

The Synthesis and Characterization of some Ru(II) Complexes Containing Carbon Monoxide and Isocyanide Groups*

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Abstract

A ruthenium complex containing both carbon monoxide and isocyanide ligands was synthesized. The complex was analyzed by several methods and was characterized as the dimer $\{\text{RuCl}_2[(\text{CH}_3)_3\text{CNC}]_2(\text{CO})\}_2$. Depending on the reaction temperature, two isomers, *trans* and *cis* were observed and were studied by means of infrared spectroscopy.

Introduction

Despite the continuing interest in isocyanide complexes of the platinum group of metals [1–3], there have been only a few reports of ruthenium compounds containing isocyanide ligands since the complexes of the type $\text{RuX}_2(\text{CNR})_4$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ or CN ; $\text{R} = \text{alkyl}$ or aryl group) were described [4–8]. However, none of the ruthenium isocyanide complexes described in the literature contains also coordinated carbon monoxide. The presence of both carbon monoxide and isocyanide ligands in one complex, preferably coordinated to the same ruthenium atom may be of considerable interest. In the vast majority of the isocyanide complexes, the isocyanide assumes the role of a terminal ligand, and its coordination properties are very similar to those of carbon monoxide. According to valence-bond models, actual bonding in such systems is represented by the central canonical forms where both σ and π contributions are expected to be significant and complementary. Hence, in view of this analogy, it seemed appropriate to synthesize ruthenium complexes containing both ligands and observe the mutual influence of these ligands which would be detected by their infrared spectra.

The synthetic approach chosen for this task was not a direct one, *i.e.* substitution of CO groups by

isocyanide groups, because in this case the isocyanide fully and irreversibly displaces the carbon monoxide groups. However, if the starting ruthenium carbonyl complex had 'empty' coordination sites, then it would be possible for the isocyanide ligands to enter the coordination sphere of the metal without displacing the carbon monoxide groups. The system chosen, therefore, for this reaction were the 'red' and 'yellow' ruthenium carbonyl solutions which have been shown to contain $[\text{RuCl}_2(\text{CO})_2]$ and $[\text{RuCl}_2(\text{CO})_3]$ species respectively [9, 10].

The use of these ruthenium carbonyl solutions as an entry port to ruthenium chemistry has been quite common in the pertinent literature. Moreover, the understanding of the composition of these solutions shall be further deepened due to this type of substitution reactions [11].

Experimental

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was purchased from Alfa Chemicals (Ventron Division) and Aldrich Chemicals. No differences between these two sources were observed in their reaction with carbon monoxide. All solvents (Fluka, spectroscopic grade) were dried on molecular sieves and redistilled before use. All infrared spectra were recorded on a Perkin-Elmer 467B grating infrared spectrophotometer.

A typical experiment was carried out in the following way: 1 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in 30 ml EtOH and placed in a 3-neck, 100 ml round bottom flask equipped with a magnetic stirrer. The solution was flushed with Ar and then heated to 78 °C by means of a silicone oil bath. When reflux started, the Ar inlet was removed, a bubbler was inserted into the free neck and then connected to the carbon monoxide source.

When the solution became wine red (or lemon–yellow in some cases), the heating was stopped, the CO was replaced with N_2 or Ar and the solution was allowed to reach room temperature. When the amount of carbon monoxide displaced from the

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TABLE I. Elementary Analysis for the Various Reactions of 'red' or 'yellow' Solutions with Butyl Isocyanide

	C (%)	H (%)	N (%)	Cl (%)
$\{\text{RuCl}_2[(\text{CH}_3)_3\text{CNC}]_2(\text{CO})\}_2$ theoretical	36.0	4.8	7.7	19.4
'yellow' + $(\text{CH}_3)_3\text{CNC}$ (1:4), reflux	36.9	4.8	8.5	19.8
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:4), reflux	36.4	4.8	8.5	18.9
'yellow' + $(\text{CH}_3)_3\text{CNC}$ (1:2), room temperature (RT)	35.5	4.7	8.2	17.4
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:2), RT	35.5	4.7	8.1	17.5
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:4), RT	36.4	4.7	8.5	17.9

solution was monitored, no gas was allowed to flow through the solution.

