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Polyhedron 22 (2003) 3293–3298
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Reactions of $[Rh(Tp^*)(PPh_3)_2]$ ($Tp^* =$ hydrotris(3,5-dimethylpyrazolyl)-borate) involving fragmentation or loss of Tp*. Structures of $[Rh(Cl)_2(H)(PPh_3)_2(pz^*)]$, $[(PPh_3)_2Rh(\mu\text{-}SC_6F_5)_2Rh(SC_6F_5)(H)(PPh_3)(pz^*)]$ ($pz^* = 3,5$-dimethylpyrazole) and $[\{Rh(Cl)_2(PPh_3)_2\}_2Hg]$

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Received 16 May 2003; accepted 24 July 2003

Abstract

The complex $[Rh(Tp^*)(PPh_3)_2]$ reacts with dichloromethane to give $[Rh(Cl)(H)_2(PPh_3)_2(pz^*)]$ (**1**) and $[Rh(Cl)_2(H)(PPh_3)_2(pz^*)]$ (**2**), with C_6F_5SH to give $[(PPh_3)_2Rh(\mu\text{-}SC_6F_5)_2Rh(SC_6F_5)(H)(PPh_3)(pz^*)]$ (**3**) and with $HgCl_2$ to give $[\{Rh(Cl)_2(PPh_3)_2\}_2Hg]$ (**4**), all under mild conditions. The crystal structures show that **2** has a slightly distorted octahedral geometry, **3** has approximately square planar Rh(I) and octahedral Rh(III) geometries, with an angle of 160.7° between the two RhS_2 planes and **4** has rhodium with a square pyramidal geometry where mercury occupies a position at the apex of the pyramid; the Rh–Hg–Rh geometry is linear and, with respect to the Rh–Hg–Rh axis, the ligands (Cl, PPh_3) on one rhodium are offset by approximately 42° relative to their counterparts on the second rhodium. In **2** an intramolecular hydrogen bond exists between the pyrazole NH and one of the chloride ligands. Structure **4** is unusual in that it contains an unsupported mercury bridge.

Keywords: Rhodium; 3,5-Dimethylpyrazole; Pentafluorophenylthiolate; Mercury; Crystal structures

1. Introduction

The complex $[Rh(Tp^*)(PPh_3)_2]$ provides a potentially useful route to a wide variety of Rh(Tp*) derivatives via ligand exchange and oxidative addition. Its chemistry is expected to resemble that of the closely related compound $[Rh(Tp)(PPh_3)_2]$, reported by Hill et al. [1], who describe reactions with, inter alia, ethylene, 1,5-cod, O_2 and CS_2. In an earlier paper we have shown that $[Rh(Tp^*)(PPh_3)_2]$ combines with HX ($X = C_2Ph$, 4-$NO_2C_6H_4CO$, $SnPh_3$) to give $[Rh(Tp^*)(H)(X)(PPh_3)]$ in moderate to good yield [2]. The structure of $[Rh(Tp^*)(PPh_3)_2]$ has been reported both by us and by Connelly et al. [3]. Here we describe reactions of $[Rh(Tp^*)(PPh_3)_2]$ with Ph_3SiH/CH_2Cl_2, C_6F_5SH and $HgCl_2$ in which Tp* is either broken up to give 3,5-dimethylpyrazole (pz*), which appears in the product as a neutral ligand, or is lost altogether.

2. Experimental

2.1. Materials

$[Rh(Tp^*)(PPh_3)_2]$ was prepared from $[Rh(Cl)(PPh_3)_3]$ and KTp* according to a procedure described in an earlier paper [2]. Ph_3SiH and C_6F_5SH were purchased from Aldrich Chemicals. Dichloromethane was distilled from P_2O_5. Other solvents and materials were of the

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doi:10.1016/S0277-5387(03)00475-3

highest available purity and were used without further treatment.

