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Rhodium pentafluorophenylthiolate complexes derived from $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$

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Abstract

The thiolate bridges of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ are readily split by a variety of phosphines, phosphites and nitrogen-containing compounds to give $[Rh(SC_6F_5)(PR_3)_3]$, $[Rh(SC_6F_5)\{P(OR')_3\}_3]$, $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L)]$ and $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L')]$, ($PR_3 = PMe_2Ph$, $PMePh_2$; $P(OR')_3 = P(OMe)_3$, $P(OEt)_3$; L (sterically nonhindering) = pyridine, 3-methylpyridine, isoquinoline, *N*-methylimidazole, acetonitrile; L' (sterically hindering) = 2-methylpyridine, 2,6-dimethylpyridine, quinoline). With H_2 under ambient conditions both $[Rh(SC_6F_5)(PR_3)_3]$ and $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L)]$ combine reversibly, $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L')]$ does not react and $[Rh(SC_6F_5)\{P(OR')_3\}_3]$ (in the presence of free $P(OR')_3$) is converted into $[RhH\{P(OR')_3\}_4]$. $[Rh(SC_6F_5)(PR_3)_3]$ and $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L)]$ react with phenylacetylene to give $[RhH(SC_6F_5)(C_2Ph)(PR_3)_3]$ and $[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(L)]$, respectively, while with C_6F_5SH $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L)]$ forms $[RhH(SC_6F_5)_2(PPh_3)(L)_2]$, and further reaction gives $[Rh(SC_6F_5)_3(L)_3]$. Although $[cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L')]$ is unreactive towards C_6F_5SH it combines with PhC_2H with loss of C_6F_5SH yielding $[trans\text{-}Rh(C_2Ph)(PPh_3)_2(L)]$. Other reagents which split the $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ bridge are carbon monoxide and t-butyl isocyanide. Products were characterised by ^1H and ^{31}P NMR spectroscopy and in many cases were not isolated.

Introduction

The ability of dinuclear S-bridged rhodium thiolate complexes to undergo conversion into mononuclear species following treatment with an appropriate reagent has some bearing on methods of their synthesis and on homogeneous catalysis by systems derived from them. Various routes to the dinuclear thiolate complexes are known [1–13] but the conversion of a dinuclear into a mononuclear structure has been less frequently reported [1–3,6]. Both dinuclear and mononuclear rhodium(I) thiolate complexes have been shown to possess activity as catalysts for the hydrogenation and hydroformylation of alkenes under mild conditions [14–19], this property being contingent on their ability to undergo readily both

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oxidative addition (of H_2) and reductive elimination reactions. The complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PMe_2Ph)_2]$, a moderately active hydrogenation catalyst, undergoes oxidative addition of CH_3I at one rhodium centre leaving the thiolate bridge intact [20], suggesting that the catalytically active species behaves similarly in the presence of H_2. Mononuclear complexes $[Rh(SR)(PPh_3)_3]$ having catalytic properties steadily lose activity during catalysis at the same time being converted into the dinuclear form [19].

The conditions under which the thiolate bridge of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ is broken and the reactivity of the resulting mononuclear species with respect to oxidative addition are reported in the present study; a preliminary communication [21] of part of this work dealt more specifically with the influence of steric effects on the course of a number of reactions.

Experimental

$[RhH(PPh_3)_4]$ was prepared by the method of Robinson *et al.* [22]. Toluene, pyridine, 2-methylpyridine, 3-methylpyridine, 2,6-dimethylpyridine and quinoline were distilled from calcium hydride; triethyl phosphite was dried over sodium and distilled, dichloromethane was distilled from P_2O_5; ether, THF, cyclohexene and triethylamine were dried over calcium hydride. Other reagents were of the highest available purity and used without further treatment. All operations (other than those involving H_2) were performed under a nitrogen atmosphere.

NMR spectra were recorded on a Bruker AC 200 FT NMR spectrometer at 200.13 MHz for ^1H and 81.01 MHz for ^{31}P measurements. IR spectra were recorded on a Perkin–Elmer 580 spectrometer.

^1H and ^{31}P NMR studies

Solutions of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ (5–20 mg) in 0.5 ml toluene-d_8 (^1H measurements) or 3.5 ml toluene/toluene-d_8 (^{31}P measurements) at room temperature were treated with bridge-splitting reagents (phosphines, phosphites and ^{t}BuNC, 1 drop; L or L′, various quantities) and transferred to an NMR tube which was then stoppered and sealed with Parafilm. Spectra were recorded either at 22, −25 (^1H) or −50°C (^{31}P). Subsequent reactions were carried out *in situ*. For the reaction of [*cis*-$Rh(SC_6F_5)(PPh_3)_2$(N-MeIm)] * with C_6F_5SH one equivalent of C_6F_5SH was added to a cooled (~ −40°C) solution of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ (10 mg) and *N*-MeIm (1 drop) in an NMR tube; spectra were recorded at −25 (^1H) and −50°C (^{31}P). In other experiments C_6F_5SH, PhC_2H, ^{i}PrSH or CH_3CO_2H (1 drop of each) or H_2 (bubbled through the solution for 2–5 min) were added at room temperature to a solution of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ plus bridge-splitting reagent in an NMR tube, and, following warming to 75°C in a number of cases, a spectrum was again recorded. Further treatment with L or L′ involved addition of ~ 1 ml of the liquid followed by warming to 75°C for 2 min. (*Note*: PMe_2Ph, $PMePh_2$ and *N*-MeIm combine with C_6F_5SH to give solids which can be redissolved by shaking the reaction mixture.)

