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LOW OXIDATION STATE RUTHENIUM CHEMISTRY

III *. THE REACTIONS OF AMINES WITH $[Ru(CO)_3Cl_2]_2$ AND RELATED COMPLEXES

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Summary

Carbamoyl complexes of ruthenium(II), $Ru(CO)_2(RNH_2)_2Cl(CONHR)$, have been isolated from the reactions of $[Ru(CO)_3Cl_2]_2$ with the amines RNH_2 (R = Bu^t, Bu^n, p-MeC_6H_4, p-$MeOC_6H_4$). By reaction of the carbamoyl complex (R = p-MeC_6H_4) with triphenylphosphine and hydrochloric acid the derivatives $Ru(CO)_2(PPh_3)_2Cl(CONHR)$ and $[Ru(CO)_3(RNH_2)_2Cl]^+Cl^-$ have been obtained. The complex $Ru(PPh_3)_3Cl_2$ did not give fully characterizable products in reactions with aromatic amines and carbon monoxide, but reacted with hydrazines and CO to give the complexes $[Ru(PPh_3)L(NH_2{-}NH_2)Cl_2]_2$ (L = PPh_3, CO) and $Ru(PPh_3)_2L(PhNH{-}NH_2)Cl_2$ (L = $PhNH{-}NH_2$, CO).

Introduction

During our studies on the reactions of organic azides RN_3 with carbonyl complexes of transition metals in low oxidation states, we prepared isocyanate derivatives by treatment of RN_3 with coordinated carbon monoxide [1] (eq. 1a), a reaction discovered by Collman [2]:

$$L_nMCO + RN_3 \rightarrow L_nM(RNCO) + N_2 \qquad (1a)$$

$$L_nM(RNCO) + HX \rightarrow [L_nM(CONHR)]^+(X^-) \qquad (1b)$$

Protonation of the isocyanate complexes with mineral acids readily gave carbamoyl derivatives [1] (eq. 1b). It is well known that carbamoyl complexes can be obtained by nucleophilic attack of aliphatic amines on coordinated car-

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* For part II see ref. 13.

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bon monoxide [3] and the reaction of $COCl_2$ with primary amines is the commonest route to organic isocyanates [4] (eq. 2):

$$COCl_2 + 3\ RNH_2 \xrightarrow{-RNH_2\cdot HCl} RNHCOCl \xrightarrow{-RNH_2\cdot HCl} RNCO \qquad (2)$$

Moreover a carbamoyl palladium complex has been suggested [3] as an intermediate during the reaction of amines with CO in the presence of palladium(II) chloride to give isocyanates [5]. We thus undertook a study of the reactions of amines with a dichlorocarbonyl complex, $[Ru(CO)_3Cl_2]_2$, with the objective of producing chlorocarbamoyl complexes, which would give isocyanate derivatives by loss of HCl.

Chlorocarbamoyl complexes of palladium and platinum have been recently reported [3b]. We have also studied the reactions of $Ru(PPh_3)_3Cl_2$ with amines, and the reactions of the products with carbon monoxide.

Results and discussion

Reactions of $[Ru(CO)_3Cl_2]_2$ with amines

$[Ru(CO)_3Cl_2]_2$ reacts with primary amines giving chlorocarbamoyl complexes according to eq. 3 (Table 1):

$$[Ru(CO)_3Cl_2]_2 + 8\ RNH_2 \xrightarrow{CHCl_3} 2\ Ru(CO)_2(RNH_2)_2Cl(CONHR) + 2\ RNH_2\cdot HX$$

$$(R = Bu^t,\ I;\ Bu^n,\ II;\ p\text{-}MeC_6H_4,\ III;\ p\text{-}MeOC_6H_4,\ IV) \qquad (3)$$

Secondary amines did not give readily characterizable products. These reactions usually involve aliphatic amines and cationic carbonyl complexes [3] and it was of interest that aromatic amines also react, although under slightly more drastic conditions (at reflux) than those for the aliphatic amines (room temperature). A cationic ruthenium—carbonyl complex is probably involved as an intermediate even in reaction 3, and this point is considered below. In all cases the reaction also gives the salts $RNH_2\cdot HX$. Even when reaction 3 ($R = p\text{-}MeC_6H_4$) was carried out in THF at 100°C and under CO pressure (20 atm), compound III was the only product isolated.

