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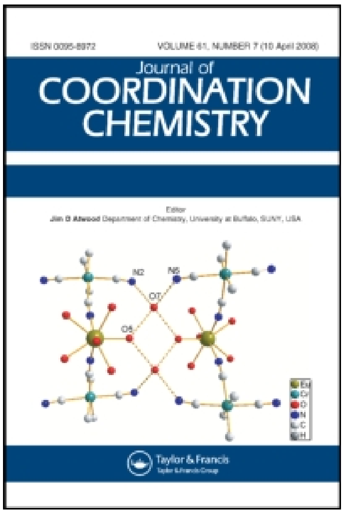

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Ruthenium(II) unsymmetrical N_2O_2 tetradentate Schiff-base complexes: synthesis, characterization, and catalytic studies

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Ruthenium(II) unsymmetrical N_2O_2 tetradentate Schiff-base complexes: synthesis, characterization, and catalytic studies

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A series of six-coordinate ruthenium(II) complexes [Ru(CO)(L^x)(B)] (B = PPh_3, $AsPh_3$ or Py; L^x = unsymmetrical tetradentate Schiff base, x = 5–8; L^5 = salen-2-hyna, L^6 = Cl-salen-2-hyna, L^7 = valen-2-hyna, L^8 = *o*-hyac-2-hyna) have been prepared by reacting [RuHCl(CO)$(EPh_3)_2$(B)] (E = P or As) with unsymmetrical Schiff bases in benzene under reflux. The new complexes have been characterized by analytical and spectroscopic (infrared, electronic, ^{1}H, ^{31}P, and ^{13}C NMR) data. An octahedral structure has been assigned for all the complexes. The new complexes are efficient catalysts for the transfer hydrogenation of ketones and also exhibit catalytic activity for the carbon–carbon coupling reactions.

Keywords: Ruthenium(II) complexes; Unsymmetrical Schiff base; Spectroscopic characterization; Catalytic activity

1. Introduction

Analytical, biological, and industrial applications of Schiff-base complexes have made this field attractive [1–8]. These complexes exhibit catalytic activity in chemical transformations such as Kharasch addition, enol ester synthesis, alkyne dimerization, olefin metathesis, and atom transfer radical polymerization [9–13]. Transition metal complexes have also been used as antimicrobials [14, 15] and sensor materials [16]. Unsymmetrical Schiff bases have advantages because of the possibility of fine-tuning structures by introducing different electron withdrawing and/or donating groups on the periphery of both imine units. Unsymmetrical Schiff bases have been reported to give improved enantioselective behavior in various organic transformations as compared with their symmetrical derivatives [17].

Ruthenium-mediated transfer hydrogenation (TH) of ketones under basic conditions employing *i*-PrOH or other H_2-donor solvents has emerged as an atom-economical

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methodology for the synthesis of secondary alcohols [18]; ruthenium-based catalytic systems are effective in TH of ketones [19]. A number of transition metal phosphine complexes have been used as catalysts in TH of aldehydes [20] and ketones [21] because of steric and electronic properties of such ligands [22].

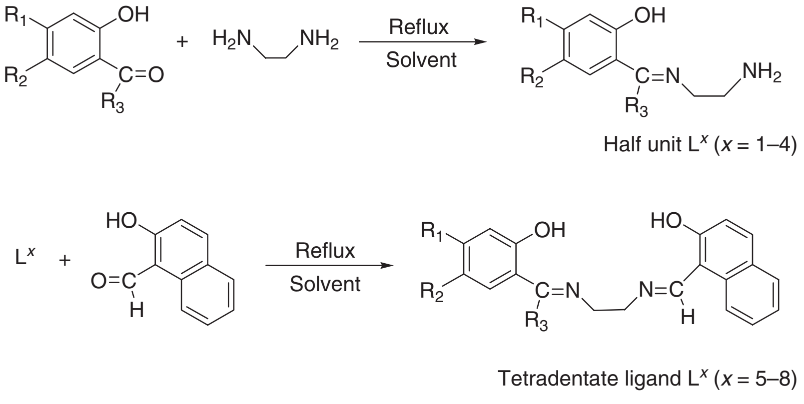
Transition-metal-catalyzed coupling reactions are important processes in organic chemistry and have been extensively studied as a powerful method for the formation of carbon–carbon bonds, applied in the synthesis of many compounds, especially complex natural products, supramolecular chemistry, and materials science [23–25]. Palladium- or nickel-catalyzed Suzuki–Miyaura cross-coupling [26–28] is the most important strategy for the construction of unsymmetrical biaryl compounds. Several reports are available on the catalytic activity of ruthenium complexes, mostly for oxidation and TH reactions, not for coupling reactions. To study the catalytic activity of ruthenium complexes for TH and coupling reactions, we synthesized unsymmetrical Schiff bases, salicylaldehyde ethylenediamine 2-hydroxy-1-naphthaldehyde (salen-2-hyna), 5-chloro salicylaldehyde ethylenediamine 2-hydroxy-1-naphthaldehyde (Cl-salen-2-hyna), *o*-vanillin ethylenediamine 2-hydroxy-1-naphthaldehyde (valen-2-hyna), *o*-hydroxy acetophenone ethylenediamine 2-hydroxy-1-naphthaldehyde (*o*-hyac-2-hyna), and their ruthenium(II) complexes containing $PPh_3/AsPh_3$ co-ligands and explored their catalytic activities. The complexes were characterized by analytical and spectral [infrared (IR), electronic, ^{1}H, ^{31}P, and ^{13}C NMR] methods.

