

The reaction of $[\text{RhH}(\text{PPh}_3)_4]$ with thiols: a ^1H and ^{31}P NMR study

Laurence Carlton* and Zaid Bulbulia

Department of Chemistry, University of the Witwatersrand, Johannesburg (Republic of South Africa)

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Abstract

In toluene or THF at -40°C $[\text{RhH}(\text{PPh}_3)_4]$ reacts with RSH ($\text{R} = \text{Pr}^i, \text{Ph}, \text{CH}_2\text{Ph}$) to give the unstable dihydro complex $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_3]$. At 20°C decomposition of this complex with loss of H_2 occurs via a five-coordinate species $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2]$ to give $[\text{Rh}(\text{SR})(\text{PPh}_3)_3]$, which then dimerises to give the stable product $[\text{Rh}_2(\mu\text{-SR})_2(\text{PPh}_3)_4]$. In toluene/pyridine the initial product is $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2(\text{py})]$. Loss of H_2 gives $[\text{cis-Rh}(\text{SR})(\text{PPh}_3)_2(\text{py})]$, which then undergoes further reaction with thiol. Where the formation of a five-coordinate dihydro species is prevented by the presence of a chelating ligand NArS- ($\text{NArS} = 2\text{-pyridylmethanethiolate}, \text{pyrimidine-2-thiolate}, \text{benzthiazole-2-thiolate}$ and purine-6-thiolate) a thermally stable dihydrobis(triphenylphosphine)rhodium thiolate complex can be isolated.

Introduction

Rhodium(I) thiolate complexes of the form $[\text{Rh}_2(\mu\text{-SR})_2\text{L}_4]$ ($\text{L} = \text{CO}, \text{phosphine}, \text{phosphite}$) have received attention as a result of their ability to catalyse reactions such as alkene hydrogenation [1] and hydroformylation [2]. Preparative routes to these complexes have included the reaction of $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$ [3,4], $[\text{RhCl}_2(\text{CO})_2]^-$ [5] and $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ [6] with RSH and $[\text{RhH}(\text{PPh}_3)_4]$ with allylic aryl sulphides [7]. Only where R is a strongly electron-withdrawing group such as C_6F_5 are terminal thiolate complexes e.g. $[\text{Rh}(\text{SR})(\text{CO})(\text{PPh}_3)_2]$ obtained [8]. Rhodium(III) thiolate complexes dimerise less readily; the oxidative addition of $p\text{-CH}_3\text{C}_6\text{H}_4\text{SH}$ to $[\text{RhCl}(\text{PPh}_3)_3]$ gives unbridged $[\text{RhClH}(\text{SC}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_2]$ [9]. Where R is an electron-donating group bridging is more likely to occur; the complex $[\text{H}_2\{\text{P}(\text{OMe})_3\}(\text{CO})\text{Rh}(\text{III})(\mu\text{-SBu}^t)_2\text{Rh}(\text{I})(\text{CO})\{\text{P}(\text{OMe})_3\}]$ has been proposed as an intermediate in the $[\text{Rh}_2(\mu\text{-SBu}^t)_2(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2]$ -catalysed hydroformylation of alkenes [2].

The properties of rhodium thiolate complexes having hydride and P-donor ligands clearly merit further investigation. To this end we have examined the reaction of $[\text{RhH}(\text{PPh}_3)_4]$ with thiols under various conditions by low temperature ^1H and ^{31}P NMR spectroscopy.

Experimental

$[\text{RhH}(\text{PPh}_3)_4]$ [10] and 2-pyridylmethanethiol [11,12] were prepared by published methods. Other thiols were purchased from Aldrich and used without further purification. Solvents were obtained from various sources. Toluene and THF were distilled from sodium, and pyridine and ether were distilled from CaH_2 . Acetone (AR grade) was not further purified. All operations were performed under nitrogen.

NMR spectra were recorded on a Bruker AC 200 FT spectrometer, at 200.13 MHz for ^1H (5 mm probe) and 81.01 MHz for ^{31}P (10 mm probe). IR spectra were recorded on a Perkin Elmer 580 spectrometer.

