

# Organometallic Thermodynamics. Redox Couples Involving Metal-Metal Bonds

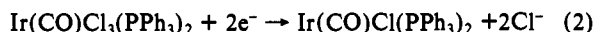
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**Abstract:** Formal potentials for couples involving the oxidation or reduction of  $\text{Mn}_2(\text{CO})_{10}$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ , or  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$  have been measured. For two-electron couples, such as  $2[\text{Mn}(\text{CO})_5(\text{NCCH}_3)]^+/\text{Mn}_2(\text{CO})_{10}$  ( $E^{\circ'} = -0.30 \pm 0.03$  V vs SSCE (saturated sodium chloride calomel electrode) in  $\text{CH}_3\text{CN}$ ,  $\mu = 0.1$ ) or  $\text{Mn}_2(\text{CO})_{10}/2[\text{Mn}(\text{CO})_5]^-$  ( $E^{\circ'} = -0.69 \pm 0.01$  V), the values were obtained by an equilibration technique. For one-electron couples such as  $\text{Mn}(\text{CO})_5/[\text{Mn}(\text{CO})_5]^-$  ( $E_{1/2} = -0.08 \pm 0.08$  V), they were measured by fast-scan microelectrode cyclic voltammetry. The free energy changes for the homolytic dissociation of  $\text{Mn}_2(\text{CO})_{10}$  ( $28 \pm 4$  kcal/mol),  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$  ( $25 \pm 5$  kcal/mol), and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$  ( $22 \pm 3$  kcal/mol) in  $\text{CH}_3\text{CN}$  ( $\mu = 0.1$ ) were calculated by combining the potentials for the one- and two-electron couples. When these quantities are included with the potentials for intermediate one-electron couples such as  $[\text{Mn}_2(\text{CO})_{10}]^{+0}$  ( $E_{1/2} = 1.50$  V), it is possible to construct complete or nearly complete Latimer diagrams which interrelate the various oxidation states. An overall pattern of reactivity toward electron transfer emerges from these diagrams. Oxidation-reduction mechanisms involving dissociation,  $\text{Mn}_2(\text{CO})_{10} \rightarrow 2\text{Mn}(\text{CO})_5$ , followed by electron transfer are inaccessible on reasonable time scales in solution at room temperature but could be important at higher temperatures although CO loss,  $\text{Mn}_2(\text{CO})_{10} \rightarrow \text{Mn}_2(\text{CO})_9 + \text{CO}$ , is competitive. Once formed in  $\text{CH}_3\text{CN}$ , the monomers  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$  and  $\text{Mn}(\text{CO})_5$  are unstable with respect to disproportionation, for example, into  $[\text{Mn}(\text{CO})_5(\text{NCCH}_3)]^+$  and  $[\text{Mn}(\text{CO})_5]^-$ , while  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$  is stable. Large overvoltages exist in the two-electron oxidations of the metal-metal bonds, e.g., for  $\text{Mn}_2(\text{CO})_{10} + 2\text{CH}_3\text{CN} \rightarrow 2\text{Mn}(\text{CO})_5(\text{NCCH}_3)^+ + 2e^-$ , the overvoltage is +1.80 V, and in their reductions,  $\text{Mn}_2(\text{CO})_{10} + 2e^- \rightarrow 2[\text{Mn}(\text{CO})_5]^-$ , at electrodes, or in solution. These overvoltages exist because the reactions occur by one-electron steps to or from the electrode or to or from a reagent in solution and occur through intermediates, which are thermodynamically unstable, e.g.,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2^+$  or  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2^-$ . A related situation exists in the oxidation of the adjacent anions, to the metal-metal bonds, e.g.,  $2[\text{Mn}(\text{CO})_5]^- \rightarrow \text{Mn}_2(\text{CO})_{10} + 2e^-$ , or in the reduction of the adjacent cations,  $2[\text{Mn}(\text{CO})_5(\text{NCCH}_3)]^+ + 2e^- \rightarrow \text{Mn}_2(\text{CO})_{10}$ , since these reactions occur via the unstable intermediates  $\text{Mn}(\text{CO})_5$ ,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ , or  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ .

## Introduction

The systematic development of organometallic chemistry has been inhibited, in part, by the absence of comprehensive thermodynamic data. Where such data are available,<sup>1</sup> insight has been gained into chemical reactivity and they have aided in the design of catalytic cycles. These data are difficult to acquire for reactions which are kinetically irreversible. This situation occurs frequently in organometallic redox chemistry, for example, where typically there are compositional and structural changes that lead to high kinetic barriers and slow reactions. Examples are the loss of metal-metal bonding with the gain or loss of electrons and oxidative addition, eqs 1 and 2. Because these reactions are typically slow at electrodes, electrochemical techniques such as cyclic voltammetry cannot be applied to the determination of reduction potentials in a direct manner.



We have developed a redox equilibration technique for measuring formal potentials for two-electron couples involving the oxidation or reduction of  $\text{Mn}_2(\text{CO})_{10}$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ , or  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ . Fast-scan, microelectrode cyclic voltammetry has been used to measure potentials for one-electron couples involving the monomers  $\text{Mn}(\text{CO})_5$ ,  $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ , or  $\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ . When the results of the two are combined, a powerful quantitative basis is made available for describing the properties of these compounds toward electron transfer and for calculating free energy changes for their homolytic dissociation.<sup>2</sup>

## Experimental Section

**Materials.** The compound dimanganese decacarbonyl was purchased from Aldrich and purified by sublimation. The compounds bis(dicarbonyl)( $\eta^5$ -cyclopentadienyl)iron] and bis(tricarbonyl)( $\eta^5$ -cyclo-

pentadienyl)molybdenum] were purchased from Aldrich and purified by recrystallization from cyclohexane/isopentane. The purified compounds were stored in a freezer at 0 °C.

Solutions containing the anions  $[\text{Mn}(\text{CO})_5]^-$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$ , or  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$  were prepared by controlled-potential electrolysis. They were prepared by electrochemical reduction of 0.1 M  $[\text{N}(\eta\text{-C}_5\text{H}_5)_4](\text{PF}_6)/\text{CH}_3\text{CN}$  solutions containing  $\text{Mn}_2(\text{CO})_{10}$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ , or  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ . The reductions were performed in a three-compartment electrolysis cell in a drybox at the peak potentials for the two-electron reductions of the dimer. After the current had decreased to the baseline, UV-vis and FTIR spectra were used to confirm that the reactions were complete.

The oxidation products  $[\text{Mn}(\text{CO})_5(\text{NCCH}_3)](\text{PF}_6)$ ,  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCCH}_3)](\text{PF}_6)$ , and  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{NCCH}_3)](\text{PF}_6)$  were prepared by literature procedures.<sup>3</sup> The polypyridyl complexes of osmium and ruthenium and all of the bipyridinium ions were prepared as hexafluorophosphate salts by literature procedures.<sup>4</sup>

Spectrograde acetonitrile was purchased from Burdick and Jackson and used as received. Tetra-*n*-butylammonium hexafluorophosphate

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Table I.  $E_{1/2}$  Values in 0.1 M TBAH/CH<sub>3</sub>CN vs SSCE<sup>a</sup>

couple	$E_{1/2}$ , V	ref
Os(bpy)(PPh <sub>3</sub> ) <sub>2</sub> (CO)H <sup>+0</sup>	-1.47	4a
Ru(bpy) <sub>3</sub> <sup>2+/+</sup>	-1.35	4b
Ru(4,4'-(CONEt <sub>2</sub> ) <sub>2</sub> -bpy) <sub>3</sub> <sup>2+/+</sup>	-1.18	4c
Os(5,5'-(CONEt <sub>2</sub> ) <sub>2</sub> -bpy)(PPh <sub>3</sub> ) <sub>2</sub> (CO)H <sup>+0</sup>	-1.11	4a
Os(bpym)(PPh <sub>3</sub> ) <sub>2</sub> (CO)H <sup>+0</sup>	-1.04	4a
Ru(5,5'-(COOEt) <sub>2</sub> -bpy) <sub>3</sub> <sup>2+/+</sup>	-1.01	4c
Os(bpy)(PPh <sub>3</sub> ) <sub>2</sub> (CO)H <sup>+0</sup>	-0.95	4a
Os(5,5'-(COOEt) <sub>2</sub> -bpy)(PPh <sub>3</sub> ) <sub>2</sub> (CO)H <sup>+0</sup>	-0.80	4a
QQ <sup>2+/+</sup> <sup>b</sup>	-0.62	4d
TQ <sup>2+/+</sup> <sup>c</sup>	-0.55	4d
PQ <sup>2+/+</sup> <sup>d</sup>	-0.44	4e
DQ <sup>2+/+</sup> <sup>e</sup>	-0.35	4d
Fe( $\eta^5$ -C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> <sup>+0</sup>	-0.12	4f
Os(bpy) <sub>2</sub> Cl <sub>2</sub> <sup>+0</sup>	-0.04	4g
Ru(bpy) <sub>2</sub> Cl <sub>2</sub> <sup>+0</sup>	+0.31	4h
Fe(Cp) <sub>2</sub> <sup>+0</sup>	+0.37	4i
Fe(p-COOEtCp) <sub>2</sub> <sup>+0</sup>	+0.48	4f
Os(bpy) <sub>3</sub> <sup>3+/2+</sup>	+0.85	4j
Ru(bpy) <sub>2</sub> (PPh <sub>3</sub> )Cl <sub>2</sub> <sup>+0</sup>	+0.90	4h
Fe(bpy) <sub>3</sub> <sup>3+/2+</sup>	+1.05	4j

<sup>a</sup>The ligand abbreviations are bpy = 2,2'-bipyridine, bpym = 2,2'-bipyrimidine, bpz = 2,2'-bipyrazine, Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>. <sup>b</sup>1,1'-Butylene-2,2'-bipyridinium ion. <sup>c</sup>1,1'-Propylene-2,2'-bipyridinium ion. <sup>d</sup>1,1'-Dimethyl-4,4'-bipyridinium ion. <sup>e</sup>1,1'-Ethylene-2,2'-bipyridinium ion.

