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SYNTHETIC AND SPECTROSCOPIC ASPECTS OF SOME MALEONITRILE DITHIOLATE COMPLEXES OF RUTHENIUM(II)

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ABSTRACT

Reactions of $[RuH(CO)Cl(PPh_3)_3]$ with $Na_2S_2C_2(CN)_2$ (referred hereafter as Na_2mnt) lead to the formation of $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]^-$ which, upon treatment with $[RuCp(EPh_3)_2Cl]$, yields neutral complexes with the general formulation $[RuH(CO)(EPh_3)_2\{S_2C_2(CN)_2\}RuCp(EPh_3)]$ (E = P, As, Sb). These complexes have been characterized by various physico-chemical techniques (elemental analyses, IR, ^1H, ^{13}C and ^{31}P NMR and electronic spectra).

INTRODUCTION

Transition metal hydridocarbonyl complexes have been the subject of intense interest in recent years, since they are the key intermediates in hydroformylation reactions[1-2]. In this regard, the Ru(II) complex $[RuH(CO)Cl(PPh_3)_3]$ has received special attention[3-5]. Usually, the complex $[RuH(CO)Cl(PPh_3)_3]$ undergoes three types of reactions: (A) substitution of a triphenylphosphine molecule by a neutral ligand yielding $[RuH(CO)Cl(PPh_3)_2L]$ (L = CO, RNC, etc.) where L in most of the cases goes trans to the hydride ion; (B) substituion reactions involving chloride ion abstraction leading to the formation of cationic or neutral complexes[6-8] of the type $[RuH(CO)(PPh_3)_{3-n}L_{1+n}]^{x+}$ (where $x = 1$, $L = P(OR)_3$, $n = 1$; $x = 1$, $L = PPh_2(OR)$, $n = 3$; $x = 0$, $L = S_2CY^-$, $Y = NR_2$, $n = 1, 2$); (C) insertion of arenediazonium salts, 2-vinylpyridine, methyl sorbate, dimethyl fumarate, acrylonitrile, carbon disulphide, dialkyl- and diarylcarbodiimides, 1,3-diaryltriazines and acetylenes in the Ru-H bond to yield the corresponding inserted complexes[9-16]. In a few cases both the chloride ion and a triphenylphosphine molecule are substituted resulting in the formation of cationic complexes[17-21]. Although, reactions of $[RuH(CO)Cl(PPh_3)_3]$ with dithiocarbamates (S_2CNR_2), with other dialkyl and diaryl carbodiimides have extensively been studied[6-8,22], however, its reaction with 1,1-dithiolato anions like $S_2CS_2^{2-}$, S_2CNCN^2, $S_2CC(CN)_2^{2-}$, and other related species have not been studied. We thought it worth, to do a detailed study of the reactions of $[RuH(CO)Cl(PPh_3)_3]$ under varying reaction conditions with maleonitrile dithiolate ligand $[S_2CC(CN)_2^{2-}]$.

Furthermore, due to high affinity of the soft Ru(II) centre towards sulfur donor sites[23-26], the reaction products are expected to have uncoordinated nitrile groups. It will be interesting to exploit the nucleophile character of remote uncoordinated nitrile groups of these complexes. Reactions of $[RuH(CO)(PPh_3)_2L]^-$ (L = dithiolate ligand, mnt) with $[RuCp(L'_2)Cl]$ [L'_2 = PPh_3, $AsPh_3$, $SbPh_3$, diphenylphosphinomethane (dppm), diphenylphosphinoethane (dppe)] may result in the formation of neutral cyano bridged di- or polynuclear complexes.

In this communication we report the results of reactions of Na_2mnt with $[RuH(CO)Cl(PPh_3)_3]$ and reactions of $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]^-$ with $[RuCp(EPh_3)_2Cl]$.

RESULTS AND DISCUSSION

Reactions of $[RuH(CO)Cl(PPh_3)_3]$ with Na_2mnt in 1:1 methanol-benzene give reddish-brown anionic complexes:

$$[RuH(CO)Cl(PPh_3)_3] + Na_2S_2C_2(CN)_2 + XCl \xrightarrow{CH_3OH/C_6H_6\ (1:1)} [RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]X + NaCl$$

(I)

X = PPh_4, $AsPh_4$ or Bu_4N

The anionic complex $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]^-$ further reacts with

$[RuCp(EPh_3)_2Cl]$ (E = P, As, Sb) to yield neutral complexes with the general formula $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(EPh_3)]$.

$$[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]^- + [RuCp(EPh_3)_2Cl] \longrightarrow [RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(EPh_3)] + EPh_3 + Cl^-$$

(II)

The resulting complexes from the above reactions are non-hygroscopic, air-stable microcrystalline solids. They are slightly soluble in benzene, methanol, acetone, soluble in halogenated solvents, dimethyl formamide and dimethyl sulfoxide and insoluble in diethyl ether and petroleum ether. The ionic behaviour of the complexes was confirmed by testing their dilute solutions with an anion exchanger (Dowex-50) whereby the anionic species were absorbed on the resin. Analytical and spectral data of the complexes are given in Table I.

