

Metal ion-mediated selective activations of C–H and C–Cl bonds. Direct aromatic thiolation reactions via C–S bond cleavage of dithioacids

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Abstract. The reactions of potassium salt of dithiocarbonate, $R'OCS_2K$, **4** ($R' = Me, Et, {}^nPr, {}^iBu, {}^tPr, {}^iBu, -CH_2Ph$) with the low-spin $ctc-Ru^{II}(L)_2Cl_2$ **1**, $ctc-Os^{II}(L)_2Br_2$ **2** and $mer-[Co^{II}(L)_3](ClO_4)_2 \cdot H_2O$ **3** [$L = 2-(arylazo)pyridine, NC_5H_4-N=N-C_6H_4(R)$, $R = H, o-Me/Cl, m-Me/Cl, p-Me/Cl$; ctc : *cis-trans-cis* with respect to halides, pyridine and azo nitrogens respectively) in boiling dimethylformamide solvent resulted in low-spin diamagnetic $Ru^{II}(L')_2$, **5**, $Os^{II}(L')_2$ **6** and $[Co^{III}(L')_2]ClO_4$ **7** respectively ($L' = o-S-C_6H_3(R)N=NC_5H_4N$). In the complexes **5**, **6** and **7** ortho carbon-hydrogen bond of the pendant phenyl ring of the ligands (L') has been selectively and directly thiolated via the carbon–sulphur bond cleavage of **4**. The newly formed tridentate thiolated ligands (L') are bound to the metal ion in a meridional fashion. In the case of cobalt complex (**7**), during the activation process the bivalent cobalt ion in the starting complex **3** has been oxidised to the trivalent Co^{III} state. The reactions are highly sensitive to the nature and the location of the substituents present in the active phenyl ring. The presence of electron donating Me group at the ortho and para positions of the pendant phenyl ring with respect to the activation points can only facilitate the thiolation process. The complexes (**1c**, **2c** and **3c**) having chloride group at the ortho position of the active phenyl ring underwent the thiolation reaction selectively via the carbon–chloride bond activation process. The rate of carbon–chloride activation process has been found to be much faster compared to the C–H bond activation. The reactions are sensitive to the nature of the solvent used, taking place only in those having high boiling and polar solvents. The rate of the reactions is also dependent on the nature of the R' group present in **4**, following the order: $Me \sim Et > {}^nPr > {}^iBu > {}^tPr > {}^iBu \gg -CH_2Ph$. The molecular geometry of the complexes in solution has been established by 1H and ${}^{13}C$ NMR spectroscopy. The thiolated complexes (**5**, **6**, **7**) exhibit metal to ligand charge-transfer transitions in the visible region and intraligand $\pi-\pi^*$ and $n-\pi^*$ transitions in the UV region. In acetonitrile solution the complexes display reversible $M^{III} \rightleftharpoons M^{II}$ reductions at 0.43 V for Ru (**5a**), 0.36 V for Os (**6a**) and –0.13 V for Co (**7a**) vs saturated calomel electrode (SCE).

Keywords. Ruthenium; osmium; cobalt; activation, thiolation.

1. Introduction

Metal-ion mediated activations of the carbon–hydrogen and carbon–chloride bonds are fundamentally important chemical reactions since these may lead to the formation of interesting new molecules which are otherwise difficult or even impossible to synthesize

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by the conventional synthetic routes¹⁻⁴. We have recently observed an unusual reaction where ruthenium, osmium and cobalt ions mediated activations of the selective ortho-carbon-hydrogen and carbon-chloride bonds of the pendant phenyl ring of coordinated 2-(arylamino)pyridine ligand $[C_6H_4(R)N=NC_5H_4N, L]$ in the complexes $[Ru(L)_2Cl_2]$, $[Os(L)_2Br_2]$ and $[Co(L)_3]^{2+}$ facilitate the direct and spontaneous aromatic thiolation reaction via the carbon-sulphur bond cleavage of dithiocarbonate and dithiocarbamate molecules.

In the activation process the metal ion acts as a pivot. Its presence helps to create a suitable chemical platform for the interacting molecules which in turn lead to the fascinating chemical transformations.

The conversion of $-C_6H_4-H \rightarrow -C_6H_4-S^-$ is conventionally a multistep process^{5,6} whereas the metal ions assisted C-H and C-Cl bond activation processes lead to one-pot synthesis of aromatic thiols.

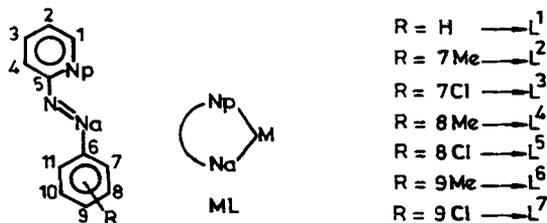
Metal ion mediated cleavage of C-S bond of organic molecules and concomitant formation of new C-S centre are important from both the industrial⁷⁻⁹ and biological¹⁰⁻¹³ points of view.

In this article we summarise our recent results on the transition metal ions prompted direct aromatic thiolation reactions.

