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# Coordination behavior of ligand based on NNS and NNO donors with ruthenium(III) complexes and their catalytic and DNA interaction studies

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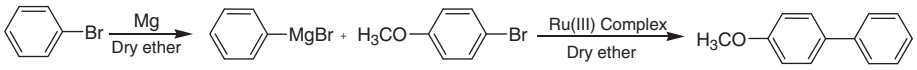
## HIGHLIGHTS

- A new series of ruthenium(III) Schiff base complexes were synthesized.
- Spectral studies have proved the binding modes of ligand with central metal ion.
- The complexes have used as catalysts in the transfer hydrogenation and coupling reaction.
- The synthesized complexes cleaved DNA even at lower concentrations.

## GRAPHICAL ABSTRACT

Ruthenium(III) Schiff base complexes containing 2-acetylpyridine thiosemicarbazone/semicarbazone were synthesized and characterized. They have been assigned an octahedral structure. The new complexes were found to be efficient catalyst for transfer hydrogenation and Kumada–Corriu coupling reactions. The complexes also successfully cleaved the DNA.

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## ABSTRACT

Reactions of 2-acetylpyridine-thiosemicarbazone $HL^1$, 2-acetylpyridine-4-methyl-thiosemicarbazone $HL^2$, 2-acetylpyridine-4-phenyl-thiosemicarbazone $HL^3$ and 2-acetylpyridine-semicarbazone $HL^4$ with ruthenium(III) precursor complexes were studied and the products were characterized by analytical and spectral (FT-IR, electronic, EPR and EI-MS) methods. The ligands coordinated with the ruthenium(III) ion via pyridine nitrogen, azomethine nitrogen and thiolate sulfur/enolate oxygen. An octahedral geometry has been proposed for all the complexes based on the studies. All the complexes are redox active and display an irreversible and quasireversible metal centered redox processes. Further, the catalytic activity of the new complexes has been investigated for the transfer hydrogenation of ketones in the presence of isopropanol/KOH and the Kumada–Corriu coupling of aryl halides with aryl Grignard reagents. The DNA cleavage efficiency of new complexes has also been tested.



## Introduction

Derivatives of semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen/sulfur donor ligands [1,2]. In particular, transition metal complexes of thiosemicarbazones have been receiving considerable interest largely because of their biological activities [3,4]. Thiosemicarbazones usually react as chelating ligands with transition metal ions by bonding through the sulfur and the azomethine nitrogen atoms and in some cases they behave as tridentate ligands and bond through the sulfur and two nitrogen atoms [5–7]. Complexation of the thiosemicarbazone usually occurs via dissociation of the acidic thiol proton, resulting in the formation of a five-membered chelate ring. Thiosemicarbazones and semicarbazones of aromatic aldehydes or ketones are known to act as tridentate ligands can yield cyclometallated complexes having two fused five-membered chelate rings at the metal center [8,9].

Among transition metal complexes ruthenium complexes have been widely used as catalysts in various catalytic reactions such as hydrogenation, oxidation, isomerization, polymerization, nucleophilic addition to multiple bonds and carbon–carbon bond formation [10,11]. The ability of ruthenium to assume a wide range of oxidation states and coordination geometries provides unique opportunities for catalysis. Reduction of carbonyl compounds is an important transformation in organic synthesis from both academic and industrial points of view [12]. Transfer hydrogenation of ketones by using an alcohol, preferably isopropyl alcohol, is an

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interesting alternative to the classical hydrogenation process requiring the use of dihydrogen gas [13,14]. Ruthenium(II) complexes containing diphosphine and 1,2 diamine ligands, in the presence of a base and isopropanol, are excellent catalysts for the hydrogenation of ketones under mild conditions [15]. Pincer type ruthenium(II) complexes containing the monoanionic terdentate NCN/PCP ligands as active catalysts for the transfer hydrogenation of ketones [16].

Carbon–carbon bond formation in the presence of a transition metal catalyst is a key step in many synthetic protocols of organic chemicals, natural products, as well as in a variety of industrial processes. One important example of such a catalytic transformation is the Grignard cross-coupling reaction that has been used in a wide range of synthetic and industrial applications. For example, the coupling of aromatic Grignard compounds with aryl halides offers a convenient synthetic access to biaryls, terphenyls and oligoaryls that have become important building blocks for the synthesis of natural products, liquid crystals, polymers and ligands in transition metal complexes [17,18]. A number of nickel and palladium complexes have been reported to catalyze the coupling of Grignard reagents with aryl bromides and iodides [19,20].

Metallopharmaceuticals are known to act on DNA by inhibiting DNA replication and transcription. Thus, studies on the interaction of metal complexes with DNA may reveal useful information on the rational drug design and development of sensitive chemical probe for DNA [21]. Various transition metal complexes derived from pyrimidine [22], polyamines [23], 1,10-phenanthroline [24], *N*-methyl-2-aminomethylpyrrolidine [25], aminoacid derivatives [26], macrocycles [27], diamines [28] and Schiff bases [29] have been reported as good candidates for DNA structural probes, DNA cleavage studies, DNA molecular light switches and new therapeutics. Recently, the DNA cleavage properties of ruthenium complexes have been investigated extensively [30]. Even though, few reports are available about the catalytic properties of ruthenium [31–34], it is still interesting for further investigation with new ligand system. Hence, we describe here the synthesis and characterization of ruthenium(III) complexes containing 2-acetylpyridine thiosemicarbazone/semicarbazone. Further the redox behavior, catalytic and DNA cleavage property of the synthesized complexes have been investigated.

