Reactions of [RuH(CO)Cl(EPh$_3$)$_3$] (E = PPh$_3$, AsPh$_3$) with 1-Piperidinecarbonitrile and 1,4-Piperazinedicarbonitrile in the Presence of an Anion (BF$_4^-$, PF$_6^-$, BPh$_4^-$ and CH$_3$C$_6$H$_4$SO$_3^-$)

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Abstract

Reactions of 1-piperidinecarbonitrile and 1,4-piperazinecarbonitrile with [RuH(CO)Cl(EPh$_3$)$_3$] (E = P, As) have been carried out in the presence of suitable anions such as BF$_4^-$, PF$_6^-$, BPh$_4^-$ and CH$_3$C$_6$H$_4$SO$_3^-$. The reaction products have been characterized using various physicochemical techniques: elemental analyses, magnetic measurements, melting points, conductivity measurements, IR, UV–Vis, ^{1}H and ^{13}C NMR spectroscopy.

Introduction

Interest in the nucleophilicity of the nitrogen atom in 1,4-piperazinedicarbonitrile and 1-piperidinecarbonitrile (hereafter referred as ppz and ppd, respectively) has led us to synthesize a number of complexes [1] where the absence of π-backbonding from Ru(II) to N≡C–N< has been suggested. Furthermore the ligands act in the nitrile form rather than in the carbodiimide form. To study further the extent of backbonding from the Ru(II) metal center into these saturated ligands, we wished to react them with [RuH(CO)Cl(PPh$_3$)$_3$], where one of the phosphine molecules and the Cl$^-$ ion are substitutively labile [2–4]. The substituents ppz and ppd, if bonded *trans* to the hydride and CO moiety, should exhibit some influence on the properties of the latter from which one can deduce information related to the π-backbonding properties of ppz and ppd. This paper reports the results of these reactions.

Experimental

The reactions were carried out under an oxygen-free dry nitrogen atmosphere. All the chemicals used were Analar grade. The starting materials [RuH(CO)-Cl(PPh$_3$)$_3$] and [RuH(CO)Cl(AsPh$_3$)$_3$] were prepared and purified by the literature method [3]. 1-Piperidinecarbonitrile and 1,4-piperazinedicarbonitrile (Aldrich) were used as such without further purification. Carbon, hydrogen, nitrogen analyses and other physical measurements were carried out as described elsewhere [1].

Reactions Procedures

(A) Reaction of 1-piperidinecarbonitrile with [RuH(CO)Cl(PPh$_3$)$_3$] in the presence of a suitable anion

1-Piperidinecarbonitrile (0.209 mmol) in benzene (5 ml) was added to a suspension of [RuH(CO)Cl-(PPh$_3$)$_3$] (200 mg; 0.20 mmol) in benzene (25 ml). The reaction mixture was heated under reflux for 4 h whereby the colour of the solution gradually changed to yellow–orange. The solution was cooled to room temperature and filtered to remove any residue. The filtrate, thus obtained, was reduced to about 5 ml under reduced pressure. A suitable anion (BF$_4^-$, PF$_6^-$, BPh$_4^-$ or PTS$^-$) in methanol (25 ml) was added to it and left overnight for slow crystallization. The shiny crystals were separated by centrifugation, washed with methanol, water, methanol, diethyl ether and dried *in vacuo*. The analyses corresponded to the formula [RuH(CO)(pipd)$_2$(PPh$_3$)$_2$]X (X = BF$_4^-$, BPh$_4^-$, PF$_6^-$ or PTS$^-$).

(B) Reaction of 1,4-piperazine dicarbonitrile with [RuH(CO)Cl(PPh$_3$)$_3$] in the presence of a suitable anion

The reaction of [RuH(CO)Cl(PPh$_3$)$_3$] with 1,4-piperazine dicarbonitrile was carried out by procedure (A) given above except that ppz was added in place of ppd.

