

cules (4), (5) and (7)]; however, the carboxyl oxygen involved in the chelate ring may also be bonded to the barium cation [molecule (3)]; both carboxyl oxygens may be bonded to the same barium [molecule (1)], to two different bariums [molecules (2) and (6)], or to the barium and the other neodymium ion [molecule (8)]. There is a pair of intramolecular hydrogen bonds in the complex molecule (represented by dashed lines in Fig. 1). The structure is held together by an elaborate network of intermolecular hydrogen bonds. The crystal packing is shown in Fig. 2 (the disordered waters OW8, OW9, OW10 and OW11 have been omitted for the sake of clarity).

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## Carbonyl( $\eta^5$ -cyclopentadienyl)bis(trimethyl phosphite)ruthenium(II) Tetrafluoroborate

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**Abstract.** [Ru(CO){P(OCH<sub>3</sub>)<sub>3</sub>}<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)] [BF<sub>4</sub>],  $M_r = 529.13$ , monoclinic,  $P2_1/c$ ,  $a = 11.455$  (2),  $b = 11.648$  (4),  $c = 15.709$  (2) Å,  $\beta = 99.40$  (1)°,  $V = 2067.87$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.700$  g cm<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 9.577$  cm<sup>-1</sup>,  $F(000) = 1064$ ,  $T = 296$  K,  $R = 0.039$  for 2941 observed reflections. The crystal structure of the title compound consists of discrete [Ru(CO){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)]<sup>+</sup> cations and [BF<sub>4</sub>]<sup>-</sup> anions. The cation displays a typical 'three-legged piano stool' geometry about ruthenium with significant distances Ru—P1 2.258 (1), Ru—P2 2.260 (1), Ru—C1 1.880 (6), C1—O1 1.115 (6) Å, and angles Ru—C1—O1 176.9 (5), C1—Ru—P1 90.3 (2), C1—Ru—P2 89.8 (2) and P1—Ru—P2 92.2 (1)°.

**Introduction.** The [Ru(L)(PR<sub>3</sub>)<sub>2</sub>(Cp)] system is extensively studied, particularly for  $L = PPh_3$  because the starting material [RuCl(PPh<sub>3</sub>)<sub>2</sub>(Cp)] is easily synthesized and handled (Bruce, Hameister, Swincer, Wallis & Ittel, 1982) and both its chloride and phosphine ligands are substitutionally labile (Albers, Robinson & Singleton, 1987). We are interested in the chemistry of [Ru(L)(PR<sub>3</sub>)<sub>2</sub>(Cp)] complexes with smaller ancillary phosphines such as trimethyl phosphite (Ashby, Bruce, Tomkins & Wallis, 1979; Bruce, Cifuentes, Snow & Tiekink, 1989; Treichel, Komar & Vincenti, 1984). We recently obtained single crystals of [Ru(CO){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)] [BF<sub>4</sub>]

(I) during attempted slow recrystallization of [Ru(C<sub>2</sub>H<sub>2</sub>){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)] [BF<sub>4</sub>], evidently *via* the oxidation of the C<sub>2</sub>H<sub>2</sub> ligand by traces of air (Bruce, Swincer & Wallis, 1979). Compound (I) has not previously been reported.

