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[(CO)H(PPh3)2-Arachno-OsB3H8]

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[(CO)H(PPh3)2-*arachno*-OsB3H8]

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Abstract

A single-crystal X-ray diffraction study of the species 2-carbonyl-2-hydrido-*trans*-2,2-bis(triphenylphosphine)-2-osma-*arachno*-tetraborane confirms the structure as a tetraborane(10) butterfly with a *trans*-[(CO)H(PPh3)2Os] group replacing a BH$_2$ group at a wing-tip or 2-position. It is compared with the previously reported ruthenaborane analogue (CO)H(PPh3)2-*arachno*-RuB3H8.

Comment

During our investigations of the chemistry of met-allaboranes, we have prepared the osmahexaborane (CO)(PPh3)2OsB5H9, which is available in *ca* 80% yield from the reaction of LiB5H8 and OsHCl(CO)(PPh3)3 (Bould, Greenwood & Kennedy, 1983). We have found that the residues from the preparation show, from ^{11}B NMR, evidence of other metallaborane products and we have attempted to identify some of these. The products include the title compound, (I), an *arachno*-osmatetraborane cluster, and what appear to be a novel *arachno*-osmapentaborane cluster and a novel *nido*-osmadecaborane cluster. Compound (I) is formed in a very low yield (2%) and is more conveniently available in 65% yield from the reaction of TlB3H8 and OsHCl(CO)(PPh3)3 (Bould *et al.,* 1983).

(I)
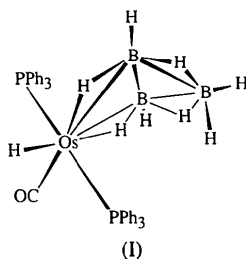
The structure (Fig. 1) is typical of an *arachno* met-allatetraborane with the metal in the 'wing-tip' position of the cluster with a distorted octahedral disposition of the ligands about the metal center (Kennedy, 1984; Alcock, Burns, Claire & Hill, 1992). The Os moiety thus replaces a BH$_2$ group in B4H$_{10}$. This is in contrast to the 1-metallatetraboranes in which the metal moiety replaces a BH$_3$ group in the 1-position (Bould, Greenwood, Kennedy & McDonald, 1985; Bould, Kennedy & McDonald, 1992; Housecroft, Owen, Raithby & Shaykh, 1990). The overall dimensions of the cluster are very similar to those of the structurally characterized ruthenaborane analogue (CO)H(PPh3)2-*arachno*-RuB3H8 (Alcock *et al.,* 1992) (Table 3), with some small differences.
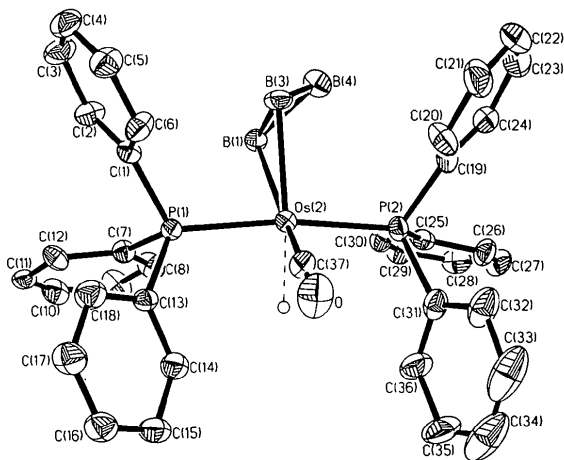
Fig. 1. The molecular structure and atomic labeling scheme for [(CO)H(PPh3)2OsB3H8]. Displacement ellipsoids are shown at the 30% probability level. The metal hydride position was located and refined, and is shown as a sphere of arbitrary size.

The *M*—B(1) and *M*—B(3) distances in the osma-borane are equal whereas the ruthenaborane shows a lengthening of the Ru—B vector *trans* to the metal hydride of 0.045 Å, which has been attributed by Alcock *et al.* (1992) to the *trans* effect of the hydride.

Fig. 2. An illustration of the metallaborane core of the molecule, including the H-atom positions.

