$\mathrm{(CO)^+}$, 86696-04-0; $\mathrm{Cu(1\text{-}MePz)_2(CO)^+}$, 86696-05-1; $\mathrm{CuL_2(CO)^+}$ (L = 3,5-dimethylpyrazole), 86696-06-2; $\mathrm{CuL_2(CO)^+}$ (L = picoline), 86696-07-3; $\mathrm{Cu(1\text{-}MeIm)_3(CO)^+}$, 86696-08-4; $\mathrm{Cu(2\text{-}MeIm)_3(CO)^+}$, 86696-09-5; $\mathrm{Cu(4\text{-}MeIm)_3(CO)^+}$, 86696-10-8; $\mathrm{CuL_3(CO)^+}$ (L = 1,2-dimethylimidazole), 86696-11-9; $\mathrm{Cu(Pz)_3(CO)^+}$, 86696-12-0; $\mathrm{Cu(1\text{-}MePz)_3(CO)^+}$, 86696-13-1; $\mathrm{CuL_3(CO)^+}$ (L = 3,5-dimethylpyrazole), 86696-14-2; $\mathrm{CuL_3(CO)^+}$ (L = 2-picoline), 86696-15-3; $\mathrm{Cu(CH_3CN)_4BF_4}$, 15418-29-8; CO, 630-08-0; 1-benzyl-3,5-dimethylpyrazole, 1134-81-2; 3,5-dimethylpyrazole, 67-51-6.

Supplementary Material Available: Final hydrogen atom positions, listings of observed and calculated structure factors, and final thermal parameters for 6 and 8 (29 pages). Ordering information is given on any current masthead page.

Mechanisms of the Photoreactions of $\mathrm{Cp_2Fe_2(CO)_4}$ with Phosphines and Chlorocarbons

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Abstract: Irradiation ($\lambda > 500$ nm) of $\mathrm{Cp_2Fe_2(CO)_4}$ (Cp = η^5-$\mathrm{C_5H_5}$) in the presence of $\mathrm{PR_3}$ (R = Ph, O-*i*-Pr) in cyclohexane solution at room temperature yields a single product, $\mathrm{Cp_2Fe_2(CO)_3(PR_3)}$. The reaction with $\mathrm{PPh_3}$ (366 nm) is inhibited by excess CO. A reaction intermediate was trapped by irradiating $\mathrm{Cp_2Fe_2(CO)_4}$ in the presence of $\mathrm{P(O\text{-}\mathit{i}\text{-}Pr)_3}$ at −78 °C in ethyl chloride or THF solution. The infrared spectrum of the intermediate has $\nu(\mathrm{C{\equiv}O}) = 1720\ \mathrm{cm^{-1}}$, and its electronic spectrum does not exhibit a $\sigma \rightarrow \sigma^*$ band. The evidence suggests that the intermediate is $\mathrm{Cp(CO)_2Fe{-}CO{-}Fe(CO)(P(O\text{-}\mathit{i}\text{-}Pr)_3)Cp}$, a molecule in which a single CO bridges the Fe atoms and in which there is no direct Fe–Fe bond. The mechanism of the photoreaction of $\mathrm{PR_3}$ with $\mathrm{Cp_2Fe_2(CO)_4}$ is proposed to involve formation of the CO-bridged intermediate $\mathrm{Cp_2Fe_2(CO)_4(PR_3)}$, followed by loss of CO to give the product $\mathrm{Cp_2Fe_2(CO)_3(PR_3)}$. The 366-nm photoreaction of $\mathrm{Cp_2Fe_2(CO)_4}$ with $\mathrm{CCl_4}$ or $\mathrm{CHCl_3}$ to give $\mathrm{CpFe(CO)_2Cl}$ occurs mainly by a $\mathrm{CpFe(CO)_2}$ radical pathway, because the chlorine atom abstraction is not inhibited by 6 atm of CO.

