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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
Disorder in solvent or counterion
R factor = 0.062
wR factor = 0.151
Data-to-parameter ratio = 19.1

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

trans-Carbonylchlorobis(tri-m-tolylphosphino)-rhodium(I) dichloromethane solvate

The title compound, $[RhCl\{P(C_7H_7)_3\}_2(CO)]\cdot CH_2Cl_2$, where $P(C_7H_7)_3$ is tri-m-tolylphosphine, crystallizes with a dichloromethane molecule in the asymmetric unit. Important geometrical parameters are Rh—P = 2.3229 (15) and 2.3269 (15) Å, Rh—Cl = 2.3659 (15) Å, Rh—C = 1.793 (6) Å, C—Rh—Cl = 174.6 (2)°, P—Rh—C = 90.33 (17)° and 92.68 (17)°, and Rh—C≡O = 176.2 (5)°. The effective cone angles for the phosphine ligands were calculated to be 160 and 155°.

Comment

The original Vaska complex, $[IrCl(PPh_3)_2(CO)]$, was first reported in 1959 (Angoletta, 1959) but was later correctly formulated by Vaska & Di Luzio (1961). This class of symmetrical square-planar complexes 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-$[MCl(AX_3)_2(CO)]$ (M = Rh, Ir; A = P, As, Sb; X = alkyl, aryl, aroyl, etc; Roodt et al., 2003). We report here the rhodium analogue, (I), of Vaska's complex, with tri-m-tolylphosphine as ligand, as another complex in this range. The compound is one of the few crystallographic examples of these complexes which does not show disorder along the carbonyl/chloro axis (Cambridge Structural Database (CSD), Version 5.25, January 2004 update; Allen, 2002). The coordination around the Rh atom shows a slightly distorted square-planar arrangement (Fig. 1 and Table 1). The Rh atom is displaced 0.0303 (16) Å from the coordination plane (r.m.s. deviation of fitted atoms = 0.0534 Å).

(I)
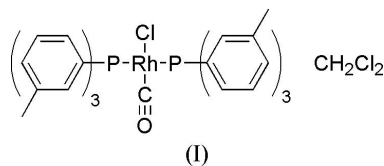
The most widely used method for determining ligand steric behaviour at a metal centre is by calculating the cone angle, as described previously (Tolman, 1977; Otto et al., 2000). For the current study, actual M—P bond distances were used, yielding effective cone angles (θ_E). The substituents of the phosphine may have different orientations, resulting in variations in cone angle sizes, as observed by Ferguson et al. (1978), and may not necessarily be a true indication of the steric properties of the phosphine in solution compared with the solid state. The
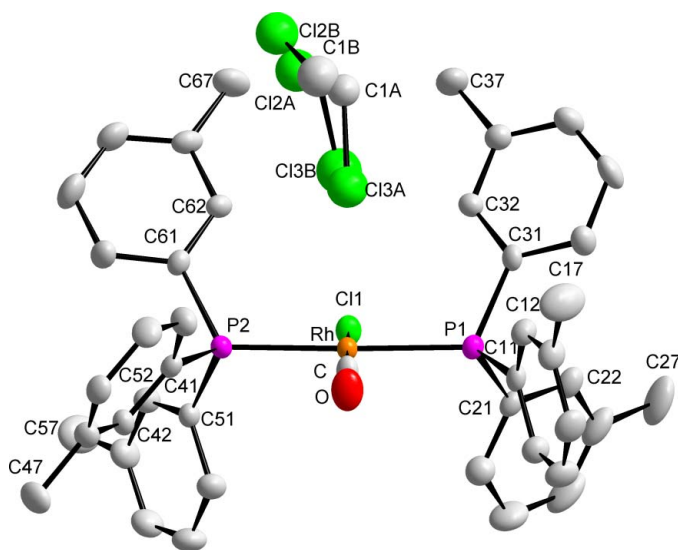
Figure 1
The structure of (I). Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. For the C atoms, the first digit indicates the ring number and the second digit indicates the position of the atom in the ring. Both disorder components are shown for the solvent molecule.

values of 160 and 155° obtained for tri-*m*-tolylphosphine are larger than the 145° cone angle obtained for tri-*p*-tolyl-phosphine (Otto *et al.*, 1999) (data extracted and calculated from the CSD). The $^1J(Rh-P)$ coupling of 126 Hz is in agreement with the $^1J(Rh-P)$ of 118 Hz for the tri-*p*-tolyl-phosphine complex reported earlier.

