

***trans*-Carbonylchlorobis[tris(*p*-fluorophenyl)phosphine]rhodium(I),
[Rh(C₁₈H₁₂F₃P)₂(CO)Cl]**

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Abstract. $M_r = 798.9$, triclinic, $P\bar{1}$, $a = 9.933$ (1), $b = 12.194$ (3), $c = 14.535$ (3) Å, $\alpha = 90.26$ (2), $\beta = 90.96$ (2), $\gamma = 103.64$ (2)°, $V = 1710.4$ (6) Å³, $Z = 2$, $D_x = 1.55$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.772$ mm⁻¹, $T = 295$ K, $F(000) = 800$, $R = 0.037$ for 5044 observed reflexions. The Rh atom exhibits a planar configuration, with the Cl atom and the CO group in *trans* positions.

Introduction. Rhodium catalysts formed *in situ* from [RhCl(diolefin)]₂ and phosphines have been used for the hydrogenation (Marko & Heil, 1974; Nagy-Magos, Vastag, Heil & Marko, 1978) and hydroformylation (Oro, Manrique & Royo, 1978) of olefins. The catalytic activity is determined by the electronic and steric effects of the phosphine ligand.

We have observed that the addition of P(*p*-FC₆H₄)₃ and [RhCl(nbd)]₂ (Rh:P 1:2) to methanol results in the formation of an orange substance of composition RhCl(nbd)[P(*p*-FC₆H₄)₃]₂ which corresponds to that found by Oro & Heras (1979) employing P(*p*-ClC₆H₄)₃ as ligand (nbd is norbornadiene).

The reaction of RhCl(nbd)[P(*p*-FC₆H₄)₃]₂ with MeOH yields a new compound, whose structure we now report.

Experimental. Yellow crystal, Enraf–Nonius CAD-4 diffractometer; cell dimensions refined by least-squares fit to the θ values of 25 reflexions; 11016 reflexions within $1 < \theta < 32^\circ$ collected at 295 K, monochromatic Mo $K\alpha$ radiation, $\omega/2\theta$ scans; two reflexions monitored periodically showed no crystal decomposition; Lorentz–polarization corrections, 5044 I considered observed [$I > 2\sigma(I)$], no absorption corrections; scattering factors for neutral atoms and anomalous-dispersion corrections for Rh, Cl and P from *International tables for X-ray Crystallography* (1974); structure solved by Patterson and Fourier methods; following anisotropic full-matrix least-squares refinement, minimizing $\sum w|F_o - |F_c||^2$, with unit weights, a difference synthesis calculated with reflexions having $\sin \theta/\lambda < 0.5$ Å⁻¹ showed all H atoms as the highest peaks of the map; final refinement with isotropic temperature factors for H atoms gave $R = 0.037$.

Discussion. The final positional parameters are listed in Table 1.* The present study has confirmed the formation of a new compound, namely Rh(CO)Cl[P(*p*-FC₆H₄)₃]₂.

* Lists of structure factors, anisotropic thermal parameters and bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38307 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and isotropic thermal parameters

For non-hydrogen atoms $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ (Å² × 10⁴). For H atoms U_{iso} values (Å² × 10²) are listed.

