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Articles

Bis(4,4′-bis(diethylamino)-2,2′-bipyridine)dichlororuthenium(III): A New Starting Material for Ruthenium Polypyridyl Complexes Exhibiting Low Redox Potentials

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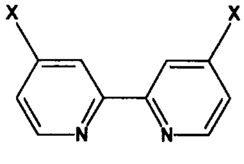
The synthesis and characterization of $[Ru((Et_2N)_2bpy)_2Cl_2]Cl$, where $(Et_2N)_2bpy$ is 4,4′-bis(diethylamino)-2,2′-bipyridine, is described. The utility of this complex as a starting material is illustrated by the syntheses of $[Ru((Et_2N)_2bpy)_2(bpy)](PF_6)_2$ and $[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)](PF_6)_2$, where bpy is 2,2′-bipyridine and py-bzimH is 2-(2-pyridyl)benzimidazole. The bis-$(Et_2N)_2bpy$ complexes are noteworthy because of their low Ru(III/II) potentials. The $(Et_2N)_2bpy$ complexes also undergo ligand-localized oxidations which may influence the Ru(III/II) couple. An improved synthesis of the $(Et_2N)_2bpy$ ligand is also reported.

Introduction

Recent work in our laboratory has focused on the design and synthesis of substitutionally inert ruthenium(II) complexes to be used in the study of proton-coupled electron-transfer reactions. Initial model systems have been based on ruthenium polypyridyl complexes which possess a single ionizable proton on one of the coordinated ligands. In many respects, ruthenium polypyridyl complexes are ideally suited for the study of redox reactions. A well-established methodology exists for the synthesis of a wide variety of ruthenium polypyridyl complexes,[1,2] and the resulting complexes generally undergo rapid, reversible electron-transfer reactions. For these reasons ruthenium polypyridyl complexes have seen wide use in the study of electron transfer.[3]

Polypyridine ligands such as 2,2′-bipyridine (**Ia**) are good π-acids. While this property is important in terms of the photophysical properties of ruthenium(II) polypyridyl complexes,[3] the high Ru(III/II) potentials exhibited by these complexes can make the study of proton-coupled electron transfer in aqueous solvents difficult. Specifically, the use of electrochemistry to study these complexes under aqueous conditions is hampered by the limitations of the solvent window due to the oxidation of water.



Ia: X = H
Ib: X = $N(CH_2CH_3)_2$

One approach to lowering the redox potentials of ruthenium polypyridyl complexes is to introduce electron-donating substituents on the polypyridyl ligand. The introduction of substituents to polypyridine ligands is most easily accomplished at the 4-position on the pyridine ring; hence, a variety of 4,4′-disubstituted 2,2′-bipyridine ligands have been synthesized and coordinated to ruthenium.[3] For a series of $[Ru(X_2bpy)_3]^{2+}$ complexes, the lowest Ru(III/II) potential was observed with the ligand 4,4′-bis(diethylamino)-2,2′-bipyridine ($(Et_2N)_2bpy$, **Ib**).[4]

In order to develop a general route to complexes of the type $[Ru((Et_2N)_2bpy)_2L\text{-}L']^{n+}$, where L-L′ represents a bidentate ligand other than $(Et_2N)_2bpy$, we have synthesized $[Ru((Et_2N)_2bpy)_2Cl_2]Cl$. The utility of this complex as a starting material is illustrated by the syntheses of $[Ru((Et_2N)_2bpy)_2(bpy)](PF_6)_2$ and $[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)](PF_6)_2$.

Experimental Section

Materials. Reagent grade solvents and chemicals were used in the synthesis of the ruthenium complexes. Acetonitrile and methylene chloride were distilled from P_2O_5 and stored over 4-Å molecular sieves. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was synthesized by a literature procedure[5] and recrystallized two times from aqueous ethanol. The chromatographic separations were carried out using neutral aluminum oxide, 80–200 mesh (Aldrich), or silica gel (Aldrich) and reagent grade solvents.

