reducing agents, which can transfer an electron to the parent compound, thus initiating an electron transfer chain reaction,[3,4,48] as shown in reactions 8–11. These reactions are indeed photocatalytic in the case of complex I since quantum yields higher than 1 were obtained for all PR_3 ligands. The quantum yields strongly depend on the steric and electronic properties of PR_3 (Table II). Φ is largest for the basic and not very bulky $P(nBu)_3$ ligand and decreases when the ligand becomes less basic and bulkier. The size of L′ will mainly influence the rate of reaction 9, its nucleophilic character that of reaction 10.

$$(CO)_4CoM(CO)_3(bpy) \xrightarrow{h\nu} Co(CO)_4 + M(CO)_3(bpy) \quad (8)$$

$$M(CO)_3(bpy) + L' \longrightarrow L'M(CO)_3(bpy) \quad (9)$$

$$L'M(CO)_3(bpy) + (CO)_4CoM(CO)_3(bpy) \longrightarrow [L'M(CO)_3(bpy)]^{+} + [(CO)_4CoM(CO)_3(bpy)]^{-} \quad (10)$$

$$[(CO)_4CoM(CO)_3(bpy)]^{-} \longrightarrow M(CO)_3(bpy) + [Co(CO)_4]^{-} \quad (11)$$

Similar photocatalytic disproportionation reactions have been observed by us for the analogous complexes $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$, which also produce $Mn(CO)_3(\alpha\text{-diimine})$ radicals upon irradiation into the MLCT band.[14] Stiegman and Tyler[3,4,49] and McCullen and Brown[50] observed photodisproportionation of the dimers $Mn_2(CO)_{10}$, $Cp_2M_2(CO)_6$ (M = Mo, W), and $Cp_2Fe_2(CO)_4$ in the presence of an electron-donating ligand or in a coordinating solvent. In that case, however, the reducing agent is most probably a 19-electron radical species with the unpaired electron mainly localized at the central metal atom. In the case of complex II the disproportionation is not photocatalytic. This is understandable in view of the above observation that the $Re(CO)_3(bpy)$ radicals are only short-lived because of a fast back-reaction to the parent compound. However, although the quantum yields for complex II are much lower than for complex I, their values show a similar dependence on the steric and electronic properties of the PR_3 ligands (Table II). This again points to a similar reaction mechanism for both complexes. A very interesting result of this study is the photodisproportionation of complex II in toluene at $T \leq 230$ K. This reaction was suppressed by addition of CBr_4, which means that the primary photoprocess is homolysis of the Co–Re bond. The $Re(CO)_3(bpy)$ radicals, produced by this reaction, cannot form an adduct according to reaction 9, since toluene is only a very weak base. Apparently, this radical can already transfer an electron to the parent compound or to $Co(CO)_4$ without formation of such a radical adduct. As far as we know, such a reaction has never been observed before. In all cases known, the 16- or 17-electron radicals first form an adduct with a basic ligand before transferring an electron to the parent compound.

All reactions described in this article are therefore the result of a homolytic cleavage of the metal–metal bond from the $^3\sigma\sigma^*$ states of the complexes. Apparently these states, which become populated by energy transfer from the lowest ^{3}MLCT states (see Figure 1), have a much weaker metal–metal than metal (Mn or Re)–CO bond here, since under no circumstances was release of CO observed upon irradiation into the MLCT band (see Introduction).

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Registry No. I, 117828-09-8; II, 117828-10-1; $P(nBu)_3$, 998-40-3; $P(cHx)_3$, 2622-14-2; $P(OMe)_3$, 121-45-9; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0; CBr_4, 558-13-4; $Mn_2(CO)_6(bpy)Br$, 97570-76-8; $Mn(CO)_3(bpy)Br$, 38173-71-6; $[Mn(CO)_3(bpy)(2\text{-}MeTHF)]^+$, 117828-12-3; $[Mn(CO)_3(bpy)(P(nBu)_3)]^+$, 117828-13-4; $[Mn(CO)_3(bpy)(P(cHx)_3)]^+$, 117828-14-5; $[Mn(CO)_3(bpy)(PPh_3)]^+$, 117894-33-4; $[Mn(CO)_3(bpy)(P(OMe)_3)]^+$, 117828-15-6; $[Mn(CO)_3(bpy)(P(OPh)_3)]^+$, 117828-16-7; $Re(CO)_3(bpy)Br$, 40231-87-6; $[Re(CO)_3(bpy)(2\text{-}MeTHF)]^+$, 117828-17-8; $[Re(CO)_3(bpy)(P(nBu)_3)]^+$, 117828-18-9; $[Re(CO)_3(bpy)(P(cHx)_3)]^+$, 117828-19-0; $[Re(CO)_3(bpy)(PPh_3)]^+$, 117828-20-3; $[Re(CO)_3(bpy)(P(OMe)_3)]^+$, 117828-21-4; $[Re(CO)_3(bpy)(P(OPh)_3)]^+$, 117828-22-5; $[Re(CO)_3(bpy)]^+$, 117828-11-2; 2-MeTHF, 96-47-9.

