

## Structure of Dichlorotris(triphenylphosphine)osmium(II), $[\text{OsCl}_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_3]$

BY AKHIL R. CHAKRAVARTY, F. ALBERT COTTON\* AND DEREK A. TOCHER

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, USA

(Received 9 October 1984; accepted 1 January 1985)

**Abstract.**  $M_r = 1047.99$ , monoclinic,  $P2_1/n$ ,  $a = 12.890$  (8),  $b = 16.631$  (11),  $c = 20.879$  (12) Å,  $\beta = 92.93$  (6)°,  $V = 4470$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.558$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7093$  Å,  $\mu = 31.201$  cm<sup>-1</sup>,  $F(000) = 2096$ ,  $T = 296$  K,  $R = 0.035$  for 4589 ( $I > 3\sigma$ ) reflections. The structure consists of discrete molecules. The geometry about the osmium atom is that of a distorted square pyramid, which consists of *trans* Cl atoms and *trans* P atoms on the base and an apical P atom. The structure and bond lengths and angles compare well with those of the ruthenium analog.

**Introduction.** In the course of our investigations into the synthesis of diosmium compounds containing metal-to-metal bonds (Chakravarty, Cotton & Tocher, 1984, and references therein) we have examined a number of potential monomeric starting materials. One such candidate was the coordinatively unsaturated monomer  $\text{OsCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$ . As a first step in our investigations we sought to determine accurately the geometry about the metal atom in the solid state. The square-pyramidal geometry about the metal atom had previously been inferred from variable-temperature nuclear magnetic resonance experiments (Hoffman & Caulton, 1975) and by analogy with the ruthenium complex,  $\text{RuCl}_2[\text{P}(\text{C}_6\text{H}_5)_3]_3$ , whose structure was reported many years ago (La Placa & Ibers, 1965). The results of that structure determination are now reported here.

**Experimental.** Complex prepared by literature method (Hoffman & Caulton, 1975) and recrystallized from methanol in inert atmosphere. Well formed crystal,  $0.40 \times 0.30 \times 0.30$  mm, Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator. Automatic search routine located and centered 25 intense reflections in range  $15 < 2\theta < 32^\circ$ , from which unit-cell dimensions were derived; systematic absences uniquely defined space group as  $P2_1/n$ ; 7823 unique reflections,  $5 < 2\theta < 50^\circ$ , 4589 ( $I > 3\sigma$ ) collected,  $0 < h < 15$ ,  $0 < k < 19$ ,  $-24 < l < 24$ ; three intensity standards checked every hour of exposure time, 24% decay during data collection; empirical absorption correction,

$\psi$  scan for each of nine reflections near  $\chi = 90^\circ$  measured, each reflection measured at  $10^\circ$  intervals from  $\psi = 0$  to  $\psi = 360^\circ$ , normalized transmission factors 0.98 to 0.74; structure solved by conventional heavy-atom methods (Bino, Cotton & Fanwick, 1979). All nonhydrogen atoms refined with anisotropic thermal parameters;  $R = 0.035$ ,  $wR = 0.046$ ,  $w = 1/\sigma^2(|F_o|)$ , scale factor = 1.238;  $\Delta_{\text{max}}/\sigma = 0.04$ ,  $\Delta\rho$  excursion in final difference Fourier map  $0.691 \text{ e \AA}^{-3}$ ; atomic scattering factors and  $f'$ ,  $f''$  values from *International Tables for X-ray Crystallography* (1974). All computations were carried out on the departmental VAX-11/780 with Enraf–Nonius VAX SDP software (Enraf–Nonius, 1979).

**Discussion.** The positional parameters and equivalent isotropic thermal parameters are given in Table 1. Bond distances and angles are given in Table 2.† An ORTEP drawing (Johnson, 1965) of the molecule is presented in Fig. 1, together with the numbering scheme used.

The structure consists of discrete mononuclear molecules (shortest Os–Os distance  $> 10$  Å). The osmium(II) ion is found near the center of gravity of a distorted square pyramid composed of *trans* Cl atoms and *trans* P atoms on the base and an apical P atom [P(3)]. The basal Os–P distances, 2.410 (2) and 2.366 (2) Å, are significantly longer than the apical Os–P distance of 2.235 (2) Å. These distances are essentially indistinguishable from those found for the ruthenium analog, *viz* 2.412 (6), 2.374 (6) and 2.230 (8) Å, respectively (La Placa & Ibers, 1965). Similarly, the *M*–Cl distances are comparable, 2.383 (2) and 2.399 (2) Å for the Os compound, compared to 2.387 (7) and 2.388 (7) Å for the Ru compound. The P–C bond distances fall in the range 1.817 (8) to 1.849 (8) Å, with a mean of 1.836 [8] Å.

The angles about the Os atom are consistent with the interpretation of the structure as a square pyramid.

† Lists of structure factors, anisotropic thermal parameters and complete tables of bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39995 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

\* To whom all correspondence should be addressed.

