Journal of Organometallic Chemistry, 332 (1987) 213–220
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Monocarbonyl complexes of rhodium(I) with (S–S) donor ligands. Reactions with I_2 and CH_3I

J.V. Heras, E. Pinilla and P. Ovejero

*Facultad de Ciencias Químicas, Departamento de Química Inorgánica, Universidad Complutense,
28040 Madrid (Spain)*

(Received March 3rd, 1987)

Abstract

A new rhodium(I) complex [Rh(NBD)(S–S)] in which (S–S) = S_2COMe^- and (NBD) = norbornadiene (bicyclo[2.2.2]octa-2,5-diene) has been obtained. This compound reacts with CO to give dicarbonyl derivative $[Rh(S_2COMe)(CO)_2]$, which undergoes total or partial replacement of CO upon treatment with the phosphine ligands $P(4\text{-}XC_6H_4)_3$ (X = Cl, F, CH_3, CH_3O). Reactions of monocarbonyl complexes $[Rh(S\text{–}S)(CO)(P(4\text{-}XC_6H_4)_3)]$ (S–S = S_2COMe^-, $S_2CNEt_2^-$) with I_2 yield the new oxidative addition compounds, $[RhI_2(S\text{–}S)(CO)(P(4\text{-}XC_6H_4)_3)]$. However, when CH_3I is used new compounds of the type $[RhI(S\text{–}S)(CH_3CO)(P(4\text{-}XC_6H_4)_3)]$ are formed by insertion of an Me group into Rh–CO bond.

Introduction

A few Rh^{III} complexes containing 1,1-dithiocarbonate ligands are known [1,2], but Rh^I complexes with these ligands have been not described.

In a previous paper we reported the preparation of new *N*,*N*-dialkyldithiocarbamate rhodium(I) complexes stabilized by the presence of high π-acceptor capacity ligands [3]. We now describe the preparation of the diolefin complex $[Rh(NBD)(S_2COMe)]$ and its substituted derivatives $[Rh(S_2COMe)(CO)_2]$, $[Rh(S_2COMe)(CO)(P(4\text{-}XC_6H_4)_3)]$ and $[Rh(S_2COMe)(P(4\text{-}XC_6H_4)_3)_2]$ (X = Cl, F, CH_3, CH_3O). Because of the high electronic density around the rhodium atom we expected to observe oxidative reactions for these complexes. The reactions of monocarbonyl complexes $[Rh(S\text{–}S)(CO)(P(4\text{-}XC_6H_4)_3)]$ (S–S = S_2COMe^-, $S_2CNEt_2^-$) with I_2 and CH_3I have been studied.

Results and discussion

[Rh(NBD)(S₂COMe)] and [Rh(S₂COMe)(CO)₂] complexes

The reaction of dimer complex $[RhCl(NBD)]_2$ with KS_2COMe in toluene yield a garnet microcrystalline product, unstable in the air, formulated as [Rh(NBD)-

0022-328X/87/$03.50

Table 1

Analytical data and some physical properties for the new compounds

Complex	Colour	Analysis (Found (calc) (%))		Conductivity [a]	$\nu(C\equiv O)$	$\nu(C=O)$ [c]
		C	H	Ω_M (ohm^{-1} cm^2 mol^{-1})	(cm^{-1})	(cm^{-1})
Rh(NBD)(S_2COMe)	garnet	35.42 (35.77)	3.60 (3.64)	4.3		1235
Rh(S_2COMe)(CO)$_2$	brown-green	17.11 (18.05)	1.10 (1.12)	4.5	2050, 2000 [b]	1245
Rh(S_2COMe)(CO)(P(4-ClC$_6$H$_4$)$_3$)	yellow	39.52 (41.76)	2.95 (2.48)	58	1980	1245
Rh(S_2COMe)(CO)(P(4-FC$_6$H$_4$)$_3$)	ochre	43.01 (43.31)	2.68 (2.70)	41.58	1978	1235
Rh(S_2COMe)(CO)(P(4-CH$_3$C$_6$H$_4$)$_3$)	ochre	53.10 (53.12)	4.35 (4.42)	4.5	1975	1240
Rh(S_2COMe)(CO)(P(4-CH$_3$OC$_6$H$_4$)$_3$)	yellow	48.21 (48.80)	4.05 (4.06)	1.63	1970	[d]
Rh(S_2COMe)(P(4-ClC$_6$H$_4$)$_3$)$_2$	yellow-ochre	46.77 (48.46)	2.62 (2.86)	16		1250
Rh(S_2COMe)(P(4-FC$_6$H$_4$)$_3$)$_2$	yellow-ochre	54.12 (54.14)	3.16 (3.20)	28		1230
Rh(S_2COMe)(P(4-CH$_3$C$_6$H$_4$)$_3$)$_2$	yellow-ochre	64.31 (64.52)	5.45 (5.49)	3.6		1240
Rh(S_2COMe)(P(4-CH$_3$OC$_6$H$_4$)$_3$)$_2$	yellow-ochre	57.25 (57.75)	4.91 (4.92)	7		[d]

