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Studies on Ruthenium and Rhodium Complexes Containing 1,2- bis (N-Methylbenzimidazolyl)Benzene and Catalytic Transfer Hydrogenation

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Abstract

Reactions of ruthenium(III) chloride and rhodium(III) halides with 1,2-bis(N-methylbenzimidazolyl)benzene (N-N) in stoicheiometric amounts in methanol produced binuclear complexes of the compositions $[RuCl_2(\mu\text{- Cl})\ (N\text{-}N)]_2$ and $[RhX_3(N\text{-}N)]_2.\ nH_2O$ (n = 0, X = Br ; n = 1, X = Cl). $[RhI_3(N\text{-}N)]_2$ was prepared by stirring a mixture of rhodium trichloride with fifteen fold excess of sodium iodide and the N-heterocycle, N-N in methanol. Ruthenium chloride and rhodium halides in 2-methoxyethanol/alcohol reacted with N-N in presence of CO to produce complexes of the types $[RuCl_2(CO)_2(N\text{-}N)]$, $[Rh_2Cl_2(CO)_2(N\text{-}N)]$ and $[Rh(CO)_2(N\text{-}N)]Br$. The

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complexes were characterized by elemental analyses, molar conductivity measurements, IR, electronic, ^{1}H- and ^{13}C- NMR spectral studies and by mass spectra. Probable structures have been proposed for the complexes. The complex $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ in DMF was found to reduce nitro compounds to corresponding amines using formic acid as the hydrogen donor.

Keywords: 1,2-bis(N-methylbenzimidazolyl) benzene, ruthenium and rhodium complexes, carbonyl.

Introduction

Benzimidazole and its derivatives have been prepared in view of their wide pharmacological potency. The compounds have interesting anti-inflammatory, antimicrobial, antitumour, anticancer and neuroprotective properties.[1-8] It has been shown that 1, 3, 5 –tri(phenyl-2-benzimidazolyl)benzene derivatives exhibit charge transfer property. They are also found to be blue emitters and effective chelating ligands for metal ions such as Cu(I) and Pt(II).[9-11] The complexes of ruthenium are of potential importance in view of their catalytic activity towards several reactions such as polymerization, photosplitting of water and solar energy conversions,[12] hydroformylation,[13] isomerisation and related reactions involving organic substrates.[14-16]

Complexes of rhodium(I) and rhodium(III) containing nitrogen heterocycles have received considerable attention in view of their possible application in catalytic hydrogenation, hydrosilation and water gas shift reactions, liquid crystals and also in inorganic synthesis and photochemistry.[17-24] The palladium complexes containing the N-heterocycle, 1,2-bis(N-methylbenzimidazolyl) benzene have been reported earlier.[25] In continuation of this work here in we describe the synthesis and characterization of halo and carbonyl complexes of ruthenium and rhodium containing 1,2-bis(N-methylbenzimidazolyl) benzene (N-N ; Figure 1).

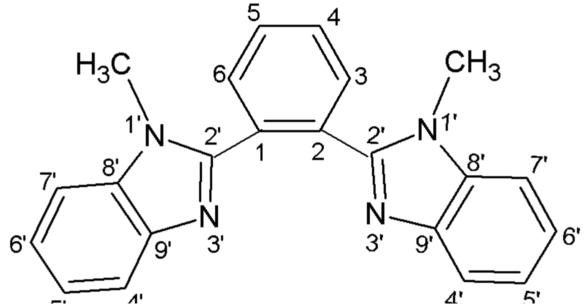

Fig 1

Experimental

Reagents

1,2-bis(N-methylbenzimidazolyl) benzene (N-N) was prepared according to literature method.[26] Hydrated ruthenium(III) and rhodium(III) chlorides were procured from Arora Matthey Ltd, Kolkata. Hydrated rhodium (III) bromide was prepared as described elsewhere.[27] The solvents employed were procured from Merck and were purified according to literature methods.[28]

Measurements

The IR (nujol mull) and Far-IR (polyethylene powder) spectra of the complexes were recorded on a Nicolet 400D and Bruker IFS 113V spectrometers respectively. Electronic spectra of the complexes in methanol were recorded on a Hitachi U-3400 spectrophotometer. The molar conductivity measurements were determined using an Elico model CM-82T conductivity cell. The ^1H and ^{13}C NMR spectra of the compounds in DMSO–d_6 were recorded at ambient temperature on Bruker 400 MHz FT NMR spectrometer using TMS as the internal standard at NMR Research centre, IISc, Bangalore. TGA was carried out on a Mettler TAHE – 20 Thermal analyzer with a scan rate of 5°C min^{-1} in air. The FAB-mass spectra and CHN analyses were carried out at CDRI Lucknow, India.