2.2. Preparation of [Rh(Cl)(H)$_2$(PPh$_3$)$_2$(pz*)] (1)

A mixture of [Rh(Tp*)(PPh$_3$)$_2$] (EtOH) (0.050 g, 0.051 mmol) and Ph$_3$SiH (0.050 g, 0.192 mmol) in dichloromethane (3 ml) was heated in a sealed flask at 60–70 °C for 90 min. The solution was cooled and treated with a mixture of ~1:1:2 hexane/ethanol/diethyl ether (~2 ml) and allowed to stand at room temperature for 1 day to give colourless crystals. Yield: 0.031 g (80%). ^{1}H NMR(CD_2Cl_2/CH_2Cl_2, 27 °C): δ −16.47 (ddt, J(H–H) 10.5, J(P–H) 14.7, J(Rh–H) 14.7 Hz, 1H), −17.81 (ddt, J(H–H) 10.5, J(P–H) 14.5, J(Rh–H) 23.0 Hz, 1H). ^{31}P NMR (CD_2Cl_2/CH_2Cl_2, 27 °C): δ 45.54 (d, J(Rh–P) 118.3 Hz). ^{103}Rh NMR (CD_2Cl_2/CH_2Cl_2, 27 °C): 387 ppm. *Anal.* Calc. for $C_{41}H_{40}ClN_2P_2Rh$: C, 64.70; H, 5.30; N, 3.68. Found: C, 65.08; H, 5.48; N, 3.32%. From solutions containing the reagents in higher concentration and with more prolonged heating it was possible, using the above procedure, to obtain yellow crystals of a product identified as [Rh(Cl)$_2$(H)(PPh$_3$)$_2$(pz*)] (**2**) in yields of up to 67%. ^{1}H NMR (CD_2Cl_2/CH_2Cl_2, 27 °C): δ −15.13 (dt, J(P–H) 11.3, J(Rh–H) 12.9 Hz). ^{31}P NMR (CD_2Cl_2/CH_2Cl_2, 27 °C): δ 29.15 (J(Rh–P) 100.9 Hz). ^{103}Rh NMR (CD_2Cl_2/CH_2Cl_2, 27 °C): δ 2091. *Anal.* Calc. for $C_{41}H_{39}Cl_2N_2P_2Rh$: C, 61.90; H, 4.94; N, 3.52. Found: C, 62.13; H, 4.97; N, 3.25%.

2.3. Preparation of [(PPh$_3$)$_2$Rh(μ-SC$_6$F$_5$)$_2$Rh(SC$_6$F$_5$)(H)(PPh$_3$)(pz*)] (3)

A solution of [Rh(Tp*)(PPh$_3$)$_2$](EtOH) (0.050 g, 0.051 mmol) in dichloromethane (2 ml) at room temperature was treated with pentafluorophenylthiol (0.011 g, 0.055 mmol) in dichloromethane (2 ml). A color change to dark red was observed. The mixture was allowed to stand for 15 min, then concentrated to ~1 ml. Ethanol (~0.5 ml) and hexane (~0.5 ml) were added. The product was isolated after 3 h as red–brown crystals. Yield: 0.028 g (59% based on Rh; 82% based on S). ^{1}H NMR (CD_2Cl_2/CH_2Cl_2, −25 °C): δ −9.83 (dd, J(P–H) ~10.8, J(Rh–H) ~10.8 Hz). ^{31}P NMR (CD_2Cl_2/

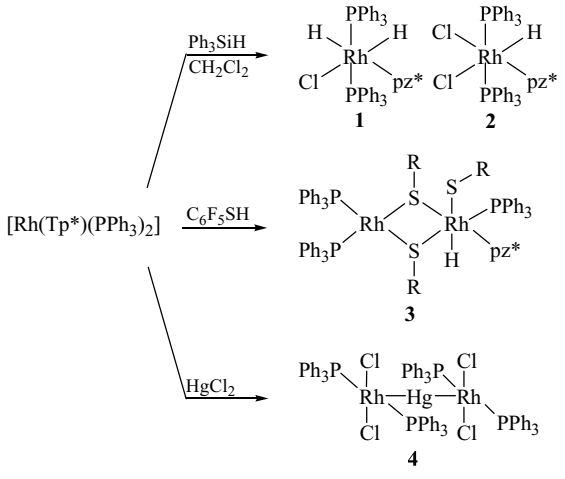
Table 1
Crystal data and structure refinement for **2**, **3** and **4**

