Journal of Organometallic Chemistry, 87 (1975) 241—245
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

NEW ISOCYANIDE COMPLEXES OF RHENIUM

MARIA FRENI and PIERFRANCESCO ROMITI

Centro di studio per la sintesi e la struttura dei composti dei metalli di transizione nei bassi stati di ossidazione del C.N.R., Istituto di Chimica Generale dell'Università, Via G. Venezian 21, 20133 Milan (Italy)

(Received September 13th, 1974)

Summary

New rhenium compounds $Re(CNR)_5I$, $Re(CNR)_4I_3$, $Re(CNR)_3I_3$, $Re(CNR)_3Br_3$, $Re(CNR)_4(CO)I_2$, $Re(CNR)_2(CO)_4I$ and $[Re(CNR)_4(CO)_2]^+$ (CNR = *p*-tolylisocyanide) have been isolated and characterized. Their magnetic properties and IR spectra are reported.

Introduction

A particularly large number of rhenium complexes with basic ligands have been isolated during recent years. However, the only known complexes of this metal with isocyanides, are the hexakis(isocyanide)rhenium(I) salts [1]. The ease with which potassium hexaiodorhenate reacts in acetone solution with carbon monoxide to give carbonyl metallates [2], and the well known affinity for carbon monoxide of isocyanide, lead us to suppose that treatment of potassium hexaiodorhenate with isocyanide in solution would produce new rhenium isocyanide complexes.

Results and discussion

When potassium hexaiodorhenate is treated with excess *p*-tolylisocyanide in ethanol or acetone solution a yellow crystalline, diamagnetic, non-electrolytic compound, $Re(CNR)_5I$ (I) is formed. If however, hexaidorhenate is heated in ethanol for a short time with a deficiency of isocyanide, a compound precipitates which, after dissolution in methylene chloride, and addition of hexane, gives pure brown crystalline $Re(CNR)_4I_3$ (II), a diamagnetic non-electrolyte whose molecular weight is in accord with it being a heptacoordinated derivative of rhenium(III).

The diamagnetic, non-electrolyte $Re(CNR)_3I_3$ (III), was obtained from the mother liquor of II by addition of water. The corresponding bromo compound, $Re(CNR)_3Br_3$ (IV), was the sole product isolated when potassium hexabromorhenate was treated with isocyanide.

When compound II is refluxed in ethanol under CO, $Re(CNR)_3(CO)I_2$ (V), a heptacoordinated non-electrolyte, was obtained in poor yield. Since V is a derivative of Re^{II} it should be paramagnetic; this is supported by its NMR spectrum.

Compound I is the product of complete substitution of iodopentacarbonylrhenium with isocyanide. A heptacoordinated compound, which is a diamagnetic, non-electrolyte, $Re(CO)_3(CNR)_2I$ (VI), is also formed from *p*-tolylisocyanide and diiodotetracarbonylrhenate $[Re(CO)_4I_2]^-$ [3]. On the other hand, when tetrabutylammonium tetraiododicarbonylrhenate $[Re(CO)_2I_4][(C_4H_9)_4N]$ [3] is treated with *p*-tolylisocyanide, reduction of Re^{III} to Re^I occurs with the formation of hexacoordinated, diamagnetic, $[Re(CNR)_4(CO)_2]I$ (VII), the ionic nature of which was established by a double exchange reaction with sodium tetraphenylborate. In this case both the excess negative charge on the rhenium atom and the steric hindrance due to the four CNR groups are probably responsible for prevention of heptacoordination.

IR spectra

The IR spectrum of compound I (Nujol mull) shows two broad bands in the C—N stretching region at 2050 and 1870 cm^{-1}. In dichloromethane solution there are three bands in the C—N stretching region at 2180m, 2080s, and 2040m cm^{-1}. These values are relatively low compared with those for pure isocyanide (2150 cm^{-1}) and are related to the low oxidation number of rhenium (+1), which permits some π back donation from the metal to the ligand, in this compound. The compound is C_{3v} type, for which three active IR bands are predicted in the C—N bond stretching region. This agrees with our observations. Compound II shows four bands in the C—N stretching region, at 2180m, 2140s, 2100s and 2020m cm^{-1}, in agreement with a structure of C_s type. In this case, however, the relatively low stretching frequency values compared with those of pure isocyanide (2150 cm^{-1}) do not agree with the high oxidation number for rhenium (+3). We assume, therefore, that there is practically no difference in electronegativity between iodine and rhenium, so that the charge on the rhenium atom is actually much smaller than its oxidation number would lead one to predict.

The bond between isocyanide and metal is not therefore exclusively σ but also shows some double bond character. Compound III (Nujol mull) shows a broad unresolved band in the C—N stretching region at ca. 2100 cm^{-1}, consisting of a shoulder at 2150 cm^{-1}, and two strong bands at 2060 and 2030 cm^{-1}. This is consistent with a *trans* structure of C_{2v} type which should possess three active bands.

The IR spectrum of compound IV in Nujol, on the other hand, shows only one strong sharp band at 2200 cm^{-1}, higher than the band present in the free isocyanide. This confirms what has been said about π back donation of the metal to the ligand which must be almost absent here due to the greater electronegativity of Br compared to I. From the IR spectrum we may assume that this compound is of the *cis* or C_{3v} type for which only two bands should be present in the C—N stretching region.

