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Synthesis, characterization and catalytic property of ruthenium–terpyridyl complexes

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ABSTRACT

The known compound 4′-(carboxyphenyl)-2,2′:6,2″-terpyridine (LH) was prepared and complexed with $RuCl_3.3H_2O$. The resulting complex $[Ru(LH)Cl_3]$ was then allowed to react separately with 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), triphenylphosphine (PPh_3) and 1,2-bis-(diphenylphosphino)ethane (dppe). The compositions of corresponding complexes $[Ru(LH)bpyCl](BF_4)$ **1**, $[Ru(LH)phenCl](BF_4)$ **2**, $[Ru(LH)(PPh_3)(CH_3CN)_2]\ (BF_4)_2$ **3** and $[Ru(LH)(dppe)Cl](BF_4)$ **4** were assigned on the basis of their FAB-mass spectra, elemental analysis, spectroscopic (IR, NMR) data and X-ray diffraction measurements. The diamagnetic, cationic complexes displayed strong MLCT transitions in the visible region with significant shift in MLCT band energy corresponding to the strength of substituted ligands. The redox behaviour of the complexes was investigated using cyclic voltammetry measurements. Among all the complexes, **3** efficiently catalyzed the synthesis of propargylamine via three components coupling reaction.

1. Introduction

It is well reported that 4′ substituted terpyridine (terpy) derivatives provides ideal building block with which to assemble the multicomponent molecular systems around photoactive transition metal centers [1]. The main advantages of the terpy module over a bpy analogue owe to its facile functionalization [2], ability to construct linear arrays [3] and facilitate the formation of achiral metal complexes. Thus, the problem inherent in the use of $[Ru(bpy)_3]^{2+}$ as structural motif providing diastereomeric complexes as a mixture of *fac* and *mer* isomer could be minimized by the use of a tridentate ligand. The polypyridyl complexes have shown several interesting properties such as photochemistry, electron transfer reaction, catalysis and photosensitizers [4,5]. In this regard, a number of luminescent and redox active compounds using bridging polypyridyl ligands have been prepared and their properties extensively studied [6–11]. Based on this and in view of our earlier interest in ruthenium polypyridyl complexes [12], it was initially planned to synthesize a ruthenium terpyridyl complex appended with three substitutable chloro groups. Recently, Crabtree et al. have reported Beckmann rearrangement for one pot synthesis of amides using terpyridines–ruthenium complexes as catalyst [13]. In view of this novel report, it was considered worthwhile to explore the catalytic potential of the prepared complexes for the synthesis of propargylamines via three – components coupling of aldehydes, alkyne and amines. Propargylamines are used as important synthetic intermediates for the preparation of polyfunctional amino derivatives and possess diverse biologically activities [14,15]. Classical methods for the preparation of propargylamines have exploited the relatively high acidity of a terminal acetylenic C–H bond to form alkynyl–metal reagents by the reaction with strong bases such as butyllithium, organomagnesium compounds or lithium diisopropylamide in multiple steps [16,17]. These reagents are highly moisture sensitive and require their stoichiometric quantities under strictly controlled reaction conditions.

In recent years, enormous work has been done which extended the scope of the direct addition of alkynes to carbon–nitrogen double bonds either preformed (imines) or in one-pot (from aldehyde and amine) by employing various complexes and salts of transition metals such as iron, zinc, copper, ruthenium–copper, indium, silver, gold, mercury and nickel [18–26]. The synthesis of propargylamines using new transition metal complexes as catalyst has enthused organic chemists to employ multi-component strategies. However, longer reaction time that is frequently required for full conversions has limited such exploitation. Therefore, rapid and reliable controlled microwave assisted approach is adopted for high-speed production of new chemicals [27] as such irradiation accelerates the process with considerable increase in yield of the product. Thus, in view of the above reports the newly prepared complexes were investigated as a catalyst for the synthesis of propargylamines using multi-component approach. However, among all the complexes, only **3** efficiently catalyzed the synthesis of several propargylamines employing different aldehydes, amines and alkyne under controlled microwave irradiation.

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2. Experimental

2.1. Materials

The chemicals 2-acetylpyridine, 4-carboxybenzaldehyde, $RuCl_3{\cdot}3H_2O$, 1,2-bis-(diphenylphosphino)-ethane, 2,2′-bipyridine, triphenylphosphine, 1,10-phenanthroline, phenylacetylene and sodium tetrafluoroborate were purchased from Sigma–Aldrich, USA. The aldehydes, morpholine, piperidine, KOH, aqueous ammonia solution and solvents were of AR grade. The ligand 4′-(carboxyphenyl)-2,2′:6,2″-terpyridine (LH) and *Ru(LH)Cl₃ (precursor)* were prepared using published procedures [28,29], respectively.

2.2. Physical measurements

Elemental analysis was performed using a Exeter Analytical CHN analyzer (model CE-440). However, UV–Vis spectra of the complexes were recorded at 25 °C using JASCO V630 spectrophotometer. The infrared spectra of complexes were recorded on Varian 3100 FTIR spectrometer and ^1H and ^{31}P NMR spectra (δ ppm) were recorded on JEOL AL-300 MHz spectrometer using TMS as internal reference. FAB mass spectra were recorded on JEOL/SX 102/Da-600. Cyclic voltammetric measurements of complexes (10^{-4} M, DMF) were performed using a CHI 620c electrochemical analyzer. A glassy carbon working electrode, platinum wire auxiliary electrode and Ag/AgCl reference electrode were used in a standard three-electrode configuration and tetrabutylammonium perchlorate (TBAP) was used as a supporting electrolyte.

MW study was made using CEM – Discover single mode microwave reactor (Benchmate model, USA) with infrared temperature probe and adjustable 0–300 W output power.