2. Results and discussion

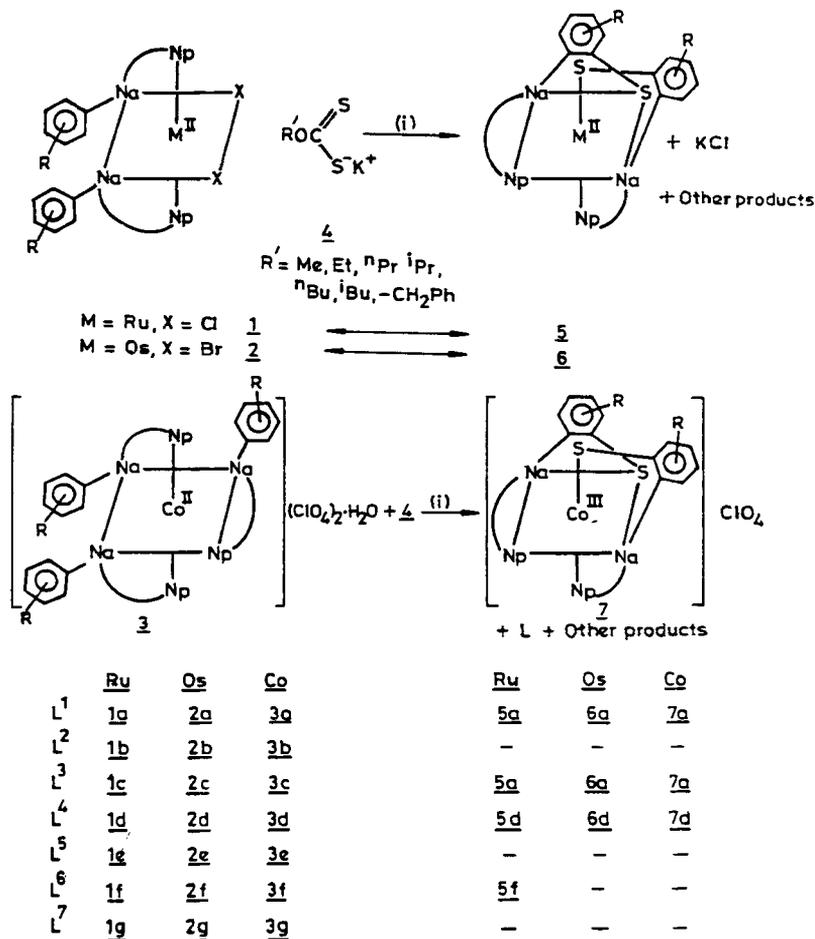
2.1 Synthesis

The seven substituted arylazopyridine ligands used for the present study are abbreviated as L^1-L^7 . The ligands, L bind to the metal ions in a bidentate neutral N_p, N_a manner forming a five-membered chelate ring ML.



The reactions of *ctc*- $Ru^{II}(L^1)_2Cl_2$ **1a** and *ctc*- $Os^{II}(L^1)_2Br_2$ **2a** (*ctc*: *cis-trans-cis* with respect to chlorides or bromides, pyridine and azo nitrogens respectively) with the potassium salt of ethyl dithiocarbonate $EtOC(S)S^-K^+$ (**4**) in a ratio 1:2 in boiling *N,N*-dimethylformamide (dmf) solvent result in red-brown and green solutions respectively (scheme 1). The progress of the reactions was monitored by TLC and approximately 3 h and 1 h time were required to complete the reactions for the ruthenium and osmium complexes respectively. Chromatographic purifications of the red-brown and green solutions on silica gel column yield pure complexes **5a** and **6a** respectively, where ortho-carbon atom of the pendant phenyl ring of both the coordinated ligands has been selectively and directly thiolated via the cleavage of the carbon-sulphur bond of the dithiocarbonate molecule (**4**), scheme 1.

The reaction of **4** with the meridional *tris* complex $[Co^{II}(L^1)_3][ClO_4]_2 \cdot H_2O$ **3a** in boiling dmf solvent for 4 h results in a greenish solution corresponding to the complex **7a**



Scheme 1. (i) dmf, heat

(scheme 1), where one of the coordinate ligands (L^1) has been liberated from the coordination sphere of the starting complex **3a** and the ortho-carbon atom of the pendant phenyl ring of other two ligands selectively and directly thiolated. The liberated L has been recovered quantitatively by column chromatography. In course of the reaction the cobalt ion has been oxidised from its bivalent state in **3a** to the trivalent state in the complex **7a**. Since the reaction here specifically takes place under atmospheric conditions, the oxygen in the air may be responsible for the metal oxidation.

The formation of the final thiolated product **5a** has been authenticated by the single crystal X-ray structure of the complex ¹⁴.

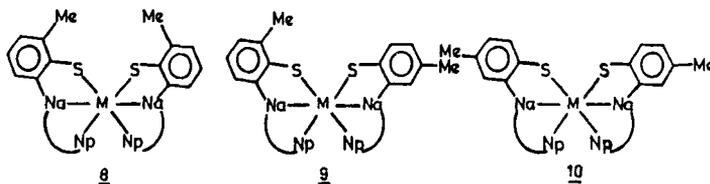
Thus the ruthenium, osmium and cobalt ions mediated selective ortho-C–H bond activation of the pendant phenyl ring of the coordinated ligands leads to the change of usual neutral bidentate N_p, N_a , mode of the azopyridine ligand (L^1) to the mononegative tridentate N_p, N_a, S^- mode (L^7) in the final thiolated complexes (**5a**, **6a**, **7a**). Two of such newly generated tridentate ligands bind to the metal ion in a meridional fashion.

The starting complexes **1b**, **2b** and **3b** where one of the ortho-carbon atoms (C-7) of the pendant phenyl ring is blocked by a methyl group, have failed to perform the C–H bond activation reaction under identical reaction conditions (scheme 1). In view of the

availability of the other ortho C–H bond (C-11–H), the free rotation of the active phenyl ring along the C-6–Na_a bond might have facilitated the thiolation at the other C-11–H site, but that did not happen in practice.

In case of the starting complexes **1c**, **2c** and **3c** where one of the ortho-carbon atoms (C-7) of the active phenyl ring is blocked by a chloride group, have failed to show the activation reaction at the other available C-11–H point. On the other hand the complexes have performed the thiolation reactions via the C-7–Cl bond activation pathway which eventually result in the products identical to **5a**, **6a** and **7a**. Thus the introduction of chloride group at one of the ortho-carbon atoms (C-7) develops a competitive situation in the complexes between the C-7–Cl bond activation and the activation of C-11–H bond. Although the C-7–H bond activation reaction in the complexes **1a**, **2a** and **3a** and C-(7)–Cl bond activation in the complexes **1c**, **2c** and **3c** afford the identical products **5a**, **6a** and **7a** respectively, the rate of the reactions and the yields are much higher for C–Cl bond activation process.

Under identical reaction conditions (scheme 1) the starting complexes **1d**, **2d** and **3d**, where one methyl group is present at the meta position (C-8) of the phenyl ring of L, undergo the thiolation reaction very effectively. Here the reactions completed in 1 h. Since free rotation along the C-6–Na single bond is allowed, the presence of a meta methyl group in both the ligands of the complexes leads to the possibility of developing three isomers **8–10**.



However, the solution ¹H NMR studies indicate the presence of an intimate mixture of isomers **8** and **9** in the ratio 2:1 and 3:4 for **5d** and **6d** respectively and for the cobalt complex (**7d**) all the possible three isomers **8**, **9** and **10** are present in the ratio 4:1:6. All our attempts to separate the individual isomers from the respective mixture have failed altogether.

The starting complexes **1e**, **2e**, **3e** and **1g**, **2g**, **3g** having electron withdrawing chloride group at the meta and para positions of the active phenyl ring respectively and did not undergo the thiolation reaction (scheme 1) even after refluxing in boiling dmf for 24 h.

The starting complexes having electron donating methyl group at the para position of the phenyl ring (**1f**, **2f** and **3f**) do not prefer to undergo the thiolation reaction (scheme 1). Under identical reaction conditions to those in scheme 1 more than 8 h were required to get only 10% pure ruthenium complex **5f** but the osmium and cobalt complexes (**2f** and **3f**) did not yield the corresponding thiolated products at all.