Preparation of the complexes [RuCl$_2$(μ-Cl)(N-N)]$_2$ [N-N = 1,2- bis(N-methylbenzimidazolyl) benzene]

Hydrated ruthenium tri-chloride (1 mmol) in methanol (15 mL) was treated with N-N (1 mmol) in 1:1 mole ratio in methanol (10 mL). On refluxing the mixture for 4 h, a brown solid separated. The solid was washed with methanol and dried in vacuo. Yield: 65%.

[RuCl$_2$(CO)$_2$(N-N)]

Carbon monoxide was bubbled through 2-methoxy ethanol (10 mL) solution of hydrated ruthenium tri-chloride (1 mmol) at refluxing temperature till the solution turned lemon yellow. To the resulting carbonylated solution, N-N (4 mmol) was added and the passage of CO was continued when a yellow solid separated. It was filtered and the solid was washed with 2-methoxy ethanol and dried in vacuo. Yield: 90%.

[RhX$_3$(N-N)]$_2$ nH$_2$O (n = 0, X = Br ; n = 1, X = Cl)

RhX$_3$ (X = Cl or Br) (1 mmol) in methanol (5 mL) was treated with N-N (1 mmol) in methanol (5 mL). The mixture was refluxed for 4 h when a brown solid separated. The solid was washed with methanol and dried in vacuo. Yield: 75%.

[RhI$_3$(N-N)]$_2$

RhCl$_3$ (1 mmol) in methanol (5 mL) was treated with sodium iodide (15 mmol) and N-N (1 mmol) in methanol (5 mL). The mixture was stirred for 4 h when a brown solid separated. The solid was filtered, washed with methanol and dried in vacuo. Yield: 75%.

[Rh$_2$Cl$_2$(CO)$_2$ (N-N)] and [Rh (CO)$_2$ (N-N)] Br

RhX$_3$ (X = Cl or Br) (1 mmol) was dissolved in ethanol (10 mL) and CO was passed through the solution at warm temperature till the solution turned lemon yellow. To the carbonylated solution of rhodium tri-chloride / rhodium tri-bromide, N-N (1 mmol) in ethanol (5 mL) was added and the passage of CO was continued when a brown solid got separated. The solid was washed with ethanol and dried in vacuo. Yield: 70%.

Catalytic transfer hydrogenation reaction

The $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ (1 mmol) was dissolved in 15 mL of DMF. To this 1 mmol of substrate (nitro compoud) and 10 mL of formic acid were added. The reaction was maintained at refluxing temperature. After the reaction, the product was separated and characterized by TLC, melting point and IR spectral measurements.[29,30]

Results and discussion

The halides of ruthenium and rhodium react with N-N (`I`) to produce yellow/brown complexes of the compositions $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$, $[RhX_3(N\text{-}N)]_2.nH_2O$ (n = 1, X = Cl; n = 0, X = Br or I). Carbonyl complexes were prepared by passing carbon monoxide through the solutions of metal salts in methoxy ethanol / alcohol at warm / refluxing temperature and then adding N-N to obtain the complexes of the compositions $[RuCl_2(CO)_2(N\text{-}N)]$, $[Rh_2Cl_2(CO)_2(N\text{-}N)]$ and $[Rh(CO)_2(N\text{-}N)]Br$. The complexes are insoluble in common organic solvents but are soluble in dimethyl formamide in which they behave as non-electrolytes except for $[Rh(CO)_2(N\text{-}N)]Br$ complex which showed 1:1 electrolytic behavior (Table 1) in DMF. The thermogravimetric analysis (TGA) of the complex, $[RhCl_3(N\text{-}N)]_2.H_2O$ showed weight loss in the range 80-100° C corresponding to the loss of a water molecule implying its hydrated nature.[31-33]

