

trans*-Carbonylchlorobis[tris(2,6-dimethylphenyl)phosphito]rhodium(I)*Reinout Meijboom, Alfred Muller and Andreas Roodt***

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

Disorder in main residue

R factor = 0.044

wR factor = 0.093

Data-to-parameter ratio = 19.5

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

The title compound, $[\text{RhCl}\{\text{P}(\text{OC}_6\text{H}_3)_2\}_2(\text{CO})]$, where $\text{P}(\text{OC}_6\text{H}_3)_2$ is tris(2,6-dimethylphenyl)phosphite, crystallizes with two independent molecules, both disordered over inversion centres. The Rh1–P1 and Rh2–P2 bond distances are 2.3097 (7) and 2.2995 (7) Å, respectively. The effective cone angle for the phosphite ligands was calculated as 182°.

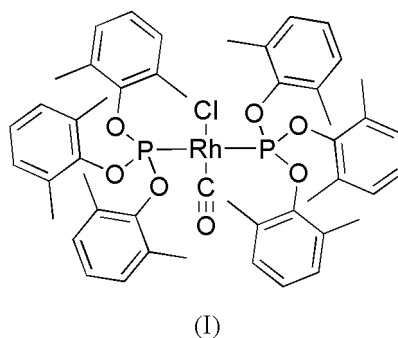
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Comment

Symmetrical square-planar complexes of Rh, Ir, Pd and Pt 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 into determining which factors govern a disordered packing mode and reports the structure of *trans*-chlorocarbonylbis[tri(2,6-dimethylphenyl)phosphite]-rhodium(I), (I), one of the few phosphite-containing Vaska-type structures known to date [Cambridge Structural Database (CSD) Version 5.25 (January 2004 update); Allen, 2002].



The title compound crystallizes with two independent molecules lying on inversion centres, resulting in a statistical disorder in both of the Cl–Rh–CO moieties. The coordination around the Rh atom shows a slightly distorted square-planar arrangement (Fig. 1 and Table 1).

The most widely used method for determining ligand steric behaviour at a metal centre is by calculating the cone angle, as described previously (Tolman, 1977; Otto *et al.*, 2000). For this study, actual M –P bond distances were used, yielding effective cone angles (Θ_E). The substituents of the phosphite may have different orientations, resulting in variations in cone angle sizes, as observed by Ferguson *et al.* (1978), and may not necessarily be a true indication of the steric properties of the phosphite in solution compared with the solid state. The value of 182° obtained for tri(2,6-dimethylphenyl)phosphite is compared with other similar structures in Table 2 and is

virtually the same as the 181° cone angle for tri(2-*tert*-butylphenyl)phosphite (data extracted and calculated from CSD) in *trans*-carbonylchlorobis[tri(2-*tert*-butylphenyl)phosphite]-rhodium(I) (Fernández *et al.*, 1998), the only other non-bridged phosphite structure reported to date.

Table 2 also compares bond distances of the other similar complexes, and shorter M–P bond distances are observed for the phosphites than, for example, for the benzylphosphine analogue, also manifested in the $^1J_{(\text{Rh}-\text{P})}$ coupling of 214 Hz for (I) compared with 124 Hz for the phosphine complex. This difference is probably due to the electron-withdrawing nature of phosphites, which enhances π back-bonding between the metal and the P atom and, as a result, weakens the M–Cl bond.

Interesting to note is the difference in values of $\nu(\text{CO})$ for the solid and solution states of the title compound. This difference may be the result of packing in the unit cell, which slightly distorts the Rh–C≡O angle (Table 1).

Experimental

$[\text{RhCl}(\text{CO})_2]_2$ was prepared according to the method described by McCleverty & Wilkinson (1990). $\text{P}(\text{OC}_8\text{H}_9)_3$ was prepared by reaction of the 2,6-dimethylphenol with PCl_3 in the presence of NEt_3 . All chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of $\text{P}(\text{OC}_8\text{H}_9)_3$ (90.7 mg, 0.230 mmol) in acetone (1.5 ml) was added slowly to a yellow solution of $[\text{RhCl}(\text{CO})_2]_2$ (21.4 mg, 0.055 mmol) in acetone (3.0 ml). Gas evolution was immediately observed and crystals formed while the solution turned colourless. The supernatant liquor was decanted and the solids were washed with pentane (3×2 ml), leaving crystals of the pure title compound, suitable for X-ray analysis. Yield: 94.3 mg; 86.9%. ^1H NMR (CDCl_3 , 300 MHz, p.p.m.): 6.97 (s, 18H), 2.29 (s, 36H); ^{13}C NMR (CDCl_3 , 75.45 MHz, p.p.m.): 149.72, 130.55, 129.05, 124.85, 18.91; ^{31}P NMR{H} (CDCl_3 , 121.46 MHz, p.p.m.): 111.12 [d , $^1J_{\text{Rh}-\text{P}} = 214$ Hz]; IR (DCM) $\nu(\text{CO})$: 2004 cm^{-1} ; (KBr) $\nu(\text{CO})$: 1991 cm^{-1} .

