

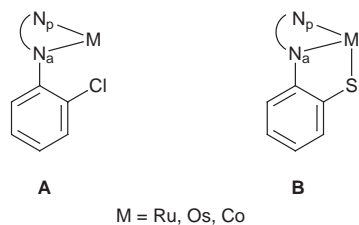
# Ruthenium-, osmium- and cobalt-ion mediated selective activation of a C–Cl bond. Direct and spontaneous aromatic thiolation reaction via C–S bond cleavage

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The reactions of KSC(S)OEt and NaSC(S)NEt<sub>2</sub> with the complexes [RuL<sub>2</sub>Cl<sub>2</sub>] **1a**, [OsL<sub>2</sub>Br<sub>2</sub>] **1b** and [CoL<sub>3</sub>][ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O **1c** [L = 2-(*o*-chlorophenylazo)pyridine, 2-(*o*-ClC<sub>6</sub>H<sub>4</sub>N=N)C<sub>5</sub>H<sub>4</sub>N] in boiling dimethylformamide solvent resulted in [Ru<sup>II</sup>L'<sub>2</sub>] **3a**, [Os<sup>II</sup>L'<sub>2</sub>] **3b** and [Co<sup>III</sup>L'<sub>2</sub>][ClO<sub>4</sub>] **3c** respectively [L' = 2-(*o*-SC<sub>6</sub>H<sub>4</sub>N=N)C<sub>5</sub>H<sub>4</sub>N]. In complexes **3** the *o*-carbon–chlorine bond of the pendant phenyl ring of the parent ligand L has been selectively and directly thiolated via carbon–sulfur bond cleavage of the dithiocarbonate and dithiocarbamate molecules. Two such newly formed tridentate thiolated ligands (L') are bound to the metal ions in a meridional fashion. The reactions are spontaneous in the case of dithiocarbonate as thiolating agent, but relatively slow and incomplete for dithiocarbamate. During the thiolation reaction the metal ion in the cobalt complex is oxidised from the starting Co<sup>II</sup> in **1c** to Co<sup>III</sup> in the final product **3c**. The reactions are highly sensitive to the nature of the solvent used, taking place only in those having high boiling points and polarities. The meridional configuration (*cis-trans-cis* with respect to sulfur, azo and pyridine nitrogens respectively) of **3** has been established by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The complexes exhibit two MLCT transitions in the visible region and intraligand (π–π\*, n–π\*) transitions in the UV region. In acetonitrile solution they display reversible M<sup>III</sup>–M<sup>II</sup> reduction potentials at 0.43 V for Ru (**3a**), 0.36 V for Os (**3b**) and –0.14 V for Co (**3c**) versus the saturated calomel electrode.

Metal ion-mediated transformation of organic molecules is an important chemical process as this provides facile synthetic routes for the formation of many interesting molecules which are otherwise difficult or even impossible to synthesize by conventional synthetic procedures.<sup>1</sup> In this process the metal ion creates a suitable chemical platform for the interacting molecules which in turn may facilitate the formation of unusual products. Here we report one example of such reactions where the transition-metal ion (Ru<sup>II</sup>/Os<sup>II</sup>/Co<sup>II</sup>) mediated selective activation of the *o*-carbon–chlorine bond of the pendant phenyl ring of co-ordinated ligand (**A**) has been directly and spontaneously thiolated (**B**) via C–S bond cleavage of dithiocarbonate and dithiocarbamate molecules.

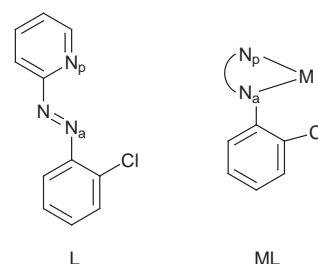


Although the conversion of RC<sub>6</sub>H<sub>5</sub> into RC<sub>6</sub>H<sub>4</sub>S<sup>–</sup> is conventionally a multistep process,<sup>2</sup> the metal ion-prompted C–Cl bond activation process here leads to spontaneous one-pot synthesis of co-ordinated aromatic thiols. To the best of our knowledge this work demonstrates the first example of transition-metal ion mediated aromatic thiolation via activation of a carbon–chloride bond. Metal ion-mediated cleavage of C–S bonds of organic molecules and concomitant formation of new carbon–sulfur centres are important from industrial,<sup>3</sup> biological<sup>4</sup> and synthetic organic chemistry points of view.<sup>5</sup>

