The *nido*–osmaboranes [2,2,2-(CO)-(PPh₃)₂-*nido*-2-OsB₅H₉] and [6,6,6-(CO)(PPh₃)₂-*nido*-6-OsB₉H₁₃]

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The structural characterization of the osmahexaborane 2-carbonyl-2,2-bis(triphenylphosphine)-*nido*-2-osmahexaborane(9), [Os(B₅H₉)(C₁₈H₁₅P)₂(CO)], (I), a metallaborane analogue of B₆H₁₀, confirms the structure proposed from NMR spectroscopy. The structure of the osmadecaborane 6-carbonyl-6,6-bis(triphenylphosphine)-*nido*-6-osmadecaborane(13), [Os(B₉H₁₃)(C₁₈H₁₅P)₂(CO)], (IV), is similarly confirmed. The short basal B—B distance of 1.652 (8) Å in (I), not bridged by an H atom, mirrors that in the parent hexaborane(10) [1.626 (4) Å].

Comment

Several metallahexaboranes, species in which a transition metal moiety has replaced a BH group in hexaborane(10), are known (Kennedy, 1984). So far, however, only the species [(PPh₃)₂(CO)-*nido*-OsB₅H₉], (I) (Bould *et al.*, 1983), and [(PPh₃)₂(CO)-*nido*-IrB₅H₈], (II) (Greenwood *et al.*, 1979), are available in sufficient yields and stability to be useful reagents. These are important systems because the parent hexaborane(10) is not stable at room temperature and is very air sensitive. Although one report of the derivatization of (II) has been reported (Bould, Rath, Fang & Barton, 1996), species (I) is the only metallahexaborane to have been the subject of significant derivative chemistry, including the construction of polymetallaboranes and studies of cluster degradation. Indeed, structures of several derivatives of (I) have been reported (Bould *et al.*, 1991; Barton *et al.*, 1996, 1997), but until recently, crystals of appropriate quality of the parent, (I), were unavailable. Compound (I) was isolated in high yield (85%) from the reaction of Na[B₅H₈] and [(CO)(PPh₃)₃HClOs]. Minor products also isolated from the reaction mixture were [(CO)H(PPh₃)₂-*arachno*-OsB₃H₈] (Bould, Rath & Barton, 1996) and [(CO)(PPh₃)₂-*nido*-OsB₄H₇(BH₂·PPh₃)], (III) (Barton *et al.*, 1997). An additional minor reaction by-product was also formed, namely, [(CO)(PPh₃)₂-*nido*-OsB₉H₁₃], (IV).

We report herein the structure of the important metallahexaborane starting material, (I), and also of the related osmadecaborane [(CO)(PPh₃)₂-*nido*-OsB₉H₁₃], (IV), for comparison purposes.
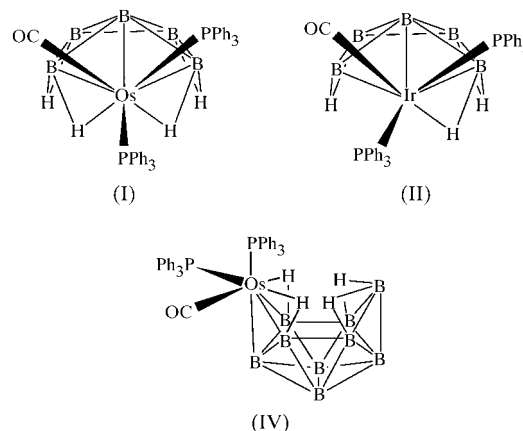
Single-crystal X-ray diffraction analysis confirms the expected pentagonal-based pyramidal structure for (I) (Fig. 1), which had been proposed previously from NMR spectroscopy (Bould *et al.*, 1983). All cage-bound H atoms were located from the difference map and refined freely in reasonable positions, with the exception of the Os—H—B bridging H atoms, although four bridging H atoms are indicated by NMR spectroscopy and required from electron-counting considerations. The bridging H atoms, which were not located from the difference Fourier syntheses, lie approximately *trans* to C37 and P1, as indicated by NMR spectroscopy [²J(³¹P–¹H) (*trans*) 40 Hz for μ-H26; Bould *et al.*, 1983].

