

Table 2. Bond lengths (Å) and interbond angles (°)

Pt—Cl(1)	2.324 (2)	Pt—Cl(2)	2.316 (2)
Pt—S(1)	2.231 (1)	Pt—S(2)	2.244 (2)
S(1)—C(1)	1.809 (7)	S(1)—C(3)	1.841 (5)
S(2)—C(2)	1.807 (9)	S(2)—C(5)	1.852 (5)
F(1)—C(4)	1.318 (7)	F(2)—C(4)	1.321 (8)
F(3)—C(4)	1.331 (8)	F(4)—C(6)	1.332 (7)
F(5)—C(6)	1.320 (7)	F(6)—C(6)	1.328 (7)
C(3)—C(4)	1.522 (8)	C(3)—C(5)	1.533 (7)
C(5)—C(6)	1.516 (8)		
Cl(1)—Pt—Cl(2)	91.5 (1)	Cl(1)—Pt—S(1)	178.4 (1)
Cl(1)—Pt—S(2)	89.4 (1)	Cl(2)—Pt—S(1)	88.1 (1)
Cl(2)—Pt—S(2)	179.1 (1)	S(1)—Pt—S(2)	91.0 (1)
Pt—S(1)—C(1)	107.3 (3)	Pt—S(1)—C(3)	103.8 (2)
C(1)—S(1)—C(3)	101.9 (3)	Pt—S(2)—C(2)	104.9 (3)
Pt—S(2)—C(5)	103.9 (2)	C(2)—S(2)—C(5)	99.9 (3)
S(1)—C(3)—C(4)	107.6 (4)	S(1)—C(3)—C(5)	110.0 (4)
C(4)—C(3)—C(5)	118.1 (5)	F(1)—C(4)—F(2)	107.9 (5)
F(1)—C(4)—F(3)	108.1 (5)	F(1)—C(4)—C(3)	110.8 (5)
F(2)—C(4)—F(3)	107.4 (5)	F(2)—C(4)—C(3)	111.3 (5)
F(3)—C(4)—C(3)	111.2 (5)	S(2)—C(5)—C(3)	112.1 (4)
S(2)—C(5)—C(6)	109.5 (4)	C(3)—C(5)—C(6)	116.4 (5)
F(4)—C(6)—F(5)	107.0 (5)	F(4)—C(6)—F(6)	106.4 (5)
F(4)—C(6)—C(5)	112.9 (5)	F(5)—C(6)—F(6)	107.7 (5)
F(5)—C(6)—C(5)	111.9 (5)	F(6)—C(6)—C(5)	110.6 (5)

respectively pseudo-axial and pseudo-equatorial, the corresponding Pt—S—C—CF<sub>3</sub> torsion angles being 88.8 (4) and -163.1 (4)°. The conformation in the crystal corresponds to that proposed by Cross *et al.* (1980) for the most abundant isomer in solution; they also suggest that it is the least sterically crowded.

The Pt—S distances [2.231 (1) and 2.244 (2) Å] and the Pt—Cl distances [2.324 (2) and 2.316 (2) Å] (Table 2) are respectively slightly shorter and slightly longer on average than corresponding distances in *cis*-[Pt{CF<sub>3</sub>SCH<sub>2</sub>CH(CH<sub>3</sub>)SCF<sub>3</sub>}Cl<sub>2</sub>] [Pt—S 2.239 (3) and

2.260 (4) Å; Pt—Cl 2.290 (4) and 2.295 (3) Å] (Manojlović-Muir, Muir & Solomun, 1977). Evidently replacement of electron-withdrawing CF<sub>3</sub> substituents on S by electron-releasing CH<sub>3</sub> causes only a minor alteration in the  $\sigma$ -electron framework of these complexes, with a stronger Pt—S and weaker Pt—Cl bonding. This contrasts with the effect of a similar substituent replacement at donor phosphorus in platinum(II) complexes (Macleod, Manojlović-Muir, Millington, Muir, Sharp & Walker, 1975): increased electron release at P weakens both the *trans*-Pt—Cl and the Pt—P bonding substantially, a result which has been interpreted in terms of significant Pt—P back-donation (Manojlović-Muir, 1978).