When we attempted the reactions with the bromo complex, $[Ru(CO)_3Br_2]_2$ in bromoform as solvent, rates were lower and the products more difficult to purify. Only compound V, $[Ru(CO)_2(p\text{-}MeC_6H_4NH_2)Br(CONHC_6H_4Me\text{-}p)]_x$, gave acceptable elemental analyses. This compound is possibly dimeric with bridging bromines ($x = 2$), having only five ligands per metal atom. The observed mol.wt. is distinctly higher than that required for a monomer (Table 1), but not satisfactory for a dimeric formulation. However the mol.wt.'s were not very satisfactory even for the 6-coordinated derivatives, being slightly higher in some cases than required; a fact for which we have no explanation. Compounds I and III react with triphenylphosphine in benzene to give the corresponding carbamoyl derivatives with triphenylphosphine ligands (eq. 4):

$$Ru(CO)_2(RNH_2)_2Cl(CONHR) + 2\ PPh_3 \rightarrow \underset{(VI)}{Ru(CO)_2(PPh_3)_2Cl(CONHR)} + 2\ RNH_2 \qquad (4)$$

However only compound VI ($R = p\text{-}MeC_6H_4$) could be easily isolated (see ex-

TABLE 1

ANALYTICAL DATA FOR CARBAMOYL COMPLEXES OF RUTHENIUM

No.	Compound	Colour	Melting point (°C)	Analyses found (calcd.) (%)					Mol.wt. in $CHCl_3$
				C	H	N	Cl or Br	O	
I	$Ru(CO)_2(Bu^tNH_2)_2Cl(CONHBu^t)$	white	152	40.47 (41.04)	7.50 (7.29)	9.50 (9.56)	8.52 (8.10)	—	557 (439)
II	$Ru(CO)_2(Bu^nNH_2)_2Cl(CONHBu^n)$	white	149	39.7 (41.0)	6.90 (7.29)	9.03 (9.56)	8.64 (8.10)	—	515 (439)
III	$Ru(CO)_2(p\text{-}MeC_6H_4NH_2)_2Cl(CONHC_6H_4Me\text{-}p)$	white	165—70	52.90—53.96 (53.23)	4.59—4.46 (4.78)	7.80—7.91 (7.76)	7.12 (6.54)	8.38 (8.86)	593 (541)
IV	$Ru(CO)_2(p\text{-}MeOC_6H_4NH_2)_2Cl(CONHC_6H_4OMe\text{-}p)$	white	140—44	47.91 (48.90)	4.21 (4.41)	7.03 (7.14)	—	—	414 (589)
V	$[Ru(CO)_2(p\text{-}MeC_6H_4NH_2)Br(CONHC_6H_4Me\text{-}p)]_x$	pale-yellow	>230	42.35 (42.67)	4.09 (3.56)	5.92 (5.87)	16.88 (16.70)	—	650 (478)
VI	$Ru(CO)_2(PPh_3)_2Cl(CONHC_6H_4Me\text{-}p)$	white	154	63.40—66.11 (64.87)	4.30—4.54 (4.45)	1.78—1.65 (1.64)	4.5—4.9 (4.17)	5.51 (5.64)	822 (851)
VII	$[Ru(CO)_3(p\text{-}MeC_6H_4NH_2)_2Cl]^+Cl^-$	white	—	43.03 (43.34)	3.47 (3.83)	5.72 (5.96)	15.13 (15.10)	—	—

perimental), and these derivatives appear to be rather unstable, especially in solution. When reaction 4 was conducted in chloroform only the white *cis*-$Ru(CO)_2(PPh_3)_2Cl_2$ was isolated. Like I—V, compound VI is a non-conductor in nitrobenzene.

The presence of the carbamoyl ligand in these compounds was confirmed by oxygen analyses (compounds III and VI) and by reaction of compound III with hydrochloric acid in a non polar solvent, such as benzene, in which the product is insoluble (eq. 5) (cf. ref. 3) (Table 1):

$$\underset{\text{(III)}}{Ru(CO)_2(RNH_2)_2Cl(CONHR)} + 2\,HCl \rightarrow \underset{\text{(VII: R = }p\text{-MeC}_6\text{H}_4\text{)}}{[Ru(CO)_3(RNH_2)_2Cl]^+Cl^-} + RNH_2 \cdot HCl \qquad (5)$$

The IR data for compound VII (Table 2) are in accordance with its formulation; in particular three $\nu(C{\equiv}O)$ bands were present in the carbonyl stretching region. The ^1H NMR data of compound VII are not reported because this derivative is unstable in solution, nucleophilic attack by the anion giving a non ionic product which has not been fully investigated. Our formulation of VII as an ionic compound is based only on the 6-coordination of this cation. Compound VII is probably the cationic intermediate formed during reaction 1. Compounds I—VI presumably should produce isocyanate complexes of formula $Ru(CO)_2L_2(RNCO)$ by loss of HCl. We found that reaction did take place with strong organic or inorganic bases but the products could not be characterized. Ruthenium—isocyanate complexes having L = PPh_3 and R = $\mathrm{Ar}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}$ have been made by another route [6], but their stability was attributed to the formation of a metallacycle involving the $>C{=}O$ group of the aroyl isocyanate ligand.

