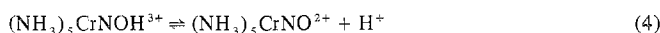


or $\text{Cr}(\text{NH}_3)_5\text{NO}^{2+}$ should proceed by similar mechanisms (based on similar rate behavior and the large yields of dimer), then no satisfactory conclusion can be made about the mechanism beyond the rate-determining step. However both reactions produce primarily Cr(III) polymers and give rise to unstable, coordinated NH_2OH complexes.

One possible explanation for the small contribution which the $1/[\text{H}^+]$ term in the rate law makes to the overall reaction may be a preequilibrium involving a protonated nitrosyl



While we have no spectrophotometric evidence to indicate

protonation of the nitrosyl, reaction 4 cannot be ruled out on the basis of the Lewis basicity of NO^- .²⁸ If reaction 4 is important, it predicts that a substantial amount of the nitrosyl is protonated at 1 M HClO_4 , while the unprotonated form becomes important beyond pH 2.

Unlike the reduction of coordinated nitro complexes, the reduction of the nitrosyls appears to be cleanly controlled with relation to the overall stoichiometry. Although the sequence of reactions occurring after the rate-determining step has not been solved, one can conclude that (1) large amounts of polymeric chromium(III) species are produced upon reduction of the chromium nitrosyls and (2) there is more than one pathway to dimer (or trimer) formation. A dramatic difference is observed for the products of the Cr^{2+} reduction of ruthenium nitrosyls⁶ (NH_3) as compared with the chromium nitrosyls (NH_2OH), and this emphasizes the control that the metal center has on the extent of the reduction of the nitrosyl ligand.

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Contribution from the "Groupe d'Etude et d'Application des Complexes metalliques," Laboratoire de Chimie de Coordination du CNRS 31030 Toulouse Cedex, France

Dinuclear-Bridged d^8 Metal Complexes. III. Behavior of the $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)_2]$ Compound toward Amines¹

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The complex $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)_2]$ provides an excellent starting material for the preparation of $[\text{RhCl}(\text{CO})\text{L}]_2$ complexes where L = diethylamine, *n*-propylamine, pyridine, and 3,5-lutidine. The $\text{RhCl}(\text{CO})(\alpha\text{-pic})_2$ and $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-lut})$ (pic = picoline; lut = lutidine) compounds are also prepared and the role of steric requirements of entering ligands is shown. The $\text{RhCl}(\text{CO})(\text{PR}_3)(2,6\text{-lut})$ derivatives are obtained from $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-lut})$ or $[\text{RhCl}(\text{CO})\text{PR}_3]_2$ complexes by action of PR_3 or 2,6-lutidine, respectively. Isolation of the $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NH}_2\text{Et}_2)]_2$ compound affords strong evidence for the general scheme of reaction mechanisms previously suggested. A rationalization of results obtained with phosphine and amine ligands is proposed.

Introduction

Di- μ -chloro-tetracarbonyldirrhodium undergoes chloro-bridge splitting by amines L to give the mononuclear species *cis*- $\text{RhCl}(\text{CO})_2\text{L}$.^{2,3} Any attempt to obtain further direct substitution of a carbonyl group was unsuccessful and, in the particular case of L = NC_5H_5 ,³ excess of ligand leads to the $\text{RhCl}(\text{CO})_2\text{L}_2$ compound. Dinitrogen-containing ligands

not only brought about the splitting but also acted as bridges between the two dicarbonylrhodium(I) moieties.³⁻⁶ In addition, the reactivity of amines toward di- μ -chloro-di- η -1,5-cyclooctadienedirrhodium has been extensively studied,⁷⁻¹⁰ splitting of the bridge occurs to form $\text{C}_8\text{H}_{12}\text{RhCl}$,^{7,8} and further addition of ligand leads to cationic species $[\text{C}_8\text{H}_{12}\text{-RhL}_2]^+$.^{8,10} By carbonylation $[\text{Rh}(\text{CO})_2\text{L}_2]^+$ complexes

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were obtained⁹⁻¹¹ and further substitution of a carbonyl group by triphenylphosphine gave $[\text{RhL}_2(\text{CO})(\text{PPh}_3)]^+ \text{ } ^{9,11}$. More recently, Mestroni, *et al.*, were able to convert $[\text{Rh}(\text{CO})_2\text{L}_2]^+$ complexes in nonelectrolyte *cis*- $\text{L}_2\text{Rh}(\text{CO})\text{Cl}$ compounds.¹² However, at the present time, dinuclear chloro-bridged amine complexes are unknown.

As in the case of tertiary phosphine ligands, the $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)_2]$ is shown now to be a particularly convenient starting material in the preparation of various dinuclear or mononuclear aminorhodium complexes.

Experimental Section

The $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)_2]$ compound (I) was prepared as previously described¹³ by mixing equimolar quantities of $[\text{RhCl}(\text{CO})_2]_2$ ¹⁴ and $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$.¹⁵ This complex was recrystallized from a yellow solution of toluene-hexane in yields of 80-90%.

All solvents were distilled and used under nitrogen atmosphere. Various amines were purchased from the Fluka Co. The ligands $\text{P}(\text{CH}_3)_3$ ¹⁶ and $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ ¹⁷ were prepared according to published methods. Rhodium trichloride trihydrate was purchased from the "Compagnie des Metaux precieux." Microanalyses were carried out by the "Service Central de Microanalyses du C.N.R.S." division of Montpellier.

