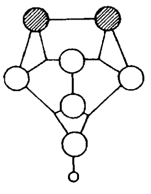
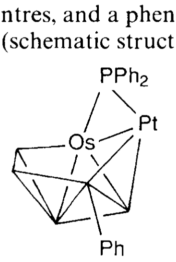
* For a definition of *styx* see ref. 31.



XII

Preparation and Structure of $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3**.—An interesting variation on the *nido*-seven-vertex osmaplatinaborane structural theme of compound **2** (schematic structure **V**) is afforded by the species $[2\text{-}(CO)\text{-}2,7\text{-}(PPh_3)_2\text{-}\mu\text{-}2,7\text{-}(PPh_2)\text{-}nido\text{-}2,7\text{-}OsPtB_5H_7\text{-}4\text{-}Ph]$ **3** which is closely related to **2**, but which has a $\{PPh_2\}$ bridge linking the two metal centres, and a phenyl group bound to the cluster in the 4 position (schematic structure **XIII** and Fig. 3).



XIII

Compound **3** was obtained as air-stable orange crystals in small quantities (yield *ca.* 3%) from a reaction mixture designed in principle to yield a diplatinaosmaborane species according to the stoichiometry of equation (4), but in the event this resulted

$$\underset{\mathbf{2}}{[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]} + [PtCl_2(PMe_2Ph)_2] + 2\,NaH \longrightarrow [(CO)(PPh_3)_2Os(PMe_2Ph)HClPtB_5H_5Pt(PMe_2Ph)_2] + 2H_2 + 2NaCl \quad (4)$$

in a complex mixture of products in low yield, of which we have only been able to characterize one (compound **3**). The other less-abundant components consist of other metallaboranes and dimetallaboranes, as judged by their NMR behaviour; two of these compounds, **4** and **5**, yielded nicely detailed NMR behaviour, but their constitution is uncertain (see NMR and Experimental sections below). Single-crystal X-ray diffraction analysis allied with NMR spectroscopy (see below, Table 5) revealed the constitution $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$* for **3**, for the formation of which an overall stoichiometry may be written as in equation (5). It can be seen

$$PPh_3 + \underset{\mathbf{2}}{[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]} + NaH \longrightarrow PMe_2Ph + \underset{\mathbf{3}}{[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]} + H_2 + NaCl \quad (5)$$

that **3** is derived from **2** by an exchange of PPh_3 for PMe_2Ph on platinum, by the elimination of HCl, and by a migration of one of the phenyl groups from a PPh_3 to give a PPh_2 unit and a boron-bound phenyl group. Compound **3** was also formed in 1.5% yield when compound **2** was thermolysed at 140 °C for 1.5 h in xylene solution, indicating that the presence of added base may not be necessary for HCl elimination.

Crystals of **3** suitable for X-ray diffraction analysis were grown by diffusion of pentane into a CH_2Cl_2 solution. A drawing of the molecular structure is in Fig. 3, and selected interatomic distances and angles are in Tables 3 and 4 respectively. Cluster hydrogen atoms were not locatable in the diffraction analysis, but their positioning in Fig. 3 (see also Table 10) by potential-well calculations,[19,20] and their incidence as determined by NMR spectroscopy (Table 5 below), are mutually self-consistent, thereby confirming the overall formulation.

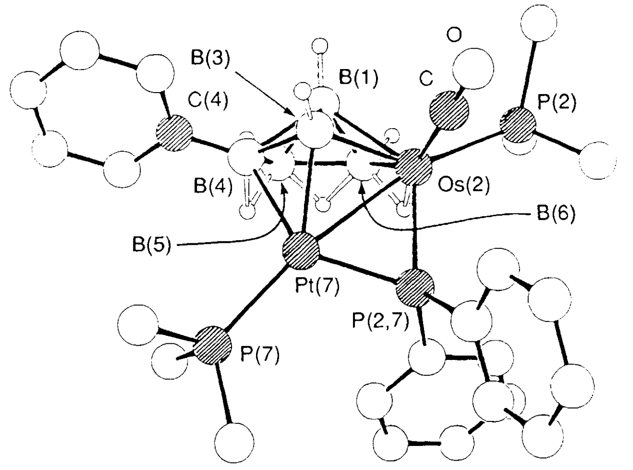
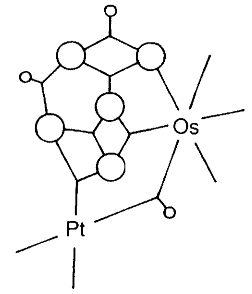
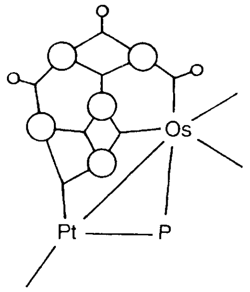


Fig. 3 Crystallographically determined molecular structure of $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3** with selected P-organyl atoms omitted for clarity. The cluster hydrogen atoms were not detected crystallographically, but are located at the positions shown in the diagram by potential-well calculations.[19,20]

The basic *nido*-type $OsPtB_5$ seven-vertex cluster structure is readily apparent, with the Pt(7)–B(5) and Pt(7)–B(6) distances being non-bonding at 346(2) and 356(2) pm respectively (compare **2** above), and the Os(2)–B(4) fold in the Os(2)B(3)-B(4)B(5)B(6) surface being significantly different from 180°, at 124.9(3)°. In contrast to compound **2**, the Os–B as well as the two B–B open face linkages are now bridged by hydrogen (compare structure **XI** for B_7H_{11} above and in ref. 18). In cluster electronic terms the basic cluster of **3** can in principle be derived from that of **2** by a shift of a proton from the two-electron Pt(7)–Os(2) linkage to the Os(2)–B(6) linkage (schematic structure **XV**, **3**, compared to **IX** and **XIV**, **2**), although the disparity between the Os(2)–B(1) distances for the two species suggests that this simple comparison should not be extended too far. In this simple approach, the Pt(7)–Os(2) linkage would thereby become a straightforward two-electron two centre bond, the distance of 268.7(1) pm being comparable to the (limited) range of such distances reported in the literature; in fact it tends toward the low end of the range which centres around 280 pm. However, this is, as far as we are aware, the first osmium–platinum phosphido-bridged compound to be reported and so direct comparisons are precluded. Also in this context a referee has pointed out that this is merely a cluster connectivity and that cluster bonding is characterized by non-localized molecular orbitals; nevertheless the short distance does suggest substantial localization.



XIV



XV

Of particular interest in compound **3** is the formation of the

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* Note that in refs. 10 and 11 this species has been wrongly transcribed as $[(CO)(PPh_3)(PPh_2)Os(PMe_2Ph)PtB_5H_7Ph]$.

