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Unprecedented examples of double-addition of aromatic amines across a ruthenium(II)-coordinated nitrile function: Isolation and X-ray structures of ruthenium complexes of amidinate and cyclometalated amidine

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Abstract

The present report examplifies a novel type of aromatic amine addition reactions at a ruthenium(II) complexed acetonitrile. The electrophilic cationic complex, *cis*-$[L_2Ru(CH_3CN)_2](ClO_4)_2$ (**1**) [L = 2-(phenylazo)pyridine] reacts with aromatic primary amines only in neat to produce a violet amidinate complex, $[L_2Ru–N(Ar)–C(CH_3)–N(Ar)]^+$ (**2**) of ruthenium(II). Along with it a blue *ortho*-metalated ruthenium(II) amidine complex, $[L_2Ru–N(H)=C(CH_3)–N(H)Ar]^+$ (**3**) is also formed. X-ray structures of the two representative complexes are reported. The transformation **1** → **2** is unprecedented, involves multiple steps and occurs with addition of two equivalents of $ArNH_2$ across a coordinated nitrile function. In this complex, amidinate ligand binds to ruthenium(II) center as a σ,σ symmetrical bidentate chelate. The formation of **3** is a combination of nucleophilic amine addition and cyclometalation. ^1H and ^{13}C NMR spectra of the products are examined, which are consistent with their formulations and structures. Optical spectra and redox properties of the newly synthesized complexes are reported. Visible range spectra of **2** and **3** are dominated by moderately intense metal-to-ligand charge transfer transitions. The complexes show multiple redox responses. The anodic potential response occurs at a high positive potential, which is attributed to a Ru(II)/Ru(III) couple. The cathodic potential responses are due to reductions of the coordinated diazo ligands.

Keywords: Reactions of coordinated nitrile; Double-addition of aromatic amines; Ruthenium amidinates; Cyclometalated amidine

1. Introduction

The nature of chemical reactions of organic substrates can vastly be affected by their coordination to metal ions [1]. It is now known that organonitriles are activated by metal coordination toward addition reactions leading to a variety of synthetic transformations of RCN species [2]. During the recent past we have been interested in the aromatic amine fusion reactions that are mediated by transition metal ions [3,4]. Herein we report an unprecedented type of aromatic amine fusion reaction to a ruthenium(II)-complexed acetonitrile. The reaction resulted in the formation of a ruthenium complex of amidinate ligand directly due to double-amine fusion across a coordinated nitrile function, along with it a cyclometalated amidine complex is formed. The chemical transformations, concerning us here, are shown in Scheme 1.

Amidinates, as ligand, have attracted considerable attention in recent years not only because of their versatile coordination abilities [5] but also some of their transition metal complexes have been found to be useful [6,7]. We wish to add here that while the chemistry associated with the metal mediated addition of a variety of nucleophiles to coordinated nitriles was 1:1 type, the observed addition of two nucleophiles to metal coordinated one nitrile group

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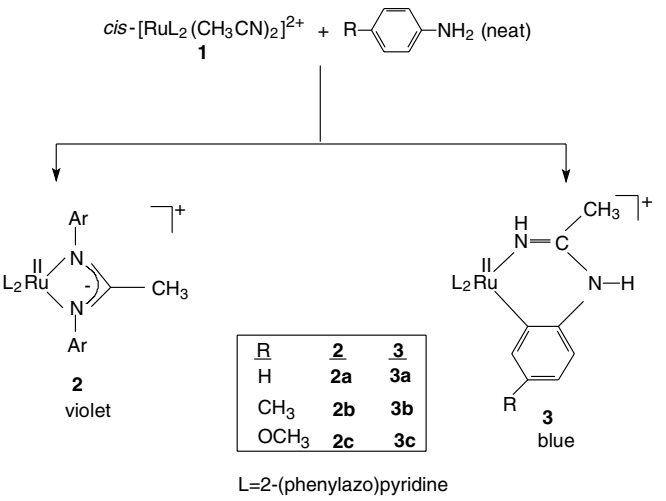
is indeed scarce in the literature [8]. Furthermore, nucleophilic addition reaction to organonitriles coordinated to bivalent ruthenium compounds is relatively uncommon [9].

2. Results and discussion

It is now known that organonitriles are activated toward nucleophilic attack by coordination to metal ions and the nitrile complexes undergo a variety of chemical transformations which otherwise do not occur [2a]. In our present study a stable ruthenium(II) diacetonitrile complex, *cis*-$[L_2Ru(CH_3CN)_2](ClO_4)_2$ (**1**), was chosen as the reactant [10]. Due to the presence of two excellent π-acceptor 2-(phenylazo) pyridine (L) ligands, it was anticipated that the metal complex would behave formally as an electron deficient center for the promotion of nucleophilic addition reaction. The complex, **1** reacted freely with neat aromatic monoamines, $ArNH_2$, on an oil bath (100–110 °C). The initial brown color of **1** gradually became violet in 30 min; the reaction was further continued for 1.5 h for completion. The crude product, after initial work up, was purified finally on a preparative TLC (silica gel) plate from which two major bands; a violet (**2**) (yield: ca. 35%) and a blue (**3**) (yield: ca. 30%) were isolated. Both the complexes, thus obtained, are fairly soluble in common organic solvents and their solutions behave as 1:1 electrolyte in acetonitrile. Notably, the above reactions did not proceed at all in common organic solvents even in the presence of high excess (>20 times) of aromatic amines. Our attempts to carry out these reactions in solvents like acetonitrile, methanol, 2-methoxy ethanol and dimethyl formamide failed to produce the desired products. Thin layer chromatography (TLC) experiment on the crude mass, obtained after solvent evaporation, showed the presence of several overlapping minor bands which could not be purified and their identities remained uncertain.