The procedure for the kinetic study is described elsewhere [23].

* Abbreviations: py, pyridine; 2-Mepy, 2-methylpyridine; 3-Mepy, 3-methylpyridine; 2,6-Me_2py, 2,6-dimethylpyridine; quin, quinoline; isoquin, isoquinoline; *N*-MeIm, *N*-methylimidazole.

Preparation of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$

A stirred suspension of $[RhH(PPh_3)_4]$ (0.60 g, 0.52 mmol) in Et_2O (7 ml) at room temperature was treated with C_6F_5SH (0.11 g, 0.55 mmol); the mixture quickly darkened and after 10 min a clear dark brown solution was obtained, and this was treated with hexane (4 ml) and allowed to stand at room temperature for 15 h. The product was obtained as red-brown crystals, which were washed with hexane and dried under vacuum. Yield 0.39 g (0.47 mmol, 91%). Found: C, 62.3; H, 4.1. $C_{84}H_{60}F_{10}P_4Rh_2S_2$ calc.: C, 61.0; H, 3.7%.

Preparation of $[RhH_2(SC_6F_5)(PPh_3)_3]$

A stirred suspension of $[RhH(PPh_3)_4]$ (0.070 g, 0.061 mmol) in Et_2O (~ 0.3 ml) at room temperature was treated with C_6F_5SH (0.02 g, 0.1 mmol); a change in colour from yellow to dark brown immediately took place. Stirring was continued for ~ 3 min and the mixture centrifuged to give a brown solid, which was washed with Et_2O (0.5 ml) and hexane. The product, a dark brown powder was dried under vacuum. Yield 0.051 g (0.047 mmol, 77%). Found: C, 64.9; H, 4.4. $C_{60}H_{47}F_5P_3RhS$ calc.: C, 66.1; H, 4.3%. IR (Nujol mull) ν(Rh–H) 2132w, 1998m cm^{-1}.

Preparation of [cis-$Rh(SC_6F_5)(PPh_3)_2(py)](0.5CH_2Cl_2)$

A solution of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ (0.017 g, 0.020 mmol) in 2–3% pyridine/CH_2Cl_2 (~ 2 ml) (the complex does not dissolve readily in CH_2Cl_2 and it is necessary first to powder the crystals and then, after shaking vigorously with the solvent, to remove undissolved material using a centrifuge or by filtration through cotton wool) was concentrated to ~ 0.5 ml and treated with hexane (~ 0.5 ml). Small orange crystals began to form. After 30 min at room temperature the solution was removed and the product washed with hexane and dried under vacuum. Yield 0.08 g (0.008 mmol, 40%). Found: C, 60.7; H, 3.7; N, 1.6. $C_{47.5}H_{36}ClF_5NP_2RhS$ calc.: C, 60.2; H, 3.8; N, 1.5%.

Preparation of $[RhH(SC_6F_5)_2(PPh_3)(py)_2]$

A suspension of $[RhH(PPh_3)_4]$ (0.056 g, 0.049 mmol) in ~ 10% pyridine/Et_2O (~ 3 ml) at room temperature was treated with C_6F_5SH (0.022 g, 0.11 mmol) and shaken to give a clear red solution. Hexane was added and the solution allowed to stand at −20°C for 2 h. Orange lumps were formed, which, on washing with hexane, gave the product as an orange powder, which was dried under vacuum. Yield 0.026 g (0.028 mmol, 57%). Found: C, 51.5; H, 2.6; N, 3.0. $C_{40}H_{26}F_{10}N_2PRhS_2$ calc.: C, 52.1; H, 2.8; N, 3.0%. IR (Nujol mull) ν(Rh–H) 2130 cm^{-1}.

Preparation of $[Rh(SC_6F_5)_3(py)_3]$

A solution of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ (0.016 g, 0.019 mmol) in 2–3% pyridine/CH_2Cl_2 (~ 2 ml) was treated with C_6F_5SH (0.008 g, 0.04 mmol) and allowed to stand at room temperature for 30 min. Hexane was added and the solution kept at −20°C for 15 h, forming red crystals. The product was washed with hexane and dried under vacuum. Yield 0.010 g (0.011 mmol, 56%). Found: C, 41.7; H, 1.5; N, 4.4. $C_{33}H_{15}F_{15}N_3RhS_3$ calc.: C, 42.3; H, 1.6; N, 4.5%.

Preparation of [Rh(SC_6F_5)$_3$(3-Mepy)$_3$]

A solution of [$Rh_2(\mu$-$SC_6F_5)_2(PPh_3)_4$] (0.014 g, 0.014 mmol) in 2–3% 3-Mepy/CH_2Cl_2 (~2 ml) was treated with C_6F_5SH (0.007 g, 0.035 mmol) and allowed to stand at room temperature for 30 min. Hexane was added and the solution kept at −20°C for 15 h, forming a red powder. The product was washed with hexane and dried under vacuum. Yield 0.008 g (0.008 mmol, 58%). Found: C, 44.1; H, 2.1; N, 3.8. $C_{36}H_{21}F_{15}N_3RhS$ calc.: C, 44.1; H, 2.2; N, 4.3%.