The above observations thus 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 reactions in scheme 1 are highly solvent dependent. In acetonitrile, benzene, dichloromethane, tetrahydrofuran, 2-methyltetrahydrofuran, ethanol, methanol and 2-methoxyethanol the reactions do not take place at all, whereas in dimethylformamide, methylformamide, dimethylsulfoxide and hexamethylphosphoramide $P(NMe_2)_3O$ these occur. 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 thiolating agent **4**, no change in the starting complexes **1**, **2** and **3** is observed even under boiling. This may suggest the absence of direct participation of the solvent to form any solvent-dependent reactive intermediate prior to the activation process.

The rate of the reactions (scheme 1) is also dependent on the nature of the R' group present in the dithiocarbonate **4**. The progress of the reactions was monitored quantitatively to semiquantitatively by TLC as well as spectrophotometrically in dmf solvent using different R' groups in **4**. The reactivity order was as follows: Me ~ Et > nPr > nBu > iPr > iBu >> 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 reactions.

In order to find other suitable thiolating agents, the reactions were tested with benzenethiol, carbondisulfide, S_8 , thiirane and dithiocarbamate instead of **4** but these failed to yield the desired products **5**, **6** and **7**. In case of C–Cl bond activation in the complexes **1c**, **2c** and **3c**, it is observed that the dithiocarbamate can also act as a thiolating agent. However, here the rate of the reactions and yields are much lesser compared to the dithiocarbonate **4**.

The free ligands L did not undergo the transformation $NC_5H_4N=NC_6H_4(R) \rightarrow NC_5H_4N=NC_6H_3(R)S^-$. This reveals the essential role of the metal ions in the activation processes.

All the complexes (**5**, **6** and **7**) are diamagnetic (low-spin t_{2g}^6 , $S = 0$). Ruthenium and osmium complexes (**5** and **6**) are electrically neutral but the cobalt complexes (**7**) exhibit 1:1 conductivity in acetonitrile solvent.

IR spectra of the cobalt complexes display a strong and broad band near 1100 cm^{-1} and a strong and sharp band near 630 cm^{-1} due to the presence of ionic perchlorate. The N=N stretching frequency of the free ligands L appears near 1430 cm^{-1} . The same $\nu_{N=N}$ frequency has been shifted to the lower values in the complexes ($\nu_{N=N}$, $\sim 1380\text{ cm}^{-1}$ for the cobalt complexes **7**, 1280 cm^{-1} for the ruthenium complexes **5** and 1200 cm^{-1} for the osmium complexes **6**) due to $d\pi(M) \rightarrow \pi^*(L')$ back-bonding where $\pi^*(L')$ is primarily dominated by the azo function¹⁵. This indicates that the $M \rightarrow L$ back-bonding follows the order: Co < Ru < Os.

In the visible region the complexes (**5**, **6** and **7**) exhibit two transitions. The lower energy band is broad and moderately intense while the higher energy band is sharp and intense (figure 1). Based on the intensities of these two allowed visible bands, the transitions are considered to be charge-transfer in nature¹⁶. Since in the complexes ruthenium(II), osmium(II) and cobalt(III) are in the low-spin t_{2g}^6 configuration, the two visible bands may therefore be due to $d\pi(M)$ to ligand LUMO and LUMO + 1 MLCT transitions respectively. According to the extended-Huckel calculations, the ligand LUMO involves the sulphur and the azo group, and the LUMO + 1 is mainly on the pyridine with some azo contribution.

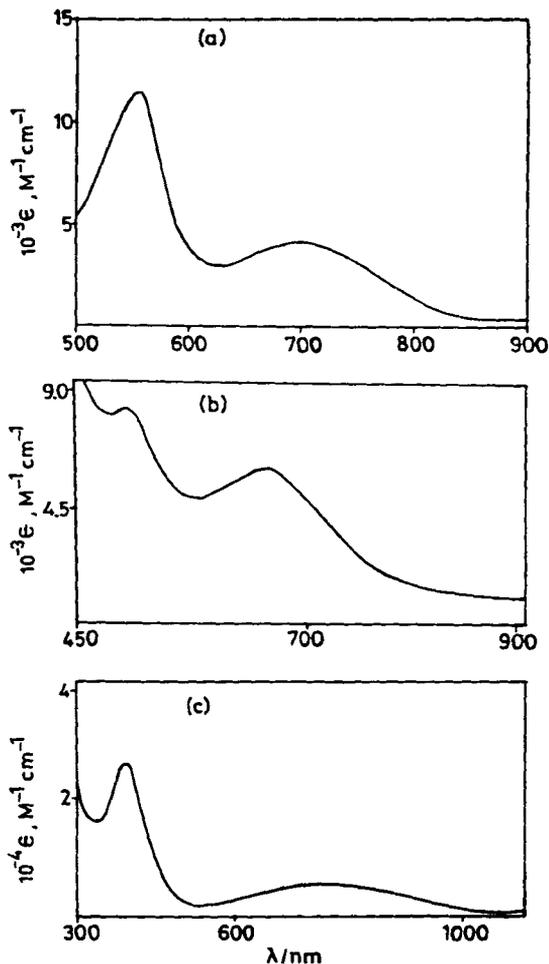


Figure 1. Electronic spectra of (a) $[\text{Ru}^{\text{II}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **5a** in dichloromethane, (b) $[\text{Os}^{\text{II}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **6a** in dichloromethane and (c) $[\text{Co}^{\text{III}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ (ClO_4) **7a** in acetonitrile.

2.2 ^1H NMR spectra

^1H NMR spectra of the complexes (**5a**, **6a** and **7a**) in CDCl_3 solvent exhibit similar four doublets and four triplets having equal intensities (figure 2). The individual proton resonances are assigned on the basis of their relative intensities, spin-spin structure and also from the effect of substituents¹⁷. The spectrum of ruthenium complex (**5a**) exhibits distinct four doublets and four triplets (figure 2a). The osmium complex (**6a**) displays two distinct doublets [H(1) and H(8)] and two triplets [H(2) and H(10)]. The other two doublets due to H(4) and H(11) protons and two triplets due to H(3) and H(9) protons overlap one another and are centred at δ 7.72 and 7.11 ppm respectively, which can be easily understood from the relative integration values (figure 2b). The corresponding cobalt complex (**7a**) shows three distinct doublets [H(1), H(4) and H(11)] and four