Scheme 1.

The ORTEP and atom numbering scheme for the cationic part of a representative complex **2b** is shown in Fig. 1 and its bond parameters are collected in Table 1. Structural analysis reveals the coordination of an *N*-aryl amidinate ligand, formed due to addition of two equivalents of aryl amine to a coordinated acetonitrile. Associated with it are the two coordinated L ligands, which complete six coordination around the central ruthenium(II) ion. Bite angle of the amidinate chelate (62.13(9)°) is much smaller than that of the L ligand (av. 76.99(9)°) but is similar to those of reported amidinate complexes [6]. The two C–N bond lengths, N(31)–C(32) (1.329(4) Å) and N(33)–

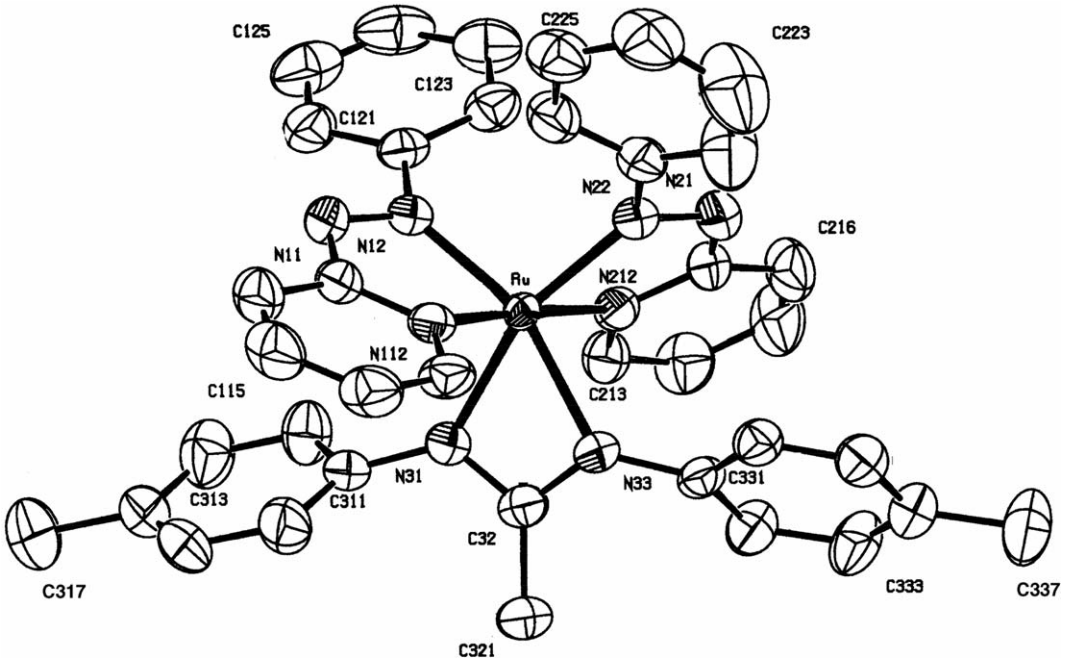


Fig. 1. ORTEP and atom numbering scheme for **2b**. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for the complexes **2b** and **3b**

2b					
Ru–N(12)	1.994(3)	Ru–N(22)	2.007(2)	Ru–N(112)	2.022(3)
Ru–N(212)	2.036(2)	Ru–N(33)	2.110(2)	Ru–N(31)	2.088(2)
N(11)–N(12)	1.305(4)	N(21)–N(22)	1.297(4)	N(31)–C(32)	1.329(4)
N(33)–C(331)	1.414(4)	C(32)–N(33)	1.337(4)	N(31)–C(311)	1.416(4)
N(212)–Ru–N(22)	77.18(9)	N(112)–Ru–N(12)	76.79(10)	N(33)–Ru–N(31)	62.13(9)
3b					
Ru–N(12)	1.981(3)	Ru–N(22)	2.145(3)	Ru–N(112)	2.035(3)
Ru–N(31)	2.073(3)	Ru–N(212)	2.053(3)	Ru–C(332)	2.068(3)
N(11)–N(12)	1.312(4)	N(21)–N(22)	1.265(4)	N(31)–C(32)	1.298(4)
N(33)–C(331)	1.411(4)	C(32)–N(33)	1.341(4)	C(331)–C(332)	1.394(4)
N(212)–Ru–N(22)	74.28(11)	N(12)–Ru–N(112)	76.35(11)	N(31)–Ru–C(332)	88.05(12)

C(32) (1.337(4) Å) are almost identical and are intermediate between a typical C–N (1.47 Å) and C=N (1.27 Å), which indicates strong delocalization of electronic charge along the NCN skeleton. The coordination mode of the amidinate ligand in **2b** may best be described as σ,σ symmetrical bidentate chelate [5]. *N*-aryl bond lengths, viz. N(31)–C(311) (1.416(4) Å) and N(33)–C(331) (1.414(4) Å) are single bonds. Amongst the six metal–nitrogen bonds, the two Ru–N(azo) lengths are short and notably the two –N=N– lengths are elongated considerably due to strong dπ–pπ interactions between ruthenium(II) and the π*(azo) of the L ligand [11]. Consequently, the $\nu_{N=N}$ stretching in these complexes appears at considerable low (ca. 1290 cm^{-1}) frequencies.

