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# Ruthenium-mediated selective activation of a C–H bond. Direct aromatic thiolation in the complexes $[Ru^{II}\{o\text{-}SC_6H_3(R)N{=}NC_5H_4N\}_2]$ (R = H, Me or Cl)

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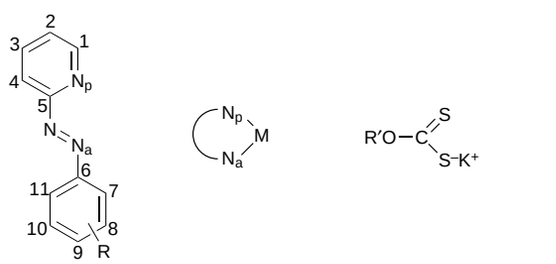
The reaction of the complexes *ctc*-$[Ru^{II}L_2Cl_2]$ (L = arylazopyridine, $RC_6H_4N{=}NC_5H_4N$, where R = H, *m*-Me, *p*-Me or *p*-Cl; *ctc* = *cis*-*trans*-*cis* with respect to chlorides, pyridine and azo nitrogens respectively) with $KS_2COR'$ (R′ = Me, Et, $Pr^n$, $Bu^n$ or $CH_2Ph$) in boiling dimethylformamide afforded $[Ru^{II}\{o\text{-}SC_6H_3(R)N{=}NC_5H_4N\}_2]$ where the *o*-carbon atom of the pendant phenyl ring of both ligands L has been selectively and directly thiolated. The newly formed tridentate thiolated ligands are bound in a meridional fashion. When one methyl group is present at the *meta* position of the pendant phenyl ring of L the reaction resulted in two isomeric complexes due to free rotation of the singly bonded *meta*-substituted phenyl ring with respect to the azo group. The molecular geometry of the complexes in solution has been determined by $^1$H NMR spectroscopy. This revealed the presence of an intimate mixture of the two isomers in solution in a 2:1 ratio. In the visible region the complexes exhibit two metal-to-ligand charge-transfer transitions at ≈700 and ≈560 nm respectively and in the UV region intraligand (π–π*, n–π*) transitions. In acetonitrile solution the complexes exhibit one reversible ruthenium(II) ⟷ ruthenium(III) oxidation couple near 0.4 V and an irreversible oxidative response near 1 V due to oxidation of the co-ordinated thiol group. Reduction of the co-ordinated azo groups occurs at *ca.* −0.8 and −1.4 V respectively. Coulometric oxidation of the complexes $[Ru^{II}\{o\text{-}SC_6H_3(R)N{=}NC_5H_4N\}_2]$ at 0.6 V *versus* the saturated calomel electrode in dichloromethane produced unstable ruthenium(III) congeners. When R = *p*-Me, the presence of trivalent ruthenium in the oxidised solution was evidenced by a rhombic EPR spectrum having $g_1 = 2.359$, $g_2 = 2.300$ and $g_3 = 1.952$.

Metal-mediated activation of the carbon–hydrogen bond is a fundamentally important chemical reaction[1] which may lead to the formation of interesting new molecules otherwise difficult or even impossible to synthesize by conventional routes. We have recently observed an unusual reaction where the *o*-carbon atom of the pendant phenyl ring of a co-ordinated arylazopyridine ligand $C_6H_4(R)N{=}NC_5H_4N$ (L) in the complex $[Ru^{II}L_2Cl_2]$ has been regiospecifically and directly thiolated to give $[Ru^{II}\{o\text{-}SC_6H_3(R)N{=}NC_5H_4N\}_2]$, *via* carbon–sulfur bond cleavage of the dithiocarbonate $KS_2COEt$. Metal-assisted carbon–sulfur bond cleavage and concomitant formation of a new carbon–sulfur centre is very important in biological systems[2] as well as in industry.[3] Preliminary synthetic aspects of this fascinating ruthenium-mediated selective and direct aromatic thiolation process (where R = H) have been communicated.[4] Herein we report a detailed account including the substrate, solvent and reagent dependencies, $^1$H NMR spectroscopic characterisation of the final product, metal- and ligand-centred electroactivities and spectroelectrochemical correlations.




$L^1$ R = H
$L^2$ R = 8-Me
$L^3$ R = 9-Me
$L^4$ R = 9-Cl

**1** ML

**2**
R′ = Me, Et, $Pr^n$, $Bu^n$ or $PhCH_2$

## Results and Discussion

### Synthesis

The four substituted arylazopyridine ligands used are abbreviated as $L^1$–$L^4$. The ligand L binds to the metal ions in a bidentate N,N′ manner forming a five-membered chelate ring ML **1**.