Table 3 Selected interatomic distances (pm) for $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3** with e.s.d.s in parentheses

(*i*) From the metal atoms

Os(2)–Pt(7)	268.7(1)	P(3)–Os(2)	232.6(3)
P(1)–Pt(7)	228.5(3)	B(1)–Os(2)	245.6(14)
P(3)–Pt(7)	229.6(3)	B(3)–Os(2)	218.8(14)
B(3)–Pt(7)	215.1(13)	B(6)–Os(2)	230.8(14)
B(4)–Pt(7)	243.3(14)	C–Os(2)	189.0(11)
P(2)–Os(2)	237.9(3)		

(*ii*) Phosphorus–carbon

C(111)–P(1)	185.9(7)	C(221)–P(2)	188.0(8)
C(121)–P(1)	185.5(7)	C(231)–P(2)	185.5(6)
C(131)–P(1)	188.8(7)	C(311)–P(3)	186.5(7)
C(211)–P(2)	186.6(6)	C(321)–P(3)	184.6(6)

(*iii*) To boron

B(3)–B(1)	178.3(18)	B(4)–B(3)	177.5(19)
B(4)–B(1)	183.4(19)	B(5)–B(4)	183.0(19)
B(5)–B(1)	177.2(20)	C(41)–B(4)	161.9(15)
B(6)–B(1)	180.8(19)	B(6)–B(5)	179.2(21)

(*iv*) Carbonyl

C–O	115.4(12)

Table 4 Selected interatomic angles (°) for $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3** with e.s.d.s in parentheses

(*i*) At the metal atoms

P(1)–Pt(7)–Os(2)	167.0(1)	B(3)–Os(2)–Pt(7)	51.1(3)
P(3)–Pt(7)–Os(2)	55.0(1)	B(3)–Os(2)–P(2)	142.8(3)
P(3)–Pt(7)–P(1)	115.9(1)	B(3)–Os(2)–P(3)	101.8(3)
B(3)–Pt(7)–Os(2)	52.4(4)	B(3)–Os(2)–B(1)	44.7(5)
B(3)–Pt(7)–P(1)	139.3(4)	B(6)–Os(2)–Pt(7)	90.4(4)
B(3)–Pt(7)–P(3)	103.9(4)	B(6)–Os(2)–P(2)	88.9(4)
B(4)–Pt(7)–Os(2)	81.0(3)	B(6)–Os(2)–P(3)	115.3(4)
B(4)–Pt(7)–P(1)	104.8(3)	B(6)–Os(2)–B(1)	44.5(5)
B(4)–Pt(7)–P(3)	133.9(3)	B(6)–Os(2)–B(3)	84.5(5)
B(4)–Pt(7)–B(3)	45.1(5)	C–Os(2)–Pt(7)	101.9(3)
P(2)–Os(2)–Pt(7)	165.7(1)	C–Os(2)–P(2)	86.4(3)
P(3)–Os(2)–Pt(7)	53.9(1)	C–Os(2)–P(3)	96.7(3)
P(3)–Os(2)–P(2)	114.0(1)	C–Os(2)–B(1)	107.1(5)
B(1)–Os(2)–Pt(7)	78.9(3)	C–Os(2)–B(3)	79.6(5)
B(1)–Os(2)–P(2)	110.0(3)	C–Os(2)–B(6)	146.5(5)
B(1)–Os(2)–P(3)	130.8(3)		

(*ii*) Other selected atoms

B(3)–B(1)–Os(2)	59.7(6)	Os(2)–B(3)–Pt(7)	76.5(4)
B(4)–B(1)–Os(2)	100.8(7)	Os(2)–P(3)–Pt(7)	71.1(1)
B(5)–B(1)–Os(2)	109.1(8)	B(3)–B(4)–Pt(7)	59.1(6)
B(4)–B(3)–Pt(7)	75.9(6)	B(5)–B(4)–Pt(7)	107.6(8)
B(4)–B(3)–Os(2)	113.9(8)	B(5)–B(4)–B(3)	111.0(10)
B(4)–B(5)–B(1)	61.2(8)	C(41)–B(4)–Pt(7)	127.1(8)
B(6)–B(5)–B(1)	61.0(8)	C(41)–B(4)–B(1)	128.1(9)
B(6)–B(5)–B(4)	107.2(10)	C(41)–B(4)–B(3)	122.9(10)
B(1)–B(6)–Os(2)	72.1(7)	C(41)–B(4)–B(5)	116.5(10)
B(5)–B(6)–B(1)	58.9(8)		

four-electron PPh_2 bridge to the Os–Pt bond and the appearance of a phenyl group instead of BH(*exo*) at the 6 position. Although the compound was isolated in low yield, the incidence of both these features in the same molecule suggests that they derive from a concerted process. The replacement by an aromatic linkage of BH(*exo*) under relatively mild conditions has precedent in platinaborane chemistry in the *aufbau* synthesis of $[(PMe_2Ph)_2Pt_2B_{16}H_{15}(C_6H_4Me)(PMe_2Ph)]$ by thermolysis of $[(PMe_2Ph)_2PtB_8H_{12}]$ in toluene solution.[32] As mentioned above this is, as far as we are aware, the first report of a PPh_2-bridged metal–metal link in polyhedral boron chemistry, although a metal–boron one has been reported, in $[(C_5Me_5)Rh(PPh_2)B_8H_9(PHPh_2)]$,[33] and boron–boron ones are known, for example in $B_{10}H_{13}(PPh_2)$[34] and in the $[B_{10}H_{12}(PPh_2)]^-$ anion.[35] In these species the two-orbital cluster contribution of the $\{Ph_2P\}$ moiety induces *arachno*-type behaviour, and it would be interesting in this context to consider a description of **3** in eight-vertex $\{PtOsB_5P\}$ cluster terms; however, this approach is complicated because the osmium centre would thereby have a four-orbital contribution to the eight-vertex cluster, thus rendering a straightforward Wadian[30] interpretation untenable. Furthermore, in the *arachno*-phosphinoboranes the two vertices to which the phosphido group is attached are not mutually bonded, whereas in **3** the metal atoms show a strong bonding interaction suggesting that the phosphorus atom is better regarded as a localized edge-bridging species and that its cluster-bonding role is limited to the extra electron that is formally released to be donated by the Pt and Os vertices to the cluster, where it replaces the one-electron bridging hydrogen atom. The extra electron may be regarded as being localized in a two-electron platinum–osmium bond (see end of preceding paragraph).