Low temperature studies

Reactions were performed in situ and monitored by ^{31}P and ^1H NMR spectroscopy. $[\text{RhH}(\text{PPh}_3)_4]$ (20–30 mg for ^{31}P studies, 10–12 mg for ^1H studies) was dissolved in the appropriate solvent (toluene/toluene- d_8 , toluene/toluene- d_8 /pyridine or THF) in an NMR tube and the tube and contents cooled to $< -40^\circ\text{C}$ by suspension over liquid nitrogen. The thiol (Pr^iSH , PhSH or PhCH_2SH , 1–2 drops) was added to the cooled solution and the tube stoppered and sealed with Parafilm. The tube was shaken to mix the contents and quickly transferred to the spectrometer at -40°C (for $^{31}\text{P}\{^1\text{H}\}$ measurements) or -25°C (for ^1H measurements). After recording of the spectrum the sample was taken out, warmed to $20\text{--}30^\circ\text{C}$ for ca. 2 min and then returned to the spectrometer and a low temperature spectrum was again recorded. This procedure was repeated with warming to $50\text{--}60^\circ\text{C}$ for ca. 5 min.

Kinetic studies

$[\text{RhH}(\text{PPh}_3)_4]$ (0.020 g) was dissolved in 6/1 toluene/toluene- d_8 (3.5 ml) or 6/1 pyridine/toluene- d_8 (3.5 ml) in a 10 mm NMR tube to give a 0.005 M solution. This was cooled to $< -40^\circ\text{C}$ and Pr^iSH (2 drops) was added * and the tube sealed, shaken, and transferred to the spectrometer at -60°C (toluene solution) or -30°C (pyridine/toluene solution). A $^{31}\text{P}\{^1\text{H}\}$ spectrum was recorded, the sample was taken out, warmed in a water bath at 20°C , and quickly returned to the spectrometer. The time spent by the solution at room temperature (from immersion in the bath to its return to the cooled probe) was either 1 or 2 min. Observations were made during a period of up to 14 min (total) at 20°C . $^{31}\text{P}\{^1\text{H}\}$ data were obtained with an acquisition time of 0.41 s and relaxation delay of 1.0 s; 512 transients were recorded prior to transformation.

* In a study involving an excess of PPh_3 (0.23 g, to give a solution of 0.25 M) the phosphine was added and dissolved at $< -40^\circ\text{C}$ after mixing of the hydride and thiol.

Table 1

³¹P spectral data for the thiolate complexes ^a

Complex	Signal	δ P ^b	$J(\text{Rh-P})$ ^c	$J(\text{P-P})$
[RhH ₂ (SPr ⁱ)(PPh ₃) ₃]	dd	35.79	113.0	19.4
	dt	27.96	89.1	19.4
[RhH ₂ (SPh)(PPh ₃) ₃]	dd	37.51	111.9	19.4
	dt	28.27	89.3	19.4
[RhH ₂ (SCH ₂ Ph)(PPh ₃) ₃]	dd	38.79	112.8	19.7
	dt	29.45	90.9	19.7
[Rh(SPr ⁱ)(PPh ₃) ₃]	dt	40.22	159.0	39.5
	dd	30.37	161.5	39.5
[Rh(SPh)(PPh ₃) ₃]	dt	40.59	169.2	35.0
	dd	28.63	149.7	35.0
[Rh(SCH ₂ Ph)(PPh ₃) ₃] ^d	dt	38.97	164.0	37.2
	dd	27.55	158.0	37.2
[Rh ₂ (μ -SPr ⁱ) ₂ (PPh ₃) ₄]	d	43.64	166.8	
[Rh ₂ (μ -SPh) ₂ (PPh ₃) ₄]	d	44.49	168.5	
[Rh ₂ (μ -SCH ₂ Ph) ₂ (PPh ₃) ₄]	d	46.29	173.3	
[RhH ₂ (SPr ⁱ)(PPh ₃) ₂ (py)] ^e	d	50.03	119.0	
[RhH ₂ (SPh)(PPh ₃) ₂ (py)] ^e	d	48.81	116.3	
[RhH ₂ (SCH ₂ Ph)(PPh ₃) ₂ (py)] ^e	d	51.74	117.6	
[<i>cis</i> -Rh(SPr ⁱ)(PPh ₃) ₂ (py)] ^e	dd	55.37	173.3	40.7
	dd	47.44	165.7	40.7
[<i>cis</i> -Rh(SPh)(PPh ₃) ₂ (py)] ^e	dd	53.16	168.4	42.4
	dd	48.78	172.1	42.4
[<i>cis</i> -Rh(SCH ₂ Ph)(PPh ₃) ₂ (py)] ^e	dd	56.39	172.9	40.0
	dd	48.24	166.2	40.0
[RhH ₂ (SCH ₂ py)(PPh ₃) ₂] ^f	d	48.04	117.6	
[RhH ₂ (Spyrim)(PPh ₃) ₂] ^g	d	48.41	116.6	
[RhH ₂ (Sbt)(PPh ₃) ₂] ^g	d	47.82	117.2	
[RhH ₂ (Spur)(PPh ₃) ₂] ^h	d	51.81	115.2	

