Journal of Organometallic Chemistry, 322 (1987) 369–376
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

LIGATING PROPERTIES OF THIONITROSOAMINES

III. CARBONYL COMPLEXES OF RHODIUM(I) AND RHODIUM(III) CONTAINING *N*-THIONITROSODIMETHYLAMINE

GIUSEPPE TRESOLDI*, SERGIO SERGI, SANDRA LO SCHIAVO and PASQUALE PIRAINO
Dipartimento di Chimica Inorganica e Struttura Molecolare dell'Università, 98100 Messina (Italy)

(Received September 30th, 1986)

Summary

Me_2NNS reacts with $[Rh(CO)_2Cl]_2$ to produce the complex *cis*-$Rh(SNNMe_2)(CO)_2Cl$ (**1**). The latter undergoes reversible CO substitution by Me_2NNS to give the complex *trans*-$Rh(SNNMe_2)_2(CO)Cl$ (**2a**). Complexes **1** and **2a**, in solution lose CO and Me_2NNS, respectively, to give the complex *trans*-$(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CO)]_2$ (**3**). Complex **1** can also be prepared by bubbling CO through a CH_2Cl_2 solution of $Rh(SNNMe_2)(diene)Cl$ (diene = 1,5-cyclooctadiene (**4a**), norbornadiene (**4b**)) obtained by a bridge-splitting reaction of Me_2NNS with $[Rh(diene)Cl]_2$. **1** and **2a** react with EPh_3 (E = P, As, Sb) to give the complexes *trans*-$Rh(EPh_3)_2(CO)Cl$. The complexes *trans*-$Rh(E'Ph_3)_2(CO)X$ (X = Cl, E' = As, Sb; X = Br, NCS, E' = As) undergo reversible $E'Ph_3$ displacement upon treatment with Me_2NNS to give the complexes *trans*-$Rh(SNNMe_2)_2(CO)X$ (X = Cl (**2a**), Br (**2b**), NCS (**2c**)). Oxidative additions of Br_2, I_2, or $HgCl_2$ to **2a** produce stable adducts, while the reaction of **2a** with CH_3I gives an inseparable mixture of the adduct $Rh(SNNMe_2)_2(CO)(CH_3)ClI$ and the acetyl derivative $Rh(SNNMe_2)_2(CH_3CO)ClI$. A mixture of the acetyl derivative $(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CH_3CO)I]_2$ and the adduct $(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CO)(CH_3)I]_2$ is obtained by treating **1** with CH_3I. The IR spectra of all the compounds are consistent with *S*-coordination of Me_2NNS. Because of the restricted rotation around the N–N bond, the ^1H NMR spectra of the new compounds exhibit two quadruplets in the range 3.5–4.3δ when $^4J(HH) = 0.7\text{–}0.5$ Hz. When $^4J(HH) < 0.5$ Hz, the perturbing effect of the quadrupolar relaxation of the ^{14}N nucleus obscures the spin–spin coupling and two broad signals are observed in the range 3.6–4δ.

Introduction

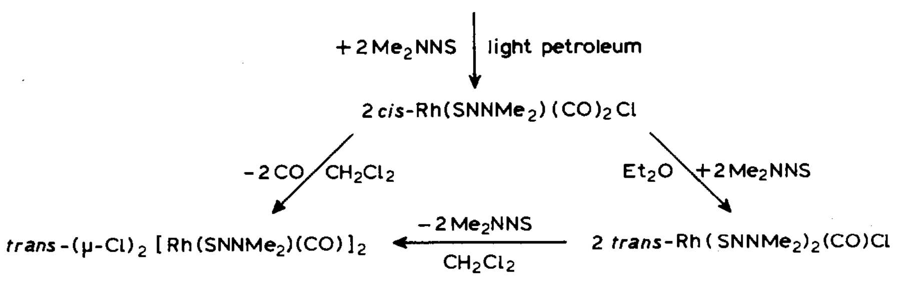
The presence of the *N*-thionitrosodimethylamine ligand favours a *cis* geometry or the complexes $MLL'X_2$ ($M = Pd^{II}$, Pt^{II}, X = anionic ligand, L = *N*-thionitrosodimethylamine, L′ = neutral ligand) because of the ligand is sterically undemanding and its electronic structure can promote π-back-donation [1,2]. In addition the dipolar form of the ligand [3] plays an important role in determining the metal–ligand bond strength of some complexes [2,4].