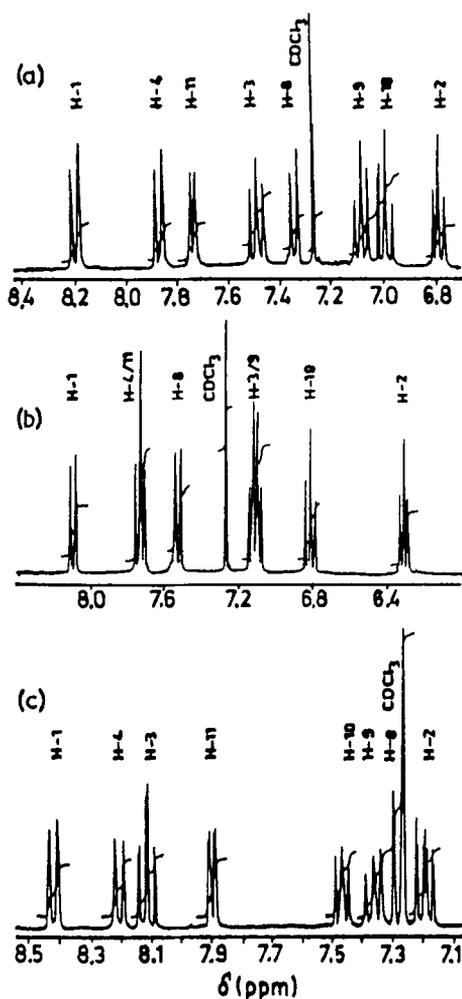


Figure 2. ^1H NMR spectra in CDCl_3 of (a) $[\text{Ru}^{\text{II}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **5a**, (b) $[\text{Os}^{\text{III}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **6a** and (c) $[\text{Co}^{\text{III}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2](\text{ClO}_4)$ **7a**.

triplets [H(3), H(10), H(9) and H(2)]. The fourth doublet [H(8)] merges partially with the CDCl_3 peak at δ 7.26 (figure 2c).

A direct comparison of the ^1H NMR spectra of complexes **5**, **6** and **7** with that of the free **L** reveals the absence of H(7) signal of the phenyl ring in the transformed thiolated ligand **L'** which is present in the complexes (**5**, **6** and **7**). Thus the newly formed **L'** ligand in **5a**, **6a** and **7a** exhibits two doublets [H(1) and H(4)] and two triplets [H(2) and H(3)] from the pyridine ring and two doublets [H(8) and H(11)] and two triplets [H(9) and H(10)] from the phenyl ring which can account for the observed eight protons having equal intensities. The absence of H(7) proton therefore supports the metal ion-mediated activation of the ortho-carbon–hydrogen [C–H(7)] bond of the pendant phenyl ring of **L** in the final complexes.

Since the NMR spectra of the complexes show only eight signals corresponding to one thiolated ligand L' , it can therefore be inferred that they basically represent half of the molecule i.e. each half of the molecule is equivalent due to localised symmetry around the metal centre.

The aromatic region of the spectra of the complexes **5d**, **6d** and **7d** are complicated due to the presence of isomers in solution, however the well resolved upfield methyl

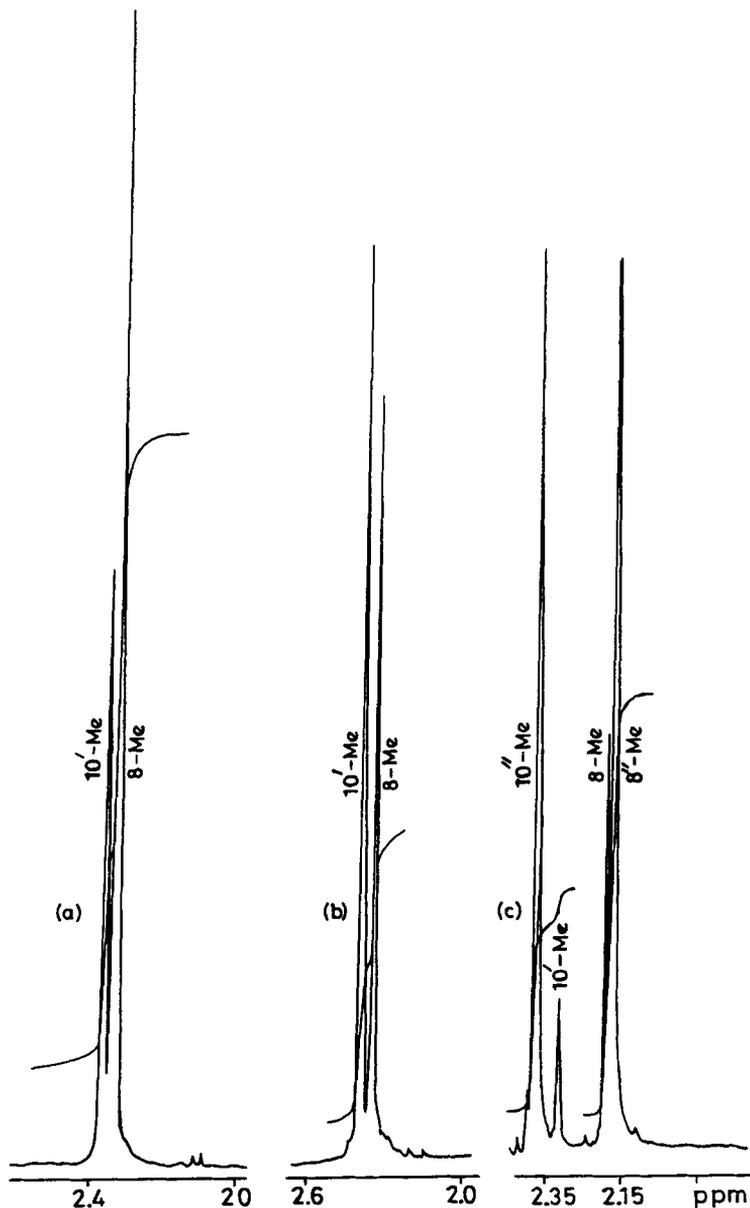


Figure 3. ^1H NMR spectra (Me signals only) in CDCl_3 of (a) $[\text{Ru}^{\text{II}}(\text{o-SC}_6\text{H}_3(\text{m-Me})\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **5d**, (b) $[\text{Os}^{\text{III}}(\text{o-SC}_6\text{H}_3(\text{m-Me})\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **6d** and (c) $[\text{Co}^{\text{III}}(\text{o-SC}_6\text{H}_3(\text{m-Me})\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ (ClO_4) **7d**.

signals indicate the percentage composition of the particular isomers in solution. The presence of the methyl group at the *meta* position of the active phenyl ring in both the ligands of **5d**, **6d** and **7d** develops the possibility of three isomers **8–10** through free rotation of the singly bonded *meta*-substituted phenyl rings. From the symmetry point of view one methyl signal is expected for each of the isomers **8** and **9** and two equally intense peaks for **10**. Since the NMR spectra of ruthenium (**5d**) and osmium (**6d**) complexes display two unequally intense methyl peaks at δ , 2.32/2.37 and 2.35/2.42 having intensity ratios 2:1 and 3:4 [figures 3(a) and 3(b)] respectively, isomers **8** and **9** are therefore predominant in solution. In the case of cobalt-complex **7d**, four methyl signals are observed and from the intensity distribution it appears that all the three possible isomers **8**, **9** and **10** are present in solution in the ratio 4:1:6 respectively [figure 3(c)]. The downfield aromatic portion of the spectra is overcrowded due to partial overlapping of the aromatic protons of the isomers, which precluded unequivocal assignments of the signals. However, the direct comparisons of the intensity of the aromatic proton signals with that of the clearly observable CH₃ protons (~ 2 ppm) for the complexes (**5d**, **6d** and **7d**) reveal the presence of the calculated number of aromatic protons in each case.