Examination of the *ORTEP* drawing, Fig. 1, clearly indicates that it is the phenyl rings, C(21)–C(26) and C(41)–C(46), that block the sixth coordination site to any ligation. It has been shown (Hoffman & Caulton, 1975) that the energy barrier for intramolecular phosphine exchange is 48.07 (24) kJ mol<sup>-1</sup> and this structure is consistent with the trigonal-bipyramidal intermediate having apical chlorine atoms and three equatorial phosphines, as would have been expected.

We are grateful to the National Science Foundation for support.

Table 1. Positional parameters and their *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )*
Os(1)	0.32584 (2)	0.24453 (2)	0.90178 (1)	1.969 (5)
Cl(1)	0.2808 (2)	0.3553 (1)	0.8335 (1)	4.16 (5)
Cl(2)	0.3833 (2)	0.1694 (1)	-0.0048 (1)	3.29 (5)
P(1)	0.5094 (2)	0.2518 (1)	0.88554 (9)	2.40 (4)
P(2)	0.6670 (2)	0.2295 (1)	0.4499 (1)	2.27 (4)
P(3)	0.2802 (2)	0.1460 (1)	0.8331 (1)	2.17 (4)
C(1)	0.5614 (6)	0.3156 (5)	0.8223 (4)	2.9 (2)
C(2)	0.6431 (8)	0.2923 (6)	0.7847 (4)	4.7 (2)
C(3)	0.6778 (9)	0.3462 (7)	0.7375 (5)	6.3 (3)
C(4)	0.6307 (9)	0.4219 (7)	0.7295 (5)	6.2 (3)
C(5)	0.5530 (8)	0.4444 (6)	0.7695 (5)	5.7 (3)
C(6)	0.5180 (7)	0.3915 (5)	0.8158 (5)	4.0 (2)
C(11)	0.5797 (6)	0.1571 (5)	0.8799 (4)	2.7 (2)
C(12)	0.6216 (6)	0.1206 (5)	0.9366 (4)	3.3 (2)
C(13)	0.6629 (7)	0.0432 (5)	0.9346 (5)	4.2 (2)
C(14)	0.6662 (7)	0.0040 (6)	0.8755 (5)	4.3 (2)
C(15)	0.6255 (7)	0.0389 (6)	0.8187 (5)	4.3 (2)
C(16)	0.5814 (6)	0.1164 (5)	0.8204 (4)	3.3 (2)
C(21)	0.5752 (6)	0.3014 (5)	0.9547 (4)	2.7 (2)
C(22)	0.5169 (7)	0.3386 (6)	0.0011 (5)	4.5 (2)
C(23)	0.5691 (8)	0.3761 (6)	0.0529 (5)	4.9 (2)
C(24)	0.6756 (8)	0.3757 (6)	0.0611 (5)	5.0 (3)
C(25)	0.7339 (7)	0.3398 (6)	0.0148 (5)	4.4 (2)
C(26)	0.6837 (7)	0.3031 (5)	0.9614 (5)	3.8 (2)
C(31)	0.5675 (6)	0.1631 (4)	0.4128 (4)	2.6 (2)
C(32)	0.5162 (6)	0.1073 (5)	0.4512 (4)	3.1 (2)
C(33)	0.4290 (7)	0.0646 (5)	0.4237 (5)	3.6 (2)
C(34)	0.3977 (7)	0.0762 (5)	0.3602 (5)	4.1 (2)
C(35)	0.4510 (8)	0.1292 (6)	0.3208 (5)	4.8 (3)
C(36)	0.5383 (7)	0.1722 (5)	0.3482 (4)	3.3 (2)
C(41)	0.7136 (6)	0.1685 (5)	0.5177 (4)	2.8 (2)
C(42)	0.2634 (7)	0.4053 (5)	0.0036 (5)	4.1 (2)
C(43)	0.3041 (7)	0.4514 (6)	0.0554 (5)	5.0 (2)
C(44)	0.2945 (7)	0.4265 (6)	0.1191 (5)	5.6 (3)
C(45)	0.2453 (9)	0.3541 (6)	0.1322 (5)	5.3 (3)
C(46)	0.7057 (7)	0.1929 (5)	0.5814 (4)	3.6 (2)
C(51)	0.5856 (6)	0.3042 (5)	0.4881 (4)	2.4 (2)
C(52)	0.6347 (7)	0.3713 (5)	0.5168 (4)	3.4 (2)
C(53)	0.5749 (8)	0.4275 (6)	0.5504 (5)	4.7 (2)
C(54)	0.4674 (8)	0.4156 (5)	0.5539 (5)	4.4 (2)
C(55)	0.4199 (8)	0.3504 (6)	0.5237 (5)	4.5 (2)
C(56)	0.4001 (7)	0.2942 (5)	0.4913 (4)	3.8 (2)
C(61)	0.6422 (6)	0.3520 (5)	0.3038 (4)	3.0 (2)
C(62)	0.5681 (6)	0.3770 (5)	0.3461 (4)	3.2 (2)
C(63)	0.4629 (7)	0.3708 (5)	0.3280 (5)	4.1 (2)
C(64)	0.4318 (7)	0.3388 (6)	0.2683 (5)	5.1 (2)
C(65)	0.5060 (8)	0.3151 (6)	0.2247 (5)	5.0 (2)
C(66)	0.6141 (7)	0.3213 (5)	0.2429 (4)	3.7 (2)
C(71)	0.2945 (6)	0.0401 (4)	0.8568 (4)	2.5 (2)
C(72)	0.3847 (7)	0.0183 (5)	0.8945 (4)	3.0 (2)
C(73)	0.5931 (8)	0.0643 (5)	0.0946 (4)	4.0 (2)
C(74)	0.6613 (8)	0.1225 (5)	0.1207 (5)	4.5 (2)
C(75)	0.2500 (8)	0.3990 (5)	0.6573 (5)	4.3 (2)
C(76)	0.7710 (7)	0.0193 (5)	0.1689 (4)	3.7 (2)
C(81)	0.3450 (6)	0.1448 (5)	0.7563 (4)	2.5 (2)
C(82)	0.3817 (7)	0.2163 (5)	0.7319 (4)	3.1 (2)
C(83)	0.4335 (7)	0.2161 (6)	0.6731 (4)	4.2 (2)
C(84)	0.4462 (7)	0.1437 (7)	0.6411 (5)	4.7 (2)
C(85)	0.4082 (7)	0.0724 (6)	0.6642 (4)	4.2 (2)
C(86)	0.3569 (7)	0.0715 (5)	0.7232 (4)	3.4 (2)

