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Synthetic Approaches to an Isostructural Series of Redox-Active, Metal Tris(bipyridine) Core Dendrimers

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Several types of six-armed, metal tris(bipyridine) core dendrimers were synthesized. Bis-4,4′-alkoxy bipyridine dendrons were prepared and employed to make tris(bipyridine) dendrimers. Although the ruthenium-centered and iron-centered dendrimers displayed quasi-reversible cyclic voltammetry, the analogous cobalt-centered complex did not. The synthesis of 4,4′-disubstituted bipyridines containing $-CH_2OR$ groups proceeded in low yield. The reactions of the dicarbanion of 4,4′-dimethyl bipyridine prepared with LDA and mesylate, triflate, and bromide groups were found to result in no or poor yields of carbon−carbon bond formation. Use of KDA in place of LDA resulted in much higher yields of dendritic bipyridines.

Introduction

Redox active core dendrimers are useful in several structural and behavioral studies of this class of molecules. By probing the rate and driving force for electron transfer to/from these molecules, one can learn about how the dendritic arms encapsulate the core. This information can facilitate conclusions about how the primary structure of the dendrimer leads to its conformations. Encapsulation of a core by a dendrimer also has potential utility, including mimicking metalloprotein behaviors, attenuating molecular exciton quenching in luminescent thin films, and understanding charge-trapping behaviors in molecular electronics.[1−4]

We and others have sought to prepare several types of redox-active core dendrimers to study these various phenomena. These include illustrating the effect of dendrimer architecture on rate and driving force for electron transfer,[1,3,5,6] comparison of structural features in dendrimer isomers,[7] and illustration of the behaviors of several types of redox active cores in dendrimers including Fe_4S_4, Mo_6Cl_8,[8] Re_6Se_8,[9−11] ferrocene,[12−17] and porphyrins.[18−37]

It is of interest to systematically vary the redox potential in an isostructural series of dendrimers. This set of molecules would permit various studies such as measurement of homogeneous electron-transfer rates between two different core moieties. The idea of an isostructural series allows for the comparison of dendrimers with a similar conformational manifold; thus, the

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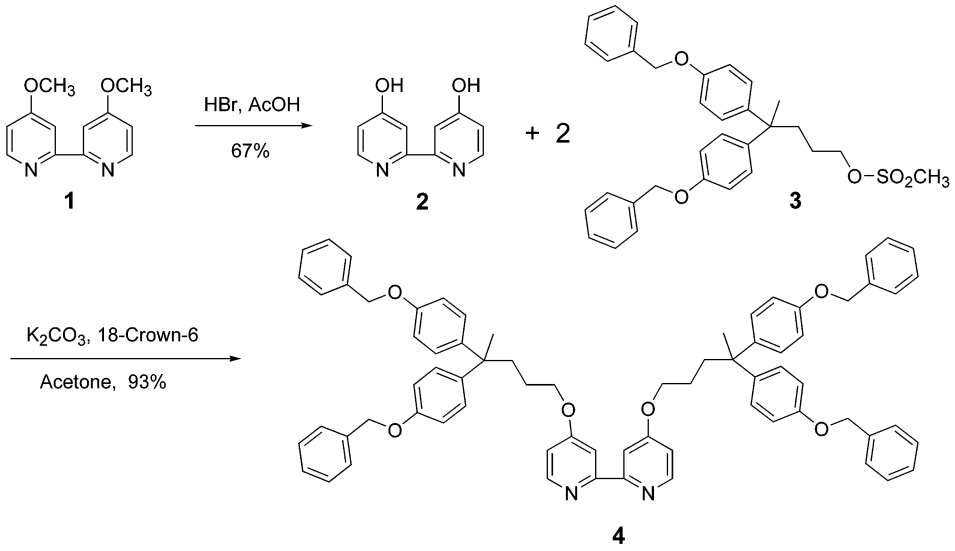
SCHEME 1



effects of differences in redox potential can be separated from those due to conformational differences between molecules.

To this end, we sought to prepare a series of metal tris(bipyridine) core dendrimers that contain different central metal atoms. Bipyridine-based metal complexes as well as the related terpyridine- and phenanthroline-based complexes have been used in the core, branches, and periphery of dendrimers.[38−53] However, as will be illustrated in this paper, no synthetic methodology could be adopted from this work that was amenable to the synthesis of an isostructural series of bipyridine-based, redox active molecules. Synthetic and electrochemical investigations are presented here that illustrate an efficient route to an isostructural series of redox-active metal tris(bipyridine) core dendrimers.

Results and Discussion

A. Dendrimers Containing a Bipyridine−OR Linkage. Bis(phenoxy)isovalerate-based dendrons can be easily converted to molecules with an electrophilic mesylate focal group (e.g., molecule **3**). Thus, a bipyridine derivative presenting a nucleophilic group seemed a good way to synthesize tris(bipyridine) core dendrimers. The route employed to do so is shown in Scheme 1. We determined that treatment with HBr/acetic acid at reflux converted 4,4′-dimethoxy bipyridine to 4,4′-dihydroxy bipyridine in acceptable yield. This molecule reacted with the focally substituted mesylate **3** in excellent yield to give **4**. Thus, from a synthetic standpoint, this route was extremely attractive for the synthesis of the dendritic bipyridine. Further, both 4,4′-dimethoxy bipyridine (generation zero or G0) and **4** (generation 1 or G1) could be converted to the ruthenium, iron, and cobalt tris(bipyridine) complexes (Scheme 2).