(TBAH) was prepared by the metathesis of tetra-*n*-butylammonium bromide (Aldrich) and hexafluorophosphoric acid (Aldrich) in water, and recrystallized from hot ethanol and dichloromethane/diethyl ether followed by drying in vacuo at 80 °C for 2 days.

**Instrumentation.** A PAR 273 potentiostat and a Hewlett-Packard 7015B X-Y recorder were used for all conventional electrochemical measurements. All potentials are reported versus the saturated sodium chloride calomel electrode, SSCE (0.236 V vs NHE). For rapid-scan microelectrode cyclic voltammetry a PAR 175 universal programmer and a home-built current follower were used in conjunction with a two-electrode cell configuration. The data were recorded on a Tektronix 2230 100-MHz digital storage oscilloscope. Microelectrodes were prepared by literature techniques.<sup>5</sup> The 10- $\mu$ m-diameter platinum wire was purchased from Goodfellow Metals.

Infrared spectra were obtained by using a Nicolet 20DX FTIR spectrometer with a 0.1-mm path length NaCl solution cell. A Hewlett-Packard 8451A diode array spectrophotometer and an air-tight 0.1-cm quartz cell were used for UV-vis measurements.

**Procedures.** All electrochemical measurements were performed inside a Vacuum Atmospheres inert atmosphere drybox. Solutions for conducting the redox equilibration experiments were also prepared inside the drybox. In the redox equilibration experiments, solutions containing the two reagents were mixed and the resulting solution was allowed to sit for several hours until equilibrium had been reached. The equilibrated solutions were added to IR or UV-vis cells, sealed with rubber septa, and removed from the drybox for measurement.

The details of a typical redox equilibration experiment were as follows. Stock solutions  $1.27 \times 10^{-3}$  M in Mn<sub>2</sub>(CO)<sub>10</sub> and  $2.55 \times 10^{-3}$  M in TQ<sup>2+</sup><sup>4d</sup> (Table I) were prepared in 0.1 M TBAH/CH<sub>3</sub>CN. A solution  $2.54 \times 10^{-3}$  M in [Mn(CO)<sub>5</sub>]<sup>-</sup> was generated by controlled-potential electrolysis of Mn<sub>2</sub>(CO)<sub>10</sub> at -1.5 V vs SSCE. Exhaustive electrolysis of the TQ<sup>2+</sup>-containing solution at -0.6 V vs SSCE gave a solution  $2.55 \times 10^{-3}$  M in TQ<sup>+</sup>. For the equilibration experiments, 2 mL of the stock solution containing Mn<sub>2</sub>(CO)<sub>10</sub> was mixed with 2 mL of the solution containing TQ<sup>+</sup>. In a second solution, 2 mL of the [Mn(CO)<sub>5</sub>]<sup>-</sup> solution was mixed with 2 mL of the stock solution containing TQ<sup>2+</sup>. The solutions were allowed to equilibrate for several hours. After that period, UV-vis or FTIR solution cells were introduced into the drybox and filled with the stock solution containing Mn<sub>2</sub>(CO)<sub>10</sub>, sealed with rubber septa, and removed from the drybox, and the UV-vis or FTIR spectrum was recorded. The cell was reintroduced into the drybox and rinsed with 0.1 M TBAH/CH<sub>3</sub>CN, and a second solution added. This procedure was repeated until the spectra of all six solutions had been recorded. Over

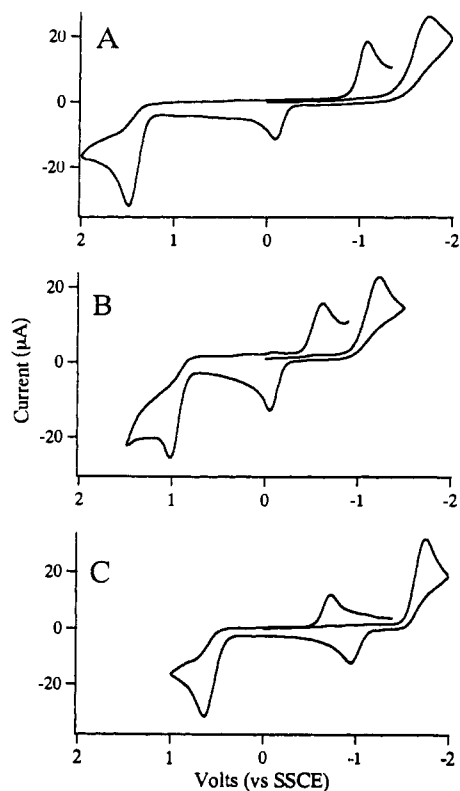


Figure 1. Cyclic voltammograms recorded in 0.1 M TBAH/CH<sub>3</sub>CN at a 0.2-cm-diameter Pt disk electrode at a scan rate of 200 mV s<sup>-1</sup>: (A)  $2.0 \times 10^{-3}$  M Mn<sub>2</sub>(CO)<sub>10</sub>, (B)  $2.0 \times 10^{-3}$  M [Mo( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub>, (C)  $2.0 \times 10^{-3}$  M [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>.

the time span of the experiment, the solutions were stable, and there was no leakage of air into the cell.<sup>4d</sup>

For measurements at temperatures other than ambient, the same procedure was followed. Solution compositions at equilibrium were determined by UV-vis measurements. The cell was sealed before removal from the drybox. It was allowed to equilibrate in a constant temperature bath for at least 1 h, at -15, 20, or 60 °C, before measurements were conducted. Complications arising from decomposition of Mn<sub>2</sub>(CO)<sub>10</sub> at 60 °C were overcome by using a kinetics program that monitored absorbances at the maxima for Mn<sub>2</sub>(CO)<sub>10</sub> at 270 and 380 nm at 10-min intervals. Decomposition led to absorbance decreases at both maxima. Equilibrium was taken to have been reached when the absorbances had reached their maximum values.

Temperature-dependent electrochemical measurements were made in a thermostated, three-compartment cell.<sup>6</sup> The cell was constructed with a water bath surrounding the three compartments and a purge line for air-sensitive materials. A sufficiently long salt bridge to the SSCE reference electrode was used so that the reference couple was isothermal and unaffected by the temperature changes that occurred in the working electrode compartment of the cell.

Rapid-scan, microelectrode cycle voltammetry was performed inside a drybox. The first scan on freshly polished electrodes was recorded. The electrodes became passive after a series of scans. This complication prevented the use of a flow cell and background subtractions.<sup>5f</sup>

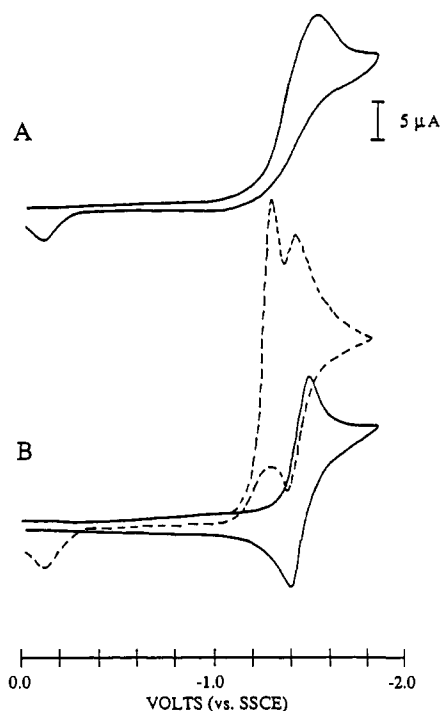
## Results

**Cyclic Voltammetry.** The cyclic voltammetric properties of Mn<sub>2</sub>(CO)<sub>10</sub> are well documented in the literature.<sup>7</sup> The voltammogram in Figure 1A is in agreement with previous reports. In 0.1 M TBAH/CH<sub>3</sub>CN, Mn<sub>2</sub>(CO)<sub>10</sub> undergoes a two-electron, irreversible reduction to give [Mn(CO)<sub>5</sub>]<sup>-</sup> at  $E_p^c = -1.45$  V vs SSCE. Irreversible oxidation of [Mn(CO)<sub>5</sub>]<sup>-</sup> occurs at  $E_p^a = -0.12$  V to give Mn<sub>2</sub>(CO)<sub>10</sub>. At  $E_p^a = 1.55$  V, Mn<sub>2</sub>(CO)<sub>10</sub> undergoes an irreversible, two-electron oxidation to give [Mn(CO)<sub>5</sub>]-

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**Figure 2.** Same as Figure 1 but with a scan rate of  $100 \text{ mV s}^{-1}$ : (A)  $1 \times 10^{-3} \text{ M Mn}_2(\text{CO})_{10}$ , (B) (solid line)  $1 \times 10^{-3} \text{ M [Os(bpy)(PPh}_3)_2(\text{CO)H]}^+$ , (dashed line)  $1 \times 10^{-3} \text{ M [Os(bpy)(PPh}_3)_2(\text{CO)H]}^+$  and  $1 \times 10^{-3} \text{ M Mn}_2(\text{CO})_{10}$ .

