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Di-μ-bromo-tetrabromotetrakis(trimethylphosphine)dirhodium(III)

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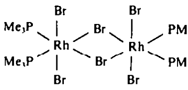
Abstract

The title structure, $[Rh_2Br_6(C_3H_9P)_4]$ (1), consists of neutral $[\mu\text{-}Br_2\text{-}\{RhBr_2(PMe_3)_2\}_2]$ bromide-bridged rhodium dimers. The Rh—P bond lengths are 2.273 (5) and 2.266 (5) Å.

Comment

As part of an investigation of the products arising from the irradiation of $[Rh\{P(CH_3)_3\}_2(CO)Cl]$ (2) (Tanaka, 1989) in the presence of aromatic hydrocarbons, a reaction mixture containing both phenylrhodium(III) hydride complexes and the starting complex, (2), was treated with an excess of dibromomethane in an attempt to obtain the corresponding phenylrhodium(III) bromide derivatives. On standing, red crystals of the neutral Rh^{III} dimer, di-μ-bromo-tetrabromotetrakis(trimethylphosphine)dirhodium(III), (1), precipitated from the reaction mixture. In this paper, the structure of $[Rh_2\{P(CH_3)_3\}_4Br_6]$, (1), is reported.



(1)

The structure consists of neutral Rh dimers. The Rh atoms are bridged by two Br^- ligands and are each coordinated to other Br^- ligands in positions *trans* to each other and *cis* to the bridging ligands and the two trimethylphosphine ligands. The trimethylphosphine ligands are *cis* to each other and *trans* to the bridging ligands. The chloro complex $[Rh_2(^nBu_3P)_4Cl_6]$ (Muir, Muir & Rivera, 1974) has an analogous arrangement around one of the Rh atoms, but has *trans* phosphines and *cis* chloro ligands around the other. The Rh—P bond lengths in the present structure [2.273 (5) and 2.266 (5) Å] are longer than the *cis* Rh—P bonds in the chloro structure [2.256 (15) Å] but shorter than the *trans* Rh—P bonds [2.321 (12) Å].

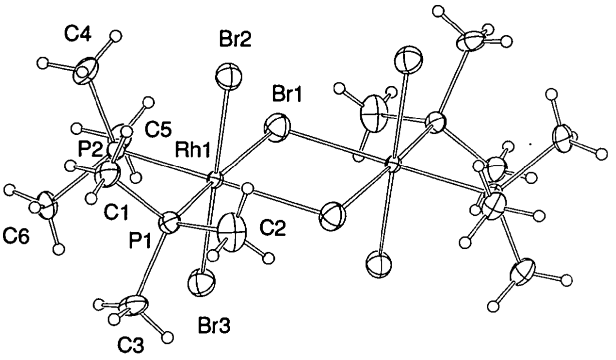


Fig. 1. *ORTEP* (Johnson, 1965) plot of $[Rh_2\{P(CH_3)_3\}_4Br_6]$.

Experimental

$[Rh\{P(CH_3)_3\}_2(CO)Cl]$ was synthesized in 65% yield (after sublimation and recrystallization from ether) using an analogous procedure to that outlined for the synthesis of $[Rh(PPh_3)_2(CO)Cl]$ from $[Rh_2(CO)_4Cl_2]$ (McCleverty & Wilkinson, 1966). A solution of $[Rh\{P(CH_3)_3\}_2(CO)Cl]$ (0.5 ml, 125 m*M*) in benzene/tetrahydrofuran (1:3 *v*/*v*) was irradiated under nitrogen at 233 K for 48 h with a 125 W medium-pressure mercury-vapour lamp. The resulting mixture was treated with dibromomethane (100 μl, 253 K, 2 d) and then warmed to room temperature. Crystals of $[Rh_2\{P(CH_3)_3\}_4Br_6]$ (1) precipitated from the reaction mixture over several days.

Crystal data

$[Rh_2Br_6(C_3H_9P)_4]$
$M_r = 989.58$
Orthorhombic
Pcab
$a = 10.971\ (2)$ Å
$b = 15.562\ (2)$ Å
$c = 16.459\ (3)$ Å
$V = 2810.0\ (11)$ Å^3
$Z = 4$
$D_x = 2.339$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 10\text{–}15°$
$\mu = 9.730$ mm^{-1}
$T = 294$ K
Prism
0.22 × 0.22 × 0.15 mm
Red

Data collection

Enraf-Nonius CAD-4*F* diffractometer
$\omega\text{-}2/3\theta$ scans
Absorption correction: empirical
$T_{min} = 0.313$, $T_{max} = 0.410$
2811 measured reflections
2024 independent reflections

1351 observed reflections $[I > 2.5\sigma(I)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity variation: none

