Bis[1,2-bis(diethylphosphino)ethane](η^2-dihydrogen)hydridoosmium(II) Tetraphenylborate

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Abstract. $[OsH(C_{10}H_{24}P_2)_2(H_2)]C_{24}H_{20}B$, $M_r = 925 \cdot 0$, monoclinic, $P2_1/c$, $a = 16 \cdot 343$ (3), $b = 13 \cdot 804$ (2), $c = 21 \cdot 704$ (5) Å, $\beta = 111 \cdot 68$ (2)°, $V = 4550$ Å³, $D_x = 1 \cdot 350$ g cm⁻³, $Z = 4$, $\lambda(Mo\,K\alpha) = 0 \cdot 71069$ Å, $\mu = 29 \cdot 7$ cm⁻¹, $F(000) = 1904$, $T = 298$ K, $R(wR) = 0 \cdot 0457$ (0·0514) for 4708 reflections with $I \geq 3\sigma(I)$. The structure of the cation is disordered with the two bis(diethylphosphino)ethane ligands existing in essentially a 3:1 ratio of conformations involving disorder of both the P and the ethyl C atoms with the exception of one PEt_2 group. Bond lengths to the major axial P positions are 2·357 (3) and 2·338 (4) Å with a P—Os—P angle of 169·6 (2)° while the Os—P distances and P—Os—P angle for the major equatorial positions are 2·328 (3) and 2·338 (6) Å and 164·1 (2)° giving the Os a flattened pentagonal bipyramidal geometry (pseudo-octahedral if its η^2-H_2 ligand is considered as one vertex).

Introduction. There is much current interest in the range of H—H distances possible for the novel η^2-dihydrogen ligand (Kubas, 1988; Hamilton & Crabtree, 1988; Bautista, Earl, Maltby, Morris, Schweitzer & Sella, 1988). The distances determined by neutron diffraction are 0·82 (1) Å for $[W(CO)_3(H_2)(P^iPr_3)_2]$ (Kubas, Unkefer, Swanson & Fukushima, 1986) and 0·816 (16) Å for $[Fe(H)(H_2)(PPh_2CH_2-CH_2PPh_2)_2]BPh_4$ (Ricci, Koetzle, Bautista, Hofstede, Morris & Sawyer, 1989). If the dppe ligands in the latter complex are replaced by depe ligands (depe $= PEt_2CH_2CH_2PEt_2$), then the H—H bond is thought to lengthen due to enhanced $d\pi(Fe) \rightarrow \sigma^*(H_2)$ back-bonding. Similarly if Fe is replaced by Os, the H—H bond is also thought to lengthen because of strengthened $\sigma(H_2) \rightarrow d^2sp^3(Os)$ bonding (Bautista, Earl, Morris & Sella, 1987). The H—H distance in *trans*-$[Os(H)(depe)_2(H_2)]BPh_4$ has been estimated by an NMR method to fall in the unprecedented range of H—H distances of between 1·12 to 1·40 Å (Bautista *et al.*, 1988). We needed an X-ray structure of the title complex before proceeding to a neutron diffraction study which would allow the accurate determination of the H—H distance. As described in this paper, disorder

of the ligands prevented further progress toward this goal.

