

*Journal of Organometallic Chemistry*, 431 (1992) 103–115  
 Elsevier Sequoia S.A., Lausanne  
 JOM 22559

## Rhodium pentafluorophenylthiolate complexes derived from $[\text{Rh}_2(\mu\text{-SC}_6\text{F}_5)_2(\text{PPh}_3)_4]$

Laurence Carlton

*Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg (South Africa)*

(Received October 24, 1991)

### Abstract

The thiolate bridges of  $[\text{Rh}_2(\mu\text{-SC}_6\text{F}_5)_2(\text{PPh}_3)_4]$  are readily split by a variety of phosphines, phosphites and nitrogen-containing compounds to give  $[\text{Rh}(\text{SC}_6\text{F}_5)(\text{PR}_3)_3]$ ,  $[\text{Rh}(\text{SC}_6\text{F}_5)(\text{P}(\text{OR}')_3)_3]$ ,  $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L})]$  and  $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L}')]_2$ , ( $\text{PR}_3 = \text{PMc}_2\text{Ph}$ ,  $\text{PMcPh}_2$ ;  $\text{P}(\text{OR}')_3 = \text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OEt})_3$ ;  $\text{L}$  (sterically nonhindering) = pyridine, 3-methylpyridine, isoquinoline, *N*-methylimidazole, acetonitrile;  $\text{L}'$  (sterically hindering) = 2-methylpyridine, 2,6-dimethylpyridine, quinoline). With  $\text{H}_2$  under ambient conditions both  $[\text{Rh}(\text{SC}_6\text{F}_5)(\text{PR}_3)_3]$  and  $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L})]$  combine reversibly,  $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L}')]_2$  does not react and  $[\text{Rh}(\text{SC}_6\text{F}_5)(\text{P}(\text{OR}')_3)_3]$  (in the presence of free  $\text{P}(\text{OR}')_3$ ) is converted into  $[\text{RhH}(\text{P}(\text{OR}')_3)_4]$ .  $[\text{Rh}(\text{SC}_6\text{F}_5)(\text{PR}_3)_3]$  and  $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L})]$  react with phenylacetylene to give  $[\text{RhH}(\text{SC}_6\text{F}_5)(\text{C}_2\text{Ph})(\text{PR}_3)_3]$  and  $[\text{RhH}(\text{SC}_6\text{F}_5)(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\text{L})]$ , respectively, while with  $\text{C}_6\text{F}_5\text{SH}$   $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L})]$  forms  $[\text{RhH}(\text{SC}_6\text{F}_5)_2(\text{PPh}_3)(\text{L})]$ , and further reaction gives  $[\text{Rh}(\text{SC}_6\text{F}_5)_3(\text{L})_3]$ . Although  $[\text{cis-Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)_2(\text{L}')]_2$  is unreactive towards  $\text{C}_6\text{F}_5\text{SH}$  it combines with  $\text{PhC}_2\text{H}$  with loss of  $\text{C}_6\text{F}_5\text{SH}$  yielding  $[\text{trans-Rh}(\text{C}_2\text{Ph})(\text{PPh}_3)_2(\text{L})]$ . Other reagents which split the  $[\text{Rh}_2(\mu\text{-SC}_6\text{F}_5)_2(\text{PPh}_3)_4]$  bridge are carbon monoxide and *t*-butyl isocyanide. Products were characterised by  $^1\text{H}$  and  $^{31}\text{P}$  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

Correspondence to: L. Carlton, Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.

oxidative addition (of  $H_2$ ) and reductive elimination reactions. The complex  $[Rh_2(\mu-S^tBu)_2(CO)_2(PMe_2Ph)_2]$ , 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  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$  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  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$  (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  $^tBuNC$ , 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  $-50^\circ C$  ( $^{31}P$ ). 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 ( $\sim -40^\circ C$ ) solution of  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$  (10 mg) and *N*-MeIm (1 drop) in an NMR tube; spectra were recorded at  $-25$  ( $^1H$ ) and  $-50^\circ C$  ( $^{31}P$ ). In other experiments  $C_6F_5SH$ ,  $PhC_2H$ ,  $^iPrSH$  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  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$  plus bridge-splitting reagent in an NMR tube, and, following warming to  $75^\circ C$  in a number of cases, a spectrum was again recorded. Further treatment with L or L' involved addition of  $\sim 1$  ml of the liquid followed by warming to  $75^\circ C$  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<sub>2</sub>py, 2,6-dimethylpyridine; quin, quinoline; isoquin, isoquinoline; *N*-MeIm, *N*-methylimidazole.

