$$\Delta G^{*} = \frac{\lambda_i + \lambda_o}{4} + \frac{\Delta G^{\circ}_r}{2} + \frac{(\Delta G^{\circ}_r)^2}{4(\lambda_i + \lambda_o)} \qquad (13)$$

reaction where the redox partners are preassembled. ΔG°_r is the standard free energy change for internal electron transfer within the binuclear complex. The solvent reorganization term is given by eq 14,[34] where e is the electronic charge, a_1 and a_2 are the radii

$$\lambda_o = e^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (14)$$

of the two reactants (assumed to be spherical), r is the distance between the metal ions in the transition state, and D_{op} and D_s are the optical and static dielectric constants of the medium, respectively. If λ_i, ΔG_r°, a_1, and a_2 do not change much along a series of compounds and the third term in eq 13 is small compared to $(\lambda_i/4) + (\Delta G_r^{\circ}/2)$, then it can be shown that eq 15 should be

$$\Delta G^{*} = \text{int} - \text{slope}/d \qquad (15)$$

obeyed where slope = 45 kcal if d is expressed in angstroms.[37] The experimental values of the slopes are 33.4 and 30.9 kcal for ruthenium and iron, respectively. For optical electron transfer in $(bpy)_2ClRuLRuCl(bpy)_2^{3+}$, the slope found previously was 27.7 kcal in acetonitrile (theoretical value 43.5 kcal).[38] The disagreement between theory and experiment is not unexpected in view of all the approximations used in deriving eq 15. Undoubtedly, other factors such as changes in the redox potentials of the metal centers and differences in inner-shell reorganization energies as the bridging ligand varies also contribute to the variation in rate. However, when the contributions of these factors are relatively constant for a series of related compounds, then the outer-sphere reorganization terms, although small compared to the inner-sphere terms of cobalt–ammine complexes, appear to determine the relative rate constants of intramolecular electron transfer.

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Studies of the Photochemical Behavior of $Fe_3(CO)_{11}^{2-}$ in Solution

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Abstract: Irradiation (λ = 504 nm) of $Fe_3(CO)_{11}^{2-}$ in the presence of PPh_3 in CH_3CN solution yields $Fe(CO)_4^{2-}$ + $Fe(CO)_3(PPh_3)_2$ + CO. The reaction is inhibited in the presence of excess CO. The mechanism of the photoreaction is proposed to involve loss of CO to give $Fe_3(CO)_{10}^{2-}$; in the presence of PPh_3, $Fe_3(CO)_{10}^{2-}$ reacts to give $2Fe(CO)_3(PPh_3)_2 + Fe(CO)_4^{2-}$. The fact that the primary photoprocess does not involve cluster fragmentation is attributed to the presence of the face-bridging CO ligands in $Fe_3(CO)_{11}^{2-}$, which inhibit geometrical rearrangement of photogenerated diradical species and facilitate metal–metal bond formation. Ultraviolet irradiation (λ ≤ 313 nm) of $Fe_3(CO)_{11}^{2-}$ in 1 M NaOH solutions gives the following reaction: $Fe_3(CO)_{11}^{2-} \rightarrow Fe(CO)_4^{2-} + 2Fe(OH)_2 + 2H_2 + 7CO$. The first step in the mechanism of this photoreaction is not known; one possibility is that the metal cluster fragments directly at these higher excitation energies; alternatively, initial Fe–CO dissociation may precede fragmentation. In either case, it is proposed that photogenerated $Fe(CO)_n$ (n = 3 or 4) fragments are oxidized to $Fe(OH)_2$ in the basic aqueous medium, thereby producing H_2.

