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Synthesis, characterization and solution behavior of a systematic series of pentapyridyl-supported Ru^{II} complexes: Comparison to bimetallic analogs

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Abstract

A series of Ru^{II} complexes stabilized with the pentapyridyl ligand Py₅Me₂ (Py₅Me₂ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine) and with an axial X ligand (X = Cl[−], H₂O, N₃[−], MeCN) were prepared and characterized in the solid state and in non-aqueous solution. The cyclic voltammograms of these complexes in MeCN reflect a reversible substitution of the axial X ligand with MeCN. Irreversible ligand substitution of [(Py₅Me₂)RuN₃]⁺ is also observed in propylene carbonate, but only at oxidizing potentials that decompose the azide ligand. The monometallic chloride and azide species are compared with analogous Ru₂ metal–metal bonded complexes, which have been reported to undergo irreversible chloride dissociation upon reduction.

Graphical Abstract

A series of pentapyridyl-supported Ru(II) complexes are synthesized and characterized using X-ray crystallography, UV-Vis, ¹H NMR and cyclic voltammetry. Moreover, these monometallic species are compared with previously reported bimetallic analogues with regards to their structure and ligand substitution behavior.

Introduction

Pentadentate N-donor ligands and their variants have been extensively studied for their ability to support metal complexes having a vacant coordination site that facilitates small molecule activation or catalysis.^{1–25} In particular, the pentapyridyl ligand Py₅Me₂ (2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine), whose complexes with varying metal centers²⁶ or with varying sixth axial ligands²⁷ were extensively characterized by the Stack group in 2002, has been found to promote interesting reactivity, e.g., supporting molybdenum, cobalt, and

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nickel complexes that can reduce water to generate hydrogen.^{28–32} In addition to being utilized to support monometallic^{33,34} and heterobimetallic^{35–43} structures, this ligand has recently been shown to support silver nitrene transfer catalysts⁴⁴ and iron/nickel oxidation catalysts.^{45,46} There are only two existing reports on ruthenium–Py₅Me₂ complexes. In a 2014 study published by Kojima and coworkers,⁴⁷ Ru^{II}–aquo and Ru^{III}–hydroxo complexes were investigated and a Pourbaix diagram was presented for the Ru^{II/III} couple. Moreover, the Ru^{III}–hydroxo complex was shown to oxidize hydroquinones and ascorbic acid in aqueous conditions. More recently, Sala, Bofill and colleagues reported the partial cyclic voltammogram of a Py₅Me₂-supported Ru^{II}–chloro complex in acetonitrile and compared the electrochemical properties of the Ru^{II}–aquo complex with those of other analogous complexes in aqueous media.⁴⁸ However, Ru complexes stabilized with this pentapyridyl platform have not been explored for further reactivity.

Previous research in our laboratory has focused on bimetallic complexes with metal–metal bonds that can support reactive oxo and nitrido groups capable of oxygen atom and nitrene transfer.^{49–54} A topic of special interest is the role of the metal–metal bond in these complexes, which can be best elucidated by direct comparisons with monometallic analogues (Scheme 1).^{53,55}

Hence, we aim to study Py₅Me₂-supported monometallic Ru complexes and to draw reactivity comparisons with their bimetallic analogues. As a first step towards this goal, we report here (1) the preparation of a systematic series of [Ru(Py₅Me₂)X]ⁿ⁺ complexes, (2) crystal structures of the entire family of compounds, (3) characterization of their properties in non-aqueous solution, and (4) a comparison of the structural and electrochemical features of these compounds to analogous metal-metal bonded Ru₂ compounds. The compounds described here are: [Ru(Py₅Me₂)N₃]PF₆ (**1**), [Ru(Py₅Me₂)Cl]PF₆ (**2**), [Ru(Py₅Me₂)(OH₂)](PF₆)₂ (**3**), and [Ru(Py₅Me₂)(NCCH₃)](PF₆)₂ (**4**).