^a Solution in toluene/toluene-*d*₈ (6/1) at -40°C unless otherwise stated; ^b Chemical shifts in ppm relative to PPh₃ at -4.7 (at room temperature the PPh₃ resonance occurs at δ -4.7 relative to H₃PO₄ as external standard) unless otherwise stated; ^c Coupling constants (absolute magnitude) in Hz; ^d In THF at -40°C; ^e In toluene/toluene-*d*₈/pyridine (7/1/2) at -40°C; ^f In C₆H₆/C₆D₆ at 22°C, ref. H₃PO₄ (ext). ^g In CHCl₃/CDCl₃ at -40°C; ^h In CHCl₃/CDCl₃ at 22°C, ref. H₃PO₄ (ext).

Preparation of [Rh₂(μ -SPrⁱ)₂(PPh₃)₄]

A suspension of [RhH(PPh₃)₄] (0.084 g) in Et₂O (4 ml) at room temperature was treated with an excess of PrⁱSH and the mixture stirred for 15 min. The product, a yellow powder, was collected by filtration and washed with Et₂O. Yield 0.023 g (45%). ¹H NMR (C₆D₆): δ 8.0–6.4 (mult, aromatic), 3.64 (sept, Prⁱ methine), 0.89 (d, Prⁱ methyl); ³¹P{¹H} NMR (toluene, 22°C) δ 41.67 (d, J 167.1 Hz) (δ relative to H₃PO₄ external standard).

Preparation of [RhH₂(SCH₂py)(PPh₃)₂] ^{*}

A suspension of [RhH(PPh₃)₄] (0.136 g) in Et₂O (5 ml) at room temperature was treated with an excess of 2-pyridylmethanethiol and the mixture stirred for 30 min.

^{*} Abbreviations: SCH₂py, 2-pyridylmethanethiolate; Spyrim, pyrimidine-2-thiolate; Sbt, benzthiazole-2-thiolate; Spur, purine-6-thiolate; py, pyridine.

Table 2

¹H spectral data for the dihydrothiolate complexes ^a

Complex	Signal	δ H ^b	$J(\text{P}-\text{H}_{\text{trans}})$ ^c	$J(\text{Rh}-\text{H})$	$J(\text{P}-\text{H})$	$J(\text{H}-\text{H})$
[RhH ₂ (SPr ⁱ)(PPh ₃) ₃]	dmult	-10.32	155.7			
	mult	-11.33				
[RhH ₂ (SPh)(PPh ₃) ₃]	dmult	-9.90	152.1			
	mult	-12.06				
[RhH ₂ (SCH ₂ Ph)(PPh ₃) ₃]	dmult	-10.47	152.3			
	mult	-11.35				
[RhH ₂ (SPr ⁱ)(PPh ₃) ₂ (py)] ^d	mult	-11.64				
	mult	-17.01				
[RhH ₂ (SPh)(PPh ₃) ₂ (py)] ^d	ddt	-12.27		18.0	14.9	9.5
	ddt	-16.71		14.6	14.5	9.5
[RhH ₂ (SCH ₂ Ph)(PPh ₃) ₂ (py)] ^d	ddt	-11.71		17.4	15.1	9.2
	ddt	-17.07		14.8	15.0	9.2
[RhH ₂ (SCH ₂ py)(PPh ₃) ₂] ^e	ddt	-11.90		18.2	16.9	9.5
	ddt	-15.92		14.5	15.5	9.5
[RhH ₂ (Spyrim)(PPh ₃) ₂] ^f	ddt	-16.05		23.2	14.6	10.7
	ddt	-16.37		15.0	14.4	10.7
[RhH ₂ (Sbt)(PPh ₃) ₂] ^g	ddt	-16.88		18.3	13.5	10.8
	ddt	-17.46		15.3	14.3	10.8
[RhH ₂ (Spur)(PPh ₃) ₂] ^g	mult	-13.94				
	mult	-15.73				

^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 Solution in ca. 5% pyridine/toluene-*d*₈ at -25 °C;^e In C₆D₆ at 22 °C; ^f In CDCl₃ at 22 °C; ^g In CDCl₃ at -25 °C.