**Experimental.** [Ru(CO){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)] [BF<sub>4</sub>] (I) was prepared and crystallized by passing a stream of nitrogen gas saturated with diethyl ether over [Ru( $\eta^2$ -HC≡CH){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)] [BF<sub>4</sub>] (Frank & Selegue, 1990) dissolved in a minimum of dichloromethane. A 0.42 × 0.47 × 0.53 mm crystal suitable for X-ray diffraction was cut from one of the resulting large, pale yellow crystals. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  2022 vs,  $\nu(\text{BF})$  1094 vs cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  4.43 (*t*, <sup>3</sup> $J_{\text{PH}} = 1.0$  Hz, 5 H, Cp), 3.53 (virtual *t*, <sup>3</sup> $J_{\text{PH}} + ^5J_{\text{PH}} = 5.3$  Hz, 18 H, POCH<sub>3</sub>). Data were measured with an Enraf-Nonius CAD-4 diffractometer controlled by a MicroVAX computer, graphite-monochromated Mo  $K\alpha$  radiation;  $\omega$ - $2\theta$  scan technique. Cell parameters were determined by least-squares refinement of 25 reflections ( $6 < \theta < 16^\circ$ ). A total of 3989 reflections ( $2 < \theta < 25^\circ$ ) were measured in the range  $-13 \leq h \leq 13$ ,  $0 \leq k \leq 13$ ,  $0 \leq l \leq 18$ . Minor variation (max. 13%) was noted in the net intensities of three reference reflections (135, 137, 133) measured every 5000 s. Of 3773 unique reflections, 2941 satisfied  $I \geq 3\sigma(I)$ . An empirical absorption correction was applied using

Table 1. Positional parameters and equivalent isotropic *B* values for the non-hydrogen atoms of [Ru(CO){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)][BF<sub>4</sub>] (I)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>eq</sub> (Å <sup>2</sup> )*
Ru	0.20350 (3)	-0.01295 (3)	-0.25126 (2)	3.19 (1)
P1	0.1573 (1)	0.0256 (1)	-0.11988 (8)	3.36 (2)
P2	0.3922 (1)	0.0465 (1)	-0.2107 (1)	3.89 (4)
F1	0.2285 (9)	0.0482 (6)	0.4551 (6)	18.5 (4)
F2	0.1316 (5)	-0.0909 (6)	0.4032 (4)	13.2 (3)
F3	0.3207 (5)	-0.1019 (5)	0.4559 (4)	12.2 (2)
F4	0.2584 (7)	-0.0138 (9)	0.3342 (4)	20.7 (5)
O1	0.1319 (4)	0.2239 (4)	-0.3130 (3)	6.8 (2)
O2	0.0322 (3)	-0.0211 (3)	-0.1038 (2)	4.2 (1)
O3	0.1565 (3)	0.1583 (3)	-0.0989 (2)	4.2 (1)
O4	0.2357 (4)	-0.0248 (3)	-0.0358 (2)	4.7 (1)
O5	0.4750 (3)	-0.0609 (3)	-0.1941 (3)	5.5 (1)
O6	0.4313 (3)	0.1182 (3)	-0.1254 (3)	5.4 (1)
O7	0.4470 (3)	0.1274 (4)	-0.2749 (3)	5.8 (1)
C1	0.1599 (5)	0.1369 (5)	-0.2879 (4)	4.3 (2)
C2	-0.0750 (5)	0.0232 (5)	-0.1538 (5)	5.7 (2)
C3	0.1327 (6)	0.1990 (5)	-0.0167 (4)	5.4 (2)
C4	0.2761 (7)	-0.1369 (6)	-0.0292 (4)	7.5 (3)
C5	0.6038 (6)	-0.0510 (8)	-0.1700 (6)	8.4 (3)
C6	0.4191 (6)	0.2391 (6)	-0.1203 (5)	7.2 (2)
C7	0.4363 (6)	0.1047 (7)	-0.3652 (4)	7.0 (2)
Cp1	0.0578 (5)	-0.1298 (5)	-0.3134 (4)	5.3 (2)
Cp2	0.1317 (6)	-0.1938 (5)	-0.2503 (4)	5.7 (2)
Cp3	0.2446 (6)	-0.1984 (5)	-0.2721 (5)	5.7 (2)
Cp4	0.2413 (6)	-0.1381 (6)	-0.3511 (5)	6.2 (2)
Cp5	0.1261 (7)	-0.0979 (6)	-0.3758 (4)	6.2 (2)
B	0.2376 (8)	-0.0380 (7)	0.4077 (5)	5.8 (2)

\*The equivalent isotropic displacement parameter is defined as (4/3) Tr(β·G), where β<sub>ij</sub> = 2π<sup>2</sup>a<sub>i</sub>\*a<sub>j</sub>\*U<sub>ij</sub> and G<sub>ij</sub> = a<sub>i</sub>·a<sub>j</sub>, where a<sub>i</sub> and a<sub>j</sub> are basis vectors in direct space.