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Luminescent Tetrametallic Complexes of Ruthenium

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Tetrametallic complexes constructed around the metal core $Ru(dpp)_3^{2+}$ (where dpp = 2,3-bis(2-pyridyl)pyrazine) have been prepared and characterized. The complexes, which have the general formula $Ru[(dpp)ML_2]_3^{n+}$, where $ML_2 = Ru^{II}(bpy)_2$ (n = 8), $Ru^{II}(phen)_2$ (n = 8), and $Ru^{II}(tpy)Cl$ (n = 5) and bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, and tpy = 2,2′:6′,2″-terpyridine, are prepared from the reaction of $Ru(dpp)_3^{2+}$ with ML_2Cl_2 in ethanol/water. The tetrametallic complexes luminesce at room temperature in acetonitrile with emissions characteristic of a single ruthenium center with excited-state lifetimes in the 100-ns range. Electrochemically, the most facile reductions occur at the dpp ligand, and the lowest energy oxidation is a single peak associated with the three peripheral ruthenium centers.

Introduction

In an earlier publication,[3] we described the preparation of the highly luminescent complex $Ru(dpp)_3^{2+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine). The significance of this complex is that it can form the core of new polymetallic species that may have application in excited-state energy- and electron-transfer reactions.[4] Multidentate bridging ligands have only recently received much attention in the construction of polymetallic systems.[5] However, the extent of electronic coupling present in the ground state of

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these bimetallic complexes depends on the metal–metal distance as well as the degree of conjugation in the π-system of the bridging ligand. Gafney and co-workers[5k] have suggested that the communication across the bridge could be predicted by comparing the oxidation potential of complexes of the type $L_2Ru^{II}BL^{2+}$ (L = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen); BL = dpp, 2,2′-bipyrimidine (bpm), or 2,3-bis(2-pyridyl)quinoxaline (dpq)) to the first oxidation potential of the analogous $[L_2Ru^{II}]_2BL^{4+}$ complexes. A small difference in oxidation potential between the mono- and bimetallic complexes has been interpreted as a small change in t_2 orbital energies due to weak electronic communication between the two metal sites in the bimetallic complex.[5k] Where communication is large, the bimetallic complex is more difficult to oxidize (e.g., for L = bpy and BL = bpm,[5a–c] $\Delta E = 0.17$ V). In cases where the communication is small, so is the difference in oxidation potential (e.g., for L = bpy and BL = dpp[5k] or dpq,[5c,6] $\Delta E = 0.01$ and 0.06 V, respectively).

The degree of communication between the metals in bimetallic systems is readily predicted as well from the room-temperature emission spectra. When substantial electronic coupling is present, the normal emission observed in the monometallic system (e.g., $Ru(bpy)_2bpm^{2+}$) is not observed in the bimetallic system (e.g., $[Ru(bpy)_2]_2bpm^{4+}$).[5a–c] Presumably, this arises from the coupling of other excited states and deactivation processes into the manifold of the first metal center. However, weakly coupled systems (e.g., $[Ru(bpy)_2]_2dpq^{4+}$) show emission at room temperature in acetonitrile in both mono- and bimetallic complexes.[6]

The preparation of $Ru(dpp)_3^{2+}$[3] has made it possible to readily extend the synthesis of bimetallic complexes to tetrametallic systems. As with the bimetallic systems, the data in the literature concerning electronically coupled polymetallic systems show the same tendency to lose room-temperature emission as the metal centers increase their interaction. In the extreme cases of strong electronic coupling, Hunziker and Ludi[5a] have reported no emission for $Ru[(bpm)Ru(bpy)_2]_3^{8+}$. In the case where virtually no electronic coupling is observed between metal centers by electrochemical studies, Schmehl et al.[7] have shown emission spectra for $Fe[(L\text{–}L)Ru(bpy)_2]_3^{8+}$ systems (L = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane) that look very much like the unperturbed emission spectra of $Ru(bpy)_2(L\text{–}L)^{2+}$.

