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# INFRARED SPECTRA AND REACTIVITY OF DI-$\mu$-HALOBIS(HALOTRICARBONYLRUTHENIUM)

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## SUMMARY

The IR spectra of the di-$\mu$-halobis(halotricarbonylruthenium) complexes of formula $[Ru(CO)_3X_2]_2$ (X=Cl, Br) have been studied in different solvents and a tentative assignment of the bands observed made. The change with time of the IR spectra in chloroform solution observed by several authors is due to the interaction of the compounds with the ethanol present in the solvent as stabilizer.

The reactions of $[Ru(CO)_3X_2]_2$ (X=Cl, Br) with oxygenated solvents, nitrogen and phosphorous ligands are described. Some complexes of type $RuX_2(CO)_3L$ and $RuX_2(CO)_2L_2$ (L=nitriles, pyridine or triphenylphosphine) have been isolated and characterized.

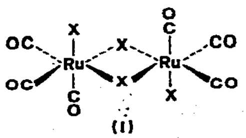
## INTRODUCTION

Di-$\mu$-halobis(halotricarbonylruthenium) complexes of formula $[Ru(CO)_3X_2]_2$ (X=Cl, Br) have been synthesized by several methods[1-8]. The IR spectra reported by various authors[1-9] differ in the carbonyl stretching region, and this had led to conflicting conclusions about the molecular structure[3,5-8]. The purpose of this paper is to suggest an explanation of the IR discrepancies, and to report the results obtained by studying the reactions of these compounds with various ligands.

## RESULTS AND DISCUSSION

### *IR spectra*

The di-$\mu$-halobis(halotricarbonylruthenium) complexes used in this study were synthesized by treating $Ru_3(CO)_{12}$ with halomethanes. The molecular structure, according to the X-ray diffraction studies by Merlino and Montagnoli[10,11], is (I) ($C_{2h}$ symmetry).



(I)

(*continued on p.* 364)

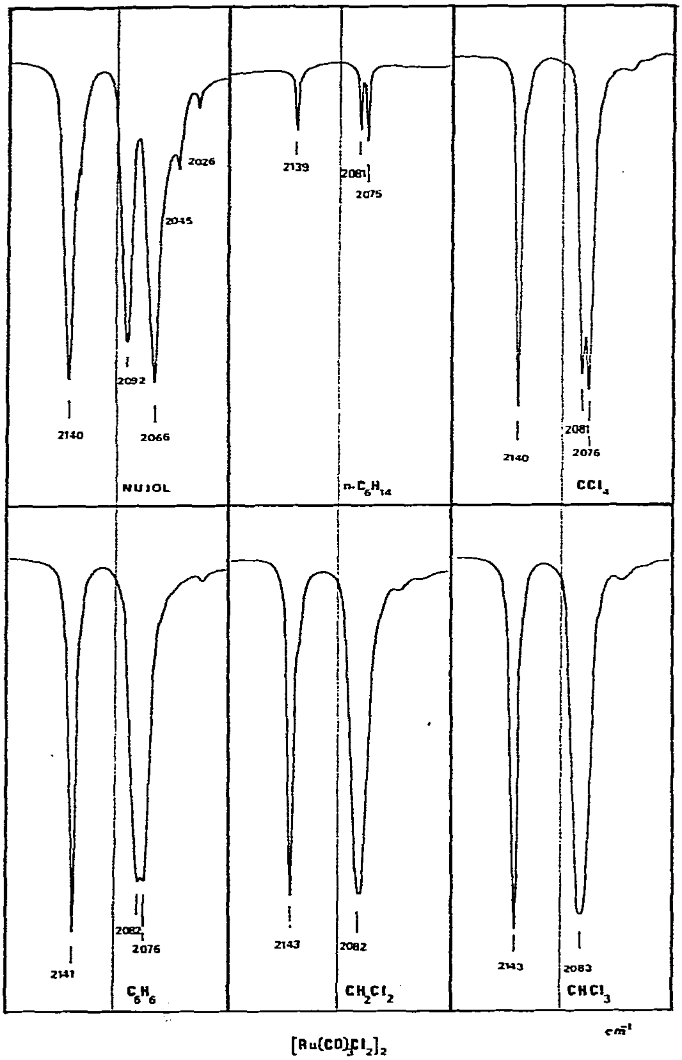


Fig. 1a. IR spectra in the carbonyl stretching region of $[Ru(CO)_3Cl_2]_2$ in various solvents.