Results and Discussion

The ligand Py₅Me₂^{41,56} and the complexes **2**⁴⁷ and **3**⁴⁷ were synthesized using modified literature procedures as described in the Supporting Information. Compound **1** was synthesized by reaction of **3** with excess NaN₃ in water,⁵⁷ and **4** was synthesized by reaction of **2** with AgPF₆ in CH₃CN. Compounds **1** and **3** crystallize readily by slow cooling in a mixture of acetone and water (mixture of acetonitrile and water for **4**), though it should be noted that repeated recrystallization of **1** by this method causes some degradation of the compound. Crystal structures of **2** and **3** have been reported,^{47,48} though the latter compound was reported as its triflate salt and we present here the crystal structure of the PF₆[−] salt. The new crystal structures of **1**, **3**, and **4** are presented in Figure 1 with selected bond distances given in Table 1.

The bond lengths in Table 1 indicate an axially compressed pseudooctahedral d⁶ Ru^{II} center. Although the bond angles and bond lengths are roughly similar among the four complexes, the greatest deviations arise in the Ru–X bond lengths, where they decrease in the following order: Ru–Cl[−] > Ru–OH₂ > Ru–N₃[−] > Ru–NCMe. The complexes that bear an axial N-donor as the X ligand tend to have a shorter Ru–X bond length and a Ru–N_{ax} bond length

slightly elongated by ~ 0.025 Å. It should be noted that the asymmetric unit of **3** contains two additional water molecules with intermolecular O...O distances of 2.776 and 2.745 Å, values indicative of hydrogen bonding. For the azide moiety in **1**, the distal N=N bond length is longer than the proximal N=N bond length (1.241(7) vs. 1.176(6) Å) and the Ru–N₃ bond distance is comparable to that of other monometallic Ru–N₃ complexes stabilized with N-donor ligands (see Table 3).

UV-vis spectra were taken in acetone for the $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{n+}$ complexes to minimize solvent substitution of the dicationic species (Figure 2). Complexes bearing a neutral X ligand give fainter yellow solutions than do complexes bearing an anionic X ligand at the same concentrations. This is reflected in the lower λ_{max} values beyond the visible region and smaller molar extinction coefficients for complexes **3** and **4** (Table 2). Represented in these spectra are the MLCT bands, and a stronger π -donating capability of the X ligands correlates with smaller energy gaps for these transitions. The shoulder at ~ 450 nm for the azido complex likely results from a $\text{Ru} \rightarrow \text{N}_3$ π^* charge transfer transition.

The ^1H NMR spectra in CD_3CN for **1** and **2** (Figure 3) exhibit a distinctive doublet of doublets between 9 and 10 ppm due to the ortho-pyridine C–H resonances of the equatorial pyridine groups. A second feature with a similar splitting pattern is unexpectedly observed in the spectrum of **3** in the same chemical shift region; however, comparison to the spectrum of **4**, the acetonitrile complex, confirmed the assignment of the more downfield peak in the spectrum of **3** to the CD_3CN -substituted complex (**4**). These spectra lead to the conclusion that substitution of the X ligand with acetonitrile occurs readily and reversibly in **3**; adding exogenous water to this solution resulted in a relative diminishing of this downfield peak. From integrations of the ^1H NMR signals, it is possible to determine the equilibrium constant for the following reaction:

In the cyclic voltammograms of the $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{n+}$ complexes acquired in acetonitrile (Figure 4), a reversible $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ oxidation wave is observed at $E_{1/2}$ values of 171, 385, 630 and 924 mV vs. Fc/Fc^+ for **1**, **2**, **3** and **4**, respectively. This trend reflects the relative electron-richness of the Ru^{II} center and the π -donating capability of the X ligands; the azide ligand is expected to be the strongest π -donor, consistent with the lowest-energy MLCT feature of **1**. The $E_{1/2}$ value of the acetonitrile complex is higher than that of the azido complex by ~ 750 mV, which reflects the dicationic nature of **4**. The $E_{1/2}$ value for **2** roughly agrees with the previously reported value of 0.78 V vs. SCE.^{48,58}

Notably, a reversible feature at 924 mV corresponding to the $E_{1/2}$ value for **4** is present in *all other* voltammograms. Although this is expected for **3** on the basis of the NMR data described above, the NMR spectra of **1** and **2** show no indications of **4** being present, even in the presence of excess Bu_4NPF_6 mimicking the high ionic strength conditions of the CV experiments. These observations lead us to conclude that oxidation of **1** or **2** initiates axial ligand exchange forming a small amount of **4**. A similar effect has been observed for

