Ruthenium(II) α-Diimine Complexes with One, Two, and Three 4,4′-Bis(hydroxymethyl)-2,2′-bipyridine and 4,4′-Bis(chloromethyl)-2,2′-bipyridine Ligands: Useful Starting Materials for Further Derivatization

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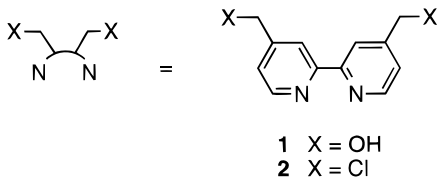
Although Ru(II) tris(bipyridine) complexes and related α-diimine analogues find wide use in chemistry, many common ligand and metal complex derivatives are difficult to synthesize. The halomethyl bpy ligands and their inert metal complexes are one such example. These compounds are desirable since they serve as useful starting materials for a variety of more elaborate derivatives. Although 4,4′-bis(halomethyl)-2,2′-bipyridine ligands readily chelate to labile metal ions, they are not compatible with the higher temperatures and polar solvents typically required to effect ligand substitution at more inert Ru centers. Alternate routes to these targets involving solvento and other substitution labile intermediates yield products, but yields are typically low due to difficulties in purification. This report describes a new route to Ru(II) halomethyl bpy complexes involving chelation of the more robust 4,4′-bis(hydroxymethyl)-2,2′-bipyridine, bpy$(CH_2OH)_2$, followed by conversion to the corresponding chloromethyl species on the metal using oxalyl chloride and DMF in THF or CH_3CN solution. This new "OH to Cl" methodology is demonstrated for Ru(II) complexes with two, four, and six functionalities with both bpy and phen ancillary ligands. Complexes of the general formula $[L_nRu\{bpy(CH_2X)_2\}_{3-n}](PF_6)_2$ (L = bpy, phen; X = OH, Cl; $n = 0-2$) have been prepared in good yield and are conveniently purified by precipitation. These Ru α-diimine complexes have already been utilized as multifunctional metalloinitiators for controlled cationic and radical polymerizations. They promise to be valuable for bpy derivatization generally.

Introduction

Ruthenium(II) tris(bipyridine) complexes, $[Ru(bpy)_3]^{2+}$, and related derivatives are ubiquitous in chemistry.[1] The stability and unique photophysical properties of these systems have been exploited for artificial photosynthesis,[2] in sensors,[3] in photorefractive materials,[4] in studies of electron transfer in proteins[5] and DNA,[6] and for a wide range of other purposes. Despite their prevalence, many common bpy analogues are difficult to prepare and their metal complexes can be challenging to purify. Of particular interest to us are metal complexes with pendant functionalities that can be used as metalloinitiators for living polymerization reactions for the generation of metal complexes with well-defined macroligands. Since both radical[7] and cationic[8] reactions can be initiated by electrophilic halide functionalities, complexes of halomethyl bpys, specifically 4,4′-bis(halomethyl)-2,2′-bipyridine, bpy$(CH_2X)_2$ (**2**) (Figure 1), were targeted. One route to these complexes involves the synthesis of the halomethyl bpy ligand followed by chelation to the



1 X = OH
2 X = Cl

Figure 1. Functionalized bipyridine ligands bpy$(CH_2OH)_2$ (**1**) and bpy$(CH_2Cl)_2$ (**2**).

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appropriate metal ion.[9] This approach has been complicated first by the fact that, traditionally, halomethyl bpy ligands have been very difficult to access cleanly and in high yield. Recent developments in the synthesis of halomethyl bipyridine ligands have addressed this problem for both mono- and difunctional bpys with different substitution patterns.[10] The highly reactive nature of halomethyl bpy ligands presents a second set of challenges for synthesis by chelation. Some of the bromide derivatives are especially prone to intermolecular self-reaction between the electrophilic "benzylic" halide and the nucleophilic nitrogen centers. Moreover, synthesis of complexes by reaction with metal complexes and halide ligands in polar solvents is only practical for labile metal complexes that form rapidly under very mild conditions. Meyer and co-workers described the successful generation of Fe and Zn complexes of 4,4′-bromomethyl-2,2′-bipyridine in aqueous solution.[9] Synthesis of labile complexes of the less reactive chloromethyl bpy ligand **2** is also straightforward.[8] Unfortunately reactive halomethyl bpy ligands are incompatible with the elevated temperatures and nucleophilic aqueous and alcohol reaction media typically required to effect substitution at more inert Ru centers. Routes to Ru bpy complexes that avoid nucleophilic solvents have been described. For example, reaction of $(bpy)_2RuCl_2 \cdot 2H_2O$ with AgOTf in acetone solution precipitates AgCl and forms a solvento species that may be further reacted with the halide ligand **2**.[9,11] Reaction with $AgPF_6$ in dimethoxyethane (DME) solution offers a similar route, this time through a labile bidentate solvento intermediate.[12] While methods employing silver salts were more effective in generating the desired product **8** in reasonable yield, it proved difficult to separate the complex from minor byproducts without significant losses in yield. Recrystallization and chromatography on alumina or ion-exchange resins were ineffective in separating out impurities. In some cases purification procedures partially degraded the electrophilic products; hence these routes seemed impractical.

