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Key indicators

Single-crystal X-ray study

T = 100 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

Disorder in main residue

R factor = 0.018

wR factor = 0.047

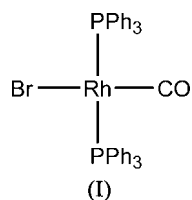
Data-to-parameter ratio = 19.5

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.*trans*-Bromocarbonylbis(triphenylphosphine)-
rhodium

The title compound, $[\text{RhBr}(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})]$, can be characterized as a rhodium(I) Vaska-type compound based only on the spectroscopic $[\nu_{\text{KBr}}(\text{CO}), ^{31}\text{P}]$ data. A low-temperature X-ray crystallographic analysis shows that the compound possesses a crystallographically imposed centre of symmetry with a statistically disordered Br atom and CO group. The essentially different occupancies for the Br atom and the CO group [0.283 (2) and 0.717 (2), respectively] suggest that the compound exists as a mixture of rhodium(0), rhodium(I) and rhodium(II) complexes.

Comment

Rhodium(I) Vaska-type compounds have attracted significant interest in the past few years (Otto & Roodt, 2004; Roodt *et al.*, 2003; Moloy & Petersen, 1995; CSD, Version 5.27, Allen, 2002). The increased activity in this field is partially due to the role that rhodium(I) complexes can play in catalytic cycles (Hua & Tanaka, 2004; Crous *et al.*, 2005). The chloro (Muir & Ibers, 1969; Del Pra *et al.*, 1979; Ceriotti *et al.*, 1983; Chen *et al.*, 1991; Dunbar & Haefner, 1992) and iodo (Basson *et al.*, 1990) derivatives have been reported for the triphenylphosphine ligand, but the bromo derivative has received little or no attention in the literature. In this paper, the crystal structure of the title bromo derivative, (I), is presented.



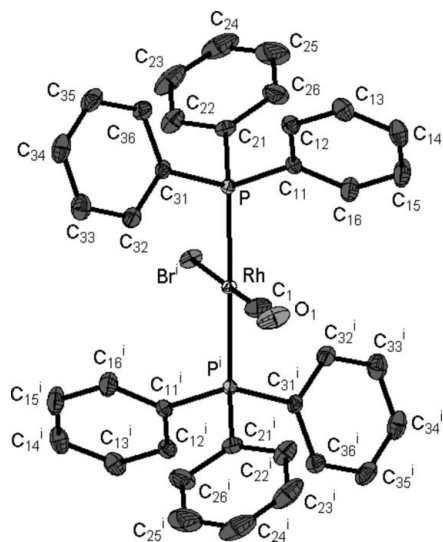
A typical bonding pattern in (I) (Fig. 1) is observed for the triphenylphosphine ligand. The Rh–P bond length is 2.3302 (3) Å (Table 1), while the Br atom and carbonyl group are disordered. Rh lies on a centre of symmetry. A low-temperature study (100 K) was necessary to resolve this disorder successfully (Fig. 2).

Structurally, the rhodium(I) Vaska-type compounds present an interesting dilemma, with an observed disorder for the carbonyl and chloro ligands in the solid state (Table 2). This disorder has an irregular nature since differing tertiary aryl phosphine ligands can induce either a disordered or a non-disordered structure. In contrast, the iodo derivative (Basson *et al.*, 1990) exhibits no disorder, though a polymorph containing a disordered iodo and carbonyl group may exist.

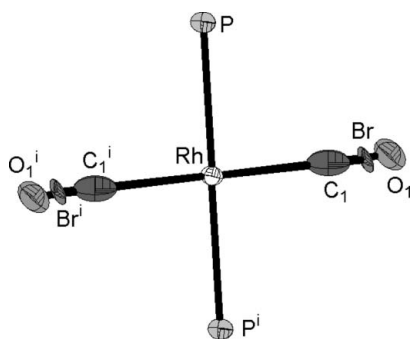
Additional experimental data were necessary to confirm the molecular formula of the title compound. Three possible

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Figure 1

Representation of (I) as a rhodium(I) Vaska-type complex, showing the numbering scheme and displacement ellipsoids at the 50% probability level [symmetry code: (i) $1 - x, -y, 1 - z$]. H atoms have been omitted for clarity.