Photochemical reactions of $\mathrm{Cp_2Fe_2(CO)_4}$ (Cp = η^5-$\mathrm{C_5H_5}$), a molecule in which there are two bridging carbonyl ligands,[2] have been reported in several papers.[3-6] For example, Gianotti has shown[3] that $\mathrm{Cp_2Fe_2(CO)_4}$ reacts photochemically with chlorocarbon solvents (eq 1). One reasonable possibility for the

$$\mathrm{Cp_2Fe_2(CO)_4} \xrightarrow[h\nu]{\mathrm{R{-}Cl}} \mathrm{2CpFe(CO)_2Cl} \qquad (1)$$

mechanism of this reaction involves homolytic cleavage of the Fe–Fe unit, followed by abstraction of Cl from R–Cl by the $\mathrm{CpFe(CO)_2}$ radical fragment.[3,4] However, there is some evidence that $\mathrm{CpFe(CO)_2}$ fragments are not formed on irradiation, namely, the observation that the photoreactions of $\mathrm{Cp_2Fe_2(CO)_4}$ with nucleophiles give monosubstituted products (eq 2). Caspar and

$$\mathrm{Cp_2Fe_2(CO)_4} + \mathrm{L} \xrightarrow[h\nu]{} \mathrm{Cp_2Fe_2(CO)_3L} + \mathrm{CO} \qquad (2)$$

Meyer have recently shown that two primary photoproducts result from either UV or visible flash photolysis of $\mathrm{Cp_2Fe_2(CO)_4}$ in cyclohexane or benzene.[7] They observed $\mathrm{CpFe(CO)_2}$ fragments as well as a long-lived intermediate that decayed by first-order kinetics. The long-lived intermediate reacted with donor ligands to give substituted products of the type $\mathrm{Cp_2Fe_2(CO)_3L}$.

Owing to our interest in metal cluster photochemistry, we decided to investigate further the photoreactions of $\mathrm{Cp_2Fe_2(CO)_4}$ with phosphines and chlorocarbons. The objective of our work was to determine whether 17-electron $\mathrm{CpFe(CO)_2}$ fragments are involved as intermediates in these reactions or whether some other pathway predominates. A preliminary account of our findings has appeared.[8]

Experimental Section

$\mathrm{Cp_2Fe_2(CO)_4}$ was obtained from ROC/RIC. Phosphine and phosphite derivatives of the type $\mathrm{Cp_2Fe_2(CO)_3(PR_3)}$ were prepared by a standard method.[6] Triphenylphosphine ($\mathrm{PPh_3}$) and trimethyl phosphite ($\mathrm{P(OMe)_3}$) were obtained from MCB. Tri-*n*-butylphosphine ($\mathrm{P(\mathit{n}\text{-}C_4H_9)_3}$) and triisopropyl phosphite ($\mathrm{P(O\text{-}\mathit{i}\text{-}Pr)_3}$) were obtained from Aldrich. Ethyl chloride was obtained from Eastman.

Electronic absorption spectra were recorded with a Cary 17 spectrophotometer. Infrared spectra were recorded with Perkin-Elmer 225 and Beckman IR-12 instruments. A 1000-W high-pressure Hg–Xe arc lamp was used for the 336-, 450-, and 505-nm and "broad-band" irradiations. The 366-nm Hg line was isolated by using a Corning CS 7-83 filter; the 450- and 505-nm lines were isolated by using dielectric interference filters obtained from Edmund Scientific Co. For the broad-band irradiations, Pyrex (λ >320 nm) and Corning CS 3-69 (λ >500 nm) filters were used. EPR spectra were recorded with a Varian E-line Century Series spectrometer, equipped with a 12-in. magnet. Temperature regulation was provided by an Air Products Heli-Trans system, and frequencies were determined with a PRD Electronics, Inc., frequency meter.

Ferrioxalate actinometry was used for quantum yield determinations at 366 nm.[9] The procedure was modified to adopt the precautions suggested by Bowman and Demas.[10] Reineke actinometry was used for quantum yields at 450 and 505 nm.[11] In all cases the quantum yields were determined by monitoring the disappearance of the 525-nm band in $\mathrm{Cp_2Fe_2(CO)_4}$. The absorption spectra of the phosphine substitution products $\mathrm{Cp_2Fe_2(CO)_3(PR_3)}$ overlap with the spectrum of $\mathrm{Cp_2Fe_2(CO)_4}$ at 525 nm. Thus, to minimize the error in the quantum yield measurement of the substitution reaction, only the first 10% of the reaction was monitored. At such small conversions the absorption by the product is

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small. Typical photon fluxes into the photolysis solution were 1 × 10^{-7}, 2 × 10^{-7}, and 2 × 10^{-7} einsteins/min at 366, 450, and 505 nm, respectively.

