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OCTAHEDRAL RUTHENIUM (II) CARBONYL COMPLEXES WITH NITROGEN, SULPHUR AND TIN DONOR LIGANDS

J. V. KINGSTON,* J. W. S. JAMIESON† and G. WILKINSON
Inorganic Chemistry Laboratories, Imperial College, London S.W.7.

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Abstract—The reaction of a carbonyl-containing ruthenium solution with amines leads to isolation of the amino–carbonyl complexes: $[Ru(C_6H_5NH_2)_2(CO)_2X_2]$, $[Ru(C_6H_5CH_2NH_2)_2(CO)_2X_2]$, $[Ru(phen)(CO)_2X_2]$ ($X = Cl, Br$), $[Ru(dipy)(CO)_2Cl_2]$ and $[Ru\{C_6H_4(S)NH_2\}_2(CO)_2]$. Preparation of the trihalostannato–carbonyl complexes $[Ru(py)_2(CO)_2(SnX_3)_2]$ ($X = Cl, Br$), and $[Ru(Et_2S)_3(CO)_2SnCl_3]X$ ($X = Cl, Ph_4B$) via the carbonyl-containing solution is also reported.

INTRODUCTION

A NUMBER of ruthenium complexes have been prepared(1–3) by the use of the deep red solution which CHATT *et al.*(4) obtained by passing carbon monoxide through a refluxing solution of ruthenium trichloride. The interaction of this carbonyl-containing ruthenium solution with (a) various amines and thioamines, and (b) with anhydrous stannous chloride to produce a lemon-coloured solution which is then reacted with both amine and sulphide ligands, is now reported. The bidentate chelating agents 2,2′-dipyridyl, 1,10-phenanthroline and 2-aminothiophenol have been used as well as the monodentate ligands aniline, benzylamine, pyridine and diethyl sulphide.

Some anionic trihalostannato–carbonyl complexes of Ru(II) $[RuX_2(CO)_2(SnX_3)_2]^{2-}$ have previously been prepared(3,5) Isolation of the neutral complexes $[Ru(py)_2(CO)_2(SnX_3)_2]$ ($X = Cl, Br$) and the cationic species $[Ru(Et_2S)_3(CO)_2(SnCl_3)]X$ ($X = Cl, Ph_4B$) has now been accomplished.

Amine carbonyl complexes

When carbon monoxide is passed into a boiling solution of ruthenium trichloride in ethanol for 5 hr, a deep red solution is formed.(4) Subsequent addition of aniline (3 moles) gives the blue complex $[Ru(C_6H_5NH_2)_2(CO)_2Cl_2]$. The complexes $[Ru(C_6H_5CH_2NH_2)_2(CO)_2Cl_2]$, $[Ru(dipy)(CO)_2Cl_2]$, $[Ru(phen)(CO)_2Cl_2]$ and

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* Present address: Department of Chemistry, La Trobe University, Melbourne, Australia.

† On sabbatical leave from Department of Chemistry, St. John's College, University of Manitoba, Winnipeg, Canada.

(1) T. A. STEVENSON and G. WILKINSON, *J. inorg. nucl. Chem.* **28,** 945 (1966).

(2) S. D. ROBINSON and G. WILKINSON, *J. chem. Soc.* 300 (1966).

(3) J. V. KINGSTON and G. WILKINSON, *J. inorg. nucl. Chem.* **28,** 2709 (1966).

(4) J. CHATT, B. L. SHAW and A. E. FIELD, *J. chem. Soc.* 3466 (1964).

(5) J. F. YOUNG, Ph.D. Thesis, University of London (1965).

$[Ru\{C_6H_4(S)NH_2\}_2(CO)_2]$ have been prepared in a similar manner. The bromo complexes have been prepared by prior treatment of ruthenium trichloride in ethanol with an excess of lithium bromide; carbonylation then gives a green solution. All of the complexes formed by these methods have been found to be non-electrolytes in nitrobenzene and monomers in acetone solution.