*Preparation of  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$* 

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)  $\nu(Rh-H)$  2132w, 1998m  $cm^{-1}$ .

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

A solution of  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$  (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  $-20^\circ C$  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)  $\nu(Rh-H)$  2130  $cm^{-1}$ .

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

A solution of  $[Rh_2(\mu-SC_6F_5)_2(PPh_3)_4]$  (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  $-20^\circ C$  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<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(3-Mepy)<sub>3</sub>]*

A solution of [Rh<sub>2</sub>(μ-SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (0.014 g, 0.014 mmol) in 2–3% 3-Mepy/CH<sub>2</sub>Cl<sub>2</sub> (~ 2 ml) was treated with C<sub>6</sub>F<sub>5</sub>SH (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<sub>36</sub>H<sub>21</sub>F<sub>15</sub>N<sub>3</sub>RhS calc.: C, 44.1; H, 2.2; N, 4.3%.

*Preparation of [Rh(SC<sub>6</sub>F<sub>5</sub>)<sub>3</sub>(N-MeIm)<sub>3</sub>]*

A solution of [Rh<sub>2</sub>(μ-SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (0.014 g, 0.014 mmol) in 2–3% N-MeIm/CH<sub>2</sub>Cl<sub>2</sub> (~ 2 ml) was treated with C<sub>6</sub>F<sub>5</sub>SH (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<sub>30</sub>H<sub>18</sub>F<sub>15</sub>N<sub>6</sub>RhS<sub>3</sub> calc.: C, 38.7; H, 1.9; N, 8.9%. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.59, 6.64, 6.34, 3.56 ppm.

*Preparation of [trans-Rh(SC<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)]*

A stirred suspension of [RhH(PPh<sub>3</sub>)<sub>4</sub>] (0.080 g, 0.069 mmol) in Et<sub>2</sub>O (4 ml) at room temperature was treated with C<sub>6</sub>F<sub>5</sub>SH (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<sub>43</sub>H<sub>30</sub>F<sub>5</sub>OP<sub>2</sub>RhS calc.: C, 60.4; H, 3.5%. IR (Nujol mull) ν(CO) 1984 cm<sup>-1</sup>.

*Preparation of [Rh(SC<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>(<sup>t</sup>BuNC)<sub>3</sub>]*

A stirred suspension of [RhH(PPh<sub>3</sub>)<sub>4</sub>] (0.100 g, 0.087 mmol) in Et<sub>2</sub>O (5 ml) at room temperature was treated with C<sub>6</sub>F<sub>5</sub>SH (0.022 g, 0.11 mmol) to give a dark brown solution. <sup>t</sup>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<sub>57</sub>H<sub>57</sub>F<sub>5</sub>N<sub>3</sub>P<sub>2</sub>RhS calc.: C, 63.6; H, 5.3; N, 3.9%. IR (CHCl<sub>3</sub>) ν(CN) 2190w, 2140s, 2124sh, 2100sh. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 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<sub>2</sub>(μ-SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub>] (I) is formed in high yield as red-brown crystals by the reaction of [RhH(PPh<sub>3</sub>)<sub>4</sub>] with C<sub>6</sub>F<sub>5</sub>SH in ether at room temperature. In toluene solution at temperatures ≤ –25°C the reaction, when monitored

Table 1

<sup>31</sup>P NMR spectral data for the pentafluorophenylthiolate complexes <sup>a</sup>