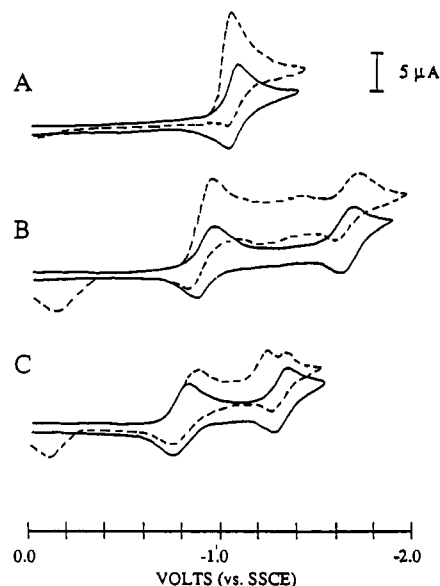
$(\text{NCCH}_3)^+$ . At  $E_p^c = -1.1 \text{ V}$ ,  $[\text{Mn}(\text{CO})_5(\text{NCCH}_3)]^+$  is reduced irreversibly to give  $\text{Mn}_2(\text{CO})_{10}$ .

The same pattern of waves was observed for  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2$ , with irreversible reduction occurring at  $E_p^c = -1.10 \text{ V}$ , and irreversible oxidation at  $E_p^a = 0.90 \text{ V}$ , Figure 1B. Oxidation of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$  occurred at  $E_p^a = -0.01 \text{ V}$ , and reduction of  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{NCCH}_3)]^+$  at  $E_p^c = -0.68 \text{ V}$ .<sup>8</sup>

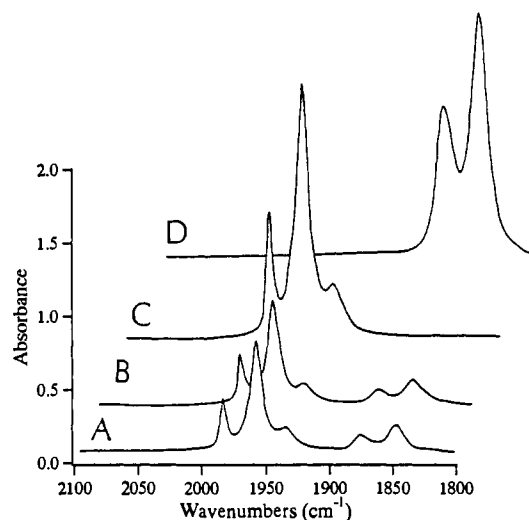
For  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2$ , there was an irreversible reduction at  $E_p^c = -1.80 \text{ V}$  and an irreversible oxidation at  $E_p^a = 0.55 \text{ V}$ , Figure 1C. The anion  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$  was oxidized irreversibly at  $E_p^a = -0.93 \text{ V}$ , and the cation  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCCH}_3)]^+$  reduced irreversibly at  $E_p^c = -0.68 \text{ V}$ .<sup>8</sup>

**Redox Catalysis and Redox Equilibration.** The irreversibilities of the two-electron reductions or oxidations precluded the measurement of  $E_{1/2}$  values by cyclic voltammetry. The potentials of these couples were measured by redox equilibration. Couples of known potential were mixed with the couple to be measured, and the equilibrium constant was determined after the system had reached equilibrium. The couples that were available for the redox equilibration experiments and their  $E_{1/2}$  values are listed in Table I. These couples undergo rapid, reversible electron transfer at  $E_{1/2}$  values that extend from  $+1.05$  to  $-1.47 \text{ V}$  in stepwise intervals that vary from  $0.37$  to  $0.03 \text{ V}$ . Four different types of couples were available: (1) oxidative, M(III/II) couples of polypyridyl complexes of Ru, Os, or Fe, (2) the Fe(III/II) couples of ferrocene or ferrocene derivatives, (3) bipyridinium dication/cation couples, and (4) reductive, polypyridyl-based couples of complexes of Ru or Os. All potentials cited in Table I were measured in  $0.1 \text{ M TBAH/CH}_3\text{CN}$  vs the SSCE reference electrode.

An initial screening of the appropriate potential range for the redox equilibration experiments was made by searching for redox catalysis.<sup>9</sup> Examples are shown in Figures 2 and 3. The effect

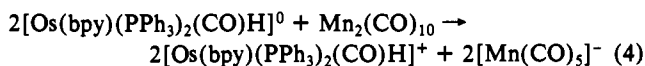
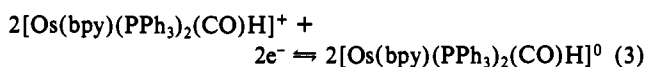


**Figure 3.** Same as Figure 2: (A) (solid line)  $1 \times 10^{-3} \text{ M [Os(5,5'-(CO}_2\text{NEt}_2)_2\text{-bpy)(PPh}_3)_2(\text{CO)H]}^+$ , (dashed line) with  $1 \times 10^{-3} \text{ M added Mn}_2(\text{CO})_{10}$ , (B) (solid line)  $1 \times 10^{-3} \text{ M [Os(bpyz)(PPh}_3)_2(\text{CO)H]}^+$ , (dashed line) with  $1 \times 10^{-3} \text{ M added Mn}_2(\text{CO})_{10}$ , (C) (solid line)  $1 \times 10^{-3} \text{ M [Os(5,5'-(CO}_2\text{Et)}_2\text{-bpy)(PPh}_3)_2(\text{CO)H]}^+$ , (dashed line) with  $1 \times 10^{-3} \text{ M added Mn}_2(\text{CO})_{10}$ . The ligand bpyz is 2,2'-bipyrazine.



**Figure 4.** Fourier transform infrared absorption spectra of solutions in  $0.1 \text{ M TBAH/CH}_3\text{CN}$ : (A) initially  $1.27 \times 10^{-3} \text{ M}$  in  $\text{Mn}_2(\text{CO})_{10}$  and  $2.55 \times 10^{-3} \text{ M}$  in  $\text{TQ}^+$ , (B) initially  $2.54 \times 10^{-3} \text{ M}$  in  $[\text{Mn}(\text{CO})_5]^+$  and  $2.55 \times 10^{-3} \text{ M}$  in  $\text{TQ}^{2+}$ , (C)  $2.54 \times 10^{-3} \text{ M}$  in  $\text{Mn}_2(\text{CO})_{10}$ , (D)  $5.08 \times 10^{-3} \text{ M}$  in  $[\text{Mn}(\text{CO})_5]^+$ .

of added  $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO)H}]^+$  on the reduction of  $\text{Mn}_2(\text{CO})_{10}$  is shown in Figure 2B. This reduction occurs via a sharp, irreversible wave at  $E_p^c = -1.30 \text{ V}$  consistent with electron-transfer catalysis, eqs 3 and 4. The reversible wave at  $E_{1/2} = -1.47 \text{ V}$  is a  $\pi^*(\text{bpy})$ -based reduction in  $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO)H}]^+$ . Catalysis occurs by reduction of  $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO)H}]^+$  to  $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO)H}]^0$  at the electrode followed by its reduction of  $\text{Mn}_2(\text{CO})_{10}$ .



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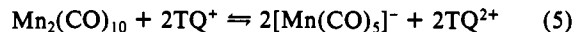
Table II. Equilibrium Constants and Formal Potentials in 0.1 M TBAH/CH<sub>3</sub>CN

reaction	<i>K</i>	<i>E</i> <sup>o</sup> , V vs SSCE <sup>a</sup>
Mn <sub>2</sub> (CO) <sub>10</sub> + 2TQ <sup>+</sup> ⇌ 2[Mn(CO) <sub>5</sub> ] <sup>-</sup> + 2TQ <sup>2+</sup>	1.6 (±0.3) × 10 <sup>-5</sup>	-0.69 (±0.01)
Mn <sub>2</sub> (CO) <sub>10</sub> + 2e <sup>-</sup> → 2[Mn(CO) <sub>5</sub> ] <sup>-</sup>		
Mn <sub>2</sub> (CO) <sub>10</sub> + 2PQ <sup>2+</sup> + 2CH <sub>3</sub> CN ⇌ 2[Mn(CO) <sub>5</sub> (NCCH <sub>3</sub> )] <sup>+</sup> + 2PQ <sup>+</sup>	5 (±5) × 10 <sup>-5</sup>	-0.30 (±0.3)
2Mn(CO) <sub>5</sub> (NCCH <sub>3</sub> ) <sup>+</sup> + 2e <sup>-</sup> → Mn <sub>2</sub> (CO) <sub>10</sub> + 2CH <sub>3</sub> CN		
[Fe(Cp)(CO) <sub>2</sub> ] <sub>2</sub> + 2[Ru(bpy) <sub>3</sub> ] <sup>+</sup> ⇌ 2[Fe(Cp)(CO) <sub>2</sub> ] <sup>-</sup> + 2[Ru(bpy) <sub>3</sub> ] <sup>2+</sup>	7.8 (±0.6) × 10 <sup>-4</sup>	-1.44 (±0.05)
[Fe(Cp)(CO) <sub>2</sub> ] <sub>2</sub> + 2e <sup>-</sup> → 2[Fe(Cp)(CO) <sub>2</sub> ] <sup>-</sup>		
[Fe(Cp)(CO) <sub>2</sub> ] <sub>2</sub> + 2DQ <sup>2+</sup> + 2CH <sub>3</sub> CN ⇌ 2[Fe(Cp)(CO) <sub>2</sub> (NCCH <sub>3</sub> )] <sup>+</sup> + 2DQ <sup>+</sup>	1.7 (±0.3) × 10 <sup>-5</sup>	-0.20 (±0.02)
[Fe(Cp)(CO) <sub>2</sub> (NCCH <sub>3</sub> )] <sup>+</sup> + 2e <sup>-</sup> → [Fe(Cp)(CO) <sub>2</sub> ] <sub>2</sub> + 2CH <sub>3</sub> CN		
[Mo(Cp)(CO) <sub>3</sub> ] <sub>2</sub> + 2PQ <sup>2+</sup> ⇌ 2[Mo(Cp)(CO) <sub>3</sub> ] <sup>+</sup> + 2PQ <sup>2+</sup>	1.19 (±0.01) × 10 <sup>-4</sup>	-0.56 (±0.01)
[Mo(Cp)(CO) <sub>3</sub> ] <sub>2</sub> + 2e <sup>-</sup> → 2[Mo(Cp)(CO) <sub>3</sub> ] <sup>-</sup>		
[Mo(Cp)(CO) <sub>3</sub> ] <sub>2</sub> + 2[Os(bpy) <sub>2</sub> Cl <sub>2</sub> ] <sup>+</sup> + 2CH <sub>3</sub> CN ⇌ 2[Mo(Cp)(CO) <sub>3</sub> (NCCH <sub>3</sub> )] <sup>+</sup> + 2Os(bpy) <sub>2</sub> Cl <sub>2</sub>	4.2 (±0.3) × 10 <sup>-3</sup>	-0.07 (±0.06)
[Mo(Cp)(CO) <sub>3</sub> (NCCH <sub>3</sub> )] <sup>+</sup> + 2e <sup>-</sup> → [Mo(Cp)(CO) <sub>3</sub> ] <sub>2</sub> + 2CH <sub>3</sub> CN		

<sup>a</sup> Calculated by using eq 7.

