

displaced out of the polymer by the other counterion. Both these effects, the enhanced quenching and its reversal, may find important applications in solar energy conversion systems.

Two goals of utmost importance in this context might be achieved by the use of polyelectrolytes:

(a) As is shown in this communication, the rate of quenching of the fluorophor of interest can be greatly enhanced. Although the exact mode of the quenching reaction was not explored in this study, it is conceivable that redox quenching will occur with the appropriate quencher, as it does in the absence of the polyelectrolyte. We are currently involved in fast laser experiments aimed at elucidating the exact quenching mechanism in the presently discussed specific system.

(b) Inhibition of the back reaction between the reduced quencher and oxidized sensitizer might be achieved. As is shown above the monovalent cations are bound much more loosely to the potential field of the polyion than are the divalent cations. It is possible therefore that the reduced quencher (e.g., Cu^+) could be more easily displaced from the potential field than the oxidized sensitizer (say $\text{Ru}(\text{bpy})_3^{3+}$) and thus their back reaction would be inhibited. Once both these effects are achieved in a single system the efficiency of energy conversion is certain to increase.

The implications of the type of behavior described above as a model for various biological systems are also obvious. In fact, the physical property that exhibits such a behavior does not necessarily have to be light emission. Any physical property

that depends exclusively on the mutual presence of the two entities in close proximity is expected to show similar behavior.

References and Notes

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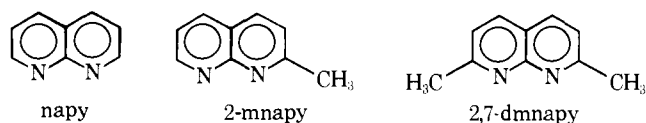
Electrochemical and Spectral Investigations of Ruthenium(II) Complexes of 1,8-Naphthyridine and Its 2-Methyl and 2,7-Dimethyl Derivatives

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Abstract: Complexes of ruthenium(II) having empirical formulas of $[\text{Ru}(\text{napy})_4](\text{PF}_6)_2$, $[\text{Ru}(2\text{-mnapy})_4](\text{PF}_6)_2$, and $[\text{Ru}(2,7\text{-dmnapy})_3](\text{PF}_6)_2$ were prepared and characterized by electrochemical methods, UV-visible, and ^1H NMR spectroscopy. Solutions of the complexes are intensely colored and exhibit visible absorptions near 450 nm characteristic of metal to ligand charge transfer transitions. Ruthenium(II) in the tris 2,7-dmnapy complex is stabilized appreciably by π -back-bonding as evidence by the reversible electrode potential, $\text{Ru}(\text{III})/\text{Ru}(\text{II})$, of 1.37 V vs. SSCE while in contrast the tetrakis napy and 2-mnapy compounds display less anodic potentials of 1.05 and 1.08 V. The lability of the napy and 2-mnapy complexes to substitution is manifested in the more anodic voltammetric waves which appear with time upon dissolution in acetonitrile. The ^1H NMR spectrum as well as the infrared spectrum of the recovered solvolysis product give strong evidence for the presence of coordinated acetonitrile.

Metal complexes with 1,8-naphthyridine (napy), 2-methyl-1,8-naphthyridine (2-mnapy), and 2,7-dimethyl-1,8-naphthyridine (2,7-dmnapy) have been extensively stud-



ied.² Interest in this series of ligands arose from a desire to study the unusual manifestations caused by the formation of a four-membered chelate ring when the two nitrogen sites bind to a central metal. The salient result was the characterization of complexes possessing abnormally high coordination num-

bers,^{2a,3} which are favored as a result of the small "bite" of 2.2 Å for the ligands.⁴

Although the 1,8-naphthyridines, 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen) are all heterocyclic amines, the chemistry of the naphthyridine complexes of iron(II)^{2a,7,8} differs significantly from $\text{Fe}(\text{phen})_3^{2+}$ and $\text{Fe}(\text{bipy})_3^{2+}$. Among the important contrasts are the stoichiometry, magnetic behavior, and the absence of a charge transfer band for the napy complexes. While no rigorous solvolysis study of $\text{Fe}(\text{napy})_4^{2+}$ has been reported, the Mössbauer and UV-visible spectral data^{2a,9} have been suggestive of dissociation of the chelate in acetonitrile to a monodentate form with the vacated site thus occupied by a solvent molecule, e.g., $[\text{Fe}(\text{napy})_4(\text{CH}_3\text{CN})]^{2+}$.⁹ In variance to this behavior, the $\text{Fe}(\text{bpy})_3^{2+}$

and $\text{Fe}(\text{phen})_3^{2+}$ species are notably substitution inert species although acid-catalyzed reactions have been studied.¹⁰ The inherent difference between these two classes of ligands lies in the strained four-membered chelate ring of the naphthyridines which manifests itself in the weak ligand field tendency of the naphthyridines toward the first row transition metals^{2a,7} as well as a lability toward substitution.

The importance of π -back-bonding or synergic bonding in phen and bipy complexes has been studied extensively¹⁰ while such information for napy complexes is derived from a limited number of studies of carbonyl complexes.^{11,12} The electronic solution spectra of $\text{Fe}(\text{2,7-dmnapy})_3^{2+}$ and $\text{Fe}(\text{2-mnapy})_4^{2+}$ ^{7,8} are devoid of an absorption attributable to a metal to ligand charge transfer (MLCT) transition, the existence of which is usually taken as strong evidence for metal-ligand π involvement.^{10,13,14} Although the $\text{Fe}(\text{napy})_4^{2+}$ species exhibits a medium intensity band, there is doubt as to the correctness of its assignment as a MLCT transition.^{2a} The net import of this information is that to date no strong evidence or claim can be made for the participation of the naphthyridine ligands in π -back-bonding.

It has become increasingly evident in recent years that d^6 ruthenium(II), as a donor metal ion, exhibits an especially good propensity for π -back-bonding with unsaturated ligands.^{15,16} The $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{bipy})_3^{2+}$ species are noteworthy examples of the stabilization of low oxidation states by unsaturated ligands.^{17,18} Thus, the $\text{Ru}(\text{III})/\text{Ru}(\text{II})$ couple has served as an effective monitor of π -back-bonding involvement between metal and ligand.^{17,19} Additionally, ruthenium(II) complexes containing unsaturated ligands have received considerable interest because of their photoluminescence^{20,21} and photogalvanic effects.²²

It was the goal of the research reported herein to investigate the π -bonding capabilities of the naphthyridine ligands. To accomplish this, we have synthesized ruthenium(II) complexes containing napy, 2-mnapy, and 2,7-dmnapy, and have studied their spectral and electrochemical behavior. In addition, we anticipated that the electrochemical studies of the complexes in acetonitrile would shed further light on the lability of the ligands toward substitution.