Introduction

Ultraviolet irradiation of hydrido transition-metal complexes in solution often leads to hydrogen production.[1] A system of this type that attracted our interest was reported by Hieber and Schubert in 1965.[2]

$$3HFe(CO)_4^- + H_2O \xrightarrow{\text{UV}} 2H_2 + Fe_3(CO)_{11}^{2-} + CO + OH^- \qquad (1)$$

It occurred to us that a study of the solution photochemistry of $Fe_3(CO)_{11}^{2-}$ might allow us to find conditions whereby the trinuclear species could be photofragmented to three molecules of $HFe(CO)_4^-$ (for $H_2Fe(CO)_4$, pK_a(1) = 4.4; pK_a(2) = 14),[3] as in eq 2. The CO_2 and two of the $HFe(CO)_4^-$ ions in eq 3 presumably

$$Fe_3(CO)_{11}^{2-} + 3CO + OH^- + \xrightarrow{h\nu} 3HFe(CO)_4^- + 2CO_2 \qquad (2)$$

would come from the known reaction of $Fe(CO)_5$ with OH^-.[4] Coupling the reactions described by eq 1 and 2 would result in a photochemical water-gas shift cycle (eq 3).

$$H_2O + CO \xrightarrow[Fe_3(CO)_{11}^{2-}]{h\nu} H_2 + CO_2 \qquad (3)$$

With this goal in mind, we began an investigation of the photochemical behavior of $Fe_3(CO)_{11}^{2-}$ in aqueous and nonaqueous solutions. Although we have not achieved the desired cyclic photoprocess (eq 3), we have found that the solution photochemistry of $Fe_3(CO)_{11}^{2-}$ is rich; visible irradiation of the trinuclear species in the presence of PPh_3 gives $Fe(CO)_4^{2-}$ and $Fe(CO)_3(PPh_3)_2$; and H_2, $Fe(CO)_4^{2-}$, $Fe(OH)_2$, and CO are produced by ultraviolet irradiation of the cluster dianion in basic aqueous solution. In this paper we report the characterizations of these and related photoreactions as well as a brief discussion of their probable mechanisms.

Experimental Section

The iron–carbonyl anions decompose when exposed to air. All manipulations were carried out in a nitrogen atmosphere glovebox or on a vacuum line. Solvents were rigorously dried by standard techniques.[5]

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$[Ni(NH_3)_6][Fe_3(CO)_{11}]$ was prepared by the method of Hieber and Brendal.[4] This salt was used for the photolyses done in aqueous solution. The compound was dissolved in NaOH solution, and the Ni^{2+} was precipitated as $Ni(OH)_2$ and removed by filtration. This avoided the possibility of any interference by the Ni^{2+} during the photolysis. For photolyses in organic solvents the PPN^+ salt of $Fe_3(CO)_{11}^{2-}$ was used (PPN^+ = triphenylphosphine)iminium cation). This salt was obtained by adding a solution of [PPN]Cl in methanol to the solution of $Fe_3(CO)_{11}^{2-}$ prepared in the reaction of OH^- with $Fe_3(CO)_{12}$.[4] $[PPN]_2[Fe_3(CO)_{11}]$ was recrystallized in the following manner using a swivel-frit assembly on a vacuum line. The compound was dissolved in the minimum amount of hot CH_2Cl_2. Petroleum ether (30–60 °C) was vacuum distilled into the hot CH_2Cl_2 solution just to the point of $[PPN]_2[Fe_3(CO)_{11}]$ crystallization. Upon being cooled, the compound crystallized; the crystals were filtered and then washed with petroleum ether. If this procedure was done quickly, pure crystals of $[PPN]_2[Fe_3(CO)_{11}]$ were obtained. However, $Fe_3(CO)_{11}^{2-}$ is oxidized slowly in CH_2Cl_2 to give $Fe_4(CO)_{13}^{2-}$. If $Fe_3(CO)_{11}^{2-}$ in CH_2Cl_2 solution was allowed to stand for long periods of time, then the tetranuclear dianion was found as an impurity in the recrystallized product.

