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CARBONYLRHODIUM(I) COMPLEXES WITH HETEROCYCLIC NITROGEN COMPOUNDS

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Summary

Crystalline complexes of rhodium(I) of the type $[Rh(CO)_2(N—N)][RhX_2(CO)_2]$ (N—N = 2,2′-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline; X = Cl, Br) have been prepared. An ionic chain-like structure involving metal—metal interactions has been established by measurement of the reflectance spectra, absorption electronic spectra and electrical conductivities. The IR spectra have been examined over the 50—4000 cm^{-1} range.

Introduction

Carbonylrhodium(I) complexes have been thoroughly investigated because of their application as catalysts in the hydroformylation reaction [1]. Some of these complexes in the solid state have a chain-like structure involving metal—metal interaction [2,3]. The complexes with *N*-heterocyclic ligands exhibit biological activity [4]. $Rh_2Cl_2(CO)_4$ (bipy) was obtained for the first time by Lawson and Wilkinson [5] by treating $Rh_2Cl_2(CO)_4$ with bipyridyl in benzene. The same complex and $Rh_2Cl_2(CO)_4(bipy)_2$ and $Rh_2Cl_2(CO)_4(bipy)_3$ were obtained in benzene by Varshavski [6]. Gillard et al. [4] prepared $Rh_2Cl_2(CO)_4$ (N—N) where N—N = 2,2′-bipyridyl and 1,10-phenanthroline in a similar way. Varshavski suggested structure I for the $Rh_2Cl_2(CO)_4(bipy)$ compound with 2,2′-bipyridyl, whereas Gillard suggested structure II. In addition, on the basis of the IR spectra Gillard suggested a chain-like structure for these compounds. Until now it has been difficult to prepare very pure compounds by the method used. Gillard maintains that the compounds containing 2 or 3 bipyridyl molecules per 2 rhodium atoms are mixtures of $Rh_2Cl_2(CO)_4(bipy)$ and bipyridyl. We describe below the preparation of $[Rh(CO)_2(N—N)][Rh(CO)_2X_2]$ in the crystalline form from the reaction between the allylrhodium(III) compounds, olefinic rhodium(I) complexes and formic acid in the presence of the appropriate ligand (N—N = 2,2′-bipyridyl, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline or 2,9-dimethyl-1,10-phenanthroline; X = Cl,Br).

Experimental

All compounds were prepared from $RhCl_3 \cdot xH_2O$ supplied by the International Enzymes Co. The following compounds were prepared by published procedures: $RhCl_2$(2-Me-allyl) [7], $Rh_2Cl_2(CO)_4$ [8], $Rh_2Cl_2(COD)_2$ [9], $Rh_2Cl_2(C_8H_{14})_4$ [10], $Rh_2Br_2(COD)_2$ [11], $Rh_2Cl_2(allyl)_4$ [12], $Rh_2Br_2(allyl)_4$ [12,13].

$Rh_2Cl_2(CO)_4$(N—N). In an ampoule were placed 0.08 g $RhCl_2$(2-Me-allyl), 0.693 g 1,10-phenanthroline or equivalent amount of another heterocyclic base (Rh/N—N ratio 1/1) and 2 cm^3 anhydrous formic acid under argon. The rhodium compound dissolved on careful heating, and the ampoule was then heated in a water bath for about 5 h. Upon slow cooling long needles with metallic lustre precipitated out. The yields varied from 60 to 80% based on the rhodium used.

$Rh_2X_2(CO)_4$(N—N). These were prepared by the method described above with $Rh_2X_2(COD)_2$, $Rh_2Cl_2(C_8H_{14})_4$, $Rh_2X_2(CO)_4$ (X = Cl, Br) as starting materials. The rhodium concentrations were similar to those above, but the Rh/N—N ratio was 2/1. The yield was 60—80% based on the rhodium taken. The products are soluble in anhydrous formic acid slightly soluble in methanol, ethanol, formamide, DMF, DMSO, acetone and other polar organic solvents, very slightly soluble in water and insoluble in non-polar solvents. The crystals vary in color from red-brown or dark-brown to black with metallic lustre. When powdered they are blue-green or green, except for the compound with 4,7-diphenyl-1,10-phenanthroline and $Rh_2Br_2(CO)_4$(bipy), which have the same color in the crystal and in the powder.

The analytical and physical data of the $Rh_2X_2(CO)_4$(N—N) complexes are listed in Table 1.

