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Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.010\text{ \AA}$

R factor = 0.048

w R factor = 0.091

Data-to-parameter ratio = 10.1

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

trans-Carbonylchlorobis(tribenzylphosphine)-rhodium(I)

The title compound, $[\text{RhCl}(\text{PBz}_3)_2(\text{CO})]$ [PBz_3 = tribenzylphosphine, $\text{P}(\text{C}_7\text{H}_7)_3$], which is the first reported tribenzylphosphine–rhodium(I) structure, has pseudo-square-planar coordination geometry, with Rh–P bond distances of 2.3164 (15) and 2.3156 (16) Å. The Rh–Cl, Rh–C and C–O bond distances are 2.3654 (15), 1.783 (6) and 1.162 (6) Å, respectively, and the angles P–Rh–P, P–Rh–Cl (2 occurrences) and C–Rh–Cl are 177.67 (6), 90.86 (5), 87.11 (5) and 178.55 (17)°, respectively. Effective cone angles for PBz_3 are 170 and 172°, while the Tolman cone angles are 171 and 173°. Each tribenzylphosphine has one benzyl C atom close to the coordination plane, with C–P–Rh–CO torsion angles of -1.6 (3) and -30.2 (3)°, and with the benzyl C atoms in a *gauche* conformation relative to the P··P axis. DFT (density functional theory) calculations, optimizing the geometry of the complex in the gas phase, approximately reproduce this conformation, showing that it is only slightly affected by the crystal-packing arrangement.

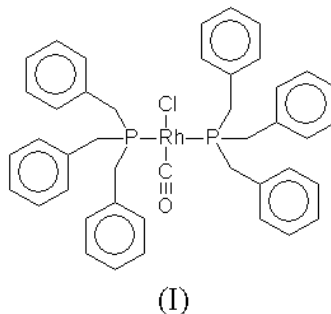
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Comment

Complexes with the general formula *trans*- $[\text{MClXL}_2]$ ($M = \text{Rh}, \text{Ir}, \text{Pd}, \text{Pt}$; $X = \text{Me}, \text{CO}$; $L =$ tertiary phosphine or arsine) often crystallize with the metal 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). This study is part of an investigation aiming to elucidate the factors governing a disordered packing. It should also be noted that, to our knowledge, the title compound, (I), is the first reported rhodium structure containing the PBz_3 ligand.



The Rh atom is in a general position and there is no disorder of the Cl–Rh–CO moiety. All angles within the Rh coordination sphere are close to those expected for a square-planar environment (Table 1). There are two intramolecular Rh··H agostic interactions, one on each side of the coordination plane, with Rh··H distances of 3.04 and 2.92 Å and H–Rh–P angles of 75 and 107°, respectively, giving a

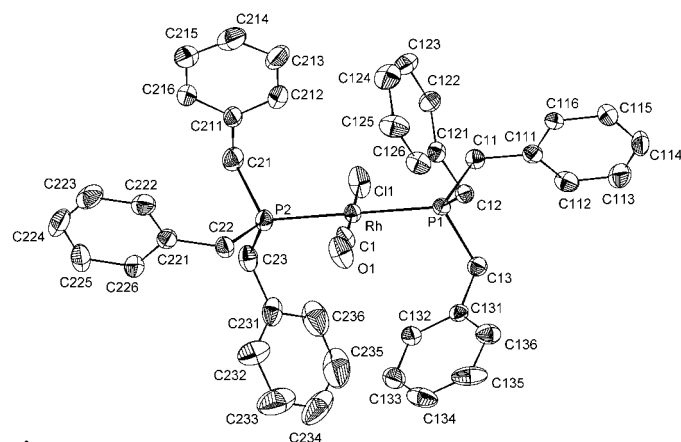


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids (30% probability). H atoms have been omitted for clarity.

pseudo-octahedral environment around Rh. High anisotropy is observed for atoms C234 and C235, lying on the periphery of the molecule. This is the result of weak packing forces ($\text{H}\cdots\text{H}$, $\text{H}\cdots\text{C}$ and one $\text{H}\cdots\text{Cl}$), allowing for high flexibility of the PBz_3 ligands, and is especially observed in one PBz_3 ligand, indicating some freedom of packing in this region; it may also explain some observed short $\text{C}\cdots\text{C}$ distances (Albertsson *et al.*, 1980). The $\text{Rh}-\text{P}$, $\text{Rh}-\text{Cl}$ and $\text{Rh}-\text{CO}$ bonds, together with bonds in the PBz_3 ligand, are within normal ranges for this type of complex (Allen & Kennard, 1993).