	x	y	z	U_{eq}/U_{iso}
O	0.01849 (42)	0.80576 (34)	0.31582 (30)	786 (17)
C	0.11784 (50)	0.84827 (39)	0.27805 (35)	492 (17)
Rh	0.27754 (4)	0.91177 (3)	0.22240 (3)	354 (1)
Cl	0.49834 (12)	0.98816 (10)	0.15800 (9)	485 (4)
P(1)	0.22456 (12)	1.08776 (9)	0.23488 (8)	386 (4)
P(2)	0.32477 (12)	0.73567 (9)	0.21071 (8)	373 (4)
C(11)	0.06709 (44)	1.08542 (35)	0.29847 (30)	402 (14)
C(12)	0.07153 (49)	1.12159 (41)	0.38924 (33)	498 (17)
C(13)	-0.04871 (61)	1.10957 (49)	0.43947 (41)	602 (22)
C(14)	-0.17125 (54)	1.06277 (44)	0.39751 (42)	573 (20)
C(15)	-0.18346 (55)	1.02629 (52)	0.30835 (45)	659 (23)
C(16)	-0.06244 (54)	1.03797 (49)	0.25917 (41)	582 (21)
F(11)	-0.29008 (34)	1.05080 (30)	0.44631 (26)	843 (15)
C(17)	0.19126 (47)	1.14933 (37)	0.12443 (32)	441 (16)
C(18)	0.10159 (65)	1.22081 (52)	0.11585 (41)	664 (24)
C(19)	0.07865 (72)	1.26597 (60)	0.03121 (47)	799 (29)
C(110)	0.14675 (65)	1.23795 (54)	-0.04330 (41)	699 (24)
C(111)	0.23593 (63)	1.16961 (56)	-0.03826 (40)	681 (25)
C(112)	0.25865 (53)	1.12431 (45)	0.04667 (35)	540 (19)
F(12)	0.12279 (44)	1.28284 (39)	-0.12577 (25)	1067 (20)
C(113)	0.35445 (45)	1.19750 (35)	0.29433 (30)	412 (15)
C(114)	0.33734 (55)	1.30756 (40)	0.30395 (39)	544 (19)
C(115)	0.43215 (60)	1.38825 (42)	0.35354 (42)	609 (21)
C(116)	0.54453 (52)	1.35813 (40)	0.39166 (34)	518 (17)
C(117)	0.56779 (52)	1.25276 (43)	0.38282 (37)	555 (19)
C(118)	0.47051 (49)	1.17231 (40)	0.33434 (35)	472 (17)
F(13)	0.63709 (35)	1.43706 (25)	0.44192 (24)	772 (13)
C(21)	0.48306 (44)	0.72945 (34)	0.27370 (30)	392 (14)
C(22)	0.51027 (53)	0.78829 (43)	0.35659 (35)	519 (18)
C(23)	0.61905 (55)	0.77736 (46)	0.41291 (36)	564 (20)
C(24)	0.70167 (47)	0.70911 (41)	0.38533 (33)	490 (17)
C(25)	0.68258 (53)	0.65361 (45)	0.30266 (36)	527 (19)
C(26)	0.57242 (52)	0.66388 (42)	0.24681 (34)	483 (17)
F(22)	0.36848 (42)	0.57436 (31)	-0.17149 (22)	897 (16)
C(27)	0.34070 (45)	0.68502 (35)	0.09347 (31)	415 (15)
C(28)	0.35355 (57)	0.75944 (42)	0.01996 (34)	532 (19)
C(29)	0.36497 (63)	0.72297 (47)	-0.06924 (37)	604 (21)
C(210)	0.35969 (55)	0.61127 (48)	-0.08383 (36)	591 (20)
C(211)	0.34538 (60)	0.53420 (46)	-0.01506 (40)	615 (21)
C(212)	0.33549 (57)	0.57194 (42)	0.07510 (38)	543 (19)
F(21)	0.80638 (30)	0.69492 (27)	0.44246 (21)	668 (12)
C(213)	0.19668 (45)	0.61782 (35)	0.26027 (33)	441 (15)
C(214)	0.20971 (55)	0.58368 (45)	0.35042 (39)	562 (19)