Photolyses were performed in special two-arm evacuable cells. $[PPN]_2[Fe_2(CO)_{11}]$ was placed in one side arm, and organic solvents were vacuum distilled into the other side arm. Several freeze-pump-thaw cycles were used to degas the solvents. Only after this degassing was the solvent allowed to mix with the $[PPN]_2[Fe_3(CO)_{11}]$ in the other side arm. Thick-walled quartz or glass cells equipped with Kontes quick-release Teflon valves were used for the photolyses done under CO pressure. Pressures up to 6 atm were obtainable in these cells. All photolyses were performed at room temperature.

Electronic absorption spectra were recorded on a Cary 17 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 225 instrument. A 1000-W high-pressure Hg–Xe arc lamp in conjunction with Corning cutoff filters or interference filters and a low-pressure Hg lamp were used for the irradiations.

Ferrioxalate actinometry was used for quantum yield determinations at 254, 313, and 366 nm.[6] The procedure was modified to adopt the precautions suggested by Bowman and Demas.[7] Reineke actinometry was employed for quantum yields at 504 nm.[8] In all cases, the quantum yields were determined by monitoring the disappearance of the 485-nm band in $Fe_3(CO)_{11}^{2-}$ (504 nm for $[PPN]_2[Fe_3(CO)_{11}]$ in CH_3CN solution). Quantitative measurements of the amounts of CO and H_2 evolved during irradiations ($\lambda < 313$ nm) of $Fe_3(CO)_{11}^{2-}$ in aqueous NaOH solutions were done as follows. The total volume of gas evolved in the reaction was measured by Toepler pumping the stirred photolyzed solution into a known volume and manometrically measuring the pressure. The gases were then passed through a heated CuO column. This oxidized the H_2 to H_2O and the CO to CO_2. The H_2O was condensed in a Dry Ice–acetone cooled trap, and the amount of CO_2 (which has considerable vapor pressure at −78 °C) was measured by Toepler pumping into a known volume and measuring the pressure. The amount of H_2 was computed by differences from the total amount of gas and the amount of CO found. Typically, 0.03–0.08 mmol of H_2 and CO_2 were collected, and the measurements were reproducible to within 10%. To measure the amount of Fe(II) formed in these strongly alkaline solutions, we used the analytical reagent 4,7-dihydroxy-1,10-phenanthroline (G. Frederick Smith Chemical Co.). Schilt, Smith, and Heimbuch have described the use of this reagent.[9] The formation of $Fe(CO)_4^{2-}$ by irradiation of $Fe_3(CO)_{11}^{2-}$ in nonaqueous solvents was followed directly by using infrared spectroscopy ($\nu_{CO} = 1750$ cm^{-1}). Hieber has reported[2] that $Fe_3(CO)_{11}^{2-}$ slowly reacts with H_2O, according to eq 4. Control experiments

$$Fe_3(CO)_{11}^{2-} \xrightarrow{H_2O} 3Fe(OH)_2 + 4H_2 + 11CO \qquad (4)$$

showed that corrections for this thermal reaction were unnecessary on the time scale of the photolyses.

Results

The prominent features in the electronic absorption spectrum of $Fe_3(CO)_{11}^{2-}$ in an aqueous 1 M NaOH solution are a band at 485 nm and a shoulder at 340 nm (Figure 1). The two bands in $Fe_3(CO)_{11}^{2-}$ are blue shifted with respect to their counterparts in $Fe_3(CO)_{12}$, thereby ruling out an MLCT assignment. Based on our study of $Fe_3(CO)_{12}$,[10] we suggest that the lowest energy band (485 nm) is due to a $\sigma^{*\prime} \rightarrow \sigma^*$ transition and the shoulder at 340 nm to $\sigma \rightarrow \sigma^*$.