The X-ray structure of the compound **2b** revealed that there is a twofold axis of symmetry in this compound. The ^1H NMR spectra of **2** are resolved and data are collected in Table 2, a representative spectrum is displayed in Fig. 2a. The ^1H NMR spectrum of **2a** showed only one methyl resonance at δ, 2.0. The compound **2b**, on the other hand, displayed two methyl resonances at δ, 2.3 and 2.0. The intensity of the methyl resonance at δ, 2.3 is twice that of the resonance at δ, 2.0. Accordingly, the latter resonance is assigned to amidinate methyl protons whereas the former is assigned to aryl-methyl protons signal [12a]. The four-pyridyl proton signals appeared in the range δ, 8.7–7.8. The resonance near δ, 170 in the ^{13}C NMR spectra (Supplementary Fig. S1) of these complexes is assigned to the middle carbon of NCN skeleton of the amidinate ligand [13].

A view of cationic part of the molecule, **3b** is shown in Fig. 3. This is a mixed trischelate comprising of two bidentate neutral N∧N donor ligands and an *ortho*-metalated amidine ligand formed via $ArNH_2$ addition to one of the two coordinated CH_3CN. The imine nitrogen of amidine together with the *ortho*-carbon of the aryl ring binds to the central metal atom forming a six member chelate ring. Such a binding mode of an amidine ligand is rare [13b]. The complex as a whole is monocationic, and the crystallographic asymmetric unit also contains one unit of perchlorate. The bond parameters of **3b** are collected in Table 1. The two diazo lengths along with the two Ru–N (azo) lengths are notably different. For example, the Ru–N(22) bond (2.145(3) Å), which is *trans* to the C-bonded aryl group, is appreciably longer than the Ru–N(12) length, 1.981(3) Å. Notably, the N(21)–N(22) length, 1.265(4) Å of one of the two coordinated L ligands is almost similar to that observed (1.258(5) Å) in the uncoordinated salt $[HL]ClO_4$, however this length (N(11)–N(12), 1.312(4) Å) in the second coordinated L ligand is elongated appreciably [12b]. These may be attributed to the strong *trans* influence of C-bonded aryl function, which is also responsible for weaker Ru-azo back bonding interaction [14]. The Ru–N (pyridyl) as well as Ru–N (imine) lengths are normal.

Due to unsymmetrical nature of the coordinated amidine ligand, the symmetry in the complexes **3** is lost and as a result a large number of resonances were observed in their ^1H NMR spectra due to the presence of several unique protons [12]. Eight distinct pyridyl proton resonances of the two coordinated L ligands were observed in the range δ, 8.5–7.3 (Table 2, Fig. 2b). Two broad singlet resonances at δ, 8.3 and 5.8 are assigned to the N–H (imine) and N–H (amine) resonances of the amidine ligand, respectively [9b,4a]. The C(333)–H resonance in **3b** is a singlet and it became doublet in the unsubstituted complex, **3a**. This result further confirms *ortho*-metalation of the aryl ring of the amidine ligand. While the complex, **3a** displayed a methyl resonance at δ, 2.0 the complex, **3b**, on the other hand, showed two methyl resonances at δ, 2.4 and 2.0. The ^{13}C NMR of the complexes **3** (Supplementary Fig. S1), showed a resonance systematically near δ, 151 assignable to the carbon bonded to ruthenium [15].

The synthetic reactions were carried out in neat $ArNH_2$. The primary step of these transformations involves addition of one equivalent of the aromatic amine across the ruthenium(II) coordinated acetonitrile function to yield an amidine intermediate [A], $[RuL_2(CH_3CN)[NH{=}C(CH_3)N(H)Ar]^{2+}$ [9b]. The formation of the complex **2** from [A] involved several steps: addition of second equivalent of aromatic amine at the intermediate [A], release of ammonia and proton loss is the plausible steps involved in this transformation [16]. Our proposal on the reaction