Experimental. Large white block-shaped crystals were cut, shaped to size and sealed in 0·2–0·3 mm Lindemann capillaries in a glove bag under dry argon. Unit-cell dimensions were obtained by least-squares fit of the diffracting positions of 25 reflections ($12 \cdot 7 < \theta < 15 \cdot 2$°) on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. Intensity-data collection [rectangular block, *ca* 0·25 × 0·3 × 0·35 mm; ω–2θ scans over ω-scan ranges $(0 \cdot 70 + 0 \cdot 35 \tan\theta)$°; octants h, k, $\pm l$ with $2\theta \leq 50$°, $h\ 0 \rightarrow 19$, $k\ 0 \rightarrow 16$, $l\ -23 \rightarrow 23$; three standard reflections collected every 7000s of exposure time; scan rates selected to give $I/\sigma(I) \geq 25$ within a max. scan time of 75 s and backgrounds by 25% extension on either side of peak measured for half the time taken to collect the peak] gave 8788 reflections. Lorentz, polarization and corrections for slow crystal decay [24% loss in intensity of standards; max. rescale factor (on F_{obs}) = 1·323] applied to all data collected. Owing to crystal decay and disorder in the Os cation, no absorption corrections were performed. Exclusion of 1183 systematically absent or zero F_{obs} data and averaging 261 symmetry-equivalent data ($R_{merge} = 0 \cdot 035$) gave a final data set of 7062 reflections.

Structure solution: Patterson for Os, least-squares and Fourier calculations for remaining atoms. Initially an ordered model for the depe ligands was applied. However, residual peaks in F and ΔF maps as well as bond-length and temperature-factor differences for the P and ethyl C atoms indicated disorder. Several cycles of refinement of population parameters and alternative partial-atom peaks indicated that the ethane C atoms, the $P(2)Et_2$ moiety and the ethyl groups bonded to $P(3)$ were ordered while the atoms $P(1)$, $P(3)$ and $P(4)$ and the ethyl groups on $P(1)$ and $P(4)$ could be resolved into two sites essentially in the ratio 3:1. Some of the resulting C sites were common to both orientations and were refined with full occupancy parameters. Other occupancy parameters were tied to the population parameters of the P positions to which they were

Table 1. *Final atomic positional* ($\times 10^4$, *for* Os $\times 10^5$) *and isotropic thermal parameters* ($\times 10^3$)