The reaction of potassium *O*-ethyl dithiocarbonate with the starting complex *ctc*-$[RuL^1{}_2Cl_2]$ **3a** (*ctc* = *cis*-*trans*-*cis* with respect to chlorides, pyridine and azo nitrogens respectively) in a ratio of 2.5:1 in boiling dimethylformamide (dmf) for 3 h results in a red-brown solution (Scheme 1). Chromatographic purification of the red-brown solution on a silica gel column yields pure complex **4a** in 70% yield, where the *o*-carbon atom of the pendant phenyl ring of both $L^1$ ligands in **3a** has been selectively thiolated ($C_6H_4H \longrightarrow C_6H_4SM$). Thus through this C–H activation process the bidentate N,N′ form of the parent ligand has been selectively transformed into a tridentate N,N′,S ligand. The newly formed tridentate ligands are bound to the ruthenium centre in a meridional fashion. The crystal structure of **4a** shows that during this conversion process (**3a** ⟶ **4a**) an overall internal geometrical reorganisation has taken place (in the starting complex **3** the pyridine and azo nitrogens are mutually *trans* and *cis* respectively whereas in **4a** they are in reverse orientation).[4]

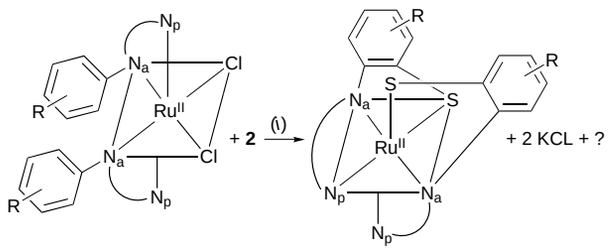
In the case of the starting complex **3b**, in which one methyl group is present at the *meta* position of the each active phenyl ring, the reaction in Scheme 1 is very facile under identical experimental conditions, being complete in 1 h. In view of the presence of this methyl group, free rotation along the C–N bond can lead to the formation of three possible isomers **5**–**7**. Indeed, an intimate mixture of isomers **5** and **6** has been detected in solution. Solution NMR study indicates that these two isomers exist in a 2:1 ratio (see below). All attempts to separate them either on a TLC plate or by column chromatography have failed.

The *para*-substituted ligands ($L^3$, $L^4$) in starting complexes **3c**

**Table 1** Microanalytical [a] and electronic spectral data [b]

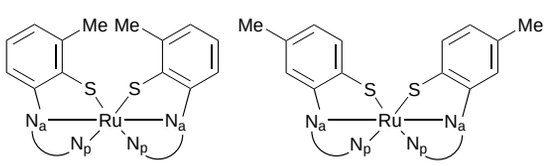
| Compound | Elemental analysis (%) C | H | N | S | UV/VIS λ/nm (ε/dm³ mol⁻¹ cm⁻¹) |
|---|---|---|---|---|---|
| **4a** | 49.85 (49.9) | 3.10 (3.00) | 15.89 (15.9) | 12.15 (12.1) | 710 (4980), 560 (13 220), 375 (26 990), 263 (37 960) |
| **4b** | 51.75 (51.7) | 3.55 (3.60) | 15.15 (15.1) | 11.4 (11.5) | 726 (4900), 562 (12 800), 384 (25 000), 260 (23 400) |
| **4c** | 51.8 (51.7) | 3.50 (3.60) | 15.15 (15.1) | 11.4 (11.5) | 706 (4600), 561 (12 700), 387 (26 900), 259 (21 800) |

[a] Calculated values are in parentheses. [b] In chloroform at 298 K.

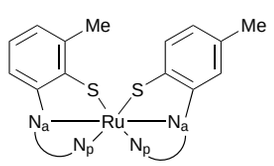



**3a** L = $L^1$ **4a**
**3b** L = $L^2$ **4b**
**3c** L = $L^3$ **4c**
**3d** L = $L^4$ **4d**

**Scheme 1** (*i*) Heat, dmf



**5** **6**



**7**

and **3d** surprisingly do not readily undergo the thiolation reaction. Complex **3c**, an electron-donating methyl group is present at the *para* position, reacts unexpectedly slowly and incompletely. Under identical reaction conditions to those in Scheme 1 more than 8 h were required to get only 10% pure **4c**. Further increase in the reflux time did not improve the yield. When an electron-withdrawing chloride group is present at the *para* position the reaction was not observed. This behaviour is not understood at present, however the results clearly indicate the simultaneous influence of positional and electronic factors of the substituents in the active phenyl ring on the C–H activation process.

The conversion of complex **3** into **4** is highly solvent dependent. In acetonitrile, benzene, dichloromethane, tetrahydrofuran, 2-methyltetrahydrofuran, ethanol, methanol and 2-methoxyethanol the reaction does not take place at all, whereas in dimethylformamide, methylformamide, dimethyl sulfoxide and hexamethylphosphoramide $P(NMe_2)_3O$ it occurs. This implies that both the boiling point and relative permittivity of the solvents are important. Dimethylformamide appears to be the best choice for maximum yield in the minimum time. In the absence of compound **2**, no change in the starting complex **3** is observed even under boiling. This may suggest the absence of direct participation of the solvent to form any solvent-containing reactive intermediates prior to the activation process.

The rate of the reaction is also dependent on the nature of the R′ group present in the dithiocarbonate **2**. The progress of the reaction was monitored qualitatively to semiquantitatively by TLC as well as spectrophotometrically in dmf solvent for all three complexes **3a**–**3c** using the different R′ groups in **2**. The reactivity order was as follows: Me ≈ Et > $Pr^n$ > $Bu^n$ > benzyl. This indicates that the nature of the leaving group (R′) of the thiolating agent plays an important role in the kinetic stability of the reaction.

In order to find other suitable thiolating agents, the reaction was tested with benzenethiol, carbon disulfide, $S_8$, thiirane, dithiocarbamate, $NaS_2P(OEt)_2$ and $NaS_2PPh_2$ instead of **2** but these failed to give the desired product **4**. The free L also did not undergo the transformation $NC_5H_4N{=}NC_6H_5 \longrightarrow NC_5H_4N{=}NC_6H_4SH$.

