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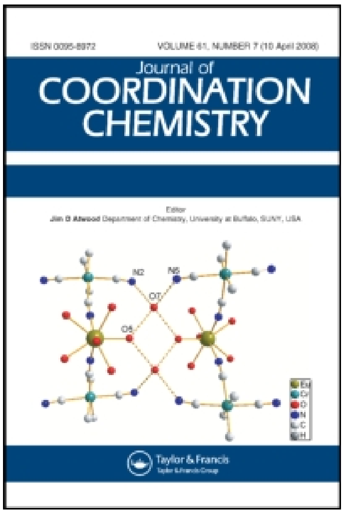

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Studies on ruthenium(III) chalcone thiosemicarbazone complexes as catalysts for carbon-carbon coupling

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Studies on ruthenium(III) chalcone thiosemicarbazone complexes as catalysts for carbon–carbon coupling

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New six-coordinate ruthenium(III) complexes $[RuX(EPh_3)_2(L)]$ ($X = Cl$ or Br; $E = P$ or As; L = chalcone thiosemicarbazone) have been prepared by reacting $[RuX_3(EPh_3)_3]$ ($X = Cl$ or Br; $E = P$ or As) with chalcone thiosemicarbazones in benzene under reflux. The new complexes have been characterized by analytical and spectroscopic (IR, electronic, mass, and EPR) data. The redox behavior of the complexes has also been studied. Based on the above data, an octahedral structure has been assigned for all the complexes. The new complexes exhibit catalytic activity for carbon–carbon coupling reactions.

Keywords: Chalcone thiosemicarbazone; Ruthenium(III) complexes; Spectroscopic studies; Carbon–carbon coupling reactions

1. Introduction

Transition metal-catalyzed coupling reactions have been extensively studied since they represent a powerful method for the formation of carbon–carbon bonds. This strategy has been applied to the synthesis of many organic compounds, especially complex natural products, in supramolecular chemistry and in materials science [1–3]. The importance of biaryl units [2] as components of pharmaceuticals, herbicides, and natural products, as well as in the field of engineering materials such as conducting polymers, molecular wires, and liquid crystals has attracted enormous interest. Palladium and nickel-catalyzed Suzuki–Miyaura cross-coupling [4–6] is the most important and efficient strategy for the construction of unsymmetrical biaryl compounds. This cross-coupling methodology allows the use of organic solvents and inorganic bases, tolerates many functional groups, is not affected by steric hindrance of the substrates, and is suitable for industrial processes [7].

Though several reports are available on catalytic activity of ruthenium complexes, most of them have been studied for oxidation and reduction reactions [8–14] not for

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coupling reactions. Hence, in an attempt to study the catalytic activity of ruthenium complexes for carbon–carbon coupling reaction, we synthesize a series of six-coordinate ruthenium(III) chalcone thiosemicarbazone complexes containing PPh_3/$AsPh_3$ co-ligands and explore their catalytic activities. Characterizations of the complexes were accomplished by analytical and spectroscopic (IR, electronic, mass, and EPR) methods.

2. Experimental

2.1. *Materials and methods*

All reagents used were of analar or chemically pure grade. Solvents were freshly distilled by literature methods [15]. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlo Erba 1108 analyzer at the Central Drug Research Institute (CDRI), Lucknow, India. MALDI-TOF mass spectral measurements were performed with a Voyager-De pro instrument. FT-IR spectra were recorded in KBr pellets with a Nicolet FT-IR spectrophotometer from 400 to 4000 cm^{-1}. Electronic spectra of the complexes were recorded on a Shimadzu UV-Vis 1650 PC spectrophotometer at 200–600 nm using CH_2Cl_2 as solvent. Magnetic susceptibility measurements of the complexes were made on an EG and G-PARC vibrating sample magnetometer. Room temperature EPR spectra of powder samples were recorded with a JEOL JES-FA200 instrument at X-band frequencies using 2,2′-diphenyl-1-picrylhydrazyl radical (DPPH) as internal standard. Cyclic voltammetric measurements were carried out with a BAS CV-27 electrochemical analyzer in acetonitrile using $[NBu_4]ClO_4$ (TBAP) as supporting electrolyte under nitrogen. A three electrode cell was employed with glassy carbon working electrode, a platinum wire as counter electrode, and Ag/AgCl as reference electrode. Melting points were recorded on a Technico micro heating table and are uncorrected. The starting complexes $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, and $[RuBr_3(AsPh_3)_3]$ were prepared according to literature methods [16, 17].

