

***trans*-Carbonylchlorobis[tris(2-methylphenyl)phosphito]rhodium(I)****Reinout Meijboom, Alfred Muller and Andreas Roodt\***Department of Chemistry and Biochemistry,  
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**Key indicators**Single-crystal X-ray study  
 $T = 292$  K  
Mean  $\sigma(C-C) = 0.005$  Å  
Disorder in main residue  
 $R$  factor = 0.040  
 $wR$  factor = 0.093  
Data-to-parameter ratio = 19.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $[\text{Rh}\{\text{P}(\text{OC}_7\text{H}_7)_3\}_2\text{Cl}(\text{CO})]$ , where  $\text{P}(\text{OC}_7\text{H}_7)_3$  is tris(2-methylphenyl)phosphite, crystallizes disordered over an inversion centre. Important geometrical parameters are  $\text{Rh}-\text{P} = 2.2905$  (9) Å,  $\text{Rh}-\text{Cl} = 2.402$  (4) Å,  $\text{Rh}-\text{C} = 1.764$  (10) Å, and  $\text{C}-\text{Rh}-\text{Cl} = 177.7$  (5)°,  $\text{P}-\text{Rh}-\text{Cl} = 85.84$  (12)° and  $\text{Rh}-\text{C}\equiv\text{O} = 174.7$  (15)°. The effective cone angle for the phosphite ligand was calculated to be 167°.

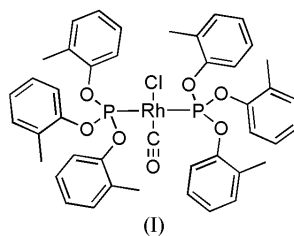
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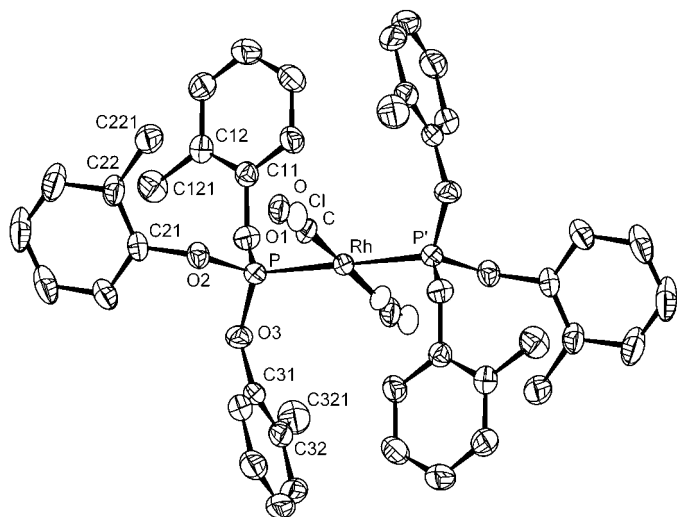
**Comment**

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 in Vaska-type complexes, *i.e.*  $[\text{M}(\text{CO})\text{Cl}(\text{AX}_3)_2]$  ( $M = \text{Rh}, \text{Ir}$ ;  $A =$  group 15 donor atom P, As, Sb;  $X =$  alkyl, aryl, aroyl, *etc.*; Roodt *et al.*, 2003). The current study reports the structure of *trans*-carbonylchlorobis[tris(2-methylphenyl)phosphito]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 as an independent molecule lying on an inversion centre, resulting in statistical disorder of the  $\text{Cl}-\text{Rh}-\text{CO}$  moiety. 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  $M-\text{P}$  bond distances were used, yielding effective cone angles ( $\Theta_E$ ). 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 167° obtained for tris(2-methylphenyl)phosphite is smaller than those for the few other similar structures known to date (Table 2). This is due to the smaller/fewer substituents on the


**Figure 1**

The structure of (I), showing the 50% statistical disorder of the Cl–Rh–CO moiety. Displacement ellipsoids are drawn at the 30% probability level. 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. Atom P' is generated by the symmetry operation  $(1 - x, -y, 1 - z)$ .

benzene rings for the title compound, introducing more flexibility in the aryl substituents.

Table 2 also compares bond distances of the other similar complexes, and shorter  $M-P$  bond distances are observed in the phosphites than, for example, for the tribenzylphosphine analogue (Muller *et al.*, 2002), also manifested in the  $^1J_{Rh-P}$  coupling of 212 Hz for (I) compared with 124 Hz for the phosphine complex. The  $^1J_{Rh-P}$  coupling is in good agreement with the  $^1J_{Rh-P}$  of 214 Hz for the tris(2,6-dimethylphenyl)-phosphite complex reported earlier (Meijboom *et al.*, 2004). This may be indicative that additional *ortho*-methyl groups on the benzene rings have little or no effect, other than steric contribution; moreover, the difference in coupling constants between phosphite and phosphine complexes is probably due to the electron-withdrawing nature of phosphites, which enhances  $\pi$  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  $\nu(CO)$  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