Our interest in obtaining inert metal polymerization initiators and the lack of efficient routes to the desired targets prompted us to develop new syntheses of Ru halomethyl bpy complexes. This report describes a strategy involving chelation of the robust 4,4′-bis(hydroxymethyl)-2,2′-bipyridine ligand, $bpy(CH_2OH)_2$ (**1**) (Figure 1), followed by conversion of the hydroxyls to electrophilic halides while on the metal. Since chloro functionalities are generated after the nucleophilic bpy nitrogens are protected by complexation, self-reaction of the bpy ligand cannot compete as a side reaction. Other investigators have also described benefits in performing organic transformations on Ru α-diimine complexes after, rather than before, chelation of the ligands.[13] The use of this "OH to Cl" methodology is described herein for Ru complexes with two, four, and six functionalities and for complexes with both bpy and phen ancillary ligands (Figure 2). Both the electrophilic halide derivatives as well as the nucleophilic hydroxymethyl precursor complexes should serve as useful starting points for bpy derivatization.

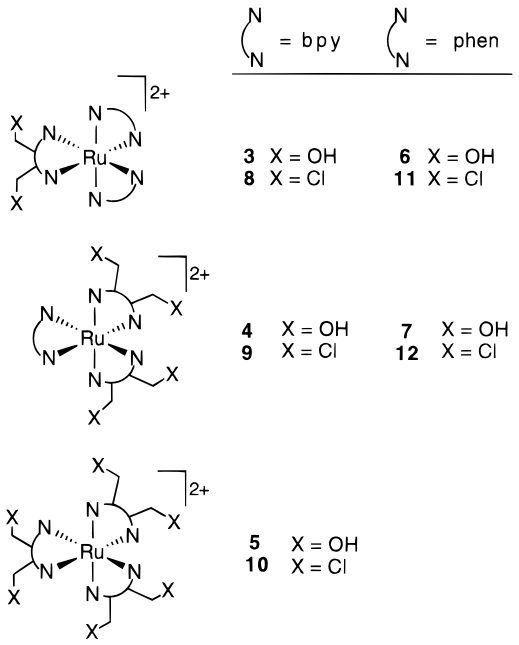
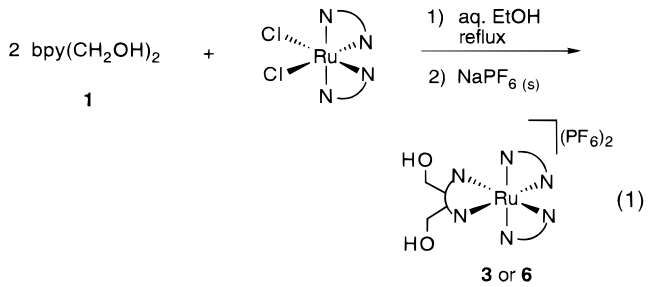


Figure 2. Ruthenium(II) complexes with $bpy(CH_2OH)_2$ (**1**) and $bpy(CH_2Cl)_2$ (**2**) ligands.

Results and Discussion

Homologous series of Ru^{II} complexes with the general formulas $[(bpy)_nRu\{bpy(CH_2X)_2\}_{3-n}](PF_6)_2$ (X = OH or Cl and $n = 0-2$) and $[(phen)_nRu\{bpy(CH_2X)_2\}_{3-n}](PF_6)_2$ (X = OH or Cl and $n = 0-2$) were prepared (Figure 2). Following a three-step procedure reported by Beer et al.,[14] 4,4′-bis(hydroxymethyl)-2,2′-bipyridine (**1**) could be made in multigram quantities (~6 g) for use in the syntheses of the di-, tetra-, and hexaol complexes **3**−**7**. The orange diol complex $[(bpy)_2Ru\{bpy(CH_2OH)_2\}](PF_6)_2$ (**3**) was prepared in 91% yield by reaction of excess **1** with commercially available $(bpy)_2RuCl_2 \cdot 2H_2O$ in refluxing ethanol, followed by precipitation with $NaPF_6$ (Experimental Section, method A) (eq 1). The diol complex



$[(phen)_2Ru\{bpy(CH_2OH)_2\}](PF_6)_2$ (**6**) was prepared from $(phen)_2RuCl_2$[15] in an analogous manner; however additional water was required in the reaction medium and higher reaction temperatures were necessary. The diol complex **3** may also be prepared in comparable yield (79%) and purity starting from $RuCl_3 \cdot xH_2O$ using the sequential addition approach (Experimental Section, method B) described below for the tetraol

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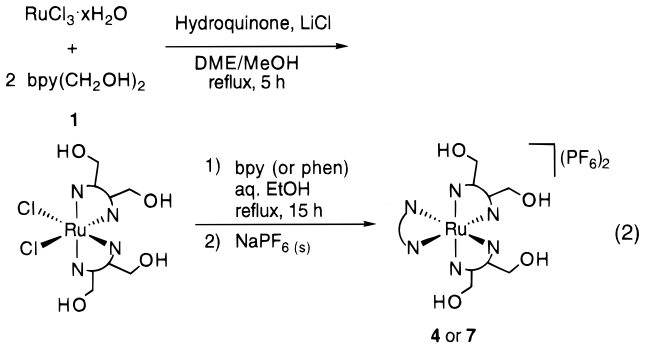
complex **4**. It is important to note that the workup procedures for the synthesis of **3** and **4** vary due to solubility differences of the respective intermediates and products.