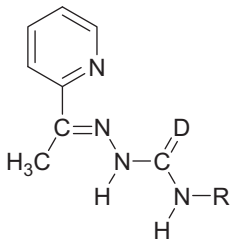
## 2. Experimental

### 2.1. Materials and reagents

All the reagents used were chemically pure and AR grade. The solvents were purified and dried according to standard procedures. $RuCl_3{\cdot}H_2O$ was purchased from Loba Chemie Pvt. Ltd. The starting complexes $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$ and $[RuBr_3(AsPh_3)_3]$ [35–37] and 2-acetylpyridine thiosemicrabazone/semicarbzone Schiff base ligands (Fig. 1) were prepared according to the literature procedures [38,39]. DNA cleavage studies were carried out according to reported procedure [40].

### 2.2. Physical measurements

Microanalysis of carbon, hydrogen and nitrogen was carried out using Vario EL III Elemental analyzer at SAIF – Cochin India. The IR spectra of the ligand and their complexes were recorded as KBr pellets on a Nicolet Avatar model in 400–4000 $cm^{-1}$ range. Electronic spectra of the ligand and their complexes have been recorded in dichloromethane using a Shimadzu UV – 1650 PC spectrophotometer in 200–800 nm range. $^1H$ NMR spectra were recorded in Jeol GSX – 400 instrument using DMSO as the solvent. Electron paramagnetic resonance spectra (EPR) of the powder samples were recorded with




| Ligand | D | R |
|---|---|---|
| $HL^1$ | S | H |
| $HL^2$ | S | $CH_3$ |
| $HL^3$ | S | $C_6H_5$ |
| $HL^4$ | O | H |

**Fig. 1.** Structure of Schiff base ligands.

a JEOL JES-FA200 X-band frequencies at room temperature using 2, 2-diphenyl-1-picrylhydrazyl radical (DPPH) as internal standard at Pondicherry University, Pondicherry, India. The EI-MS spectra were recorded by the EI technique at using JEOL JMS600H instrument in the HRMS facility NIIST, Thiruvananthapuram. Cyclic voltammetric measurements were carried out with a BAS CV-27 electrochemical analyzer in acetonitrile and $[(n\text{-}C_4H_9)_4N](ClO_4)$(TBAP) used as supporting electrolyte under nitrogen atmosphere. Three electrode cells was employed with glassy carbon working electrode, a platinum wire as counter electrode and an Ag/AgCl as reference electrode. Melting points were recorded on a Technico micro heating table and are uncorrected. The catalytic yields were determined using ACME 6000 series GC-FID with DP-5 column of 30 m length, 0.53 mm diameter and 5.00 μm film thickness.

### 2.3. Synthesis of ruthenium(III) Schiff base complexes

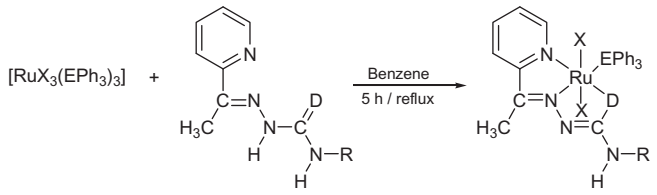
The general procedure for the preparation of the complexes is as follows. To a solution of 0.1 mmol $[RuX_3(EPh_3)_3]$ (E = P or As; X = Cl or Br) in benzene was added 0.1 mmol ligand (mole ratio of ruthenium complex and ligand is 1:1, respectively) and the mixture was refluxed for 5 h. The product was separated by the addition of small amount of petroleum ether (60–80 °C). The resulting complexes were recrystallized from $CH_2Cl_2$/petroleum ether and dried under vacuum. The overall yield obtained for all the complexes were 67–78%.

### 2.4. Typical procedures for transfer hydrogenation of ketones

The catalytic transfer hydrogenation reactions were also studied using ruthenium(III) Schiff base complexes as a catalyst, ketone as substrate and KOH as base at 1:500:2.5 molar ratios. The procedure was described as follows. A mixture containing ketone (5.0 mmol), the ruthenium complex (0.01 mmol) and KOH (0.025 mmol) was heated to reflux in 10 ml of *i*-PrOH for 2 h. After completion of reaction the catalyst was removed from the reaction mixture by the addition of petroleum ether followed by filtration and subsequent neutralization with 1 M HCl. The ether layer was filtered through a short path of silica gel by column chromatography. The filtrate was subjected to GC analysis and the hydrogenated product was identified and determined with authentic samples.

