Structure of
Carbonyl[(ferrocenecarbonyl)trifluoroacetonato-κO,κO]triphenylphosphinerhodium(I)
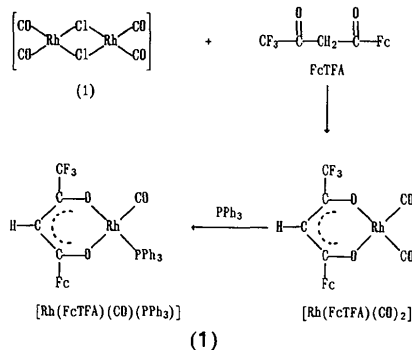
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Abstract. [Rh($C_{14}H_{10}F_3FeO_2$)(CO){P(C_6H_5)$_3$}], $M_r =$ 716.28, triclinic, $P\bar{1}$, $a = 10.439$ (2), $b = 12.605$ (1), $c = 13.307$ (1) Å, $\alpha = 107.77$ (1), $\beta = 100.45$ (1), $\gamma = 107.76$ (1)°, $V = 1513.5$ (4) Å^3, $Z = 2$, $D_m = 1.57$, $D_x = 1.52$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 11.17$ cm^{-1}, $F(000) = 720$, $T = 298$ K, final $R = 0.045$ for 6083 observed reflections. The title complex has a square-planar geometry about the Rh atom. The structure determination shows that the complex is formed by triphenylphosphine substitution of the carbonyl group *trans* to the O atom nearest to the more electronegative CF$_3$ group (relative to the ferrocenyl group). This result is not in agreement with the expected *trans* influence of the two O atoms of the chelate ring; this may be explained in terms of the steric hindrance of the more bulky ferrocenyl group.

Experimental. The title complex was prepared as shown in the scheme below. An equivalent amount of FcTFA (Weinmayr, 1958) was added to (1)

(1)

(Rusina & Vlcek, 1965) dissolved in dimethylformamide. Cold water was added to precipitate [Rh(FcTFA)(CO)$_2$] which was extracted with *n*-hexane. The *n*-hexane solution was dried with CaCl$_2$, filtered and allowed to evaporate to dryness. 0.072 g of triphenylphosphine in 20 cm^3 *n*-hexane was added to 0.039 g of [Rh(FcTFA)(CO)]$_2$ in 10 cm^3 *n*-hexane.