TABLE 1.—COLOUR AND CARBONYL STRETCHING FREQUENCIES OF THE RUTHENIUM COMPLEXES

Complex	Colour	ν(CO) (cm^{-1})
$Ru(C_6H_7N)_2(CO)_2Cl_2$	blue	2070, 2004, 1988†
$Ru(C_6H_7N)_2(CO)_2Br_2$	green	2070 (w), 2008 (w), 1965 (s)
$Ru(C_6H_5CH_2)_2(CO)_2Cl_2$	pale green	2060 (w), 2005 (w), 1955 (s)
$Ru(C_6H_5CH_2NH_2)_2(CO)_2Br_2$	dark green	2058, 2002
$Ru(dipy)(CO)_2Cl_2$	red brown	2066, 2005*
$Ru(phen)(CO)_2Cl_2$	red brown	2066, 2005*
$Ru(phen)(CO)_2Br_2$	light brown	2066, 2005*
$Ru(C_6H_4(S)NH_2)_2(CO)_2$	light brown	2035, 1970
$Ru(py)_2(CO)_2(SnCl_3)_2$	yellow	2071, 2005
$Ru(py)_2(CO)_2(SnBr_3)_2$	orange yellow	2058, 1992
$[Ru(Et_2S)_3(CO)_2SnCl_3]Cl$	green–yellow	1990 (m), 1955 (s)*
$[Ru(Et_2S)_3(CO)_2SnCl_3][(C_6H_5)_4B]$	green–yellow	1985 (m), 1955 (s)

* Dichloromethane solution.

† Bands strong unless otherwise stated.

The complexes $[Ru(C_6H_5NH_2)_2(CO)_2Cl_2]$, $[Ru(C_6H_5NH_2)_2(CO)_2Br_2]$ and $[Ru(C_6H_5CH_2NH_2)_2(CO)_2Cl_2]$ show three bands in the carbonyl region of the i.r. spectrum (Table 1). The presence of three carbonyl bands suggests that these products may be mixtures of the *cis* and *trans* forms, but attempts to separate them by recrystallization gave products having only weaker bands at the higher frequencies; complete separation was not achieved.

The dark green complex $[Ru(C_6H_5CH_2NH_2)_2(CO)_2Br_2]$ which showed only two carbonyl bands at 2002 cm^{-1} and 2058 cm^{-1} is probably the *cis* form. Attempts to prepare the *trans*-$[Ru(C_6H_5CH_2NH_2)_2(CO)_2Br_2]$ were unsuccessful.

Similar dicarbonyl complexes(1) using triphenylphosphine, -stibine and -arsine have previously been isolated, as well as complexes of the type $[Ru(L)_3(CO)Cl_2]$. Although complexes of this latter type might have been expected with the monodentate ligands aniline and benzylamine none have been isolated; nor has it been possible to prepare complexes of the types $[Ru(L)_3(CO)Cl_2]$ and $[Ru(L)(CO)_3Cl_2]$ by treatment of the complexes $[Ru(L)_2(CO)_2Cl_2]$ with excess of either amino ligand or carbon monoxide, even at high pressure.

Complexes such as [Ru(dipy)$_3$]Cl$_2$ and [Ru(phen)$_3$]Cl$_2$ are known(6) but the reddish-brown [Ru(dipy)(CO)$_2$Cl$_2$] and [Ru(phen)(CO)$_2$Cl$_2$] and the light brown [Ru(phen)(CO)$_2$Br$_2$] appear to be the first ruthenium carbonyl complexes with bidentate nitrogenous ligands. They show carbonyl bands in the i.r. spectrum which are similar to those of *cis*-[Ru(py)$_2$(CO)$_2$Cl$_2$] and similar *cis* complexes(1); thus it is probable that they are octahedral with *cis* carbonyl groups. These 2,2′-dipyridyl and 1,10-phenanthroline complexes seem to be quite stable and even with an excess of bidentate ligand the cationic species [Ru(dipy)$_2$(CO)$_2$]Cl$_2$ and [Ru(phen)$_2$(CO)$_2$]Cl$_2$ are not obtained.