### 2.5. Typical procedures for Kumada–Corriu reactions

Magnesium turnings (320 mg) were placed in a two-neck-round-bottomed flask with a calcium chloride guard tube. A crystal




(E = P or As; X = Cl or Br; D = S or O; R = H, $CH_3$ or $C_6H_5$)

**Scheme 1.** Synthesis of ruthenium(III) Schiff base complexes.

of iodine was added to activate the surface of the magnesium. Bromobenzene (0.5 ml of a total of 1.3 ml, 12 mmol) in 5 ml of anhydrous diethyl ether was added with stirring and heated under reflux. Turbidity after 5 min indicated the initiation of the reaction. The remaining bromobenzene in 5 ml of ether was added drop wise and the reaction mixture was refluxed for 40 min. To this reaction mixture, 1.03 ml (10 mmol) of 4-bromoanisole in 5 ml of anhydrous diethyl ether and the ruthenium complex (0.03 mmol) was added and the mixture was stirred for 6 h. The reaction mixture was quenched with 10 ml of $H_2O$, and the mixture was diluted with diethyl ether. After separation of organic and aqueous phases, the organic phase was washed with 50 ml of $H_2O$, and then dried over $MgSO_4$, filtered and evaporation of solvent. The crude product was purified by column chromatography on silica gel to afford of 4-phenyl anisole.

## 3. Result and discussion

The reactions of $[RuX_3(EPh_3)_3]$ (E = P or As; X = Cl or Br) with 2-acetylpyridine thiosemicarbazone/semicarbazone in 1:1 molar ratio in dry benzene afforded new hexa-coordinated low-spin ruthenium(III) Schiff base complexes (Scheme 1). The analytical data (Table 1) are in good agreement with the general molecular formula proposed. In all the reactions, the Schiff base ligand behaves as mono negative tridentate ligands by replacing two molecules of triphenylphosphine or triphenylarsine and one molecule of chloride or bromide ion from the precursors. All the complexes are air-stable, non-hygroscopic in nature, insoluble in water and highly soluble in common solvents such as chloroform, dichloromethane, acetonitrile and dimethyl sulphoxide. Attempts made to grow single crystals of the complexes went unsuccessful.

### 3.1. Infrared spectroscopic analysis

The important IR absorption frequencies of the ligands and their metal complexes along with their assignment are listed in Table 2.

**Table 2**
IR absorption frequencies ($cm^{-1}$) and electronic spectral data (nm) of free ligands and ruthenium(III) Schiff base complexes.

| Compound | $\nu_{NH}$ | $\nu_{CN}$ | $\nu_{CO}$ | $\nu_{CS}$ | λmax |
|---|---|---|---|---|---|
| $HL^1$ | 3183 | 1609 | – | 836 | 297, 234 |
| $HL^2$ | 3187 | 1580 | – | 834 | 360, 341, 241 |
| $HL^3$ | 3194 | 1598 | – | 801 | 329, 279, 238 |
| $HL^4$ | 3174 | 1585 | 1686 | – | 336, 310, 260 |
| $[RuCl_2(PPh_3)L^1]$ | – | 1574 | – | 747 | 492, 364, 331, 283, 237 |
| $[RuCl_2(PPh_3)L^2]$ | – | 1560 | – | 745 | 496, 367, 268, 238, 236 |
| $[RuCl_2(PPh_3)L^3]$ | – | 1565 | – | 743 | 487, 350, 260, 254 |
| $[RuCl_2(PPh_3)L^4]$ | – | 1583 | 1332 | – | 460, 354, 238 |
| $[RuCl_2(AsPh_3)L^1]$ | – | 1573 | – | 741 | 490, 314, 309 |
| $[RuCl_2(AsPh_3)L^2]$ | – | 1565 | – | 740 | 480, 343, 310 |
| $[RuCl_2(AsPh_3)L^3]$ | – | 1562 | – | 741 | 496, 350, 308, 253 |
| $[RuCl_2(AsPh_3)L^4]$ | – | 1579 | 1336 | – | 459, 340, 256 |
| $[RuBr_2(AsPh_3)L^1]$ | – | 1574 | – | 737 | 488, 332, 324, 307 |
| $[RuBr_2(AsPh_3)L^2]$ | – | 1569 | – | 741 | 491, 352 |
| $[RuBr_2(AsPh_3)L^3]$ | – | 1560 | – | 745 | 498, 360, 334, 269, 212 |
| $[RuBr_2(AsPh_3)L^4]$ | – | 1580 | 1336 | – | 462, 346, 313, 243 |

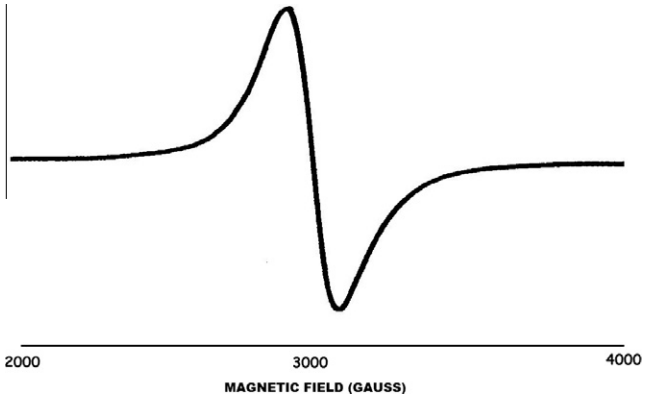



**Fig. 2.** EPR spectrum of $[RuCl_2(PPh_3)L^1]$.

The free ligands showed a strong band in the region 1580–1609 $cm^{-1}$ due to $\upsilon_{C=N}$. This band has been shifted to lower frequencies 1560–1583 $cm^{-1}$ in the metal complexes indicating the coordination of the ligands to metal through the azomethine nitrogen atom [41]. The bands due to $\upsilon_{N-H}$ and $\upsilon_{C=S}$ appeared around 3174–3194 $cm^{-1}$ and 801–836 $cm^{-1}$ in the free ligands has disappeared on complexation and a new band appeared around 737–747 $cm^{-1}$. These observation attributed to thioenolization of the —NH—C=S group and subsequent coordination through the deprotonated sulfur [42,43]. The semicarbazone ligand ($HL^4$) $\upsilon_{C=O}$