Discussion of results

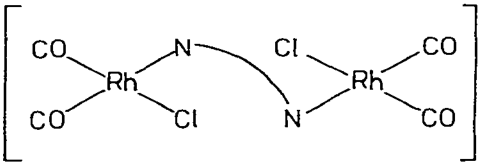
The infrared spectra of $Rh_2Cl_2(CO)_4$(phen) and $Rh_2Cl_2(CO)_4$(bipy) are identical to those reported in references [4—6]. All the compounds prepared

TABLE 1

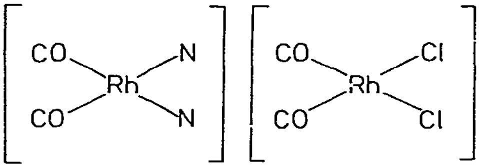
ANALYTICAL AND PHYSICAL DATA OF THE COMPLEXES $Rh_2X_2(CO)_4$(N—N)

Compound	M.p. (°C)	Color	Analysis (Found (calcd.) (%))			
			C	H	X	Rh
$Rh_2Cl_2(CO)_4$(phen)	120—123 (dec.)	red-brown	33.0 33.78	1.5 1.42	12.1 12.46	36.2 36.17
$Rh_2Cl_2(CO)_4(Me_2phen)$	124—125 (dec.)	brown	35.5 36.21	1.7 2.02	11.5 11.88	33.4 34.47
$Rh_2Cl_2(CD)_4(Ph_2phen)$	158—160 (dec.)	yellow- brown	46.8 46.63	2.2 2.24	9.5 9.83	27.0 28.5
$Rh_2Cl_2(CO)_4$(bipy)	120—123 (dec.)	brown	30.5 30.86	1.5 1.48	12.7 13.01	37.6 37.77
$Rh_2Br_2(CO)_4$(phen)	160—163 (dec.)	red-brown	29.0 29.11	1.3 1.22	22.9 24.29	30.8 31.28
$Rh_2Br_2(CO)_4$(bipy)	165—168 (dec.)	dark- brown	26.4 26.53	1.4 1.27	24.6 25.21	32.2 32.47

exhibit ionic structures (structure II) found by Gillard et al. [4] for the com-



Structure I



Structure II

plex with phenanthroline and bipyridyl. This is demonstrated by the electrical conductivities of the compounds under examination. It is 44.1 cm^2 ohm^{-1} mol^{-1} for $[Rh(CO)_2(phen)]^+[Rh(CO)_2Br_2]^-$, for the 9.5×10^{-4} *M* solution at 25° C. Additional evidence is provided by the solubilities of these compounds in strongly polar solvents. The infrared spectra in the valence vibration range $\nu(CO)$ are very similar for all the complexes studied (Table 2). In the far infrared two valence vibration bands $\nu(Rh—X)$ appear, which indicates the *cis* structure of the $[Rh(CO)_2Cl_2]^-$ anion [14]. This shows that all compounds under investigation have ionic structures. The absorption electronic spectra (Table 3) in methanolic solutions and in anhydrous formic acid differ considerable from the diffuse reflectance spectra (Fig. 3). The latter spectra exhibit a

TABLE 2

INFRARED SPECTRA OF THE COMPLEXES $Rh_2X_2(CO)_4(N—N)$

Compound	$\nu(Rh—X)$ (cm^{-1})	$\nu(C=O)$ (cm^{-1})
$Rh_2Cl_2(CO)_4(phen)$	281vs, 311vs	1910v, 1956s, 1958vs, 1985vs, 2015vs, 2036vs, 2054vs, 2058vs, 2070m, 2084vs, 2094vs
$Rh_2Br_2(CO)_4(phen)$	199vs, 225s	1955m, 1963m(sh), 1980vs, 1994vs, 2016vs, 2036vs, 2054vs, 2058vs, 2070m(sh), 2084vs, 2092vs
$Rh_2Cl_2(CO)_4(dipy)$	283vs, 311vs	1908m, 1963vs, 1986s, 2012s, 2024s, 2054vs, 2060vs, 2078s(sh), 2084vs, 2094s(sh)
$Rh_2Br_2(CO)_4(dipy)$	200s, 224m	1980vs, 1990vs, 2012vs, 2020vs, 2053vs, 2066vs, 2080vs.
$Rh_2Cl_2(CO)_4(Me_2phen)$	287vs, 313s(sh) 317s	1955w, 1975m, 1984s, 1998m, 2014vs, 2038w(sh), 2048vs, 2078vs, 2092m(sh), 2143vw
$Rh_2Cl_2(CO)_4(Ph_2phen)$	289vs, 313s	1943w, 1965vs, 1978m(sh), 1994vs, 2025w, 2051vs, 2058vs(sh), 2074m, 2086w, 2108vs, 2143vw

