ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 7, pp. 482–485. © Pleiades Publishing, Ltd., 2009.

Aromatic Ring Aminated Trischelates of Ruthenium(II): Synthesis and Spectral Characterization[1]

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Received June 30, 2008

Abstract—Aromatic ring amination reactions in the ruthenium complex of 1-methyl-2-(phenylazo)imidazole is described. The substitutionally inert cationic brown complex [Ru(HAaiMe)$_3$](ClO$_4$)$_2$ (**I**) reacts smoothly with aromatic amines neat and in the presence of air produce cationic and intense blue complexes [Ru(ArNH-AaiMe)$_3$](ClO$_4$)$_2$ (**II**) (ArNH-AaiMe = 1-methyl-2-[(4-(arylamino)phenyl)azo] imidazole, Ar = C_6H_5 (**IIa**), *p*-C_6H_4Me (IIb)). These were purified on a preparative TLC plate (large plates of thin layer chromatography). The results are compared with those of the starting complex, [Ru(HAaiMe)$_3$](ClO$_4$)$_2$ (**I**). The transformation **I** $\longrightarrow$ **II** involves aromatic ring amination at the *para* carbon (with respect to the diazo function) of the pendant phenyl rings of all three coordinated azoimine ligands in **I**. The ruthenium complex **II** is characterized by intense blue solution color. The lowest energy transitions in these complexes appear near 600 nm, which have been attributed to intraligand charge-transfer transitions. IR spectra of the complexes show –C=N– and –N=N– stretching at 1590 and 1370 cm^{-1} which is red shifted by 40 and 90 cm^{-1} from the free ligand value and supports Ru-azo nitrogen π bonding interection. The ^{1}H NMR spectral measurements suggest methyl and aromatic ring protons. Considering three arylazoimidazole moities there are forty eight different carbon atoms in the molecule which gives a total of that different peaks in the ^{13}C (^{1}H) NMR spectrum. In the ^{1}H–^{1}H COSY spectrum of the present complex, absence of any off-diagonal peaks extending from δ = 14.12 and 9.55 ppm confirms their assignment of no proton on N(1) and N(3), respectively. Contour peaks in the ^{1}H–^{13}C HMQC spectrum in the present complex assign them hydrogen carbon atoms relationship, respectively. The electrons are believed to be added successively to the three azo functions.

DOI: 10.1134/S1070328409070033

INTRODUCTION

This work originated from my recent interest on metal-promoted aromatic ring amination reactions [1–4] on the coordinated ligand 1-methyl-2-(phenylazo)imidazole (**HAaiMe**). Amine fusion reactions of the above type occurring either at *ortho* or at *para* carbon (relative to the azo fragment) of the pendent phenyl ring.

For example, when a labile [Co^{II}]$^{2+}$ complex was reacted with ArNH$_2$, it produced a green cobalt(III) complex, [Co(L^1)$_2$]$^+$ [5–9]. This transformation involves elimination of a bidentate ligand from the parent complex, which is followed by *ortho*-amination of the rest two coordinated ligands. It is to be noted here that *ortho*-amination of the ligand leads to the formation of a bischelating tridentate anionic ligand, two of which are coordinated to the cobalt(III) cation in its complex. It thus appeared that ligand dissociation from the mediator complex might be responsible for the above *ortho*-amination reaction. Although complete *ortho*-amination reaction was observed in the case of [Co(Pap)$_3$]$^{2+}$, but Goswami et al. did not have an example of complete *para*-amination reactions. They, however, were successful to observe the *para*-amination reactions, only partially, in the cases of a rhodium(III) and a chromium(II) complex [10–13]. To achieve *para*-amination, we chose a cationic trischelate [Ru(HAaiMe)$_3$](ClO$_4$)$_2$ (**I**) as the mediator complex. The reference ruthenium complex is known [6, 14–19] to be substitutionally inert. The primary aim of this report is to present the results on the reaction of ArNH$_2$ with **I**. In this case all the coordinated ligands have undergone amination exclusively at the *para*-carbon.