Preparations. 4,4′-Dichloro-2,2′-bipyridine 1,1′-dioxide was prepared by a literature procedure.[6] $[Ru((Et_2N)_2bpy)_3](PF_6)_2$ and $[Ru(bpy)_2((Et_2N)_2bpy)](PF_6)_2$ were prepared from $RuCl_3{\cdot}3H_2O$ and $Ru(bpy)_2Cl_2{\cdot}2H_2O$, respectively, by standard literature procedures.[7]

4,4′-Bis(diethylamino)-2,2′-bipyridine. The ligand was prepared by the procedure of Maerker and Case,[8] except that the intermediate 1,1′-dioxide was not crystallized. 4,4′-Dichloro-2,2′-bipyridine 1,1′-dioxide (18 g, 79 mmol) was added to 144 mL of 1:1 diethylamine/water and heated in a sealed tube at 130 °C for 15 h. After cooling to room temperature, the reaction mixture was placed on a rotary evaporator to remove water and unreacted diethylamine. A minimum of acetone was

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(7) $[Ru(X_2bpy)_3]^{2+}$, $[Ru(X_2bpy)_2(bpy)]^{2+}$, and $[Ru(X_2bpy)(bpy)_2]^{2+}$ complexes are typically prepared by reacting $RuCl_3{\cdot}3H_2O$, $Ru(bpy)Cl_4$, or $Ru(bpy)_2Cl_2{\cdot}2H_2O$, respectively, with an excess of the X_2bpy ligand in any of a number of solvents. For example, see: Rillema, D. P.; Blanton, C. B.;Shaver, R. J.; Jackman, D. C.; Boldaji, M.; Bundy, S.; Worl, L. A.; Meyer, T. J. *Inorg. Chem.* **1992**, 31, 1600.

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added to the residual oil to precipitate undesired salts which were removed by suction filtration. The acetone was removed by rotary evaporation to yield the crude 4,4′-bis(diethylamino)-2,2′-bipyridine 1,1′-dioxide as an oil. The oil was combined with 50 mL of phosphorus trichloride in 300 mL of chloroform and heated at reflux for 75 min. The solution was allowed to cool to room temperature and suction filtered to remove solid that had formed during the reaction. The filtrate was extracted with water and the aqueous layer was neutralized with 40% NaOH to produce the desired solid. The light brown product was isolated by suction filtration to give 12 g (51% yield). ^{13}C NMR in $CDCl_3$ (ppm vs TMS): 157.69, 153.18, 149.45, 106.03, 103.81, 43.53, 12.23; mp = 145 °C (literature: 156–157 °C).[8]

$[Ru((Et_2N)_2bpy)_2Cl_2]Cl$. $RuCl_3\cdot 3H_2O$ (0.61 g, 2.3 mmol), LiCl (1.6 g, 38 mmol), and $(Et_2N)_2bpy$ (1.45 g, 4.9 mmol) were combined in 15 mL of DMF and gently heated at or near reflux for 12 h under N_2. The reaction mixture was allowed to cool, and 20 mL of acetone was added. The solution was added dropwise to 300 mL of stirring anhydrous diethyl ether, and the resulting solid was isolated by suction filtration and dried under vacuum. Roughly half of the crude solid was dissolved in 30 mL of CH_2Cl_2 and suction filtered to remove insolubles (presumably LiCl). The filtrate was passed down a 5 cm × 8 cm silica gel column prepared with CH_2Cl_2. The initial eluent was 2% methanol/CH_2Cl_2 until the first band (red) was removed. The eluent was changed to 9% methanol/CH_2Cl_2 to remove the next band (dark purple), which contained the desired complex. A third band, which was also purple, did not contain the desired complex. The desired band was collected and the solvent was removed by rotary evaporation. The residue was dissolved in minimal CH_2Cl_2 and added dropwise to stirring diethyl ether, precipitating the product. The product was isolated by suction filtration and air-dried. This procedure was repeated for the remainder of the crude solid, giving a total of 1.34 g (65% yield based on ruthenium). Anal. Calcd for $[Ru(C_{18}H_{26}N_4)_2Cl_2]Cl\cdot 4H_2O$: C, 49.34; H, 6.90. Found: C, 49.23; H, 6.51.

