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DPPM-RU-RAAIR: DPPM (DIPHENYLPHOSPHINIMETHANE)-RUTHENIUM(II)-BIS-{1-(ALKYL)-2-(ARYLAZO)IMIDAZOLE (RAAIR)} COMPLEXES: [RU(DPPM)(RAAR)$_2$] : SYNTHESIS, SPECTRAL STUDY AND ELECTROCHEMISTRY.

Prithwiraj Byabartta*

Inorganic Chemistry Research Laboratory (Icrl), Epartment of Chemistry, Jogesh Chandra Chaudhuri College, 30-Prince Anwar Shah Road, Kolkata.

***Corresponding Author: Prithwiraj Byabartta**
Inorganic Chemistry Research Laboratory (Icrl), Epartment of Chemistry, Jogesh Chandra Chaudhuri College, 30- Prince Anwar Shah Road, Kolkata.

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ABSTRACT

Silver assisted aquation of blue cis-trans-cis-$RuCl_2(RaaiR)_2$[1] leads to the synthesis of solvento species, blue-violet cis-trans-cis-$[Ru(OH_2)_2(RaaiR')_2](ClO_4)_2$ [RaaiR = p-R-C_6H_4- N=N-C_3H_2-NN,[2], abbreviated as N,N/-chelator, where N(imidazole) and N(azo) represent N and N/, respectively; R = p-Me that have been reacted with DPPM in warm EtOH resulting in red-violet dithiocyanato complexes of the type, [Ru(DPPM)(RaaR)$_2$].[3] The solution structure and stereoretentive transformation in each step have been established from ^{1}H n.m.r. results. All the complexes exhibit strong MLCT transitions in the visible region. They are redox active and display one metal-centred oxidation and successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

KEYWARDS: 1-alkyl-2-(arylazo)imidazole, DPPM, ruthenium(II), MLCT, NMR, CV, IR.

INTRODUCTION

The elimination of functional groups from organic molecules has immense significance in chemistry, including the synthesis of natural products.[1,2] In this context, decarbonylation reactions have become an indispensable aspect in the advancement of chemical synthesis. The key challenge of the decarbonylation reaction lies in the high bond dissociation energy of the C−C bond. Complexes of platinum group metals have been used to address this issue, as the metal center destabilizes the C−C bond through single- or two-electrontransfer processes. Hence, the platinum-group metals have drawn considerable attention over the decades.[3−5] Among the platinum-group metals, ruthenium exhibits the largest range of stable oxidation states (from −II to + VIII).[6] Hence, there is interest in the exploration of new ruthenium-based catalysts capable of decarbonylation reactions, especially after an initial report by Dolphin and co-workers on the stoichiometric decarbonylation using a ruthenium−porphyrin-based complex.[7] An iridium-catalyzed decarbonylation method has also been reported by Tsuji and co-workers, wherein a variety of functional groups were tolerated under mild reaction conditions.[8] In this way, effective synthetic decarbonylation processes can be beneficial for the generation of fuel-grade alkanes and should be attractive alternatives to existing expensive hydrogenation methodologies.[9] Bhattacharya and co-workers,[10-33] Jayanthi et al.,[11] and Dinger et al.[12] have worked on ruthenium complexes wherein in situ solvent oxidation and decarbonylation had led to CO-coordinated Ru(II) complexes. These groups had proposed CO generation via either Ruassisted methyl oxidation or solvent oxidation in azo and hydrazone complexes. However, their findings lacked substantial experimental evidence to support the mechanism of Ru-assisted solvent oxidation. Thus, further experimental investigations into the precise mechanism of these Ru-assisted alcohol dehydrogenation reactions and CO coordination are needed.[11,12] These literature reports prompted us to synthesize some new ruthenium azo complexes and examine the possiblesolvent oxidation (by using 13C-labeled ethanol) and subsequent decarbonylation. We here focus on the synthesis of organometallic ruthenium complexes (1 & 2) derived from arylazo functionalized ligands, wherein an in situ solvent oxidation and subsequent decarbonylation to generate an alkane would be possible. To further see whether this decarbonylation is specific for ruthenium, we attempted to observe similar in situ decarbonylation in an organoiridium complex (3) using the same organic ligand. However, it is also known that arylazo complexes of the platinum-group metals have been the subject of substantial interest because of their rich redox and