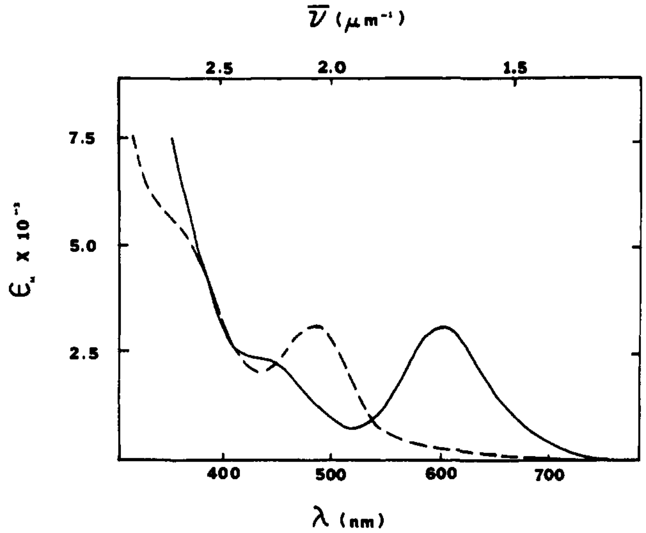

Figure 1. Electronic absorption spectra of $[Ni(NH_3)_6][Fe_3(CO)_{11}]$ in 1 M NaOH (- - -) and $Fe_3(CO)_{12}$ in 2-methylpentane (—) at 25 °C. The 485-nm band in the spectrum of $Fe_3(CO)_{11}^{2-}$ shifts to 504 nm for the PPN^+ salt in CH_3CN solution.

Table I. Quantum Yields for $Fe_3(CO)_{11}^{2-}$ Photoreactions

$$Fe_3(CO)_{11}^{2-} \xrightarrow{1\ M\ NaOH\ (aq)} Fe(CO)_4^{2-} + 2Fe(OH)_2 + 7CO + nH_2$$

wavelength, (nm)	504	366	313	254
quantum yield	*a*	*a*	5.5×10^{-3}	1.1×10^{-2}

$$Fe_3(CO)_{11}^{2-} \xrightarrow{PPh_3/CH_3CN} Fe(CO)_4^{2-} + 2Fe(CO)_3(PPh_3)_2 + CO$$

wavelength (nm)	504	366	313	254
quantum yield	5.1×10^{-3}	5.0×10^{-3}	*b*	*b*

[a] Too small to measure. [b] At these wavelengths absorption by the PPN^+ cation prohibited measurement.

When a 1 M NaOH solution containing $Fe_3(CO)_{11}^{2-}$ is irradiated ($\lambda \leq 313$ nm), the characteristic brown color of the dianion disappears to give a colorless solution. Vigorous evolution of CO and H_2 from the solution (confirmed by mass spectral analysis) accompanies the bleaching, and a white precipitate of $Fe(OH)_2$ is formed, the latter material being extremely air sensitive. The photoreaction stoichiometry is given by eq 5. In a typical ex-

$$Fe_3(CO)_{11}^{2-} \xrightarrow[1\ M\ NaOH]{\lambda \leq 313\ nm} Fe(CO)_4^{2-} + 2Fe(OH)_2 + 7CO + 2H_2 \qquad (5)$$

periment, exhaustive photolysis of $Fe_3(CO)_{11}^{2-}$ (9.8×10^{-6} mol) yielded CO (6.4×10^{-5} mol) and H_2 (1.48×10^{-5} mol); in an experiment in which Fe(II) was analyzed, 2.5×10^{-7} mol $Fe_3(CO)_{11}^{2-}$ gave 4.75×10^{-7} mol of Fe(II). The other iron-containing product is $Fe(CO)_4^{2-}$, as shown by adjusting the pH to 8 followed by irradiation, thereby giving $Fe_3(CO)_{11}^{2-}$ according to eq 1. In this photochemical experiment the colorless solution quickly yielded a brown product with an absorption band maximum (485 nm) characteristic[2] of $Fe_3(CO)_{11}^{2-}$.