The infrared spectra were recorded with a Perkin-Elmer 225 grating spectrometer either in hexadecane solutions or in cesium bromide pellets; in the carbonyl stretching region the spectra were calibrated by water vapor lines.

The proton magnetic resonance spectra were recorded on a Varian Associates A-60A and for nuclear Overhauser effect and variable-temperature probe experiments on an HA 100 spectrometer. Dichloromethane, deuteriochloroform, and deuteriotoluene were used as solvents and tetramethylsilane was used as internal standard.

Molecular weight measurements were determined in benzene using a Mechrolab osmometer.

Melting points were determined in air.

Preparation of Complexes. $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NH}(\text{C}_2\text{H}_5)_2)]_2$. Compound I (0.398 g, 1.02 mmol) was dissolved in 10 ml of toluene and 0.168 ml of diethylamine (2.04 mmol) was added at room temperature. The solution became brown. By crystallization at -20° brown product was obtained, washed with hexane, and dried *in vacuo*. A 0.400-g quantity of crystals was obtained (yield $\approx 72\%$).

Elemental analysis and molecular weight measurements were consistent with the proposed formula. *Anal.* Calcd: C, 31.42; H, 5.66; Cl, 13.25; N, 5.23; mol wt 535. Found: C, 31.67; H, 5.54; Cl, 13.02; N, 5.25; mol wt 519.

$[\text{RhCl}(\text{CO})(\text{NH}(\text{C}_2\text{H}_5)_2)]_2$. $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NH}(\text{C}_2\text{H}_5)_2)]_2$ was dissolved in toluene. The solution was left under vacuum in a vacuum line and warmed to $70-80^\circ$ during 24 hr. A dark brown solid appeared which was filtered off, washed with toluene, and dried *in vacuo*. The yield calculated with regard to $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NH}(\text{C}_2\text{H}_5)_2)]_2$ is $\approx 90\%$. This product is almost insoluble in the most common solvents. *Anal.* Calcd: C, 25.07; H, 4.64; Cl, 14.80; N, 5.85. Found: C, 26.17; H, 4.81; Cl, 14.75; N, 5.73.

$[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NH}_2\text{-}n\text{-C}_3\text{H}_7)]_2$ and $[\text{RhCl}(\text{CO})(\text{NH}_2\text{-}n\text{-C}_3\text{H}_7)]_2$. Compound I (0.316 g, 0.81 mmol) was dissolved in 20 ml of toluene and the solution cooled to -20° ; 0.133 ml (1.62 mmol) of *n*-propylamine was added slowly. The solution became light brown; it was cooled to -80° . After 1 hr there appeared fine yellow crystals, which were filtered off, washed with cooled hexane, and dried rapidly *in vacuo*. The product was unstable: upon slow heating above -20° the solid became dark brown, so no elemental analysis was undertaken. The dark solid obtained and heated under reduced pressure was identified by elemental analysis as $[\text{RhCl}(\text{CO})(n\text{-C}_3\text{H}_7\text{-}$

$\text{NH}_2)]_2$. *Anal.* Calcd: C, 21.30; H, 4.03; Cl, 15.72; N, 6.21. Found: C, 22.01; H, 4.11; Cl, 16.08; N, 6.07. We obtained 0.270 g of product, which is insoluble in the most usual solvents (yield $\approx 75\%$ with regard to I).

$[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NC}_5\text{H}_5)_2]$ and $[\text{RhCl}(\text{CO})(\text{NC}_5\text{H}_5)_2]$. A 0.226-g sample of I (0.58 mmol) was dissolved in 10 ml of toluene. The solution was cooled to -40° and 0.0935 ml (1.16 mmol) of pyridine was added dropwise. The solution became light yellow. Fine yellow crystals gradually appeared, which were filtered off, washed with cooled hexane, and dried in a stream of nitrogen gas. Upon slow heating to reach room temperature the crystals became brown-yellow. Elemental analysis of this product revealed a mixture of complexes. For instance this analysis is consistent with a 50:50 mixture of $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NC}_5\text{H}_5)_2]$ and $[\text{RhCl}(\text{CO})(\text{NC}_5\text{H}_5)_2]$. *Anal.* Calcd for $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NC}_5\text{H}_5)_2]$: C, 35.13; H, 3.32; Cl, 12.96; N, 5.12. Calcd for $[\text{RhCl}(\text{CO})(\text{NC}_5\text{H}_5)_2]$: C, 29.36; H, 2.06; Cl, 14.44; N, 5.71. Found: C, 32.04; H, 2.45; Cl, 13.89; N, 5.34.

However, when pyridine (0.083 ml) was added to a hot solution ($\approx 60^\circ$) of I (0.200 g), a maroon solid appeared immediately. It was filtered off, washed with toluene, and dried *in vacuo*. A 0.215-g amount of product was obtained (yield $\approx 85\%$). Elemental analysis of this solid was consistent with the $[\text{RhCl}(\text{CO})(\text{NC}_5\text{H}_5)_2]$ formula. *Anal.* Calcd: C, 29.36; H, 2.06; Cl, 14.44; N, 5.71. Found: C, 30.15; H, 2.29; Cl, 14.12; N, 5.43.

$[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(3,5\text{-NC}_7\text{H}_9)_2]$ and $[\text{RhCl}(\text{CO})(3,5\text{-NC}_7\text{H}_9)_2]$. Preparation and stability of these complexes are similar to those of $[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NC}_5\text{H}_5)_2]$ and $[\text{RhCl}(\text{CO})(\text{NC}_5\text{H}_5)_2]$. *Anal.* Calcd for $[\text{RhCl}(\text{CO})(\text{NC}_7\text{H}_9)_2]$: C, 35.13; H, 3.32; N, 5.12. Found: C, 36.10; H, 3.42; N, 4.86.