	[Rh(Cl)$_2$(H)(PPh$_3$)$_2$(pz*)] (**2**)	[(PPh$_3$)$_2$Rh(μ-SC$_6$F$_5$)$_2$Rh-(SC$_6$F$_5$)(H)(PPh$_3$)(pz*)] (tol)$_2$ (**3**)	[{Rh(Cl)$_2$(PPh$_3$)$_2$}$_2$Hg](CH$_2$Cl$_2$)$_2$ (**4**)
Empirical formula	$C_{41}H_{39}Cl_2N_2P_2Rh$	$C_{91}H_{70}F_{15}N_2P_3Rh_2S_3$	$C_{74}H_{64}Cl_8HgP_4Rh_2$
Formula weight	795.49	1871.40	1767.14
Temperature (K)	173(2)	293(2)	173(2) *K*
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*P*nma	$P\bar{1}$	$P2/c$
Unit cell dimensions			
a (Å)	16.2568(19)	13.640(4)	20.087(4)
b (Å)	23.703(3)	17.521(5)	13.731(3)
c (Å)	9.6221(11)	18.854(5)	25.836(6)
α (°)	90	73.571(5)	90
β (°)	90	82.377(5)	90.806(4)
γ (°)	90	74.078(6)	90
Volume (Å^3)	3707.7(8)	4149(2)	7125(3)
Z	4	2	2
Density (calculated) (Mg/m^3)	1.425	1.498	1.647
Absorption coefficient (mm^{-1})	0.723	0.613	3.039 mm^{-1}
F(0 0 0)	1632	1896	3496
Crystal size (mm)	0.27 × 0.20 × 0.16	0.18 × 0.08 × 0.04	0.36 × 0.33 × 0.08
θ range for data collection (°)	1.72–27.00	1.13–25.00	1.01–26.00
Index ranges	$-20 \leqslant h \leqslant 20$	$-16 \leqslant h \leqslant 15$	$-24 \leqslant h \leqslant 15$
	$-30 \leqslant k \leqslant 24$	$-18 \leqslant k \leqslant 20$	$-16 \leqslant k \leqslant 16$
	$-12 \leqslant l \leqslant 12$	$-20 \leqslant l \leqslant 22$	$-31 \leqslant l \leqslant 31$
Reflections collected	21 748	22 313	37 749
Independent reflections	4148 (R_{int} = 0.0270)	14 479 (R_{int} = 0.1109)	13 958 [R_{int} = 0.0676]
Completeness to θ_{max} (%)	99.9	99.1	99.8
Max. and Min. transmission	0.8931 and 0.8287	0.9759 and 0.8977	0.7931 and 0.4075
Data/restraints/parameters	4148/0/233	14 479/1/789	13 958/14/808
Goodness-of-fit on F^2	1.092	0.882	1.034
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0434$	$R1 = 0.0739$	$R1 = 0.0606$
	$wR2 = 0.1227$	$wR2 = 0.1480$	$wR2 = 0.1249$
R indices (all data)	$R1 = 0.0511$	$R1 = 0.2249$	$R1 = 0.1160$
	$wR2 = 0.1277$	$wR2 = 0.1951$	$wR2 = 0.1478$
Largest difference peaks (e Å^{-3})	1.103 and −1.969	0.740 and −0.805	2.440 and −2.056

CH_2Cl_2, −25 °C): δ 47.30 (dd, *J*(Rh–P) 177.3, *J*(P–P) 41.2 Hz), 38.15 (dd, *J*(Rh–P) 169.1, *J*(P–P) 41.2 Hz), δ 37.58 (d, *J*(Rh–P) 121.6 Hz). ^{103}Rh NMR (CD_2Cl_2/CH_2Cl_2, −25 °C): δ 2117, 239 ppm. *Anal.* Calc. for $C_{77}H_{54}F_{15}$ $N_2P_3Rh_2S_3$: C, 54.82; H, 3.23; N, 1.66. Found: C, 55.12; H, 3.38; N, 1.57%.

