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Structure of Carbonyl-*mer*-trichloro-*trans*-bis(triphenylphosphine)iridium(III),$C_{37}H_{30}Cl_3IrOP_2$

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(*Received* 25 *March* 1983; *accepted* 13 *June* 1983)

Abstract. $M_r = 851{\cdot}16$, monoclinic, $C2/c$, $a = 24{\cdot}209$ (3), $b = 9{\cdot}561$ (2), $c = 22{\cdot}233$ (3) Å, $\beta = 140{\cdot}33$ (2)°, $V = 3285$ (2) Å^3, $Z = 4$, $D_m = 1{\cdot}71$ (2), $D_x = 1{\cdot}721$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo }K\alpha) = 44{\cdot}2$ cm^{-1}, $F(000) = 1672$, $T = 298$ K, $R = 0{\cdot}024$ for 2461 independent observed reflections. The X-ray study of the title compound has shown the presence of two triphenylphosphine ligands in *trans* positions, the other ligands lying on the equatorial plane of the coordination octahedron.

Introduction. The title compound was obtained as an unexpected by-product from substitution reactions on $[Ir(CO)_3(PPh_3)]_2$, carried out in chlorinated solvents (Angoletta, Bellon, Demartin & Manassero, 1981; Angoletta, Bellon, Demartin & Sansoni, 1981). The present structural study was undertaken to determine the precise stoichiometry of the new iridium derivative and its stereochemistry.

Experimental. D_m at room temperature by flotation in K_2HgI_4, air-stable yellow prismatic crystal, approximately 0·2 × 0·2 × 0·3 mm, Nonius CAD-4 automatic diffractometer, graphite-monochromatized Mo $K\alpha$, standard CAD-4 centering, indexing and data collection programs, lattice parameters and the orientation matrix refined by least-squares fit of 25 reflections ($8 < \theta < 12°$), 2874 independent reflections, 2θ sphere of 50°, ω scan, $\Delta\omega = 1{\cdot}5 + 0{\cdot}35 \tan\theta$, background counted for half of the peak scanning time, h −28–28, k 0–11, l 0–26; three standard reflections revealed no crystal decay; Lorentz, polarization and absorption corrections applied, absorption correction by an empirical method based on a set of φ scans of reflections having χ values near 90° (North, Phillips & Mathews, 1968), maximum and minimum relative transmission factors 1·00 and 0·83; conventional Patterson and Fourier methods, refinement by full-matrix least squares minimizing $\sum w(F_o - |F_c|)^2$, 2461 reflections with $I \geq 3\sigma(I)$, anisotropic thermal parameters for non-hydrogen atoms; contribution of scattering amplitudes of all hydrogen atoms in their expected positions (C—H = 0·95 Å) included in the last cycles of the refinement, with assigned isotropic thermal parameter of 5·00 Å^2, no refinement of hydrogen coordinates attempted; 201 parameters refined, final R and R_w values 0·024 and 0·029 respectively,* $w_{hkl} = 1/\sigma^2(F_o)$, $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (AI)^2]^{\frac{1}{2}}/\text{Lp}$; A, the ignorance factor, is 0·04, maximum shift/e.s.d. = 0·32, maximum peak in final difference Fourier = 1·6 e Å^{-3} (close to Ir); scattering factors and anomalous-dispersion correction from *International Tables for X-ray Crystallography* (1974); all calculations performed on PDP 11/34 using the *Enraf–Nonius Structure Determination Package* (Enraf–Nonius, 1979).

Discussion. Final atomic parameters are given in Table 1; relevant intramolecular distances and angles are reported in Table 2; a view of the molecule of $IrCl_3CO[P(Ph)_3]_2$ and the atomic numbering are shown in Fig. 1.

The molecular structure of the title compound consists of a six-coordinate Ir^{III} ion with octahedral geometry, the two triphenylphosphine ligands being *trans* to each other. The molecule displays C_2 symmetry, with Ir, C, O and Cl(2) atoms lying on a twofold crystallographic axis; however, the idealized symmetry

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38659 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/83/091225-02$01.50

of the coordination sphere is C_{2v}. Almost straight linearity can be observed for the atomic system P—Ir—P′ [angle 179·86 (4)°]. The bending of the *trans* chlorine atoms Cl(1) and Cl(1′) towards the carbonyl ligand [Cl(1)—Ir—Cl(1′) 175·18 (4)°] is probably related to a dominant electrostatic repulsion among the most electronegative chlorine ligands.

The two triphenylphosphine groups are almost in eclipsed conformation; the phenyl-plane arrangement seems dictated by possible intramolecular interactions between α-hydrogens of the phenyl rings and chlorine atoms as suggested by Cl(1′)···H(32), Cl(2)···H(26) and Cl(2)···H(32) contacts [2·60 (1), 2·80 (2) and 2·83 (1) Å, respectively], which are shorter than the sum of the van der Waals radii.