## Results and Discussion

### Synthesis

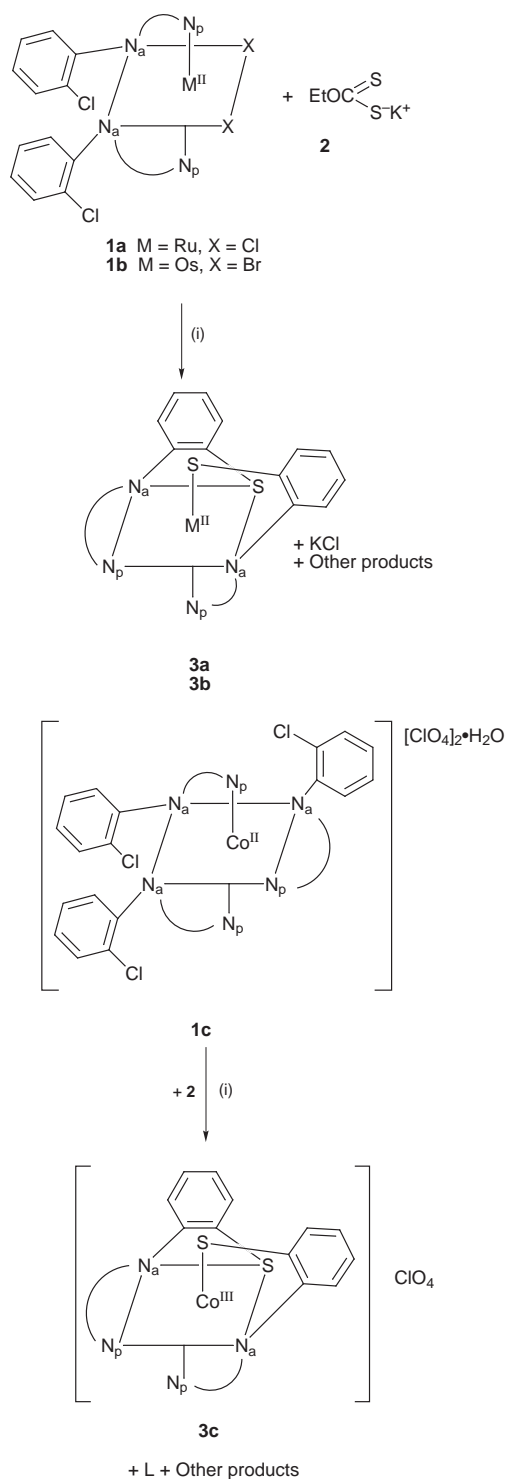
The ligand L binds to the metal ions in a bidentate N<sub>p</sub>, N<sub>a</sub> manner forming a five-membered chelate ring ML. The reac-



tion of potassium *O*-ethyl dithiocarbonate **2** with the starting complexes *cis-trans-cis* [Ru<sup>II</sup>L<sub>2</sub>Cl<sub>2</sub>] **1a** and *cis-trans-cis* [Os<sup>II</sup>L<sub>2</sub>Br<sub>2</sub>] **1b** (*cis-trans-cis* with respect to chlorides or bromides, pyridine and azo nitrogens respectively) in a ratio of 2:1 in boiling dimethylformamide (dmf) solvent spontaneously result in red-brown and green solutions respectively (Scheme 1). Chromatographic purifications of these solutions on silica gel column afford pure complexes **3a** and **3b** respectively in 85 and 80% yield, where the *ortho*-carbon atom of the pendant phenyl ring of both ligands has been selectively and directly thiolated (C<sub>6</sub>H<sub>4</sub>Cl to C<sub>6</sub>H<sub>4</sub>SM) via cleavage of the carbon–sulfur bond of the dithiocarbonate **2**.

The reaction of salt **2** with the meridional tris complex [Co<sup>II</sup>-L<sub>3</sub>][ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O **1c** in boiling dmf solvent for 15 min results in a greenish solution corresponding to **3c** (Scheme 1), where one of the ligands has been liberated from the co-ordination sphere of the starting complex **1c** and the *ortho*-carbon–chlorine bonds of the pendant phenyl rings of the other two ligands selectively and spontaneously thiolated. The liberated L has been recovered quantitatively by column chromatography. In the course of the reaction the cobalt ion has been oxidised from its bivalent state in **1c** to the trivalent state in the complex **3c**. Since the reaction specifically takes place under atmospheric conditions, the oxygen in air may be responsible for the metal oxidation.