The orange-brown compound [Ru{C$_6$H$_4$(S)NH$_2$}$_2$(CO)$_2$] is similar to the dithiocarbamate complexes(3) and it would seem to have a six co-ordinate structure with 2-aminothiophenol as a uninegative bidentate ligand. No complex containing only one molecule of the chelating agent could be isolated even when a deficiency of the ligand was used.

Complexes analogous to [Ru(C$_6$H$_5$NH$_2$)$_2$(CO)$_2$Cl$_2$] with R$_2$S (R is CH$_3$—, C$_2$H$_5$— or *i*-C$_3$H$_7$—) could not be isolated. On evaporation, the yellow-green R$_2$S reaction solutions gave only mixtures, which showed carbonyl bands in the i.r. spectrum.

Trihalostannato-carbonyl complexes

When the red solution is refluxed for 1 hr with anhydrous stannous chloride (6 moles excess) a lemon-coloured solution is obtained. This solution contains the anionic complex [RuCl$_2$(CO)$_2$(SnCl$_3$)$_2$]$^{2-}$ which was characterized by precipitation of the tetramethylammonium and tetraphenylarsonium salts.(3) Treatment of the lemon-coloured solution with pyridine (3 moles) in ethanol gives the yellow complex [Ru(C$_5$H$_5$N)$_2$(CO)$_2$(SnCl$_3$)$_2$]. This compound is stable for long periods in air; it is soluble in both acetone and dichloromethane and can be recrystallized without decomposition from an ethanol–acetone solution. It is a monomer in acetone solution and a non-electrolyte in nitrobenzene. The i.r. spectrum shows two carbonyl bands of approx. equal intensity at 2005 cm^{-1} and 2071 cm^{-1} which are very similar to those observed(3) for [RuCl$_2$(CO)$_2$(SnCl$_3$)$_2$]$^{2-}$. Thus it is probable that the two complexes have similar structure.

When the green bromo–carbonyl solution (prepared by the use of lithium bromide, as above) was refluxed with a solution of anhydrous stannous bromide in ethanol a yellow solution was obtained. After filtration and allowing the solution to stand overnight, pyridine was added slowly with shaking to precipitate the yellow-orange tribromostannato complex [Ru(C$_5$H$_5$N)$_2$(CO)$_2$(SnBr$_3$)$_2$]. This complex is a non-electrolyte in nitrobenzene and shows carbonyl bands at 1992 cm^{-1} and 2058 cm^{-1} which are similar to those of the trichlorostannato complexes.

Addition of diethyl sulphide (3 moles) to the ruthenium–tin solution gave a greenish-yellow crystalline precipitate which, on the basis of analysis and the observation that it is a uni-univalent electrolyte in nitrobenzene, appears to be

$$[\mathrm{Ru(Et_2S)_3(CO)_2(SnCl_3)}]\mathrm{Cl}.$$

The i.r. spectrum shows two bands in the carbonyl stretching region at 1955 cm^{-1}(s) and 1990 cm^{-1}(m). When the compound was dissolved in aqueous acetone solution and treated with a solution of sodium tetraphenylborate the yellow compound

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(6) W. W. Brandt, F. P. Dwyer and E. C. Gyarfas, *Chem. Rev.* **54**, 959 (1954).

$[Ru(Et_2S)_3(CO)_2(SnCl_3)][Ph_4B]$ was precipitated and also shown to be a uni-univalent electrolyte in nitrobenzene.

Attempts to prepare the dicarbonyltrichlorostannato complexes

$$[Ru(Et_2S)_2(CO)_2Cl_2]$$

and

$$[Ru(Et_2S)_2(CO)_2(SnCl_3)_2]$$

were unsuccessful.

EXPERIMENTAL

Microanalysis and molecular weight determinations (Mechrolab osmometer, 37°) were by the Microanalytical Laboratory, Imperial College. M.p.'s were determined with a Kofler hot-stage microscope and are uncorrected. I.r. spectra were taken in mulls (Nujol and hexachlorobutadiene) and whenever possible in dichloromethane, using a Grubb–Parsons Spectromaster grating instrument. Magnetic data were obtained by the standard Guoy method at room temperature. Molar conductivities (Λ_M) are for 0·001 M solution.