TABLE 3

ELECTRONIC SPECTRA OF THE COMPLEXES $RhX_2(CO)_4(N—N)$

Compound	Absorption spectra in HCOOH	Reflectance spectra in MgO
	(cm^{-1} 10^{-3}) (ϵ)	(cm^{-1} 10^{-3})
$Rh_2Cl_2(CO)_4$(phen)	25.9 [a](sh), 28.1 (4.1 X 10^3), 30.3(sh), 30.8(sh) 33.9(sh), 36.2 (5.3 X 10^4)	14.3 [a], 23.8, 27.0, 36.2, 43.9
$Rh_2Br_2(CO)_4$(phen)	25.6 [a](sh), 28.3 (2.5 X 10^3), 29.6(sh), 31.2(sh), 33.9(sh), 37.0 (3.0 X 10^4)	14.5 [a], 23.7(sh), 25.3, 33.3, 45.0
$Rh_2Cl_2(CO)_4$(dpiy)	25.8 [a] (1.4 X 10^3), 31.7(sh), 32.4 (1.7 X 10^4) 39.2 (2.2 X 10^4)	15.5 [a], 17.1(sh), 23.9, 31.6, 35.2(sh), 45.0(sh)
$Rh_2Br_2(CO)_4$(dipy)	26.0 [a] (1.2 X 10^3), 32.1 (1.4 X 10^4), 33.0(sh) 40.3 (2.8 X 10^4)	16.0 [a], 17.2(sh), 24.6, 31.1, 35.3(sh), 45.0(sh)
$Rh_2Cl_2(CO)_4(Me_2phen)$	26.3 [a](sh), 27.6(sh), 31.2 (1.0 X 10^4), 35.6 (3.6 X 10^4), 40.0 (2.4 X 10^4)	15.8 [a], 24.3(sh), 27.0(sh), 28.2(sh), 35.5, 43.9
$Rh_2Cl_2(CO)_4(Ph_2phen)$	25.0 [a](sh), 27.0(sh), 28.0(sh), 30.3(sh), 33.7 (5.2 X 10^4), 34.3 (5.2 X 10^4)	19.2 [a], 26.9(sh), 30.5, 34.4, 45.5

[a] Metal to ligand charge transfer.

strong band between 13000 and 19000 cm^{-1} which does not appear in the absorption spectra. This shows that in the solid state there is a direct metal—metal interaction, that is, the compounds have a column-like structure with alternate square-planar cations and anions (Fig. 1). This has been observed in many similar compounds [15—17]. The absorption electronic spectra of the d^8 electron complexes, among others rhodium(I) have been discussed in a number of papers [18—20]. Because of the relatively low spin-orbit coupling constant, the spectra of the rhodium(I) compounds are relatively simple [18]. Above 20000 cm^{-1} the bands resulting from M → L charge transfer transitions $2a_{1g}$ (z^2) → $2a_{2u}(\pi^*)$ (D_{4h}) appear (Fig. 2). For the compounds in which interactions between the planar components occur, the charge transfer band energies are considerably reduced (Fig. 2). An increase in the rhodium—rhodium interaction results in a shift of the first charge transfer band towards lower energies. This

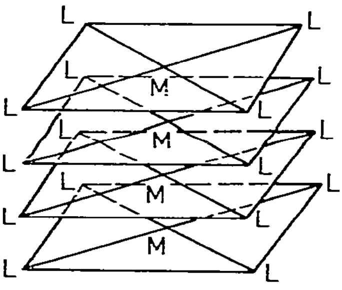


Fig. 1. Columnar structure of the planar complexes.

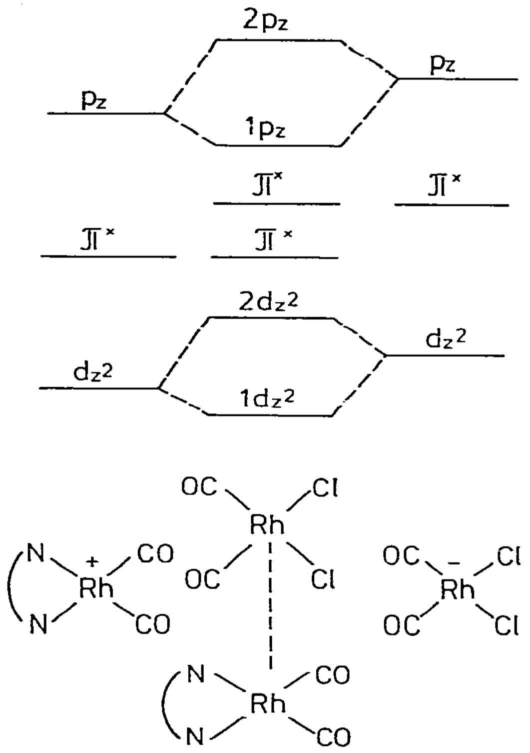


Fig. 2. A partial MO orbital diagram for the interaction of planar $[Rh(CO)_2(N—N)]^+$ and $[RhCl_2(CO)_2]^-$ units.