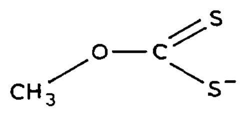
[a] In acetone solution. [b] In dichloromethane solution. [c] ν(CO) of S_2COMe ligand. [d] The band is oclused by the absorption band of phosphine ligand.

(S_2COMe)] on the basis of its analytical data (Table 1). The new compound is a non-electrolyte in acetone solution.

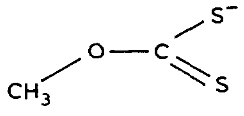
The ^1H NMR spectrum shows two multiplets centered at 1.20 and 4.00 ppm, these positions not being significantly different from those found in [Rh(NBD)(S_2CNR_2)] [3]. These signals are attributed respectively to $>CH_2$ and $>CH + \geq CH$ protons of NBD ligand, and the second set also includes the signal from the CH_3 group of methyl xanthate (S_2COMe).

The IR spectrum shows the absortion bands attributed to NBD and S_2COMe ligands.

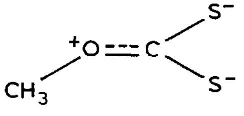
Chatt et al. proposed three resonance forms (**a**, **b** and **c**) for the ligands of the type RS_2CO^- and suggested that forms **a** and **b** are the most representative of a bidentate coordination. The other form (**c**) is present when the ligand is coordinated in a monodentate fashion [4].



(**a**)



(**b**)



(**c**)

From the position of ν(CO) stretching band it is possible to decide between these coordination modes. The IR spectrum of [Rh(NBD)(S_2COMe)] shows a strong ν(CO) absorption at 1235 cm^{-1}; its position suggests bidentate coordination of the methylxanthate group.

The NBD ligand in the [Rh(NBD)(S_2COMe)] complex is readily displaced by CO to give the dicarbonyl complex [Rh(S_2COMe)($CO)_2$]. The product is unstable in the air, and its solutions in toluene or acetone decompose rapidly. Its IR spectrum in the solid state shows two much split bands in the carbonyl stretching region (Table 1). However, the IR spectrum of the solution obtained by reaction in CH_2Cl_2 shows only two bands in this region, at 2050 and 2000 cm^{-1} (Table 1). This fact and the dichroism observed in the dicarbonyl complex is tentatively accounted for by the assumption that there are metal–metal interactions in solid state [5].

The band assigned to ν(CO) stretching vibration of methylxanthate ligand appears at 1245 cm^{-1}, and so we suggest that bidentate coordination is also present in this complex.

[Rh(S_2COMe)(CO)L] and [Rh(S_2COMe)L_2] complexes

The phosphine ligands of the type P(4-$XC_6H_4)_3$ (X = Cl, F, CH_3, CH_3O) react with [Rh(S_2COMe)($CO)_2$] and cause the replacement of one CO group when a 1/1 molar ratio is employed. However, when an excess of phosphine is used complete replacement of carbonyl groups is possible for P(4-$XC_6H_4)_3$ with X = Cl or F. For the more basic phosphines P(4-X=$C_6H_4)_3$ (X = CH_3, CH_3O) complete substitution is only possible under a UV irradiation. This can be understood if the substitution process occurs via a pentacoordinate intermediate [3].

The new complexes are moderately air-stable, soluble in organic solvents such as dichloromethane and acetone, and behave as non-electrolytes in acetone solution (Table 1).