The same experiment was repeated but with the bpy-modified complexes mentioned in the caption to Figure 3 which had *E*<sub>1/2</sub> values for the first π\* reduction at -1.10 or -0.80 V. As *E*<sub>1/2</sub> for this reduction was made more positive in the catalyst, the extent of catalysis at constant sweep rate decreased.<sup>9c</sup> For [Os(5,5'-(CO<sub>2</sub>Et)<sub>2</sub>-bpy)(PPh<sub>3</sub>)<sub>2</sub>(CO)H]<sup>+</sup>, Figure 3C, slow catalysis occurred at the first ligand-based reduction and rapid catalysis at the second. From the results of these experiments it can be estimated that *E*<sup>o</sup> < -0.8 V vs SSCE for the Mn<sub>2</sub>(CO)<sub>10</sub>/2-[Mn(CO)<sub>5</sub>]<sup>-</sup> couple.

In order to define the potential more precisely, redox equilibration experiments were undertaken. An infrared spectrum of a solution initially containing TQ<sup>+</sup> and Mn<sub>2</sub>(CO)<sub>10</sub> in 0.1 M TBAH/CH<sub>3</sub>CN in the ν<sub>CO</sub> region is shown in Figure 4A. The peaks at 2045, 2011, and 1985 cm<sup>-1</sup> are ν<sub>CO</sub> stretches for Mn<sub>2</sub>(CO)<sub>10</sub>, and the peaks at 1900 and 1894 cm<sup>-1</sup> are ν<sub>CO</sub> stretches for [Mn(CO)<sub>5</sub>]<sup>-</sup>. Under the conditions of the experiment, equilibrium between Mn<sub>2</sub>(CO)<sub>10</sub> and [Mn(CO)<sub>5</sub>]<sup>-</sup> was reached within 6 h. After equilibration, the concentrations of Mn<sub>2</sub>(CO)<sub>10</sub> and [Mn(CO)<sub>5</sub>]<sup>-</sup> were determined by measuring the areas under the CO bands and comparing them with preestablished calibration curves. The concentrations of TQ<sup>+</sup> and TQ<sup>2+</sup> were surmised by mass balance by assuming the equilibrium in eq 5, and the four concentrations used to calculate the equilibrium constant in eq 6. The same value for the equilibrium constant, *K*(CH<sub>3</sub>CN,



$$K = \frac{[\text{Mn}(\text{CO})_5]^-]^2 [\text{TQ}^{2+}]^2}{[\text{Mn}_2(\text{CO})_{10}] [\text{TQ}^+]^2} \quad (6)$$

*μ* = 0.1 M, 22 ± 2°C) = 1.6 (±0.3) × 10<sup>-5</sup>, was obtained regardless of the direction in which the equilibrium was approached. The formal potential for the Mn<sub>2</sub>(CO)<sub>10</sub>/2[Mn(CO)<sub>5</sub>]<sup>-</sup> couple was calculated from the equilibrium constant and the potential of the equilibrating couple by using eq 7 in which *E*<sup>o</sup><sub>ref</sub> (≈ *E*<sub>1/2</sub>) is the potential for the equilibrating couple, *F* is the Faraday constant, *T* is the temperature (K), and *n* is the electrochemical stoichiometry. Equilibrium constants and formal potentials are listed in Table II.

$$E^o(\text{Mn}_2(\text{CO})_{10}/2[\text{Mn}(\text{CO})_5]^-) = E^o_{\text{ref}} + (RT/nF) \ln K \quad (7)$$

The equilibrium constant was also measured by using UV-vis spectrophotometry. The result of one such experiment is shown in Figure 5. In these experiments the concentrations of Mn<sub>2</sub>(CO)<sub>10</sub> (λ<sub>max</sub> = 346, ε = 16 950 M<sup>-1</sup> cm<sup>-1</sup>) and TQ<sup>+</sup> (λ<sub>max</sub> = 508 nm, ε = 3450 M<sup>-1</sup> cm<sup>-1</sup>) were established by absorbance measurements at their λ<sub>max</sub> values. The components [Mn(CO)<sub>5</sub>]<sup>-</sup> and TQ<sup>2+</sup> are transparent in these spectral regions. The same equilibrium constant was obtained within experimental error. The value cited in Table II is the average value obtained for six separate experiments using both techniques. The uncertainties in Table II are standard deviations.

A measurable equilibrium was reached between the PQ<sup>2+</sup>/<sup>+</sup> couple (*E*<sub>1/2</sub> = -0.45 V) and Mn<sub>2</sub>(CO)<sub>10</sub>/2[Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup>, Figure 6, but the equilibration time was noticeably longer.

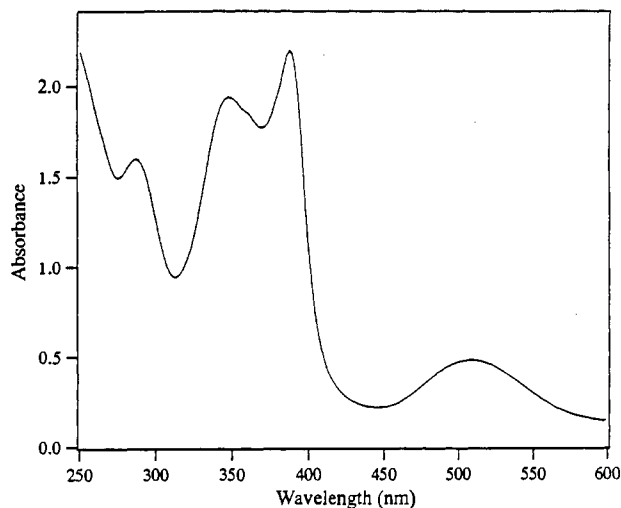


Figure 5. UV-vis absorption spectra of a solution that was initially 1.27 × 10<sup>-3</sup> M in Mn<sub>2</sub>(CO)<sub>10</sub> and 2.55 × 10<sup>-3</sup> M in TQ<sup>+</sup> in 0.1 M TBAH/CH<sub>3</sub>CN.

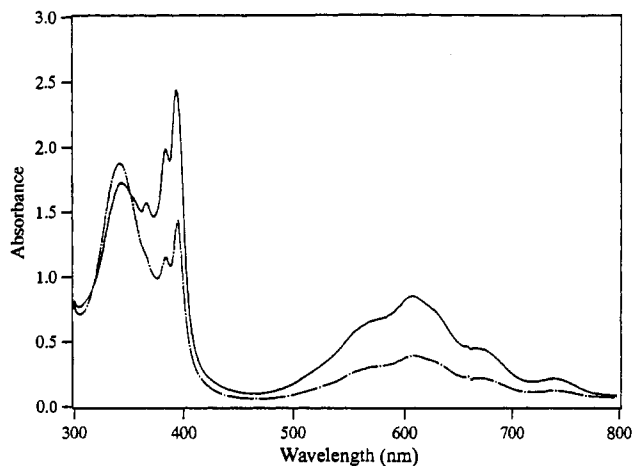
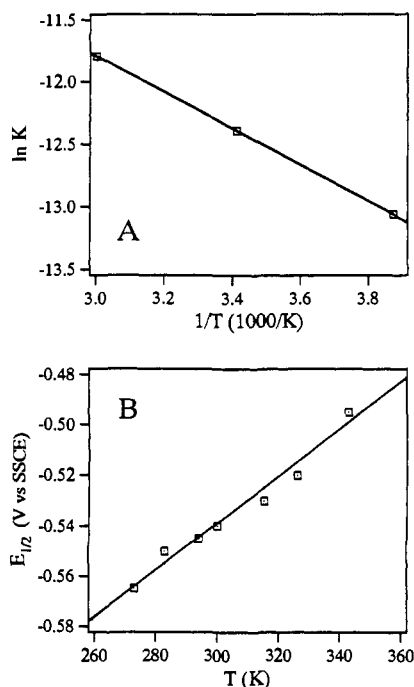


Figure 6. UV-vis absorption spectra of solutions 3 h after mixing the reactants in 0.1 M TBAH/CH<sub>3</sub>CN: (solid line) a solution initially 2.03 × 10<sup>-3</sup> M in [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup> and 2.21 × 10<sup>-3</sup> M in PQ<sup>+</sup>, (dashed-dotted line) a solution initially 1.03 × 10<sup>-3</sup> M in Mn<sub>2</sub>(CO)<sub>10</sub> and 2.21 × 10<sup>-3</sup> M in PQ<sup>2+</sup>.