One methyl peak has been observed for the complex **5f** at δ , 2.33 as imposed symmetry makes the two ligands equivalent. All the seven aromatic proton signals are well resolved. The expected two doublets and two triplets from the pyridine ring and two doublets and one singlet from the phenyl ring are observed distinctly.

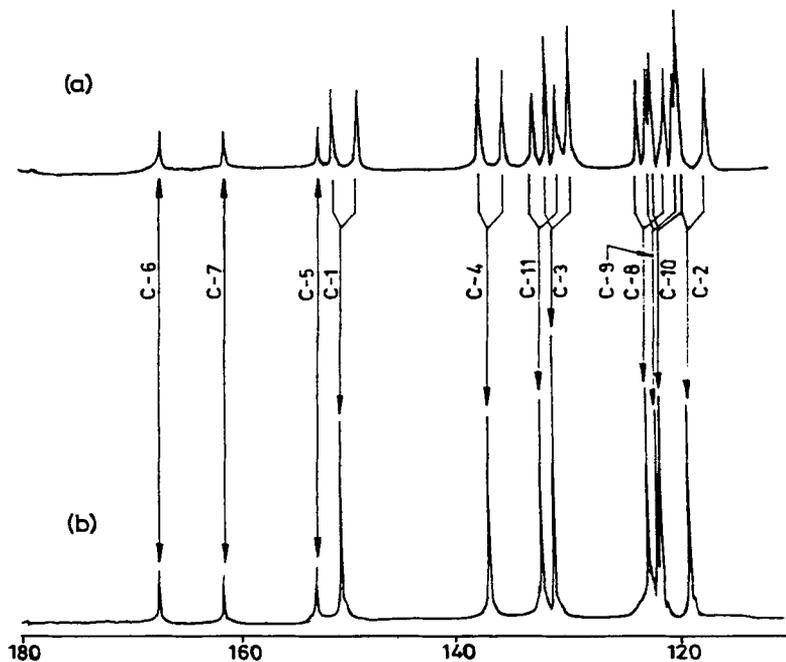


Figure 4. ¹³C NMR spectra in (CD₃)₂SO of [Ru^{III}(*o*-SC₆H₄N=NC₅H₄N)₂] **5a** (a) coupled (b) decoupled.

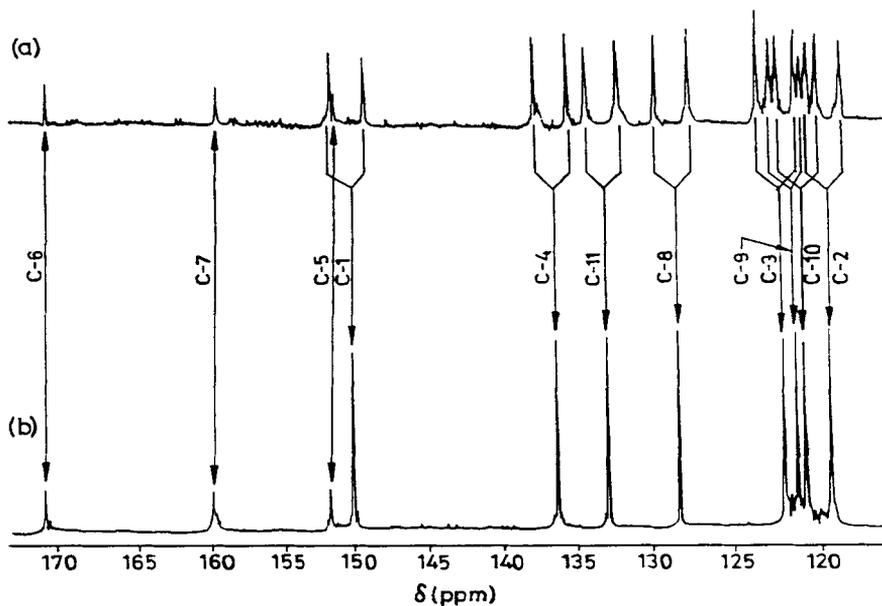


Figure 5. ^{13}C NMR spectra in $(\text{CD}_3)_2\text{SO}$ of $[\text{Os}^{\text{III}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2]$ **6a** (a) coupled (b) decoupled.

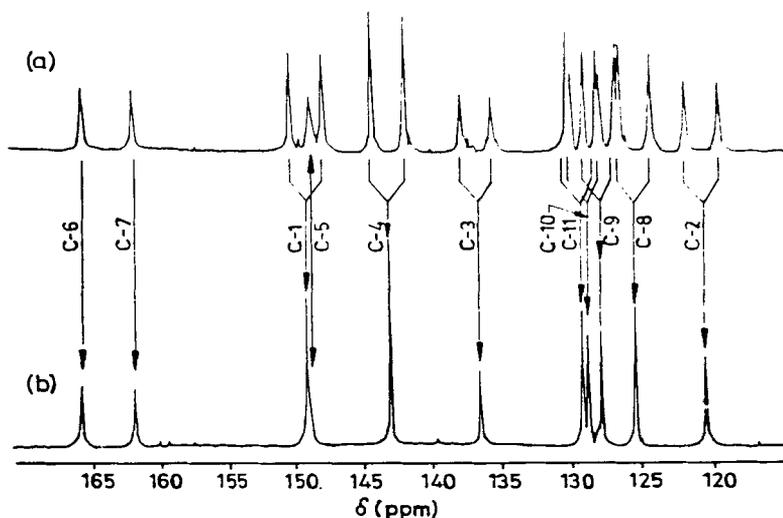


Figure 6. ^{13}C NMR spectra in $(\text{CD}_3)_2\text{SO}$ of $[\text{Co}^{\text{III}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2](\text{ClO}_4)$ **7a** (a) coupled (b) decoupled.