$Cp_2Fe_2(CO)_2(P(OMe)_3)_2$ was synthesized by adding 0.5 g of $Cp_2Fe_2(CO)_4$ to 1.0 mL of $P(OMe)_3$ in 125 mL of benzene which had previously been degassed by a nitrogen purge. The solution was then photolyzed ($\lambda > 500$ nm). The nitrogen purge was maintained during the photolysis. After 2 or 3 h of irradiation, the solution was concentrated and cooled. The greenish black $Cp_2Fe_2(CO)_2(P(OMe)_3)_2$ crystals were filtered from solution and dried in vacuo. Anal. Calcd for $C_{18}H_{28}Fe_2O_8P_2$: C, 39.6; H, 5.13; P, 11.34. Found: C, 39.45; H, 5.14; P, 11.22. The IR spectrum of $Cp_2Fe_2(CO)_2(P(OMe)_3)_2$ in cyclohexane solution exhibits CO stretching bands at 1718 and 2012 cm^{-1}.

Photolyses were done in special two-arm evacuable cells equipped with Kontes quick-release valves. One side was a glass bulb and the other side was a quartz spectrophotometer cell. Photolysis solutions in the glass bulb were degassed by three freeze–pump–thaw cycles. Electronic absorption spectral measurements were made after transferring the solution into the quartz cell. Thick-walled quartz or glass cells equipped with Kontes quick-release valves were used for irradiation experiments under CO pressure. Pressures up to 6 atm were obtained in these cells.

The infrared spectrum of the intermediate generated by irradiation of $Cp_2Fe_2(CO)_4$ with phosphines in low-temperature solution was recorded by using a Beckman low-temperature infrared cell. An aliquot of the solution containing the intermediate was transferred from the photolysis cell to the cell of the low-temperature apparatus. This procedure was carried out in a glovebag filled with nitrogen. The pipette used for the transfer and the infrared cell were precooled by placing them on a slab of dry ice in the glovebag. With practice, the transfer could be made without warming the reaction solution. After the infrared cell was filled, it was transferred to the cold head of the low-temperature apparatus (also in the glovebag). The cold head was precooled to avoid warming the solution. This rather elaborate procedure for obtaining the infrared spectrum of the intermediate was necessary because the intermediate only forms when the photolysis solution is freeze–pump–thaw degassed; the intermediate does not form if the solution has only been degassed by a nitrogen purge. As freeze–pump–thawing of the low-temperature infrared cell is not possible, the yellow intermediate could not be generated in situ in the infrared cell. Hence, the procedure above was used.

The electronic spectrum of the intermediate was obtained in a similar fashion by transferring the reaction solution to a quartz cell in an optical Dewar filled with a dry ice/acetone mixture. The Dewar has been described previously.[12]

Results

Irradiation ($\lambda > 500$ nm) of $Cp_2Fe_2(CO)_4$ in the presence of triisopropyl phosphite in cyclohexane solution at room temperature gives $Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3)$; the product was identified by IR measurements ($\nu(C{\equiv}O)$ = 1757, 1939, and 1961 cm^{-1} in cyclohexane solution; these values accord closely with those reported earlier).[6] A similar photoreaction occurs between $Cp_2Fe_2(CO)_4$ and PPh_3 (98 ± 2% conversion)[8] or tri-*n*-butylphosphine. Once again, infrared spectral measurements confirmed that only monosubstituted derivatives are formed. Slightly less than quantitative (86 ± 5%)[8] conversion occurs with $P(O\text{-}i\text{-}Pr)_3$ as reactant because the monosubstituted derivative slowly decomposes when irradiated. Although the decomposition products were not identified, the infrared spectrum of the photolysis solution showed that no new carbonyl bands were present. Thus, the disubstituted complex $Cp_2Fe_2(CO)_2(P(O\text{-}i\text{-}Pr)_3)_2$ is not one of the photolysis products. The reaction of $Cp_2Fe_2(CO)_4$ (1.5 × 10^{-3} M) with PPh_3 (10^{-2} M) in toluene is inhibited under 1 atm of CO at 366 nm. The quantum efficiency of the reaction is 36% lower under these conditions.