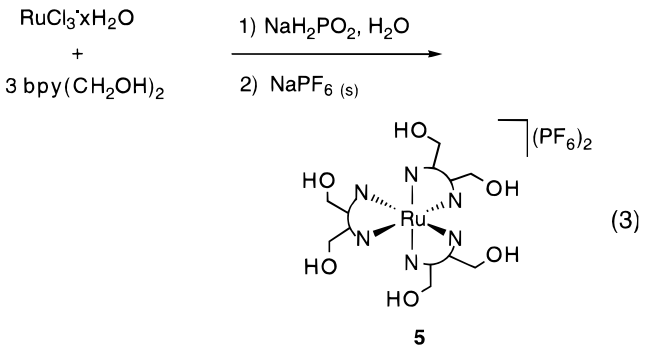
The Ru^{II} tetraol complexes $[(bpy)Ru\{bpy(CH_2OH)_2\}_2](PF_6)_2$ (**4**) and $[(phen)Ru\{bpy(CH_2OH)_2\}_2](PF_6)_2$ (**7**) were prepared in two steps employing a procedure first reported by Meyer et al. for the synthesis of bis(4-vinyl-4′-methyl-2,2′-bpy)Ru^{II} complexes (eq 2).[16] In the first step, a mixture of $RuCl_3 \cdot xH_2O$, the



(2)

diol ligand **1**, hydroquinone, and excess LiCl was allowed to react in refluxing DME/MeOH solution. Reaction times of ~5 h provide the products in good yield; for longer reaction times, larger amounts of a brown insoluble impurity are formed. After extraction of organic byproducts, the resulting dark purple intermediate, $[bpy(CH_2OH)_2]_2RuCl_2$, was combined with either bpy or phen in refluxing 70% aqueous ethanol solution. Addition of excess $NaPF_6$ provided the orange-red bpy tetraol complex **4** in 87% yield. The phen tetraol complex **7** proved far more difficult to prepare in pure form, though it was attained in 76% yield with minor impurities. Reaction stoichiometry appears to be extremely important in the formation of the $[bpy(CH_2OH)_2]_2RuCl_2$ intermediate. Addition of too much diol ligand **1** results in impurities in the NMR spectrum in regions where the hexaol complex **5** appears, whereas addition of too little diol ligand produced impurities coincident with the resonances attributable to the diol complexes **3** or **6**. Precise identification of these impurities is complicated by the fact they are present in small amounts and many resonances overlap with those arising from the major, desired product. Purification of the diol ligand **1** by recrystallization from water and drying in vacuo for several days prior to use serves to minimize the presence of these unwanted byproducts; however, we were unable to remove them entirely from the preparation of **7**. Other investigators have prepared similar mixed ligand complexes, $(bpy')Ru(bpy'')_2$, by forming $(bpy')RuCl_3$ first, followed by reaction with 2 equiv of the second bpy analogue, bpy″.[17] Attempts to prepare the phen tetraol complex **7** by this route gave crude product in lower yield (~50%) with a larger amount of impurity.

Although the hexaol $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$ (**5**) can also be prepared using the same two-step approach that was described for the tetraol complex **4**, the method reported by Broomhead et al.[18] for the synthesis of homoleptic Ru^{II} tris(bpy) complexes is more convenient and provides **5** in higher yield (77%) (eq 3). In this reaction, a refluxing aqueous solution of NaH_2PO_2 reduces $RuCl_3$ in the presence of $bpy(CH_2OH)_2$ (**1**). Addition of excess $NaPF_6$ to the reaction mixture results in the precipitation of the red hexaol complex **5**. It is also possible to perform this reaction using excess benzyl alcohol as the reductant, thus

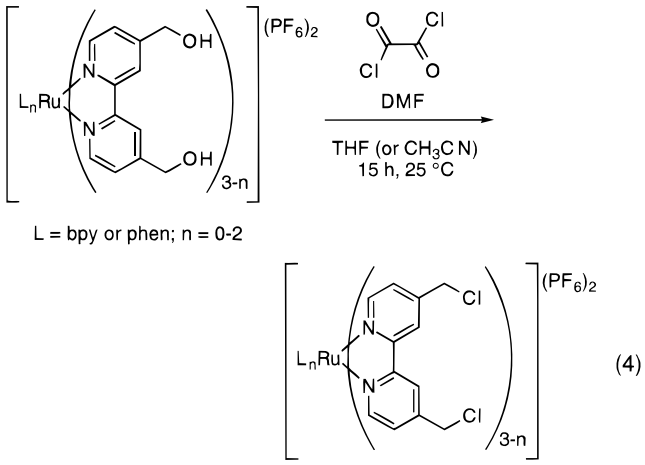


(3)

forming benzaldehyde as a byproduct. However, separation of the Ru product from these organic reagents proved difficult and resulted in depressed yields.