The product, a yellow powder, was collected by filtration and washed with Et₂O. Yield 0.065 g (73%). IR (Nujol mull): $\nu(\text{Rh}-\text{H})$ 2030, 1974 cm⁻¹. NMR data are given in Tables 1 and 2.

Preparation of [RhH₂(Spyrim)(PPh₃)₂]

A mixture of [RhH(PPh₃)₄] (0.090 g, 0.078 mmol) and pyrimidine-2-thiol (0.010 g, 0.09 mmol) in acetone (5 ml) at room temperature was stirred for 90 min to give a suspension of a pale yellow solid. The product was separated by use of a centrifuge and washed with acetone. Yield 0.041 g (71%). IR (Nujol mull): $\nu(\text{Rh}-\text{H})$ 2038, 2012(sh) cm⁻¹.

Preparation of [RhH₂(Sbt)(PPh₃)₂]

A mixture of [RhH(PPh₃)₄] (0.097 g 0.084 mmol) and benzthiazole-2-thiol (0.014 g, 0.084 mmol) in acetone (5 ml) at room temperature was stirred for 5 min to give a brown suspension. The product was filtered off and washed with acetone. Yield 0.018 g (27%). IR (Nujol mull): $\nu(\text{Rh}-\text{H})$ 2048 (sh), 2026 cm⁻¹.

Preparation of [RhH₂(Spur)(PPh₃)₂]

A mixture of [RhH(PPh₃)₄] (0.091 g, 0.079 mmol) and purine-6-thiol (0.013 g, 0.076 mmol) in acetone (5 ml) at room temperature was stirred for 15 hr to give a yellow suspension. The product was filtered off washed and with acetone. Yield 0.046 g (76%). IR (Nujol mull): $\nu(\text{Rh}-\text{H})$ 2060(sh), 2045 cm⁻¹.

Results and discussion

Solutions of $[\text{RhH}(\text{PPh}_3)_4]$ in toluene give well-resolved $^{31}\text{P}\{^1\text{H}\}$ NMR spectra only at temperatures below -60°C ; these show a dt and dd characteristic of a tris(phosphine) complex, i.e. $[\text{RhH}(\text{PPh}_3)_3]$, and also a signal from free triphenylphosphine. At room temperature the signals are broadened to the point at which