	x	y	z	$U/U_{eq}(\text{Å}^2)$
Os	23564 (3)	27662 (2)	61228 (2)	46·3 (1)
P1	2680 (4)	4404 (2)	6004 (2)	54 (2)
P1b	2066 (13)	4344 (11)	5763 (8)	70 (5)*
P2	2316 (2)	3339 (2)	7120 (1)	48·9 (9)
P3	2817 (4)	2216 (3)	5285 (2)	39·5 (14)
P3b	2502 (12)	2119 (12)	5191 (8)	41 (5)*
P4	2307 (6)	1119 (3)	6356 (3)	53 (2)
P4b	1879 (12)	1199 (11)	6172 (8)	51 (4)*
C1	2181 (11)	5131 (7)	6490 (6)	90 (6)
C2	2452 (8)	4662 (7)	7195 (5)	67 (4)
C3	2936 (8)	871 (7)	5358 (5)	67 (4)
C4	2265 (9)	426 (7)	5628 (6)	77 (5)
C1a	3977 (11)	4674 (12)	6396 (8)	88 (5)*
C1b	4191 (13)	5707 (15)	6372 (10)	124 (7)*
C1c	2345 (12)	5032 (12)	5217 (8)	93 (5)*
C1de	1294 (11)	4940 (11)	4866 (8)	120 (5)*
C1f	737 (38)	4644 (40)	4903 (26)	89 (16)*
C1g	2978 (34)	5072 (34)	5523 (24)	68 (13)*
C1h	3715 (30)	5002 (31)	6006 (23)	59 (11)*
C2a	3187 (10)	2961 (8)	7929 (5)	86 (5)
C2b	4130 (8)	2995 (9)	7950 (6)	89 (5)
C2c	1378 (9)	3119 (10)	7361 (7)	90 (6)
C2d	503 (10)	3391 (12)	6860 (9)	124 (8)
C3a	3837 (7)	2672 (8)	5276 (5)	69 (4)
C3b	4227 (8)	2099 (9)	4828 (6)	89 (6)
C3c	2077 (8)	2374 (9)	4401 (5)	73 (4)
C3d	1171 (8)	1794 (12)	4195 (7)	106 (6)
C4af	3292 (8)	634 (9)	7091 (6)	89 (3)*
C4b	3356 (10)	−401 (11)	7218 (8)	90 (5)*
C4c	1374 (11)	575 (13)	6527 (9)	101 (6)*
C4dg	543 (12)	797 (14)	5911 (9)	148 (6)*
C4e	2457 (28)	486 (31)	6977 (20)	61 (12)*
C4h	506 (38)	−98 (41)	6088 (28)	98 (19)*
B1	7403 (8)	2656 (8)	1177 (6)	57 (4)
C111	6591 (6)	3296 (7)	1248 (5)	54 (3)
C112	6315 (7)	4200 (7)	936 (5)	63 (4)
C113	5688 (8)	4769 (7)	1045 (6)	73 (5)
C114	5323 (7)	4461 (8)	1491 (7)	80 (5)
C115	5573 (7)	3586 (8)	1820 (5)	72 (5)
C116	6187 (7)	3018 (8)	1686 (5)	68 (4)
C121	8258 (7)	3053 (7)	1802 (5)	60 (4)
C122	8473 (7)	2677 (8)	2433 (5)	71 (4)
C123	9138 (8)	3047 (10)	2983 (7)	86 (5)
C124	9635 (9)	3773 (12)	2905 (7)	101 (6)
C125	9473 (8)	4178 (9)	2288 (7)	84 (6)
C126	8785 (7)	3811 (8)	1749 (6)	72 (5)
C131	7489 (7)	2789 (6)	448 (5)	54 (4)
C132	8312 (8)	2644 (7)	384 (6)	66 (4)
C133	8350 (11)	2650 (7)	−268 (8)	89 (7)
C134	7621 (11)	2769 (8)	−821 (7)	79 (5)
C135	6835 (10)	2870 (8)	−763 (6)	77 (5)
C136	6787 (8)	2888 (7)	−135 (5)	66 (4)
C141	7223 (7)	1499 (7)	1215 (4)	53 (4)
C142	7890 (8)	825 (7)	1495 (5)	67 (4)
C143	7680 (10)	−190 (8)	1466 (5)	83 (6)
C144	6837 (11)	−525 (9)	1163 (6)	81 (6)
C145	6198 (9)	118 (9)	875 (6)	73 (5)
C146	6375 (7)	1109 (7)	903 (5)	63 (4)

*Atoms refined isotropically. Anisotropically refined atoms are given in terms of the equivalent isotropic U_{eq}, where $U_{eq} = \frac{1}{3}$ trace U. Population parameters for the major (x) and minor ($1-x$) P and ethyl C atom positions were: P1 0·78 (1), P3 0·75 (1) and P4 0·077 (2) (*cf.* *Experimental*).

bonded.* Blocked least-squares refinement [two blocks; $\sum w\Delta F^2$ minimized; Os, major P positions, ordered C atoms in the cation and all non-H atoms in the anion with anisotropic thermal parameters; phenyl H atoms in calculated positions with common $U_{iso} = 0·096$ (8) Å²; $N_{variables} = 454$] converged (max. $\Delta/\sigma = 0·15$) to final agreement indices $R(wR) =$

* In the resulting ethyl group, atoms C(na)–C(nd) are common to one orientation; atoms C(ne)–C(nh) to the alternative orientation. Sites common to both orientations are given corresponding two-letter designations – C(1de), C(4af) and C(4dg).