All alcohol complexes, **3**−**7**, are thermally robust and exhibit no reactivity toward air or moisture. These complexes are highly soluble in polar organic solvents such as acetonitrile and acetone and are less soluble in ethanol, THF, CH_2Cl_2, and water. Generally, alcohol complexes could be purified by precipitation either from hot/cold H_2O or from acetone/hexanes.

Chlorination of the alcohol complexes **3**−**7** was achieved using oxalyl chloride and DMF (4 molar equiv each per OH moiety) in THF or CH_3CN by a modification of the procedure first described by Ireland et al. for natural product synthesis[19] (eq 4). The reaction proceeds cleanly in very high yield. The



(4)

byproducts, CO, CO_2, and HCl, are easily separated from the desired products **8**−**12** by evaporation followed by washing with water. As for the alcohol complexes, most chloride complexes may be purified by recrystallization from acetone/hexanes. By subjecting the crude phen tetraol complex **7** to the chlorination procedure and subsequent purification, it is also possible to generate analytically pure phen tetra-Cl complex **12**. A number of other approaches to the synthesis of the halide complex **8** were also attempted before the efficient oxalyl chloride method was discovered. Among other procedures, the following were explored: (1) CCl_4 or CBr_4 and PPh_3; (2) TsCl or MsCl, base (pyridine, collidine, or NaH), and LiX in a variety of polar aprotic solvents (CH_3CN, DMA, DMF); (3) $SOCl_2$; and (4) concentrated HCl at ~100 °C for days. Although many of these alternative methods also generate the desired halide complex product, they suffer from the fact that it is very difficult to separate the di-Cl complex **8** from unreacted starting materials,

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reagents, or reaction byproducts. For example, heating the Ru diol complex **3** in concentrated HCl for extended periods of time effected chlorination, but even after several days at 100 °C, a considerable amount of partially halogenated intermediate remained as determined by electrospray mass spectroscopy.

The solubility properties and ^{1}H NMR spectra of the chlorides **8**−**12** are very similar to their alcohol precursors. It is important to note that the methylene resonances of the chloro products exhibit only a slight downfield chemical shift ($0.01 < \Delta\delta < 0.09$ ppm) as compared to the corresponding alcohols. Complexes with electrophilic chloromethyl groups are susceptible to hydrolysis when subjected to aqueous conditions either at elevated temperatures or for extended periods of time, as evidenced by a smaller broad shoulder on the "benzylic" resonance or broadening at the base of this peak in the ^{1}H NMR spectra. Partially hydrolyzed chloride complexes may be converted back to the pure chlorides by resubjecting them to the halogenation procedure.

Conclusion

This study reports new routes to a series of Ru^{II} tris(α-diimine) reagents with different numbers of nucleophilic and electrophilic functionalities. Both in terms of yields and simplicity, the OH to Cl conversion on the metal constitutes a dramatic improvement over other routes to these compounds. These reagents are of tremendous value to us in exploring the compatibility of different living polymerization methodologies. Thus far the halide-substituted Ru complexes **8**−**10** have been used as metalloinitiators for the polymerization of styrene by atom-transfer radical polymerization[7a,b] and for the polymerization of oxazolines by a cationic mechanism.[8a,d] The alcohol ligand **1** serves to initiate caprolactone polymerizations,[20] whereas the hexafunctional Ru complex **10** as well as an α-halo ester derivative formed from **5** have proven successful as initiators for the polymerization of acrylate monomers.[7c] As these results attest, the hydroxymethyl- and chloromethyl-functionalized ligands **1** and **2** and their Ru complexes **3**−**12** are compatible with a variety of different reaction mechanisms—cationic, anionic, and radical. Thus, they should prove to be widely useful for inert metal bipyridine complex derivatization.

Experimental Section

General Procedures. 4,4′-Hydroxymethyl-2,2′-bipyridine (**1**) was prepared by the method of Beer et al.[14] THF and CH_2Cl_2 used in reactions were purified by passage through alumina solvent purification columns,[21] and CH_3CN was dried over CaH_2 and distilled prior to use. $RuCl_3 \cdot xH_2O$ and $(bpy)_2RuCl_2 \cdot 2H_2O$ were purchased from Strem, 4,4′-dimethyl-2,2′-bipyridine was obtained from GFS Chemicals, and all other reagents and solvents were used as received from Aldrich or Acros. ^{1}H NMR spectra were recorded on a GE QE 300 spectrometer in CD_3CN unless otherwise indicated. UV/vis spectra were taken in CH_3CN solution with an HP 8452A diode array spectrophotometer. IR spectra were measured on the samples using KBr pellets with a Nicolet Impact 400 D. Elemental analyses were performed using a Perkin-Elmer Series II CHNS/O Analyzer 2400. The high-resolution mass spectra were analyzed for solids on a VG 70SQ spectrometer by Drs. W. E. Cotham and M. Walla at the Mass Spectrometry Laboratory at the University of South Carolina. All OH and Cl complexes may be purified by preciptation from acetone/hexanes.

