

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

Hg—Br	3.127 (1)	Hg—C(1)	2.105 (6)
Hg—C(2)	2.110 (6)	P(1)—O(1)	1.472 (5)
P(1)—C(1)	1.740 (7)	P(1)—C(3)	1.799 (6)
P(1)—C(9)	1.797 (10)	P(2)—O(2)	1.477 (4)
P(2)—C(2)	1.728 (8)	P(2)—C(15)	1.819 (9)
P(2)—C(21)	1.809 (6)	O(1)—Li	1.909 (11)
O(2)—Li <sub>a</sub>	1.883 (12)	O(3)—Li	1.939 (12)
O(4)—C(27)	1.436 (14)	O(4)—C(30)	1.377 (13)
O(4)—Li	1.997 (18)	C(3)—C(4)	1.348 (11)
C(3)—C(8)	1.341 (11)	C(4)—C(5)	1.375 (11)
C(5)—C(6)	1.319 (13)	C(6)—C(7)	1.304 (14)
C(7)—C(8)	1.397 (12)	C(9)—C(10)	1.390 (12)
C(9)—C(14)	1.377 (12)	C(10)—C(11)	1.357 (18)
C(11)—C(12)	1.354 (17)	C(12)—C(13)	1.355 (16)
C(13)—C(14)	1.367 (18)	C(15)—C(16)	1.359 (10)
C(15)—C(20)	1.363 (15)	C(16)—C(17)	1.406 (15)
C(17)—C(18)	1.349 (17)	C(18)—C(19)	1.349 (12)
C(19)—C(20)	1.397 (16)	C(21)—C(22)	1.360 (11)
C(21)—C(26)	1.356 (10)	C(22)—C(23)	1.386 (10)
C(23)—C(24)	1.330 (13)	C(24)—C(25)	1.318 (15)
C(25)—C(26)	1.397 (11)	C(27)—C(28)	1.415 (28)
C(28)—C(29)	1.402 (20)	C(29)—C(30)	1.417 (28)
Li—O(2a)	1.883 (12)		
Br—Hg—C(1)	89.2 (2)	Br—Hg—C(2)	92.6 (2)
C(1)—Hg—C(2)	176.9 (3)	O(1)—P(1)—C(1)	113.0 (3)
O(1)—P(1)—C(3)	110.2 (3)	C(1)—P(1)—C(3)	108.3 (3)
O(1)—P(1)—C(9)	111.3 (3)	C(1)—P(1)—C(9)	106.4 (4)
C(3)—P(1)—C(9)	107.5 (3)	O(2)—P(2)—C(2)	112.3 (3)
O(2)—P(2)—C(15)	112.7 (3)	C(2)—P(2)—C(15)	109.1 (3)
O(2)—P(2)—C(21)	11.05 (3)	C(2)—P(2)—C(21)	106.0 (3)
C(15)—P(2)—C(21)	105.8 (4)	P(1)—O(1)—Li	151.0 (5)
P(2)—O(2)—Li <sub>a</sub>	147.6 (6)	C(27)—O(4)—C(30)	107.5 (9)
C(27)—O(4)—Li	121.5 (8)	C(30)—O(4)—Li	126.8 (7)
Hg—C(1)—P(1)	111.4 (4)	Hg—C(2)—P(2)	117.5 (4)
P(1)—C(3)—C(4)	120.4 (5)	P(1)—C(3)—C(8)	125.7 (6)
C(4)—C(3)—C(8)	113.9 (7)	C(3)—C(4)—C(5)	123.1 (8)
C(4)—C(5)—C(6)	121.4 (8)	C(5)—C(6)—C(7)	117.5 (8)
C(6)—C(7)—C(8)	121.6 (9)	C(3)—C(8)—C(7)	122.4 (9)
P(1)—C(9)—C(10)	124.0 (7)	P(1)—C(9)—C(14)	118.5 (6)
C(10)—C(9)—C(14)	117.4 (9)	C(9)—C(10)—C(11)	120.3 (9)
C(10)—C(11)—C(12)	122.5 (10)	C(11)—C(12)—C(13)	117.1 (13)
C(12)—C(13)—C(14)	122.6 (11)	C(9)—C(14)—C(13)	120.0 (8)
P(2)—C(15)—C(16)	124.2 (8)	P(2)—C(15)—C(20)	117.0 (5)
C(16)—C(15)—C(20)	118.7 (9)	C(15)—C(16)—C(17)	120.3 (10)
C(16)—C(17)—C(18)	120.2 (8)	C(17)—C(18)—C(19)	119.8 (10)
C(18)—C(19)—C(20)	120.3 (11)	C(15)—C(20)—C(19)	120.6 (8)
P(2)—C(21)—C(22)	120.5 (5)	P(2)—C(21)—C(26)	121.3 (6)
C(22)—C(21)—C(26)	117.9 (6)	C(21)—C(22)—C(23)	120.5 (7)
C(22)—C(23)—C(24)	120.6 (9)	C(23)—C(24)—C(25)	120.0 (8)
C(24)—C(25)—C(26)	120.8 (8)	C(21)—C(26)—C(25)	120.2 (8)
O(4)—C(27)—C(28)	108.3 (10)	C(27)—C(28)—C(29)	106.0 (17)
C(28)—C(29)—C(30)	109.7 (17)	O(4)—C(30)—C(29)	107.6 (9)
O(1)—Li—O(3)	115.2 (7)	O(1)—Li—O(4)	100.9 (6)
O(3)—Li—O(4)	105.3 (6)	O(1)—Li—O(2a)	110.6 (6)
O(3)—Li—O(2a)	109.9 (6)	O(4)—Li—O(2a)	114.7 (7)