The goal in preparing and studying these molecules was to access at least three metal tris(bipyridine) complexes with different redox potentials and quasi-reversible electron-transfer kinetics. These molecules were thus examined by cyclic voltammetry (Figure 1). The ruthenium and iron complexes (**5** and **6**) showed the type of electrochemistry desired. Although the cobalt complex (**7**) showed the expected, ligand-centered reduction below −1500 mV, the metal-centered reduction was irreversible. Thus, although synthetically attractive, this complex did not display the desired electrochemical behavior.

B. Dendrons Containing a Bipyridine−CH_2OR Linkage. It was hypothesized that the alkoxy−bipyri-

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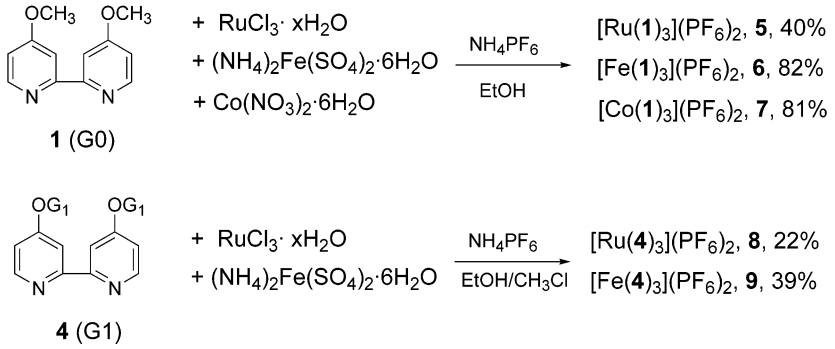
SCHEME 2



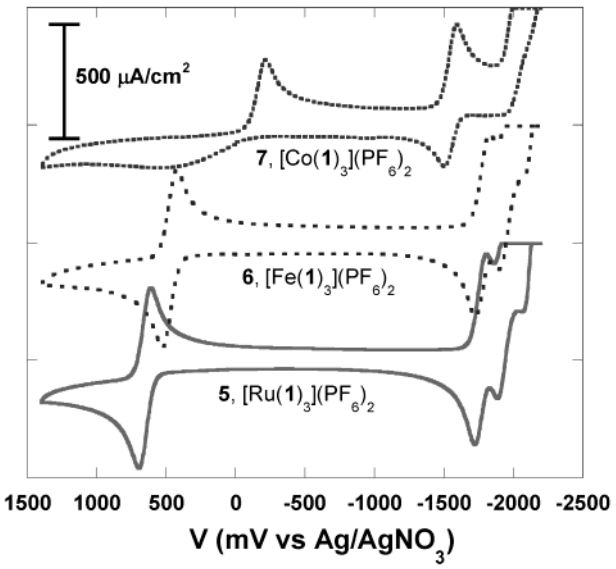


FIGURE 1. Cyclic voltammograms of compounds **5**, **6**, and **7** (scan rate 200 mV/s, argon-purged acetonitrile solution, 100 mM tetrabutylammonium tetrafluoroborate supporting electrolyte, platinum as working electrode).

dine linkage gave rise to the poor electrochemical behavior for the cobalt complex, **7** (vide infra). To remedy this, a route to an alkyl-substituted bipyridine derivative was sought. Fraser et al. reported the conversion of 4,4′-dimethyl 2,2′-bipyridine (**10**) to the electrophilic bisbromomethyl derivative (**12**) via the bistrimethylsilylmethyl bipyridine (**11**).[54] Molecule **12** could then be reacted with nucleophiles to form bipyridine derivatives. When this molecule was reacted with the focally substituted dendritic alkoxide (Scheme 3), the yield was unacceptably low (32%). Yields were not improved by varying the hydride used (NaH versus KH), addition of 18-crown-6, or variation of the solvent (dimethyl formamide versus tetrahydrofuran). Because of these observations, this approach was not pursued further.

C. Dendrimers Containing a Bipyridine−CH_2R Linkage. Another method for the synthesis of substituted bipyridines is the direct deprotonation of **10** followed by reaction with electrophiles.[54,55] We discovered that, although this reaction is acceptable for the synthesis of dialkyl bipyridines (Scheme 4) from the alkyl bromide, reaction of the analogous mesylate or triflate was unsuccessful at producing the desired product. The G1 dendritic mesylate could, however, be converted into the bromide (**18**) very efficiently using Finkelstein chemistry (Scheme 5). However, the use of lithium diisopropyl amide as base to deprotonate 4,4′-dimethyl bipyridine followed by reaction with **18** led to a disappointingly low yield of the desired product **19**. From the model studies above, we reckoned that the structure and reactivity of the biscarbanion rather than the leaving group was to blame for the poor yield. Indeed, when potassium diisopropyl amide was substituted, an excellent yield of **19** was obtained. This reaction was run and quenched at −78 °C given the known temperature sensitivity of the KDA[56] and likely that of the resulting potassium dicarbanion. The disubstituted, G1 bipyridine (**19**) could be converted into metal, tris(bipyridine) complexes of ruthenium, iron, and cobalt (Scheme 6).