**Table 1**
Analytical data of free ligands and ruthenium(III) Schiff base complexes.

| Compound | Colour | M. Pt (°C) | Calculated (found) (%) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | N | S |
| $HL^1$ | Yellow | 180 | 49.46(49.32) | 5.18(5.26) | 28.84(28.69) | 16.50(16.32) |
| $HL^2$ | Yellow | 170 | 51.90(51.78) | 5.80(5.72) | 26.90(26.29) | 15.39(15.78) |
| $HL^3$ | Yellow | 185 | 62.20(62.46) | 5.21(5.56) | 26.72(26.54) | 11.85(11.63) |
| $HL^4$ | Yellow | 210 | 53.92(53.45) | 5.65(5.43) | 31.44(31.65) | – |
| $[RuCl_2(PPh_3)L^1]$ | Brown | 235 | 49.76(49.58) | 3.85(3.62) | 8.92(8.43) | 5.10(5.58) |
| $[RuCl_2(PPh_3)L^2]$ | Brown | 160 | 50.54(50.43) | 4.08(4.43) | 8.73(8.54) | 4.99(4.68) |
| $[RuCl_2(PPh_3)L^3]$ | Brown | 170 | 54.62(54.73) | 4.61(4.99) | 7.96(7.35) | 4.55(3.56) |
| $[RuCl_2(PPh_3)L^4]$ | Brown | 230 | 51.07(51.53) | 3.95(3.99) | 9.16(9.35) | – |
| $[RuCl_2(AsPh_3)L^1]$ | Brown | 160 | 46.50(46.56) | 3.60(3.38) | 8.34(7.59) | 4.77(4.71) |
| $[RuCl_2(AsPh_3)L^2]$ | Brown | 258 | 47.30(41.39) | 3.82(3.52) | 8.17(8.52) | 4.67(4.68) |
| $[RuCl_2(AsPh_3)L^3]$ | Brown | 158 | 51.41(51.57) | 3.77(3.54) | 7.49(7.35) | 4.28(4.67) |
| $[RuCl_2(AsPh_3)L^4]$ | Brown | 160 | 47.64(47.45) | 3.69(3.86) | 8.54(8.67) | – |
| $[RuBr_2(AsPh_3)L^1]$ | Brown | 261 | 41.07(41.38) | 3.18(3.53) | 7.36(7.58) | 4.21(4.61) |
| $[RuBr_2(AsPh_3)L^2]$ | Brown | 250 | 41.87(41.56) | 3.38(3.56) | 7.23(7.45) | 4.14(4.23) |
| $[RuBr_2(AsPh_3)L^3]$ | Brown | 160 | 45.94(45.94) | 3.37(3.79) | 6.60(6.12) | 3.83(3.68) |
| $[RuBr_2(AsPh_3)L^4]$ | Brown | 180 | 41.95(41.94) | 3.24(3.79) | 7.52(7.12) | – |

**Table 3**
EPR spectral data of the ruthenium(III) Schiff base complexes.

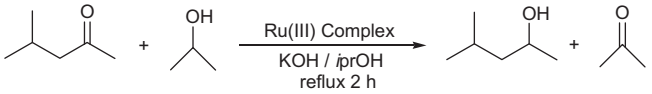
| Complex | $g_x$ | $g_y$ | $g_z$ | $\langle g^* \rangle$ |
|---|---|---|---|---|
| $[RuCl_2(PPh_3)L^1]$ | – | 2.30 | – | – |
| $[RuCl_2(PPh_3)L^2]$ | – | 2.71 | – | – |
| $[RuCl_2(PPh_3)L^3]$ | – | 2.21 | – | – |
| $[RuCl_2(AsPh_3)L^1]$ | – | 2.62 | – | – |
| $[RuCl_2(AsPh_3)L^2]$ | – | 2.22 | – | – |
| $[RuBr_2(AsPh_3)L^3]$ | – | 2.23 | – | – |

$\langle g^* \rangle = \left[1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2\right]^{1/2}$.

appeared around 1686 $cm^{-1}$ in free ligands has disappeared on complexation and new band appeared around 1332–1336 $cm^{-1}$ which due to ketoenolization [44]. The band at 3380–3427 $cm^{-1}$ in the spectra has been assigned to terminal —NH—R group [45]. All the ruthenium(III) complexes show strong vibrations near 530, 690, 745 and 1550 $cm^{-1}$ which are attributed to $PPh_3/AsPh_3$ [46].