The slightly larger e.s.d.'s for the osmaborane could possibly obscure a similar but smaller *trans* effect in the osmaborane. The P(1)—*M*(2)—P(2) angle for the *trans* phosphine ligands is significantly closer to 180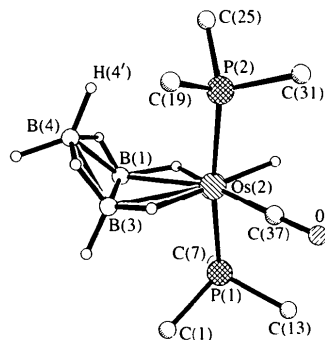° in the osmaborane [172.21 (7)°] than in the ruthenaborane [161.8 (1)°] although, as with the latter compound, the deviations from the ideal octahedral angles are greater for the phosphine [P(2)] in the *cis* position with respect to the *endo*-terminal H atom H(4') (Fig. 2).

Experimental

The reaction between LiB₅H₈ and [OsHCl(CO)(PPh₃)₃] was carried out on a 0.5 mmol scale in tetrahydrofuran (thf) solution essentially according to the literature method (Bould *et al.*, 1983) using the same conditions and similar procedures. Compound (I) was obtained as follows: the thf was removed under vacuum, the solid obtained redissolved in CH₂Cl₂/pentane solution (1:3), filtered through silica gel, the filtrate applied to a preparative thin-layer-chromatography plate and developed using diethyl ether/pentane (1:1) as the mobile phase giving two bands (under UV illumination) at R_f = 0.8 (identified by NMR spectroscopy as Ph₃PBH₃) and R_f = 0.5 [compound (I), 9 mg, 0.011 mmol, 2% yield]. Colourless crystals of (I) were obtained by slow diffusion of pentane into a dichloromethane solution of the compound at 273 K.

Crystal data

[Os(B₃H₈)(H)(CO)-
(C₁₈H₁₅P)₂]
M_r = 784.25
Monoclinic
$P2_1/n$
a = 17.116 (4) Å
b = 9.960 (3) Å
c = 21.416 (5) Å
β = 108.59 (2)°
V = 3460 (2) Å³
Z = 4
D_m = 1.505 Mg m⁻³

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 8.5–11.0°
μ = 3.806 mm⁻¹
T = 298 (2) K
Hexagonal plate
0.4 × 0.2 × 0.1 mm
Colorless

Data collection

Siemens *R*3/*mv* diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan (*SHELXA*;
  Sheldrick, 1993)
  T_{min} = 0.319, T_{max} = 0.756
6347 measured reflections
6129 independent reflections
4231 observed reflections
  [$F > 4\sigma(F)$]

R_{int} = 0.05
θ_{max} = 25.0°
h = 0 → 20
k = 0 → 11
l = −25 → 24
3 standard reflections
  monitored every 100 reflections
  intensity decay: 50% (crystal decay)

Refinement

Refinement on F^2
$R(F)$ = 0.0471
$wR(F^2)$ = 0.1129
S = 0.935
6129 reflections
400 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + 0.0588P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.987 e Å⁻³
$\Delta\rho_{min}$ = −0.924 e Å⁻³