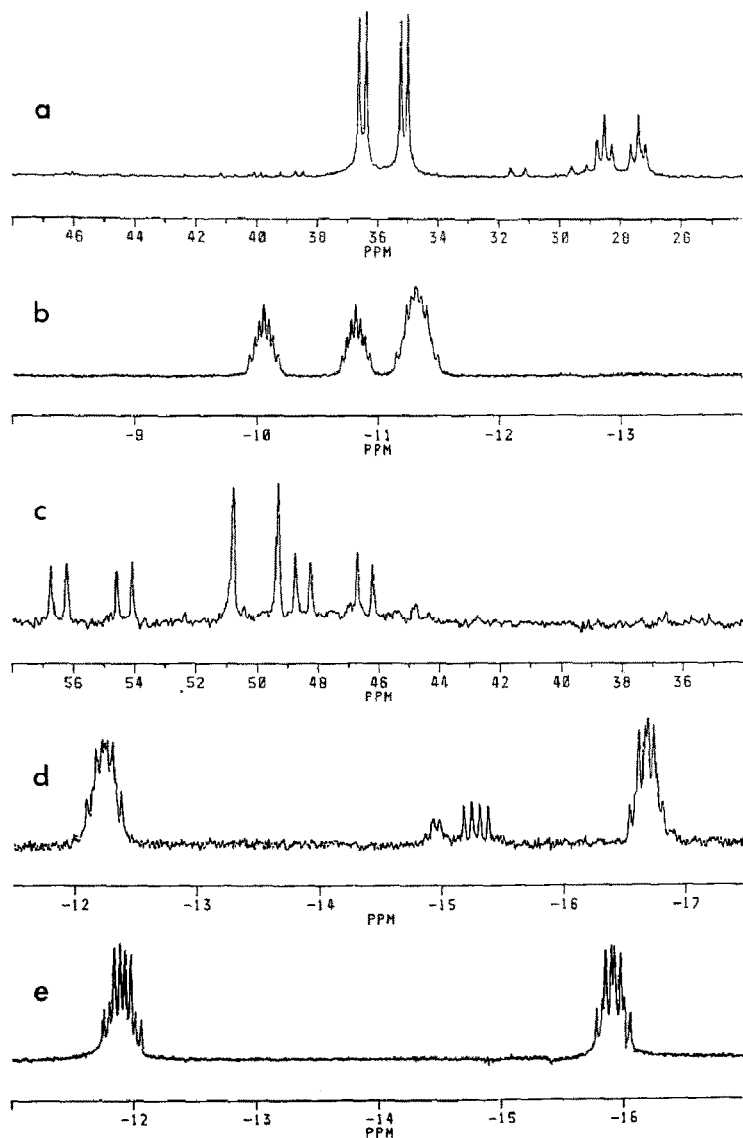
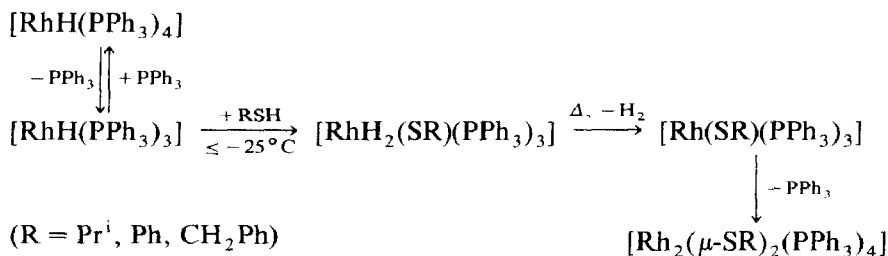


Fig. 1. (a) $^{31}\text{P}\{^1\text{H}\}$ spectrum of $[\text{RhH}(\text{PPh}_3)_4]$ and Pr^iSH in toluene at -40°C showing signals from $[\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_3]$; (b) ^1H spectrum of $[\text{RhH}(\text{PPh}_3)_4]$ and PhCH_2SH in toluene at -25°C showing hydride resonances of $[\text{RhH}_2(\text{SCH}_2\text{Ph})(\text{PPh}_3)_3]$; (c) $^{31}\text{P}\{^1\text{H}\}$ spectrum of $[\text{RhH}(\text{PPh}_3)_4]$ and Pr^iSH in 20% pyridine/toluene at -40°C after warming to $30\text{--}40^\circ\text{C}$ for ca. 2 min; The signals are from $[\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_2(\text{py})]$ and $[\text{cis-Rh}(\text{SPr}^i)(\text{PPh}_3)_2(\text{py})]$; (d) ^1H spectrum of $[\text{RhH}(\text{PPh}_3)_4]$ and PhSH in ca. 5% pyridine/toluene at -25°C showing hydride resonances of $[\text{RhH}_2(\text{SPh})(\text{PPh}_3)_2(\text{py})]$ (major signals); (e) high field portion of the ^1H spectrum of $[\text{RhH}_2(\text{SCH}_2\text{py})(\text{PPh}_3)_2]$ (C_6D_6 , 22°C).

they are almost undetectable, indicating interconversion between $[\text{RhH}(\text{PPh}_3)_4]$ and $[\text{RhH}(\text{PPh}_3)_3]$. The $^{31}\text{P}\{^1\text{H}\}$ spectra recorded from mixtures of $[\text{RhH}(\text{PPh}_3)_4]$ and excess RSH ($\text{R} = \text{Pr}^i, \text{Ph}, \text{CH}_2\text{Ph}$) in toluene at -40°C show strong signals due to $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_3]$ and very weak signals (dt and dd, $J(\text{Rh}-\text{P})$ characteristic of a Rh^{I} complex) due to $[\text{Rh}(\text{SR})(\text{PPh}_3)_3]$ (Table 1 and Fig. 1,a). Signals due to $[\text{RhH}(\text{PPh}_3)_3]$ are no longer seen, indicating that the reaction is substantially complete within a few minutes at -40°C . After warming ($20-30^\circ\text{C}$, 2 min) new signals characteristic of $[\text{Rh}_2(\mu\text{-SR})_2(\text{PPh}_3)_4]$ [7] are observed which, after further warming ($50-60^\circ\text{C}$, 5 min) form the only significant features of the spectra. The hydride resonances of $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_3]$. (Table 2 and Fig. 1,b) appear in the region $\delta = -9$ to -13 ppm of the ^1H spectra (recorded at -25°C in order to optimise resolution) and are lost on warming.