Then, 0.64 g and 1.28 g of $(\text{CH}_3)_3\text{CNC}$, corresponding to a twofold and fourfold molar excess respectively, were dissolved in 30 ml EtOH and added dropwise to the red (or yellow) ruthenium solution. The reaction mixture was thoroughly stirred for ~1 h at room temperature, until vigorous precipitation occurred. In cases in which higher temperatures were desired, the reaction mixture was refluxed for about the same length of time. Upon completion, the reaction mixture was filtered, and the resulting crystals washed thoroughly with ethanol and ether, and dried in air overnight. The crystals were stored in small glass bottles at room temperature.

Elemental analysis of the various samples was performed at the Elemental Analysis Laboratory at the Hebrew University in Jerusalem.

The amount of CO released was measured by connecting the gas outlet placed on top of the cooling column to a gas burette filled with a dilute solution of CuSO_4 , so that the blue color of the solution would give good readings of the volume displaced by CO. The total volume displaced allowed the calculation of the overall amount of CO released during the substitution reaction.

Results and Discussion

A summary of the elemental analyses performed on the various reaction products is shown in Table I. Even though several parameter variations may be observed in the reaction conditions, the content of the four elements seems to be practically identical in all cases. These results are compared to the theoretical values obtained for the compound $\{\text{RuCl}_2[(\text{CH}_3)_3\text{CNC}]_2(\text{CO})\}_2$ and the similarity is striking. The most significant information obtained here is not only the identification of the compound formed by the substitution reaction of the butylisocyanide with the 'red' or 'yellow' solutions, but the realization that the reaction product is the same for both systems. The final product resulting from this substitution reaction contains only one CO group in spite

TABLE II. Relationship Between the Number of Moles of CO Evolved Upon Addition of One Mole of $(\text{CH}_3)_3\text{CNC}$

Reaction	CO evolved/ $(\text{CH}_3)_3\text{CNC}$ added
'yellow' + $(\text{CH}_3)_3\text{CNC}$ (1:4), reflux	1:1
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:4), reflux	0.5:1
'yellow' + $(\text{CH}_3)_3\text{CNC}$ (1:2), RT	1:1
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:2), RT	0.5:1
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:4), RT	0.5:1

of the fact that the ruthenium compound forming the 'yellow' solution contains three CO groups while that of the 'red' solution contains only two. This implies that the binding energy of the last CO group to the ruthenium atom is greater than the substituting capabilities of the isocyanide ligand.

Additional support for the nature of the reaction product is furnished by the results summarized in Table II. Here, the amount of CO released from the reaction mixture was calculated and was expressed as moles of CO evolved upon addition of one mole of $(\text{CH}_3)_3\text{CNC}$. In cases in which the 'red' solution was used as the starting ruthenium carbonyl compound, the ratio between CO evolved and $(\text{CH}_3)_3\text{CNC}$ added was 0.5:1, independent of the reaction conditions or extent of the butylisocyanide excess. On the other hand, when the 'yellow' solution was used, the ratio was in all cases 1:1. On the basis of these observations it is clear that the carbonyl compound in the 'yellow' solution contains an additional CO group compared to the compound in the 'red' solution. Therefore it is possible to confirm the assumptions made in a previous paper [10], in which it was stated that the 'red' solution contains $[\text{RuCl}_2(\text{CO})_2]$ species and the 'yellow' solution contains $[\text{RuCl}_2(\text{CO})_3]$ species.