Preparation of [Rh(SC_6F_5)$_3$(N-MeIm)$_3$]

A solution of [$Rh_2(\mu$-$SC_6F_5)_2(PPh_3)_4$] (0.014 g, 0.014 mmol) in 2–3% *N*-MeIm/CH_2Cl_2 (~2 ml) was treated with C_6F_5SH (0.007 g, 0.035 mmol) and allowed to stand at room temperature for 30 min. Hexane was added and the solution allowed to stand at room temperature for 15 h, forming red crystals. The product was washed with hexane and dried under vacuum. Yield 0.007 g (0.007 mmol, 53%). Found: C, 37.7; H, 1.8; N, 8.8. $C_{30}H_{18}F_{15}N_6RhS_3$ calc.: C, 38.7; H, 1.9; N, 8.9%. ^{1}H NMR ($CDCl_3$) δ 8.59, 6.64, 6.34, 3.56 ppm.

*Preparation of [*trans-*Rh(SC_6F_5)(PPh_3)$_2$(CO)]*

A stirred suspension of [$RhH(PPh_3)_4$] (0.080 g, 0.069 mmol) in Et_2O (4 ml) at room temperature was treated with C_6F_5SH (0.022 g, 0.11 mmol) to give a dark brown solution. CO (at atmospheric pressure) was introduced into the reaction tube and the colour of the solution quickly changed to yellow. Hexane (4 ml) was added and the solution concentrated (by evaporation in a stream of nitrogen) to ~3 ml and allowed to stand at room temperature for 4 h. The product was obtained as yellow crystals, which were washed with hexane and dried under vacuum. Yield 0.041 g (0.048 mmol, 70%). Found: C, 60.3; H, 3.4. $C_{43}H_{30}F_5OP_2RhS$ calc.: C, 60.4; H, 3.5%. IR (Nujol mull) ν(CO) 1984 cm^{-1}.

Preparation of [Rh(SC_6F_5)(PPh_3)$_2$(^{t}BuNC)$_3$]

A stirred suspension of [$RhH(PPh_3)_4$] (0.100 g, 0.087 mmol) in Et_2O (5 ml) at room temperature was treated with C_6F_5SH (0.022 g, 0.11 mmol) to give a dark brown solution. ^{t}BuNC (0.06 g, 0.7 mmol) was added and a change in colour to orange was observed. After 10 min the solution was concentrated to ~2 ml and allowed to stand at room temperature for 15 h. The product was obtained as yellow crystals, which were washed with hexane and dried under vacuum. Yield 0.049 g (0.046 mmol, 52%). Found: C, 63.2; H, 5.3; N, 3.9. $C_{57}H_{57}F_5N_3P_2RhS$ calc.: C, 63.6; H, 5.3; N, 3.9%. IR ($CHCl_3$) ν(CN) 2190w, 2140s, 2124sh, 2100sh. ^{1}H NMR (CD_3CN, 22°C) δ 7.71 (mult 30 H), 0.93 (s, 27 H); (toluene, 22°C) δ 0.75; (toluene, −70°C) δ 0.89, 0.77, 0.48 ppm.

Results and discussion

The complex [$Rh_2(\mu$-$SC_6F_5)_2(PPh_3)_4$] (I) is formed in high yield as red-brown crystals by the reaction of [$RhH(PPh_3)_4$] with C_6F_5SH in ether at room temperature. In toluene solution at temperatures $\leq$ −25°C the reaction, when monitored

Table 1

^{31}P NMR spectral data for the pentafluorophenylthiolate complexes [a]