These observations suggest the following reaction sequence (Scheme 1):



Scheme 1

In THF solution the $^{31}\text{P}\{^1\text{H}\}$ spectra obtained from mixtures of $[\text{RhH}(\text{PPh}_3)_4]$ and Pr^iSH or PhSH are not significantly different from those obtained from toluene

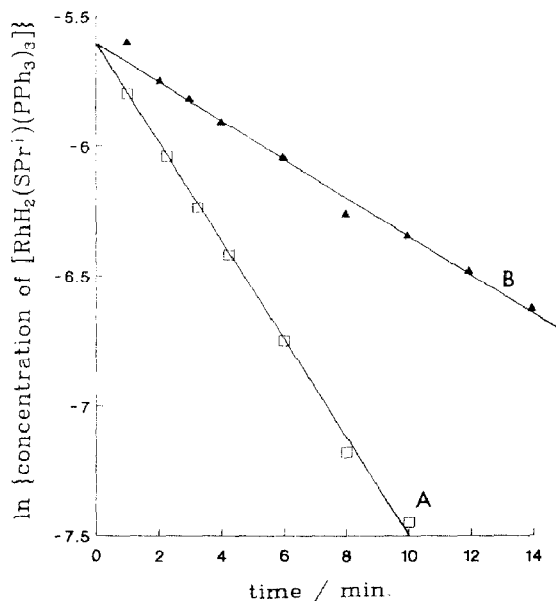


Fig. 2. Plot of $\ln\{\text{concentration of } [\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_3]\}$ vs. time. Data were obtained from a mixture of $[\text{RhH}(\text{PPh}_3)_4]$ (0.005 M) and excess Pr^iSH in toluene at 20°C (A), and from a similar mixture with excess PPh_3 (0.25 M) (B). Concentrations were determined from $^{31}\text{P}\{^1\text{H}\}$ spectra recorded at -60°C .

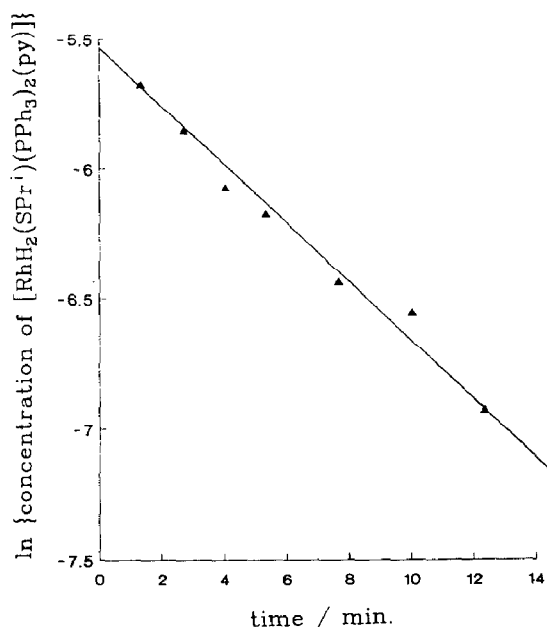


Fig. 3. Plot of $\ln\{\text{concentration of } [\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_2(\text{py})]\}$ vs. time. Data were obtained from a mixture of $[\text{RhH}(\text{PPh}_3)_4]$ (0.005 M) and excess Pr^iSH in 80% pyridine/toluene at 20°C . Concentrations were determined from $^{31}\text{P}\{^1\text{H}\}$ spectra recorded at -30°C .

solutions under the same conditions. With PhCH_2SH the spectrum obtained after warming the reaction mixture to $30\text{--}40^\circ\text{C}$ for 1 min shows the presence only of $[\text{Rh}(\text{SCH}_2\text{Ph})(\text{PPh}_3)_3]$ and $[\text{Rh}_2(\mu\text{-SCH}_2\text{Ph})_2(\text{PPh}_3)_4]$ (approximate ratio 2/1). On further warming ($50\text{--}60^\circ\text{C}$, 5 min) signals due to the former are no longer observed.