Table 2. *Selected bond lengths* (Å), *bond angles* (°) *and contact distances* (Å)

Os–P1	2·357 (3)	P1–C1	1·849 (16)	P3b–C3	1·85 (2)
–P1b	2·303 (15)	–C1a	2·006 (17)	–C3a	2·25 (2)
–P2	2·328 (3)	–C1c	1·812 (18)	–C3c	1·63 (2)
–P3	2·338 (6)	–C1g	1·60 (6)	P4–C4	1·827 (14)
–P3b	2·303 (20)	–C1h	1·88 (5)	–C4af	1·920 (12)
–P4	2·338 (4)	P1b–C1	1·87 (2)	–C4c	1·86 (2)
–P4b	2·315 (16)	–C1c	1·71 (3)	–C4e	1·55 (4)
P1···P1b	0·95 (2)	–C1de	2·06 (2)	P4b–C4	1·87 (2)
P3···P3b	0·50 (2)	–C1f	2·32 (5)	–C4c	1·58 (3)
P4···P4b	0·68 (2)	–C1g	2·02 (6)	–C4dg	2·12 (3)
		P2–C2	1·841 (10)	–C4e	1·92 (4)
		–C2a	1·879 (10)	C1–C2	1·57 (2)
		–C2c	1·819 (17)	C3–C4	1·55 (2)
		P3–C3	1·867 (10)		
		–C3a	1·789 (15)		
		–C3c	1·863 (10)		
P1–Os–P2	82·0 (1)	P1b–Os–P2	85·5 (5)	P1–Os–P1b	23·5 (5)
–P3	94·4 (2)	–P3b	98·3 (6)	P3–Os–P3b	12·3 (5)
–P4	169·6 (2)	–P4b	150·2 (6)	P4–Os–P4b	16·7 (5)
P2–Os–P3	164·1 (2)	P2–Os–P3b	174·9 (4)		
–P4	96·5 (2)	–P4b	98·6 (5)		
P3–Os–P4	84·2 (2)	P3b–Os–P4b	79·8 (7)		

0·0457 (0·0514) for 4708 reflections with $I \geq 3\sigma(I)$. Weights given by $[\sigma^2(F) + 0·00422F^2]^{-1}$ and the most significant feature in a final ΔF map was a peak of 1·0 e Å^{-3} close (1 Å) to Os; the highest peak in the vicinity of the disordered Et groups was of height 0·6 e Å^{-3} near C(1de).* Programs: Enraf–Nonius *SDP* package (Frenz, 1981) and *SHELX76* (Sheldrick, 1976) on PDP 11/23 and Gould 9705 computers. Scattering factors from *International Tables for X-ray Crystallography* (1974) were stored in the programs. Selected atomic positional parameters and bond lengths and bond angles are given in Tables 1 and 2.†

Discussion. A view of the molecule showing the disordered ethyl and P positions is given in Fig. 1. To our knowledge no other osmium structures have been determined containing the bis(diethylphosphino)ethane ligand or any phosphines containing ethyl groups, most structures containing the bulky triphenylphosphine or tricyclohexylphosphine ligands.

In the present structure the Os–P distances to the major P positions are 2·357 (3) and 2·338 (4) Å along one axis, P(1)–Os–P(4), and 2·328 (3) and 2·338 (6) Å along an essentially orthogonal axis, P(2)–Os–P(3), with *trans* P–Os–P angles of 169·6 (2) and 164·1 (2)° respectively. For comparison, the Os–P distances in the seven-coordinate pentagonal bipyramidal $[OsH_4(PMe_2Ph)_3]$ structure (which has been determined by both X-ray and neutron experiments) are 2·305 (3) and 2·291 (3) Å (axial) and

* See previous footnote.

† Lists of H-atom coordinates, anisotropic thermal parameters, bond lengths and bond angles and final structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51830 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
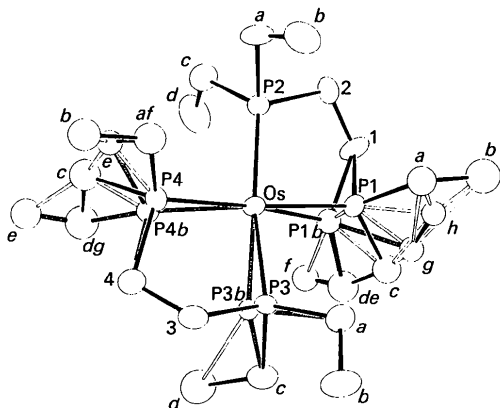
Fig. 1. *ORTEP* (Johnson, 1965) view of the cation showing the disordered arrangements of the bis(diethylphosphino)ethane ligands. Anisotropic thermal ellipsoids have been drawn at the 50% probability level. See footnotes for origin of atom designations.