Irradiation ($\lambda > 500$ nm) of $Cp_2Fe_2(CO)_4$ and $P(OMe)_3$ in cyclohexane solution at room temperature results in quantitative conversion to $Cp_2Fe_2(CO)_2(P(OMe)_3)_2$ (eq 3). Neither electronic

$$Cp_2Fe_2(CO)_4 + 2P(OMe)_3 \xrightarrow[\lambda > 500\ nm]{} Cp_2Fe_2(CO)_2(P(OMe)_3)_2 + 2CO \quad (3)$$

absorption nor infrared spectroscopic measurements provided any evidence for the intermediacy of the monosubstituted complex in this photoreaction.

Table I. Quantum Yield Data for $Cp_2Fe_2(CO)_4$ Photoreactions

irradatn λ, nm	reactants[a]	product	ϕ[b]
366	CCl_4	$CpFe(CO)_2Cl$	0.42
	$CHCl_3$	$CpFe(CO)_2Cl$	0.19
	PR_3	$Cp_2Fe_2(CO)_3(PR_3)$	0.11
450	CCl_4	$CpFe(CO)_2Cl$	0.11
	$CHCl_3$	$CpFe(CO)_2Cl$	0.075
	PR_3	$Cp_2Fe_2(CO)_3(PR_3)$	0.065
505	CCl_4	$CpFe(CO)_2Cl$	0.067
	$CHCl_3$	$CpFe(CO)_2Cl$	0.074
	PR_3	$Cp_2Fe_2(CO)_3(PR_3)$	0.045

[a] Chlorocarbon reactants are solvents; the PR_3 (R = O-*i*-Pr) photoreactions were performed in cyclohexane solution with PR_3 in 100-fold excess. [b] Quantum yield (±10%) for the disappearance of $Cp_2Fe_2(CO)_4$.

We have found that $Cp_2Fe_2(CO)_3(P(OMe)_3)$ reacts photochemically with $P(OMe)_3$ in cyclohexane solution to give $Cp_2Fe_2(CO)_2(P(OMe)_3)_2$. This photoreaction is much faster than the reaction of $P(OMe)_3$ with $Cp_2Fe_2(CO)_4$. $P(OMe)_3$ will also react with $Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3)$ (eq 4). However, $P(O\text{-}i\text{-}Pr)_3$ does not react photochemically with $Cp_2Fe_2(CO)_3(P(OMe)_3)$.

$$Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3) + 2P(OMe)_3 \xrightarrow[\lambda > 500\ nm]{} Cp_2Fe_2(CO)_2(P(OMe)_3)_2 + P(O\text{-}i\text{-}Pr)_3 + CO \quad (4)$$

Irradiation ($\lambda > 500$ nm) of a solution of $Cp_2Fe_2(CO)_4$ and triisopropyl phosphite in ethyl chloride solution at −78 °C does not yield the green $Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3)$.[13] A photoreaction does occur, however, to produce a yellow intermediate species. When the solution is warmed to room temperature, the yellow intermediate disappears and the solution turns green. Similar observations were made with $P(n\text{-}C_4H_9)_3$ and $P(OMe)_3$ as reactants. Infrared spectral measurements showed that the green product is the monosubstituted binuclear species in the case of $P(O\text{-}i\text{-}Pr)_3$ or $P(n\text{-}C_4H_9)_3$; however, the disubstituted product forms in the case of $P(OMe)_3$.