TABLE 1

NUMBER, SPECIES AND IR ACTIVITY OF $[Ru(CO)_3X_2]_2$ (X=Cl, Br)

| *Species* | *IR* | *ν(C≡O) or ν(Ru–C)* | *δ(Ru–C–O)* | *ν(Ru–X)* |
|---|---|---|---|---|
| $A_g$ | ia | 2 | 3 | 2 |
| $B_g$ | ia | 1 | 3 | 1 |
| $A_u$ | a | 1 | 3 | 1 |
| $B_u$ | a | 2 | 3 | 2 |

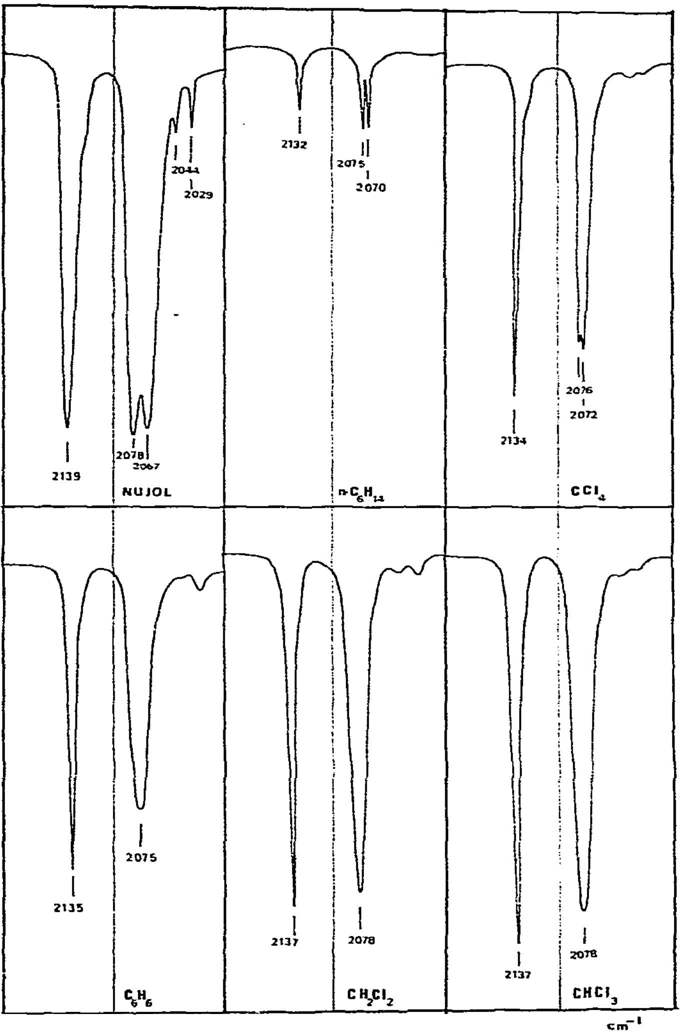


Fig. 1b. IR spectra in the carbonyl stretching region of $[Ru(CO)_3Br_2]_2$ in various solvents.

TABLE 2

IR ABSORPTIONS ($cm^{-1}$) IN THE CARBONYL STRETCHING REGION OF $[Ru(CO)_3X_2]_2$ ($X=Cl, Br$)[a]

| *Medium* | $[Ru(CO)_3Cl_2]_2$ | $[Ru(CO)_3Br_2]_2$ |
|---|---|---|
| Nujol | 2140, 2092, 2066 | 2139, 2078, 2067 |
| n-Hexane | 2139, 2081, 2075 | 2132, 2075, 2070 |
| Carbon tetrachloride | 2140, 2082, 2076 | 2134, 2076, 2072 |
| Benzene | 2141, 2082, 2076 | 2135, 2075 |
| Chloroform[b] | 2143, 2083 | 2137, 2078 |
| Methylene chloride | 2143, 2082 | 2137, 2078 |

[a] Only the bands of high intensity are reported. [b] Free of ethanol.

TABLE 3

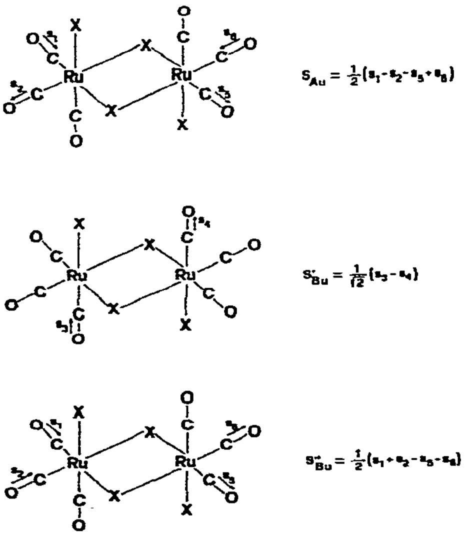
IR ABSORPTIONS ($cm^{-1}$) IN THE 650–150 $cm^{-1}$ REGION OF $[Ru(CO)_3X_2]_2$ (X=Cl, Br)[a]

| *Complex* | *δ(Ru–C–) and ν(Ru–C)* | *ν(Ru–X$_t$)* | *ν(Ru–X$_b$)* |
|---|---|---|---|
| $[Ru(CO)_3Cl_2]_2$ | 610, 576, 565, 476<br>464, 458, 436, 411 | 331 | 290, 260 |
| $[Ru(CO)_3Br_2]_2$ | 604, 562, 555, 473<br>459, 443, 426, 407 | 234 | 211, 195 |

[a] Nujol mull.