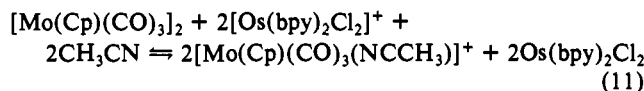
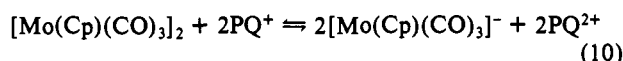
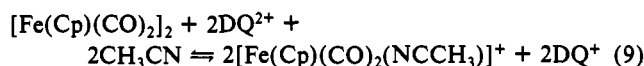
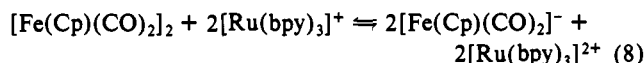
Problems arose from competing secondary reactions involving the loss of CO from [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup> to give [Mn(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup> with ν<sub>CO</sub> = 2066 and 1977 cm<sup>-1</sup>. As shown in Figure 6, equilibration was largely, but not quite, complete after 3 h. In order to calculate *K*, we utilized data acquired 24 h after mixing. At this point, decomposition was not significant, and equilibrium had been reached. A conservative estimate for the uncertainty in *E*<sup>o</sup> introduced by decomposition is ±50 mV.

The redox equilibration method was also applied to the two-electron couples involving [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> and [Mo(η<sup>5</sup>-



**Figure 7.** (A) Same as in Figure 5, the temperature dependence of the equilibrium in eq 5 and (B)  $E_{1/2}$  for the  $TQ^{2+/+}$  couple vs SSCE. The linear correlation in (A) is to the expression  $\ln K = -1450/T - 7.4$  from which  $\Delta S = 15$  eu. The correlation in (B) is to the expression  $E_{1/2}$  (V) =  $(9.1 \times 10^{-4})T - 0.81$  from which  $\Delta S = 21$  eu for the  $TQ^{2+/+}$  couple.

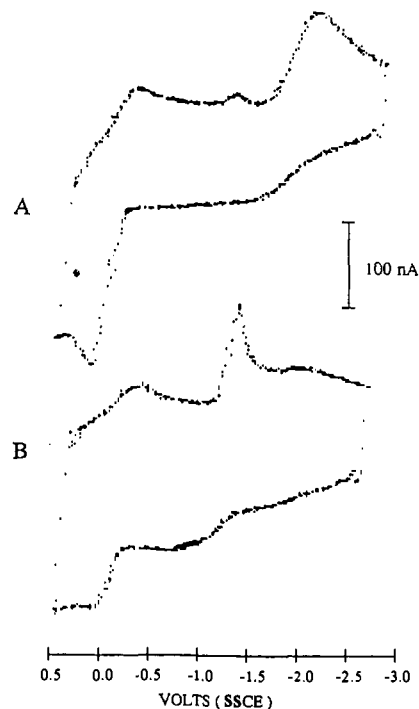
$C_5H_5(CO)_3]_2$ . The equilibria that were investigated are shown in reactions 8–11; Cp is  $\eta^5-C_5H_5$ . The data are presented else-



where.<sup>10</sup> The equilibrium constants and formal potentials derived from the measurements are listed in Table II. Corraine and Atwood recently reported values for the two-electron reductions of the dimers.<sup>11</sup> They estimated these values by combining literature values for metal–metal bond strengths with the oxidation potentials of the anions reported by Tilsted and Parker.<sup>16</sup> Their estimates agree well with our values which were obtained by direct measurement.

The equilibrium constant for the reaction in eq 5 was measured at a series of temperatures and electrolyte concentrations. In experiments where temperature was varied, equilibrium constants were measured at  $-15$ ,  $20$ , and  $60$  °C following equilibration of solutions that were initially  $5 \times 10^{-4}$  M in  $Mn_2(CO)_{10}$  and  $1 \times 10^{-3}$  M in  $TQ^+$ . A plot of  $\ln K$  vs  $1/T$  is shown in Figure 7A. The temperature dependence of  $E_{1/2}$  for the  $TQ^{2+}/TQ^+$  couple vs SSCE is shown in Figure 7B. The equilibrium constants measured in  $0.5$  and  $0.1$  M TBAH/ $CH_3CN$  were the same to within the experimental uncertainty of the measurements.

**Microelectrode Cyclic Voltammetry.** Cyclic voltammograms at scan rates of up to  $10\,000$  V  $s^{-1}$  were acquired in an attempt



**Figure 8.** Cyclic voltammograms recorded at scan rates of  $5000$  V  $s^{-1}$  in  $0.5$  M TBAH/ $CH_3CN$  at a  $10\text{-}\mu\text{m}$ -diameter Pt disk electrode: (A)  $5 \times 10^{-3}$  M  $Mn_2(CO)_{10}$ , (B)  $5 \times 10^{-3}$  M  $[Mn(CO)_5(NCCH_3)]^+$ .

to measure the potentials for the one-electron couples involving the metal–metal-bonded dimers. The acquisition of data at high scan rates was made possible by utilizing  $10\text{-}\mu\text{m}$ -diameter platinum electrodes.<sup>5</sup> In Figure 8 are shown cyclic voltammograms obtained at  $5000$  V  $s^{-1}$ . At this high scan rate the oxidation of  $[Mn(CO)_5]^-$  to  $Mn(CO)_5$ , which occurs at  $E_p^a = 0.01$  V, is chemically reversible because rereduction of  $Mn(CO)_5$  to  $[Mn(CO)_5]^-$  is more rapid than dimerization to give  $Mn_2(CO)_{10}$ .<sup>12</sup> In Figure 8B, reduction of  $[Mn(CO)_5(NCCH_3)]^+$  to  $Mn(CO)_5(NCCH_3)$  occurs at  $E_p^c = -1.3$  V. The appearance of the reduction wave for  $[Mn(CO)_5(NCCH_3)]^+$  in Figure 8A is the result of a competition between one-electron oxidation of  $[Mn(CO)_5]^-$  to give  $Mn(CO)_5$ , and further one-electron oxidation of  $Mn(CO)_5(NCCH_3)$  to give  $[Mn(CO)_5(NCCH_3)]^+$  which is spontaneous at this potential, Scheme I. Oxidation of  $Mn(CO)_5$  or reduction of  $[Mn(CO)_2(NCCH_3)]^+$  are expected to occur through the solvent-coordinated, 19-electron complex  $Mn(CO)_5(CH_3CN)$ .<sup>13,19</sup>

From our measurements,  $E_{1/2} = -0.08 \pm 0.08$  V vs SSCE for the  $Mn(CO)_5^{0/-}$  couple on the basis of the results of six separate experiments. In our initial communication, a value of  $E_{1/2} = -0.15$  V vs SSCE was reported.<sup>2</sup> The discrepancy between the two values is within the uncertainty of the experiment. There were no systematic variations in  $E_{1/2}$  when the electrolyte concentration was varied from  $0.1$  to  $0.5$  M. If they exist, ionic strength effects are also within the limits of uncertainty.

Rapid-scan cyclic voltammograms were also recorded in solutions which were  $5 \times 10^{-3}$  M in  $[Fe(\eta^5-C_5H_5)(CO)_2]_2$  in  $0.1$  M TBAH/ $CH_3CN$ . At a scan rate of  $879$  V  $s^{-1}$ , the characteristic, irreversible reduction of  $[Fe(\eta^5-C_5H_5)(CO)_2]_2$  to  $[Fe(\eta^5-C_5H_5)(CO)_2]^-$  was observed at  $E_p^c = -2.3$  V vs SSCE. In addition, what appeared to be the reductive component of the wave for the  $[Fe(\eta^5-C_5H_5)(CO)_2]^0/[Fe(\eta^5-C_5H_5)(CO)_2]^-$  couple was observed at  $E_{1/2} = -0.90$  V.

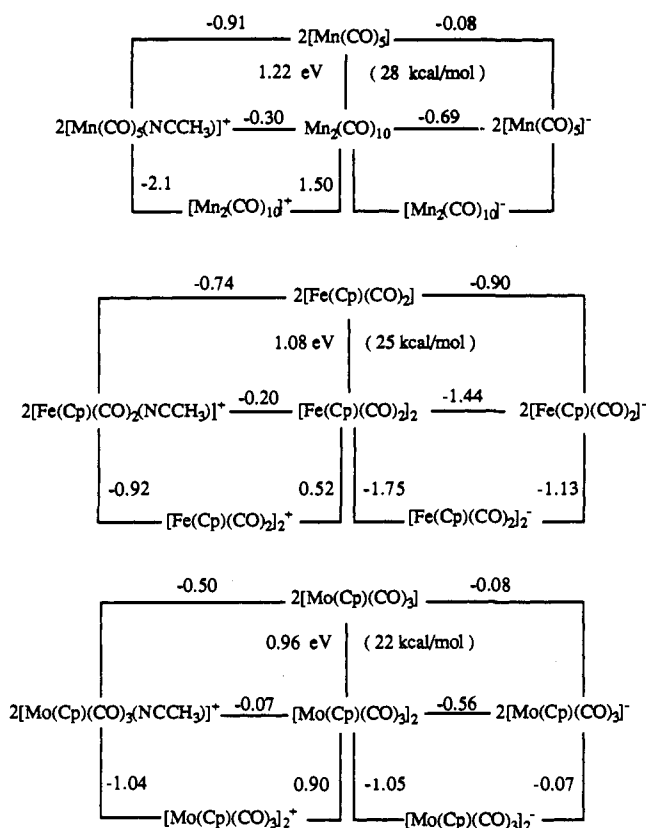
(12) (a) Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *C49*. (b) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259. (c) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 3748. (d) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakura, S. *J. Am. Chem. Soc.* **1983**, *105*, 6749.

(13) (a) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087. (b) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Organometallics* **1987**, *6*, 1886. (c) Kuchynka, D. J.; Kochi, D. J. *Inorg. Chem.* **1989**, *28*, 855.