When the same reactions are carried out in toluene/pyridine (4/1) at -40°C the $^{31}\text{P}\{^1\text{H}\}$ spectra show the principal component of the mixture to be $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2(\text{py})]$, with small quantities of $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_3]$ and for $\text{R} = \text{Ph}$ and CH_2Ph some $[\text{cis-Rh}(\text{SR})(\text{PPh}_2)_3(\text{py})]$ (very small quantities in the case $\text{R} = \text{CH}_2\text{Ph}$) (Table 1). On warming ($20\text{--}30^\circ\text{C}$, 2 min) the following changes are observed: $\text{R} = \text{Pr}^i$, signals due to $[\text{cis-Rh}(\text{SR})(\text{PPh}_3)_2(\text{py})]$ appear (Fig. 1,c); $\text{R} = \text{Ph}$, signals due to $[\text{cis-Rh}(\text{SR})(\text{PPh}_3)_2(\text{py})]$ disappear, to be replaced by two doublets at δ 50.92 (J 134.2 Hz) and δ 32.44 (J 105.4 Hz); $\text{R} = \text{CH}_2\text{Ph}$, a new signal (doublet) is found at δ 31.5 (J 109.6 Hz). The Rh–P coupling constants indicate the presence of rhodium(III). In all three cases the signal from $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2(\text{py})]$ is

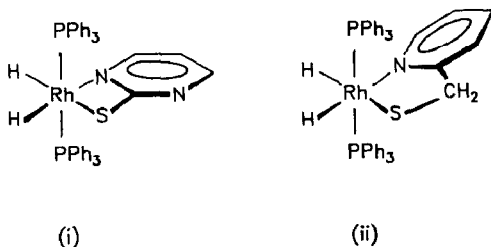
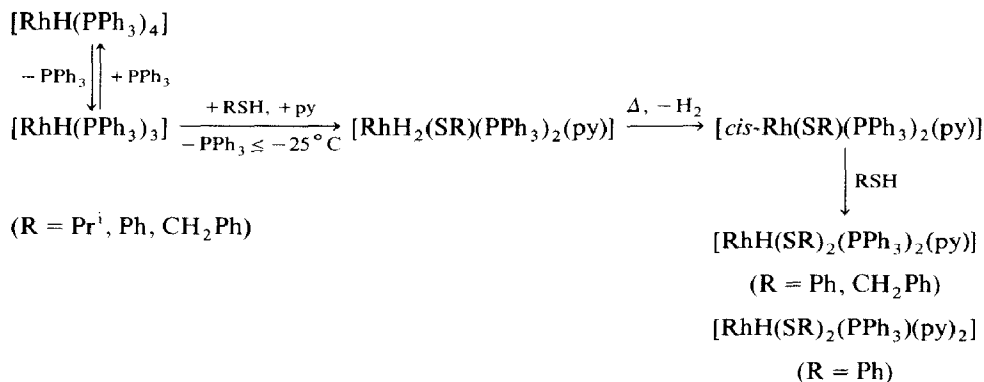


Fig. 4. The structures of $[\text{RhH}_2(\text{Spyrim})(\text{PPh}_3)_2]$, (i) and $\text{RhH}_2(\text{SCH}_2\text{py})(\text{PPh}_3)_2$, (ii).

substantially reduced in intensity. In the ^1H spectra (recorded from reaction mixtures in $\sim 5\%$ pyridine/toluene at -25°C) the intensity of the hydride signals from $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2(\text{py})]$ (Fig. 1,d) decreases on warming, and this is accompanied in the case of $\text{R} = \text{Ph}$ by the unequal growth of two signals at $\delta -14.99$ (dt, J 12.5, 9.3 Hz) and $\delta -15.31$ (dd, J 27.0, 13.5 Hz). These signals clearly arise from the same species as the doublets in the $^{31}\text{P}\{^1\text{H}\}$ spectrum, and suggest $(\text{RhH}(\text{SPh})_2(\text{PPh}_3)_2(\text{py}))$ (phosphines mutually *trans*) and $[\text{RhH}(\text{SPh})_2(\text{PPh}_3)(\text{py})_2]$ as products of the oxidative addition of a second thiol to $[\text{cis-Rh}(\text{SPh})(\text{PPh}_3)_2(\text{py})]$.