The number, symmetry species and IR activity of the normal modes for structure (I) are reported in Table 1. The IR spectra of the compounds in the solid state have been examined in the 2200–150 $cm^{-1}$ region (Nujol), while their spectra in solution have been examined only in the carbonyl stretching region owing to limited solubility. The frequencies in the carbonyl stretching region are listed in Table 2 and the spectra shown in Fig. 1 (a and b), while the frequencies of the Ru–C–O bending, Ru–C stretching and of the terminal and bridging Ru–X stretching modes are listed in Table 3.

As shown in Table 1, in the carbonyl stretching region, three IR bands are expected and three bands are observed in Nujol, n-hexane, carbon tetrachloride and benzene, having nearly the same intensity according to the calculation of the band intensity by the method of oscillating dipoles. In methylene chloride and chloroform solution, owing to the higher solvent polarity, the two bands at lower frequency for the chloro and bromo derivatives are unresolved, and the spectra in these solvents show only two bands, a sharp one at higher frequency and a second at lower frequency, the latter being broadened probably because of overlap of two bands.



$$S_{Au} = \frac{1}{2}(s_1 - s_2 - s_5 + s_6)$$

$$S'_{Bu} = \frac{1}{\sqrt{2}}(s_3 - s_4)$$

$$S''_{Bu} = \frac{1}{2}(s_1 + s_2 - s_5 - s_6)$$

Fig. 2. Stretching symmetry coordinates of carbonyl groups.

According to El-Sayed and Kaesz[12], if the carbonyl group is regarded as an oscillating dipole the vibration modes in which the similar ends of the dipoles are facing each other (→M←) should in general have a higher stretching frequency with respect to the modes in which the similar ends of the dipole (→M→) are opposed. Representing the vibration modes as symmetry coordinates, it is possible to attribute the higher frequency band to the $S''_{B_u}$ vibration (Fig. 2), but for the other two bands, very close to each other, it is impossible to establish the assignment to $S'_{B_u}$ and $S_{A_u}$ vibrations.

As shown in Table 2, there is a shift towards higher frequencies of the bands in going from non-polar solvents such as n-hexane to polar ones such as chloroform. Hales and Irving[13] have taken this to imply an interaction of dipolar type between the halogen atoms of the complex and the solvent; in particular, they have observed a different behaviour of carbonyl groups in *cis* or *trans* position, in complexes of type $M(CO)_4X_2$, having an octahedral structure. Unfortunately, the frequency shifts in our compounds are very small (about 3 $cm^{-1}$) and nearly equal for the three bands, and therefore do not give significant information about the molecular structure.

As shown in Table 1, nine bands are expected in the Ru–C–O deformation and Ru–C stretching region, and eight of them are observed. It is very difficult to attribute these bands to the various vibration modes owing to the considerable coupling. However, the bands at higher frequencies may be attributed to the Ru–C–O deformation and the ones at lower frequencies assigned essentially to Ru–C stretching modes.

In the Ru–X stretching region three bands are observed, in agreement with the theory (Table 1). The bands at 331 and 234 $cm^{-1}$, for the chloro and the bromo derivative, respectively, are assigned to the terminal Ru–X stretching of $B_u$ species. The Ru–Br/Ru–Cl stretching ratio (0.7) is quite similar to the observed value for other analogous compounds[14]. The two bands at 290, 260 and 211, 195 $cm^{-1}$ for the chloro and the bromo derivatives, respectively, are assigned to the vibration of bridging halogens, corresponding to $A_u$ and $B_u$ species.

Our spectral data (Table 2) are not in agreement with those reported by other authors[2], who did not for $CCl_4$ solutions observe the splitting of the intense band at lower frequency in the carbonyl region; furthermore, our present data in $CHCl_3$ solution are different from those we obtained previously[4,7] and from the data recorded by others authors[3,5,6,8].