Complex	Signal	δ(P) [b]	J(Rh–P) [c]	J(P–P)
$[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$	d	43.85	176.4	
$[Rh(SC_6F_5)(PPh_3)_3]$ [d]	dt	39.66	172.0	36.8
	dd	26.14	149.0	36.8
$[Rh(SC_6F_5)(PMe_2Ph)_3]$ [d]	dt	7.71	138.3	29.3
	dd	3.17	94.8	29.3
$[Rh(SC_6F_5)(PMePh_2)_3]$ [d]	dt	26.69	167.5	41.2
	dd	16.42	141.1	41.2
$[Rh(SC_6F_5)(P^nBu_3)_3]$ [d]	dt	22.83	166.4	41.0
	dd	8.48	137.8	41.0
$[Rh(SC_6F_5)(P(OMe)_3)_3]$	dt	144.46	240.8	57.2
	dd	138.43	216.9	57.2
$[Rh(SC_6F_5)(P(OEt)_3)_3]$ [d]	dt	143.82	238.8	55.5
	dd	136.91	211.6	55.5
$[RhH_2(SC_6F_5)(PPh_3)_3]$ [d]	dd	38.30	112.7	18.5
	dt	24.37	86.6	18.5
$[RhH_2(SC_6F_5)(PMe_2Ph)_3]$ [d]	dd	9.18	103.7	26.3
	dt	−10.18	126.2	26.3
$[RhH_2(SC_6F_5)(PMePh_2)_3]$ [d]	dd	28.59	110.3	21.6
	dt	5.7	88.9	21.6
$[RhH_2(SC_6F_5)(P^nBu_3)_3]$ [d]	dd	19.52	104.5	23.2
	dt	−0.07	87.5	23.2
$[RhH(SC_6F_5)(C_2Ph)(PMe_2Ph)_3]$ [d]	dd	−0.50	94.4	22.4
	dt	−20.37	74.4	22.4
$[RhH(SC_6F_5)(C_2Ph)(PMePh_2)_3]$ [d]	dd	18.51	97.6	20.1
	dt	−9.93	77.7	20.1
$[RhH(SC_6F_5)_2(PMe_2Ph)_3]$ [d]	dt	8.28	112.4	31.3
	dd	3.85	95.2	31.3
[*cis*-$Rh(SC_6F_5)(PPh_3)_2$(py)]	dd	50.06	166.1	44.8
	dd	47.51	178.1	44.8
[*cis*-$Rh(SC_6F_5)(PPh_3)_2$(2-Mepy)]	dd	49.33	167.4	44.8
	dd	46.86	179.8	44.8
[*cis*-$Rh(SC_6F_5)(PPh_3)_2$(3-Mepy)]	dd	50.17	165.7	44.6
	dd	47.61	178.4	44.6
[*cis*-$Rh(SC_6F_5)(PPh_3)_2(2,6\text{-}Me_2py)$]	dd	48.23	170.6	45.5
	dd	45.19	180.0	45.5
[*cis*-$Rh(SC_6F_5)(PPh_3)_2$(quin)]	dd	49.67	175.9	44.6
	dd	47.83	169.3	44.6
[*cis*-$Rh(SC_6F_5)(PPh_3)_2$(isoquin)]	dd	50.13	165.6	44.3
	dd	47.75	177.8	44.3
[*cis*-$Rh(SC_6F_5)(PPh_3)_2$(*N*-MeIm)]	dd	50.80	170.0	44.1
	dd	46.89	175.6	44.1
[*cis*-$Rh(SC_6F_5)(PPh_3)_2(NCCH_3)$] [d]	dd	51.09	177.6	45.8
	dd	46.86	165.8	45.8
$[RhH_2(SC_6F_5)(PPh_3)_2$(py)]	d	47.59	119.0	
$[RhH_2(SC_6F_5)(PPh_3)_2$(3-Mepy)]	d	47.74	118.3	
$[RhH_2(SC_6F_5)(PPh_3)_2$(isoquin)]	d	47.83	118.6	
$[RhH_2(SC_6F_5)(PPh_3)_2$(*N*-MeIm)] [d]	d	47.56	118.5	
$[RhH_2(SC_6F_5)(PPh_3)_2(NCCH_3)]$ [d]	d	46.94	116.3	
$[RhH(SC_6F_5)_2(PPh_3)(py)_2]$	d	43.80	133.9	
$[RhH(SC_6F_5)_2(PPh_3)(3\text{-}Mepy)_2]$	d	43.50	134.0	
$[RhH(SC_6F_5)_2(PPh_3)(isoquin)_2]$	d	43.98	133.4	
$[RhH(SC_6F_5)_2(PPh_3)(N\text{-}MeIm)_2]$ [d]	d	47.85	133.9	

Table 1 (continued)

Complex	Signal	δ(P) [b]	J(Rh–P) [c]	J(P–P)
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(py)]$	d	41.77	103.9	
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(3\text{-Mepy})]$ [d]	d	45.97	103.7	
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(isoquin)]$	d	42.28	104.0	
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(N\text{-MeIm})]$	d	42.89	104.1	
$[trans\text{-}Rh(SC_6F_5)(PPh_3)_2(CO)]$	d	30.22	130.9	
$[Rh(SC_6F_5)(PPh_3)_2(^tBuNC)_3]$ [e]	d	32.36	154.8	

[a] Solution in toluene/toluene-d_8 (10/1) at 22°C unless otherwise stated. [b] Chemical shifts in ppm relative to 80% H_3PO_4 (external standard) unless otherwise stated. [c] Coupling constants (absolute magnitude) in Hz. [d] Recorded at −50°C, chemical shift relative to PPh_3 at δ −4.70 ppm. [e] Recorded at −70°C, chemical shift relative to PPh_3 at −4.70 ppm.

by ^1H and ^{31}P NMR spectroscopy, is seen to proceed via an oxidative addition product (eq. 1).

$$[RhH(PPh_3)_4] \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} [RhH(PPh_3)_3] \xrightarrow{C_6F_5SH} \underset{(II)}{[RhH_2(SC_6F_5)(PPh_3)_3]} \qquad (1)$$

The $^{31}P\{^1H\}$ spectrum of II consists of a dd (2P) and dt (1P) (Table 1) while the high-field region of the ^1H spectrum (Table 2) shows two multiplets, one with $J = 154.8$ Hz characteristic of a hydride positioned *trans* to phosphine; II therefore has two phosphines mutually *trans* and two hydrides mutually *cis*.

At room temperature II loses H_2 (the rate constant for the decomposition of II, prepared *in situ* from $[RhH(PPh_3)_4]$ and C_6F_5SH, in toluene at 20°C is 0.0025 s^{-1}) to form a tris(phosphine)rhodium(I) thiolate complex III, which subsequently dimerises (eq. 2).

$$\underset{(II)}{II} \underset{+H_2}{\overset{\Delta,\ -H_2}{\rightleftharpoons}} \underset{(III)}{[Rh(SC_6F_5)(PPh_3)_3]} \underset{+PPh_3}{\overset{-PPh_3}{\rightleftharpoons}} \underset{(I)}{[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]} \qquad (2)$$

Results similar to these were obtained in an earlier study of the reaction of $[RhH(PPh_3)_4]$ with ^iPrSH, PhSH and $PhCH_2SH$ [23]. In the presence of a large excess of PPh_3 I can be reconverted (incompletely) to III on warming and, under an atmosphere of H_2, III is reconverted to II. The presence of III is shown by a dd and dt in $^{31}P\{^1H\}$ spectra recorded at −50°C, where the magnitudes of the ^{103}Rh–^{31}P coupling constants are indicative of a rhodium(I) complex. By carrying out the reaction of $[RhH(PPh_3)_4]$ with C_6F_5SH in the minimum possible volume of ether and isolating the product within a few minutes of mixing the reagents II can be obtained in good yield as a brown powder. The solid is fairly stable and can be stored for several months under nitrogen at −20°C.