Experimental Section

1. Preparations. (a) **General.** The ruthenium trichloride ($\text{RuCl}_3 \cdot n\text{H}_2\text{O}$; 40.00% Ru) was used as obtained from Matthey Bishop. The ammonium hexafluorophosphate (96%) was obtained from Alfa-Ventron while the "Spectro" grade acetonitrile and the tetraethylammonium chloride were from Eastman Chemicals. All other solvents were of reagent grade and used as obtained unless stated otherwise. The 2,7-dmnapy was prepared by the method of Paudler and Kress²³ while the 2-mnapy and napy were synthesized using the procedure of Hamada and Takeuchi.²⁴ Ligand purity was ascertained by C, H, and N analysis and ¹H NMR spectroscopy.

Preparation of $\text{K}_2[\text{Ru}(\text{Cl})_5\text{H}_2\text{O}]$. A modification of the procedure of Mercer and Buckley²⁵ was employed. Commercial RuCl_3 (2.00 g, 7.95 mmol) was refluxed in ~ 60 mL of concentrated HCl for 4 h. Potassium chloride (1.78 g, 24 mmol) was added to the solution producing the immediate precipitation of a black solid. The material was collected by suction filtration, redissolved in ~ 250 mL of 6 N HCl, and filtered and the filtrate was allowed to evaporate to a smaller volume. Deep red crystals were recovered which were washed with 95% ethanol and ether.

Preparation of $[(\text{CH}_3\text{CH}_2)_4\text{N}]\text{PF}_6$. Ammonium hexafluorophosphate (96%, 136 g, 0.8 mol) dissolved in ~ 300 mL of H_2O was added to an aqueous tetraethylammonium chloride (132 g, 0.8 mol) solution (250 mL) producing an immediate precipitation of a white solid. The material was recrystallized twice from ethanol-water (1:1), dried for 12 h at 100 °C, and stored in a desiccator.

(b) Ruthenium(II) Compounds. Preparation of $[\text{Ru}(\text{napy})_4](\text{PF}_6)_2$ and $[\text{Ru}(\text{napy})_4](\text{ClO}_4)$. The synthesis involved hydrogenation of ruthenium chloride in methanol to produce a "blue chlororuthenate(II) solution"^{26,27} which was added to the ligand to generate the desired te-

trakis-1,8-naphthyridineruthenium(II) ion. For a typical preparation, commercial ruthenium chloride (0.389 g, 1.54 mmol) was dissolved in 25 mL of anhydrous methanol in a Parr glass bottle and a trace of Adams' catalyst (PtO_2) added. The bottle was evacuated and then pressurized to ~ 3 atm with hydrogen. The solution was agitated for 1.5 h at which time the solution was deep blue. The pressure was released, and the bottle stoppered and introduced into an argon-purged glove box. The blue solution was filtered into a stirred and degassed solution containing 1,8-napy (1.04 g, 7.68 mmol) and glycerol (25 mL) at 50 °C. An immediate color change to dark red was observed. The heating and stirring were continued for 8 h. At this point 30 mL of H_2O was added and the solution divided into two equal parts. Saturated aqueous NH_4PF_6 was added to one portion and saturated aqueous NaClO_4 to the other with concomitant precipitation of red solids. Recrystallization for both salts was effected from boiling methanol, followed by partial evaporation to produce deep red crystals which were collected by vacuum filtration, washed with ethanol and anhydrous ether, and dried in vacuo overnight.

Preparation of $[\text{Ru}(\text{2-mnapy})_4](\text{PF}_6)_2$ and $[\text{Ru}(\text{2-mnapy})_4](\text{ClO}_4)_2$. The procedure for $[\text{Ru}(\text{napy})_4]^{2+}$ was followed with recrystallization of the ClO_4^- salt accomplished from hot methanol and the PF_6^- salt effected from an acetone-ethanol (1:1) mixture.

Preparation of $[\text{Ru}(\text{2,7-dmnapy})_3](\text{PF}_6)_2$ and $[\text{Ru}(\text{2,7-dmnapy})_3](\text{ClO}_4)_2$. The $\text{K}_2[\text{RuCl}_5\text{H}_2\text{O}]$ (0.208 g, 0.558 mmol) was suspended in ~ 30 mL of hot glycerol, stirred, and heated to 95–100 °C. The red complex slowly dissolved and formed a green solution which was added to the 2,7-dmnapy (0.353 g, 2.23 mmol) dissolved in ~ 15 mL of glycerol. Initially a reddish-brown solution formed which on heating to 70 °C for 6 h transformed to an intense orange. At this point ~ 50 mL of water was added and the resulting solution divided into two parts. To one part was added a saturated aqueous NH_4PF_6 solution causing precipitation of an orange solid. This material was collected, redissolved in ~ 30 mL of acetone, and precipitated by addition of 200 mL of anhydrous ether. The resulting golden powder was recovered by vacuum filtration and dried in vacuo for 12 h. To the second part was added a saturated aqueous NaClO_4 solution which caused the precipitation of an orange solid. This material was collected, redissolved in a 1:1 (v/v) mixture of hot absolute ethanol and acetone, filtered, and allowed to evaporate to a smaller volume. Orange crystals were collected by vacuum filtration and dried in vacuo for 12 h.

Reaction of $[\text{Ru}(\text{napy})_4](\text{PF}_6)_2$ with Acetonitrile. A quantity (0.2 g) of the tetrakis napy complex was dissolved in ~ 10 mL of acetonitrile, refluxed for 2 h, filtered, and then added to ethyl ether (150 mL) at -35 °C. An oil suspension resulted which eventually yielded a yellow solid. The material was collected by vacuum filtration, washed with ethyl ether, and dried in vacuo overnight.

2. Measurements. An Industrial Instruments Model RC-16B2 conductance bridge was used to determine the molar conductivity, Λ_m , of reagent grade acetone solutions of the new complexes at a concentration of 10^{-3} M. The experimental results were compared to the value for $[\text{Ru}(\text{bipy})_3](\text{PF}_6)_2$, a known 1:2 electrolyte, at the same approximate concentration.

The infrared (4000–600 cm^{-1}) spectra of Nujol-Fluorolube mulls of the complexes supported between sodium chloride windows were obtained with a Perkin-Elmer Model 621 double-beam grating spectrophotometer.

