metal-organic papers

trans-Carbonylchlorobis[tris(2-methylphenyl)phosphito]rhodium(I)

Reinout Meijboom, Alfred Muller and Andreas Roodt*

Department of Chemistry and Biochemistry, Rand Afrikaans University, Auckland Park, Johannesburg, South Africa 2006

Correspondence e-mail: aroo@rau.ac.za

Key indicators

Single-crystal X-ray study

$T = 292$ K

Mean σ(C–C) = 0.005 Å

Disorder in main residue

R factor = 0.040

wR factor = 0.093

Data-to-parameter ratio = 19.0

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

The title compound, $[Rh\{P(OC_7H_7)_3\}_2Cl(CO)]$, where $P(OC_7H_7)_3$ is tris(2-methylphenyl)phosphite, crystallizes disordered over an inversion centre. Important geometrical parameters are Rh—P = 2.2905 (9) Å, Rh—Cl = 2.402 (4) Å, Rh—C = 1.764 (10) Å, and C—Rh—Cl = 177.7 (5)°, P—Rh—Cl = 85.84 (12)° and Rh—C≡O = 174.7 (15)°. The effective cone angle for the phosphite ligand was calculated to be 167°.

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. trans*-$[M(CO)Cl(AX_3)_2]$ (M = Rh, 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*-carbonylchloro-bis[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].

(I)
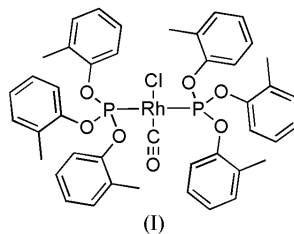
The title compound crystallizes as an independent molecule lying on an inversion centre, resulting in statistical disorder of the Cl—Rh—CO moiety. The coordination around the Rh atom shows a slightly distorted square-planar arrangement (Fig. 1 and Table 1).

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—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 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
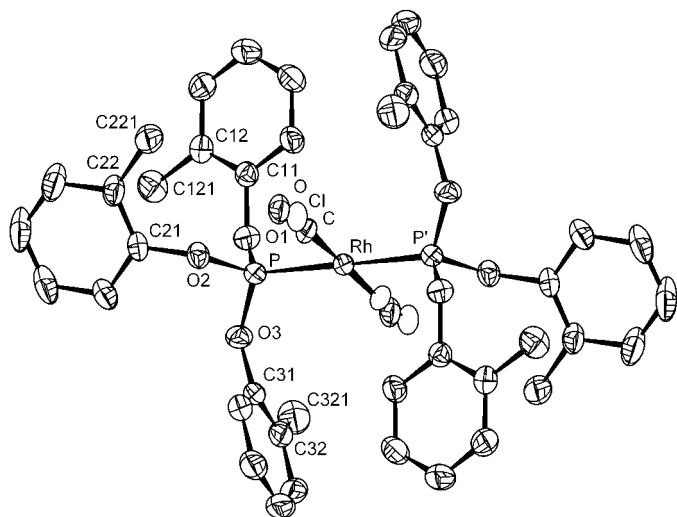
Figure 1
The structure of (I), showing the 50% statistical disorder of the Cl—Rh—CO moiety. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. For the C atoms, the first digit indicates ring number and the second digit indicates the position of the 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 aroyl 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 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 $\nu(CO)$ 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$_7$H$_7$)$_3$ was prepared by reaction of 2-methylphenol with PCl$_3$ in the presence of NEt$_3$, analogous to the synthesis of tris(2-butylpenyl)phosphite (Van Leeuwen & Robeck, 1983). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of P(OC$_7$H$_7$)$_3$ (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 × 2 ml) to leave the pure title compound. Crystals suitable for X-ray analysis were grown from CH$_2$Cl$_2$ (yield: 88 mg, 66%; m.p. 398 K). ^{1}H 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$_2$Cl$_2$) ν(CO): 2011 cm^{-1}; (KBr) ν(CO): 1999 cm^{-1}; UV–Vis (CH$_2$Cl$_2$) λ_{max}: 267.3 (100), 358.0 (40%) nm.

Crystal data

[Rh(C$_{21}$H$_{21}$O$_3$P)$_2$Cl(CO)]	$Z = 1$
$M_r = 871.07$	$D_x = 1.379$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.1871$ (16) Å	Cell parameters from 828
$b = 10.785$ (2) Å	reflections
$c = 13.101$ (3) Å	$\theta = 2.7–24.3°$
$\alpha = 102.12$ (3)°	$\mu = 0.59$ mm^{-1}
$\beta = 104.65$ (3)°	$T = 292$ (2) K
$\gamma = 102.46$ (3)°	Plate, yellow
$V = 1049.1$ (5) Å^3	0.48 × 0.22 × 0.11 mm

Data collection

Bruker SMART 1K CCD diffractometer	4966 independent reflections
	3453 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	$\theta_{max} = 28.3°$
	$h = -10 \rightarrow 10$
$T_{min} = 0.764$, $T_{max} = 0.938$	$k = -14 \rightarrow 10$
7011 measured reflections	$l = -15 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.1712P]$
$wR(F^2) = 0.093$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
4966 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
262 parameters	$\Delta\rho_{min} = -0.45$ e Å^{-3}
H-atom parameters constrained	

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^i—Rh—Cl	177.7 (5)
P^i—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	$M-P$	$M-Cl$	$P-M-P$	$Cl-M-C$	Θ_E
O(2MP)^a	2.2905 (9)	2.402 (4)	180	177.7 (5)	167
O(2,6DMP)^b	2.3097 (7)	2.380 (3)	180	179.2 (6)	182
	2.2995 (7)	2.379 (3)	180	178.3 (5)	182
O(2tBP)^c	2.286	2.370	180	175.85	181
Bz^d	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) (2,6-DMP = 2,6-dimethylphenyl); (*c*) Fernández *et al.* (1998) (2tBP = 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 Å) 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: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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