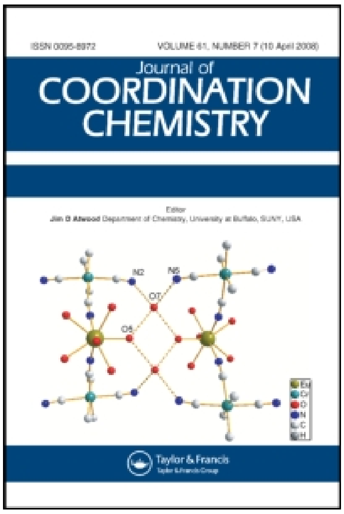

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Spectroscopic characterization and electrochemical studies of ruthenium(II) carbonyl complexes containing bidentate Schiff bases and triphenylphosphine or a nitrogen heterocycle

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Spectroscopic characterization and electrochemical studies of ruthenium(II) carbonyl complexes containing bidentate Schiff bases and triphenylphosphine or a nitrogen heterocycle

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Reactions of ruthenium(II) carbonyl complexes of the type [RuHCl(CO)(PPh$_3$)$_2$(B)] [B = PPh$_3$, pyridine (py), piperidine (pip) or morpholine (mor)] with bidentate Schiff base ligands derived from the condensation of 2-hydroxy-1-naphthaldehyde with aniline, *o*-, *m*- or *p*-toluidine in a 1 : 1 mol ratio in benzene resulted in the formation of complexes formulated as [RuCl(CO)(L)(PPh$_3$)(B)] [L = bidentate Schiff base anion, B = PPh$_3$, py, pip, mor]. The complexes were characterized by analyses, IR, electronic and ^{1}H NMR spectroscopy, and cyclic voltammetric studies. In all cases, the Schiff bases replace one molecule of phosphine and a hydride ion from the starting complexes, indicating that Ru–N bonds in the complexes containing heterocyclic nitrogenous bases are stronger than the Ru–P bond to PPh$_3$. Octahedral geometry is proposed for the complexes.

Keywords: Ruthenium(II) carbonyl Schiff base complexes; Characterization; Redox potential

1. Introduction

Ruthenium has the widest range of oxidation states (from −2 in $Ru(CO)_4^{2-}$ to +8 in RuO_4) of all the elements and displays various coordination geometries for each electronic configuration. This suggests great potential for exploitation in catalysis [1]. Interest in ruthenium chemistry thus continues [2–6] and much of this is due to the wide variety of reactions exhibited by complexes of the metal. It is well established that aniline derivatives react with aromatic aldehydes to form Schiff bases [7]. Schiff bases have played a special role as chelating ligands in main group and transition metal coordination chemistry because of their stability under a variety of redox conditions and because imine ligands are borderline Lewis bases [8–10]. The important physical and biological properties of the Schiff bases are directly related to intramolecular hydrogen bonding and proton transfer equilibria [11–15]. Derivatives of aromatic

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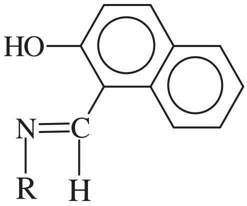


Scheme 1. R = C_6H_5, o-$C_6H_4CH_3$, m-$C_6H_4CH_3$, p-$C_6H_4CH_3$.

o-hydroxyaldehydes represent a class of compounds that has received attention because of their interesting properties and biological activity [11,16]. In particular, Schiff bases of *p*-substituted aniline and its complexes have a variety of applications in biological [17] and analytical fields [18]. In addition, tetradentate Schiff base complexes are important for designing model complexes related to synthetic and natural oxygen carriers [19]. Furthermore, carbonyl Schiff base complexes of transition metal ions, especially those of ruthenium, are important in homogeneous catalysis such as carbonylation and the oxo reaction [20–23]. Transition metal Schiff base chelates also assume importance in reactions such as hydroformylation, reduction, oxidation, epoxidation and hydrolysis [24–28]. Schiff bases also offer opportunities for inducing substrate chirality, tuning metal-centered electronic factors and enhancing the solubility and stability of homogeneous or heterogeneous catalysts [29–31].