In their IR spectra compounds I—VI show two $\nu(C{\equiv}O)$ bands of equal intensity, indicative of a *cis*-arrangement of the carbonyl groups (in some preparations, compounds III, IV and V also gave a very weak band at higher frequencies).

TABLE 2

SPECTROSCOPIC DATA FOR CARBAMOYL COMPLEXES OF RUTHENIUM

No.	IR absorption bands in nujol (cm^{-1})				^1H NMR spectra in $CDCl_3$		
	$\nu(NH)$	$\nu(NH_2)$	$\nu(C{\equiv}O)$	$\nu(C{=}O)$ + $\delta(NH, NH_2)$ [a]	$\tau(NH_2)$	$\tau(NH)$	$\tau(R)$
I	3440	3265—3240	2035—1960	1605—1580	6.6	4.1	8.68—8.71 [e]
II	3360	3280—3230	2035—1960	1590—1550	[b]	[b]	[b]
III	3435	3220—3120	2055—1985	1620—1605—1590	6.7	4.35	7.66—7.78
IV	3420	3220—3110	2050—1980	1615—1605—1585	[c]	4.3 [c]	6.27—6.34 [c]
V	3430	3210—3120	2060—1980	1625—1600—1580	[d]	4.92	7.74
VI	3330	—	2060—1970	1595—1580	—	4.7	—
VII	—	3230—3170	2130—2080 2060	1605—1575	—	—	—

[a] The absorptions due to aromatic rings are probably hidden by these medium-strong bands. [b] Broad and complex signals between τ 8 and 9.5 and between 6 and 7.5 ppm: C_6D_6 as solvent. [c] Probably overlapping with the signals due to R; deuteroacetone as solvent. [d] Not clearly detectable. [e] In deuteroacetone; in $CDCl_3$ a single signal was observed at τ 8.7 ppm, while $\tau(NH)$ and $\tau(NH_2)$ have been detected at τ 4.7 and 7 ppm respectively.

Three bands were observed for compounds I—V in the 3450—3100 cm^{-1} region. The absorption at higher frequency is attributed to ν(NH) of the carbamoyl group, since the two vibrations at lower frequencies are absent in compound VI, in which the amine has been replaced by triphenylphosphine. In the 1600 cm^{-1} region more and broad absorptions were observed, probably due to $\nu(>C{=}O)$ of the carbamoyl group and to δ(NH) of the amines and RNHCO- ligands.

The ^1H NMR spectra (Table 2) in most cases showed broad signals due to $\tau(NH_2)$ and τ(NH), these signals generally disappeared on treatment with D_2O. Compounds I, III and IV also show two distinct signals due to the *para* substituent of the aromatic amines or to the Bu^t groups; these signals were approximately in the expected 2 : 1 ratio.

Reactions of $Ru(PPh_3)_3Cl_2$ with hydrazines and carbon monoxide

$Ru(PPh_3)_3Cl_2$ reacts with pyridine to give $Ru(amine)_2(PPh_3)_2Cl_2$ [7]. It also readily reacted in benzene with aromatic amines, but the violet products isolated from these reactions did not give satisfactory elemental analyses. By carbonylation of these materials, at atmospheric pressure, we isolated products which analysed correctly as $Ru(CO)(PPh_3)(RNH_2)_2Cl_2$ (R = p-MeC_6H_4, p-$MeOC_6H_4$) (see experimental). However the IR spectra of these compounds showed a broad $\nu(C{\equiv}O)$ band below 2000 cm^{-1}, possibly due to the presence of other isomers.

