

Orthometallation in bidentate Schiff base ligands via C–H activation: synthesis of ruthenium(III) organometallic complexes

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Abstract Schiff bases obtained by the reactions of substituted aromatic aldehydes with phenyl hydrazine or 2,4-dinitrophenyl hydrazine were synthesized and characterized by spectroscopic methods. Cyclometalated Ru(III) complexes of general formula, namely $[\text{Ru}(\text{L})(\text{PPh}_3)_2\text{Cl}]$, were synthesized from the Schiff bases via C–H bond activation and characterized by spectroscopic and electrochemical studies. In addition, one molecular structure of one of the complexes was determined by X-ray crystallography. The redox behavior of the complexes was examined by electrochemical studies, and one mechanism of orthometallation was investigated.

Introduction

In recent years, the activation of chemically inert C–H bonds by the formation of ruthenium complexes, under mild conditions, has received considerable attention [1–13]. Such cyclometalated complexes are important in insertion reactions [14, 15], regio- and stereo-selective reactions, and as catalysts for organic synthesis [1, 6–9]. Although a large number of cyclometalated ruthenium(II) complexes have been reported to date, ruthenium(III)

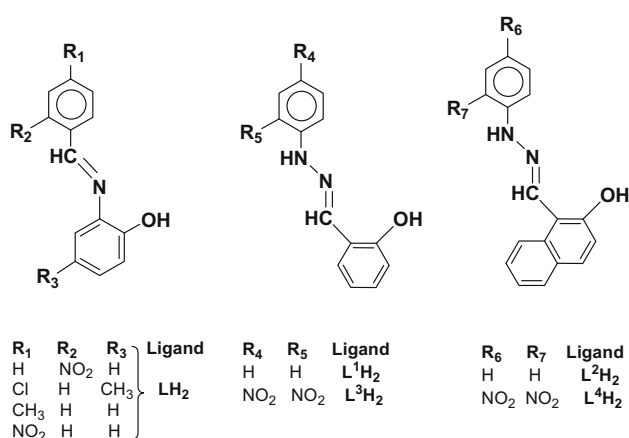
organometallic complexes are still very scarce [16–22] compared to ruthenium(II) complexes. In this regard, we have recently reported cyclometalated ruthenium(III) complexes derived from different bidentate Schiff base ligands (LH_2) obtained via condensation of substituted *o*-aminophenols and benzaldehyde (shown in Scheme 1) [10, 23, 24]. Coordination of the imine and phenolato functions of such bidentate Schiff base ligands gave rise to five-membered rings (Scheme 2a) and afforded organometallic complexes of ruthenium(III) via C–H activation in the phenyl ring of benzaldehyde. The present study stems from our interest in the synthesis of ruthenium(III) organometallics and our efforts to better understand the process of formation of Ru–C bonds with such ligands. In this work, we have chosen a bidentate ligands incorporating imine and phenolato functional groups (Scheme 1) in order to search for a new family of cyclometalated ruthenium(III) complexes. The coordination of imine and phenolato groups by these Schiff base ligands could afford six-membered rings (Scheme 2b) compared to the five-membered rings (Scheme 2a) described in our previous reports [10, 23, 24].

Herein, we report the synthesis and characterization of ruthenium(III) cyclometalated complexes, namely $[\text{Ru}(\text{L}^{1-4})(\text{PPh}_3)_2\text{Cl}]$ [where $\text{L}^1\text{H}_2 = 2\text{-}((2\text{-phenylhydrazono)methyl)phenol$, complex **1**; $\text{L}^2\text{H}_2 = 3\text{-}((2\text{-phenylhydrazono)methyl)naphthalen-2\text{-ol}$, complex **2**; $\text{L}^3\text{H}_2 = 2\text{-}((2\text{-}(2,4\text{-dinitrophenyl)hydrazono)methyl)phenol$, complex **3**; $\text{L}^4\text{H}_2 = 3\text{-}((2\text{-}(2,4\text{-dinitrophenyl)hydrazono)methyl)naphthalen-2\text{-ol}$, complex **4**; and H are dissociable protons] (Scheme 3). These complexes were characterized by IR and UV–Vis spectral studies and by elemental analysis. In addition, one molecular structure of complex **3** was determined by X-ray crystallography. The redox properties of the metal centers were investigated. A reaction model is