In this work we report the synthesis, characterization, and photophysical studies of the tetrametallic complexes, $Ru[(dpp)Ru(bpy)_2]_3^{8+}$, $Ru[(dpp)Ru(phen)_2]_3^{8+}$, and $Ru[(dpp)Ru(tpy)Cl]_3^{5+}$ (tpy = 2,2′:6′,2″-terpyridine). These complexes should have behavior intermediate to the systems discussed above.[5a,7] The systems are low molecular weight tetrametallic complexes that should display only weakly coupled metal centers. Thus, a relatively small molecule with four ruthenium(II) centers should still be capable of undergoing room-temperature emission as well as maintaining the capabilities for multielectron, ground- and excited-state reactions.

Experimental Section

Materials. The ethanol, ether, and acetonitrile used in the syntheses were analytical reagent grade and were used without further purification. Water was deionized and then redistilled from alkaline permanganate in an all-glass apparatus. Acetonitrile used in electrochemical and photophysical measurements was Burdick and Jackson Spectroquality purchased from American Scientific Products. Potassium hexafluorophosphate (Alfa Inorganics) and tetrabutylammonium perchlorate (Fisher Scientific) used to make the electrolyte for cyclic voltammetry measurements were used as supplied. The dpp ligand used in this study was prepared by the method of Goodwin and Lions.[8]

Syntheses. The monometallic starting materials ($[Ru(dpp)_3](PF_6)_2$,[3] $Ru(bpy)_2Cl_2$,[9] $Ru(phen)_2Cl_2$,[9] and $Ru(tpy)Cl_3$[10]) used in the synthesis of the polymetallic complexes were prepared by literature procedures.

{Ru[(dpp)Ru(bpy)$_2$]$_3$}(PF$_6$)$_8$. The bpy-containing tetrametallic complex was prepared by heating at reflux a column-chromatographed sample of $[Ru(dpp)_3](PF_6)_2$ (0.055 g, 0.050 mmol) with $Ru(bpy)_2Cl_2$ (0.10 g, 0.207 mmol) in 3:1 (v/v) ethanol/water for 3 h. After this time, very little luminescence characteristic of $Ru(dpp)_3^{2+}$ was observed in the aliquots taken from the reaction mixed and diluted with cold ethanol. The reaction mixture was cooled, and an excess of saturated, aqueous KPF_6 was added. Ethanol was removed by rotary evaporation, and the resulting purple precipitate was collected by vacuum filtration. The crude product was chromatographed on Sephadex CH-20 gel-filtration media in 4:1 (v/v) acetonitrile/water, and the first fraction was collected. Elemental analysis agrees with the formulation of the complex. A typical yield was 0.080 g (50%). As an additional confirmation of the tetrametallic nature of the complex, a gel-filtration, column chromatography experiment was run. A 61.6-cm column of Bio-Rad G-25 gel-permeation resin was prepared to bracket the molecular weight of the tetrametallic bpy complex by its size exclusion capabilities. The solvent used was 0.1 M $NaBF_4$ in water. The four compounds eluted from the column and the amounts of eluent required to elute them were as follows: Blue Dextran 2000 standard (MW = 2000000), 42 mL; $Ru[(dpp)Ru(bpy)_2]_3^{8+}$, 65 mL; $[Ru(bpy)_2]_2dpp^{4+}$,[6] 69.5 mL; $Ru(bpy)_3^{2+}$, 95 mL.

{Ru[(dpp)Ru(phen)$_2$]$_3$}(PF$_6$)$_8$ and {Ru[(dpp)Ru(tpy)Cl]$_3$}(PF$_6$)$_5$. The phen- and tpy-containing tetrametallic complexes were prepared by the same procedure as described above for the bpy-containing tetrametallic complex with $Ru(phen)_2Cl_2$ (0.11 g, 0.207 mmol) and $Ru(tpy)Cl_3$ (0.09 g, 0.206 mmol) substituted for $Ru(bpy)_2Cl_2$, respectively. A typical yield was 0.075 g (45%) for the phen complex and 0.054 g (41%) for the tpy complex. Elemental analysis agrees with the formulation of the complex.