Table 1 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}/U_{iso}</i>
C(215)	0.10970 (65)	0.49708 (53)	0.38850 (52)	726 (26)
C(216)	-0.00078 (61)	0.44745 (47)	0.33530 (56)	763 (26)
C(217)	-0.02017 (61)	0.47890 (52)	0.24728 (56)	745 (26)
C(218)	0.07924 (55)	0.56602 (48)	0.20908 (44)	617 (21)
F(23)	-0.09869 (40)	0.36158 (34)	0.37166 (37)	1233 (22)
H(12)	0.157 (4)	1.151 (4)	0.419 (3)	2 (1)
H(13)	-0.041 (5)	1.135 (4)	0.498 (4)	4 (2)
H(15)	-0.281 (5)	0.994 (5)	0.280 (4)	5 (2)
H(16)	-0.068 (5)	1.014 (5)	0.203 (4)	4 (2)
H(18)	0.057 (5)	1.245 (4)	0.166 (4)	3 (1)
H(19)	0.003 (5)	1.306 (5)	0.023 (4)	6 (2)
H(111)	0.278 (5)	1.155 (5)	-0.089 (4)	4 (2)
H(112)	0.322 (5)	1.080 (4)	0.051 (3)	3 (1)
H(114)	0.265 (5)	1.328 (4)	0.274 (3)	2 (1)
H(115)	0.421 (5)	1.461 (5)	0.359 (4)	4 (2)
H(117)	0.644 (5)	1.234 (4)	0.411 (3)	3 (1)
H(118)	0.486 (5)	1.103 (4)	0.335 (3)	3 (1)
H(22)	0.451 (4)	0.835 (4)	0.374 (3)	2 (1)
H(23)	0.638 (5)	0.818 (4)	0.467 (4)	3 (2)
H(25)	0.747 (5)	0.610 (4)	0.282 (3)	2 (1)
H(26)	0.554 (4)	0.622 (4)	0.192 (3)	2 (1)
H(28)	0.357 (5)	0.831 (4)	0.033 (3)	3 (1)
H(29)	0.366 (6)	0.776 (5)	-0.117 (4)	5 (2)
H(211)	0.339 (6)	0.451 (4)	-0.025 (3)	3 (1)
H(212)	0.330 (5)	0.516 (4)	0.122 (4)	4 (2)
H(214)	0.290 (6)	0.617 (5)	0.388 (4)	4 (2)
H(215)	0.130 (6)	0.470 (5)	0.449 (4)	6 (2)
H(217)	-0.094 (6)	0.449 (4)	0.208 (4)	3 (2)
H(218)	0.069 (5)	0.593 (4)	0.150 (3)	2 (1)

It appears that at room temperature the initial Rh complex $\text{RhCl}(\text{nbdt})[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$ catalyses the transfer of H from the methanol to the coordinated diolefin with formation of $\text{Rh}(\text{CO})\text{Cl}[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$ as

end product. The corresponding reaction, employing $[\text{Rh}(\text{diene})\text{Cl}]_2$ and phosphines as a catalyst, has been reported by Kollar, Toros, Heil & Marko (1980).

Fig. 1 is an ORTEP (Johnson, 1965) drawing of the molecule. Table 2 lists bond angles and lengths.

The Rh atom exhibits a practically planar configuration with an average deviation of 0.030 Å and

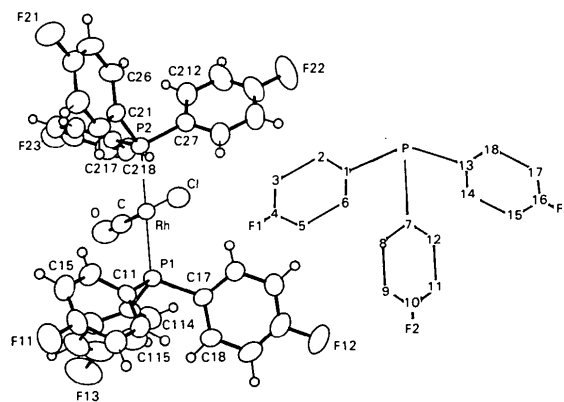


Fig. 1. Perspective drawing of $\text{Rh}(\text{CO})\text{Cl}[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$. The atom labels can be obtained from the key shown on the right, by adding either the number 1 after the chemical symbol for the lower phosphine group or the number 2 for the upper phosphine group. The labels of selected atoms are shown for reference.