Complex	Signal	$\delta(\text{P})^b$	$J(\text{Rh}-\text{P})^c$	$J(\text{P}-\text{P})$
[Rh <sub>2</sub> ( $\mu$ -SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> ) <sub>4</sub> ]	d	43.85	176.4	
[Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	dt	39.66	172.0	36.8
	dd	26.14	149.0	36.8
[Rh(SC <sub>6</sub> F <sub>5</sub> )(PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>d</sup>	dt	7.71	138.3	29.3
	dd	3.17	94.8	29.3
[Rh(SC <sub>6</sub> F <sub>5</sub> )(PMePh <sub>2</sub> ) <sub>3</sub> ] <sup>d</sup>	dt	26.69	167.5	41.2
	dd	16.42	141.1	41.2
[Rh(SC <sub>6</sub> F <sub>5</sub> )(P <sup>n</sup> Bu <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	dt	22.83	166.4	41.0
	dd	8.48	137.8	41.0
[Rh(SC <sub>6</sub> F <sub>5</sub> )(P(OMe) <sub>3</sub> ) <sub>3</sub> ]	dt	144.46	240.8	57.2
	dd	138.43	216.9	57.2
[Rh(SC <sub>6</sub> F <sub>5</sub> )(P(OEt) <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	dt	143.82	238.8	55.5
	dd	136.91	211.6	55.5
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	dd	38.30	112.7	18.5
	dt	24.37	86.6	18.5
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>d</sup>	dd	9.18	103.7	26.3
	dt	-10.18	126.2	26.3
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PMePh <sub>2</sub> ) <sub>3</sub> ] <sup>d</sup>	dd	28.59	110.3	21.6
	dt	5.7	88.9	21.6
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(P <sup>n</sup> Bu <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	dd	19.52	104.5	23.2
	dt	-0.07	87.5	23.2
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>d</sup>	dd	-0.50	94.4	22.4
	dt	-20.37	74.4	22.4
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PMePh <sub>2</sub> ) <sub>3</sub> ] <sup>d</sup>	dd	18.51	97.6	20.1
	dt	-9.93	77.7	20.1
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>d</sup>	dt	8.28	112.4	31.3
	dd	3.85	95.2	31.3
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (py)]	dd	50.06	166.1	44.8
	dd	47.51	178.1	44.8
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (2-Mepy)]	dd	49.33	167.4	44.8
	dd	46.86	179.8	44.8
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (3-Mepy)]	dd	50.17	165.7	44.6
	dd	47.61	178.4	44.6
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (2,6-Me <sub>2</sub> py)]	dd	48.23	170.6	45.5
	dd	45.19	180.0	45.5
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (quin)]	dd	49.67	175.9	44.6
	dd	47.83	169.3	44.6
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (isoquin)]	dd	50.13	165.6	44.3
	dd	47.75	177.8	44.3
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ( <i>N</i> -MeIm)]	dd	50.80	170.0	44.1
	dd	46.89	175.6	44.1
[ <i>cis</i> -Rh(SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (NCCH <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	dd	51.09	177.6	45.8
	dd	46.86	165.8	45.8
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (py)]	d	47.59	119.0	
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (3-Mepy)]	d	47.74	118.3	
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (isoquin)]	d	47.83	118.6	
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ( <i>N</i> -MeIm)] <sup>d</sup>	d	47.56	118.5	
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (NCCH <sub>3</sub> ) <sub>3</sub> ] <sup>d</sup>	d	46.94	116.3	
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )(xy) <sub>2</sub> ]	d	43.80	133.9	
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )(3-Mepy) <sub>2</sub> ]	d	43.50	134.0	
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )(isoquin) <sub>2</sub> ]	d	43.98	133.4	
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )( <i>N</i> -MeIm) <sub>2</sub> ] <sup>d</sup>	d	47.85	133.9	



Table 2

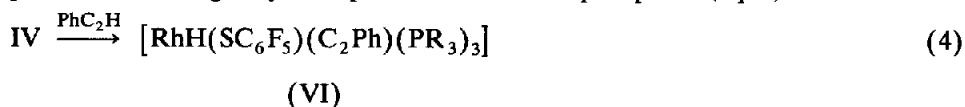
<sup>1</sup>H NMR spectral data for the hydro- and dihydropentafluorophenylthiolate complexes <sup>a</sup>

Complex	Signal	$\delta(\text{H})^b$	$J(\text{P-H})$ <i>trans</i> <sup>c</sup>	$J(\text{P-H})$ <i>cis</i>	$J(\text{Rh-H})$
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>3</sub> ]	d mult	-9.67	154.8		
	mult	-13.77			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PMe <sub>2</sub> Ph) <sub>3</sub> ]	d mult	-9.42	167.2		
	mult	-14.76			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PMePh <sub>2</sub> ) <sub>3</sub> ]	d mult	-9.08	157.0		
	mult	-14.32			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(P <sup>n</sup> Bu <sub>3</sub> ) <sub>3</sub> ]	d mult	-10.49	159.5		
	mult	-16.65			
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PMe <sub>2</sub> Ph) <sub>3</sub> ]	ddt	-8.87	189.6	~ 13	~ 13
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PMePh <sub>2</sub> ) <sub>3</sub> ]	ddt	-8.79	177.3	~ 12	~ 12
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>3</sub> ]	broad	~ -13.4			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (py)]	mult	-13.85			
	mult	-16.77			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (3-Mepy)]	mult	-13.85			
	mult	-16.70			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (isoquin)]	mult	-13.66			
	mult	-16.54			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ( <i>N</i> -MeIm)]	mult	-14.12			
	mult	-16.12			
[RhH <sub>2</sub> (SC <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (NCCH <sub>3</sub> )]	mult	-14.45			
	mult	-16.60			
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )(py) <sub>2</sub> ] <sup>d</sup>	dd	-16.99		8.9	21.1
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )(3-Mepy) <sub>2</sub> ]	dd	-16.89		8.4	20.3
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )(isoquin) <sub>2</sub> ]	dd	-16.58		8.4	20.4
[RhH(SC <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> (PPh <sub>3</sub> )( <i>N</i> -MeIm) <sub>2</sub> ]	dd	-16.16		7.0	19.9
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PPh <sub>3</sub> ) <sub>2</sub> (py)] <sup>d</sup>	dt	-15.32		12.3	16.2
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PPh <sub>3</sub> ) <sub>2</sub> (3-Mepy)] <sup>d</sup>	dt	-15.26		12.2	16.0
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PPh <sub>3</sub> ) <sub>2</sub> (isoquin)] <sup>d</sup>	dt	-15.11		12.3	16.2
[RhH(SC <sub>6</sub> F <sub>5</sub> )(C <sub>2</sub> Ph)(PPh <sub>3</sub> ) <sub>2</sub> ( <i>N</i> -MeIm)] <sup>d</sup>	dt	-14.64		12.1	14.9