spectroscopic behavior, catalytic activities, and isomerization reactions.[13−16] By comparison, the anticancer activity of platinum arylazo complexes has received rather limited attention.[17] a−c While conventional platinum anticancer drugs such as cisplatin, carboplatin, and oxaliplatin are potent against a range of tumors, their side effects like toxicity toward normal tissue and tumor resistance have motivated researchers to develop anticancer agents that diverge from the stereotypical complexes already in use.17d−f In this direction, ruthenium and iridium complexes have emerged as encouraging classes of metallodrug candidates and hold great promise for cancer chemotherapy.[18] Moreover, recent reports have revealed ruthenium complexes as remarkable antiproliferative agents, for example, the Ru(III)- based anticancer drugs indazolium trans-[tetrachlorobis(1Hindazole) ruthenate (III)] (KP1019),[32-80] its sodium salt analogue sodium trans-[tetrachlorobis(1H-indazole)ruthenate(III)] (NKP-1339),[20-32] and the new antimetastasis inhibitor imidazolium trans-[tetrachlorobis(1H-imidazole)(S-dimethyl sulfoxide)-ruthenate(III)] (NAMI-A),[21] which all have proceeded into the clinical stages of drug development. Furthermore, iridium complexes have been reported to generate reactive oxygen species and to induce apoptosis by acting on mitochondria as well as exerting anticancer effects through interaction with DNA.[22−24] Phenylazo ligands have a crucial role in cytotoxicity against the A2780 ovarian and A549 lung-cancer cell lines as reported by Dougan et al. during investigation of η6 -areneruthenium(II) derivatives containing phenylazo ligands.17a The azo derivatives of ruthenium were found to be more cytotoxic as compared to the oxadiazole derivatives, on human glioblastoma cell lines, inspiring further study of azo-coordinated complexes.17c The redox reactions of the metal-coordinated azo ligands have been known to increase the cytotoxicity of half-sandwich organometallic (arene)-ruthenium(II) complexes.17a,c As compared to the free arylazo ligand, the transitionmetal chelated azo complexes target cancer cells better than normal cells due to increased lipophilicity on chelation; this prompts the design and exploration of more metal-coordinated azo compounds.[25] Significant in vitro cytotoxic results of azovanadium complexes have also been reported in our earlier works, which further stimulates us to design and study azofunctionalized complexes.[26] Another class of pharmacophoric interest are triphenylphosphine (PPh3)-coordinated metal complexes, as they exhibit excellent potential in chemotherapy by influencing mitochondrial metabolism.27a−g Using hydrophobic PPh3-ligated complexes results in complexes with good cytotoxicity, presumably due to their increasing vehiculation property.[27] h−j Some ruthenium phosphine complexes are known to inhibit the human topoisomerase IB enzyme (a potential biological target for complexes).[27] h It has been demonstrated that the presence of a PPh3 ligand is important also to facilitate the binding of the Ru complex to DNA and then distort its secondary and tertiary structure.[27] j,k Also, wide investigations of platinum, ruthenium, copper, and gold complexes have led to conclusions that mixed-ligand complexes possessing PPh3 are highly cytotoxic in contrast to the phosphine-free ones, which inhibited cell proliferation only in relatively high concentrations.[27] h,l−q Thus, the wide cytotoxic activity of azo- and PPh3-derived complexes stimulated us to investigate mixed azo- and PPh3-coordinated complexes. Ruthenium is a component of mixed-metal oxide (MMO) anodes used for cathodic protection of underground and submerged structures, and for electrolytic cells for chemical processes such as generating chlorine from salt water. The fluorescence of some ruthenium complexes is quenched by oxygen, which has led to their use as optode sensors for oxygen. Ruthenium red, $[(NH_3)_5Ru\text{-}O\text{-}Ru(NH_3)_4\text{-}O\text{-}Ru(NH_3)_5]^{6+}$, is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy and electron microscopy. The beta-decaying isotope 106 of ruthenium is used in radiotherapy of eye tumors, mainly malignant melanomas of the uvea. Ruthenium-centered complexes are being researched for possible anticancer properties. Compared with platinum complexes, those of ruthenium show greater resistance to hydrolysis and more selective action on tumors. NAMI-A and KP1019 are two drugs undergoing clinical evaluation against metastatic tumors and colon cancers. Because of its ability to harden platinum and palladium, ruthenium is used in platinum and palladium alloys to make wear-resistant electrical contacts. In this application, only thin plated films are used to achieve the necessary wear-resistance. Because of its lower cost and similar properties compared to rhodium, the use as plating material for electric contacts is one of the major applications. The thin coatings are either applied by electroplating or sputtering. Ruthenium dioxide and lead and bismuth ruthenates are used in thick-film chip resistors. These two electronic applications account for 50% of the ruthenium consumption. Only a few ruthenium alloys are used other than those with other platinum group metals. Ruthenium is often used in small quantities in those alloys to improve some of their properties. The beneficial effect on the corrosion resistance of titanium alloys led to the development of a special alloy containing 0.1% ruthenium. Ruthenium is also used in some advanced high-temperature single-crystal superalloys, with applications including the turbine blades in jet engines. Several nickel based superalloy compositions are described in the literature. Among them are EPM-102 (with 3% Ru) and TMS-162 (with 6% Ru), as well as TMS-138 and TMS-174. both containing 6% rhenium. Fountain pen nibs are frequently tipped with alloys containing ruthenium. From 1944 onward, the famous Parker 51 fountain pen was fitted with the "RU" nib, a 14K gold nib tipped with 96.2% ruthenium and 3.8% iridium.