The aqueous solution photolyses were done in strong base to avoid protonation of $Fe(CO)_4^{2-}$ and the subsequent photolysis of $HFe(CO)_4^-$ (eq 1). The 7 mol of CO presumably come from the decomposition of photogenerated iron–carbonyl fragments, $Fe(CO)_4$ and $Fe(CO)_3$. The Fe(0) is oxidized to Fe(II) and H_2 is the reduction product. Attempts to trap the $Fe(CO)_3$ and the $Fe(CO)_4$ fragments with CO in aqueous solution failed. The

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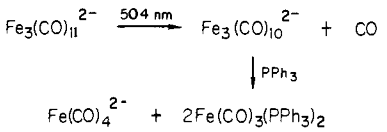
Scheme I



quantum yields for the reaction (eq 5) at various wavelengths are given in Table I.

No reaction was observed upon irradiation of $Fe_3(CO)_{11}^{2-}$ under several atmospheres of CO in CH_3CN solution. However, when $Fe_3(CO)_{11}^{2-}$ is irradiated ($\lambda = 504$ nm) with a fivefold excess of PPh_3 in acetonitrile solution,[11] the disappearance of $Fe_3(CO)_{11}^{2-}$ is accompanied by the appearance of a yellow precipitate of $Fe(CO)_3(PPh_3)_2$. An infrared spectrum of the yellow compound in CH_3CN solution showed a single band at 1880 cm^{-1} in the carbonyl stretching region. For comparison, Clifford and Mukherjee reported[12] that $Fe(CO)_3(PPh_3)_2$ has a CO band at 1884.4 cm^{-1} in CS_2. As $Fe(CO)_3(PPh_3)_2$ is virtually insoluble in cold CH_3CN, the precipitate was filtered from a cold solution, dried, and then weighed. In a typical experiment, 0.05055 g of $(PPN)_2Fe_3(CO)_{11}$ yielded 0.03770 g of $Fe(CO)_3(PPh_3)_2$ upon exhaustive photolysis; i.e., the mol ratio $Fe_3(CO)_{11}^{2-}$:$Fe(CO)_3(PPh_3)_2$ was 1.8:1. A mass spectral analysis of the gas above the photolysis solution showed that CO (but no H_2) was evolved in the reaction. A quantitative study showed an approximate 1:1 mol ratio of CO:$Fe_3(CO)_{11}^{2-}$ (2.4×10^{-2} mmol of $[PPN]_2[Fe_3(CO)_{11}]$ gave 2.1×10^{-2} mmol of CO in a Toepler-pump experiment).

Infrared spectroscopic monitoring of the photoreaction between $Fe_3(CO)_{11}^{2-}$ and PPh_3 showed, in addition to the band at 1880 cm^{-1} due to $Fe(CO)_3(PPh_3)_2$, the appearance of a band at 1750 cm^{-1} due to $Fe(CO)_4^{2-}$.[13] In experiments where the CH_3CN had not been rigorously dried, bands at 2000, 1910, and 1880 cm^{-1} also appeared, due to $HFe(CO)_4^-$.[13] No other carbonyl stretching bands were present. In particular, the absence of bands at 2055, 1978, and 1943 cm^{-1} and at 2064, 1976, and 1959 cm^{-1} showed that neither $Fe(CO)_4(PPh_3)$[12] nor $Fe(CO)_4(CH_3CN)$[14] formed. Control experiments showed that $Fe(CO)_4(PPh_3)$ did not react with PPh_3 to give $Fe(CO)_3(PPh_3)_2$ when irradiated at 504 nm.