2.4. Preparation of [{(PPh$_3$)$_2$(Cl)$_2$Rh}$_2$Hg](CH$_2$Cl$_2$)$_2$ (4)

A mixture of [Rh(Tp*)(PPh$_3$)$_2$](EtOH) (0.050 g, 0.051 mmol) and $HgCl_2$ (0.015 g, 0.055 mmol) in dichloromethane (2 ml) was stirred at room temperature for 15 min. The dark red solution was filtered through cotton wool, to remove some unreacted $HgCl_2$ and traces of metallic mercury, and treated with ethanol (2 ml). The solution was concentrated and allowed to stand at −20 °C for 1 day to give red crystals, together with a grey powder. The product was recrystallised from dichloromethane/ethanol. Yield: 0.016 g (36% based on Rh). ^{31}P NMR (CD_2Cl_2/CH_2Cl_2, 27 °C): δ 36.04 (d, *J*(Rh–P) 104.6 Hz, ^{199}Hg satellites *J*(^{119}Hg–^{31}P) 327 Hz). *Anal.* Calc. for $C_{74}H_{64}Cl_8HgP_4Rh_2$: C, 50.29; H, 3.65. Found: C, 50.06; H, 3.85%.



Scheme 1. Tp* = hydrotris(3,5-dimethylpyrazolyl)borate, pz* = 3,5-dimethylpyrazole, R = pentafluorophenyl.

2.5. NMR spectroscopy

Spectra were recorded on a Bruker DRX 400 Spectrometer equipped with a 5 mm triple resonance inverse probe with a dedicated ^{31}P channel and extended decoupler range operating at 400.13 MHz (^{1}H), 161.98 MHz (^{31}P) and 12.65 MHz (^{103}Rh). ^{103}Rh spectra were obtained by indirect detection using ^{31}P. Chemical shifts were referenced to TMS (^{1}H), 85% H_3PO_4 (^{31}P) and Ξ = 3.16 MHz (^{103}Rh).

2.6. X-ray structure determination

Intensity data were collected at 20 °C (**3**) and −100 °C (**2**, **4**) on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50 kV, 30 mA) (see Table 1). The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program SAINT+ [4] and absorption corrections were made using the program SADABS [5]. The crystal structures were solved by direct