Thus the selective activation of the carbon–chlorine bond of the phenyl ring leads to a change from the usual neutral bidentate mode (N<sub>p</sub>, N<sub>a</sub>) of the parent ligand L to the mono-



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

negative tridentate ( $N_p$ ,  $N_a$ ,  $S^-$ ) form,  $L'$  in complexes **3a–3c**. Two such transformed tridentate ligands bind to the metal ion in a meridional fashion.

The reactions (Scheme 1) are very sensitive to the nature of the solvent used. Although spontaneous in dmf solvent, they do not occur in common organic solvents such as chloroform, dichloromethane, benzene, acetonitrile, methanol, ethanol, 2-methoxyethanol, ethyl benzoate, tetrahydrofuran and water. They can take place in other high-boiling and polar solvents like dimethyl sulfoxide,  $P(NMe_2)_3O$ , 1-methylpyrrolidin-2-one and *N*-methylformamide with varying degrees of efficiency. Dimethylformamide was found to be the best choice from a practical point of view, *i.e.* to get the maximum yield in the minimum time.

In order to find other suitable thiolating agents the reactions (Scheme 1) were tested with benzenethiol, carbon disulfide (the precursor of dithiocarbonate **2**),  $S_8$ , thiirane and dithiocarbamate instead of **2** but the desired thiolated product **3** was found to form only in the case of dithiocarbamate. Although the sodium salt of diethyldithiocarbamate can perform the thiolation reaction in boiling dmf solvent, the rate is very slow compared to that with **2**. It takes approximately 4 h to yield 50% thiolated product **3**. In the absence of thiolating agent **2** the starting complexes **1a–1c** remain unchanged in the above-mentioned polar solvents even under reflux. Hence, the formation of any solvent-dependent reactive intermediates prior to the activation process may be ruled out.

Under identical reaction conditions (Scheme 1) but in the absence of metal ions, free  $L$  does not undergo the transformation  $NC_5H_4N=NC_6H_4Cl \rightarrow NC_5H_4N=NC_6H_4S^-$ . This implies the direct involvement of the metal ion in the activation process. The newly formed tridentate thiolated ligand  $L'$  cannot be removed intact from the metal complexes **3** by using  $H_2O_2$ ,  $HBr$ ,  $HCl$  and  $HCN$ .

The microanalytical data of the products **3** (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 (low-spin  $Ru^{II}/Os^{II}/Co^{III}$ ,  $t_{2g}^6$ ,  $S = 0$ ). In acetonitrile solvent **3a** and **3b** are non-conducting but **3c** behaves as a 1:1 electrolyte (conductivity  $\Lambda_M = 155 \Omega^{-1} cm^2 mol^{-1}$ ).

#### Infrared spectra

The  $N=N$  stretching frequency of free  $L$  appears at  $1425 cm^{-1}$ .<sup>6</sup> It is shifted to lower values on complexation ( $1380 cm^{-1}$  for **3c**,  $1280 cm^{-1}$  for **3a**, and  $1200 cm^{-1}$  for **3b**) due to  $d_\pi(M) \rightarrow \pi^*(L')$  backbonding.<sup>6</sup>  $Co < Ru < Os$ . Two distinct  $M-S$  stretching frequencies have been observed for each of the complexes **3a–3c** near  $350 cm^{-1}$ .<sup>7</sup> The perchlorate anion in the cobalt complex **3c** is evidenced by a strong and broad band near  $1100 cm^{-1}$  and a strong and sharp band near  $625 cm^{-1}$ .

#### Electronic spectra

Electronic spectra of ruthenium and osmium complexes **3a** and **3b** were recorded in dichloromethane solution but for the cobalt complex **3c** acetonitrile solvent was used due to solubility problems. The spectral data are listed in Table 1. In the visible region the complexes display two moderately intense bands. Since  $Ru^{II}/Os^{II}$  and  $Co^{III}$  in the complexes are in the low-spin  $t_{2g}^6$  configuration, the bands may be considered as metal-to-ligand charge-transfer transitions.<sup>8</sup> In the UV region the complexes show very intense transitions which are presumably due to intraligand  $\pi-\pi^*$  and  $n-\pi^*$  transitions.<sup>9</sup>

#### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of the ligand  $L$  and the complexes **3a–3c** were recorded in  $CDCl_3$  solvent. The chemical shifts and coupling constants are given in Table 2 and the spectra are displayed in Fig. 1. The individual proton resonances are assigned on the basis of their relative intensities, spin-spin structure and electronic environments.<sup>10</sup> Free  $L$  should exhibit four doublets and four triplets. Although the signals are not resolved properly, the expected four doublets and four triplets have been identified from the relative integration values [Fig. 1(a)].