Electronic absorption spectral measurements made during the low-temperature photolysis of $Cp_2Fe_2(CO)_4$ with $P(O\text{-}i\text{-}Pr)_3$ show that the bands due to $Cp_2Fe_2(CO)_4$ (λ_{max} = 525 and 350 nm) disappear. Eventually, the spectrum consists only of a rising absorption into the ultraviolet region. This is the spectrum we assign to the yellow intermediate. No bands or shoulders are discernible between 300 and 800 nm. When the solution is warmed, the electronic spectrum of $Cp_2Fe_2(CO)_3P(O\text{-}i\text{-}Pr)_3$ appears (λ_{max} = 568 and 370 nm). The infrared spectrum of the yellow intermediate in THF at −78 °C in the region 1900–1700 cm^{-1} shows a band at 1720 cm^{-1}. When the solution is warmed, the band at 1720 cm^{-1} disappears. No EPR signals attributable to the intermediate were found in measurements made at temperatures as low as 15 K. Finally, we note that if phosphine is not present in the low-temperature photolysis solution, the yellow intermediate is not observed.

When CCl_4 (0.5 mL) is vacuum distilled into a THF solution of the yellow intermediate (prepared by irradiation of $P(O\text{-}i\text{-}Pr)_3$ and $Cp_2Fe_2(CO)_4$ at −78 °C) and the solution warmed to room temperature in the dark, the only product is $CpFe(CO)_2Cl$. This product was identified by its infrared spectrum (2012 and 2055 cm^{-1} in CCl_4). Bands attributable to $Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3)$ were not observed. In a related reaction, addition of $P(OMe)_3$ (0.5 mL) to the yellow intermediate ($P(O\text{-}i\text{-}Pr)_3/Cp_2Fe_2(CO)_4$/−78 °C), followed by warming to room temperature in the dark, resulted in the formation only of $Cp_2Fe_2(CO)_2(P(OMe)_3)_2$ (IR spectral measurements showed that $Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3)$ was not present).

Irradiation of solutions of $Cp_2Fe_2(CO)_4$ in CCl_4 or $CHCl_3$ (10^{-4} M) at room temperature gives $CpFe(CO)_2Cl$ (eq 5). CpFe-

$$Cp_2Fe_2(CO)_4 \xrightarrow[\lambda > 500\ nm]{CCl_4\ or\ CHCl_3} 2CpFe(CO)_2Cl \quad (5)$$

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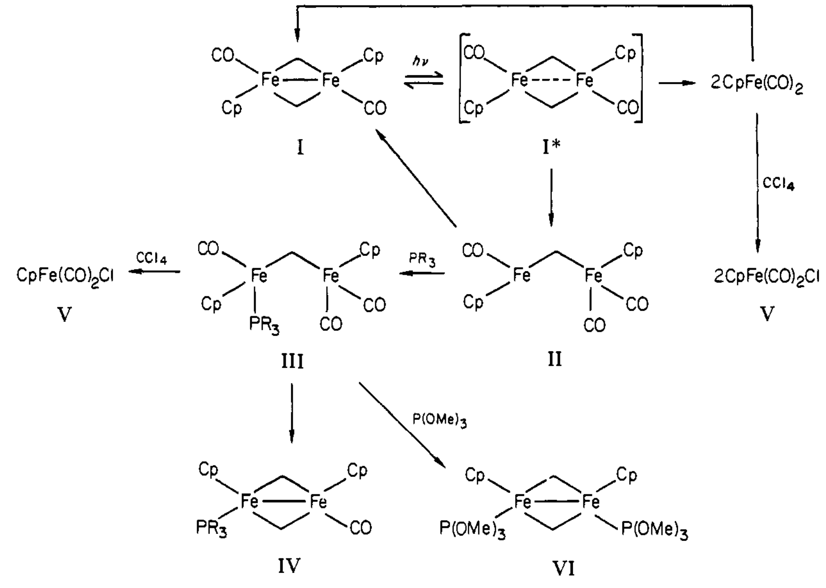
(12) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042.

(13) Similar results were obtained by using THF as solvent.

Scheme I



$(CO)_2Cl$ was identified by its infrared spectrum in the carbonyl region (2012 and 2060 cm^{-1} in $CHCl_3$).[14] The quantum yields for the reaction (eq 5) at various wavelengths are set out in Table I. The quantum yields are corrected for the dark reaction of $Cp_2Fe_2(CO)_4$ with solvent.[14] In contrast to the reaction with PPh_3, the reaction of $Cp_2Fe_2(CO)_4$ with CCl_4 (366 nm) is not inhibited by excess CO. We observed no decrease in the quantum efficiency of the reaction with CO pressures up to 6 atm.