The thiolate bridge of I is cleaved by a variety of σ-donor compounds including phosphines and phosphites. With PMe_2Ph and $PMePh_2$ bridge-breaking occurs readily at room temperature and is accompanied by replacement of PPh_3 (eq. 3).

$$\underset{(I)}{I} \xrightarrow[-PPh_3]{+PR_3} \underset{(IV)}{[Rh(SC_6F_5)(PR_3)_3]} \qquad (3)$$

Table 2

^{1}H NMR spectral data for the hydro- and dihydropentafluorophenylthiolate complexes [a]

Complex	Signal	δ(H) [b]	*J*(P–H *trans*) [c]	*J*(P–H *cis*)	*J*(Rh–H)
$[RhH_2(SC_6F_5)(PPh_3)_3]$	d mult	−9.67	154.8		
	mult	−13.77			
$[RhH_2(SC_6F_5)(PMe_2Ph)_3]$	d mult	−9.42	167.2		
	mult	−14.76			
$[RhH_2(SC_6F_5)(PMePh_2)_3]$	d mult	−9.08	157.0		
	mult	−14.32			
$[RhH_2(SC_6F_5)(P^nBu_3)_3]$	d mult	−10.49	159.5		
	mult	−16.65			
$[RhH(SC_6F_5)(C_2Ph)(PMe_2Ph)_3]$	ddt	−8.87	189.6	~13	~13
$[RhH(SC_6F_5)(C_2Ph)(PMePh_2)_3]$	ddt	−8.79	177.3	~12	~12
$[RhH(SC_6F_5)_2(PMe_2Ph)_3]$	broad	~−13.4			
$[RhH_2(SC_6F_5)(PPh_3)_2(py)]$	mult	−13.85			
	mult	−16.77			
$[RhH_2(SC_6F_5)(PPh_3)_2(3\text{-Mepy})]$	mult	−13.85			
	mult	−16.70			
$[RhH_2(SC_6F_5)(PPh_3)_2(isoquin)]$	mult	−13.66			
	mult	−16.54			
$[RhH_2(SC_6F_5)(PPh_3)_2(N\text{-MeIm})]$	mult	−14.12			
	mult	−16.12			
$[RhH_2(SC_6F_5)(PPh_3)_2(NCCH_3)]$	mult	−14.45			
	mult	−16.60			
$[RhH(SC_6F_5)_2(PPh_3)(py)_2]$ [d]	dd	−16.99		8.9	21.1
$[RhH(SC_6F_5)_2(PPh_3)(3\text{-Mepy})_2]$	dd	−16.89		8.4	20.3
$[RhH(SC_6F_5)_2(PPh_3)(isoquin)_2]$	dd	−16.58		8.4	20.4
$[RhH(SC_6F_5)_2(PPh_3)(N\text{-MeIm})_2]$	dd	−16.16		7.0	19.9
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(py)]$ [d]	dt	−15.32		12.3	16.2
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(3\text{-Mepy})]$ [d]	dt	−15.26		12.2	16.0
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(isoquin)]$ [d]	dt	−15.11		12.3	16.2
$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(N\text{-MeIm})]$ [d]	dt	−14.64		12.1	14.9

[a] Solution in toluene-d_8 at −25°C unless otherwise stated. [b] Chemical shifts in ppm relative to TMS. [c] Coupling constants (absolute magnitude) in Hz. [d] Recorded at 22°C.

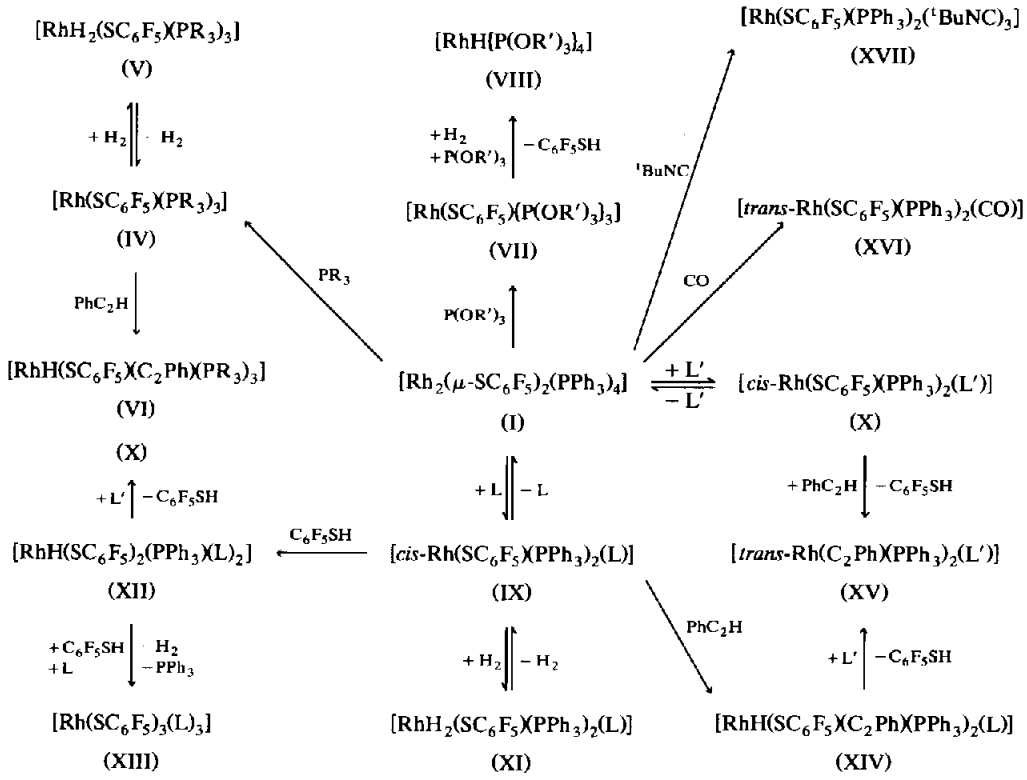
The bridge is not readily broken by P^nBu_3 and IV ($R = {}^nBu$) is formed only slowly on warming to 75°C.