EXPERIMENTAL

RuCl$_3$ · nH$_2$O was obtained from Arora Matthey, and was digested thrice with concentrated HCl before use. Ligand 1-alkyl-2-(arylazo)imidazoles **RAaiR'** and [Ag(Bipy)$_2$](ClO$_4$) were synthesised by reported procedure [10–16]. *ctc*-RuCl$_2$(RAaiR')$_2$ was prepared by known method. The purification of solvents for electrochemical and spectral work and [nBu$_4$N][ClO$_4$] were prepared as described earlier [2]. All other chemicals

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and solvents used for the preparative work were of reagent grade and were used as received. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. Solution electronic spectra were recorded on a JASCO UV-VIS-NIR V–570 spectrophotometer. IR spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000–200 cm^{-1}). The ^1H NMR spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10^{-3} mol/l in acetonitrile. FAB mass spectrum at 298 K was recorded on a SX 102 DA6000 mass spectrum.

Synthesis of [Ru(HAaiMe)$_3$](ClO$_4$)$_2$ (I). [Ru(HAaiMe)$_2$Cl$_2$](ClO$_4$)$_2$ (0.19 g, 0.20 mmol) was solvated by reacting with ethanol, then filtered through G4 gouch crucible. This solution and HAaiMe (0.134 g, 0.20 mmol) was heated on a steam bath for 4 h. The initial reddish-brown color of the mixture gradually became deep-red. The mixture was cooled and washed thoroughly with diethyl ether for several times. Finally, it was purified by thin layer chromatographic technique using a 40% chloroform–acetonitrile mixture as the eluent (first, chromatographed and then the solvent was separated and dried). The intense red product, thus obtained, was recrystallized from a toluene–acetonitrile mixture. Yield **I** was 0.19 g (80%).

Synthesis of [Ru(ArNHAaiMe)$_3$](ClO$_4$)$_2$ (IIa). A mixture of I (0.20 g, 0.23 mmol) and $PhNH_2$ (0.5 ml) was heated on a steam bath for 4 h. The initial brown color of the mixture gradually became ink-blue. The mixture was cooled and washed thoroughly with diethyl ether for several times. Finally, it was purified on a preparative TLC plate using a 40% chloroform–acetonitrile mixture as the eluent (firstly, chromatographed and then the solvent was separated and dried). The intense blue product, thus obtained, was recrystallized from a toluene–acetonitrile mixture. Yield IIa was 0.19 g (70%).

For [Ru(ArNHAaiMe)$_3$](ClO$_4$)$_2$ ($C_{48}H_{48}N_{15}Cl_2O_8Ru$) (**IIa**)

anal. calcd, %:	C 54.55;	H 3.77;	N 14.97.
Found, %:	C 54.32;	H 3.54;	N 14.76.

MS: *m/z* 924; UV-Vis spectra (λ_{max}, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1})): 597 (48800), 496 (34449), 282 (39998); FTIR (KBr; ν, cm^{-1}): 3420 ν(N–H), 1600 ν(C=C), 1590 ν(C=N), 1320 ν(N=N), 1190, 1089, 640 $\nu(ClO_4)$; ^1H NMR ($CDCl_3$; δ, ppm): 8.3 (d., 7.11H), 7.99 (d., 8, 10H), 8.43 (d., 13, 17H), 7.93 (t., 14, 16H), 7.6 (t., 15H), 7.32 (d., 4H), 7.61 (d., 5H), 1.67 (s., N–Me); ^{13}C (H) NMR ($CDCl_3$; δ, ppm): 128.3 (7, 11C), 127.99 (8, 10C), 128.43 (13, 17C), 131.93 (14, 16C), 130.6 (t., 15C), 127.32 (d., 4C), 127.61 (d., 5C), 61.67 (s., N–Me).

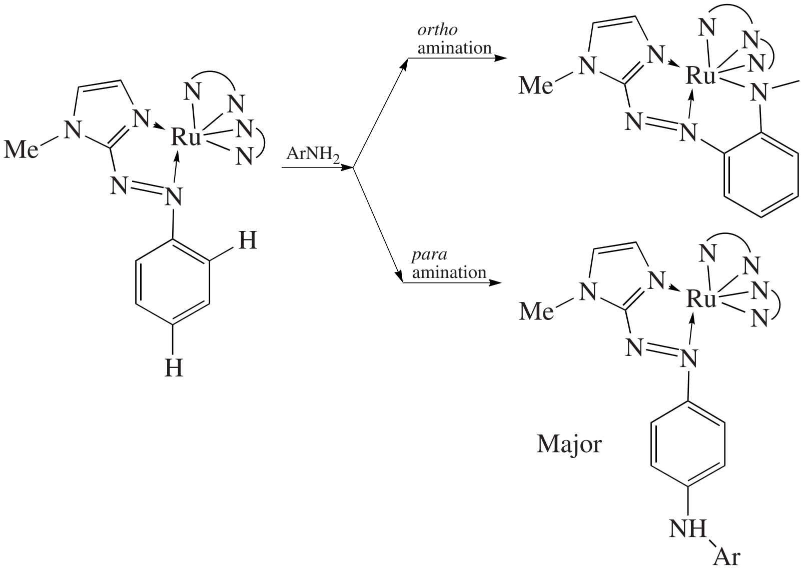
For [Ru(ArNHMeAaiMe)$_3$] (ClO$_4$)$_2$($C_{51}H_{51}N_{15}Cl_2O_8Ru$) (**IIb**)