The microanalytical data of the products **4** (Table 1) are in good agreement with the calculated values and thus confirm the composition. Solid-state magnetic moment measurements at 298 K indicate that the complexes are uniformly diamagnetic ($t_{2g}^6$, $S = 0$). In acetonitrile, dimethylformamide and methanol the complexes are non-conducting. The IR, electronic, $^1$H NMR and electrochemical behaviours of **4a** are akin to those of the other complexes **4**, therefore it is inferred that **4a**–**4c** have very similar gross molecular structures.

### Infrared spectroscopy

The IR spectra of complexes **4** display several intense bands in the region 4000–300 $cm^{-1}$. No attempt was made to assign all the bands. However, two strong bands near 1595 and 1585 $cm^{-1}$ are assigned to ν(C=C) and ν(C=N) stretching frequencies respectively, and the ν(N=N) stretching frequency of the ligand is observed near 1280 $cm^{-1}$. The ν(N=N) of free L appears at 1425 $cm^{-1}$,[5] thus this frequency is appreciably lowered in complexes **4**. This is attributed to the presence of strong $d_\pi$ ($Ru^{II}$) ⟶ π*(L) back bonding in the ground state of ruthenium(II). The N=N frequency of the thiolato ligand present in complexes **4** cannot be checked as the free form is not available. However, a 150 $cm^{-1}$ shift of ν(N=N) in **4** compared to that in free L strongly supports the π-acidic nature of the present tridentate ligand. The complexes display two Ru–S stretching bands at 360 and 340 $cm^{-1}$ as expected.[6]

### Electronic spectra

The solution electronic spectra of the complexes were studied in chloroform solvent in the region 300–900 nm. The spectral data are listed in Table 1 and spectra are shown in Fig. 1. The complexes display several absorption bands in the specified region which may be due to the presence of different donor and acceptor levels. All exhibit one moderately intense broad band in the region 706–726 nm and a strong relatively sharper band near 560 nm. The band near 700 nm is sensitive to the nature of the substituents present, while that at 560 nm remains more or less unaffected. Based on the intensities of these two allowed visible bands (Table 1) the transitions are assigned to be charge

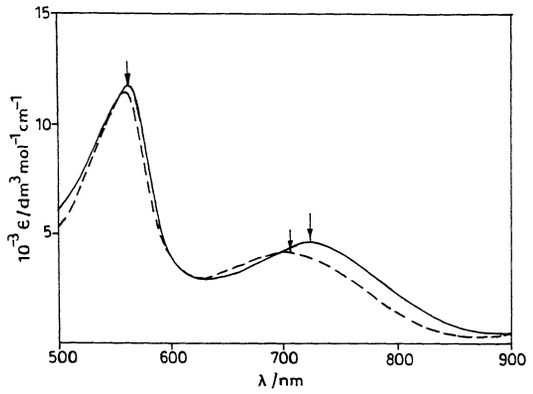



**Fig. 1** Electronic spectra of [Ru$^{II}${*o*-$SC_6H_3$(Me-*m*)N=$NC_5H_4N$}$_2$] **4b** (——) and [Ru$^{II}${*o*-$SC_6H_3$(Me-*p*)N=$NC_5H_4N$}$_2$] **4c** (– – – – –) in chloroform

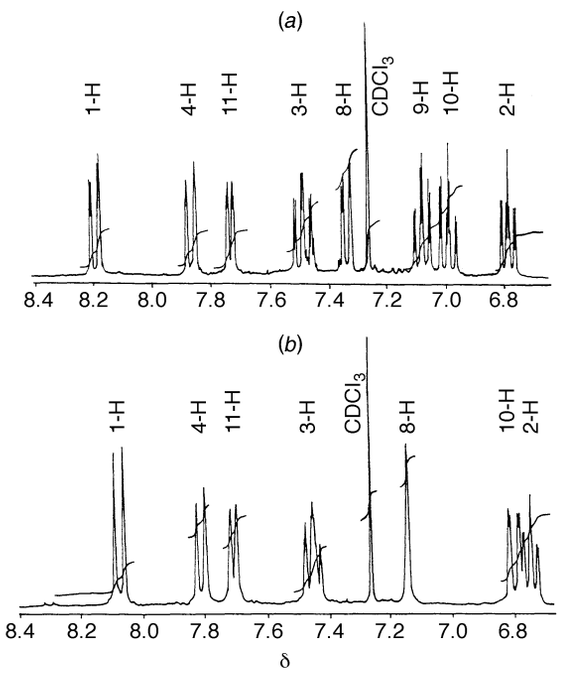



**Fig. 2** Proton NMR spectra in $CDCl_3$ of (*a*) [Ru$^{II}$(*o*-$SC_6H_4N$=$NC_5H_4N$)$_2$] **4a** and (*b*) [Ru$^{II}${*o*-$SC_6H_3$(Me-*p*)N=$NC_5H_4N$}$_2$] **4c**