2.3. Synthesis and purification

2.3.1. Synthesis of precursor [Ru(LH)Cl₃]

A solution of ligand (LH) (0.353 g, 1.0 mmol) and $RuCl_3{\cdot}3H_2O$ (0.261 g, 1.0 mmol) in ethanol (20 mL) was refluxed for 8 h. The solution was then cooled to room temperature and solid mass thus obtained was filtered and dried in *vacuo*. It was assigned a composition $[Ru(LH)Cl_3]$ on the basis of its analytical and spectroscopic data. Yield: 0.336 g (60%). Soluble in DMSO, DMF and hot ethanol. *Anal.* Calc. for $C_{22}H_{15}N_3O_2Cl_3Ru$: C, 47.10; H, 2.67; N, 7.49. Found: C, 47.07 3; H, 2.65; N, 7.51%. IR (KBr pellet, cm^{-1}) 1716 (ν_{COOH}), 1601($\nu_{CH=N}$).

2.3.2. Synthesis of [Ru(LH)(bpy)Cl]BF₄ **1**

The precursor complex $Ru(LH)Cl_3$ (0.560 g, 1 mmol) and 2,2′-bipyridine (0.156 g, 1.0 mmol) were taken together in ethanol (10 mL) and the mixture was heated at reflux with stirring for 10 h. The resulting solution was then reduced to ~5 mL. A methanolic solution of $NaBF_4$ was then added to it. The resulting solid was separated from the solution by filtration and finally washed with water and ethanol and then dried in *vacuo*. The crude product was then purified by column chromatography using SiO_2 as supporting material with MeCN, aqueous saturated solution of KNO_3 and water (v/v ratio of 14:2:1) as eluent. To the eluate thus obtained, a methanolic solution of $NaBF_4$ was added which gave red coloured solid product. It was then filtered and repeatedly washed with water and finally with a little ethanol followed by diethyl ether. The complex was found soluble in DMSO, DMF, C_2H_5OH, CH_3OH and CH_3CN. Yield: 0.197 g (27%). *Anal.* Calc. for $C_{32}H_{23}N_5O_2BF_4ClRu$: C, 52.49; H, 3.14; N, 9.56. Found: C, 52.45; H, 3.12; N, 9.59%. FAB MS: *m/z*: 731 $[M]^+$, 645 $[M–BF_4]^+$, 609 $[M–BF_4–Cl]^+$. IR (KBr pellet, cm^{-1}) 1721 (ν_{COOH}), 1606 ($\nu_{CH=N}$), 1084 ($\nu_{BF_4^-}$). ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 10.11 (d, 1H, H_a, J = 5.1 Hz), 9.22 (s, 2H, H_m,$H_{m'}$), 8.93 (m, 3H, H_d, H_l,$H_{l'}$), 8.63 (d, 1H, H_e, J = 8.1 Hz), 8.37 (m, 3H, H_h,H_i,$H_{i'}$), 8.17 (m, 2H, H_j,$H_{j'}$), 8.05 (dd, 3H, H_b, H_k,$H_{k'}$), 7.77 (t, 1H, H_c, J = 8.1 Hz), 7.63 (d, 2H, H_o,$H_{o'}$, J = 4.8 Hz), 7.38 (m, 3H, H_g, H_n,$H_{n'}$), 7.07 (t, 1H, H_f, J = 6.3 Hz).

2.3.3. Synthesis of [Ru(LH)(phen)Cl]BF₄ **2**

This complex was prepared using procedure given for the complex **1**, except that 1,10-phenanthroline (0.180 g, 1.0 mmol) was used in place of 2,2′-bipyridine. The complex containing BF_4^- as counter anion was isolated and purified similarly using column chromatography. The brown coloured solid was obtained after reducing the volume of the corresponding eluate and by the addition of an aqueous solution of $NaBF_4$. It was then filtered and washed with water followed by ethanol and diethyl ether. The complex was found soluble in DMSO, DMF, C_2H_5OH, CH_3OH and CH_3CN. The solution of complex in CH_3CN: H_2O (1: 1, v/v) gave block shaped dark brown crystals after its slow evaporation. Yield: 0.367 g (45%). *Anal.* Calc. for $C_{34}H_{23}N_5O_2BF_4ClRu$: C, 54.01; H, 3.04; N, 9.26. Found: C, 54.03; H, 3.01; N, 9.28%. FAB MS: *m/z*: 755$[M]^+$, 669$[M–BF_4]^+$, 634$[M–BF_4–Cl]^+$. IR (KBr pellet, cm^{-1}) 1716 (ν_{COOH}), 1605 ($\nu_{CH=N}$), 1083 ($\nu_{BF_4^-}$). ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 10.33 (d, 1H, H_a, J = 5.1 Hz), 9.28 (s, 2H, H_m,$H_{m'}$), 8.94–9.00 (m, 3H, H_c,H_l,$H_{l'}$), 8.38–8.46 (m, 5H, H_b,H_j,$H_{j'}$,H_k,$H_{k'}$), 8.23 (m, 3H, H_i,-$H_{i'}$,H_f), 7.96–8.01 (m, 2H, H_d, H_e), 7.82 (d, 1H, H_h, J = 5.1 Hz), 7.50 (d, 2H, H_o,$H_{o'}$, J = 5.4 H_z), 7.40–7.45 (m, 1H, H_g), 7.23–7.28 (m, 2H, H_n,$H_{n'}$). Its solution in DMF emitted at room temperature (λ_{em} = 600 nm) after excitation at λ_{ex} 520 nm.