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(11) Corraine, M. S.; Atwood, J. D. *Organometallics* **1991**, *10*, 2315.

Scheme 1

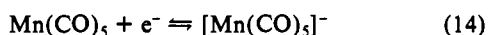
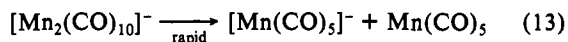


### Discussion

**Electrochemistry.** In CH<sub>3</sub>CN, Mn<sub>2</sub>(CO)<sub>10</sub> undergoes an irreversible electrochemical oxidation to give [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup> and an irreversible reduction to give [Mn(CO)<sub>5</sub>]<sup>-</sup>. The loss of structural integrity is typical for metal–metal bonds where electrons are gained or lost from orbitals that are largely bonding or antibonding with regard to the metal–metal interaction. There was no evidence for an intermediate [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>0/-</sup> couple by rapid-scan, cyclic voltammetry even at scan rates of up to 10000 V s<sup>-1</sup>. Likewise, the reduction of Mn<sub>2</sub>(CO)<sub>10</sub> is chemically irreversible even in propionitrile at low temperatures.<sup>14c</sup>

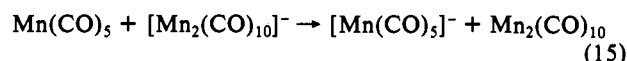
For the irreversible reduction wave for Mn<sub>2</sub>(CO)<sub>10</sub> that appears at E<sub>p</sub><sup>c</sup> = -1.45 V, the peak to half-peak potential separation, |E<sub>p</sub> - E<sub>p/2</sub>| = 136 mV, is considerably in excess of the 59 mV expected for a diffusion-controlled reaction. Both the peak shape and scan rate dependence are consistent with initial slow electron transfer with a transfer coefficient, α<sub>n</sub> = 0.4. Oxidation of [Mn(CO)<sub>5</sub>]<sup>-</sup> at the electrode is rapid, |E<sub>p</sub> - E<sub>p/2</sub>| = 59 mV as expected for a diffusion-controlled reaction. The reduction of [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup> is also slow, |E<sub>p</sub> - E<sub>p/2</sub>| = 94 mV.

The mechanism that has been proposed for electrochemical reduction of Mn<sub>2</sub>(CO)<sub>10</sub> is shown in eqs 12–14.<sup>7</sup> The electron-



transfer reaction in eq 15 could also play a role depending on the rate of cleavage of the Mn–Mn <sup>1/2</sup> bond in [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>-</sup>. The reactions involving Mn(CO)<sub>5</sub> are in competition with recombi-

nation to give the metal–metal bond, eq 16.



Oxidation of either Mn<sub>2</sub>(CO)<sub>10</sub> or [Mn(CO)<sub>5</sub>]<sup>-</sup> to give [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup> is electrochemically irreversible, but rapid with |E<sub>p</sub> - E<sub>p/2</sub>| = 59 mV. The irreversibility arises because the metal–metal bond cleaves following oxidation. The [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>+0</sup> couple has been reported to be quasi-reversible in propionitrile at high scan rates (>100 V s<sup>-1</sup>)<sup>14c</sup> or in 1,2-difluorobenzene at moderate scan rates.<sup>15</sup>

On the basis of the electrochemical results, it can be inferred that the reductions of Mn<sub>2</sub>(CO)<sub>10</sub> or [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup> at the electrode occur by slow, rate-limiting electron transfer while the oxidations of Mn<sub>2</sub>(CO)<sub>10</sub> or [Mn(CO)<sub>5</sub>]<sup>-</sup> are rapid, diffusion-controlled processes.

The value of E<sub>1/2</sub> = -0.08 V vs SSCE for the Mn(CO)<sub>5</sub>/[Mn(CO)<sub>5</sub>]<sup>-</sup> couple is within experimental error of the value of -0.143 V obtained by Tilset and Parker by using derivative cyclic voltammetry and kinetic shift factors.<sup>16</sup> A value of 0.08 V was reported by Kuchynka and Kochi, by fast-scan, microelectrode cyclic voltammetry.<sup>13c</sup> The discrepancy between our value and theirs may lie in the waveform distortions that exist at high scan rates.

Both [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub> and [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> have also been the subject of detailed electrochemical investigations.<sup>8</sup> Early results obtained at mercury electrodes may have been complicated by adsorption and the formation of mercury compounds.<sup>17</sup> More recently, reversible, one-electron oxidations<sup>14b</sup> and reductions<sup>14a</sup> have been reported for [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>.

Attempts to establish potentials for the one-electron couples involving [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>] by rapid-scan, microelectrode voltammetry were complicated by an overlap in potentials. Oxidation of [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sup>-</sup> gave both [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>(NCCH<sub>3</sub>)]<sup>+</sup> and [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>], and their reduction waves at E<sub>p</sub><sup>c</sup> = -0.30 V and at E<sub>p</sub><sup>c</sup> = -0.20 V overlapped and could not be resolved. The acetonitrile complex appears because Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub> is unstable with respect to disproportionation and is oxidized (as Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>(NCCH<sub>3</sub>))<sup>18</sup> at any potential required to oxidize the anion (see below). Because of the overlap problem, the E<sub>1/2</sub> value determined by Tilset and Parker for the [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sup>0/-</sup> couple was adopted.<sup>16</sup>

The estimate made of E<sub>1/2</sub> for the Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub><sup>0/-</sup> couple by Tilset and Parker utilized the rate constant for dimerization of Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub> in order to use kinetic shift factors. This could lead to some error in their calculated E<sub>1/2</sub> values because the dimerization rate constants have not been measured in 0.1 M TBAH/CH<sub>3</sub>CN. From the results of flash photolysis experiments these rate constants are solvent dependent.<sup>24</sup> Despite this, our results for Mn(CO)<sub>5</sub> and Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> agree well with theirs, and their value for Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub> appears to be within the experimental uncertainty of the value that we could have determined directly in the absence of the overlap problem.

The apparent reversibility of the [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>/[Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup> couple at scan rates as low as 879 V s<sup>-1</sup> is inconsistent with the reported dimerization rate constant of 3 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> determined by flash photolysis,<sup>19</sup> and even less consistent with reversibility at rates as low as 1 V s<sup>-1</sup> reported earlier.<sup>8f</sup>

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**Table III.** Free Energies of Dissociation in 0.1 M TBAH/CH<sub>3</sub>CN at 22 ± 2 °C

compound	$\Delta G^{\circ'}_{M-M}$ , kcal mol <sup>-1</sup>	$K_{M-M}$
Mn <sub>2</sub> (CO) <sub>10</sub>	28 ± 4	2.4 × 10 <sup>-21</sup>
[Fe(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> ] <sub>2</sub>	25 ± 5	4.0 × 10 <sup>-19</sup>
[Mo(η <sup>5</sup> -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>3</sub> ] <sub>2</sub>	22 ± 3	7.1 × 10 <sup>-17</sup>

It is possible that the cathodic wave observed at  $E_p = -0.9$  V is due to reduction of the long-lived CO-bridged complex that was reported to form following flash photolysis of [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>.<sup>19,20</sup> If so, access to this intermediate is also possible via oxidation of [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup> at an electrode.

The equilibration reactions are reversible; no products other than [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(NCCH<sub>3</sub>)<sup>+</sup>, [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup>, or [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> were detected. Despite the experimental complications, the  $E_{1/2}$  value determined by Tilset and Parker for the [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>0/-</sup> couple is consistent with the reversible wave observed by rapid-scan cyclic voltammetry.<sup>16</sup>

**Stabilities of the Metal-Metal Bonds. Free Energies of Dissociation.** When the results of the redox equilibration and fast-scan experiments are combined, it is possible to calculate the free energy change associated with dissociation of the metal-metal bonds. The relationship between this quantity,  $\Delta G^{\circ'}_{M-M}$ , and the formal potentials for the one- and two-electron couples is shown in eq 17. The values of  $\Delta G^{\circ'}_{M-M}$ , the free energy change in 0.1 M TBAH/CH<sub>3</sub>CN calculated by this method, and the associated equilibrium constants,  $K_{M-M}$ , are listed in Table III.

$$\Delta G^{\circ'}(\text{Mn}_2(\text{CO})_{10}) \text{ (eV)} = -2[E^{\circ'}(\text{Mn}_2(\text{CO})_{10}/2[\text{Mn}(\text{CO})_5]^-) - E^{\circ'}(\text{Mn}(\text{CO})_5/[\text{Mn}(\text{CO})_5]^-)] \quad (17)$$

From the temperature dependence of  $K$ ,  $\Delta S^{\circ'} = 15$  eu in 0.1 M TBAH/CH<sub>3</sub>CN for the equilibrium in eq 5. When this value is combined with  $\Delta S^{\circ'}$  for the TQ<sup>2+/+</sup> couple, a value of  $\Delta S^{\circ'} = -14$  eu is derived for the Mn<sub>2</sub>(CO)<sub>10</sub>/2[Mn(CO)<sub>5</sub>]<sup>-</sup> couple. In order to calculate the entropic change associated with dissociation of the metal-metal bond in Mn<sub>2</sub>(CO)<sub>10</sub>, it would be necessary to measure the temperature dependence of the Mn(CO)<sub>5</sub><sup>0/-</sup> couple. It was not possible to perform these measurements with any degree of accuracy because of the large uncertainties in the rapid-scan experiments.

An independent estimate of  $\Delta S \approx 32$  eu for the metal-metal bond equilibrium has been made by flash photolysis in cyclohexane.<sup>12a</sup> This may be a reasonable value for  $\Delta S^{\circ'}$  in CH<sub>3</sub>CN since both components in the reaction are neutral and  $\Delta S$  should be relatively independent of solvent. If this value is adopted,  $\Delta H^{\circ'}_{M-M} \approx 38$  kcal mol<sup>-1</sup> for Mn<sub>2</sub>(CO)<sub>10</sub> at 298 K.