IR spectra, UV-visible, ^1H, ^{13}C and ^{31}P NMR studies have been used to deduce the bonding mode and tentative structure of the complexes.

IR Spectra

IR spectra of the free ligand, Na_2mnt, exhibit bands at 2180, 1430, 1120 and 860 cm^{-1} corresponding to $\upsilon(C\equiv N)$, $\upsilon(C=C)$, $\upsilon_{asym}(C\text{-}S)$ and $\upsilon_{sym}(C\text{-}S)$, respectively[27]. Shifts in the positions of these bands have been used to elucidate the site of coordination in the complexes. IR spectra of the mononuclear complexes exhibited bands in the region 2180-2185 cm^{-1}. The presence of the bands in this region suggested that the ligand mnt^{2-} coordinated through its sulfur atoms with the ruthenium metal centre in these complexes. The $\upsilon(C=C)$ and $\upsilon_{asym}(C\text{-}S)$ bands appeared as shoulders with the phosphine phenyl ring vibrations and $\upsilon_{sym}(C\text{-}S)$ appeared at 850 cm^{-1}. In the IR spectra of the binuclear complex $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(EPh_3)]$, a sharp band was present at 2165 cm^{-1}. This band has been assigned to $\upsilon(C\equiv N)$. The shift in the position of this band results from the coordination of the nitrile group of the monomeric complex with another ruthenium centre. The decrease in the stretching frequency of $\upsilon(C\equiv N)$ may be due to the donation of electron density from ruthenium into the ligand π^* orbitals. The presence of a single sharp

Table I. Elemental Analyses and other Physical Measurements of the Complexes

Compound	Mol. wt.	Yield %	Colour (M.pt. °C)	ANALYTICAL DATA				IR BANDS (cm^{-1})			^1H NMR	^{13}C NMR	^{31}P NMR	λ_{max} (nm)
				%C (calc)	%H (calc)	%N (calc)	%S (calc)	υCN	υRu-H	υ(C≡O)	(δ ppm)	(δ ppm)	(δ ppm)	
$[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]PPh_4$ $C_{65}H_{51}N_2OP_3RuS_2$	1133	65	BW (165)	68.50 (68.84)	4.32 (4.50)	2.48 (2.47)	5.35 (5.64)	2182	1998	1940	11.7 7.2-7.8	128-132 205	-	465 350
$[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]AsPh_4$ $AsC_{65}H_{51}N_2OP_2RuS_2$	1177	60	BW (220)	66.32 (66.27)	4.35 (4.33)	2.39 (2.37)	5.56 (5.43)	2182	2005	1945	-	-	43.4	450 365
$[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(PPh_3)]$ $C_{64}H_{51}N_2OP_3Ru_2S_2$	1222	60	DB (170)	62.80 (62.8)	4.32 (4.17)	2.39 (2.29)	5.22 (5.23)	2165	1995	1930	11.3 7.2-7.8	84.5,128- 132, 205	-	460 350
$[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(AsPh_3)]$ $AsC_{64}H_{51}N_2OP_2Ru_2S_2$	1266	55	BW (172)	60.6 (60.66)	4.22 (4.2)	2.15 (2.21)	5.06 (5.05)	2160	1990	1930	-	-	-	458 355
$[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(SbPh_3)]$ $C_{64}H_{51}N_2OP_2Ru_2S_2Sb$	1313	52	BR (205)	58.6 (58.5)	3.80 (3.88)	2.12 (2.13)	4.98 (4.87)	2160	1998	1935	-	-	-	455 350

BW-brown, BR-brown red, DB-dark brown

band in the IR spectra of the binuclear complexes in the nitrile stretching frequency region suggests that both nitrile groups of the ligand mnt^{2-} of the mononuclear complex are involved in the coordination with the metal centre.

Shifts in the positions of υ(Ru-H) and υ(C≡O) were also observed in the IR spectra of all the complexes. The band due to υ(Ru-H) exhibited a shift towards lower wave number whereas υ(C≡O) exhibited a shift towards the higher wave number side. These shifts indicated a reduction in the Ru-H bond order and Ru-C π interaction, suggesting that Ru-H and Ru-C bond orders are sensitive to the positive charge residing on the metal centre.

Characteristic bands due to EPh_3 were present in their usual positions in the IR spectra of all the complexes.