Irradiation ($\lambda > 320$ nm) of a cyclohexane solution of $Cp_2Fe_2(CO)_4$ and $Mn_2(CO)_{10}$ gives a yellow product that exhibits three strong infrared absorption bands in the carbonyl stretching region (2082, 1993, and 1975 cm^{-1}). This yellow product was identified as the cross-coupled species $(CO)_5Mn{-}Fe(CO)_2Cp$ by comparison of its infrared spectrum to the reported literature spectrum.[15] Irradiation of the solution at wavelengths ($\lambda > 500$ nm) where only $Cp_2Fe_2(CO)_4$ absorbs produces no net photolysis.

The other cross-coupling reactions that we investigated in cyclohexane solution are shown in eq 6 and 7. In each case, the disappearance of the starting materials and the appearance of the products were followed by infrared spectroscopy.[6]

$$Cp_2Fe_2(CO)_4 + Cp_2Fe_2(CO)_2(P(OMe)_3)_2 \xrightarrow[\lambda > 500\text{ nm}]{} Cp_2Fe_2(CO)_3(P(OMe)_3) \quad (6)$$

$$2Cp_2Fe_2(CO)_3(P(OMe)_3) \xrightarrow[\lambda > 500\text{ nm}]{} Cp_2Fe_2(CO)_2(P(OMe)_3)_2 + Cp_2Fe_2(CO)_4 \quad (7)$$

When a CH_2Cl_2 solution of $Cp_2Fe_2(CO)_4$ ($\simeq 10^{-3}$ M) containing equimolar concentrations ($\simeq 0.1$ M) of CCl_4 and PPh_3 (or $P(OMe)_3$) is irradiated ($\lambda > 500$ nm), the only product is $CpFe(CO)_2Cl$. A similar result holds when $Cp_2Fe_2(CO)_4$ is irradiated in the presence of equimolar concentrations of $CHCl_3$ and phosphine.

Discussion

We propose that $Cp_2Fe_2(CO)_4$ reacts photochemically by the pathways outlined in Scheme I. The first step in this pathway is excitation of $d\pi\sigma^*$ or $\sigma\sigma^*$ states (collectively denoted I*); in these states the Fe–Fe bond is expected to be very weak. Two primary photoproducts result from I*: one is a 17-electron $CpFe(CO)_2$ fragment and the other is a binuclear intermediate (II) that contains a single bridging CO. We suggest that the reactions of $Cp_2Fe_2(CO)_4$ with chlorocarbons involve the $CpFe(CO)_2$ radical pathway, whereas the reactions with phosphines and phosphites proceed primarily through intermediate II.

We do not believe that simple homolytic cleavage of the bridged Fe–Fe unit is the productive photochemical step in the reactions with nucleophilic ligands, because near quantitative conversion to the monosubstituted complex occurs with PPh_3 or $P(O\text{-}i\text{-}Pr)_3$.[16] It is conceivable that only monosubstituted products could result from homolytic cleavage of the Fe–Fe unit if two substituted fragments, $CpFe(CO)(PR_3)$, were sterically unable to combine to form a dimer. However, a Stern–Volmer analysis rules out this alternative, at least for R = PPh_3.[8] Thus, it is necessary to postulate an intermediate other than the $CpFe(CO)_2$ fragment in the PR_3 substitution reactions of $Cp_2Fe_2(CO)_4$. Intermediate II is formed when one of the bridging Fe–CO bonds of I* is broken.