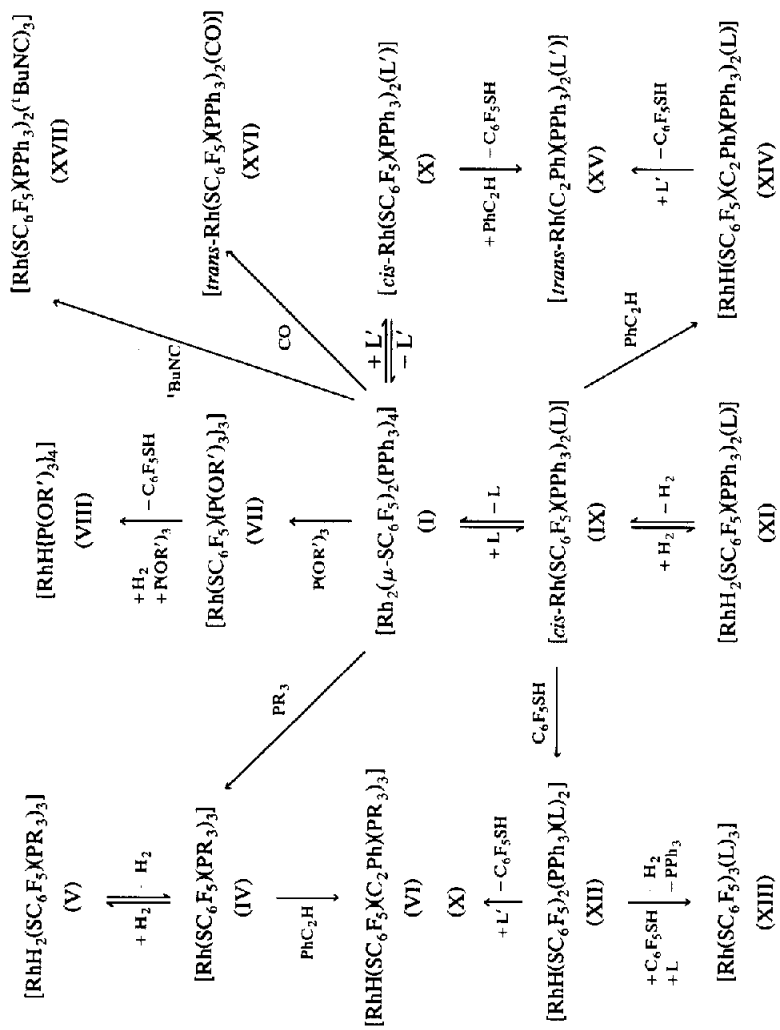
<sup>a</sup> Solution in toluene-*d*<sub>6</sub> at -25°C unless otherwise stated. <sup>b</sup> Chemical shifts in ppm relative to TMS.<sup>c</sup> Coupling constants (absolute magnitude) in Hz. <sup>d</sup> Recorded at 22°C.

The bridge is not readily broken by P<sup>n</sup>Bu<sub>3</sub> and IV (R = <sup>n</sup>Bu) is formed only slowly on warming to 75°C.

Complex IV (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PMePh<sub>2</sub>) in toluene solution undergoes oxidative addition reactions with H<sub>2</sub>, PhC<sub>2</sub>H and C<sub>6</sub>F<sub>5</sub>SH, binding H<sub>2</sub> readily and reversibly to give [RhH<sub>2</sub>(SC<sub>6</sub>F<sub>5</sub>)(PR<sub>3</sub>)<sub>3</sub>] (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 = <sup>n</sup>Bu). With PhC<sub>2</sub>H IV (PR<sub>3</sub> = PMe<sub>2</sub>Ph, PMePh<sub>2</sub>) gives a product VI having a hydride positioned *trans* to phosphine (eq. 4).



