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trans-Carbonylchlorobis[tris(pentafluorophenyl)phosphine)]rhodium(I)

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The title compound, *trans*-[RhCl($C_{18}F_{15}P$)$_2$(CO)], crystallizes with one independent molecule in the asymmetric unit. Important geometric parameters are Rh—P = 2.2797 (14) and 2.2993 (14) Å, Rh—Cl = 2.3642 (12) Å, Rh—C = 1.824 (4) Å, C—Rh—Cl = 174.12 (13)°, P—Rh—C = 91.73 (13) and 93.71 (13)°, P—Rh—P = 169.38 (4)° and Rh—C≡O = 176.7 (4)°. The effective cone angles (θ_E) for the phosphine ligands were calculated to be 172 and 173°.

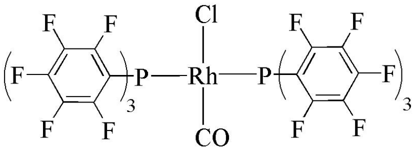
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
R factor = 0.049
wR factor = 0.106
Data-to-parameter ratio = 14.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The original Vaska complex, *trans*-[IrCl(PPh_3)$_2$(CO)], was first reported in 1959 (Angoletta, 1959), but later correctly formulated by Vaska in 1961 (Vaska & Di Luzio, 1961). This class of symmetrical square-planar complexes often crystallize with the metal atom on a crystallographic centre of symmetry, thus imposing a disordered packing arrangement (Otto, 2001; Otto *et al.*, 2000; Chen *et al.*, 1991; Kuwabara & Bau, 1994). The present study is part of an ongoing investigation aimed at determining which factors govern a disordered packing mode in Vaska-type complexes, *i.e.* *trans*-[MCl(CO)(AX_3)$_2$] (M is Rh or Ir, A is P, As or Sb, and X is alkyl, aryl or aroyl; Roodt *et al.*, 2003). Here, we report the title rhodium analogue, (I), of Vaska's complex, with tris(pentafluorophenyl)phosphine as the ligand, as another complex in this series.



(I)

Compound (I) is one of the few crystallographic examples of these complexes not to show disorder along the carbonyl–chloro axis [Cambridge Structural Database (CSD), Version 5.26, February 2005 update; Allen, 2002]. The coordination around the Rh atom in (I) shows a distorted square-planar arrangement (Fig. 1 and Table 1), with the Rh atom displaced by 0.1374 (13) Å from the coordination plane (r.m.s. deviation of fitted atoms 0.0385 Å).

The most widely used method for determining ligand steric behaviour at a metal centre is the calculation of the Tolman cone angle (θ_T), as described previously (Tolman, 1977; Otto *et al.*, 2000). For the current study, actual Rh—P bond distances were used, with a van der Waals radius of 1.47 Å for F (1.20 Å for H in the other ligands of Table 2). This gave effective cone angles (θ_E) of 172 and 173° for atoms P1 and P2, respectively, which is similar to the cone angle, θ_T, of 173°, calculated by

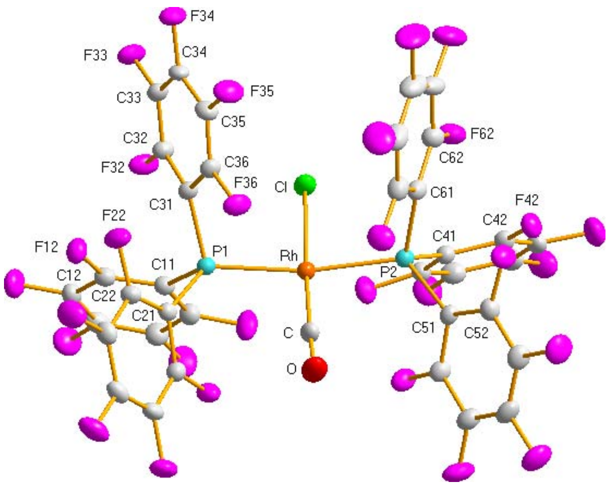


Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 30% probability level. For the C atoms, the first digit indicates the ring number and the second digit indicates the position of the atom in the ring. For the F atoms, the number is the same as that of the corresponding C atom.

creating a dummy atom at a distance of 2.28 Å from the P atom (Otto *et al.*, 2000). It is significantly smaller than the value of 184° previously reported for this ligand (Tolman, 1977). The effective cone angles, as well as other geometric properties, are given in Table 2. Comparison of the structure of (I) with that of the isomorphous Ir analogue (Selke *et al.*, 1995), as well as with *ortho*-fluorinated triphenylphosphine derivatives (Corcoran *et al.*, 2000), is given in Table 2. As expected, the *M*—P bond weakens with a decreasing number of F atoms in the ligand, as seen from the *M*—P bond distances in Table 2.

Another interesting feature of this series is that the *ortho*-substituted complexes yield disorder of the Cl—Rh—C≡O group, suggesting that the fluorine substituents in the *ortho*-position do not make a significant contribution to the factors determining the disordered packing mode. The corresponding *para*-fluorinated triphenylphosphine derivative was reported previously (Monge *et al.*, 1983) and this compound did not show disorder of the Cl—Rh—C≡O group. This suggests that the presence of F atoms in the 4-position of the phenyl rings might contribute to the disordered packing, whether due to electronic, or more probably steric, effects. Close-contact interactions between the various F atoms in (I) are indeed observed, most of them involving those in the 3- and 4-positions.