Table 2. Selected bond distances (Å) and angles (°) with e.s.d.'s

Ru—C1	1.880 (6)	C1—Ru—P1	90.3 (2)
Ru—Cp0*	1.904 (6)	C1—Ru—P2	89.8 (2)
Ru—P1	2.258 (1)	P1—Ru—P2	92.2 (1)
Ru—P2	2.260 (1)	C1—Ru—Cp0*	126.8 (3)
C1—O1	1.115 (6)	Cp0*—Ru—P1	123.4 (2)
P—O	1.581 (7)††	Cp0*—Ru—P2	124.1 (2)
C—O	1.43 (2)††	Ru—C1—O1	176.9 (5)
Cp—Cp	1.40 (1)†§	O—P—O	120 (3)††
B—F	1.30 (5)†	Ru—P—O	116 (4)†
		P—O—C	122 (1)††
		Cp—Cp—Cp	108.0 (9)†§
		F—B—F	109 (5)†

\*Cp0 is the centroid of the Cp1—Cp5 cyclopentadienyl ring.

†Average value reported with σ<sub>n</sub>.

‡Phosphite ligands.

§Cp represents any cyclopentadienyl carbon atom.

CAMEL (Flack, 1977) with correction factors: max. 1.50, min. 1.29, av. 1.34; no extinction correction was made. Scattering factors for Ru, P and F were corrected for *f*' and *f*'' (Cromer & Waber, 1974). All calculations were made using an IBM 3084 computer system. The ruthenium atom was located using Patterson methods and the remaining non-hydrogen atoms by using DIRDIF (Beurskens *et al.*, 1984). Full-matrix least-squares refinement on *F* magnitudes with weights  $w = 4I/[\sigma^2(I)]$ , where  $[\sigma^2(I)]$  included a term (0.02I)<sup>2</sup>. Anisotropic thermal parameters were refined for all non-hydrogen atoms. One

hydrogen atom on each of six methyl groups was located in a difference Fourier map, and all remaining hydrogens were placed in idealized positions with  $d(C-H) = 1.00$  Å and  $B(H) = B_{eq}$  (attached C) + 1.00. Hydrogen positions and thermal parameters were subsequently adjusted after each two least-squares cycles of refinement. At convergence,  $R = 0.039$ ,  $wR = 0.053$  for 244 variables,  $S = 3.11$ ,  $(\Delta/\sigma)_{max} = -0.17$  for β(2,2) of F4,  $(\Delta\rho)_{max} = 0.09$  e Å<sup>-3</sup> near BF<sub>4</sub><sup>-</sup>. Atomic parameters are listed in Table 1, and selected bond distances and angles are in Table 2. An ORTEP (Johnson, 1976) plot with the numbering scheme is shown in Fig. 1.\*

**Discussion.** The structure of (I) consists of well separated [Ru(CO){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)]<sup>+</sup> cations and [BF<sub>4</sub>]<sup>-</sup> anions. Bonding distances and angles in the cation are typical of an [RuL<sub>3</sub>(Cp)] 'piano-stool' or pseudooctahedral structure (Bruce, Humphrey, Snow & Tiekink, 1986), with L—Ru—L 'basal' angles averaging 91 (1)° (Table 2). The [BF<sub>4</sub>]<sup>-</sup> ion is reasonably well ordered.