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*Acta Cryst.* (1984). **C40**, 39–41

## Structure of Carbonyldichloro(cyclopropyl)bis(methyldiphenylphosphine)iridium(III), [IrCl<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>)(CO){P(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>]

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**Abstract.**  $M_r = 732.6$ , rhombohedral,  $R\bar{3}$ ,  $a = 17.863$  (5) Å,  $\alpha = 108.97$  (2)°,  $V = 4468$  (7) Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 1.63$  g cm<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 47.7$  cm<sup>-1</sup>,  $F(000) = 2151$  electrons (with anomalous

dispersion),  $T = 295$  K,  $R = 0.060$  for 2866 averaged reflections. The Ir atom is six-coordinate with the chloro ligands having a *cis* configuration and the phosphine ligands having a *trans* configuration. The cyclopropyl ligand is  $\sigma$  bonded to the Ir atom and has a mean C—C bond length of 1.56 (2) Å.

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**Introduction.** Structural characterization of transition-metal  $\sigma$ -cyclopropyl complexes is important in order to determine the effect of the metal on C—C bonding within the cyclopropyl ring. The lack of structural information on such molecules prompted our investigation of *cis*-Pt(CHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> (Jones & Ibers, 1982). The present study reports the structure of IrCl<sub>2</sub>(CHCH<sub>2</sub>CH<sub>2</sub>)(CO)(PMePh<sub>2</sub>)<sub>2</sub>, one product of the reaction of cyclopropylmethanoic chloride (C<sub>3</sub>H<sub>5</sub>-COCl) with [IrCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub> after treatment of the latter with PMePh<sub>2</sub> (Jones & Ibers, 1983).

**Experimental.** Crystals obtained through recrystallization from a toluene/hexane mixture; colorless rhomboid, 0.3 × 0.3 × 0.2 mm; Enraf-Nonius CAD-4 diffractometer,  $\omega$ -2 $\theta$  scan mode, scan width 0.45° + 0.35° tan  $\theta$  in 2 $\theta$ ; two standard reflections (4,  $\bar{1}$ , 4, 7,  $\bar{1}$ , 4) measured after every 2 h of data collection showed no significant variations in intensities; (sin  $\theta$ )/ $\lambda_{\text{max}}$  = 0.5384 Å<sup>-1</sup>; empirical and necessarily approximate absorption correction based on  $\psi$ -scan data from nine reflections, relative transmission factors 0.58–1.0 (North, Phillips & Mathews, 1968);  $\pm h$ (-19 to +19),  $\pm k$ (0 to +19),  $\pm l$ (-19 to +19), 13 052 measured intensities, 3984 unique, 2866 observed [ $I \geq 2\sigma(I)$ ]; solution by Patterson and Fourier techniques, full-matrix least-squares refinement on  $F$ ; phenyl H atoms included as fixed contribution to structure factors; methyl and cyclopropyl H atoms could not be located from difference Fourier syntheses and were not included; 325 refined parameters;  $w = 1/\sigma(F)^2$ ,  $R(F) = 0.060$ ,  $wR(F) = 0.077$ ,  $S = 1.88$  electrons; scattering factors, including real and imaginary anomalous-dispersion corrections for the nonhydrogen atoms, from *International Tables for X-ray Crystallography* (1974); all calculations carried out with *ORTEP* (Johnson, 1976) and the Enraf-Nonius *SDP* crystallographic computing package (Frenz, 1979); maximum  $\Delta/\sigma = 3.3\%$  in the final cycle, the largest  $\Delta\rho$  peak in the final difference electron density map [4.1 (2) e Å<sup>-3</sup>; 0.94, 0.02, 0.02] is 1.2 Å from the origin of the unit cell and is not interpretable in terms of solvent disorder.\*

**Discussion.** As illustrated in Fig. 1, IrCl<sub>2</sub>(CHCH<sub>2</sub>CH<sub>2</sub>)(CO)(PMePh<sub>2</sub>)<sub>2</sub> is a monomer in which the Ir atom has a six-coordinate octahedral geometry. The *trans* arrangement of the phosphine ligands along with the *cis* configuration of the chloro ligands is consistent with the molecular geometry deduced from <sup>1</sup>H NMR, <sup>31</sup>P{<sup>1</sup>H} NMR and IR spectroscopy

\* Lists of structure amplitudes, anisotropic thermal parameters, hydrogen-atom positions and bond distances and angles in the phenyl rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38808 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Jones & Ibers, 1983). The final positional parameters are listed in Table 1, the nonphenyl bond distances and angles are given in Table 2, and the phenyl distances and angles [mean C—C = 1.38 (4) Å, range = 1.30 (2)–1.44 (2) Å; mean C—C—C = 120 (2)°, range = 116 (2)–122 (2)°] have been deposited. The crystal packing is displayed in Fig. 2; all intermolecular contacts involving nonhydrogen atoms are greater than 3.3 Å.