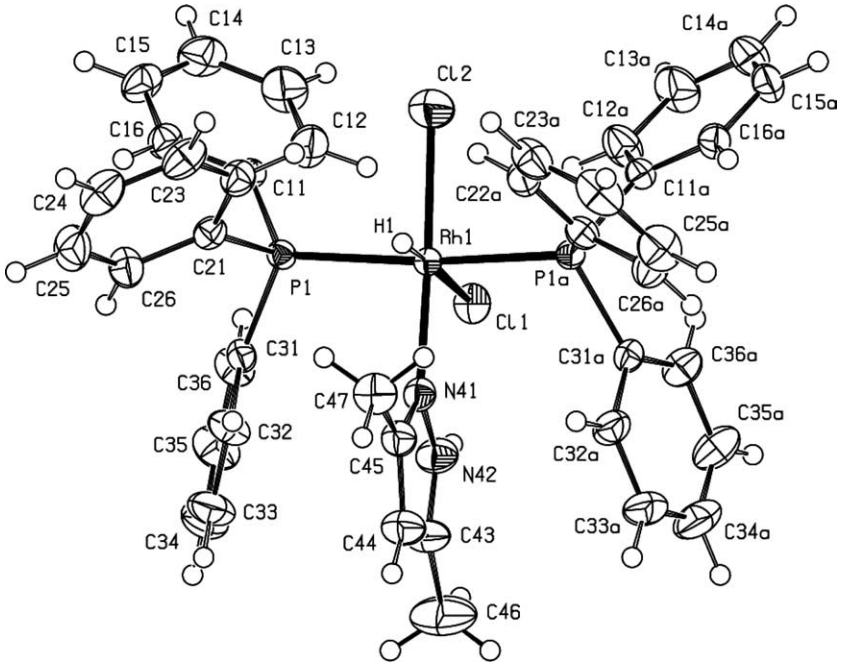


Fig. 1. ORTEP diagram of [Rh(Cl)$_2$(H)(PPh$_3$)$_2$(pz*)] (**2**); thermal ellipsoids are shown at the 50% probability level.

methods using SHELXTL [6]. Non-hydrogen atoms were first refined isotropically followed by anistropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Diagrams were generated using PLATON [7].

3. Results and discussion

Three reactions of $[Rh(Tp^*)(PPh_3)_2]$ ($Tp^* =$ hydrotris(3,5-dimethylpyrazolyl)-borate) in which the Tp* ligand is either fragmented, to give a neutral pz* (1,3-dimethylpyrazole) ligand or lost altogether are outlined in Scheme 1. Such fragmentation is not uncommon and has been found to occur, for example, in reactions of KTp^R with compounds of Rh [8] and Cu [9] and in the reaction of $[Rh(Tp^{iPr})(dppe)]$ with O_2 [10].

On warming with triphenylsilane in toluene at 50 °C for 1 day $[Rh(Tp^*)(PPh_3)_2]$ gives $[Rh(Tp^*)(H)_2(PPh_3)]$ as the major product (in solution), identified by comparison of its NMR data with those of an authentic sample (toluene, 300 K: ^1H, δ −16.69 dd (J 31.0, 16.6 Hz); ^{31}P δ 58.58 d (J 151.3)).

When the reaction is carried out in dichloromethane the product $[Rh(Cl)(H)_2(PPh_3)_2(pz^*)]$ (**1**) is obtained in good yield, clearly formed by a process involving the solvent. Indeed the reaction (as monitored by ^1H and ^{31}P NMR) proceeds in dichloromethane in the absence of Ph_3SiH, but more slowly. The rate of the reaction (with or without Ph_3SiH) is significantly enhanced in the presence of the free radical scavenger quinol, indicating