### 3.2. Electronic spectroscopic analysis

The electronic spectra of the complexes were recorded in dichloromethane solution in the region 200–800 nm (Table 2). All the ruthenium(III) Schiff base complexes display strong band in the visible region in the range 459–498 nm due to charge transfer transition. The bands in the 307–367 nm regions are due to $n$–$\pi^*$




**Scheme 2.** Transfer hydrogenation of ketones.

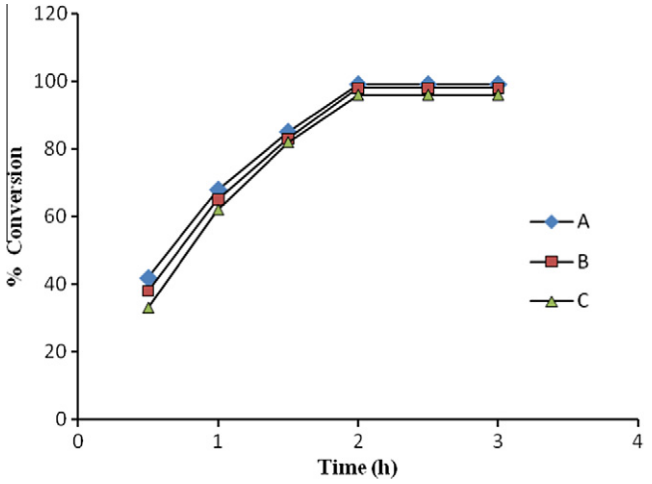



**Fig. 4.** Catalytic transfer hydrogenation of cyclohexanone (A), acetophenone (B) and isobutylmethyl ketone (C) in different time intervals.

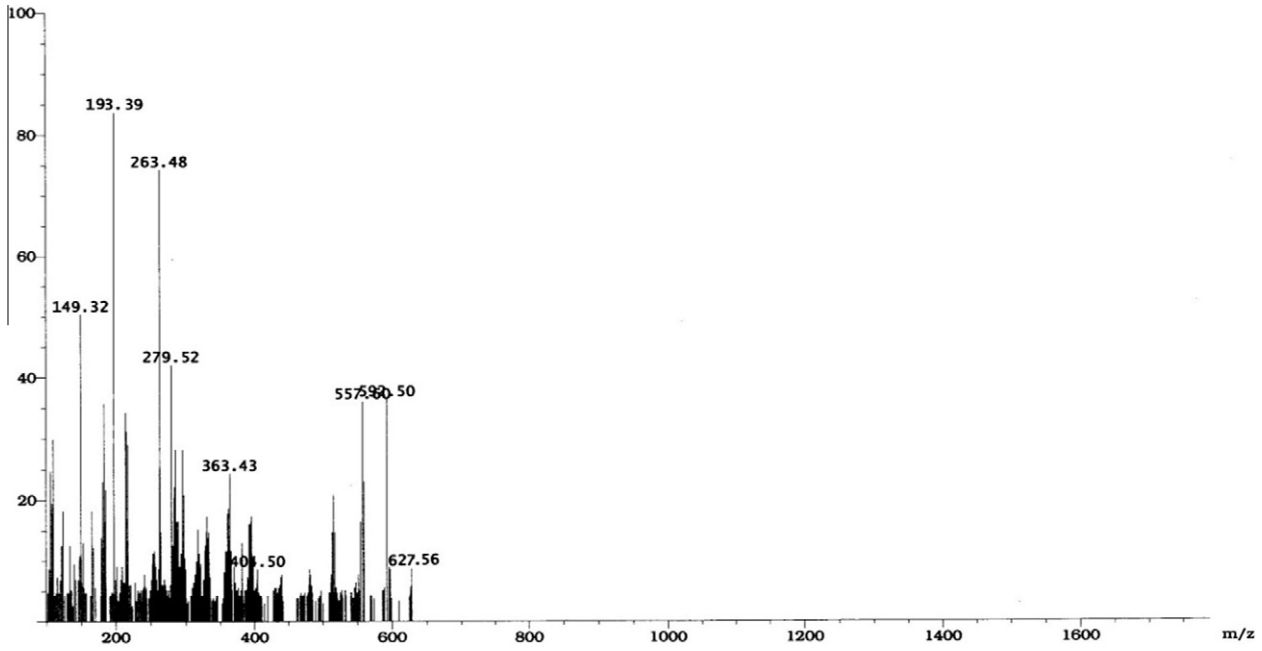



**Fig. 3.** EI-Mass spectrum of $[RuCl_2(PPh_3)L^1]$.

**Table 4**
Electrochemical spectral data of the ruthenium(III) Schiff base complexes.[a]

| Complex | $Ru^{III}/Ru^{IV}$ $E_{pa}$(V) | $E_{pa}$(V) | $Ru^{III}/Ru^{II}$ $E_{pc}$(V) | $E_f$(V) | $\Delta E_p$(mV) |
|---|---|---|---|---|---|
| $[RuCl_2(PPh_3)L^2]$ | 0.50 | −0.80 | −0.65 | −0.73 | 150 |
| $[RuCl_2(AsPh_3)L^2]$ | 0.55 | −0.90 | −0.60 | −0.75 | 300 |
| $[RuCl_2(AsPh_3)L^3]$ | 0.60 | −0.95 | −0.55 | −0.75 | 400 |
| $[RuBr_2(AsPh_3)L^1]$ | 0.65 | −0.90 | −0.53 | −0.71 | 370 |
| $[RuBr_2(AsPh_3)L^3]$ | 0.70 | −0.96 | −0.52 | −0.74 | 440 |
| $[RuBr_2(AsPh_3)L^4]$ | 0.60 | −0.98 | −0.75 | −0.86 | 230 |

[a] Working electrode, glassy carbon electrode; reference electrode, Ag–AgCl electrode; supporting electrolyte $[NBu_4]ClO_4$ (0.01 M); concentration of the complex, 0.001 M; scan rate, 100 mV $s^{-1}$; $E_f = 0.5(E_{pa} + E_{pc})$, $\Delta E_p = E_{pa} - E_{pc}$.