We describe here part of a study of the effect of the metal nature on the bond mode of the ligand and on the stability of the complexes. The synthesis and the characterization of the mononuclear rhodium(I) complexes $Rh(SNNMe_2)(CO)LCl$ ($L = SNNMe_2$, $X = Cl$, Br, NCS; $L = CO$, $X = Cl$) and mononuclear rhodium(III) complexes $Rh(SNNMe_2)_2(CO)X_2Cl$ ($X_2 = Br_2$, I_2, $HgCl_2$), binuclear rhodium(I) complex *trans*-$(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CO)]_2$ and binuclear rhodium(III) complex $(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CO)I_2]_2$ are described, along with the results of oxidative addition of MeI to these rhodium(I) complexes.

Results and discussion

As depicted in Scheme 1, *N*-thionitrosodimethylamine reacts with $[Rh(CO)_2Cl]_2$ to give *cis*-$Rh(SNNMe_2)(CO)_2Cl$ (**1**), and further reaction of **1** with Me_2NNS gives the *trans*-$Rh(SNNMe_2)_2(CO)Cl$ (**2a**). Complexes **1** and **2** in solution lose CO (1 h) and Me_2NNS (2 d), respectively, to give a brown insoluble product formulated, on the basis of the analytical and IR data ($\nu(CO)$ at 2050s, $\nu(Rh\text{–}Cl)$ at 280m cm^{-1}), as *trans*-$(\mu\text{-}Cl)_2[Rh(CO)(SNNMe_2)]_2$ (**3**).

Complex **1** is a yellow solid soluble in dichloromethane, chloroform, acetone and diethyl ether; it is stable in the solid state for some days but only for about 1 h in solution. Its IR spectrum shows strong bands at 2075 and 2000 cm^{-1} due to $\nu(CO)$ stretches, and 1120 and 780 cm^{-1} assigned to $\nu(N\text{–}N)$ and $\nu(N\text{–}S)$, respectively. The last band is close to those exhibited by the *N*-thionitrosodimethylamine-palladium(II) and -platinum(II) complexes [1,2], suggesting that the coördination of the thionitrosoamine ligand occurs through the sulfur atom. Complex **2a** is a red solid, moderately soluble in acetone, chloroform and dichloromethane; it is stable in the solid state for some weeks and for about 2 d in solution. The IR spectrum shows, besides the bands associated with the thionitrosoamine moiety, the $\nu(CO)$ at 1975s cm^{-1}. Comparison of the far-infrared spectra of **1** and **2a** reveals that the dicarbonyl compound has the $\nu(Rh\text{–}S)$ band at higher wavenumbers (370 cm^{-1}) than that of the monocarbonyl compound (350 cm^{-1}), while both compounds show the $\nu(Rh\text{–}Cl)$



SCHEME 1

band at the almost same frequency (Table 1). These data suggest for **2a** the *trans*-configuration with the chlorine atom *trans* to the Rh–CO bond. The ^{1}H NMR spectrum of **2a** shows broad signals at 3.65δ and 3.93δ indicating hindered rotation around the N–N bond [1–3]. The ^{1}H NMR spectrum of **1** exhibits two quadruplets, centered at 3.7δ and 4δ (^4J(HH) 0.55 Hz), attributable to the protons of the methyl groups. There have, to the best of our knowledge, been no reports of coupling between the protons of two *N*-bonded methyl groups, no doubt because the coupling constants are very small and because the perturbing effect of the ^{14}N nucleus prevents the observation of spin–spin splitting.