$\text{RhCl}(\text{CO})(2\text{-NC}_6\text{H}_7)_2$. A 0.419-g sample of I (1.08 mmol) was dissolved in 20 ml of toluene, and 0.422 ml of 2-methylpyridine (4.32 mmol) was added at room temperature. The solution became immediately light yellow. Fine yellow crystals gradually appeared after 15 min of stirring. Crystallization was achieved at -20° . The product was filtered off, washed with toluene, and dried *in vacuo*. A 0.510-g amount of yellow crystals was obtained (yield $\approx 72\%$); mp $\approx 135^\circ$ dec. *Anal.* Calcd: C, 44.27; H, 4.01; Cl, 10.05; N, 7.95; mol wt 353. Found: C, 43.78; H, 4.14; Cl, 10.40; N, 7.75; mol wt 363.

$\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-NC}_7\text{H}_9)$. A 0.195-g sample of I (0.50 mmol) was dissolved in 10 ml of toluene and 0.116 ml of 2,6-lutidine (1.00 mmol) was added at room temperature. The solution became light yellow. It was cooled to -20° . Fine yellow crystals were obtained, washed with hexane, and dried *in vacuo*. A 0.210-g quantity of product was obtained (yield $\approx 70\%$); mp 98° dec. *Anal.* Calcd: C, 39.82; H, 4.35; Cl, 11.75; N, 4.64; mol wt 302. Found: C, 39.95; H, 4.58; Cl, 11.60; N, 4.69; mol wt 308.

$\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_3)(2,6\text{-NC}_7\text{H}_9)$. (a) A 0.130-g amount of $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-NC}_7\text{H}_9)$ (0.43 mmol) was dissolved in 20 ml of toluene, and 0.043 ml (0.43 mmol) of $\text{P}(\text{CH}_3)_3$ was added at room temperature. The solution was cooled to -20° . Yellow cubic crystals were obtained, washed with hexane, and dried *in vacuo*; mp 85° dec. A 0.120-g amount of product was collected (yield $\approx 80\%$). *Anal.* Calcd: C, 37.79; H, 5.20; Cl, 10.14; H, 4.01; P, 8.86; mol wt 350. Found: C, 37.94; H, 5.20; Cl, 10.35; H, 4.08; P, 9.13; mol wt 356.

(b) A 0.0945-g sample of $[\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_3)_2]$ (0.195 mmol) was dissolved in 10 ml of toluene, and 0.045 ml of 2,6-lutidine (0.39 mmol) was added at room temperature. The solution became immediately light yellow. By crystallization at -20° yellow crystals were collected, washed with hexane, and dried *in vacuo*. The product was identified to be $\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_3)(2,6\text{-lut})$ by infrared and nmr spectra.

$\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)(2,6\text{-NC}_7\text{H}_9)$. Methods a and b of the preparation of this compound, mp 88° , are similar to those of the analogous compound $\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_3)(2,6\text{-NC}_7\text{H}_9)$. *Anal.* Calcd: C, 46.67; H, 4.91; Cl, 8.61; N, 3.40; P, 7.52; mol wt 412. Found: (method b): C, 45.91; H, 4.88; Cl, 8.63; N, 3.40; P, 7.75; mol wt 405.

Results and Discussion

Dinuclear Complexes. Addition at room temperature of the stoichiometric quantity of diethylamine (L:Rh = 1) to $\text{Y}_2\text{C}_2\text{H}_4$ (I) in toluene solution gives, after crystallization at -20° , quantitatively a yellow product. Elemental analysis, relative intensities of ethylene and amine proton nmr signals, and molecular weight are consistent with the $[\text{RhCl}$

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Table I. Infrared and Nmr Data

