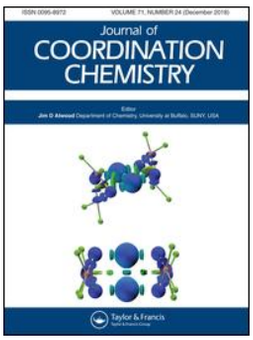

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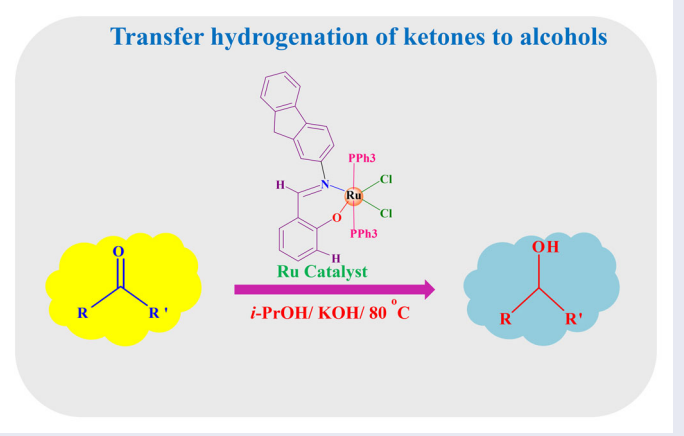
Synthesis and characterization of new ruthenium(III) complexes derived from fluoreneamine-based Schiff base ligands and their catalytic activity in transfer hydrogenation of ketones

Veerasamy Nagalakshmi[a,b], Raja Nandhini[a,b], Galmari Venkatachalam[a,b] and Kasturi Balasubramani[a,b]

[a]PG & Research Department of Chemistry, Government Arts College, Dharmapuri, Tamilnadu, India; [b]Department of Chemistry, Govt Arts College (Autonomous), Karur, Tamilnadu, India

ABSTRACT

An easy and convenient synthesis of a new series of octahedral ruthenium(III) complexes bearing Schiff base ligands of general formula $[RuCl_2(EPh_3)_2(L)]$ (where E = P, As and L = O,N-donor Schiff bases) has been reported. The composition of all complexes has been unequivocally characterized by spectral (IR, UV-vis, EPR) and ESI-MS techniques. The substituted Schiff base ligands behave as bidentate O,N-donors and coordinate to ruthenium *via* the phenolic oxygen, the azomethine nitrogen. Complexes **1–6** have been proven to catalyze the transfer hydrogenation of linear, cyclic and aromatic ketones to their corresponding secondary alcohols in the presence of *i*-PrOH/KOH at 80 °C with conversion up to 99%. The effect of other variables on the transfer hydrogenation reaction such as solvent, base, and catalyst loading is also reported.



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CONTACT Galmari Venkatachalam gvchem@gmail.com, manavaibala@gmail.com PG & Research Department of Chemistry, Government Arts College, Dharmapuri 636 705, Tamilnadu, India

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1. Introduction

Schiff base ligands, considered as privileged ligands and attractive due to their stability and the ease by which modified variations can be obtained, are once again topical in connection with a diverse range of applications such as organic synthesis [1, 2]. For several reasons, Schiff bases have been found to be among the most convenient and attractive ligands for ruthenium complexes [3–7]. Schiff base ligands have been used extensively in coordination chemistry to build complexes with transition and main group metals. The proper choice of ligands is key in manipulating the activity and selectivity of catalysts. Steric and electronic effects around the metal center can be finely adjusted through an appropriate selection of the Schiff base ligands. Experimental data suggests that the steric bulk of the Schiff base has a greater impact on catalytic performance compared to the electronic influence of Schiff base ligands [8]. The two donor atoms O,N in the ligated Schiff base exert opposite electronic effects, thus a flexible interplay between these two binding sites can be achieved and it triggers catalytic activity. Schiff base complexes of transition metals [9] having O,N-donor atoms have shown an exponential increase as inorganic catalysts for various organic transformations.

Ruthenium complexes have been recently gaining importance in a broad range of applications, and consequently there is a continuous endeavor to synthesize new complexes of ruthenium with different types of ligands, such as Schiff base [10], azo [11], pincer [12], tripodal [13] and carbenes [14, 15]. In particular, emphasis has been placed on ligands containing a phenolate oxygen, which is a recognized hard donor, and hence coordination by a phenolate oxygen is of importance with regard to stabilization of the higher oxidation states of ruthenium [16–19].