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## Structure of Dicarboxyl( $\eta^5$ -pentamethylcyclopentadienyl)iridium

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**Abstract.**  $[\text{Ir}(\text{CO})_2(\text{C}_{10}\text{H}_{15})]$ ,  $M_r = 383.45$ , monoclinic,  $P2_1/n$ ,  $a = 7.692(2)$ ,  $b = 10.565(1)$ ,  $c = 15.057(3)$  Å,  $\beta = 98.99(1)^\circ$ ,  $V = 1208.7(4)$  Å<sup>3</sup>,

multiple bonding therein; for example, it corresponds in length to the aromatic-type bond [1.72(2) Å] in  $[\text{Ph}_3\text{C}_5\text{H}_2\text{P}(\text{OCH}_3)_2]$  (Thewalt, 1969). However, the average P=O distance, 1.475(3) Å, is entirely consistent with the presence of a full double bond. A P—C bond order of more than one would necessitate a P atom with more than five bonds. Furthermore, the average Hg—C distance of 2.108(4) Å is typical of a full single bond. Ylidic ionic contributions undoubtedly contribute to the bond lengths observed in  $[\text{Hg}(\text{Br})\{\text{CH}_2\text{P}(\text{O})\text{Ph}_2\}_2\text{Li}(\text{H}_2\text{O})(\text{C}_4\text{H}_8\text{O})]_2$ .

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form a planar triangular array around the Ir atom; the OC—Ir—CO angle is only 89.0 (2)°.

**Introduction.** The original synthesis (Kang, Moseley & Maitlis, 1969) of Cp\*Ir(CO)<sub>2</sub> (Cp\* =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>) was reported to give a compound with a melting point of 418–421 K and infrared absorptions in the  $\nu$ (CO) region at 1925 and 2000 cm<sup>-1</sup>. Recently, we isolated (Chen, Daniels & Angelici, 1991), as a by-product from the reaction of Cp\*Ir( $\eta^4$ -2,5-dimethylthiophene) with Fe<sub>3</sub>(CO)<sub>12</sub>, a compound with the same composition but a different melting point (383–384 K) and IR spectrum [ $\nu$ (CO)(hexane): 1949, 2018 cm<sup>-1</sup>]. The results in this paper establish that our compound is indeed Cp\*Ir(CO)<sub>2</sub>. More recently a new synthesis of Cp\*Ir(CO)<sub>2</sub> has been described (Ball *et al.*, 1990); the IR spectrum of this compound corresponds closely to that of ours.

**Experimental.** Single crystals of Cp\*Ir(CO)<sub>2</sub> suitable for X-ray diffraction study were obtained by recrystallization from hexane solution at 193 K. A crystal with dimensions 0.55 × 0.25 × 0.15 mm was mounted on the end of a glass fiber and moved to the Enraf-Nonius CAD-4 diffractometer. The unit-cell parameters were initially determined from 25 carefully centered reflections in the range 18 < 2 $\theta$  < 32° using a  $\theta$ -2 $\theta$  scan technique. Following data collection, the cell was redetermined using 25 strong reflections in the range 25 < 2 $\theta$  < 36° and a constrained least-squares refinement. Intensities were measured for 4254 reflections with -9 ≤ *h* ≤ 9, 0 ≤ *k* ≤ 12, -17 ≤ *l* ≤ 17, and 4 < 2 $\theta$  < 50° and were corrected for Lorentz and polarization effects. The intensities of the 251, 241, and 250 reflections were measured every hour and varied by less than 1.2%. An empirical absorption correction was derived from  $\psi$  scans of seven reflections and resulted in minimum and maximum correction factors of 0.724 and 1.00. The averaging of 3819 observed equivalent reflections (*R*<sub>int</sub> = 0.012) gave 2132 unique reflections, of which 1882 were considered observed [*I* > 3 $\sigma$ (*I*)]. The position of the Ir atom was taken from a Patterson map. A subsequent difference Fourier map clearly revealed the Cp\* ligand and the two CO groups.