2. Experimental

All reagents used were Analar or chemically pure grade. Solvents were freshly distilled according to standard procedure. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlo Erba (Thermoquest, Italy) 1108 model analyzer at Central Drug Research Institute (CDRI), Lucknow, India. FT-IR spectra were recorded in KBr pellets with a Nicolet (Thermoscientific, US) FT-IR spectrophotometer from 400 to 4000 cm^{-1}. Electronic spectra were recorded on a Shimadzu (Japan) UV-Vis 1650 PC spectrophotometer from 200 to 800 nm using CH_2Cl_2. NMR spectra (^{1}H, ^{31}P, and ^{13}C) were recorded on a Jeol (Japan) GSX-400 instrument in $CDCl_3$ at room temperature. ^{1}H NMR chemical shifts were referenced to tetramethylsilane (TMS) as an internal standard and ^{13}C NMR chemical shifts were referenced to the internal solvent resonance. ^{31}P NMR spectra of the complexes were obtained using *ortho* phosphoric acid as reference. Gas chromatographic (GC) analyses were conducted on an ACME 6000 (Younglin instrument, Korea) series instrument equipped with a flame ionization detector (FID) using a DP-5 column of 30 m length, 0.53 mm diameter, and 5.00 µm film thickness. Melting points were recorded on a Technico micro heating table and are uncorrected. The starting complexes $[RuHCl(CO)(PPh_3)_3]$ [29], $[RuHCl(CO)(AsPh_3)_3]$ [30], and $[RuHCl(CO)(Py)(PPh_3)_2]$ [31] were prepared according to the literature methods.

2.1. *Preparation of new unsymmetrical tetradentate Schiff-base ligands, L^x [$x = 5$–8]*

The unsymmetrical tetradentate Schiff bases were synthesized by a two-stage process (scheme 1). In the first step, half-units L^x ($x = 1$–4) were prepared by condensing



$R_1 = R_2 = R_3 = H$; L^1 = salen; L^5 = salen-2-hyna
$R_1 = R_3 = H$, $R_2 = Cl$; L^2 = Cl-salen; L^6 = Cl-salen-2-hyna
$R_1 = OCH_3$, $R_2 = R_3 = H$; L^3 = valen; L^7 = valen-2-hyna
$R_1 = R_2 = H$, $R_3 = CH_3$; L^4 = *o*-hyac; L^8 = *o*-hyac-2-hyna

Scheme 1. Synthesis of half units and tetradentate unsymmetrical Schiff bases.

substituted benzaldehyde or *o*-hydroxy acetophenone with ethylenediamine in ethanol in 1 : 1 molar ratio [32]. In the second stage, to a well-stirred solution of L^x [x = 1–4] (4 mmol) in 50 cm^3 chloroform, 2-hydroxy-1-naphthaldehyde (4 mmol) in 30 cm^3 chloroform was added dropwise. After addition was complete, the mixture was stirred for another 30 min and refluxed for 2–3 h. The resulting solution was concentrated under vacuum to remove solvent and the product obtained was recrystallized from chloroform.