The <sup>1</sup>H NMR spectra of complexes **3a–3c** in  $CDCl_3$  solvent exhibit four doublets and four triplets having equal intensities [Fig. 1(b)–1(d)]. Direct comparison of the spectra with that of ligand  $L$  reveals that the thiolation takes place at the *C-Cl* site but not at the other possible *ortho C-H* position.<sup>11</sup> Since these spectra show only eight signals correspond to one thiolated ligand ( $L'$ ), it can be inferred that each half of the molecule is equivalent. Hence, the spectra of the complexes suggest a

**Table 1** Microanalytical and electronic spectral data

Compound	Microanalytical data <sup>a</sup> (%)				Electronic spectral data <sup>b</sup> $\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )
	C	H	N	S	
<b>3a</b>	49.8 (49.9)	3.1 (3.0)	16.0 (15.9)	12.2 (12.1)	711 (4982), 560 (13 200), 375 (26 990), 265 (37 965)
<b>3b</b>	42.6 (42.7)	2.7 (2.6)	13.7 (13.6)	10.4 (10.3)	653 (5937), 508 (8178), 357 (25 750), 315 (26 718)
<b>3c</b>	45.2 (45.0)	2.8 (2.7)	14.4 (14.3)	11.0 (10.9)	786 (4318), 664 (3339), <sup>d</sup> 404 (26 603), 280 (54 625)

<sup>a</sup> Calculated values are in parentheses. <sup>b</sup> In dichloromethane for **3a** and **3b** and in acetonitrile for **3c**. <sup>c</sup> Absorption coefficient. <sup>d</sup> Shoulder.

**Table 2** Proton NMR spectral data in  $\text{CDCl}_3$ 

Compound	$\delta$ (J/Hz) <sup>a</sup>							
	H-1	H-2	H-3	H-4	H-8	H-9	H-10	H-11
L	8.77 (d, 5.8)	7.37 (t, 7.5)	7.88 <sup>b</sup> —	7.88 <sup>b</sup> —	7.59 (d, 7.5)	7.45 (t, 6.7) (7.5)	7.43 (t, 6.7)	7.88 <sup>b</sup> —
<b>3a</b>	8.19 (d, 8.8)	6.78 (t, 6.7) (6.9)	7.49 (t, 7.0) (8.0)	7.87 (d, 8.2)	7.34 (d, 8.6)	7.08 (t, 6.9) (7.3) (7.7)	6.98 (t, 7.3) (7.7)	7.73 (d, 5.8)
<b>3b</b>	8.09 (d, 8.4)	6.31 (t, 6.8)	7.11 (t, 7.5)	7.72 (d, 7.5)	7.52 (d, 7.8)	7.11 (t, 7.5)	6.81 (t, 7.5)	7.72 (d, 7.5)
<b>3c</b>	8.42 (d, 8.4)	7.19 (t, 7.9) (8.4)	8.11 (t, 7.9) (8.4)	8.20 (d, 9.0)	7.28 (d, 8.5)	7.36 (t, 8.0) (6.8)	7.46 (t, 6.6) (7.2)	7.89 (d, 5.8)

<sup>a</sup> Tetramethylsilane as internal standard. <sup>b</sup> Complex multiplet pattern centred at  $\delta$  7.88. Owing to overlapping signals it does not seem possible to determine the  $J$  values for doublets or triplets unequivocally.

meridional geometry where the co-ordinating atoms are in *cis-trans-cis* configuration with respect to the sulfurs, azo and pyridine nitrogens respectively (Scheme 1).<sup>11</sup>

### <sup>13</sup>C NMR spectra

The decoupled and coupled <sup>13</sup>C NMR spectra of free L and complexes **3a–3c** were recorded in  $(\text{CD}_3)_2\text{SO}$  solvent. The decoupled spectra are shown in Fig. 2 and chemical shift and coupling constant values are listed in Table 3. The individual carbon resonances are assigned on the basis of their electronic environments like the proton resonances.