As part of our efforts to synthesize and characterize ruthenium(II) carbonyl complexes using simple and inexpensive Schiff base ligands [20,32,33], we report the synthesis and characterization of some stable ruthenium(II) carbonyl Schiff base complexes derived from amines such as aniline and *o*-, *m*- and *p*-toluidine with 2-hydroxy-1-naphthaldehyde. The structures of the Schiff base ligands used in this study are shown in scheme 1.

2. Experimental

2.1. *Reagents and instrumentation*

Commercially available $RuCl_3 \cdot 3H_2O$ was used as supplied. All reagents used were of analar or chemically pure grade. Solvents were purified according to standard procedures [34]. Microanalyses of the complexes were performed on Carlo-Erba 1106-model 240 or Perkin-Elmer CHN analyzer at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute (CDRI), Lucknow. IR spectra of the complexes and ligands were recorded (KBr pellets) with a Jasco 400 Plus FTIR spectrophotometer in the range 4000–400 cm^{-1}. ^1H NMR spectra were recorded using $CDCl_3$ with a Bruker 400 MHz instrument with TMS as internal reference. Electronic spectra were recorded in CH_2Cl_2 solution with a Cary 300 Bio UV–visible Varian spectrophotometer in the range 800–200 nm. Cyclic voltammograms of the complexes were recorded on a Bio Analytical System (BAS) CV-50W electrochemical analyzer using acetonitrile solutions with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte; all potentials are referred to the Ag/AgCl electrode. The three-electrode cell contained a reference Ag/AgCl electrode, a Pt wire auxiliary electrode and a glassy carbon working electrode. Solutions were purged with N_2 before each set of experiments. Melting points are uncorrected.

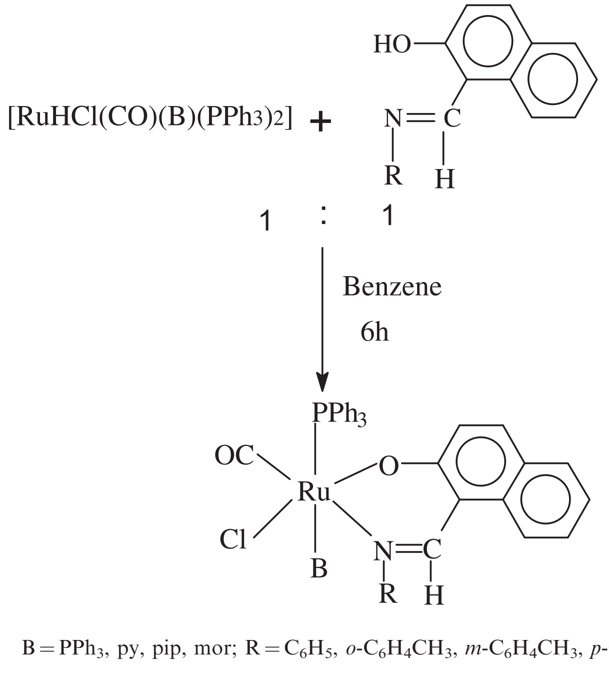
The precursor complexes [RuHCl(CO)(PPh$_3$)$_3$] [35], [RuHCl(CO)(py)(PPh$_3$)$_2$] [36], [RuHCl(CO)(pip)(PPh$_3$)$_2$] [36], [RuHCl(CO)(mor)(PPh$_3$)$_2$] [36] and the bidentate Schiff base ligands [34] were prepared according to literature procedures.