Transition metal triphenylphosphine/triphenylarsine complexes, especially ruthenium complexes, find application in classical catalytic process such as hydrogenation, isomerization, decarbonylation, reductive elimination, oxidative addition and in making C-C bonds [20]. Ruthenium complexes are currently being investigated because of their rich structural, electrochemical, catalytic and biological properties [21–29].

Furthermore, transfer hydrogenation is one of the most important methods for the reduction of ketones to alcohols, due to its valuable and atom-efficient reaction and simpler experimental procedure [30]. Ruthenium-based catalytic systems are found to be effective in the transfer hydrogenation reactions [31].

Herein we report on the reactions of the fluoreneamine Schiff base ligands with ruthenium precursor complexes. The newly synthesized complexes were fully characterized by spectroscopic and mass techniques and their ability to serve on precursors in the catalytic transfer hydrogenation of a wide range of substrates is discussed.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were obtained from commercial sources and used without further purification. $RuCl_3 \cdot 3H_2O$ and different aromatic aldehydes for catalytic studies were purchased from Sigma-Aldrich. Schiff base ligands were prepared by

2-aminofluorene with corresponding aldehydes according to reported procedures [32]. The microanalysis of carbon, hydrogen and nitrogen was carried out using a Vario EL III Elemental analyzer at SAIF, Cochin, India. The FT-IR spectra of the compounds were recorded on an Agilent Resolution pro system spectrometer from 4000 to 400 cm^{-1}. Electronic spectra of the complexes were recorded in $CHCl_3$ solution on a Cary 300 Bio UV-vis Varian spectrophotometer from 800 to 200 nm. ESR spectra were recorded in the X-band frequency on an ESR-JEOL/82 ESR spectrometer with a microwave power of 1 mW and a modulation amplitude of 160.00. The starting ruthenium(III) precursors, $[RuCl_3(PPh_3)_3]$ [33] and $[RuCl_3(AsPh_3)_3]$ [34], were prepared according to the literature reports.

2.2. Synthesis of ruthenium(III) Schiff base complexes (1-6)

Complexes **1–6** were prepared by the following general procedure. To a benzene (20 mL) solution of $[RuX_3(EPh_3)_3]$ (0.0993 g, 0.1 mmol) (X = Cl, E = P or As) was added the Schiff base ligands (0.0253-0.0335 g, 0.1 mmol) (HL_1-HL_3) in the presence of triethylamine. The solution was allowed to heat under reflux for 5 h. The solution mixture was concentrated to 3 mL under reduced pressure and cooled. The complex was separated out upon the addition of 10 mL petroleum ether (60-80 °C) and reprecipitated from CH_2Cl_2/petroleum ether and dried under vacuum.

2.2.1. $[RuCl_2(PPh3)2L_1]$ (1)

Green solid, M.p. 230 °C. Anal calcd. for $C_{56}H_{44}ONCl_2P_2Ru$: C: 68.78; H: 4.50; N: 1.43. Found: C: 68.79; H: 4.50; N: 1.44. IR (cm^{-1}): 1596 ν(–C=N), 1300 ν(C–O). UV–vis, λ_{max} (nm): 430, 320, 260.

2.2.2. $[RuCl_2(AsPh3)2L_1]$ (2)

Pale-green solid, M.p. 220 °C. Anal calcd. for $C_{56}H_{44}ONCl_2As_2Ru$: C: 62.98; H: 4.12; N: 1.31. Found: C: 62.97; H: 4.11; N: 1.30. IR (cm^{-1}): 1597 ν(–C=N), 1305 ν(C–O). UV-vis, λ_{max} (nm): 430, 330, 250.