Compd	ν_{CO} , cm^{-1}		Other freq, cm^{-1} (CsBr)	δ (TMS), ppm; J , Hz
	Hexa- decane	CsBr		
$[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)]_2$	2023 s		$\nu_{\text{C}=\text{C}}$ 1502 m	$\delta_{\text{C}_2\text{H}_4}^b$ -3.93
$[\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(\text{NH}(\text{C}_2\text{H}_5)_2)]_2$	2014 vs		δ_{CH_2} 1420 m	
	1986 s^a		$\nu_{\text{C}=\text{C}}$ 1518 m	$\delta_{\text{C}_2\text{H}_4}^c$ -4.12, $\delta_{\text{CH}_2}^c$ -3.10, $\delta_{\text{CH}_3}^c$ -1.53, $J_{\text{HH}} = 7$
$[\text{RhCl}(\text{CO})(\text{NH}(\text{C}_2\text{H}_5)_2)]_2$		1995 vs, br		
$[\text{RhCl}(\text{CO})(\text{NH}_2\text{-}i\text{-C}_3\text{H}_7)]_2$		1995 vs, br		
$[\text{RhCl}(\text{CO})(\text{NC}_5\text{H}_9)]_2$		1995 vs, br		
$[\text{RhCl}(\text{CO})(3,5\text{-}(\text{CH}_3)_2\text{NC}_5\text{H}_9)]_2$		1995 vs, br		
$\text{RhCl}(\text{CO})(2\text{-}(\text{CH}_3)_2\text{NC}_5\text{H}_9)$	1963 vs	1950 vs	$\nu_{\text{Rh-Cl}}$ 290 m	$\delta_{\text{CH}_3}^b$ -3.22
<i>cis</i> - $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-}(\text{CH}_3)_2\text{NC}_5\text{H}_9)$	2023 s^a			$\delta_{\text{C}_2\text{H}_4}^c$ -3.42, $J_{\text{Rh-H}} = 2.1$, $\delta_{\text{CH}_3}^c$ -3.13
<i>trans</i> - $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-}(\text{CH}_3)_2\text{NC}_5\text{H}_9)$	1990 vs a			$\delta_{\text{C}_2\text{H}_4}^d$ -2.88, $J_{\text{Rh-H}} = 2.1$, $\delta_{\text{CH}_3}^d$ -2.74
				$\delta_{\text{C}_2\text{H}_4}^c$ -4.16, $\delta_{\text{CH}_3}^c$ -3.13
				$\delta_{\text{C}_2\text{H}_4}^d$ -4.09, $\delta_{\text{CH}_3}^d$ -2.78
$\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_3)(2,6\text{-}(\text{CH}_3)_2\text{NC}_5\text{H}_9)$				
<i>cis</i>	1979 s			
<i>trans</i>	1961 vs	1952 vs	$\nu_{\text{Rh-Cl}}$ 300 m	$\delta_{\text{CH}_3}^d$ -3.00, $\delta_{\text{PCH}_3}^d$ -1.35, $J_{\text{P-H}} = 10.8$, $J_{\text{Rh-H}} = 1.4$
$\text{RhCl}(\text{CO})(\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5)(2,6\text{-}(\text{CH}_3)_2\text{NC}_5\text{H}_9)$				
<i>cis</i>	1981 s			
<i>trans</i>	1962 vs	1950 vs	$\nu_{\text{Rh-Cl}}$ 295 m	$\delta_{\text{CH}_3}^d$ -3.02, $\delta_{\text{PCH}_3}^d$ -1.69, $J_{\text{P-H}} = 10.0$, $J_{\text{Rh-H}} = 1.5$

a Toluene-hexadecane solutions (30/70). b Dichloromethane solutions. c Deuteriochloroform solutions. d Deuteriotoluene solutions.

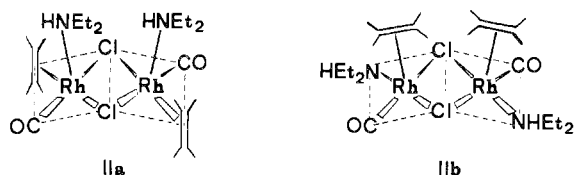


Figure 1.

$(\text{CO})(\text{C}_2\text{H}_4)(\text{NHEt}_2)]_2$ formula (hereafter referred as $W_2^{\text{NHEt}_2}$). As generally admitted, the substitution of d^8 square-planar compounds involves, in most cases, five-coordinated species.¹⁸⁻²² The structure of the W_2 compound is certainly strongly related to the geometry of the transition state implicated in the present substitution reaction. Only a few pentacoordinated model rhodium complexes have been studied.²³⁻³⁰ Thus it seems reasonable to admit, *a priori*, the two amine ligands taking up apical positions without bridge splitting (Figure 1, IIa).

As shown by the decreasing of CO stretching frequencies (see Table I), the back-coordination to carbonyl groups increases in W_2 when compared to Y_2 . However infrared ($\nu_{\text{C}=\text{C}}$ 1518 cm^{-1} in CsBr) and nmr data ($\delta_{\text{C}_2\text{H}_4}$ -4.12 ppm) when compared^{30a} to those of $Y_2^{\text{C}_2\text{H}_4}$ ($\nu_{\text{C}=\text{C}}$ 1502 cm^{-1} in

CsBr; $\delta_{\text{C}_2\text{H}_4}$ -3.93 ppm) suggest the opposite. Variations of the coupling between $\nu_{\text{C}=\text{C}}$ and δ_{CH_2} modes^{31,32} could afford for the raising of $\nu_{\text{C}=\text{C}}$ frequency from Y_2 to W_2 , but the comparable situations of ethylene groups coordinated to rhodium atoms in Y_2 and W_2 make this eventuality rather improbable. Then, in structure IIa retrodonation would be surprisingly greater for CO groups and weaker for ethylenic groups than this in $Y_2^{\text{C}_2\text{H}_4}$ when each ligand would be expected to fall under the same influence of amine. It seems, therefore, more plausible that the CO and C_2H_4 groups do not lie in the same plane due to opposite influence of amine; for instance structure IIb of C_2 symmetry for which ethylene lies in the apical position corresponds better to the experimental data. Compound IIa recalls the geometry of the rhodium carbonyl porphyrin complex³⁰ where the two rhodium atoms are bonded to two nitrogens of the porphyrin ring, whereas structure IIb is to be compared to those of $[\text{RhCl}(\text{CO})_2]_2(\text{diene})^{28}$ or $[\text{RhCl}(\text{C}_4\text{H}_6)_2]\text{C}_4\text{H}_6^{29}$ complexes. Recently, two trigonal-bipyramidal platinum-containing olefin and nitrogen ligand complexes have been reported;^{33,34} nevertheless, in our case, in the assumption of such geometry, the presence of the bridge would compel the chloro atoms being in apical and equatorial positions. However distortions and/or C_s symmetry or centrosymmetrical structures are not excluded.