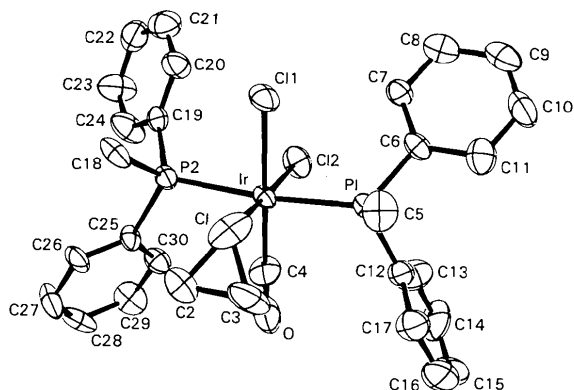


Fig. 1. Drawing of IrCl<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>)(CO)(PMePh<sub>2</sub>)<sub>2</sub> (50% probability thermal ellipsoids) along with atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Atomic coordinates and equivalent isotropic temperature factors

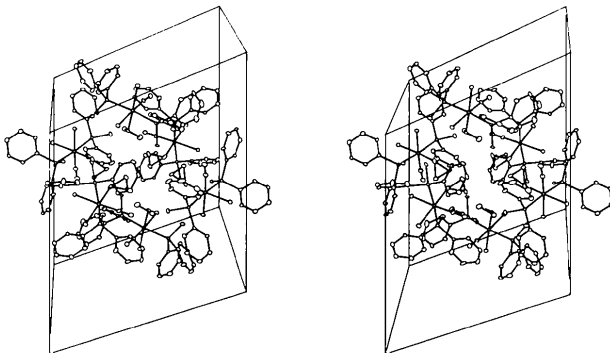
$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
Ir	0.26908 (4)	0.45380 (4)	0.13179 (4)	2.04 (1)
Cl(1)	0.1346 (3)	0.3691 (3)	0.1328 (3)	3.4 (1)
Cl(2)	0.1924 (3)	0.4752 (3)	0.0041 (3)	3.9 (1)
P(1)	0.2773 (3)	0.5830 (3)	0.2349 (3)	2.4 (1)
P(2)	0.2456 (3)	0.3141 (3)	0.0284 (3)	2.4 (1)
O	0.4403 (8)	0.5621 (8)	0.1488 (9)	4.9 (4)
C(1)	0.3350 (15)	0.4319 (15)	0.2375 (15)	3.6 (5)
C(2)	0.4178 (15)	0.4169 (15)	0.2461 (15)	4.5 (6)
C(3)	0.4305 (15)	0.5038 (15)	0.3194 (15)	5.5 (7)
C(4)	0.3760 (15)	0.5200 (15)	0.1385 (15)	3.7 (5)
C(5)	0.2968 (15)	0.5879 (15)	0.3446 (15)	3.7 (5)
C(6)	0.1795 (15)	0.6010 (15)	0.2052 (15)	2.8 (5)
C(7)	0.0961 (15)	0.5383 (15)	0.1308 (15)	3.0 (5)
C(8)	0.0227 (15)	0.5544 (15)	0.1188 (15)	4.3 (6)
C(9)	0.0343 (15)	0.6362 (15)	0.1809 (15)	4.5 (6)
C(10)	0.1173 (15)	0.6979 (15)	0.2543 (15)	5.1 (7)
C(11)	0.1915 (15)	0.6840 (15)	0.2681 (15)	4.3 (6)
C(12)	0.3684 (15)	0.6870 (15)	0.2635 (15)	2.7 (5)
C(13)	0.3617 (15)	0.7179 (15)	0.1977 (15)	5.1 (7)
C(14)	0.4269 (15)	0.7936 (15)	0.2129 (15)	5.6 (7)
C(15)	0.5061 (15)	0.8427 (25)	0.2983 (25)	7.6 (9)
C(16)	0.5151 (15)	0.8168 (15)	0.3615 (25)	6.6 (8)
C(17)	0.4457 (15)	0.7351 (15)	0.3425 (15)	4.4 (6)
C(18)	0.2282 (15)	0.2321 (15)	0.0694 (15)	3.4 (5)
C(19)	0.1453 (15)	0.2522 (15)	-0.0840 (15)	3.0 (5)
C(20)	0.0618 (15)	0.2298 (15)	-0.0926 (15)	3.8 (6)
C(21)	-0.0122 (15)	0.1772 (15)	-0.1742 (15)	4.6 (6)
C(22)	-0.0059 (15)	0.1419 (15)	-0.2518 (15)	4.6 (6)
C(23)	0.0776 (15)	0.1654 (25)	-0.2432 (15)	5.2 (7)
C(24)	0.1501 (15)	0.2182 (15)	-0.1648 (15)	4.8 (6)
C(25)	0.3365 (15)	0.3214 (15)	0.0023 (15)	2.5 (4)
C(26)	0.3784 (15)	0.2696 (15)	0.0126 (15)	3.5 (5)
C(27)	0.4434 (15)	0.2715 (15)	-0.0142 (15)	4.5 (6)
C(28)	0.4663 (15)	0.3245 (15)	-0.0501 (15)	4.5 (6)
C(29)	0.4239 (15)	0.3759 (15)	-0.0634 (15)	4.3 (6)
C(30)	0.3629 (15)	0.3774 (15)	-0.0340 (15)	3.1 (5)