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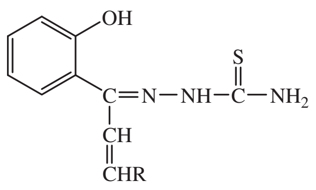
2.2. *Preparation of chalcone thiosemicarbazone ligands*

Ligands are prepared by two-step processes. In the first step, the 2′-hydroxychalcones were prepared in 80–90% yield by stirring 2-hydroxyacetophenone (0.6 cm^3, 5 mmol) with corresponding aldehydes (0.531–0.831 g, 5 mmol) in the presence of 50 cm^3 alcoholic sodium hydroxide solution (20%). After 24 h stirring, the product was precipitated by adding concentrated hydrochloric acid, filtered, and recrystallized from ethanol. In the second step, 2′-hydroxychalcones (0.224–0.284 g, 1 mmol) was reacted with thiosemicarbazide (0.425 g, 4.7 mmol) in ethanol (40 cm^3) containing concentrated hydrochloric acid (0.2 cm^3). The reaction mixture was refluxed for 8 h and the solvent was evaporated under vacuum. The resulting residue (yield 60–68%) was recrystallized from ethanol.

L^1: Yellow, m.p. 120°C, yield 80%. FT-IR (KBr, cm^{-1}): ν(C=N) 1604, ν(C–O) 1351, ν(C–S) 824.



Ligand	R
L^1	C_6H_5
L^2	$4\text{-}(OCH_3)C_6H_4$
L^3	$3,4\text{-}(OCH_3)_2C_6H_3$
L^4	$4\text{-}(CH_3)C_6H_4$

Figure 1. Structure of chalcone thiosemicarbazone ligands.

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L^2: Yellow, m.p. 128°C, yield 79%. FT-IR (KBr, cm^{-1}): ν(C=N) 1598, ν(C–O) 1339, ν(C–S) 818.
L^3: Yellow, m.p. 150°C, yield 75%. FT-IR (KBr, cm^{-1}): ν(C=N) 1581, ν(C–O) 1330, ν(C–S) 829.
L^4: Yellow, m.p. 132°C, yield 70%. FT-IR (KBr, cm^{-1}): ν(C=N) 1599, ν(C–O) 1324, ν(C–S) 810.

The general structure of chalcone thiosemicarbazone ligands is given in figure 1.

2.3. *Preparation of new ruthenium(III) chalcone thiosemicarbazone complexes*

All complexes were prepared by the following procedure. To a solution of $[RuX_3(EPh_3)_3]$ (X = Cl or Br; E = P or As) (0.1 g, 0.1 mmol) in benzene (20 cm^3), the appropriate chalcone thiosemicarbazone ligands (0.024–0.036 g, 0.1 mmol) were added in 1 : 1 molar ratio. The mixture was refluxed for 6 h on a water bath. The color of the reaction mixture gradually deepened during heating. The reaction mixture was concentrated to around 3 cm^3 by removing the solvent under reduced pressure, cooled, and the product separated by addition of 10 cm^3 of petroleum ether (60°C–80°C). The product was recrystallized from CH_2Cl_2/petroleum ether mixture, dried under vacuum, and the purity was checked by TLC.