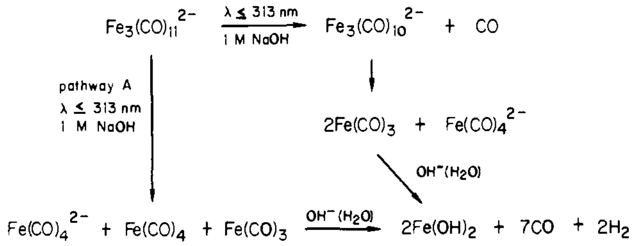
The above results establish that the photoreaction between $Fe_3(CO)_{11}^{2-}$ and PPh_3 in acetonitrile solution proceeds according to eq 6. The quantum yields for the reaction (eq 6) are given in Table I.

$$Fe_3(CO)_{11}^{2-} \xrightarrow[\lambda = 504\ nm]{PPh_3} 2Fe(CO)_3(PPh_3)_2 + CO + Fe(CO)_4^{2-} \tag{6}$$

Irradiation of $Fe_3(CO)_{11}^{2-}$ and dppe (1,2-bis(diphenylphosphino)ethane) in CH_3CN solution produces $Fe(CO)_3(dppe)$. Note that the photochemical method of preparation of $Fe(CO)_3(dppe)$ is much simpler than conventional procedures.[15] The product has IR bands at 1978, 1907, and 1888 cm^{-1} in the carbonyl region in CH_3CN solution (these positions accord closely with infrared frequencies of 1984, 1912, and 1890 cm^{-1} for $Fe(CO)_3(dppe)$ in tetrachloroethylene solution).[15]

When $[PPN]_2[Fe_3(CO)_{11}]$ is irradiated ($\lambda > 320$ nm) in CH_2Cl_2 with no phosphine present, the products formed are $Fe(CO)_4^{2-}$ and $Fe_4(CO)_{13}^{2-}$ (1980 and 1950 cm^{-1}).[13] The addition of PPh_3 to the photolysis solution (100-fold molar excess) inhibited the formation of $Fe_4(CO)_{13}^{2-}$. In this case, as in CH_3CN, $Fe(CO)_4^{2-}$ and $Fe(CO)_3(PPh_3)_2$ were the carbonyl-containing products.

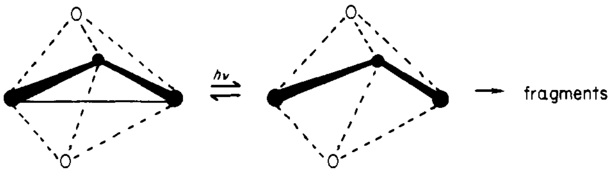
Scheme II



Discussion

Our proposed pathway for the photofragmentation of $Fe_3(CO)_{11}^{2-}$ in CH_3CN solution is outlined in Scheme I. The following experimental facts support Scheme I: (1) CO inhibits the photochemical reaction; (2) in the presence of PPh_3, the photoreaction stoichiometry is 2:1:1 mol ratio $Fe(CO)_3(PPh_3)_2$:CO:$Fe_3(CO)_{11}^{2-}$; and (3) the formation of $Fe(CO)_4^{2}$ can be observed directly by using infrared spectroscopy.

The intriguing feature of Scheme I is that cluster fragmentation is not the primary photoprocess. It is reasonable to expect that population of the $\sigma^{*\prime}\sigma^*$ state in triangular Fe_3 clusters leads to homolytic cleavage to one metal–metal bond, producing a diradical species.



In the case of $Fe_3(CO)_{12}$ (but not $Os_3(CO)_{12}$),[16] fragmentation is clearly competitive with reformation of the metal–metal bond.[17] However, if bridging groups are present, as in $Fe_3(CO)_{11}^{2-}$,[18] cluster fragmentation apparently is inhibited to such an extent that the metal–metal bond reforms. Loss of CO must then occur directly either from an electronic excited state of $Fe_3(CO)_{11}^{2-}$ or from the diradical intermediate.

It is emerging that direct cluster fragmentation is not a common reaction pathway for the lowest cluster-localized excited state of polynuclear carbonyl complexes that possess bridging ligands. For example, $Fe_3(CO)_{10}NSi(CH_3)_3$ (triply bridging $NSi(CH_3)_3$ group) photochemically substitutes H_2 or PR_3 for CO without any fragmentation.[19] Recent work in our laboratory has demonstrated[20] that the photosubstitution reactions of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ (two bridging CO ligands) do not involve 17-electron fragments as intermediates. And Geoffroy and co-workers have shown[21] that $HCCo_3(CO)_9$ (face-bridging CH group) photochemically substitutes PPh_3 for CO.