E.s.d.'s in the least significant digits are shown in parentheses in this and all subsequent tables.

Table 2. Selected bond lengths (Å) and angles (°) excluding phenyl rings

Ir—Cl(1)	2.397 (4)	C(2)—C(3)	1.56 (2)
Ir—Cl(2)	2.470 (4)	C(4)—O	1.06 (2)
Ir—P(1)	2.363 (4)	P(1)—C(5)	1.84 (1)
Ir—P(2)	2.374 (4)	P(1)—C(6)	1.82 (1)
Ir—C(1)	2.11 (2)	P(1)—C(12)	1.80 (1)
Ir—C(4)	1.83 (2)	P(2)—C(18)	1.84 (1)
Cl—C(2)	1.56 (2)	P(2)—C(19)	1.84 (2)
Cl—C(3)	1.56 (2)	P(2)—C(25)	1.81 (1)
Cl(1)—Ir—Cl(2)	95.8 (1)	C(1)—C(2)—C(3)	60 (1)
Cl(1)—Ir—P(1)	86.0 (1)	C(1)—C(3)—C(2)	60 (1)
Cl(1)—Ir—P(2)	87.4 (1)	C(2)—C(1)—C(3)	60 (1)
Cl(1)—Ir—C(1)	84.7 (5)	Ir—C(4)—O	175 (2)
Cl(1)—Ir—C(4)	176.3 (6)	Ir—P(1)—C(5)	114.0 (5)
Cl(2)—Ir—P(1)	91.0 (1)	Ir—P(1)—C(6)	119.0 (5)
Cl(2)—Ir—P(2)	89.8 (1)	Ir—P(1)—C(12)	113.0 (5)
Cl(2)—Ir—C(1)	177.9 (4)	C(5)—P(1)—C(6)	100.7 (7)
Cl(2)—Ir—C(4)	87.7 (5)	C(5)—P(1)—C(12)	104.3 (7)
P(1)—Ir—P(2)	173.4 (1)	C(6)—P(1)—C(12)	104.1 (7)
P(1)—Ir—C(1)	91.1 (4)	Ir—P(2)—C(18)	111.8 (5)
P(1)—Ir—C(4)	92.7 (5)	Ir—P(2)—C(19)	116.8 (5)
P(2)—Ir—C(1)	88.2 (4)	Ir—P(2)—C(25)	114.9 (5)
P(2)—Ir—C(4)	93.8 (5)	C(18)—P(2)—C(19)	102.5 (7)
Ir—C(1)—C(2)	120 (1)	C(18)—P(2)—C(25)	106.5 (7)
Ir—C(1)—C(3)	123 (1)	C(19)—P(2)—C(25)	103.1 (7)

Fig. 2. Stereoscopic packing diagram for  $\text{IrCl}_2(\text{C}_3\text{H}_5)(\text{CO})(\text{PMe}_2\text{Ph})_2$ . Thermal ellipsoids are at the 30% probability level and hydrogen atoms have been omitted for clarity.