Figure 2

Environment of Rh in (I) with the disordered Br atom and carbonyl group [symmetry code: (i) $1 - x, -y, 1 - z$].

compounds were available: $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]$, a rhodium(0) complex, $[\text{Rh}(\text{Br})\text{CO}(\text{PPh}_3)_2]$, a rhodium(I) Vaska-type complex, and $[\text{Rh}(\text{Br})_2(\text{PPh}_3)_2]$, a rhodium(II) complex. Since Rh^0 - and Rh^{II} -type compounds are generally prepared under dry anaerobic conditions, the likelihood of formation of these complexes was significantly reduced (see *Experimental*). Further evidence of a rhodium(I) complex was observed from the ^{31}P NMR spectra, giving a doublet corresponding to a single Rh—P species. In order to eliminate the Rh^0 and Rh^{II} complexes, a solid-state IR spectrum of the title compound was measured. A single carbonyl peak in the region $1900\text{--}2000\text{ cm}^{-1}$ was observed, indicating a rhodium(I) species. Since $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2]$ would have at least two carbonyl peaks in this region (Steyl *et al.*, 2004) and $[\text{Rh}(\text{Br})_2(\text{PPh}_3)_2]$ would have no carbonyl peaks at all, we believe that (I) is a rhodium(I) Vaska-type compound.

Thus, although the structure could be solved, the disorder posed a significant hurdle in determining of exact positions of the Br atom and the carbonyl group (owing to their positional proximity, Fig. 2).

Experimental

Sodium bromide (7 mg, 0.068 mmol) in acetone (2 ml) was added to a solution of $[\text{Rh}(\text{CO})(\text{PPh}_3)]^+$ trifluoromethanesulfonate (50 mg, 0.06 mmol) in acetone (10 ml) with constant stirring. The resulting solution was filtered and allowed to evaporate at room temperature, to yield crystals suitable for X-ray crystallography. (Yield 16 mg, 36%). Spectral data are given in the CIF.

Crystal data

$[\text{RhBr}(\text{C}_{18}\text{H}_{15}\text{P})_2(\text{CO})]$
 $M_r = 712.84$
 Triclinic, $P\bar{1}$
 $a = 9.1519(4)\text{ \AA}$
 $b = 9.5797(5)\text{ \AA}$
 $c = 10.2796(5)\text{ \AA}$
 $\alpha = 73.040(2)^\circ$
 $\beta = 89.016(2)^\circ$
 $\gamma = 69.567(2)^\circ$

$V = 804.19(7)\text{ \AA}^3$
 $Z = 1$
 $D_x = 1.472\text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 1.36\text{ mm}^{-1}$
 $T = 100(2)\text{ K}$
 Plate, yellow
 $0.37 \times 0.12 \times 0.07\text{ mm}$

Data collection

Bruker APEX 24K CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\text{min}} = 0.762, T_{\text{max}} = 0.877$

21423 measured reflections
 4011 independent reflections
 3855 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 28.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.018$
 $wR(F^2) = 0.047$
 $S = 1.07$
 4011 reflections
 206 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0192P)^2 + 0.4097P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.39\text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.54\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Rh—C1	1.861 (6)	Rh—Br	2.4533 (13)
Rh—P	2.3302 (3)	O1—C1	0.985 (7)
C1—Rh—P	88.75 (11)	P—Rh—Br	89.05 (3)
C1—Rh—Br ⁱ	179.45 (11)	O1—C1—Rh	178.6 (5)

Symmetry code: (i) $-x + 1, -y, -z + 1$.

Table 2

Comparative X-ray crystallographic data for $[\text{Rh}(X)\text{CO}(\text{PPh}_3)_2]$ complexes.

X	Rh—X	Rh—C	C=O	Disorder	Space group
Cl ^a	2.356	1.847	1.126	No	$P2_1/c$
Cl ^b	2.405	1.987	0.739	Yes	$P1$
Cl ^c	2.371	1.810	1.143	No	$P2_1/n$
Cl ^d	2.381	1.759	1.143	Yes	$P\bar{1}$
Cl ^e	2.383	1.761	1.150	Yes	$Pbca$
Br ^f	2.453	1.862	0.984	Yes	$P\bar{1}$
I ^g	2.684	1.807	1.140	No	$P2_1/n$

Notes: (a) (Muir & Ibers, 1969); (b) (Del Pra *et al.*, 1979); (c) (Ceriotti *et al.*, 1983); (d) (Chen *et al.*, 1991); (e) (Dunbar & Haefner, 1992); (f) this work; (g) (Basson *et al.*, 1990).

All H atoms were positioned geometrically ($\text{C—H} = 0.93\text{ \AA}$) and allowed to ride on their parent atoms, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}$ of

the parent atom. The bromo and carbonyl disorder was solved by initially restraining the distances from the rhodium(I) metal centre and the C atom for the respective atoms. Once the positions of the atoms were determined, the displacement parameter restraints were slackened and anisotropic refinement proceeded. Finally the positional restraints were removed and the structure further refined. The refined occupancies for the Br atom and carbonyl group are 0.283 (2) and 0.717 (2), respectively.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2004); software used to prepare material for publication: *SHELXL97*.

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