Nuclear Magnetic Resonance Investigations of Compounds **2** *and* **3**.—The measured ^{11}B and ^1H NMR data for the metallaborane clusters of **2** and **3** are summarized in Table 5, which also contains data for compound **1** for comparison. For each compound five separate ^{11}B resonance positions were apparent, and selective ^1H-$\{^{11}B\}$ NMR spectroscopy showed that each of these [except for the resonance assigned to phenyl-bound B(4) in **3**] was associated with a BH(terminal) group. For each compound the resonance at highest field was reasonably[36,37] assignable to the apical B(1) position, and the behaviour of the bridging hydrogen ^1H resonances under conditions of selective irradiation of the remaining ^{11}B resonance positions readily assigned the open-face ^{11}B resonances and also defined the bridging hydrogen positions as indicated in Table 5. These latter bridging positions were consistent with the results of single-crystal X-ray diffraction analysis (allied with potential-well calculations in the case of **3**), as discussed above.

For the dimetallic compounds **2** and **3** there was a wide variation of ^{11}B chemical shifts, both compared to each other and to compound **1**, particularly for the positions adjacent to the two metal atoms, but ^{11}B work on *nido* seven-vertex systems is so limited (this work and refs. 22 and 38) that any discussion of shielding trends would be necessarily very speculative at present. It is convenient to consider the cluster ^1H shielding behaviour as a plot of $\delta(^1H)$ *versus* $\delta(^{11}B)$ for the

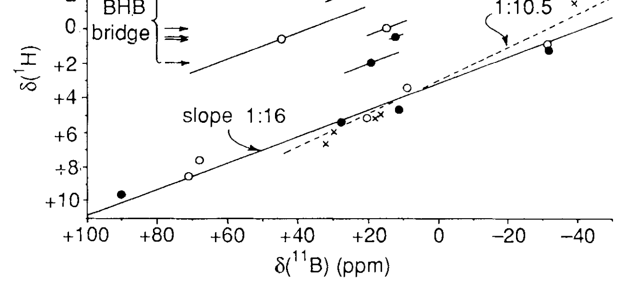

Fig. 4 Proton-boron-11 shielding correlation plot for $[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]$ **2** (○), $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3** (●), and for the parent osmaborane $[(CO)(PPh_3)_2OsB_5H_9]$ (×). For the *exo*-terminal protons, the slope $\delta(^{11}B):\delta(^1H)$ of 10.5:1 (hatched line) is as found for $[(CO)(PPh_3)_2OsB_5H_9]$ and its iron and ruthenium analogues (ref. 13), and the slope of 16:1 (solid line) is as found for a variety of larger boranes and platinaboranes (refs. 16, 36, and 39–42). The M–H–B positions are off-scale to high proton shielding [low $\delta(^1H)$ value].

Table 5 Proton and boron-11 NMR data for $[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]$ **2**, $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3** and for the parent osmaborane $[(CO)(PPh_3)_2OsB_5H_9]$ **1**

Tentative assignments	Compound **2**[a] $\delta(^{11}B)$	Compound **2**[a] $\delta(^{1}H)$	Compound **3**[b] $\delta(^{11}B)$	Compound **3**[b] $\delta(^{1}H)$	Compound **1**[c] $\delta(^{11}B)$	Compound **1**[c] $\delta(^{1}H)$
(3)	*ca.* +68	+7.57[d]	+90.1	+9.57[e]	+32.2	+6.62
(6)	+71.4	+8.56	+27.6	+5.41	+30.0	+5.85
(4)	+0.9	+3.21[d]	+13.2	—	+18.0	+5.18
(5)	+20.5	+5.14	+11.2	+4.65	+16.4	+4.96
(1)	−31.3	+ 0.87[f]	−31.7	+1.18	−39.2	−1.49
(4,5)	—	−0.10[g,h]	—	+0.45[g]	—	—
(2,6)	—		—	−10.57[i]	—	−9.03,[i] −10.59[j]
(5,6)	—	+0.53[k,l]	—	+1.97[k,m]	—	−2.24, −2.59

[a] In $CDCl_3$ solution at +21 °C. [b] In CD_2Cl_2 solution at +20 °C. [c] In $CDCl_3$ solution at +21 °C; data from ref. 13; the numbering scheme used here differs from that used in ref. 13 so that similar sites may be easily compared among $[(CO)(PPh_3)_2OsB_5H_9]$ (**1**, see Fig. 1), **2** and **3**. [d] Both these peaks exhibit doublet splittings of 11.5 ± 0.5 Hz, possibly arising from mutual coupling $^{n}J(^{1}H-^{1}H)$ or from considerably similar couplings $^{n}J(^{31}P-^{1}H)$. [e] Possible satellites, $^{2}J(^{195}Pt-^{1}H)$ *ca.* 80 Hz. [f] Satellites, $^{3}J(^{195}Pt-^{1}H)$ *ca.* 55 Hz. [g] Sharpened upon irradiation at $\nu[^{11}B(4)]$ and $\nu[^{11}B(5)]$. [h] Satellites, $^{2}J(^{195}Pt-^{1}H)$ *ca.* 70 Hz. [i] No significant coupling to ^{31}P observed [H(2,6) is *trans* to carbonyl in this compound, see footnote *j*]. [j] Doublets of doublets, $^{2}J(^{31}P-^{1}H)(cis) = 11$, $^{2}J(^{31}P-^{1}H)(trans) = 40$ Hz (ref. 13). [k] Sharpened by $\nu[^{11}B(5)]$ only, implying a very small coupling of this bridging proton to $^{11}B(6)$; in addition these bridging protons exhibit anomalously low shieldings which may indicate a transannular influence of the platinum bonding environment across the Os(2)Pt(7)B(4)B(5)B(6) open face. Similar effects are observed in the proton shielding of isomers of $[(PMe_2Ph)_2PtB_{18}H_{20}]$. [l] Satellites, $^{3}J(^{195}Pt-^{1}H)$(transoid) *ca.* 60 Hz. [m] Satellites, $^{3}J(^{195}Pt-^{1}H)$(transoid) = 61 Hz.