Cyclic voltammetry was performed on both the G0 and G1 ruthenium, iron, and cobalt tris(bipyridine) complexes (Figure 2 and Table 1). All displayed quasi-reversible electrochemical behavior. Thus, the alkyl linkage to the bipyridine avoids the slow electrochemical kinetics found in the alkoxy-substituted trisbipyridine cobalt complex. We hypothesize that, in going from alkyl to alkoxy groups on the bipyridines, the ligand field weakens as has been observed for alkoxy terpyridine cobalt complexes.[57] This effect causes the alkoxy cobalt complex to undergo a spin crossover upon oxidation, which is rate limiting. Such slowing of electrochemical kinetics has been observed in cobalt bis[poly(pyrazolyl)borate] complexes.[58] Furthermore, the G1 dendrimers displayed the expected lower current than did their G0 analogues. This result is consistent with a slowing of electron-transfer kinetics due to dendritic encapsulation.[1−4] A more complete set of electrochemical results that compares rate attenuation in these molecules as a function of generation will be reported in due course.

Experimental Section

2,2′-Bipyridinyl-4,4′-diol (2). To a solution of 4,4′-dimethoxy-2,2′-bipyridine (**1**) (2.95 g, 14 mmol) in 170 mL of glacial acetic acid was added 48 wt % HBr solution in water (24 mL,

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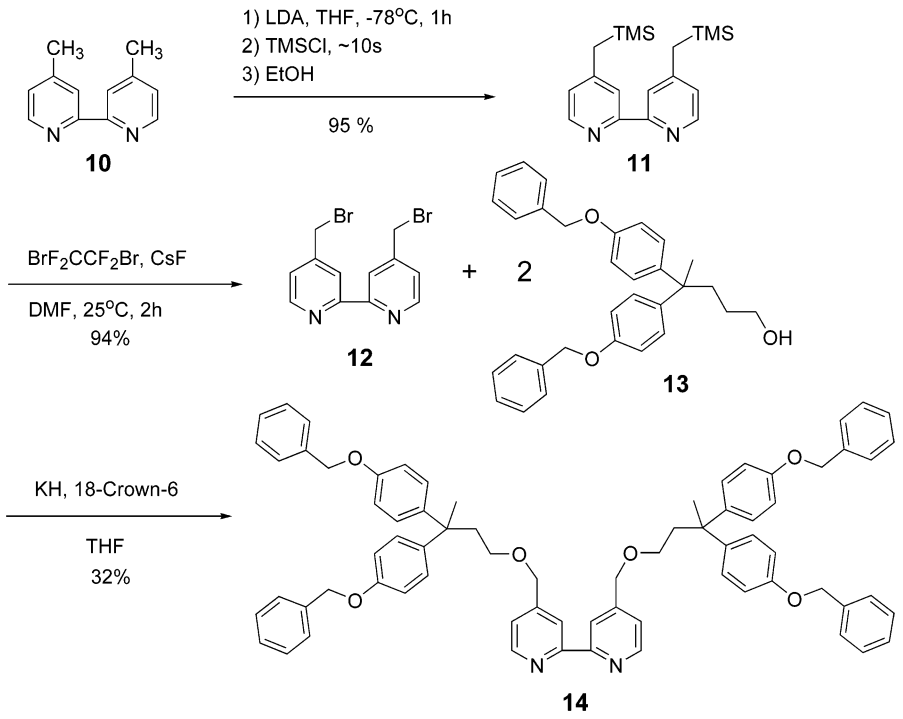
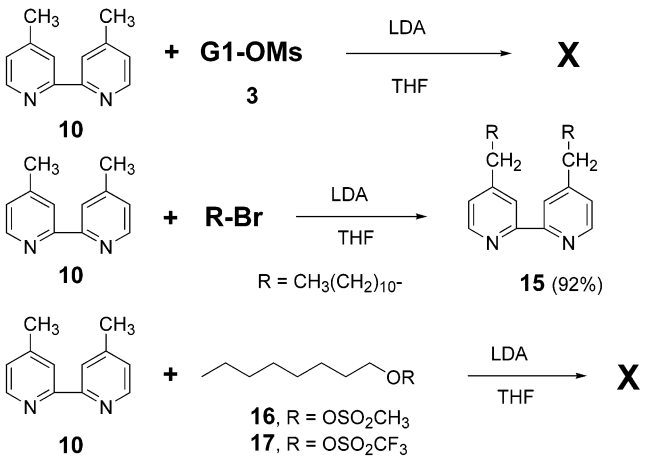
SCHEME 3



SCHEME 4



140 mmol). The mixture was refluxed overnight. After the mixture had cooled to room temperature, the solvent was removed in vacuo. The residue was dissolved in water and neutralized by adding aqueous ammonium hydroxide. This produced a white solid that was filtered and dried. This was used for the next step without further purification. Yield: 67% (1.76 g).