The decoupled spectrum of free L [Fig. 2(a)] exhibits a distinct pattern of three singlets and eight doublets (confirmed from the coupled spectrum). Similarly the decoupled spectra of the ruthenium, osmium and cobalt complexes **3a–3c**, Fig. 2(b), 2(c) and 2(d) respectively, show three singlets and eight doublets corresponding to one ligand, L'. The presence of the three singlets unambiguously supports the activation at the C–Cl bond of the ligand. The eleven signals corresponding to one transformed thiolated ligand (L') provide further support in favour of the presence of molecular symmetry around the metal centre in these complexes.

Thus the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic results along with the microanalytical, magnetic moment, conductivity and IR data collectively establish the composition and stereochemistry of complexes **3**.

### Metal redox

In acetonitrile solvent the ruthenium and osmium complexes **3a** and **3b** show quasi-reversible  $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$  and  $\text{Os}^{\text{III}}-\text{Os}^{\text{II}}$  reduction potentials,  $E_{298}^{\circ}$ , 0.43 ( $\Delta E_p = 90$ ,  $i_{\text{pa}}/i_{\text{pc}} = 1.07$ ) and 0.36 V ( $\Delta E_p = 80$  mV,  $i_{\text{pa}}/i_{\text{pc}} = 1.02$ ) versus SCE (platinum working electrode, tetrabutylammonium perchlorate as supporting electrolyte) respectively (Fig. 3). Under identical experimental conditions the cobalt complex **3c** exhibits a quasi-reversible  $\text{Co}^{\text{III}}-\text{Co}^{\text{II}}$  reduction potential,  $E_{298}^{\circ}$ ,  $-0.14$  V ( $\Delta E_p = 110$  mV,  $i_{\text{pa}}/i_{\text{pc}} = 0.92$ ) versus SCE (Fig. 3). The one-electron nature of

the couples is confirmed by constant-potential coulometry (observed Coulomb counts,  $n$ , for **3a**, **3b** and **3c** are 1.06, 1.02 and 1.08 respectively where  $n = Q/Q'$ ,  $Q$  is the calculated Coulomb count for one-electron transfer and  $Q'$  that found after exhaustive electrolysis of a  $10^{-2}$  mmol solution of the complexes). The low ( $<0$  V versus SCE) cobalt(II)–cobalt(III) oxidation potential of the complex **3c** can account for its stabilisation in the trivalent state which possibly occurs by aerial oxidation of the cobalt(II) congener of **3c** during the course of the reaction (Scheme 1). Thus chemical reduction of the cobalt(III) complex **3c** by hydrazine hydrate as well as the electrochemical reduction at  $-0.3$  V versus SCE generate the unstable cobalt(II) congener on the chemical and electrochemical timescales.

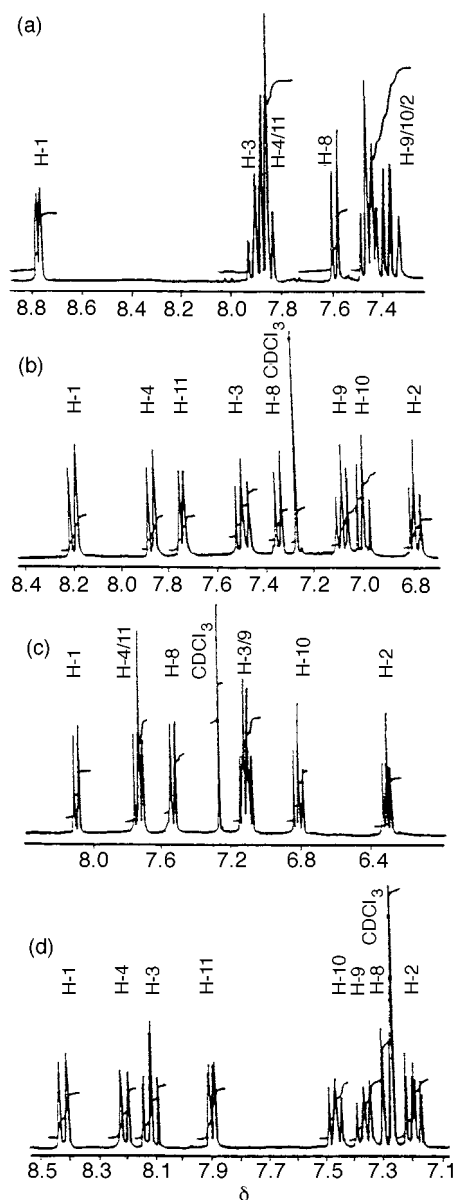
Since the reactions (Scheme 1) involve several simultaneous steps and take place in boiling dmf solvent without any tractable intermediates, the overall conversion process **1–3** is complex particularly with respect to the mechanism. However, based on the available knowledge of the chloride-substitution reactions of aromatic chloro compounds, we believe that the thiolation reaction proceeds through a nucleophilic substitution pathway.<sup>12,13</sup> Since free L is not activated towards substitution, it must be co-ordination to the azonitrogen which withdraws enough electron density to promote the nucleophilic attack. The presence of the chloride group at the *para* position of the ligand instead of the *ortho* position does not result in the thiolation reaction; this suggests that the proximity of the activation site to the metal ion is also important. The high-boiling dmf solvent is essential to facilitate all the simultaneously operating processes.