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Rh	2093.5 (3)	3117.7 (3)	858.9 (3)	43.31 (7)
Fe	7035.5 (6)	6926.9 (1)	4045.9 (1)	45.8 (1)
P	3176.1 (10)	1860.1 (8)	334.6 (9)	39.3 (2)
O(1)	3825 (3)	4066 (2)	2235 (2)	49 (1)
O(2)	1175 (3)	4287 (3)	1546 (3)	58 (1)
C(51)	2223 (4)	382 (3)	−801 (3)	42 (1)
C(1)	4030 (4)	4978 (3)	3079 (3)	45 (1)
C(31)	4753 (4)	2489 (3)	−31 (3)	41 (1)
C(5)	626 (5)	2296 (4)	−392 (4)	56 (1)
C(15)	6564 (5)	5150 (4)	3781 (4)	51 (1)
O(3)	−309 (4)	1803 (4)	−1189 (3)	83 (1)
C(3)	1729 (5)	5112 (4)	2504 (4)	54 (1)
C(32)	5325 (5)	1760 (4)	−653 (4)	51 (1)
C(36)	5425 (5)	3738 (4)	333 (4)	54 (1)
C(12)	5865 (5)	6422 (2)	5003 (4)	54 (1)
C(11)	5401 (4)	5480 (3)	3929 (3)	46 (1)
C(41)	3772 (4)	1498 (3)	1517 (3)	43 (1)
C(56)	1700 (5)	327 (4)	−1851 (4)	60 (1)
C(53)	1340 (5)	−1793 (4)	−1526 (4)	61 (1)
C(33)	6552 (5)	2269 (5)	−897 (4)	60 (1)
C(43)	3150 (7)	686 (5)	2863 (4)	73 (1)
C(42)	2766 (5)	1019 (4)	1986 (4)	56 (1)
C(2)	3027 (5)	5499 (4)	3250 (4)	55 (1)
C(14)	7726 (5)	5884 (4)	4751 (4)	56 (1)
C(54)	829 (5)	−1837 (4)	−2567 (5)	70 (1)
C(46)	5167 (5)	1664 (4)	1950 (4)	56 (1)
C(44)	4530 (7)	851 (5)	3282 (4)	76 (2)
C(13)	7292 (5)	6659 (4)	5505 (4)	56 (1)
C(52)	2042 (5)	−689 (3)	−651 (4)	50 (1)
C(34)	7210 (5)	3500 (5)	−516 (4)	60 (1)
C(35)	6658 (5)	4231 (4)	94 (4)	62 (1)
F(3)	−366 (5)	5022 (5)	2901 (6)	169 (2)
C(45)	5530 (7)	1345 (5)	2840 (5)	75 (1)
C(23)	8097 (7)	8706 (4)	4376 (5)	75 (1)
C(22)	6686 (6)	8318 (5)	3758 (6)	78 (2)
F(2)	283 (6)	6126 (6)	2117 (5)	166 (2)
F(1)	1269 (5)	6632 (5)	3770 (5)	191 (2)
C(25)	7687 (7)	7190 (5)	2769 (5)	73 (1)
C(55)	1005 (5)	−783 (5)	−2736 (4)	72 (1)
C(4)	759 (6)	5742 (6)	2841 (6)	82 (2)
C(24)	8706 (6)	8009 (5)	3759 (5)	72 (1)
C(21)	6442 (6)	7372 (6)	2752 (5)	82 (2)

Crystals of the title compound [Rh(FcTFA)(CO)(PPh$_3$)] were then obtained by slowly cooling the reaction mixture. The density was determined by flotation in sodium iodide solution. A crystal of dimensions 0.25 × 0.15 × 0.30 mm was used for data collection on an Enraf–Nonius CAD-4F diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The $\omega/2\theta$-scan technique was used with variable scan width $\Delta\omega = (0.43 + 0.34\tan\theta)°$, scan speed 5.49° min^{-1} in ω and a maximum scan time of

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

Rh—P	2.232 (1)	Rh—O(1)	2.048 (3)
Rh—O(2)	2.070 (3)	Rh—C(5)	1.801 (5)
Fe—C(12)	2.027 (4)	Fe—C(11)	2.023 (4)
Fe—C(14)	2.052 (5)	Fe—C(23)	2.039 (5)
Fe—C(21)	2.020 (5)	O(1)—C(1)	1.266 (5)
O(2)—C(3)	1.264 (5)	C(1)—C(11)	1.467 (6)
C(1)—C(2)	1.413 (5)	C(5)—O(3)	1.147 (5)
C(3)—C(2)	1.368 (6)	C(3)—C(4)	1.515 (6)
C(12)—C(11)	1.432 (6)	F(3)—C(4)	1.280 (7)
F(2)—C(4)	1.295 (8)	F(1)—C(4)	1.273 (7)