All visible and UV spectra were obtained from solutions using a Cary Model 14 recording spectrophotometer. The sample was dissolved in the indicated solvent and a spectrum obtained using matched quartz 1-cm cells at a scan speed of 10 Å/s. For Beer's law determinations, absorbance measurements of a successively diluted standard solution were obtained at constant wavelength. A least-square linear regression of a minimum of four data points was then utilized to calculate the reported molar absorptivity.

The ¹H NMR data were obtained using a Varian HA-100 NMR spectrometer at a frequency sweep time of 500 s at 30 ± 3 °C. Typically a sealed ampule of acetone-*d*₆ (Merck Sharp and Dohme) was opened in a dry glove box and a saturated solution of the appropriate complex was prepared. Tetramethylsilane served as the internal standard. This procedure was prompted by the observation of a spurious signal due to absorbed water between δ 3 and 4 ppm for samples prepared in air.

All electrochemical measurements were obtained using "spectrograde" acetonitrile dried over 4 Å molecular sieves with 0.1 M tetraethylammonium hexafluorophosphate (TEAH) as supporting electrolyte. A limited number of runs were made using reagent grade

Table I. Elemental Analysis and Conductivity Data for Naphthyridine Complexes of Ruthenium(II)

Complex	% C		% H		% N		Λ_m^a , cm ² mho	Concn, M $\times 10^3$
	Calcd	Found	Calcd	Found	Calcd	Found		
[Ru(2,7-dmnapy) ₃](ClO ₄) ₂	46.52	46.27	3.90	3.81	10.85	10.85		
[Ru(2,7-dmnapy) ₃](PF ₆) ₂	41.62	41.56	3.49	3.46	9.71	9.75	252	0.99
[Ru(napy) ₄](ClO ₄) ₂	46.83	46.69	2.94	2.74	13.65	13.48		
[Ru(napy) ₄](PF ₆) ₂	42.16	42.17	2.65	2.51	12.29	12.37	233	1.02
[Ru(2-mnapy) ₄](ClO ₄) ₂	49.32	49.08	3.68	3.50	12.78	12.73		
[Ru(2-mnapy) ₄](PF ₆) ₂	44.68	44.80	3.33	3.25	11.58	11.57	238	1.01

^a Molar conductivity obtained at $25 \pm 2^\circ\text{C}$ in acetone. [Ru(bipy)₃](PF₆)₂ was used as the standard for a 1:2 electrolyte, 233 cm² mho at a concentration of 1.02×10^{-3} M.

acetone (dried over 4 Å molecular sieves) with 0.1 M TEAH. The values reported are vs. the saturated sodium chloride calomel electrode (SSCE) at $25 \pm 2^\circ\text{C}$. A three electrode system (working electrode, auxiliary platinum wire counter electrode, and the SSCE connected by means of a luggin capillary) was used in conjunction with a Princeton Applied Research Model 174A polarographic analyzer, a Model 174/50 AC polarographic interface accessory, and a Model 122 lock-in amplifier. The working surface was a glassy carbon electrode (Princeton Applied Research) pretreated by rinsing with acetone and drying with a tissue before each run. Before the start of an experiment, the solution was degassed with N₂ and the internal resistance compensation circuit of the Model 174/50 interface was adjusted to a point just below oscillation using an oscilloscope. The mode of operation was either cyclic voltammetry, differential pulse polarography (modulation of 50 mV) or alternating current polarography (70 Hz) depending on the experiment performed.

Microanalyses for carbon, hydrogen, and nitrogen were performed by the Analytical Services Laboratory of Ohio University.

Results and Discussion

1. Preparations. The synthesis of Ru(2,7-dmnapy)₃²⁺ utilized glycerol as the medium for the reduction of [Ru(Cl)₅(H₂O)]²⁺ to Ru(II),^{28,29} while the preparation of the remaining naphthyridine complexes, Ru(napy)₄²⁺ and Ru(2-mnapy)₄²⁺, employed the useful blue ruthenium(II) species generated by the hydrogenation of commercial ruthenium chloride.^{26,27} This choice of procedures was based on the more robust behavior of the 2,7-dmnapy base in synthesis. The elemental analyses and conductivity data in Table I are consistent with a 1:2 formulation for all the complexes, [RuL_{3 or 4}]²⁺: 2PF₆⁻, while the infrared spectra of the complexes did not show the presence of water of crystallization. It is interesting to note that the ligand to ruthenium stoichiometry of 3:1 for 2,7-dmnapy and 4:1 for napy and 2-mnapy mirrors the behavior of ruthenium's congener, iron(II), with these ligands.

The following analyses were obtained with four separate reactions of acetonitrile with [Ru(napy)₄](PF₆)₂:

% C	1	2	3	4
% H	30.9	31.1	30.5	30.3
% N	2.5	2.2	2.3	2.5
	12.6	12.2	12.9	13.2

These values compare to the calculated percent carbon and nitrogen values for [Ru(napy)₄](PF₆)₂, [Ru(napy)₂(CH₃CN)₂](PF₆)₂, and [Ru(napy)(CH₃CN)₄](PF₆)₂, respectively, of 42.2, 12.3; 32.2, 11.5; and 28.0, 12.3. The analytical results indicate that the solid isolated from acetonitrile analyzed significantly lower in carbon than the tetrakis napy complex and that the loss of coordinated naphthyridine occurs. Most likely, the yellow salt is a mixture of the bis and tetrakis acetonitrile complexes suggested above and as established by polarographic techniques (vide infra). When an argon atmosphere was employed and reflux time was 24 h, neither air oxidation nor time of reflux appeared to be factors in the reaction as evidenced by analyses comparable to the above values.