The ruthenium to trimethyl phosphite distances in (I), 2.258 (1) and 2.260 (1) Å, fall in the middle of the range of Ru—P distances for 23 Ru—{P(OMe)<sub>3</sub>} structures in the Cambridge Crystallographic Database, 2.18 to 2.35 Å. In particular, the Ru—P distances are very slightly longer than those in [RuCl{P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)] [2.199 (3) and 2.234 (2) Å]

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, further bond distances and angles, least-squares-plane data and intermolecular distances less than 2.6 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53306 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

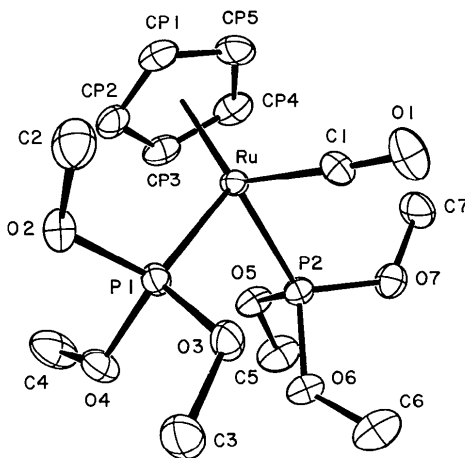


Fig. 1. ORTEP drawing (Johnson, 1976) of the [Ru(CO){P(OMe)<sub>3</sub>}<sub>2</sub>(Cp)]<sup>+</sup> cation showing the numbering system. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacements.

and two isomers of  $[\text{Ru}\{\text{C}=\text{C}(\text{CN})_2\text{CPh}=\text{C}(\text{CN})_2\}\{\text{P}(\text{OMe})_3\}_2(\text{Cp})]$  [2·231 (1) to 2·238 (2) Å; Bruce, Cifuentes, Snow & Tiekink, 1989]. This slight lengthening may be due to effective competition for  $\pi$ -backbonding electron density by the carbonyl ligand in (I).

The Ru—Cl bond distance of 1·880 (6) Å in (I) falls within the range of Ru—CO distances of 1·869 (2) Å for  $[\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{Cp})][\text{BPh}_4]$  (II; Wisner, Bartczak & Ibers, 1985), 1·890 (2) Å for  $[\text{Ru}(\text{CO})(\text{PPh}_3)_2(\text{Cp})][\text{Co}(\text{CO})_4]$  (III; Doyle & Van Engen, 1985) and 1·863 (3) Å for  $[\text{Ru}(\text{CO})(\text{PPh}_3)_2(\eta^5\text{-indenyl})][\text{ClO}_4]\cdot\text{CH}_2\text{Cl}_2$  (IV; Oro, Ciriano, Campo, Foces-Foces & Cano, 1985). Similarly, the C—O bond distance for (I), 1·115 (6) Å, does not differ significantly from the values of 1·144 (3), 1·135 (3) and 1·145 (4) Å found respectively in structures (II)–(IV). This is not surprising, as metal-carbon and carbon-oxygen distances in metal carbonyl compounds are notoriously insensitive to changes in ancillary ligands. The carbonyl stretching frequencies in the infrared spectra are better indicators of electron density available for backbonding at ruthenium, being 2022, 1987, 1978 and 1970  $\text{cm}^{-1}$  for compounds (I)–(IV), respectively.

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## Structure of (+)-(3*S*,4*R*,5*R*,1'*R*,2'*S*,5'*R*)-Tetracarbonyl{(3,4- $\eta^2$ )-5-[5'-methyl-2'-(1-methylethyl)cyclohexyloxy]-2(5*H*)-furanone}iron

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**Abstract.**  $\text{C}_{18}\text{H}_{22}\text{FeO}_7$ ,  $M_r = 406.2$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.4633$  (3),  $b = 10.7995$  (7),  $c =$

$28.056$  (1) Å,  $V = 1958.3$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.38$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 8.00$  cm<sup>-1</sup>,  $F(000) = 848$ ,  $T = 293$  K,  $R = 0.030$  for 3655 observed reflections, crystals obtained from hexane.

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