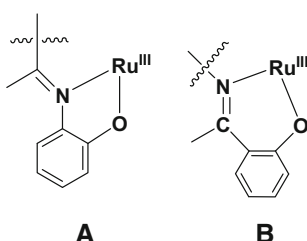
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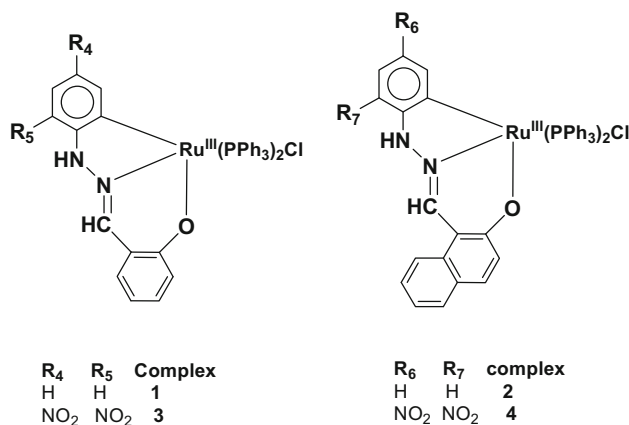
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Scheme 1 Schiff base ligands (LH₂ and L^{1–4}H₂)



Scheme 2 Five- and six-membered chelate rings



Scheme 3 Ruthenium(III) cyclometalated complexes 1–4

suggested, based on our previous reports and the results obtained in this study.

Experimental

Materials and measurements

All the solvents used were of analytical grade reagents. RuCl₃·3H₂O, triphenylphosphine (SRL, Mumbai, India),

2,4-dinitrophenylhydrazine, phenyl hydrazine, 2-hydroxy-1-naphthaldehyde (Himedia Laboratories Pvt. Ltd., Mumbai, India) and salicylaldehyde (Sisco Research Laboratory Pvt. Ltd., Mumbai, India) were used as received. Infrared spectra were obtained using KBr pellets with a Thermo Nicolet Nexus FT IR spectrometer, using 16 scans and are reported in cm⁻¹. Electronic absorption spectra were recorded in dichloromethane or acetonitrile solvents with an Evolution 600, Thermo Scientific UV–Vis spectrophotometer. Cyclic voltammetric studies were performed on a CH-600 electroanalyser in dichloromethane solutions with 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The working electrode, reference electrode and auxiliary electrode were glassy carbon, Ag/AgCl and a Pt wire, respectively. The concentration of the compounds was in the order of 10⁻³ M. The E_{1/2} value for the ferrocene/ferrocenium couple was observed at +0.51 (105) V versus Ag/AgCl (scan rate 0.01 V/s) in dichloromethane solution under the same experimental conditions.

The Schiff base ligands L^{3,4}H₂ were synthesized by the condensation of 2,4-dinitrophenylhydrazine with salicylaldehyde and 2-hydroxy-1-naphthaldehyde, respectively, in ethanol by following the procedure reported by Natarajan et al. [11]. The precursor complex [Ru(PPh₃)₃Cl₂] was synthesized by using the procedure reported earlier [10, 23, 24].

Synthesis of 2-((2-phenylhydrazono)methyl)phenol (L¹H₂)

A solution of salicylaldehyde (0.61 g, 5 mmol) in methanol (10 ml) was added to a solution of phenyl hydrazine (0.54 g, 5 mmol) in methanol (10 ml) with continuous stirring. After 1 h of stirring, the red-brown colored solid precipitate was filtered off and washed thoroughly with methanol and diethyl ether. Yield: 0.76 g (72 %). Anal. Calcd. for C₁₃H₁₂N₂O (212.09): C, 73.5; H, 5.7; N, 13.2. Found: C, 73.2; H, 5.6; N, 13.1 %. IR (KBr disk, cm⁻¹): 1590 (ν_{C=N})s, 1490 m, 1272 m, 1152w, 743 m, 680w cm⁻¹. UV–Vis (CH₂Cl₂; λ_{max}, nm (ε, M⁻¹ cm⁻¹)): 343 (13,330), 300 (6550), 240 (8390). ¹H NMR (CDCl₃, 500 MHz): δ 10.72 (s, 1H), 7.80 (s, 1H), 7.32–7.22 (m, 3H), 7.14 (d, 1H), 7.01–6.88 (m, 6H) ppm. ¹³C NMR (CDCl₃, 500 MHz): δ 157.10, 143.46, 141.29, 130.12, 129.65, 129.47, 120.98, 119.60, 118.60, 116.68, 112.72 ppm.