2. Ultraviolet-Visible Spectra. Table II presents the visible

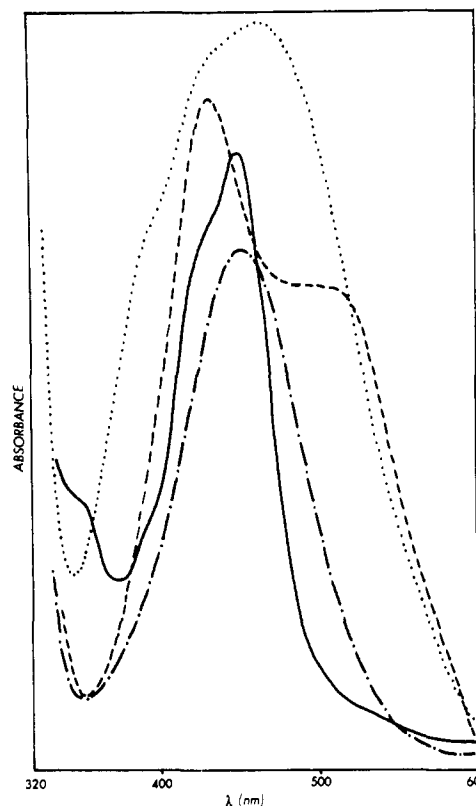


Figure 1. Visible spectra of selected complexes of ruthenium(II) in methanol: [Ru(2-mnapy)₄]²⁺ (···); [Ru(napy)₄]²⁺ (---); [Ru(2,7-dmnapy)₃]²⁺ (-·-·); [Ru(bipy)₃]²⁺ (—).

and UV maxima for the naphthyridine complexes of ruthenium(II), Ru(bipy)₃²⁺, and the ligands. The visible bands are asymmetric (Figure 1) exhibiting high molar absorptivities, and, for the Ru(napy)₄²⁺ and Ru(2-mnapy)₄²⁺ complexes, are unusually broad. These bands are not a sum of the individual ligand and metal ion absorptions and are too intense to be d-d transitions; therefore, they are assigned as MLCT transitions.

The electronic spectra^{10,11} of phen and bipy metal complexes, particularly Ru(bipy)₃²⁺, have attracted the attention of many and continue to be the subject of current research. The broadness and shape (appearance of distinct shoulders) of the visible band of Ru(bipy)₃²⁺, D₃, have been ascribed to be the result of both vibrational effects and nonadherence to octahedral symmetry.³⁰ As a result of the interaction between the metal d orbitals and the π and π* orbitals of bipyridine the number of excited states for the complex is increased.¹³ The observed visible maximum of Ru(bipy)₃²⁺ may then be regarded as a composite of several MLCT transitions of similar energy influenced by the vibrational modes of the complex.

The spectrum of the tris 2,7-dmnapy complex parallels that

Table II. Visible and Ultraviolet Spectral Data for the Naphthyridines and Complexes of Ruthenium(II)

Compd	Solvent	λ_{\max} , nm	$\bar{\nu}$, μm^{-1}	ϵ , $\text{M}^{-1} \text{cm}^{-1}$	Half-band width, cm^{-1} ^a
[Ru(2,7-dmnapy) ₃](PF ₆) ₂	Acetonitrile	455	2.20	8.67×10^3	4400
		286	3.50	5.00×10^4	
[Ru(napy) ₄](ClO ₄) ₂	Methanol	500 (sh)	2.00	7.30×10^3	7330
		434	2.30	9.56×10^3	
		304 (sh)	3.29	1.19×10^4	
		273	3.66	3.34×10^4	
[Ru(2-mnapy) ₄](PF ₆) ₂	Methanol	465	2.15	8.61×10^3	7490
		277	3.61	4.11×10^4	
[Ru(bipy) ₃](ClO ₄) ₂ ^b	Methanol	453	2.21	1.37×10^4	
		286	3.50	7.90×10^4	
		244	4.09	2.56×10^4	
[Ru(bipy) ₃](PF ₆) ₂	Acetonitrile	450	2.22	1.40×10^4	3500
		284	3.52	8.00×10^4	
		253 (sh)	3.95		
		243	4.12	2.50×10^4	
2,7-dmnapy	Methanol	315	3.18	9.18×10^3	
		308	3.25	8.60×10^3	
		303	3.31	8.25×10^3	
		248	4.03	5.30×10^3	
2-mnapy ^c	Methanol	312	3.21	6.01×10^3	
		303	3.30	5.94×10^3	
		298	3.35	5.58×10^3	
		253	3.95		
napy	Methanol	306	3.27	5.17×10^3	
		301	3.32	5.30×10^3	
		294	3.40	4.76×10^3	
		255	3.92	4.27×10^3	

^a Represents the width of the actual maximum envelope, without Gaussian resolution into separate bands. ^b Data from ref 30. ^c Data from ref 38.

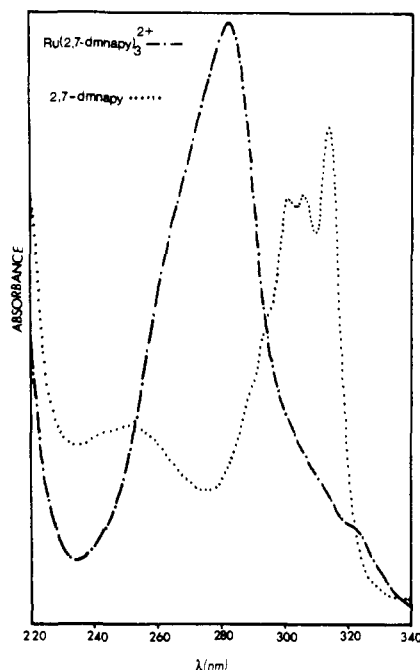


Figure 2. Ultraviolet spectra of [Ru(2,7-dmnapy)₃]²⁺ and free 2,7-dmnapy in acetonitrile.

of Ru(bipy)₃²⁺ rather closely in terms of band shape, width, and energy, presumably the result of interactions between Ru(II) and 2,7-dmnapy which are similar in nature to those found in Ru(bipy)₃²⁺. The Ru(napy)₄²⁺ species by analogy to Fe(napy)₄²⁺ is postulated to be eight coordinate with a dodecahedron environment, *D*_{2d}, surrounding the Ru(II) center. This assumption is reasonable based on the fact that the radius of Ru(II) is greater than Fe(II) and thus the metal should be able to accommodate four bidentate ligands with

ease. Also, 4d orbitals are spatially larger than 3d orbitals, facilitating better overlap of the nitrogen donor pairs when the central metal is Ru instead of Fe. The dodecahedral geometry^{31,32} results in a splitting of the d orbitals significantly different from that caused by the *D*₃ environment of Ru(bipy)₃²⁺.²⁰ As a result, eight coordination may give rise to several d → π* transitions of similar energy, perhaps, accounting for the distinctive shoulder and shape of the visible maximum of Ru(napy)₄²⁺. Additional support for eight coordination for Ru(napy)₄²⁺ comes from low-frequency infrared data³³ which show Ru(napy)₄²⁺ to be similar to Fe(napy)₄²⁺ and not six coordinate as Ru(bipy)₃²⁺.