Table 2
Selected bond lengths (Å) and angles

(a) *$[Rh(Cl)_2(H)(PPh_3)_2(pz^*)]$* (**2**)					
Bond lengths					
Rh–N(41	2.096(4)	Rh–Cl(1)	2.5645(14)	Rh–H(1)	1.45(2)
Rh–P(1)	2.3249(9)	Rh–Cl(2)	2.3583(17)		
Bond angles					
N(41)–Rh–P(1)	91.99(2)	Cl(1)–Rh–H(1)	177(1)	P(1)–Rh–P(2)	172.61(5)
N(41)–Rh–Cl(1)	88.08(12)	Cl(2)–Rh–H(1)	84(1)	P(1)–Rh–H(1)	87(1)
N(41)–Rh–Cl(2)	172.41(13)	P(1)–Rh–Cl(1)	93.18(2)	Rh–Cl(1)–H(42)	50(1)
N(41)–Rh–H(1)	89(1)	P(1)–Rh–Cl(2)	87.62(2)	Cl(1)–H(42)–N(42)	129(1)
Cl(1)–Rh–Cl(2)	99.51(6)				
(b) *$[(PPh_3)_2Rh(\mu\text{-}SC_6F_5)_2Rh(SC_6F_5)(H)(PPh_3)(pz^*)](tol)_2$* (**3**)					
Bond lengths					
Rh(1)–N(41)	2.086(8)	Rh(1)–S(3)	2.565(3)	Rh(2)–S(2)	2.374(3)
Rh(1)–P(1)	2.313(3)	Rh(1)–H(1)	1.45(4)	Rh(2)–P(2)	2.285(3)
Rh(1)–S(1)	2.353(3)	Rh(2)–S(1)	2.432(3)	Rh(2)–P(3)	2.244(3)
Rh(1)–S(2)	2.396(3)				
Bond angles					
N(41)–Rh(1)–P(1)	91.7(3)	P(1)–Rh(1)–H(1)	88(3)	Rh(1)–S(2)-Rh(2)	100.22(10)
N(41)–Rh(1)–S(1)	167.2(3)	S(1)–Rh(1)–S(2)	78.60(9)	S(1)–Rh(2)–S(2)	77.49(9)
N(41)–Rh(1)–S(2)	88.7(3)	S(1)–Rh(1)–S(3)	92.37(10)	S(1)–Rh(2)–P(2)	94.57(10)
N(41)–Rh(1)–S(3)	89.5(3)	S(1)–Rh(1)–H(1)	87(2)	S(1)–Rh(2)–P(3)	164.37(11)
N(41)–Rh(1)–H(1)	92(2)	S(2)–Rh(1)–S(3)	90.85(10)	S(2)–Rh(2)–P(2)	171.93(11)
P(1)–Rh(1)–S(1)	101.04(10)	S(2)–Rh(1)–H(1)	94(3)	S(2)–Rh(2)–P(3)	93.68(10)
P(1)–Rh(1)–S(2)	177.57(11)	S(3)–Rh(1)–H(1)	175(3)	P(2)–Rh(2)–P(3)	94.38(11)
P(1)–Rh(1)–S(3)	86.76(10)	Rh(1)–S(1)–Rh(2)	99.74(11)		
(c) *$[\{Rh(Cl)_2(PPh_3)_2\}_2Hg](CH_2Cl_2)_2$* (**4**)[a]					
Bond lengths					
Rh(1)–Cl(1)	2.325(3)	Rh(1)–Hg(1)	2.5494(8)	Rh(2)–P(3)	2.325(3)
Rh(1)–Cl(2)	2.341(3)	Rh(2)–Cl(3)	2.338(2)	Rh(2)–P(4)	2.326(3)
Rh(1)–P(1)	2.336(3)	Rh(2)–Cl(4)	2.331(3)	Rh(2)–Hg(2)	2.5446(9)
Rh(1)–P(2)	2.330(3)				
Bond angles					
P(1)–Rh(1)–P(2)	166.33(9)	Cl(1)–Rh(1)–Hg(1)	88.51(7)	P(4)–Rh(2)–Cl(3)	88.99(9)
P(1)–Rh(1)–Cl(1)	89.64(9)	Cl(2)–Rh(1)–Hg(1)	98.56(7)	P(4)–Rh(2)–Cl(4)	91.72(9)
P(1)–Rh(1)–Cl(2)	91.07(9)	Rh(1)–Hg(1)–Rh(1)	179.79(5)	P(4)–Rh(2)–Hg(2)	96.06(7)
P(1)–Rh(1)–Hg(1)	95.99(6)	P(3)–Rh(2)–P(4)	167.03(9)	Cl(3)–Rh(2)–Cl(4)	173.10(9)
P(2)–Rh(1)–Cl(1)	91.18(9)	P(3)–Rh(2)–Cl(3)	91.14(9)	Cl(3)–Rh(2)–Hg(2)	90.09(6)
P(2)–Rh(1)–Cl(2)	86.44(9)	P(3)–Rh(2)–Cl(4)	86.63(9)	Cl(4)–Rh(2)–Hg(2)	96.66(7)
P(2)–Rh(1)–Hg(1)	97.67(7)	P(3)–Rh(2)–Hg(2)	96.91(7)	Rh(2)–Hg(2)–Rh(2)	179.59(5)
Cl(1)–Rh(1)–Cl(2)	172.78(10)				

[a] Data are given for each of the two molecules forming the unit cell.

that the mechanism is probably ionic and that the reaction is accelerated by proton donors (hydrogen is required not only to form **1**, but in the fragmentation of Tp* in order to generate neutral pz*). Also formed in the reaction is an unidentified compound ($\delta(^{31}P)$ d 46.62 (J 175.2 Hz) in dichloromethane, 300 K). By slight modification of the conditions required to form **2** (higher concentrations, longer reaction times) the product $[Rh(Cl)_2(H)(PPh_3)_2(pz^*)]$ (**2**) can be obtained. The structure of **2** is shown in Fig. 1. The two axial phosphines are related by a mirror plane that intersects the equatorial ligands. An intramolecular hydrogen bond exists between the pyrazole NH(41) and Cl(1). Bond lengths and angles are given in Table 2.