Results and Discussion

The yellow shiny crystalline cationic mononuclear and dinuclear complexes obtained from the reactions between [RuH(CO)Cl(EPh$_3$)$_3$] (E = P, As) with ppd

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TABLE 1. Analytical and spectral data of the complexes

Complexes[a] Colour[b] Melting point (°C)	Analyses: found (calc.) (%)			Major IR bands (cm^{-1})			^1H NMR bands (δ values)	^{13}C NMR bands (δ values)
	C	H	N	ν(C≡N)	ν(C≡O)	ν(Ru–H)		
$[RuH(CO)(ppd)_2(PPh_3)_2]Cl$ y, 225	63.5 (63.2)	5.6 (5.4)	5.7 (6.0)	2280, 2220	1945	2005	(7.2–7.8), 3.25, 1.95, 1.85, –7.8	44.85, 127–134, 141.6, 193.5
$[RuH(CO)(ppd)_2(PPh_3)_2]BF_4$ y, 215	62.1 (61.2)	5.6 (5.3)	6.0 (5.82)	2260, 2270, 1035, 1000, 490	1940	1960	(7.2–7.8), 3.25, 1.95, 1.85, –7.8	44.85, 127–134, 141.6, 193.5
$[RuH(CO)(ppd)_2(PPh_3)_2]PF_6$ y, 205	58.0 (57.05)	5.9 (5.0)	5.2 (5.5)	2280, 2255, 1030, 1000, 490	1945	1955		
$[RuH(CO)(ppd)_2(PPh_3)_2]BPh_4$ y, 185	75.2 (74.0)	6.8 (6.0)	4.4 (4.7)	2245, 2200, 1030, 995	1925	1940	(7.2–7.8), 3.2, 1.95, 80, –7.8	
$[RuH(CO)(ppd)_2(PPh_3)_2]PTS$ yo, 220	61.8 (63.2)	5.8 (5.4)	5.5 (5.3)	2260(b), 2240	1965	2020		
$[RuH(CO)(ppd)_2(AsPh_3)_2]Cl$	59.2 (58.3)	5.4 (5.1)	5.4 (5.6)	2280, 2225	1955	2010	(7.2–7.8), 3.26, 1.95, 1.8, –7.7	44.85, 127–134, 141.6, 192.8
$[RuH(CO)(ppd)_2(AsPh_3)_2]BF_4$ y, 210	52.8 (53.1)	4.8 (4.6)	5.1 (5.05)	2280, 2260, 1030, 1000, 480	1965	1980	(7.2–7.8, 3.25, 1.95, 1.85, –7.8	44.85, 127–134, 141.6, 193.8
$[RuH(CO)(ppd)_2(AsPh_3)_2]PF_6$ y, 212	56.2 (56.1)	5.2 (4.9)	5.5 (5.3)	2275, 2220, 1030, 1000, 475	1955	1975		
$[RuH(CO)(ppd)_2(AsPh_3)_2]BPh_4$ y, 145	69.0 (68.2)	5.9 (5.5)	4.3 (4.4)	2280	1955	2010	(7.2–7.8), 3.24, 1.96, 1.8, –7.8	
$[RuH(CO)(ppd)_2(AsPh_3)_2]PTS$	59.0 (58.3)	5.2 (5.0)	4.7 (4.9)	2265, 2220	1958	2010		
$[RuH(CO)(ppz)(PPh_3)_2]_2Cl_2$ ly, 230	62.6 (62.4)	4.9 (4.7)	6.85 (6.8)	2280, 2220	1950	1970	(7.2–7.8), 3.1, –7.8	
$[RuH(CO)(ppz)(PPh_3)_2]_2(BF_4)_2$ ly, 215	57.2 (59.0)	4.8 (4.5)	6.2 (6.4)	1285, 2280, 1030, 990	1955	2000	(7.2–7.8), 3.2, –7.8	
$[RuH(CO)(ppz)(PPh_3)_2]_2(PF_6)_2$ ly, 724	56 (55.2)	4.5 (4.2)	5.7 (6.0)	2220, 2280, 1030, 1000	1975	2010		

$[RuH(CO)(ppz)(PPh_3)_2]_2(PTS)_2$ yo, 220	60.5 (61.2)	4.95 (4.7)	5.9 (5.7)	2280, 2220	1955	2015	
$[RuH(CO)(ppz)(PPh_3)_2]_2(BPh_4)_2$	65.8 (66.0)	5.6 (5.3)	4.8 (5.0)	2260, 2220	1950	2016	7.2–7.8, 3.1, –7.7
$[RuH(CO)(ppz)(AsPh_3)_2]_2Cl_2$	56.8 (56.5)	4.7 (4.3)	6.0 (6.1)	2280, 2230	1960	2010	7.2–7.8, 3.1, –7.8
$[RuH(CO)(ppz)(AsPh_3)_2]_2(BF_4)_2$	52.8 (53.7)	4.4 (4.05)	5.4 (5.8)	2280, 2225	1970 1950	2015	7.2–7.8, 3.2, –7.8
$[RuH(CO)(ppz)(AsPh_3)_2]_2(PF_6)_2$	51.3 (50.0)	4.1 (3.8)	5.3 (5.5)	2276, 2280, 1030, 1000, 480	1975	1990	
$[RuH(CO)(ppz)(AsPh_3)_2]_2(PTS)_2$	55.4 (56.2)	4.9 (4.3)	5.1 (5.3)	2270, 2225	1940	2005	
$[RuH(CO)(ppz)(AsPh_3)_2](BPh_4)_2$	60.7 (61.3)	5.1 (4.9)	4.3 (4.7)	2275, 2225	1955	2010	7.2–7.8, 3.2, –7.8