**Table 5**
Catalytic transfer hydrogenation of cyclohexanone by $[RuBr_2(AsPh_3)L^2]$/*i*-PrOH/KOH.

| Entry | Reaction time (h) | % Conversion* |
|---|---|---|
| 1 | 2 | 99[a] |
| 2 | 2 | 58[b] |
| 3 | 2 | Not detected[c] |
| 4 | 2 | Not detected[d] |

* The conversion of product determined by GC and comparing with authentic sample.
[a] Reactions were carried out at 90 °C using substrate (5 mmol), catalyst (0.01 mmol) in isopropanol, KOH (0.025 mmol).
[b] Reactions were carried out at 90 °C using substrate (5 mmol), catalyst (0.005 mmol) in isopropanol, KOH (0.025 mmol).
[c] The reaction was carried out without catalyst.
[d] The reaction was carried out without KOH.

transition of non-bonding electrons present in the nitrogen of the azomethine group in the ruthenium(III) Schiff base complexes. The bands observed around 212–297 nm is as assigned to $\pi-\pi^*$ transitions of the ligands. The pattern of the electronic spectra of all the complexes indicates the presence of an octahedral environment around the ruthenium(III) ion [47].

### 3.3. EPR spectroscopic analysis

The EPR spectra of powdered samples were recorded at room temperature. The representative spectra are shown in Fig. 2. The complexes showed no indication of any hyperfine interaction of Ru with N, As, P, Cl and Br. The spectra of all the complexes showed single isotropic resonance with g values of 2.21–2.71 (Table 3). Such isotropic lines are usually observed either due to intermolecular spin–spin exchange, which can broaden the lines or due to occupancy of the unpaired electron in a degenerate orbital [48] corresponding to the electronic configuration $(d_{xz})^2$, $(d_{yz})^2$, $(d_{xy})^1$.

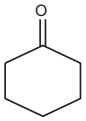
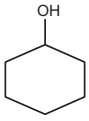
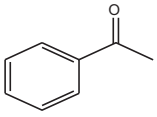
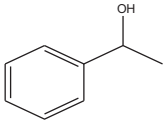
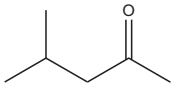
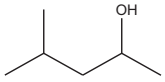
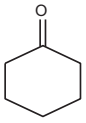
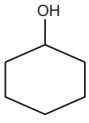
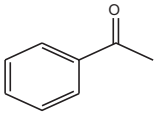
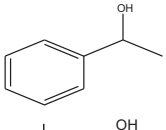
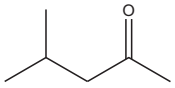
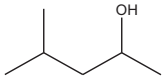
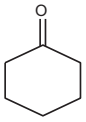
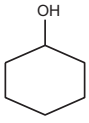
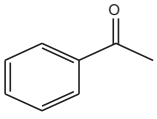
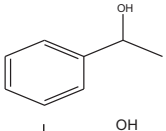
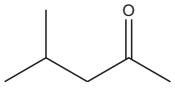
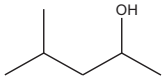
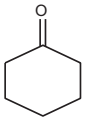
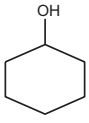
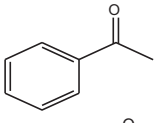
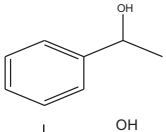
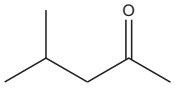
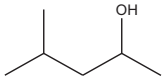
### 3.4. Mass spectroscopic analysis

The electron impact mass spectra of complexes are recorded and investigated at 70 eV of electron energy. The representative mass spectrum of complex $[RuCl_2(PPh_3)L^1]$ are given in Fig. 3. The complex is characterized by moderate to high relative intensity molecular ion peaks. It is obvious that, the molecular ion peaks are in good agreement with the suggested empirical formula as indicated from elemental analyses. The spectrum showed a molecular ion peak $M^+$ at M/Z 627, which is equivalent to its molecular weight of the complex. The molecular ion peak fragmentation with the loss of two chlorine molecules, gave a peak at M/Z 592 and 557 due to fragment ion $[RuCl(PPh_3)L_1]^+$ and $[Ru(PPh_3)L_1]^+$. Further, the fragments leading to the formation of the species $[RuL_1]^+$ which undergo demetalation to form the species $[L+H]^+$ gave fragment ion at M/Z 193.