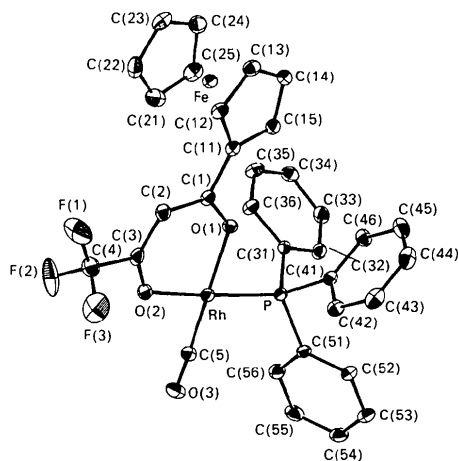|			
P—Rh—O(1)	85.9 (1)	P—Rh—O(2)	172.7 (1)
O(1)—Rh—O(2)	88.6 (1)	P—Rh—C(5)	92.7 (1)
O(1)—Rh—C(5)	177.2 (2)	O(2)—Rh—C(5)	92.9 (2)
Rh—O(1)—C(1)	128.5 (3)	Rh—O(2)—C(3)	123.7 (3)
O(1)—C(1)—C(11)	116.0 (3)	O(1)—C(1)—C(2)	124.3 (4)
C(11)—C(1)—C(2)	119.7 (4)	Rh—C(5)—O(3)	178.1 (4)
O(2)—C(3)—C(2)	130.3 (4)	O(2)—C(3)—C(4)	112.4 (4)
C(2)—C(3)—C(4)	117.3 (5)	C(1)—C(11)—C(12)	128.0 (4)
C(1)—C(2)—C(3)	124.3 (4)	C(3)—C(4)—F(3)	112.0 (5)
C(3)—C(4)—F(2)	112.8 (5)		

Fig. 1. Perspective view of the molecule showing atom labelling (H atoms omitted for clarity).

60 s per reflection. The unit-cell parameters were determined from least-squares refinement of 25 reflections with $6 < \theta < 18°$ (total measuring range 3 $< \theta < 30°$). Empirical absorption corrections (North, Phillips & Matthews, 1968) were applied with minimum and maximum correction factors of 0.94 and 1.00 respectively. The mean intensity of three standard reflections, measured over 7200 s of X-ray exposure time, varied from the initial value by $< -1\%$. All possible reflections with $(\sin\theta)/\lambda <$ 0.70 Å^{-1} in the range $0 < h < 14$, $-17 < k < 17$, $-18 < l < 18$ were measured, giving 7733 unique reflections of which 6083 were considered observed $[I > 3.0\sigma(I)]$. The structure was solved by the heavy-atom method using *SHELXS*86 (Sheldrick, 1990) and was subjected to anisotropic full-matrix least-squares refinement on F (a total of 380 parameters refined) using *SHELX*76 (Sheldrick, 1976). The H-atom positions were calculated riding on the adjacent C atoms assuming C—H = 1.08 Å, and were

refined with an overall temperature factor. Neutral-atom scattering factors were taken from Cromer & Mann (1968) and anomalous-dispersion corrections for rhodium from *International Tables for X-ray Crystallography* (1962, Vol. III, p. 216). Final $R =$ 0.045 and $wR = 0.044$ (unit weights), $(\Delta\rho)_{max} = 0.66$, $(\Delta\rho)_{min} = -0.41 \text{ e Å}^{-3}$ and $(\Delta/\sigma)_{max} = 0.35$. S was not calculated.

The final fractional coordinates are given in Table 1 and selected geometrical parameters in Table 2.* Fig. 1 shows a perspective view of the molecule (Johnson, 1976) with atomic labels.

Related literature. The present structure shows that the carbonyl group *trans* to the O atom nearest to the more electronegative CF_3 group is substituted by PPh_3. This result, which is not in agreement with polarization theory (Grinberg, 1935), is explained (Steynberg, Lamprecht & Leipoldt, 1987) in terms of the relative sizes of the substituents of the β-diketone. Dominance of the electronic effects by steric hindrance was also observed in trifluoro-2,4-hexanedionatocarbonyltriphenylphosphinerhodium(I) (Steynberg, Lamprecht & Leipoldt, 1987), trifluoro(5,5-dimethylpentanedionato)(carbonyl)-(phosphine)rhodium(I) (Leipoldt, Basson & Nel, 1983) and trifluoro(5,5,5-trimethylpentanedionato)-(carbonyl)(triphenylphosphine)rhodium(I) (Leipoldt, Basson & Potgieter, 1986). The cyclopentadienyl rings are planar within experimental error, and are almost parallel [dihedral angle 1.8 (9)°]; the average angle of deviation from a fully eclipsed conformation is 8.7°.