Unfortunately, the 3,5-difluorinated *trans*-[RhCl(CO)-$(PR_3)_2$] complex has not yet been reported. We are therefore unable to draw conclusions on the influence of the F atoms in the 3- and 5-positions of the aromatic ring of the phosphine.

The electron-withdrawing nature of the F atoms on the ligand renders the electronic properties of phosphine (I) similar to that of aromatic phosphites, as was observed by the ν(CO) value of 2004 cm^{-1} for (I). The previously reported [RhCl(CO){P(O*R*)$_3$}$_2$] compounds exhibit ν(CO) values of 2004 cm^{-1} for R = 2,6-$Me_2C_6H_3$ (Meijboom *et al.*, 2004*a*) and 2011 cm^{-1} for R = 2-$Me_2C_6H_4$ (Meijboom *et al.*, 2004*b*). Similar values for the Rh—P bond distances in the above-mentioned compounds were also observed. Surprisingly, the values of $^1J_{(Rh-P)}$ in the above-mentioned compounds were significantly different [155 Hz for (I), *versus* 214 and 212 Hz for the phosphites].

Unfortunately, due to coupling with F, as well as P and Rh, no satisfactory ^{13}C NMR spectrum could be obtained for (I).

Experimental

[RhCl(CO)$_2$]$_2$ was prepared according to the method described by McCleverty & Wilkinson (1990). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of P(C_6F_5)$_3$ (164 mg, 0.312 mmol) in dichloromethane (5.0 ml) was slowly added to a yellow solution of [RhCl(CO)$_2$]$_2$ (30 mg, 0.077 mmol) in acetone (5.0 ml). Immediately, gas evolution was observed and the solution turned lighter in colour. Slow evaporation of the solvent mixture afforded the title compound as a crystalline yellow solid. The solid was washed with pentane to give the pure compound (yield 190 mg, 99%). All analytical data were in accordance with the literature (Kemmit *et al.*, 1968; Atherton *et al.* 1995).

Crystal data

[RhCl($C_{36}F_{30}P_2$)(CO)]
M_r = 1230.67
Triclinic, $P\overline{1}$
a = 11.232 (2) Å
b = 12.274 (3) Å
c = 16.013 (3) Å
α = 74.95 (3)°
β = 89.49 (3)°
γ = 68.79 (3)°
V = 1978.6 (9) Å^3
Z = 2
D_x = 2.066 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 843 reflections
θ = 2.3–24.2°
μ = 0.76 mm^{-1}
T = 293 (2) K
Needle, yellow
0.28 × 0.1 × 0.07 mm

Data collection

Bruker SMART CCD 1K area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.816, T_{max} = 0.949
13443 measured reflections
9585 independent reflections
5904 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 28.3°
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 16$
$l = -18 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.106
S = 0.98
9585 reflections
649 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.52 e Å^{-3}
$\Delta\rho_{min}$ = −0.40 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Rh—C	1.824 (4)	P1—C21	1.838 (4)
Rh—P2	2.2797 (14)	P2—C41	1.826 (4)
Rh—P1	2.2993 (14)	P2—C61	1.839 (4)
Rh—Cl	2.3642 (12)	P2—C51	1.841 (4)
P1—C11	1.823 (4)	C—O	1.137 (5)
P1—C31	1.828 (4)		
C—Rh—P2	91.73 (13)	C—Rh—Cl	174.12 (13)
C—Rh—P1	93.71 (13)	O—C—Rh	176.7 (4)
P2—Rh—P1	169.38 (4)		
C—Rh—P1—C11	−111.59 (19)	C—Rh—P2—C41	127.88 (19)
C—Rh—P1—C21	8.32 (19)	C—Rh—P2—C51	10.14 (19)
C—Rh—P1—C31	127.72 (18)	C—Rh—P2—C61	−109.79 (19)

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Table 2
Comparative geometrical data (Å, °) for trans-[MCl(CO)L_2] complexes (M is Rh or Ir and L is a phosphine).

M	L	M—P	P—M—P	θ_T	θ_E	Type	Note
Rh	P(C_6F_5)$_3$	2.2798 (14) 2.2996 (14)	169.38 (4)	173 173	172 173	1	*a*
Ir	P(C_6F_5)$_3$	2.294 2.283	169.8	173 172	173 172	1	*b*
Rh	P(2,6-$F_2C_6H_3$)$_2$Ph	2.3100 (13)	180.0	162 166	161 165	2	*c*, 3
Ir	P(2,6-$F_2C_6H_3$)$_2$Ph	2.3045 (13)	180.0	158 159	157 158	2	*c*, 3
Ir	P(2,6-$F_2C_6H_3$)$_3$	2.3025 (12)	180.0	171	170	2	*c*

(1) No disorder in Cl—M—C≡O. (2) Statistical disorder (50%) in Cl—M—C≡O. (3) Disorder of the Ph and 2,6-$F_2C_6H_4$ substituents yields two cone angle values. (*a*) This work. (*b*) Selke *et al.*, 1995). (*c*) Corcoran *et al.*, 2000).

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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