### 3.5. Redox properties

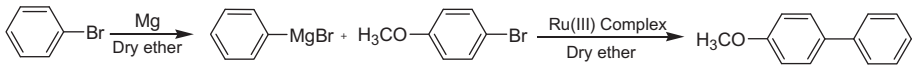
The electron transfer properties of the Ru(III) Schiff base complexes were studied by cyclic voltammetry. Voltammograms of these complexes recorded from 0 to 2.0 V for $Ru^{III}/Ru^{IV}$ and from 0 to −2.0 V for $Ru^{III}/Ru^{II}$ vs Ag–AgCl (Table 4). The voltammograms reveal a pair of redox waves for these complexes, which corresponds to +0.50 to +0.70 $Ru^{III}/Ru^{IV}$ (oxidation) and −0.52 to −0.98 $Ru^{III}/Ru^{II}$ (reduction) at the positive and negative potentials, respectively. The redox process of the complexes exhibits an irreversible oxidation and quasi-reversible reduction (The $\Delta E_p$ values for the above reduction process ranging from 150 to 440 mV). The irreversible redox processes $Ru^{III}/Ru^{IV}$ observed for these complexes may be due to short-lived oxidation state of metal ion where as a quasi-reversible process observed for the reduction

**Table 6**
Catalytic transfer hydrogenation of ketones by ruthenium(III) Schiuff base complexes.[a]

| Complex | Substrate | Product | Conversion (%)[b] |
|---|---|---|---|
| $[RuCl_2(PPh_3)(L^3)]$ |  |  | 89 |
| |  |  | 86 |
| |  |  | 85 |
| $[RuCl_2(PPh_3)(L^4)]$ |  |  | 92 |
| |  |  | 90 |
| |  |  | 89 |
| $[RuBr_2(AsPh_3)(L^1)]$ |  |  | 96 |
| |  |  | 94 |
| |  |  | 93 |
| $[RuBr_2(AsPh_3)(L^2)]$ |  |  | 99 |
| |  |  | 98 |
| |  |  | 96 |

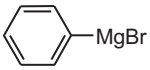
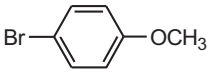
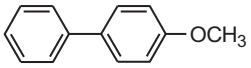
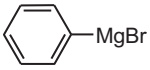
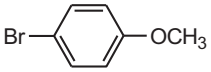
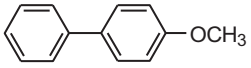
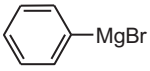
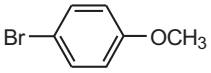
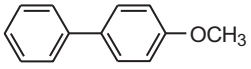
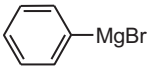
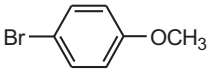
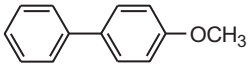
[a] Conditions: reactions were carried out at 90 °C using 5 mmol of ketone (10 ml isopropanol) and catalyst/substrate/KOH ratio 1:500:2.5.
[b] The conversion of product determined by GC and comparing with analyses of authentic samples.

$Ru^{III}/Ru^{II}$ is due to slow electron transfer and absorption of the complexes on to the electrode surface. The potentials of both the oxidation ($Ru^{III}/Ru^{IV}$) and reduction ($Ru^{III}/Ru^{II}$) have been found to be sensitive to the nature of the substituent (R) in the 2-acetylpyridine thiosemicarbazone ligands and replacement of chlorides by bromides and triphenyl phosphine by arsine. Hence from the electrochemical data it is clear that the present ligand system is ideally suitable for stabilizing the higher oxidation state of ruthenium ion.




**Scheme 3.** Kumada–Corriu reaction of aryl bromide with Grignard reagent.

**Table 7**
Kumada–Corriu reaction of 4-bromoanisole with phenylmegnesium bromide by ruthenium(III) Schiff base complexes at room temperature in diethyl ether (6 h).[a]

| Complex | Coupling partner | Aryl halide | Product | Yield (%)[b] |
|---|---|---|---|---|
| $[RuCl_2(PPh_3)L^1]$ |  |  |  | 35 |
| $[RuCl_2(AsPh_3)L^3]$ |  |  |  | 28 |
| $[RuBr_2(AsPh_3)L^2]$ |  |  |  | 48 |
| $[RuBr_2(AsPh_3)L^4]$ |  |  |  | 36 |

[a] Based on phenylmegnisium bromide (12 mmol), 4-bromoanisole (10 mmol) and ruthenium(III) Schiff base complex (0.03 mmol).
[b] The yield of product was determined using a $^1H$ NMR.

### 3.6. Catalytic transfer hydrogenation of ketones

Transfer hydrogenation of ketones in the presence of newly synthesized Ru(III) Schiff base complexes has been studied in isopropanol/KOH medium (Scheme 2). The reaction was conducted at a catalyst, substrate and base in molar ratio 1:500:2.5, respectively. $[RuBr_2(AsPh_3)L^2]$ was selected as a model catalyst for optimization of the reaction conditions. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 4) and optimized as 2 h.

To evaluate the catalytic efficiency of $[RuBr_2(AsPh_3)L^2]$, the reduction of cyclohexanone was carried out under similar reaction conditions in the absence of catalyst and found that no reasonable conversion was observed (Table 5, entry 2). The reduction of cyclohexanone was carried out with lower amount of $[RuBr_2(AsPh_3)L^2]$, the yield was low (Table 5, entry 3). Also the reaction was carried out in the absence of base, no transfer hydrogenation of cyclohexanone was observed (Table 5, entry 4). The role of KOH is to generate the catalyst from chloro precursor and the reaction mediates through the hydride species. The base facilitated the formation of the ruthenium alkoxide by abstracting the proton of alcohol and subsequently, the alkoxide underwent β-elimination to give a ruthenium hydride which is the active species in this reaction. The transfer hydrogenation of other aliphatic and aromatic ketones was then examined using the optimized reaction conditions. Among the ruthenium(III) Schiff base complexes that have been analyzed, the order of catalytic activity in terms of yield was $[RuBr_2(AsPh_3)L^2] > [RuBr_2(AsPh_3)L^1] > [RuCl_2(PPh_3)L^4] > [RuCl_2(PPh_3)L^3]$ (Table 6). In terms of substituents present in the Schiff base moiety, the order of activity is $CH_3 > H > C_6H_5$. Hence, it is inferred that inductive effect of the substituent plays a major role in deciding the catalytic activity of their corresponding complexes. It is further inferred from the results that the $AsPh_3/PPh_3$, Br/Cl ligands may also influence the catalytic efficiency by their electron donor–acceptor nature.