A wide number of ruthenium complexes containing heterocyclic nitrogeneous molecules and related ligands have been reported to date. They are of considerable

interest primarily due to variable oxidation states, building blocks for supramolecular assemblies, photo-physical properties, directional electron and energy transfer, potential anticancer property. Modification of heterocyclic ligands may be carried out by incorporating new donor centers, spectator groups, change of ring size and number of Heteroatoms. They can significantly influence the physical and chemical properties of the complex molecules. Since the discovery of important redox, photophysical and photochemical properties of ruthenium complexes having 2,2-bipyridine (bipy) as ligand, there has been continuous research activity in the direction of developing newer ruthenium–bipyridine systems with the perspective of interesting physicochemical properties. In this context different kinds of mixed ligand ruthenium–bipyridine complexes have been synthesized and studied over the last fifteen years [Rasmussen S. C., Thompson D. W., Singh V. and Petersen J. D., (1996 medical aspects)]. The basic strategies behind all these activities are either to incorporate different groups within the bipyridine moiety itself or use other types of donor sites like azoimine function along with the $Ru(bipy)_2$ core to form mixed-ligand tris-chelates to modulate the photo-redox activities of this class of complexes [Santra B. K., Thakur G. A., Ghosh P., Pramanik A. and Lahiri G. K., *Inorg. Chem.*, 1996]. The nature of chemical reactions of organic substrates can vastly be affected by their coordination to metal ions. It is now known that organonitriles are activated by metal coordination toward addition reactions leading to a variety of synthetic transformations of RCN species. Thiocyanates, as ligand, have attracted considerable attention in recent years not only because of their versatile coordination abilities but also some of their transition metal complexes have been found to be useful. The ruthenium chemistry of diimine ligands is an area of significant current interest, particularly with regard to the photophysical and photo-chemical properties exhibited by such complexes. Di-imine ligands are strong π-acceptors and are recognized stabilizers of the +2 state of ruthenium (low-spin d^6, S=0). As a consequence, an interesting aspect of the ruthenium–diimine chemistry has been to study the remarkable π-interaction between the filled t_2 orbitals of ruthenium(II) and the low-lying vacant π*-orbital of the diimine chromophore. The extent of π-interaction in these complexes depends primarily on the nature of the diimine ligands, which again depends on the nature of the groups linked to the two carbons and the two imine-nitrogens. The presence of other π-acceptor ligands within the coordination sphere may also have significant influence on the π-interaction between the diimine ligands and ruthenium(II).[1-5] For the last few years, the search for a suitable precursor to synthesize NNN^- complexes is a challenging domain and the compounds are found to be useful in this context [6-8]. Recently, we have developed the arylazopyrimidine as well as arylazoimidazole chemistry of ruthenium(II) and have synthesised dichloro componds and diaquo species. Syntheses of hetero-tris-chelates, $[Ru(bpy)_n(RaaiR')_{3-n}](ClO_4)_2$ [bpy = 2,2′-bipyridine; n = 1, n = 2) from the solvento complexes $[Ru(OH_2)_2(bpy)_2]^{2+}$ /$[Ru(OH_2)_2(RaaiR')_2]^{2+}$ containing labile reaction centres are reported from Prof. Sinha´s laboratory [8-11]. In this paper, We examine the reaction of $DPPM^-$ towards $[Ru(OH_2)_2(RaaiR)_2]^{2+}$ and the reactions of the complexes derived there-from and also studied the dinuclear adduct formation pathway. The complexes were well charecterised by C.H.N, FT-I.R, U.V-Vis, and Cyclic Voltammetrically. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