2.2.3. $[RuCl_2(PPh3)2L_2]$ (3)

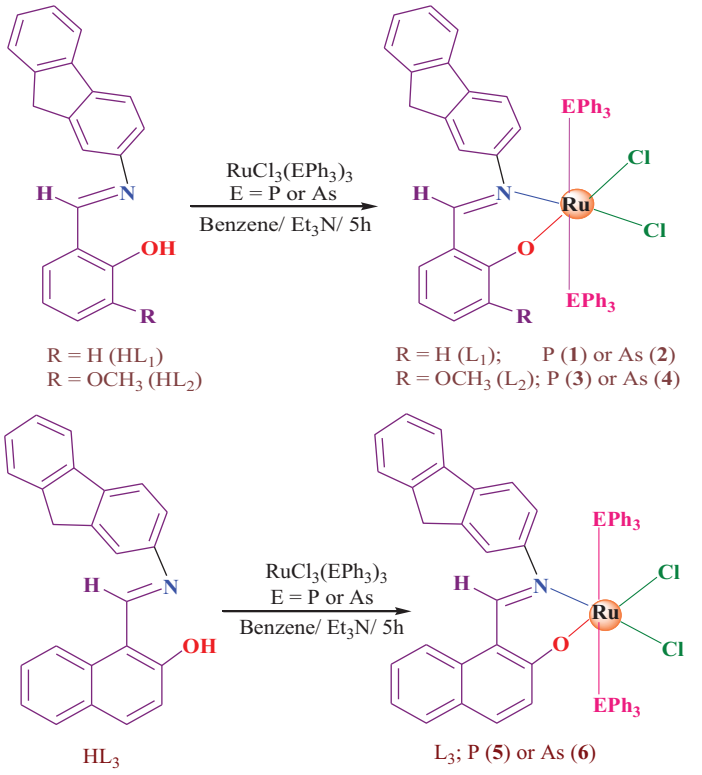
Green solid, M.p. 250 °C. Anal calcd. for $C_{57}H_{46}O_2NCl_2P_2Ru$: C: 67.92; H: 4.56; N: 1.39. Found: C: 67.93; H: 4.56; N: 1.40. IR (cm^{-1}): 1586 ν(–C=N), 1305 ν(C–O). UV-vis, λ_{max} (nm): 410, 310, 270.

2.2.4. $[RuCl_2(AsPh3)2L_2]$ (4)

Green solid, M.p. 230 °C. Anal calcd. for $C_{57}H_{46}O_2NCl_2As_2Ru$: C: 63.27; H: 4.25; N: 1.29. Found: C: 63.28; H: 4.24; N: 1.28. IR (cm^{-1}): 1578 ν(–C=N), 1306 ν(C–O). UV-vis, λ_{max} (nm): 440, 320, 250.

2.2.5. $[RuCl_2(PPh3)2L_3]$ (5)

Green solid, M.p. 210 °C. Anal calcd. for $C_{60}H_{47}ONCl_2P_2Ru$: C: 70.03; H: 4.57; N: 1.36. Found: C: 70.02; H: 4.56; N: 1.37. IR (cm^{-1}): 1597 ν(–C=N), 1336 ν(C–O). UV-vis, λ_{max} (nm): 440, 310, 265.



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

2.2.6. [$RuCl_2(AsPh3)2L_3$] (6)

Green solid, M.p. 200 °C. Anal calcd. for $C_{60}H_{47}ONCl_2As_2Ru$: C: 64.40; H: 4.20; N: 1.25. Found: C: 64.41; H: 4.20; N: 1.25. IR (cm^{-1}): 1597 ν(–C=N), 1336 ν(C–O). UV-vis, λ_{max} (nm): 420, 310, 272.

2.3. Typical procedure for transfer hydrogenation of ketones

The mixture of a ketone (5.0 mmol) and base (0.03 mmol) containing the catalyst (0.2 mol %), *i*-PrOH (6 mL) was refluxed for 5 h. After completion of the reaction, the solvent was removed under reduced pressure. The catalyst was removed by the addition of 15 mL of petroleum ether followed by filtration and subsequent neutralization with dilute HCl. The combined organic fractions were dried over anhydrous Na_2SO_4. Percentage of conversion was determined by GC analysis of the crude mixture and compared with the authentic samples.