Table 6 Proton[a] and phosphorus-31[b] NMR chemical shift and coupling-constant data for $[(CO)(PPh_3)_2HOs(PMe_2Ph)ClPtB_5H_7]$ **2**

On the platinum atom			
$\delta[^{31}P(3)]$(ppm)	−3.3	$\delta[^{1}H(Me)]$	+1.61(C), +1.74(D)[c]
$^{1}J[^{195}Pt-^{31}P]$/Hz	3339.8 ± 2	$^{2}J[^{31}P(3)-^{1}H(Me)]$/Hz	11.7 ± 0.2 (both C and D)[c]
$^{3}J[^{31}P(A)-^{31}P(3)]$[d]/Hz	9.8 ± 0.2	$^{3}J[^{195}Pt-^{1}H(Me)]$/Hz	30.4 ± 0.2(C), 40.0 ± 0.2(D)[c]
$^{3}J[^{31}P(B)-^{31}P(3)]$[d]/Hz	2.3 ± 0.2		
On the osmium atom			
$\delta[^{31}P(A)]$[c,e](ppm)	−0.3	$\delta[^{1}H(2,7)]$	−10.61
$\delta[^{31}P(B)]$[c,e](ppm)	+2.2	$^{2}J[^{31}P(3)-^{1}H(2,7)](trans)$/Hz	98.5 ± 0.3
$^{2}J[^{195}Pt-^{31}P(A)]$[c]/Hz	31.7 ± 0.2	$^{2}J[^{31}P(A\ or\ B)-^{1}H(2,7)](cis)$[c]/Hz	191 ± 0.5
$^{2}J[^{195}Pt-^{31}P(B)]$[c,e]/Hz	20 ± 2	$^{1}J[^{195}Pt-^{1}H(2,7)]$/Hz	554.7 ± 0.2
$^{2}J[^{31}P(A)-^{31}P(B)]$[c]/Hz	28.1 ± 0.2		

[a] Recorded at +21 °C in $CDCl_3$ solution. [b] Recorded at −41 °C in $CDCl_3$ solution. [c] C and D refer to chemically distinct H atoms; the two inequivalent P-methyl groups C and D arise from the chiral nature of the platinum centre and the prochiral $\{PhMe_2P(3)\}$ ligand. [d] A and B refer to the chemically distinct phosphorus atoms P(1) and P(2). On present NMR evidence it is not possible to assign $^{31}P(A)$ and $^{31}P(B)$ specifically to either position P(1) or P(2) (Fig. 2). [e] The parent osmaborane $[(CO)(PPh_3)_2OsB_5H_9]$ has $\delta(^{31}P)$ +5.6 and +13.5 ppm, with $^{2}J(^{31}P-^{31}P)$ 19.5 ± 0.2 Hz (−50 °C in $CDCl_3$ solution; ref. 13).

Table 7 Measured phosphorus-31[a] NMR chemical shift and coupling-constant data for $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3**

$\delta[^{31}P(2)]$(ppm)	+17.5	$^{1}J[^{195}Pt-^{31}P(B)]$[b]/Hz	2395 ± 5
$\delta[^{31}P(A)]$[b](ppm)	+39.5	$^{n}J[^{31}P(2)-^{31}P(A)]$[b]/Hz	53.7 ± 0.2
$\delta[^{31}P(B)]$[b](ppm)	+57.8	$^{n}J[^{31}P(2)-^{31}P(B)]$[b]/Hz	18.5 ± 1.5
$^{2}J[^{195}Pt-^{31}P(2)]$/Hz	24.3 ± 0.2	$^{2}J[^{31}P(A)-^{31}P(B)]$[b]/Hz	*ca.* 0
$^{1}J[^{195}Pt-^{31}P(A)]$[b]/Hz	3826 ± 5		

[a] Recorded at −41 °C in $CDCl_3$ solution. [b] A and B refer to the chemically distinct phosphorus atoms P(1) and P(3). On present evidence it is not possible to assign $^{31}P(A)$ and $^{31}P(B)$ to either P(1) or P(3), although evidence suggests P(A) = P(1) and P(B) = P(3) (see text).

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directly bound atoms (Fig. 4). It can be seen from this that there is a general correlation between $\delta(^{11}B)$ and $\delta(^{1}H)$ for BH(*exo*) units. It is of interest that the slope of $\delta(^{11}B):\delta(^{1}H)$ 16:1 is more similar to those found[36,39–42] for a variety of open-structured larger (8–11 vertices) boranes, metallaboranes and heteroboranes than to the slope of *ca.* 10:1 found (*a*) for smaller (4–6 vertices) osmaboranes such as **1**,[43] and (*b*) for *closo* ten- and twelve-vertex species.[42,44–46] Variation in these correlation slopes, with due allowance for anomalous heteroatom and other effects, is likely to have increasing diagnostic value as more assigned (^{11}B,^{1}H) data become available for polyhedral boron-containing compounds. In this context therefore it is of interest that compounds **1**–**3** appear to exhibit no anomalous antipodal or transannular ^{1}H deshielding effects induced by the heavy Os and/or Pt atoms, in contrast to some four-,[47] five-,[43] ten-[47] and twelve-vertex[44–48] systems. The B–H–B bridging protons are all some 3–7 ppm above the *exo*-BH shielding trends, as expected,[36] although it should be noted that this does not necessarily imply a high absolute shielding [*i.e.* $\delta(^{1}H) < 0$] in all cases particularly when $\delta(^{11}B)$ for the bridged boron atoms is large and positive.[49] The shieldings for the M–H–B bridging protons are much higher, generally some 15 ppm above the general trend.

The measured ^{1}H, ^{31}P and ^{195}Pt NMR data associated with the phosphine metal environments of **2** and **3** are summarized in Tables 6 and 7 respectively. The ^{31}P spectra in particular give nicely detailed information, but again the dearth of comparative data for phosphine-substituted polymetallaborane species precludes a useful discussion at present, or even a definitive assignment of all the ^{31}P resonances. It is, however, of interest that $^{1}J(^{195}Pt-^{31}P)$ for the PMe_2Ph ligand *trans* to the Pt–H–Os link, at *ca.* 3340 Hz, is much larger than values generally observed[9,36,50] for the same ligand *trans* to a variety of boron hydride moieties, which may indicate that the similarly larger coupling of *ca.* 3826 Hz for $^{31}P(A)$ in **3** is associated with the PPh_3 phosphorus atom P(1) which is *trans* to the Os–Pt link, and that the smaller one of *ca.* 2395 Hz associated with $^{31}P(B)$ is thereby ascribable to the PPh_2 phosphorus atom P(3) which is *trans* to the Pt(7)B(3)B(4) three-centre bond. The general similarity of this and the other NMR behaviour of compound **3** to the incompletely characterized **4** [see above, near equation (4), and Experimental section] suggest strongly that **3** and **4** are isomers, near isomers, or otherwise very closely related, but unfortunately the quite different behaviour of a further incompletely characterized compound **5** (see above and the Experimental section) precludes any definitive comment about the nature of this potentially much more interesting ten-boron open-clustered polymetallaborane species. This and closely related systems will clearly repay continued examination.