$[(bpy)_2Ru\{bpy(CH_2OH)_2\}](PF_6)_2$, 3. Method A. Preparation from $[(bpy)_2RuCl_2 \cdot 2H_2O]$. The complex $[(bpy)_2RuCl_2 \cdot 2H_2O]$ (0.390 g; 0.749 mmol) and **1** (0.365 g; 1.69 mmol) were stirred for 20 h in refluxing EtOH (18 mL). The bright orange-red mixture was cooled to 25 °C and then was concentrated in vacuo to ∼5 mL. After H_2O (50 mL) was added, the mixture was washed with EtOAc (5 × 50 mL). The aqueous layer was concentrated in vacuo to ∼15 mL. Addition of solid $NaPF_6$ (1.080 g; 6.44 mmol) precipitated an orange solid **3**, which was collected and washed with H_2O (∼10 mL total). The complex was further purified by precipitation from hot/cold H_2O: 0.624 g; 0.679 mmol; 91%.

Method B. Preparation from $RuCl_3 \cdot xH_2O$. Bipyridine (0.328 g; 2.10 mmol), $RuCl_3 \cdot xH_2O$ (0.233 g; 1.05 mmol), hydroquinone (0.289 g; 2.63 mmol), and LiCl (1.330 g; 31.38 mmol) were stirred for 6 h in refluxing DME/MeOH (10 mL/20 mL). The dark brown mixture was concentrated in vacuo to an oil (∼5 mL), and then H_2O (60 mL), EtOH (150 mL), and **1** (0.341 g; 1.58 mmol) were added. After stirring at reflux for 18 h the reaction mixture was concentrated to a red oil (∼10 mL), H_2O (30 mL) was added, and the red solution was washed with EtOAc (5 × 50 mL). Addition of solid $NaPF_6$ to the aqueous layer precipitated **3** as an orange solid, which was stirred at 0 °C for ∼10 min prior to collection by filtration and washing with H_2O (∼10 mL): 0.761 g; 0.828 mmol; 79%. ^{1}H NMR (CD_3CN, 300 MHz): δ 8.48 (d, $J = 8$ Hz, 6 H), 8.03 (m, 4 H), 7.72 (m, 4 H), 7.61 (d, $J = 6$ Hz, 2 H), 7.37 (m, 6 H), 4.78 (d, $J = 5$ Hz, 4 H), 3.77 (t, $J = 5$ Hz, 2 H). (Note: Resonances attributable to alcohol protons vary depending on the water content in CD_3CN.) IR (KBr): $\nu = 3355$ cm^{-1} (OH). UV/vis (CH_3CN), λ_{max} (ϵ) = 454 nm (17,750). Anal. calcd for $C_{32}H_{28}N_6O_2P_2F_{12}Ru$: C, 41.80; H, 3.07; N, 9.14. Found: C, 41.84; H, 3.61; N, 8.99. Accurate FAB high-resolution mass spectrum for $[[(bpy)_2Ru\{bpy(CH_2OH)_2\}](PF_6)]^+$ (*m*/*z*): calcd for $C_{32}H_{28}N_6O_2PF_6{}^{99}Ru$, 772.0975; found, 772.0977.

$[(bpy)Ru\{bpy(CH_2OH)_2\}_2](PF_6)_2 \cdot H_2O$, 4. A solid mixture of **1** (0.207 g; 0.958 mmol), $RuCl_3 \cdot xH_2O$ (0.104 g; 0.479 mmol), hydroquinone (0.133 g; 1.21 mmol), and LiCl (0.596 g; 14.1 mmol) was suspended in a DME/MeOH (5 mL/10 mL) solvent mixture. The resulting brown heterogeneous mixture was warmed to 80 °C for 5 h. After cooling, the reaction was poured into water (50 mL). The aqueous solution was washed with CH_2Cl_2 (5 × 50 mL), filtered through Celite, and then concentrated in vacuo to a volume of ∼3 mL. To the resulting thick maroon solution was added H_2O (27 mL), EtOH (70 mL), and 2,2′-bipyridine (0.130 g; 0.707 mmol), and then the reaction mixture was refluxed for 18 h. After cooling to room temperature (RT), the bright orange-red solution was concentrated in vacuo to ∼3 mL, H_2O (20 mL) was added, and the aqueous mixture was washed with CH_2Cl_2 (5 × 50 mL). (Note: If excess 2,2′-bpy is not completely removed here, it chelates Na^+ in the subsequent step and becomes extremely difficult to remove.) Addition of $NaPF_6$ (0.800 g; 4.91 mmol) to the orange aqueous layer precipitated **4** as an orange solid, which was collected, washed with H_2O (∼10 mL total), and dried in vacuo: 0.418 g; 0.419 mmol; 87% based on $RuCl_3 \cdot H_2O$. ^{1}H NMR (CD_3CN, 300 MHz): δ 8.48 (m, 6 H), 8.01 (dt, $J = 8$ Hz, $J = 2$ Hz, 2 H), 7.71 (m, 2 H), 7.61, (dd, $J = 6$ Hz, $J = 4$ Hz, 4 H), 7.35 (m, 6 H) 4.78 (d, $J = 5$ Hz, 8 H), 3.75 (t, $J = 5$ Hz, 4 H). IR (KBr): $\nu = 3388$ cm^{-1} (OH). UV/vis (CH_3CN), λ_{max} (ϵ) = 455 nm (21 652). Anal. Calcd for $C_{34}H_{34}N_6O_5P_2F_{12}Ru$: C, 40.93; H, 3.43; N, 8.42. Found: C, 40.95; H, 3.38; N, 8.40. Accurate FAB high-resolution mass spectrum for $[[(bpy)Ru\{bpy(CH_2OH)_2\}_2(PF_6)]^+$ (*m*/*z*): calcd for $C_{34}H_{32}N_6O_4PF_6{}^{102}Ru$, 835.1170; found, 835.1161.