Synthesis of 3-((2-phenylhydrazono)methyl)naphthalen-2-ol (L²H₂)

L²H₂ was synthesized from the reaction of 2-hydroxy-1-naphthaldehyde with phenyl hydrazine by following the same procedure as for ligand L¹H₂. Yield: 0.92 g (70 %).

Anal. Calcd. for $C_{17}H_{14}N_2O$ (262.11): C, 77.8; H, 5.3; N, 10.6. Found: C, 77.3; H, 5.4; N, 10.6 %. IR (KBr disk, cm^{-1}): 1602 ($\nu_{C=N}$)s, 1540 m, 1477 m, 1253w, 1160w, 813 m, 743w (ν_{PPh_3}) cm^{-1} . UV–Vis (CH_2Cl_2 ; λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)): 375 (13,630), 334 (7450), 250 (16,600). 1H NMR ($CDCl_3$, 500 MHz): δ 12.06 (s, 1H), 8.76 (s, 1H), 7.99 (d, 1H), 7.79–7.73 (m, 3H), 7.51 (d, 1H), 7.49–7.23 (m, 5H), 7.04 (d, 1H), 6.96–6.93 (t, 1H) ppm. ^{13}C NMR ($CDCl_3$, 500 MHz): δ 156.94, 143.52, 137.96, 136.71, 131.30, 131.64, 129.68, 129.21, 128.36, 127.16, 123.38, 120.96, 119.04, 119.98, 112.71 ppm.

Synthesis of complex 1

Solid $[Ru(PPh_3)_3Cl_2]$ (0.096 g, 0.10 mmol) was added directly to a hot methanol solution (30 ml) of L^1H_2 (0.025 g, 0.12 mmol). The reaction mixture was refluxed for 10–12 h. The resulting yellowish brown crystalline complex **1**, $[Ru(L^1)(PPh_3)_2Cl]$, was collected by filtration at room temperature after 2–3 days and then washed with cold methanol and diethyl ether. Yield: 0.057 g (66 %). Anal. Calcd. for $C_{49}H_{40}ClN_2OP_2Ru$ (871.13): C, 67.5; H, 4.6; N, 3.2. Found: C, 67.4; H, 4.5; N, 3.1 %. IR (KBr disk, cm^{-1}): 1605 ($\nu_{C=N}$)s, 1428 s, 1297w, 1090 s, 742 m, 695 s, 518 s (ν_{PPh_3}) cm^{-1} . UV–Vis (CH_2Cl_2 ; λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)): 375 (1050), 295 (8210).

Synthesis of complex 2

Complex **2** was prepared by reacting $[Ru(PPh_3)_3Cl_2]$ (0.096 g, 0.10 mmol) with L^2H_2 (0.031 g, 0.12 mmol) following the same procedure described for **1**. Complex **2**, formulated as $[Ru(L^2)(PPh_3)_2Cl]$, was yellowish brown in color. Yield: 0.062 g (67 %). Anal. Calcd. for $C_{53}H_{42}ClN_2OP_2Ru$ (921.15): C, 69.1; H, 4.6; N, 3.0. Found: C, 69.2; H, 4.5; N, 3.1 %. IR (KBr disk, cm^{-1}): 1605 ($\nu_{C=N}$)s, 1430 m, 1380 m, 1188w, 1090 m, 742 m, 698 s, 512 s (ν_{PPh_3}) cm^{-1} . UV–Vis (CH_2Cl_2 ; λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)): 500 (7090), 270 (27,680).

Synthesis of complex 3

A batch of solid L^3H_2 (0.036 g, 0.12 mmol) was added to a hot solution of $[Ru(PPh_3)_3Cl_2]$ (0.096 g, 0.10 mmol) in methanol (30 ml). The reaction mixture was refluxed for 4–5 h and then allowed to cool at room temperature to obtain a crystalline red-brown solid. This was filtered out and then washed with cold methanol and diethyl ether to give complex **3**, $[Ru(L^3)(PPh_3)_2Cl]$. Yield: 0.065 g (68 %). Anal. Calcd. for $C_{49}H_{38}ClN_4O_5P_2Ru$ (961.10): C, 61.2; H, 3.9; N, 5.8. Found: C, 61.1; H, 3.8; N, 5.8 %. IR (KBr disk, cm^{-1}): 1590 ($\nu_{C=N}$)s, 1480 s, 1430 m, 1328 m, 1242w, 1175w, 1090 m, 742 s, 698 s, 518 s (ν_{PPh_3}) cm^{-1} .