Experimental

General.—Reactions were generally carried out under nitrogen or using standard vacuum-line techniques; subsequent manipulations and chromatographic separations were carried out in air. Preparative thin-layer chromatography (TLC) was performed using 200 × 200 × 1 mm layers of silica gel G (Kieselgel G, Merck) which were made on glass formers as required from acetone slurries, followed by drying in air at 80 °C. The compounds $[PtCl_2(PMe_2Ph)_2]$[51] and $[(CO)(PPh_3)_2OsB_5H_9]$ **1**[13] were prepared by published routes. Infrared spectra were recorded on a Pye Unicam SP 2000 spectrophotometer with the samples prepared as pressed KBr discs.

Nuclear Magnetic Resonance Spectroscopy.—Phosphorus-31 NMR spectra at 40 MHz and proton spectra at 100 MHz were obtained at 2.34 T on a JEOL FX-100 instrument in these laboratories, the double-resonance $^{1}H-\{^{11}B\}$ experiments being carried out as described elsewhere.[52–54] The ^{31}P experiments were generally carried out at lower temperatures to maximize the 'thermal decoupling' of ^{10}B and ^{11}B from the phosphine-ligand resonances.[15] Boron-11 NMR spectra at 128 MHz were recorded using a Bruker WH-400 instrument (SERC service, University of Sheffield), and 115.5 MHz ^{11}B and 360 MHz ^{1}H spectra [in $^{1}H-\{^{11}B(\text{selective})\}$ experiments] using a Bruker WH-360 instrument (SERC service, University of Edinburgh). Chemical shifts $\delta(^{1}H)$, $\delta(^{31}P)$ and $\delta(^{11}B)$ are given in ppm, 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 $F_3B{\cdot}OEt_2$ in $CDCl_3$) respectively, Ξ being defined as in ref. 55.

Preparation of $[(CO)(PPh_3)_2\overline{HOs(PMe_2Ph)ClPt}B_5H_7]$ **2**.—To a stirred solution of $[(CO)(PPh_3)_2OsB_5H_9]$ **1** (1.1 g, 1.4 mmol), in dry tetrahydrofuran (20 cm³) at 197 K was added NaH (0.11 g; 60% dispersion in mineral oil, *ca.* 2.8 mmol). After 5 min dry CH_2Cl_2 (50 cm³) was added, followed by $[PtCl_2(PMe_2Ph)_2]$ (0.33 g, 0.60 mmol), the mixture allowed to warm slowly (*ca.* 2 h) to room temperature, and left to stir overnight. The resulting reddish solution was reduced to dryness, dissolved in CH_2Cl_2 (*ca.* 3 cm³), and applied to a preparative TLC plate, which was then developed using CH_2Cl_2–pentane (80:20) as liquid phase. A number of mobile bands resulted. The first (R_f 0.8) appeared as a thin red line in an amount too small to characterize but which was later identified as compound **3** (see below) from its $^{31}P-\{^{1}H\}$ NMR spectrum. A colourless compound also at R_f *ca.* 0.8 was the known[13] five-vertex *nido* compound $[(CO)(PPh_3)_2OsB_4H_8]$. A yellow band (R_f 0.4) was rechromatographed using CH_2Cl_2–pentane (70:30). The resulting yellow band (R_f 0.3) was removed and purified by crystallization from CH_2Cl_2–pentane to yield lemon-yellow hexagonal-prismatic crystals of $[(CO)(PPh_3)_2\overline{HOs(PMe_2Ph)ClPt}B_5H_7]$ **2** [0.55 g, 0.47 mmol, 34%; $\nu_{max}(CO)$ 1965, $\nu_{max}(PtCl)$ 340 cm⁻¹], identified by X-ray crystallography and NMR spectroscopy as described in the Results and Discussion Sections (Tables 1, 2, 6 and 8). An additional minor product (R_f 0.7) was possibly a *nido* five-vertex osmaborane: $\delta(^{11}B)$ [with corresponding *exo*-bound $\delta(^{1}H)$ in square brackets] +13.0[+5.37], −18.2[+1.23], −29.8[+0.39] and −37.1[+2.00]; $\delta(^{1}H)$(bridging)(294 K, $CDCl_3$) −1.34, −2.23, −9.05[$^{2}J(^{31}P-^{1}H)$ 41.9 Hz] and −10.32; $\delta(^{31}P)$(CH_2Cl_2–$CDCl_3$ at 188 K) +22.7(A) +15.1(B) and +9.0(C) ppm; $^{2}J[^{31}P(A)-^{31}P(B)]$ 4.9, $^{2}J[^{31}P(B)-^{31}P(C)]$ 9.8 Hz and $^{2}J[^{31}P(A)-^{31}P(C)]$ *ca.* zero.