The exceptionally broad maximum of Ru(mnapy)₄²⁺ probably represents a manifold of many possible d-π* transitions arising from an unsymmetrical coordination environment surrounding the ruthenium(II). The Mössbauer data for Fe(2-mnapy)₄²⁺¹⁰ show behavior intermediate to that of the eight-coordinate Fe(napy)₄²⁺ complex and the six-coordinate Fe(2,7-dmnapy)₃²⁺ species. This result, along with tentative infrared spectral interpretations, led Good et al.¹⁰ to favor a six-coordinate geometry consisting of two bidentate and two monodentate ligands, though an eight-coordinate species was also conceded to account for the results. This reasoning may be applied to Ru(2-mnapy)₄²⁺, but at the same time noting that ¹H NMR results (vide infra) may suggest the complex to be seven coordinate.

Figure 2 as well as the data in Table II manifest the substantial blue shift of the naphthyridines' intraligand transitions upon coordination to ruthenium(II). The result is opposite to that observed with phen and bipy where a red shift on coordination has been ascribed to a perturbation of the heterocycles' energy levels due to the presence of the positive metal center.^{34,35} The red shift observed for the ruthenium(II) complexes of phen and bipy is much smaller than that observed with first row divalent transition metals. This smaller red shift has been ascribed to enhanced metal-ligand π bonding which increases the energy separation between occupied and unoccupied π

Table III. Proton Magnetic Resonance Data for Naphthyridines and Their Ruthenium(II) Complexes

Compd	Chemical shift at position δ , ppm ^a					
	CH ₃ -2,7	H-3,6	H-4,5			
2,7-dmnapy	2.70	7.38	8.17			
Ru(2,7-dmnapy) ₃ ²⁺	2.29	7.70	8.62			
napy	9.10	H-2,7	H-3,6	H-4,5		
Ru(napy) ₄ ²⁺	9.83	7.57	7.66	8.38		
				8.45		
2-mnapy	CH ₃ -2	H-3	H-4	H-5	H-6	H-7
Ru(2-mnapy) ₄ ²⁺	2.72	7.44	8.24	8.32	7.52	9.04
	2.72 (1) ^b	7.54	8.42	8.54	7.80	9.71
	2.47 (3) ^b					

^a In deuterated acetone at 30 °C with TMS as internal standard. ^b Number indicates relative ratio of the area of the signals.

orbitals.¹³ Previous work with the first row transition metal complexes of napy and 2,7-dmnapy has not revealed significant shifts in the intraligand band region upon coordination.^{2a,7} The ultraviolet spectrum of napy in methanol is characterized by an envelope near 300 nm and a broad band centered at 257 nm. Mason³⁶ has investigated the cyclohexane solution spectrum of napy and has assigned two bands, 308 and 256 nm, as π - π^* transitions. By inference, the UV maxima of the substituted naphthyridines would also likely arise from transition of a $\pi \rightarrow \pi^*$ nature.

Taube et al.³⁷ observed that the absorption band for pyridine bound to ruthenium(II) in the $[(\text{NH}_3)_5\text{Ru}(\text{py})]^{2+}$ complex was shifted to higher energy when compared to the free and protonated ligand. Following evaluation of this result by use of a simplified molecular-orbital description, it was concluded that the hypsochromic shift resulted from an increase in the relative energy of a π^* level as a consequence of interaction with a metal d_{yz} orbital. Mason¹³ has also shown that metal-ligand π bonding increases the energy separation between the π and π^* orbitals of the ligand. Thus, the conclusion that the blue shift observed in the $\pi \rightarrow \pi^*$ band for the naphthyridines results from back-bonding which has significantly altered the separation of the π and π^* levels is not unwarranted.

3. ¹H NMR Spectra. The ¹H NMR data for the naphthyridine complexes of ruthenium(II) are presented in Table III. The spectrum of the tris(2,7-dimethyl-1,8-naphthyridine)-ruthenium(II) ion is characterized by deshielding relative to the free ligand of protons H-3,6 and H-4,5 while the protons on the 2,7-methyl positions are significantly shielded. Previous ¹H NMR work with naphthyridine complexes^{7,39,40} has shown that deshielding resulted for all ligand protons when compared to the free ligand. This change in the proton environment upon coordination results from a decrease in electron intensity induced by the positive metal center.^{41,42}

The ¹H NMR investigations of Ru(phen)₃²⁺ and Ru(bipy)₃²⁺ have indicated that the coordinated ligands' 2,9 and 6,6' protons were shielded when compared to the free ligand.^{10,43} These observations were attributed to the anisotropic influence of an aromatic ring of an adjacent ligand.⁴²⁻⁴⁶

A space-filling model of Ru(2,7-dmnapy)₃²⁺ shows that the protons of the 2,7-methyl group are in the shielding cone of an adjacent aromatic ring. It is concluded, therefore, that the proton shielding manifested in this 2,7-dmnapy complex closely parallels the behavior observed with the six-coordinate heterocyclic amine complexes of ruthenium(II) mentioned above. This magnitude of the deshielding of the 3,6 and 4,5 protons (0.32 and 0.45 ppm) is less than that observed for Cd(2,7-dmnapy)₃²⁺ (0.40 and 0.58 ppm)⁷ and may reflect the complement of back-donation present in the Ru(II) complex,⁴⁵ though insufficient reference data are available to substantiate this trend.

The tetrakis 2-mnapy compound exhibits a more complex spectrum as a result of the unsymmetrical ligand.²³ A striking

double resonance is observed for the 2-methyl protons with the ratio of areas being 1 (δ 2.72):3 (δ 2.47). This finding may indicate that the 2-mnapy complex is seven coordinate with one molecule functioning as a monodentate ligand as a result of the steric constraints of fitting four 2-mnapy molecules around a Ru(II) center.

The tetrakis napy complex displays uncomplicated resonances with the single feature being a substantial deshielding and broadening of the H-2,7 protons (0.73 ppm) upon coordination. It is evident from the spectral data (Table III) that the environment for equivalent protons on all four ligands remains the same.⁴⁷

4. Electrochemical Data. The reduction potentials, Ru(III)/Ru(II), of ruthenium complexes are known to be dependent^{17,19} upon the presence of back-bonding ligands in the coordination sphere, the potential increasing as the number of back-bonding ligands is increased.⁴⁸ Qualitatively, this change in potential can be attributed to a stabilization of the ruthenium(II) t_{2g} level by increased back-bonding whereas π bonding between ruthenium(III) and pyridine-type ligands is thought to be insignificant.¹⁹ Ultimately, the process of oxidation of Ru(bipy)₃²⁺ involves removal of an electron from the t_{2g} metal orbitals; hence the electrode potential provides evidence for the energy of the t_{2g} levels. As the ligand environment surrounding Ru(II) is varied the potential of the couple changes, thus yielding information about the relative π interaction between the metal and ligand.