$[RuBr(AsPh_3)_2(L^1)]$: Brown, d.p. 169°C, yield 77%, Anal. Calcd for $C_{52}H_{43}N_3As_2BrOSRu$ (%): C, 37.5; H, 2.9; N, 3.9. Found (%): C, 37.3; H, 2.4; N, 3.9. FT-IR (KBr, cm^{-1}): ν(C=N) 1606; ν(C–O) 1312; ν(C–S) 739; (PPh_3/$AsPh_3$) 1432, 1074, 692. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 360(10,444), 284(16,666), 240(33,333).

$[RuBr(AsPh_3)_2(L^2)]$: Brown, d.p. 150°C, yield 74%. Anal. Calcd for $C_{53}H_{45}N_3O_2As_2BrSRu$ (%): C, 37.5; H, 2.7; N, 3.7. Found (%): C, 36.4; H, 2.1; N, 3.0. FT-IR (KBr, cm^{-1}): ν(C=N) 1607; ν(C–O) 1311; ν(C–S) 739; (PPh_3/$AsPh_3$)

1432, 1085, 692. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 352(17,391), 292(26,086), 242(45,652).

[RuBr(AsPh$_3$)$_2$(L^3)]: Brown, d.p. 170°C, yield 72%. Anal. Calcd for $C_{54}H_{47}N_3O_3As_2BrSRu$ (%): C, 37.5; H, 2.2; N, 3.1. Found (%): C, 37.8; H, 2.4; N, 3.7. FT-IR (KBr, cm^{-1}): ν(C=N) 1603; ν(C–O) 1317; ν(C–S) 741; ($PPh_3/AsPh_3$) 1433, 1077, 693. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 340(14,893), 285(23,404), 250(51,063).

[RuBr(AsPh$_3$)$_2$(L^4)]: Brown, d.p. 165°C, yield 78%. Anal. Calcd for $C_{53}H_{45}N_3OAs_2BrSRu$ (%): C, 39.2; H, 3.2; N, 4.2. Found (%): C, 38.8; H, 2.8; N, 3.8. FT-IR (KBr, cm^{-1}): ν(C=N) 1606; ν(C–O) 1314; ν(C–S) 740; ($PPh_3/AsPh_3$) 1433, 1075, 693. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 362(7954), 297(10,227), 248(20,454).

[RuCl(AsPh$_3$)$_2$(L^1)]: Brown, d.p. 185°C, yield 73%. Anal. Calcd for $C_{52}H_{43}N_3OAs_2ClSRu$ (%): C, 38.1; H, 2.9; N, 3.8. Found (%): C, 38.1; H, 3.5; N, 3.8. FT-IR (KBr, cm^{-1}): ν(C=N) 1608; ν(C–O) 1313; ν(C–S) 739; ($PPh_3/AsPh_3$) 1433, 1074, 693. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 351(14,893), 284(19,361), 243(42,553).

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[RuCl(AsPh$_3$)$_2$(L^2)]: Brown, d.p. 172°C, yield 75%. Anal. Calcd for $C_{53}H_{45}N_3O_2As_2ClSRu$ (%): C, 39.1; H, 2.9; N, 3.9. Found (%): C, 40.1; H, 3.5; N, 3.8. FT-IR (KBr, cm^{-1}): ν(C=N) 1608; ν(C–O) 1311; ν(C–S) 740; ($PPh_3/AsPh_3$) 1432, 1086, 692. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 355(13,043), 281(19,782), 240(36,956).

[RuCl(AsPh$_3$)$_2$(L^3)]: Brown, d.p. 189°C, yield 75%. Anal. Calcd for $C_{54}H_{47}N_3O_3As_2ClSRu$ (%): C, 39.1; H, 3.0; N, 2.8. Found (%): C, 40.4; H, 2.9; N, 1.8. FT-IR (KBr, cm^{-1}): ν(C=N) 1603; ν(C–O) 1318; ν(C–S) 741; ($PPh_3/AsPh_3$) 1433, 1076, 693. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 345(11,702), 276(23,404), 243(44,680).