The change with time of the spectra in $CHCl_3$ solution and the different explanations of this suggested by various authors prompted us to reinvestigate this matter. Bruce and Stone[3], and Johnson *et al.*[6] have attributed the spectral behaviour in $CHCl_3$ to isomerization, while some of us[7] attribute it to a change of the structure due to an interaction with the solvent, and finally the simpler spectrum observed by Trovati *et al.*[8] was regarded as indicative of higher purity. By using chloroform carefully purified and free from stabilizing agents, we have been able to show that the above mentioned transformations are due to the ethanol present in very low concentration as a stabilizer in this solvent. Indeed the spectra in $CHCl_3$ free of ethanol do not change with time, and are quite analogous to those in $CH_2Cl_2$ solution. Furthermore, small amounts of ethanol added to $CH_2Cl_2$ solution of the complexes induce the transformations similar to those observed in stabilized chloroform (Fig. 3).

TABLE 4

PHYSICAL PROPERTIES AND IR SPECTRA OF THE COMPLEXES

| *Compound* | *M.p.* (°C) | *IR spectra* ($cm^{-1}$) | | | |
|---|---|---|---|---|---|
| | | $\nu(C{\equiv}N)$ | $\nu(C{\equiv}O)$ | $\nu(C{=}C)$ | $\nu(Ru{-}X)^c$ |
| *cis*-$RuCl_2(CO)_4$ | | | 2182 w, 2132 s, 2113 ms, 2080 s[a] | | |
| *cis*-$RuBr_2(CO)_4$ | | | 2178 w, 2124 s, 2110 m, 2078 m[a] | | |
| *cis*-$RuCl_2(CO)_3Py$ | 170–172 | | 2136 s, 2075 s, 2051 s[b] | | 322s, 303 s |
| *cis*-$RuCl_2(CO)_2Py_2$ | 264–266 | | 2070 s, 2006 s[b] | | 332 s |
| *cis*-$RuBr_2(CO)_2Py_2$ | 227–229 | | 2067 s, 2006 s[b] | | 276 s, 220 w |
| *cis*-$RuCl_2(C_2H_5CN)(CO)_3$ | 125 decomp. | 2296 w | 2141 s, 2082 s, 2064 s[b] | | 329 s, 315 m |
| *cis*-$RuBr_2(C_2H_5CN)(CO)_3$ | 125 decomp. | 2300 w | 2136 s, 2078 s, 2063 s[b] | | 226 m, 209 s |
| *cis*-$RuCl_2(C_2H_3CN)(CO)_3$ | 145 decomp. | 2285 w | 2141 s, 2084 s, 2066 s[b] | 1600 vw[c] | 339 s, 330 m |
| *cis*-$RuBr_2(C_2H_3CN)(CO)_3$ | 130 decomp. | 2285 w | 2136 s, 2080 s, 2064 s[b] | 1600 vw[c] | 235 s, 229 s |
| *cis*-$RuCl_2(C_6H_5CN)(CO)_3$ | 146–148 | 2286 mw | 2141 s, 2083 s, 2066 s[b] | | 329 s, 306 s |
| *cis*-$RuBr_2(C_6H_5CN)(CO)_3$ | 135 decomp. | 2284 mw | 2136 s, 2078 s, 2063 s[b] | | 228 s, 225 s, 210 s, 207 s |

[a] Methylene bromide.
[b] Methylene chloride.
[c] Nujol mull.