The reaction of C<sub>6</sub>F<sub>5</sub>SH with IV (PR<sub>3</sub> = PMe<sub>2</sub>Ph) gives [RhH(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>] but with IV (PR<sub>3</sub> = PMePh<sub>2</sub>) 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 <sup>1</sup>H spectrum.

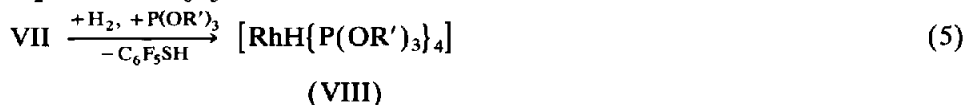


$\text{PR}_3 = \text{PMe}_2\text{Ph, PMePh}_2$   
 $\text{P(OR')}_3 = \text{P(OMe)}_3, \text{P(OEt)}_3$   
 $\text{L} = \text{py, 3-Mepy, isoquin, } N\text{-MeIm, CH}_3\text{CN}$   
 $\text{L}' = 2\text{-Mepy, 2,6-Me}_2\text{py, quin}$

Scheme 1.

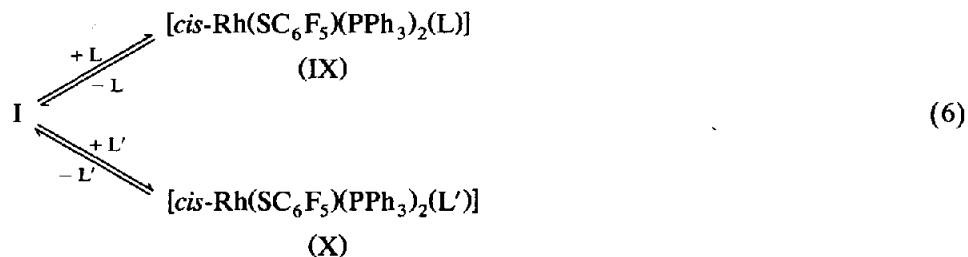


Phosphites react with I in a manner similar to phosphines, with replacement of  $\text{PPh}_3$  by  $\text{P}(\text{OR}')_3$  ( $\text{R}' = \text{Me}, \text{Et}$ ) to give  $[\text{Rh}(\text{SC}_6\text{F}_5)\{\text{P}(\text{OR}')_3\}_3]$  (VII) (Scheme 1). With  $\text{P}(\text{OPh})_3$  a reaction occurs only on heating ( $75^\circ\text{C}$ , 5 min). In the presence of  $\text{H}_2$  VII loses  $\text{C}_6\text{F}_5\text{SH}$  to give VIII (eq. 5), suggesting that an unstable intermediate



$[\text{RhH}_2(\text{SC}_6\text{F}_5)\{\text{P}(\text{OR}')_3\}_3]$  is formed. The readiness with which this complex undergoes reductive elimination can be explained by the poorer  $\sigma$ -donor ability and greater  $\pi$ -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  $[\text{RhH}(\text{PPh}_3)_4]$ ) all ligands remain attached to the metal. At temperatures of  $-50^\circ\text{C}$  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).



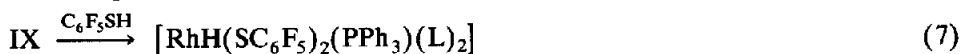
(L = py, 3-Mepy, isoquin, *N*-MeIm,  $\text{CH}_3\text{CN}$ ; L' = 2-Mepy, 2,6-Me<sub>2</sub>py, quin)

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  $^{31}\text{P}\{^1\text{H}\}$  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  $\text{CH}_2\text{Cl}_2$  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  $^{31}\text{P}$  spectra) of the species in solution varies considerably with the ligand. For 0.003–0.005 M solutions of I in toluene at  $22^\circ\text{C}$  the number of equivalents of L or L' (per equivalent of Rh) required are: py, 8; 3-Mepy, 4; isoquin, 3; *N*-MeIm, 1;  $\text{CH}_3\text{CN}$  ( $-50^\circ\text{C}$ ), 600; 2-Mepy, 15; 2,6-Me<sub>2</sub>py, 90; quin, 5. In the case of the reaction with  $\text{CH}_3\text{CN}$  measurements were made at  $-50^\circ\text{C}$  since at room temperature the signals from IX (L =  $\text{CH}_3\text{CN}$ ) are broadened and difficult to observe.