### Conclusion

We have observed ruthenium-, osmium- and cobalt-ion mediated activation of the carbon–chloride bond of the phenyl ring of L which in turn leads to direct and spontaneous one-pot synthesis of aromatic thiols *via* the carbon–sulfur bond cleavage of dithiocarbonate and dithiocarbamate molecules. The

**Table 3** Carbon-13 NMR data in (CD<sub>3</sub>)<sub>2</sub>SO

Compound	$\delta$ (J/Hz)										
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
L	148.98 (d, 714)	113.01 (d, 678)	132.48 (d, 653)	137.89 (d, 671)	135.90 (s)	147.77 (s)	162.62 (s)	117.26 (d, 664)	125.22 (d, 642)	126.91 (d, 657)	130.35 (d, 671)
3a	150.43 (d, 734)	119.22 (d, 653)	130.87 (d, 656)	136.95 (d, 656)	152.88 (s)	167.50 (s)	161.69 (s)	122.58 (d, 668)	121.80 (d, 671)	121.49 (d, 659)	132.10 (d, 650)
3b	150.21 (d, 722)	119.39 (d, 573)	122.13 (d, 654)	136.44 (d, 654)	151.81 (s)	170.75 (s)	160.03 (s)	128.46 (d, 654)	121.18 (d, 518)	120.93 (d, 671)	133.06 (d, 632)
3c	149.07 (d, 750)	120.55 (d, 675)	136.57 (d, 645)	143.12 (d, 687)	148.69 (s)	165.72 (s)	161.93 (s)	125.38 (d, 666)	127.78 (d, 708)	128.75 (d, 675)	129.19 (d, 660)

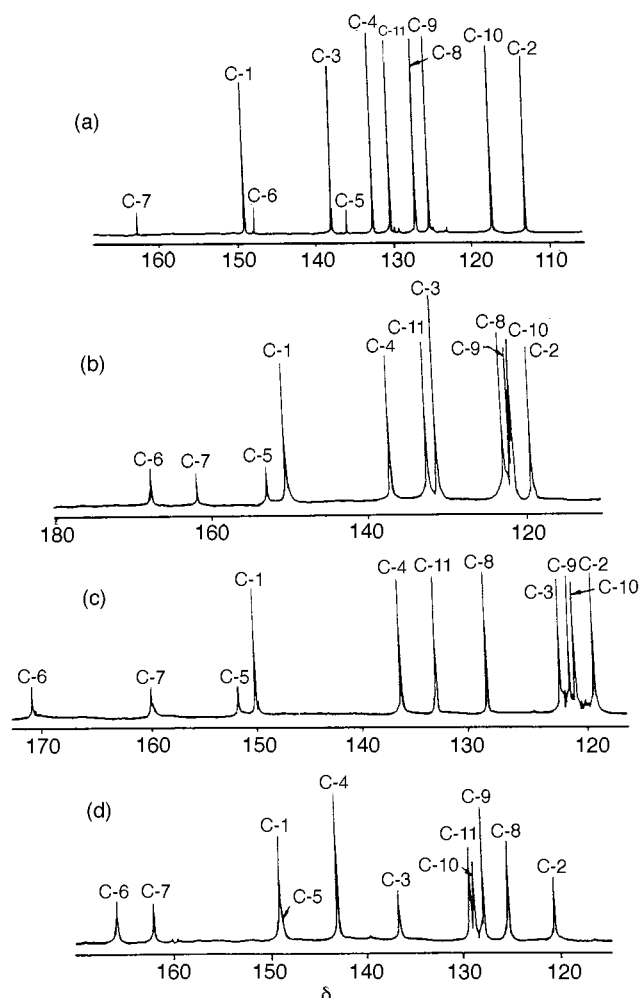
**Fig. 1** Proton NMR spectra in CDCl<sub>3</sub> of (a) free L, (b) [Ru<sup>II</sup>(*o*-SC<sub>6</sub>H<sub>4</sub>N=NC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] **3a**, (c) [Os<sup>II</sup>(*o*-SC<sub>6</sub>H<sub>4</sub>N=NC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] **3b** and (d) [Co<sup>III</sup>(*o*-SC<sub>6</sub>H<sub>4</sub>N=NC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>][ClO<sub>4</sub>] **3c**