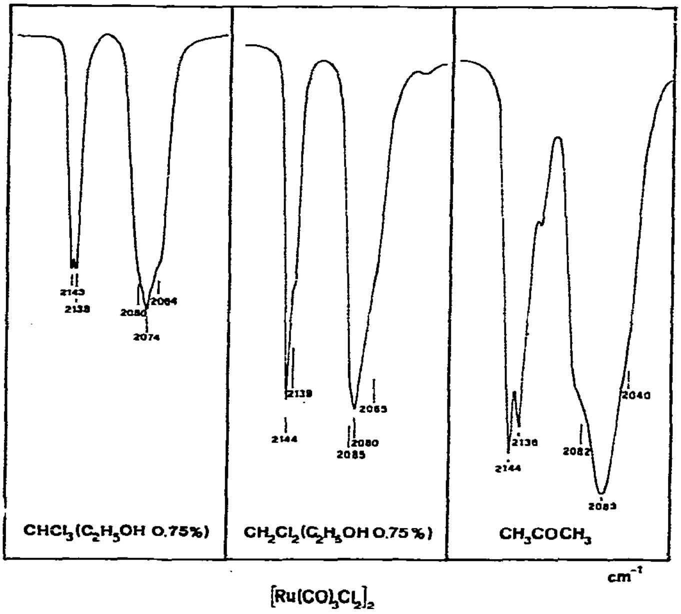


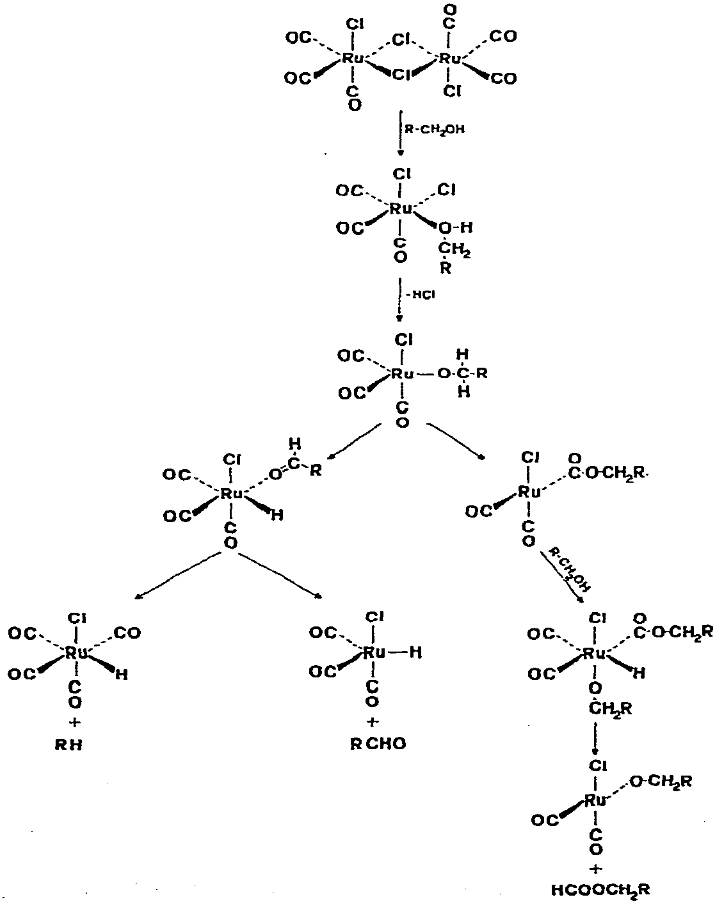
Fig. 3. IR spectra in the carbonyl stretching region of $[Ru(CO)_3Cl_2]_2$ in chloroform and methylene chloride containing ethanol and in acetone.

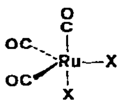
### *Interaction with oxygen containing ligands*

The pattern of the IR spectrum, in the carbonyl stretching region, of di-$\mu$-halobis(halotricarbonylruthenium), in acetone or in $CCl_4$/acetone solutions is similar to that observed in $CHCl_3$ stabilized with ethanol (Fig. 3). Using acetone we have been able to examine the Ru–X stretching region more carefully in the case of $[Ru(CO)_3Cl_2]_2$. In this region two new bands appear at 329 and 306 $cm^{-1}$, very close to the observed frequency for Ru–Cl stretchings in monomeric compounds of the type $RuCl_2(C_2H_5CN)(CO)_3$ and $RuCl_2(C_6H_5CN)(CO)_3$[15] (Table 4). In addition, the intensity of the bands of the bridging halogen atoms is decreased. Hence it is likely that acetone or ethanol cleaves the halogen bridge with formation of monomeric species which, upon evaporation of the solvent and crystallization, give back the starting dimeric compounds. This hypothesis is supported by the values of the molecular weights, determined by osmometric method in methyl ethyl ketone or ethanolic solution, which are nearly one-half of those of the dimeric compounds (Table 7).

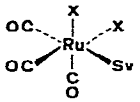
SCHEME 1

SUGGESTED MECHANISM FOR THE INTERACTION OF $[Ru(CO)_3Cl_2]_2$ WITH ALCOHOL. PATHWAYS FOR THE FORMATION OF ALDEHYDE, PARAFFIN AND ALKYL FORMATE





(II)



(III)

The monomeric species in oxygenated solvents may be a pentacoordinate form $Ru(CO)_3X_2$ (II) or a hexacoordinate one containing a molecule of solvent $Ru(CO)_3X_2Sv$ (Sv=acetone, ethanol) (III). For both the pentacoordinate structure (II) and the facial structure (III), three bands of the same intensity are predicted.

The interaction of ethanol with di-$\mu$-chlorobis(chlorotricarbonylruthenium) as indicated spectrophotometrically, was furthermore confirmed by the investigation of the products obtained by treating the dimeric compound with alcohols. With benzyl alcohol under an inert atmosphere at 150° benzaldehyde was obtained; with n-butanol at 100° and 2–3 atm of CO, propane was detected as a result of dehydrogenation and decarbonylation of the alcohol.

Moreover, in the synthesis of esters from olefins, carbon monoxide (30–50 atm), and alcohols at 190° in the presence of $[Ru(CO)_3Cl_2]_2$ as catalyst, dehydrogenation, decarbonylation and dehydration products of the alcohol used and alkyl formate were observed. The formation of these products suggests a direct interaction of the alcohol with the catalyst according to the mechanism proposed by Chatt, Shaw and Field[16] for the reaction of Ru-complexes with alcohols (Scheme 1). The presence in the same reaction of hydrogen chloride (nearly one-half the chlorine present in the catalyst), agrees also with the proposed mechanism.