[RuCl(AsPh$_3$)$_2$(L^4)]: Brown, d.p. 164°C, yield 80%. Anal. Calcd for $C_{53}H_{45}N_3OAs_2ClSRu$ (%): C, 39.7; H, 3.0; N, 4.0. Found (%): C, 38.7; H, 2.5; N, 3.5. FT-IR (KBr, cm^{-1}): ν(C=N) 1606; ν(C–O) 1314; ν(C–S) 741; ($PPh_3/AsPh_3$) 1433, 1079, 693. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 347(23,706), 290(24,568), 242(43,103).

[RuCl(PPh$_3$)$_2$(L^1)]: Brown, d.p. 180°C, yield 80%. Anal. Calcd for $C_{52}H_{43}N_3P_2ClOSRu$ (%): C, 42.6; H, 3.1; N, 4.2. Found (%): C, 43.1; H, 3.9; N, 4.9. FT-IR (KBr, cm^{-1}): ν(C=N) 1605; ν(C–O) 1314; ν(C–S) 748; ($PPh_3/AsPh_3$) 1433, 1092, 695. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 280(11,363), 235(19,772).

[RuCl(PPh$_3$)$_2$(L^2)]: Brown, d.p. 192°C, yield 75%. Anal. Calcd for $C_{53}H_{45}N_3O_2P_2ClSRu$ (%): C, 42.6; H, 3.2; N, 4.3. Found (%): C, 41.9; H, 3.6; N, 4.8. FT-IR (KBr, cm^{-1}): ν(C=N) 1602; ν(C–O) 1313; ν(C–S) 748; ($PPh_3/AsPh_3$) 1433, 1092, 695. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 270(26,595), 238(40,425).

[RuCl(PPh$_3$)$_2$(L^3)]: Brown, d.p.179°C, yield 85%. Anal. Calcd for $C_{53}H_{45}N_3O_2P_2ClSRu$ (%): C, 42.5; H, 3.3; N, 4.5. Found (%): C, 43.2; H, 2.9; N, 4.1. FT-IR (KBr, cm^{-1}): ν(C=N) 1600; ν(C–O) 1320; ν(C–S) 748; ($PPh_3/AsPh_3$) 1434, 1091, 697. UV (CH_2Cl_2, nm (ε, $dm^3\,mol^{-1}\,cm^{-1}$)): 325(7500), 275(14,500), 238(32,500).

[RuCl(PPh$_3$)$_2$(L^4)]: Brown, d.p. 170°C, yield 70%. Anal. Calcd for $C_{53}H_{45}N_3OP_2ClSRu$ (%): C, 43.3; H, 3.2; N, 4.3. Found (%): C, 42.9; H, 3.9; N, 4.5. FT-IR (KBr, cm^{-1}): ν(C=N) 1602; ν(C–O) 1314; ν(C–S) 747; (PPh$_3$/AsPh$_3$) 1433, 1092, 696. UV (CH$_2$Cl$_2$, nm (ε, dm^3 mol^{-1} cm^{-1})): 265(11,111), 239(26,666).

2.4. *Catalytic activity for carbon–carbon coupling reaction*

Magnesium turnings (0.320 g) were placed in a two-necked round-bottomed flask with a calcium chloride guard tube. A crystal of iodine was added to activate the surface of the magnesium. Bromobenzene (0.5 cm^3 of total 1.275 cm^3, 12 mmol) in 5 cm^3 of anhydrous diethyl ether was added with stirring and heated under reflux. The appearance of 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 the bromobenzene in 5 cm^3 of anhydrous diethyl ether and the ruthenium complex, (0.05 mmol) chosen for investigation, was added and the mixture was heated under reflux 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 compared with an authentic sample (m.p.: 69–72°C) [18].