[a] ppd = 1-piperidinecarbonitrile; ppz = 1,4-piperazinedicarbonitrile; PTS = *p*-toluene sulfonate. [b] y = yellow; yo = yellow orange; ly = light yellow or pale yellow.

and ppz (Table 1) are non-hygroscopic, air-stable, soluble in DMF and CH_3CN, slightly soluble in methanol, benzene, chloroform and dichloromethane, and insoluble in diethyl ether and petroleum ether. In chlorinated solvents the colour of the solutions started changing indicating either slow decomposition of the complexes or formation of a new compound. The interesting aspect of the ppz reactions is that all our attempts to synthesize complexes with ppz acting as a monodentate ligand have failed. It always acted as a bidentate ligand towards two metal ions. Nitrogen atoms of both the CN groups are equally basic with no interaction between them.

The charges on the complexes were distinguished by measuring the conductivity of the complexes in pure acetone following the procedure of Feltham and Hayter [5]. In accordance with this procedure equivalent conductance λ_e was measured over a concentration of 10^{-2}–10^{-4} eq./l, from which the equivalent conductance at zero concentration, λ_0, was determined by extrapolation (Fig. 1a). Subsequently by plotting the values of $(\lambda_0-\lambda_e)$ (Fig. 1b) as a function of $\sqrt{C}$ [5–7] the slopes of the straight lines for ppd [432] and ppz [728] were measured which compared very well with the values of Feltham and Hayter for the 1:1 and 1:2 complexes, respectively. These values provide further evidence regarding the charges on the cation.

The bonding modes in the complexes and their tentative structures have been deduced following spectral studies.

IR Spectra

It is assumed that the ligands exist in the N,N′-disubstituted nitrile (N≡C–N<) form. The possibility of their existence in the carbodiimide form (–N=C=N–) is remote. It can only contribute as a resonating structure where the lone pair of electrons on >N–CN nitrogen participate in the delocalization process (>N=C=N:⁻) [8–10]. This too is possible when the lone pair is present in pure p_z orbital. With this presumption, one expects IR active bands due to ν(C≡N), ν(C–N) and ν(N–CN) around 2250, 1000 and 400 cm^{-1}, respectively. Furthermore the spectra of the carbodiimide form should display a strong band due to ν_{asym} (N=C=N) and a weak band due to ν_{sym} (N=C=N) around 2200 and 2000 cm^{-1} [8, 10]. The spectra of ppd and ppz exhibit bands at 2240, 1010 and 410 cm^{-1}, supporting the first model [8]. It is also unlikely that the lone pair of electrons on (>N–C≡N) is involved in the resonance structure owing to the non-planarity of the molecule, because of which the non-bonding orbital containing the lone pair has some S–C character inhibiting the contribution of (>N=C=N:⁻) to the structure.

The IR spectra of the complexes of ppd show bands around 2275 (two), 1010 (two) and 450 (broad) cm^{-1}. The shift of the 2240 cm^{-1} band