transfer in nature. Since in these complexes the ruthenium(II) is in the low-spin $t_{2g}^6$ state, the spectra clearly require the presence of low-lying ligand LUMO (lowest unoccupied molecular orbital) and the LUMO +1 orbitals above the metal HOMO (highest occupied molecular orbital) to generate two metal-to-ligand charge-transfer (m.l.c.t.) transitions. According to a quick extended-Hückel calculation the ligand LUMO involves the S and the azo group, and the LUMO +1 is mainly on the pyridine with some azo contribution (results provided by a referee). Thus the lowest-energy band near 700 nm is due to the $d_\pi$ (Ru$^{II}$) ⟶ ligand LUMO transition. This explains the observed shifts in this transition with the substituent present in the activated phenyl rings (Table 1), the S and azo part of the molecule (which dominate the LUMO) being more affected by the Me substituents. For the starting complex **3** the $d_\pi$ (Ru$^{II}$) ⟶ L(π*) (where L π* is dominated by the LUMO of the azoimine chromophore) the m.l.c.t. transition occurs at 580 nm.[5] The charge-transfer transition energy is known to depend on the separation in potentials between the donor and acceptor levels.[7] In the present complexes **4** the difference in potentials between the first reduction couple (–N=N– reduction) and the reversible oxidation couple (Ru$^{II}$–Ru$^{III}$) is ≈1.2 V (Table 3) which is lower than that of the starting complex **3** (≈1.6 V).[5] In accordance with the above fact the m.l.c.t. transition which

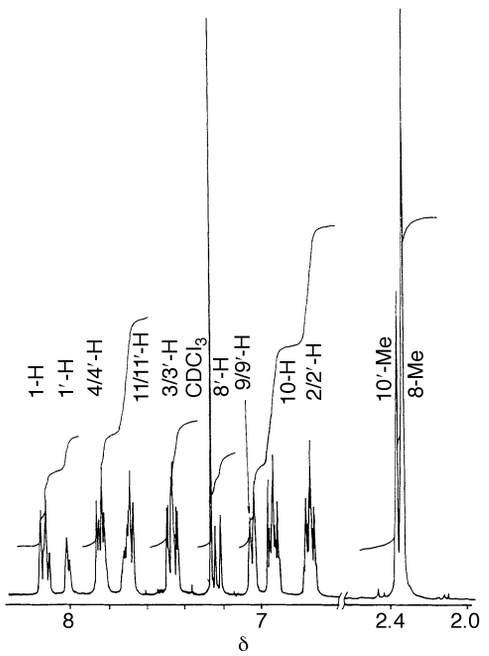



**Fig. 3** The $^1$H NMR spectrum of [Ru$^{II}${*o*-$SC_6H_3$(Me-*m*)N=$NC_5H_4N$}$_2$] **4b** in $CDCl_3$. Peaks due to isomer **5** are indicated by unprimed numbers and for **6** by primed ones

occurs at 580 nm for complex **3** is believed to take place near 700 nm for complexes **4**. This lowering in m.l.c.t. transition energy on going from **3** to **4** implies that the filled ruthenium $t_{2g}$ level becomes destabilised in the present ligand environments compared to those of **3**. The second m.l.c.t. band at 560 nm possibly originates from the $d_\pi$ (Ru$^{II}$) ⟶ LUMO +1 orbital transition. In the UV region the complexes show two bands possibly because of intraligand π–π* and n–π* transitions involving energy levels higher than those of the ligand LUMO.

At room temperature complexes **4** do not show any emission properties.

### $^1$H NMR spectra

The $^1$H NMR spectra of all the complexes were recorded in $CDCl_3$ solvent. The chemical shifts and the coupling constants are given in Table 2 and the spectra are displayed in Figs. 2 and 3. Complex **4a** exhibits four doublets and four triplets having equal intensities [Fig. 2(*a*)], *i.e.* each half of the molecule is equivalent due to localised symmetry around the ruthenium centre. The individual proton resonances were assigned on the basis of their relative intensities, spin–spin structure and also from the effect of the substituents.[8]

In the case of complex **4b** the aromatic region of the spectrum is complicated due to the presence of two isomers in solution, however the well resolved upfield methyl signals and direct comparisons of the individual methyl intensities with those of respective aromatic protons enabled us to reach reasonable conclusions. The presence of the methyl group at the *meta* position of the active phenyl ring in both ligands of **4b** yields three isomers **5**–**7** through free rotation of the singly bonded *meta*-substituted phenyl rings. The $^1$H NMR spectrum of **4b** displays two distinct methyl signals having unequal intensities. From the symmetry point of view one methyl signal is expected for each of isomers **5** and **6** and two equally intense peaks for **7**. As the spectrum displays two unequally intense methyl peaks at δ 2.32 and 2.37 respectively (Fig. 3), having intensity ratio 2:1, isomers **5** and **6** are predominant in solution. The downfield portion of the spectrum is overcrowded due to partial overlapping of the aromatic protons of isomers **5** and **6**, which precluded unequivocal assignment of the signals as doublets or triplets. However, a tentative assignment can be made by comparing the spectrum of **4b** with those of **4a** and **4c**. All pyridine protons

**Table 2** Proton NMR spectral data in $CDCl_3$

| | δ (*J*/Hz)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | H(1) | H(2) | H(3) | H(4) | H(8) | H(9) | H(10) | H(11) |
| **4a** | 8.19 (8.8)[b] | 6.78 (6.7)[c] (6.9) | 7.49 (7.0)[c] (8.0) | 7.87 (8.2)[b] | 7.34 (8.6)[b] | 7.08 (6.9)[c] (7.3) | 6.98 (7.3)[c] (7.7) | 7.73 (5.8)[b] |
| **4b**[d] | | | | | | | | |
| Isomer **5** | 8.14[b] | 6.76[c] | 7.47[c] | 7.84[b] | 2.32 (Me) | 7.05[b] | 6.93[c] | 7.70[b] |
| Isomer **6** | 8.0[b] | 6.76[c] | 7.47[c] | 7.84[b] | 7.23[b] | 7.05[b] | 2.37 (Me) | 7.70[e] |
| **4c** | 8.07 | 6.75 | 7.33 | 7.81 | 7.14[e] | 2.33 (Me) | 6.40 | 7.70 |
| | (8.8)[b] | (6.9)[c] (6.9) | (8.3)[c] (7.6) | (8.0)[b] | | | (8.4)[b] | (5.5)[b] |