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3. Results and discussion

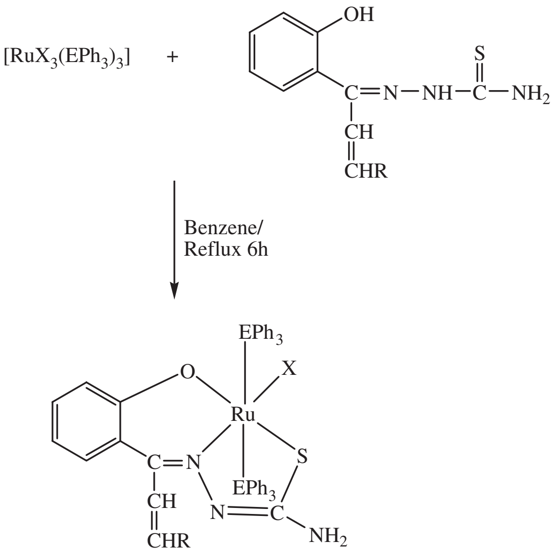
New stable ruthenium(III) chalcone thiosemicarbazone complexes of the type [RuX(EPh$_3$)$_2$(L)] (X = Cl or Br; E = P or As; L = chalcone thiosemicarbazone) are obtained from the reactions of [RuX$_3$(EPh$_3$)$_3$] (X = Cl or Br; E = P or As) with chalcone thiosemicarbazone ligands in dry benzene in 1 : 1 molar ratio (scheme 1).

In all the above reactions, the chalcone thiosemicarbazones are binegative tridentate ligands, replacing one triphenylphosphine/triphenylarsine and two chloride/bromide ions. Mass spectra of [RuCl(PPh$_3$)$_2$(L^4)] displayed molecular ion isotopic cluster at m/z 970, another isotopic cluster due to [RuCl(PPh$_3$)(L^4)]$^+$ at m/z 708, and the dominant fragment ([Ru(PPh$_3$)(L^4)]$^+$) at m/z 673, consistent with the proposed molecular formula of new ruthenium(III) chalcone thiosemicarbazone complexes.

3.1. *Infrared spectroscopic analysis*

IR spectra of new complexes, when compared with those of the free ligands, confirm the coordination of chalcone thiosemicarbazones to ruthenium. The ligands used in the present study can exhibit thione–thiol tautomerism (scheme 2).

IR spectra of the free ligands display two bands at 3333 and 3514 cm^{-1} due to ν_s and ν_{as} of terminal NH$_2$ [19], these bands remain unaltered in the corresponding metal complexes indicating non-involvement of this group in complexation. A strong band in the ligands at 1581–1604 cm^{-1} due to $\nu_{C=N}$ shifts to higher wavenumber by 5–27 cm^{-1} in the complexes [20]. The phenolic $\nu_{C–O}$ of the free ligands in the region 1351–1324 cm^{-1} shifts to lower wavenumber due to coordination to ruthenium ion



[E = P or As; X = Cl or Br; R = C_6H_5, 4-$(OCH_3)C_6H_4$, 3, 4-$(OCH_3)_2C_6H_3$ or 4-$(CH_3)C_6H_4$]

Scheme 1. Formation of ruthenium(III) chalcone thiosemicarbazone complexes.

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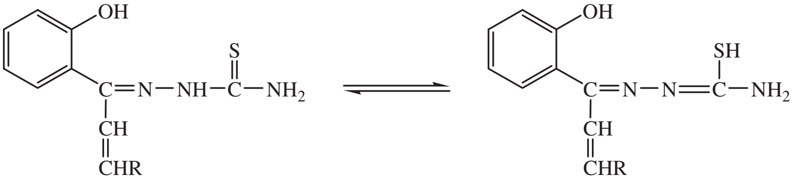

Scheme 2. Tautomerism in chalcone thiosemicarbazone.

through oxygen of the phenol [20]. Absorption due to $\nu_{O\text{–}H}$ was not observed in infrared spectra of the complexes in the region 3400–3600 cm^{-1}, suggesting deprotonation prior to coordination to ruthenium. The band due to $\nu_{C=S}$ at 830 cm^{-1} in the free ligand disappears on complexation and a new band appears around 739–748 cm^{-1}. These observations may be attributed to the coordination of thiolate sulfur after enolization followed by deprotonation [21]. Characteristic bands due to triphenylphosphine or triphenylarsine are also present.