2.2. *Synthesis of [RuCl(CO)(B)(PPh$_3$)(L)]; B = PPh$_3$, py, pip or mor; L = bidentate Schiff base anion*

To a solution of [RuHCl(CO)(PPh$_3$)$_3$] or [RuHCl(CO)(B)(PPh$_3$)$_2$] [B = py, pip, mor] (0.1 g, 0.104–0.129 mmol) in benzene (20 cm^3), Schiff base (0.025–0.034 g, 0.104–0.129 mmol) was added and the mixture refluxed for 6 h. The resulting dark-colored solution was separated from the product by addition of a small quantity of petroleum ether 60–80°C. The product was filtered off, washed with petroleum ether, recrystallized from CH$_2$Cl$_2$–petroleum ether and dried *in vacuo*. The purity of the complexes was checked by TLC. Yield: 50–70%.

3. Results and discussion

The stable ruthenium(II) complexes of general formula [RuCl(CO)(B)(PPh$_3$)(L)] prepared by reacting [RuHCl(CO)(PPh$_3$)$_3$], [RuHCl(CO)(py)(PPh$_3$)$_2$], [RuHCl(CO)(pip)(PPh$_3$)$_2$] and [RuHCl(CO)(mor)(PPh$_3$)$_2$] with the respective Schiff bases in a 1 : 1 mol ratio in benzene are shown in scheme 2. The complexes are highly colored, stable to air and light and soluble in CHCl$_3$, methylene chloride, benzene, DMF and DMSO. Satisfactory analytical data were obtained for all of the compounds. Spectroscopic data are listed in tables 1 and 2. In all reactions, the Schiff bases replaced one PPh$_3$



Scheme 2 B = PPh$_3$, py, pip, mor; R = C$_6$H$_5$, *o*-C$_6$H$_4$CH$_3$, *m*-C$_6$H$_4$CH$_3$, *p*-C$_6$H$_4$CH$_3$.

Table 1. IR and electronic spectroscopic data for the Ru(II) carbonyl Schiff base complexes.

Complex		ν(C=N)	$\Delta\nu$(C=N)	ν(C-O)	ν(C≡O)	λ_{max} (ε)
1	[RuCl(CO)(PPh$_3$)$_2$(naphanil)]	1596	28	1351	1955	672^{a} (954), 351^{c} (9373), 270^{c} (6407)
2	[RuCl(CO)(PPh$_3$)$_2$(naph-*o*-tol)]	1596	24	1349	1959	426^{b} (6619), 324^{c} (16 333), 268^{c} (36 761)
3	[RuCl(CO)(PPh$_3$)$_2$(naph-*m*-tol)]	1606	20	1356	1955	656^{a} (722), 460^{b} (2720), 324^{c} (9238), 270^{c} (28 427)
4	[RuCl(CO)(PPh$_3$)$_2$(naph-*p*-tol)]	1616	3	1336	1958	423^{b} (3076), 320^{c} (8813), 272^{c} (24 438)
5	[RuCl(CO)(py)(PPh$_3$)(naphanil)]	1606	18	1359	1943	660^{a} (1234), 450^{b} (3746), 330^{c} (21 254), 270^{c} (25 456)
6	[RuCl(CO)(py)(PPh$_3$)(naph-*o*-tol)]	1604	16	1357	1938	430^{b} (4768), 340^{c} (20 143), 265^{c} (20 142)
7	[RuCl(CO)(py)(PPh$_3$)(naph-*m*-tol)]	1602	24	1365	1945	667^{a} (953), 442^{b} (4902), 318^{c} (14 382), 265^{c} (30 656)
8	[RuCl(CO)(py)(PPh$_3$)(naph-*p*-tol)]	1616	3	1346	1944	670^{a} (869), 441^{b} (5998), 321^{c} (15 078), 311^{c} (16 061)
9	[RuCl(CO)(pip)(PPh$_3$)(naphanil)]	1617	7	1342	1945	441^{b} (1977), 313^{c} (8856), 274^{c} (23 969), 262^{c} (39 876)
10	[RuCl(CO)(pip)(PPh$_3$)(naph-*o*-tol)]	1616	4	1330	1942	433^{b} (8062), 326^{c} (22 286), 267^{c} (29 558)
11	[RuCl(CO)(pip)(PPh$_3$)(naph-*m*-tol)]	1620	6	1355	1952	448^{b} (1666), 311^{c} (6759), 271^{c} (18 333)
12	[RuCl(CO)(pip)(PPh$_3$)(naph-*p*-tol)]	1614	5	1344	1947	447^{b} (1576), 265^{c} (18 682), 249^{c} (22 255)
13	[RuCl(CO)(mor)(PPh$_3$)(naphanil)]	1602	22	1353	1943	435^{b} (4000), 325^{c} (11 168), 263^{c} (33 185)
14	[RuCl(CO)(mor)(PPh$_3$)(naph-*o*-tol)]	1601	19	1335	1944	438^{b} (2974), 311^{c} (8046), 250^{c} (25 364)
15	[RuCl(CO)(mor)(PPh$_3$)(naph-*m*-tol)]	1598	24	1362	1945	441^{b} (1755), 326^{c} (4547), 249^{c} (19 620)
16	[RuCl(CO)(mor)(PPh$_3$)(naph-*p*-tol)]	1600	19	1355	1946	436^{b} (1109), 267^{c} (8385), 238^{c} (16 438)