$[RhCl(CO)_2]_2$  was prepared according to the method described by McCleverty & Wilkinson (1990), while  $P(OC_7H_7)_3$  was prepared by reaction of 2-methylphenol with  $PCl_3$  in the presence of  $NEt_3$ , analogous to the synthesis of tris(2-butylphenyl)phosphite (Van Leeuwen & Robeck, 1983). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of  $P(OC_7H_7)_3$  (110 mg, 0.312 mmol) in pentane (1.0 ml) was added slowly to a yellow solution of  $[RhCl(CO)_2]_2$  (30 mg, 0.077 mmol) in pentane (1.0 ml). Gas evolution was observed immediately and the solution turned lighter in colour while a precipitate formed. The supernatant liquid was decanted and the solids were washed with

pentane ( $3 \times 2$  ml) to leave the pure title compound. Crystals suitable for X-ray analysis were grown from  $CH_2Cl_2$  (yield: 88 mg, 66%; m.p. 398 K).  $^1H$  NMR ( $CDCl_3$ , 300 MHz, p.p.m.): 7.35 (6H, *m*,  $J = 4.5$  Hz, ArH), 7.11 (6H, *m*,  $J = 4.7$  Hz, ArH), 7.03 (12H, *m*, ArH), 2.10 (18H, *s*,  $CH_3$ );  $^{13}C\{H\}$  NMR ( $CDCl_3$ , 75.45 MHz, p.p.m.): 149.59, 131.30, 130.13, 126.54, 124.75, 120.37, 16.53;  $^{31}P\{H\}$  NMR ( $CDCl_3$ , 121.42 MHz, p.p.m.): 114.42 (*d*,  $^1J_{Rh-P} = 212$  Hz); IR ( $CH_2Cl_2$ )  $\nu(CO)$ : 2011  $cm^{-1}$ ; (KBr)  $\nu(CO)$ : 1999  $cm^{-1}$ ; UV–Vis ( $CH_2Cl_2$ )  $\lambda_{max}$ : 267.3 (100), 358.0 (40%) nm.

### Crystal data

$[Rh(C_{21}H_{21}O_3P)_2Cl(CO)]$   
 $M_r = 871.07$   
 Triclinic,  $P\bar{1}$   
 $a = 8.1871$  (16) Å  
 $b = 10.785$  (2) Å  
 $c = 13.101$  (3) Å  
 $\alpha = 102.12$  (3)°  
 $\beta = 104.65$  (3)°  
 $\gamma = 102.46$  (3)°  
 $V = 1049.1$  (5) Å<sup>3</sup>

$Z = 1$   
 $D_x = 1.379$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 828 reflections  
 $\theta = 2.7$ – $24.3$ °  
 $\mu = 0.59$  mm<sup>-1</sup>  
 $T = 292$  (2) K  
 Plate, yellow  
 $0.48 \times 0.22 \times 0.11$  mm

### Data collection

Bruker SMART 1K CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{min} = 0.764$ ,  $T_{max} = 0.938$   
 7011 measured reflections

4966 independent reflections  
 3453 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.019$   
 $\theta_{max} = 28.3$ °  
 $h = -10 \rightarrow 10$   
 $k = -14 \rightarrow 10$   
 $l = -15 \rightarrow 17$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.040$   
 $wR(F^2) = 0.093$   
 $S = 1.02$   
 4966 reflections  
 262 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.1712P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.30$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.45$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Rh–C	1.764 (10)	P–O1	1.599 (2)
Rh–P	2.2905 (9)	P–O3	1.6041 (19)
Rh–Cl	2.402 (4)	O1–C11	1.412 (3)
P–O2	1.588 (2)		
C–Rh–P	92.1 (4)	C <sup>i</sup> –Rh–Cl	177.7 (5)
P <sup>i</sup> –Rh–P	180	O–C–Rh	174.7 (15)
C–Rh–P–O1	116.7 (5)	C–Rh–P–O3	–131.4 (5)
C–Rh–P–O2	–6.9 (5)		

Symmetry code: (i)  $1 - x, -y, 1 - z$ .

**Table 2**

Comparative geometrical data (Å, °) for *trans*- $[M(CO)Cl(PX_3)_2]$  complexes.

X	M–P	M–Cl	P–M–P	Cl–M–C	$\Theta_E$
O(2MP) <sup>a</sup>	2.2905 (9)	2.402 (4)	180	177.7 (5)	167
O(2,6DMP) <sup>b</sup>	2.3097 (7)	2.380 (3)	180	179.2 (6)	182
	2.2995 (7)	2.379 (3)	180	178.3 (5)	182
O(2 <i>t</i> BP) <sup>c</sup>	2.286	2.370	180	175.85	181
Bz <sup>d</sup>	2.3164 (15)	2.3654 (15)	177.67 (6)	178.55 (17)	170
	2.3156 (16)				172

Notes: (a) this work (2MP = 2-methylphenyl); (b) Meijboom *et al.* (2004) (2,6DMP = 2,6-dimethylphenyl); (c) Fernández *et al.* (1998) (2*t*BP = 2-*tert*-butylphenyl); data extracted from Cambridge Structural Database (Allen, 2002), no s.u. values available; (d) Muller *et al.* (2002) (Bz = benzyl).

The aromatic and methyl H atoms were placed in geometrically idealized positions ( $C-H = 0.93-0.96 \text{ \AA}$ ) and constrained to ride on their parent atoms, with  $U_{iso}(H) = 1.2U_{eq}(C)$  and  $1.5U_{eq}(C)$ , respectively. A rotating group model was used for two methyl groups.

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, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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