Cyclic voltammetry, ac polarography, and differential pulse polarography techniques were utilized to determine the half-wave potentials for the naphthyridine complexes of ruthenium(II). The diagnostic criteria usually employed to establish reversibility in cyclic voltammetry are that the separation of the anodic and cathodic peaks, ΔE ($E_p^a - E_p^c$), is equal to or less than 60 mV for a one-electron process⁴⁹ and that the ratio of anodic to cathodic current, i_p^a/i_p^c , is unity.⁵⁰ The [Ru(bipy)₃]^{3+/2+} couple is reversible⁵¹ and using the apparatus described in the Experimental Section gave a peak potential separation of 70 mV. Therefore, this value was used as our criterion of reversibility for measurements made under similar conditions.⁵² The peak position, height, and shape of ac polarograms are sensitive to the reversibility of the couple with the primary reversibility test being a frequency independent half-peak width of 90 mV for a one-electron transfer.⁵⁰

The voltammetric data scanned from +2.0 to -2.3 V for [Ru(2,7-dmnapy)₃](ClO₄)₂ are compiled in Table IV. The oxidation of Ru(II) \rightarrow Ru(III) occurs at 1.37 V vs. SSCE and is judged reversible by both cyclic voltammetric and ac polarographic criteria (Figure 3). This half-wave potential is more anodic than Ru(bipy)₃²⁺, 1.29 V, or Ru(phen)₃²⁺, 1.30 V, under the same conditions which strongly indicates that 2,7-dmnapy is participating in significant π back-bonding with ruthenium(II). No oxidation wave could be observed for the free ligand when scanned to potentials as positive as 2.2 V vs.

Table IV. Cyclic Voltammetric Data for $[\text{Ru}(2,7\text{-dmnapy})_3](\text{ClO}_4)_2$ in 0.1 M TEAH-Acetonitrile at a Glassy Carbon Electrode vs. SSCE

Wave	Assignment	$E_{1/2}$	E_p	ΔE_p , mV	i_p^a/i_p^c	Scan rate, mV/s
Oxidation	$\text{RuL}_3^{3+} \rightarrow \text{RuL}_3^{3+}$	1.37 ^a		70	0.95	200
Reduction						
I	$\text{RuL}_3^{2+} \rightarrow \text{RuL}_3^{1+}$		-1.24 ^b			500
II	$\text{RuL}_3^{1+} \rightarrow \text{RuL}_3^0$		-1.42 ^b			500
III	$\text{RuL}_3^0 \rightarrow \text{RuL}_3^{1-}$		-1.56 ^b			500
IV	2,7-dmnapy		-1.90 ^c			500
			-1.20 ^d			

^a The ac polarographic maximum coincides with 1.37 V and showed a peak half-width of 95 mV when ω was varied from 50 to 250 Hz at a scan rate of 2 mV/s. ^b Irreversible cathodic peak potential. ^c Broad distorted cathodic peak. The free ligand showed an irreversible E_p at -2.18 V while differential pulse measurements yielded a maximum at -1.95 V at a modulation of 50 mV and scan rate of 2 mV/s. ^d Desorption spike on reversal.

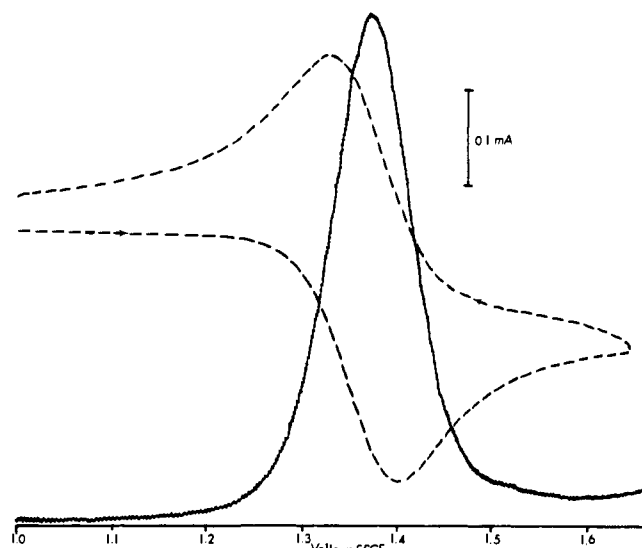


Figure 3. Cyclic voltammogram and ac polarogram of $[\text{Ru}(2,7\text{-dmnapy})_3]^{2+}$ in 0.1 M TEAH acetonitrile. The cyclic voltammogram has a $\Delta E_p = 70$ mV and the ac polarogram has a half-peak width of 95 mV.

SSCE. The $\text{Ru}(2,7\text{-dmnapy})_3^{2+}$ ion is exceedingly stable in acetonitrile as evidenced by the single ac polarographic maximum, 1.37 V, obtained on a solution that had been stored in the laboratory for 2 months.

An electrochemical investigation⁵³ of $\text{Ru}(\text{bipy})_3^{2+}$ has revealed three reversible cathodic waves thus demonstrating the existence of the species RuL_3^{+1} , RuL_3 , and RuL_3^{-1} with "effective" ruthenium oxidation states of +1, 0, and -1. A fourth observed wave was suggested to result from the reduction of bipyridine. The cathodic scan for $\text{Ru}(2,7\text{-dmnapy})_3^{2+}$ indicates four reduction peaks (Figure 4 and Table IV) with the probable assignments indicated. It should be noted that the tris 2,7-dmnapy complex shows complications in its behavior which are similar to those observed for the reduction of $\text{Ru}(\text{phen})_3^{2+}$.⁵³ The voltammograms are not reversible as evidenced by the inequality of the heights, the lack of well-formed anodic waves, and the appearance of a desorption spike on reversal. This suggests that the reduced 2,7-dmnapy complexes are unstable and undergo decomposition to yield uncoordinated ligand. The fourth peak is broad and occurs at 1.95 V, a potential where free ligand is irreversibly reduced.