The nujol mull IR spectrum of `I` (N-N) exhibited a peak at 1616 cm^{-1} due to $\nu_{C=C}$ and $\nu_{C=N}$. A peak observed at 1403 cm^{-1} is assigned to the symmetrical deformation mode of $N\text{-}CH_3$ group. The peaks at 1290, 1010 and 964 cm^{-1} are ascribed to benzimidazole ring vibrations. The IR spectra of the metal complexes are comparable to those of the uncoordinated N-N except for minor shifts in the positions of some of the bands. The spectral data of the complexes are suggestive of the coordination of N-N via the tertiary nitrogen atoms of the benzimidazole moiety.[34] The IR spectrum of $[RuCl_2(CO)_2(N\text{-}N)]$ complex displayed two ν_{CO} peaks at 1983 and 2060 cm^{-1} due to the cis location of the carbonyls.[35,36] The benzimidazole ring vibrations are observed around 1290, 1021, 969, 555 and 447 cm^{-1} (Table 1). $Rh_2Cl_2(CO)_2(N\text{-}N)$ and $[Rh(CO)_2(N\text{-}N)]Br$ complexes, in addition to the bands due to N-N also exhibit two strong bands around 2000 and 2100 cm^{-1} arising from the <u>cis</u> location of the carbonyl groups. Far-IR spectrum of $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ displayed peaks due to the presence of both bridging (b) and terminal (t) chlorides at 310 and 350 cm^{-1} respectively.[37] The $\nu_{Ru\text{-}N}$ is observed at 210 and 214 cm^{-1}. The far IR-spectra of $[RhX_3(N\text{-}N)]_2.nH_2O$ (n = 1, X = Cl; n = 0, X = Br or I) and $Rh_2Cl_2(CO)_2(N\text{-}N)$ complexes displayed peaks around 210 and 300 cm^{-1} due to bridging and terminal metal-halide stretching frequencies.

The electronic absorption spectrum of $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ complex exhibited a band at 27173 cm^{-1} due to metal-ligand charge-transfer transition and another peak at 16583 cm^{-1} due to $^2T_{2g}\rightarrow{}^4T_{1g}$ transition of d^6 Ru(III) in octahedral environment. A peak observed at 32000 cm^{-1} is assigned to metal-ligand charge transfer transition.[38] The solid state electronic spectra of $[RhX_3(N\text{-}N)]_2.nH_2O$ (n = 1, X = Cl; n = 0, X = Br or I) complexes displayed weak bands around 20600 and 27000 cm^{-1} and these are assigned to $^1A_{1g}\rightarrow{}^1T_{1g}$ and $^1A_{1g}\rightarrow{}^1T_{2g}$ transitions of octahedral spin paired d^6 Rh(III) systems.[39,40]

The magnetic moment for $[RuCl_2(\mu\text{-}Cl)N\text{-}N]_2$ at ambient temperature is found to be 1.72 BM and is in the expected range for low spin d^5 Ru(III) systems.[41-42] The X-band ESR spectrum of $[RuCl_2(\mu\text{-}Cl)N\text{-}N]_2$ complex has been recorded at ambient temperature and 77 K. The spectral profiles are typical of axial type ($g_{\parallel} > g_{\perp}$) implying a $d_{x2\text{-}y2}$ ground state.[41] The spectral features resemble those of six-coordinate octahedral ruthenium(III) complexes. The ESR signals corresponding to $g_{\parallel}$ and $g_{\perp}$ are centred around 2.26 and 1.95 respectively and the $g_{\parallel}$ value of the complex, indicates considerable covalent character in the metal-ligand bond.