2.2. *Synthesis of new ruthenium(II) unsymmetrical Schiff-base complexes*

All complexes were prepared by the following procedure. To a solution of $[RuHCl(CO)(EPh_3)_2(B)]$ (0.10 g, 0.10 mmol) in benzene (20 cm^3), the appropriate unsymmetrical Schiff base (29–46 mg, 0.10 mmol) was added in 1 : 1 molar ratio in a 100 cm^3 round-bottomed flask. The mixture was refluxed for 5 h on a water bath. The reaction mixture gradually changed to deep color during heating. Then, the contents were concentrated to 3 cm^3 under reduced pressure, cooled, and the product was separated by the addition of 10 cm^3 of petroleum ether (60–80°C). The product was recrystallized from CH_2Cl_2–petroleum ether (60–80°C). The compounds were dried under vacuum and the purity of the complexes was checked by TLC.

2.3. *Procedure for catalytic TH*

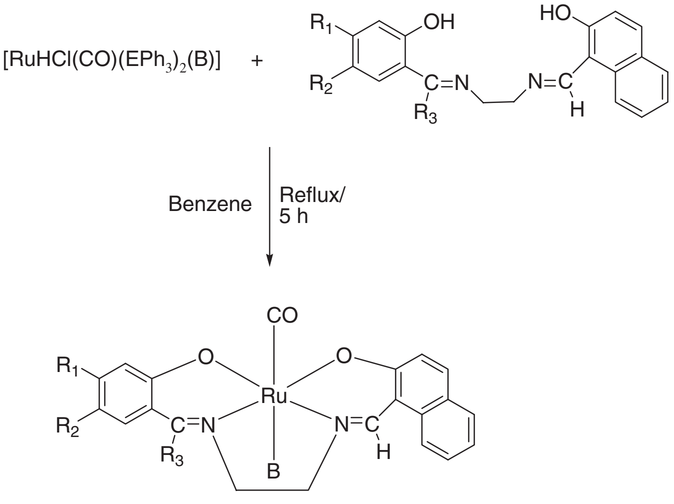
Catalytic TH reactions were studied using ruthenium(II) unsymmetrical Schiff-base complex as a catalyst, ketone as substrate, and KOH as base at 1 : 300 : 2.5 molar ratios with the following procedure. A mixture containing ketone (3.75 mmol), ruthenium complex (0.0125 mmol), and KOH (0.03 mmol) in 10 cm^3 of *i*-prOH was refluxed on a water bath for appropriate time at 95°C. At completion the catalyst was removed from the reaction mixture by the addition of petroleum ether, followed by filtration and subsequent neutralization with 1 M HCl. Then, the ether layer was filtered through a small bed (2 cm^3) of silica gel by column chromatography, the filtrate was concentrated to ≈1 cm^3, subjected to GC analysis, and the hydrogenated product was identified and determined with authentic samples.

2.4. *Procedure for catalytic activity of carbon–carbon coupling reaction*

Magnesium turnings (320 mg) were placed in a two-neck-round-bottomed flask with a calcium chloride guard tube. A crystal of iodine was added to activate the surface of the magnesium. Bromobenzene (0.50 cm^3 of a total of 1.3 cm^3, 12 mmol) in 5 cm^3 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 cm^3 of ether was added dropwise and the reaction mixture was refluxed for 40 min. To this reaction mixture, 1.03 cm^3 (10 mmol) of bromobenzene in 5 cm^3 of anhydrous diethyl ether and the ruthenium complex (0.05 mmol) was added and the mixture was refluxed for 6 h. The reaction mixture was cooled and hydrolyzed with a saturated solution of aqueous ammonium chloride. The ether extract on evaporation of the solvent gave the crude product, which was chromatographed to get pure biphenyl and was compared with an authentic sample (m.p.: 69–72°C).

3. Results and discussion

New six-coordinate ruthenium(II) unsymmetrical tetradentate Schiff-base complexes [Ru(CO)(L^x)(B)] were obtained as shown in scheme 2. Analytical data of the new



(B = PPh_3, $AsPh_3$ or Py; R_1 = H or OCH_3, R_2 = H or Cl, R_3 = H or CH_3)

Scheme 2. Formation of new ruthenium(II) unsymmetrical Schiff-base complexes.

complexes (table 1) agree well with the proposed molecular formulas. In all reactions, Schiff bases are dianionic tetradentate ligands, replacing two molecules of triphenylphosphine or triphenylarsine, a hydride and a chloride from [RuHCl(CO)(EPh$_3$)$_2$(B)]. The products obtained from reactions of [RuHCl(CO)(PPh$_3$)$_3$] with the Schiff bases contained one triphenylphosphine, whereas the corresponding reactions with [RuHCl(CO)(PPh$_3$)$_2$(py)] yielded new complexes with no triphenylphosphine ligands, indicating labile nature of the Ru–P bond compared with the Ru–N bond in these complexes. The difference in the strength of Ru–P and Ru–N bonds may be explained on the basis of the better σ donating ability of the nitrogen bases [33, 34] compared to triphenylphosphine.