Crystal data

$[\text{RhCl}(\text{C}_{48}\text{H}_{54}\text{O}_6\text{P}_2)(\text{CO})]$	$Z = 2$
$M_r = 955.22$	$D_x = 1.386 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.3892$ (5) Å	Cell parameters from 997 reflections
$b = 13.1262$ (5) Å	$\theta = 2.3$ – 19.9°
$c = 14.6675$ (6) Å	$\mu = 0.55 \text{ mm}^{-1}$
$\alpha = 83.685$ (2) $^\circ$	$T = 293$ (2) K
$\beta = 89.773$ (2) $^\circ$	Plate, yellow
$\gamma = 75.016$ (2) $^\circ$	$0.26 \times 0.12 \times 0.07 \text{ mm}$
$V = 2289.45$ (16) Å 3	

Data collection

Bruker SMART 1K CCD diffractometer	$R_{\text{int}} = 0.070$
ω scans	$\theta_{\text{max}} = 28.3^\circ$
27 501 measured reflections	$h = -14 \rightarrow 16$
11 343 independent reflections	$k = -17 \rightarrow 16$
6184 reflections with $I > 2\sigma(I)$	$l = -19 \rightarrow 19$

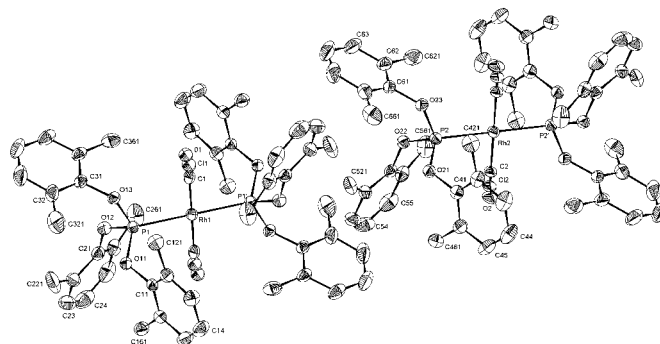


Figure 1

The two independent molecules of (I), with 30% probability displacement ellipsoids; H atoms have been omitted for clarity. For the C atoms, the first digit indicates ring number and the second digit indicates the position of the atom in the ring. Both disordered components are shown for each molecule.

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.91$	$(\Delta/\sigma)_{\text{max}} < 0.001$
11343 reflections	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
583 parameters	$\Delta\rho_{\text{min}} = -0.44 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, $^\circ$).

Rh1–C1	1.771 (9)	P1–O12	1.597 (2)
Rh1–P1	2.3097 (7)	P1–O11	1.6056 (19)
Rh1–Cl1	2.380 (3)	O23–P2	1.5943 (19)
Rh2–C2	1.773 (8)	O22–P2	1.596 (2)
Rh2–P2	2.2995 (7)	O21–P2	1.607 (2)
Rh2–Cl2	2.379 (3)	C1–O1	1.128 (12)
P1–O13	1.5923 (19)	C2–O2	1.139 (11)
P1 ⁱ –Rh1–P1	180	C2 ⁱⁱ –Rh2–Cl2	178.3 (5)
C1 ⁱ –Rh1–Cl1	179.2 (6)	O1–C1–Rh1	174.2 (19)
P2–Rh2–P2 ⁱⁱ	180	O2–C2–Rh2	176.1 (19)
Cl1–Rh1–P1–O11	–114.49 (15)	Cl2–Rh2–P2–O21	66.04 (13)
Cl1–Rh1–P1–O12	120.93 (15)	Cl2–Rh2–P2–O22	–59.21 (14)
Cl1–Rh1–P1–O13	5.00 (15)	Cl2–Rh2–P2–O23	–175.41 (13)

Symmetry codes: (i) $-x, -y, 1 - z$; (ii) $-1 - x, -1 - y, -z$.

Table 2

Comparison of geometry for *trans*- $[\text{MCl}(\text{CO})(\text{PX}_3)_2]$ complexes..

2,6DMP = 2,6-dimethylphenyl, 2tBP = 2-*tert*-butylphenyl and Bz = benzyl.

X	M–P(Å)	M–Cl(Å)	P–M–P($^\circ$)	Cl–M–C($^\circ$)	$\Theta_{\text{E}}(^\circ)$
O(2,6DMP)†	2.3097 (7)	2.380 (3)	180	179.2 (6)	182
	2.2995 (7)	2.379 (3)	180	178.3 (5)	182
O(2tBP)‡	2.286	2.370	180	175.85	181
Bz§	2.3164 (15)	2.3654 (15)	177.67 (6)	178.55 (17)	170
	2.3156 (16)				172

† This work. ‡ Fernández *et al.* (1998). § Muller *et al.* (2002).

The aromatic and methyl H atoms were placed in idealized positions (C–H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{C})$, respectively.

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: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Brendt, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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