UV–Vis (CH_2Cl_2 ; λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)): 510 (5510), 415 (8820), 317 (15,310), 270 (23,930).

Synthesis of complex 4

Complex **4** was synthesized by the reaction of L^4H_2 (0.042 g, 0.12 mmol) with $[Ru(PPh_3)_3Cl_2]$ (0.095 g, 0.10 mmol) through the same procedure as for **3**. Yield: 0.063 g (62 %). Anal. Calcd. for $C_{53}H_{40}ClN_4O_5P_2Ru$ (1011.12): C, 62.9; H, 3.9; N, 5.5. Found: C, 62.8; H, 4.0; N, 5.6 %. IR (KBr disk, cm^{-1}): 1582 ($\nu_{C=N}$)s, 1483 m, 1433 m, 1343w, 745 s, 694 s, 522 s (ν_{PPh_3}) cm^{-1} . UV–Vis (CH_2Cl_2 ; λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)): 560 (6210), 415 (18,010), 327 (18,325), 262 (36,125).

X-ray crystallography

A reddish brown crystal of complex **3** was obtained via slow evaporation of a solution in dichloromethane/methanol mixture (9:1) which was suitable for diffraction study. The X-ray data collection and processing was performed on a Bruker Kappa Apex-II CCD diffractometer using graphite monochromated Mo– $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 296 K. The crystal structure was solved by direct methods. All calculations were performed using the SHELXTL software package for structure solution and refinement [25]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model.

Results and discussion

Synthesis and general properties

The Schiff bases L^nH_2 ($n = 1-4$) were prepared in high yields through the condensation reactions of different aromatic aldehydes with phenyl hydrazine and 2,4-dinitrophenyl hydrazine in ethanol using the reported procedures [11] (Figs. S1–S7). Cyclometalated ruthenium(III) complexes $[Ru(L^{1-4})(PPh_3)_2Cl]$ (**1–4**) (Scheme 3) were obtained through the addition of solid $[Ru(PPh_3)_3Cl_2]$ to hot methanolic solutions of the corresponding Schiff bases $L^{1-4}H_2$. Complexes **1** and **2** were yellowish brown in color, while **3** and **4** were reddish brown. All four complexes are highly soluble in dichloromethane, DMF and DMSO but less soluble in water.

The infrared spectra of complexes **1** and **3** are shown in Figs. S8 and S9, respectively, and data for all the complexes are deposited in Table S1. All four complexes displayed a band in the range 1606–1582 cm^{-1} assigned to the azomethine ($\nu_{C=N}$) group [10, 11, 23, 24], plus three

strong peaks in the ranges 742–750, 694–698 and 512–523 cm^{-1} attributed to ruthenium bound PPh_3 groups [10, 23, 24] (Table S1).

The electronic absorption spectra of complexes **1–2** and **3–4** in dichloromethane solutions are displayed in Figs. S10 and S11, respectively. Complexes **1** and **2** showed bands at ca. 375 and 500 nm, respectively (Table S2). These are probably due to ligand-to-metal charge transfer (LMCT) transitions [21, 22, 26]. Complex **3** showed charge transfer bands at ca. 317, 415 and 510 nm, while for complex **4**, these bands were redshifted to 327, 415 and 560 nm (Table S2). These bands are also assigned to LMCT transitions [21, 22, 26].

Crystal structure of complex **3**

The molecular structure of complex **3**, $[\text{Ru}(\text{L}^3)(\text{PPh}_3)_2\text{Cl}]$ is shown in Fig. 1, and selected structural data are listed in Table 1. Selected bond lengths and angles are given in Table 2. In crystal structure of complex **3**, the carbanion (C49), phenolato oxygen (O1), imine nitrogen (N2) and Cl1 constitute the equatorial plane, while the phosphine groups occupy at the axial positions (trans to each other). The P(1)–Ru(1)–P(2), N(2)–Ru(1)–Cl(1) and C(49)–Ru(1)–O(1) bond angles clearly indicate a distorted octahedral geometry around the ruthenium center.