Complex IV ($PR_3 = PMe_2Ph$, $PMePH_2$) in toluene solution undergoes oxidative addition reactions with H_2, PhC_2H and C_6F_5SH, binding H_2 readily and reversibly to give $[RhH_2(SC_6F_5)(PR_3)_3]$ (V) (Scheme 1); reconversion of V to IV occurs on flushing the solution with nitrogen for a few minutes. Hydrogen is held more strongly by V ($R = {}^nBu$). With PhC_2H IV ($PR_3 = PMe_2Ph$, $PMePh_2$) gives a product VI having a hydride positioned *trans* to phosphine (eq. 4).

$$\text{IV} \xrightarrow{PhC_2H} [RhH(SC_6F_5)(C_2Ph)(PR_3)_3] \quad (4)$$

(VI)

The reaction of C_6F_5SH with IV ($PR_3 = PMe_2Ph$) gives $[RhH(SC_6F_5)_2(PMe_2Ph)_3]$ but with IV ($PR_3 = PMePh_2$) the results are less clear-cut: a product appears to be formed reversibly at −50°C but no high field signals are found in the ^{1}H spectrum.



PR_3 = PMe_2Ph, $PMePh_2$
$P(OR')_3$ = $P(OMe)_3$, $P(OEt)_3$
L = py, 3-Mepy, isoquin, *N*-MeIm, CH_3CN
L' = 2-Mepy, 2,6-Me_2py, quin

Scheme 1.

Phosphites react with I in a manner similar to phosphines, with replacement of PPh_3 by $P(OR')_3$ (R' = Me, Et) to give $[Rh(SC_6F_5)\{P(OR')_3\}_3]$ (VII) (Scheme 1). With $P(OPh)_3$ a reaction occurs only on heating (75°C, 5 min). In the presence of H_2 VII loses C_6F_5SH to give VIII (eq. 5), suggesting that an unstable intermediate

$$\text{VII} \xrightarrow[-C_6F_5SH]{+H_2,\ +P(OR')_3} [RhH\{P(OR')_3\}_4] \quad (5)$$

(VIII)

$[RhH_2(SC_6F_5)\{P(OR')_3\}_3]$ is formed. The readiness with which this complex undergoes reductive elimination can be explained by the poorer σ-donor ability and greater π-acidity [24] of the phosphite ligand leading to a lower electron density at the metal than in the analogous phosphine-containing complex II. In VIII (unlike $[RhH(PPh_3)_4]$) all ligands remain attached to the metal. At temperatures of −50°C and above the stereochemical nonrigidity of VIII causes all phosphites to appear equivalent on the NMR timescale [25] and the hydride resonates as a doublet of quintets. *

With nitrogen-containing aromatic compounds and with acetonitrile I reacts to give *cis*-bis(phosphine)rhodium(I) pentafluorophenylthiolate complexes (eq. 6).

$$\text{I} \underset{-L}{\overset{+L}{\rightleftharpoons}} [cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L)] \quad \text{(IX)}$$

$$\text{I} \xrightarrow[-L']{+L'} [cis\text{-}Rh(SC_6F_5)(PPh_3)_2(L')] \quad \text{(X)} \qquad (6)$$

(L = py, 3-Mepy, isoquin, *N*-MeIm, CH_3CN; L' = 2-Mepy, 2,6-Me_2py, quin)

Although these two classes of compound appear virtually identical their properties differ markedly, correlating with the sterically hindering or nonhindering nature of the ligands L and L'. In the $^{31}P\{^1H\}$ spectra of IX and X the nonequivalence of the two phosphines is shown by the appearance of their signals each as a doublet of doublets. When L = py IX can be isolated as an orange microcrystalline powder from solution in CH_2Cl_2 containing 2–3% pyridine. In solution in the absence of an excess of pyridine IX (L = py) is rapidly reconverted to I. With other ligands L and L' products IX cannot readily be isolated. The minimum concentration of L or L' required to convert I to IX or X such that these products constitute > 95% (measured from ^{31}P spectra) of the species in solution varies considerably with the ligand. For 0.003–0.005 *M* solutions of I in toluene at 22°C the number of equivalents of L or L' (per equivalent of Rh) required are: py, 8; 3-Mepy, 4; isoquin, 3; *N*-MeIm, 1; CH_3CN (−50°C), 600; 2-Mepy, 15; 2,6-Me_2py, 90; quin, 5. In the case of the reaction with CH_3CN measurements were made at −50°C since at room temperature the signals from IX (L = CH_3CN) are broadened and difficult to observe.