2.3 ^{13}C NMR spectra

The decoupled and coupled ^{13}C NMR spectra of complexes **5a**, **6a** and **7a** were recorded in $(\text{CD}_3)_2\text{SO}$ solvent. The spectra are shown in figures 4–6. The individual carbon

resonances are assigned on the basis of their electronic environments like the proton resonances. The decoupled spectra of the ruthenium (**5a**) and osmium (**6a**) complexes, figures 4b and 5b respectively have shown eleven distinct peaks. The corresponding coupled spectra (figures 4a and 5a) indicate the presence of three singlets and eight doublets.

The decoupled spectrum of the cobalt complex (**7a**) exhibits ten distinct and one partially overlapping peak (figure 6b). The coupled spectrum (figure 6a) shows three distinct singlets [the C(5) singlet which merges with the C(1) singlet in the decoupled spectrum has now appeared clearly here] and eight-doublets. The free L^I should have two singlets [C(5) and C(6)] and nine doublets. Thus the change of one doublet [C(7)] to the corresponding singlet while going from L^I in the starting complexes (**1a**, **2a** and **3a**) to L^I in the final complexes **5a**, **6a** and **7a** further unequivocally establishes the activation of the C(7)–H bond of the phenyl ring of L^I in the complexes.

2.4 Metal redox

In acetonitrile solvent, ruthenium and osmium complexes (**5a** and **6a**) show reversible $Ru^{III} \rightleftharpoons Ru^{II}$ and $Os^{III} \rightleftharpoons Os^{II}$ reduction potentials at 0.43 and 0.36 V vs SCE (platinum working electrode, tetrabutyl ammonium perchlorate as electrolyte) respectively (figure 7). Under identical experimental conditions the cobalt complex (**7a**) exhibits reversible $Co^{III} \rightleftharpoons Co^{II}$ reduction potential at –0.14 V vs SCE (figure 7). The low (< 0 V vs SCE) cobalt(II)–cobalt(III) oxidation potential of the complex **7a** can account for its stabilization in the trivalent state which possibly occurs by the aerial

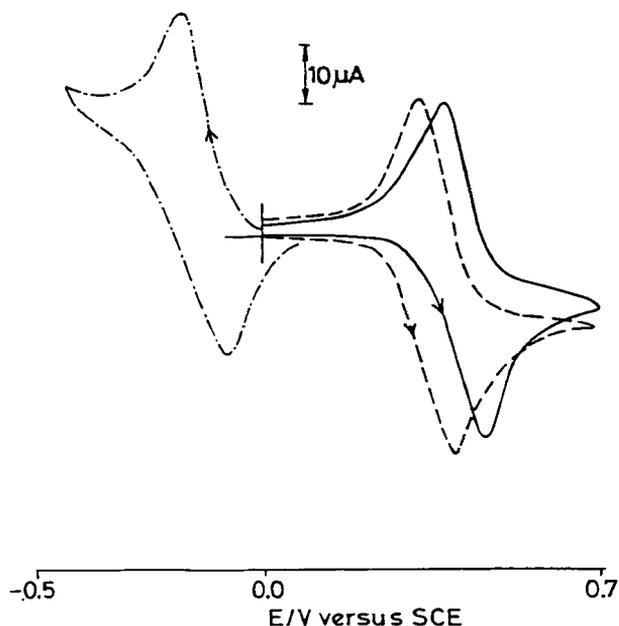


Figure 7. Cyclic voltammograms of $\approx 10^{-3}$ M solution of complexes $[Ru^{II}(o-SC_6H_4N=NC_5H_4N)_2]$ **5a**, $[Os^{II}(o-SC_6H_4N=NC_5H_4N)_2]$ **6a** and $[Co^{III}(o-SC_6H_4N=NC_5H_4N)_2]$ (ClO_4) **7a** in acetonitrile at 298 K.

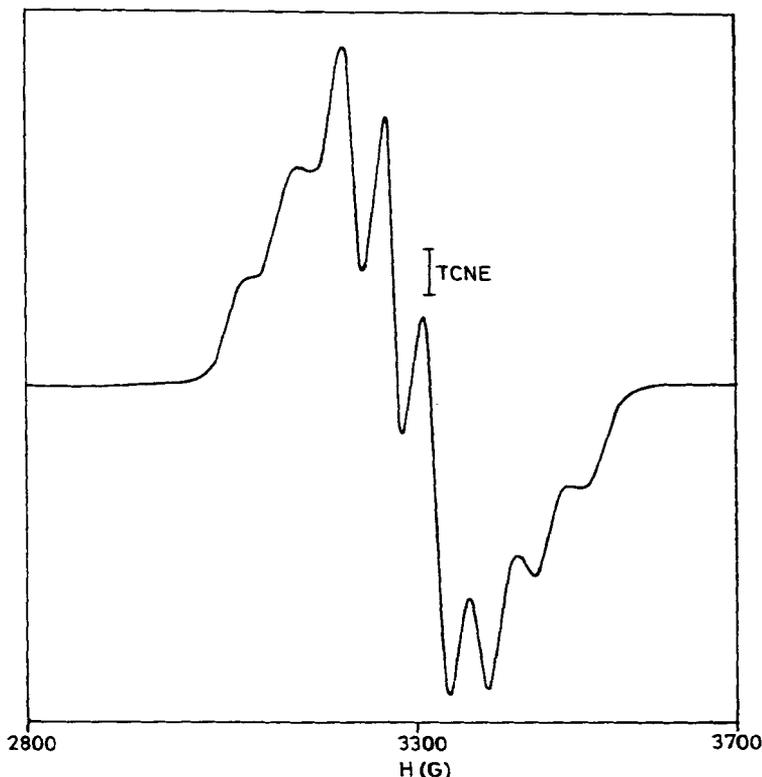


Figure 8. X-band EPR spectrum of coulometrically reduced complex $[\text{Co}^{\text{II}}(o\text{-SC}_6\text{H}_4\text{N}=\text{NC}_5\text{H}_4\text{N})_2] 7\text{a}^-$ in acetonitrile solution at 77 K.

oxidation of the Co^{II} congener of **7a** during the course of the reaction (scheme 1). Thus the chemical reduction of the Co^{III} complex **7a** by hydrazine hydrate as well as the electrochemical reduction at -0.3 V vs SCE generate unstable Co^{II} congener.

In order to confirm that the reduced solution consists of $\text{Co}(\text{II})$ species as opposed to the reduced ligand, the X-band EPR spectrum of the fresh reduced solution (produced coulometrically in acetonitrile solvent followed by quick freezing at 77 K) was examined. It comprises eight lines (figure 8) characteristic of hyperfine splitting by ^{59}Co nucleus (^{59}Co , 100% natural abundance, $I = 7/2$). The centre-field g value and the average hyperfine splitting are 1.99 and 56 G respectively.