\* Spectral data for  $[\text{RhH}\{\text{P}(\text{OR}')_3\}_4]$  ( $\delta$  in ppm;  $J$  in Hz),  $\text{R}' = \text{Me}$ :  $\delta(\text{H})$  (toluene  $22^\circ\text{C}$ )  $-11.70$   $J(\text{P-H})$  35.3,  $J(\text{Rh-H})$  9.5;  $\delta(\text{P})$  (toluene  $-50^\circ\text{C}$ ) 168.20  $J(\text{Rh-P})$  212.4;  $\text{R}' = \text{Et}$ :  $\delta(\text{H})$  (toluene  $-25^\circ\text{C}$ )  $-11.77$   $J(\text{P-H})$  33.6,  $J(\text{Rh-H})$  9.8;  $\delta(\text{P})$  (toluene  $-50^\circ\text{C}$ ) 162.92  $J(\text{Rh-P})$  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  $\sim 4/1$  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  $-S^tBu$ , 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



(XII)

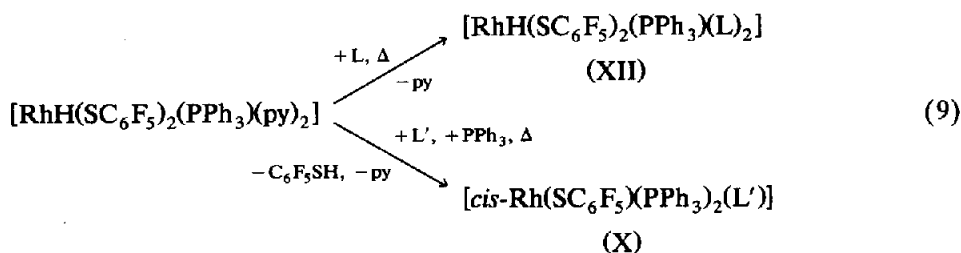
single phosphine in XII is shown by the hydride signal in the  $^1H$  spectrum which appears as a dd. In the absence of a large excess of L further reaction of XII with the thiol rapidly occurs (eq. 8), where an unstable intermediate  $[RhH(SC_6F_5)_2(PPh_3)(L)(HSC_6F_5)]$  may be formed by exchange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



(XIII)

can be prepared in 57% yield by the addition of  $C_6F_5SH$  to a suspension of  $[RhH(PPh_3)_4]$  in  $\sim 10\%$  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.

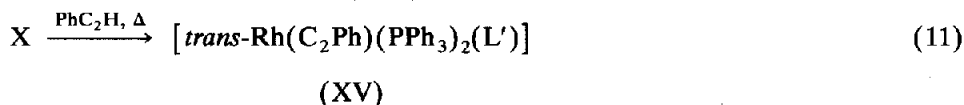
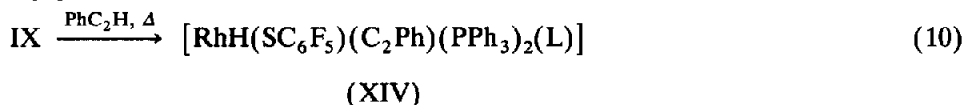
When a solution of XII ( $L = py$ ; the complex prepared *in situ* in toluene from IX and  $C_6F_5SH$ ) is treated with a large excess (20–25% by volume) of L ( $L = 3-Mepy, isoquin, N-MeIm$ ) and warmed to  $75^\circ C$  for 2 min a ligand exchange takes place to give XII ( $L = 3-Mepy, etc.$ ). However 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).



( $L = 3-Mepy, isoquin, N-MeIm, L' = 2-Mepy, 2,6-Me_2py, quin$ )

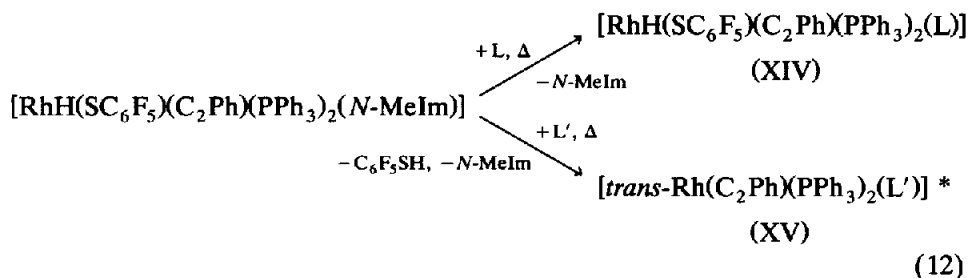
In view of the similarity in electronic properties of 2-Mepy and 3-Mepy and also of quin and isoquin these divergent results would appear to arise as a consequence largely of steric differences between ligands L and  $L'$ .