Table 2
^{1}H NMR data of complexes **2** and **3** in $CDCl_3$

Compound	N–H proton		Chemical shift[a,b,c] in ppm		
	Imine	Amine	Pyridyl proton	Aromatic proton	Methyl proton
2a			8.70(d, 1H, $J = 5.3$), 8.49(d, 1H, $J = 8.0$), 8.20(t, 1H, $J = 7.0$), 7.87(t, 1H, $J = 7.0$)	7.38(t, 1H, $J = 7.7$), 7.15(m, 2H), 7.10(m, 2H), 7.01(t, 1H, $J = 7.3$), 6.58(d, 2H, $J = 8.0$), 6.20(d, 2H, $J = 7.5$)	2.0(s)
3a	8.31(s) (1H)	5.88(s) (1H)	8.57(d, 1H, $J = 5.6$), 8.51(d, 1H, $J = 8.0$), 8.43(d, 1H, $J = 8.0$), 8.08(d, 1H, $J = 5.0$), 7.94(t, 1H, $J = 7.0$), 7.82(t, 1H, $J = 7.2$), 7.39(t, 1H, $J = 7.4$), 7.34(t, 1H, $J = 6.0$)	7.18(t, 2H, $J = 7.9$), 7.08(t, 2H, $J = 7.8$), 7.00(d, 2H, $J = 7.9$), 6.92(m, 2H), 6.71(t, 1H, $J = 6.3$), 6.29(d, 1H, $J = 7.4$)	2.0(s)
2b			8.67(d, 1H, $J = 5.2$), 8.49(d, 1H, $J = 8.0$), 8.21(t, 1H, $J = 7.9$), 7.84(t, 1H, $J = 6.2$) 6.06(d, 2H, $J = 8.2$)	7.38(t, 1H, $J = 7.5$), 7.16(t, 2H, $J = 7.8$), 6.88(d, 2H, $J = 8.1$), 6.58(d, 2H, $J = 8.0$),	2.0(s), 2.3(s)[d]
3b	8.32(s) (1H)	5.74(s) (1H)	8.56(d, 1H, $J = 5.9$), 8.50(d, 1H, $J = 8.0$), 8.45(d, 1H,$J = 8.0$), 8.08(d, 1H, $J = 4.9$), 7.94(t, 1H, $J = 7.8$), 7.83(t, 1H, $J = 7.7$), 7.47(t, 1H, $J = 6.6$), 7.39(t, 1H, $J = 7.3$)	7.17(t, 2H, $J = 7.9$), 7.08(t, 2H, $J = 7.8$), 6.99(d, 2H, $J = 8.0$), 6.86(d, 1H, $J = 8.2$), 6.70(d, 1H, $J = 7.8$), 6.07(s, 1H)	2.0(s), 2.4(s)[d]
2c			8.66(d, 1H, $J = 5.4$), 8.48(d, 1H, $J = 8.0$), 8.20(t, 1H, $J = 7.2$), 7.84(t, 1H, $J = 6.0$) 6.12(d, 2H, $J = 8.7$)	7.40(t, 1H, $J = 7.4$), 7.14(t, 2H, $J = 7.9$), 6.65(d, 2H, $J = 6.9$), 6.60(d, 2H, $J = 7.8$),	1.9(s), 3.76(s)[e]
3c	8.72(s) (1H)	5.58(s) (1H)	8.55(d, 1H, $J = 5.6$), 8.49(d, 1H, $J = 7.8$), 8.43(d, 1H, $J = 8.0$), 8.12(d, 1H, $J = 5.5$), 7.94(t, 1H, $J = 7.6$), 7.81(t, 1H, $J = 7.7$), 7.44(t, 1H, $J = 6.5$), 7.38(t, 1H, $J = 7.3$)	7.14(m, 3H), 7.05(m, 2H), 6.89(d, 2H, $J = 7.9$), 6.42(d, 1H, $J = 5.9$), 5.82(s, 1H)	2.0(s), 3.57(s)[e]

[a] Solvent $CDCl_3$.
[b] Multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet).
[c] The coupling constant (J in Hz) are given in parentheses.
[d] CH_3 of toluidine.
[e] OCH_3 of anisidine.

pathways is based on the previous results on the similar reactions of amines with organonitriles catalyzed by lanthanide(III) ions. However, our experimental conditions did not allow us to detect ammonia in the gasses evolved from the reference reaction mixture. The complex **3**, on the other hand, is a result of cyclometalation due to C–H activation of the amidine intermediate. Successive steps for the formation of the complexes **2** and **3** from the amidine intermediate, [A] are shown in Scheme 2. The fact that the compounds **2** and **3** are not inter-convertible also supports the proposed reaction scheme. Since the reactions proceed only in neat aromatic amine it may be possible that amine acts not only as a nucleophile but also as a suitable solvent for these transformations.

Electronic spectra of the ruthenium complexes, recorded in dichloromethane solution, showed several intense absorptions in the visible and ultraviolet regions (Table 3). Two representative spectra of **2b** and **3b** are shown in Fig. 4. The absorptions in the UV-region are assigned to transitions within the ligand orbitals. The color of the