2.5 Probable reaction pathways

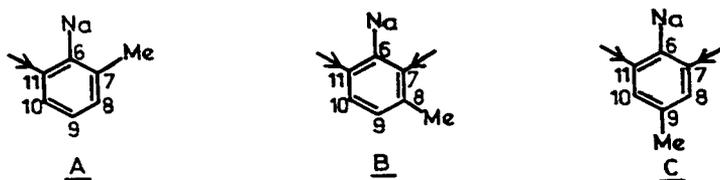
2.5a C-H bond activation: The mechanism of the metal ions mediated selective activation of the ortho C-H bond of the phenyl ring of the ligands (L') in the complexes **5**, **6** and **7** is not clearly understood. This may be primarily due to the following two factors: (i) the reactions take place only at a higher temperature (boiling dmf), (ii) the reactions proceed without any tractable stable intermediates. However, the following observations help to understand the reaction pathway to a certain extent: (i) the reactions are highly sensitive to the electronic nature of the substituents present in the active phenyl

ring, (ii) the reactions are strictly dependent on the specific position of the substituents in the phenyl ring with respect to the active ortho-C-H bond, (iii) high boiling polar solvent is essential to carry out the reactions.

It has been observed that the presence of electron donating methyl group at the ortho and para positions of the phenyl ring with respect to the activation positions (C-7 and C-11) facilitates the thiolation reaction. Since the meta methyl (C-8) group (**B**) can only satisfy the above requirements, the starting complexes **1d**, **2d** and **3d** therefore result in isomeric mixture of thiolated complexes where both the active sites C-7 (ortho with respect to C-8 methyl group) and C-11 (para with respect to C-8 methyl group) have been thiolated.

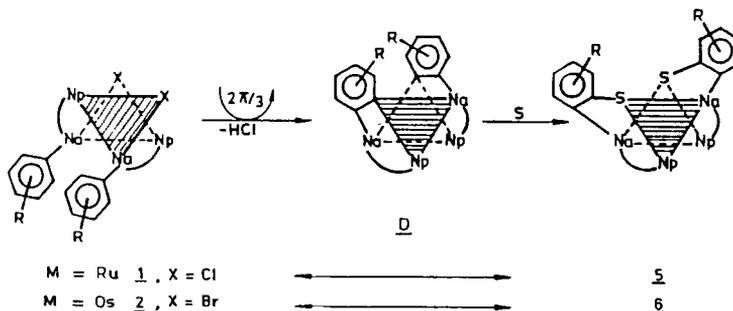
The rate of the thiolation reactions (scheme 1) when electron donating methyl group present at the ortho and para positions with respect to the activation points is much faster compared to the unsubstituted active phenyl ring.

The other two methyl positions in the pendant phenyl ring such as C-7 (A) and C-9 (C) are basically meta with respect to the activation points C-7 and C-11, thus did not



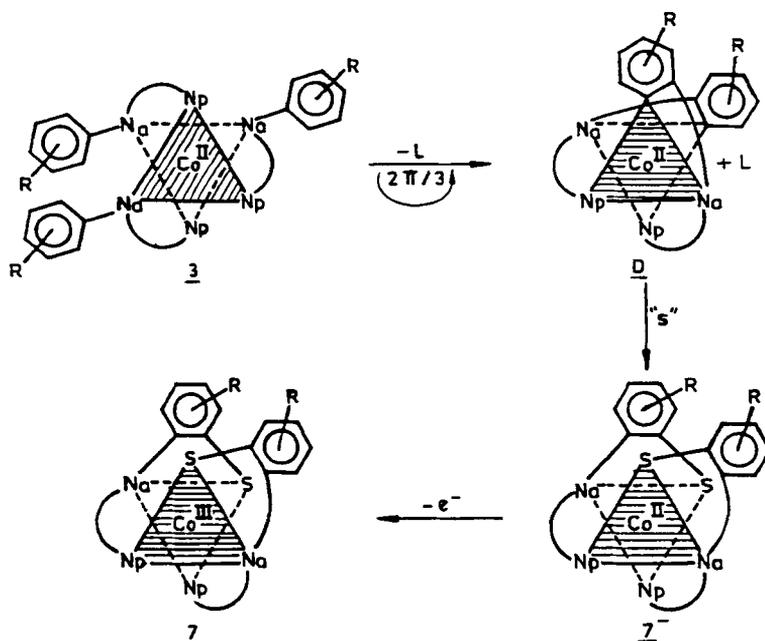
prefer to do the reactions. Therefore an optimum electron density at the activation points (C-7 and/or C-11) is necessary to carry out the reactions. Since the methyl group is an ortho and para oriented electron donating function, its meta position (A and C) with respect to C-7 and C-11 cannot help to achieve the required electron density at the activation sites. The presence of an electron withdrawing chloride group at any position of the phenyl ring (ortho, meta or para) has altogether failed to perform the reactions. This is due to the fact that the chloride group being an electron withdrawing function cannot help the active points (C-7 and C-11) to have the necessary electron density by any means.

Based on the above observations it may be considered that the attack of an electrophile at the active sites is the first step of the activation process. We therefore logically assume that the reactions proceed via the reactive orthometallated species, **D** (schemes 2a, b) where the metal ion acts as an electrophile. Orthometallation from the



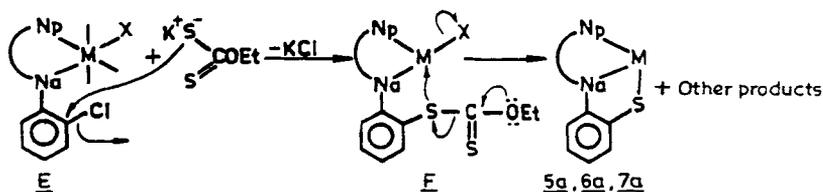
Scheme 2a

pendant phenyl ring is well documented¹⁸. The assumed four-membered orthometalated intermediate (**D**) is expected to be reactive from a thermodynamic point of view and which in turn may be responsible for its invisible existence. Insertion of sulphur (generated by the cleavage of C-S bond of dithiocarbonate, **4**) into the reactive metal-carbon bond may lead to the thiolated products (**5**, **6** and **7**). In case of cobalt complex (**7**) an addition step regarding the oxidation of $\text{Co}^{\text{II}} \rightarrow \text{Co}^{\text{III}}$ is involved (scheme 2b).



Scheme 2b.