Table 2. Bond lengths (Å) and bond angles (°) in $\text{RhCl}(\text{CO})[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$

X = 1 for the lower phosphine group, and 2 for the upper phosphine group in Fig. 1. Standard deviations are 0.002 Å and 0.2° for lengths and angles involving Rh atoms, and 0.007 Å and 0.5° for others.

	(<i>X</i> = 1)	(<i>X</i> = 2)		(<i>X</i> = 1)	(<i>X</i> = 2)
Rh—Cl		2.381	C(X7)—C(X8)	1.390	1.393
—P(<i>X</i>)	2.334	2.310	—C(X12)	1.392	1.392
—C		1.800	C(X8)—C(X9)	1.387	1.384
C—O		1.150	C(X9)—C(X10)	1.370	1.366
P(<i>X</i>)—C(<i>X</i> 1)	1.825	1.823	C(X10)—C(X11)	1.353	1.361
—C(X7)	1.833	1.832	—F(X2)	1.360	1.360
—C(X13)	1.828	1.839	C(X11)—C(X12)	1.391	1.400
C(X1)—C(X2)	1.386	1.389	C(X13)—C(X14)	1.399	1.390
—C(X6)	1.392	1.387	—C(X18)	1.381	1.390
C(X2)—C(X3)	1.389	1.376	C(X14)—C(X15)	1.381	1.392
C(X3)—C(X4)	1.350	1.363	C(X15)—C(X16)	1.365	1.350
C(X4)—C(X5)	1.362	1.365	C(X16)—C(X17)	1.364	1.361
—F(X1)	1.366	1.363	—F(X3)	1.364	1.365
C(X5)—C(X6)	1.388	1.381	C(X17)—C(X18)	1.384	1.393
P(<i>X</i>)—Rh—P(<i>X</i>)		178.7	P(<i>X</i>)—C(X7)—C(X12)	119.0	121.4
Cl—Rh—P(<i>X</i>)	93.4	87.9	P(<i>X</i>)—C(X7)—C(X8)	122.2	120.0
Cl—Rh—C		175.2	C(X8)—C(X7)—C(X12)	118.9	118.5
C—Rh—P(<i>X</i>)	89.6	89.2	C(X7)—C(X8)—C(X9)	120.7	121.0
Rh—P(<i>X</i>)—C(X7)	114.2	115.7	C(X8)—C(X9)—C(X10)	118.1	118.3
Rh—P(<i>X</i>)—C(X1)	113.8	111.7	C(X9)—C(X10)—F(X2)	117.3	118.7
Rh—P(<i>X</i>)—C(X13)	115.8	116.2	C(X9)—C(X10)—C(X11)	123.4	123.4
C(X7)—P(<i>X</i>)—C(X13)	105.4	102.4	C(X11)—C(X10)—F(X2)	119.4	117.9
C(X1)—P(<i>X</i>)—C(X13)	103.1	102.3	C(X10)—C(X11)—C(X12)	118.4	118.0
C(X1)—P(<i>X</i>)—C(X7)	103.0	107.2	C(X7)—C(X12)—C(X11)	120.5	120.8
P(<i>X</i>)—C(X1)—C(X6)	120.4	123.9	P(<i>X</i>)—C(X13)—C(X18)	120.4	119.7
P(<i>X</i>)—C(X1)—C(X2)	121.8	117.6	P(<i>X</i>)—C(X13)—C(X14)	121.5	121.4
C(X2)—C(X1)—C(X6)	117.6	118.3	C(X14)—C(X13)—C(X18)	118.1	118.7
C(X1)—C(X2)—C(X3)	121.2	120.9	C(X13)—C(X14)—C(X15)	121.1	121.1
C(X2)—C(X3)—C(X4)	118.5	118.9	C(X14)—C(X15)—C(X16)	118.1	118.0
C(X3)—C(X4)—F(X1)	118.9	119.0	C(X15)—C(X16)—F(X3)	118.2	118.4
C(X3)—C(X4)—C(X5)	123.5	122.3	C(X15)—C(X16)—C(X17)	123.2	123.4
C(X5)—C(X4)—F(X1)	117.6	118.7	C(X17)—C(X16)—F(X3)	118.5	118.1
C(X4)—C(X5)—C(X6)	117.5	118.6	C(X16)—C(X17)—C(X18)	117.9	118.8
C(X1)—C(X6)—C(X5)	121.8	120.9	C(X13)—C(X18)—C(X17)	121.6	120.0