One of the Fe atoms in II is coordinatively unsaturated (16 electrons). This coordinatively unsaturated Fe can react with a phosphine to give III, which we propose is the thermally unstable yellow intermediate. The spectroscopic properties of the yellow intermediate are consistent with structure III. The infrared band at 1720 cm^{-1} is appropriate for a molecule with a bridging CO ligand,[17] and the absence of a $\sigma \rightarrow \sigma^*$ band in the electronic spectrum indicates that the Fe–Fe bond has been broken.[18] Finally, note that in the absence of phosphine, III will not form. In our proposed scheme the photosubstitution is completed by dissociation of CO from III, followed by reformation of the Fe–Fe bond. Complex III is kinetically stable at −78 °C, and these last steps occur at reasonable rates only at higher temperatures.[19]

The observed CO inhibition of the PR_3 substitution reactions cannot be explained by a mechanism in which $CpFe(CO)_2$ is the reactive intermediate. However, the inhibition is consistent with

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[14] Noack, K. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1383.

[15] King, R. B.; Treichel, P. M.; Stone, F. G. A. *Chem. Ind.* (*London*) **1961**, 747.

[16] Note that $Cp_2Fe_2(CO)_3(P(OMe)_3)$ undergoes rapid photosubstitution with $P(OMe)_3$ to give disubstituted product. Control experiments showed that $Cp_2Fe_2(CO)_3(P(OMe)_3)$ does not react with $P(OMe)_3$ at room temperature in the dark. It is reasonable to suggest that the larger phosphines do not form disubstituted products because the coordinatively unsaturated iron atom in the monosubstituted intermediate analogous to II is sterically crowded in such cases.

[17] Chini, P. *Pure Appl. Chem.* **1970**, *23*, 489.

[18] Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042.

[19] Recent studies have shown that many of the substitution reactions of 17-electron species are associatively activated (Shi, Q.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032. McCullen, S. B.; Walker, H. W.; Brown, T. L. *Ibid.* **1982**, *104*, 4007). Thus, one alternative to structure III is the 19-electron intermediate $CpFe(CO)_2(PR_3)$, formed by bimolecular attack of PR_3 on $CpFe(CO)_2$ and kinetically stable at −78 °C. The argument would be that the abnormally low (terminal) CO stretch at 1720 cm^{-1} is attributable to the extraordinary amount of π-backbonding due to the increased electron density on the Fe. While attractive because of its mechanistic simplicity (there is no need to postulate two pathways), it is not likely that III is a 19-electron species, because it is EPR silent in frozen solutions.

the intermediate formation of species II, because coordination of CO to the vacant coordination site in II would compete with coordination of PR_3 at the site and the quantum yield would decrease. The quantum yield data in Table I show that the CCl_4 photoreaction becomes more efficient relative to the PR_3 photoreaction as the irradiation wavelength decreases. This result is entirely reasonable in the context of our proposal of two reaction channels, because relatively more radicals should be formed from the more energetic excited states.

The finding that the long-lived intermediate generated by flash photolysis reacts with CCl_4[7] coupled with our discovery that CCl_4 reacts with III to give only $CpFe(CO)_2Cl$ establish that it is not necessary to postulate 17-electron fragment intermediates as primary photoproducts based only on an observation that a chlorine abstraction product forms. In our scheme the chlorocarbon could react directly either with II or III (in the latter case by displacing phosphine) to give $CpFe(CO)_2Cl$, thereby explaining why $CpFe(CO)_2Cl$ is the only product in the photolysis of $Cp_2Fe_2(CO)_4$ with equimolar amounts of CCl_4 and PR_3. However, the fact that 6 atm of CO does not markedly inhibit the reaction with CCl_4 suggests that the reaction of II with chlorocarbons is not very efficient compared to the radical pathway.

The relatively long-lived photoproduct observed by Caspar and Meyer was proposed[7] to be $Cp_2Fe_2(CO)_3$, formed by Fe–CO bond dissociation. This particular photoproduct absorbs strongly in the visible, and it reacts with CO and other ligands. Because II should have a visible absorption band attributable to charge-transfer excitation from the coordinatively saturated iron to the 16-electron ("CpFeCO") center,[20] the flash photolysis results[7] can be accommodated equally well in terms of our mechanistic scheme.