The reactions of $[\mathrm{Rh(CO)_2Cl}]_2$ with $\mathrm{Me_2NNS}$ to give **1** or **2a** and the reactions of **1** with $\mathrm{EPh_3}$ ($\mathrm{EPh_3 = PPh_3, AsPh_3, SbPh_3}$) to give *trans*-$\mathrm{Rh(EPh_3)_2(CO)Cl}$ were monitored by IR spectroscopy. When a solution of $\mathrm{Me_2NNS}$ in dichloromethane was slowly added to a solution of $[\mathrm{Rh(CO)_2Cl}]_2$ in the same solvent, the ν(CO) bands of the starting material were gradually replaced by two bands at 2080s and 2010s cm^{-1}. The addition of $\mathrm{Me_2NNS}$ solution was stopped when the ν(CO) bands of $[\mathrm{Rh(CO)_2Cl}]_2$ disappeared in order to prevent formation of the monocarbonyl derivative. When $\mathrm{Me_2NNS}$ or $\mathrm{EPh_3}$ ($\mathrm{EPh_3 = PPh_3, AsPh_3, SbPh_3}$) was added to the dichloromethane solution of **1** the ν(CO) band of **2a** or of the *trans*-$\mathrm{Rh(EPh_3)_2(CO)Cl}$ complex appeared. The reversible reaction of CO with **2a** in $\mathrm{CH_2Cl_2}$ solution to give **1** was also monitored by IR spectroscopy (ν(CO) of **2a** 1985s cm^{-1}). When CO was bubbled through a suspension of **2a** in diethyl ether, the yellow solution of **1** initially formed gave, **2a** after some minutes, as red solid.

Because of the limited stability of **1** in solution, the reaction depicted in Scheme 1 produced the monocarbonyl derivative in low yields, and better yields were obtained in light petroleum in which **1** is insoluble. A more convenient preparation of **1** utilized the route depicted in Scheme 2.

$$1/2[\mathrm{Rh(diene)Cl}]_2 \xrightarrow[\mathrm{CH_2Cl_2/Et_2O}]{+\mathrm{Me_2NNS}} \mathrm{Rh(SNNMe_2)(diene)Cl} \xrightarrow[\mathrm{CH_2Cl_2}]{+\mathrm{CO}}$$

$$cis\text{-}\mathrm{Rh(SNNMe_2)(CO)_2Cl}$$

SCHEME 2. diene = 1,5-cyclooctadiene, norbornadiene.

The reactions of $[\mathrm{Rh(diene)Cl}]_2$ with $\mathrm{Me_2NNS}$ gave the complexes $\mathrm{Rh(SNNMe_2)(diene)Cl}$ (diene = 1,5-cyclooctadiene (**4a**), norbornadiene (**4b**)) as red needles soluble in dichloromethane, chloroform and moderately soluble in acetone. Bubbling of CO through a dichloromethane solution of **4a** or **4b** gave the dicarbonyl derivative in high yield [5]. The reactions of $\mathrm{Me_2NNS}$ with **4a** and **4b** also brought about diene substitution, but gave a brown insoluble solid which could not be isolated pure.

IR spectra of **4a** and **4b** have the ν(Rh–Cl) band at 325 and 320 cm^{-1}, respectively. In the ^{1}H NMR spectra the resonances of the methyl protons are observed as two quadruplets in the range 3.5–3.9δ (^4J(HH) 0.5 Hz).

Scheme 3 shows an alternative and more convenient method for the synthesis of **2a**, and *trans*-$\mathrm{Rh(SNNMe_2)_2(CO)Br}$ (**2b**), and *trans*-$\mathrm{Rh(SNNMe_2)_2(CO)(SCN}$ (**2c**).

$$trans\text{-}\mathrm{Rh(E'Ph_3)_2(CO)X} \xrightleftharpoons[+\mathrm{E'Ph_3,\ CH_2Cl_2}]{+\mathrm{Me_2NNS,\ Et_2O}} trans\text{-}\mathrm{Rh(SNNMe_2)_2(CO)X}$$

SCHEME 3. X = Cl, E′ = As, Sb; X = Br, SCN, E′ = As.