Parameters refined included the scale factor, a secondary-extinction coefficient (refined value 2.7 × 10<sup>-7</sup>), and all positional and atomic displacement factors for the non-H atoms. H atoms were not included in the calculations. Magnitudes of *F* were used in full-matrix least-squares refinement where the function minimized was  $\sum w(|F_o| - |F_c|)^2$ . The final cycle of refinement gave *R* = 0.018, *wR* = 0.028, and a goodness-of-fit *S* = 1.48, where  $w = 4I/[\sigma^2(I) + 0.0004 I^2]$ . The maximum final shift/e.s.d. = 0.01, and the maximum final difference electron density was

Table 1. Positional parameters and equivalent isotropic atomic displacement coefficients with e.s.d.'s in parentheses

$$B_{\text{eq}} = (1/3) \sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )
Ir	0.13696 (2)	0.28053 (2)	0.11369 (1)	1.453 (4)
O(1)	-0.1384 (5)	0.1161 (4)	0.0079 (3)	4.6 (1)
O(2)	-0.1060 (5)	0.3224 (5)	0.2481 (3)	4.7 (1)
C(1)	-0.0314 (7)	0.1783 (6)	0.0494 (3)	2.8 (1)
C(2)	-0.0130 (7)	0.3074 (6)	0.1964 (4)	2.7 (1)
C(3)	0.3698 (6)	0.2580 (5)	0.0424 (3)	2.0 (1)
C(4)	0.4319 (6)	0.2428 (5)	0.1364 (3)	2.0 (1)
C(5)	0.3965 (6)	0.3585 (5)	0.1787 (3)	2.2 (1)
C(6)	0.3225 (6)	0.4480 (5)	0.1105 (3)	2.2 (1)
C(7)	0.3062 (6)	0.3849 (5)	0.0260 (3)	2.0 (1)
C(8)	0.3869 (7)	0.1591 (5)	-0.0289 (3)	2.6 (1)
C(9)	0.5250 (7)	0.1273 (5)	0.1795 (4)	2.8 (1)
C(10)	0.4490 (8)	0.3917 (6)	0.2774 (3)	3.4 (1)
C(11)	0.2819 (7)	0.5859 (5)	0.1250 (4)	3.3 (1)
C(12)	0.2452 (7)	0.4456 (5)	-0.0642 (3)	2.8 (1)

0.7 (1) e Å<sup>-3</sup>. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were performed on a Digital Equipment Co. MicroVAX II using the CAD-4/SDP programs (Enraf-Nonius, 1985). The final atomic coordinates and temperature factors are given in Table 1.†

**Discussion.** An ORTEP drawing of Cp\*Ir(CO)<sub>2</sub> is shown in Fig. 1. Bond distances and selected bond angles are given in Table 2. The Cp\* ring centroid (RC) and the two carbonyl groups are disposed about the Ir atom in a planar triangular arrangement with the two CO groups at angles of 135.4 (2) and 135.6 (2)° from the Ir—RC vector, the C(1)—Ir—C(2) angle is 89.0 (2)°. In general, the structure is similar to that of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(CO)(PPh<sub>3</sub>) (Bennett, Pratt & Tuggle, 1974). The Ir—C(CO) distances of 1.841 (5) and 1.847 (6) Å are slightly longer than that [1.800 (8) Å] in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(CO)(PPh<sub>3</sub>) but fall in the general range of Ir—CO distances (Orpen *et al.*, 1989). The C—O distances [1.157 (7) and 1.147 (7) Å] in Cp\*Ir(CO)<sub>2</sub> appear to be slightly shorter than that [1.176 (9) Å] in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(CO)(PPh<sub>3</sub>). The longer Ir—C(CO) and shorter C—O distances in Cp\*Ir(CO)<sub>2</sub> suggest that there is less  $\pi$  back-bonding from the Ir to the CO groups in Cp\*Ir(CO)<sub>2</sub> than in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(CO)(PPh<sub>3</sub>). This would result from a lower electron density on the Ir in Cp\*Ir(CO)<sub>2</sub> than in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ir(CO)(PPh<sub>3</sub>). That the Ir atom in Cp\*Ir(CO)<sub>2</sub> is less electron-rich is supported by the lower basicity