maximum deviation of 0.081 Å, the Cl atom and the CO group being located at *trans* positions.

The packing of the crystal is determined only by van der Waals interactions.

The bond lengths and angles are as expected for the triarylphosphine ligand. The Rh–C and Rh–P lengths are similar to those found by La Placa & Ibers (1965) in Rh(CO)[P(Ph)₃]₃; thus the F atoms have no influence on the Rh–P bond.

Most of the calculations were carried out with XRAY70 (Stewart, Kundell & Baldwin, 1970). Thanks are due to the staff of the Computing Center of JEN (Madrid) for the facilities provided on the Univac 1100/80 computer.

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Structure of the Rhombohedral Form (α Form) of Arsenious Methylxanthate,*[As(C₂H₃OS₂)₃]

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Abstract. $M_r = 396.4$, $R\bar{3}$, $a = 14.639$ (7), $c = 12.384$ (7) Å, $V = 2298$ (2) Å³, $Z = 6$, $D_x = 1.719$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 3.11$ mm⁻¹, $T = 298$ K, $F(000) = 1188$, $R = 0.035$ for 1227 unique reflections ($2\theta < 60^\circ$). The structure is isostructural with that of arsenious ethylxanthate [Carrai & Gottardi (1960). *Z. Kristallogr.* **113**, 373–384]. The As(S₂COCH₃)₃ molecule is located on a threefold rotation axis passing through the As atom. Each As atom is coordinated with six S atoms in a distorted octahedral arrangement at distances of 2.298 (1) Å \times 3 and 2.992 (1) Å \times 3; the three shorter As–S bonds make an angle of 90.56 (3)° with each other. Difference electron density maps revealed sharp residual peaks of 0.35 e Å⁻³ on the shorter As–S bonds, indicating a 4p³-type covalent bond nature of the As atom. A pair of molecules approach closely with S...S contacts of 3.650 (2) Å \times 6 to form a loosely bound dimeric unit.

Introduction. Metal xanthates, $M(\text{S}_2\text{COR})_n$, where M = metal and R = alkyl, are an interesting group of metal complexes which show various kinds of S

coordination around metals. Although structural information on metal ethylxanthates and their higher homologues has been accumulated (Rao, 1971), no structures of methylxanthates have thus far been reported. Methylxanthates are the simplest among xanthate homologues and, therefore, are most suitable for a detailed study of the structural chemistry of xanthates. The present paper describes the crystal and molecular structure of the rhombohedral form (α form) of arsenious methylxanthate [abbreviated as As(MeX)₃ in the following]. It is designated as the α form because a monoclinic form (β form) has been found.

Experimental. Powder of As(MeX)₃ was precipitated by acidifying an aqueous solution of sodium arsenite and potassium methylxanthate until pH = 1.0 with HCl while cooling with ice. Recrystallization from an ether solution gave rhombohedral and prismatic colourless crystals; preliminary Weissenberg photographs showed that the former (α form) belong to the rhombohedral space group $R\bar{3}$ or $R3$, and the latter (β form) to the monoclinic space group $P2_1/a$. A parallelepiped with rhombohedral faces (edges 0.46 \times 0.50 \times 0.60 mm) was mounted on a Rigaku automated four-circle diffractometer; cell parameters determined with 42 reflections within the 2θ range 50 to 55° (Mo $K\alpha_1$,

* IUPAC name: tris(*O*-methyl dithiocarbonato)arsenic(III).

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