TABLE 1

ANALYTICAL AND CHARACTERISTIC IR AND ^{1}H NMR DATA

Complex		Analyses (Found (calc)(%))			IR (cm^{-1}) ^{a}		^{1}H NMR	
		C	H	N	ν(CO)	ν(M–X)	δ(N–CH$_3$) (ppm)	^4J(HH) (Hz)
cis-Rh(SNNMe$_2$)(CO)$_2$Cl	**(1)**	16.94	2.12	9.88	2075s	370w ^{b}	3.70q	
		(16.88)	(2.12)	(9.85)	2000s	308m ^{c}	4.00q	0.55
trans-Rh(SNNMe$_2$)$_2$(CO)Cl	**(2a)**	17.30	3.45	16.12	1975s	350w ^{b}	3.65br	
		(17.32)	(3.49)	(16.16)		300m ^{c}	3.93br	
trans-Rh(SNNMe$_2$)$_2$(CO)Br	**(2b)**	15.35	3.10	14.38	1978s	350w ^{b}		
		(15.35)	(3.09)	(14.32)				
trans-Rh(SNNMe$_2$)$_2$(CO)(NCS)	**(2c)**	19.50	3.30	18.90	2080s ^{d}	460w ^{e}	3.74br	
		(19.51)	(3.27)	(18.96)	1985s	354br ^{b}	4.04br	
					810m ^{f}			
trans-(μ-Cl)$_2$[Rh(SNNMe$_2$)(CO)]$_2$	**(3)**	14.10	2.40	10.85	2050s	280m ^{c}		
		(14.04)	(2.35)	(10.92)				
Rh(SNNMe$_2$)(1,5-COD)Cl	**(4a)**	35.50	5.40	8.40		345w ^{b}	3.80q	
		(35.67)	(5.39)	(8.32)		325m ^{c}	3.64q	
Rh(SNNMe$_2$)(NBD)Cl	**(4b)**	33.80	4.45	8.80		340m ^{b}	3.84q	0.50
		(33.71)	(4.40)	(8.74)		320w ^{c}	3.52q	0.50
Rh(SNNMe$_2$)$_2$(CO)ClBr$_2$	**(5a)**	11.85	2.45	11.00	2085s	375w ^{b}		
		(11.86)	(2.39)	(11.06)		310m ^{c}		
Rh(SNNMe$_2$)$_2$(CO)ClI$_2$	**(5b)**	10.05	2.05	9.30	2075s	375w ^{b}	3.93q	
		(10.00)	(2.01)	(9.33)		305m ^{c}	4.25q	0.65
Rh(SNNMe$_2$)$_2$(CO)Cl(HgCl$_2$)	**(6)**	9.75	2.00	8.98	2040s	300w ^{c}		
		(9.71)	(1.96)	(9.06)		240br ^{g}		
(μ-Cl)$_2$[Rh(SNNMe$_2$)(CO)I$_2$]$_2$	**(7)**	7.05	1.25	5.50	2060s	285m ^{c}	3.80br	
		(7.06)	(1.18)	(5.49)			4.08br	

[a] Nujol mulls. [b] ν(Rh–S). [c] ν(Rh–Cl). [d] ν(C–N). [e] δ(SCN). [f] δ(RhCO). [g] γ(Hg–Cl).

The reactions depicted are reversible, and require use of diethyl ether as solvent and a considerable excess of ligand to drive them to completion. These reactions can be reversed by adding $E'Ph_3$ to a dichloromethane solution of complexes **2a**, **2b**, **2c**. The red compounds **2b** and **2c** are stable for some weeks in the solid state; **2b** decomposes rapidly in acetone or chlorinated solvents, while **2c** is stable for about an hour in acetone solution. In the infrared spectrum strong $\nu(CO)$ bands are observed at 1978 and 1985 cm^{-1}, respectively. The compound **2c** shows also a strong band at 2080 cm^{-1} due to $\nu(CN)$, a band of medium intensity at 810 cm^{-1} due to $\nu(C-S)$ and a weak band at 460 cm^{-1} assigned to $\delta(NCS)$, consistent with the presence of the Rh-NCS bond [6]. The ^1H NMR spectrum of **2c** shows two broad peaks due to the methyl protons of the thionitrosoamine ligand at 3.74 and 4.04δ.

Complex **2a** undergoes oxidative addition reactions with hydrogen chloride, halogens, methyl iodide and $HgCl_2$. Oxidative additions to **2a** result in increase in the $\nu(CO)$ and the $\nu(N-N)$ stretching frequencies. These results can be explained in terms of decreased Rh-CO back-donation for $\gamma(CO)$ and on increased contribution of the dipolar form to the over-all electronic structure of Me_2NNS ligand coordinated to rhodium(III) (for $\nu(N-N)$).

Bubbling of dry hydrogen chloride through a cold acetone solution of **2a** gave a yellow solid. Because of the very low stability of this compound (it decomposes in a few minutes) it was characterized only by its IR spectrum, which showed bands at 2310 cm^{-1}, assigned to $\nu(Rh-H)$, at 2100s cm^{-1}, due to $\nu(CO)$, and at 320 cm^{-1}, assigned to $\nu(Rh-Cl)$.