### 3.7. Catalytic Kumada–Corriu reactions

The system chosen for the study is the coupling of phenyl magnesium bromide with 4-bromoanisole to give 4-phenylanisole as the product. Bromobenzene was first converted into the corresponding Grignard reagent. Then 4-bromoanisole, followed by the ruthenium(III) Schiff base complex, were added and the mixture was stirred for 6 h (Scheme 3). After work up, the crude product was purified by column chromatography on silica gel to afford 28–48% yield of 4-phenylanisole (Table 7). The product was characterized by $^1H$ NMR and comparison with literature data [49]. The present catalyst systems are able to couple aryl bromides with aryl Grignard reagents at room temperature in a low catalyst loading for good yields.

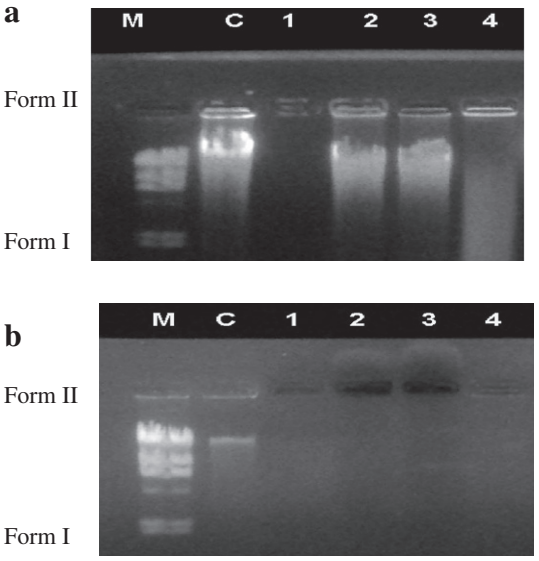



**Fig. 5.** Agarose gel electrophoresis diagram showing the cleavage DNA of Escherichia coli by Ru(III) Schiff base complex in TAE Buffer (4.84 g Tris base, pH = 8, 0.5 M EDTA/1 L). Lane M, DNA alone; Lane C, Control DNA (untreated complex). (a) Lane 1, $[RuBr_2(PPh_3)L^2]$ 10 μg/ml; Lane 2, $[RuBr_2(AsPh_3)L^1]$ 10 μg/ml and Lane 3 and 4, $[RuCl_2(PPh_3)L^3]$ 10 and 50 μg/ml concentrations. (b) Lane 1 and 2 $[RuBr_2(AsPh_3)L^1]$ 100 and 200 μg/ml and Lane 3 and 4 $[RuCl_2(PPh_3)L^3]$ 100 and 200 μg/ml concentrations.

### 3.8. DNA cleavage studies by gel electrophoresis

The potential of the present complexes to cleavage DNA was studied by gel electrophoresis using supercoiled DNA of Escherichia coli in TAE buffer (pH 8). When circular plasmid DNA is subjected to gel electrophoresis, relatively fast migration will be

observed for the intact supercoil form (Form I). If scission occurs on one strand (nicking), the supercoil will relax to generate a slower-moving open circular form (Form II). If both strands are cleaved, a linear form (Form III) that migrates between Forms I and II will be generated [50]. Fig. 5 shows the gel electrophoresis separation of plasmid DNA after incubation with each of Ru(III) complexes and irradiation at UV. Fig. 5a Shows $[RuBr_2(PPh_3)L^2]$ completely cleaved DNA at 10 μg/ml and $[RuBr_2(AsPh_3)L^1]$ was inactive at same concentration (lanes 1 and 2). For the complex $[RuCl_2(PPh_3)L^3]$, the amount of Form I of DNA diminished gradually, whereas that of Form II increased when concentration of the complex increased. This shows that the complex is inactive at 10 μg/ml concentration and displayed partial cleavage at 50 μg/ml concentration (lanes 3 and 4). At higher concentration, the complexes $[RuBr_2(AsPh_3)L^1]$ and $[RuCl_2(PPh_3)L^3]$ (Fig. 5b lanes 1–4) completely cleave the DNA.

## 4. Conclusion

In this work we have synthesized series of new ruthenium(III) 2-acetylpyridine thiosemicarbazone/semicarbazone complexes bearing triphenylphosphine/arsine. The characterization of all the complexes was accomplished by analytical and spectral (FT-IR, electronic, EPR and EI-MS) methods. Spectral studies are confirmed the coordination mode of the ligand to the metal through NNS/NNO donors and reveal the presence of an octahedral geometry around the ruthenium center. The catalytic efficiency of the complexes was determined for transfer hydrogenation and Kumada–Corriu coupling reactions. The complexes also efficiently cleaved the DNA, even at low concentration.

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