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Os(2)	0.4224 (1)	0.1135 (1)	0.1744 (1)	0.034 (1)
P(1)	0.3630 (1)	0.2057 (2)	0.0684 (1)	0.032 (1)
P(2)	0.4979 (1)	0.0382 (2)	0.2810 (1)	0.039 (1)
O	0.5722 (5)	0.0358 (9)	0.1355 (3)	0.084 (2)
C(1)	0.2900 (5)	0.0976 (8)	0.0093 (4)	0.034 (2)
C(2)	0.2073 (5)	0.1209 (9)	−0.0124 (4)	0.048 (2)
C(3)	0.1546 (6)	0.0315 (11)	−0.0558 (5)	0.067 (3)
C(4)	0.1845 (7)	−0.0807 (10)	−0.0792 (5)	0.064 (3)
C(5)	0.2671 (6)	−0.1025 (9)	−0.0579 (4)	0.057 (2)
C(6)	0.3196 (6)	−0.0183 (9)	−0.0137 (4)	0.049 (2)
C(7)	0.3080 (5)	0.3657 (8)	0.0616 (4)	0.038 (2)
C(8)	0.3035 (6)	0.4372 (9)	0.1157 (4)	0.056 (3)
C(9)	0.2678 (7)	0.5645 (10)	0.1089 (5)	0.063 (3)
C(10)	0.2343 (6)	0.6206 (10)	0.0473 (5)	0.057 (2)
C(11)	0.2385 (5)	0.5504 (9)	−0.0071 (4)	0.044 (2)
C(12)	0.2726 (5)	0.4240 (8)	−0.0016 (4)	0.043 (2)
C(13)	0.4389 (5)	0.2521 (8)	0.0285 (4)	0.034 (2)
C(14)	0.5069 (6)	0.3253 (10)	0.0634 (4)	0.052 (2)
C(15)	0.5660 (6)	0.3694 (10)	0.0355 (5)	0.059 (3)
C(16)	0.5555 (6)	0.3387 (10)	−0.0294 (5)	0.056 (2)
C(17)	0.4889 (6)	0.2691 (10)	−0.0637 (5)	0.062 (3)
C(18)	0.4291 (6)	0.2267 (10)	−0.0376 (4)	0.056 (2)
C(19)	0.4878 (6)	−0.1432 (9)	0.2926 (4)	0.049 (2)
C(20)	0.5037 (7)	−0.2275 (10)	0.2466 (4)	0.062 (3)
C(21)	0.4935 (7)	−0.3642 (11)	0.2491 (5)	0.074 (3)
C(22)	0.4668 (7)	−0.4204 (11)	0.2964 (6)	0.077 (3)
C(23)	0.4510 (7)	−0.3375 (12)	0.3420 (5)	0.072 (3)
C(24)	0.4641 (6)	−0.1993 (11)	0.3421 (4)	0.055 (3)
C(25)	0.4850 (5)	0.1188 (9)	0.3541 (4)	0.044 (2)
C(26)	0.5383 (5)	0.0859 (10)	0.4175 (4)	0.053 (2)
C(27)	0.5324 (6)	0.1509 (11)	0.4716 (4)	0.060 (3)
C(28)	0.4737 (7)	0.2496 (11)	0.4659 (4)	0.064 (3)
C(29)	0.4225 (6)	0.2862 (10)	0.4040 (4)	0.058 (3)
C(30)	0.4272 (5)	0.2212 (9)	0.3487 (4)	0.044 (2)
C(31)	0.6072 (6)	0.0679 (10)	0.2979 (4)	0.050 (2)
C(32)	0.6655 (6)	−0.0332 (14)	0.3018 (5)	0.078 (3)
C(33)	0.7464 (9)	−0.001 (2)	0.3086 (7)	0.119 (7)
C(34)	0.7739 (9)	0.126 (3)	0.3156 (7)	0.128 (8)
C(35)	0.7192 (9)	0.2238 (18)	0.3131 (6)	0.111 (5)
C(36)	0.6362 (6)	0.1987 (14)	0.3040 (5)	0.076 (3)
C(37)	0.5126 (6)	0.0668 (10)	0.1503 (5)	0.061 (3)
B(1)	0.2822 (5)	0.1129 (11)	0.1801 (4)	0.039 (2)
B(3)	0.3085 (6)	−0.0444 (11)	0.1563 (5)	0.046 (3)
B(4)	0.2745 (7)	−0.0289 (12)	0.2286 (5)	0.055 (3)

Table 2. *Selected geometric parameters (Å, °)*

P(1)—C(1)	1.820 (8)	P(2)—C(19)	1.839 (9)
P(1)—C(13)	1.827 (8)	O—C(37)	1.202 (11)
P(1) C(7)	1.834 (8)	Os(2)—C(37)	1.837 (12)
P(2)—C(31)	1.813 (10)	Os(2)—P(1)	2.358 (2)
P(2)—C(25)	1.834 (8)	Os(2)—P(2)	2.359 (2)
O—C(37)—Os(2)	179.1 (8)	P(1)—Os(2)—B(1)	85.4 (2)
B(3)—B(1)—B(4)	62.2 (6)	C(37)—Os(2)—B(1)	60.2 (4)
B(3)—B(1)—Os(2)	68.9 (4)	P(2)—Os(2)—B(1)	101.2 (2)
B(4)—B(1)—Os(2)	106.7 (6)	C(1)—P(1)—C(13)	104.9 (3)
B(1)—B(3)—B(4)	59.8 (5)	C(1)—P(1)—C(7)	103.8 (4)
B(1)—B(3)—Os(2)	69.1 (4)	C(13)—P(1)—C(7)	99.6 (3)
B(4)—B(3)—Os(2)	105.4 (6)	C(1)—P(1)—Os(2)	115.4 (3)
C(37)—Os(2)—B(3)	119.6 (4)	C(13)—P(1)—Os(2)	113.3 (3)
P(1)—Os(2)—B(3)	91.2 (2)	C(7)—P(1)—Os(2)	117.8 (2)
P(2)—Os(2)—B(3)	96.5 (2)	C(31)—P(2)—C(25)	98.9 (4)
C(37)—Os(2)—P(1)	88.3 (3)	C(31)—P(2)—C(19)	105.6 (4)
C(37)—Os(2)—P(2)	86.6 (3)	C(25)—P(2)—C(19)	105.8 (4)