3.2. *Electronic spectroscopic analysis*

Electronic spectra of the ruthenium(III) chalcone thiosemicarbazone complexes were recorded in CH_2Cl_2 from 600 to 200 nm. Most complexes showed two to three bands in the region 362–235 nm. The ground state of ruthenium(III) is $^2T_{2g}$ and the first excited doublet levels in the order of increasing energy are $^2A_{2g}$ and $^2A_{1g}$ arising from $t_{2g}^4\,e_g^1$ configuration. In most of the ruthenium(III) complexes, prominent charge transfer

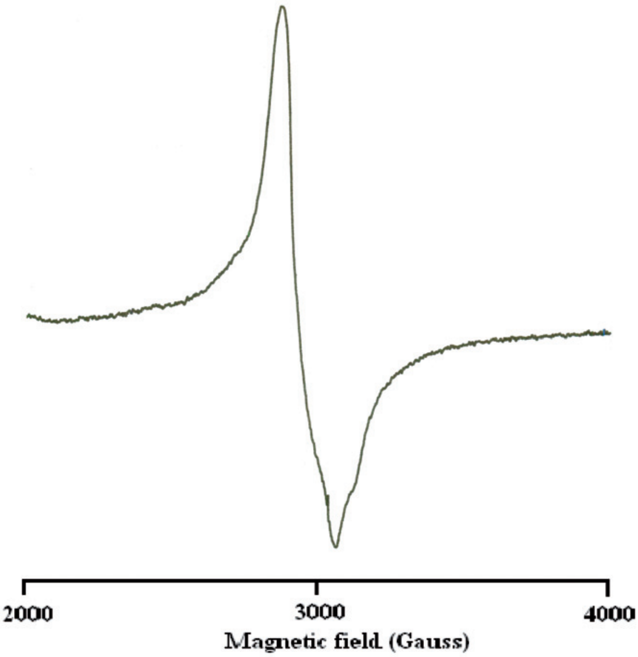

Figure 2. EPR spectrum of [RuCl(PPh$_3$)$_2$(L^3)].

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bands of the type $L_{\pi y} \rightarrow T_{2g}$ obscure the weaker bands due to d–d transitions [22]. It is therefore difficult to assign conclusively the bands of ruthenium(III) complexes in the visible region. However, we assign the bands below 362 nm as being due to charge-transfer transitions based on the extinction coefficient values, which are characteristic of ruthenium(III) octahedral complexes [23–26].

3.3. *Magnetic moments*

The magnetic moment of the complexes has been measured at room temperature using a vibrating sample magnetometer. The values lie between 1.72 and 2.12 BM, indicating the presence of one unpaired electron and +3 oxidation state for ruthenium in all these complexes [27].

3.4. *EPR spectroscopic analysis*

Solid state EPR spectra of the complexes (figure 2) were recorded in X-band frequencies at room temperature and the '*g*' values are given in table 1. Most of the complexes showed only one signal with '*g*' values between 2.01 and 2.45, indicating symmetry around the ruthenium. Such isotropic lines are usually due to either intermolecular spin exchange which can broaden the lines or occupancy of the unpaired electron in a degenerate orbital. However, a few of the complexes, [RuCl(AsPh$_3$)$_2$(L^1)] and [RuCl(AsPh$_3$)$_2$(L^2)], showed spectra characteristic of an axially symmetric system with $g_\perp$ around 2.01–2.45 and $g_\parallel$ around 2.09–2.14. For an octahedral field with tetragonal distortion, $g_x = g_y \neq g_z$ and, hence, two values for 'g' indicate tetragonal distortion in these complexes. Overall, the position of lines and nature of the EPR spectra of the complexes are characteristic of low-spin ruthenium(III) octahedral complexes [26, 28, 29].