$\text{Ru}^{\text{II}}(\text{bpy})(\text{CO})_2\text{Cl}_2$, where loss of the chloride ligand forms the species $[\text{Ru}^{\text{III}}(\text{bpy})(\text{CO})(\text{CH}_3\text{CN})_2\text{Cl}]^{2+}$ at oxidative potentials, although a detailed mechanism for the substitution process was not described.^{59,60} In a similar case of a Ru–aquo species supported by pentadentate EDTA (ethylenediaminetetraacetate), substitution of the water ligand with acetonitrile is found to be kinetically favored at the Ru^{III} center compared to the Ru^{II} .^{61,62} We therefore examined the ‘oxidatively-induced’ ligand substitution in **1** and **2** more closely to determine whether it is a kinetic or thermodynamic phenomenon and whether a mechanistic model can be described.

First, we examined the CVs of **1** and **2** more quantitatively. At a scan rate of 100 mV/s, the ratios of the $\text{Ru}^{\text{II/III}}$ oxidative peak currents of **4** to those of the parent complexes are 0.22 for **1** and 0.13 for **2** (see S3 & S4), corresponding to 18 % and 12 % ligand substitution in **1** and **2**, respectively. The $i_{\text{pa}} / i_{\text{pc}}$ ratios for the $\text{Ru}^{\text{II/III}}$ redox couples of **1** and **2** are 0.98 and 1.0, respectively, and these ratios remain constant upon multiple scans, indicating that the X^- ligand is displaced reversibly and that an irreversible pathway involving a $\text{X}^\bullet$ radical is not likely. At faster scan rates up to 2.4 V/s, the redox couple of **4** persists in the voltammograms of **2**, and the relative ratio of peak currents described above remain the same. These data are consistent with a kinetic activation toward axial ligand substitution upon oxidation to Ru^{III} . Further support of this idea comes from a chemical oxidation experiment. We have found that adding 1.5 equivalents of oxidant (ceric ammonium nitrate) to a solution of **2** in CD_3CN and then quenching with 1.5 equivalents of reductant (decamethyl ferrocene) led to complete recovery of the chloride complex with no substitution based on NMR studies (data not shown).

The data described above are consistent with an $\vec{E}\overleftarrow{C}\overleftarrow{E}$ mechanism for **1** and **2** as shown in Scheme 2.⁶³ In this mechanism, first the complexes undergo a one-electron oxidation, followed by solvolysis yielding a solvated Ru^{III} species. The $\text{Ru}^{\text{III}}\text{-NCCH}_3$ species is then re-reduced to Ru^{II} (hence the $\overleftarrow{E}$ symbol), since it is more oxidizing than the $\text{Ru}^{\text{III}}\text{-Cl}$ or $\text{Ru}^{\text{III}}\text{-N}_3$ species. The bottom equation in Scheme 2 indicates the equilibrium constants for the cross-reaction, oxidation of **1** or **2** by $[\text{Ru}(\text{Py}_5\text{Me}_2)(\text{NCCH}_3)]^{3+}$; these are easily determined from the $E_{1/2}$ values of the compounds as 5.3×10^{12} for **1** and 1.3×10^9 for **2**.

To gain further insights into the nature of ligand substitution from oxidized **1** and **2**, we acquired CVs of the compounds in propylene carbonate, PC (Figure 5). The voltammograms of **1** and **2** in PC display only a single $\text{Ru}^{\text{II/III}}$ couple attributable to the parent complexes at 203 and 408 mV, respectively. No waves attributable to a $[\text{Ru}(\text{Py}_5\text{Me}_2)(\text{PC})]^{2+}$ complex are observed. However, the formation of such a PC adduct itself is clearly not unfavorable because the CV of **3** in PC, like in CH_3CN , shows two oxidative waves with the one appearing at a higher potential, 789 mV, which can be assigned to the PC adduct.

Further evidence for this assignment is shown in Figure 6, in which the CV of **1** was measured with variable scan windows. Increasing the oxidative window from ~ 1.25 V to ~ 1.75 V vs Fc/Fc^+ causes a second oxidation of **1** to be observed. During the first scan, the $\text{Ru}^{\text{II/III}}$ redox event for **1** is followed by an irreversible wave at ~ 1.5 V attributable to

destruction of the azide ligand.⁵ This process generates the PC complex, which is prominently visible upon the second scan (Scheme 3).