2·334 (3) Å (equatorial, X-ray data) with an axial P—Os—P angle of 165·2 (1)° (Hart, Bau & Koetzle, 1977) while in the pentagonal bipyramidal trihydrides [Re(dppe)$_2$H$_3$] and [Re(dppe)H$_3$(PPh$_3$)$_2$] the axial P—Re—P bond angles are smaller with values of 167·4 (5) and 159·1° respectively [the equatorial P—Re—P angle in the bis(diphenylphosphino)ethane structure is 151·5 (5)°; Albano & Bellon, 1972]. Thus, despite the smaller POsP bond angle the shorter Os—P distances in the present compound suggest that P(2) and P(3) are the axial atoms in a pentagonal bipyramid with P(1) and P(4) and the *trans*-related hydride and dihydrogen (with a long H—H bond from NMR data) in the equatorial plane. The disorder, however, prevented any location of the H atoms so that the above interpretation of the structure is still somewhat in doubt.

The tetraphenylborate ion is a slightly 'stretched' tetrahedron with two Ph—B—Ph angles of 102·3 (8) and 103·8 (8)° and four angles averaging 112·8°; the average B—C distance is 1·643 (8) Å.

References

ALBANO, V. G. & BELLON, P. L. (1972). *J. Organomet. Chem.* **37**, 151–157.
BAUTISTA, M. T., EARL, K. A., MALTBY, P. A., MORRIS, R. H., SCHWEITZER, C. T. & SELLA, A. (1988). *J. Am. Chem. Soc.* **110**, 7031–7036.
BAUTISTA, M. T., EARL, K. A., MORRIS, R. H. & SELLA, A. (1987). *J. Am. Chem. Soc.* **109**, 3780–3782.
FRENZ, B. A. (1981). *Enraf–Nonius Structure Determination Package.* College Station, Texas, USA.
HAMILTON, D. G. & CRABTREE, R. H. (1988). *J. Am. Chem. Soc.* **110**, 4126–4133.
HART, D. W., BAU, R. & KOETZLE, T. F. (1977). *J. Am. Chem. Soc.* **99**, 7557–7564.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
KUBAS, G. J. (1988). *Acc. Chem. Res.* **21**, 120–128.
KUBAS, G. J., UNKEFER, C. J., SWANSON, B. I. & FUKUSHIMA, E. (1986). *J. Am. Chem. Soc.* **108**, 7000–7009.
RICCI, J. S., KOETZLE, T. F., BAUTISTA, M. T., HOFSTEDE, T., MORRIS, R. H. & SAWYER, J. F. (1989). In preparation.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Amminetris(η-methylcyclopentadienyl)uranium(III)

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Abstract. [U(C$_6$H$_7$)$_3$(NH$_3$)], $M_r = 492·43$, monoclinic, *Im*, $a = 12·129$ (3), $b = 24·197$ (5), $c = 8·725$ (3) Å, $\beta = 92·85°$, $V = 2557·5$ Å^3, $Z = 6$, $D_x = 1·92$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 90·2$ cm^{-1}, $F(000) = 1386$, $T = 296$ K, $R = 0·037$ [4247 data, $F^2 > 3\sigma(F^2)$]. There are two independent molecules, one of which is across the mirror plane. The U atom is bonded to three cyclopentadienyl rings and to an ammonia molecule, with $\langle$U—C$\rangle$, $\langle$U—ring$\rangle$ and $\langle$U—N$\rangle$ distances of 2·81 (5), 2·55 (3) and 2·61 (3) Å, respectively.