3.5. *Electrochemistry*

Electrochemical properties of the new complexes have been examined by cyclic voltammetry under N_2 at glassy carbon working electrode in acetonitrile. $[NBu_4]ClO_4$ (0.05 M) as supporting electrolyte and redox potentials are referenced to Ag/AgCl. The cyclic voltammetric data are given in table 2. As the ligands used in this work are inactive at the used potential range, we believe that the redox processes observed for these complexes are metal-centered only.

All the complexes show one reversible reduction couple. $[RuBr(AsPh_3)_2(L^2)]$ and $[RuBr(AsPh_3)_2(L^3)]$ exhibit one reversible oxidation couple, whereas $[RuBr(AsPh_3)_2(L^4)]$ and $[RuCl(AsPh_3)_2(L^1)]$ show an irreversible oxidation peak.

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Table 1. EPR data of ruthenium(III) chalcone thiosemicarbazone complexes.

Complex	g_x	g_y	g_z	$\langle g^* \rangle$
$[RuBr(AsPh_3)_2(L^1)]$	–	2.15	–	–
$[RuBr(AsPh_3)_2(L^2)]$	–	2.18	–	–
$[RuBr(AsPh_3)_2(L^3)]$	–	2.16	–	–
$[RuBr(AsPh_3)_2(L^4)]$	–	2.17	–	–
$[RuCl(AsPh_3)_2(L^1)]$	2.45	2.45	2.14	2.35
$[RuCl(AsPh_3)_2(L^2)]$	2.45	2.45	2.09	2.33
$[RuCl(AsPh_3)_2(L^3)]$	–	2.09	–	–
$[RuCl(AsPh_3)_2(L^4)]$	–	2.15	–	–
$[RuCl(PPh_3)_2(L^1)]$	–	2.04	–	–
$[RuCl(PPh_3)_2(L^2)]$	–	2.05	–	–
$[RuCl(PPh_3)_2(L^3)]$	–	2.16	–	–
$[RuCl(PPh_3)_2(L^4)]$	–	2.01	–	–

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

Table 2. Electrochemical data for some ruthenium(III) chalcone thiosemicarbazone complexes.

	Ru(IV)–Ru(III)				Ru(III)–Ru(II)			
Complex	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	E_f (V)	ΔE_p (mV)
$[RuBr(AsPh_3)_2(L^2)]$	0.95	0.73	0.84	220	−0.58	−0.47	−0.53	110
$[RuBr(AsPh_3)_2(L^3)]$	0.78	0.70	0.74	80	−0.70	−0.50	−0.60	200
$[RuBr(AsPh_3)_2(L^4)]$	0.78	–	–	–	−0.64	−0.38	−0.51	260
$[RuCl(AsPh_3)_2(L^1)]$	1.02	–	–	–	−0.68	−0.41	−0.55	270
$[RuCl(AsPh_3)_2(L^3)]$	–	–	–	–	−0.57	−0.44	−0.51	130
$[RuCl(PPh_3)_2(L^1)]$	–	–	–	–	−0.68	−0.47	−0.58	210
$[RuCl(PPh_3)_2(L^4)]$	–	–	–	–	−0.55	−0.42	−0.49	130

Supporting electrolyte, $[NBu_4]ClO_4$ (0.05 M); complex, 0.001 M; solvent, CH_3CN; $\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively; $E_f = 0.5(E_{pa} + E_{pc})$; scan rate: 100 mV s^{-1}.