Well defined products have been isolated from the reactions of $Ru(PPh_3)_3Cl_2$ with hydrazines (eq. 6) (Table 3):

$$Ru(PPh_3)_3Cl_2 + RNH{-}NH_2 \rightarrow [Ru(RNH{-}NH_2)_n(PPh_3)_2Cl_2]_m \qquad (6)$$

(VIII): R = Ph; $n = 2$; $m = 1$
(IX): R = H; $n = 1$; $m = 2$

Compound IX is probably dimeric with bridging hydrazine, but the phenylhydrazine derivative VIII adopts a monomeric structure because of the steric effect of the phenyl substituent. Such a proposal was made for the ruthenium complexes [e.g. compound IX] isolated from the reaction of $RuCl_3(Ph_3)_3$ with hydrazines [8].

Support for these formulations came from the reactions of these compounds with carbon monoxide in which one molecule of PhNH—NH_2 was displaced from compound VIII, and one phosphine replaced by CO in compound IX (eq. 7):

$$Ru(PhNH{-}NH_2)_2(PPh_3)_2Cl_2 + CO \rightarrow \underset{(X)}{Ru(PhNH{-}NH_2)(CO)(PPh_3)_2Cl_2} + PhNH{-}NH_2 \qquad (7)$$

$$[Ru(NH_2{-}NH_2)(PPh_3)_2Cl_2]_2 + CO \rightarrow \underset{(XI)}{[Ru(NH_2{-}NH_2)(CO)(PPh_3)Cl_2]_2} + PPh_3$$

The IR data for compounds VIII—XI (Table 4) agree with our formulations, and the ν(Ru—Cl) bands suggest a *trans* configuration of chlorines. In no case did we observe a reaction between CO and the coordinated amine or hydrazine.

TABLE 3

ANALYTICAL DATA FOR HYDRAZINE DERIVATIVES OF RUTHENIUM [a]

No.	Compound	Colour	Analyses found (calcd.) (%)				Mol. wt. [b]
			C	H	N	Cl	
VIII	$Ru(PPh_3)_2(PhNH{-}NH_2)_2Cl_2$	brown	62.77 (63.10)	4.82 (5.05)	5.95 (6.14)	7.25 (7.76)	750 (912)
IX	$[Ru(PPh_3)_2(NH_2{-}NH_2)Cl_2]_2$	yellow-orange	59.39 (59.34)	4.76 (4.67)	3.49 (3.85)	8.41 (9.77)	1140 (1456)
X	$Ru(CO)(PPh_3)_2(PhNH{-}NH_2)Cl_2$	yellow	62.24 (62.02)	4.43 (4.56)	3.82 (3.36)	8.05 (6.52)	834 [c] (832)
XI	$[Ru(CO)(PPh_3)(NH_2{-}NH_2)Cl_2]_2$	pale-yellow	46.19 (46.15)	3.85 (3.85)	5.21 (5.66)	—	978 (988)

[a] All compounds are non conductors in nitrobenzene solution. [b] $CHCl_3$ as solvent. [c] Benzene as solvent.

TABLE 4

IR ABSORPTION BANDS IN NUJOL (cm^{-1}) FOR HYDRAZINE DERIVATIVES OF RUTHENIUM

No.	ν(NH)	ν(CO)	ν(Ru—Cl)
VIII	3280(sh), 3250m, 3170vw	—	320
IX	3290(sh), 3280m, 3200vw, 3160vw	—	320
X	3270m	1940	330
XI	[a]	1960	330

[a] Several bands in the 3300—3100 cm^{-1} region.

Experimental

All reactions were carried out under nitrogen. Reaction mixtures were worked up in the air, unless otherwise stated. Solvents were dry and purified.

The starting complexes $[Ru(CO)_3Cl_2]_2$ [9], $[Ru(CO)_3Br_2]_2$ [10] and $Ru(PPh_3)_3Cl_2$ [11] were prepared by published procedures. IR spectra were obtained using a Perkin—Elmer 457 instrument. ^1H NMR spectra were recorded on a Varian 60 spectrometer with Me_4Si as internal standard. Elemental analyses were carried out in the analytical laboratory of Milan University, except for oxygen analyses which were carried out by Pascher's Analytical Laboratories, Bonn.

$Ru(CO)_2(Bu^tNH_2)_2Cl(CONHBu^t)$ (I)

To a suspension of $[Ru(CO)_3Cl_2]_2$ (0.2 g) in chloroform (15 ml) was added Bu^tNH_2 (0.5 ml). A clear solution was immediately formed. After few minutes a white product precipitated, and after 1 h this was filtered off and shown to be $Bu^tNH_2 \cdot HCl$ by comparison of its IR spectrum with that of an authentic sample. The chloroform solution was evaporated almost to dryness and n-hexane added to give a white precipitate. This was filtered off, washed repeatedly with water (ca. 100 ml) to remove $Bu^tNH_2 \cdot HCl$, then with n-hexane, and was dried in vacuo (yield ca. 60%). The compound can be crystallized from chloroform/n-hexane in the presence of free Bu^tNH_2.