Commercial ruthenium trichloride trihydrate (Johnson-Matthey and Co. Ltd.) was used but identical complexes were obtained by using the chloro complex from repeated evaporation to dryness with concentrated hydrochloric acid. All reactions were carried out in the absence of air.

Analyses of the new ruthenium complexes are given in Table 2.

In the following preparations a standard quantity, 0·5 g, of $RuCl_3 \cdot 3H_2O$ was used.

Ruthenium (II) complexes

Dichlorodicarbonylbis(aniline)ruthenium (II). Aniline (0·3 g) in ethanol (20 ml) was added slowly to the red solution. No immediate colour change was observed but on shaking the colour changed slowly from red to green and finally to deep blue. The blue compound which precipitated slowly was washed with ethanol and ether and dried *in vacuo* over silica gel. Yield 50 per cent. The *complex* is diamagnetic and a non-electrolyte in nitrobenzene.

Dibromodicarbonylbis(aniline)ruthenium (II). As the chloro complex except that an initial green solution was obtained by passing carbon monoxide for 5 hr through a boiling solution of hydrated ruthenium trichloride and excess lithium bromide (6:1 mole ratio) in ethanol. Addition of aniline (0·3 g) in ethanol (20 ml) gave the green crystalline complex in almost quantitative yield. The *complex* is diamagnetic and a non-electrolyte in nitrobenzene.

Dichlorodicarbonylbis(benzylamine)ruthenium (II). Benzylamine (0·4 g) in ethanol (20 ml) was added slowly to the red solution. An immediate colour change from red to green occurred and the pale green complex was precipitated. It was washed with ethanol and ether and dried over phosphorus pentoxide. Yield 90 per cent. The *complex* is diamagnetic and a non-electrolyte in nitrobenzene.

Dibromodicarbonylbis(benzylamine)ruthenium (II). As the aniline bromo complex except that benzylamine (0·4 g) in ethanol (20 ml) was used instead of aniline. Yield 90 per cent. The green crystalline *complex* is diamagnetic and a non-electrolyte in nitrobenzene.

Dichlorodicarbonyl(2,2′-dipyridyl)ruthenium (II). To the hot red solution was added 2,2′-dipyridyl (0·8 g) in ethanol (10 ml). When the filtrate was allowed to cool slowly, reddish-brown crystals of the complex were precipitated. Yield 80 per cent. The *complex* is a non-electrolyte in nitrobenzene.

Dichlorodicarbonyl(1,10-phenanthroline)ruthenium (II). Addition of 1,10-phenanthroline hydrate (0·8 g) in ethanol (10 ml) to the hot red solution gave the reddish-brown crystalline complex on cooling. Yield 50 per cent. The *complex* is a non-electrolyte in nitrobenzene.

Dibromodicarbonyl(1,10-phenanthroline)ruthenium (II). As the chloro complex except that the initial carbonyl solution contained an excess of lithium bromide (6:1 mole ratio). Yield 75 per cent. The light brown *complex* is a non-electrolyte in nitrobenzene.

Dicarbonylbis(2-aminothiophenol)ruthenium (II). To the hot red solution 2-aminothiophenol (0·3 g) in ethanol (10 ml) was added slowly with stirring. An immediate colour change from red to green occurred and a small quantity of black material was precipitated. The light brown *complex* which was obtained on allowing the filtrate to stand in the cold, was washed with ethanol and ether and dried *in vacuo* over silica gel. Yield 30 per cent. The *complex* is diamagnetic and a non-electrolyte in nitrobenzene.