When the reaction was performed at room temperature, the resulting crystals were orange, but upon heating (or when the reaction mixture was refluxed) the product became light yellow. Since no quantitative differences were found between these two forms to suggest two independent compounds, it was concluded that they were actually two isomers of the

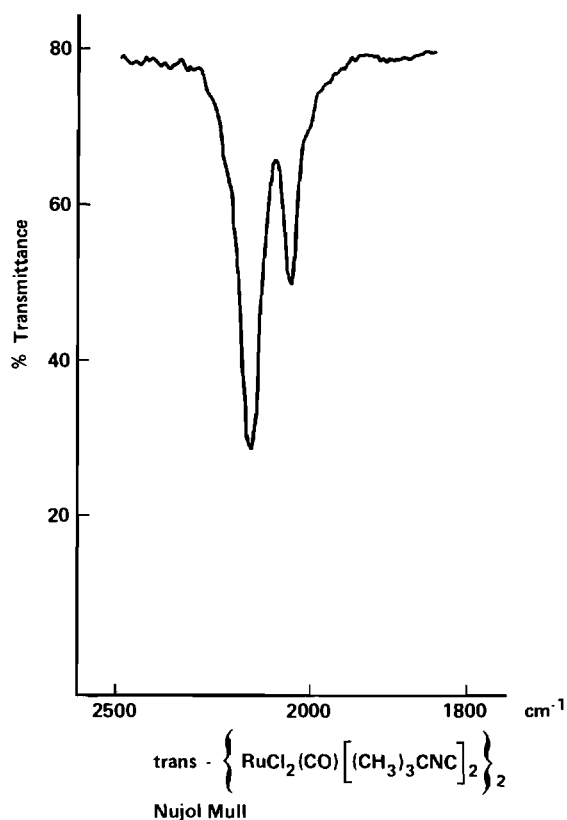


Fig. 1. Infrared spectrum of the orange crystals of *trans*- $\left\{ \text{RuCl}_2 \left[(\text{CH}_3)_3\text{CNC} \right]_2 (\text{CO}) \right\}_2$.

same compound, *trans*- $\left\{ \text{RuCl}_2 \left[(\text{CH}_3)_3\text{CNC} \right]_2 (\text{CO}) \right\}_2$ and *cis*- $\left\{ \text{RuCl}_2 \left[(\text{CH}_3)_3\text{CNC} \right]_2 (\text{CO}) \right\}_2$. Figure 1 shows the infrared spectrum of the orange *trans* isomer in which two main bands are observed in the 1800–2500 cm^{-1} region. The 2051 cm^{-1} is a medium absorption band and it corresponds to a symmetric CO stretch, while the strong 2158 cm^{-1} band corresponds to a symmetric isocyanide stretch [8]. Figure 2 shows the infrared spectrum of the light yellow *cis* isomer in which three main bands are observed in the same region. The CO band is practically unchanged and it occurs at 2052 cm^{-1} , but the isocyanide band appears as a doublet at 2167

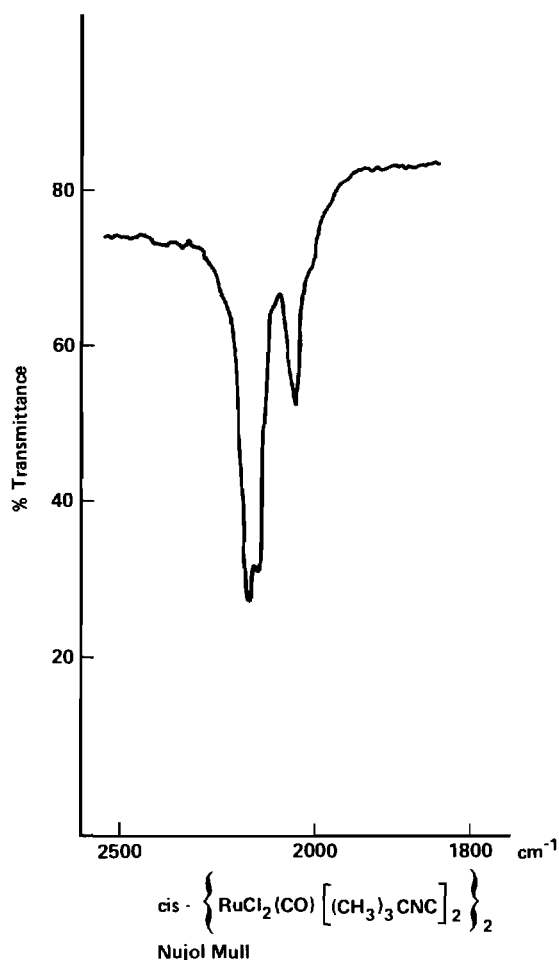


Fig. 2. Infrared spectrum of the light yellow crystals of *cis*- $\left\{ \text{RuCl}_2 \left[(\text{CH}_3)_3\text{CNC} \right]_2 (\text{CO}) \right\}_2$.