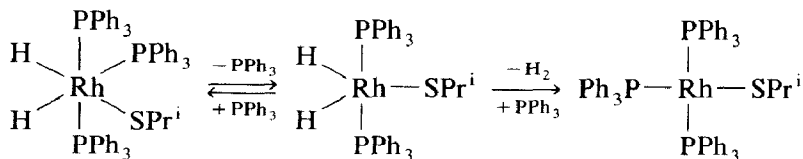
These findings are consistent with the following reaction sequence (Scheme 2):



Scheme 2

Further warming ($50\text{--}60^\circ\text{C}$, 5 min) causes a loss in intensity of signals from coordinated phosphine and growth of the signal from free phosphine, suggesting that the product $[\text{Rh}(\text{SR})_3(\text{py})_3]$ may be formed. The presence of the dinuclear complex $[\text{Rh}_2(\mu\text{-SR})_2(\text{PPh}_3)_4]$ is not observed in the reactions using pyridine.

The rate of decomposition of $[\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_3]$ in toluene at 20°C was examined by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy by using the intensity of the signal at δ 35.79 ppm as a measure of concentration. The rate constant for the decomposition in the presence of 0.005 M PPh_3 (liberated in the reaction of $[\text{RhH}(\text{PPh}_3)_4]$ with the thiol) is 0.0031 s^{-1} (Fig. 2,A) while in the presence of 0.25 M PPh_3 is 0.0012 s^{-1} (Fig. 2,B). These results indicate that the species undergoing reductive elimination of H_2 cannot be $[\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_3]$, but must be formed from it by loss of phosphine (Scheme 3):



Scheme 3

The ability of hydride to labilise ligands in the *trans* position is well known [13]. In the complexes $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2\text{L}]$ ($\text{L} = \text{PPh}_3, \text{py}$) phosphine can readily be exchanged for pyridine and vice versa by suitable adjustment of the relative concentrations of the free ligands. Dihydro complexes with pyridine as the *trans* ligand undergo loss of H_2 at similar rates to those having phosphine as the *trans*

ligand; the rate constant for the decomposition of $[\text{RhH}_2(\text{SPr}^i)(\text{PPh}_3)_2(\text{py})]$ in 80% pyridine/toluene at 20°C is 0.002 s^{-1} (Fig. 3). This suggests a common mechanism for decomposition, involving an unstable five-coordinate dihydro intermediate. The stability with respect to loss of H_2 of a six-coordinate dihydro species will therefore most clearly be shown by a complex with a *trans* ligand showing little tendency to dissociate, i.e. a chelating ligand.

The reaction of $[\text{RhH}(\text{PPh}_3)_4]$ with NArSH ($\text{NArSH} = 2\text{-pyridylmethanethiol}$, pyrimidine-2-thiol, benzthiazole-2-thiol and purine-6-thiol) in ether or acetone gives $[\text{RhH}_2(\text{NArS})(\text{PPh}_3)_2]$ as thermally stable yellow powders. (Spectral data are in the Tables and Fig. 1,e). In these complexes chelate binding of the ligand NArS^- gives four- or five-membered ring structures (Fig. 4). These compounds are analogues of the stable dihydro complexes $[\text{RhH}_2(\text{L-L})(\text{PPh}_3)_2]$ ($\text{L-L} = \text{diphenyltriazene}$ [14], di(μ -chloro)bis(triphenylphosphine)rhodium [15] and pyridine-2-carboxylate [16]) which have a chelating ligand *trans* to hydrogen.

Conclusion

The ease with which complexes $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2\text{L}]$ ($\text{L} = \text{ligand trans to hydride} = \text{PPh}_3 \text{ or py}$) decompose with loss of H_2 is related to the ease with which the *trans* ligand L dissociates to give a five-coordinate species $[\text{RhH}_2(\text{SR})(\text{PPh}_3)_2]$. Where loss of the *trans* ligand is prevented by its attachment to the thiol (to give a single chelating ligand) the dihydro complexes are stable and can readily be isolated.

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