The Ir—P bond lengths [2.363 (4) and 2.374 (4) Å] are comparable with the Ir—P bond lengths (*trans* to P) in *mer*- $\text{IrCl}_3(\text{PMe}_2\text{Ph})_3$  [2.363 (1) and 2.384 (1) Å; Robertson & Tucker, 1981] and fall within the range (2.29–2.42 Å) of Ir—P (*trans* to P) bond lengths for  $\text{Ir}^{\text{III}}-\text{PPh}_3$  complexes as compiled by Robertson & Tucker (1981). For the rest of the coordination sphere the structures of  $\text{IrCl}_2(\text{CHF}_2)(\text{CO})(\text{PPh}_3)_2$  (Schultz, McArdle, Khare & Eisenberg, 1974) and  $\text{IrCl}(\text{CHF}_2)(\text{OCOCF}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$  (Schultz, Khare, Meyer & Eisenberg, 1974) provide good examples for comparison. The Ir—Cl(1) bond length [2.397 (4) Å] *trans* to the CO ligand of the title compound is equal within experimental error to the corresponding bond lengths in  $\text{IrCl}_2(\text{CHF}_2)(\text{CO})(\text{PPh}_3)_2$  [2.375 (8) Å] and  $\text{IrCl}(\text{CHF}_2)(\text{OCOCF}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$  [2.393 (4) Å] and the Ir—Cl(2) bond length [2.470 (4) Å] *trans* to the  $\sigma$ -bonded cyclopropyl is equal to the equivalent bond length in  $\text{IrCl}_2(\text{CHF}_2)(\text{CO})(\text{PPh}_3)_2$  [2.475 (10) Å]. We

attribute the 0.073 Å difference between the two Ir—Cl distances to the stronger *trans* influence of the  $\sigma$ -bonded cyclopropyl group relative to the coordinated CO ligand. In addition the Ir—C(1) [2.11 (2) Å cyclopropyl] and the Ir—C(4) [1.83 (2) Å carbonyl] bond lengths are equal within experimental error to their counterparts in  $\text{IrCl}_2(\text{CHF}_2)(\text{CO})(\text{PPh}_3)_2$  [2.19 (3) and 1.85 Å\*] and  $\text{IrCl}(\text{CHF}_2)(\text{OCOCF}_2\text{Cl})(\text{CO})(\text{PPh}_3)_2$  [2.09 (2) and 1.84 (2) Å].

The four equatorial atoms along with the Ir atom [Cl(1), Cl(2), Ir, C(1), C(4)] are planar to within 0.06 (1) Å. The cyclopropyl ligand is oriented perpendicular to this plane (dihedral angle = 94°). All of the cyclopropyl C—C bond lengths and C—C—C bond angles are equal within the accuracy of the experiment; the mean values [mean C—C = 1.56 (2) Å; mean C—C—C = 60 (1)°] are comparable with those found in  $\text{Pt}(\text{CHCH}_2\text{CH}_2)_2(\text{PMe}_2\text{Ph})_2$  [1.51 (1) Å and 60.0 (1)°; Jones & Ibers, 1982] and in the nickel  $\sigma$ -cyclopropyl complex 2,2'-bipyridyl-3,3',7,7-tetramethyl-*trans*-5-nickelatricyclo[4.1.0.0<sup>2,4</sup>]heptane [1.52 (1) Å and 60.0 (5)°; Binger, Doyle, McMeeking, Kruger & Tsay, 1977], a compound containing functionalized cyclopropyl rings. The undistorted geometries of the  $\sigma$ -bonded cyclopropyl ligands along with the proven chemical stability of these entities (Jones & Ibers, 1983) throws doubt on their role as intermediates in the metal-assisted rearrangement of cyclopropanes to olefins.

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\* In the refinement of  $\text{IrCl}_2(\text{CHF}_2)(\text{CO})(\text{PPh}_3)_2$  the Ir—C—O fragment was treated as a rigid group (Schultz, McArdle, Khare & Eisenberg, 1974).

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