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<sub>6</sub>F<sub>5</sub>SH has been lost (eq. 11).



This suggests that an unstable intermediate [RhH(SC<sub>6</sub>F<sub>5</sub>)(C<sub>2</sub>Ph)(PPh<sub>3</sub>)<sub>2</sub>(L')] is formed which, owing to steric congestion, undergoes reductive elimination of C<sub>6</sub>F<sub>5</sub>SH 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<sub>2</sub>H 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<sub>6</sub>F<sub>5</sub>SH takes place (eq. 12).



(L = *py*, 3-Mepy, isoquin; L' = 2-Mepy, 2,6-Me<sub>2</sub>*py*, quin)

Here again steric effects would appear largely to determine the outcome, although the reasons for loss of C<sub>6</sub>F<sub>5</sub>SH rather than PhC<sub>2</sub>H are likely to include the greater opportunities for *dπ-pπ* interactions afforded by the C<sub>2</sub>Ph ligand.

Attempts to bring about a reaction between IX or X and <sup>1</sup>PrSH or CH<sub>3</sub>CO<sub>2</sub>H by heating mixtures in toluene to 75°C for 2 min proved unsuccessful. In this respect IX differs from [Rh(SC<sub>6</sub>F<sub>5</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub>], which reacts with both <sup>1</sup>PrSH (on warming) and CH<sub>3</sub>CO<sub>2</sub>H (to give in each case mixtures of products) and [RhH(PPh<sub>3</sub>)<sub>3</sub>], which combines readily with both reagents, the reaction with <sup>1</sup>PrSH being rapid even at -40°C [23,26].

Complex I reacts rapidly with CO and with <sup>1</sup>BuNC in toluene at room temperature to give [*trans*-Rh(SC<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>(CO)] (XVI) and a product with the stoichiometry Rh(SC<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>(<sup>1</sup>BuNC)<sub>3</sub> (XVII) respectively. In the <sup>1</sup>H spectrum of XVII in toluene at room temperature the *t*-butyl protons appear as a sharp singlet

\* <sup>31</sup>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<sub>2</sub>*py*, δ 33.30 J(Rh-P) 162.9; L' = quin, δ 35.13, J(Rh-P) 161.7.

which, on lowering the temperature to  $-70^{\circ}\text{C}$ , is transformed into three lines; the  $^{31}\text{P}\{^1\text{H}\}$  spectrum at  $-70^{\circ}\text{C}$ , shows a doublet and a signal from free  $\text{PPh}_3$  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  $[\text{Rh}(\text{SC}_6\text{F}_5)(\text{PPh}_3)(^t\text{BuNC})_3](\text{PPh}_3)$ . Both XVI and XVII can readily be prepared by the reaction of CO or  $^t\text{BuNC}$  with a mixture of  $[\text{RhH}(\text{PPh}_3)_4]$  and  $\text{C}_6\text{F}_5\text{SH}$  in  $\text{Et}_2\text{O}$ . XVI reacts with neither  $\text{H}_2$  nor  $\text{C}_6\text{F}_5\text{SH}$  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  $60\text{--}70^{\circ}\text{C}$  for 2 min).

The strongly  $\pi$ -acidic ligands CO,  $^t\text{BuNC}$  and  $\text{P}(\text{OR}')_3$  react with I to give mononuclear complexes that either do not readily undergo oxidative addition or (in the case of VII with  $\text{H}_2$ ) react to give stable  $\text{Rh}^{\text{I}}$  complexes. With these ligands in the complex the  $\text{Rh}^{\text{III}}$  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  $d\pi\text{--}p\pi$  interactions. Rhodium(I) complexes having  $\text{PMe}_2\text{Ph}$  or a combination of  $\text{PPh}_3$  and L ligands are sufficiently electron-rich to react with  $\text{C}_6\text{F}_5\text{SH}$  and  $\text{PhC}_2\text{H}$  to give stable products. In each case ligands are present that can stabilise a reduced metal fragment, therefore the stability of the  $\text{Rh}^{\text{III}}$  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  $\text{H}_2$  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  $\text{L}'$  (Scheme 1) involving a reductive elimination of  $\text{C}_6\text{F}_5\text{SH}$  would appear to be governed almost entirely by steric effects. The increased steric congestion resulting from the exchange of L for  $\text{L}'$  is evidently sufficient to labilise the molecule with respect to reductive elimination (of  $\text{C}_6\text{F}_5\text{SH}$ ) without leading to the expulsion of  $\text{L}'$  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  $\text{L}'$  and in the absence of  $\text{L}'$  the  $\text{Rh}^{\text{III}}$  complex is stable.