5. Acetonitrile Solvolysis. Upon dissolution of $[\text{Ru}(\text{napy})_4](\text{PF}_6)_2$ and $[\text{Ru}(2\text{-mnapy})_4](\text{PF}_6)_2$ in acetonitrile for spectral and for polarographic measurements, it was noticed that the initially red solution faded with time to orange and finally to yellow. The differential pulse polarographic results for $\text{Ru}(\text{napy})_4^{2+}$ and $\text{Ru}(2\text{-mnapy})_4^{2+}$ (Table V) confirm the

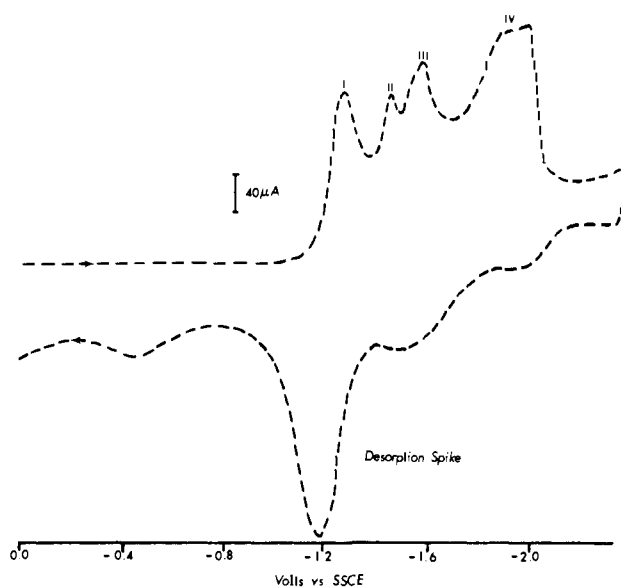


Figure 4. Cyclic voltammogram from 0.0 to -2.2 V for $[\text{Ru}(2,7\text{-dmnapy})_3]^{2+}$ in 0.1 M TEAH acetonitrile. I = $\text{RuL}_3^{2+} \rightarrow \text{RuL}_3^{1+}$; II = $\text{RuL}_3^{1+} \rightarrow \text{RuL}_3^0$; III = $\text{RuL}_3^0 \rightarrow \text{RuL}_3^{1-}$; IV = 2,7-dmnapy.

presence of several oxidizable species whose relative concentration changed with time.

These voltammetric changes are believed to be indicative of acetonitrile substitution of coordinated naphthyridine. The initial peaks at 1.05 and 1.08 V which eventually disappear are assigned as the half-wave potentials for the $\text{Ru}(\text{napy})_4^{2+}$ and $\text{Ru}(2\text{-mnapy})_4^{2+}$ species, respectively. The remaining peaks most probably correspond to solvation products containing coordinated acetonitrile and naphthyridine. This tentative assignment is supported by the known stabilizing effect (increase in $E_{1/2}$ values) when successive replacement of bipy by acetonitrile occurs in the coordination sphere of $\text{Ru}(\text{II})$ complexes.⁵⁴

The UV-visible spectrum of the refluxed acetonitrile solutions of the tetrakis napy complex also suggest replacement of coordinated napy by the solvent. The UV region shows free ligand maxima which are significantly displaced from the absorption band ascribed to coordinated napy in the tetrakis ruthenium(II) complex. A shift of the visible λ_{max} from 434 nm to 365 nm is further indication of acetonitrile solvolysis. A similar effect is also observed in the series, $\text{Ru}(\text{bipy})_3^{2+}$, 450 nm, $\text{Ru}(\text{bipy})_2(\text{py})(\text{CH}_3\text{CN})^{2+}$, 437 nm, $\text{Ru}(\text{bipy})_2(\text{CH}_3\text{CH})_2^{2+}$, 425 nm, where progressive replacement by acetonitrile shifts the charge transfer band to higher energy.⁵⁴

Some comments on the yellow salt recovered from an ace-

Table V. Voltammetric Data for [Ru(napy)₄](PF₆)₂ and [Ru(2-mnapy)₄](PF₆)₂ in 0.1 M TEAH-Acetonitrile at a Glassy Carbon Electrode vs. SSCE

	$E_{1/2}^a$	Assignment
[Ru(napy) ₄](PF ₆) ₂	1.05 ^b	[Ru(napy) ₄] ²⁺
	1.27 ^c	Solvolysis product
	1.47 ^d	Solvolysis product
	1.68 ^d	Solvolysis product
[Ru(2-mnapy) ₄](PF ₆) ₂	1.08 ^b	[Ru(2-mnapy) ₄] ²⁺
	1.26 ^c	Solvolysis product
	1.47 ^d	Solvolysis product

^a Differential pulse measurements at modulation of 50 mV. ^b Initial peak which disappears with time. ^c Peak which increases then decreases with time. ^d Peak increases with time.

tonitrile solution of Ru(napy)₄²⁺ seem in order. The analyses of this salt (preparations) suggested it to be a mixture, a result later confirmed by differential pulse measurements which showed two peaks at 1.47 and 1.68 V. That the recovered complexes contain coordinated acetonitrile is shown by the ¹H NMR spectrum of the yellow solid in acetone-*d*₆. Signals were observed at δ 2.47 and 2.73 which are similar to the prior observation for coordinated acetonitrile in phen and bipy mixed ligand Ru(II) complexes.⁵⁵ The tetrakis napy complex does not absorb in this region, and therefore the signals at δ 2.47 and 2.73 are representative of the presence of coordinated acetonitrile in the recovered yellow solid. The yellow complex also absorbed weakly in the infrared region at 2292 cm⁻¹ as compared to the ν(C≡N) observed for acetonitrile at 2266 cm⁻¹.⁵⁶ The observation of an increase in the C≡N frequency is well documented and is indicative of coordinated acetonitrile.⁵⁶⁻⁵⁸

Summary and Conclusions

The existence of metal to ligand charge transfer bands for the naphthyridine complexes of ruthenium(II), Ru(napy)₄²⁺, Ru(2-mnapy)₄²⁺, and Ru(2,7-dmnapy)₃²⁺ suggests that the ground-state configuration has significant charge transfer character and, therefore, metal to ligand π bonding contributes to the stability of the complex. Also demonstrating the ability of the naphthyridines to participate in π back-bonding are the considerably anodic potentials of the complexes. Ruthenium(II) in the tris 2,7-dmnapy complex is stabilized appreciably by π back-bonding as evidenced by the potential of 1.37 V, while in contrast the napy and 2-mnapy tetrakis compounds display less anodic potentials of 1.05 and 1.08 V. This difference in potential of ~0.30 V may arise from the steric considerations of placing four ligands about the ruthenium(II) center with less effect of π overlap and inherently weaker σ donor and π acceptance behavior of the napy and 2-mnapy ligands. That the intraligand transitions of the coordinated naphthyridines shift to higher energy is also a noteworthy observation supporting ligand π involvement with the metal. This interaction results in an increased separation of the π and π* levels on the ligand. Interestingly, the ¹H NMR spectrum of Ru(2,7-dmnapy)₃²⁺ shows an upfield shift for the methyl protons indicative of the anisotropic diamagnetic shielding by adjacent ligands.