Taken together, the variable-solvent data indicate that oxidation of **1** and **2** in *acetonitrile* induces a kinetically-driven axial ligand substitution but this process does not occur in PC. We may conclude at this point that the rate of oxidatively-induced axial ligand substitution in this case depends on the identity of the incoming ligand (acetonitrile vs the more sterically-demanding PC), which is an observation most commonly affiliated with an associative ligand-exchange mechanism. This process could proceed via a seven-coordinate intermediate, analogs of which have been proposed for Mo(Py₅Me₂) compounds.⁶⁴ Another possibility involves one of the equatorial pyridyl arms falling off, which opens up a site for the incoming ligand. This type of species has been proposed as an intermediate in the isomerization of [Ru^{II}(κ -N⁵-bpy2PYMe)Cl]⁺ (bpy2PYMe = 1-(2-pyridyl)-1,1-bis(6-2,2'-bipyridyl)ethane) upon oxidation to Ru^{III}.⁴⁸ An intermediate with a decoordinated pyridyl arm is also proposed in studies on the redox reactivity of cobalt chloride complexes supported with pentadentate N-donor ligands.^{24,65} Our data do not allow us to discriminate between these two possible mechanisms.

Comparison of [Ru(Py₅Me₂)X]ⁿ⁺ complexes to metal–metal bonded diruthenium complexes.

It is useful to make comparisons between analogous complexes of a mononuclear vs. binuclear nature. Appropriate diruthenium structures supported by N,N-donor ligands were screened from the CCDC database.

Structural features of **1** are compared to those of other Ru–azido complexes supported by five N-donor ligands in Table 3. Also included in Table 3 are binuclear azido complexes with Ru–Ru bonds supported by N-donor ligands. In each case, the Ru–Ru bond is *trans* to the Ru–N₃ connection; by comparing mono-Ru and di-Ru complexes, we can learn about the *trans* influence of the Ru–Ru bond. Also of note is the influence of structure on the Ru–N–N₂ angle, related to the extent to which the azide ligand is activated by the metal.^{66,67} As seen in Table 3, the Ru–N₃ distance in **1** compares well with those of other mono-Ru azido complexes, as well as with the distances in Ru₂(II,III) complexes. However, the Ru₂(III,III) compound Ru₂(DMBA)₄(N₃)₂ has a Ru–N₃ distance that is longer by ~ 0.2 Å. Thus, while the Ru–Ru bond in Ru₂(II,III) compounds does not appear to have a strong *trans* influence on the Ru–N₃ bond, the Ru(III)–Ru(III) bond does. However, the Ru–N–N₂ angle must also be taken into account. The larger Ru–N–N₂ angles of the Ru₂(II,III) compounds, which appear to be sterically enforced, are consistent with a high degree of activation at the azide ligands, commensurate with relatively short Ru–N₃ bond distances. These two structural features are roughly correlated as seen in Figure 7. It is worth noting that the difference between the distal N=N bond length and the proximal N=N bond length in the azide moiety of these complexes does not lead to a correlation that is as statistically significant.

Mono- and di-Ru complexes differ substantially in the nature of their redox-dependent ligand substitution chemistry. As we have shown here, oxidation of **2** from Ru(II) to Ru(III) at 385 mV vs. Fc/Fc⁺ facilitates reversible substitution of the Cl[–] ligand, which appears to be a kinetic phenomenon. Other Ru complexes behave similarly.^{59–62} In contrast, reduction of

$\text{Ru}_2(\text{II,III})\text{-Cl}$ complexes to the $\text{Ru}_2(\text{II,II})$ oxidation state typically causes irreversible Cl^- dissociation.^{68,69} In Ru_2 complexes, this effect appears to be mainly electrostatic and thermodynamic in nature.