The CH_2 spacers between the P atom and phenyl rings in the PBz_3 ligand introduce additional flexibility compared to a PPh_3 ligand. This increases the ligand cone angle size and is expected to influence, for example, the reactivity of the complex. The individual benzyl groups may have different orientations, resulting in variations in cone-angle sizes, as observed earlier (Ferguson *et al.*, 1978). The most widely used method for describing ligand steric behaviour at a metal centre is the Tolman cone angle (Tolman, 1977), using an $M-\text{P}$ bond distance of 2.28 Å, $\text{C}-\text{H}$ bond distances of 0.97 Å, and 1.2 Å as the van der Waals radius of hydrogen. For the calculation of effective cone angles, actual $\text{Rh}-\text{P}$ bond distances, as determined from crystallographic data, are used (Otto *et al.*, 2000). Values obtained from effective cone-angle calculations for the title compound, 171 and 173°, are in agreement with the value of 165° proposed by Tolman (1977) for PBz_3 , and also correlate with recent work (Johansson *et al.*, 2002), where an effective cone angle of $165\pm 12^\circ$ was postulated. Only one of the benzyl C atoms is used in the cone-angle calculation, while the phenyl rings of the other two substituents contribute to the large cone angle. The cone-angle values may not be a true indication of the ligand influence on the metal centre behaviour, since the phenyl rings used to calculate cone angles are not in the close vicinity of the metal. In Table 2, the title compound is compared with other closely related Ni^{II} , Pd^{II} and Pt^{II} complexes containing two of the bulky tribenzylphosphine ligands in a *trans* configuration. The Tolman (θ_T) and effective (θ_E) cone angles for (I) correlate with those calculated by Johansson *et al.* (2002), but deviate

substantially from some other reported values (Bendiksen *et al.*, 1982).

The two $\text{C}-\text{P}-\text{Rh}-\text{CO}$ torsion angles, representing the least deviation from the coordination plane for the title compound, are $-1.6(3)$ and $-30.2(3)^\circ$, *i.e.* one $\text{P}-\text{C}$ bond is close to the coordination plane for one of the ligands and one is slightly out of the plane for the other. This was previously observed in *trans*- $[\text{PtCl}_2(\text{XPh}_3)_2]$ ($\text{X} = \text{P}, \text{As}$) (Johansson *et al.*, 2000; Johansson & Otto, 2000), *trans*- $[\text{MX}_2(\text{PBz}_3)_2]$ ($M = \text{Pt}, \text{X} = \text{Cl}^-, \text{I}^-, \text{NCS}^-$; $M = \text{Pd}, \text{X} = \text{I}^-$; Johansson *et al.*, 2002), *trans*- $[\text{PtH}(\text{OPh})(\text{PBz}_3)_2]$ (Seligson *et al.*, 1991) and $[\text{PdX}_2(\text{PBz}_3)_2]$ ($\text{X} = \text{N}_3^-, \text{CN}^-$; Bendiksen *et al.*, 1982). The orientation of the benzyl C atoms relative to the $\text{P}-\text{Rh}-\text{P}$ axis are thus *gauche*. In previous studies, it was observed that the orientation of the benzyl C atoms relative to the $\text{P}-\text{M}-\text{P}$ axis were *anti*, implying a pseudo-inversion centre in the complex, except in the case of *trans*- $[\text{Pt}(\text{NCS})_2(\text{PBz}_3)_2]$, where a *gauche* conformation was also observed (Johansson *et al.*, 2002). DFT calculations on the title complex in the gas phase result in $\text{C}-\text{P}-\text{Rh}-\text{CO}$ torsion angles of -17.4 and 6.2° , which are fairly close to the observed values, implying that the conformation in the crystal structure is only slightly affected by the packing arrangement. A local minimum is also observed when the $\text{P}-\text{C}$ bond is close to the coordination plane, but with the $\text{C}-\text{P}-\text{Rh}-\text{Cl}$ torsion angles close to zero, *i.e.* $\text{Cl}-\text{Rh}-\text{CO}$ is rotated by approximately 180° compared to the global minimum. The energy difference between the global and local minima is 18.5 kJ mol^{-1} , which may be too large for a disordered packing for the title compound. The global minimum structure has one agostic interaction on one side of the coordination plane ($\text{Rh}\cdots\text{H} = 2.59 \text{ \AA}$) and two on the other side ($\text{Rh}\cdots\text{H} = 3.05$ and 3.12 \AA). The calculations indicate interactions between the metal and the H atoms, since the Mulliken charges are 0.19 for these three H atoms, compared to 0.11 for H atoms further away.

Experimental

$[\text{RhCl}(\text{CO})_2]_2$ (Lebedev National Rubber Research Institute) and PBz_3 (Aldrich) were used as received. PBz_3 (157 mg, 0.52 mmol), dissolved in acetone (5 ml), was added to a solution of $[\text{RhCl}(\text{CO})_2]_2$ (50 mg, 0.13 mmol) in acetone (10 ml). Slow evaporation of the solution yielded yellow crystals suitable for X-ray analysis. ^{31}P NMR (CDCl_3): 18.1 p.p.m. [$d, {}^1J(\text{Rh}-\text{P}) = 124 \text{ Hz}$]; IR (DCM), $\nu(\text{CO})$: 1968 cm^{-1} . Quantum chemical geometry optimizations were performed with the density-functional B-P86 method, as implemented in the *Turbomole* 5.5 software (Hertwig & Koch, 1997; Treutler & Ahlrichs, 1995). Basis sets at the def-SVP level were used for Rh, Cl and P, and at 6-31g* for the other atoms. Two starting structures, one direct from the crystal structure data and one modified with an *anti* conformation along the $\text{P}\cdots\text{P}$ axis, reproduced approximately the same final geometry of the complex in the gas phase. However, a starting structure with $\text{O}-\text{C}-\text{Rh}-\text{Cl}$ rotated by approximately 180° compared to the crystal structure found a local minimum in this region, with a somewhat larger energy compared to the global minimum. Accurate energies were calculated with single-point calculations on the optimized structures, by the B3LYP method, and using basis sets def-TZVPP for Rh and def-TZVP for the other atoms, as implemented in *Turbomole* 5.5.