EXPERIMENTAL

Published methods were used to prepare RaaiR [7-8], *ctc*-$RuCl_2(RaaiR)_2$ [7-8], *ctc*-$[Ru(OH_2)_2(RaaiR)_2](ClO_4)_2$. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, India). The purification of MeCN and preparation of $[n\text{-}Bu_4N][ClO_4]$ respectively used as solvent and supporting electrolyte in electrochemical experiments were done following the literature method. 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. I.r. 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 n.m.r spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}$ M in acetonitrile. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE). Reported potentials are uncorrected for the junction effect.

Preparation of DPPM-bis-{1-methyl-2-(p-tolylazoimidazolee} ruthenium(II), ctc-$Ru(DPPM)(MeaaiMe)_2$ CAUTION ! Perchlorates of heavy metal ions with organic ligands are potentially explosive. The syntheses involve in some cases the use of perchlorate ions. Three independent methods were employed to synthesise.

Method (a). To an EtOH blue-violet solution (15 cm^3) of ctc-$[Ru(OH_2)_2(MeaaiMe)_2](ClO_4)_2$ (0.1 g, 0.14 mmol) was added 0.019 g (0.27 mmol) of solid DPPM, and the mixture was stirred at 343-353 K for 12 h. The violet

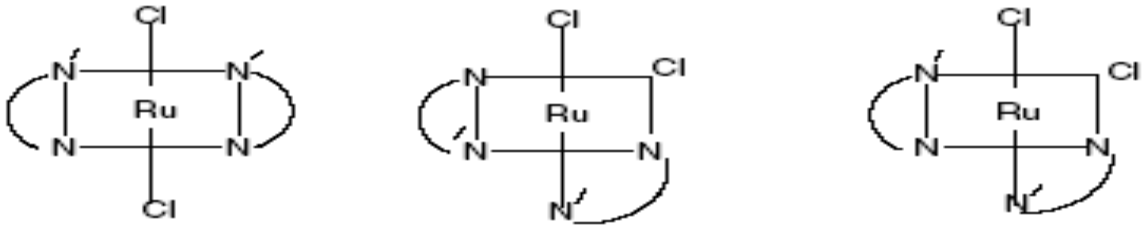
solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (12 h). The precipitate was collected by filtration, washed thoroughly with H_2O and dried in vacuo over $CaCl_2$. Analytically pure (7b) was obtained after chromatography over an alumina (neutral) column on eluting the red-violet band with toluene-acetonitrile (4:1, v/v) and evaporating slowly in air. The yield was 0.088 g (80%).

Method (b). To a suspension of ctc-$RuCl_2(MeaaiMe)_2$ (4b) (0.1 g, 0.18 mmol) in EtOH (25 cm^3) was added an aqueous solution of $AgNO_3$ and stirred at room temperature (300 K) for 2 h. The AgCl which precipitated was filtered through a G-4 sintered crucible. An EtOH solution of DPPM (0.025 g, 0.35 mmol) was added to the filtrate, and the resulting mixture was stirred at room temperature for 8 h under a N_2 atmosphere. The violet solution was concentrated by slow evaporation and the precipitate was processed as in Method (a); yield, 0.047 g (45%).