The short B4—B5 distance of 1.652 (8) Å in (I) compares closely with that in (III) [1.649 (10) Å] and with the basal 'single' bond in the parent borane, B₆H₁₀ [1.626 (4) Å; Huffman, 1974]. This determination confirms that the B—B bond opposite the Os atom is the unbridged one. The B3—B4 and B5—B6 distances of 1.753 (6) and 1.730 (6) Å, respectively, suggest hydrogen-bridged B—B bonds, whereas the shorter B4—B5, at 1.652 (8) Å, does not. Thus the bridging H
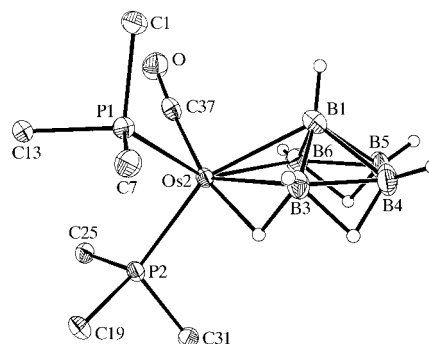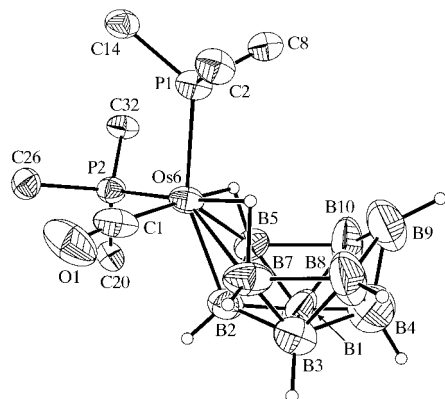

Figure 1
A perspective view of a single molecule of (I), with displacement ellipsoids drawn at the 40% probability level and H atoms shown as small spheres of arbitrary radii. The phenyl groups, with the exception of the *ipso*-C atoms, have been omitted for clarity. The Os2—H—B6 bridging H atom, shown to be present by NMR spectroscopy, was not located from the X-ray data.

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atoms in (I) are symmetrically disposed, in spite of the observation of four separate resonances in the bridging H atom region of the ^{1}H NMR spectrum. The latter is clearly due to the asymmetric disposition of the two PPh$_3$ ligands on Os.

The short B4—B5 distance in (I) implies that the metallaborane species may have some Lewis base character, as has been noted in hexaborane(10) (Solomon & Porter, 1972; Brennan *et al.*, 1973). Some evidence for this has, for example, been adduced in the reaction of (II) with Fe$_2$(CO)$_9$ to yield *closo*-[B$_5$H$_4$PPh$_3${Fe(CO)$_3$}{Ir(CO)PPh$_3$}] *via* an initial [(PPh$_3$)$_2$-(CO)IrB$_5$H$_8${μ-(Fe(CO)$_4$)}] intermediate (Bould, Rath, Fang & Barton, 1996).

The molecular structure of (IV) is shown in Fig. 2. Again, as with (I), two of the four cage-bound bridging H atoms were not located in the difference map, although they are shown by NMR spectroscopy to be present bridging B9—B8 and B9—B10 (see *Experimental*). The hydrogen-bridged Os—B distances in (I) and (IV) are comparable: Os2—B3 2.291 (4) Å and Os2—B6 2.301 (4) Å in (I), and Os6—B5 2.317 (11) Å and Os6—B7 2.300 (12) Å in (IV). This gives support to the assumption that the two bridging H atoms not located in the X-ray structure are indeed present in (I).

The cluster in (IV) is seen to be a conventional *nido*-metalladecaborane cage, with the metal vertex in a 'prow' position on the open face of the ten-vertex 'boat'. The structure of a similar osmadecaborane, [(PMe$_2$Ph)$_3$-*nido*-OsB$_9$H$_{13}$], (V), has been reported previously by Beckett *et al.* (1986). The main variance between the two structures arises from the differing metal ligation sphere. The smaller steric requirement of the PMe$_2$Ph ligand effects a smaller Os—P distance in (V) compared with (IV) [by *ca* 0.035 (3) Å]. The slight difference between the long B5—B10 and B7—B8 distances in (IV) [2.026 (19) and 1.93 (2) Å, respectively], which might be attributed to the asymmetry introduced by the presence of the equatorial carbonyl ligand, is, however, mirrored in (V) [2.083 (11) and 2.016 (10) Å]. It is noteworthy that the orientations of the ligands on Os in (IV) and (I) are similar

and both asymmetrical. Representations of (I), (II) and (IV) are given in the Scheme above to illustrate the orientation of the ligands relative to the boron cages in the three systems.