The FAB-mass spectra of $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ and $[RhX_3(N\text{-}N)]_2.nH_2O$ (n = 1, X = Cl; n = 0, X = Br or I) have revealed that the complexes are binuclear in nature. For the ruthenium complex, the molecular ion peak corresponding to the dimer is observed at m/z 1094. The m/z peaks at 1055, 983, 855, 682, 647, 531 and 441, probably arise due to the fragmented species $[Ru_2Cl_5(N\text{-}N)_2\text{-}2H]$, $[Ru_2Cl_3(N\text{-}N)_2\text{-}4H]$, $RuCl_3(N\text{-}N)_2$, $Ru_2Cl_4[(N\text{-}N)\text{-}2H]$, $Ru_2Cl_3[(N\text{-}N)\text{-}2H)$, $RuCl_3[(N\text{-}N)\text{-}CH_3]$ and Ru(N-N) respectively. In addition, peaks due to the association of fragments are observed at 1130, 1177, 1316 and 1430 which correspond to $Ru_2Cl_7(N\text{-}N)_2$, $Ru_2Cl_8(N\text{-}N)_2(CH_3\text{-}2H)$, $Ru_3Cl_9(N\text{-}N)_2(CH_3)$ and $Ru_5Cl_6(N\text{-}N)_2(CH_3)\text{-}2H$ species respectively.

Table 1: Analytical and IR spectral data of I (N-N) and complexes of ruthenium and rhodium

Compound	Color	M.P. (^{0}C)	Λ^a (Ω^{-1} cm^2 mol^{-1})	Analytical data Found (calcd.%) *			I.r. Spectral data (cm^{-1})		
				C	H	N	$\delta_{N\text{-}CH3}$	$\nu_{C=C}$ & $\nu_{C=N}$	ν_{M-Xt} / ν_{M-Xb} / ν_{CO}
N-N	White	250	-	78.14(78.08)	5.37(5.36)	16.57(16.56)	1403	1545,1616	----
$[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$	Brown	>260	10	48.48(48.40)	3.26(3.30)	10.30(10.20)	1409	1545,1621	350 / 308
$[RuCl_2(CO)_2(N\text{-}N)]$	Yellow	> 250	13	50.90(50.89)	3.25(3.20)	9.87(9.89)	1409	1545,1616	1983, 2060
$[RhCl_3(N\text{-}N)]_2.\ H_2O$	Brown	> 270	21	46.73(46.70)	3.61(3.56)	9.97(9.90)	1403	1550,1621	351 / 300
$[RhBr_3(N\text{-}N)]_2$	Brown	> 260	18	40.46(40.42)	2.75(2.77)	8.46(8.57)	1403	1550,1621	258 / 211
$[RhI_3(N\text{-}N)]_2$	Brown	> 260	21	32.05(32.10)	2.40(2.20)	6.75(6.80)	1403	1548,1616	255 / 210
$[Rh_2Cl_2(CO)_2(N\text{-}N)]$	Brown	> 250	11	43.10(43.00)	2.75(2.70)	8.36(8.34)	1409	1548,1621	2102, 2024
$[Rh(CO)_2(N\text{-}N)]Br$	Brown	> 250	70	49.93(49.90)	3.21(3.14)	9.76(9.70)	1409	1547,1616	2112, 2010

[a] Molar conductance of Ca. 10^{-3} M solutions in DMF around 25^{0}C; *Calculated values are in parentheses.

The mass spectrum of $[RhBr_3(N\text{-}N)]_2$ displayed a peak at m/z 1307 corresponding to binuclear nature of the complex. Other peaks of m/z values 1295, 1202, 1040, 939, 883, 861 and 521 correpond to fragmented species $Rh_2Br_5(N\text{-}N)_2\text{-}CH_3)\text{-}2H^+$, $Rh_2Br_4(N\text{-}N)$, $Rh_2Br_2(N\text{-}N)_2$, $RhBr_2(N\text{-}N)_2$, $Rh_2(N\text{-}N)_2$, $RhBr(N\text{-}N)_2$ and $RhBr(N\text{-}N + H^+)$ respectively.