The Ru–C(19) bond distance is consistent with the values reported by Chakravorty et al. [17] and Bhattacharya et al. [2]. However, the Ru–C(19) bond length is lower than the values reported in other ruthenium cyclometalated complexes [16, 21, 22, 27, 28]. The Ru–O_{Ph} bond distance was also lower compared to the reported values [17, 20–23]. The other bond distances including Ru–P [21, 22, 28],

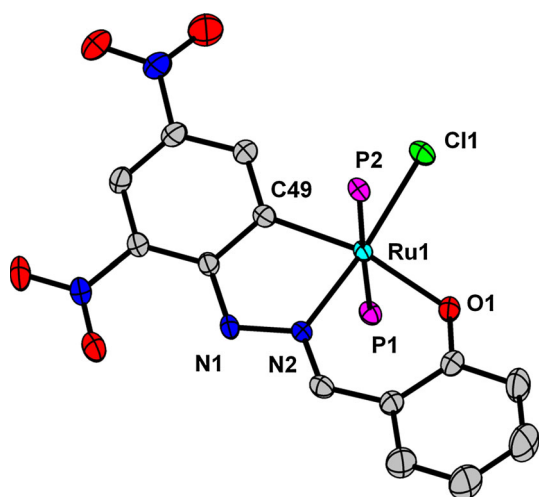


Fig. 1 ORTEP diagram (30 % probability level) of the complex **3**. All the hydrogen atoms and phenyl rings of PPh_3 groups are omitted for clarity

Table 1 Crystal data and structural refinement parameters for complex **3**

Empirical formula	$\text{C}_{49}\text{H}_{37}\text{ClN}_4\text{O}_5\text{P}_2\text{Ru}$
Formula weight (g mol^{-1})	960.29
Space group	$P2_1/c$
Temperature/K	296(2)
λ (Å) (Mo–K α)	0.71073
Crystal system	Monoclinic
a (Å)	12.814(3)
b (Å)	21.064(5)
c (Å)	17.278(3)
α (°)	90.00
γ (°)	90.00
β (°)	110.677(9)
V (Å ³)	4363.2(17)
Z	4
ρ_{calc} (g cm^{-3})	1.462
Crystal size (mm)	$0.27 \times 0.21 \times 0.17$
$F(000)$	1960.0
Theta range for data collection	1.59–28.49
Index ranges	$-15 < h < 17,$ $-28 < k < 28,$ $-22 < l < 22$
Data/restraints/parameters	10,843/0/559
GOF^a on F^2	1.013
$R1^b$ [$I > 2\sigma(I)$]	0.0365
$R1$ [all data]	0.0688
$wR2^c$ [$I > 2\sigma(I)$]	0.1137
$wR2$ [all data]	0.1515

^a $\text{GOF} = [\sum[w(F_o^2 - F_c^2)^2]/M - N]^{1/2}$ (M = number of reflections, N = number of parameters refined)

^b $R1 = \sum \|F_o - F_c\| / \sum F_o$

^c $wR2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum [(F_o^2)^2]]^{1/2}$

Table 2 Selected bond distances (Å) and angles (°) for complex **3**

Bond length (Å)	Bond angle (°)		
Ru(1)–N(2)	2.042(2)	C(49)–Ru(1)–O(1)	165.50(9)
Ru(1)–P(1)	2.4018(10)	N(2)–Ru(1)–Cl(1)	173.86(6)
Ru(1)–P(2)	2.3958(10)	O(1)–Ru(1)–Cl(1)	99.12(5)
Ru(1)–O(1)	2.047(2)	N(2)–Ru(1)–P(1)	89.50(7)
Ru(1)–Cl(1)	2.3593(8)	C(49)–Ru(1)–P(1)	91.80(8)
Ru(1)–C(49)	2.016(3)	O(1)–Ru(1)–P(1)	87.22(6)
		P(2)–Ru(1)–P(1)	178.49(2)
		C(49)–Ru(1)–Cl(1)	95.34(7)

Ru–Cl [16, 22, 23, 28] and Ru–N_{imine} [17, 20–22] were similar to previously reported results, as were the bond angles P(1)–Ru–P(2) [21, 28] and N_{imine}–Ru–Cl [21, 28].