Spectroscopy. Absorption spectra of gravimetrically prepared samples in acetonitrile were recorded at room temperature on a Bausch-Lomb Spectronic 2000 spectrophotometer. Emission spectra were recorded at room temperature in acetonitrile with a SPEX Industries Model 5 spectrofluorometer. Emission quantum yields were not measured due to the position of the emission peaks near the red-sensitive limit of the photomultiplier tube. Excited-state lifetimes were determined in acetonitrile at room temperature with equipment and procedures described previously.[3,6]

Electrochemistry. Cyclic voltammetry measurements and coulometry were accomplished with an IBM EC 225/3A or a PAR Model 273 electrochemistry system. Measurements were made at a sweep rate of 100 mV/s. Millimolar solutions of the tetrametallic complexes were prepared in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The solutions were deoxygenated with N_2 gas prior to voltammetric measurements. Voltammograms were recorded under a N_2 atmosphere at a Pt working electrode vs a saturated calomel electrode and were uncorrected for junction potential. Coulometry used a large surface area Pt basket electrode as the working electrode. Coulometric results were corrected for background current flow (always minimal) and were checked against well-characterized mono- and bimetallic complexes.

Conductivity. Solution conductivities were recorded on a Yellow Springs Instruments Co. Inc. Model 32 conductance meter using either an Altex/Beckman conductivity cell (0.1/cm cell constant) or a YSI 3403 conductivity cell (1.0/cm cell constant) with acetonitrile as the solvent. The procedures and data treatment have been reported by other researchers.[11] The solution conductivities of representative mono- and bimetallic complexes were measured for comparative purposes.

The conductivity results are consistent with the complex formulation and parallel the work of others.[5c,11] Plots of specific conductivity vs the square root of the equivalent concentration result in straight lines (correlation coefficients >0.98) with slopes dependent on the ionic charge of

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Table I. Absorption and Emission Spectra of Tetra-, Bi-, and Monometallic Complexes of Ru with dpp[a]

complex	λ_{max},[b] nm	$10^4\epsilon$,[c] M^{-1} cm^{-1}	λ_{max}^{em},[d] nm	τ,[e] ns
$Ru(dpp)_3^{2+}$[f]	455	1.65	621	183
$Ru(bpy)_2(dpp)^{2+}$[g]	463 (sh) 440	1.15 1.19	658	276
$Ru(phen)_2(dpp)^{2+}$[h]	465 (sh) 435	1.06 1.39	654	252
$[(bpy)_2Ru]_2(dpp)^{4+}$[g]	524 426	2.25 1.98	758	134
$[(phen)_2Ru]_2(dpp)^{4+}$[h]	526 424	2.34 2.10	746	153
$Ru[(dpp)Ru(bpy)_2]_3^{8+}$	534 422	4.96 3.64	772	89
$Ru[(dpp)Ru(phen)_2]_3^{8+}$	539 419	5.14 3.57	760	87
$Ru[(dpp)Ru(tpy)Cl]^{5+}$	564 344	2.38 3.11	758	84

[a] Measured in acetonitrile at room temperature unless otherwise indicated. [b] Absorption maximum. [c] Molar extinction coefficient of absorption band. [d] Emission maximum. [e] Lifetime of emissive state in nanoseconds; uncertainty is approximately 10%. [f] Reference 3. [g] Reference 5k. [h] Reference 6a.

the species. For example, the 2:1 electrolyte $[Ru(bpy)_3](PF_6)_2$ has a slope of 810 mhos $L^{1/2}$ $equiv^{-1/2}$ and the 8:1 electrolyte $\{Ru[(dpp)Ru(bpy)_2]_3\}(PF_6)_8$ has a slope of 3720 mhos $L^{1/2}$ $equiv^{-1/2}$ compared to the theoretical values of 822 and 3263 mhos $L^{1/2}$ $equiv^{-1/2}$, respectively, from the Onsager equation.