[a] Tetramethylsilane is the internal standard. [b] Doublet. [c] Triplet. [d] Owing to overlapping signals it does not seem possible to determine the *J* values for doublets or triplets unequivocally. [e] Singlet.

**Table 3** Electrochemical data at 298 K[a]

| | | Ligand | | | $\tilde{\nu}$(m.l.c.t.)/$cm^{-1}$ | |
|---|---|---|---|---|---|---|
| Compound | $Ru^{III}$–$Ru^{II}$ couple $E^\circ_{298}$/V ($\Delta E_p$/mV) | oxidation $E_{pa}$/V | Ligand reductions $E^\circ_{298}$/V ($\Delta E_p$/mV) | $\Delta E$[b]/V | Obs.[c] | Calc.[d] |
| **4a** | 0.43 (70) | 1.04 | −0.80 (60)<br>−1.37 (80) | 1.23 | 14 080 | 12 920 |
| **4b** | 0.37 (60) | 1.04 | −0.83 (60)<br>−1.39 (80) | 1.20 | 13 770 | 12 680 |
| **4c** | 0.34 (70) | 1.01 | −0.85 (60)<br>−1.40 (70) | 1.19 | 14 160 | 12 600 |

[a] Conditions: solvent, acetonitrile; supporting electrolyte, $NEt_4ClO_4$; reference electrode, SCE; solute concentration, $10^{-3}$ mol $dm^{-3}$; working electrode, platinum. Cyclic voltammetric data: scan rate, 50 mV $s^{-1}$; $E^\circ_{298} = 0.5$ ($E_{pc} + E_{pa}$) where $E_{pc}$ and $E_{pa}$ are the cathodic and anodic peak potentials respectively. [b] Calculated by using equation (5) of the text. [c] In $CHCl_3$ solution. [d] Using equation (4) of the text.

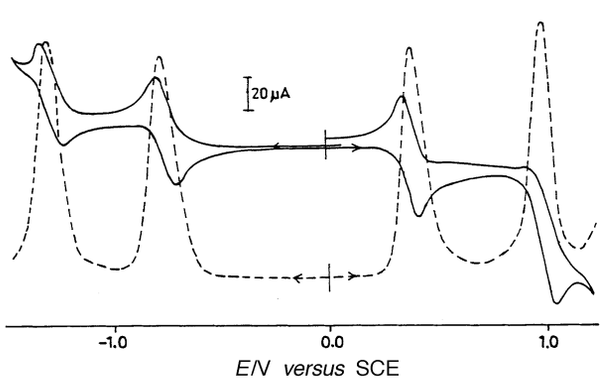



**Fig. 4** Cyclic voltammograms and differential-pulse voltammograms (scan rate 50 mV $s^{-1}$) of a ≈$10^{-3}$ mol $dm^{-3}$ solution of complex **4a** in acetonitrile

except $H^1$ for the isomers **5** and **6** appear together. Phenyl-ring protons such as $H^{10}$ (triplet) for isomer **5** and $H^8$ (doublet) for isomer **6** appear separately, while $H^9$ (doublet) for both isomers and $H^{11}$ (doublet for **5** and singlet for **6**) appear together (Fig. 3, Table 2).

One methyl peak has been observed for complex **4c** at δ 2.33 as imposed symmetry makes the two ligands equivalent. All the seven aromatic proton signals are well resolved. Two doublets and two triplets from the pyridine ring and two doublets and one singlet from the phenyl ring are observed distinctly as expected [Fig. 2(*b*), Table 2].

## Electron-transfer properties

The electron-transfer properties of complexes **4** have been studied in acetonitrile solution by cyclic voltammetry (CV) using a platinum working electrode. The complexes are electroactive with respect to the metal as well as the ligand centres and display the same four redox processes in the potential range ±1.5 V *versus* saturated calomel electrode (SCE) (tetraethylammonium perchlorate as electrolyte, 298 K). Representative voltammograms are shown in Fig. 4. The peak-to-peak separations of the couples lie in the range 60–80 mV. Reduction potential data are listed in Table 3. The assignments of the responses to specific couples are based on the following considerations.