2.3.4. Synthesis of [Ru(LH)(PPh₃)(MeCN)₂] (BF₄)₂ **3**

The complex **3** was prepared by the addition of a solution of PPh_3 (0.262 g, 1 mmol) in dichloromethane (5 mL) to a solution of $[Ru(LH)Cl_3]$ in ethanol (15 mL) and the mixture was heated at reflux with stirring for ~6 h. An aqueous saturated solution of $NaBF_4$ was then added to it which gave orange coloured solid. The solid product thus obtained was washed with water and ethanol and dried in *vacuo*. It was then purified using column chromatography similar to that used for complex **1**. The solid thus obtained was then dissolved in CH_3CN:H_2O (1:1, v/v) mixture and its solution was slowly evaporated then red coloured parallelopiped shaped crystals were obtained. The crystals were soluble in DMSO, DMF, C_2H_5OH, CH_3OH and CH_3CN. Yield: 0.709 g (45%). *Anal.* Calc. for $C_{44}H_{36}N_5O_2PB_2F_8Ru$: C, 54.43; H, 3.71; N, 7.21. Found: C, 54.39; H, 3.69; N, 7.19%. FAB MS: *m/z*: 970$[M]^+$, 883$[M–BF_4]^+$, 797$[M–2BF_4]^+$ IR (KBr pellet, cm^{-1}) 2398 (ν_{CN}), 1709 (ν_{COOH}), 1606 ($\nu_{CH=N}$), 1080($\nu_{BF_4^-}$). ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 9.13 (d, 2H, H_l,$H_{l'}$, J = 5.1 Hz), 8.76 (s, 2H, H_m,$H_{m'}$), 8.63 (d, 2H, H_i,$H_{i'}$, J = 8.1 Hz), 8.14–8.21 (m, 4H, H_j,$H_{j'}$,H_k,$H_{k'}$), 7.70 (m, 2H, H_o,$H_{o'}$), 7.41 (m, 2H, H_n,$H_{n'}$), 7.24 (m, 9H, H_q), 6.95 (m, 6H, H_p), 2.07 (s, 6H, H_r). ^{31}P NMR (300 MHz, DMSO-d_6, δ ppm): 32.56.

2.3.5. Synthesis of [Ru(LH)(dppe)Cl]BF₄ **4**

The complex **4** was also prepared by the addition of a solution of dppe (0.398 g, 1 mmol) in dichloromethane (5 mL) to an ethanolic solution (15 mL) of $[Ru(LH)Cl_3]$ (0.560 g, 1 mmol). The mixture was then heated at reflux with stirring for 8 h. Finally, it was precipitated as BF_4^- salt upon addition of aqueous saturated solution of $NaBF_4$ to it. This complex was washed with water, dried in *vacuo* and purified by column chromatography. Yield: 0.584 g (61%). *Anal.* Calc. for $C_{48}H_{39}N_3O_2P_2ClBF_4Ru$: C, 59.18; H, 4.00; N, 4.31. Found: C, 59.15; H, 3.97; N, 4.34%. FAB MS: *m/z*: 973$[M]^+$, 886$[M–BF_4]^+$, 850$[M–BF_4–Cl]^+$. IR (KBr pellet, cm^{-1}) 1708 (ν_{COOH}), 1609 ($\nu_{CH=N}$), 1081 ($\nu_{BF_4^-}$). ^1H NMR (300 MHz, DMSO-d_6, δ ppm): 9.09 (d, 2H, H_l,$H_{l'}$, J = 6 Hz), 8. 54 (s, 2H, H_m,$H_{m'}$), 8.24 (d, 2H, H_i,$H_{i'}$), 7.79–8.00 (m, 4H, H_k,$H_{k'}$,H_j,$H_{j'}$), 7.65 (d, 2H, H_o,$H_{o'}$, J = 5.3 Hz), 7.57 (m,

2H, H_n,$H_{n'}$), 7.39–6.91 (m, 20H, H_a), 1.35–1.23 (m, 4H, H_b), ^{31}P NMR (300 MHz, DMSO-d_6, δ ppm): 28.06.

*2.3.6. General procedure for the Synthesis of propargylamines **8***

Aldehyde **5** (1 mmol), amine **6** (1.1 mmol), alkyne **7** (1.2 mmol), complex **3** (10 mol%) and chlorobenzene (2 mL) were placed in a sealed pressure regulation 10 mL vial with "snap-on" cap and the mixture was irradiated in single-mode microwave synthesis system using 250 W power at 130 °C for 10 min. After completion of the reaction (as monitored by TLC), the solvent was evaporated in *vacuo* and water (20 mL) was added to the reaction mixture. The product was extracted with ethylacetate (3 × 10 mL). The combined organic phase was dried over anhydrous $MgSO_4$, filtered and the solvent was evaporated in *vacuo*. The residue was then purified by column chromatography on silica gel (ethyl acetate: hexane = 1:9 v/v) to afford the pure propargylamine.

4-(1,3-Diphenyl-prop-2-ynyl)-morpholine **8a**: Yield: 55%. *Anal.* Calc. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.30; H, 6.85; N, 5.09%. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 2.62–2.64 (m, 4H, 2 × CH_2), 3.72–3.75 (m, 4H, 2 × CH_2), 4.78 (s, 1H, CH), 7.25–7.39 (m, 6H, H–Ar), 7.49–7.52 (m, 2H, H–Ar), 7.61 (d, 2H, J = 7.2 Hz, H–Ar). ^{13}C NMR (300 MHz, $CDCl_3$, δ ppm) 49.8, 62.0, 67.1, 84.9, 88.4, 122.9, 127.7, 128.0, 128.2, 128.3, 128.5, 131.7, 137.7. The spectrum is depicted as S10.

The physical and spectral data of all the products are in full agreement with their assigned structures and the characterization data of products 8b–8h are given as S11.

2.4. X-ray structural studies

Single crystal X-ray diffraction data for the complexes were collected in the temperature range of 100(2) to 293(2) K on a Oxford diffraction XCALIBUR-EOS diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Intensities of these reflections were measured periodically to monitor crystal decay. The crystal structures were solved by direct methods and refined by full matrix least squares (SHELX-97) [30]. Drawings were carried out using MERCURY [31]. The crystal refinement data is shown in Table 1. The X-ray quality crystals of only two complexes [Ru(LH)-phenCl]BF_4·H_2O·CH_3CN **2** and [Ru(LH)(CH_3CN)$_2$$PPh_3$]($BF_4$)$_2$ **3** could be obtained.

Table 1
Summary of crystallographic data for complexes **2** and **3**.

