Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

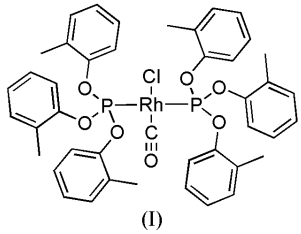
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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°.

Received 18 June 2004
Accepted 25 June 2004
Online 9 July 2004

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*-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].



(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

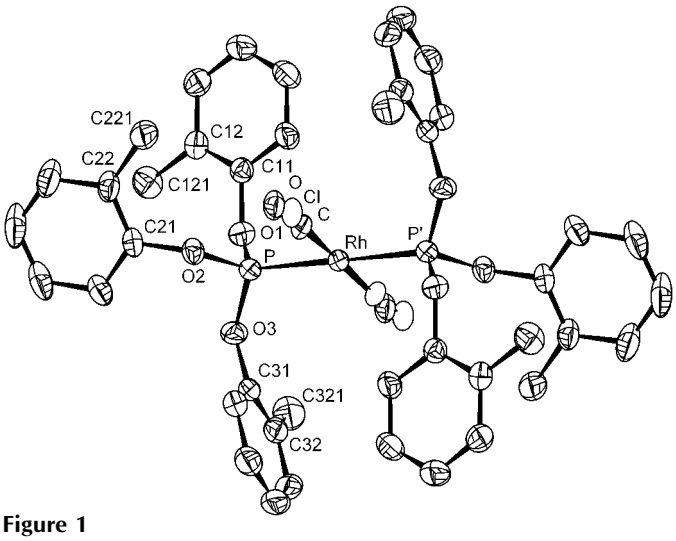


Figure 1
The structure of (I), showing the 50% statistical disorder of the Cl—Rh—CO moiety. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. For the C atoms, the first digit indicates ring number and the second digit indicates the position of the 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 $^1J_{\mathrm{Rh-P}}$ coupling of 212 Hz for (I) compared with 124 Hz for the phosphine complex. The $^1J_{\mathrm{Rh-P}}$ coupling is in good agreement with the $^1J_{\mathrm{Rh-P}}$ 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 ν(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-butylpenyl)phosphite (Van Leeuwen & Robeck, 1983). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of $P(OC_7H_7)_3$ (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 × 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). ^{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*, $^1J_{(\mathrm{Rh-P})}$ = 212 Hz); IR (CH_2Cl_2) ν(CO): 2011 cm^{-1}; (KBr) ν(CO): 1999 cm^{-1}; UV–Vis (CH_2Cl_2) $\lambda_{\max}$: 267.3 (100), 358.0 (40%) nm.

Crystal data

$[Rh(C_{21}H_{21}O_3P)_2Cl(CO)]$	Z = 1
M_r = 871.07	D_x = 1.379 Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
a = 8.1871 (16) Å	Cell parameters from 828 reflections
b = 10.785 (2) Å	θ = 2.7–24.3°
c = 13.101 (3) Å	μ = 0.59 mm^{-1}
α = 102.12 (3)°	T = 292 (2) K
β = 104.65 (3)°	Plate, yellow
γ = 102.46 (3)°	0.48 × 0.22 × 0.11 mm
V = 1049.1 (5) Å^3	

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	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.1712P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$= 0.040	
$wR(F^2)$ = 0.093	
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$^{\mathrm{i}}$—Rh—Cl	177.7 (5)
P$^{\mathrm{i}}$—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(2*t*BP)[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) (2,6DMP = 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 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).

Financial assistance from the South African National Research Foundation, SASOL and the Research Fund of RAU is gratefully acknowledged. The University of the Witwatersrand (Professor D. Levendis and Dr D. Billing) is thanked for the use of its diffractometer. Part of this material is based on work supported by the South African National Research Foundation under grant number GUN 2053397. Opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NRF.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Brandenburg, K. (2001). *DIAMOND*. Release 2.1e. Crystal Impact GbR, Bonn, Germany.
Bruker (1998). *SADABS* (Version 2004/1) and *SMART-NT* (Version 5.050). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1999). *SAINT-Plus.* Version 6.02 (including *XPREP*). Bruker AXS Inc., Madison, Wisconsin, USA.
Chen, Y., Wang, J. & Wang, Y. (1991). *Acta Cryst.* C**47**, 2441–2442.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Ferguson, G., Roberts, P. J., Alyea, E. C. & Khan, M. (1978). *Inorg. Chem.* **17**, 2965–2967.
Fernández, E., Ruiz, A., Claver, C., Castillon, S., Polo, A. Piniella, J. F. & Alvarez-Larena, A. (1998). *Organometallics*, **17**, 2857–2864.
Kuwabara, E. & Bau, R. (1994). *Acta Cryst.* C**50**, 1409–1411.
McCleverty, J. A. & Wilkinson, G. (1990). *Inorg. Synth.* **28**, 84–86.
Meijboom, R., Muller, A. & Roodt, A. (2004). *Acta Cryst.* E**60**, m455–m457.
Muller, A. J., Roodt, A., Otto, S., Oskarsson, Å. & Yong, S. (2002). *Acta Cryst.* E**58**, m715–717.
Otto, S. (2001). *Acta Cryst.* C**57**, 793–795.
Otto, S., Roodt, A. & Smith, J. (2000). *Inorg. Chim. Acta*, **303**, 295–299.
Roodt, A., Otto, S. & Steyl, G. (2003). *Coord. Chem. Rev.* **245**, 121–137.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Tolman, C. A. (1977). *Chem. Rev.* **77**, 313–348.
Van Leeuwen, P. W. N. M. & Robeck, C. F. (1983). *J. Organomet. Chem.* **258**, 343–350.