3. Results and discussion

The reactions of 1:1 molar ratio of $[RuX_3(EPh_3)_3]$ (X = Cl, E = P or As) and Schiff base ligands (HL_1-HL_3) in dry benzene afforded new six-coordinate low spin ruthenium(III) Schiff base complexes. The reaction proceeds as shown in Scheme 1. All the

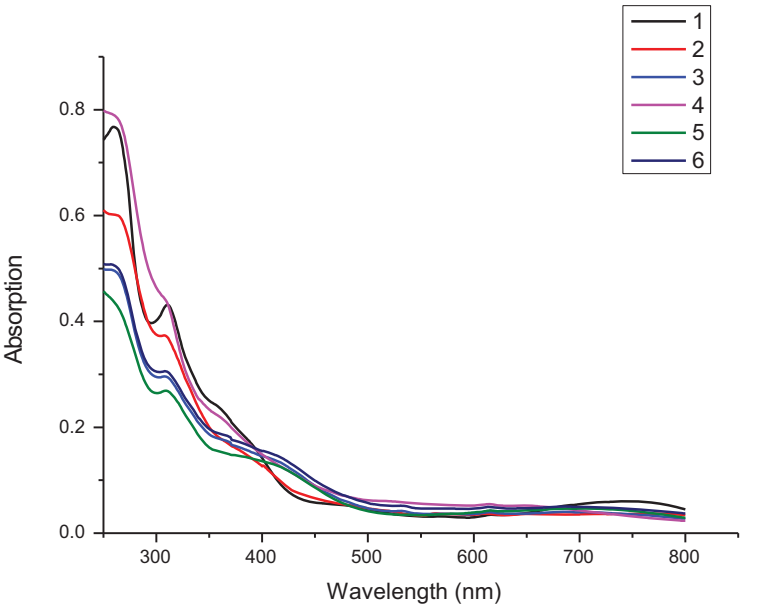


Figure 1. UV-vis spectra of **1–6** in $CHCl_3$ (10^{-5} M).

complexes are air-stable, non-hygroscopic in nature, insoluble in water and highly soluble in common solvents such as dichloromethane, acetonitrile and chloroform. The data obtained from elemental analysis are in good agreement with the compositions proposed for the molecular structure of the ruthenium complexes.

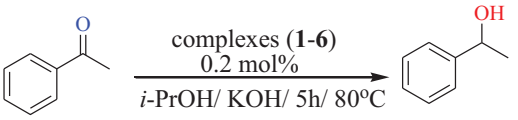
3.1. Characterization of the complexes

The IR spectra of the free Schiff base ligands display a strong band at 1610-1615 cm^{-1} that is attributed to the ν(C=N) stretching. Coordination of the Schiff bases to the ruthenium ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link. Hence, this band undergoes a shift to lower frequency to 1578–1597 cm^{-1} after complexation, indicating coordination of the azomethine nitrogen to ruthenium atom [35, 36]. This fact is further supported by increase in the absorption frequency of the phenolic ν(C-O) band from 1276–1296 cm^{-1} in the free ligands to 1300–1336 cm^{-1} in the ruthenium complexes, confirming that the other coordination site of Schiff base is phenolic oxygen in all the complexes. FT-IR of **1–6** are given in Figures S1–S6.

Electronic spectra of **1-6** have been recorded in chloroform and the representative spectra are depicted in Figure 1. Complexes showed a moderate intense band in the visible region. The absorption bands around 420–440 nm are due to metal-to-ligand charge-transfer (MLCT) transition [37, 38]. The high intensity bands around 250–270 nm and 310–330 nm were assigned to π–π* and n–π* transitions, respectively, due to non-bonding electron present on the nitrogen of the azomethine group of the ligands.

The electron paramagnetic resonance spectral studies are performed both in pure powder samples and in solution at room temperature and liquid nitrogen

Table 1. Transfer hydrogenation of acetophenone to 1-phenylethanol catalyzed by complexes (1–6).[a]



Entry	Complex	Conversion[b] (%)
1	**1**	99
2	**2**	85
3	**3**	80
4	**4**	75
5	**5**	72
6	**6**	70
7	–	No desired product

[a]Reaction conditions: reactions were carried out using acetophenone (5 mmol), catalyst (0.2 mol%), base (0.03 mmol).
[b]Conversion was monitored by GC analysis and are average of two runs.