### *Reaction with carbon monoxide*

Treatment of a $CH_2Br_2$ solution of the di-$\mu$-halobis(halotricarbonylruthenium) at 20–120° with carbon monoxide (80–100 atm) gives monomeric *cis*-$RuX_2(CO)_4$ (X=Cl, Br) compounds. The bromo derivative, $RuBr_2(CO)_4$ was obtained pure by crystallization, but the chloroderivative, $RuCl_2(CO)_4$, identified by its IR spectrum in solution (Table 4) could not be isolated, since in the absence of carbon monoxide it is rapidly converted into the dimeric form. The highest conversion of the dimer into the monomer is obtained at room temperature and high carbon monoxide pressure, as shown by studying the equilibrium (1) in a high-pressure IR cell[17].

$$[Ru(CO)_3Cl_2]_2 + 2\,CO \rightleftharpoons 2\,RuCl_2(CO)_4 \tag{1}$$

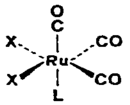
The IR spectra of the bromo and chloro derivatives correspond closely to those reported by Calderazzo and L'Eplattenier[18] and Johnson *et al.*[6] for the compound obtained by reacting $Ru(CO)_5$ with bromine and $Ru_3(CO)_{12}$ with chlorine, respectively.

### *Reaction with triphenylphosphine*

Treatment of $[Ru(CO)_3X_2]_2$ at 0° with triphenylphosphine ($[Ru(CO)_3X_2]_2/PPh_3 = 1/2$) causes cleavage of the halogen bridge and carbon monoxide is released, with formation of monomeric compounds of the type $RuX_2(CO)_2(PPh_3)_2$ (X=Cl, Br). The IR spectra in the carbonyl and Ru–X stretching regions suggest that these compounds have the carbonyl groups in *cis* positions and are identical with the products obtained by other authors under different conditions[1,3,19].

*Reaction with pyridine*

Different compounds were obtained by treating $[Ru(CO)_3X_2]_2$ with pyridine using a stoichiometric amount of the ligand at room temperature or an excess of pyridine at temperatures between 50 and 70° (Table 4). In the first case complexes of the type $RuX_2(CO)_3Py$ were formed by cleavage of the halogen bridge. The presence in the IR spectra in the carbonyl stretching region of three bands of the same intensity and two bands in the Ru–X stretching region suggests for the products the facial structure (IV) of $C_s$ symmetry.



(IV)
( X=Cl,Br; L=py,RCN)

At higher temperature and with an excess of pyridine, the products are the known complexes $RuX_2(CO)_2Py_2$, having the carbonyl groups in *cis* position (two bands in the 2200–1900 $cm^{-1}$ region) and the halogen atoms in *trans* position (one band in the Ru–X stretching region)[3,19].

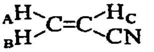
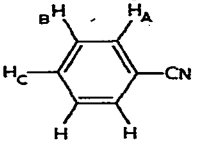
While for pyridine complexes only very small spectral differences have been observed between coordinated and free pyridine[20], our complexes $RuX_2(CO)_3Py$ and $RuX_2(CO)_2Py_2$ show considerable shifts of the ligand bands in the 900–1200 $cm^{-1}$ region. This may arise from a change of the symmetry of the coordinated molecule in the crystalline state of the complexes or from a pertubation of the electronic density of the pyridine ring as a consequence of coordination.

*Reaction with nitriles*

The halogen bridge of $[Ru(CO)_3X_2]_2$ complexes is readily cleaved by nitriles such as propionitrile, benzonitrile and acrylonitrile in 1,2-dichloroethane solution and complexes of the type $RuX_2(RCN)(CO)_3$ (X=Cl, Br; R=$C_2H_5$, $C_6H_5$, $CH_2$=

TABLE 5

PROTON NMR DATA FOR FREE NITRILES AND *cis*-$RuCl_2(RCN)(CO)_3$ COMPLEXES (IV) [δ (PPM)[a]]

| *Nitrile* | $\delta_A$ *RCN* | $\delta_A$ *(IV)* | $\Delta\delta_A$ | $\delta_B$ *RCN* | $\delta_B$ *(IV)* | $\Delta\delta_B$ | $\delta_C$ *RCN* | $\delta_C$ *(IV)* | $\Delta\delta_C$ |
|---|---|---|---|---|---|---|---|---|---|
| $\underset{B}{CH_3}-\underset{A}{CH_2}-CN$ | 2.36 | 2.92 | −0.56 | 1.20 | 1.48 | −0.28 | | | |
|  | 6.07 | 6.57 | −0.50 | 6.20 | 6.70 | −0.50 | 5.73 | 6.11 | −0.38 |
|  | 7.51 | 7.85 | −0.34 | 7.44 | 7.70 | −0.26 | 7.56 | 7.98 | −0.42 |

[a] From TMS at 60 MHz in $CDCl_3$.