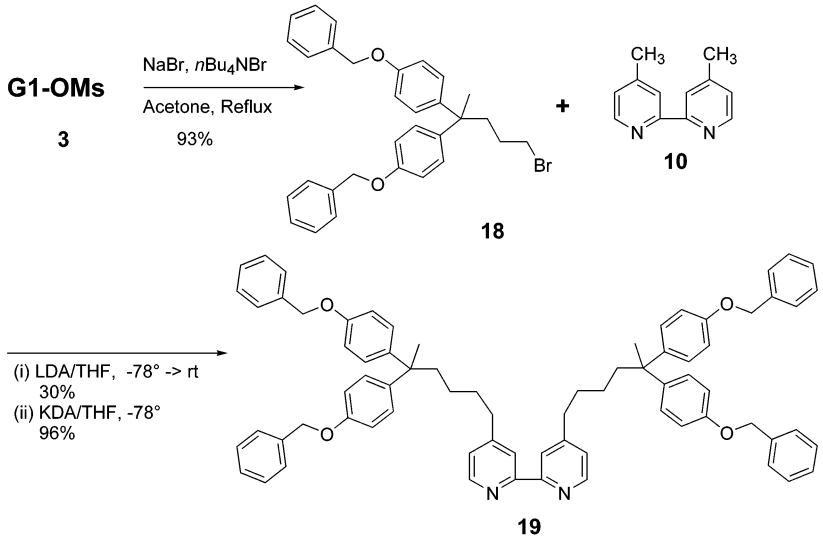
G1-OBpy (4). To a suspension of **2** (0.50 g, 2.66 mmol) in 60 mL of dry acetone were added G1-OMs (**3**)(3.13 g, 5.9 mmol), anhydrous potassium carbonate (1.1 g, 7.98 mmol), and a catalytic amount of 18-crown-6. The mixture refluxed and stirred vigorously for 36 h. After the mixture had cooled to room temperature, the solid residue was filtered and the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography with CH_2Cl_2 followed by 2:1 ethyl acetate−hexane eluent: yield 93% (2.62 g); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.50−1.80 (m, 10H), 2.22 (m, 4H), 4.06 (t, 4H), 5.03 (s, 8H), 6.80 (br, 2H), 6.89 (d, 8H, J = 6.9 Hz), 7.20 (d, 8H, J = 6.9 Hz), 7.30−7.50 (m, 20H), 7.94 (s, 2H), 8.47 (br, 2H, J = 4.7 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 25.0, 28.3, 38.6, 45.1, 68.8, 70.3, 107.2, 111.5, 114.4, 127.7, 128.1, 128.5, 128.8, 137.3, 142.0, 150.2, 156.9, 157.7, 166.3.

$[Ru(1)_3](PF_6)_2$ (5). To a solution of 4,4′-dimethoxy-2,2′-bipyridine (**1**) (0.50 g, 2.3 mmol) in 30 mL of pure ethanol was added ruthenium-trichloride hydrate (40−43% Ru) (0.15 g, 0.72 mmol) in 5 mL of pure ethanol. The reaction mixture was refluxed for 5 days. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, and a solution of NH_4PF_6 (1.18 g, 7.23 mmol) in a small amount of methanol was added dropwise with stirring. The mixture was stirred for 2 h and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of CH_2Cl_2 and added dropwise with stirring to 150 mL of petroleum ether. The orange precipitate was filtered, washed with ethanol, and dried: yield 40% (0.30 g); ^{1}H NMR (CD_3CN) δ (ppm) 3.99 (s, 6H), 6.94 (d, 2H), 7.52 (d, 2H), 7.98 (s, 2H); ^{13}C NMR (CD_3CN) δ (ppm) 57.7, 111.9, 114.6, 153.3, 159.5, 167.9. MALDI-TOF MS (matrix, DHB); m/z calcd, 895.14 (M − PF_6); found, 892.68. FAB-MS (matrix, NBA); m/z calcd, 895.14 (M − PF_6); found, 895.10. Anal. Calcd for $C_{36}H_{36}F_{12}N_6O_6P_2Ru$: C, 41.59; H, 3.49; N, 8.08. Found: C, 41.48; H, 3.34; N, 8.11.

$[Fe(1)_3](PF_6)_2$ (6). To a solution of 4,4′-dimethoxy-2,2′-bipyridine (**1**) (0.50 g, 2.3 mmol) in 30 mL of pure ethanol was added $(NH_4)_2FeSO_4SO_4\cdot 6H_2O$ (0.28 g, 0.72 mmol) in 5 mL of water. The reaction mixture was refluxed for 24 h. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, and a solution of NH_4PF_6 (1.18 g, 7.23 mmol) in a minimum amount of methanol was added dropwise while stirring. The mixture was stirred for 2 h and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and added dropwise while stirring to 150 mL of petroleum ether. The purple precipitate was filtered, washed with ethanol, and dried: yield 82% (0.59 g); ^{1}H NMR (CD_3CN) δ (ppm) 4.01 (s, 6H), 6.98 (d, 2H), 7.23 (d, 2H), 8.06 (s, 2H); ^{13}C NMR (CD_3CN) δ (ppm) 57.7, 111.9, 115.0, 155.6, 161.4, 169.1. MALDI-TOF MS (matrix, DHB); m/z calcd, 849.17 (M − PF_6); found, 847.20. FAB-MS (matrix, NBA); m/z calcd, 849.17 (M − PF_6); found, 849.20. Anal. Calcd for $C_{36}H_{36}F_{12}FeN_6O_6P_2$: C, 43.48; H, 3.65; N, 8.45. Found: C, 43.40; H, 3.62; N, 8.42.