Addition of X_2 (X = Cl, Br, I) in diethyl ether to an acetone solution of **2a** gives adducts of formula $Rh(SNNMe_2)_2(CO)ClX_2$; the stability of these rhodium(III) complexes increases from the chloro to the iodo derivative. Thus, whereas the chloro derivative decomposes as a solid and in solution too rapidly for satisfactory analyses to be obtained, the bromo derivative **5a** is stable in the solid state but decomposes rapidly in solution, and the iodo derivative **5b** is stable in acetone solution (in which it is a non-electrolyte) for 1 h. The infrared spectra of these compounds show strong $\nu(CO)$ bands, at 2100, 2085 and 2075 cm^{-1}, respectively, and $\nu(Rh-Cl)$ bands of medium intensity, in the range 320–305 cm^{-1}. The ^1H NMR spectrum of **5b** is similar to that of **1**, and exhibits two quadruplets at 3.93 and 4.25 ($^4J(HH)$ 0.65 Hz).

Treatment of **2a** with $HgCl_2$ gives the orange adduct $Rh(SNNMe_2)_2(CO)Cl(HgCl_2)$ (**6**), which is insoluble in the common organic solvents, and shows in the IR spectrum a $\nu(CO)$ band at 2040s cm^{-1}, a $\nu(Rh-Cl)$ band at 300m cm^{-1}, and a broad band at 240 cm^{-1} assigned to the $\nu(Hg-Cl)$ [7].

When an excess of CH_3I was added to complex **2a** in CH_2Cl_2 the colour of the solution turns from red to orange, the $\nu(CO)$ band of the starting compound disappears, and two bands at 2060s and 1690br cm^{-1} appear. The intensities of these bands changes with time (the former decreases while the latter increases) but stabilize after 15 min. Addition of diethyl ether to the resultant solution gives an orange solid which analyzes for $Rh(SNNMe_2)_2(CO)(CH_3I)Cl$. The complex, which is non-electrolyte in acetone solution, exhibits in the IR spectrum (Nujol) a strong band at 2040 and a broad band at 1680 cm^{-1}, attributable to the $\nu(CO)$ stretch of a terminal carbonyl and of an acetyl derivative, respectively. We suggest that the solid obtained is a mixture of the acetyl derivative $Rh(SNNMe_2)_2(CH_3CO)ClI$ and the adduct $Rh(SNNMe_2)_2(CO)(CH_3)ClI$ [8]. Attempted fractional crystallization and chromatography on silica gel failed to effect any separation.

The reaction of **1** with CH_3I was also monitored by IR spectroscopy. Upon addition of CH_3I to a dichloromethane solution of complex **1** the intensity of the band at 2010 cm^{-1} declined while that of the band at 2080 cm^{-1} did not changes significantly. When a large excess of CH_3I was added the band at 2010 disappeared and two bands appear at 2080s and 1710br cm^{-1}. The same reaction in neat CH_3I readily gave a yellow compound, which analyzes as $Rh(SNNMe_2)(CO)(CH_3I)Cl$; the IR spectrum of which showed had $\nu(CO)$ bands at 2065s and 1710b cm^{-1}. By comparison with published data [9], and bearing in mind that **1** loses CO to give **3**, we formulate this product as a mixture of the acetyl derivative $(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CH_3CO)I]_2$ and the adduct $(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CH_3)(CO)I]_2$.

In order to confirm this suggestion we treated compound **1** with I_2. On the basis of the analytical IR and ^1H NMR data (Table 1) the dark brown product was formulated as $(\mu\text{-}Cl)_2[Rh(SNNMe_2)(CO)I_2]_2$.

Experimental

The compounds $[Rh(CO)_2Cl]_2$ [10], *trans*-$Rh(CO)(AsPh_3)_2Cl$ [11], $[Rh(COD)Cl]_2$ [12], $[Rh(NBD)Cl]_2$ [13] and Me_2NNS [3] were prepared by published methods.

The complex *trans*-$Rh(CO)(AsPh_3)_2X$ (X = Br, NCS) were prepared as follows: A solution of 1.2 mmol of KX, in about 10 cm^3 of H_2O and 612 mg (2 mmol) of $AsPh_3$ were added to an acetone solution (40 cm^3) of $[Rh(CO)_2Cl]_2$ (194.4 mg, 0.5 mmol). After 5 h the precipitate was filtered off washed with acetone and diethyl ether, and redissolved in CH_2Cl_2. The solution was filtered then hexane was added. The yellow solid obtained was dried over P_2O_5.