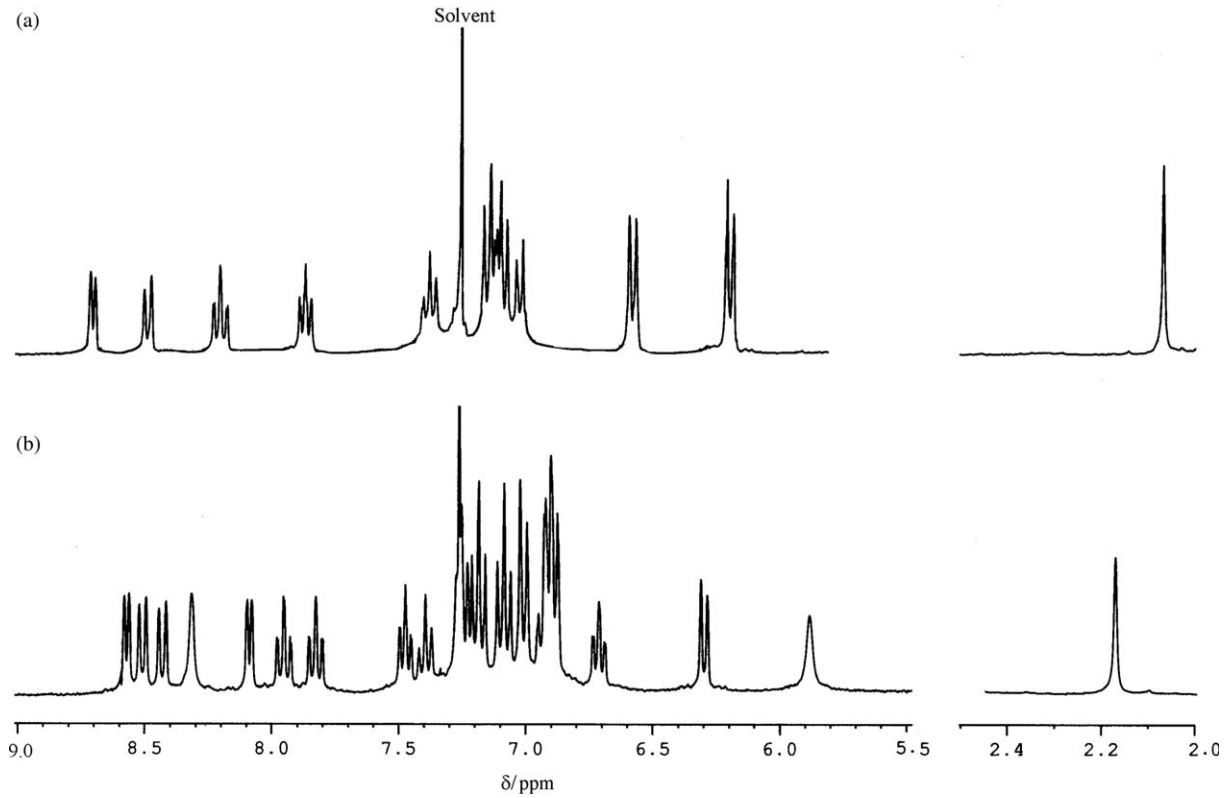


Fig. 2. ^{1}H NMR spectra of (a) **2a** and (b) **3a** in $CDCl_3$ at 298 K.

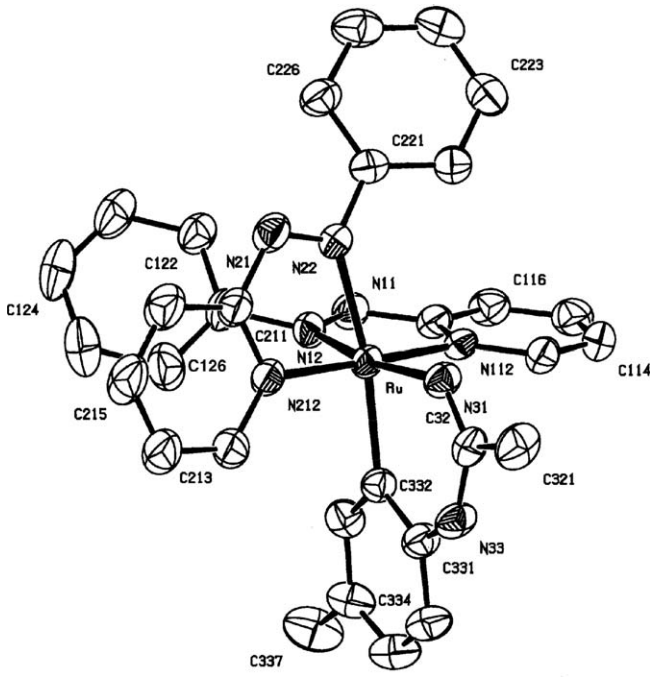


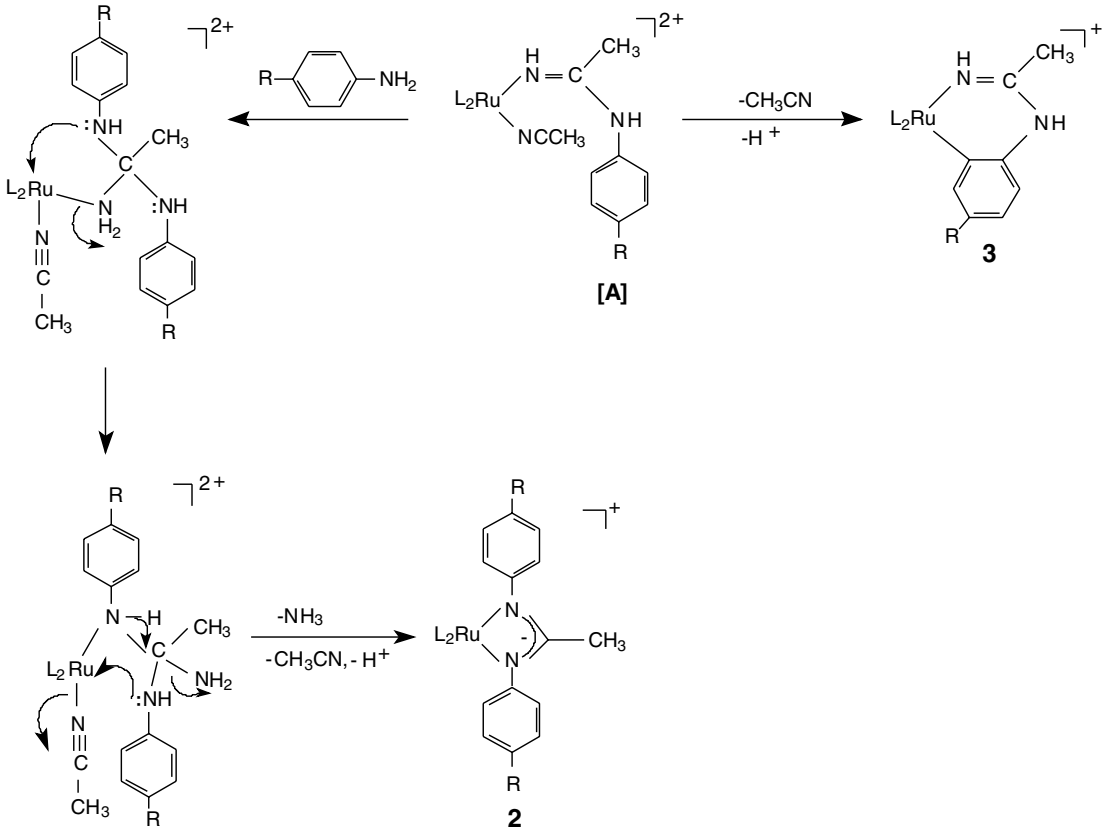
Fig. 3. ORTEP and atom numbering scheme for **3b**. Hydrogen atoms are omitted for clarity.