Since the first estimate of the M-M bond strength in Mn<sub>2</sub>(CO)<sub>10</sub> by Cotton and Monchamp,<sup>21a</sup> there have been many attempts to measure this enthalpic change. Values ranging from 19 to 41 kcal mol<sup>-1</sup> have been obtained by using a variety of techniques. The values derived from electron impact studies<sup>21d-8</sup> are now

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believed to be unreasonably low.<sup>21m</sup> A value derived from thermochemical data has large uncertainties.<sup>21j</sup>

Our value is within experimental error of the original estimate. It is also consistent with a value obtained by time-resolved, photoacoustic calorimetry in hexanes.<sup>21i</sup> A more recent gas-phase estimate gave 41 kcal mol<sup>-1</sup>, with an uncertainty of 9 kcal mol<sup>-1</sup>.<sup>21m</sup> If the near constancy in  $\Delta H^{\circ'}_{M-M}$  implied by the gas-phase and solution experiments is correct, the Mn<sub>2</sub>(CO)<sub>10</sub>/2[Mn(CO)<sub>5</sub>] equilibrium is nearly medium independent and the solvation enthalpies for Mn<sub>2</sub>(CO)<sub>10</sub> and Mn(CO)<sub>5</sub> must be the same to within a few kilocalories per mole.

On the basis of the values of  $\Delta G^{\circ'}_{M-M}$  listed in Table III, the metal-metal bonds in these compounds are weak compared to typical chemical bonds. In the cis and trans CO-bridged isomers of [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> there is no direct metal-metal bonding,<sup>22</sup> and  $\Delta G^{\circ'}_{M-M}$  is a measure of the strength of the electronic coupling that exists through the CO bridges. On the basis of the results of NMR and infrared measurements, a nonbridged isomer also exists. Since the nonbridged isomer is in measurable equilibrium with the cis and trans isomers,  $\Delta G^{\circ'}_{M-M}$  for [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> also provides a reasonable estimate of the metal-metal bond strength. It is in agreement with a previous determination of  $\Delta H_{M-M}$ .<sup>23</sup>

**Reduction Potentials. Latimer Diagrams.** Latimer diagrams, for couples that interrelate Mn<sub>2</sub>(CO)<sub>10</sub>, [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>, or [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub> and their adjacent oxidation states are shown in Scheme I. The potentials cited came from the following sources: (1) The two-electron couples came from the redox equilibration experiments. (2) The [Mn(CO)<sub>5</sub>]<sup>0/-</sup> and [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>0/-</sup> couples came from microelectrode cyclic voltammetry, and [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sup>0/-</sup> from ref 16. (3) The one-electron oxidative couples [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)<sup>+</sup>/Mn(CO)<sub>5</sub> were calculated from  $\Delta G^{\circ'}_{M-M}$  and  $E^{\circ'}$  values for the analogous two-electron couples Mn<sub>2</sub>(CO)<sub>10</sub>/2[Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)<sup>+</sup>]. (4) The one-electron couples [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>+0</sup>, [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub><sup>+0</sup>, or [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub><sup>+0</sup> were taken as  $E^{\circ'} - 0.03$  V and [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub><sup>0/-</sup> or [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub><sup>0/-</sup> as  $E_p^{\circ} + 0.03$  V. The justification for using peak potentials to calculate  $E_{1/2}$  values was based on the properties of the waves. They point to diffusion-controlled, heterogeneous electron transfers at the electrode followed by rapid, irreversible chemical steps. This approximation is known to be valid for the couples [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub><sup>+0</sup>, [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub><sup>0/-</sup>, and [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>+0</sup> where  $E_{1/2}$  values are known by direct measurement in noncoordinating solvents.<sup>14,15</sup> The approximation is not valid for reduction of Mn<sub>2</sub>(CO)<sub>10</sub> because of the evidence from the wave shape for slow heterogeneous electron transfer. Chemical shift factors were not included in the calculations of  $E_{1/2}$  for the one-electron dimer couples. The potentials cited are only estimates of the thermodynamic potentials.

The values cited for the couples [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)<sup>+</sup>/Mn(CO)<sub>5</sub> and 2[Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)<sup>+</sup>]/Mn<sub>2</sub>(CO)<sub>10</sub> are consistent with estimates made earlier on the basis of a flash photolysis procedure.<sup>24</sup> In that study it was estimated that  $E^{\circ} < -0.8$  V for [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)<sup>+</sup>/Mn(CO)<sub>5</sub> and  $E^{\circ} < -0.2$  V for 2[Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)<sup>+</sup>]/Mn<sub>2</sub>(CO)<sub>10</sub>.

**Implications for Reactivity.** The thermodynamic data in the Latimer diagrams reveal much about the reactivity of the metal-metal bonds toward electron transfer.

**Reactivity via the Monomers.** On the basis of the equilibrium constant for dissociation of Mn<sub>2</sub>(CO)<sub>10</sub> (Table III) and assuming that  $K = 10^9$  M<sup>-1</sup> s<sup>-1</sup> for recombination of Mn(CO)<sub>5</sub>, the half-time

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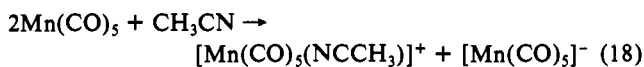
(24) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *187*.



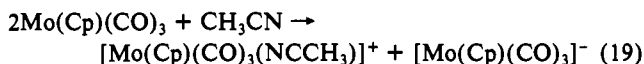
for dissociation at 298 K is  $\sim 5 \times 10^5$  h. The half-times for the Fe and Mo dimers are less but still appreciable. This means that any mechanism that relies on dissociation *prior* to electron transfer of the metal–metal bond is necessarily very slow at room temperature.

At higher temperatures, dissociation could be more important. By using  $\Delta H^\circ_{M-M} \approx 38$  kcal mol<sup>-1</sup> for Mn<sub>2</sub>(CO)<sub>10</sub>,  $K_{\text{dis}}$  increases from  $2.4 \times 10^{-21}$  at 295 K to  $3.8 \times 10^{-17}$  at 353 K. For a solution initially  $2 \times 10^{-3}$  M in Mn<sub>2</sub>(CO)<sub>10</sub> this corresponds to an increase in the equilibrium concentration of Mn(CO)<sub>5</sub> from  $2 \times 10^{-12}$  M at 295 K to  $2.7 \times 10^{-10}$  M at 353 K. This concentration level is near that required for direct observation by NMR given the paramagnetic character of the monomers.<sup>25</sup> At higher temperatures, loss of CO is known to occur and provides a basis for the reactivity of Mn<sub>2</sub>(CO)<sub>10</sub> toward both oxidation and substitution.<sup>21k,26–28</sup>

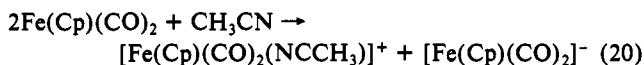
From the potentials for the couples [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup>/Mn(CO)<sub>5</sub>, etc., the monomers are strong reducing agents. They are accessible photochemically,<sup>12,19,20,24</sup> and their strong reducing character is shown by reactions in which they abstract halogen atoms from halocarbon solvents.<sup>24,29</sup> They have both enhanced oxidizing and reducing strengths compared to the parent metal–metal bonds.<sup>30</sup> This leads to an instability toward disproportionation in CH<sub>3</sub>CN for both Mn(CO)<sub>5</sub> and Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub> while Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub> is stable.



$$\Delta G^\circ = -19.0 \text{ kcal mol}^{-1}$$



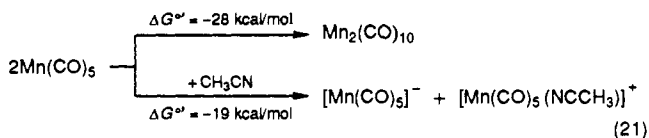
$$\Delta G^\circ = -9.7 \text{ kcal mol}^{-1}$$



$$\Delta G^\circ = 3.7 \text{ kcal mol}^{-1}$$

The instability toward disproportionation is driven by the binding of the donor solvent CH<sub>3</sub>CN to the cations, and by the solvation of the ions that are produced. These calculations provide a rationale for the photochemically- or thermally-induced disproportionations of Mn<sub>2</sub>(CO)<sub>10</sub>, [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub>, or Co<sub>2</sub>(CO)<sub>8</sub> in polar solvents, or of Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub> in the presence of halide ions.<sup>12,18,24,29</sup>

Both disproportionation and metal–metal bond formation are thermodynamically spontaneous and competitive reactions for the monomers when they are prepared thermally or photochemically.



Metal–metal bond formation is known to be rapid.<sup>12</sup> Disproportionation would be favored by prior binding of the solvent or of an added ligand followed by outer-sphere electron transfer.<sup>31,18</sup>

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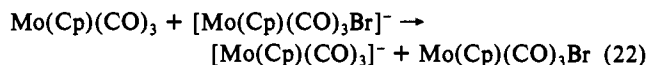
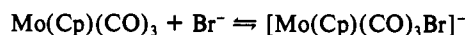
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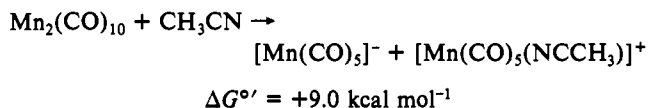
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(29) (a) Wrighton, M. S.; Bredesen, D. *J. Organomet. Chem.* **1973**, *50*, C35. (b) Wrighton, M. A.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

(30) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258.