The $W_2^{\text{NHEt}_2}$ complex, in the solid state as in toluene solution, loses ethylene very slowly under reduced pressure to give a dark brown product, for which elemental analysis is consistent with a $[\text{RhCl}(\text{CO})(\text{NHEt}_2)]_n$ formula. Low solubility of this complex has prevented infrared and nmr determinations in solution; infrared analysis in CsBr pellets has revealed a broad CO stretching at 1995 cm^{-1} . By analogy with $[\text{RhCl}(\text{CO})(\text{PR}_3)]_2$ complexes,^{1a} although no molecular weight determination has been made, it would seem that we are in the presence of a dinuclear complex ($n = 2$). Here also^{1a} a double square-planar structure (*cis* or

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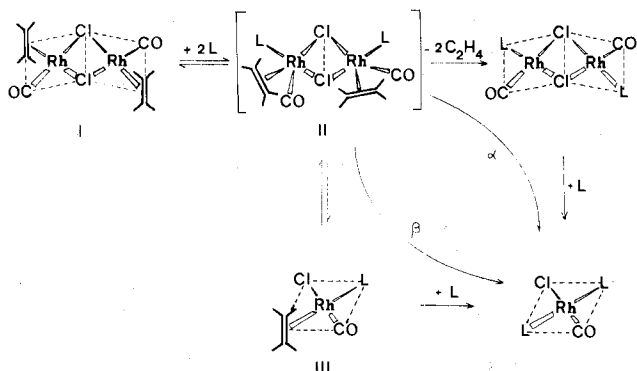


Figure 2.

trans, bent or entirely planar) can be retained. Addition at low temperature ($\approx -30^\circ$) of *n*-propylamine, 3,5-lutidine, and pyridine gives in a similar manner the corresponding W_2 complexes; these compounds lose ethylene at room temperature and all attempts to obtain exact elemental analysis were unsuccessful. Pure Y_2^{amine} complexes are prepared at higher temperature and in the case where the products are left for a long time under reduced pressure. Under these conditions, elemental analyses of the new $[\text{RhCl}(\text{CO})(\text{amine})]_2$ complexes were satisfactory.

Finally, W_2 compounds particularly studied in the case of $L = \text{diethylamine}$, appear as stabilized intermediates in the substitution of ethylene in $Y_2^{\text{C}_2\text{H}_4}$ by amines.

Influence of Steric Hindrance. A previously proposed scheme^{1a} (Figure 2) of the formation of $Y_2^{\text{PR}_3}$ complexes is recalled now, isolation of the W_2 complex affording a new strong argument in favor of a double pentacoordinate intermediate such as II.

As admitted in the case of substitution of bulky phosphines,^{1a} due to slow formation of intermediate II, free ligand could react with compound Y_2 or III to afford $\text{RhCl}(\text{CO})\text{L}_2$ mononuclear species (X_2). With α -picoline, the reaction was slow and incomplete, and by further addition of ligand to reach the $L:\text{Rh} = 2$ ratio, the X_2 compound $\text{RhCl}(\text{CO})(2\text{-NC}_6\text{H}_7)_2$ was obtained almost quantitatively by crystallization from a clear solution. In addition, as the compounds $[\text{RhCl}(\text{CO})(\text{amine})]_2$ (*vide supra*) have been found to be almost insoluble, the Y_2 complex, if formed, would be expected to be of low solubility and its precipitation would favor its formation while preserving it from fast further attack by free ligand. Then, it seems that, in this case, path α can be excluded and that intermediate III is clearly involved in the reaction of substitution.

In nuclear magnetic resonance, a single methyl signal was detected in agreement with a trans configuration in which the picoline plane is normal to the molecular plane, the two methyl groups being syn or anti in regard to the square plane. In addition, CO (1963 cm^{-1} in hexadecane) and Rh-Cl (290 cm^{-1} in CsBr) stretching frequencies, when compared to those of corresponding phosphine complexes *trans*- $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ ^{35,36} are in agreement with mutually trans picoline ligands. Recently Mestroni and coworkers¹² have been able to prepare the *cis*- $\text{L}_2\text{Rh}(\text{CO})\text{Cl}$ compounds ($\text{L}_2 = 1,10\text{-phenanthroline}$ or $2,2'\text{-bipyridine}$) for which the CO stretching frequencies were found to be 1989 cm^{-1} (CHCl_3) and 1977 cm^{-1} (CH_3CN) respectively. Now, the presently proposed method for amine ligands leads to the first example of a mononuclear-disubstituted rhodium(I) complex *trans*- $\text{RhCl}(\text{CO})\text{L}_2$ ($L = \alpha\text{-picoline}$).