Isolation of $[(CO)(PPh_3)(\overline{PPh_2)Os(PPh_3)Pt}B_5H_7Ph]$ **3**.—Under rigorously anhydrous conditions, a sample of compound **2** (0.326 g, 0.28 mmol) was dissolved in tetrahydrofuran (40 cm³), and NaH (0.022 g, 60% dispersion in mineral oil; 0.56 mmol) added, followed by $[PtCl_2(PMe_2Ph)_2]$ (0.15 g, 0.28 mmol). No reaction was noticeable after stirring for 4 h at room temperature. Undried CH_2Cl_2 (40 cm³) was then added, whereupon effervescence occurred and the yellow solution commenced to redden. Stirring was continued for 36 h, the solution was filtered, reduced in volume (rotary evaporator), and subjected to preparative TLC using CH_2Cl_2–pentane (60:40) as eluting medium. Four components were recovered: yellow compound **2** (R_f 0.4; 90 mg; 27% recovery), the dark orange-red compound **3** (R_f 0.6; 10.5 mg, 3% yield; $\nu_{max}(CO)$ 1970 cm⁻¹], a possible isomer or ligand variant of **2** or **3** (compound **4**, R_f 0.3, trace quantities) and a yellow component **5**, possibly a $\{Pt(OsB_5)_2\}$ species [R_f 0.5; *ca.* 2 mg; $\nu_{max}(CO)$ 950 cm⁻¹]. Compound **3** (*ca* 1.5 mg) was also isolated from a sample of **2** (100 mg) that had been heated in xylene solution at 140 °C for 1.5 h while the reaction was monitored by NMR spectroscopy; under these conditions almost complete decomposition of **2** occurred with no significant quantities of other metallaboranes being apparent. Compound **3** was identified as described in the Results and Discussion section (Table 3–5 and 7). Compound **4** had the following NMR properties ($CDCl_3$ solution): $\delta(^{11}B)$ [with corresponding *exo*-bound $\delta(^{1}H)$ in square brackets] *ca.* +90[+9.66],*ca.* +30[+5.55],*ca.* +10[+4.75],*ca.* +10[+0.44] and *ca.* −30[+1.28]; $\delta(^{1}H)$(bridging) −10.64; $\delta(^{31}P)$ +17.5(A), +39.5(B) and +57.8(C) ppm, $^{1}J[^{195}Pt-^{31}P(B)]$ 3826, $^{1}J[^{195}Pt-^{31}P(C)]$ 2395, $^{n}J[^{195}Pt-^{31}P(A)]$ 24 ± 1, $^{n}J[^{31}P(A)-^{31}P(B)]$ 54 ± 1 and $^{n}J[^{31}P(A)-^{31}P(C)]$ 18.5 ± 1.5 Hz. Component **5** had the following NMR properties: $\delta(^{11}B)$ (+21 °C, CD_2Cl_2) [with corresponding *exo*-bound $\delta(^{1}H)$ in square brackets] +73.6[+7.15], +29.0[+5.43], *ca.* +23 [+6.42], *ca.* +23[+4.86], *ca.* +10[+6.58], *ca.* +10[+4.65] *ca.* 0[+5.08], *ca.* −2[+3.83], −38.3[+0.16] and −42.3 [−1.37]; $\delta(^{1}H)$(bridging)(+21 °C, CD_2Cl_2) −1.68, −2.07, −8.48, − 9.07 and −9.64; $\delta(^{31}P)$(−50 °C, $CDCl_3$) +19.1(A), +9.8(B), + 4.2(C) and +1.3(D); $^{n}J(^{195}Pt-^{31}P)$ 140 ± 4, 37 ± 2, 21 ± 1 and 3238 ± 2 Hz for A, B, C and D respectively; $^{n}J[^{31}P(A)-^{31}P(D)]$ 59 ± 1, $^{n}J[^{31}P(B)-^{31}P(C)]$ 11 ± 1 Hz. Infrared $\nu(CO)$ 1950 cm⁻¹ (CH_2Cl_2 solution).

X-Ray Crystallography.—Crystals of compounds **2** and **3** were obtained by diffusion of pentane into CH_2Cl_2 solutions: **2** formed bright yellow prismiatic blocks, the selected crystal being regular with dimensions *ca.* 0.8 × 0.2 × 0.2 mm; **3** formed deep red blocks, the crystal used being regular with dimensions *ca.* 0.3 × 0.2 × 0.5 mm. All crystallographic measurements were made on a Syntex $P2_1$ diffractometer. Accurate cell dimensions and their standard deviations were obtained by least-squares treatment of the setting angles for 15 strong reflections having $35 < 2\theta < 40°$. Intensities of all independent reflections within the range $4 < 2\theta < 45°$ were measured in the ω–2θ scan mode with scan speeds varying between 2 and 29° min⁻¹ for **2** (3 and 29° min⁻¹ for **3**) according to a pre-scan intensity and running from 1° below $K\alpha_1$ to 1° above $K\alpha_2$. Reflections were corrected for Lorentz, polarization and transmission factors (T_{min} 0.1946, T_{max} 0.4596 for **2** and T_{min}

Table 8 Fractional atomic coordinates and e.s.d.s for $[(CO)(PPh_3)_2\overline{HOs(PMe_2Ph)ClPt}B_5H_7]$ **2**