	Complex **2**	Complex **3**
Empirical formula	$C_{36}H_{26}N_6ClO_3BF_4Ru$	$C_{44}H_{36}N_5O_2B_2F_8Ru$
Formula weight	813.96	974.15
T (K)	150(2)	293(2)
λ (Å)	0.71073	0. 71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.5999(4)	12.4520(13)
b (Å)	12.0751(6)	13.6700(12)
c (Å)	14.3605(7)	14.9784(15)
α (°)	90.177(4)	90.311(8)
β (°)	95.159(4)	114.501(10)
γ (°)	98.717(4)	102.047(8)
V (Å^3)	1638.53(13)	2256.8(4)
Z	2	2
Absorption coefficient (mm^{-1})	0.703	0.465
$F(000)$	832	948
Crystal size (mm)	0.28 × 0.23 × 0.18	0.34 × 0.31 × 0.3
Theta range for data collection	3.30–25.00°	2.03–28.77°
Reflections collected/unique	11732/5765 [R_{int} = 0.0586]	15479/9586 [R_{int} = 0.0684]
Completeness to theta (%)	99.8	96.6
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Goodness-of-fit (GOF) on F^2	0.943	1.035
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0557, wR_2 = 0.1291	R_1 = 0.0880, wR_2 = 0.2295
R indices (all data)	R_1 = 0.0802, wR_2 = 0.1363	R_1 = 0.1116, wR_2 = 0.2458
Largest difference in peak and hole (e A^{-3})	1.656 and −1.135	2.148 and −1.36

3. Result and discussion

3.1. Synthesis

The synthetic route for the preparation of complexes is summarized in scheme 1. The ligand was prepared using published procedure [28]. The complexes were prepared by direct reaction of precursor complex [Ru(LH)Cl_3] in ethanol with different ligands in equimolar ratio. The yields were good to moderate. The desired ruthenium(II) complexes were isolated as tetrafluoroborate salts and purified using column chromatography. These complexes were found soluble in solvents such as DMSO, DMF, ethanol, methanol, acetonitrile, and acetone. The composition of the complexes were initially identified by their elemental and spectroscopic data. The structure of the complexes were further supported by their ^{1}H NMR and ^{1}H–^{1}H COSY NMR spectra. The numbering of protons are same as shown in scheme 1. The ^{1}H NMR spectrum of 1 (S1) showed all protons which were assigned in view of earlier reports for terpy complexes [32,33]. The proton of bpy marked as H_a appeared at δ = 10.11 ppm (J = 5.1 Hz) as doublet. Its ^{1}H–^{1}H COSY NMR spectrum (S2) showed that H_a proton coupled with its neighbouring H_b proton. The H_b proton appeared at δ = 8.05 ppm as multiplet owing to its coupling with H_a and H_c (δ = 7.77 ppm) protons. The protons marked as H_k and $H_{k'}$ also appeared at δ = 8.05 ppm. However, peak observed at δ = 8.63 ppm (J = 8.1 Hz) is assigned to H_d proton which appeared as doublet owing to its coupling with H_c proton. The protons marked as H_e, H_l and $H_{l'}$ appeared together as multiplet at δ = 8.93 ppm. The peak observed at δ = 7.07 ppm as triplet is assigned to H_f proton. However, H_o and $H_{o'}$ protons are observed at δ = 7.63 ppm (J = 4.8 Hz) as doublet and showed its coupling with H_n and $H_{n'}$ protons. The latter both protons together with H_g proton appeared at δ = 7.38 ppm. The Protons marked as H_h, H_i and $H_{i'}$ appeared at δ = 8.37 ppm. The terpy (LH) protons H_j and $H_{j'}$ appeared as multiplet at δ = 8.17 ppm where as H_m and $H_{m'}$ protons appeared together at δ = 9.22 ppm. In a similar way, protons of complex **2** were also assigned and its spectrum is depicted in S3 along with the assignment of the different protons supported by its ^{1}H–^{1}H COSY NMR spectrum (S4). The assignments were made in view of reported data [34] and also in view of the position and integration intensity of the peaks. The peaks observed at δ =7.24–6.95 ppm were assigned to PPh_3 protons of the complex **3** (S5) in view of earlier report [35]. The assignment is also supported by its ^{1}H–^{1}H COSY NMR spectrum (S6). In the spectrum of this complex, methyl protons of acetonitrile appeared at δ = 2.07 ppm as singlet. The protons of dppe in complex **4** appeared as multiplet from δ 7.39–6.91 ppm (S7) were found in consistence with the earlier report [36]. Its ^{1}H–^{1}H COSY NMR spectrum (S8) supported the assigned structure of this complex. The presence of phosphorus nuclei in complexes **3** and **4** was also supported by their ^{31}P NMR spectra which showed peaks at δ (ppm) 32.56 for PPh_3 and 28.06 for dppe, respectively(S9a,S9b). Thus, ^{1}H NMR spectra of the complexes together with their ^{1}H–^{1}H COSY NMR spectra tentatively assigned the presence of different types of protons in their structures. However, some of the peaks overlapped together and calls for separate NMR study using high field NMR spectrometer.

3.2. Molecular structures of complexes **2** and **3**

The molecular structure of the complex **2**, a triclinic system with space group $P\bar{1}$ is shown in Fig. 1. The Selected bond lengths and bond angles are given in Table 2. The bond length of LH (N3, N4 and N5) to Ru(II) centre varies from 1.956 to 2.068 Å. The central nitrogen atom (N4) of LH ligand lies at shortest distance of 1.956 Å from ruthenium centre. It could be considered in view that to optimize the chelation of this ligand with metal centre, this bond shortens but the terminal Ru–N bonds lengthen to relieve strain hence it retains a typical terpyridine bite angle (N–Ru–N) of ~79°[37]. The bond length of phenanthroline nitrogen to ruthenium centre varies from 2.046 to 2.072 Å. The bond distance of Ru(1)–Cl(1) was found to be 2.398 Å.

The complex **3** crystallized in triclinic crystal system with space group $P\bar{1}$. A red colour rod shaped crystal was chosen for the diffraction study and resulting molecular structure of the complex **3** is shown in Fig. 2. The selected bond angles and bond distances are given in Table 2. The coordination sphere of this complex showed asymmetrical bond distances with different donors. The bond distance between ruthenium and nitrogen (N1, N2, N3) are in the range 1.966–2.097 Å. The ruthenium ion in each structure occupied a distorted octahedral environment with a terpy bite angle found in consistence with the value reported for other terpy–ruthenium complexes [38–41]. Both coordinated acetonitrile groups were bonded to Ru(II) centre at different distance varying from 2.059 to 2.115 Å.