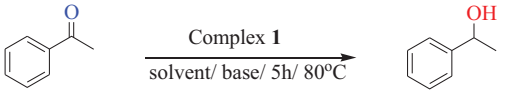
temperature, respectively, at X-band frequency. Complexes **1-3** exhibit well-defined single isotropic feature near g = 2.10 to 2.17 at room temperature. However, the EPR spectral profiles of the complexes in dichloromethane solution at 77 K show rhombic spectra with three different 'g' values ($g_x \neq g_y \neq g_z$) (Figures S7–S9). Overall the position of lines and nature of the EPR spectra of the complexes are characteristic of low spin ruthenium(III) octahedral complexes [39–42]. The electrospray ionization (ESI) mass spectra of **1** and **6**, obtained in positive mode, give peaks at m/z = 977 and 1118, respectively (Figures S10 and S11). The loss of one chloride atom for ruthenium complexes is quite common under ESI-MS conditions [43–45].

3.2. Catalytic transfer hydrogenation of ketones

Catalytic transfer hydrogenation is being increasingly used in industry because of its selectivity, efficiency, scope, simplicity, economic viability and also the growing awareness of the need for green chemistry. In general, recent aims have been to improve catalyst turnover and selectivity, either through more active catalysts or ones that can be recycled, to enable lower costs and higher purity products, as well as more productive, less wasteful processes. Ruthenium complexes catalyzed transfer hydrogenation reactions require the Ru-H an intermediate species and hence complexes with Ru-H bond or with potential for the *in-situ* formation of such a bond are suitable candidates for these catalytic reactions. Given the propensity toward *in situ* formation of ruthenium-hydrido species in the present family of complexes, we wish to explore their catalytic activity in transfer hydrogenation of ketones. In order to optimize the reaction conditions, the effect of solvents, bases, time, temperature and catalyst:substrate ratios were studied.

We started our study by examining the transfer hydrogenation of acetophenone to 1-phenylethanol using synthesized ruthenium Schiff base complexes. All complexes efficiently catalyze the transfer hydrogenation of acetophenone with maximum conversion within 5 h. Among the tested complexes, **1** is highly efficient in the transfer hydrogenation of ketones to alcohol with high conversion of 99%. The result of

Table 2. Effect of the catalyst, solvent and base.[a]



Entry	Catalyst (mol%)	Solvent	Base	Conversion[b](%)
1	0.2	*i*-PrOH	KOH	99
2	0.1	*i*-PrOH	KOH	81
3	0.05	*i*-PrOH	KOH	70
4	0.02	*i*-PrOH	KOH	45
5	0.2	*i*-PrOH	–	0
6	–	*i*-PrOH	KOH	0[c]
7	0.2	*i*-PrOH	NaOH	96
8	0.2	*i*-PrOH	Na_2CO_3	65
9	0.2	*i*-PrOH	K_2CO_3	53
10	0.2	*i*-PrOH	Et_3N	Trace
11	0.2	*i*-PrOH	Pyridine	Trace
12	0.2	Methanol	KOH	45
13	0.2	Ethanol	KOH	30

[a]Reaction conditions: reactions were carried out using acetophenone (5 mmol), catalyst, base (0.03 mmol), solvent (6 mL).
[b]Conversion determined by GC analysis.
[c]Reaction carried out in the absence of catalyst.

transformations is given in Table 1. The lowest conversion observed is 72% for **6**. The catalytic process is more efficient with **1** followed by **2**, **3**, **4**, **5** and **6** showing the least activity among all six complexes. It was observed that the efficiency of catalysts was simply dependent on the structure of Schiff base ligands. The electron donating substituent (-OCH_3) group present in the Schiff base ligand in **2** and bulky naphthyl group in **3** shows less activity than the catalyst **1**. Further, it is observed that the complex catalyst containing PPh_3 group shows higher activity than the complexes possessing $AsPh_3$.

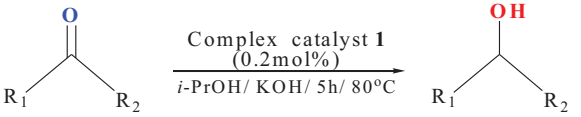
The effect of methanol, ethanol and isopropanol on the hydrogenation of acetophenone was investigated. When no catalyst was added, the blank reaction with solvent isopropanol exhibited no conversion in 5 h (entry 7, Table 1).