$Ru(CO)_2(Bu^nNH_2)_2Cl(CONHBu^n)$ (II)

This compound was prepared as described for I but with a 3 h reaction time. Evaporation to dryness of the chloroform solution and prolonged scratching of the oily residue in presence of n-hexane gave a white powder. This was filtered off, washed repeatedly with water and n-hexane, and dried in vacuo.

$Ru(CO)_2(p\text{-}MeC_6H_4NH_2)_2Cl(CONHC_6H_4Me\text{-}p)$ (III)

(a) To a suspension of $[Ru(CO)_3Cl_2]_2$ (0.2 g) in chloroform (20 ml) was added p-$MeC_6H_4NH_2$ (0.6 g). The solution was refluxed for 2 h during which a little white precipitate formed (and was shown to be p-$MeC_6H_4NH_2 \cdot HCl$ by IR spectroscopy). The solution was evaporated almost to dryness, and addition of n-hexane followed by scratching gave a white powder. This was filtered off, washed repeatedly with water to remove p-$MeC_6H_4NH_2 \cdot HCl$ and then with ethyl ether and finally dried in vacuo (yield ca. 70%).

TABLE 4

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No.	ν(NH)	ν(CO)	ν(Ru—Cl)
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This compound was prepared as described for I but with a 3 h reaction time. Evaporation to dryness of the chloroform solution and prolonged scratching of the oily residue in presence of n-hexane gave a white powder. This was filtered off, washed repeatedly with water and n-hexane, and dried in vacuo.

$Ru(CO)_2(p\text{-}MeC_6H_4NH_2)_2Cl(CONHC_6H_4Me\text{-}p)$ (III)

(a) To a suspension of $[Ru(CO)_3Cl_2]_2$ (0.2 g) in chloroform (20 ml) was added $p\text{-}MeC_6H_4NH_2$ (0.6 g). The solution was refluxed for 2 h during which a little white precipitate formed (and was shown to be $p\text{-}MeC_6H_4NH_2 \cdot HCl$ by IR spectroscopy). The solution was evaporated almost to dryness, and addition of n-hexane followed by scratching gave a white powder. This was filtered off, washed repeatedly with water to remove $p\text{-}MeC_6H_4NH_2 \cdot HCl$ and then with ethyl ether and finally dried in vacuo (yield ca. 70%).

$Ru(CO)(PPh_3)_2(PhNH{-}NH_2)Cl_2$ *(X)*

Compound VIII (0.16 g) was added to benzene (20 ml) while CO was bubbled through. The initial brown solution became yellow. After two days the solution was evaporated to small volume, and on addition of n-hexane the yellow product precipitated. It was filtered off, washed with n-hexane and dried in vacuo.

$[Ru(CO)(PPh_3)(NH_2{-}NH_2)Cl_2]_2$ *(XI)*

Compound IX (0.1 g) was suspended in chloroform (25 ml) while CO was bubbled through. After 12 h the lemon-yellow solution was evaporated to small volume, and addition of n-hexane gave a pale-yellow product precipitated, which was filtered off, washed with n-hexane, and dried in vacuo.

Reactions of $Ru(PPh_3)_3Cl_2$ *with aromatic amines and carbon monoxide*

$Ru(PPh_3)_3Cl_2$ (0.25 g) and p-$MeC_6H_4NH_2$ (0.14 g) were added to benzene (20 ml). After 6 h the red-violet solution was evaporated to small volume and n-hexane was added. The red-violet precipitate (0.1 g) was filtered off, washed with n-hexane and some of it was dissolved in benzene (15 ml) while CO was bubbled through. After 5 h the solution was evaporated to small volume and addition of n-hexane gave a grey precipitate. This was filtered off, washed with n-hexane, and dried in vacuo. It (m.p. 140°C) analysed as $Ru(CO)(PPh_3)(p\text{-}MeC_6H_4NH_2)_2Cl_2$, found: C, 58.70; H, 4.48; N, 3.93; Cl, 9.90; mol. wt., 714 in $CHCl_3$. Calcd.: C, 58.50; H, 4.88; N, 4.13; Cl, 10.49%; mol. wt., 676. $\nu(C{\equiv}O)$ 1990(br) cm^{-1}, nujol mull. Similar results were obtained when p-$MeOC_6H_4NH_2$ was used.

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