From the reaction of $[Rh(Tp^*)(PPh_3)_2]$ with pentafluorophenyl thiol a dinuclear product **3** is obtained (Scheme 1) having Rh(I) and Rh(III) centres bridged by two SC_6F_5 groups. The Rh(III) centre has an attached pz* fragment of the original Tp*, present as a neutral ligand, with a hydrogen most probably acquired from the thiol. The asymmetry of the Rh(III) centre causes the two (diastereotopic) phosphines attached to the Rh(I) centre to exhibit different values of $\delta(^{31}P)$. The presence of two different rhodium oxidation states in a dinuclear thiolate bridged complex is unusual but not unknown [11].

The structure of **3** is shown in Fig. 2; selected bond lengths and angles are given in Table 2. The unit cell contains both enantiomeric forms, related to each other by an inversion centre. Two rhodium complexes containing pentafluorophenyl thiolate as a bridging ligand ($[Rh_2(\mu\text{-}SC_6F_5)_2(1,5\text{-cod})_2]$ [12] and $[Rh_2(C_5Me_5)_2(\mu\text{-}SC_6F_5)_3]^+$ [13]) have been structurally characterised and show Rh–S–Rh angles that are significantly smaller than for **3**. Complexes containing bridging SC_6H_5, for example $[Rh_2(\mu\text{-}SC_6H_5)_2(CO)_2(PMe_3)_2]$ [14] also show Rh–S–Rh angles (79.2°, 80.2°) that are up to 20° smaller than for **3**. The angle between the planes defined by S(1)–Rh(1)–S(2) and S(1)–Rh(2)–S(2) is also larger for **3** (160.7°) than for $[Rh_2(\mu\text{-}SC_6F_5)_2(1,5\text{-cod})]$ (118.4°) and $[Rh_2(\mu\text{-}SC_6H_5)_2(CO)_2(PMe_3)_2]$ (114.9°). It is likely that the bulky ligands of **3**, and the fact that one rhodium is six-coordinate, prevent a closer approach of the two Rh atoms.

Mercuric chloride reacts with $[Rh(Tp^*)(PPh_3)_2]$ to give a mercury bridged dirhodium complex (**4**) from which the Tp* ligand has been entirely lost (Scheme 1 and Fig. 3). To our knowledge this is the first such complex in which the mercury bridge between the rhodium atoms is unsupported by additional bonds (several examples are known of structures in which the bridge is supported [15–20]). The unit cell contains two non-identical molecules (one only is shown in Fig. 3; data for both are given in Table 2) which show only minor structural differences. The geometry at rhodium is square pyramidal, with rhodium lying 0.1991(2) and 0.2102(2) Å (for the two forms, respectively) above the mean plane defined by the two phosphorus and two chlorine atoms. When viewed along the Rh–Hg–Rh axis the chloride and phosphine ligands on Rh(1) are offset by approximately 42° with respect to the same ligands on Rh(2).

