

the averaging was mainly in the equatorial plane. These dynamical effects manifested by changes in the M-L distances and the L-M-L angles result in deviation from the idealized 120° TBP geometry. As a consequence, (1) g_1 and g_2 and (2) A_1 and A_2 are averaged into an effective g_{\perp} and A_{\perp} (see Figure 4 in ref 14). In other words, temperature-dependent metal-ligand vibrations are operative and they (1) average the g_1 and g_2 values due to a modulation of the α angular parameter and/or (2) produce a jumping of the effective C_{2v} axis between the three equatorial positions. This results in the observed axial spectrum. This vibrational averaging of the C_{2v} model accounts for the lack of a strong temperature dependence of g_{\perp} and A_{\perp} because they average two lines which depend on T but (to a first approximation) this average is independent of T . In addition, the vibronic effects would be expected to produce a smearing of A_{\parallel} and a value of g_{\parallel} that increases with increasing temperature (vibronic activity). This has been observed here and was first measured by Barbucci et al.¹⁹ in a single-crystal study of a TBP complex. Moreover, this proposal of dynamical averaging is consistent with earlier experimental observations.^{12,13}

Conclusion

The results of our experiments and computer simulations suggest that a vibrational effect may be producing the apparent axial appearance of the EPR spectra in five-coordinate complexes of Cu(II) containing tetradentate tripod ligands.⁸⁻¹² This result is a natural extension of our chemical intuitive feeling that the Cu(II) ion prefers a metal $x^2 - y^2$ ground state,^{10,23} which is also supported by structural data on Cu(II) complexes containing systematically varied tripod ligands.¹⁰ Thus, as in the usual Jahn-Teller effect, it appears that appropriate vibrational modes may be admitted allowing deviation from the z^2 ground state that has been forced upon Cu(II) by a constraining tripod ligand. Finally, it may be noted that both intra- and intermolecular effects may be present and play a role in the dynamical processes.^{18,24,25}

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(24) For several discussions of related problems, see: *Faraday Discuss. Chem. Soc.* **1980**, No. 69.

(25) Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, 1970; pp 465-466.

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Mixed-Ligand Iron(II) Complexes Containing 2,2'-Bipyrimidine. Spectroscopic, Electrochemical, and Coulombic Modification of Highly Absorbing Metal Complexes by Ligand Substitution

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There have been several recent articles concerning the synthesis and characterization of M(bpym)_{3-n}L_{2n} (where M = Cr,¹ Co,² Mo,³ W,¹ Ru,⁴⁻⁸ Fe⁹⁻¹¹ or Ni¹² and bpym =

2,2'-bipyrimidine) systems and their possible use as precursor complexes for the formation of polymetallic systems. The 2,2'-bipyrimidine ligand serves as an effective bidentate ligand in either mono- or polymetallic systems, and results from previous studies indicate that this bidentate ligand is more effective at electronically communicating two metal centers than most of the monodentate bridges.¹³⁻¹⁶

We report here the synthesis, electronic absorption spectroscopy, magnetic susceptibility, and electrochemistry of a series of Fe(bpym)_{3-n}(CN)_{2n}⁽²⁻²ⁿ⁾⁺ complexes that, in addition to serving as possible backbones for polymetallic complexes, might also serve as effective visible-light-absorbing, energy-transfer antenna fragments in intramolecular sensitization processes.⁶

Experimental Section

Procedures for the preparation of mixed-ligand complexes of Fe(II) with CN⁻ and 2,2'-bipyridine have been previously described.¹⁷⁻¹⁹ The preparation of mixed-ligand complexes of Fe(II) with CN⁻ and 2,2'-bipyrimidine was achieved by modification of those procedures. Complete procedural details are described here for the preparation of the newly characterized mixed-ligand complexes of Fe(II), as well as for the tris(2,2'-bipyrimidine)iron(II) complex.

Materials. Analytical reagent grade compounds were used for all preparations described in this work. Water, which was used as the solvent for synthesis and electrochemistry, was redistilled from alkaline permanganate in an all-glass apparatus. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA, with satisfactory results obtained for all complexes. The bpym was purchased from Alfa Inorganics and had a proton-decoupled, ¹³C NMR spectrum in D₂O corresponding to C_α and C_γ (159.0 ppm) and C_β (123.4 ppm) vs. Me₄Si.