Some of the complexes showed only reduction couple (table 2). The reduction couples (Ru^{III}–Ru^{II}) are quasi-reversible with peak-to-peak separation values (ΔE_p) ranging from 110 to 270 mV. The high peak-to-peak separation is attributed to slow electron transfer and adsorption of the complexes onto the electrode surface [30]. The ΔE_p (80–220 mV) observed for oxidation (Ru^{III}–Ru^{IV}) couple in $[RuBr(AsPh_3)_2(L^2)]$ and $[RuBr(AsPh_3)_2(L^3)]$ indicate that the oxidation is quasi-reversible. The irreversible oxidation observed in some complexes is presumably due to the short-lived oxidized state of the metal ion [31] or due to oxidative degradation [32] followed by electrode deposition. Based on the analytical and spectroscopic data, an octahedral structure (scheme 1) has been tentatively proposed for all of the ruthenium(III) chalcone thiosemicarbazone complexes.

3.6. *Catalytic activity*

The new ruthenium(III) complexes were tested as catalysts for aryl–aryl coupling. The system chosen for the study is the coupling of phenylmagnesium bromide with bromobenzene to give biphenyl as the product. Bromobenzene was first converted to the corresponding Grignard reagent. Then, bromobenzene followed by the test complex was added and the mixture was heated under reflux for 6 h. After work up, the reaction mixture gave biphenyl.

The yields of the biphenyl formed from the coupling reactions varied from 14% to 17% (table 3) depending on the catalyst used. A blank reaction without ruthenium catalyst produced 1% biphenyl, an insignificant amount 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 reactions. The catalytic activity of ruthenium(III) complexes towards coupling reactions is less than its activity for oxidation and transfer hydrogenation reactions [33]. This may be due to the fact that the active species derived from ruthenium complexes are less stable in the case of coupling reactions, as the effectiveness of the catalysts is directly related to their ability to generate the corresponding active species [34]. The product yields are not much differed for different catalysts used, due to the formation of identical active species in all reactions. Coupling reactions catalyzed by ruthenium complexes containing PPh_3 or $AsPh_3$ yielded almost equal quantity of biphenyl.

Table 3. Catalytic activity of ruthenium(III) complexes.

	Yield of biphenyl	
Complex	*g*	%
$[RuBr(AsPh_3)_2(L^1)]$	0.221	15
$[RuBr(AsPh_3)_2(L^4)]$	0.244	16
$[RuCl(AsPh_3)_2(L^2)]$	0.235	14
$[RuCl(AsPh_3)_2(L^3)]$	0.217	17
$[RuCl(PPh_3)_2(L^3)]$	0.270	17
$[RuCl(PPh_3)_2(L^4)]$	0.210	14
No catalyst	0.021	01

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4. Conclusion

Several new ruthenium(III) complexes were synthesized using chalcone thiosemicarbazones formed from derivatives of 2′-hydroxychalcones and thiosemicarbazide. The new complexes have been characterized by analytical and spectroscopic data. An octahedral structure has been tentatively proposed for all the complexes. Some of the ruthenium(III) chalcone thiosemicarbazone complexes have been tested for C–C coupling reactions. Though ruthenium(III) complexes with Schiff-base ligands have been reported as catalysts for aryl–aryl coupling reactions [35], ruthenium(III)-thiosemicarbazone complexes have been rarely seen as catalysts for this kind of reaction. Several transition metal thiosemicarbazone complexes have been found in recent literature [36–42], but with triphenylphosphine as co-ligand is rare [43]. In our system, the presence of labile triphenylphosphine ligand makes the complexes catalytically active and the activity may be tuned in the future by changing the electronic environment around the metal by altering the substituents in the thiosemicarbazone ligand.

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Supplementary material

Representative mass spectrum, electronic spectra, and cyclic voltammogram of ruthenium(III) chalcone thiosemicarbazone complexes have been provided as supplementary materials.

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