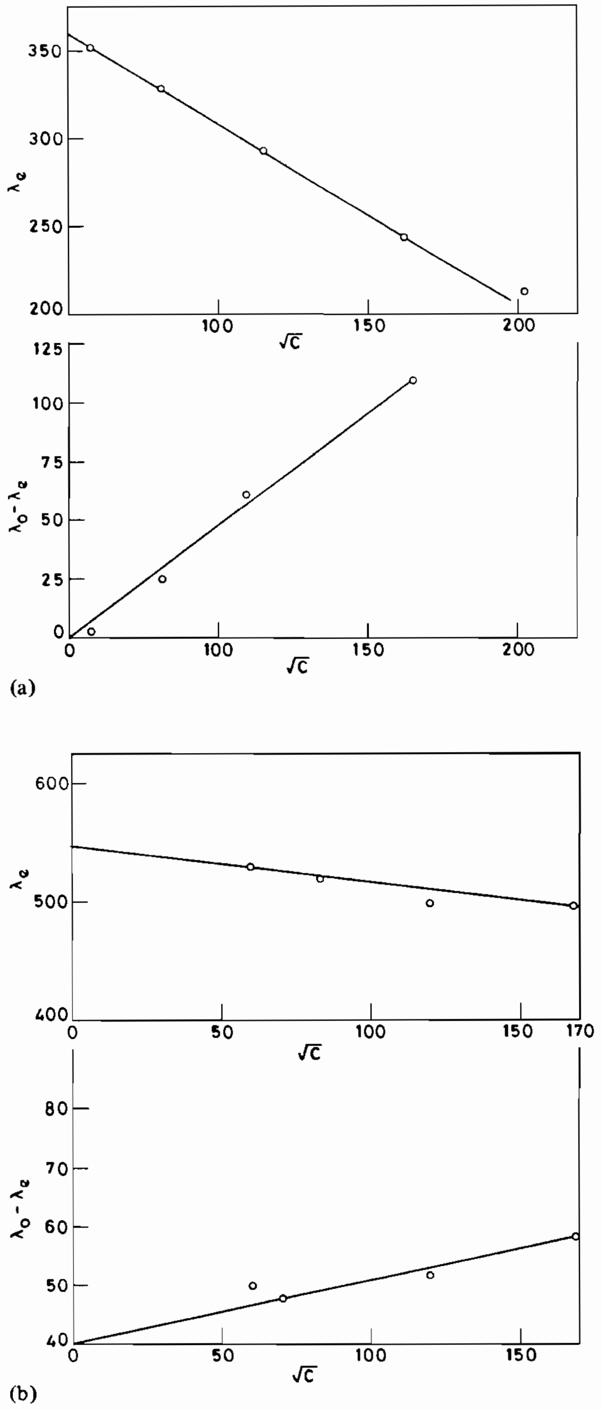


Fig. 1. Plots of λ_e vs. $\sqrt{C}$ and $(\lambda_0 - \lambda_e)$ vs. $\sqrt{C}$ for (a) [RuH(CO)(ppz)$(PPh_3)_3]_2Cl_2$ and (b) [RuH(CO)$(ppd)_2(PPh_3)_2$]Cl.

towards the higher wave numbers with respect to the parent molecule reflects (i) direct coordination of the metal ion [Ru(II)] to the nitrogen of the nitrile group, (ii) the absence of backbonding from Ru(II) or its coordination with the bond of the (N≡C–N<) group. (The latter should cause a shift of the ν(C≡N) position towards lower wave numbers.) There is a distinct splitting of these bands suggesting 'neighbour interaction'. Thus it is likely that the two ligand molecules ppd or ppz are bonded to the metal center in the *cis* positions causing intramolecular 'neighbour interaction' which will result in the split in the IR bands [ν_{asym}(C≡N) and ν_{sym}(C≡N)]. Although similar splitting is also observed in the band at 1010 cm^{-1}, one of the splitted band shifts to lower wave number (*c.* 990 cm^{-1}) while the other shifts to higher wave numbers (*c.* 1030 cm^{-1}). This splitting pattern suggest that the position of the original band (C–N) at 1010 cm^{-1} is practically unaffected on coordination and the amide nitrogen (>N–CN) is not involved in complexation. The broadness of the 430 cm^{-1} band also implies 'neighbour' interaction of (N≡C–N<) groups in the coordinated state.

The positions of ν(Ru–H) and ν(C≡O) in the spectra of the complexes with respect to those in the chloro complex shift toward lower and higher wave numbers, respectively (Table 1). In a couple of complexes it became difficult to distinguish the two bands because of the large shifts in their positions. These shifts imply the reduction in the Ru–H bond order and metal to carbon interaction in the ppd substituted products. We have previously shown [1] that there is reasonably good evidence of non-involvement of Ru(II) electrons in the backbonding with ppd molecules. Substitution of a PPh_3 molecule (π-acceptor) and Cl^- ion (π-donor) by bonded ppd molecules should lead to no change in the positions of ν(Ru–H) and ν(C≡O) ligands, or it should cause an increase in the Ru–H bond order and Ru–C π interaction. Though the lack of data at this stage regarding the factors influencing the backbonding of Ru to CO or H^- prevents us from suggesting any definite reason for reduction in the Ru–H bond order and M → C interaction, it appears that the bond orders of Ru–H and Ru–C are very sensitive to the positive charge residing on the metal center. The observed shifts in the band positions of ν(Ru–H) and ν(C≡O) are therefore attributed to the increased positive charge on the metal center of the substituted products.