Results and Discussion

Characterization of the Complexes. In multimetal systems with similar repeating units, elemental analysis alone is not sufficient to characterize the system. While the elemental analysis of the tetrametallic systems is consistent with the proposed formulation, mixed salts and lower molecular weight units need to be ruled out. The gel-permeation chromatography and the solution conductivity experiment for $\{Ru[(dpp)Ru(bpy)_2]_3\}(PF_6)_8$, described in the Experimental Section, placed the size of the molecular ion larger than that of the bimetallic unit $[Ru(bpy)_2]_2dpp^{4+}$ and placed the overall charge of the complex ion as 8+. These data are consistent with the formulation of this ion as a tetrametallic unit.

Electronic Spectroscopy. The electronic spectral properties in acetonitrile solution of the tetrametallic and related bi- and monometallic complexes are summarized in Table I. The lower energy transition is assigned to the Ru(II) → dpp($d_\pi \rightarrow p_\pi^*$) metal-to-ligand charge-transfer transition. When the dpp ligand is bound to only one metal center (monometallic complexes), this transition occurs in the 455–465-nm region. When dpp bridges more than one metal center (bimetallic and tetrametallic complexes), the stabilization of the π^*-acceptor orbital on dpp shifts the MLCT transition to lower energy, 524–564 nm. The higher energy transition is probably also MLCT in nature, involving the bpy, phen, or tpy π^* orbital as the electron acceptor in the optical transition.

The emission maxima in Table I parallel the lowest energy absorption maxima. These transitions are assigned as p_{π^*}(dpp) → d_π(Ru(II)) transitions, as reported previously[5-7] for similar compounds. In the case of the emission maxima, the range for nonbridging dpp ligands is 621–658 nm (some distinction is observed for dpp bound to a $Ru(dpp)_2$ center as opposed to a $Ru(bpy)_2$ or $Ru(phen)_2$ center) while bridging dpp ligands show MLCT emission maxima in the 746–772-nm region. The similarity in the absorption and emission maxima for the bi- and tetrametallic complexes is consistent with the similarity in chromophores (i.e., RuL_2 bound to a bridging dpp, where $L_2 = (bpy)_2$, $(phen)_2$, or (tpy)Cl) and lack of electronic coupling between the metal centers.[5k] This shift also reflects almost exclusively the stabilization of the π^* system in dpp in going from a terminal to a bridging ligand. As an example, for $Ru(dpp)_3^{2+}$ vs $Ru[(dpp)Ru(bpy)_2]_2^{8+}$, there is a shift of 0.39 V in the reduction potentials for dpp in the two complexes and a 0.39-eV shift in the energy of the emission maxima.

Table II. Electrochemical Data for Tetra-, Bi-, and Monometallic Complexes of Ruthenium

	E,[a] V		
complex	Ru(III)/Ru(II)[b]	dpp redn[c]	2nd dpp/bpy/phen/tpy redn[d]
$Ru(dpp)_3^{2+}$[e]	1.68	−0.95 −1.12 −1.39	
$[(bpy)_2Ru]_2(dpp)^{4+}$[f]	1.38 1.56	−0.66	−1.14
$[(phen)_2Ru]_2(dpp)^{4+}$[g]	1.44 1.65	−0.64	−1.13, −1.38
$Ru(tpy)(dpp)Cl^{+}$[h]	0.94	−1.21	∼−1.5
$[(tpy)ClRu]_2(dpp)^{2+}$[h]	0.94 1.14	−0.85	−1.32, ∼−1.6
$Ru[(dpp)Ru(bpy)_2]_3^{8+}$	1.50	−0.56 −0.74 −0.89	−1.12, −1.24, −1.37, −1.51, −1.65
$Ru[(dpp)Ru(phen)_2]_3^{8+}$	1.43	*i*	*i*
$Ru[(dpp)Ru(tpy)Cl]_3^{5+}$	1.06	−0.60 −0.72 −0.84	

[a] Reduction potential (vs SCE) obtained from cyclic voltammetry in acetonitrile (0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte). [b] Ru(III)/Ru(II) couple. [c] Couple for ligand reduction corresponding to placing an electron in a low-lying π^* orbital of bound dpp. [d] Couple for ligand reduction corresponding to placing an electron in a low-lying π^* orbital of bound dpp/bpy/phen/tpy. [e] Reference 3. [f] Reference 5k. [g] Reference 6a. [h] Gettliffe, G.; Petersen, J. D. Unpublished observations. [i] Broad, unresolved reductions beginning at ∼−0.5 V.