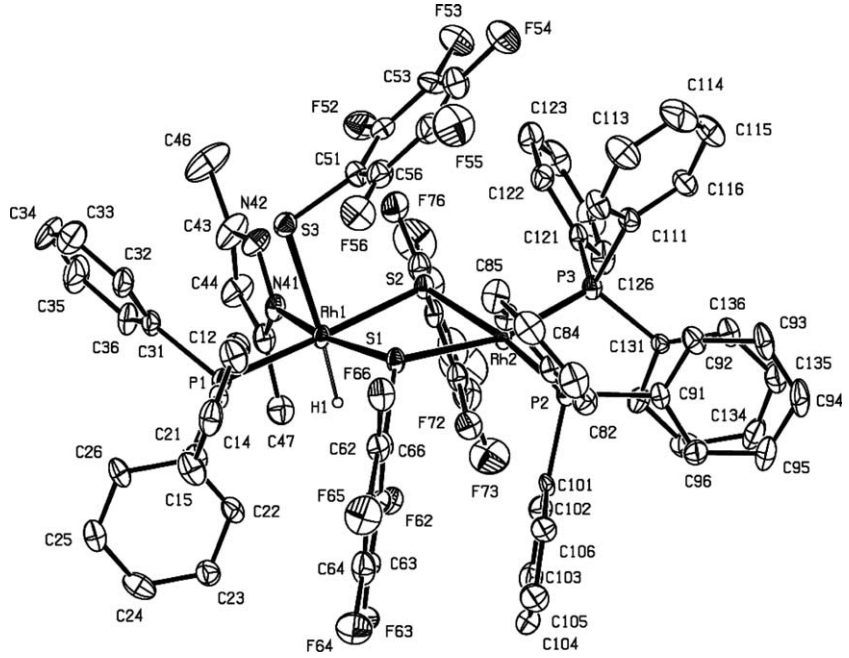


Fig. 2. ORTEP diagram of $[(PPh_3)_2Rh(\mu\text{-}SC_6F_5)_2Rh(SC_6F_5)(H)(PPh_3)(pz^*)]$ (**3**); thermal ellipsoids are shown at the 20% probability level; hydrogens (other than H(1)) and cocrystallised toluene are omitted.

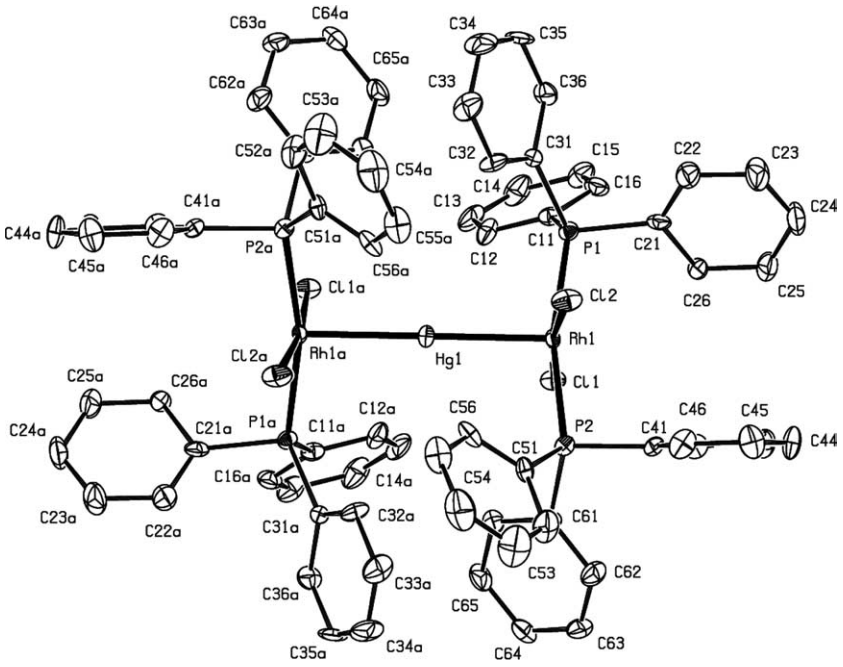


Fig. 3. ORTEP diagram of [{Rh(Cl)$_2$(PPh$_3$)$_2$}$_2$Hg] (**4**); thermal ellipsoids are shown at the 50% probability level; hydrogens and cocrystallised CH_2Cl_2 are omitted.

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre for the structures of **2**, **3** and **4** with CCDC numbers: 210529, 210530 and 210531, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the University of the Witwatersrand for financial support.

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