Instrumentation. Cyclic voltammograms were recorded on an IBM Instruments Inc. Model EC/225 voltammetric analyzer using a glassy-carbon working electrode (IBM). Voltammograms in non-aqueous solution were recorded in DMF (Fisher Scientific Co.) with 0.1 M TEAP (Fisher Scientific Co.) as a supporting electrolyte. Voltammograms in water were recorded in pH 7.00 buffer solution (Fisher Scientific Co.) for comparison with the pH-dependent hexacyanoferrate(III/II) reduction potential. The supporting electrolyte was 0.1 M KCl for aqueous voltammograms, and they were recorded at 10-100 mV/s vs. SCE.

Magnetic susceptibility measurements were made on solid samples with use of the Faraday method. A Cahn Model RG automatic electrobalance and Alfa Scientific 7500 M electromagnet were used. HgCo(SCN)₄ was used as a calibrant.²⁰ Diamagnetic corrections for molar susceptibilities were made with use of Pascal's constants.²¹

(1) Moore, K. J.; Petersen, J. D. *Polyhedron* **1983**, 2, 279.

(2) Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta*, in press.

(3) Overton, C.; Connor, J. A. *Polyhedron* **1982**, 1, 53.

(4) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, 17, 2660.

(5) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, 99, 7370.

(6) Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982**, 21, 3706.

(7) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Inorg. Chem.* **1982**, 21, 2589.

(8) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, 22, 1614.

(9) Bly, D. D.; Mellon, M. G. *Anal. Chem.* **1963**, 35, 1386.

(10) Watanabe, J.; Saji, T.; Aoyagui, S. *Bull. Chem. Soc. Jpn.* **1982**, 55, 327.

(11) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

(12) Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta*, in press.

(13) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, 20, 3125.

(14) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, 18, 1017.

(15) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, 102, 1289.

(16) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, 17, 1782.

(17) Schilt, A. A. *J. Am. Chem. Soc.* **1960**, 82, 3000.

(18) Barbieri, G. A. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1934**, 20, 273.

(19) Parry, R. W. *Inorg. Synth.* **1970**, 12, 247.

(20) Sullivan, S.; Thorpe, A. N.; Hambricht, P. *J. Chem. Educ.* **1971**, 48, 345.

Room temperature was controlled at 21.5 ± 0.1 °C.

Proton-decoupled ^{13}C NMR spectra were obtained in D_2O (Aldrich, 99.8 atom % D) with a JEOL FX 90Q spectrometer operating at 22.49 MHz. An insert containing dioxane (Fisher Scientific Co.) in D_2O was used as an external reference.

All electronic absorption spectra were recorded on a Bausch and Lomb Spectronic 2000 or a Cary Model 14 spectrophotometer using matched quartz cells. Formation constants for $\text{Fe}(\text{bpym})_3^{2+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ were determined by titrating a deoxygenated stock solution of Fe^{2+} with a solution containing the ligand. The lowest energy MLCT transition was used to measure the absorbance, and six to eight points were used to calculate the formation constant (K) and the molar extinction coefficient of the MLCT bands.

Syntheses. $[\text{Fe}(\text{bpym})_3](\text{ClO}_4)_2$. Tris(2,2'-bipyrimidine)iron(II) perchlorate was prepared by the stoichiometric addition of 0.50 g (3.18 mmol) of solid 2,2'-bipyrimidine (Alfa Chemicals) to 20 mL of an argon-deaerated, aqueous solution containing 0.13 g (1.03 mmol) of FeCl_2 at 50–60 °C. The dark red reaction mixture was diluted to 40 mL with argon-deaerated H_2O and heated at 50–60 °C under argon for an additional 90 min. The solution was then cooled to room temperature, and saturated, aqueous NaClO_4 was added to precipitate the product. The red product was collected by vacuum filtration, washed thoroughly with generous portions of methanol to remove excess ligand, and dried by washing with diethyl ether. The product was further dried and stored under vacuum; yield 0.61 g (79%); $\mu_{\text{eff}} = 0.62 \mu_{\text{B}}$; $^{13}\text{C}\{^1\text{H}\}$ NMR (ppm) C_α 163.8, C_β 125.3, C_γ 160.8.