band results from the $(d_{z^2}) \rightarrow (\pi^*)$ transition (Fig. 2) from the d_{z^2} orbital of rhodium to the π^* orbitals of the ligand, i.e. amine or X or CO, which accounts for its considerable width. An increase in energy of this transition in the series: $Rh_2Br_2(CO)_4$(phen) < $Rh_2Cl_2(CO)_4$(phen) < $Rh_2Cl_2(CO)_4$(2,9-Me_2-phen) < $Rh_2Cl_2(CO)_4$(4,7-Ph_2phen) indicates that the rhodium—rhodium interaction is decreased in the compounds containing substituted phenanthrolines. The phenyl rings can not lie in the phenanthroline plane and, so cause more steric hindrance than the methyl groups. For this reason, the energy of the above transition is highest for the 4,7-diphenyl-1,10-phenanthroline complex. The conductivity of compressed solid $Rh_2Cl_2(CO)_4$(phen) in the 80—310 K temperature range is 4.0×10^{-9} ohm^{-1} cm^{-1} (77 K)—5.2×10^{-9} ohm^{-1} cm^{-1} (310 K), and increases above room temperature. The conductivity of this compound is higher than that of $[Rh(CNR)_4][PF_6]$ [21]. Spectrophotometric studies showed that for all the complexes examined absorbance vs. concentration data do not follow Beer's law over the concentration range 10^{-3}—10^{-5} M in formic acid (85%) or methanol solution. This behaviour can be attributed either to anion—cation association or to decomposition due to reaction with solvents. In such solvents the compounds are more stable under a CO atmosphere. Their reactions in solution are now under examination.

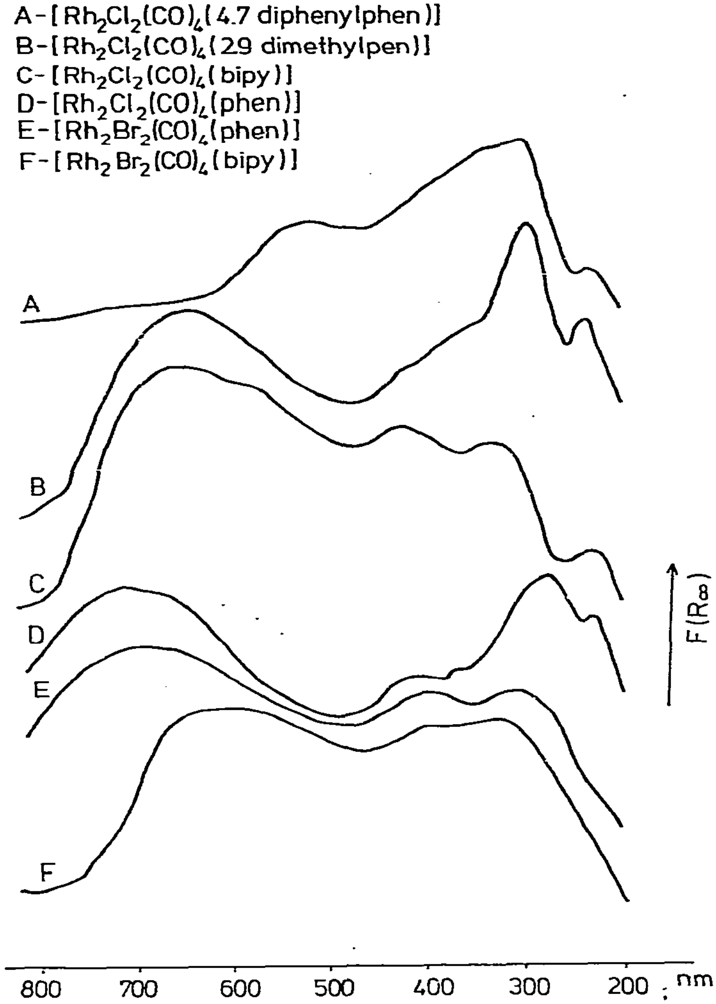


Fig. 3. Reflectance spectra.

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