* Spectral data for $[RhH\{P(OR')_3\}_4]$ (δ in ppm; J in Hz), R' = Me: δ(H) (toluene 22°C) −11.70 J(P–H) 35.3, J(Rh–H) 9.5; δ(P) (toluene −50°C) 168.20 J(Rh–P) 212.4; R' = Et: δ(H) (toluene −25°C) −11.77 J(P–H) 33.6, J(Rh–H) 9.8; δ(P) (toluene −50°C) 162.92 J(Rh–P) 209.8.

Complexes IX bind H_2 reversibly under ambient conditions to give products (XI, Scheme 1) in which the phosphines are mutually *trans* (appearing as a doublet in the $^{31}P\{^1H\}$ spectrum) and the hydrides are mutually *cis* (shown by their differing chemical shifts); complexes X do not bind H_2. With a large excess of PPh_3 XI is converted to II. Complex XI (L = py) is also formed by the reaction of $[RhH(PPh_3)_4]$ with C_6F_5SH in ~ 4/1 toluene/pyridine and decomposes at room temperature to give IX (L = py) as the first product (followed by further reaction with thiol, *vide infra*). There is no evidence for the formation of a five-coordinate dimeric thiolate-bridged structure of the type reported by Kalk *et al.* for complexes of Rh^I with –SPh or –S^{t}Bu, phosphine and carbonyl ligands [7,8].

Differences in the properties of IX and X are also found in their reactivity towards C_6F_5SH and PhC_2H. IX combines with C_6F_5SH forming an oxidative addition product (eq. 7), while with X no changes are observed. The presence of a

$$\text{IX} \xrightarrow{C_6F_5SH} [RhH(SC_6F_5)_2(PPh_3)(L)_2] \quad (7)$$

(XII)

single phosphine in XII is shown by the hydride signal in the ^1H spectrum which appears as a dd. In the absence of a large excess of L further reaction of XII with the thiol rapidly occurs (eq. 8), where an unstable intermediate $[RhH(SC_6F_5)_2(PPh_3)(L)(HSC_6F_5)]$ may be formed by exchange of L for C_6F_5SH. XII (L = py)

$$\text{XII} \xrightarrow[-H_2,\ -PPh_3]{+C_6F_5SH,\ +L} [Rh(SC_6F_5)_3(L)_3] \quad (8)$$

(XIII)

can be prepared in 57% yield by the addition of C_6F_5SH to a suspension of $[RhH(PPh_3)_4]$ in ~ 10% pyridine/Et_2O, from which it is obtained as an orange powder; with other ligands L products XII cannot readily be isolated. Complexes XIII (L = py, *N*-MeIm) are obtained as red crystals or (L = 3-Mepy) red powder.

When a solution of XII (L = py; the complex prepared *in situ* in toluene from IX and C_6F_5SH) is treated with a large excess (20–25% by volume) of L (L = 3-Mepy, isoquin, *N*-MeIm) and warmed to 75°C for 2 min a ligand exchange takes place to give XII (L = 3-Mepy, etc). However on similar treatment with L′ the outcome is quite different: a reductive elimination of C_6F_5SH occurs, accompanied by replacement of py by L′ to give X (eq. 9).

$$[RhH(SC_6F_5)_2(PPh_3)(py)_2] \begin{cases} \xrightarrow[-py]{+L,\ \Delta} [RhH(SC_6F_5)_2(PPh_3)(L)_2] \quad \text{(XII)} \\ \xrightarrow[-C_6F_5SH,\ -py]{+L',\ +PPh_3,\ \Delta} [\textit{cis}\text{-}Rh(SC_6F_5)(PPh_3)_2(L')] \quad \text{(X)} \end{cases} \quad (9)$$

(L = 3-Mepy, isoquin, *N*-MeIm, L′ = 2-Mepy, 2,6-Me_2py, quin)

In view of the similarity in electronic properties of 2-Mepy and 3-Mepy and also of quin and isoquin these divergent results would appear to arise as a consequence largely of steric differences between ligands L and L′.

With phenylacetylene in toluene IX reacts on warming to 75°C for 1 min to give an oxidative addition product (eq. 10), while X reacts to give a product from which C_6F_5SH has been lost (eq. 11).

$$\text{IX} \xrightarrow{PhC_2H,\ \Delta} [RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(L)] \quad (10)$$

(XIV)

$$\text{X} \xrightarrow{PhC_2H,\ \Delta} [\textit{trans}\text{-}Rh(C_2Ph)(PPh_3)_2(L')] \quad (11)$$

(XV)

This suggests that an unstable intermediate $[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(L')]$ is formed which, owing to steric congestion, undergoes reductive elimination of C_6F_5SH rather than ejection of L'. Attempts to isolate XIV (L = *N*-MeIm) yielded an impure brown oil.