C(37)—Os(2)—B(3)	119.6 (4)	C(31)—P(2)—Os(2)	110.7 (3)
P(1)—Os(2)—B(3)	91.2 (2)	C(25)—P(2)—Os(2)	120.6 (3)
P(2)—Os(2)—B(3)	96.5 (2)	C(19)—P(2)—Os(2)	113.4 (3)

Table 3. *A comparison of selected distances (Å) and angles (°) for [(CO)H(PPh$_3$)$_2$OsB$_3$H$_8$] and [(CO)H-(PPh$_3$)$_2$RuB$_3$H$_8$]*

	M = Os	M = Ru
B(1)—B(3)	1.75 (2)	1.738 (9)
B(1)—B(4)	1.783 (14)	1.802 (10)
B(3)—B(4)	1.827 (13)	1.808 (9)
M(2)—B(1)	2.441 (8)	2.439 (6)
M(2)—B(3)	2.437 (10)	2.484 (6)
P(1)—M(2)—P(2)	172.21 (7)	161.8 (1)
B(1)—B(4)—B(3)	58.0 (5)	57.6 (3)
B(1)—M(2)—B(3)	42.1 (3)	41.3 (2)
M(2)—B(1)—B(3)/B(1)—B(3)—B(4)	123.5	124.4

The structure was solved by the Patterson method. Full-matrix least-squares refinement was carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. All H atoms connected to B atoms were located from the difference Fourier synthesis and were included in the final refinement. The positional parameters of the hydride H(2) were refined. The phenyl H atoms were calculated using a riding model (*AFIX*43 in *SHELXL*93; Sheldrick, 1993*b*). All H atoms were assigned fixed isotropic displacement parameters of 0.08 Å^2. Attempts were made to resolve the disorder resulting in larger displacement ellipsoids for C(33)–C(36), but the disorder models could not be refined successfully.

Data reduction and structure solution were carried out using the *SHELXTL-Plus* (VMS) software package (Sheldrick, 1991). Least-squares refinement was achieved by using *SHELXL*93.

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trans(S)-(*S*-Methyl-D-penicillaminato)(D-penicillaminesulfinato)cobalt(III) Monohydrate

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Abstract

The title complex {[3-methylthio-D-valinato(1−)]-[3-sulfino-D-valinato(2−)]cobalt(III) monohydrate, [Co(C$_5$H$_9$NO$_4$S)(C$_6$H$_{12}$NO$_2$S)].H$_2$O}, containing thioether and sulfinato moieties, has two different types of donor S atoms situated in *trans* positions to each other. The Co atom is octahedrally surrounded by the N, O and S atoms of each tridentate ligand. The complex molecule has been resolved spontaneously by crystallization. The absolute configuration of the coordinated S atom in the thioether ligand is *R*(S). The lengthening of the Co—S distances [2.376 (3) and 2.366 (3) Å] for the thioether ligand depends on the strong *trans* influence of the sulfinato group.

Comment

In the course of our investigations on the stereochemical and spectrochemical properties of Co^{III} complexes with sulfur-containing ligands, we have recently prepared the title complex, (I). It is difficult to prepare stably the *trans*(S) isomer of a Co^{III} complex with two thiolate and/or sulfinate groups because of the *trans* influence of these donor S atoms. Moreover, reports on the investigation of Co^{III} complexes containing two different types of donor S atoms are scarce. In order to elucidate the geometry adopted by (I), we have determined its structure crystallographically.

(I)