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Table 2

^{1}H NMR spectral data (δ in ppm)

Complex	NBD protons		Xanthate protons	Phosphine protons		Acetyl protons	Dithiocarbamate protons	
Rh(NBD)(S_2COMe)	4.00 m	($\geqslant$CH + $\geqslant$CH)						
	1.20 m	(> CH_2)						
Rh(S_2COMe)(CO)(P(4-ClC_6H_4)$_3$)			4.20 s	7.20–7.70 m	(^{1}H aromatic)			
Rh(S_2COMe)(CO)(P(4-$CH_3OC_6H_4$)$_3$)			3.70 s	6.70–7.80 m	(^{1}H aromatic)			
				3.80 s	(4-CH_3O)			
Rh(S_2COMe)(P(4-$CH_3OC_6H_4$)$_3$)$_2$			3.70 s	6.80–7.70 m	(^{1}H aromatic)			
				3.80 s	(4-CH_3O)			
RhI_2(S_2COMe)(CO)(P(4-ClC_6H_4)$_3$)			4.35 s	7.40–7.80 m	(^{1}H aromatic)			
RhI_2(S_2COMe)(CO)(P(4-$CH_3OC_6H_4$)$_3$)			3.75 s	6.80–8.20 m	(^{1}H aromatic)			
				3.85 s	(4-CH_3O)			
RhI(S_2COMe)(CH_3CO)(P(4-ClC_6H_4)$_3$)			4.30 s	7.20–7.80 m	(^{1}H aromatic)	3.20 s		
RhI(S_2COMe)(CH_3CO)(P(4-$CH_3OC_6H_4$)$_3$)			3.65 s	6.70–7.70 m	(^{1}H aromatic)	2.70 s		
				3.75 s	(4-CH_3O)			
RhI(S_2CNEt$_2$)(CH_3CO)(P(4-FC_6H_4)$_3$)				6.70–7.60 m	(^{1}H aromatic)	3.10 s	1.16 t	(CH_3)
							3.53 q	(CH_2)

Table 3. Analytical data and some physical properties for the new compounds

Complex	Colour	Analysis (Found (calc) (%))			Conductivity [a] Ω_M (ohm^{-1} cm^2 mol^{-1})	ν(C≡O) (cm^{-1})	ν(C=O) [b] (cm^{-1})	ν(CN) [c] (cm^{-1})	ν(C=O) [d] (cm^{-1})
		C	H	N					
$RhI_2(S_2COMe)(CO)(P(4\text{-}ClC_6H_4)_3)$	dark brown	29.15 (29.38)	1.70 (1.74)		2.3	2075			1265
$RhI_2(S_2COMe)(CO)(P(4\text{-}FC_6H_4)_3)$	red-brown	31.05 (31.18)	1.81 (1.85)		2	2070			1260
$RhI_2(S_2COMe)(CO)(P(4\text{-}CH_3C_6H_4)_3)$	red-brown	36.70 (36.18)	3.12 (3.01)		29.7	2080			1260
$RhI_2(S_2COMe)(CO)(P(4\text{-}CH_3OC_6H_4)_3)$	dark-brown	34.10 (34.12)	2.65 (2.84)		2.6	2075			1290
$RhI_2(S_2CNEt_2)(CO)(P(4\text{-}ClC_6H_4)_3)$	red-brown	32.40 (32.05)	2.47 (2.44)	1.60 (1.55)	8.8	2070		1510	
$RhI_2(S_2CNEt_2)(CO)(P(4\text{-}FC_6H_4)_3)$	red-brown	33.90 (33.95)	1.61 (1.64)	2.58 (2.59)	18	2065		1515	
$RhI_2(S_2CNEt_2)(CO)(P(4\text{-}CH_3C_6H_4)_3)$	red-brown	38.40 (38.73)	1.22 (1.67)	3.62 (3.70)	22	2060		1515	
$RhI_2(S_2CNEt_2)(CO)(P(4\text{-}CH_3OC_6H_4)_3)$	red-brown	35.89 (36.63)	1.43 (1.58)	3.48 (3.50)	4.3	2060		1495	
$RhI(S_2COMe)(CH_3CO)(P(4\text{-}ClC_6H_4)_3)$	ochre	35.61 (35.41)	2.40 (2.41)		5.4		1720		1265
$RhI(S_2COMe)(CH_3CO)(P(4\text{-}FC_6H_4)_3)$	ochre	37.62 (37.93)	2.54 (2.58)		6.9		1710		1260
$RhI(S_2COMe)(CH_3CO)(P(4\text{-}CH_3C_6H_4)_3)$	yellow	43.81 (43.85)	3.96 (3.94)		29.6		1710		1265
$RhI(S_2COMe)(CH_3CO)(P(4\text{-}CH_3OC_6H_4)_3)$	yellow	41.12 (40.98)	3.61 (3.68)		62.7		1712		1290
$RhI(S_2CNEt_2)(CH_3CO)(P(4\text{-}ClC_6H_4)_3)$	orange	38.20 (38.14)	3.06 (3.17)	1.72 (1.78)	3		1708	1515	
$RhI(S_2CNEt_2)(CH_3CO)(P(4\text{-}FC_6H_4)_3)$	orange	41.21 (40.73)	1.91 (1.89)	3.42 (3.39)	3		1705	1515	
$RhI(S_2CNEt_2)(CH_3CO)(P(4\text{-}CH_3O_6H_4)_3)$	orange	46.19 (46.37)	1.90 (1.93)	4.53 (4.68)	1.4		1710	1515	
$RhI(S_2CNEt_2)(CH_3CO)(P(4\text{-}CH_3OC_6H_4)_3)$	yellow-orange	43.60 (43.49)	1.87 (1.81)	4.52 (4.39)	3.2		1700	1495	