ν is in units of cm^{-1}, λ_{max} in nm, ε in M^{-1} cm^{-1}; a = $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$, b = charge transfer, c = ligand–centered transition; $\Delta\nu$(C=N), in cm^{-1}, is the difference in energy between the ligand and its respective complex.

Table 2. ^{1}H NMR data for the complexes (δ, ppm).

Complex		–C_6H_5	–HC=N	–CH_3	–CH_2	–NH
1	[RuCl(CO)$(PPh_3)_2$(naphanil)]	6.9–7.7 (m)	8.2 (s)			
2	[RuCl(CO)$(PPh_3)_2$(naph-*o*-tol)]	6.85–7.7 (m)	8.3 (s)	2.08 (s)		
3	[RuCl(CO)$(PPh_3)_2$(naph-*m*-tol)]	7.1–7.9 (m)	8.4 (s)	2.1 (s)		
4	[RuCl(CO)$(PPh_3)_2$(naph-*p*-tol)]	7.2–7.8 (m)	8.4 (s)	2.09 (s)		
7	[RuCl(CO)(py)(PPh_3)(naph-*m*-tol)]	6.9–7.8 (m)	8.35 (s)	2.05 (s)		
8	[RuCl(CO)(py)(PPh_3)(naph-*p*-tol)]	6.75–7.8 (m)	8.35 (s)	2.2 (s)		
9	[RuCl(CO)(pip)(PPh_3)(naphanil)]	7.2–7.8 (m)	8.2 (s)		1.4 (s)	9.10 (s)
13	[RuCl(CO)(mor)(PPh_3)(naphanil)]	7.0–7.8 (m)	8.3 (s)		4.1^{a} (s) 3.3^{b}(s)	9.15 (s)
16	[RuCl(CO)(mor)(PPh_3)(naph-*p*-tol)]	7.0–7.9 (m)	8.35 (s)	2.25 (s)	3.7^{a} (s) 2.6^{a} (s)	9.25 (s)

a = protons nearer to oxygen; b = protons nearer to nitrogen.

group and a hydride from the starting complexes. The Schiff bases behave as monobasic bidentate ligands in all cases. The heterocyclic nitrogen bases (pyridine, piperidine, morpholine) remained intact because the Ru–P bond is more labile than the Ru–N bond, because of the better σ donating ability of the nitrogen bases compared to triphenylphosphine [36].