Photolysis ($\lambda = 504$ nm) of $Fe_3(CO)_{11}^{2-}$ in CH_2Cl_2 yields $Fe_4(CO)_{13}^{2-}$ in addition to $Fe(CO)_4^{2-}$. In the absence of good nucleophiles, $Fe_3(CO)_{10}^{2-}$ produced by photodissociation of CO from $Fe_3(CO)_{11}^{2-}$ may fragment to $2Fe(CO)_3$ and $Fe(CO)_4^{2-}$; any $Fe(CO)_3$ formed could react with $Fe_3(CO)_{11}^{2-}$ (eq 7). Such a

$$Fe_3(CO)_{11}^{2-} + Fe(CO)_3 \rightarrow Fe_4(CO)_{13}^{2-} + CO \tag{7}$$

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(11) $Fe_3(CO)_{11}^{2-}$ in CH_3CN solution reacts in the dark at room temperature with PPh_3 when the phosphine is present in large excess. However, when the mol ratio of PPh_3:$Fe_3(CO)_{11}^{2-}$ is kept below 5:1, the dark reaction is negligible.

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reaction is likely in view of the fact that $Fe(CO)_5$ reacts with $Fe_3(CO)_{11}^{2-}$ at elevated temperatures to produce $Fe_4(CO)_{13}^{2-}$.[22]

$$\mathrm{Fe_3(CO)_{11}^{2-} + Fe(CO)_5 \xrightarrow{\Delta} Fe_4(CO)_{13}^{2-} + 3CO} \tag{8}$$

Dissociation of CO from $Fe(CO)_5$ is known to occur readily at high temperatures, so the thermal reaction probably also proceeds by attack of an $Fe(CO)_n$ (n = 3 or 4) fragment on $Fe_3(CO)_{11}^{2-}$. Evidence that Fe—CO dissociation is still the primary photoprocess in CH_2Cl_2 solution is our observation that 1 atm of CO inhibits the photoreaction.

The aqueous solution photochemistry of $Fe_3(CO)_{11}^{2-}$ is readily understood in terms of either of the pathways outlined in Scheme II. Direct fragmentation of the $Fe_3(CO)_{11}^{2-}$ cluster could occur at the relatively high excitation energies involved (pathway A). Pathway B is similar to the mechanism in Scheme I in that Fe–CO dissociation is the primary photoprocess. Note that two Fe(0) fragments are formed along either pathway. In the absence of trapping agents these fragments are expected to be unstable with respect to oxidation; such redox decomposition gives two molecules of $Fe(OH)_2$ and two molecules of H_2.

Acknowledgment. This research was supported by National Science Foundation Grant No. CHE78-10530.

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Electronic Spectra of Copper(II)-Imidazole and Copper(II)-Pyrazole Chromophores