^{1}H NMR Spectra

Because of the poor solubility of these complexes in C_6H_6-d_6 and their tendency to react with halogenated solvents, the NMR spectra were recorded in DMSO-d_6. We could obtain only a few well resolved ^{1}H, ^{13}C and ^{31}P NMR spectra.

In the ^{1}H NMR spectra of the monomeric complexes, the phenyl ring protons of PPh_3 resonated as a broad multiplet in the region δ 7.2 - 7.8 ppm. The hydride group in these complexes, resonated at about δ -11.7 ppm as a triplet. The presence of a triplet suggested that the hydride ligand is cis to two equivalent phosphine ligands[28-29]. In the ^{1}H NMR spectra of the binuclear complex, an additional band was present at δ 4.6 ppm. This band has been assigned to Cp protons. The band due to Cp protons exhibited a downfield shift, relative to that in the parent complex[30]. This may result from the change in electron density on the metal centre due to backbonding from ruthenium to the ligand antibonding orbitals. The hydride group resonated at about δ -11.5 ppm as a triplet and the phenyl ring protons as a broad multiplet in the range δ 7.2 - 7.8 ppm in the ^{1}H NMR spectra of the binuclear complexes.

^{13}C NMR Spectra

The ^{13}C NMR spectra of the mononuclear complexes exhibited bands in the region δ 116.2, 125, 128-132 and 206 ppm. The former two resonances have been assigned to nitrile and alkene carbon atoms of the ligand mnt^{2-}, respectively[31]. The bands in the region δ 128 - 132 ppm have been assigned to phenyl carbons of EPh_3 and the one at δ 206 ppm has been assigned to the carbonyl carbon atom. The ^{13}C NMR spectra of the binuclear complexes exhibited resonances at about the same positions as those of mononuclear complexes except that a new resonance was observed at δ 84.5 ppm assignable to Cp carbon resonances and the nitrile carbon atom exhibited a downfield shift (δ 119 ppm) as compared to that in the mononuclear complex. The downfield shift of the nitrile carbon resonance suggests the coordination of the pendant nitrile group of the monomeric complex with another ruthenium centre. This observation supports the conclusions drawn from IR and ^1H NMR studies.

^{31}P NMR Spectra

We could obtain well resolved ^{31}P NMR spectra only for the mononuclear complex $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]AsPh_4$. ^{31}P NMR spectra of this complex exhibited a peak at δ 43.4 ppm. This peak has been assigned to ^{31}P nuclei of the PPh_3 groups in the complex. It was observed that this signal exhibited a downfield shift as compared to that in the parent complex[4]. This downfield shift may be attributed to lesser donation of electron density from metal to phosphorus through back bonding. Since only one signal is observed in the ^{31}P NMR spectra of the complex, it suggested that the two triphenylphosphine groups are trans to each other.

Electronic Spectra

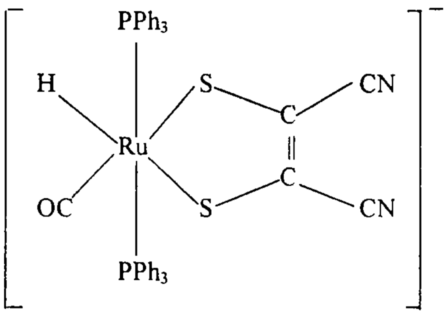
Filled orbitals of proper symmetry of Ru(II) (d^6 configuration) in mono and binuclear complexes may interact with low-lying π* orbitals of the ligand mnt^{2-}. One may, therefore, expect a MLCT transition ($t_{2g} \rightarrow \pi^*$) in these complexes. The energy of these transitions should vary with the nature of the π acceptor ligand.

The electronic spectra of the mono and binuclear complexes (Table I) exhibited bands in the region 450-470 nm. Because neither the precursor complex, $[RuH(CO)Cl(PPh_3)_3]$, nor the ligand, mnt^{2-}, possess this band, it has been assigned to a $d\pi$ - π^* (Ru→ mnt^{2-}) MLCT transition. This band did not exhibit any solvatochromic effect, indicating no change in the dipole moments of the molecule in the ground state and transition state. Alongwith this band, a broad band in the range 320-360 nm was also present in the electronic spectra of all the complexes. This band has been assigned to the M→CO charge transfer band. It can not be assigned to a M-PPh$_3$ MLCT band since it falls well below 250 nm.