activation process is highly dependent on the nature of the solvents and the thiolating agents. Although the reaction is spontaneous in the case of dithiocarbonate, it proceeds slowly in the case of dithiocarbamate as thiolating agent.

## Experimental

### Materials

Commercial ruthenium trichloride (S.D. Fine Chemicals,

**Fig. 2** Carbon NMR spectra (decoupled) in (CD<sub>3</sub>)<sub>2</sub>SO of (a) free L, (b) [Ru<sup>II</sup>(*o*-SC<sub>6</sub>H<sub>4</sub>N=NC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] **3a**, (c) [Os<sup>II</sup>(*o*-SC<sub>6</sub>H<sub>4</sub>N=NC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>] **3b** and (d) [Co<sup>III</sup>(*o*-SC<sub>6</sub>H<sub>4</sub>N=NC<sub>5</sub>H<sub>4</sub>N)<sub>2</sub>][ClO<sub>4</sub>] **3c**

Bombay, India) was converted into RuCl<sub>3</sub>·3H<sub>2</sub>O by repeated evaporation to dryness with concentrated hydrochloric acid.<sup>14</sup> Osmium tetroxide was obtained from Johnson Matthey, London. Cobalt carbonate (J. T. Baker, Colorado, USA) was converted into cobalt perchlorate by a standard method. The ligand L and the starting complex [CoL<sub>3</sub>][ClO<sub>4</sub>]<sub>2</sub>·H<sub>2</sub>O **1c** were prepared according to the reported procedure.<sup>15</sup> The starting ruthenium (**1a**) and osmium (**1b**) complexes were prepared for the first time following procedures reported for related complexes.<sup>16,17</sup> Potassium *O*-ethyl dithiocarbonate was prepared according to the reported procedure.<sup>18</sup> Other chemicals and solvents were reagent grade and used as received. Silica gel (60–120 mesh) used for chromatography was of BDH quality. For spectroscopic/electrochemical studies HPLC grade solvents were used. Commercial tetrabutylammonium bromide was converted into pure tetrabutylammonium perchlorate by following an available procedure.<sup>19</sup> Dinitrogen gas was purified by

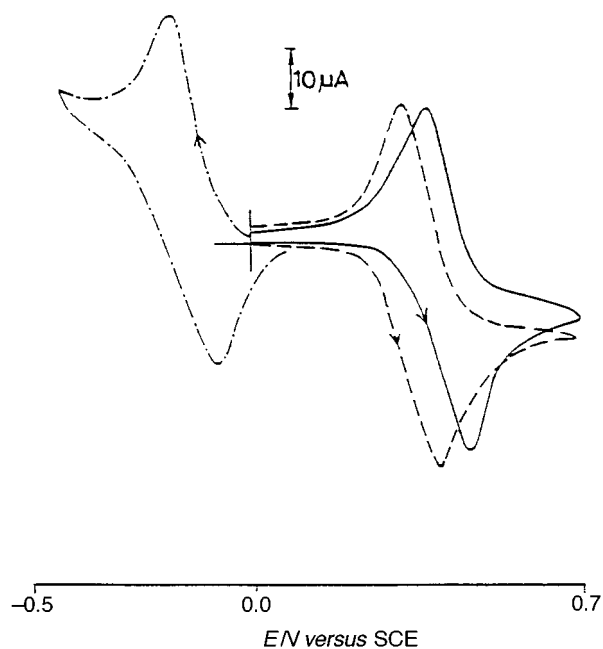


Fig. 3 Cyclic voltammograms of  $\approx 10^{-3}$  mol dm $^{-3}$  solutions of complexes **3a** (—), **3b** (---) and **3c** (-.-.-) in acetonitrile at 298 K