Atom	*x*	*y*	*z*
Os	0.142 19(4)	0.191 21(3)	0.375 66(3)
Pt	0.032 14(4)	0.196 20(4)	0.512 32(3)
P(1)	0.184 0(2)	0.317 0(2)	0.393 6(2)
P(2)	0.053 3(2)	0.189 7(2)	0.257 0(2)
P(3)	0.005 8(2)	0.198 2(2)	0.640 7(2)
Cl	−0.111 6(2)	0.236 1(2)	0.479 2(2)
C	0.244 4(12)	0.177 8(3)	0.320 1(8)
O	0.306 8(8)	0.167 0(6)	0.289 8(7)
B(1)	0.196 7(12)	0.107 4(9)	0.462 3(11)
B(3)	0.169 6(12)	0.190 7(9)	0.501 4(9)
B(4)	0.125 1(13)	0.113 0(11)	0.541 4(11)
B(5)	0.118 0(13)	0.036 8(11)	0.469 5(12)
B(6)	0.133 9(12)	0.075 3(9)	0.377 3(11)
H(1)	0.274 5(106)	0.098 5(79)	0.460 2(88)
H(3)	0.221 9(103)	0.238 7(80)	0.556 0(89)
H(4)	0.121 8(109)	0.102 5(84)	0.587 2(97)
H(5)	0.117 2(103)	−0.017 5(86)	0.507 9(91)
H(6)	0.144 4(103)	0.044 7(80)	0.318 7(91)
H(45)	0.078 1(111)	0.053 5(87)	0.505 0(97)
H(56)	0.053 6(104)	0.058 7(78)	0.405 0(91)
C(31)	−0.071 6(12)	0.267 6(9)	0.666 0(11)
H(311)	−0.130 7(12)	0.261 4(9)	0.630 4(11)
H(312)	−0.044 1(12)	0.320 3(9)	0.656 1(11)
H(313)	−0.086 0(12)	0.262 3(9)	0.726 7(11)
C(32)	−0.042 7(12)	0.116 5(9)	0.673 0(11)
H(321)	−0.001 2(12)	0.071 2(9)	0.660 4(11)
H(322)	−0.105 3(12)	0.109 3(9)	0.643 1(11)
H(323)	−0.051 0(12)	0.119 4(9)	0.735 0(11)
C(111)	0.167 8(7)	0.379 9(6)	0.313 0(6)
C(112)	0.199 9(7)	0.359 4(6)	0.241 7(6)
C(113)	0.194 3(7)	0.406 9(6)	0.178 6(6)
C(114)	0.156 5(7)	0.474 9(6)	0.186 9(6)
C(115)	0.124 4(7)	0.495 4(6)	0.258 2(6)
C(116)	0.130 0(7)	0.447 8(6)	0.321 3(6)
H(112)	0.229 2(7)	0.306 8(6)	0.235 3(6)
H(113)	0.219 1(7)	0.391 0(6)	0.123 4(6)
H(114)	0.152 1(7)	0.511 7(6)	0.138 0(6)
H(115)	0.095 1(7)	0.548 0(6)	0.264 6(6)
H(116)	0.105 2(7)	0.463 7(6)	0.376 5(6)
C(121)	0.302 2(6)	0.328 2(6)	0.409 6(6)
C(122)	0.338 0(6)	0.395 6(6)	0.393 6(6)
C(123)	0.426 4(6)	0.408 1(6)	0.409 7(6)
C(124)	0.478 8(6)	0.353 3(6)	0.441 8(6)
C(125)	0.443 0(6)	0.285 9(6)	0.457 8(6)
C(126)	0.354 7(6)	0.273 4(6)	0.441 7(6)
H(122)	0.297 4(6)	0.438 0(6)	0.368 7(6)
H(123)	0.454 1(6)	0.460 3(6)	0.397 3(6)
H(124)	0.547 2(6)	0.363 0(6)	0.454 3(6)
H(125)	0.483 6(6)	0.243 4(6)	0.482 7(6)
H(126)	0.326 9(6)	0.221 2(5)	0.454 1(6)
C(131)	0.142 3(6)	0.368 3(4)	0.473 6(6)
C(132)	0.197 0(6)	0.406 8(4)	0.525 5(6)
C(133)	0.161 9(6)	0.448 0(4)	0.584 3(6)
C(134)	0.072 0(6)	0.450 8(4)	0.591 2(6)
C(135)	0.017 3(6)	0.412 3(4)	0.539 3(6)
C(136)	0.052 4(6)	0.371 0(4)	0.480 5(6)
H(132)	0.266 6(6)	0.404 6(4)	0.520 2(6)
H(133)	0.204 3(6)	0.477 8(4)	0.624 5(6)
H(134)	0.044 8(6)	0.482 7(4)	0.636 8(6)
H(135)	−0.052 3(6)	0.414 4(4)	0.544 7(6)
H(136)	0.010 1(6)	0.341 2(4)	0.440 3(6)
C(211)	0.117 3(6)	0.174 4(4)	0.171 5(4)
C(212)	0.159 6(6)	0.108 2(4)	0.164 1(4)
C(213)	0.214 5(6)	0.097 0(4)	0.102 9(4)
C(214)	0.227 1(6)	0.152 0(4)	0.049 0(4)
C(215)	0.184 9(6)	0.218 2(4)	0.056 3(4)
C(216)	0.130 0(6)	0.229 4(4)	0.117 6(4)
H(212)	0.149 8(6)	0.065 6(4)	0.205 8(4)
H(213)	0.247 2(6)	0.045 7(4)	0.097 2(4)
H(214)	0.269 6(6)	0.143 2(4)	0.001 5(4)
H(215)	0.194 7(6)	0.260 8(4)	0.014 6(4)
H(216)	0.097 3(6)	0.280 7(4)	0.123 3(4)
C(221)	−0.019 9(6)	0.262 9(4)	0.231 4(6)
C(222)	−0.063 3(6)	0.265 3(4)	0.158 4(6)
C(223)	−0.122 2(6)	0.320 8(4)	0.140 6(6)
C(224)	−0.137 7(6)	0.374 0(4)	0.195 8(6)
C(225)	−0.094 4(6)	0.371 7(4)	0.268 8(6)
C(226)	−0.035 5(6)	0.316 2(4)	0.286 5(6)
H(222)	−0.051 2(6)	0.224 1(4)	0.115 6(6)
H(223)	−0.155 7(6)	0.322 6(4)	0.084 1(6)
H(224)	−0.183 3(6)	0.417 0(4)	0.182 0(6)
H(225)	−0.106 4(6)	0.412 9(4)	0.311 5(6)
H(226)	−0.001 9(6)	0.314 4(4)	0.343 0(6)
C(231)	−0.027 5(6)	0.115 7(4)	0.249 6(6)
C(232)	−0.043 7(6)	0.078 0(4)	0.180 1(6)
C(233)	−0.108 5(6)	0.025 3(4)	0.175 3(6)
C(234)	−0.157 1(6)	0.010 2(4)	0.239 9(6)
C(235)	−0.140 9(6)	0.047 8(4)	0.309 4(6)
C(236)	−0.076 1(6)	0.100 6(4)	0.314 2(6)
H(232)	−0.006 0(6)	0.089 7(4)	0.130 1(6)
H(233)	−0.121 0(6)	−0.003 9(4)	0.121 5(6)
H(234)	−0.207 2(6)	−0.030 7(4)	0.236 1(6)
H(235)	−0.178 5(6)	0.036 1(4)	0.359 4(6)
H(236)	−0.063 5(6)	0.129 7(4)	0.368 0(6)
C(331)	0.098 1(6)	0.216 8(6)	0.704 6(6)
C(332)	0.151 8(6)	0.274 0(6)	0.684 6(6)
C(333)	0.221 8(6)	0.293 9(6)	0.734 3(6)
C(334)	0.238 0(6)	0.256 8(6)	0.804 1(6)
C(335)	0.184 2(6)	0.199 6(6)	0.824 1(6)
C(336)	0.114 3(6)	0.179 6(6)	0.774 3(6)
H(332)	0.139 3(6)	0.302 8(6)	0.630 6(6)
H(333)	0.263 4(6)	0.338 2(6)	0.718 9(6)
H(334)	0.292 2(6)	0.272 2(6)	0.842 6(6)
H(335)	0.196 8(6)	0.170 8(6)	0.877 1(6)
H(336)	0.072 6(6)	0.135 4(6)	0.789 8(6)

0.2509, T_{max} 0.4665 for **3**). For **2** the 5349 reflections having $I > 2\sigma(I)$ were retained for the structure analysis; 1462 below this threshold were rejected as 'unobserved'. Using the same criterion for **3**, 6565 were retained and 573 rejected for the structure analysis.

Non-hydrogen atoms were located from Patterson and difference syntheses. Full-matrix least-squares refinement, with anisotropic thermal parameters for platinum, osmium, phosphorus, (chlorine for **2**), and the carbonyl ligand, and isotropic ones for the remaining non-hydrogen atoms converged at *R* 0.045 for **2**. Organic groups were included in the refinement as rigid groups (C–C 139.5 pm, C–C–C 120° for phenyl) as allowed by the SHELX programs.[56] The least-squares weights were obtained from counting statistics such that $w^{-1} = \sigma^2(F_o)$. All the borane hydrogen atoms were located from a difference map and were included in the refinement with fixed thermal parameters (*U* 70 pm^2. The final *R* was 0.043, *R′* 0.046 for **2**. Similar procedures for **3** gave *R* 0.039, *R′* 0.0392.

Crystal data. **2**, $C_{45}H_{49}B_5ClOOsP_3Pt$, M = 1173.60, monoclinic, space group $P2_1/n$, a = 1.5397(3), b = 1.8489(3), c = 1.7189(3) nm, β = 92.568(13)°, U = 4.888(1) nm^3, Z = 4, D_c = 1.595 g cm^{-3}, $F(000)$ = 2272, Mo-Kα graphite-monochromatized radiation (λ = 71.069 pm), μ(Mo-Kα) = 5.672 mm^{-1}.