**Ruthenium(II)–ruthenium(III) couple.** All the complexes display one reversible wave with characteristic anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak potentials near 0.4 V. The anodic and cathodic peak heights are equal and vary as the square root of the scan rate. This reversible oxidation process is assigned to the ruthenium(III)–ruthenium(II) couple, equation (1). Its one-

$$[Ru^{III}L_2]^+ + e^- \rightleftharpoons [Ru^{II}L_2] \quad (1)$$

electron nature was confirmed by constant-potential coulometry. The peak potentials ($E_{pa}$ and $E_{pc}$) are virtually independent of the scan rate. The presence of trivalent ruthenium in the oxidised solution was confirmed by the characteristic rhombic EPR spectrum of the ruthenium(III) complex (Fig. 5). The formal potential of the couple varies depending on the R group present in the ligand as expected (Table 3). The ruthenium(II)–ruthenium(III) oxidation potential of the starting complex **3** appears near 1.1 V.[5] Thus thiolation of the *o*-carbon atom of the pendant phenyl ring of L in **4** decreases the $Ru^{II}$–$Ru^{III}$ oxidation potential by ≈0.7 V. The parent azopyridine ligand (L in **3**) is known to stabilise low-valent metal complexes (bivalent in the case of ruthenium), due to its high π-acidic character and this is always reflected in the high $Ru^{II}$–$Ru^{III}$ oxidation potential.[9] The lowering of the oxidation potential in the present complexes **4** is due to the presence of the σ-donor thiol group in the tridentate form of the azopyridine ligand in the complexes. Complexes **4** exhibit the lowest oxidation potential in an environment formed by the azopyridine moiety.

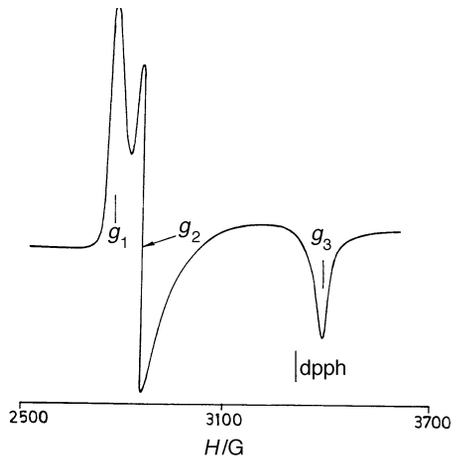



**Fig. 5** X-Band EPR spectrum of the coulometrically oxidised $[Ru^{III}\{o\text{-}SC_6H_3(Me\text{-}p)N{=}NC_5H_4N\}_2]^+$, in dichloromethane solution at 77 K. G = $10^{-4}$ T

**Ligand oxidation.** All complexes **4** exhibit a second irreversible oxidation response (anodic peak, $E_{pa}$) near 1.0 V *vs.* SCE. No significant response on scan reversal in cyclic voltammetry is observed (Fig. 4, Table 3) for the complexes in this region. The oxidised complex thus decomposes rapidly on the cyclic voltammetric time-scale. Although the anodic current height ($i_{pa}$) of this irreversible process is ≈2.0 times that of the previous reversible ruthenium(II)–ruthenium(III) process, the differential pulse voltammogram shows the second oxidation wave to have the same height as that of the first, implying a one-electron process (Fig. 4). This irreversible oxidation process could be due to either $Ru^{III} \longrightarrow Ru^{IV}$ oxidation or oxidation of the co-ordinated thiol group. Here the potential difference between the two successive oxidation processes is ≈0.7 V. The average potential differences between the two successive redox processes of the ruthenium centre ($Ru^{II/III} - Ru^{III/IV}$) in mononuclear complexes having C, N, O, thioether donor centres have been observed in many cases to be in the range 1.3–1.5 V.[10] Therefore it seems reasonable to consider this irreversible response as due to oxidation of the co-ordinated thiol group.

**Ligand reduction.** All the complexes display two successive reversible one-electron reductions near −0.8 and −1.3 V (Fig. 4, Table 3). The azopyridine ligand in **3** is known to act as a potential electron-transfer carrier.[5] Each ligand can accommodate two electrons in one electrochemically accessible LUMO which is primarily azo in character. As two electroactive azo groups are present in complexes **4**, four successive one-electron reductions are expected for each complex. In practice two one-electron reductions are observed experimentally which are assigned to the reductions of the azo groups of the ligands as shown in equations (2) and (3). The other two reductions are

$$[Ru^{II}L_2] + e^- \rightleftharpoons [Ru^{II}L(L^{\cdot -})]^- \quad (2)$$

$$[Ru^{II}L(L^{\cdot -})]^- + e^- \rightleftharpoons [Ru^{II}L^{\cdot -}{}_2]^{2-} \quad (3)$$

not detected, presumably due to solvent cut-off. Complexes **4** also exhibit the lowest reduction potentials for the azo function of the co-ordinated azopyridine.[11]

### Spectroelectrochemical correlation

The complexes display lowest m.l.c.t. transitions of the type $t_2$ (Ru) ⟶ ligand LUMO (where LUMO is dominated by the azo group and S of the ligand) near 700 nm (Table 1), reversible ruthenium(III)–ruthenium(II) reduction potentials near 0.4 V and first ligand (−N=N−) reduction potentials near −0.8 V (Table 3). The m.l.c.t. transition involves excitation of the electron from the filled $t_{2g}^6$ orbital of ruthenium to the π* orbital of the azo function (the first ligand reduction). The energy of this band can be predicted with the help of equations (4) and (5).[12]

$$\tilde{\nu}(\text{m.l.c.t.}) = 8065(\Delta E^\circ) + 3000 \quad (4)$$

$$\Delta E^\circ = E^\circ_{298}(Ru^{III}\text{–}Ru^{II}) - E^\circ_{298}(L) \quad (5)$$