3.1. *Infrared spectroscopic analysis*

IR absorptions for the ligands and complexes are shown in table 2. A strong band at 1644–1634 cm^{-1} in free Schiff base is characteristic of the azomethine. If the Schiff base coordinates through nitrogen, there must be a reduction in the azomethine frequency owing to the lowering of electron density upon coordination. In the spectra of complexes, this band shifts to 1639–1611 cm^{-1}, indicating coordination through nitrogen [35]. A strong band at 1303–1315 cm^{-1} in the free Schiff bases is assigned to phenolic C–O stretch. In ruthenium complexes, this band shifts to 1355–1318 cm^{-1} showing coordination through the phenolic oxygen [36]. This is further supported by the disappearance of ν_{OH} around 3401–3422 cm^{-1} in the complexes. Hence, from IR spectroscopic data carbonyl and phenolic oxygen are involved in coordination to ruthenium. Strong absorption around 1945–1923 cm^{-1} has been assigned to the carbonyl group in the ruthenium complexes. For complexes containing heterocyclic nitrogen [37], a medium intensity band appeared at 1030 cm^{-1}.

3.2. *Electronic spectroscopic analysis*

The electronic spectra of the complexes in dichloromethane showed three to four bands at 423–233 nm (table 2). Bands around 423–310 nm have been assigned to charge

Table 1. Analytical data of ruthenium(II) unsymmetrical Schiff-base complexes.

			Calcd (found) (%)		
Complex	Yield (%)	d.p. (°C)	C	H	N
[Ru(CO)(PPh$_3$)(L^5)]	87	161–163	66.19(66.09)	4.41(4.34)	3.96(3.91)
[Ru(CO)(PPh$_3$)(L^6)]	84	145–148	63.11(63.02)	4.07(4.01)	3.77(3.69)
[Ru(CO)(PPh$_3$)(L^7)]	82	150–152	65.12(64.99)	4.51(4.48)	3.80(3.74)
[Ru(CO)(PPh$_3$)(L^8)]	78	146–150	66.56(66.49)	4.60(4.51)	3.88(3.80)
[Ru(CO)(AsPh$_3$)(L^5)]	73	158–161	62.32(62.25)	4.16(4.05)	3.73(3.68)
[Ru(CO)(AsPh$_3$)(L^6)]	76	160–164	59.58(59.44)	3.85(3.78)	3.56(3.49)
[Ru(CO)(AsPh$_3$)(L^7)]	79	140–142	61.40(61.27)	4.25(4.18)	3.58(3.52)
[Ru(CO)(AsPh$_3$)(L^8)]	88	134–138	62.74(62.69)	4.14(4.06)	3.66(3.59)
[Ru(CO)(Py)(L^5)]	85	191–194	59.53(59.47)	4.03(3.98)	8.01(7.93)
[Ru(CO)(Py)(L^6)]	81	187–190	55.86(55.81)	3.60(3.53)	7.51(7.41)
[Ru(CO)(Py)(L^7)]	78	179–183	58.47(58.45)	4.18(4.10)	7.57(7.42)
[Ru(CO)(Py)(L^8)]	76	182–185	60.21(60.13)	4.30(4.25)	7.80(7.73)

Table 2. IR absorption frequencies (cm^{-1}) and electronic spectroscopic data (nm) of free ligands and their ruthenium(II) unsymmetrical Schiff-base complexes.