Crystal data

[RhCl(C ₂ H ₅ P) ₂ (CO)]	Z = 2
<i>M_r</i> = 775.11	<i>D_x</i> = 1.371 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 10.031 (1) Å	Cell parameters from 1993 reflections
<i>b</i> = 10.165 (1) Å	θ = 2–21°
<i>c</i> = 18.9910 (19) Å	μ = 0.64 mm ⁻¹
α = 93.36 (3)°	<i>T</i> = 293 K
β = 90.37 (3)°	Cuboid, yellow
γ = 103.69 (3)°	0.09 × 0.08 × 0.03 mm
<i>V</i> = 1877.8 (4) Å ³	

Data collection

Bruker SMART diffractometer	4389 reflections with <i>I</i> > 2σ(<i>I</i>)
ω scans	<i>R</i> _{int} = 0.032
Absorption correction: multi-scan (SADABS; Siemens, 1998)	θ_{\max} = 31.7°
<i>T</i> _{min} = 0.85, <i>T</i> _{max} = 0.95	<i>h</i> = -14 → 14
19116 measured reflections	<i>k</i> = -14 → 14
11180 independent reflections	<i>l</i> = -21 → 27

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.048	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0462 <i>P</i>) ²]
<i>wR</i> (<i>F</i> ²) = 0.091	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>S</i> = 0.88	(Δ/σ) _{max} < 0.001
4389 reflections	Δρ _{max} = 0.78 e Å ⁻³
433 parameters	Δρ _{min} = -0.50 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Rh—P1	2.3164 (15)	Rh—Cl	2.3654 (15)
Rh—P2	2.3156 (16)	Cl—O1	1.162 (6)
Rh—C1	1.783 (6)		
P1—Rh—P2	177.67 (6)	P2—Rh—Cl	87.11 (5)
P1—Rh—C1	90.54 (17)	Cl—Rh—Cl	178.55 (17)
P2—Rh—C1	91.48 (17)	Rh—C1—O1	179.3 (6)
P1—Rh—C1	90.86 (5)		

Table 2

Comparison of torsion angles (θ_{Tor1} and θ_{Tor2}), cone angles (θ_T and θ_E) (°) and the type of conformation for various *trans*-[*M*(*X*)(*Y*)(PBz₃)₂] complexes.

<i>M</i> (<i>X</i>)	θ_{Tor1}	θ_{Tor2}	θ_T	θ_E	Conformation	Ref.
Ni(Cl)	1.72 (11)	-1.72 (11)		167		
	14.05 (8)	-14.05 (8)		162	<i>anti</i>	<i>a</i> *
Pd(I)	0.8 (4)	-3.0 (4)	157	155	<i>anti</i>	<i>b</i>
Pd(CN)	18.63 (5)	-18.63 (5)	232	182	<i>anti</i>	<i>c</i> *
Pd(N ₃)	12.24 (5)	-12.24 (5)	200	163	<i>anti</i>	<i>c</i> *
Pt(Cl)	1.6 (2)	-1.6 (2)	164	162		
	1.08 (15)	-1.08 (15)	160	160	<i>anti</i>	<i>b</i>
Pt(I)	-2.1 (3)	3.9 (3)	156	155		
			161	163	<i>anti</i>	<i>b</i>
Pt(NCS)	-0.8 (2)	-15.2 (2)	179	178		
			167	165	<i>gauche</i>	<i>b</i>
Rh(CO)(Cl)	-1.6 (3)	-30.2 (3)	170	171		
			172	173	<i>gauche</i>	<i>d</i>

Notes: (*a*) Novoa de Armas *et al.* (2000); (*b*) Johansson *et al.* (2002); (*c*) Bendiksen *et al.* (1982); (*d*) this work. * Calculated data extracted from CSD (Allen & Kennard, 1993).

The first 50 frames of data were recollected at the end of the data collection to check for decay; none was found. Both the minimum and maximum residual electron densities lie within 1 Å of the Rh atom.

Data collection: SMART (Siemens, 1998); cell refinement: SAINT; data reduction: SAINT (Siemens, 1998); program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: CRYSTALS (Watkin *et al.*, 2001); molecular graphics: DIAMOND (Brandenburg & Brendt, 2000); software used to prepare material for publication: CRYSTALS.

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