cis- $[\text{Fe}(\text{bpym})_2(\text{CN})_2]$. *cis*-Dicyanobis(2,2'-bipyrimidine)iron(II) was prepared by initial formation of $\text{Fe}(\text{bpym})_3^{2+}$ in aqueous solution (as previously described), followed by addition of 0.134 g (2.06 mmol) of solid KCN. The solution was then heated at 65–70 °C for 24 h under argon. After the solution was cooled to room temperature, the volume was reduced to 10 mL by the use of a rotary evaporator. Ethanol (~50 mL) was added to induce precipitation. After cooling at 0 °C for 12 h, the red precipitate was collected by vacuum filtration.

The neutral *cis*-dicyanobis(2,2'-bipyrimidine)iron(II) complex was isolated from possible cationic byproducts by dissolving the precipitate in a minimum amount of water and passing the solution down a Sephadex C-25 cation-exchange column with water. The colored solution that eluted was collected and then passed down a Dowex 1-X4 anion-exchange column to remove anionic byproducts (i.e., $\text{Fe}(\text{bpym})(\text{CN})_4^{2-}$). The neutral *cis*-dicyanobis(bipyrimidine)iron(II) readily eluted through both cation and anion columns with water, and the solution was evaporated to dryness. Final purification was achieved by placing the product on a 2-mL fritted funnel and quickly washing with 1 mL of 0 °C water, followed by excess ethanol and then ether, and the compound was dried under vacuum: yield 0.06 g (13%); $\mu_{\text{eff}} = 0.61 \mu_{\text{B}}$; $^{13}\text{C}\{^1\text{H}\}$ NMR (ppm) C_α 166.3, 160.5, C_β 124.4, C_γ 158.9, 158.7.

$\text{K}_2[\text{Fe}(\text{bpym})(\text{CN})_4]$. Preparation of potassium tetracyano(2,2'-bipyrimidine)iron(II) was achieved by formation of $\text{Fe}(\text{bpym})_3^{2+}$ in aqueous solution (as previously described, but at a 3 times larger scale), followed by addition of 0.79 g (12.08 mmol) of solid KCN. The resulting solution was heated an additional 24 h under argon. After the solution was cooled to room temperature, the reaction mixture was extracted with several portions of chloroform to remove excess 2,2'-bipyrimidine from solution, and the aqueous product was reduced to 10 mL by rotary evaporation over a warm-water bath. The concentrated solution was cooled to 0 °C for 12 h and the brown precipitate collected by vacuum filtration, washed with ethanol and then ether, and dried under vacuum: yield 0.79 g (58%); $\mu_{\text{eff}} = 0.47 \mu_{\text{B}}$; $^{13}\text{C}\{^1\text{H}\}$ NMR (ppm) C_α 162.9, C_β 123.5, C_γ 157.0.

Results and Discussion

The preparation of the mixed-ligand complexes of Fe(II) with cyanide and 2,2'-bipyrimidine closely paralleled those for the analogous complexes with cyanide and 2,2'-bipyridine. However, many of the properties, such as stability and solubility, differed for the analogous species. Solubility differences in the formation of the neutral dicyanobis(bipyrimidine)iron(II) (insoluble in H_2O) and dicyanobis(bipyrimidine)iron(II) (soluble in H_2O) required ion-exchange separations for the isolation and purification of the latter complex from the other

Table I. Electronic Spectra and Assignments for $\text{Fe}(\text{bpy})_{3-n}(\text{CN})_{2n}^{(2-2n)+}$ and $\text{Fe}(\text{bpym})_{3-n}(\text{CN})_{2n}^{(2-2n)+}$ Complexes