$[Ru((Et_2N)_2bpy)_2(bpy)](PF_6)_2$. $[Ru((Et_2N)_2bpy)_2Cl_2]Cl\cdot 4H_2O$ (0.050 g, 0.058 mmol), bpy (0.030 g, 0.19 mmol), and triethylamine (0.1–0.2 mL, 1 mmol) were combined in 50 mL of 50% ethanol/water and heated at reflux for 2 h under N_2. The reaction mixture was allowed to cool and the ethanol was removed by rotary evaporation. The product was precipitated by the addition of excess NH_4PF_6(aq) and isolated by suction filtration. The crude product (0.060 g) was purified on a neutral alumina column with 1:2 acetonitrile/toluene as the eluent. Three bands appeared, and the first band (red) corresponded to the desired complex. The band was isolated and the solvent removed by rotary evaporation. The residue was redissolved in a minimum of acetonitrile and added dropwise to stirring anhydrous diethyl ether. The precipitate was isolated by suction filtration and air-dried, yielding 0.036 g of the desired complex (55% yield based on ruthenium). Anal. Calcd for $[Ru(C_{18}H_{16}N_4)_2(bpy)](PF_6)_2$: C, 48.29; H, 5.29. Found: C, 48.39; H, 5.26.

$[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)](PF_6)_2$. $[Ru((Et_2N)_2bpy)_2Cl_2]Cl\cdot 4H_2O$ (0.20 g, 0.23 mmol) and 2-(2-pyridyl)benzimidazole (0.15 g, 0.77 mmol) were combined in 200 mL of 50% ethanol/water and heated at reflux under N_2 for 26 h. The reaction mixture was allowed to cool, and the volume was reduced to roughly 130 mL by rotary evaporation. Approximately 200 mg of NH_4PF_6 dissolved in 3 mL of H_2O was added to the reaction mixture, and the resulting precipitate was isolated by suction filtration. The solid was washed with water and washed/dried with anhydrous diethyl ether. The crude solid was purified on a neutral alumina column (4 cm × 12.5 cm) with acetonitrile as the eluent. The first band (red) was collected, and the solvent was removed on a rotary evaporator. The product was redissolved in 5 mL of acetonitrile and added dropwise to 250 mL of stirring anhydrous diethyl ether, precipitating the product. The product was isolated by suction filtration and dried under vacuum, yielding 165 mg of solid composed of both the protonated and deprotonated complexes.[9] A 70-mg portion was dissolved in 40% water/acetone that had been acidified to pH 1–2 with concentrated HPF_6. The solution volume was reduced on a rotary evaporator until the product precipitated. The product was isolated by suction filtration, washed/dried with anhydrous diethyl ether, and dried under vacuum. The HPF_6 treatment was repeated for the remaining solid to give a total of 153 mg (56% yield based on ruthenium). Anal. Calcd for $[Ru(C_{18}H_{16}N_4)_2(C_{12}H_9N_3)](PF_6)_2$: C, 48.73; H, 5.20. Found: C, 48.45; H, 5.19.

Measurements. Electrochemical measurements were obtained on a Princeton Applied Research Model 173 potentiostat equipped with a Model 175 Linear Programmmer. Cyclic voltammograms were recorded on a Houston Instrument Model 200 x-y recorder. The working electrode was a platinum disk electrode (Bioanalytical Systems) which was polished routinely with 0.05 micron alumina micropolish. A platinum wire served as the auxiliary electrode. The half-wave potential ($E_{1/2}$) is defined as $(E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the peak anodic and peak cathodic potentials, respectively. Potentials were measured vs a saturated sodium calomel electrode (SSCE). The SSCE reference electrode was periodically checked against the ferrocenium/ferrocene couple.[11] ^1H and ^{13}C NMR spectra were obtained at 300 MHz on a Varian Gemini spectrometer in chloroform-*d* and dimethyl-d_6 sulfoxide solutions, respectively.

Results

Synthesis. Several research groups have reported complexes containing the ligand 4,4′-bis(diethylamino)-2,2′-bipyridine,[4,12–14] referencing the five-step procedure of Maerker and Case for synthesis of the ligand. We found a recent modification of the Maerker and Case procedure to give better yields of the 4,4′-dichloro-2,2′-bipyridine 1,1′-dioxide intermediate.[6] The 4,4′-dichloro-2,2′-bipyridine 1,1′-dioxide was converted into the desired ligand by the Maerker and Case procedure, except that the intermediate 4,4′-bis(diethylamino)-2,2′-bipyridine 1,1′-dioxide was not crystallized. The final 4,4′-bis(diethylamino)-2,2′-bipyridine was obtained in overall 18% yield based on starting 2,2′-bipyridine.