Compound	$\nu_{C\equiv O}$	$\nu_{C=N}$	$\nu_{C–O}$	λ_{max} (ε) ($\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$)
L^5	–	1636	1303	–
L^6	–	1634	1310	–
L^7	–	1642	1316	–
L^8	–	1644	1315	–
$[Ru(CO)(PPh_3)(L^5)]$	1942	1626	1353	390(8318), 310(11,630), 237(21,956)
$[Ru(CO)(PPh_3)(L^6)]$	1938	1615	1351	395(8157), 311(10,886), 240(21,242)
$[Ru(CO)(PPh_3)(L^7)]$	1940	1611	1345	400(7392), 311(10,868), 235(22,890)
$[Ru(CO)(PPh_3)(L^8)]$	1938	1616	1348	396(7984), 310(11,630), 236(22,182)
$[Ru(CO)(AsPh_3)(L^5)]$	1928	1622	1343	401(7289), 308(12,238), 236(22,274)
$[Ru(CO)(AsPh_3)(L^6)]$	1937	1634	1350	419(6993), 402(7168), 311(10,849), 233(23,956)
$[Ru(CO)(AsPh_3)(L^7)]$	1923	1635	1353	421(6894), 401(7257), 311(10,916), 233(23,892)
$[Ru(CO)(AsPh_3)(L^8)]$	1945	1639	1355	420(6913), 401(7263), 311(10,864), 234(23,215)
$[Ru(CO)(Py)(L^5)]$	1927	1623	1342	423(6795), 310(11630), 235(22,890)
$[Ru(CO)(Py)(L^6)]$	1938	1616	1318	399(7458), 310(11,613), 292(18,213), 235(22,890)
$[Ru(CO)(Py)(L^7)]$	1934	1614	1348	422(6812), 401(7289), 272(15,968), 234(23,215)
$[Ru(CO)(Py)(L^8)]$	1936	1635	1349	419(6993), 310(11,642), 234(23,198)

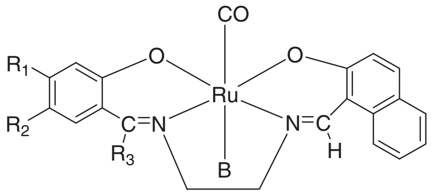
transfer transitions from the metal t_{2g} level to the unfilled π^* molecular orbital of the ligand [38]. Other high-intensity bands in the region below 300 nm are characterized as ligand-centered transitions and have been designated as π–π^* and n–π^* transitions for the electron localized on the azomethine of the Schiff bases [39]. This assignment is in conformity with the assignment made for similar octahedral complexes.

3.3. ^{1}H NMR spectroscopic analysis

Coordination of the unsymmetrical Schiff base to ruthenium is further confirmed by ^{1}H NMR spectra (Supplementary material). A singlet at 8.91–9.22 ppm has been assigned to the azomethine proton; the position of the azomethine signal in the complexes is downfield compared to the free ligands, indicating deshielding of the azomethine proton due to coordination [40]. A singlet at 2.36 ppm is assigned to methyl. Multiplets around 6.98–7.52 ppm in the complexes are assigned to aromatic protons of triphenylphosphine, triphenylarsine, pyridine, and Schiff-base ligand [35]. In addition, methylene protons appeared in the region 3.59–3.83 ppm for all the complexes [37]. The absence of a resonance around 12 ppm in the complexes indicates the deprotonation of the phenolic group of the Schiff bases on complexation, and coordination to ruthenium.

3.4. ^{31}P NMR spectroscopic analysis

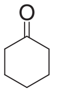
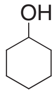
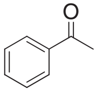
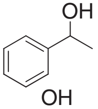
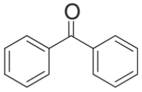
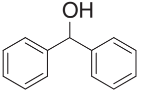
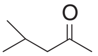
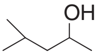
To confirm the triphenylphosphine group present in the complexes, the ^{31}P NMR spectra were recorded for few complexes (Supplementary material). A signal around 20–22 ppm in the spectra of $[Ru(CO)(PPh_3)(L^5)]$ and $[Ru(CO)(PPh_3)(L^6)]$ revealed the presence of triphenylphosphine; $[Ru(CO)(Py)(L^6)]$ does not exhibit such signal.



(B = PPh_3, $AsPh_3$ or Py; R_1 = H or OCH_3, R_2 = H or Cl, R_3 = H or CH_3)

Figure 1. Proposed structure of new ruthenium(II) unsymmetrical Schiff-base complexes.

Table 3. Catalytic activity of the TH of ketones by $[Ru(CO)(PPh_3)(L^8)]$ with *i*-PrOH[a].

Substrate	Product	Time (h)	Conversion (%)[b]
		2	94
		4	92
		6	53
		4	87

[a] Conditions: reactions were refluxed using 3.75 mmol of ketone (10 cm^3 isopropanol); catalyst : ketone : KOH ratio 1 : 300 : 2.5.

[b] Yield of product was determined using a ACME 6000 series GC-FID with a DP-5 column of 30 m length, 0.53 mm diameter, and 5.00 μm film thickness and by comparing with the authentic samples.

