Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

A new polymorph of *trans*-carbonylchlorobis[tris(4-fluorophenyl)phosphine]rhodium(I)

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Received 31 March 2006
Accepted 28 April 2006

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.027
wR factor = 0.067
Data-to-parameter ratio = 19.4

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

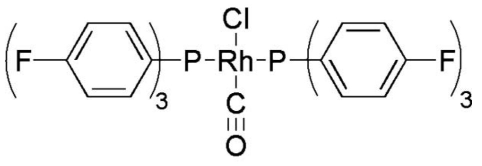
In the title compound, *trans*-[RhCl{P(4-FC_6H_4)$_3$}$_2$(CO)], where 4-FC_6H_4 is 4-fluorophenyl, the Rh—P bond distances are 2.3118 (5), 2.3220 (5), 2.3136 (5) and 2.3233 (5) Å, and the Rh—Cl bond distances are 2.3689 (5) and 2.3694 (5) Å. The effective cone angles (θ_E) for the phosphine ligands were calculated to be 155 and 156°.

Comment

The original Vaska complex, *trans*-[Ir(CO)Cl(PPh_3)$_2$], was initially reported by Angoletta (1959), but was later correctly formulated by Vaska & Di Luzio (1961). They recognized the importance of it as a model compound for studies in homogeneous catalysis. Several crystalline forms of the rhodium(I) analogue of Vaska's complex have been described in the past (Roodt *et al.*, 2003), utilizing a range of known phosphines.

This class of square-planar complexes (usually including Rh, Ir, Pd and Pt) often crystallizes 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 into determining which factors govern a disordered packing mode in Vaska-type complexes, *i.e.* *trans*-[M(CO)Cl(AX_3)$_2$] (M = Rh or Ir; A = group 15 donor atom P, As or Sb; X = alkyl, aryl, aroyl, *etc.*; Roodt *et al.*, 2003).

Several polymorphs of the triphenylphosphine analogue, [Rh(CO)Cl(PPh_3)$_2$], have been reported by our group in the past (Kemp *et al.* 1995). Here, we report a new polymorph of the rhodium analogue, (I), of Vaska's complex with tris(4-fluorophenyl)phosphine as ligand. In contrast with the previously reported structure (Monge *et al.*, 1983), which crystallizes in the triclinic space group $P\overline{1}$ (Z = 2) with one independent molecule, the current reported polymorph crystallizes with two independent molecules in the triclinic space group $P\overline{1}$ (Z = 4).



(I)

The title compound is one of the few crystallographic examples of these complexes which does not show disorder along the Cl—Rh—C≡O axis [Cambridge Structural Database (CSD), Version 5.27, January 2006 update; Allen, 2002]. The coordination polyhedra around the Rh atoms of (I) show distorted square-planar arrangements (Fig. 1 and Table 1),

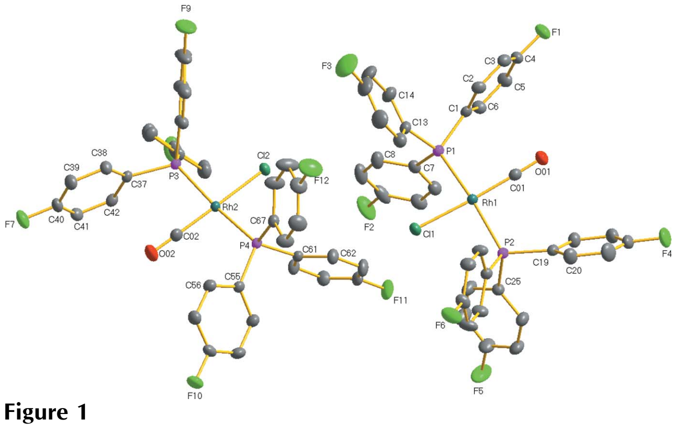


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

illustrated by the slight displacement of the Rh atoms [0.0514 (6) and 0.0494 (6) Å] from the plane defined by the two P, the Cl and the C atoms. Compound (I) shows comparable bond lengths (Table 2) with the polymorph reported by Monge *et al.* (1983). In addition, Table 2 gives the bond lengths of the four previously reported PPh_3 polymorphs for comparison. Significant differences between the polymorphs are shown in the superimposed line drawings of the structure reported by Monge *et al.* (1983) and the two independent molecules of the current study (Fig. 2).

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 by Tolman (1977) and Otto *et al.* (2000). For the current study, actual Rh—P bond distances were used, with a van der Waals radius of 1.20 Å for H (Otto *et al.*, 2000), yielding effective cone angles (θ_E). The substituents of the phosphine may have different orientations, resulting in variations in cone-angle sizes, as observed by Ferguson *et al.* (1978), and these may not necessarily be a true indication of the steric properties of the phosphine in solution. The values of 155° (for P1, P3 and P4) and 156° (for P2) obtained for tris(4-fluorophenyl)phosphine are comparable with the cone angles of 154 and 156° for the polymorph reported by Monge *et al.* (1983), as well as the average cone angle of 155° obtained for triphenylphosphine (data extracted and calculated from the CSD; 5 hits).