CH) are formed (Table 4). The IR spectra show three bands of the same intensity in the carbonyl stretching region and two bands in the Ru–X stretching region: the data are consistent with structure (IV) having the CO groups and the halogen atoms in *cis* postion.

Coordination of the nitriles through the $\pi$ electron cloud must be considered but the shift of the CN stretching bands towards higher frequencies with respect to the free nitriles is in agreement with a coordination of the ligand through the nitrogen lone pair[21]. The NMR spectra (Table 5), in which a slight shift of the proton resonance towards lower fields with respect to the free ligand is observed, confirm that the coordination of the nitriles occurs through the nitrogen lone pair[22]. Coordination via the nitrile $\pi$-electrons should result in a much greater downfield shift[22]. In the acrylonitrile complexes, for which coordination to the metal through the C=C $\pi$ electrons is possible, the same kind of complexation occurs as shown by the presence of a nearly unperturbed C=C stretching band at 1600 $cm^{-1}$.

## EXPERIMENTAL

The compounds $[Ru(CO)_3Cl_2]_2$ and $[Ru(CO)_3Br_2]_2$ were prepared from $Ru_3(CO)_{12}$ and $CHCl_3$ or $CHBr_3$ according to literature procedures[7].

n-Hexane, benzene, carbon tetrachloride and acetone were distilled before use. Chloroform was carefully purified from ethanol by Budde's procedure[23]. Methylene chloride was purified according to Maryott *et al.*[24].

The IR spectra in the 4000–200 $cm^{-1}$ region were recorded with a Perkin–Elmer 225 spectrophotometer and those in the 400–150 $cm^{-1}$ with a Perkin–Elmer 301 spectrophotometer. The IR spectra of the products at high temperature and under high pressure of carbon monoxide were recorded with a Perkin–Elmer 221 spectrophotometer, using a high pressure IR cell of our own construction[17].

All proton NMR spectra were measured with a JEOL Model C 60 HL high-resolution spectrometer at 60 MHz.

Elemental analyses (Table 6) were carried out by Dr. A. Nuti, Facoltà di Farmacia, University of Pisa, Italy. Ruthenium analyses were carried out by reducing to the metal using a standard hydrogen reduction technique[25]. Molecular weights (Table 7) in solution were measured with a Mechrolab Osmometer.

### Reaction of $[Ru(CO)_3Cl_2]_2$ with alcohols

0.5 g of $[Ru(CO)_3Cl_2]_2$ was treated with 10 ml of n-butanol or benzyl alcohol at 100–150° under nitrogen. The gaseous and liquid products were analyzed by gas-chromatography. Benzaldehyde was characterized as its (2,4-dinitrophenyl)hydrazone.

### Reaction of $[Ru(CO)_3Br_2]_2$ with CO

A saturated methylene bromide solution of $[Ru(CO)_3Br_2]_2$ (0.5 g) was heated in an open glass vial introduced in an autoclave for 24 h at 70° under carbon monoxide (100 atm). The conversion of the product into *cis*-$Ru(CO)_4Br_2$ was quantitative.