$[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$, 5. A solution of NaH_2PO_2 was prepared according to the method of Broomhead et al.[18] by slow addition of NaOH pellets to aqueous hypophosphorous acid (50% w/w; 1 mL) until a viscous cloudy suspension resulted, followed by dropwise addition of H_3PO_2 until the mixture clarified again. The clear NaH_2PO_2 solution (0.47 mL), the diol ligand **1** (0.673 g; 3.11 mmol), $RuCl_3 \cdot xH_2O$ (0.230 g; 1.04 mmol), and H_2O (9.1 mL) were combined and heated at reflux for 30 min. After the orange-red solution was allowed to cool to RT, it was passed through a plug of glass wool and then was poured onto solid $NaPF_6$ (1.74 g; 10.4 mmol) to precipitate the red, microcrystalline hexaol complex **5**, which was collected and washed with H_2O (∼10 mL) before drying under vacuum: 0.828 g; 0.799 mmol; 77% based on $RuCl_3 \cdot H_2O$. ^{1}H NMR (CD_3CN, 300 MHz): δ 8.45 (s, 6 H), 7.64 (d, $J = 6$ Hz, 6 H), 7.33 (d, $J = 6$ Hz, 6 H), 4.78 (d, $J = 5$ Hz, 12 H), 3.70 (t, $J = 5$ Hz, 6 H). IR (KBr): $\nu = 3346$ cm^{-1} (OH). UV/vis (CH_3CN), λ_{max} (ϵ) = 459 nm (15,291). Anal. Calcd for

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$C_{36}H_{36}N_6O_6P_2F_{12}Ru$: C, 41.59; H, 3.49; N, 8.08. Found: C, 41.38; H, 3.98; N, 7.62. Accurate FAB high-resolution mass spectrum for $[[Ru\{bpy(CH_2OH)_2\}_3](PF_6)]^+$ (*m*/*z*): calcd for $C_{36}H_{36}N_6O_6PF_6{}^{102}Ru$, 895.1382; found, 895.1394.

$[(phen)_2Ru\{bpy(CH_2OH)_2\}](PF_6)_2\cdot H_2O$, 6. $(Phen)_2RuCl_2$ was synthesized by modification of the procedures described by Hackett and Meyer.[15] $RuCl_3\cdot xH_2O$ (0.53 g; 2.10 mmol), phenanthroline (0.75 g; 4.16 mmol), LiCl (2.64 g; 62.28 mmol), and hydroquinone (0.60 g; 5.45 mmol) were stirred in refluxing DMF (25 mL) for 8 h. After the reaction mixture was cooled to RT, acetone (125 mL) was added and the resultant solution was further cooled to −22 °C for ∼15 h. A dark green-black microcrystalline solid was collected by filtration and then was washed with water (3 × 25 mL) until the aqueous filtrate was colorless. After washing with Et_2O (3 × 25 mL), the green-black solid was dried in vacuo: 0.93 g, 1.75 mmol; 83%. The diol ligand **1** (0.42 g; 1.93 mmol) and $(phen)_2RuCl_2$ (0.50 g; 0.94 mmol) were suspended in a 2:1 EtOH/water mixture (60 mL). After heating at reflux for 18 h, the hot reaction mixture was filtered through paper and then was cooled to 0 °C. Solid $NaPF_6$ (1.58 g, 9.41 mmol) was added, and the heterogeneous mixture was stirred for 3 h at 0 °C. The resulting orange precipitate was collected by filtration and then was washed with refluxing ethanol (10 mL) followed by hexanes before drying in vacuo: 0.73 g; 0.75 mmol; 79%. Samples for analysis were further purified by dissolving in refluxing water, followed by cooling to −22 °C. A yellow solid impurity was removed by filtration, and then the aqueous solution was concentrated on the rotovap, followed by azeotroping with toluene, and drying in vacuo. ^1H NMR (CD_3CN, 300 MHz): δ 8.63 (d, $J = 9$ Hz, 2 H), 8.53 (d, $J = 9$ Hz, 2 H), 8.49 (s, 2 H), 8.23 (m, 4 H) 7.87 (d, $J = 5$ Hz, 2 H), 7.77 (m, 4 H), 7.54 (m, 4 H), 7.21 (d, $J = 5$ Hz, 2 H), 4.76 (d, $J = 3$ Hz, 4 H), 3.68 (t, $J = 6$ Hz, 2 H). IR (KBr): $\nu = 3421$ cm^{-1} (OH). UV/vis (CH_3CN) λ_{max} (ϵ) = 450 nm (13 100). Anal. Calcd for $C_{36}H_{30}N_6O_3P_2F_{12}Ru$: C, 43.86; H, 3.07; N, 8.53. Found: C, 43.79; H, 3.08; N, 8.35. Accurate FAB high-resolution mass spectrum for $[[(phen)_2Ru\{bpy(CH_2OH)_2\}](PF_6)]^+$ (*m*/*z*): calcd for $C_{36}H_{28}N_6O_2PF_6{}^{99}Ru$, 820.0975; found, 820.0956.