Initial attempts to synthesize $Ru((Et_2N)_2bpy)_2Cl_2$ were based on the well known synthesis of $Ru(bpy)_2Cl_2$, where ruthenium trichloride is allowed to react with 2 equiv of 2,2′-bipyridine in *N,N*-dimethylformamide, and $Ru(bpy)_2Cl_2$ is precipitated by the addition of acetone.[15] When attempting to use this procedure to synthesize $Ru((Et_2N)_2bpy)_2Cl_2$, we found that acetone failed to precipitate the dichloride. Instead, a solid was obtained by adding the reaction mixture to diethyl ether, and the product was purified by column chromatography. A cyclic voltammogram of the product showed two reversible waves at roughly the potentials expected for the $[Ru((Et_2N)_2bpy)_2Cl_2]^{+/0}$ and $[Ru((Et_2N)_2bpy)_2Cl_2]^{2+/+}$ couples (see below); however, current measurements indicated that the complex had been isolated in a higher oxidation state. Elemental analysis confirmed that the ruthenium(III) complex had been obtained as a tetrahydrated chloride salt.

The ruthenium(II) complexes $[Ru((Et_2N)_2bpy)_2(bpy)](PF_6)_2$ and $[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)](PF_6)_2$ were prepared by treating $[Ru((Et_2N)_2bpy)_2Cl_2]Cl$ with an excess of the appropriate ligand in ethanol/water. Reaction times under these conditions were typically 15–25 h; however, the reaction time could be decreased significantly by the addition of triethylamine as a reducing agent. The complexes were characterized by elemental analysis, by ^{13}C NMR (supplemental material), and by comparison of the Ru(III/II) potentials to those of the analogous 2,2′-bipyridine complexes.

Electrochemistry. The cyclic voltammogram of $[Ru((Et_2N)_2bpy)_2Cl_2]Cl$ in acetonitrile showed three distinct redox processes in the potential range –0.5 to 1.5 V vs SSCE. Two reversible waves at –0.31 and 1.20 V vs SSCE were assigned as the $[Ru((Et_2N)_2bpy)_2Cl_2]^{+/0}$ and $[Ru((Et_2N)_2bpy)_2Cl_2]^{2+/+}$ couples, respectively, based on related assignments for $Ru(bpy)_2Cl_2$ ($Ru^{III/II} = 0.32$ V; $Ru^{IV/III} = 1.95$ V).[16,17] An irreversible oxidation observed at 1.0 V vs SSCE is characteristic of the oxidation of

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(9) The presence of protonated and deprotonated complexes was detected by cyclic voltammetry of the mixed product: $E_{1/2}$ in 0.1 M TBAH/acetonitrile is 0.18 and 0.51 V vs SSCE for $[Ru((Et_2N)_2bpy)_2(py\text{-}bzim)]^{2+/+}$ and $[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)]^{3+/2+}$, respectively.[10]

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Table 1. Cyclic Voltammetry Data for Analogous $Ru((Et_2N)_2bpy)_2$ and $Ru(bpy)_2$ Complexes

	$E_{1/2}$ (V vs SSCE)[a]	
	L = bpy	L = $(Et_2N)_2$bpy
$[RuL_2Cl_2]^{+/0}$	0.32[b]	–0.31
$[RuL_2Cl_2]^{2+/+}$	1.95[b]	1.20
$[RuL_2((Et_2N)_2bpy)]^{3+/2+}$	0.90	0.33
$[RuL_2((Et_2N)_2bpy)]^{4+/3+}$		1.40
$[RuL_2(bpy)]^{3+/2+}$	1.28	0.60
$[RuL_2(bpy)]^{4+/3+}$		1.55[c]
$[RuL_2(py\text{-}bzimH)]^{3+/2+}$	1.17[d]	0.51

[a] Measured in 0.1 M TBAH/acetonitrile at a platinum disk electrode; scan rate = 100 mV·s^{-1}. [b] Reference 16. [c] Quasireversible; obscured by ligand oxidation. [d] Haga, M. *Inorg. Chim. Acta* **1983**, *75*, 29.

free chloride which is present as the counterion in this complex. Increasing the potential range beyond 1.6 V revealed an irreversible oxidation which we assigned as oxidation of the coordinated $(Et_2N)_2$bpy ligands (see Discussion). A cyclic voltammogram of the free ligand in acetonitrile showed two irreversible oxidations at 1.2 and 1.5 V vs SSCE.