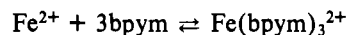
compd	solvent	λ_{max} , ^a nm	$10^{-3}\epsilon$, ^a		ref
			$\text{M}^{-1}\text{cm}^{-1}$	assignt	
$\text{Fe}(\text{bpym})_3^{2+}$	H_2O	(530)	2.7	MLCT	<i>b</i>
		481	3.0	MLCT	
		363	5.0	MLCT	
		243	49.4	$\pi-\pi^*$	
$\text{Fe}(\text{bpy})_3^{2+}$	H_2O	523	8.6	MLCT	17, 23
		(495)	(7.8)	MLCT	
		(415)	(2.4)	MLCT	
		(387)	(3.7)	MLCT	
$\text{Fe}(\text{bpym})_2(\text{CN})_2$	H_2O	351	6.5	MLCT	<i>b</i>
		298	70.0	$\pi-\pi^*$	
		545	3.38	MLCT	
		380	6.14	MLCT	
$\text{Fe}(\text{bpy})_2(\text{CN})_2$	EtOH	244	32.9	$\pi-\pi^*$	17
		570	6.93	...	
		(506)	(3.0)	...	
		373	6.79	...	
$\text{Fe}(\text{bpym})(\text{CN})_4^{2-}$	H_2O	533	1.79	MLCT	<i>b</i>
		403	4.69	MLCT	
		243	20.3	$\pi-\pi^*$	
		373	2.30	...	
$\text{Fe}(\text{bpy})(\text{CN})_4^{2-}$	95% EtOH	535	2.95	...	17
		373	2.30	...	

^a Values in parentheses are for shoulders. ^b This work.

constituents of the reaction mixture.

The absorption maxima and extinction coefficients in the electronic spectra of $\text{Fe}(\text{bpym})_3^{2+}$, *cis*- $\text{Fe}(\text{bpym})_2(\text{CN})_2$, $\text{Fe}(\text{bpym})(\text{CN})_4^{2-}$, and similar Fe(II) complexes are summarized and assigned in Table I. The MLCT bands observed in the 400–600-nm range are typical of Fe(II)-bpy or Fe(II)-phen complexes.^{22,23}

With the exception of the $\text{Fe}(\text{bpym})_3^{2+}$ ion, all of the complexes are thermally stable in aqueous solution. The thermal decomposition of $\text{Fe}(\text{bpym})_3^{2+}$ corresponds to ligand dissociation. The equilibrium constant for the process



was found to be $\sim 1 \times 10^7 \text{ M}^{-3}$. For the analogous bpy complex, we measured a lower limit value of 10^{15} M^{-3} using the procedures described in the Experimental Section. This latter value compares favorably with previous reported values²⁴ of 10^{15} – 10^{17} M^{-3} obtained under various conditions with more sophisticated measurement procedures.

The difference of $\sim 10^8$ in formation constants between the closely related $\text{Fe}(\text{bpym})_3^{2+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ complexes is surprising. However, it should be noted that both complexes have formation constants of $\sim 10^{15}$ in acetonitrile. Apparently, the remote nitrogen atoms in the bpym ligand make the periphery of the $\text{Fe}(\text{bpym})_3^{2+}$ complex hydrophilic rather than hydrophobic, as is the case for $\text{Fe}(\text{bpy})_3^{2+}$. In aqueous solution, bound bpym can be involved in hydrogen bonding to the solvent; therefore, solvent-assisted loss of one bpym ligand is likely to be an important process. This type of reaction has also been suggested for the bipyrazine complex, $\text{Fe}(\text{bpz})_3^{2+}$.^{25,26} The $\text{Fe}(\text{bpym})_2(\text{H}_2\text{O})_2^{2+}$ complex, which results from bpym loss, should be high spin and should rapidly lose the other bpym ligands. This instability of $\text{Fe}(\text{bpym})_3^{2+}$ has been used in the preparation of bimetallic Fe(II) complexes, since addition of Fe(II) and bpy to a solution of $\text{Fe}(\text{bpym})_3^{2+}$ leads to the

(22) Jørgensen, C. K. *Acta Chem. Scand.* **1957**, *11*, 166.