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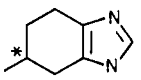
Abstract: Solution spectra covering the 50 000–20 000-cm^{-1} region are reported for tetrakis complexes of Cu(II) with various imidazole and pyrazole ligands. Such complexes exhibit three ligand to metal charge-transfer (LMCT) absorptions, which originate from the sp^2-type nitrogen lone pair (n) and from two π-symmetry ring orbitals, one (HOMO, π_1) with mostly carbon character and the other (π_2) with substantial nitrogen character. The π-symmetry absorptions are relatively weak and poorly resolved for solutions containing tetrakis complexes of Cu(II) with either unsubstituted imidazole or pyrazole. Alkylation of either type of ligand causes the π-symmetry absorptions to be prominent well-resolved features of the solution spectra. Tetragonal Cu(II) complexes containing alkylated ligands of *either* type exhibit absorptions at approximately 46 000 cm^{-1} (ligand $\pi \rightarrow \pi^*$ and n(ligand) $\rightarrow$ Cu(II) LMCT), 33 000 cm^{-1} (π_2(ligand) $\rightarrow$ Cu(II) LMCT), 29 000 cm^{-1} (π_1(ligand) $\rightarrow$ Cu(II) LMCT), and 16 000 cm^{-1} (ligand field transitions). The electronic structures, ligand $\pi \rightarrow \pi^*$ absorptions, and ligand $\rightarrow$ Cu(II) LMCT absorptions are very similar for imidazoles and pyrazoles. Published LMCT spectra of various pyrazolylborate– and pyrazolylgallate–Cu(II) complexes have been reassigned from the above point of view. The LMCT absorptions exhibited by a pseudotetrahedral Cu(II) complex of this type are red shifted by 10 000–12 000 cm^{-1} relative to planar Cu(II) reference complexes. Analogous absorptions in the visible–near-UV spectra of type 1 copper proteins are thought to result from Cu(II)–imidazole ligation. Finally, circular dichroism spectra are presented of solutions containing Cu(II) and (+)-5-methyl-4,5,6,7-tetrahydrobenzimidazole.

In a previous paper we have characterized the ligand to metal charge-transfer (LMCT) absorptions of several model Cu(II)–imidazole (ImH) complexes.[1] These transitions originate from the three highest lying imidazole orbitals, i.e., the σ-symmetry nitrogen donor lone pair (n) and two π-symmetry ring orbitals (π_1, π_2). The solid-state spectra of tetragonal Cu(II)–ImH chromophores exhibit prominent n(ImH) $\rightarrow$, π_2(ImH) $\rightarrow$, and π_1(ImH) $\rightarrow$ Cu(II) LMCT absorptions at ~220, ~260, and ~330 nm, respectively; the $\pi \rightarrow \pi^*$ absorption of free and complexed ImH appears at ~205 nm. The $\pi \rightarrow$ M bands were not well-resolved features in the solution spectra of the same complexes, in contrast to the $\sigma \rightarrow$ M bands. We interpreted the broadening of the $\pi \rightarrow$ M bands as indicating that the Cu(II)–ImH units of the solution complexes adopt a range of conformations around the Cu–N axis. The $\sigma \rightarrow$ M absorption should be rather insensitive to such rotations. We report here an extension of these studies to Cu(II) complexes of 4,5-disubstituted imidazoles such as 4,5-diisopropylimidazole, 4,5-diethylimidazole, and 4,5,6,7-tetrahydrobenzimidazole. Solution spectra of these complexes exhibit well-resolved π_2(ImH) $\rightarrow$ Cu(II) and π_1(ImH) $\rightarrow$ Cu(II) bands. We also report preliminary circular dichroism spectra for the Cu(II) complex of (+)-5-methyl-4,5,6,7-tetrahydrobenzimidazole.



Finally, we present an analysis of the LMCT spectra of Cu(II)–pyrazole (Pz) complexes. The electronic structures of ImH and Pz are very similar, and we show that the LMCT spectra of Cu(II)–Pz complexes mirror those of Cu(II)–ImH complexes and also have considerable bioinorganic relevance. In particular, the LMCT spectra of an approximately tetrahedral Cu(II)–Pz chromophore allow the convincing prediction that analogous low energy absorptions are to be expected from the Cu(II)–ImH units in the type 1 copper proteins.[2]

Experimental Section

Preparation of 4,5-Diethylimidazole. Propionoin was prepared by the acyloin condensation[3] of ethyl propionate and converted to 4,5-diethylimidazole by reaction with refluxing formamide.[4] After removal of the

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[2] Solomon, E. I.; Hare, J. W.; Dooley, D. M.; Dawson, J. H.; Stephens, P. J.; Gray, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 168–178.

[3] Snell, J. M.; McElvain, S. M. "Organic Syntheses"; Wiley: New York, 1943; Collected Vol. II, pp 114–115.

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