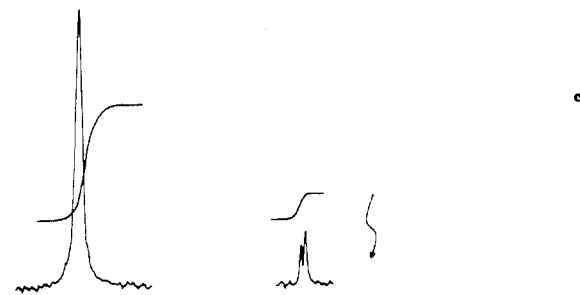
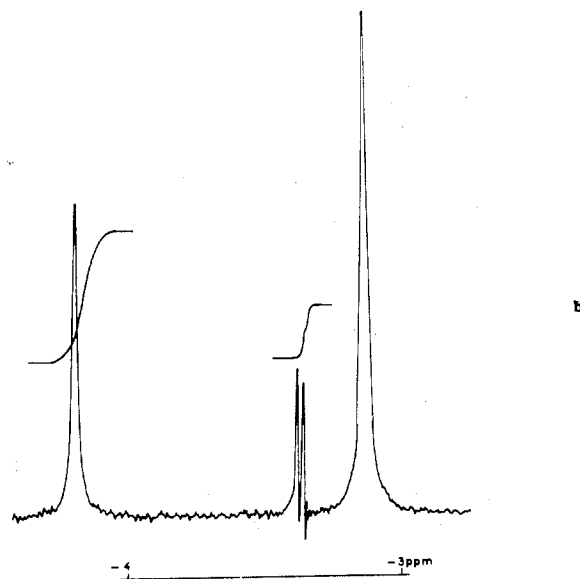
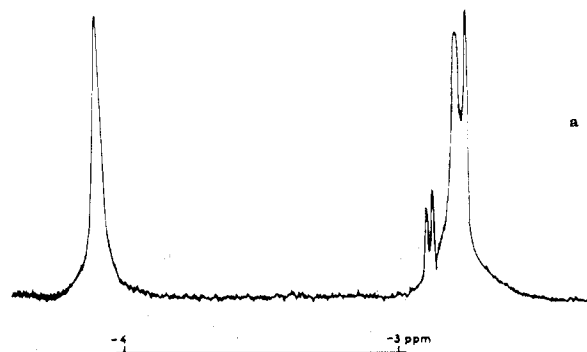
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Figure 3. Nmr spectra of *cis*- and *trans*- $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-lut})$: a, in C_7D_8 solution; b, in CDCl_3 solution; c, nuclear Overhauser effect experiment.

In addition, use of the very sterically hindered 2,6-lutidine ligand affords exclusively isolation of intermediate III, $\text{RhCl}(\text{CO})(\text{C}_2\text{H}_4)(2,6\text{-lut})$, of the path β , even in the presence of excess of ligand. Elemental analysis and molecular weight are consistent with this mononuclear structure formulation. Moreover, from infrared and nmr data, a mixture of two isomers is detected in deuteriotoluene solution: one A ($\nu_{\text{CO}} 1990\text{ cm}^{-1}$, $\delta_{\text{C}_2\text{H}_4} -4.09\text{ ppm}$, $\delta_{\text{CH}_3} -2.78\text{ ppm}$) and the other B ($\nu_{\text{CO}} = 2023\text{ cm}^{-1}$, $\delta_{\text{C}_2\text{H}_4} -2.88\text{ ppm}$, $\delta_{\text{CH}_3} -2.74\text{ ppm}$) (see Table I and Figure 3) almost in the ratio 60:40. *A priori*, three isomers are to be considered (Figure 4).

Splitting of the signal at -2.88 ppm is due to a coupling of ethylene protons with the ^{103}Rh nucleus ($I = 1/2$) as shown by its unchanged value when changing the solvents or recording spectra at 60 or 100 MHz. Similarly the signal at -4.09 ppm is split but only at low temperature ($J_{\text{Rh-H}} = 2.1\text{ Hz}$).

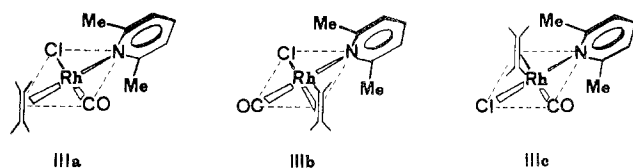


Figure 4.

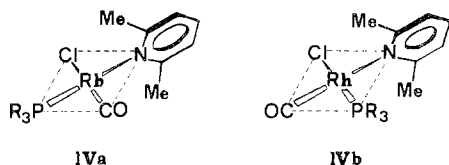


Figure 5.