Mechanism of C–H activation

The proposed mechanism of C–H bond activation is depicted in Scheme 4. During the reaction of $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ with Schiff base ligands, we observed that bidentate ligands having imine and phenolato functions became tridentate, such that cyclometalated ruthenium complexes were obtained via orthometallation. Coordination of bidentate ligands with $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ is well known in the literature [29–35]. Bidentate ligands can stabilize Ru(II) or Ru(III) depending upon the nature of the donor atoms [29–35]. Cenini et al. [29] and Bhattacharya and coworkers [33] reported facile oxidation of the metal center due to coordination of primary ammine nitrogen and phenolato oxygen. After the coordination of bidentate ligands (shown in Scheme 1), the metal would be prone to oxidation in the presence of air. The presence of a properly oriented C–H bond close to the metal center could lead to an electrophilic attack on the carbon atom of the phenyl ring with concomitant formation of a Wheland intermediate [10–13]. In the present case, during the C–H bond activation, electrophilic attack of the metal center is proposed, although both electrophilic and nucleophilic attacks have been reported in the literature [10–13]. This assignment is supported by the fact that the formation of complexes **3**, **4** was faster than that of complexes **1**, **2**. Hence, the presence of $-\text{NO}_2$ substituents on the ligand ($\text{L}^{3,4}\text{H}_2$) increases the acidity of

the ligated proton. Hence, electrophilic attack of the metal and the liberation of HCl are facilitated (Scheme 4).

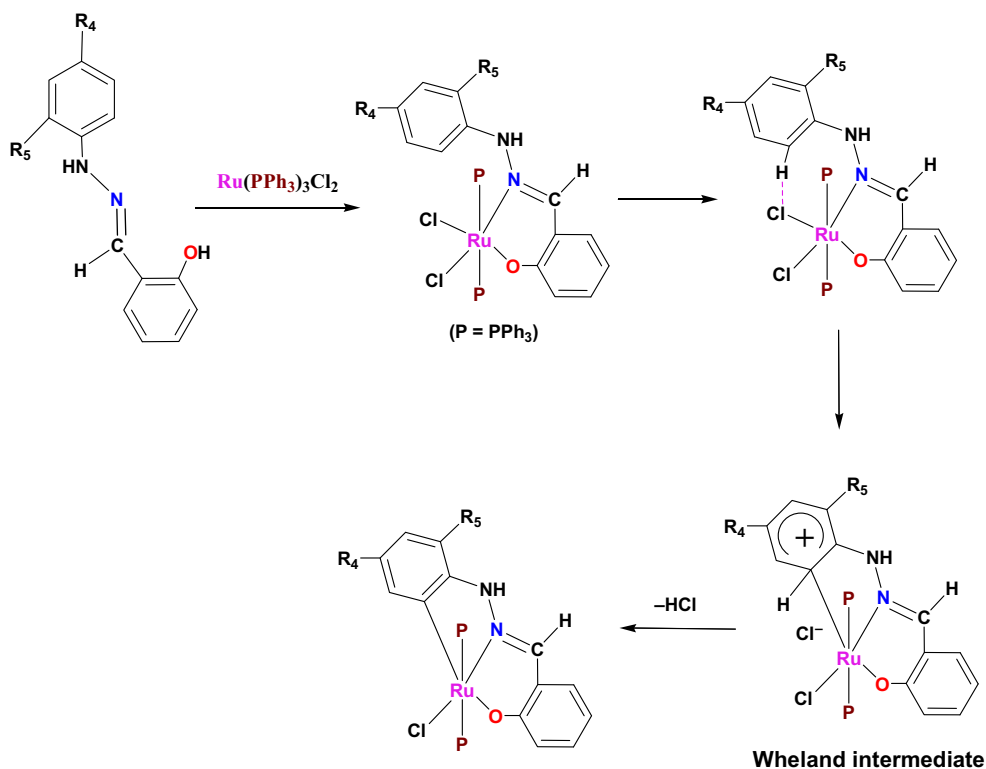
Electrochemistry

We have investigated the electrochemical properties of complexes **1–4** in dichloromethane solution. Complexes **1** and **2** displayed quasi-reversible cyclic voltammetric responses, with $E_{1/2}$ values +1.0 and +0.66 V versus Ag/AgCl, respectively. These responses can be assigned to the Ru(III)/Ru(IV) couples [10, 21, 22]. Complex **2** was oxidized more easily compared to complex **1**. Quasi-reversible couples for **1** and **2** were also found, with $E_{1/2}$ values of -0.29 and -0.60 V versus Ag/AgCl, respectively, which are assigned to Ru(III)/Ru(II) couples [10, 22, 28]. Moreover, a cathodic response near -0.98 V was observed for complex **1** (shown in Fig. 2).