* Lists of least-squares planes and deviations, anisotropic thermal parameters, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55232 (37 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL0523]

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Structure du *trans*-Dichlorobis(pyridine)palladium(II)

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Abstract. [PdCl$_2$(C$_5$H$_5$N)$_2$], M_r = 335.51, monoclinic, C2/c, a = 8.774 (1), b = 15.474 (2), c = 8.635 (1) Å, β = 90.56 (1)°, V = 1172.3 (3) Å^3, Z = 4, D_m = 1.87 (3), D_x = 1.90 Mg m^{-3}, λ(Mo Kα) = 0.7107 Å, μ = 1.991 mm^{-1}, F(000) = 656, T = 295 (1) K, final R = 0.033 for 1086 independent observed reflections. The title compound exhibits twofold internal geometry: the Pd atom, and the N(1), C(3), N(2) and C(6) atoms of two independent pyridine molecules lie on the binary axis. The complex consists of discrete molecules with Pd showing the usual square-planar coordination with two Cl atoms at 2.297 (1) Å, and two N atoms of the pyridine molecules at 2.024 (6) Å (av.). The Pd atoms are spaced at intervals of 5.835 (1) Å. The two pyridine molecules, defined by the P1 mean plane [atoms N(1), C(1), C(2) and C(3)] and the P2 mean plane [atoms N(2), C(4), C(5) and C(6)], make a dihedral angle of 160.0 (5)°. These mean planes make dihedral angles with the P3 mean plane [defined by the atoms N(1), N(2), Pd and Cl] of 131.9 (3) and 68.1 (3)°, respectively.

Partie expérimentale. Les cristaux du composé cité en titre été obtenus lors d'un essai de synthèse d'un complexe du Pd^{II} avec le ténonitrozole en présence de pyridine. Masse volumique par flottaison. Cristal parallélépipédique: 0,22 × 0,30 × 0,38 mm. Diffractomètre Enraf–Nonius CAD-4. Dimensions de la maille déterminées sur monocristal avec 25 réflexions telles que 5 ≤ θ ≤ 22°. 0,024 ≤ (sinθ)/λ ≤ 0,703 Å^{-1}.

Balayage $\theta/2\theta$ d'amplitude s = (0,8 + 0,35tgθ)°. − 12 ≤ h ≤ 12, 0 ≤ k ≤ 21, 0 ≤ l ≤ 12. Réflexions de contrôle de l'intensité: 463 et 332. Variation des intensités de contrôle < 1%. 1713 réflexions indépendantes mesurées, 627 indépendantes inobservées [I ≤ 3σ(I)]. R_{int} = 0,023. Résolution de la structure: méthodes directes à l'aide de *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Affinement basé sur les F à l'aide du programme *CRYSTALS* (Watkin, Carruthers & Betteridge, 1988). Coordonnées des H: série de Fourier des ΔF. Facteurs de diffusion des *International Tables for X-ray Crystallography* (1974, Tome IV). Paramètres affinés: x, y, z de tous les atomes; U_{ij} de Pd, Cl, N et C; U_{iso} général initialement affecté aux atomes H. Corrections d'absorption (valeurs maxima et minima: 1,046 et 0,95) à l'aide du programme *DIFABS* (Walker & Stuart,
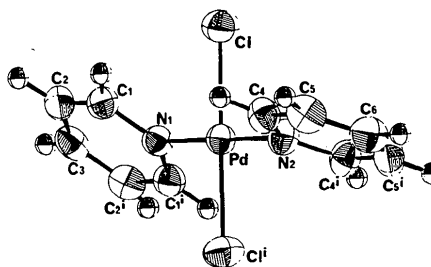

Fig. 1. Vue en perspective de la molécule et numérotation des atomes.