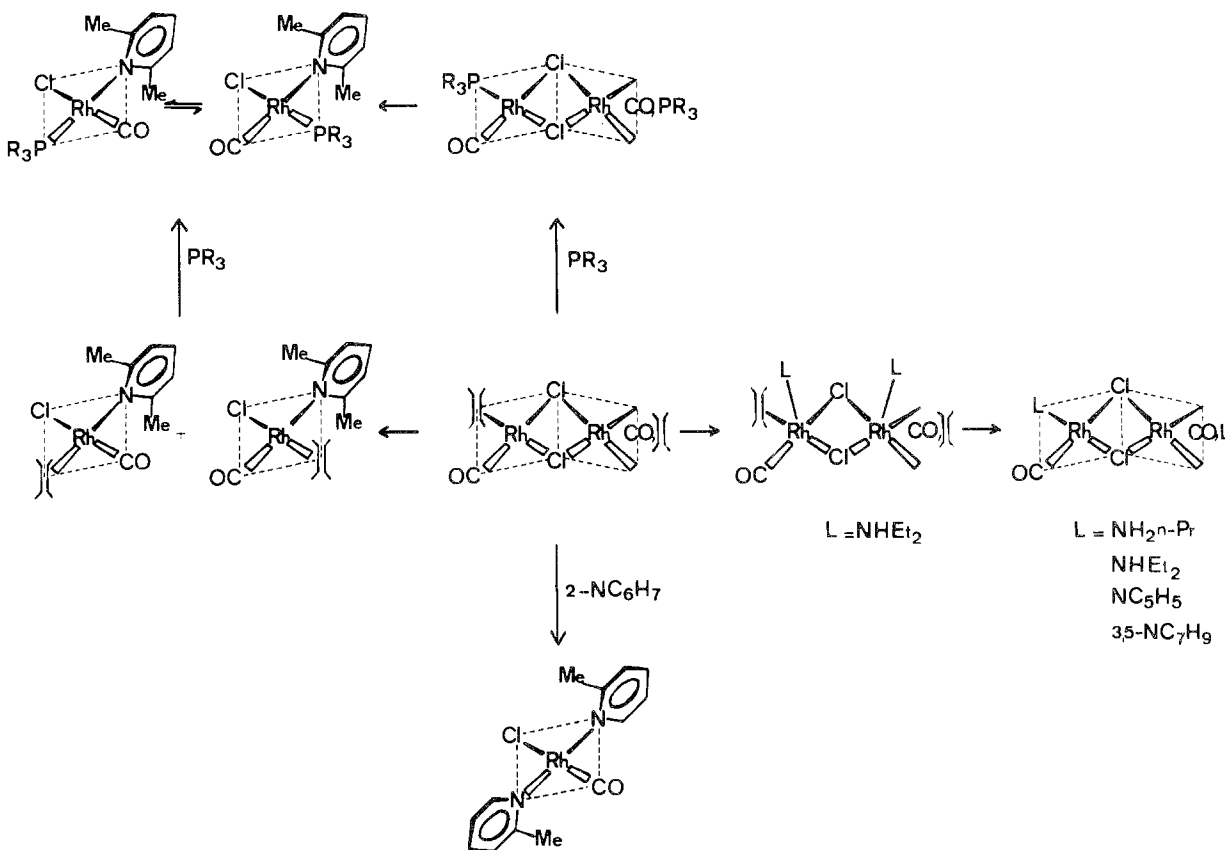


Figure 6. General scheme of isolated complexes.

An exchange phenomenon is certainly involved; however, no detailed study to reach the exchange mechanism has been performed. According to literature data³⁷⁻³⁹ the C-C bond of ethylene lies approximately perpendicular to the coordination square plane. Similarly, existence of a single methyl-lutidine signal for each isomer is in favor of the lutidine plane being normal to the square plane. For isomers IIIb and IIIc distances between ethylenic and methyl protons appear equally small and in any case shorter than in isomer IIIa; indeed by a nuclear Overhauser effect⁴⁰ experiment, in carefully degassed CDCl₃, irradiation of methyl signals induces a decrease of 50% of the intensity of ethylene signal at -3.42 ppm (compound B) whereas intensity of the ethylene signal

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at -4.09 ppm (compound A) is reduced by only $\approx 15\%$ (Figure 3). Moreover, since these compounds are formed by an attack of $Y_2C_2H_4$ with bridge splitting, it seems reasonable to retain a structure having ethylene and CO groups in mutually cis positions and to retain therefore isomer IIIb as being compound B. Concerning isomer IIIa (A), distances of ethylenic and methyl protons are still sufficiently short to induce a weak nuclear Overhauser effect as shown by molecular models. In addition, the surprisingly high difference between shifts of ethylenic protons in IIIa and IIIb is probably not due to the back-coordination only. Indeed, the ring current induced by the aromatic amine brings about a higher absolute value for the induced magnetic field in the trans position than in the cis position.

Reactivity of $RhCl(CO)(C_2H_4)(2,6-lut)$ toward Phosphines.

The presence of an ethylene group in $RhCl(CO)(C_2H_4)(2,6-lut)$ suggests a facile replacement by phosphines to prepare mononuclear-disubstituted complexes of type X_2 . We have restricted our study to the case of $P(CH_3)_2C_6H_5$ and $P(CH_3)_3$ ligands. The $RhCl(CO)(PR_3)(2,6-lut)$ compounds have been also prepared by attack⁴¹ of $[RhCl(CO)(PR_3)]_2$ compounds by 2,6-lutidine. Elemental analysis, molecular weight, infrared in the solid state, and nmr measurements are in good agreement with the proposed formula. However the infrared spectrum in solution exhibits two CO stretchings, one of which lies at the same frequency as that of the corresponding Y_2 . The lack of a shoulder at 1992 cm^{-1} present in Y_2 infrared spectra and observation of separate nmr signals when some Y_2 or 2,6-lutidine is added to the solution of X_2 show clearly that no dissociation of X_2 giving rapid dynamical equilibrium between X_2 and Y_2 is involved. So, the two bands observed

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in infrared spectra agree with the existence of two isomers (IVa and IVb, Figure 5). Under these conditions the single methyl nmr signal suggests a dynamical equilibrium between the two isomers; fast rates of interconversion have certainly precluded the observation at -100° of the signals corresponding to each isomer. Assignment of CO frequencies remains however possible. The 1961 (or 1962) cm^{-1} carbonyl frequency is comparable with those observed in *trans*-RhCl(CO)(PR₃)₂³⁵ as in *trans*-RhCl(CO)(α -pic)₂ and is in agreement with structure IVa. In the solid state isomer IVa is only present as shown by CsBr pellets exhibiting a single ν_{CO} at 1950 cm^{-1} and a single $\nu_{\text{Rh-Cl}}$ at 295 cm^{-1} .³⁶ Concerning isomer IVb, as in the case of the RhCl(CO)(C₂H₄)(2,6-lut) compound, we retain the CO and PR₃ groups in mutually *cis* positions. The carbonyl stretching frequency at 1979 (and 1981) cm^{-1} appears, when compared to those of *trans* isomers, surprisingly high. Some such compounds are known: *cis*-RhCl(CO)(PPh₃)₂⁴² (ν_{CO} 1980 cm^{-1} in Nujol), *cis*-(Ph₂PCH₂CH₂PPh₂)Rh(CO)Cl⁴³ (ν_{CO} 2010 cm^{-1} in CH₂Cl₂) (see also ref 44), and *cis*-(1,10-phen)Rh(CO)Cl¹² (ν_{CO} 1989 cm^{-1} in CHCl₃). *Trans* influences⁴⁵ of ligands in isomers IVa and IVb justify the observed order of the CO frequencies, but clearly the high polarizable CO ligand appears to afford a particularly strong response to this influence.