All of the $(Et_2N)_2$bpy ruthenium(II) complexes reported here exhibited reversible Ru(III/II) couples in acetonitrile at potentials significantly lower than the analogous bpy complexes (see Table 1). Complexes containing at least one $(Et_2N)_2$bpy ligand also exhibited a broad, irreversible oxidation wave at 1.5–1.7 V vs SSCE, and the peak anodic currents ($i_{p,a}$) were more than two times $i_{p,a}$ for the Ru(III/II) couples. These waves were assigned as ligand oxidations. $[Ru((Et_2N)_2bpy)_3]^{2+}$ and $[Ru((Et_2N)_2bpy)_2(bpy)]^{2+}$ exhibited an additional reversible or quasi-reversible couple at potentials roughly 1 V more anodic than the Ru(III/II) couples (see Table 1), with peak currents comparable to the Ru(III/II) couples. These couples were assigned as Ru(IV/III) couples. The $[Ru((Et_2N)_2bpy)_2(bpy)]^{4+/3+}$ couple was somewhat obscured by the irreversible ligand oxidation.

Discussion

Our objective was to develop a synthetically useful route to ruthenium polypyridyl complexes that would exhibit low Ru(III/II) couples. The ability of diethylamino-substituted polypyridine ligands to stabilize ruthenium(III) manifested itself in the attempted synthesis of $Ru^{II}((Et_2N)_2bpy)_2Cl_2$, where the ruthenium(III) complex, $[Ru^{III}((Et_2N)_2bpy)_2Cl_2]^+$, was isolated from a substantially reducing medium (refluxing *N,N*-dimethylformamide). While it is interesting to note that an attempted synthesis of $Os((Et_2N)_2bpy)_2Cl_2$ also yielded the metal(III) complex,[12] the isolation of the ruthenium(III) complex is even more remarkable given that Ru(III/II) potentials are generally 400 mV more positive than the Os(III/II) potentials for complexes with the same ligand environments.[18,19] Both the ruthenium and osmium complexes were isolated as extensively hydrated salts, presumably due to hydrogen-bonding to the diethylamino groups.

$[Ru((Et_2N)_2bpy)_2Cl_2]Cl$ is an effective starting material for the synthesis of bis-$(Et_2N)_2$bpy complexes; however, since the dichloride is isolated as the ruthenium(III) complex, the loss of chloride is not as facile as it is for $Ru(bpy)_2Cl_2$. For example, the reaction to form $[Ru((Et_2N)_2bpy)_2(bpy)]^{2+}$ from $[Ru((Et_2N)_2bpy)_2Cl_2]^+$ and excess bpy in 50% ethanol/water takes 15–25 h to go to completion, while the analogous reaction with $Ru(bpy)_2Cl_2$ is complete within several hours. Addition of triethylamine as a reducing agent decreases the reaction time for the preparation of $[Ru((Et_2N)_2bpy)_2(bpy)]^{2+}$ to roughly 2 h. Triethylamine was not used in the synthesis of $[Ru((Et_2N)_2bpy)_2(py\text{-}bzimH)]^{2+}$ in order to avoid complications due to deprotonation of py-bzimH.[10]

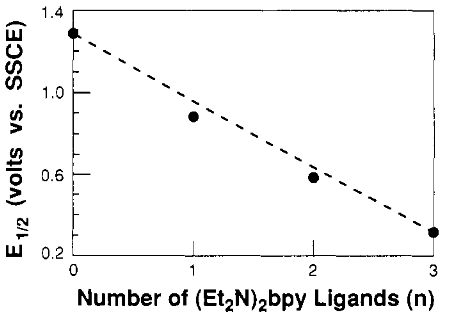
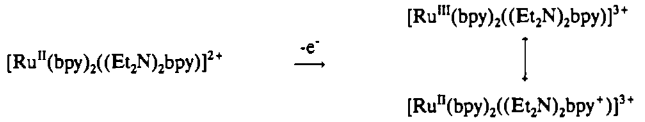


Figure 1. Plot of $E_{1/2}$ for the Ru(III/II) couple vs the number of $(Et_2N)_2$bpy ligands in the family of complexes $[Ru((Et_2N)_2bpy)_n(bpy)_{3-n}]^{2+}$ (*n* = 0–3). Potentials were measured in 0.1 M TBAH/acetonitrile as reported in the Experimental Section.