Atomic coordinates are in Table 8, selected interatomic distances and angles in Tables 1 and 2.

3, $C_{55}H_{52}B_5OOsP_3Pt$, M = 1261.28, triclinic, space group $P\bar{1}$ (no. 2), a = 1.4491(7), b = 1.7730(4), c = 1.0763(3) nm, α = 82.08(2), β = 102.71(3), γ = 105.42(4)°, U = 2.591(2) nm^3, Z = 2, D_c = 1.617 g cm^{-3}, $F(000)$ = 1228, Mo-Kα, graphite-monochromatized radiation (λ = 71.069 pm), μ(Mo-Kα) = 5.306 mm^{-1}.

Table 9 Fractional atomic coordinates and e.s.d.s for $[(CO)(PPh_3)(PPh_2)Os(PPh_3)PtB_5H_7Ph]$ **3**

Atom	*x*	*y*	*z*
Pt(7)	0.318 23(3)	0.275 79(2)	0.105 23(4)
Os(2)	0.484 26(3)	0.232 69(2)	0.115 50(4)
P(1)	0.185 7(2)	0.307 8(2)	0.145 9(2)
P(2)	0.637 4(2)	0.199 3(2)	0.179 4(2)
P(3)	0.464 5(2)	0.324 5(2)	0.236 0(2)
B(1)	0.363 7(9)	0.127 1(7)	0.000 7(12)
B(3)	0.358 2(9)	0.226 8(7)	−0.041 4(12)
B(4)	0.251 0(9)	0.157 8(7)	−0.008 4(12)
B(5)	0.281 2(12)	0.075 2(8)	0.100 5(13)
B(6)	0.408 6(11)	0.103 8(7)	0.168 4(13)
C	0.541 4(7)	0.305 5(6)	−0.008 4(9)
O	0.577 9(6)	0.346 5(4)	−0.086 1(7)
C(111)	0.206 5(6)	0.387 7(3)	0.251 7(7)
C(112)	0.270 0(6)	0.459 1(3)	0.222 2(7)
C(113)	0.285 6(6)	0.522 2(3)	0.294 9(7)
C(114)	0.237 8(6)	0.514 0(3)	0.397 0(7)
C(115)	0.174 3(6)	0.442 6(3)	0.426 4(7)
C(116)	0.158 7(6)	0.379 5(3)	0.353 8(7)
C(121)	0.104 2(6)	0.219 8(3)	0.213 2(7)
C(122)	0.147 0(6)	0.165 8(3)	0.297 0(7)
C(123)	0.088 5(6)	0.096 1(3)	0.343 8(7)
C(124)	−0.012 7(6)	0.080 4(3)	0.304 8(7)
C(125)	−0.055 5(6)	0.134 4(3)	0.221 0(7)
C(126)	0.003 0(6)	0.204 1(3)	0.175 2(7)
C(131)	0.105 4(6)	0.344 7(4)	0.000 1(6)
C(132)	0.040 5(6)	0.388 5(4)	0.009 3(6)
C(133)	−0.018 7(6)	0.413 5(4)	−0.100 8(6)
C(134)	−0.012 9(6)	0.394 8(4)	−0.220 2(6)
C(135)	0.052 0(6)	0.351 0(4)	−0.229 4(6)
C(136)	0.111 1(6)	0.326 0(4)	−0.119 3(6)
C(211)	0.630 4(6)	0.184 6(3)	0.035 5(6)
C(212)	0.618 2(6)	0.129 5(3)	−0.045 3(6)
C(213)	0.645 8(6)	0.116 2(3)	−0.155 1(6)
C(214)	0.735 7(6)	0.158 1(3)	−0.184 0(6)
C(215)	0.798 0(6)	0.213 2(3)	−0.103 3(6)
C(216)	0.770 3(6)	0.226 5(3)	0.006 5(6)
C(221)	0.742 7(6)	0.275 2(4)	0.259 8(7)
C(222)	0.815 2(6)	0.253 8(4)	0.355 9(7)
C(223)	0.891 7(6)	0.311 5(4)	0.415 0(7)
C(224)	0.895 6(6)	0.390 6(4)	0.378 0(7)
C(225)	0.823 1(6)	0.412 1(4)	0.281 9(7)
C(226)	0.746 6(6)	0.354 4(4)	0.222 8(7)
C(231)	0.645 0(6)	0.109 1(3)	0.286 9(6)
C(232)	0.674 7(6)	0.047 2(3)	0.253 3(6)
C(233)	0.679 6(6)	−0.018 8(3)	0.339 1(6)
C(234)	0.654 7(6)	−0.023 1(3)	0.458 3(6)
C(235)	0.625 0(6)	0.038 7(3)	0.491 9(6)
C(236)	0.620 1(6)	0.104 8(3)	0.406 2(6)
C(311)	0.531 3(6)	0.430 1(3)	0.238 8(7)
C(312)	0.543 0(6)	0.468 7(3)	0.347 8(7)
C(313)	0.596 3(6)	0.546 7(3)	0.353 4(7)
C(314)	0.637 7(6)	0.586 1(3)	0.249 9(7)
C(315)	0.625 9(6)	0.547 4(3)	0.140 8(7)
C(316)	0.572 7(6)	0.469 5(3)	0.135 3(7)
C(321)	0.471 4(6)	0.293 0(3)	0.407 9(4)
C(322)	0.387 2(6)	0.271 4(3)	0.460 2(4)
C(323)	0.392 6(6)	0.244 5(3)	0.589 0(4)
C(324)	0.432 1(6)	0.239 1(3)	0.665 5(4)
C(325)	0.566 3(6)	0.260 7(3)	0.613 3(4)
C(326)	0.561 0(6)	0.287 6(3)	0.484 5(4)
C(41)	0.150 9(4)	0.138 2(4)	−0.113 5(6)
C(42)	0.153 1(4)	0.161 4(4)	−0.242 2(6)
C(43)	0.066 5(4)	0.150 6(4)	−0.332 6(6)
C(44)	−0.022 4(4)	0.116 6(4)	−0.294 3(6)
C(45)	−0.024 6(4)	0.093 4(4)	−0.165 5(6)
C(46)	0.062 0(4)	0.104 2(4)	−0.075 1(6)

Atomic coordinates are in Table 9, selected interatomic distances and angles in Tables 3 and 4.

Additional material available from the Cambridge Crystallographic Data Centre, comprises thermal parameters and remaining interatomic distances and angles.

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