Experimental

Compound (I) was isolated in high yield (85%) from the reaction of Na[B$_5$H$_8$] and [(CO)(PPh$_3$)$_3$HClOs]. Single crystals of (I) were not grown directly from solutions of the compound; they arose from attempts to grow single crystals of [(PPh$_3$)$_2$(CO)-*nido*-OsB$_4$H$_7$-(BH$_2$·PPh$_3$)], (III). In solution at ambient temperature, (III) loses PPh$_3$ to form an equilibrium mixture from which (I) preferentially crystallizes. Compound (IV), previously unreported, was isolated as a minor product from the preparation of (I). Soluble residues from the preparation of (I) gave, after reduction in volume, a grey precipitate. Preparative thin-layer chromatography (TLC) of the filtrate (silica gel, Aldrich standard TLC grade, with gypsum binder and fluorescent indicator) gave a series of colourless bands, identified as, in order, [(CO)(PPh$_3$)$_2$OsB$_4$H$_8$], (III), [(CO)H(PPh$_3$)$_2$-*arachno*-OsB$_3$H$_8$] and [BH$_3$PPh$_3$] (Bould *et al.*, 1983; Bould, Rath & Barton, 1996; Barton *et al.*, 1997; Nainan & Ryschkewitsch, 1969). Repeated TLC on solutions of the grey precipitate gave an orange band, which was identified as (IV). Orange single crystals were obtained by diffusion of hexane into a CD$_2$Cl$_2$ solution of the compound. NMR data (CD$_2$Cl$_2$, 300 K, Bruker 500 AMX spectrometer, p.p.m.) in the order, assignment $\delta(^{11}$B) [$\delta(^1$H) in square brackets]: B1,3 12.5 [4.42], B2 -28.5 [-0.26], B4 -28.2 [2.04], B5 8.9 [5.27], B7 14.5 [4.90], B(8 or 10) 0.81 [2.69], B(10 or 8) -2.5 [2.56], B9 6.5 [2.53]; additional ^{1}H data, p.p.m.: H(6/5) -10.26 [$^2J(^{31}$P–^{1}H) 35 Hz], H(6/7) -8.80, H(89/910) -4.54 and -4.45; $\delta(^{31}$P), p.p.m.: 8.7 and 14.9.

Compound (I)

Crystal data

[Os(B$_5$H$_9$)(C$_{18}$H$_{15}$P)$_2$(CO)]	$D_x = 1.544$ Mg m^{-3}
$M_r = 805.87$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 8192
$a = 16.0054$ (1) Å	reflections
$b = 13.0200$ (1) Å	$\theta = 2$–33°
$c = 17.2445$ (1) Å	$\mu = 3.80$ mm^{-1}
$\beta = 105.29$ (1)°	$T = 153$ (2) K
$V = 3466.39$ (4) Å^3	Irregular, colourless
$Z = 4$	$0.25 \times 0.20 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	9460 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.041$
Absorption correction: empirical (*SADABS*; Blessing, 1995)	$\theta_{max} = 30°$
$T_{min} = 0.450$, $T_{max} = 0.751$	$h = -22 \rightarrow 22$
31 883 measured reflections	$k = -18 \rightarrow 18$
5075 independent reflections (plus 4866 Friedel-related reflections)	$l = -24 \rightarrow 24$
	Intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0182P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.03$	$\Delta\rho_{max} = 2.20$ e Å^{-3}
9961 reflections	$\Delta\rho_{min} = -1.78$ e Å^{-3}
443 parameters	Absolute structure: Flack (1983)
H atoms treated by a mixture of independent and constrained refinement	Flack parameter = 0.002 (4)

Figure 2
A perspective view of a single molecule of (IV), with displacement ellipsoids drawn at the 40% probability level and H atoms shown as small spheres of arbitrary radii. The phenyl groups, with the exception of the *ipso*-C atoms, have been omitted for clarity. The two H atoms bridging B9—H—B8 and B9—H—B10, shown to be present by NMR spectroscopy, were not located from the X-ray data.

Table 1
Selected geometric parameters (Å, °) for (I).