To study the binding mode of the Schiff bases, IR spectra of the Schiff bases were compared to spectra of known ruthenium(II) complexes. Free Schiff bases show a very strong absorption around 1626–1609 cm^{-1}, characteristic of the azomethine (>C=N) group [37]. If the Schiff bases coordinate through the nitrogen atom, a lowering of the azomethine (>C=N) frequency is expected due to reduction in electron density upon coordination. In the IR spectra of all of the complexes the azomethine stretch is observed at lower frequencies (1620–1596 cm^{-1}), indicating coordination of nitrogen to ruthenium [32,38]. This is further supported by comparison of the energies of the azomethine (>C=N) stretching vibration of particular ligands (table 1) with those of their respective ruthenium(II) complexes; a shift of 4–28 cm^{-1} to lower energy is observed for the complexes, as expected [39,40].

A strong band observed at around 1314–1326 cm^{-1} in the free Schiff bases has been assigned to phenolic C–O stretching. On complexation, this band shifts to higher frequency, indicating that the other coordination site is the phenolic oxygen atom [32,33,37,38,41]. This is further supported by the disappearance of the free ligand ν(OH) band around 3360–3438 cm^{-1} in the spectra of the complexes, indicating deprotonation of Schiff bases prior to coordination [11]. For all complexes, a strong band in the region 1939–1959 cm^{-1} is due to the terminally coordinated carbonyl group [32,36], seen at higher frequency than in the starting complexes. With [Ru(Cl) (CO)(B)(PPh_3)(L)] (B = py, pip, mor), IR spectra show a medium intensity band around 1090 cm^{-1}, characteristic of coordinated nitrogenous bases [33,42]. Characteristic bands for the coordination of triphenylphosphine are also present at around 1432–1436 cm^{-1} [41].

Electronic spectra of the complexes were recorded in dichloromethane. All complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) in an octahedral environment is $^{1}A_{1g}$, arising from the t_{2g}^{6} configuration. Excited states corresponding to the $t_{2g}^{5}e_{g}^{1}$ configuration are $^{3}T_{1g}$, $^{3}T_{2g}$, $^{1}T_{1g}$ and $^{1}T_{2g}$. Hence, four bands corresponding to $^{1}A_{1g} \rightarrow {}^{3}T_{1g}$, $^{1}A_{1g} \rightarrow {}^{3}T_{2g}$, $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ are possible, in order of increasing energy. The electronic spectra show bands at around 672–656 nm, assigned to $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$.

Table 3. Cyclic voltammetric data for the complexes; supporting electrolyte $[NBu_4]ClO_4$ (0.05 M); concentration of complex 0.001 M; all potentials referenced to Ag/AgCl; $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively; scan rate $100\,mV\,s^{-1}$.

Complex		Ru(III)/Ru(II)				Ru(II)/Ru(I)			
		E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)	$E_{1/2}$ (V)	E_{pc} (V)	E_{pa} (V)	ΔE_p (mV)	$E_{1/2}$ (V)
1	$[RuCl(CO)(PPh_3)_2(naphanil)]$	1.02	0.95	70	0.98	−1.02	−0.70	−360	0.86
2	$[RuCl(CO)(PPh_3)_2$(naph-*o*-tol)]	1.03	0.95	80	0.99	−1.07	−0.72	−300	0.90
3	$[RuCl(CO)(PPh_3)_2$(naph-*m*-tol)]	0.98	0.92	60	0.95	−1.04	−0.71	−330	0.88
4	$[RuCl(CO)(PPh_3)_2$(naph-*p*-tol)]	0.94	0.85	80	0.89	−1.00	−0.67	−330	0.84
7	$[RuCl(CO)(py)(PPh_3)$(naph-*m*-tol)]	1.00	0.93	70	0.96	−1.07	−0.80	−270	0.94
9	$[RuCl(CO)(pip)(PPh_3)(naphanil)]$	0.93	0.86	70	0.89	−1.02	−0.74	−280	0.88
10	$[RuCl(CO)(pip)(PPh_3)$(naph-*o*-tol)]	1.02	0.94	80	0.98	−1.00	−0.69	−310	0.85
11	$[RuCl(CO)(pip)(PPh_3)$(naph-*m*-tol)]	0.97	0.91	60	0.94	−1.04	−0.66	−380	0.85
12	$[RuCl(CO)(pip)(PPh_3)$(naph-*p*-tol)]	0.96	0.88	80	0.92	−1.02	−0.74	−280	0.88
15	$[RuCl(CO)(mor)(PPh_3)$(naph-*m*-tol)]	1.02	0.94	80	0.93	−1.04	−0.71	−330	0.88