The manner in which XII (L = py) reacts with L and L' is paralleled by the reaction of XIV (L = *N*-MeIm, chosen because the reaction using it proceeds most readily to completion; the complex prepared *in situ* from IX and PhC_2H in toluene) with these ligands. With the sterically nonhindering L an exchange of *N*-MeIm for L occurs on warming to 75°C for 2 min while with the sterically hindering L' a reductive elimination of C_6F_5SH takes place (eq. 12).

$$[RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(N\text{-MeIm})] \begin{cases} \xrightarrow[-N\text{-MeIm}]{+L,\ \Delta} [RhH(SC_6F_5)(C_2Ph)(PPh_3)_2(L)] \\ \qquad\qquad (XIV) \\ \xrightarrow[-C_6F_5SH,\ -N\text{-MeIm}]{+L',\ \Delta} [\textit{trans}\text{-}Rh(C_2Ph)(PPh_3)_2(L')]\ * \\ \qquad\qquad (XV) \end{cases} \quad (12)$$

(L = py, 3-Mepy, isoquin; L' = 2-Mepy, 2,6-Me_2py, quin)

Here again steric effects would appear largely to determine the outcome, although the reasons for loss of C_6F_5SH rather than PhC_2H are likely to include the greater opportunities for $d\pi$–$p\pi$ interactions afforded by the C_2Ph ligand.

Attempts to bring about a reaction between IX or X and ^iPrSH or CH_3CO_2H by heating mixtures in toluene to 75°C for 2 min proved unsuccessful. In this respect IX differs from $[Rh(SC_6F_5)(PMe_2Ph)_3]$, which reacts with both ^iPrSH (on warming) and CH_3CO_2H (to give in each case mixtures of products) and $[RhH(PPh_3)_3]$, which combines readily with both reagents, the reaction with ^iPrSH being rapid even at −40°C [23,26].

Complex I reacts rapidly with CO and with ^{t}BuNC in toluene at room temperature to give $[\textit{trans}\text{-}Rh(SC_6F_5)(PPh_3)_2(CO)]$ (XVI) and a product with the stoichiometry $Rh(SC_6F_5)(PPh_3)_2(^tBuNC)_3$ (XVII) respectively. In the ^1H spectrum of XVII in toluene at room temperature the t-butyl protons appear as a sharp singlet

* ^{31}P spectral data for XV (toluene/L' 22°C) (δ in ppm; J in Hz): L' = 2-Mepy, δ 34.62 J(Rh–P) 162.8; L' = 2.6-Me_2py, δ 33.30 J(Rh–P) 162.9; L' = quin, δ 35.13, J(Rh–P) 161.7.

which, on lowering the temperature to −70°C, is transformed into three lines; the $^{31}P\{^1H\}$ spectrum at −70°C, shows a doublet and a signal from free PPh_3 both of which disappear at room temperature. This is consistent with the properties of a nonrigid five-coordinate complex in which the isocyanides are individually bound to the metal rather than fused together in some way and which interacts with a phosphine that is not firmly attached. The product may therefore be better represented as $[Rh(SC_6F_5)(PPh_3)(^tBuNC)_3](PPh_3)$. Both XVI and XVII can readily be prepared by the reaction of CO or ^{t}BuNC with a mixture of $[RhH(PPh_3)_4]$ and C_6F_5SH in Et_2O. XVI reacts with neither H_2 not C_6F_5SH under ambient conditions.

A number of compounds were found not to split the thiolate bridge of I, namely thiophene, tetrahydrofuran, triethylamine and cyclohexene (in 25–95% mixtures with toluene and with heating to 60–70°C for 2 min).

The strongly π-acidic ligands CO, ^{t}BuNC and $P(OR')_3$ react with I to give mononuclear complexes that either do not readily undergo oxidative addition or (in the case of VII with H_2) react to give stable Rh^I complexes. With these ligands in the complex the Rh^{III} oxidation state is disfavoured for reasons that are clearly electronic in nature, involving a decrease in the electron density at the metal caused by substantial $d\pi$–$p\pi$ interactions. Rhodium(I) complexes having PMe_2Ph or a combination of PPh_3 and L ligands are sufficiently electron-rich to react with C_6F_5SH and PhC_2H to give stable products. In each case ligands are present that can stabilise a reduced metal fragment, therefore the stability of the Rh^{III} complex is unlikely to depend on the existence of an unfavourable transition state for the elimination reaction (a condition which has been shown to apply in the case of chloroethyl(8-quinolinecarbonyl-*C*,*N*)(pyridine)rhodium [27]). The ability of III, IV and IX to bind H_2 reversibly is consistent with activity in the catalysis of alkene hydrogenation, where III is moderately effective [19].

The conversion of XII and XIV to X and XV respectively by treatment with L′ (Scheme 1) involving a reductive elimination of C_6F_5SH would appear to be governed almost entirely by steric effects. The increased steric congestion resulting from the exchange of L for L′ is evidently sufficient to labilise the molecule with respect to reductive elimination (of C_6F_5SH) without leading to the expulsion of L′ or the prevention of its binding to the metal. The prior dissociation of a neutral ligand to give an unstable five-coordinate intermediate, although a prerequisite of numerous reductive elimination reactions [23,27,28], is unlikely to promote reductive elimination here since the ligand most likely to be lost is L′ and in the absence of L′ the Rh^{III} complex is stable.

Conclusion

The thiolate bridge of $[Rh_2(\mu\text{-}SC_6F_5)_2(PPh_3)_4]$ is split by a variety of reagents to give products whose abilities to undergo oxidative addition and subsequent reductive elimination reaction vary greatly. This wide range of reactivity appears to be a function of the electron density at the metal, governed by the σ-donor and π-acceptor properties of the phosphine, phosphite, *N*-donor aromatic or carbonyl ligands in the complex. In two series of complexes in which the *N*-donor ligand is varied while other factors are held constant, it is clear that steric effects can also

have a marked influence on the stability of a rhodium(III) complex with respect to reductive elimination.

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