$[Co(1)_3](PF_6)_2$ (7). To a solution of 4,4′-dimethoxy-2,2′-bipyridine (**1**) (0.50 g, 2.3 mmol) in 30 mL of pure ethanol was

SCHEME 5



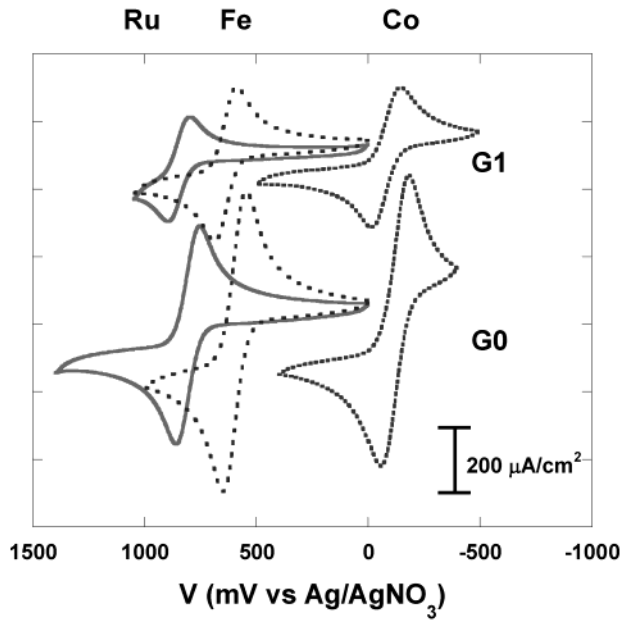
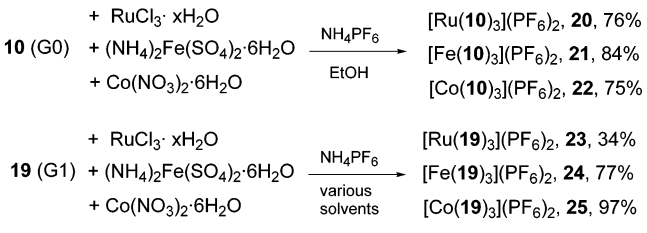


FIGURE 2. Cyclic voltammograms of compounds **20**, **21**, and **22** (bottom) and **23**, **24**, and **25** (top) and CV of the three G0 complexes and the three G1 complexes (identical conditions to those reported in Figure 1).

SCHEME 6



added $Co(NO_3)_2 \cdot 6H_2O$ (0.21 g, 0.72 mmol) in 5 mL of ethanol. The reaction mixture was heated to reflux under Ar for 24 h. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2, and a solution of NH_4PF_6 (1.18 g, 7.23 mmol) in a minimum amount of methanol was added dropwise while stirring. The mixture was stirred for 2 h and extracted with water two times. The combined organic layers were evaporated

TABLE 1. Electrochemical Data

compound	E_{pa} (mV)	E_{pc} (mV)	$E_{1/2}$ (mV)	ΔE (mV)
$[Ru(\mathbf{1})_3](PF_6)_2$, **5**	+680	+579	+630	101
$[Fe(\mathbf{1})_3](PF_6)_2$, **6**	+500	+394	+447	106
$[Co(\mathbf{1})_3](PF_6)_2$, **7**	irrev.[a]	−211	NA[b]	NA[b]
$[Ru(\mathbf{4})_3](PF_6)_2$, **8**	+680	+577	+629	103
$[Fe(\mathbf{4})_3](PF_6)_2$, **9**	+491	+400	+446	91
$[Ru(\mathbf{10})_3](PF_6)_2$, **20**	+860	+754	+807	106
$[Fe(\mathbf{10})_3](PF_6)_2$, **21**	+649	+547	+598	102
$[Co(\mathbf{10})_3](PF_6)_2$, **22**	−60	−181	−121	121
$[Ru(\mathbf{19})_3](PF_6)_2$, **23**	+895	+805	+850	90
$[Fe(\mathbf{19})_3](PF_6)_2$, **24**	+686	+590	+638	96
$[Co(\mathbf{19})_3](PF_6)_2$, **25**	−20	−143	−82	123

[a] Not determined in a fit of the irreversible wave. [b] Not applicable.

to dryness under reduced pressure. The residue was dissolved in a minimum amount of CH_2Cl_2 and added dropwise while stirring to 150 mL of petroleum ether. The yellow precipitate was filtered, washed with ethanol, and dried: yield 81% (0.58 g); ^{1}H NMR (CD_3CN) δ (ppm) 6.66 (s, 6H), 40.79 (s 2H), 77.08 (s, 2H), 91.96 (br, 2H). MALDI-TOF MS (matrix, DHB); *m*/*z* calcd, 852.17 (M − PF_6); found, 852.21. FAB-MS (matrix, NBA); *m*/*z* calcd, 852.17 (M − PF_6); found, 852.21. Anal. Calcd for $C_{36}H_{36}CoF_{12}N_6O_6P_2$: C, 43.34; H, 3.64; N, 8.42. Found: C, 43.47; H, 3.64; N, 8.48.