Scheme 1


$$[Ru^{II}(bpy)_2((Et_2N)_2bpy)]^{2+} \xrightarrow{-e^-} \begin{array}{c} [Ru^{III}(bpy)_2((Et_2N)_2bpy)]^{3+} \\ \updownarrow \\ [Ru^{II}(bpy)_2((Et_2N)_2bpy^{+})]^{3+} \end{array}$$

Cyclic voltammograms of the bis-$(Et_2N)_2$bpy complexes confirmed that the Ru(III/II) potentials had been lowered substantially relative to the analogous bis-bpy complexes. Observation of the Ru(IV/III) couples for some of these complexes also indicates a relatively electron-rich metal center. The observation of ligand oxidation waves at roughly 1.6 V vs SSCE for all of the $(Et_2N)_2$bpy complexes is noteworthy. The assignments of the ligand oxidations were based on (1) the irreversible nature of the oxidations, (2) the large anodic currents relative to the Ru(III/II) couples, and (3) the potentials relative to oxidation of the free ligand. The anodic shift for the oxidation of coordinated $(Et_2N)_2$bpy relative to free $(Et_2N)_2$bpy is expected on the basis of electrostatic and bonding effects of the proximate metal. Anodic shifts of 0.4–0.9 V have been observed for related redox-active metal/ligand systems.[20,21]

The relative proximity of the metal-based and ligand-based redox couples suggests that the possibility exists for electronic coupling between these states, as illustrated in Scheme 1 for the complex $[Ru^{II}(bpy)_2((Et_2N)_2bpy)]^{2+}$. In terms of molecular orbital theory, the $[Ru(bpy)_2((Et_2N)_2bpy)]^{3+/2+}$ couple involves removal of an electron from a metal-based HOMO which could have appreciable ligand character.[22]

The term "noninnocent" has been used to designate ligands which can complicate the assignment of oxidation states in metal complexes.[23] The noninnocent role of the $(Et_2N)_2$bpy ligand may be indicated in the relationship between the Ru(III/II) potential and the number of $(Et_2N)_2$bpy ligands in the family of complexes $[Ru((Et_2N)_2bpy)_n(bpy)_{3-n}]^{2+}$. Haga has shown that very good linear relationships are obtained when the Ru(III/II) potential is plotted against n for families of complexes of the type $[Ru(bpy)_n(X\text{-}X')_{3-n}]^{m+}$, where X-X′ is one of a variety of bidentate ligands.[24] Lever has generalized this ligand additivity relationship to include many of the ligands that have been coordinated to ruthenium, generating a ligand electrochemical series based on the Ru(III/II) couple.[25]

The plot of Ru(III/II) potential vs the number of $(Et_2N)_2$bpy ligands for the family of complexes $[Ru((Et_2N)_2bpy)_n(bpy)_{3-n}]^{2+}$ (*n* = 0–3) shown in Figure 1 deviates significantly from linearity.

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Lever has suggested that such deviations may be due to extraordinary synergistic interactions between the metal and ligand, such as the mixing of metal-based and ligand-based redox states. The extent of mixing between the metal-based and ligand-based orbitals should decrease as the energy between these orbitals increases, as reflected by the difference in the Ru(III/II) and ligand-based redox potentials for the $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})_n(\mathrm{bpy})_{3-n}]^{2+}$ complexes. Since the difference in potential between the Ru(III/II) couple and the ligand oxidation is greatest for $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})_3]^{2+}$, the extent of mixing between the metal-based and ligand-based orbitals should be minimized for this complex. The dashed line in Figure 1 is drawn to show the hypothetical linear relationship between the Ru(III/II) potential and the number of $(\mathrm{Et_2N})_2\mathrm{bpy}$ ligands, assuming no ligand-orbital mixing for $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})_3]^{2+}$. A cathodic shift in the Ru(III/II) potentials for the complexes $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})_n(\mathrm{bpy})_{3-n}]^{2+}$ ($n = 1, 2$) relative to the line is consistent with resonance stabilization due to mixing of the $\mathrm{Ru^{III}}$ and $(\mathrm{Et_2N})_2\mathrm{bpy}^+$ states; however, the possibility of contributions due to specific ligand-solvent interactions must also be considered.[25]

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Supplementary Material Available: ^{1}H-NMR spectra for the complexes $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})_3](\mathrm{PF_6})_2$, $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})_2(\mathrm{bpy})](\mathrm{PF_6})_2$, and $[\mathrm{Ru}((\mathrm{Et_2N})_2\mathrm{bpy})(\mathrm{bpy})_2](\mathrm{PF_6})_2$ (3 pages). Ordering information is given on any current masthead page.