complex **2** is violet while that of **3** is blue. A strong visible range transition for **2** appeared near 570 nm and that for **3** appeared near 600 nm. By analogy with the reported ruthenium(II)–L systems, the lowest energy transition in each case is attributed to $Ru(d\pi) \rightarrow \pi^*(azo)$ MLCT transition [17]. The donor $Ru(d\pi)$ orbital of **2** is more stabilized than that of **3** (see below) and is responsible for the red shift of MLCT transition energy in moving from **2** to **3**. We note that MLCT band of both **2** and **3** are associated with a shoulder at higher energy.

Electrochemical properties of the complexes were studied by cyclic voltammetry in dichloromethane (0.1 M TBAP). Voltammetric data are collected in Table 3. The complexes showed a reversible oxidative response on the positive of SCE and two reversible reductive responses at the negative potentials (Fig. 5). Notably, the anodic potential response of **2** is more anodic than that of **3** by 160–170 mV. The cathodic potential responses are attributed to successive reductions of L ligands while, the anodic potential response is due to Ru(II)–Ru(III) oxidation [17]. The oxidation of the present complexes occur at high anodic potentials, making the ruthenium(III) species strong oxidants and reactive. The color of the coulometrically oxidized solutions of $[\mathbf{2a}]^+$ and $[\mathbf{3a}]^+$ are orange and brownish pink, respectively. These are not stable enough for their isolation. These transformed to a mixture of products, which have not been characterized.

3. Conclusion

We have presented the results of an unprecedented type of organoamine addition reaction on a ruthenium(II)-coordinated acetonitrile. Two excellent π-acceptor ancillary



Scheme 2.

Table 3
Electronic spectra and cyclic voltammetric data of complexes **2** and **3** in dichloromethane

Compound	Electronic spectra[a]	Cyclic voltammetry[c,d]	
	abs[λ_{max}/nm (ε/M^{-1} cm^{-1})]	Oxidation $E_{1/2}$/V (ΔE_p/mV)	Reduction $-E_{1/2}$/V (ΔE_p/mV)
2a	555 (7350), 465[b] (3510) 320 (27100), 235 (28500)	1.04 (100)	0.37 (105) 1.00 (85)
3a	600 (8500), 485[b] (4420) 335 (30000), 235 (35950)	0.87 (90)	0.52 (70) 1.20 (100)
2b	560 (10950), 470[b] (3350) 325 (29740), 230 (36900)	1.02 (100)	0.31 (95) 1.02 (80)
3b	595 (6700), 480[b] (3425) 340 (23190), 235 (29400)	0.86 (80)	0.49 (90) 1.22 (80)
2c	560 (9500), 480[b] (4200) 315 (26900), 230 (31850)	1.00 (80)	0.37 (90) 1.03 (70)
3c	595 (6270), 485[b] (3890) 340 (21575), 235 (28430)	0.84 (100)	0.53 (90) 1.24 (80)

[a] Solvent, dichloromethane.
[b] Shoulder.
[c] Solvent, dichloromethane; supporting electrolyte, TBAP.
[d] Potentials are referenced to SCE: scan rate, 50 mV s^{-1}.

diazo ligands in the starting complex play the key role in making the coordinated nitriles sufficiently electrophilic for nucleophilic double-addition reactions. Such a chemical transformation of coordinated organonitrile, to the best of our knowledge, was not available in the literature. In the present context we wish to note that nitriles in complexes where the metal ion is in low oxidation state, e.g., Ru(II) are sluggish addition reactions. Addition reactions in such complexes are reported in the presence of additional Lewis acids such as Ag^{+} or Cu^{2+} [18].

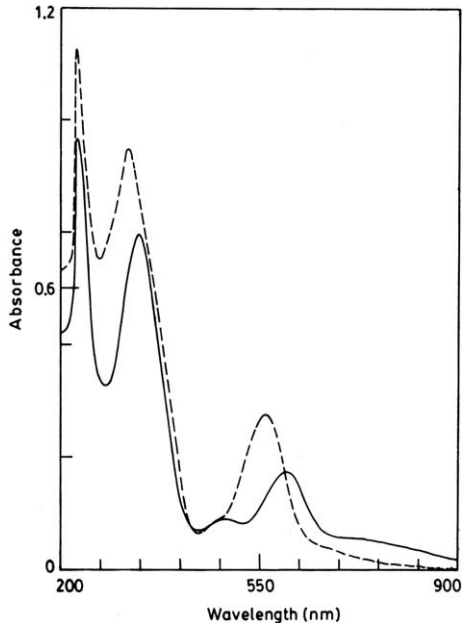


Fig. 4. UV-vis spectra of **2b** (---) and **3b** (—) in dichloromethane.

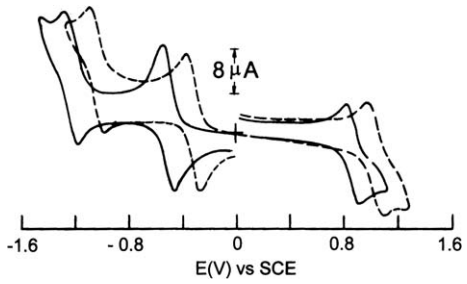


Fig. 5. Segmented cyclic voltammograms of **2b** (---) and **3b** (—) in dichloromethane (0.1 M TBAP).