3.5. ^{13}C NMR spectroscopic analysis

^{13}C NMR spectra revealed the presence of an expected number of signals corresponding to different types of carbon atoms present in the compounds. The spectral (Supplementary material) data showed a strong resonance at 168.36–170.52 ppm assigned as –C=N. Multiplets around 126.27–143.31 ppm are assigned to aromatic carbons. The methylene carbons appear in the region 42.45–44.58 and 38.53–40.82 ppm. Sharp singlets at 55.62 and 21.97–22.04 ppm are assigned to methoxy and methyl carbons, respectively. The spectra confirm the formation of new ruthenium(II) unsymmetrical Schiff-base complexes.

Based on analytical and spectroscopic data, an octahedral structure (figure 1) is proposed for all the ruthenium(II) unsymmetrical Schiff-base complexes.

3.6. Catalytic TH of ketones

Catalytic TH of various ketones in the presence of $[Ru(CO)(PPh_3)(L^8)]$ has been studied in isopropanol–KOH using a molar ratio 1 : 2.5 : 300 for the catalyst, KOH, and ketone in 10 cm^3 of isopropanol. The catalyst performed efficiently for both aliphatic and aromatic ketones with high conversion and turnover (table 3). Cyclohexanone was

Table 4. Catalytic activity of ruthenium(II) unsymmetrical Schiff-base complexes for coupling reaction.

	Yield of biphenyl[a]	
Complex	(g)	(%)
[Ru(CO)(PPh_3)(L^7)]	0.289	15.7
[Ru(CO)(PPh_3)(L^8)]	0.251	13.6
[Ru(CO)($AsPh_3$)(L^7)]	0.248	13.4
[Ru(CO)($AsPh_3$)(L^8)]	0.251	13.6
[Ru(CO)(Py)(L^6)]	0.302	16.3
[Ru(CO)(Py)(L^7)]	0.246	13.3
No catalyst	0.021	01.2

[a] Based on phenylmagnesium bromide: 12 mmol.

converted into cyclohexanol in 94% yield and acetophenone was converted into 1-phenyl ethanol in 92% yield. Similarly, benzophenone and isobutyl methyl ketone underwent TH to afford the corresponding alcohol in 53% and 87% yields. In the absence of base, no TH of ketones was observed.

3.7. *Catalytic coupling reactions*

The ruthenium(II) unsymmetrical Schiff-base complexes were also tested as catalysts for aryl–aryl coupling [41, 42]. The system chosen is the coupling of phenylmagnesium bromide with bromobenzene to give biphenyl. Bromobenzene was first converted to the corresponding Grignard reagent. Then bromobenzene, followed by the test complex, was added and the mixture was refluxed for 6 h. After work up, the reaction mixture gave biphenyl.

Yields of biphenyl formed from the coupling reactions varied from 13% to 16% (table 4) depending upon the catalyst. Reactions without ruthenium catalyst produced 1.2% biphenyl, insignificant compared to the yields of biphenyl obtained from the reactions catalyzed by ruthenium complexes. This shows the catalytic role of ruthenium complexes in the coupling. The yields of biphenyl obtained from the reactions catalyzed by the ruthenium(II) complexes are low due to (1) active species derived from ruthenium complexes are less stable, as the effectiveness of the catalysts is directly related to their ability to generate the corresponding active species [43] and (2) bromobenzene undergoes dehalogenation to form benzene as side product. That product yields are not much differed for different catalysts may be due to similar active species formed in all reactions.

4. Conclusions

Several new ruthenium(II) unsymmetrical Schiff-base complexes were synthesized and characterized by analytical and spectroscopic techniques. An octahedral structure has been tentatively proposed for all complexes. The complexes showed efficient catalytic activity for TH reactions and moderate activity for carbon–carbon coupling reactions.

Although some ruthenium complexes have been reported in recent literature [44–52], ruthenium(II) unsymmetrical Schiff-base complexes have been rarely seen as catalysts for this kind of TH and carbon–carbon coupling reactions. The presence of a labile triphenylphosphine makes the complexes catalytically active and activity may be tuned by changing the electronic environment around the metal by altering the substituents in unsymmetrical Schiff-base ligand.

Supplementary material

^{1}H and ^{31}P NMR spectra of representative ruthenium(II) unsymmetrical Schiff-base complexes have been provided as supplementary materials.

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