$[(phen)Ru\{bpy(CH_2OH)_2\}_2](PF_6)_2$, 7. The tetraol complex **7** was prepared by the same method described for bpy tetraol complex **4** except that 1,10-phenanthroline was used instead of 2,2′-bipyridine. Crude **7** was obtained as a red powder: 0.326 g; 0.317 mmol; 77% based on $RuCl_3\cdot xH_2O$. Since it was not possible to prepare this compound in analytically pure form, crude **7** was carried on to the chloride preparation **12** as described below. Spectral data of the crude compound are provided for reference. ^1H NMR (CD_3CN, 300 MHz): δ 8.60 (dd, $J =$ 8 Hz, $J = 1$ Hz, 2 H), 8.50 (s, 2 H), 8.47 (s, 2 H), 8.23 (s, 2 H), 8.10 (dd, $J = 5$ Hz, $J = 1$ Hz, 2 H), 7.74 (m, 4 H), 7.41 (dd, $J = 12$ Hz, $J = 6$ Hz, 4 H), 7.15 (d, $J = 5$ Hz, 2 H), 4.83 (d, $J = 5$ Hz, 4 H), 4.77 (d, $J = 5$ Hz, 4 H), 3.75 (t, $J = 5$ Hz, 2H), 3.67 (t, $J = 5$ Hz, 2H). IR (KBr): $\nu = 3414$ cm^{-1} (OH). UV/vis (CH_3CN), λ_{max} (ϵ) = 455 nm (15 200). Accurate FAB high-resolution mass spectrum for $[[(phen)Ru\{bpy(CH_2OH)_2\}_2](PF_6)]^+$ (*m*/*z*): calcd for $C_{36}H_{32}N_6O_4PF_6{}^{99}Ru$, 856.1186; found, 856.1163.

$[(bpy)_2Ru\{bpy(CH_2Cl)_2\}](PF_6)_2$, 8. The di-Cl complex **8** was prepared by the method of Ireland et al.[19] with the following modifications. DMF (0.13 mL; 1.7 mmol) was added dropwise to an oxalyl chloride (0.15 mL; 1.7 mmol)/THF (10 mL) mixture at 0 °C. The reaction mixture was slowly warmed to RT as it effervesced. After stirring for 15 min at RT, the reaction was cooled again to 0 °C for the addition of $[(bpy)_2Ru\{bpy(CH_2OH)_2\}](PF_6)_2$ (**3**) (0.20 g; 0.21 mmol). The reaction mixture was stirred at RT for 15 h and then was concentrated in vacuo. Addition of H_2O (∼10 mL) to the resulting red-orange oil produced the orange solid **8**, which was collected by filtration and then was washed with additional H_2O, prior to drying in vacuo: 0.18 g; 0.19 mmol; 87%. (Note: Acetonitrile may be substituted for THF in chloride preparations. Though NMR spectra of crude products are complex, after purification, comparable yields and purities were obtained for these alternate conditions.) ^1H NMR (300 MHz, CD_3CN): δ 8.56 (d, $J = 2$ Hz, 2 H), 8.49 (d, $J = 8$ Hz, 4 H), 8.05 (m, 4 H), 7.70 (m, 6 H), 7.40 (m, 6 H), 4.79 (s, 4 H). UV/vis (CH_3CN), λ_{max} (ϵ) = 453 nm (15,800). Anal. Calcd for $C_{32}H_{26}N_6Cl_2P_2F_{12}Ru$: C, 40.18; H, 2.74; N, 8.79. Found: C, 40.32; H, 3.23; N, 8.40. Accurate FAB high-resolution mass spectrum for $[[(bpy)_2Ru\{bpy(CH_2Cl)_2\}](PF_6)]^+$ (*m*/*z*): calcd for $C_{32}H_{26}N_6{}^{37}Cl_2PF_6{}^{104}Ru$, 813.0292; found, 813.0303.

$[(bpy)Ru\{bpy(CH_2Cl)_2\}_2](PF_6)_2$, 9. The tetra-Cl complex **9** was prepared as described above for **8** using $[(bpy)Ru\{bpy(CH_2OH)_2\}_2](PF_6)_2$ (**4**) (0.26 g; 0.27 mmol), DMF (0.33 mL; 4.3 mmol), $(COCl)_2$ (0.37 mL; 4.2 mmol), and THF (30 mL). Yield: 0.24 g; 0.23 mmol; 86%. ^1H NMR (300 MHz, CD_3CN): δ 8.55 (s, 4 H), 8.48 (d, $J = 8$ Hz, 2 H), 8.06 (t, $J = 8$ Hz, 2 H), 7.69 (t, $J = 5$ Hz, 6 H), 7.40 (m, 6 H), 4.80 (s, 8 H). UV/vis (CH_3CN), λ_{max} (ϵ) = 456 nm (15,227). Anal. Calcd for $C_{34}H_{28}N_6Cl_4P_2F_{12}Ru$: C, 38.77; H, 2.68; N, 7.98. Found: C, 38.47; H, 3.11; N, 7.88. Accurate FAB high-resolution mass spectrum for $[[(bpy)Ru\{bpy(CH_2Cl)_2\}_2](PF_6)]^+$ (*m*/*z*): calcd for $C_{34}H_{28}N_6{}^{35}Cl_2{}^{37}Cl_2PF_6{}^{104}Ru$, 912.9767; found, 912.9796.