Method (c). To a CH_2Cl_2-Me_2CO (1:1, v/v, 30 cm^3) solution of ctc-$RuCl_2(MeaaiMe)_2$ (4b) (0.1 g, 0.18 mmol) was added an H_2O-Me_2CO solution of **DPPM** (0.024 g, 0.35 mmol). The mixture was stirred at 343-353 K for 30 h. The resulting violet solution was processed as in method (a) to give analytically pure dithiocyanato complexes; yield, 0.021 g (20%). The high yield in method (a) has prompted us to follow this route for the syntheses of the other complexes (3b-3e). The yields varied in the range 65-85%.

RESULTS AND DISCUSSION

Diaquo complexes ctc-$[Ru(OH_2)_2(RaaiR)_2](ClO_4)_2$, prepared by Ag+-assisted aquation of ctc-$RuCl_2(RaaiR)_2$, were reacted with **DPPM** (excess amount >3 mol) under stirring at 343-353 K in aqueous alcohol to give Ru(**DPPM**)$(RaaiR)_2$ (**3**) in good yield (65-85%). The synthetic routes are shown in Scheme 1. The dithiocyanato were synthesized in low yield either directly on stirring in ethanol-acetone mixture for 30 h or in situ synthesis of the aquo complex by $AgNO_3$ followed by the reaction with **DPPM**. The composition of the complexes is supported by microanalytical results. Room temperature solid state magnetic susceptibility measurements show that the complexes are diamagnetic (t_{2g}^6, S = 0). The violet dithicyanato complexes are soluble in common organic solvents but insoluble in H_2O. In MeCN, they show as non-electrolytic behaviour is found for type complexes as indicated by their very low Λ_M values (10-20 Ω^{-1} cm^{-1} mol^{-1}).



I.r. spectra of the complexes, **Ru(DPPM)(RaaiR)$_2$** (**3**) show a 1:1 correspondence to the spectra of the dichloro analogue, *ctc*-$RuCl_2(RaaiR)_2$ except the appearance of intense stretching at 1300-1335 and 1250-1280 cm^{-1} with concomitant loss of ν(Ru-Cl) at 320-340 cm^{-1}. They are assigned to $\nu(DPPM)_{as}$ [5,6,15]. The ν(N=N) and ν(C=N) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively. Other important frequencies are $\nu(H_2O)$ at 3350-3400 cm^{-1} The solution electronic spectra of these new complexes were recorded in dry acetonitrile. Dithiocyanato complexes (**3-5**) exhibit multiple transitions in the uv-visible region. They display intense MLCT transition in the 550-560 nm range . The transitions are blue shifted by ~ 40 nm as compared with corresponding dichloro derivatives, $RuCl_2(RaaiR)_2$ [6,8,11]. The ^1H n.m.r. spectra of Ru(DPPM)$_2$(RaaiR)$_2$ (**3**) complexes were unambiguously assigned on comparing with $RuCl_2(RaaiR)_2$ [7-9]. The aryl protons (7-H—11-H) are downfield shifted by 0.1-0.7 ppm as compared to those of the parent dichloro derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9) and C(10)-position. The aryl protons resonate asymmetrically indicative of a