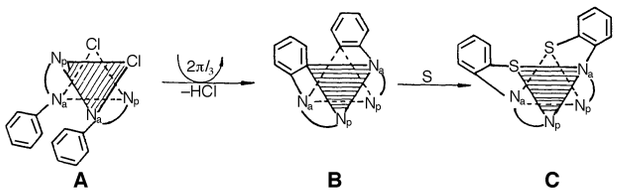
Here $E^\circ_{298}(Ru^{III}\text{–}Ru^{II})$ is the formal potential (in V) of the reversible ruthenium(III)–ruthenium(II) couple, $E^\circ_{298}(L)$ is the first ligand reduction and $\tilde{\nu}$(m.l.c.t.) is the wavenumber of the charge-transfer band in $cm^{-1}$. The factor 8065 is used to convert the potential difference $\Delta E$ from V into $cm^{-1}$ and the term 3000 $cm^{-1}$ is of empirical origin. The calculated m.l.c.t. energies and experimentally observed m.l.c.t. transitions are given in Table 3, and there is a linear relationship between the $\tilde{\nu}$(m.l.c.t.) and $\Delta E$. The involvement of the sulfur in the LUMO along with the azo group may explain why the redox–charge transfer energy correlation gives errors that all lie outside those quoted by Chakravorty and co-workers[12] for other azopyridine ligand systems.

### Electrogeneration of the trivalent ruthenium congener

Coulometric oxidation of complexes **4** in dichloromethane solution at 0.6 V *versus* SCE using a platinum-gauze working electrode produces a light red solution and the observed Coulomb count corresponds to a one-electron transfer ('*n*' values: **4a**, 0.97; **4b**, 1.02; **4c**, 0.95; $n = Q/Q'$ where $Q'$ is the calculated Coulomb count for a one-electron transfer and $Q$ that found after exhaustive electrolysis of $10^{-2}$ mmol of solute). The resulting oxidised solution shows a cyclic voltammogram which is identical to that of the starting bivalent complex, $[Ru^{II}L_2]$; this may be due to the stereoretentive nature of the oxidation process. Although the complexes exhibit reasonably low ruthenium(II)–ruthenium(III) oxidation potentials, the oxidised solution is unstable. However, in one case (R = *p*-Me) we have succeeded in recording the X-band EPR spectrum of the oxidised species by quickly freezing the solution (liquid $N_2$). The rhombic nature of the spectrum (Fig. 5) at 77 K ($g_1 = 2.359$, $g_2 = 2.300$, $g_3 = 1.952$) is characteristic of trivalent ruthenium(III) in a distorted-octahedral environment (low-spin $Ru^{III}$, $t_{2g}^5$, $S = \frac{1}{2}$).[13]

The mechanism of this ruthenium-mediated selective activation of the C–H bond of the phenyl ring of L is not yet clearly understood, primarily due to two reasons: (*i*) the reaction occurs under drastic conditions and (*ii*) it does not proceed with any tractable intermediate. In ruthenium chemistry cyclometallation of the pendant phenyl ring of azobenzene,[14] azobenzene thioether[15] and azophenol[16] ligands and cyclopalladation of azopyridine[17] are known. On the basis of the above evidence we assume that the reaction here may proceed through the orthometallated species (**B**) as reactive intermediate (Scheme 2). In the starting complex **3** (structure confirmed crystallographically[18]) the phenyl ring of both L units (which are active sites for the thiolation reaction) exists far away from the chlorides (the leaving groups) with the pyridine and azo nitrogens being mutually *trans* and *cis* respectively (**A**).

In the final product **C**, however, the relative orientation of the respective nitrogens is exactly the opposite. Since **A** does not isomerise to the corresponding dichloro species of **C** (where the pyridine and azo nitrogens are *cis* and *trans* respectively) under similar reaction conditions but in the absence of compound **2**, it may be considered that as a first step of the reaction the chlorides are replaced through formation of the four-membered orthometallated species **B** in the presence of **2**. To facilitate the formation of **B**, proximity of the phenyl rings of **L** and the chloride ions is essential and can only be achieved *via* a geometrical reorientation possibly through a Bailar twist mechanism (Scheme 2). This satisfies the positional requirements




**Scheme 2**

needed for the first step of the activation process which eventually leads to the formation of **C** *via* the insertion of sulfur (generated by cleavage of the C–S bond of dithiocarbonate **2**) into the reactive metal–carbon σ bond. Bearing the proximity of these groups in complex **3** in mind, the reaction of **2** with the other stable isomers of **3** such as *ttt* (where both phenyl rings are close to chlorides) and *ccc* (where one phenyl ring is close to one chloride ion) were performed in dmf solvent. Instead of undergoing the direct thiolation reaction both isomers are rapidly isomerised to the *ctc* isomer (known to be the most stable isomer of the starting complex **3**[5]) which subsequently gives product **4**. The invisibility of the proposed orthometallated intermediate **B** (if it exists) is evidently due to its extreme reactivity in the presence of the incoming sulfur group, which may originate from the presence of an unfavourable four-membered cyclometallated ring.

## Conclusion

We have observed ruthenium-mediated intramolecular selective activation of a C–H bond of a phenyl ring. This process is highly dependent on the nature of the substrate, reagent and solvent. Suitably placed substituents in the active phenyl ring lead to the formation of isomeric products due to the specificity of the activation process.

The newly formed thiolato derivative of the well known strongly π-acidic azopyridine ligand (L) destabilises the metal $t_{2g}$ orbital to a great extent which in turn reduces the ruthenium(III)–ruthenium(II) reduction potential by ≈0.7 V and lowers the ($d_\pi$) $Ru^{II} \longrightarrow$ ligand LUMO m.l.c.t. transition energy reasonably compared to the starting complex **3**.