$[Ru(4)_3](PF_6)_2$ (8). This complex was prepared analogous to **5**, alternatively using chloroform/ethanol solvent mixture (2:1 v/v), and was purified by neutral alumina column chromatography with 10:1 CH_2Cl_2−methanol eluent: yield 24% (0.11 g); ^{1}H NMR (acetone-d_6) δ (ppm) 1.50−1.80 (m, 10H), 2.24 (m, 4H), 4.16 (t, 4H), 5.03 (s, 8H), 6.90 (d, 8H), 7.02 (d, 2H), 7.13 (d, 8H), 7.10−7.43 (m, 20H), 7.74 (d, 2H), 8.24 (br, 2H); ^{13}C NMR (acetone-d_6) δ (ppm) 24.7, 27.5, 37.9, 44.7, 69.7, 70.0, 111.5, 114.4, 127.7, 127.7, 128.0, 128.4, 128.6, 137.8, 142.0, 152.4, 157.1, 158.7, 166.4. MALDI-TOF MS (matrix, DHB); *m*/*z* calcd, 3416.39 (M − PF_6); found, 3413.55. FAB-MS (matrix, NBA); *m*/*z* calcd, 3416.39 (M − PF_6); found, 3418.4. Anal. Calcd for $C_{216}H_{204}F_{12}N_6O_{18}P_2Ru$: C, 72.81; H, 5.77; N, 2.36. Found: C, 72.60; H, 5.93; N, 2.34.

$[Fe(4)_3](PF_6)_2$ (9). This complex was prepared analogous to **6**, alternatively using chloroform/ethanol solvent mixture (2:1 v/v). The purple solid was dissolved in a minimum amount of CH_2Cl_2 and added dropwise while stirring to 150 mL of toluene. The purple precipitate was filtered, washed with ethanol, and dried: yield 39% (0.22 g); ^{1}H NMR (acetone-d_6) δ (ppm) 1.59−1.70 (br, 10H), 2.20−2.30 (m, 4H), 4.15−4.20 (br, 4H), 5.03 (s, 8H), 6.90 (d, 8H, J = 7.2 Hz), 7.05−7.14 (m,

10H), 7.25−7.45 (m, 22H), 8.30 (s, 2H); ^{13}C NMR (acetone-d_6) δ (ppm) 24.6, 27.5, 37.9, 44.7, 69.7, 70.0, 111.4, 114.4, 127.7, 127.8, 128.0, 128.4, 128.6, 137.8, 142.0, 154.8, 157.1, 160.6, 167.5. FAB-MS (matrix, NBA); *m*/*z* calcd, 3370.42 (M − PF_6); found, 3372.20.

G1-O−CH_2Bpy (14). To a suspension of KH (0.14 g, 3.5 mmol) and a catalytic amount of 18-crown-6 in 20 mL of dry THF at 0 °C was added G1-OH (**13**) (0.8 g, 1.77 mmol) in 10 mL of dry THF. After 1 h, 4,4′-bis-bromomethyl-2,2′-bipyridine (**12**) (0.2 g, 0.58 mmol) in 5 mL of dry THF was added and allowed to warm to room temperature. After 12 h, ethanol was added slowly to quench the reaction followed by water. The solution was extracted with ethyl acetate three times, and the combined organic layers were evaporated to dryness under reduced pressure. The crude product was purified by column chromatography with CH_2Cl_2 followed by ethyl acetate eluents: yield 32% (0.2 g); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.40−1.50 (m, 4H), 1.50−1.70 (m, 6H), 2.10−2.20 (m, 4H), 3.50 (t, 4H), 4.53 (s, 4H), 5.01(s, 8H), 6.87 (d, 8H), 7.13 (d, 8H), 7.28−7.46 (m, 22H), 8.30 (s, 2H), 8.65 (d, 2H).

***n*-Octyl Mesylate (16).** To a solution of *n*-octyl alcohol (3.0 g, 23 mmol), triethylamine (9.7 mL, 69 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in CH_2Cl_2 at 0 °C was added methanesulfonyl chloride (5.3 g, 46 mmol). The mixture was stirred for 1 h and then allowed to warm to room temperature. After an additional 2 h, water was added to quench the reaction. The solution was extracted with CH_2Cl_2 two times, and the combined organic layers were evaporated to dryness under reduced pressure. The crude product was purified by plug column chromatography with CH_2Cl_2 eluent: yield 83% (4.25 g); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.90 (t, 3H), 1.20−1.85 (m, 12H), 3.00 (s, 3H), 4.20 (t, 2H). This spectrum matched that published previously.[59]

***n*-Octyl Triflate (17).**[60,61] To a solution of *n*-octyl alcohol (3.0 g, 23 mmol), triethylamine (9.7 mL, 69 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in CH_2Cl_2 at 0 °C was added trifluoromethanesulfonic anhydride (13 g, 46 mmol). After 2 h, water was added to quench the reaction. The solution was extracted with CH_2Cl_2 two times, and the combined organic layers were evaporated to dryness under reduced pressure. The crude product was purified by plug column chromatography with pentane eluent: yield 63% (4 g); ^{1}H NMR ($CDCl_3$) δ (ppm) 0.90 (t, 3H), 1.30−1.88 (m, 12H), 4.54 (t, 2H, J = 6.6 Hz). This spectrum matched that published previously.[61]