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Refinement

Refinement on F
$R = 0.056$
$wR = 0.063$
$S = 1.48$
1351 reflections
111 parameters
$w = 2.20/[\sigma^2(F_o) + 0.00074F_o^2]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.57$ e Å^{-3}
$\Delta\rho_{\min} = -1.72$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) for Br and Rh and from *SHELX76* (Sheldrick, 1976) for all other atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Rh(1)	−0.1422 (1)	−0.0475 (1)	0.4439 (1)	1.56
Br(1)	−0.0116 (2)	0.0919 (1)	0.4447 (1)	4.30
Br(2)	−0.2772 (2)	0.0137 (2)	0.5479 (1)	4.05
Br(3)	−0.0083 (2)	−0.1126 (2)	0.3408 (1)	4.32
P(1)	−0.2531 (4)	−0.1694 (3)	0.4588 (3)	2.55
C(1)	−0.4157 (17)	−0.1602 (14)	0.4585 (12)	3.74
C(2)	−0.225 (2)	−0.2157 (16)	0.5558 (12)	5.40
C(3)	−0.2203 (16)	−0.2565 (11)	0.3878 (13)	3.83
P(2)	−0.2574 (4)	0.0000 (3)	0.3383 (3)	2.31
C(4)	−0.3955 (17)	0.0541 (12)	0.3680 (13)	3.76
C(5)	−0.1782 (18)	0.0797 (12)	0.2760 (12)	3.60
C(6)	−0.310 (2)	−0.0800 (14)	0.2638 (10)	4.29

Table 2. *Selected geometric parameters* (Å, °)

Br(1)—Rh(1)	2.601 (2)	Br(2)—Rh(1)	2.456 (2)
Br(3)—Rh(1)	2.462 (2)	P(1)—Rh(1)	2.266 (5)
P(2)—Rh(1)	2.273 (5)	C(1)—P(1)	1.790 (19)
C(2)—P(1)	1.779 (18)	C(3)—P(1)	1.825 (18)
C(4)—P(2)	1.801 (19)	C(5)—P(2)	1.829 (18)
C(6)—P(2)	1.841 (19)		
Br(2)—Rh(1)—Br(1)	90.2 (1)	Br(3)—Rh(1)—Br(1)	91.1 (1)
Br(3)—Rh(1)—Br(2)	178.6 (1)	P(1)—Rh(1)—Br(1)	173.4 (1)
P(1)—Rh(1)—Br(2)	85.7 (1)	P(1)—Rh(1)—Br(3)	92.9 (1)
P(2)—Rh(1)—Br(1)	92.2 (1)	P(2)—Rh(1)—Br(2)	94.0 (1)
P(2)—Rh(1)—Br(3)	86.5 (1)	P(2)—Rh(1)—P(1)	93.3 (2)
C(1)—P(1)—Rh(1)	117.9 (7)	C(2)—P(1)—Rh(1)	110.1 (8)
C(2)—P(1)—C(1)	102. (1)	C(3)—P(1)—Rh(1)	116.5 (6)
C(3)—P(1)—C(1)	104.7 (9)	C(3)—P(1)—C(2)	103 (1)
C(4)—P(2)—Rh(1)	114.4 (7)	C(5)—P(2)—Rh(1)	112.7 (6)
C(5)—P(2)—Rh(1)	103.6 (9)	C(6)—P(2)—Rh(1)	117.6 (6)
C(6)—P(2)—C(4)	103 (1)	C(6)—P(2)—C(5)	103 (1)

The crystal was mounted on a glass fibre with cyanoacrylate resin. The scan width and horizontal counter aperture were (1.10 + 0.34tanθ)° and (2.70 + 1.05tanθ) mm, respectively. The absorption correction was according to Coppens, Leiserowitz & Rabinovich (1965) and used 10×12×12 sampling points with maximum and minimum corrections of 3.195 and 2.439, respectively. Data reduction and application of Lorentz, polarization and absorption corrections were carried out using the Enraf-Nonius *SDP* system (Frenz, 1985). The structure was solved by heavy-atom methods using *SHELX76* (Sheldrick, 1976) and the solutions were extended by difference Fourier methods. H atoms were included at calculated sites with group isotropic displacement parameters and all other atoms were refined anisotropically. All calculations were carried out using *SHELX76*.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55822 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1014]

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Two Crystalline Polymorphs of Chloro[tris(2-cyanoethyl)phosphine]gold(I), [$AuCl(C_9H_{12}N_3P)$]

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Abstract

Polymorph (1) has Au—Cl and Au—P bond lengths of 2.295 (3) and 2.225 (3) Å, respectively, with a P—Au—Cl bond angle of 177.8 (1)°. Polymorph (2) has Au—Cl and Au—P bond lengths of 2.315 (2) and 2.243 (2) Å, respectively, with a P—Au—Cl bond angle of 177.1 (1)°. Polymorph (2) crystallizes with two of the C≡N groups alongside the Au^{I} center in the asymmetric unit.

Comment

We have been studying the coordination and reaction chemistry of complexes containing tris(2-cyanoethyl)phosphine (Khan, King, Fackler &

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