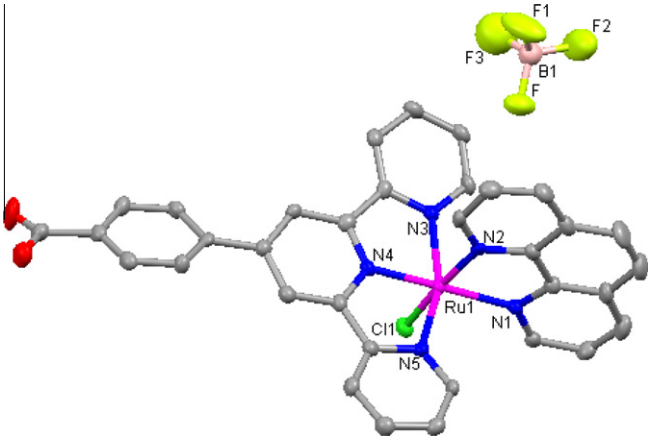
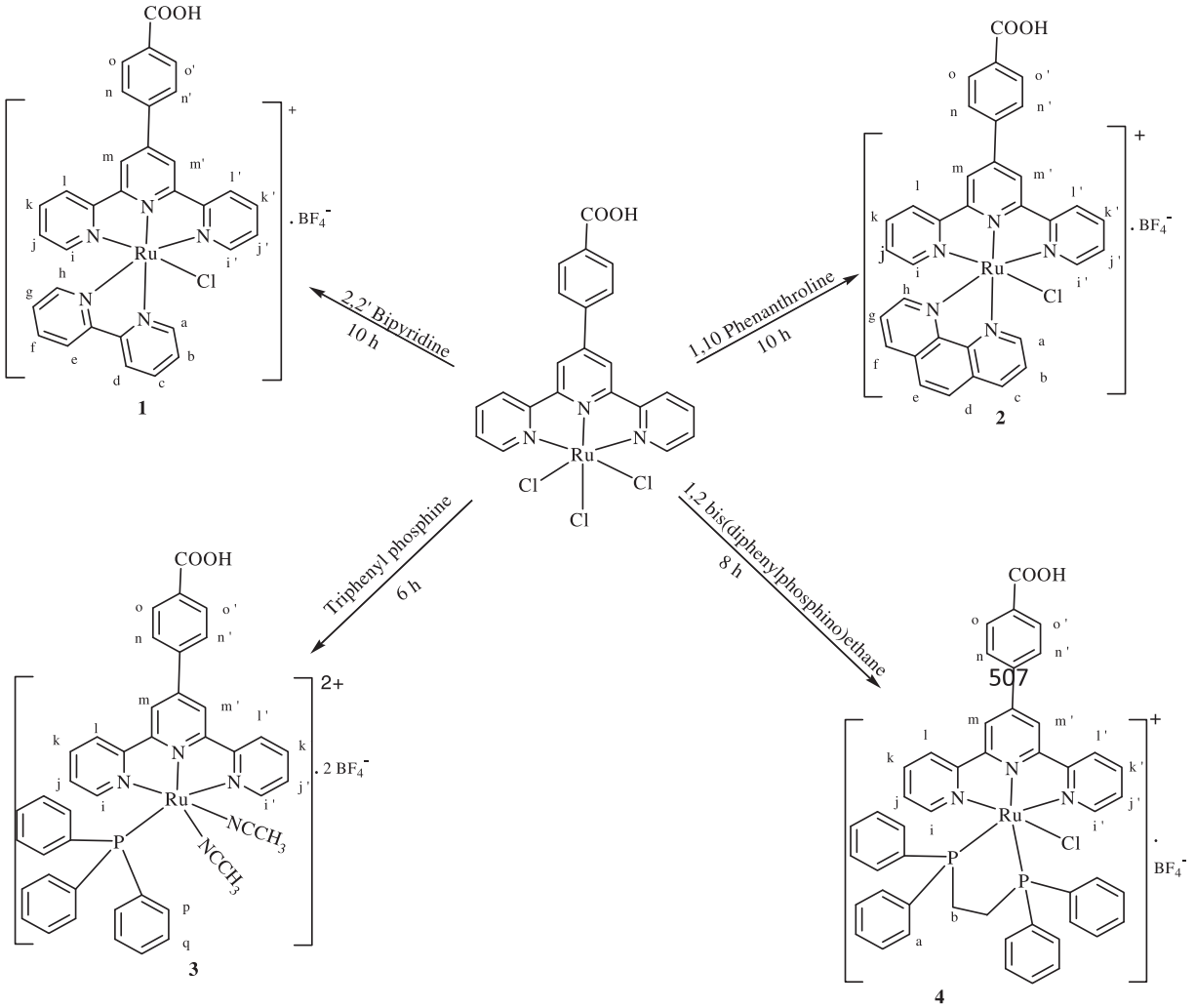


Fig. 1. Molecular structure of complex **2** (30% probability ellipsoid), hydrogen atoms are omitted for clarity.



Scheme 1.

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **2** and **3**.