The ^{1}H NMR spectrum of `N-N` in DMSO-d$_6$ exhibited a multiplet at δ 7.8 due to middle benzene ring protons (H-3 to 6). Further, the spectrum revealed that the corresponding protons of the two benzimidazole moieties of the heterocycle are equivalent. The resonances due to H-4' and H–7' are observed as doublets at δ 7.50 and 7.47 respectively and the signals due to H-5' and H-6' as triplets at δ 7.20 and 7.14 respectively (Table 2). The N-CH$_3$ resonance appeared as a singlet at δ 3.48. The PMR spectra of the ruthenium(II) and rhodium(III) and rhodium(I) complexes exhibited peaks due to coordinated N-N and these have undergone minor shifts as compared to those of I (N-N).[34]

The ^{13}C NMR spectrum of N-N exhibited ten signals in the chemical shift (δ) range 110.0 – 158.4 due to ring protons and another peak at δ 30.63 due to N-CH$_3$. The assignments of the signals are made with the aid of off-resonance proton decoupled spectrum of N-N (Table 3). The resonances due to C-8' and C-9' in the coordinated heterocycle are shifted up-field. The other carbon signals are shifted either up-field or downfield relative to those of the uncoordinated N-heterocycle. The negative coordination induced shifts, (c.i.s = δ_{complex} - δ_{ligand}) are attributed to greater metal-to-ligand π-back donation, whereas positive c.i.s to ligand–to–metal π-donation. The carbon-2' resonance of $[RhCl_3(N\text{-}N)]_2.H_2O$ has undergone up-field shift where as that of bromo and iodo complexes has undergone downfield shift.[43-45] The ^{13}C NMR spectra of the carbonyl complexes of rhodium(I) have displayed resonances at δ 188 (chloro) and δ 189 (bromo) and of ruthenium(II) at δ 210 due to coordinated CO.

Stereochemistry

The analytical data, IR, ^{1}H and ^{13}C NMR spectral results have indicated that the N-N is coordinated to the metal ion. The N-N is planar and can serve as chelating or bridging bi-dentate ligand.[41] The far-IR spectrum of $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ complex has indicated the presence of both bridging and terminal chlorides. The FAB-mass spectrum of $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ has supported the di-nuclear nature of the complex with each ruthenium in an octahedral environment (Figure 2).

Table 2 ^{1}H NMR spectral data of N-N (Figure 1) and complexes in DMSO-d_6 (δ in ppm)^a

Compound ^{b}	Benzimidazole ring					Benzene ring	
	H – 4'	H – 5'	H –6'	H – 7'	N–CH_3	H –3,6	H – 4,5
N-N	7.50 d	7.20 t	7.14 t	7.47 d	3.48 s	7.80 m	7.80 m
$[RuCl_2(CO)_2(N\text{-}N)]$	7.36 d (-0.14)	7.04t (-0.16)	6.95 t (-0.19)	6.66 d (-0.81)	3.39 (-0.09)	7.76 m (-0.04)	7.48 m (-0.32)
$[RhCl_3(N\text{-}N)]_2\ H_2O$	7.36 cm (-0.14)	7.04 cm (-0.16)	6.95 cm (-0.19)	6.66 cm (-0.81)	3.65 s (0.17)	7.76 m (-0.04)	7.48 m (-0.32)
$[RhBr_3(N\text{-}N)]_2$	7.62 d (0.12)	7.14 t (-0.06)	6.78 t (-0.36)	7.00 d (-0.47)	4.00 s (0.52)	8.17 m (0.37)	8.00 m (0.20)
$[RhI_3(N\text{-}N)]_2$	7.65 d (0.15)	7.15 t (-0.05)	6.77 t (-0.37)	7.02 d (-0.45)	4.00 s (0.21)	8.15 m (0.35)	8.00 m (0.20)
$[Rh_2Cl_2(CO)_2(N\text{-}N)]$	7.85 cm (0.35)	7.35 cm (0.15)	7.35 cm (0.21)	7.85 cm (0.38)	3.88 s (0.40)	8.16 m (0.36)	8.00 m (0.20)
$[Rh(CO)_2(N\text{-}N)]Br$	7.28 cm (-0.22)	7.00 cm (-0.20)	7.00 cm (-0.14)	7.28 cm (-0.19)	3.86 s (0.38)	7.78 m (-0.02)	7.49 m (-0.31)

^{a}Values in parentheses are co-ordination induced shifts (c.i.s) = $\delta_{complex} - \delta_{ligand}$

^{b}s = singlet ; d = doublet; t = triplet; m = multiplet; cm = complex multiplet