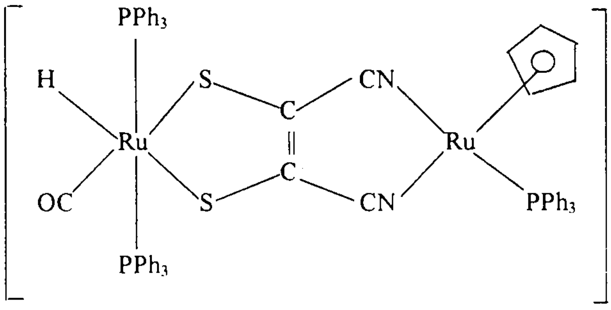
Based on the analytical and spectral data it appears that one of the PPh$_3$ molecules and a Cl ion are substituted by the two sulfur atoms of mnt^{2-} in the complex [RuH(CO)Cl(PPh$_3$)$_3$], leading to the formation of [RuH(CO)(PPh$_3$)$_2${S$_2$C$_2$(CN)$_2$}]$^-$ **(I)**. This anion, upon treatment with [RuCp(EPh$_3$)$_2$Cl], leads to the formation of the binuclear complex [RuH(CO)(PPh$_3$)$_2${S$_2$C$_2$(CN)$_2$}RuCp(EPh$_3$)] **(II)**. Since the mononuclear complex **(I)** contains two uncoordinated nitrile groups and two coordinated thiol groups, it is expected, therefore, that at least two molecules of [RuCp(EPh$_3$)$_2$Cl], should have been coordinated with **(I)**. In contrast, it coordinated with only one molecule of [RuCp(EPh$_3$)$_2$Cl]. This may be due to considerable steric requirements of these moieties. It is obvious from models of the dinuclear complexes that the steric requirements on the coordinated sulfur in the complex **(I)** is more than that on the nitrogen atom of the nitrile group. Most probably, the incoming moiety attacks the nitrile nitrogen atom in the complex **(I)**. It seems definite that the interaction of [RuCp(EPh$_3$)$_2$Cl], with the complex **(I)** is taking place and it is most likely that the coordination site is the nitrile group of the anion. Tentatively, we have proposed the following structures in Fig. 1 to these complexes.

EXPERIMENTAL

Analar grade chemicals were used throughout. All the reactions were carried out under nitrogen atmosphere. The starting complex [RuH(CO)Cl(PPh$_3$)$_3$][33] and the ligand Na$_2$mnt[34] were prepared and purified by literature methods. C, H and N analyses were performed by the Microanalysis Division, RSIC, Central Drug Research Institute, Lucknow. Sulfur determinations in the complexes were made following the literature procedure[35]. IR spectra of the complexes in KBr pellets were recorded on Perkin-Elemer-383 and 880 spectrophotometers. UV-visible and NMR (^{1}H, ^{13}C and ^{31}P) spectra of the



(I)



(II)

Fig. 1. Proposed Structures of the Complexes (I) and (II)

complexes were recorded on Shimadzu UV-160 and Brucker WM-400 FT NMR spectrophotometers, respectively.

Preparation of $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]Ph_4P$

To a suspension of $[RuH(CO)Cl(PPh_3)_3]$ (0.250 g, 0.26 mmole) in methanol-benzene (25 mL, 1:1), Na_2mnt (0.0465 g, 0.25 mmole) was added and the resulting solution was heated to reflux for about 4 h, whereupon it turned to reddish-brown. The solution was cooled to room temperature. After filtration to remove any solid residue, it was concentrated to 10 mL under reduced pressure. Tetraphenylphosphonium chloride (0.100 g, 0.25 mmole) dissolved in methanol (10 mL) was added to the concentrated solution which was then left for slow crystallization. After a few hours a reddish-brown microcrystalline compound separated out. It was centrifuged, washed thoroughly with methanol and diethyl ether and dried in *vacuo*. It melts at 165°C and analysed for $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}]Ph_4P$; yield, 0.182 g (65%).

The tetraphenylarsonium and tetrabutylammonium salts were prepared following the same procedure.

Preparation of $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(PPh_3)]$

To a suspension of $[RuH(CO)Cl(PPh_3)_3]$ (0.250 g, 0.26 mmole) in methanol-benzene (25 mL, 1:1), Na_2mnt (0.0465 g, 0.25 mmole) was added and the resulting solution was heated to reflux for about 4 h. It turned reddish-brown. After cooling to room temperature, the solution was filtered to remove any solid residue. The filtrate was treated with $[RuCp(EPh_3)_2Cl]$ (0.184 g, 0.25 mmole) and allowed to reflux for about 0.5 h, whereupon the ruthenium cyclopentadienyl complex dissolved and an orange-brown microcrystalline compound separated out. It was isolated by centrifugation, washed thoroughly with methanol, diethyl ether and dried in *vacuo*. It melts at 170°C and analyses for $[RuH(CO)(PPh_3)_2\{S_2C_2(CN)_2\}RuCp(PPh_3)]$; yield, 0.192 g (60%).

The triphenylarsine and triphenylstibine containing complexes were prepared following the same above procedure.

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