For complexes **3** and **4**, the Ru(III)/Ru(IV) couple [10, 21, 22] was observed with $E_{1/2}$ values of +0.93 and +0.78 V, respectively, versus Ag/AgCl. Similar to the above results, complex **4** is oxidized more easily than **3**. The Ru(III)/Ru(II) couple was also observed with an $E_{1/2}$ value of -0.19 V (for **3** and **4**) versus Ag/AgCl (shown in Fig. 3) [10, 22, 28].

Comparing $E_{1/2}$ values for the Ru(III)/Ru(II) redox couple in complexes **1–4**, there is better stabilization of Ru(II) in complexes **3** and **4** which may be due to the

Scheme 4 Proposed mechanism for cyclometalation (where $\text{R}_4, \text{R}_5 = \text{H}$ or NO_2)



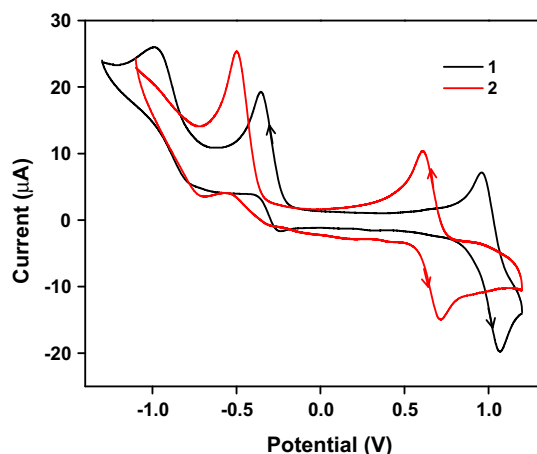


Fig. 2 Cyclic voltammograms of 10^{-3} M solutions of complexes **1** (black line) and **2** (red line) in dichloromethane, in the presence of 0.1 M TBAP using working electrode, glassy carbon; reference electrode, Ag/AgCl; auxiliary electrode, platinum wire; scan rate, 0.1 V/s. (Color figure online)

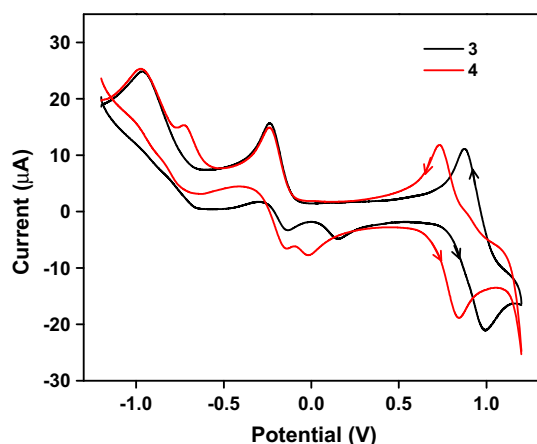


Fig. 3 Cyclic voltammograms of 10^{-3} M solutions of complexes **3** (black line) and **4** (red line) in dichloromethane, in the presence of 0.1 M TBAP using working electrode, glassy carbon; reference electrode, Ag/AgCl; auxiliary electrode, platinum wire; scan rate, 0.1 V/s. (Color figure online)

presence of the electron withdrawing $-\text{NO}_2$ substituent on the ring attached to the Ru center via C–H bond in both of these complexes. We also observed some cathodic peaks at -0.96 V (for complex **3**), -0.72 and -0.97 V (for **4**) versus Ag/AgCl.

Conclusions

In conclusion, a new family of cyclometalated ruthenium(III) complexes were synthesized via C–H bond activation of Schiff bases. Bidentate chelation of the ligand followed by electrophilic attack of the metal to the phenyl

carbon gave rise to ruthenium–carbon bond formation. Electrochemical studies showed better stabilization of Ru(II) in the complexes in which the schiff base ligand carried a nitro substituent.

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