(23) Madeja, K.; König, E. *J. Inorg. Nucl. Chem.* **1963**, *25*, 377.

(24) Irving, H.; Mellor, D. H. *J. Chem. Soc.* **1962**, 5222 and references therein.

(25) Lever, A. B. P.; Lewis, J.; Nyholm, R. J. *J. Chem. Soc.* **1964**, 1187.

(26) Gillard, R. D.; Knight, D. W.; Williams, P. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 375.

(21) Earnshaw, A. "Introduction to Magnetochemistry"; Academic Press: New York, 1968.

Table II. Cyclic Voltammetry of Fe(II) Complexes Containing Cyano, 2,2'-Bipyridine, and/or 2,2'-Bipyrimidine Ligands

complex	solvent	$E_{1/2}$, V ^a	ΔE , mV ^b	ref
Fe(CN) ₆ ⁴⁻	H ₂ O ^c	0.174	123	<i>d</i>
Fe(bpym)(CN) ₄ ²⁻	H ₂ O	0.482	60	<i>d</i>
Fe(bpym) ₂ (CN) ₂	H ₂ O	0.876	62	<i>d</i>
Fe(bpy) ₃ ²⁺	H ₂ O	0.825	64	<i>d</i>
		0.810	...	28
	DMF	1.07	75	<i>d</i>
		1.06	...	26
Fe(bpym) ₃ ²⁺	DMF	1.33 ^e	100	<i>d</i>

^a Potential estimated from average of oxidation and reduction waves for Fe(III/II) vs. SCE at 10 mV/s scan rate. ^b Peak-to-peak separation between oxidation and reduction waves for Fe(III/II) at 10 mV/s. ^c pH 7.00. ^d This work. ^e Irreversible.

formation of [Fe(bpym)₂]₂(bpym)⁴⁺.²⁷

The thermal instability of the Fe(bpym)₃²⁺ complex does not appear to manifest itself in aqueous solutions of Fe-(bpym)₂(CN)₂ and Fe(bpym)(CN)₄²⁻. Neither of the last two ions undergo any appreciable decomposition in aqueous solution.

The cyclic voltammograms of the mixed-ligand complexes of Fe(II) with cyanide and 2,2'-bipyrimidine show single reversible waves when scanned from -0.3 to +1.2 V (vs. SCE) in aqueous solution. The $E_{1/2}$ values for Fe(bpym)_{3- n} (CN)_{2 n} ^{(2-2 n)⁺} ($n = 1-3$) and Fe(bpy)₃²⁺ in aqueous solution and DMF are listed in Table II. In aqueous solution, the $E_{1/2}$ value of the Fe(III)/Fe(II) couple shifts anodically in the order Fe(CN)₆⁴⁻ < Fe(bpym)(CN)₄²⁻ < Fe(bpy)₃²⁺ < Fe-(bpym)₂(CN)₂ and is dependent on scan rate. The Fe-(bpym)₃²⁺ wave was not observable in aqueous solution due to the onset of solvent oxidation at more positive potential. Comparative electrochemistry of Fe(bpym)₃²⁺ and Fe(bpy)₃²⁺ was conducted in DMF/0.1 M TEAP. The single irreversible wave for the Fe(bpym)₃^{3+/2+} couple at +1.31 V (vs. SCE) occurred 0.25 V more positive than for the Fe(bpy)₃^{3+/2+} wave at +1.06 V (vs. SCE). Although both oxidation and reduction waves are observed in the voltammogram, the reduction peak is much smaller at all scan rates. The peak-to-peak separation of the oxidation and reduction waves was ~100 mV at a scan rate of 10 mV/s and is larger at faster scan rates.

A comparison of the potential of the Fe(bpym)₃^{3+/2+} couple with that of the Fe(bpy)₃^{3+/2+} couple shows that the relative delocalization of electron density toward the nitrogen aromatic ring systems and away from the metal is greater for bpym than for bpy. The 0.25-V increase in the reduction potential for Fe(bpym)₃²⁺ shows that the Fe(III) complex of bpym is not as stable as the corresponding bpy analogue. In fact, the instability of the Fe(bpym)₃³⁺ complex as shown by cyclic voltammetry suggests that the stability of Fe(bpym)₃²⁺ is probably due predominantly to the π -acceptor ability of bpym. Since the structural difference in bpym and bpy is the substitution of a N atom for a CH group at a site remote to metal coordination, it is not surprising that the bpym ligand is more π -electron withdrawing.