Experimental

$[RhCl(CO)_2]_2$ was prepared according to the literature procedure of McCleverty & Wilkinson (1990). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of $P(4\text{-}FC_6H_4)_3$ (32 mg, 0.10 mmol) in dichloromethane (2 ml) was added to a yellow solution of $[RhCl(CO)_2]_2$ (10 mg, 0.025 mmol) in dichloromethane (2.0 ml). Gas evolution was observed immediately and the solution turned lighter in colour. The volatiles were evaporated at room temperature, and the yellow residue was recrystallized from acetone (5.0 ml) to give crystals suitable for X-ray analysis in a quantitative yield. The analytical data were identical to those reported in the literature (Monge *et al.*, 1983).

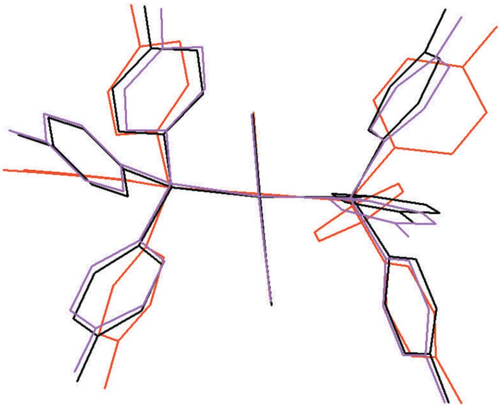


Figure 2
Superimposed line drawings of the polymorph reported by Monge *et al.* (1983) in red and the two independent molecules of the current study, in black and violet for molecules 1 and 2, respectively.

Crystal data

$[RhCl(C_{18}H_{12}F_3P)(CO)]$
$M_r = 798.86$
Triclinic, $P\overline{1}$
$a = 11.0530$ (4) Å
$b = 12.0560$ (4) Å
$c = 26.5140$ (9) Å
$\alpha = 83.685$ (2)°
$\beta = 84.150$ (2)°
$\gamma = 73.725$ (2)°

$V = 3361.6$ (2) $Å^3$
$Z = 4$
$D_x = 1.578$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.75$ mm^{-1}
$T = 150$ (2) K
Block, yellow
0.30 × 0.11 × 0.06 mm

Data collection

Bruker X8 APEXII area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.807$, $T_{max} = 0.957$

59610 measured reflections
16749 independent reflections
14119 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.067$
$S = 1.01$
16749 reflections
865 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 2.075P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.52$ e $Å^{-3}$
$\Delta\rho_{min} = -0.35$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Rh1—C01	1.816 (2)	Rh2—C02	1.818 (2)
Rh1—P1	2.3118 (5)	Rh2—P3	2.3136 (5)
Rh1—P2	2.3220 (5)	Rh2—P4	2.3233 (5)
Rh1—Cl1	2.3689 (5)	Rh2—Cl2	2.3694 (5)
C01—O01	1.145 (2)	C02—O02	1.145 (2)
C01—Rh1—P1	91.41 (6)	C02—Rh2—P3	90.30 (6)
C01—Rh1—P2	92.43 (6)	C02—Rh2—P4	92.37 (6)
P1—Rh1—P2	171.800 (18)	P3—Rh2—P4	172.352 (18)
O01—C01—Rh1	177.75 (18)	O02—C02—Rh2	177.4 (2)
Cl1—Rh1—P1—C7	−64.98 (7)	Cl2—Rh2—P3—C43	−65.98 (7)
Cl1—Rh1—P1—C13	59.55 (8)	Cl2—Rh2—P3—C49	59.03 (7)
Cl1—Rh1—P1—C1	178.11 (7)	Cl2—Rh2—P3—C37	177.64 (7)
Cl1—Rh1—P2—C31	−47.54 (7)	Cl2—Rh2—P4—C61	−45.51 (7)
Cl1—Rh1—P2—C25	71.67 (7)	Cl2—Rh2—P4—C67	74.95 (7)
Cl1—Rh1—P2—C19	−168.99 (7)	Cl2—Rh2—P4—C55	−167.51 (7)

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Table 2
Comparative geometrical data (Å) for compounds of the general formula *trans*-[RhCl{PR_3}$_2$(CO)].

PR_3	Rh—P	Rh—Cl	Rh—C	Reference
PPh_3†	2.313 (7) 2.349 (7)	2.380 (11)	1.74 (3)	(*a*)
PPh_3‡	2.322 (1)	2.382 (1)	1.77 (1)	(*b*)
PPh_3†	2.363 (2) 2.304 (2)	2.405 (4)	1.99 (1)	(*c*)
PPh_3†	2.333 (1) 2.327 (1)	2.395 (1)	1.821 (5)	(*d*)
$P(4-FC_6H_4)_3$†	2.3118 (5) 2.3220 (5)	2.3689 (5)	1.816 (2)	(*e*)
	2.3136 (5) 2.3233 (5)	2.3694 (5)	1.818 (2)	
$P(4-FC_6H_4)_3$†	2.334 (2) 2.310 (2)	2.381 (2)	1.800 (2)	(*f*)

† Non-disordered. ‡ Disordered. References: (*a*) Kemp *et al.* (1995); (*b*) Dunbar & Haefner (1992); (*c*) Del Prada *et al.* (1979); (*d*) Rheingold & Geib (1987); (*e*) this work; (*f*) Monge *et al.* (1983).

H atoms were placed in geometrically idealized positions, with C—H = 0.97 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); 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).

Financial assistance from the South African National Research Foundation, the Research Fund of the University of the Free State and SASOL is gratefully acknowledged. Part of this material is based on work supported by the South African National Research Foundation (SA NRF, GUN 2038915). Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF.

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