The complex *trans*-$Rh(CO)(SbPh_3)_2Cl$ was prepared by treatment of $[Rh(CO)Cl]_2$ (97 mg, 0.25 mmol) with $SbPh_3$ (353 mg, 1 mmol) in diethyl ether (100 cm^3). The yellow precipitate was filtered off, washed with diethyl ether, and dried over P_2O_5.

All the other chemicals were used as obtained from commercial sources. Elemental analyses were carried by Microanalytical Laboratory of the Organic Chemistry Institute of Milan. Conductance measurements were performed with acetone solutions at 20°C using a WTW LBR conductivity meter. Infrared spectra were recorded with a Perkin–Elmer 783 spectrometer using CsI plates and a polystyrene film for calibration. A Bruker SY 80 spectrometer was used for recording of the ^1H NMR spectra.

Analyses and characteristic IR and ^1H NMR data are listed in Table 1.

Preparation of cis-$Rh(SNNMe_2)(CO)_2Cl$ (1)

Method A. A cold (−10°C) dilute light petroleum (b.p. 40–60°C) solution of Me_2NNS was added dropwise to a cold solution of $[Rh(CO)_2Cl]_2$ (194 mg, 0.5 mmol) in the same solvent (10 cm^3) until the IR spectrum showed the disappearance of the $\nu(CO)$ band of the starting material. A yellow precipitate formed was separated, washed with light petroleum, and dried over P_2O_5 (Yield ca. 60%).

Method B. When CO was bubbled through a CH_2Cl_2 solution (20 cm^3) of $Rh(SNNMe_2)(diene)Cl$ (0.5 mmol) (diene = 1,5-cyclooctadiene (**4a**), norbornadiene (**4b**)) the red colour of the solution turned to yellow. Addition of light petroleum gave a yellow solid, which was treated as above (Yield ca. 80%).

Preparation of trans-$Rh(SNNMe_2)_2(CO)Cl$ (2a)

Method A. To a stirred diethyl ether solution (60 cm^3) of **1** (142 mg, 0.5 mmol) a solution of Me_2NNS in the same solvent was added until complete precipitation of the dark red solid. This was separated, washed with diethyl ether, and dissolved in acetone. The solution was filtered and diethyl ether/hexane (1/1) was added, to give **2a** as red solid, which was dried over P_2O_5 (Yield ca. 50%).

Method B. To a stirred suspension of *trans*-$Rh(CO)(AsPh_3)_2Cl$ (388 mg, 0.5 mmol) in diethyl ether were added 360 mg (4 mmol) of Me_2NNS were added. The red solid was separated, washed several times with diethyl ether and dried (Yield ca. 80%).

Preparation of trans-(μ-Cl)$_2$[Rh(SNNMe$_2$)(CO)]$_2$ (3)

When a diethyl ether solution of **1** was kept at room temperature a brown precipitate formed after about an hour. It was separated, washed with diethyl ether, and dried (Yield ca. 60%).

Preparation of Rh(SNNMe$_2$)(diene)Cl (4a, 4b)

A solution of $[Rh(diene)Cl]_2$ (0.5 mmol) (diene = 1,5-cyclooctadiene, norbornadiene) in dichloromethane (20 cm^3) was filtered and a diethyl ether solution of Me_2NNS (0.1 *M*) then added slowly. The addition was stopped when $Rh(SNNMe_2)$(1,5-cyclooctadiene)Cl (**4a**) or $Rh(SNNMe_2)$(norbornadiene)Cl (**4b**) separated as red needles. These were filtered off, washed with diethyl ether, and dried (Yield **4a** ca. 90%, **4b** ca. 60%).

Preparation of Rh(SNNMe$_2$)$_2$(CO)ClX$_2$ (5a, 5b)

To an acetone solution (40 cm^3) of **2a** (87 mg, 0.25 mmol) was added a diethyl ether solution (10 cm^3) of X_2 (0.5 mmol) (X = Br, I). The solution was concentrated to 10 cm^3 and light petroleum was added to give $Rh(SNNMe_2)_2(CO)ClBr_2$ (**5a**) or $Rh(SNNMe_2)_2(CO)ClI_2$ (**5b**) as an orange solid, which was filtered off, washed with diethyl ether, and dried (Yield **5a** ca. 70%, **5b** ca. 80%).