anal. calcd, %:	C 54.5;	H 3.7.
Found, %:	C 54.3;	H 3.5.

FTIR (KBr; ν, cm^{-1}): 3410 ν(N–H), 1620 ν(C=C), 1599 ν(C=N), 1327 ν(N=N), 1190, 1089, 649 $\nu(ClO_4)$; ^1H NMR ($CDCl_3$; δ, ppm): 8.13 (d., 7, 11H), 7.99 (d., 8, 10H), 8.13 (d., 13, 17H), 7.93 (t., 14, 16H), 1.62 (t., 15-Me), 7.32 (d., 4H), 7.61 (d., 5H), 1.97 (s., N–Me).

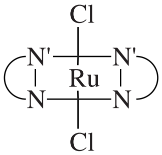
RESULTS AND DISCUSSION

Isolation and complete characterization of the products follow the reactions:

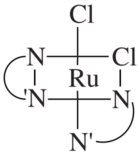


Complex **I**, was reacted with neat $ArNH_2$ on a steam bath in air. The initial brown color of the ruthenium trischelate $[Ru(RAaiR')_3](ClO_4)_2$, where R = H; R' = Me, gradually became ink-blue in 4 h. The crude product, after initial workup, was finally purified on a preparative TLC plate. An intense blue band of composition $[Ru(HL)_3](ClO_4)_2$ (**II**), where HL = ArNHAaiMe, was collected in 60–70% yield. The above reaction does not proceed at all in the presence of solvent and is sluggish in an inert atmosphere. A similar amination reaction was also tried on the neutral complex $[RuCl_2(RAaiR)_2]$, which notably was unreactive to $ArNH_2$.

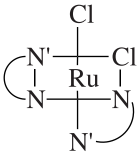
Greater electrophilicity of the cationic complexes appears to be crucial for the amination reactions. Among the major three isomers ***ctc***, ***tcc***, ***ccc***:



tcc



ctc



ccc

ctc-isomer is used in the synthetic purpose. It is probable that nucleophilic attack of deprotonated $[ArNH]^-$ at the *para* carbon of the pendant phenyl group of HAaiMe is the primary and key step for this fusion reaction. Nucleophilic substitution on an aryl ring is otherwise not common. It is believed that the phenyl ring of HAaiMe becomes electrophilic upon coordination. In the aforesaid reactions, the coordinated ligands undergo fusion with an amine function exclusively at the *para*-carbon (relative to the azo functionality) of the pendant phenyl ring.

The results have confirmed the regioselective nature of the amination reaction. Moreover these have also demonstrated that the site selectivity of the above reactions may be controlled by the proper selection of the mediator complex. These complexes are diamagnetic (Ru(II), t_2^6). In the resultant complex, the transformed ligand HL bears an uncoordinated donor amine function, which is separated from a coordinated acceptor azo function by a conjugated spacer. Metal complexes of such ligands having both donor and acceptor chromophores are of current interest. One of the most important observations in the IR spectra of the complexes of HL is the appearance of ν(N–H) in the range 3420–3250 cm^{-1}.

The dihalo complexes showed sharp bands, while those for the trischelates are broad. The abilities of the azo ligands to act as strong π-acceptors toward low valent metal ions are well documented. The azo imine orbitals in these complexes are strongly involved in π-interactions. Thus, the ν(N = N) stretching frequencies in the complexes of HL are appreciably lowered [8, 15] comparing to that for the free HL. *ctc*-Isomer is required among the major three isomers.