$[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)_2$, 10. The hexa-Cl complex **10** was prepared as described above for **8** using $[Ru\{bpy(CH_2OH)_2\}_3](PF_6)_2$ (**5**) (0.062 g; 0.058 mmol), DMF (0.12 mL; 1.4 mmol), $(COCl)_2$ (0.12 mL; 1.4 mmol), and THF (10 mL). Yield: 0.058 g; 0.051 mmol; 85%. ^1H NMR (300 MHz, CD_3CN): δ 8.54 (s, 6 H), 7.68 (d, $J = 6$ Hz, 6 H), 7.43 (d, $J = 6$ Hz, 6 H), 4.80 (s, 12 H). UV/vis (CH_3CN), λ_{max} (ϵ) = 461 nm (16,480). Anal. Calcd for $C_{36}H_{30}N_6Cl_6P_2F_{12}Ru$: C, 37.59; H, 2.63; N, 7.31. Found: C, 37.65; H, 2.91; N, 7.13. Accurate FAB high-resolution mass spectrum for $[[Ru\{bpy(CH_2Cl)_2\}_3](PF_6)]^+$ (*m*/*z*): calcd for $C_{36}H_{30}N_6{}^{35}Cl_3{}^{37}Cl_3PF_6{}^{104}Ru$, 1010.9271; found, 1010.9288.

$[(phen)_2Ru\{bpy(CH_2Cl)_2\}](PF_6)_2$, 11. The di-Cl complex **11** was prepared as described above for **8** using $[(phen)_2Ru\{bpy(CH_2OH)_2\}](PF_6)_2$ (**6**) (0.21 g; 0.22 mmol), DMF (0.14 mL; 1.8 mmol), and $(COCl)_2$ (0.16 mL; 1.8 mmol) and was purified by precipitation from acetone/hexanes: 0.13 g; 0.13 mmol; 77%. ^1H NMR (300 MHz, CD_3CN): δ 8.65 (d, $J = 9$ Hz, 2 H), 8.57 (s, 2 H), 8.54 (d, $J = 9$ Hz, 2 H), 8.23 (m, 4 H), 7.85 (d, $J = 5$ Hz, 2 H), 7.78 (m, 4 H), 7.59 (m, 4 H), 7.30 (d, $J = 5$ Hz, 2 H), 4.77 (s, 4 H). UV/vis (CH_3CN), λ_{max} (ϵ) = 450 nm (17 780). Anal. Calcd for $C_{36}H_{26}N_6Cl_2P_2F_{12}Ru$: C, 43.04; H, 2.61; N, 8.34. Found: C, 43.37; H, 3.20; N, 8.24. Accurate FAB high-resolution mass spectrum for $[[(phen)_2Ru\{bpy(CH_2Cl)_2\}](PF_6)]^+$ (*m*/*z*): calcd for $C_{36}H_{26}N_6{}^{35}Cl_2PF_6{}^{99}Ru$, 856.0297; found, 856.0338.

$[(phen)Ru\{bpy(CH_2Cl)_2\}_2](PF_6)\cdot H_2O$, 12. The phen tetra-Cl complex **12** was prepared from the phen tetra-ol complex **7** (0.149 g; 0.145 mmol), $(COCl)_2$ (0.200 mL; 2.29 mmol), and DMF (0.18 mL; 2.32 mmol) by the method described above for **8**. The complex was obtained as an orange powder. Crude yield: 0.139 g, 89%. The product was precipitated from acetone/hexanes to yield a red oil. The solvents were decanted off, and the product was dried under high vacuum to yield a red glassy solid. Yield: 0.119 g; 0.109 mmol; 75%. ^1H NMR (CD_3CN, 300 MHz): δ 8.60 (m, 6 H), 8.24 (s, 2 H), 8.06 (dd, $J = 5$ Hz, $J = 1$ Hz, 2 H), 7.83 (d, $J = 6$ Hz, 2 H), 7.75 (d, $J = 5$ Hz, 1 H), 7.73 (d, $J = 5$ Hz, 1 H), 7.49 (d, $J = 6$ Hz, 4 H), 7.25 (dd, $J = 6$ Hz, $J = 2$ Hz, 2 H), 4.84 (s, 4 H), 4.74 (s, 4 H). UV/vis (CH_3CN), λ_{max} (ϵ) = 455 nm (17,440). Anal. Calcd for $C_{36}H_{30}N_6OCl_4P_2F_{12}Ru$: C, 39.47; H, 2.76; N, 7.67. Found: C, 39.40; H, 2.58; N, 7.63. Accurate FAB high-resolution mass spectrum for $[[(phen)Ru\{bpy(CH_2Cl)_2\}_2](PF_6)]^+$ (*m*/*z*): calcd for $C_{36}H_{28}N_6{}^{35}Cl_4PF_6{}^{99}Ru$, 927.9831; found, 927.9865.

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