Table I includes the lifetimes of the complexes determined in acetonitrile at room temperature with equipment described elsewhere.[6a] The complexes were excited with laser radiation of the same wavelength as the lowest energy absorption maximum and were monitored at the maximum of the emission. The data were analyzed by a linearized unweighted least-squares method, and in each case the correlation coefficient was greater than 0.99. The length of the excited-state lifetime decreases as the energy of the excited state decreases, which is qualitatively consistent with energy-gap-law considerations.[12] No quantitative comparison to the energy-gap law can be made since the nonradiative decay rate requires measurement of emission quantum yields as well as excited-state lifetimes. However, if one assumes that $1/\tau$ is dominated by k_{nr} (a reasonable assumption given the weak emission), the plot of ln $(1/\tau)$ vs E_{em} for the last seven entries in Table I gives a correlation coefficient of 0.92.

The fact that the tetrametallic complexes are luminescent at room temperature is unique. One explanation is that the forced nonplanarity of the dpp bridging ligand interrupts electronic communication and allows each peripheral metal center to act as a isolated molecular unit.[5k] However, current studies in our laboratories on mixed iron/ruthenium systems[13] and the report by Fuchs et al.[5l] using the planar bridging ligand 4′,7′-phenanthrolino-5′,6′:5,6-pyrazine may suggest a different explanation centered around the localization of the MLCT transition into the α,α'-diimine structure of the ligand.

Table II summarizes the electrochemical data for the dpp-containing mono-, bi-, and polymetallic complexes. The Ru(II)/Ru(III) couples vary between 1.06 and 1.68 V vs SCE and are dependent on the average environment surrounding the ruthenium center. The oxidation reported in Table II for the tetrametallic complex corresponds to the peripheral metal centers. No oxidation of the core $Ru(dpp)_3$ unit is observed within the solvent window (∼2.0 V vs SCE), which is not surprising since it involves an 11+ to 12+ charge change for $Ru[(dpp)Ru(bpy)_2]_3^{8+}$

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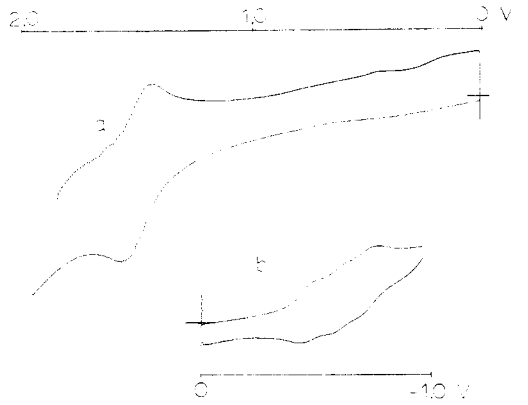

Figure 1. (a) Oxidative and (b) reductive cyclic voltammograms of $Ru[(dpp)Ru(bpy)_2]_3^{8+}$ in acetonitrile (0.1 M TBAH) vs SCE.

and $Ru[(dpp)Ru(phen)_2]_3^{8+}$ and an 8+ to 9+ charge change for $Ru[(dpp)Ru(tpy)Cl]_3^{5+}$ and since the Ru center is bound to three strongly π-accepting dpp bridging ligands. The increase in first oxidation potential in going from mono- to bi- to tetrametallic complexes can be ascribed to a small electrostatic effect. In our laboratories, the oxidation of $Ru(bpy)_2dpp^{2+}$ occurs at 1.33 V and the first oxidation of $[(bpy)_2Ru]_2(dpp)^{4+}$ occurs at 1.38 V. If the 0.05-V difference is due to electrostatic effects, two additional metals would suggest a 0.15-V difference between mono- and tetrametallic complexes. Experimentally, the difference observed is 0.17 V. The oxidative cyclic voltammogram for one of the three tetrametallic complexes, $Ru[(dpp)Ru(bpy)_2]_3^{8+}$, is illustrated in Figure 1a. The ligand reductions are specific and appear to depend on three criteria: (1) the nature of the ligand, (2) the charge on the complex at the time of reduction, and (3) whether or not the ligand is terminal or bridging. In the latter case, for example, a bridging dpp ligand will undergo reduction 0.4 V more easily than a nonbridging dpp ligand in a similar environment. This shift in reduction potential allows easy identification of polymetallic systems. The reductive cyclic voltammogram for $Ru[(dpp)Ru(bpy)_2]_3^{8+}$ is illustrated in Figure 1b. The cyclic voltammograms in Figure 1 are on the same scale and display the expected deviation in peak height characteristic of the simultaneous oxidations of three metal centers.