2.5b *C-Cl bond activation*: The carbon-chloride bond activation process in the complexes **1c**, **2c** and **3c** possibly proceed through the nucleophilic addition of the thiolating agent **4** at the C-Cl point of the pendant phenyl ring (**E**, scheme 3) followed by



Scheme 3.

the elimination of the Cl^- group¹⁹. The presence of strong electron pool in the direction of the metal ion via the electron withdrawing azo group linked to the phenyl ring ortho to the activation point might be the driving force for the nucleophilic addition step (**E**)²⁰. In the

absence of metal ion the free L^3 does not have this electronic advantage to undergo the nucleophilic addition reaction. It thus failed to perform the thiolation reaction. Once the intermediate **F** is formed, the subsequent processes such as cleavage of C–S bond of **4**, the formation of M–S bond and removal of the halide groups from the ruthenium and osmium complexes and the removal of one L^3 in case of the cobalt complex might have taken place consecutively. Since the overall conversion process is associated with several bond-breaking and bond-forming steps, the high boiling dmf solvent is needed to facilitate all those simultaneously operating processes.

The rate of formations of the thiolated products in case of dithiocarbamate as the thiolating agent is much slower compared to the dithiocarbonate (**4**), which is possibly due to the second step (**F**, scheme 3) where the C–S bond breaking process is involved.

3. Experimental

3.1 Materials

Commercial ruthenium trichloride (SD Fine Chemicals, Bombay, India) was converted into $RuCl_3 \cdot 3H_2O$ by repeated evaporation to dryness with concentrated hydrochloric acid. Osmium tetroxide was obtained from Johnson Matthey and Co. Ltd., London. Cobalt carbonate (JT Baker, Colorado, USA) was converted into cobalt perchlorate by standard method. The ligands L^1 – L^7 and the starting cobalt complexes (**3**) were prepared according to the reported procedures²¹. The starting ruthenium (**1**) and osmium (**2**) complexes were prepared by following the reported procedures^{15,22}. Potassium salt of dithiocarbonate (**4**) was prepared according to the reported procedure²³. 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 procedure²⁴. Dinitrogen gas was purified by successive bubbling through alkaline dithionite and concentrated sulphuric acid.

3.2 Physical measurements

Solution electrical conductivity was checked using Systronic 305 conductivity bridge. Electronic spectra (900–200 nm) were recorded using a Shimadzu-UV –160 A spectrophotometer. IR spectra were recorded on a Nicolet spectrophotometer with the 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 (SCE) were used in the three-electrode configuration. The supporting electrolyte was $[NBu_4]ClO_4$ and the solute concentration $\approx 10^{-3}$ M. The half-wave potential, E_{298}^0 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 mVs^{-1} . All experiments were carried out under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. 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). Spectra were calibrated by using tetracyano ethylene (tcne) ($g = 2.0023$). The elemental analyses were carried out with a Carlo Erba (Italy) elemental analyser.

3.3 Preparation of complexes

$[Ru^{II}(o-SC_6H_4N=NC_5H_4N)_2]$ **5a**: A 100 mg, 0.18 mmol sample of *ctc*- $[RuL^1_2Cl_2]$, **1a** was dissolved in 20 ml of dmf solvent. To this solution the potassium salt of *o*-ethyl dithiocarbonate (**4**) 60 mg, 0.38 mmol was added. The resulting solution was heated to reflux for 3 h. The initial blue solution gradually turned to a red brown colour. It was evaporated to dryness under reduced pressure and the solid mass thus obtained was dried *in vacuo* over P_4O_{10} . The dried product was dissolved in a small volume of chloroform and was 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 dryness under reduced pressure to afford a dark crystalline solid, which was recrystallised from dichloromethane–hexane (5:1). Yield: 70%.

The complexes **5d** and **5f** were prepared by following the above method except for the reflux time. Approximately 1 h and 8 h respectively were required to get the desired products. Yield: 90% for **5d** and 10% for **5f**.

The complex **5a** was also obtained starting from **1c** through the carbon–chloride bond activation process. Here within 15 m, 85% product (**5a**) was formed under identical experimental conditions as mentioned above.

$[Os^{II}(o-SC_6H_4N=NC_5H_4N)_2]$ **6a**: The complex *ctc*- $[Os^{II}L^1_2Br_2]$ **2a** (100 mg, 0.14 mmol) was dissolved in 20 ml of dmf under warm condition. To this solution the potassium salt of *o*-ethyl dithiocarbonate (45 mg, 0.28 mmol) was added. The mixture was heated to reflux for 1 h. The initial blue-violet colour of **2a** was gradually changed to light green. The solvent was then removed under reduced pressure and the solid mass thus obtained was dried under *in vacuo* over P_4O_{10} . The dried product was dissolved in 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. Finally the product was recrystallised from dichloromethane–hexane (1:8). Yield was (65%).

The complex **6d** was prepared by following the above method except the reflux time. Here only 0.5 h was needed to complete the reaction. The yield was 90%.

The complex **6a** was also obtained starting from **2c** via the C–Cl bond activation process. Here 80% product (**6a**) was formed within 15 m under identical experimental conditions as mentioned above.

$[Co^{III}(o-SC_6H_4N=NC_5H_4N)_2](ClO_4)$ **7a**: The complex *mer*- $[Co^{III}(L)_3](ClO_4)_2 \cdot H_2O$ **3a** (100 mg, 0.12 mmol) was dissolved in dmf (15 ml) and the potassium salt of *o*-ethyl dithiocarbonate (40 mg, 0.25 mmol) was added to it. The mixture was then heated to reflux for 4 h. The initial brown colour of **3a** gradually changed to a greenish colour. 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 by 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. The evaporation of the solvents under reduced pressure afforded a crystalline solid. The pure product was dried *in vacuo* over P₄O₁₀. Finally the product was recrystallised from acetonitrile–benzene (1:6). Yield 65%.

The complex **7d** was synthesized by following the above procedure and it took 1 h to yield 90% product.

The complex **7a** was also prepared from the starting **3c** complex following the C–Cl bond activation method and only 10 min time was needed to achieve 85% product.

4. Conclusions

This study shows that the metal ions mediated selective activations of the C–H and C–Cl bonds of the phenyl ring lead to the one-pot synthesis of aromatic thiols via the C–S bond cleavage of dithiocarbonate and dithiocarbamate molecules which is conventionally a multistep process. Suitably placed substituents in the active phenyl ring facilitate the formation of isomeric products due to the selectivity of the activation process. We have observed that the rate of thiolation reaction is much faster in case of C–Cl bond activation process compared to the C–H bond activation. The thiolation process is highly sensitive to the natures of the substrate, the thiolating agent and the solvent.

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