Conclusions

Investigations of a variety of $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{n+}$ complexes reveal that dicationic complexes **3** and **4** have lower chemical shift values for the ortho-pyridine C–H resonances, higher UV-vis MLCT energy levels and higher $E_{1/2}^{\text{II/III}}$ values compared to the monocationic complexes **1** and **2**. For these complexes, reversible ligand substitution takes place under oxidative conditions in MeCN. The onset of ligand substitution at the Ru^{III} center rather than at the Ru^{II} center is thought to proceed through an $\vec{E} \text{ C E} \leftarrow$ mechanism. The sterically bulkier O-donor PC is less capable of ligand substitution compared to the N-donor MeCN, suggesting an associative ligand substitution mechanism. These results contrast with those observed for metal–metal bonded $\text{Ru}_2(\text{II,III})$ complexes, which show irreversible ligand dissociation upon one-electron reduction.

Experimental Section

All manipulations were performed under a nitrogen atmosphere using a Schlenk line unless specified otherwise. ^1H NMR spectra were obtained using Bruker Avance III 400 or Bruker Avance III 500 spectrometers. For ^1H NMR, chemical shifts are reported relative to the residual protiated solvent peaks (δ 1.94 for CD_3CN). Cyclic voltammograms were taken on a BASi Potentiostat using Epsilon software in dry, degassed CH_3CN solutions with 1.0 mM complex and 0.1 M tetrabutylammonium hexafluorophosphate. The electrodes were as follows: glassy carbon (working), Pt wire (auxiliary), and Ag/Ag^+ in CH_3CN (reference). The potentials were referenced versus the ferrocene/ferrocenium redox couple obtained with exogenous ferrocene. Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, IN, USA. Electrospray ionization (ESI) mass spectrometry data were obtained with a Thermo Q Exactive Plus mass spectrometer. UV/vis spectra were acquired on a StellarNet Miniature BLUE-Wave dip-probe spectrometer.

Synthesis of 1.

To 125.0 mg $[\text{Ru}(\text{Py}_5\text{Me}_2)(\text{OH}_2)](\text{PF}_6)_2$ (0.1466 mmol) and 249.4 mg sodium azide (3.836 mmol) was added 60 mL of degassed water and the mixture was heated to reflux for 2.5 hours. The color of the solution changed from yellow to orange-like yellow, and then to bright orange and then to yellowish orange. After 2.5 hours, the solution was cooled with an ice bath and the orange precipitate was filtered, washed with cold water and washed again with hexanes. Yield: 71.4 mg (67%). The compound is soluble in acetone, acetonitrile, methanol and dichloromethane. It is moderately soluble in chloroform. ^1H NMR (δ in CD_3CN , 400 MHz): 9.51 (dd, $J = 5.8, 1.2$ Hz, 4H), 7.95 (dd, $J = 8.2, 0.9$ Hz, 4H), 7.93 – 7.82 (m, 7H), 7.48 (ddd, $J = 7.3, 5.8, 1.4$ Hz, 4H), 2.73 (s, 6H) ppm. Calc'd (%) for $\text{C}_{29}\text{H}_{25}\text{N}_8\text{ORuPF}_6$: C, 47.61; H, 3.44; N, 15.32. Found: C, 47.40; H, 3.45; N, 15.23. UV-Vis (acetone): λ_{max} [nm] = 454 (sh), 400. ESI-MS: $m/z = 587.1243$ $[\text{M} - \text{PF}_6]^+$.

Synthesis of 4.

To 196.5 mg of $[\text{Ru}(\text{Py}_5\text{Me}_2)\text{Cl}](\text{PF}_6)$ (0.271 mmol) was added 82.4 mg AgPF_6 (0.326 mmol) and 50 mL of degassed, dry acetonitrile. The mixture was heated to reflux for 4 hours; the color of the resulting solution stayed dark yellow throughout the reaction. Since NMR revealed starting material impurities after the 4 hours, an additional 4.7 mg AgPF_6 (0.019 mmol) was added and the mixture was further heated to reflux for an additional 6 hours. After cooling, the mixture was filtered and the yellow product was recovered from the filtrate via recrystallization in a mixture of water and acetone. Yield: 77.7 mg (33%). The compound is soluble in acetone and acetonitrile. It does not dissolve in methanol, dichloromethane or chloroform. ^1H NMR (δ in CD_3CN , 400 MHz): 9.38 (dd, $J = 5.7, 0.6$ Hz, 4H), 8.05 – 7.99 (m, 7H), 7.96 (ddd, $J = 8.3, 7.2, 1.4$ Hz, 4H), 7.51 (ddd, $J = 7.2, 5.8, 1.4$ Hz, 4H), 2.76 (s, 6H) ppm. Calc'd (%) for $\text{C}_{31}\text{H}_{28}\text{N}_6\text{RuP}_2\text{F}_{12}$: C, 42.52; H, 3.22; N, 9.60. Found: C, 42.44; H, 3.21; N, 9.61. UV-Vis (acetone): λ_{max} [nm] = 374. ESI-MS: $m/z = 293.0705$ $[\text{M} - 2\text{PF}_6]^{2+}$, 580.0839 $[\text{M} - \text{MeCN} + \text{Cl} - 2\text{PF}_6]^+$, 731.1066 $[\text{M} - \text{PF}_6]^+$.