The last column in Table II corresponds to a combination of the second reduction of dpp ligand(s) and reductions of the nonbridging type ligands (bpy, phen, and tpy). Without spectroelectrochemical studies, specific assignments are difficult, but some tentative assignments can be made. For the complex $[(bpy)_2Ru]_2(dpp)^{4+}$, the reduction at −1.14 V could be either the second dpp reduction or the reduction of one of the bpy ligands. Since the first bpy reduction in $Ru(bpy)_3^{2+}$ occurs at −1.35 V, the −1.14-V reduction is probably the second dpp reduction. However, the former complex does involve an overall complex charge change of 3+ to 2+ compared to 2+ to 1+ for $Ru(bpy)_3^{2+}$. A further piece of data supporting the −1.14-V reduction as the second dpp reduction comes from the similar reduction observed for $[(phen)_2Ru]_2(dpp)^{4+}$ (−1.13 V) and $Ru[(dpp)Ru(bpy)_2]_3^{8+}$ (−1.12 V) with 2+ to 1+ and 5+ to 4+ charge changes, respectively. In addition, the spacings between the first, second, and third reductions for $Ru[(dpp)Ru(bpy)_2]_3^{8+}$, 0.18 and 0.15 V, and the fourth, fifth, and sixth reductions, 0.12 and 0.13 V, suggest that the first six reductions of this tetrametallic complex may only involve the three bridging dpp ligands. In contrast, the positions of the reduction peaks for $Ru(tpy)(dpp)Cl^+$ and $[(tpy)ClRu]_2(dpp)^{2+}$ seem to indicate that overall charge is important for ligand reductions.

As an additional analytical measurement for confirming the tetrametallic nature of $Ru[(dpp)Ru(bpy)_2]_3^{8+}$, $Ru[(dpp)Ru(phen)_2]_3^{8+}$, and $Ru[(dpp)Ru(tpy)Cl]_3^{5+}$, coulometric determinations were carried out. On the oxidative side, the systems are unstable when more than two electrons/mol are removed from the complexes. Yet coulometric determinations still show $n > 2.5$ for the 1.50-, 1.43-, and 1.06-V oxidations of the three tetrametallic systems, indicating that the single oxidative wave observed in the voltammograms corresponds to the oxidation of all three peripheral ruthenium centers. In the case of $Ru[(dpp)Ru(tpy)Cl]_3^{5+}$, the first dpp reductions are set apart enough from the other ligand reductions to enable a determination of $n = 2.99 \pm 0.10$ for the three bridging-ligand reduction waves.

The instability of the tetrametallic complexes toward multielectron oxidations in unfortunate since they otherwise would be low molecular weight multielectron reducing agents. The reversibility of the first three reductions in all of these complexes does suggest that these systems could be used as ground-state, multielectron oxidizing agents. More importantly, the predictability of excited-state energy based on the chromophores present and the ability of ground- (and excited-) state redox potentials by variation of metal center, bridging ligand, and terminal ligand open the door for further design and synthesis of heteropolymetallic complexes with specifically controlled ground- and excited-state properties.

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Registry No. $\{Ru[(dpp)Ru(bpy)_2]_3\}(PF_6)_8$, 117827-98-2; $\{Ru[(dpp)Ru(phen)_2]_3\}(PF_6)_8$, 117800-10-9; $\{Ru[(dpp)Ru(tpy)Cl]_3\}(PF_6)_5$, 117828-00-9; $[Ru(dpp)_3](PF_6)_2$, 100334-03-0; $Ru(bpy)_2Cl_2$, 19542-80-4; $Ru(phen)_2Cl_2$, 85718-09-8; $Ru(tpy)Cl_3$, 72905-30-7; $Ru(tpy)(dpp)Cl^+$, 117828-01-0; $[(tpy)ClRu]_2(dpp)^{2+}$, 117828-02-1; $Ru(tpy)(dpp)Cl^{2+}$, 117800-11-0; $[(tpy)ClRu]_2(dpp)^{4+}$, 117800-12-1; $Ru[(dpp)Ru(bpy)_2]_3^{8+}$, 117800-13-2; $Ru[(dpp)Ru(phen)_2]_3^{8+}$, 117800-14-3; $Ru[(dpp)Ru(tpy)Cl]_3^{5+}$, 117800-15-4.