### Reaction of $[Ru(CO)_3X_2]_2$ ($X = Cl, Br$) with triphenylphosphine

$[Ru(CO)_3X_2]_2$ (0.4 mmole) and triphenylphosphine (ca. 0.8 mmole) suspend-

TABLE 6

ANALYTICAL DATA FOR THE COMPLEXES

| *Compound* | *Analysis found (calcd.) (%)* | | | | | *Mol.wt.*[a] *found (calcd.)* |
|---|---|---|---|---|---|---|
| | *C* | *H* | *Hal* | *N* | *Ru* | |
| *cis*-$RuBr_2(CO)_4$ | 13.01 | | 41.82 | | 27.60 | |
| | (12.88) | | (42.90) | | (27.10) | |
| *cis*-$RuCl_2(CO)_2(PPh_3)_2$ | 60.21 | 3.92 | 9.50 | | | |
| | (60.64) | (4.02) | (9.42) | | | |
| *cis*-$RuBr_2(CO)_2(PPh_3)_2$ | 53.90 | 3.37 | 17.41 | | | |
| | (54.24) | (3.59) | (19.00) | | | |
| *cis*-$RuCl_2(CO)_3Py$ | 29.10 | 1.43 | 21.30 | 4.30 | | 345.0[b] |
| | (28.67) | (1.50) | (21.26) | (4.18) | | (335.1) |
| *cis*-$RuCl_2(CO)_2Py_2$ | 37.49 | 2.50 | 20.28 | 7.15 | | |
| | (37.29) | (2.61) | (18.36) | (7.25) | | |
| *cis*-$RuBr_2(CO)_2Py_2$ | 30.65 | 2.20 | 34.40 | 5.92 | 20.17 | 478.9[b] |
| | (30.31) | (2.12) | (33.64) | (5.89) | (21.27) | (475.1) |
| *cis*-$RuCl_2(C_2H_5CN)(CO)_3$ | 22.44 | 1.49 | 23.50 | 4.00 | 29.03 | |
| | (23.16) | (1.62) | (22.79) | (4.50) | (32·49) | |
| *cis*-$RuBr_2(C_2H_5CN)(CO)_3$ | 18.58 | 1.10 | 38.84 | 3.74 | | 360.8[c] |
| | (18.01) | (1.26) | (39.95) | (3.50) | | (400.0) |
| *cis*-$RuCl_2(C_2H_3CN)(CO)_3$ | 23.60 | 0.87 | 22.99 | 4.35 | | |
| | (23.32) | (0.97) | (22.95) | (4.53) | | |
| *cis*-$RuBr_2(C_2H_3CN)(CO)_3$ | 18.79 | 0.71 | 38.90 | 3.05 | 24.45 | 436.4[b] |
| | (18.11) | (0.76) | (40.16) | (3.52) | (25.39) | (398.0) |
| *cis*-$RuCl_2(C_6H_5CN)(CO)_3$ | 33.33 | 1.78 | 20.04 | 4.17 | | |
| | (33.44) | (1.40) | (19.74) | (3.90) | | |
| *cis*-$RuBr_2(C_6H_5CN)(CO)_3$ | 26.71 | 1.18 | 35.08 | 3.58 | 22.20 | 425.7[b] |
| | (26.81) | (1.13) | (35.67) | (3.12) | (22.55) | (448.0) |

[a] Mechrolab determinations.
[b] In benzene.
[c] In chloroform.

TABLE 7

MOLECULAR WEIGHTS OF $[Ru(CO)_3X_2]_2$ (X=Cl, Br) IN VARIOUS SOLVENTS[a]

| *Compound* | *Mol.wt. calcd.* | *Mol.wt. found* | *Solvent* |
|---|---|---|---|
| $[Ru(CO)_3Cl_2]_2$ | 512.08 | 412.3 | 1,2-Dichloroethane |
| | | 228.0 | Methyl ethyl ketone |
| | | 198.0 | Ethanol |
| $[Ru(CO)_3Br_2]_2$ | 689.92 | 575.3 | 1,2-Dichloroethane |
| | | 305.0 | Methyl ethyl ketone |
| | | 251.0 | Ethanol |

[a] Mechrolab determinations.

ed in methylene chloride (10 ml) were allowed to react under nitrogen at 0° until dissolution was complete (6 h). The solution was then concentrated under reduced pressure and the products of formula $RuX_2(CO)_2(PPh_3)_2$ were precipitated by adding pentane, and recrystallized as white crystals from methylene chloride/benzene solution.

*Reaction of* $[Ru(CO)_3X_2]_2$ *with pyridine*

*cis-Dichloro(tricarbonyl)pyridineruthenium(II).* $[Ru(CO)_3Cl_2]_2$ (0.6 mmole) and pyridine (1.2 mmoles) were allowed to react under nitrogen for 30 min in methylene chloride solution at room temperature until dissolution was complete. $RuCl_2(CO)_3Py$ was recrystallized from methylene chloride/pentane solution.

*cis-Dihalo(dicarbonyl)dipyridineruthenium(II).* These were made as described above for the triphenylphosphine complexes but using a large excess of pyridine (10 mmoles) in 1,2-dichloroethane. Pale yellow crystals were deposited after refluxing (5 h).and evaporation of the solvent. Recrystallization from a methylene chloride/pentane mixture gave the pure complexes (70% yield). The carbon monoxide evolved during the reaction was found to correspond very closely to one mole per mole of ruthenium.

*General procedure for the synthesis of* $RuX_2(CO)_3(RCN)$ $(X=Cl, Br; R=C_2H_5, CH_2{=}CH, C_6H_5)$

$[Ru(CO)_3X_2]_2$ (1 mmole) and a large excess of the ligand (50–70 mmoles) in 15–20 ml of 1,2-dichloroethane were allowed to react under nitrogen at 70° until dissolution was complete (3–5 h). The solutions were then concentrated under reduced pressure and the products were precipitated by adding n-pentane. The white or pale-yellow crystalline compounds were filtered, washed with n-pentane and dried under high vacuum. Purification was effected by recrystallization from methylene chloride/pentane solution. The yields of pure products were 70–80%.

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