The solution color of the ruthenium complexes of HL is blue, and these are characterized by a strong absorption near 600 nm. The spectrum of the free ligand HL consists of two high-energy transitions at 415 and 270 nm, respectively. The UV-Vis spectrum of the cationic trischelate, $[Ru(HL)_3]^{2+}$, comprises a strong absorption in the range 590–600 nm, which is associated with a shoulder near 500 nm. There is also a strong band in the UV region. The intensity of the lowest energy transition in these complexes is unusually high, which varies with the change of substitution R on the ligand HL. The broad transition at 492 nm for $[Ru(RAaiR)_3]^{2+}$ was assigned to a metal-to-ligand charge transfer (**MLCT**) transition. Comparison of the above spectra indicates that the MLCT transition in $[Ru(RAaiR)_3]^{2+}$ also appeared at 494 nm. The band near 600 nm is due to an additional allowed transition, which is responsible for the intense blue color of its solution. The ligand HL has the donor amine as well as the azo acceptor functions, which are separated by a conjugated spacer. The acceptor property of the azo-chromophore is augmented upon coordination to the ruthenium center.

The ^1H NMR spectra of the trischelates are very complex due to overlapping of unique proton resonances. The N–H resonance was observed near δ = 6.0. 1-Me appears as a singlet at 4.2 ppm; the methylene protons, $1\text{-}CH_2\text{–}(CH_3)$, show AB type sextet (~4.4, 4.6 ppm) and methyl gives a triplet at 1.5 ppm (7.0–8.0 Hz). $1\text{-}C_2(Ph)$ protons appear at AB type quartets (~5.5, 5.7 ppm).

The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the molecule. Carbon atoms neighbouring the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrogen atom and π electron delocalisation in the magnetic environment. The non-protonated carbon atoms at C(2), C(9), C(12), and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum effected by the magnetic interection of two bulky phenyl rings environment and the two methyl substituted imidazole rings and the π electron delocalization on the =N–C–C=N– and =N–C–C=C–C–. The methyl carbon atom of the imidazole ring resonates at 60 ppm, resonably compare to the other carbon atoms resonance.

The COSY spectrum reveals the ^1H–^1H coupling interections in the molecule. It is usually plotted as three dimentional contours, where the conventional spectrum is represented along the diagonal. The cross peaks along both the sides of the diagonal identify the nuclei that are coupled to each other. On the contrary, the protons that are decoupled from the adjacent ones due to the lack of α-protons will show no coorelation in the spectrum. However, extending horizontal and vertical lines from δ = 8.32 (C(7)H) and 8.68 ppm (C(13)H) encounter cross peaks at δ = 7.12 and 7.23 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. COSY spectrum also turns out very helpful in the accurate assignment of proton resonance in the aromatic region. The doublet of the C(7)H and C(11)H protons show coupling interection with the doublet at $\delta = 7.12$ and 7.68 ppm (C(9)H and C(10)H).

The ^{1}H–^{13}C heteronuclear multiple-quantum coherence (HMQC) spectrum provides information regarding the interection between the protons and the carbon atoms to which they are directly attached. In the present complexes, the absence of any contours at $\delta = 147.12$, 160.76, 155.67, and 157.68 ppm assign them to the C(2),C(6), C(9), and C(12) carbon atoms, respectively. This is because they belong to the non-protonated carbon atoms on the imidazole, phenyl and arylamine rings. The doublets at $\delta = 7.92$, 7.45, 7.82, and 7.68 ppm (H(4), H(5), H(7), and H(8)) show contours at $\delta = 148.42$, 147.55, 144.82, and 140.68 ppm [C(4), C(5), C(7), and C(8)] which help to distinguish these carbon resonance, which are close to each other.

Thus, in this work we have achieved regioselective *para*-amination at coordinated 2-(phenylazo)imidazole ligands in $[Ru(HAaiMe)_3]^{2+}$. The role of the mediator complex with respect to site selectivity of the amination reaction has been established. This seems reasonable since prior coordination of an amine residue at the vacant site of the metal ion would bring it in close proximity to the *ortho*-CH of the pendent phenyl ring. In the absence of any such vacant site at the metal center, as it occurs in the case of a substitutionally inert mediator complex, $ArNH_2$ cannot approach the *ortho*-carbon and hence fusion occurs only at the *para*-carbon. ^{1}H NMR study suggests quartet splitting of ethyl substitution. ^{13}C NMR gives the molecular skeleton in solution phase. ^{1}H–^{1}H COSY spectrum as well as the contour peaks in the ^{1}H–^{13}C HMQC spectrum of the present complexes, assign their accurate structure.

ACKNOWLEDGMENTS

The Ministerio De Education Y Ciencia, Madrid (grant no. SB2004-0060) is thanked for financial support and Prof. C. Sinha, M. Laguna, B. Guchait, Pravas, Latika Byabartta for constant help and valuable comments on this work.

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