The iridium—chlorine bond lengths are identical, thus suggesting that the *trans* influence of the π-acceptor carbonyl ligand is not relevant. The iridium—phosphorus distance [2·408 (1) Å] is comparable to that found in other Ir^{III} complexes, such as $IrCl_2(CHF_2)(CO)[P(Ph)_3]_2$ (Schultz, McArdle, Khare & Eisenberg, 1974) and $(bdpps)Cl_3Ir$ (bdpps = *o*-$Ph_2PC_6H_4$-*t*-CH=$CHC_6H_4PPh_2$-*o*) (Robertson, Tucker & Whimp, 1980).

Table 1. *Coordinates and equivalent isotropic thermal parameters for the non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}\sum_i \sum_j B_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i.\, \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Ir	0·0000	0·08186 (3)	0·2500	1·849 (4)
Cl(1)	0·11131 (5)	0·0923 (1)	0·41667 (5)	3·08 (3)
Cl(2)	0·00000	−0·1660 (2)	0·25000	2·77 (4)
P	0·11222 (4)	0·0815 (1)	0·26893 (5)	1·95 (2)
O	0·0000	0·3972 (5)	0·2500	2·8 (2)
C	0·0000	0·2785 (7)	0·2500	4·7 (1)
C(11)	0·1311 (2)	0·2615 (5)	0·2612 (2)	2·4 (1)
C(12)	0·1659 (2)	0·3565 (5)	0·3315 (2)	3·3 (1)
C(13)	0·1717 (3)	0·4961 (6)	0·3216 (3)	4·4 (2)
C(14)	0·1438 (3)	0·5436 (5)	0·2436 (3)	5·0 (2)
C(15)	0·1117 (3)	0·4513 (6)	0·1754 (3)	4·7 (2)
C(16)	0·1050 (2)	0·3097 (5)	0·1833 (2)	3·4 (1)
C(21)	0·2178 (2)	0·0163 (5)	0·3802 (2)	2·2 (1)
C(22)	0·2924 (2)	0·0946 (5)	0·4392 (3)	3·5 (1)
C(23)	0·3723 (2)	0·0368 (6)	0·5198 (3)	4·0 (2)
C(24)	0·3790 (2)	−0·0990 (6)	0·5431 (2)	3·5 (1)
C(25)	0·3055 (3)	−0·1782 (6)	0·4849 (3)	4·5 (2)
C(26)	0·2262 (2)	−0·1218 (5)	0·4055 (3)	3·9 (2)
C(31)	0·0948 (2)	−0·0190 (5)	0·1856 (2)	2·3 (1)
C(32)	0·0227 (2)	−0·1017 (5)	0·1158 (2)	2·7 (1)
C(33)	0·0150 (2)	−0·1792 (5)	0·0570 (2)	3·3 (1)
C(34)	0·0776 (2)	−0·1748 (6)	0·0667 (2)	3·8 (1)
C(35)	0·1491 (2)	−0·0922 (7)	0·1348 (2)	5·0 (1)
C(36)	0·1587 (2)	−0·0157 (7)	0·1949 (3)	4·1 (1)

Table 2. *Relevant geometrical parameters with e.s.d.'s in parentheses* (Å *and* deg)

Ir—Cl(1)	2·373 (1)	P—C(11)	1·822 (5)
Ir—Cl(2)	2·370 (2)	P—C(21)	1·819 (4)
Ir—P	2·408 (1)	P—C(31)	1·824 (5)
Ir—C	1·880 (7)	C—O	1·135 (8)
		$C—C_{(phenyl, av)}$	1·379 (3)
Cl(1)—Ir—Cl(2)	92·42 (3)	Ir—P—C(11)	108·30 (14)
Cl(1)—Ir—Cl(1′)	175·18 (4)	Ir—P—C(21)	116·99 (15)
Cl(1)—Ir—P	87·41 (4)	Ir—P—C(31)	118·37 (15)
Cl(1)—Ir—C	87·58 (3)	C(11)—P—C(21)	105·05 (20)
Cl(2)—Ir—P	89·92 (3)	C(11)—P—C(31)	106·24 (21)
P—Ir—P′	179·86 (4)	C(21)—P—C(31)	100·66 (21)
P—Ir—C	90·08 (3)		

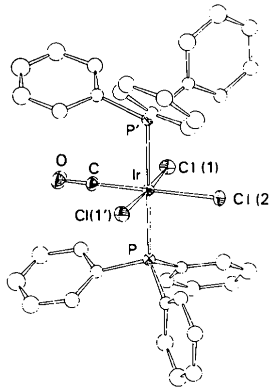

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule.

We thank the Italian CNR for financial support; the courtesy of Professor M. Angoletta, who prepared the crystals, is also acknowledged.

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