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Key indicators

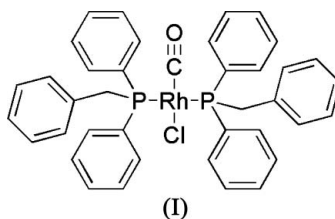
Single-crystal X-ray study
 $T = 150\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.023
 wR factor = 0.057
Data-to-parameter ratio = 20.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*trans*-Bis(benzylidiphenylphosphine)carbonyl-
chlororhodium(I)

In the title compound, *trans*-[RhCl(C₁₉H₁₇P)₂(CO)], selected geometrical parameters are: Rh–P = 2.3204 (5) and 2.3365 (5) Å, Rh–Cl = 2.3687 (5) Å and Rh–C = 1.8007 (15) Å, and P–Rh–P = 179.005 (16)°, P–Rh–Cl = 88.807 (15)° and 90.529 (15)°, and Rh–C≡O = 176.43 (13)°. The effective cone angles for the phosphine ligands were calculated to be 156 and 160°.

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Comment

The original Vaska complex, *trans*-[Ir(CO)Cl(PPh₃)₂], was initially reported by Angoletta (1959), but was later correctly formulated by Vaska & Di Luzio (1961). This class of symmetrical square-planar complexes (usually including Rh, Ir, Pd and Pt) often crystallize with the metal atom on a crystallographic inversion centre, 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(AX₃)₂] ($M = \text{Rh, Ir}$; $A = \text{group 15 donor atom P, As, Sb}$; $X = \text{alkyl, aryl, aroyl, etc.}$; Roodt *et al.*, 2003). We report here the rhodium analogue, (I), of Vaska's complex with benzylidiphenylphosphine as ligand, as another complex in this series.



The title compound is one of the few crystallographic examples of these complexes which does not show disorder along the Cl–Rh–C≡O axis [Cambridge Structural Database (CSD), Version 5.26, February 2005 update; Allen, 2002]. The coordination polyhedron around the Rh atom of (I) shows a distorted square-planar arrangement (Fig. 1 and Table 1), illustrated by the displacement of the Rh atom by 0.1417 (2) Å from the mean plane of the Cl, C and two P atoms.

The most widely used method for determining ligand steric behaviour at a metal centre is the calculation of the Tolman cone angle (θ_T), as described previously by Tolman (1977) and Otto *et al.* (2000). For the present study, actual Rh–P bond distances were used, with a van der Waals radius of 1.20 Å for H, yielding effective cone angles (θ_E). The substituents of the

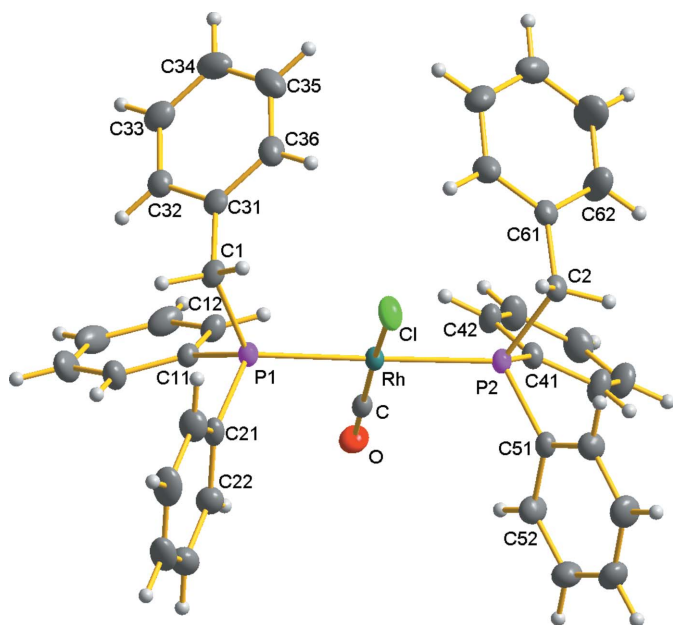


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. For the C atoms, the first digit indicates the ring number and the second digit indicates the position of the atom in the ring.

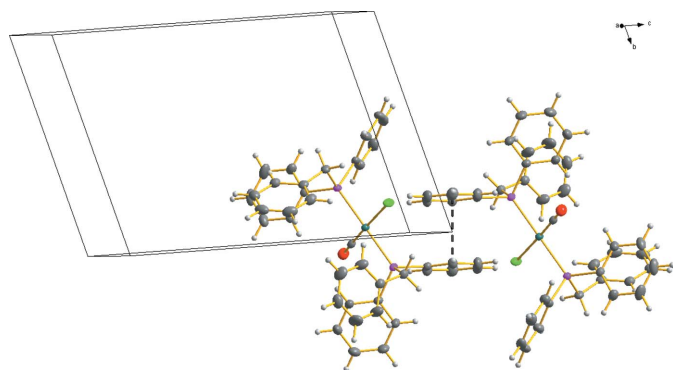


Figure 2
The π -stacking between two molecules of (I). The interaction is indicated by a dashed line.

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. The values of 156 and 160° obtained here for benzyldiphenylphosphine are larger than the 148° cone angle obtained for triphenylphosphine (data extracted and calculated from the CSD).

