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trans-Carbonyliodotris(triphenylstibine-*κSb*)rhodium(I)

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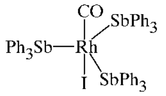
The crystal structure of the title compound, $[RhI(C_{18}H_{15}Sb)_3(CO)]$, represents a rare example of a crystallographically characterized five-coordinate Rh^I–$SbPh_3$ complex. The compound crystallizes with the I—Rh—CO core on a threefold rotation axis, with three crystallographically equivalent triphenylstibine ligands. Selected geometric parameters are: Rh—I = 2.7159 (8), Rh—Sb = 2.5962 (4), Rh—C_{CO} = 1.825 (6) and C_{CO}—O 1.153 (6) Å, and Sb—Rh—I = 89.374 (10) and Sb—Rh—C_{CO} = 90.626 (10)°. The cone angle of the $SbPh_3$ ligand was determined as 137°, according to the Tolman model.

Comment

Although stibine complexes of Rh have been known since the 1950s (Vallarino, 1957), surprisingly few crystallographic studies of these complexes have been reported to date. As has been pointed out in earlier investigations (Ugo *et al.*, 1969; Otto & Roodt, 2002), several experimental problems may arise during the characterization of these complexes, making X-ray crystallography the method of choice. As part of our systematic investigation of these systems (Otto *et al.*, 2002; Otto & Roodt, 2002), we obtained single crystals of *trans*-carbonyliodotris(triphenylstibine-*κSb*)rhodium(I), (I), and the crystal structure is presented here.



(I)

Compound (I) (Fig. 1) crystallizes with an almost perfect trigonal–bipyramidal geometry in the trigonal space group $P\overline{3}$. The packing in the crystal is governed by van der Waals forces alone; no significant intermolecular interactions are observed. The OC—Rh—I core is situated along the threefold rotation axis, resulting in three crystallographically equivalent $SbPh_3$ ligands around the Rh atom with angles of exactly 120°. Accordingly, the OC—Rh—I core is exactly linear and the C1—Rh—Sb and I—Rh—Sb angles are close to 90°, at 90.626 (10) and 89.374 (10)°, respectively.

An I—Rh—Sb—C11 torsion angle of 175.77 (10)° indicates phenyl ring 1 (C11–C16) points almost directly towards the CO moiety, whereas rings 2 (C21–C26) and 3 (C31–C36) are staggered with respect to the Rh—I bond, with I—Rh—Sb—C21 and I—Rh—Sb—C31 torsion angles of −63.88 (11) and 57.89 (9)°, respectively. These specific geometric orientations may account for the observation that the $SbPh_3$ ligands are marginally displaced towards the larger I ligand.

Based on molecular models, Tolman (1977) predicted that increasing the M—L or L—C (M is a metal and L is a ligand) bond lengths by 0.1 Å (for ligands containing donor atoms other than P) would result in a 3–5° decrease in the cone angle of the ligand. In this regard, the effective cone angle, as defined earlier (Otto *et al.*, 2000), utilizes the observed Rh—Sb bond distance, and the cone angle for $SbPh_3$ in (I) was calculated as 137°. This value is in excellent agreement with both Tolman's prediction and the average of 139° for six independent $SbPh_3$ ligands obtained during a previous study (Otto & Roodt, 2002).

In Table 2, compound (I) is compared with related *trans*-$[Rh(X)CO(LPh_3)_n]$ (n = 2 or 3; L is Sb or P) complexes, illustrating the effect of different X ligands on the geometric parameters of four- and five-coordinate $SbPh_3$ complexes of Rh^I. From these data, it is clear that the Rh—Sb bond length of 2.5962 (4) Å in (I) is comparable with the value of

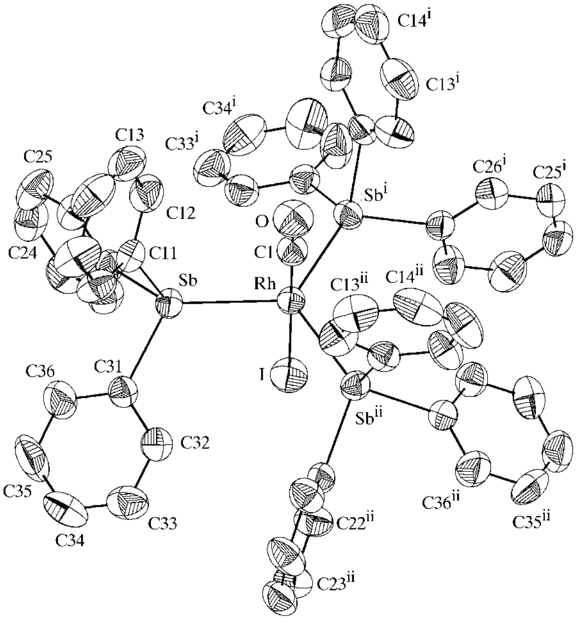


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity. The complex is numbered with the first digit of the phenyl rings referring to the number of the ring (1–3) and the second digit referring to the number of the atom within the ring (1–6) [symmetry codes: (i) $-x+y, 1-x, z$; (ii) $1-y, x-y+1, z$].