Table 3 ^{13}C NMR spectral data of N-N (Figure 1) and complexes in dmso-d_6 (δ in ppm)*

Compound	Benzimidazole ring								Benzene ring		
	C-2'	C-4'	C-5'	C-6'	C-7'	C-8'	C-9'	N – CH$_3$	C-1,2	C-3,6	C- 4,5
N-N	152.18	118.96	122.20	121.65	110.30	135.60	142.38	30.63	130.75	131.33	129.82
[RuCl$_2$(CO)$_2$(N-N)] [a]	152.09 (-0.09)	121.34 (2.38)	124.81 (2.61)	122.19 (0.54)	111.15 (0.85)	135.16 (-0.44)	140.21 (-2.17)	29.65 (-0.98)	126.30 (-4.45)	132.81 (1.48)	129.90 (0.08)
[RhCl$_3$(N-N)]$_{2.}$ H$_2$O	151.53 (-0.65)	121.50 (2.54)	124.34 (2.14)	122.18 (0.53)	111.04 (0.74)	135.27 (-0.33)	139.82 (-2.56)	33.53 (2.90)	125.90 (-4.85)	132.46 (1.13)	129.28 (-0.54)
[RhBr$_3$(N-N)]$_2$	153.31 (1.13)	121.51 (2.55)	123.70 (1.50)	122.74 (1.09)	111.00 (0.70)	134.88 (-0.72)	141.04 (-1.34)	33.70 (3.07)	128.58 (-2.17)	133.11 (1.78)	130.93 (1.11)
[RhI$_3$(N-N)]$_2$	153.30 (1.12)	121.48 (2.52)	123.68 (1.48)	122.73 (1.08)	110.99 (0.69)	134.87 (-0.73)	141.03 (-1.35)	33.70 (3.07)	128.58 (-2.17)	133.09 (1.76)	130.91 (1.09)
[Rh$_2$Cl$_2$(CO)$_2$(N-N)] [b]	152.60 (0.42)	120.60 (1.64)	124.50 (2.30)	121.80 (0.15)	110.90 (0.60)	134.70 (-0.90)	139.90 (-2.48)	32.80 (2.17)	127.20 (-3.55)	132.42 (1.09)	129.70 (-0.12)
[Rh (CO)$_2$(N-N)] Br [c]	151.33 (-0.85)	121.50 (2.54)	124.50 (2.30)	123.20 (1.55)	111.00 (0.70)	134.90 (-0.70)	140.30 (-2.08)	33.70 (3.07)	127.56 (-3.19)	132.50 (1.17)	129.60 (-0.22)

* Values in parentheses are co-ordination induced shifts : c. i.s = $\delta_{complex} - \delta_{ligand}$

[a] δ_{CO} = 210 ppm, [b] δ_{CO} = 188 ppm, [c] δ_{CO} = 189 ppm

The di-carbonyl complex RuCl$_2$(CO)$_2$(N-N) displayed two ν_{CO} peaks implying the cis location of the carbonyl groups. The complex is proposed to have octahedral geometry (III) with N-N functioning as chelating bi-dentate ligand.

The di-carbonyl complex $RuCl_2(CO)_2(N\text{-}N)$ displayed two ν_{CO} peaks implying the cis location of the carbonyl groups. The complex is proposed to have octahedral geometry (Figure 3) with N-N functioning as chelating bi-dentate ligand.

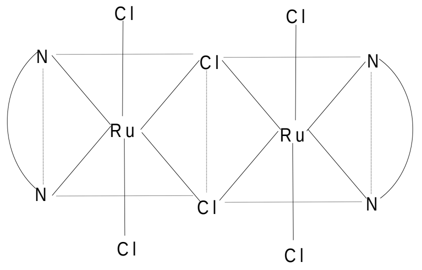

Fig 2

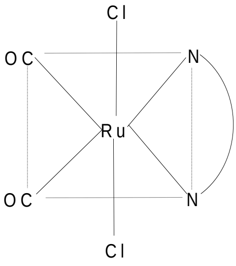

Fig 3

Based on molar conductivity, FAB-mass, IR and electronic spectral data, the complexes of rhodium are suggested to have di-halobridged structure (Figure 4) with each rhodium in an octahedral environment and N-N acting as chelating bi-dentate.