It is interesting to note 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 crystal structure, which slightly distorts the $Rh-C\equiv O$ and $P1-Rh-P2$ angles (Table 1). The fact that the title compound crystallizes with a molecule of dichloromethane could also be responsible for the observed ordered packing mode. However, the *meta* substituents on the phenyl rings could also be responsible for this, since it is unlikely that the relative orientations of the six rings will be symmetrical.

Large thermal motion of the dichloromethane solvate molecule, held only by weak intermolecular hydrogen bonding, is observed. This was treated isotropically as disordered over two partially occupied sites with occupancies refined to 0.426 (11) and 0.574 (11).

Experimental

$[RhCl(CO)_2]_2$ was prepared according to the method described by McCleverty & Wilkinson (1990). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of $P(C_7H_7)_3$ (94.1 mg, 0.312 mmol) in dichloromethane (5.0 ml) was added slowly to a yellow solution of $[RhCl(CO)_2]_2$ (28.8 mg, 0.074 mmol) in acetone (5.0 ml). Immediately, gas evolution was observed and the colour of the solution became lighter. Slow evaporation of the solvent afforded the title compound as a crystal-line yellow solid, which was washed with pentane to give the pure compound (yield: 113 mg, 99%). ^1H NMR (CDCl$_3$, 300 MHz, p.p.m.):

7.32, 7.15, 6.89 (ArH), 4.86 (CH$_2$Cl$_2$), 1.99 (CH$_3$); $^{13}C\{H\}$ NMR (CDCl$_3$, 75.4 MHz, p.p.m.): 137.5, 135.5, 132.9, 131.6, 130.7, 127.7 (ArC), 21.5 CH$_3$); $^{31}P\{C\}$ (CDCl$_3$, 121.5 MHz, p.p.m.): 30.33 [d, $^1J_{(Rh-P)}$ = 126 Hz]; IR (CH$_2$Cl$_2$) ν(CO): 1976 cm^{-1}; (KBr) ν(CO): 1981 cm^{-1}; UV–Vis (CH$_2$Cl$_2$): λ_{max}274 (100), 268 (22%) nm.

Crystal data

$[RhCl(C_{21}H_{21}P)_2(CO)]\cdot CH_2Cl_2$	$Z = 2$
$M_r = 859.99$	$D_x = 1.386$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.061$ (2) Å	Cell parameters from 814
$b = 11.763$ (2) Å	reflections
$c = 19.337$ (4) Å	$\theta = 2.6-22.6°$
$\alpha = 100.87$ (3)°	$\mu = 0.72$ mm^{-1}
$\beta = 100.71$ (3)°	$T = 293$ (2) K
$\gamma = 108.14$ (3)°	Block, yellow
$V = 2061.0$ (9) Å^3	$0.60 \times 0.22 \times 0.12$ mm

Data collection

Bruker SMART 1K CCD diffractometer	8864 independent reflections
ω scans	5105 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.047$
SADABS (Bruker, 1998)	$\theta_{max} = 27.0°$
$T_{min} = 0.672$, $T_{max} = 0.919$	$h = -12 \rightarrow 12$
13219 measured reflections	$k = -14 \rightarrow 15$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0525P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.062$	$+ 1.6693P]$
$wR(F^2) = 0.151$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
8864 reflections	$\Delta\rho_{max} = 0.84$ e Å^{-3}
464 parameters	$\Delta\rho_{min} = -0.73$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Rh—C	1.792 (6)	Rh—Cl1	2.3659 (15)
Rh—P1	2.3231 (16)	C—O	1.156 (6)
Rh—P2	2.3266 (16)		
C—Rh—P1	90.40 (18)	C—Rh—Cl1	174.6 (2)
C—Rh—P2	92.62 (18)	O—C—Rh	176.3 (6)
P1—Rh—P2	176.88 (6)		
C11—P2—Rh—C	−6.3 (3)	C41—P2—Rh—C	0.6 (3)
C21—P2—Rh—C	−132.7 (3)	C51—P2—Rh—C	−118.8 (3)
C31—P2—Rh—C	117.1 (3)	C61—P2—Rh—C	121.3 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C32—H32···Cl1	0.93	2.81	3.543 (6)	137
C67—H67C···Cl2A	0.96	2.75	3.505 (10)	137
C67—H67C···Cl2B	0.96	2.69	3.547 (9)	149

The aromatic, methylene and methyl H atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ for the aromatic and methylene H atoms, and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl H atoms. The methyl H atoms were located in a difference Fourier map and they were then refined as rigid rotors.

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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