## Conclusion

The thiolate bridge of  $[\text{Rh}_2(\mu\text{-SC}_6\text{F}_5)_2(\text{PPh}_3)_4]$  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  $\sigma$ -donor and  $\pi$ -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.

### Acknowledgment

I thank the University of the Witwatersrand for financial support.

### References

- 1 W. Hieber and K. Heinicke, *Z. Naturforsch., Teil B*, 16 (1961) 554.
- 2 J. Cooke, M. Green and F.G.A. Stone, *J. Chem. Soc. A*, (1968) 170.
- 3 E.S. Bolton, R. Havlin and G.R. Knox, *J. Organomet. Chem.*, 18 (1969) 153.
- 4 B.F.G. Johnson, J. Lewis, P.W. Robinson and J.R. Miller, *J. Chem. Soc. A*, (1969) 2693.
- 5 J.V. Kingston and G.R. Scollary, *J. Inorg. Nucl. Chem.*, 33 (1971) 4373.
- 6 R.D.W. Kemmitt and G.D. Rimmer, *J. Inorg. Nucl. Chem.*, 35 (1973) 3155.
- 7 A. Maisonnat, P. Kalck and R. Poilblanc, *J. Organomet. Chem.*, 73 (1974) C36.
- 8 P. Kalck and R. Poilblanc, *Inorg. Chem.*, 14 (1975) 2779.
- 9 H. Schumann, G. Cielusek and J. Pickardt, *Angew. Chem., Int. Ed. Engl.*, 19 (1980) 70.
- 10 P.J. Blower and J.R. Dilworth, *Coord. Chem. Rev.*, 76 (1987) 121.
- 11 P. Kalck, F. Senocq, M. Siani and A. Thorez, *J. Organomet. Chem.*, 350 (1988) 77.
- 12 D. Cruz-Garriz, J. Garcia-Alejandre, J. Torrens, C. Alvarez, R.A. Toscano, A. Thorez and R. Poilblanc, *Transition Met. Chem.*, 16 (1991) 130.
- 13 J. Garcia, H. Torrens, H. Adams, N.A. Bailey and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1991) 74.
- 14 P. Kalck, R. Poilblanc, R.-P. Martin, A. Rovera and A. Gaset, *J. Organomet. Chem.*, 195 (1980) C9.
- 15 P. Kalck, J.M. Frances, P.M. Pfister, T.G. Southern and A. Thorez, *J. Chem. Soc., Chem. Commun.*, (1983) 510.
- 16 P. Escaffre, A. Thorez, P. Kalck, B. Besson, R. Perron and Y. Colleuille, *J. Organomet. Chem.*, 302 (1986) C17.
- 17 C. Claver, P. Kalck, M. Ridmy, A. Thorez, L.A. Oro, M.T. Pinillos, M.C. Apreda, F.H. Cano and C. Foces-Foces, *J. Chem. Soc., Dalton Trans.*, (1988) 1523.
- 18 C. Claver, A.M. Masdeu, N. Ruiz, C. Foces-Foces, F.H. Cano, M.C. Apreda, L.A. Oro, J. Garcia-Alejandre and H. Torrens, *J. Organomet. Chem.*, 398 (1990) 177.
- 19 L. Carlton, *Phosphorus Sulfur*, 59 (1991) 231.
- 20 A. Mayanza, J.-J. Bonnet, J. Galy, P. Kalck and R. Poilblanc, *J. Chem. Res. (S)*, (1980) 146.
- 21 L. Carlton, *J. Organomet. Chem.*, 415 (1991) C19.
- 22 N. Ahmad, J.J. Levison, S.D. Robinson and M.F. Uttley, *Inorg. Synth.*, XV (1974) 58.
- 23 L. Carlton and Z. Bulbulia, *J. Organomet. Chem.*, 389 (1990) 139.
- 24 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd Edition, Wiley, New York, 1972, Chap. 22.
- 25 P. Meakin, E.L. Muetterties and J.P. Jesson, *J. Am. Chem. Soc.*, 94 (1972) 5271.
- 26 S.D. Robinson and M.F. Uttley, *J. Chem. Soc., Dalton Trans.*, (1973) 1912.
- 27 J.W. Suggs, M.J. Wovkulich and S.D. Cox, *Organometallics*, 4 (1985) 1101.
- 28 D. Milstein, *Acc. Chem. Res.*, 17 (1984) 221.