In Nujol compound V shows a broad unresolved band at ca. 2100 cm^{-1}, and a broad unresolved band in the C—O stretching region at about 1900 cm^{-1}. Compound VI shows (Nujol mull) two bands in C—N stretching region at 2200 and 2178 cm^{-1}, and four bands in the C—O region at 2110 m, 2060 s, 1980 s and 1940 m cm^{-1}. We may assume a formulation of C_s type. Compound VII shows only one strong band in the C—N stretching region at 2040 cm^{-1}, and one band in the C—O region at 1885 cm^{-1}. We may thus conclude that the structure of the cation is of D_{4h} type. Analytical data for compounds I -VII are given in Table 1.

Experimental

Molecular weights were recorded on a Mechrolab model 301-A osmometer in $CHCl_3$ solution. IR spectra were recorded on a Perkin—Elmer model 457 spectrometer.

Iodopentakis(p-tolylisocyanide)rhenium (I)

Potassium hexaiodorhenate (1 g) was dissolved in acetone (20 ml), and *p*-tolylisocyanide (1 g) was added to the solution. After stirring for 1 h at room temperature a mixture (1/1) of ethanol and water was added to the brown solution. The yellow crystals of $Re(CNR)_5I$ which separated were recrystallized from acetone and ethanol/water (1/1). The compound is soluble in acetone, dichloromethane, chloroform, methanol and ethanol but insoluble in other common organic solvents.

Triiodotetrakis(p-tolylisocyanide)rhenium (II)

Potassium hexaiodorhenate (1 g) was suspended in ethanol (20 ml) and treated with *p*-tolylisocyanide (0.4 g) at room temperature for 1 h. The brown crystals which separated were dissolved in dichloromethane (20 ml). On addition of hexane (20 ml) brown crystals separated which corresponded to $Re(CNR)_4I_3$. The product is soluble in dichloromethane and chloroform but insoluble in other common organic solvents.

Triiodotris(p-tolylisocyanide)rhenium (III)

Black crystals which correspond to $Re(CNR)_3I_3$ separated from the mother liquor of II by addition of water. The product is soluble in ethanol, methanol, acetone but insoluble in other common organic solvents.

Tribromotris(p-tolylisocyanide)rhenium (IV)

A suspension of potassium hexabromorhenate (1 g) in ethanol (20 ml) was treated with *p*-tolyisocyanide (0.4 g) at room temperature, for 24 h. On addition of water green crystals of $Re(CNR)_3Br_3$ separated. The product is soluble in methanol, ethanol, acetone but insoluble in other common organic solvents.

TABLE 1

ANALYTICAL DATA

Compound		Colour	M.p. (°C)	Mol. wt found (calcd.)	Analysis found (calcd.) (%)			
					C	H	N	I
$Re(CNR)_5I$	(I)	yellow	149	890 (898)	53.2 (53.5)	3.60 (3.90)	7.78 (7.72)	13.6 (14.2)
$Re(CNR)_4I_3$	(II)	brown	138	1100 (1035)	37.5 (37.3)	2.50 (2.71)	5.20 (5.41)	37.7 (36.8)
$Re(CNR)_3I_3$	(III)	black	125	914 (918)	32.4 (31.7)	2.33 (2.29)	4.60 (4.57)	39.6 (40.5)
$Re(CNR)_3Br_3$	(IV)	green	166	790 (777)	37.1 (36.9)	2.67 (2.70)	5.48 (5.40)	
$Re(CNR)_4(CO)I_2$	(V)	orange	206		42.1 (42.2)	3.00 (2.99)	5.80 (5.97)	
$Re(CNR)_2(CO)_4I$	(VI)	white	104		35.5 (36.7)	2.30 (2.14)	4.00 (4.22)	
$[Re(CNR)_4(CO)_2]I$	(VII)	yellow	204		46.1 (46.3)	3.30 (3.19)	6.20 (6.39)	15.0 (14.5)

Diiodomonocarbonyltetrakis(p-tolylisocyanide)rhenium (V)

Compound II (1 g) was suspended in ethanol (20 ml) and the mixture was refluxed under carbon monoxide for 2 h. Upon cooling, orange crystals of $Re(CNR)_4(CO)I_2$ separated.

Iodotetracarbonylbis(p-tolylisocyanide)rhenium (VI)

A mixture of $[Re(CO)_4I_2][(C_4H_9)_4N]$ [3] (1 g) and *p*-tolylisocyanide (0.4 g) was refluxed in ethanol (20 ml) for 2 h. On addition of hexane at room temperature white crystals of $Re(CO)_4(CNR)_2I$ separated. The compound is soluble in acetone, dichloromethane, chloroform but insoluble in other commom organic solvents.

Dicarbonyltetrakis(p-tolylisocyanide)rhenium iodide (VII)

A mixture of $[Re(CO)_2I_4][(C_4H_9)_4N]$ [3] (1 g) and *p*-tolylisocyanide (0.8 g) was refluxed in 40 ml of ethanol for 2 h. On cooling, the orange crystals which separated were treated with a solution of KOH in ethanol, to give yellow crystals of $[Re(CO)_2(CNR)_4]I$.

References

1 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, Wiley, London, 1969.

2 M. Freni, D. Giusto and P. Romiti, Atti Accad. Naz. Lincei, Mem. Cl. Sci. Fiz. Mat. Natur. Sez. 49 (1970) 420.

3 M. Freni, P. Romiti, V. Valenti and P. Fantucci, J. Inorg. Nucl. Chem., 34 (1972) 1195.