Other high-intensity bands observed at around 460–423 nm are assigned to charge transfer transitions arising from the excitation of electrons from the metal t_{2g} level to the unfilled π molecular orbitals of the ligands (table 1). Absorption spectra were also characterized by intense ligand-centered bands with maxima in the 351–238 nm region. These bands have been designated as π–π^* and n–π^* transitions of electrons localized on the azomethine group of the Schiff bases. These assignments are in accordance with assignments for similar ruthenium(II) octahedral complexes based on molar extinction coefficients [32,38,43–45].

The bonding arrangement is further supported by ^{1}H NMR spectra (table 2). A multiplet observed at around 6.85–7.8 ppm in all complexes is assigned to the aromatic protons of the phenyl groups of triphenylphosphine, the Schiff base ligands and the heterocyclic nitrogenous bases. The signal due to the azomethine proton appears as a sharp singlet in the region 8.3–8.4 ppm. The positions of the azomethine signal in the complexes are downfield in comparison with those of the free ligands, suggesting deshielding of the azomethine proton due to its coordination to ruthenium through the azomethine nitrogen atom [32]. Spectra of complexes **9**, **13** and **16** show a singlet in the region 9.1–9.25 ppm assigned to the NH proton of piperidine and morpholine. This signal was not found in complexes **1**–**4**, **7** and **8**. Spectra of complexes **13** and **16** show two signals for methylene protons. The signal in the region 2.6–3.3 ppm is due to methylene protons nearer to nitrogen, and the other in the region 3.7–4.1 ppm to methylene protons nearer to oxygen. The signal for the methylene proton in the complex **9** appears as a broad singlet at 1.4 ppm. As the methyl protons are attached to the phenyl ring, the signal for these protons in complexes **2**–**4**, **7**, **8** and **16** appear upfield in the region 2.05–2.25 ppm. The absence of a resonance in the region 11.5–12.0 ppm in the complexes indicates deprotonation of the phenolic OH group of the Schiff bases on complexation and coordination to ruthenium through the phenolic oxygen atom [37].

As one of the aims of this study was to ascertain whether it was possible to stabilize higher oxidation states of ruthenium with these ligands, we also investigated the electrochemical behavior of the complexes. Redox properties were studied by cyclic voltammetry in acetonitrile solutions at a glassy carbon working electrode with 0.1 M TBAP as supporting electrolyte. All potentials are referenced to Ag/AgCl (table 3). The complexes show well-defined waves in the range 0.89 to 0.99 V (Ru^{III}–Ru^{II}) and -0.84 to -0.94 V (Ru^{II}–Ru^{I}). Oxidation couples were reversible, having peak-to-peak separation values (ΔE_p) ranging from 60 to 80 mV, close to that anticipated for a Nernstian, one-electron transfer process [46–48]. For a scan rate (SR) of 100 mV s^{-1}, the ratio i_p/SR (i_p = peak current) was approximately one, the peak separation being independent of the scan rate. This indicates that the electron transfer is reversible or approaches reversibility and mass transfer is limited. On the negative side, the reduction couples observed were *quasi*-reversible with very high peak-to-peak separation values ranging from 270 to 380 mV. Little variation in redox potential due to replacement of pyridine by piperidine or morpholine was observed.

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