† Tables of complete bond angles, least-squares planes, anisotropic thermal parameters, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55863 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0570]

Table 2. Bond distances (Å) and selected bond angles (°) with e.s.d.'s in parentheses

Ir—C(1)	1.841 (5)	C(3)—C(7)	1.435 (7)
Ir—C(2)	1.847 (6)	C(3)—C(8)	1.518 (7)
Ir—C(3)	2.240 (5)	C(4)—C(5)	1.424 (7)
Ir—C(4)	2.276 (5)	C(4)—C(9)	1.509 (7)
Ir—C(5)	2.239 (4)	C(5)—C(6)	1.446 (7)
Ir—C(6)	2.278 (5)	C(5)—C(10)	1.519 (7)
Ir—C(7)	2.278 (5)	C(6)—C(7)	1.424 (7)
O(1)—C(1)	1.157 (7)	C(6)—C(11)	1.513 (8)
O(2)—C(2)	1.147 (7)	C(7)—C(12)	1.509 (7)
C(3)—C(4)	1.431 (7)		
RC*—Ir—C(1)	135.4 (2)	C(3)—C(7)—C(6)	107.7 (4)
RC—Ir—C(2)	135.6 (2)	C(4)—C(3)—C(7)	109.1 (4)
C(1)—Ir—C(2)	89.0 (2)	C(3)—C(4)—C(5)	106.8 (4)
Ir—C(1)—O(1)	178.6 (5)	C(4)—C(5)—C(6)	109.0 (4)
Ir—C(2)—O(2)	179.1 (5)	C(5)—C(6)—C(7)	107.4 (4)

\* RC is the centroid of the pentamethylcyclopentadienyl ring.

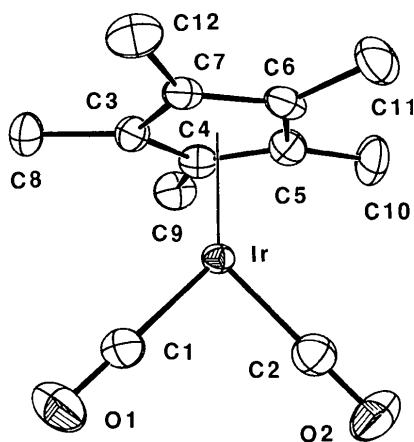


Fig. 1. ORTEP drawing of Cp\*Ir(CO)<sub>2</sub>, with ellipsoids drawn at the 50% probability level.

of the Ir atom in Cp\*Ir(CO)<sub>2</sub> toward protonation by CF<sub>3</sub>SO<sub>3</sub>H as compared with the basicity of (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ir(CO)(PPh<sub>3</sub>) (Sowa, Zanotti, Facchin & Angelici, 1991).

The cyclopentadienyl C atoms [C(3) through C(7)] of the Cp\* ring lie in one plane (± 0.02 Å); the five methyl C atoms are an average of 0.10 Å out of this plane away from the Ir atom. The perpendicular distance from the Ir atom to the Cp\* ring plane is 1.906 (5) Å. The plane of the Cp\* ring is essentially perpendicular [89.1 (2)°] to the plane defined by O(1)—C(1)—Ir—C(2)—O(2).

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## Structure of *cis*-(1,2-Ethanediamine)(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate

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**Abstract.** *cis*-(1,2-Ethanediamine-κ<sup>2</sup>N,N')(1,4,8,11-tetraazacyclotetradecane-κ<sup>4</sup>N,N',N'',N''')chromium(III) triperchlorate, [Cr(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)(C<sub>10</sub>H<sub>24</sub>N<sub>4</sub>)](ClO<sub>4</sub>)<sub>3</sub>, *M<sub>r</sub>* = 610.77, orthorhombic, *Pbna* (non-standard setting of *Pbcn*), *a* = 12.145 (2), *b* =

13.832 (3), *c* = 14.624 (4) Å, *V* = 2456.8 Å<sup>3</sup>, *Z* = 8 (half molecules), *D<sub>m</sub>* = 1.643, *D<sub>x</sub>* = 1.651 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71069 Å, μ = 8.47 cm<sup>-1</sup>, *F*(000) = 1172, *T* = 293 K, *R* = 0.073 for 1635 independent observed reflections. When coordinated to Cr<sup>III</sup> in a *cis* configuration, the cyclam ligand (1,4,8,11-tetraazacyclotetradecane) adopts the *RRRR* and

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