Complex ***2***			
Ru(1)–N(4)	1.956(4)	Ru(1)–N(3)	2.069(4)
Ru(1)–N(2)	2.046(4)	Ru(1)–N(1)	2.072(4)
Ru(1)–N(5)	2.068(4)	Ru(1)–Cl(1)	2.398(14)
N(4)–Ru(1)–N(2)	98.32(17)	N(4)–Ru(1)–N(5)	79.56(17)
N(2)–Ru(1)–N(5)	93.09(16)	N(4)–Ru(1)–N(3)	79.06(17)
N(2)–Ru(1)–N(3)	86.64(16)	N(5)–Ru(1)–N(3)	158.35(16)
N(4)–Ru(1)–N(1)	177.19(18)	N(2)–Ru(1)–N(1)	79.99(16)
N(5)–Ru(1)–N(1)	98.25(17)	N(3)–Ru(1)–N(1)	103.00(17)
N(4)–Ru(1)–Cl(1)	89.17(12)	N(2)–Ru(1)–Cl(1)	171.40(12)
N(3)–Ru(1)–Cl(1)	90.67(12)	N(5)–Ru(1)–Cl(1)	92.42(12)
Complex ***3***			
Ru(1)–N(2)	1.966(5)	Ru(1)–P(1)	2.340(16)
Ru(1)–N(3)	2.075(4)	P(1)–C(35)	1.829(6)
Ru(1)–N(1)	2.097(4)	P(1)–C(23)	1.837(6)
Ru(1)–N(5)	2.115(5)	P(1)–C(29)	1.840(6)
Ru(1)–N(4)	2.059(5)	N(4)–Ru(1)–N(1)	103.16(18)
N(2)–Ru(1)–N(4)	175.51(17)	N(3)–Ru(1)–N(1)	158.31(19)
N(2)–Ru(1)–N(3)	79.45(17)	N(2)–Ru(1)–N(5)	88.25(17)
N(4)–Ru(1)–N(3)	97.57(18)	N(4)–Ru(1)–N(5)	88.23(18)
N(2)–Ru(1)–N(1)	79.46(18)	N(3)–Ru(1)–N(5)	86.96(17)
N(1)–Ru(1)–N(5)	87.39(17)	C(35)–P(1)–C(23)	101.9(3)
N(2)–Ru(1)–P(1)	92.16(13)	C(35)–P(1)–C(29)	105.9(3)
N(4)–Ru(1)–P(1)	91.41(14)	C(23)–P(1)–C(29)	104.7(3)
N(3)–Ru(1)–P(1)	93.93(13)	C(35)–P(1)–Ru(1)	114.6(2)
N(1)–Ru(1)–P(1)	91.87(14)	C(23)–P(1)–Ru(1)	117.2(2)
N(5)–Ru(1)–P(1)	179.08	C(29)–P(1)–Ru(1)	111.3(2)

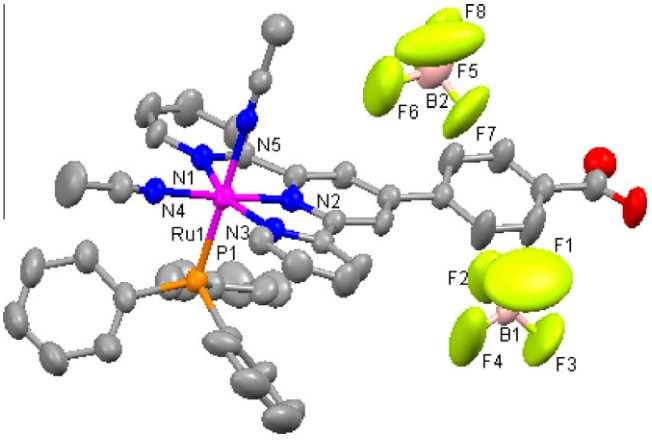


Fig. 2. Molecular structure of complex **3** (30% probability ellipsoid), hydrogen atoms are omitted for clarity.

3.3. Absorption and emission spectra

The absorption spectra of the complexes recorded in DMF (10^{-4} M) are depicted in Fig. 3 and spectral data are shown in Table 3. The absorptions in UV region were assigned to intraligand π–π* transitions within terpy, bpy, phen and phenyl rings of PPh_3 and dppe in view of earlier reports [42,43]. However, broad absorption bands observed at lower energy were assigned to Ru (dπ)–terpy/bpy/phen/PPh_3/dppe (π*) metal to ligand charge transfer (MLCT) transitions observed at λ_{max} 517, 520, 469 and 495 nm for **1**, **2**, **3** and **4**, respectively. These bands were red shifted as compared to the band observed from the precursor complex at λ_{max} 407 nm. Thus, spectral features of the complexes were found sensitive to the nature of substituted ligands, from weaker σ donor and stronger π acceptor ligands (bpy, phen) to stronger σ donor and weaker π acceptor ligands (PPh_3, dppe). The emission spectrum obtained from complex **2** in DMF (10^{-4} M) is depicted in Fig. 4. However no detectable luminescence could be obtained under similar condition

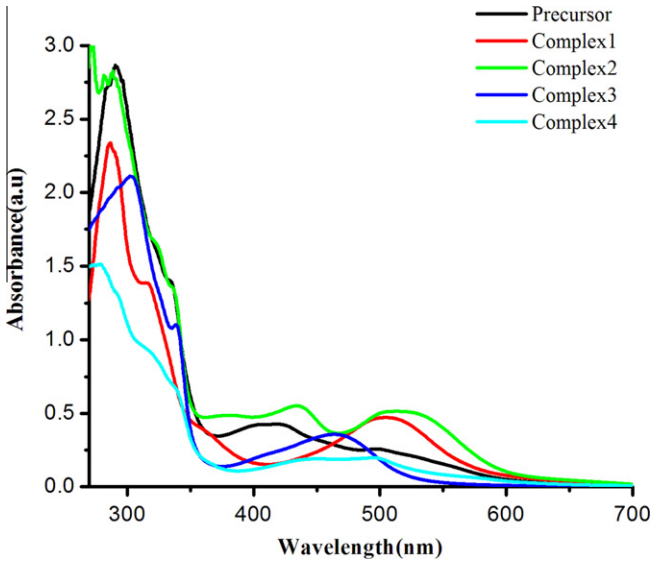


Fig. 3. Overlaid UV–Vis absorption spectra of complexes **1**, **2**, **3** and **4** in DMF (10^{-4} M).

Table 3
Electronic spectral data for complexes **1**, **2**, **3** and **4**.