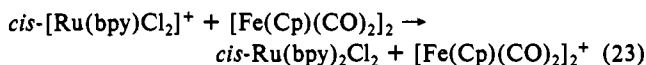


**Reactivity of the Dimers.** All three metal–metal bonds are stable with respect to disproportionation, with the free energy of disproportionation being +11.3 kcal mol<sup>-1</sup> for [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub>, and +28.5 kcal mol<sup>-1</sup> for [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub>. The reverse reactions are used to prepare the metal–metal bonds.<sup>13c</sup>

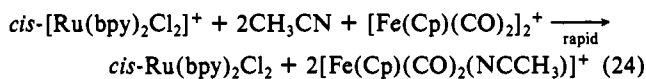


One-electron oxidation or reduction at solid electrodes is rapid, except for [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>0/-</sup>. The two-electron processes occur via the one-electron intermediates as shown by the appearance of their couples in noncoordinating solvents. This explains the patterns of irreversible waves that appear in the cyclic voltammograms in Figure 1. For example, for Mn<sub>2</sub>(CO)<sub>10</sub>, initial, one-electron oxidation to give [Mn<sub>2</sub>(CO)<sub>10</sub>]<sup>+</sup> does not occur until  $E_{1/2} = 1.52$  V, yet  $E_{1/2} = -0.30$  for the two-electron couple. This creates an overvoltage of 1.82 V for the oxidation of Mn<sub>2</sub>(CO)<sub>10</sub> to [Mn(CO)<sub>5</sub>(NCCH<sub>3</sub>)]<sup>+</sup>. Likewise, reduction of [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> to 2[Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup> cannot occur until the potential for reduction to [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sup>-</sup> is reached at -1.77 V. This causes an overvoltage of 0.33 eV.

The same factors lead to an inhibition to electron transfer in solution as illustrated by the oxidation of [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> by [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>.<sup>24</sup> The slow step in this reaction is the initial electron transfer as shown by the rate law which is first order in both reactants.



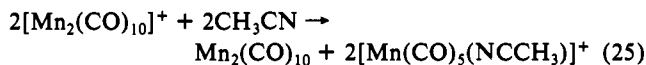
$$\Delta G^\circ = +4.8 \text{ kcal mol}^{-1}$$



$$\Delta G^\circ = -28.3 \text{ kcal mol}^{-1}$$

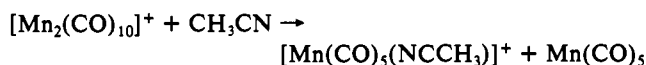
On this basis, the reactivity order toward oxidation of the metal–metal bonds should follow the potentials of the one-electron couples, [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub> > [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub> > Mn<sub>2</sub>(CO)<sub>10</sub>.

The one-electron intermediates are powerful oxidants and powerful reductants. They are *highly* unstable with respect to disproportionation in polar, coordinating solvents.



$$\Delta G^\circ = -83 \text{ kcal mol}^{-1}$$

This instability is driven by the formation of a strong bond with the solvent in the (dπ)<sup>4</sup> or (dπ)<sup>6</sup> cationic products and by the re-formation of the metal–metal bond. The one-electron cations are also unstable with regard to dissociation. The coordinating solvent plays an important role. In CH<sub>2</sub>Cl<sub>2</sub>, [Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>]<sub>2</sub><sup>+</sup> is stable on the cyclic voltammetric time scale, but in CH<sub>3</sub>CN, it dissociates rapidly.<sup>14b</sup>

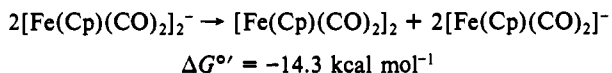


$$\Delta G^\circ = -27 \text{ kcal mol}^{-1}$$

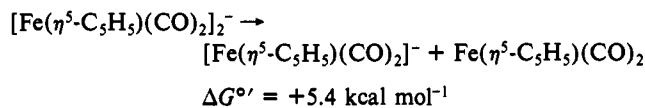
Where data are available, the one-electron-reduced anions are also unstable toward disproportionation;  $\Delta G^\circ = -22.5$  kcal mol<sup>-1</sup> for [Mo(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]<sub>2</sub><sup>-</sup>.

(31) Hughey, J. L.; Meyer, T. J. *Inorg. Chem.* **1975**, *14*, 947.

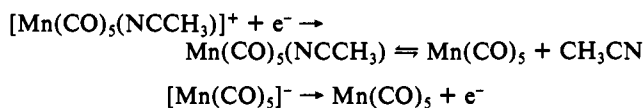




The anion  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2^-$  is stable with respect to dissociation, but  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2^-$  is not ( $\Delta G^{\circ'} = -0.27 \text{ kcal mol}^{-1}$ ).

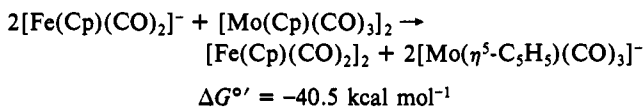


**The Adjacent Oxidation States.** The requirement of one-electron oxidation or reduction of the  $(d\pi)^4$  or  $(d\pi)^6$  cations or the corresponding anions also causes the overvoltages that occur in their voltammograms.

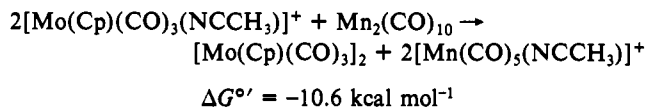


Overvoltages are +1.82 V for  $2[\text{Mn}(\text{CO})_5(\text{NCCH}_3)]^+/\text{Mn}_2(\text{CO})_{10}$  and +0.51 V for  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2/2[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ . For electron transfer in solution the order of reactivity as one-electron oxidants should fall in the order  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{NCCH}_3)]^+ > [\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCCH}_3)]^+ > [\text{Mn}(\text{CO})_5(\text{NCCH}_3)]^+$  and as reductants  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^- \gg [\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ ,  $\text{Mn}(\text{CO})_5^-$ . This assumes that reorganizational energies are comparable or negligible.

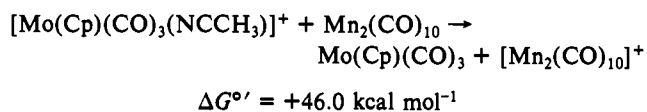
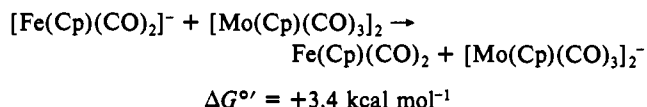
The anion  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]^-$  is capable of reducing either  $\text{Mn}_2(\text{CO})_{10}$  or  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]_2^-$ .



The cation  $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3(\text{NCCH}_3)]^+$  is capable of oxidizing either  $\text{Mn}_2(\text{CO})_{10}$  or  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]_2^-$ .



These results are qualitatively consistent with the results reported recently by Corraïne and Atwood.<sup>11</sup> A kinetic inhibition is expected in either case since the initial one-electron steps are non-spontaneous and the  $\Delta G^{\circ'}$  values represent minimum free energies of activation.



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**Registry No.** TQ<sup>+</sup>, 67509-62-0; PQ<sup>2+</sup>, 4685-14-7; DQ<sup>2+</sup>, 2764-72-9; TBAH, 3109-63-5;  $\text{Mn}_2(\text{CO})_{10}$ , 10170-69-1;  $\text{Mn}(\text{CO})_5(\text{NCCH}_3)^+$ , 27674-37-9;  $[\text{Fe}(\text{Cp})(\text{CO})_2]_2$ , 12154-95-9;  $[\text{Ru}(\text{bpy})_3]^+$ , 56977-24-3;  $[\text{Fe}(\text{Cp})(\text{CO})_2(\text{NCCH}_3)]^+$ , 46134-92-3;  $[\text{Mo}(\text{Cp})(\text{CO})_3]_2$ , 12091-64-4;  $[\text{Os}(\text{bpy})_2\text{Cl}_2]^+$ , 15702-72-4;  $[\text{Mo}(\text{Cp})(\text{CO})_3(\text{NCCH}_3)]^+$ , 68868-63-3;  $[\text{Mn}(\text{CO})_5]^-$ , 14971-26-7;  $[\text{Fe}(\text{Cp})(\text{CO})_2]^-$ , 12107-09-4;  $[\text{Mo}(\text{Cp})(\text{CO})_3]^-$ , 12126-18-0;  $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ , 84117-36-2;  $[\text{Os}(\text{bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]$ , 139759-59-4;  $[\text{Os}(5,5'-(\text{CO}_2\text{NEt}_2)_2\text{-bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ , 139869-56-0;  $[\text{Os}(\text{bpyz})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ , 89689-63-4;  $[\text{Os}(5,5'-(\text{CO}_2\text{Et})_2\text{-bpy})(\text{PPh}_3)_2(\text{CO})\text{H}]^+$ , 139759-65-2;  $[\text{Mn}(\text{CO})_5]$ , 14971-26-7;  $[\text{Mn}_2(\text{CO})_{10}]^+$ , 119886-99-6;  $[\text{Mn}_2(\text{CO})_{10}]^-$ , 64539-72-6;  $[\text{Fe}(\text{Cp})(\text{CO})_2]_2$ , 55009-40-0;  $[\text{Fe}(\text{Cp})(\text{CO})_2]_2^+$ , 91760-55-3;  $[\text{Fe}(\text{Cp})(\text{CO})_2]_2^-$ , 91864-52-7;  $[\text{Mo}(\text{Cp})(\text{CO})_3]$ , 12079-69-5;  $[\text{Mo}(\text{Cp})(\text{CO})_3]_2^+$ , 139759-60-7;  $[\text{Mo}(\text{Cp})(\text{CO})_3]_2^-$ , 139759-61-8;  $\text{CH}_3\text{CN}$ , 75-05-8; Fe, 7439-89-6; Mo, 7439-98-7; Mn, 7439-96-5.