General Methods for X-ray Crystallography.

Single-crystal X-ray diffraction was conducted at the University of Wisconsin, Madison, Department of Chemistry, Molecular Structure Laboratory. All data collections were performed on a Bruker Quazar APEX-II diffractometer with $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$). The crystal was kept at 100.0 K during data collection. Using Olex2⁷⁹, the structure was solved with the ShelXT⁸⁰ structure solution program using Intrinsic Phasing and refined with the ShelXL⁸¹ refinement package using Least Squares minimisation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
50% probability thermal ellipsoid depictions of Py₅Me₂-supported Ru^{II} complexes **1**, **3**, and **4**. Hydrogen atoms and counter ions have been omitted for clarity.

Figure 2. UV-Vis spectra of 0.04 mM $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{n+}$ complexes in acetone at room temperature.

Figure 3. ^1H -NMR spectra of $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{n+}$ complexes in CD_3CN at room temperature. The peaks arise from the ortho-H resonance of the equatorial pyridines in the Py_5Me_2 ligand.

Figure 4. Cyclic voltammograms of $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{n+}$ complexes in $0.1 \text{ M Bu}_4\text{NPF}_6 / \text{CH}_3\text{CN}$, 100 mV/s scan rate. The $E_{1/2}^{\text{II/III}}$ value for the unsubstituted parent complex is displayed on the corresponding voltammogram.

Figure 5.

Cyclic voltammograms of $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{\text{n}+}$ complexes in 0.1 M Bu_4NPF_6 / PC, 100 mV/s scan rate. The $E_{1/2}^{\text{II/III}}$ values are displayed on the corresponding voltammogram.

Figure 6.

Cyclic voltammograms of $[\text{Ru}(\text{Py}_5\text{Me}_2)\text{N}_3]^+$ (1) in $0.1 \text{ M Bu}_4\text{NPF}_6 / \text{PC}$, 100 mV/s scan rate with different potential windows. The two green voltammograms, both taken during a single measurement, indicate the first (middle graph) and second (bottom graph) potential sweeps, respectively.

Figure 7. Correlation diagram for Ru-N₃ bond distances versus Ru-N-N₂ bond angles in the monometallic (blue) and bimetallic Ru₂(II,III) (red) azido complexes listed in Table 3.

Scheme 1.

Representative depictions of a bimetallic Ru–Ru complex (left) and a monometallic Ru complex (right) bearing N-donor ligands and a terminal oxo, nitrido or nitrene moiety.

Scheme 2.

Proposed $\vec{E}\overleftarrow{CE}$ mechanism for reversible ligand substitution of MeCN for X^- ($\text{X}^- = \text{Cl}^-$, N_3^-).

Scheme 3.

Proposed mechanism for the electrochemical features of **1** in PC.

Table 1.

Structural parameters for $[(\text{Py}_5\text{Me}_2)\text{Ru}^{\text{II}}\text{X}]^{\text{n}+}$ complexes stabilized with the hexafluorophosphate counteranion.