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2.5981 (5) Å found in the analogous five-coordinate Cl complex, but is slightly longer than the values of 2.568 (2) Å in the acetyl complex and 2.5655 (2) Å in the four-coordinate Cl complex. Not many Rh—I bond distances are known for complexes of this kind, but the Rh—I bond length of 2.7159 (8) Å in (I) is considerably longer than the value of 2.683 (1) Å determined for *trans*-[RhI(CO)(PPh$_3$)$_2$] (Basson *et al.*, 1990). This may be a result of the increased steric crowding in the five-coordinate complex or the increased electron density introduced by the three SbPh$_3$ ligands. A similar observation was made in relation to the Rh—Cl bond distances of the four- and five-coordinate triphenylstibine complexes (Otto & Roodt, 2002) listed in Table 2, where an elongation from 2.315 (3) to 2.4094 (18) Å was induced by the increase in coordination number.

Experimental

NaI (17 mg, 0.113 mmol) was added to a nitrogen-flushed solution of the [Rh(μ-Cl)(CO)$_2$]$_2$ dimer (20 mg, 0.051 mmol) in acetone (5 ml). The reaction medium immediately took on a deep-red colour and was stirred for a further 5 min after addition. Stirring was then discontinued and SbPh$_3$ (126 mg, 0.357 mmol) dissolved in acetone (7 ml) was added carefully so as to avoid the least disturbance to the solution. Deep-red rectangular crystals of (I) soon started separating from the solution; yields > 80% based on Rh were obtained. Spectroscopic analysis, IR (KBr, ν): 1977 cm^{-1} (CO); IR (dichloromethane, ν): 1978 cm^{-1} (CO).

Crystal data

[RhI(C$_{18}$H$_{15}$Sb)$_3$(CO)]
M_r = 1316.97
Trigonal, $P\overline{3}$
a = 14.462 (2) Å
c = 13.902 (3) Å
V = 2518.2 (7) Å^3
Z = 2
D_x = 1.737 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4642 reflections
θ = 2.2–24.8°
μ = 2.56 mm^{-1}
T = 293 (2) K
Parallelepiped, dark red
0.29 × 0.10 × 0.08 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.493, $T_{\max}$ = 0.815
24 940 measured reflections

5324 independent reflections
2651 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.094
$\theta_{\max}$ = 31.8°
$h = -18 \rightarrow 21$
$k = -20 \rightarrow 20$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.056$
S = 0.86
5324 reflections
185 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0154P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max}$ = 0.43 e Å^{-3}
$\Delta\rho_{\min}$ = −0.67 e Å^{-3}

H atoms were treated as riding, with C—H = 0.93 Å. Even though the structure contains solvent-accessible voids of 115 Å^3, both the minimum and maximum residual electron-density peaks were smaller than 1 e Å^{-3}, indicating that no molecular fragments remain unaccounted for.

Table 1
Selected geometric parameters (Å, °).

Rh—C1	1.825 (6)	Sb—C21	2.143 (3)
Rh—Sb	2.5962 (4)	Sb—C31	2.129 (3)
Rh—I	2.7159 (8)	C1—O	1.153 (6)
Sb—C11	2.140 (3)		
C1—Rh—Sb	90.626 (10)	C21—Sb—C31	96.21 (12)
Sb—Rh—I	89.374 (10)	C11—Sb—Rh	112.73 (9)
C11—Sb—C21	99.57 (12)	C21—Sb—Rh	124.39 (8)
C11—Sb—C31	101.04 (12)	C31—Sb—Rh	118.84 (8)
I—Rh—Sb—C11	175.77 (10)	I—Rh—Sb—C31	57.89 (9)
I—Rh—Sb—C21	−63.88 (11)		

Table 2
Comparative X-ray data for *trans*-[Rh(X)CO(LPh$_3$)$_n$] complexes.

X	n	L	Rh—C1 (Å)	Rh—L (Å)	Rh—X (Å)	Reference
Cl	2	Sb	1.797 (13)	2.5655 (2)	2.315 (3)	*a*
Cl	3	Sb	1.875 (7)	2.5981 (5)	2.4094 (18)	*a*
I	2	P	1.81 (1)	2.326 (2)	2.683 (1)	*b*
I	3	Sb	1.825 (6)	2.5962 (4)	2.7159 (8)	*c*
COCH$_3$	3	Sb	1.91 (2)	2.568 (2)	2.095 (16)	*d*

References: (*a*) Otto & Roodt (2002); (*b*) Basson *et al.* (1990); (*c*) this work; (*d*) Lamprecht *et al.* (1986).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1526). Services for accessing these data are described at the back of the journal.

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