magnetically anisotropic environment even in the solution phase. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. Imidazole 4- and 5-H appear as doublet at the lower frequency side of the spectra (7.0-7.2 ppm for 4-H; 6.9-7.1 ppm for 5-H). The aryl-Me (R = Me) in $Ru(NNN)_2(MeaaiR)_2$ (**3**) appears as a single signal at 2.30 ppm and is in consonance with stereoretentive nucleophilic substitution during synthesis of DPPM complexes from *ctc*-$RuCl_2(RaaiR)_2$ via aquo derivatives. Isomerisation of the ctc-isomer may lead to ccc-configuration belonging to C_1-symmetry and would give two equally intense Ar-Me signals, which is however not the case here. The dithiocyanato complexes exhibit a quasi-reversible ($\Delta E_p \geq 100$ mV) oxidative response in the potential range 1.0-1.3 V. This is assigned to the Ru(III)/Ru(II) couple. The one-electron stoichiometry of this couple is confirmed by constant potential electrolysis vs SCE and the electron count ratio equals 0.94. The potential $E^M_{1/2}$ is dependent on the substituent type R. The present series of complexes show higher $E^M_{1/2}$ values than that of precursor dichloro derivatives by ~ 0.4 V. The better electron withdrawing property of NNN^- over Cl^- stabilises the dπ shell of the metal and thus shifts the metal-centred redox process to more anodic values. The stronger π-acidic nature of RaaiR′ compared to α-diimine system leads to better stabilisation of Ru(II) in the present series of complexes. The cyclic voltammogram of $Ru(DPPM)_2(RaaiR')_2$ exhibit some unusual behaviour on repetitive cycles. The reduction sweep shows a new wave that has a counter oxidative wave on the second sweep. The second and consecutive cycles increase the peak height with subsequent decrease of the primary couple. The assignment is based on earlier observations of similar Ru-bipyridine [21] and Ru-azopyridine [11] systems. The potential values of the present set of complexes lie between bipyridine and azopyridine analogous complexes and follow the order azopyridine > azoimidazole > bipyridine. This is in line of π-acidity order of these different ligand systems. The one-electron stoichiometry of the couples is assigned by comparison of current heights in differential pulse voltammetry experiments. Successive reductions on the negative side of SCE were observable and one-electron nature was confirmed by comparing the current heights of these process with that of couple II in the differential pulse voltammetry experiments and are assigned to the reduction of coordinated ligand. The azo group in RaaiR′ may accommodate two electrons and hence two coordinated ligands should exhibit four reductive responses. However, within the available potential window two reductions were clearly observable.

Table 1: Microanalytical (C.H.N)[a] and FT-IR spectroscopic[b] data.

Complexes	C H N	ν(N=N)ν(C=N)ν(C=C)ν(NNN)
$Ru(NNN)_2(H\text{-}aaiMe)_2$, **3a**	42.4 3.5 24.8 (42.3) (3.4) (24.7)	1365 1570 1600 1300
$Ru(NNN)_2(p\text{-}Me\text{-}aaiMe)_2$, **3b**	44.4 4.0 23.6 (44.5) (4.1) (23.7)	1367 1580 1602 1320
$Ru(NNN)_2(p\text{-}Cl\text{-}aaiMe)_2$, **3c**	37.8 2.84 22.1 (37.7) (2.7) (22.0)	1370 1590 1610 1325
$Ru(NNN)_2(H\text{-}aaiEt)_2$, 4a	44.3 4.2 23.5 (44.5) (4.1) (23.7)	1375 1585 1613 1320
$Ru(NNN)_2(p\text{-}Me\text{-}aaiEt)_2$, 4b	37.8 4.84 22.1 (37.7) (2.7) (22.0)	1380 1590 1609 1310
$[Ru(NNN)_2(p\text{-}Cl\text{-}aaiEt)_2]$, **4c**	34.1 4.3 19.9 (34.0) (2.4) (19.8)	1370 1570 1609 1300
$Ru(NNN)_2(H\text{-}aaiBz)_2$, 5[a]	34.0 3.1 18.0 (34.1) (3.0) (18.1)	1365 1575 1606 1310
$Ru(NNN)_2(p\text{-}Me\text{-}aaiBz)_2$, **5b**	31.1 3.81 18.1 (31.2) (1.82) (18.2)	1380 1570 1609 1320
$Ru(NNN)_2(p\text{-}Cl\text{-}aaiBz)_2$, **5c**	34.2 3.2 18.1 (34.1) (3.0) (18.1)	1370 1575 1609 1310

[a] Calculated values are in parenthesis; On KBr disk.

Table 2: UV-Vis[a] and cyclic voltammetric[b] data.