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Registry No. $Cp_2Fe_2(CO)_4$, 12154-95-9; $Cp_2Fe_2(CO)_2(P(OMe)_3)_2$, 71579-40-3; $Cp_2Fe_2(CO)_3(P(O\text{-}i\text{-}Pr)_3)$, 33218-96-1; $CpFe(CO)_2Cl$, 12107-04-9; $Mn_2(CO)_{10}$, 10170-69-1; $(CO)_5Mn\text{-}Fe(CO)_2Cp$, 12088-73-2; Fe, 7439-89-6; $P(OMe)_3$, 121-45-9; PPh_3, 603-35-0; $P(n\text{-}Bu)_3$, 998-40-3; $P(O\text{-}i\text{-}Pr)_3$, 116-17-6; CCl_4, 56-23-5; $CHCl_3$, 67-66-3.

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(20) As formulated, II would be expected to exhibit some degree of Fe(18-electron) → Fe(16-electron) charge transfer in its ground state. Thus, II could be viewed as a species in which there is metal–metal interaction of a donor–acceptor type. Relatively intense bands in the visible region are commonly observed in the absorption spectra of molecules that feature interactions of this sort.

Effects of Phenoxide Ligation on Iron–Sulfur Clusters. Preparation and Properties of $[Fe_4S_4(OAr)_4]^{2-}$ Ions and the Structure of $[(C_2H_5)_4N]_2[Fe_4S_4(OC_6H_5)_4]$

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Abstract: The phenoxide-ligated tetranuclear iron–sulfur clusters $[Fe_4S_4(OAr)_4]^{2-}$ (I, R = phenyl; II, R = *p*-tolyl) have been synthesized by reaction of $[Fe_4S_4(SR)_4]^{2-}$ or $[Fe_4S_4Cl_4]^{2-}$ with HOAr or NaOAr, respectively. The preparation, reactivity, and electronic properties of these compounds are described, as is the crystal structure of the Et_4N^+ salt of I. $[Et_4N]_2[Fe_4S_4(OPh)_4]$ crystallizes in the monoclinic space group C_{2h}^5—$P2_1/n$ with $Z = 4$ and unit-cell parameters $a = 17.610$ (4) Å, $b = 11.600$ (3) Å, $c = 22.810$ (6) Å, $\beta = 106.41$ (1)°, and $V = 4469.9$ Å^3 (−150 °C). The structure was refined to $R = 0.066$ and $R_w = 0.107$, using 6032 independent reflections with $F_o^2 > 3\sigma(F_o^2)$. The structure of I consists of an $[Fe_4S_4]^{2+}$ cubane core distorted toward D_{2d} symmetry, with a terminal phenoxide ligand completing the approximately tetrahedral coordination about each iron atom. The most notable structural feature is the short Fe–O distance (mean 1.865 (17) Å). Isotropically shifted resonances are observed in the ^1H NMR spectra of I and II; the directions and relative magnitudes of these shifts are consistent with significant delocalization of spin into the π system of the phenyl rings. At any temperature, the magnitude of the isotropic shifts is approximately twice that observed for the arenethiolate analogues. The magnitude of the isotropic shifts *increases* with increasing temperature, consistent with an antiferromagnetically coupled system. Variable-temperature magnetic susceptibility measurements are in agreement with the NMR data and give values of μ_{eff}/Fe of $\sim 1.3\mu_B$ at 25 °C. Zero field Mössbauer spectra of solid I show a single quadrupole doublet with parameters $\delta = 0.50$ and $\Delta E_Q = 1.21$ mm/s. Electrochemical data indicate that substitution of arenethiolate by phenolate ligands results in substantial *negative* shifts of first and second reduction potentials of the $[Fe_4S_4]^{2+}$ core. Reaction of I with PhSH, monitored by ^1H NMR spectroscopy, generates the mixed-ligand species $[Fe_4S_4(OPh)_{4-n}(SPh)_n]^{2-}$ (n = 0–4), with an approximately statistical distribution of ligands among the species present. The accumulated results are consistent with a relatively covalent Fe–O interaction in I and II. The biological implications for tyrosyl coordination to 4Fe–4S centers are discussed.

The iron–molybdenum protein of nitrogenase is now thought to contain two types of metal–sulfur clusters.[2-6] The iron–molybdenum cofactor[7-9] consists of a molybdenum–iron–sulfur cluster[10] whose structure is as yet unknown, depsite extensive

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