[a] In acetone solution. [b] ν(CO) of acetyl group Rh-$COCH_3$. [c] ν(CN) of S_2CNEt_2 ligand. [d] ν(CO) of S_2COMe ligand.

The IR spectra in the solid state in all cases show bands attributed to the coordinated triarylphosphine ligands. The presence of a bidentate group S_2COMe^- in all cases is also evident from the appearance of bands, in the range 1230–1250 cm^{-1}, assigned to ν(CO) stretching vibration. For the monocarbonyl compounds the IR spectrum shows one strong band at 1970–1980 cm^{-1} assigned to the ν(CO) stretching vibration of CO group. These positions are not significantly different from those for another monocarbonyl complexes of Rh^I [3]. A relationship between the basicity of the phosphine ligand and the ν(CO) frequency is also apparent.

The ^1H NMR spectra (Table 2) show peaks characteristics of the phosphine ligands. The CH_3 group of methylxanthate ligand gives a single resonance whose position is very dependent upon the basicity of phosphine ligand.

Reactions of monocarbonyl complexes [Rh(S–S)(CO)L] (S–S = S_2COMe^-, $S_2CNEt_2^-$), (L = $P(4\text{-}XC_6H_4)_3$; X = Cl, F, CH_3, CH_3O) with I_2 and CH_3I

Reaction of the complexes [Rh(S–S)(CO)L] with an excess of I_2 in toluene gives the compounds of the type [RhI_2(S–S)(CO)L] (I), formulated on the basis of their spectroscopic and analytical data (Table 3). The complexes are relatively stable in air in the solid state, behave as non-electrolytes in freshly made acetone solutions, and are soluble in solvents as dichloromethane or acetone, but decompose in the solutions.

The IR spectra of the complexes (Table 3) show a strong absorption in 2075 cm^{-1} region characteristic of $\nu(C\equiv O)$ stretching of the terminal carbonyl group. The increase of ~ 100 cm^{-1} in this frequency with respect to that of the parent compounds [Rh(S–S)(CO)L] is consistent with an increase in the formal oxidation state of the rhodium atom. Again, no important changes are observed in these values as the basicity of the phosphine is varied. The positions of the ν(CO) and ν(CN) frequencies (Table 3) suggest a bidentate coordination for the (S–S) ligand [4].

The ^1H NMR spectra (Table 2) of the complexes I show the characteristic signals of the ligands present.

Reaction of compounds [Rh(S–S)(CO)L] with a slight excess of CH_3I immediately gives a microcrystalline solid formulated as [RhI(S–S)(CH_3CO)L] (II) on the basis of its analytical and spectroscopic data (Table 3). The new compounds are air stable and soluble in organic solvents. Their conductivity data (Table 3) in freshly made acetone solution show that they are neutral species.

The IR spectra of the solid compounds (Table 3) do not show bands characteristic of the presence of CO terminal group, but there is a strong absorption in the region ~ 1700 cm^{-1} in all cases, which is attributed to a ν(C=O) stretching vibration. This observation can be attributed to insertion of a CO group in to the Rh–CH_3 bond.

The ^1H NMR of these compounds (Table 2) show the peaks for the protons of the (S–S) and phosphine ligands. An additional singlet in the 2.70–3.20 ppm region is observed in all cases, as expected for an acetyl group.

IR monitoring of freshly made solutions of II after treatment with excess carbon monoxide at atmospheric pressure provides evidence for the formation of two new rhodium(III) species. These solutions rapidly decompose even under dry nitrogen. The carbonyl stretching region shows four absorption bands in the range 2060–1660 cm^{-1}; the two higher frequency bands are attributed to ν(CO) stretching vibrations of CO terminal groups, and the lower frequencies to Rh-$COCH_3$ groups.