The IR spectra of ppz and its complexes are similar to those of ppd and its complexes. The two >N–C≡N groups in ppz are too far apart to interact through inductive or resonance effects and bring about either splitting or broadening of the NCN bands.

The characteristic bands due to PPh_3, $AsPh_3$, PF_6^-, BF_4^-, BPh_4^- and PTS are exhibited in the spectra of their respective compounds. Unfortunately the bands due to ν(Ru–N), ν(Ru–C) and ν(Ru–P) could not be conclusively assigned because of the presence of a large number of bands in the lower wave number region.

Electronic Spectra

The electronic spectra of the complexes of the ppd and ppz exhibited broad medium intensity bands in the region 312–260 nm. They did not display any bands in the visible region. These have been assigned as MLCT bands (M → CO). It will be highly impossible to assign them to M → N–C, N or M → EPh_3 MLCT transitions since the latter transitions occur below 250 nm. These bands did not show any solvatochromic effect suggesting no change in the dipole moment of the molecule in the ground and excited states. This supports our assignment because the presence of ruthenium to ppd and ppz charge transfer bands would change the dipole moment of the excited state. Bands below 250 nm have not been assigned.

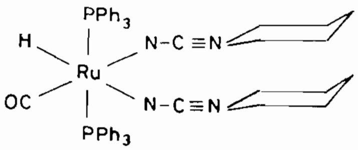
NMR Spectra

Investigations of chemical shifts in proton and ^{13}C NMR spectra of these complexes were largely complicated by two basic problems: (i) their very low solubility in a number of solvents viz. deuterated alcohols, C_6D_6, acetone d^6, etc., (ii) slow reaction of the complexes by chlorinated solvents like $CDCl_3$. Thus their NMR spectra, if taken in $CDCl_3$ or any other chlorinated solvent, did not exhibit any signal of hydride if they were not taken immediately after dissolving them. So only in a couple of complexes were we able to observe a good NMR spectrum (Table 1).

^1H NMR spectra of chloro and ppd complexes are shown in Table 1. They exhibit signals around δ 7.2–7.8(m) (EPh_3), δ 3.25(b), δ 1.85–1.95(b), (CH_2 protons of ppd ring) and δ 3.2 (CH_2 protons of ppz ring). In a couple of complexes we were able to obtain a hydride signal at δ (–7.87(t)) if the spectra were taken immediately after dissolving the complexes in $CDCl_3$. The signals due to the position of EPh_3 and ppd or ppz signals are well in keeping with the literature values [1]. Only a perturbation was observed for the hydride ion which shows deshielding of the hydride hydrogen in the complex with respect to the parent complex. The direction of the shift reflects the lower degree of polarization of electron density towards the hydride ion which would cause weakening of the metal hydride bond. This further supports the conclusions obtained from IR spectral studies.

^{13}C NMR spectra of the ppd complexes exhibited signals at about δ 44.8 (CH_2 carbons of ppd ring), δ 127–134(m) (EPh_3 carbon), δ 141.6 (>N–C≡N carbon) and δ 193.8 (carbonylcarbon). The deshielding of the complexed (>N–C≡N) group versus ligand (δ 117 ppm) indicates that on complexation of the nitrogen of CN with ruthenium, the electron density on the carbon atom is polarized towards nitrogen resulting in deshielding of the carbon nucleus. It further suggests non-involvement of the nitrogen lone pair (>N–CN) in bonding with the metal center because in the case of involvement the possibility of deshielding should have been much less.

Based on the physicochemical data it appears certain that ruthenium is coordinated through the nitrogen atom of the CN group. Although the molecules could be present in a number of conformers (chair–chair, chair–boat boat–boat etc), one can rule out the possibility of their existing in the boat form on the following grounds: (i) the steric interaction between the two CN groups in 1,4 position, (ii) lone pair–lone pair repulsion on the two nitrogen atoms. Thus the boat form will be energetically unfavourable. Therefore we suggest the complex is in the chair–chair form with two ppz in the *cis* position, supporting the previous observations. Similarly in the ppd complexes the chair–chair form with the two ppd molecules *cis* to each other is preferred with the NCN group substituent occupying an equatorial position to avoid interaction with the neighbouring CH_2 groups.



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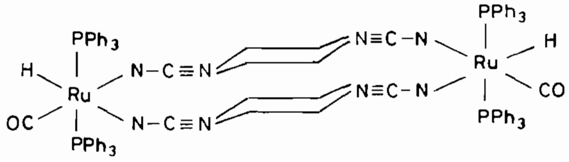

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