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-160A spectrophotometer, IR spectra on a Nicolet spectrophotometer with the samples prepared as KBr pellets. Magnetic susceptibility was measured with a PAR vibrating-sample magnetometer. The NMR spectra were obtained with a 300 MHz Varian FT spectrometer. Cyclic voltammetric measurements were carried out using a PAR model 362 scanning-potentiostat electrochemistry system, with platinum-wire working electrode, platinum-wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) in the three-electrode configuration. The supporting electrolyte was NBu $_4$ ClO $_4$  and the solute concentration  $\approx 10^{-3}$  mol dm $^{-3}$ . The half-wave potential,  $E_{298}^{\circ}$ , 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,  $i_{pa}$  and  $i_{pc}$  are the anodic and cathodic peak currents 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. All experiments were carried out under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. The elemental analyses were carried out with a Carlo Erba (Italy) elemental analyser.

#### Preparation of complexes

[Ru $^{II}$ (*o*-SC $_6$ H $_4$ N=NC $_5$ H $_4$ N) $_2$ ] **3a**. A sample (100 mg, 0.17 mmol) of *ctc*-[RuL $_2$ Cl $_2$ ] **1a** was dissolved in dmf solvent (20 cm $^3$ ) and potassium *O*-ethyl dithiocarbonate **2** (55 mg, 0.34 mmol) was added. The resulting solution was heated to reflux for 10 min. The initial blue solution immediately turned red-brown. It was evaporated to dryness under reduced pressure and the solid mass thus obtained dried *in vacuo* over P $_4$ O $_{10}$ . The dried product was dissolved in a small volume of chloroform and subjected to chromatography on a silica gel (60–120 mesh) column. A red-brown band was eluted with chloroform–acetonitrile (10:1). The collected eluent was evaporated to dry-

ness under reduced pressure to afford a dark crystalline solid, which was recrystallised from dichloromethane–hexane (5:1). Yield: 74 mg (85%).

[Os $^{II}$ (*o*-SC $_6$ H $_4$ N=NC $_5$ H $_4$ N) $_2$ ] **3b**. The complex *ctc*-[Os $^{II}$ L $_2$ Br $_2$ ] **1b** (100 mg, 0.13 mmol) was dissolved in dmf (20 cm $^3$ ) under warming and potassium *O*-ethyl dithiocarbonate (42 mg, 0.26 mmol) added. The mixture was heated to reflux for 10 min. The initial blue-violet colour of **1b** spontaneously changed to light green. The solvent was then removed under reduced pressure and the solid mass thus obtained dried *in vacuo* over P $_4$ O $_{10}$ . The dried product was dissolved in a small volume of dichloromethane and purified by using a silica gel (60–120 mesh) column. A light green band was eluted with dichloromethane–acetonitrile (20:1). The light green solution was collected and evaporation of the solvents under reduced pressure afforded a crystalline solid which was recrystallised from dichloromethane–hexane (1:8). Yield: 62 mg (80%).

[Co $^{III}$ (*o*-SC $_6$ H $_4$ N=NC $_5$ H $_4$ N) $_2$ ][ClO $_4$ ] **3c**. The complex *mer*-[Co $^{III}$ L $_3$ ][ClO $_4$ ] $_2$ ·H $_2$ O **1c** (100 mg, 0.11 mmol) was dissolved in dmf (15 cm $^3$ ) and potassium *O*-ethyl dithiocarbonate (35 mg, 0.22 mmol) added. The mixture was then heated to reflux for 15 min. The initial brown colour of **1c** immediately changed to greenish. The solvent was removed under reduced pressure and the solid mass thus obtained dried *in vacuo* over P $_4$ O $_{10}$ . The dried product was extracted by the minimum volume of chloroform and purified by using a silica gel column (60–120 mesh). With benzene (as eluent) a yellow solution due to liberated L separated first. Using chloroform–acetonitrile (8:1) as eluent a greenish band was eluted. Evaporation of the solvents under reduced pressure afforded a crystalline solid which was dried *in vacuo* over P $_4$ O $_{10}$  and recrystallised from acetonitrile–benzene (1:6). Yield: 55 mg (85%).

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