\*  $B_{eq} = (4/3) [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$ .

Table 2. Some important bond distances (Å) and angles (°) in the molecule OsCl<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub>

E.s.d.'s are given in parentheses.

Os(1)–Cl(1)	2.383 (2)	P(2)–C(31)	1.833 (7)
–Cl(2)	2.399 (2)	–C(41)	1.817 (8)
–P(1)	2.410 (2)	–C(51)	1.837 (7)
–P(2)	2.366 (2)	P(3)–C(61)	1.849 (8)
–P(3)	2.235 (2)	–C(71)	1.838 (7)
P(1)–C(1)	1.847 (8)	–C(81)	1.847 (7)
–C(11)	1.824 (7)		
–C(21)	1.831 (8)		
Cl(1)–Os(1)–Cl(2)	160.65 (8)	Os(1)–P(2)–C(31)	122.2 (3)
–P(1)	94.96 (7)	–C(41)	100.1 (2)
–P(2)	85.62 (7)	–C(51)	126.0 (3)
–P(3)	97.87 (7)	Os(1)–P(3)–C(61)	114.5 (2)
Cl(2)–Os(1)–P(1)	82.97 (7)	–C(71)	120.8 (3)
–P(2)	89.26 (7)	–C(81)	116.7 (3)
–P(3)	101.43 (7)		
P(1)–Os(1)–P(2)	158.07 (7)	C(1)–P(1)–C(11)	104.5 (4)
–P(3)	99.99 (7)	–C(21)	97.8 (4)
P(2)–Os(1)–P(3)	101.65 (7)	C(11)–P(1)–C(21)	103.3 (4)
Os(1)–P(1)–C(1)	121.7 (3)	C(31)–P(2)–C(41)	100.7 (3)
–C(11)	117.4 (3)	–C(51)	100.9 (3)
–C(21)	109.2 (3)	C(41)–P(2)–C(51)	102.2 (4)
		C(61)–P(3)–C(71)	100.8 (4)
		–C(81)	100.6 (4)
		C(71)–P(3)–C(81)	100.4 (3)

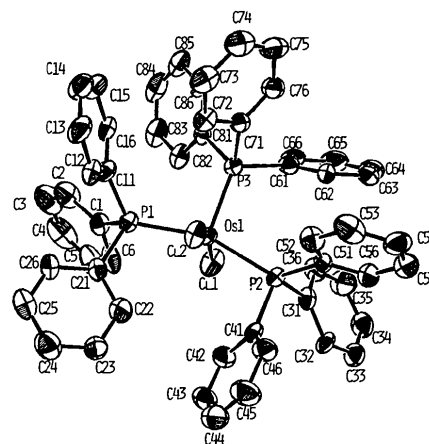


Fig. 1. An *ORTEP* (Johnson, 1965) diagram of the OsCl<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>3</sub> molecule. Atoms are represented by thermal vibration ellipsoids at the 50% level and the atomic labeling scheme is defined.

## References

- BINO, A., COTTON, F. A. & FANWICK, P. E. (1979). *Inorg. Chem.* **18**, 3558–3562.
- CHAKRAVARTY, A. R., COTTON, F. A. & TOCHER, D. A. (1984). *Inorg. Chem.* In the press.
- Enraf–Nonius (1979). *Structure Determination Package*. Enraf–Nonius, Delft.
- HOFFMAN, P. R. & CAULTON, K. G. (1975). *J. Am. Chem. Soc.* **97**, 4221–4228.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- LA PLACA, S. J. & IBERS, J. A. (1965). *Inorg. Chem.* **4**, 778–783.