Complexes	λ_{max} (nm) ($10^{-4}\varepsilon$, M^{-1}, cm^{-1})
Precursor	294 (2.86), 332 (1.39), 407 (0.42)
1	286 (2.34), 317 (1.37), 364 (0.36), 517 (0.46)
2	288 (2.76), 324 (1.6), 336 (1.30) 434(0.56), 520 (0.50)
3	298 (2.10), 339 (1.08), 469 (0.35)
4	298 (2.12), 314 (2.10), 495 (0.22)

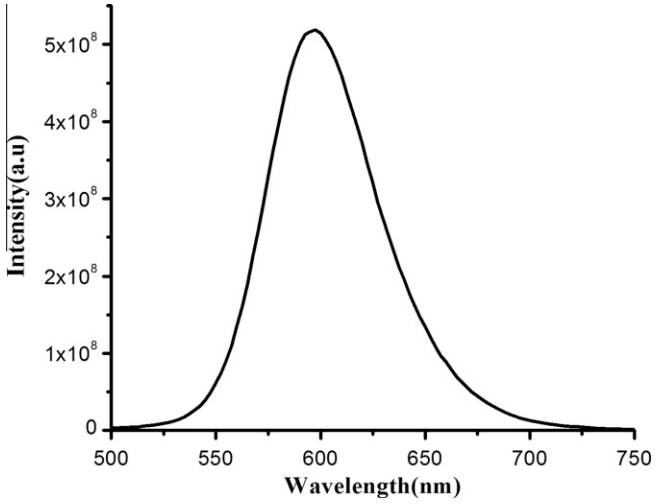


Fig. 4. Fluorescence spectrum of complex **2** in DMF (10^{-4} M).

from complexes **1**, **3** and **4**. This observation is not unusual, having been observed in several earlier reported ruthenium complexes [44].

3.4. Electrochemistry

Electrochemical properties of the complexes was studied in DMF (10^{-4} M) using cyclic voltammetry. The cyclic voltammograms of **1** and **2** are shown in Fig. 5 and redox data are presented in Table 4. These complexes are found redox active and their metal

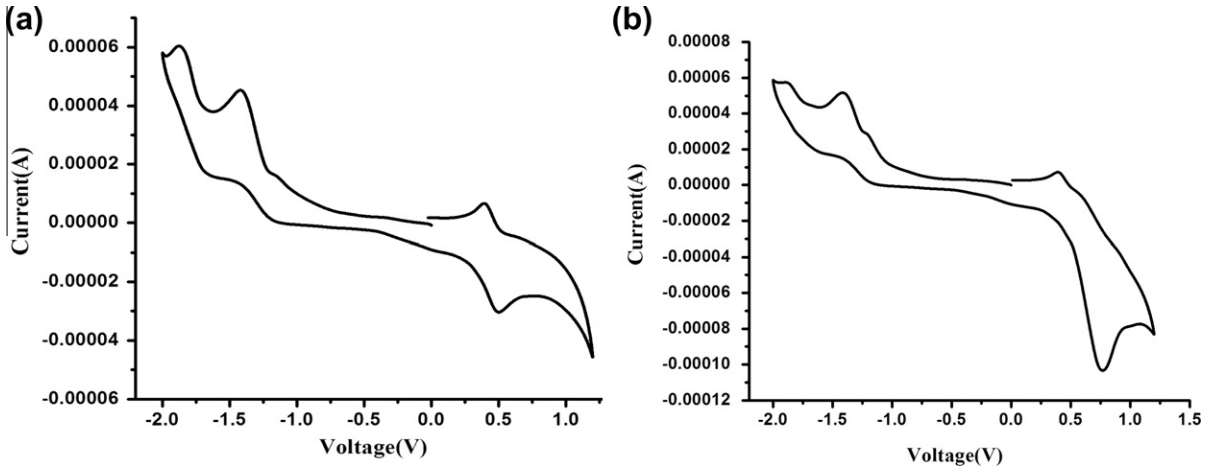
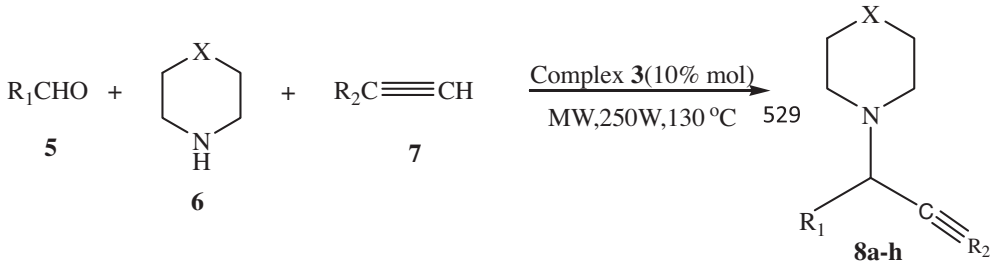


Fig. 5. Cyclic voltammograms of representative complexes (a) **1**, and (b) **2** in DMF (10^{-4} M).

Table 4
Electrochemical data for complexes **1**, **2**, **3** and **4** at 298 K.

$E°_{298}/V(\Delta E_p/V)$				ν_{MLCT} (cm^{-1})	
Complex	Ru^{III}–Ru^{II}	Ligand reduction	$\Delta E° = E°_{298}(Ru^{III}Ru^{II})-\Delta E°_{298}(L)$	Observed	Calculated
1	0.5	−1.42	1.92	19342	18484
2	0.74	−1.38	2.12	19230	20097
3	0.79	−1.45	2.24	21321	21065
4	0.68	−1.36	2.04	20202	19452



X = O (**6**), $R_2 = C_6H_5$, $R_1 = C_6H_5$(a), $MeOC_6H_4$(b), MeC_6H_4(c) BrC_6H_4(d)

X = CH_2 (**6**), $R_2 = C_6H_5$, $R_1 = C_6H_5$(e), $MeOC_6H_4$(f), MeC_6H_4(g), BrC_6H_4(h)

Scheme 2.

Table 5
Screening of reaction parameters for the synthesis of **8a**.

Entry	Catalyst (mol%)	Solvent	Conventional			Microwave			
			Temp (°C)	Time (h)	Yield[a]	Power (Watt)	Temp (°C)	Time (min)	Yield[b]
1.	$RuCl_3$	chlorobenzene	130	8	nr[c]	300	130	20	nr[c]
2.	precursor	chlorobenzene	130	10	20	300	130	20	35
3.	**2**	chlorobenzene	130	8	trace	300	130	20	trace
4.	**3**	chlorobenzene	130	8	35	250	130	10	55
5.	**3**	chlorobenzene	125	10	15	300	130	15	55
6.	**3**	chlorobenzene	120	8	trace	200	130	20	35

[a] Used benzaldehyde:morpholine:phenylacetylene (1:1.1:1.2).
[b] Isolated yield based on benzaldehyde.
[c] nr = no reaction.