The newly synthesized bis-chelated complexes **4** are susceptible to both metal- as well as ligand-based chemical and electrochemical transformations. The complexes can act as building blocks for the formation of homo- and hetero-nuclear polymeric species. Further investigations are in progress.

## Experimental

### Materials

Commercial ruthenium trichloride (S. D. Fine Chemicals, Bombay, India) was converted into $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. The *ctc*-$[RuL_2Cl_2]$ complexes **3**, $KS_2COR'$ (R′ = Me, Et, $Pr^n$, $Bu^n$ or $CH_2Ph$), $NaS_2P(OEt)_2$ and $NaS_2PPh_2$ were prepared according to the reported procedures.[5,13,19] Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) and alumina (neutral) used for chromatography were of BDH quality. For spectroscopic/electrochemical studies commercial acetonitrile was treated with $CaH_2$ (overnight) followed by successive distillation over $Li_2CO_3$–$KMnO_4$ and $P_4O_{10}$. The solvent was stored over molecular sieves (4 Å). Commercial tetraethylammonium bromide was converted into pure tetraethylammonium perchlorate by following an available procedure.[20] Dinitrogen gas was purified by successive bubbling through alkaline dithionite and concentrated sulfuric acid.

### Physical measurements

Solution electrical conductivity was checked using a Systronic 305 conductivity bridge. Electronic spectra (900–200 nm) were recorded using a Shimadzu-UV-265 spectrophotometer, IR spectra on a Nicolet spectrophotometer with samples prepared as KBr pellets. Magnetic susceptibility was checked with a PAR vibrating-sample magnetometer. Proton NMR spectra were obtained with a 300 MHz Varian FT-NMR spectrometer. Cyclic voltammetric measurements were carried out using a PAR model 362 scanning-potentiostat electrochemistry system. A platinum-wire working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode were used in a three-electrode configuration. The supporting electrolyte was $NEt_4ClO_4$ and the solute concentration $\approx 10^{-3}$ mol $dm^{-3}$. The half-wave potential $E^\circ_{298}$ was set equal to 0.5 ($E_{pa} + E_{pc}$), where $E_{pa}$ and $E_{pc}$ are the anodic and cathodic cyclic voltammetric peak potentials respectively. The scan rate was 50 mV $s^{-1}$. The coulometric experiments were done with a PAR model 370-4 electrochemistry apparatus incorporating a 179 digital coulometer. A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were carried out under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. The EPR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid nitrogen). The spectrum was calibrated by using diphenylpicrylhydrazyl (dpph) ($g$ = 2.0037). The elemental analyses were carried out with a Carlo Erba (Italy) elemental analyser. Solution emission properties were checked using a Shimadzu RF-540 fluorescence spectrophotometer.

### Preparation of complexes

The starting complexes **3c** and **3d** were prepared for the first time following procedures reported for **3a** and **3b**.[5] Complexes **4b** and **4c** were synthesized by the following procedures.

**$[Ru^{II}\{o\text{-}SC_6H_3(Me\text{-}m)N{=}NC_5H_4N\}_2]$ 4b.** The complex *ctc*-$[RuL^2{}_2Cl_2]$ **3b** (100 mg, 0.177 mmol) was dissolved in dmf (15 $cm^3$) and heated to reflux for 5 min. To this boiling solution was added potassium *O*-ethyl dithiocarbonate (72 mg, 0.45 mmol). Heating was continued for 1 h. The initial blue colour of **3b** gradually turned to red-brown. The progress of the reaction was monitored periodically by TLC. The solvent was removed under reduced pressure and the solid mass thus obtained was dried *in vacuo* over $P_4O_{10}$. The dried product was extracted into the minimum volume of dichloromethane and purified by using a silica gel column. With dichloromethane (as eluent) a slight amount of light yellow solution due to the excess of ligand was separated first and rejected. Using dichloromethane–acetonitrile (40 : 1) as eluent a deep red-brown band was separated. It was collected and evaporation of the solvent under reduced pressure afforded a crystalline solid. Finally the product was recrystallised from dichloromethane–hexane (1 : 5). Yield: 88 mg (90%).

Complex **4c** was prepared by following the above method except for the reflux time. Approximately 8 h of heating were needed for the complete conversion of the starting blue complex **3c**. After removal of solvent under reduced pressure the solid mass was dissolved in chloroform. The solution was filtered to remove any insoluble particles and subjected to chromatography on a silica gel column. A small red-brown band was eluted by chloroform–acetonitrile (5 : 1) leaving a dark band at the top of the column, which was not even moved by methanol. The solvent was evaporated under reduced pressure and the solid mass thus obtained was recrystallised from chloroform–light petroleum (b.p. 80–100 °C) (2 : 5). Yield: 9.8 mg (10%).

## Acknowledgements

Financial support from the Department of Science and Tech-

nology, New Dehli, India, is gratefully acknowledged. We are grateful to Professor A. Q. Contractor and Dr. R. Dabke, Indian Institute of Technology (IIT), Bombay, for providing electrochemical instrumental facility. Special acknowledgement is made to the Regional Sophisticated Instrumentation Centre, IIT, Bombay for providing the NMR facility. The referees comments at the revision stage were very helpful.

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*Received* 5*th June* 1996; *Paper* 6/03955C