The proton-decoupled ¹³C NMR spectra for the Fe(II)-bpym complexes show the behavior characteristic of bpym functioning as a π -acceptor ligand. There have been previous reports describing the coordination of aromatic nitrogen heterocyclic ligands (L) to d⁶ transition-metal centers such as Fe(CN)₅L³⁻, Ru(NH₃)₅L²⁺, Ru(NH₃)₄L²⁺, or M(CO)₄L (where M = Cr, Mo, W) and the effect of coordination on the ¹³C NMR chemical shifts of the ligand.^{1,3,28-32} Bonding

between d⁶ low-spin metal centers and the aromatic nitrogen heterocyclic ligand has been described as ligand σ donation to the metal in conjunction with metal π back-bonding to the ligand.^{1,32,33}

In all Fe(II)-2,2'-bipyrimidine complexes studied, the α -carbon is shifted downfield with respect to the same α -carbon in the free ligand. This result is in agreement with other studies and appears to be independent of the π -back-bonding ability or anisotropic character of the nonaromatic nitrogen heterocyclic ligand. Downfield shifts of α -carbons and small downfield or upfield shifts of β -carbons are observed for the Fe(II)-bpym complexes. These are in general agreement with other systems where π back-bonding to the nonaromatic ligands was possible.^{1,3} The γ -carbon in bpym continues to shift upfield vs. free ligand as each bpym ligand is replaced by two CN⁻ ligands. The net conclusion is that the combined σ -donor/ π -acceptor properties of CN⁻ and bpym result in the heterocycle being a better electron acceptor for Fe(II) than the CN⁻ ligand. This interpretation is consistent with the electrochemical results as well, where increased numbers of bpym ligands lead to more positive reduction potentials.

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- (30) Malin, J. M.; Schmidt, C. F.; Toma, H. E. *Inorg. Chem.* **1975**, *14*, 2924.
 (31) Lavalley, D. K.; Baughman, M. D.; Phillips, M. P. *J. Am. Chem. Soc.* **1977**, *99*, 718.
 (32) Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta* **1982**, *65*, L177.
 (33) Ford, P.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 697.

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Ligand Substitution Processes in Tetranuclear Carbonyl Clusters. 8. Reactions of Co₄(¹²CO)₁₂/Co₄(¹³CO)₁₂ with Phosphorus Donor Ligands. Further Evidence for Cluster Integrity during Ligand Substitution Processes

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A possible mode of reaction for ligand substitution processes involving polynuclear metal carbonyl derivatives is cluster fragmentation followed by recombination. Definitive experiments designed to probe this phenomenon in dinuclear metal carbonyls of the group 7B metals have recently been published. These include studies of thermal ligand substitution reactions involving MnRe(CO)₁₀ or a mixture of Mn₂(CO)₁₀/Re₂(CO)₁₀,¹ ¹⁸⁵Re₂(CO)₁₀/¹⁸⁷Re₂(CO)₁₀,² and Mn₂(¹³CO)₁₀/Mn₂(¹²CO)₁₀.³ In these dimeric species, thermal ligand substitution reactions were demonstrated to proceed via carbon

- (27) Brewer, K. J.; Petersen, J. D., work in progress.
 (28) Saji, T.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *60*, 1.
 (29) Figard, J. E.; Paukstelis, J. V.; Byrne, E. F.; Petersen, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417.

- (1) (a) Schmidt, S. P.; Troglor, W. C.; Basolo, F. *Inorg. Chem.* **1982**, *21*, 1698. (b) Sonnenberger, D.; Atwood, J. D. *J. Am. Chem. Soc.* **1980**, *102*, 3484. (c) Poe, A. *Inorg. Chem.* **1981**, *20*, 4029. (d) Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 4031.
 (2) Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822.
 (3) Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 2499.