Comp Ound	UV-Vis spectra λ_{max} (nm)(10^{-3} ε/dm^3 mol^{-1} cm^{-1})	Cyclic Voltammetric data E/V (ΔE_p / mV) E^{M1}	$-E^{L}$
(**3a**)	551(8.379),421(8.914)[d], 373(18. 3)	1.188(110)	0.388(80), 0.651(130)
(**3b**)	548(6.773), 421(12.271)[d], 379(17.791)	1.101(115)	0.407(95), 0.691(120)
(**3c**)	555(13.919), 424(13.416)[d], 384(40.721)	1.201(107)	0.344(80), 0.673(100)
(**4a**)	550(8.796), 416(10.081)[d], 376(20.755)	1.108(120)	0.377(80), 0.632(75)
(**4b**)	547(8.752), 423(7.149)[d], 380(23.694)	1.011(80)	0.383(85), 0.647(100)
(**4c**)	550(3.996)[d], 408(10.616), 258(12.403)	1.010(110)	0.401(80) 0.711(120)
(**5a**)	555(3.118)[d], 412(13.016), 260(14.469)[d]	1.032(120)	0.351(85), 0.621(120)
(**5b**)	550(3.996)[d], 408(10.616), 258(12.403)	1.010(110)	0.401(80), 0.711(120)
(**5c**)	555(3.118)[d], 412(13.016), 260(14.469)[d]	1.032(120)	0.351(85), 0.621(120),

[a] Solvent dry MeCN; [d] shoulder; [b] Solvent dry MeCN, supporting electrolyte [^{n}Bu$_4$N][ClO$_4$] (0.1M), w.e. Pt-disk, a.e. Pt-wire, r.e. SCE, solute conc. ~10^{-3} M, scan rate 50 mVs^{-1}, E^M : metal oxidation, eqn (3), E^L : ligand reductions, $\Delta E_p = | E_{pa} - E_{pc} |$ V where E_{pa} = anodic peak potential and E_{pc} = cathodic peak potential.

Table 3: ^{1}H-n.m.r. spectral data, δ (J/Hz), ppm of the complexes in $CDCl_3$.

Compd	4-H[c]	5-H[c]	7-H[c]	11-H	8-H	10-H
(3[a])[a]	7.15 (7.5)	7.06 (7.5)	8.03 (8.1)	7.88 (8.91)	7.80 (8.1)	7.86 (6.1)
(3b)	6.98 (7.5)	6.86 (7.5)	8.17 (8.1)	8.09 (8.1)	8.04 (8.1)	8.01 (8.01)
(3c)	7.13 (8.1)	7.02 (8.1)	8.15 (7.8)	7.99 (7.0)	7.95 (7.8)	7.92 (8.8)
(4[a])[a]	7.14 (7.5)	7.00 (7.5)	8.01 (7.8)	7.95 (7.1)	7.85 (7.8)	7.89 (7.8)
(4b)	7.02 (8.1)	6.94 (8.1)	8.11 (7.5)	8.04 (6.5)	8.04 (7.5)	8.07 (6.5)
(4c)	7.13 (8.1)	7.06 (8.1)	8.14 (7.5)	8.06 (8.5)	8.06 (7.5)	8.0 (7.7)
(5[a])[a]	7.06 (7.8)	6.98 (7.8)	8.08 (8.1)	8.10 (8.3)	8.00 (8.1)	7.00 (8.1)
(5b)	6.97 (8.1)	6.85 (8.1)	8.21 (8.1)	7.80 (8.1)	8.10 (8.1)	8.50 (8.7)
(5c)	7.11 (7.8)	7.02 (7.8)	8.15 (8.1)	8.00 (6.1)	8.05 (8.1)	7.05 (8.01)

[a] δ(9-H) 7.60 ppm(m); [b] δ (9-Me); [c] doublet; [d] triplet; [e] N-Bz, AB type sextet, geminal coupling constant,4.98,4.78,; [f] 1-Me, singlet, 1.98; [g] N-Et, AB type quartet, geminal coupling constant, 4.44,4.12.

CONCLUSIONS

Di-phenyl-phosphino-methane complexes of ruthenium(II)–azoimidazole, *ctc*-Ru(DPPM)(RaaiR)$_2$ have been synthesised by stereoretentive reaction of diaquo complex [Ru(OH$_2$)$_2$(RaaiR)$_2$]$^{2+}$ with thiocyanate ion. The complexes exhibit strong MLCT transitions. Voltammetric study shows Ru(III)/Ru(II) couple along with successive ligand-based reductions. Linkage isomerisation was studied by changing the solvent and then UV-Vis spectral analysis.

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