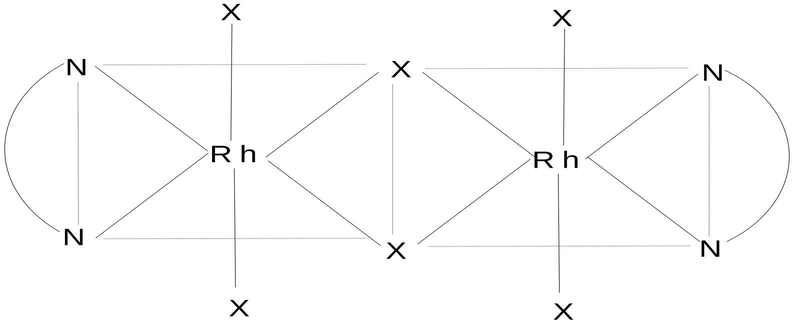

Fig 4 X = Cl, Br or I

The IR spectra of rhodium(I) carbonyl complexes have indicated the **cis** disposition of the carbonyl groups. The FAR- IR spectrum of the chloro carbonyl complex has revealed bridging nature of chlorides and this is substantiated by mass spectral data. The complex is non-electrolyte in DMF and is proposed to have binuclear structure (Figure 5) with each rhodium having a square planar environment. The bromo carbonyl being mononuclear behaved as 1:1 electrolyte in DMF and the cation is proposed to have square planar geometry (Figure 6).

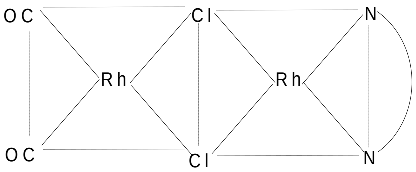

Fig 5

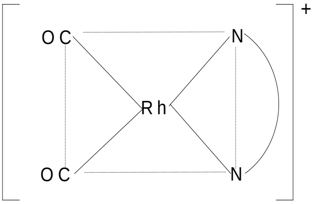

Fig 6

Catalytic transfer hydrogenation

The ruthenium complex, $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ was investigated for its catalytic activity towards reduction of nitro compounds using formic acid as the hydrogen donor. The substrates were o-, m- and p-nitro aniline, nitro benzoic acid and nitro phenols for transfer hydrogenation reactions. The reaction was carried out by taking $[RuCl_2(\mu\text{-}Cl)(N\text{-}N)]_2$ (1 mmol) as catalyst in DMF (15 ml) with nitro compounds (1 mmol) as substrates using formic acid (10 ml) as hydrogen donor. It was found that all the isomers of nitro benzoic acid and nitro phenol reduced to amino benzoic acid and amino phenol respectively. Under the given conditions, the reduction of nitro phenols was faster (10 – 15 hrs) compared to nitro benzoic acid (18 – 20 hrs). In the case of isomers of nitro aniline, p-nitro aniline reduced partially to p-phenylenediamine whereas the other isomers did not undergo reduction even after 36 hrs. The products were analyzed by TLC, MP and IR-spectra. The IR spectrum of the reduced product of p-nitro aniline showed peaks around 3100 and 1605 cm^{-1} due ν_{NH} and ν_{NO2} respectively implying partial reduction. The hydrogen transfer might be inhibited by the presence of electron donating $-NH_2$ group which tends to increase the electron density on the nitro group thereby lowering the polarization of the NO bonds.[45] This would lead to the slower rate of hydrogenation (Table 4).

Table 4: Reduction of nitro compounds using $[RuCl_2(\mu - Cl)N\text{-}N]_2$ as catalyst at 100^0C in DMF

Substrate	Reaction time in hrs.	Products	MP (°C)
p-nitro aniline	30	p-phenylenediamine	142-145
o-nitro phenol	10	o-aminophenol	176
m-nitro phenol	14	m-aminophenol	127
p-nitro phenol	13	p-aminophenol	114
o-nitro benzoic acid	26	o-amino benzoic acid	114
m-nitro benzoic acid	20	m-amino benzoic acid	176
p-nitro benzoic acid	18	p-amino benzoic acid	189

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