Analogous behaviour was observed by Siedle for the compound $[RhI_2(CH_3CO)(P)_2]$ [6], which gave two isomers on treatment with an excess CO. Thus, probably two *cis-trans* isomers of $[RhI(S{-}S)(CH_3CO)(CO)L]$ are present, but attempted isolation of these, yielded only the parent pentacoordinate compounds.

Experimental

All reactions were carried out under nitrogen. Solvents were distilled, dried, and degassed before use.

Analyses: C, H, N analyses were carried out by the Elemental Micro-Analyses Ltd. Laboratories, Amberley, Beaworth, Devon, U.K.

IR spectra in the 4000–200 cm^{-1} region were recorded on a Perkin–Elmer 325 and 1300 spectrophotometers using KBr discs. The ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Perkin–Elmer R-12 apparatus at 90 MHz. Conductance measurements were made on solutions 3×10^{-3} *M* in acetone with a Philips PR9500 conductimeter.

$[Rh(NBD)(S_2COMe)]$

$[RhCl(NBD)]_2$ (60 mg) was added to a solution of KS_2COMe (38.01 mg) [7] in toluene and the mixture was stirred for 3 min then filtered. The filtrate was evaporated to dryness, and the residual brown oil solidified by addition of cold diethyl ether and n-hexane. The garnet complex obtained was dried in vacuo.

$[Rh(S_2COMe)(CO)_2]$

Carbon monoxide was bubbled for 20 min through a solution of $[Rh(NBD)(S_2COMe)]$ in toluene at room temperature and atmospheric pressure. The initial orange colour of the solution changed to garnet. The residue obtained by evaporation was recrystallized by dissolving it in dichloromethane and adding diethyl ether and n-hexane. The crystals were dried under vacuum.

$[Rh(S_2COMe)(CO)(P(4\text{-}XC_6H_4)_3)]$ and $[Rh(S_2COMe)(P(4\text{-}XC_6H_4)_3)_2]$

To a solution of the complex $[Rh(S_2COMe)(CO)_2]$ prepared as described above, was added an equimolar amount of $P(4\text{-}XC_6H_4)_3$ (X = Cl, F, CH_3, or CH_3O). The solution was stirred for 30 min then evaporated to dryness. The oil obtained which was taken up in diethyl ether or dichloromethane, and n-hexane was added to produce crystals of the product.

When an excess of $P(4\text{-}XC_6H_4)_3$ (X = Cl or F) was employed the complex $[Rh(S_2COMe)(P(4\text{-}XC_6H_4)_3)_2]$ was obtained. For X = CH_3 or CH_3O the acetone solution was irradiated with UV light for 9 h. Concentration of the solution followed by addition of diethyl ether and then n-hexane gave a precipitate, which was filtered off and dried over P_2O_5.

These products were also made as follows:

To a suspension of KS_2COMe in toluene was added a 1/2 molar amount of $[RhCl(NBD)]_2$. The solution was filtered and the appropriate phosphine ligand was added. After 30 min stirring the solvent was partially removed and the product was crystallized by addition of diethyl ether and n-hexane.

$[RhI_2(S\text{–}S)(CO)(P(4\text{-}XC_6H_4)_3)]$ ($S\text{–}S = S_2COMe^-$, $S_2CNEt_2^-$; $X = Cl, F, CH_3, CH_3O$)

A slight excess of I_2 was added to a solution of $[Rh(S\text{–}S)(CO)(P(4\text{-}XC_6H_4)_3)]$ ($S\text{–}S = S_2COMe^-$) in toluene. After 2 h stirring at room temperature, addition of cold diethyl ether and n-hexane gave a red brown product, which was filtered off, washed with n-hexane, and vacuum dried.

For (S–S) = $S_2CNEt_2^-$ the complexes were prepared in a similar way in acetone solution, precipitated by addition of a n-heptane, and washed with the same solvent.

$[RhI(S\text{–}S)(CH_3CO)(P(4\text{-}XC_6H_4)_3)]$ ($S\text{–}S = S_2COMe^-$, $S_2CNEt_2^-$; $X = Cl, F, CH_3, CH_3O$)

An excess of CH_3I was added to a solution of $[Rh(S\text{–}S)(CO)(P(4\text{-}XC_6H_4)_3)]$ in toluene and the mixture was stirred for 4 h when X = Cl, F and 72 h for X = CH_3, CH_3O. The solvent was concentrated and the complex precipitated with cold diethyl ether and n-hexane.

For S–S = $S_2CNEt_2^-$ an analogous procedure was used but with dichloromethane as solvent. The solution was stirred for 3 h and the complex precipitated by addition of n-heptane. It was filtered off and dried over P_2O_5.

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