Os2—C37	1.869 (4)	B1—B6	1.777 (7)
Os2—B3	2.291 (4)	B1—B3	1.788 (7)
Os2—B6	2.301 (4)	B1—B5	1.808 (7)
Os2—B1	2.335 (5)	B1—B4	1.809 (8)
Os2—P2	2.3664 (9)	B3—B4	1.753 (6)
Os2—P1	2.3729 (11)	B4—B5	1.652 (8)
O—C37	1.155 (5)	B5—B6	1.730 (6)
C37—Os2—B3	134.42 (15)	B1—Os2—P2	152.23 (15)
C37—Os2—B6	80.32 (15)	C37—Os2—P1	86.53 (11)
B3—Os2—B6	79.87 (16)	B3—Os2—P1	88.02 (11)
C37—Os2—B1	93.31 (17)	B6—Os2—P1	146.59 (13)
B3—Os2—B1	45.46 (18)	B1—Os2—P1	106.00 (16)
B6—Os2—B1	45.07 (19)	P2—Os2—P1	98.46 (3)
C37—Os2—P2	101.22 (11)	B5—B4—B3	112.0 (3)
B3—Os2—P2	124.35 (12)	B4—B5—B6	111.7 (3)
B6—Os2—P2	114.12 (13)		

Compound (IV)

Crystal data

[Os(B$_9$H$_{13}$)(C$_{18}$H$_{15}$P)$_2$(CO)]	$D_x = 1.526$ Mg m^{-3}
$M_r = 853.14$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 8192
$a = 10.4617$ (1) Å	reflections
$b = 15.6821$ (1) Å	$\theta = 2$–25°
$c = 22.6315$ (3) Å	$\mu = 3.55$ mm^{-1}
$\beta = 91.08$ (1)°	$T = 223$ (2) K
$V = 3712.29$ (7) Å^3	Irregular, orange
$Z = 4$	$0.28 \times 0.20 \times 0.04$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	5001 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.01$
Absorption correction: empirical	$\theta_{max} = 25$°
(SADABS; Blessing, 1995)	$h = -12 \rightarrow 12$
$T_{min} = 0.436$, $T_{max} = 0.871$	$k = -18 \rightarrow 18$
74 813 measured reflections	$l = -26 \rightarrow 26$
6483 independent reflections	Intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 26.7668P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.18$	$(\Delta/\sigma)_{max} = 0.002$
6483 reflections	$\Delta\rho_{max} = 1.26$ e Å^{-3}
491 parameters	$\Delta\rho_{min} = -1.16$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 2
Selected geometric parameters (Å, °) for (IV).

Os6—C1	1.866 (11)	Os6—P2	2.379 (2)
Os6—B2	2.299 (11)	O1—C1	1.159 (12)
Os6—B7	2.300 (12)	B5—B10	2.026 (19)
Os6—B5	2.317 (11)	B7—B8	1.93 (2)
Os6—P1	2.357 (2)		
C1—Os6—B2	97.7 (4)	C1—Os6—P2	90.5 (3)
C1—Os6—B7	81.8 (5)	B2—Os6—P2	100.8 (3)
C1—Os6—P1	94.0 (3)	P1—Os6—P2	101.04 (8)
B2—Os6—P1	155.1 (3)		

For (I), cluster-associated H atoms were located from the difference Fourier syntheses and refined freely, with the exception of the bridging H23 atom, which was located from the Fourier synthesis and for which the positional parameters were treated as riding on Os2. The bridging H26 atom, expected to bridge between Os2 and B6, could not be located. For (IV), cage H atoms were located from the difference Fourier synthesis and, for some, the positions were refined, while for the rest, an appropriate riding model was used. The H atoms bridging B8—B9 and B9—B10 could not be located. One of the phenyl rings (C8—C13) in (IV) is disordered. This was resolved and the disordered atoms were refined with anisotropic displacement-parameter constraints (EADP command in SHELXTL; Sheldrick, 1999). Non-boron-cage H atoms for both compounds were included in idealized positions and refined with appropriate riding models (AFIX command in SHELXTL; Sheldrick, 1999). The highest residual peaks were found close to the Os atoms [0.89 and 0.99 Å for (I) and (IV), respectively].

For both compounds, data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXTL (Sheldrick, 1999); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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