G1-Br (18). To a solution of G1-OMs (**3**) (1.0 g, 1.88 mmol) in 50 mL of dry acetone were added NaBr (0.58 g, 5.64 mmol) and a catalytic amount of tetrabutylammonium bromide. The mixture was refluxed for 36 h. After the mixture cooled to room temperature, the solid residue was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in CH_2Cl_2 and extracted with water two times. The combined organic layers were dried with Na_2SO_4 and evaporated to dryness under reduced pressure: yield 93% (0.90 g); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.60−1.80 (m, 5H), 2.10 (br, 2H), 3.36 (t, 2H), 5.04 (s, 4H), 6.89 (d, 4H, J = 8.7 Hz), 7.11 (d, 4H, J = 8.7 Hz), 7.30−7.50 (m, 10H). This spectrum matched that published previously.[62]

G1-Bpy (19). To a solution of potassium *tert*-butoxide (1 M in THF, 6.24 mL, 6.24 mmol) and diisopropylamine (0.93 mL, 6.65 mmol) in 20 mL of THF cooled to −78 °C under Ar was added *n*-butyllithium (1.6 M in hexane, 3.64 mL, 5.82 mmol). The mixture was stirred for 1 h at −78 °C, and then, a solution of 4,4′-dimethyl-2,2′-bipyridine (**10**) (0.38 g, 2.08 mmol) in 10 mL of THF was added over 1 min. The mixture was stirred at −78 °C for 1 h, and a solution of G1-Br (**18**) (3.0 g, 5.82 mmol) in 10 mL of THF was added while stirring at −78 °C was continued for additional 2 h. The reaction was quenched with methanol (2 mL) and added to 20 mL of saturated aqueous NH_4Cl. The THF was removed in vacuo, and the residue was extracted with CH_2Cl_2. The combined organic layers were evaporated under reduced pressure, and the crude product was purified by column chromatography with CH_2Cl_2 followed by 10:0.2 CH_2Cl_2−ethyl acetate eluents: yield 96% (2.10 g); ^{1}H NMR ($CDCl_3$) δ (ppm) 1.20−1.31 (m, 4H), 1.59 (s, 6H), 1.64−1.71 (m, 4H), 2.08 (m, 4H), 2.63 (t, 4H J = 6 Hz), 5.03 (s, 8H), 6.89 (d, 8H, J = 6.6 Hz), 7.07−7.12 (m, 10H), 7.31−7.46 (m, 20H), 8.24 (s, 2H), 8.53 (d, 2H, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm) 24.8, 28.1, 31.3, 35.6, 42.0, 45.2, 70.2, 114.3, 121.5, 124.1, 127.8, 128.1, 128.4, 128.8, 137.4, 142.5, 149.1, 153.1, 156.1, 156.8. Anal. Calcd for $C_{74}H_{72}N_2O_4$: C, 84.38; H, 6.89; N, 2.66. Found: C, 84.49; H, 6.92; N, 2.76.

[Ru(10)$_3$](PF$_6$)$_2$ (20). This complex was prepared analogous to **5**: yield 76% (0.63 g); ^{1}H NMR (acetone-d_6) δ (ppm) 2.56 (s, 6H), 7.38 (d, 2H, J = 4.2 Hz), 7.83 (d, 2H, J = 4.2 Hz), 8.67 (s, 2H); ^{13}C NMR (acetone-d_6) δ (ppm) 20.5, 125.2, 128.7, 150.2, 151.0, 157.1. MALDI-TOF MS (matrix, DHB) *m*/*z* calcd, 799.17 (M − PF_6); found, 799.58. FAB-MS (matrix, NBA); *m*/*z* calcd, 799.17 (M − PF_6); found, 799.10.

[Fe(10)$_3$](PF$_6$)$_2$ (21). This complex was prepared analogous to **6**: yield 84% (0.66 g); ^{1}H NMR (acetone-d_6) δ (ppm) 2.58 (s, 6H), 7.39 (d, 2H, J = 3.9 Hz), 7.51 (d, 2H, J = 4.2 Hz), 8.69 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ (ppm) 21.3, 124.7, 128.8, 151.5, 152.9, 158.7. FAB-MS (matrix, NBA) *m*/*z* calcd, 753.20 (M − PF_6); found, 753.30.

[Co(10)$_3$](PF$_6$)$_2$ (22). To a solution of $Co(NO_3)_2 \cdot 6H_2O$ (0.24 g, 0.81 mmol) in 30 mL of ethanol was added 4,4′-dimethyl-2,2′-bipyridine (**10**) (0.50 g, 2.3 mmol). The reaction mixture was refluxed under Ar for 24 h. The solution was then allowed to cool to room temperature and filtered to remove any insoluble impurities. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and added dropwise with stirring to 150 mL of petroleum ether. The yellow precipitate was filtered and washed with ether and petroleum ether several times. The yellow precipitate was dissolved in water and extracted with diethyl ether several times. To the combined aqueous layers was added a solution of KPF_6 (1.49 g, 8.14 mmol) in a small amount of water. The produced yellow precipitate was filtered, dissolved in CH_2Cl_2, and extracted with water two times. The combined organic layers were evaporated to dryness under reduced pressure: yield 75% (0.55 g); ^{1}H NMR (acetone-d_6) δ (ppm) 0.36 (s, 6H), 44.77 (s, 2H), 81.55 (s, 2H), 91.48 (br, 2H); ^{13}C NMR failed to show all of the expected signals, presumably due to fast nuclear relaxation by the paramagnetic cobalt. FAB-MS (matrix, NBA) *m*/*z* calcd, 756.20 (M − PF_6); found, 756.20. Anal. Calcd for $C_{36}H_{36}CoF_{12}N_6P_2$: C, 47.96; H, 4.02; N, 9.32. Found: C, 47.94; H, 4.09; N, 9.30.