Several short contacts were observed (Table 2) around the Cl–Rh–C≡O group. In addition, π -stacking, with a distance of 3.443 Å, is observed for some phenyl rings of neighbouring molecules (Fig. 2). These interactions might contribute to factors leading to the ordered packing of (I).

It is interesting to note 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 the packing, which slightly distorts the Rh–C≡O angle (Table 1). This effect was

previously observed for a polymorph of *trans*-[Rh(CO)Cl{PPh₃}₂] (Kemp *et al.*, 1995).

Experimental

[RhCl(CO)₂]₂ was prepared according to the literature method of McCleverty & Wilkinson (1990). All other chemicals and solvents were obtained from Sigma–Aldrich and used as received. A solution of PBzPh₂ (0.100 g, 0.36 mmol) in dichloromethane (2 ml) was added to a yellow solution of [RhCl(CO)₂]₂ (35 mg, 0.09 mmol) in dichloromethane (5.0 ml). Gas evolution was observed immediately and the solution turned lighter in colour. The volatiles were evaporated at room temperature, and the yellow residue was recrystallized from acetone (5.0 ml) to give crystals suitable for X-ray analysis in a quantitative yield. ¹H NMR (CDCl₃, 300 MHz, p.p.m.): 7.52–7.09 (*m*, 15H), 4.05 (*t*, 2H, ²*J*_{PH} = 5 Hz); ³¹P NMR (CDCl₃, 121.5 MHz, p.p.m.): 30.2 (*d*, ¹*J*_{RhP} = 127 Hz); IR (CH₂Cl₂): $\nu(\text{CO})$ 1968 cm⁻¹; (KBr): $\nu(\text{CO})$ 1959 cm⁻¹.

Crystal data

[RhCl(C₁₉H₁₇P)₂(CO)]
*M*_r = 718.96
Triclinic, *P* $\bar{1}$
a = 9.5651 (12) Å
b = 11.9457 (16) Å
c = 16.4284 (18) Å
 α = 68.873 (4)°
 β = 80.939 (5)°
 γ = 73.061 (5)°
V = 1672.1 (4) Å³

Z = 2
*D*_x = 1.428 Mg m⁻³
Mo *K*α radiation
Cell parameters from 9178 reflections
 θ = 2.5–28.3°
 μ = 0.72 mm⁻¹
T = 150 (2) K
Plate, yellow
0.34 × 0.24 × 0.05 mm

Data collection

Bruker X8 APEX-II Kappa 4K
CCD diffractometer
 ω scans
Absorption correction: multi-scan
SADABS (Bruker, 1998)
*T*_{min} = 0.793, *T*_{max} = 0.965
34434 measured reflections

8287 independent reflections
7426 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.029
 θ_{max} = 28.3°
h = -12 → 12
k = -15 → 15
l = -21 → 21

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.023$
wR(*F*²) = 0.057
S = 1.03
8287 reflections
397 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.8407P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.001
 $\Delta\rho_{\text{max}} = 0.41 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Rh–C	1.8007 (15)	Rh–Cl	2.3686 (4)
Rh–P1	2.3204 (5)	O–C	1.1513 (18)
Rh–P2	2.3364 (5)		
C–Rh–P1	90.85 (5)	P2–Rh–Cl	90.529 (15)
C–Rh–P2	89.91 (5)	C1–P1–Rh	115.96 (5)
P1–Rh–P2	179.004 (14)	C2–P2–Rh	117.34 (5)
C–Rh–Cl	172.05 (5)	O–C–Rh	176.44 (14)
P1–Rh–Cl	88.807 (15)		
C–Rh–P1–C11	-26.75 (7)	C–Rh–P2–C41	32.35 (7)
C–Rh–P1–C21	93.36 (7)	C–Rh–P2–C2	153.58 (7)
C–Rh–P1–C1	-148.30 (7)	Rh–P1–C1–C31	71.70 (12)
C–Rh–P2–C51	-86.23 (7)	Rh–P2–C2–C61	-70.13 (12)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C1-H1B\cdots Cl$	0.99	2.82	3.4350 (16)	121
$C56-H56\cdots Cl^i$	0.95	2.8	3.7042 (17)	159
$C65-H65\cdots O^{ii}$	0.95	2.44	3.203 (2)	138

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

Table 3
Comparative geometrical data (Å, °) for compounds of the general formula *trans*-[Rh(CO)Cl(PR₃)₂].

PR ₃	Rh–P (Å)	θ _E (°)	Reference
PPh ₂ CH ₂ Ph ^a	2.3204 (5)	160	TW
	2.3365 (5)	156	
PPh ₂ <i>o</i> -tol ^a	2.328	169	i
	2.327	163	
PPh ₂ OMes ^a	2.310	183	ii
	2.320	244	
PPh ₂ CH ₂ NPh ₂ ^a	2.333	183	iii
	2.324	175	
PPh ₂ CH=CH ₂ ^b	2.323	151	iv
PBz ₃ ^a	2.316 (2)	170	v
	2.315 (2)	172	

Notes: (a) ordered; (b) disordered; *o*-tol: *ortho*-tolyl; Mes: mesityl. References: TW (this work); (i) Suomalainen *et al.* (2001); (ii) Chahen *et al.* (2005); (iii) Balch *et al.* (1990); (iv) Kessler *et al.* (1993); (v) Muller *et al.* (2002).

The aromatic and methylene H atoms were placed in geometrically idealized positions ($C-H = 0.95-0.99$ Å) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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