Preparation of Rh(SNNMe$_2$)$_2$(CO)Cl(HgCl$_2$) (6)

An acetone solution (30 cm^3) of **2a** (42 mg, 0.15 mmol) was added to a stirred diethyl ether suspension (150 cm^3) of $HgCl_2$ (30.5 mg, 0.15 mmol). The orange precipitate was separated, then dried P_2O_5 (Yield ca. 95%).

Preparation of (μ-Cl)$_2$[Rh(SNNMe$_2$)(CO)I$_2$]$_2$ (7)

A solution of I_2 in light petroleum was added to a solution of **1** (142 mg, 0.5 mmol) in CH_2Cl_2 (10 cm^3) was added until a dark brown solid precipitated. The solid was separated, washed with light petroleum, and dried (Yield ca. 70%).

Reaction of 2a with CH$_3$I

A solution of **2a** (87 mg, 0.25 mmol) in CH_2Cl_2 (40 cm^3) was treated with CH_3I (1 cm^3). The red solution turned orange. The solution was concentrated to about 5 cm^3 and diethyl ether was added, to produce an inseparable mixture of the acetyl derivative $Rh(SNNMe_2)_2(CH_3CO)ICl$ and the adduct $Rh(SNNMe_2)_2(CO)(CH_3)ICl$. This was filtered off, washed with diethyl ether, and dried (Yield ca. 90%).

Reaction of 1 with CH$_3$I

A solution of **1** (94.8 mg, 0.33 mmol) in CH_3I (3 cm^3) was stirred for about 1 h. The excess of CH_3I was removed by evaporation. A yellow mixture of the acetyl derivative $(\mu\text{-Cl})_2$ $[\text{Rh(SNNMe}_2)(\text{CH}_3\text{CO})\text{I}]_2$ and the adduct $(\mu\text{-Cl})_2[\text{Rh(SNNMe}_2)(\text{CO})(\text{CH}_3)\text{I}]_2$ obtained was washed with diethyl ether and dried (Yield ca. 90%).

Acknowledgements

We thank the C.N.R. and the Public Education Ministry for financial support.

References

1 G. Tresoldi, G. Bruno, F. Crucitti and P. Piraino, J. Organomet. Chem., 252 (1983) 381.
2 G. Tresoldi, G. Bruno, P. Piraino, G. Faraone and G. Bombieri, J. Organomet. Chem., 265 (1984) 311.
3 W.J. Middleton, J. Amer. Chem. Soc., 88 (1966) 3842.
4 H.W. Roesky, R. Emmert, W. Isenberg and G.M. Sheldrick, Angew. Chem. Int. Ed. Engl., 20 (1981) 591; H.W. Roesky, R. Emmert, W. Isenberg, M. Schmidt and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1983) 183.
5 L.A. Oro, M.A. Ciriano, B.E. Villaroya, A. Tiripicchio and F.J. Lahoz, J. Chem. Soc., Dalton Trans., (1985) 1891.
6 M.A. Jennings and A. Wojcicki, Inorg. Chem., 6 (1967) 1854; K. Nakamoto (Ed.), Infrared spectra of inorganic and coordination compounds, Wiley Interscience, New York, 1970, p. 188.
7 F. Faraone, G. Bruno, G. Tresoldi, G. Faraone and G. Bombieri, J. Chem. Soc., Dalton Trans., (1981) 1651.
8 A.M. Trzeciak and J.J. Ziolkowsky, Inorg. Chim. Acta, 115 (1986) L43 and references therein; F.R. Hartley, S.G. Murray, D.M. Potter and J.R. Chipperfield, J. Organomet. Chem., 306 (1986) 133 and references therein.
9 D.F. Steele and T.A. Stephenson, J. Chem. Soc., Dalton Trans., (1972) 2161.
10 R. Cramer, Inorg. Synth., 15 (1966) 17.
11 J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 214.
12 D.F. Shriver, Inorg. Synth., 19 (1979) 218.
13 E.W. Abel, M.A. Bennett and G. Wilkinson, J. Chem. Soc., (1959) 3178.