	1	2^a	3	3 (OTf)^b	4
Ru–X (Å)	2.097(4)	2.4112(8)	2.158(3)	2.123(1)	2.035(3)
Ru–N _{ax} (Å)	2.026(4)	2.008(3)	2.001(3)	2.001(1)	2.025(3)
Ru–N _{eq} (Å)	2.062(4)/	2.074(2)/	2.055(3)/	2.085(1)/	2.073(3)/
	2.072(3)/	2.074(2)/	2.076(3)/	2.062(1)/	2.078(3)/
	2.070(3)/	2.074(2)/	2.087(3)/	2.069(1)/	2.072(3)/
	2.074(4)	2.074(2)	2.065(3)	2.070(1)	2.084(3)
X–Ru–N _{ax} (°)	177.5(2)	178.98(9)	178.8(1)	178.13(5)	178.3(1)

^aData from ref. 47.

^bData from ref. 48.

Table 2.Relevant UV-Vis parameters for [(Py₅Me₂)Ru^{II}X]ⁿ⁺ complexes.

Complex	λ_{max} [nm]	ϵ [M ⁻¹ cm ⁻¹]
1	454 (sh), 400	1.5×10^4
2	398	1.5×10^4
3	385	1.2×10^4
4	374	1.2×10^4

Table 3.

Structural parameters for a series of monometallic and bimetallic azido complexes. Compounds from the literature are listed by their six-letter CSD entry code.

	1	EBAHAS	ENAZPUI^a	FUNGUQ^b	MANNIA^c	MANNOG^c	MANNUM^c	NIPLEF^d	PAOTIK^e	YOMNIZ^f	PAYKAC^g	PAYKEG^g	AQELIR^h	PAYKEG01ⁱ
Ru–Ru (Å)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	2.3445(8)	2.3472(5)	2.3166(7)	2.3429(6)
Ru–N ₃ (Å)	2.097(4)	2.123(2), 2.094(2)	2.121(8)	2.11(1)	2.115(3)	2.069(9), 2.078(8)	2.084(5)	2.158(3), 2.122(3)	2.117(5)	2.066(3)	2.076(7)	2.042(4)	2.246(4)	2.050(4)
RuN–N ₂ (Å)	1.176(6)	1.187(2), 1.196(2)	1.18(1)	1.08(1)	1.194(4)	1.16(1), 1.17(1)	1.171(7)	1.138(5), 1.181(4)	1.173(7)	1.195(4)	1.09(1)	1.101(5)	1.036(5)	1.183(6)
RuN ₂ –N (Å)	1.241(7)	1.166(2), 1.159(2)	1.15(1)	1.06(2)	1.157(4)	1.14(1), 1.14(1)	1.173(7)	1.172(6), 1.171(5)	1.193(7)	1.156(5)	1.16(2)	1.230(8)	1.158(7)	1.160(7)
Ru–N–N ₂ (°)	132.2(4)	128.5(1), 124.2(1)	116.7(7)	154(1)	137.6(3)	149.7(9), 143.5(9)	139.1(4)	120.7(3), 127.5(3)	120.9(4)	125.3(3)	171.0(8)	165.5(5)	153.6(5)	150.9(4)

^a[Ru^{II}(N₃)₂(N(O)CH(py)CH₂N(C₂H₅)C₂H₄py)], from ref. 70.

^btrans-[Ru(en)₂(N₂)(N₃)]⁺, from ref. 71.

^ctrans-[Ru(TMC)(NCCH₃)(N₃)]⁺, from ref. 72.

^dMANNIA = trans-[Ru(TMC)(NC–O–OCH₃–C₆H₄)(N₃)]⁺, MANNOG = trans-[Ru(TMC)(Ph₃PN)(N₃)]⁺, MANNUM = trans-[Ru(TMC)(NCC₆H₅)(N₃)]⁺, from ref. 73.

^e[Ru(N₄Py)(N₃)]⁺, from ref. 74.

^f[Ru(o-BQDI)(Me₃acn)(N₃)]⁺, from ref. 75.

^g[Ru(N₃)₆]^{3–}, from ref. 76.

^hPAYKAC = Ru₂(DPhF)₄N₃, PAYKEG = Ru₂(D(3,5–Cl₂Ph)F)₄N₃, from ref. 77. To account for disorder, the Ru–N_q–N_c angles instead of the Ru–N_q–Nb angles were used in the Ru–N_q–Nb–N_c fragment.

ⁱRu₂(DMBA)₄(N₃)₂, from ref. 78.

^jRu₂(D(3,5–Cl₂Ph)F)₄N₃, from ref. 67.