Conclusions

The previously reported synthesis of [RhCl(CO)(PR₃)₂]₂¹

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compounds and the present results permit the same rationalization. Addition of a nucleophilic molecule to [RhCl(CO)(C₂H₄)₂]₂ leads to a dinuclear-pentacoordinated transition state whatever the basicity and hardness of the entering ligand; isolation of the W₂ compounds whose geometry is probably strongly related to the transition state supports this proposition. Isolation of the RhCl(CO)(C₂H₄)(2,6-lut) complex shows that two paths are in competition when [RhCl(CO)L]₂ species are prepared from [RhCl(CO)(C₂H₄)₂]. By loss of ethylene in W₂ the [RhCl(CO)L]₂ compounds (Y₂) are obtained. When comparison was made to the chemistry of amines with platinum(II)-olefin complexes,^{46,47} no addition on the olefin was detected leading to the conclusion that ethylene appears to be the softest of the two electrophilic centers.

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Registry No. [RhCl(CO)(C₂H₄)(NH(C₂H₅)₂)₂]₂, 52613-54-4; [RhCl(CO)(NH(C₂H₅)₂)₂]₂, 52613-55-5; [RhCl(CO)(NH₂-*n*-C₃H₇)₂]₂, 52613-56-6; [RhCl(CO)(NC₃H₇)₂]₂, 52613-57-7; [RhCl(CO)(3,5-(CH₃)₂NC₅H₃)₂]₂, 52613-58-8; RhCl(CO)(2-(CH₃)NC₅H₄)₂, 52647-44-6; *cis*-RhCl(CO)(C₂H₄)(2,6-(CH₃)₂NC₅H₃)₂, 52613-59-9; *trans*-RhCl(CO)(C₂H₄)(2,6-(CH₃)₂NC₅H₃)₂, 52646-57-8; *cis*-RhCl(CO)(P(CH₃)₃)(2,6-(CH₃)₂NC₅H₃)₂, 52613-60-2; *trans*-RhCl(CO)(P(CH₃)₃)(2,6-(CH₃)₂NC₅H₃)₂, 52646-58-9; *cis*-RhCl(CO)(P(CH₃)₂C₆H₅)(2,6-(CH₃)₂NC₅H₃)₂, 52613-61-3; *trans*-RhCl(CO)(P(CH₃)₂C₆H₅)(2,6-(CH₃)₂NC₅H₃)₂, 52646-59-0; [RhCl(CO)(C₂H₄)₂], 12306-60-4; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; P(CH₃)₃, 594-09-2; [RhCl(CO)P(CH₃)₃]₂, 49634-24-4.

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Sulfate Coordination. Molecular Structure of Chlorosulfatonitrosylbis(triphenylphosphine)ruthenium(II), RuCl(SO₄)(NO)(PPh₃)₂

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The crystal and molecular structure of chlorosulfatonitrosylbis(triphenylphosphine)ruthenium(II), RuCl(SO₄)(NO)(PPh₃)₂, has been determined from three-dimensional X-ray data collected by counter methods using the θ - 2θ scan technique. The complex crystallizes in space group *Pbcn* (*D*_{2h}¹⁴) of the orthorhombic system with four molecules in a unit cell of dimensions $a = 19.65$ (1) Å, $b = 10.79$ (1) Å, $c = 15.73$ (1) Å; $V = 3334$ Å³; $\rho_{\text{exptl}} = 1.55$ (2) g/cm³ and $\rho_{\text{calcd}} = 1.55$ g/cm³ for $Z = 4$. The structure was solved by standard Patterson and Fourier methods and has been refined by least squares to an agreement factor R of 0.054 based on 86 variables and 1192 reflections having $F_o^2 > 2\sigma(F_o^2)$. The coordination geometry in the complex is a distorted octahedron with the sulfate ligand coordinating in a bidentate manner. Because the complex is crystallographically required to have a twofold axis of symmetry, the chloride and nitrosyl ligands are disordered as has been observed in several similar structures. The refinement procedure allows for one-half chloride and one-half nitrosyl at each position. With regard to the sulfate coordination, the average Ru-O bond length is 2.079 (7) Å, and the O-Ru-O bond angle is 68.7 (4)^o. Moreover, the ruthenium, sulfur, and coordinating oxygen atoms are coplanar. As expected, the sulfate is a slightly distorted tetrahedron. Other important structural parameters are S-O(coordinating) = 1.552 (8) Å, S-O(noncoordinating) = 1.451 (8) Å, Ru-P = 2.454 (3) Å, Ru-N(nitrosyl) = 1.80 (3) Å, and Ru-N-O = 175 (3)^o.

Introduction

The catalyzed oxidation of sulfur dioxide to sulfate using transition metal complexes is an interesting and important chemical reaction whose relevance to industrial oxygenation

processes may help in controlling SO₂ in exhaust gases. To date, studies on this oxidation reaction have focused on group VIII metal complexes, particularly those containing dioxygen as a ligand, and general reactions 1 and 2 have been

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