4. Experimental

4.1. Materials

The starting complexes *cis*-$[L_2Ru(H_2O)_2](ClO_4)_2$ and *cis*-$[L_2Ru\ (CH_3CN)_2](ClO_4)_2$ were synthesized by the published procedures [10]. Solvents and chemicals used for synthesis were of analytical grade. Supporting electrolyte (tetrabutylammonium perchlorate) and solvents for electrochemical work were obtained as before [17].

Caution. Perchlorate salts of metal complexes can be explosive. Although no detonation tendencies have been observed, care is advised and handling of only small quantities recommended.

4.2. Physical measurements

A JASCO V-570 spectrometer was used to record electronic spectra. The IR spectra were obtained with a Perkin–Elmer 783 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance DPV 300 spectrometer using TMS as the internal standard. A Perkin–Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). Electrochemical measurements were done under a dry nitrogen atmosphere on a PAR 370-4 electrochemistry system as described before [17]. All potentials in this work are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution. The value for the ferrocenium–ferrocene couple under our experimental condition was 0.40 V. ESI mass spectra were recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263).

4.3. Amine addition reactions to *cis*-$[L_2Ru(CH_3CN)_2](ClO_4)_2$, **1**

The complexes **2** and **3** were isolated from the amine fusion reaction of $ArNH_2$ on *cis*-$[L_2Ru(CH_3CN)_2](ClO_4)_2$ (**1**) in neat. Details are given below for the reaction of *cis*-$[L_2Ru(CH_3CN)_2](ClO_4)_2$ (**1**) with aniline.

A mixture of *cis*-$[L_2Ru(CH_3CN)_2](ClO_4)_2$ (**1**) (100 mg, 0.135 mmol.) and freshly distilled aniline (1 ml) was heated at 100–110 °C on an oil-bath in argon atmosphere for 1.5 h. The initial reddish brown color of the mixture gradually became violet. The product was washed thoroughly with diethyl ether and was subjected to chromatography on a preparative TLC plate using 20% acetonitrile–chloroform mixture as the eluent. Two major bands viz. a violet and a blue was separated from the TLC plate. For purification of the products, the TLC experiment need be repeated thrice. Finally the two compounds were collected by complete evaporation of the eluates. The violet compound **2a** was recrystallized from a tetrahydrofuran–hexane solvent mixture.

2a Yield: 30%. Anal. Calc. for $C_{36}H_{31}N_8RuClO_4$: C, 55.65; H, 3.99; N, 14.42. Found: C, 55.68; H, 4.02; N, 14.40%. ^{13}C NMR (298 K, $CDCl_3$): $\delta = 171.25$ (amidinate-carbon), 164.85, 155.79, 150.51, 138.26, 137.55, 131.61, 129.30, 129.13, 127.77, 127.44, 124.72, 123.47, 122.40, 16.90. IR (KBr disk): ν 1620 (NCN), 1295 (N=N), 1100, 625 (ClO_4^-) cm^{-1}. ESI-MS: m/z 676 $[M - ClO_4]^+$.

The blue compound **3a**, was recrystallized from dichloromethane–tetrahydrofuran–hexane solvent mixture.

3a Yield: 28%. Anal. Calc. for $C_{30}H_{27}N_8RuClO_4$: C, 51.47; H, 3.85; N, 15.99; Found: C, 51.45; H, 3.88; N, 16.01%. ^{13}C NMR (298 K, $CDCl_3$): δ 166.39 (iminocarbon), 164.90, 157.97, 155.45, 153.75, 150.53, 148.32, 137.91, 137.15, 136.54, 135.80, 132.16, 129.81, 129.20, 128.74, 128.57, 125.51, 125.26, 124.81, 124.28, 123.58, 123.25, 122.63, 117.55, 117.39, 23.87. IR (KBr disk): ν 3400 (N–H), 1600 (C=N), 1290 (N=N), 1125, 610 (ClO_4^-) cm^{-1}. ESI-MS: m/z 600 $[M - ClO_4]^+$.

Compounds **2b**, **3b**, **2c** and **3c** were prepared similarly by following the above procedure using the appropriate substituted aromatic amines in place of aniline. Their yields and characterization data are collected below.

2b Yield: 35%. Anal. Calc. for $C_{38}H_{35}N_8RuClO_4$: C, 56.69; H, 4.35; N, 13.92. Found: C, 56.67; H, 4.38; N, 13.94%. ^{13}C NMR (298 K, $CDCl_3$): δ 172.51 (amidinate-