The Ru(napy)₄²⁺ and Ru(2-mnapy)₄²⁺ complexes upon dissolution in acetonitrile undergo solvolysis with corresponding color changes from red to yellow indicative of a shift in the MLCT band. The replacement of naphthyridine by acetonitrile apparently stabilizes the t_{2g} level of Ru(II) thereby causing the energy of the dRu(II) → π*(napy) transition to move to higher energy. Additionally, the UV region of acetonitrile solutions of Ru(napy)₄²⁺ and Ru(2-mnapy)₄²⁺ contains absorptions for free ligand. The voltammetric changes observed for solutions of the complexes are indicative of the presence

of at least two acetonitrile solvation products for each. The ¹H NMR and infrared data obtained for the yellow salt also corroborate that acetonitrile solvolysis occurs. The tetrakis napy and 2-mnapy complexes are labile to substitution as a consequence of the strain present in the four-membered chelate ring while the inertness of Ru(2,7-dmnapy)₃²⁺ results from the steric protection provided by the two methyl groups on 2,7-dmnapy.

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Structure and Stereodynamic Behavior of (1,2-Diazine)decacarbonyl Triangulotruthenium. Evidence for Hidden Processes in Fluxional Molecules

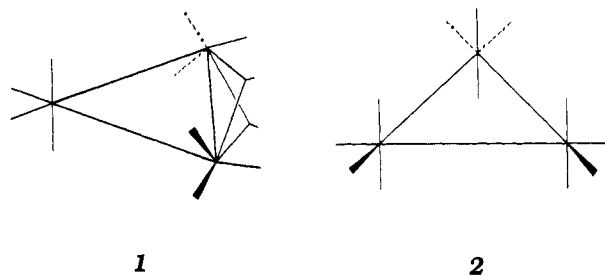
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Abstract: A derivative of $\text{Ru}_3(\text{CO})_{12}$, in which two cis axial CO ligands are replaced by the bidentate ligand 1,2-diazene (pyridazine), has been prepared and characterized structurally and stereodynamically by x-ray crystallography and ^{13}C NMR. The arrangement of the equatorial (in-plane) CO groups is changed from all terminal as in $\text{Ru}_3(\text{CO})_{12}$ and now consists of three terminal ones and three slightly unsymmetrical bridging ones. Crystal data: space group, $P\bar{1}$; $a = 9.272(2) \text{ \AA}$, $b = 13.727(2) \text{ \AA}$, $c = 8.973(1) \text{ \AA}$, $\alpha = 103.44(1)^\circ$, $\beta = 120.53(1)^\circ$, $\gamma = 90.01(1)^\circ$, $V = 947.1(3) \text{ \AA}^3$, $Z = 2$. Using 2304 data with $I > \sigma(I)$, anisotropic refinement converged with $R_1 = 0.024$ and $R_2 = 0.039$. A ^{13}C NMR study over the temperature range -156 to 75°C reveals three distinct phases of fluxionality the cumulative effect of which is to transform the seven-line slow exchange spectrum (-156°C) that is consistent with the crystal structure into a spectrum (75°C) consisting of only one sharp line. Phase one, which alters the spectrum between -156 and about -90°C , consists in the equivalencing of the six equatorial CO groups. Phase two, whose effects are observed mainly from about -115 to -80°C , involves a process that is difficult to define with certainty, but appears to introduce one axial CO group into the averaging process seen in phase one. Phase three, whose effects become evident above about -30°C , results in collapse and merging of the three separate lines of relative intensities 7:2:1 into a single line. Dynamic processes capable of accounting for these spectral changes are suggested and discussed.

The stereodynamic behavior of $\text{M}_3(\text{CO})_{12}$ molecules ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) and their multitudinous derivatives, many of which are of special interest with regard to catalysis,¹ is one of the focal points in current research on fluxionality in polynuclear organometallic and metal carbonyl type molecules. Despite a number of significant discoveries, our factual knowledge of the stereodynamic capabilities of these systems remains very fragmentary, and our comprehension of the structural and mechanistic principles underlying the observations is correspondingly incomplete. We report and analyze here an investigation designed to penetrate the superficial simplicity of the situation regarding the parent carbonyls themselves by using a judiciously designed substitution product. This work provides the first direct observation of limited and "unperceived" (in the sense that we have previously² defined that term) scrambling processes for some of the CO groups. The certain knowledge that one of these processes takes place has an important bearing on how one evaluates the recent proposal of Johnson³ for "truly concerted" scrambling in $\text{Fe}_3(\text{CO})_{12}$ and related species, an issue we shall return to later in this paper.

The crystal structures of the three parent $\text{M}_3(\text{CO})_{12}$ molecules are known. $\text{Fe}_3(\text{CO})_{12}$ has the least symmetrical structure, **1**, in the crystal,⁴ while $\text{Ru}_3(\text{CO})_{12}$ ⁵ and $\text{Os}_3(\text{CO})_{12}$ ⁶ have the D_{3h} structure **2** in which there are no bridging CO groups. It has been shown that for $\text{Fe}_3(\text{CO})_{12}$ the replacement of some CO groups by phosphorus or sulfur ligands causes the degree of asymmetry in the bridging system to vary greatly, from one case in which the bridges are essentially symmetrical to another in which they are only incipient.⁷ This observation, coupled with the fact that $\text{Fe}_3(\text{CO})_{12}$ undergoes rapid carbonyl



scrambling (even at -150°C ⁸), led us to propose, first in 1974^{4b} and later in more detail,⁸ the mechanism shown in Scheme I for total scrambling of CO groups in $\text{Fe}_3(\text{CO})_{12}$. It was also suggested^{4a,7,8} that the entire potential energy hypersurface traversed by the entire set of configurations of the types shown in Scheme I as they interconvert is so flat that a continuous range of intermediate dispositions of CO groups is present in solution. In this way the very unusual and previously unexplained infrared spectrum of $\text{Fe}_3(\text{CO})_{12}$ became understandable for the first time.⁸

It was, of course, perfectly obvious that Scheme I could equally well afford an explanation for CO scrambling, should it be observed, in $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$. However, it was not until later that ^{13}C NMR spectra were published for these molecules.⁹⁻¹² It should be noted that for $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ infrared spectra show, straightforwardly, that the structures in solution are the same as those in the crystalline compounds. After one report that $\text{Ru}_3(\text{CO})_{12}$ at room temperature has two resonances,⁹ followed by another¹⁰ that even at -50°C there is only one, a third report¹¹ showed that even