Table 6
One – pot synthesis of propagylamines[a] using complex **3** as catalyst.

Entry	R_1	Amine	R_2	Product	Time (min)	Yield (%)[b]
1.	C_6H_5	Morpholine	C_6H_5	**8a**	10	55
2.	p-$MeOC_6H_4$	Morpholine	C_6H_5	**8b**	10	50
3.	p-MeC_6H_4	Morpholine	C_6H_5	**8c**	10	48
4.	p-BrC_6H_4	Morpholine	C_6H_5	**8d**	10	52
5.	C_6H_5	Piperidine	C_6H_5	**8e**	10	56
6.	p-$MeOC_6H_4$	Piperidine	C_6H_5	**8f**	10	52
7.	p-MeC_6H_4	Piperidine	C_6H_5	**8g**	10	50
8.	p-BrC_6H_4	Piperidine	C_6H_5	**8h**	10	52

[a] Reaction condition: aldehyde (1 mmol), amine (1.1 mmol), phenylacetylene (1.2 mmol), complex **3** (10 mol%), chlorobenzene (2 mL), microwave (250 W, 130 °C).
[b] Isolated yield based on aldehyde.

based oxidation was observed between 0.49 and 0.79 V. The low value observed for metal based oxidation potential could be attributed to the presence of phenylcarboxy group at 4′-position of terpy ring and other ligands which substituted Cl atoms of the parent complex. The decrease of metal oxidation potential shows the destabilization of metal centered (dπ) HOMO of the complexes [45].

3.5. Spectroelectrochemical correlation

The lowest energy MLCT transition involves excitation of the filled t_2 electron of ruthenium(II) to the lowest π^* orbital of the terpy (LH) ligand. The energy of the MLCT transition is calculated using observed electrochemical data by using Eqs. (1) and (2) [46].

$$\nu\mathrm{MLCT} = 8065(\Delta E^\circ) + 3000 \quad (1)$$

$$\Delta E^\circ = E^\circ_{298}(\mathrm{Ru^{III}}\text{—}\mathrm{Ru^{II}}) - E^\circ_{298}(\mathrm{LH}), \quad (2)$$

ν_{MLCT} is the frequency of the lowest energy MLCT transition (in cm^{-1}). The factor 8065 in Eq. (1) is used to convert potential difference ΔE from volt to cm^{-1} and the term 3000 cm^{-1} is of empirical origin where as $E^\circ_{298}(Ru^{III}–Ru^{II})$ and $E^\circ_{298}(LH)$ are the formal potentials (in V) of the ruthenium(III)–ruthenium(II) couple as well as the first ligand reduction potential, respectively. The calculated and experimentally observed ν_{MLCT} transition frequencies for the complexes are listed in Table 4. The calculated values lie within 900 cm^{-1} of the experimentally observed energies, which are in very good agreement with the previously observed correlation in other ruthenium complexes [47].

3.6. Catalytic properties

In order to assess the efficiency of the catalysts, a typical multicomponent reaction of benzaldehyde, morpholine and phenylacetylene (scheme 2) was carried out in chlorobenzene by varying different catalyst under conventional as well as under microwave heating. The outcome is given in Table 5. It is important to mention that the free $RuCl_3$ alone could not bring about any conversion to the product even after 8 h heating at 130 °C or 20 min of MW heating (300 W) at 130 °C. The data reveals that complex **3** under conventional conditions at 130 °C brings about the reaction to afford the product **8a** in 35% yield (Table 5, entry 4). Application of a monomode MW irradiation at the same temperature, however, brought about a commendable increase in the product yield as well as a dramatic reduction in the reaction time, the best result (55%) was observed using 250 W at 130 °C in 10 min using 10 mol% of the complex **3** (entry 4, scheme 2). The use of the precursor also promoted the reaction to a reasonable extent (Table 5, entry 2, 35%), but the complex **2** did not work at all (Table 5, entry 3). The reaction was carried out under controlled microwave conditions by varying the MW power (200, 250 and 300 W) and time. The 250 W power output and reflux temperature of the solvent were important to obtain the maximum conversion of the product in 10 min. Further increase in MW power and time could not enhance the product yield. Under the optimized set of MW reaction conditions (250 W, 10 min), a number of aldehydes and amines (Scheme 2) were subsequently made to react with phenylacetylene to provide various propargylamines in appreciable yields (Table 6). It was interesting to observe that aldehydes such as benzaldehyde, *p*-methoxybenzaldehyde, *p*-methylbenzaldehyde and *p*-bromobenzaldehyde reacted smoothly with morpholine/piperidine and phenylacetylene to produce the corresponding propargylic amines in 48–56% yields (Table 6, entries 1–8). The physical and spectral data of all the products are in full agreement with their assigned structures (S11).

4. Conclusion

The Present article embodies the synthesis of four new complexes $[Ru(LH)bpyCl]^+$ **1**, $[Ru(LH)phenCl]^+$ **2**, $[Ru(LH)PPh_3(CH_3CN)_2]^{2+}$ **3** and $[Ru(LH)dppeCl]^+$ **4** obtained after the substitution of chloro groups of precursor complex $[Ru(LH)Cl_3]$ by stronger σ donor and poor π acceptors (PPh_3, dppe) and poor σ donor and stronger π acceptors (bpy, phen). The complexes have been characterized using their spectral and analytical data along with X-ray diffraction data of complexes $[Ru(LH)phenCl]^+$ **2** and $[Ru(LH)PPh_3(CH_3CN)_2]^{2+}$ **3**. The latter complex **3** catalyzes the formation of propargylamines using one-pot multicomponent approach.

Acknowledgement

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Appendix A. Supplementary data

CCDC 793026 and 760553 contains the supplementary crystallographic data for compounds **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.09.014.

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