[Ru(19)$_3$](PF$_6$)$_2$ (23). To a solution of **19** (0.54 g, 0.51 mmol) in 40 mL of ethylene glycol/DMF (1/2 v/v) was added ruthenium-trichloride hydrate (40−43% Ru) (0.15 g, 0.72 mmol) in 5 mL of DMF. The reaction mixture was refluxed for 24 h. The solution was allowed to cool to room temperature and filtered to remove any insoluble impurities. The solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and added dropwise with stirring to 150 mL of petroleum ether. The orange precipitate was filtered and washed with ether and petroleum ether several times. The orange precipitate was dissolved in a minimum amount of acetone and added while stirring to 200 mL of water. A solution of KPF_6 (0.3 g, 1.65 mmol) in a minimum amount of water was then added to the resulting orange red solution. This produced an orange precipitate, which was subsequently filtered, dissolved in CH_2Cl_2, and extracted with water two times. The combined organic layers were evaporated under reduced pressure, and the crude product was purified by column chromatography with CH_2Cl_2−ethyl acetate 10:0.2 eluent: yield 34% (0.20 g); ^{1}H NMR (CD_2Cl_2) δ (ppm) 1.22−1.27(br, 4H), 1.54−1.65 (br,

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10H), 2.08−2.12 (br, 4H), 2.72 (t, 4H, J = 8.4 Hz), 4.99 (s, 8H), 6.85 (d, 8H, J = 9 Hz), 7.08−7.15 (m, 10H), 7.31−7.46 (m, 20H), 8.08 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ (ppm) 25.0, 27.7, 31.0, 35.5, 41.8, 70.1, 114.2, 123.9, 127.8, 128.0, 128.1, 128.4, 128.7, 137.5, 142.5, 150.7, 154.7, 156.6, 156.9. MALDI-TOF MS (matrix, DHB) m/z calcd, 3404.52 (M − PF_6); found, 3410.46. FAB-MS (matrix, NBA) m/z calcd, 3404.52 (M − PF_6); found, 3405.70. Anal. Calcd for $C_{222}H_{216}F_{12}N_6O_{12}P_2Ru$: C, 75.09; H, 6.13; N, 2.37. Found: C, 74.87; H, 6.23; N, 2.34.

[Fe(19)$_3$](PF$_6$)$_2$ (24). This complex was prepared analogous to **6**, alternatively using chloroform/ethanol solvent mixture (2:1 v/v): yield 77% (0.40 g); ^{1}H NMR (CD_2Cl_2) δ (ppm) 1.22 (br, 4H), 1.54−1.65 (m, 10H), 2.10 (m, 4H), 2.73 (t, 4H, J = 6.6 Hz), 4.99 (s, 8H), 6.86 (d, 8H, J = 6.6 Hz), 7.09−7.13 (m, 10H), 7.31−7.41 (m, 22H), 8.11 (s, 2H); ^{13}C NMR (CD_2Cl_2) δ (ppm) 25.1, 27.8, 31.0, 35.5, 41.9, 45.1, 70.2, 114.2, 127.7, 127.9, 128.1, 128.3, 128.6, 137.4, 142.4, 153.2, 155.6, 156.8, 158.7. FAB-MS (matrix, NBA) m/z calcd, 3358.55 (M − PF_6); found, 3360.30. Anal. Calcd for $C_{222}H_{216}F_{12}FeN_6O_{12}P_2$: C, 76.05; H, 6.21; N, 2.40. Found: C, 75.50; H, 6.17; N, 2.34.

[Co(19)$_3$](PF$_6$)$_2$ (25). This complex was prepared analogous to **22** alternatively using chloroform/ethanol solvent mixture (2:1 v/v): yield 97% (0.77 g); ^{1}H NMR (CD_2Cl_2) δ (ppm) is shown in the Supporting Information. Additional peaks were always observed in these spectra despite repeated attempts to purify this compound by silica gel and alumina chromatography, reverse phase chromatography, selective precipitation, and gel permeation chromatography. It is suspected that these may be perhaps due to paramagnetic shifting of certain nuclei due to the presence of the cobalt as acceptable elemental and mass spectral analyses were obtained. ^{13}C NMR failed to show all of the expected signals, presumably due to fast nuclear relaxation by the paramagnetic cobalt. FAB-MS (matrix, NBA) m/z calcd, 3361.55 (M − PF_6); found, 3362.60. Anal. Calcd for $C_{222}H_{216}F_{12}CoN_6O_{12}P_2$: C, 75.99; H, 6.20; N, 2.40. Found: C, 75.86; H, 6.31; N, 2.35.

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Supporting Information Available: Experimental general considerations and relevant ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

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