carbon), 166.89, 156.44, 151.38, 141.38, 139.35, 135.55, 132.61, 130.89, 130.18, 128.87, 128.27, 124.31, 123.53, 21.94, 17.74. IR (KBr disk) ν 1610 (NCN), 1290 (N=N), 1100, 610 (ClO_4^-) cm^{-1}. ESI-MS: m/z 704 $[M - ClO_4]^+$. **3b** Yield: 30%. Anal. Calc. for $C_{31}H_{29}N_8RuClO_4$: C, 52.08; H, 4.06; N, 15.68. Found: C, 52.06; H, 4.08; N, 15.69%. ^{13}C NMR (298 K, $CDCl_3$): δ 166.34 (iminocarbon), 164.90, 157.40, 155.42, 153.68, 151, 150.47, 148.23, 137.09, 135.76, 135.69, 132.25, 132.06, 129.79, 129.12, 128.63, 128.54, 127,54, 125.46, 125.36, 125.22, 124.14, 123.22, 122.58, 116.96, 23.54, 20.81. IR (KBr disk): ν 3400 (N–H), 1590 (C=N), 1295 (N=N), 1125, 620 (ClO_4^-) cm^{-1}. ESI-MS: m/z 615 $[M - ClO_4]^+$. **2c** Yield: 35%. Anal. Calc. for $C_{38}H_{35}N_8RuClO_6$: C, 54.52; H, 4.18; N, 13.39. Found: C, 54.55; H, 4.20; N, 13.36%. ^{13}C NMR (298 K, $CDCl_3$): δ 171.78 (amidinatecarbon), 165.74, 156.79, 155.28, 150.31, 138.00, 135.81, 131.37, 128.76, 127.07, 126.23, 124.19, 122.35, 114.22, 55.45, 16.46. IR (KBr disk): ν 1635 (NCN), 1295 (N=N), 1100, 630 (ClO_4^-) cm^{-1}. ESI-MS: m/z 736 $[M - ClO_4]^+$.

3c Yield: 30%. Anal. Calc. for $C_{31}H_{29}N_8RuClO_5$: C, 50.9; H, 4.0; N, 15.3. Found: C, 51.3; H, 4.2; N, 15.1%. ^{13}C NMR (298 K, $CDCl_3$): δ 166.33 (iminocarbon), 164.94, 157.47, 155.47, 154.97, 153.72, 152.31, 150.76, 148.26, 137.05, 135.83, 132.13, 132.10, 129.82, 129.21, 128.65, 128.59, 125.44, 125.32, 124.28, 123.18, 122.63, 121.36, 118.18, 109.75, 55.13, 23.74. IR (KBr disk): ν, 3450 (N–H), 1630 (C=N), 1290 (N=N), 1120, 625 (ClO_4^-) cm^{-1}. ESI-MS: m/z 631 $[M - ClO_4]^+$.

4.4. X-ray crystallographic study

Crystallographic data for the compounds **2b** and **3b** are collected in Table 4.

2b X-ray quality crystals ($0.38 \times 0.35 \times 0.28$ mm^3) of **2b** were obtained by slow diffusion of a tetrahydrofuran solution of the compound into hexane. The data were collected on a Nonius Kappa CCD diffractometer equipped with a graphite crystal, incident beam monochromator having Mo Kα radiation ($\lambda = 0.71073$ Å), and Lorentz and polarization corrections were applied to the data. A total of 26875 reflections were collected of which 9189 were unique ($R_{int} = 0.041$) and were used in subsequent analysis. An empirical absorption correction using SCALEPACK was applied [19]. The structure was solved using the structure solution program PATTY in DIRDIF-99 [20a] and refined by full-matrix least-squares based on F^2. Refinement was performed on a LINUX PC using SHELXL-97 [20b]. Crystallographic drawings were done using the programs ORTEP [21] and PLATON [22].

3b X-ray quality crystals ($0.41 \times 0.31 \times 0.13$ mm^3) of **3b** were obtained by slow diffusion of a dichloromethane solution of the compound into tetrahydrofuran and hexane solvent mixture. The data were collected as noted above. A total of 34090 reflections were collected, of which 7828 were unique ($R_{int} = 0.071$) and were used in subsequent analysis. An empirical absorption correction using SCALEPACK was applied [19]. The structure solutions, refinement as well as the crystallographic drawing were performed as mentioned above.

Table 4
Selected crystallographic data for compounds **2b** and **3b**

	2b	**3b**
Empirical formula	$C_{38}H_{35}N_8RuClO_4$	$C_{31}H_{29}N_8RuClO_4$
F_w	804.28	714.15
T (K)	220	150
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	10.9838(2)	14.5163(11)
b (Å)	27.4166(5)	15.1004(6)
c (Å)	13.0687(2)	16.1254(11)
α (°)	90	90
β (°)	100.1170(10)	109.735(3)
γ (°)	90	90
V (Å^3)	3874.29(12)	3327.1(4)
Z	4	4
D_c (Mg m^{-3})	1.379	1.43
Crystal size (mm)	$0.28 \times 0.35 \times 0.38$	$0.13 \times 0.30 \times 0.41$
θ Range for data collections (°)	2.2–27.9	2.1–27.9
λ (Å)	0.71073	0.71073
Reflections collected	26875	34090
Unique reflections	9189	7828
Absorption correction	SCALEPACK	SCALEPACK
Largest diff. between peak and hole (e Å^{-3})	−0.87, 0.76	−1.01, 0.78
Final R indices [$I > 2\sigma(I)$]		
R_1[a]	0.050	0.051
wR_2[b]	0.126	0.127
R indices (all data)		
R_1[a]	0.084	0.086
wR_2[b]	0.138	0.139
Number of parameters (N)	472	417
Goodness-of-fit[c]	0.997	0.935

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.
[b] $wR_2 = [\sum\{w(F_o^2 - F_c^2)^2\} / \sum\{w(F_o^2)\}]^{1/2}$.
[c] GOF $= [\sum\{w(F_o^2 - F_c^2)^2\}/(M - N)]^{1/2}$, where M is the number of reflections and N is the number of parameters refined.

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Appendix A. Supplementary data

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 264209 and 264210 for complexes **2b** and **3b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax (int code): +44 1223 336 033, or email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk. ^{13}C NMR (Fig. S1) of complexes **2b** and **3b** in $CDCl_3$ is available as supporting information. Supplementary data associated with this article can be

found, in the online version, at doi:10.1016/j.jorganchem.2006.02.033.

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