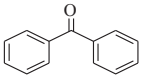
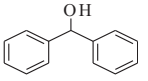
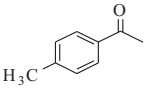
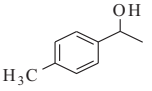
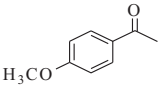
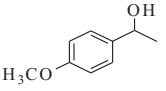
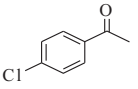
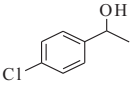
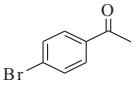
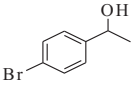
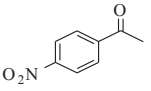
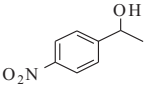
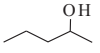
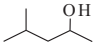
The base also plays an essential role, and in the absence of a base, no product was formed (entry 5, Table 2). KOH was found to be the effective base and its substitution by NaOH, Na_2CO_3 and K_2CO_3 led to a significant drop in yield. The results propose that KOH/isopropanol was preferred base/solvent system for transfer hydrogenation of ketones under our experimental conditions.

The reaction proceeds with high conversion 99% when the catalyst loading was 0.2 mol %. When decreasing the catalyst loading to 0.1, 0.05 mol %, the reaction proceeds with good conversions 81% and 70%, respectively. Further, the catalysis works well with low loading of catalyst 0.02 mol % and shows conversion of 45%. Thus, it was concluded that the catalyst loading of 0.2 mol % of **1** is the best compromise between optimum reaction rates. The results are collected in Table 2 and the conversions reported are averages of two runs i7n the case of all catalytic reaction.

To examine the generality of **1** as a catalyst for transfer hydrogenation, the scope of ketones with different electronic effect was investigated under similar conditions; the results are summarized in Table 3. Acetophenone with substituents of varying electronic properties were efficiently reduced to the corresponding secondary alcohols

Table 3. Transfer hydrogenation of various ketones with complex (1).[a]



Entry	Substrate	Product	Conversion[b] (%)	TON[c]
1			99	495
2			92	460
3			80	400
4			78	390
5			92	460
6			95	475
7			98	490
8			89	445
9			93	465
10			91	455
11			96	480
12			85	425
13			82	410

[a]Reaction conditions: ketone (5 mmol), catalyst (0.2 mol%, base (0.03 mmol), i-PrOH (6 mL).
[b]Conversion was monitored by GC analysis and are average of two runs.
[c]TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

in good conversions. The conversion of acetophenone to 1-phenyl ethanol is obtained in 99% conversion (entry 1). The presence of electron-withdrawing or electron-donating substituents on the aromatic ring has significant effect in the conversion. Aromatic halo-substituents have an enhancing effect on the catalytic activity, showing quantitative results on the formation of the corresponding alcohols (entries 5, 6 and 7) and catalyzed with good conversions of 92%, 95% and 98%, respectively. Whereas, electron-donating substituents (entries 3 and 4) on the ring gave lower conversions to the corresponding alcohols are 80% and 78%, respectively, than that of acetophenone. Cyclic ketones containing five- and six-membered rings were reduced effectively to give the corresponding alcohols with conversions of up to 89% and 93%. The complex catalyst also efficiently catalyzed the reduction of aliphatic ketones such as 2–butanone, 2–pentanone, diethyl ketone and 4–methylpentan–2–one to their corresponding secondary alcohols in 91%, 96%, 85% and 8 2% yield, respectively.

It is well known from the literature that the mechanism of transfer hydrogenation of ketones by ruthenium complexes has been proposed to involve the formation of ruthenium(II)-hydride as catalytic intermediate [46] and the mechanism involving Ru(III) complexes is not known. However, the present Ru(III) Schiff base complexes show an excellent catalytic performance with high conversions and the catalytic activity is comparable to the reported ruthenium complexes in terms of conversion, reaction time and catalyst loading [47].

4. Conclusion

The new family of ruthenium(III) fluoreneamine based Schiff base complexes of the type $[RuCl_2(EPh_3)_2L]$ (E = P, As and L = O,N-donor) were synthesized. The characterization of the complexes was accomplished by analytical, spectral (FT-IR, UV-vis, EPR) and ESI-MS analyses. The bulky bidentate fluoreneamine Schiff base ligand, twoPPh_3/$AsPh_3$ and two chlorine atoms are coordinated to ruthenium metal which forms octahedral geometry in these complexes. The catalytic studies showed that the synthesized ruthenium complexes are effective for the transfer hydrogenation of a range of ketones. Further, the synthesis of ruthenium complexes containing different types of fluoreneamine-based bulky Schiff base ligands are under process.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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