cm^{-1} (symmetric stretch [8]) and at 2148 cm^{-1} (asymmetric stretch). The infrared frequencies of both isomers obtained from different reaction conditions are summarized in Table III. The only parameter affecting the reaction product is temperature. The *cis* isomer may be formed either directly by conducting the reaction at higher temperature, or by refluxing a solution of the *trans* isomer. The

TABLE III. Infrared Spectroscopic Properties of $\left\{ \text{RuCl}_2 \left[(\text{CH}_3)_3\text{CNC} \right]_2 (\text{CO}) \right\}_2$

Reaction	Color	Infrared frequencies (cm^{-1})	Isomer
'yellow' + $(\text{CH}_3)_3\text{CNC}$ (1:4), reflux	light yellow	2167(s), 2148(s), 2052(m)	<i>cis</i>
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:4), reflux	light yellow	2167(s), 2148(s), 2052(m)	<i>cis</i>
'yellow' + $(\text{CH}_3)_3\text{CNC}$ (1:2), RT	orange	2158(s), 2051(m)	<i>trans</i>
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:2), RT	orange	2158(s), 2051(m)	<i>trans</i>
'red' + $(\text{CH}_3)_3\text{CNC}$ (1:4), RT	orange	2158(s), 2051(m)	<i>trans</i>

reflux
 $\text{trans} \longrightarrow \text{cis}$

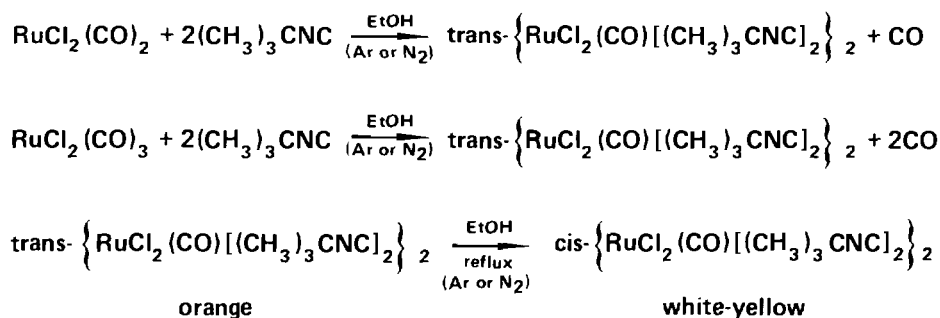


Fig. 3. General scheme of the reaction between the 'red' and 'yellow' solutions with butylisocyanide.

trans-cis conversion is not reversible, and it has been known to occur in a variety of octahedral ruthenium(II) carbonyl complexes [11–13].

Figure 3 shows the overall reaction pathway of the formation of the *trans* and *cis* isomers. There are several symmetry configurations possible for the $\{\text{RuCl}_2[(\text{CH}_3)_3\text{CNC}]_2(\text{CO})\}_2$ dimer, bearing in mind that the *trans* and *cis* isomers refer to the position of the isocyanide groups. Since two Cl atoms (one per Ru) in the dimer act as bridges between the two ruthenium centers, it leaves two Cl atoms and two CO groups to be spatially distributed within the octahedral lattice. However, these configurations have identical vibrational modes and hence are indistinguishable in their infrared spectra [8, 14].

In conclusion, we have shown here that it is possible to obtain a ruthenium complex in which two types of π -acidic ligands, especially very similar ones like carbon monoxide and isocyanide groups, may be bonded to the same Ru metal. Such complexes may prove to be very versatile in their bonding properties and their homogeneous catalytic activity.

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