TABLE 2.—ANALYTICAL DATA FOR RUTHENIUM COMPLEXES

Complex	M.p. (°C)	Found					Required				
		C	H	N	O	M (solvent)	C	H	N	O	M
$Ru(C_6H_7N)_2(CO)_2Cl_2$	185–87	40·0	3·9	7·1	7·8	428 (acetone)	40·6	3·4	6·8	7·7	414
$Ru(C_6H_7N)_2(CO)_2Br_2$*		32·7	2·5	5·3	6·6	—	33·4	2·8	5·6	6·3	—
$Ru(C_6H_5CH_2NH_2)_2(CO)_2Cl_2$	147	43·6	4·2	6·8	8·2	388 (acetone)	43·5	4·1	6·3	7·2	442
$Ru(C_6H_5CH_2NH_2)_2(CO)_2Br_2$†	213	37·1	3·6	5·1	6·5	—	36·2	3·4	5·3	6·0	—
$Ru(dipy)(CO)_2Cl_2$*		36·8	2·2	7·5	9·4	383 (acetone)	37·5	2·1	7·3	8·3	384
$Ru(phen)(CO)_2Cl_2$*		40·9	2·2	7·1	7·3	436 (acetone)	41·2	2·0	6·9	7·8	408
$Ru(phen)(CO)_2Br_2$*		34·2	2·5	6·5	8·2	—	33·8	1·6	5·6	6·4	—
$Ru(C_6H_4(S)NH_2)_2(CO)_2$	191–3	40·6	3·6	7·8	7·1	—	41·3	3·5	7·9	6·9	—
$Ru(py)_2(CO)_2(SnCl_3)_2$	184(d)	17·9	2·0	3·2	4·5	695 (acetone)	18·8	1·3	3·7	4·2	765
$Ru(py)_2(CO)_2(SnBr_3)_2$*		13·0	2·0	1·9	2·8	—	14·0	1·0	2·7	3·1	—
$[Ru(Et_2S)_3(CO)_2SnCl_3]Cl$‡	145	23·2	4·4	—	4·4		24·4	4·4	—	4·7	—
$[Ru(Et_2S)_3(CO)_2SnCl_3][(C_6H_5)_4B]$		46·3	4·8	—	—	—	47·5	5·2	—	—	—

* Stable at 250°C.

† Br, Found 28·6; Requires 30·1.

‡ Cl, Found 22·9; Requires 20·6.

Dicarbonylbis(pyridine)bis(trichlorostannato)ruthenium (II). Anhydrous stannous chloride (2 g, 6 moles) in ethanol (20 ml) was added to the red solution. After refluxing for 2 hr the lemon-coloured solution was filtered and allowed to stand overnight. The yellow complex was obtained as a copious precipitate on addition of pyridine (1·8 g) in ethanol (20 ml). The precipitate was washed with hot ethanol and ether and dried *in vacuo* over silica gel. Yield 40 per cent. The *complex* is a non-electrolyte in nitrobenzene.

Dicarbonylbis(pyridine)bis(tribromostannato)ruthenium (II). The green bromo-carbonyl solution was refluxed for 2 hr with a solution of anhydrous stannous bromide (2 g). The resultant yellow solution was filtered and allowed to stand overnight. Pyridine (2 g) in ethanol (30 ml) was slowly added with shaking to give the yellow–orange complex. Yield 40 per cent. The *complex* is a non-electrolyte in nitrobenzene.

Dicarbonyltris(diethylsulphide)trichlorostannato ruthenium(II) chloride. Anhydrous stannous chloride (2 g) in ethanol (20 ml) was added to the red solution and the resultant solution was refluxed for 2 hr. Diethyl sulphide (0·7 g) in ethanol (10 ml) was then added. The lemon-coloured complex precipitated slowly as the solution was shaken for 4 hr. After separation of the precipitate and allowing the filtrate to stand, more darkly-coloured and larger crystals were obtained. The *complex* was washed with ethanol and ether and dried *in vacuo* over silica gel. Yield 80 per cent. $\Lambda_{0\cdot0017}$ in nitrobenzene = 19 Ω^{-1}cm^{2}mole^{-1}.

Dicarbonyltris(diethylsulphide)trichlorostannato ruthenium (II) tetraphenylborate. Dicarbonyltris-(diethylsulphide)trichlorostannato ruthenium (II) chloride (0·2 g) in aqueous acetone (5 ml) was added to an aqueous acetone solution of sodium tetraphenyl borate (0·4 g). The yellow–green *complex*, which precipitated slowly to give a quantitative yield, was washed with water and ether and dried *in vacuo* over silica gel. $\Lambda_{0\cdot001}$ in nitrobenzene = 15 Ω^{-1}cm^{2}mole^{-1}.

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