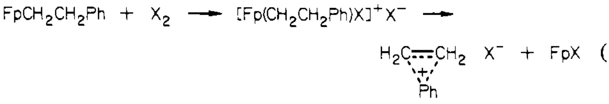
(eq 8) (Table II, expt 25, 26; Table III, expt 15, 16). However, while nucleophilic displacement of Fp· from the bulky $[FpCH_2CH_2\text{-}t\text{-}Bu]^+$ by halide ion (eq 10) may not be a facile process, FpX should be a much better leaving group than Fp·, and nucleophilic displacement of the iron(II) compound from $[Fp(CH_2CH_2\text{-}t\text{-}Bu)X]^+$ by halide ion seems the best general rationale for the halogen cleavage reactions. On this basis, halogen cleavage reactions of (*R*)-(−)-FpCHDPh should be even more likely to proceed with inversion of configuation, and it was reassuring to find that chlorination and bromination reactions in CH_2Cl_2 produced the corresponding (*S*)-(+)-benzyl halides in high yields and with >75% inversion of configuration.

Finally, the idea that the chemistry of an intermediate, $[FpRX]^+[X]^-$, might occur solely within a solvent cage had not occurred to us during our earlier work on bromination of the phenethyl system. We expected that formation of a free phenonium ion in the presence of equimolar amounts of fluoride and bromide ions would result in formation of both phenethyl fluoride and bromide, but did not consider the possibility that the phenonium ion might be formed in a solvent cage in close promixity to bromide ion and not come into contact with significant amounts of fluoride ion (the amount of fluoride available in solution was limited by the rather low solubility of the 18-crown-6 complex of potassium fluoride that was used).

In retrospect, while the present investigation was winding down, it seemed possible that the competition experiments carried out were not as conclusive as had been hoped, and further experiments were carried out with the much more soluble $n\text{-}Bu_4NF$. The results of several bromination reactions of $FpCH_2CH_2Ph$ in the presence of a tenfold excess of fluoride ion are listed in Table VI, along with the *Z* values for each solvent.[67]

As can be seen, $PhCH_2CH_2F$ was formed in yields that correlated reasonably well with the extent to which ion pairs might be expected to diffuse from a solvent cage, as indicated by the *Z* values. In C_6H_6 and CH_2Cl_2, phenethyl bromide was the predominant product, presumably formed within the solvent cage. In MeCN and Me_2CO, however, formation of phenethyl fluoride became more competitive, presumably in a process that involved diffusion of the phenethyl moiety or of the components of $[FpRX]^+[X]^-$ from the solvent cage. Since, as argued above, the normal pathway for collapse of $[FpRX]^+[X]^-$ to RX presumably involved nucleophilic attack of X^- on the α-carbon atom of R (inversion of configuration), the data for the phenethyl system now seem explicable in terms of only the phenonium ion path (i.e., eq 15).



(15)

Acknowledgment. Financial support from Queen's University and the Natural Sciences and Engineering Research Council made this research possible. W.N.R. thanks the Aluminum Co. of Canada, Ltd., for a scholarship. We also thank Professor J. K. S. Wan for assistance with the ESR measurements and Professor W. Giering for disclosure of unpublished data.

Registry No. FpMe, 12080-06-7; FpEt, 32611-65-7; Fp-*n*-Bu, 69661-74-1; $FpCH_2CH_2Ph$, 32760-31-9; Fp-*threo*-CHDCHDPh, 55102-02-8; $FpCH_2Ph$, 12093-91-3; $FpCH_2SiMe_3$, 32963-17-0; (*R*)-(−)-FpCHDPh, 77944-67-3; $FpCH_2CMe_3$, 43157-77-3; Fp-*s*-Bu, 69661-73-0; $FpCH_2CH_2CMe_3$, 43157-76-2; $(\eta^5\text{-}C_5H_5)FeCO[P(OPh)_3]Me$, 12290-98-1; $(\eta^5\text{-}C_5H_5)FeCO[P(OMe)_3]CH_2Ph$, 54496-25-2; $(\eta^5\text{-}C_5H_5)FeCO(PPh_3)CH_2Ph$, 33135-99-8; $(\eta^5\text{-}C_5H_5)FeCO(PMePh_2)CH_2Ph$, 54496-24-1; $CuCl_2{\cdot}2H_2O$, 13933-17-0; $CuBr_2$, 7789-45-9; $CuCl_2$, 7447-39-4; $CuCl_2(OPPh_3)_2$, 31240-85-4; $CuBr_2(OPPh_3)_2$, 58618-32-9; $Cu(NO_3)_2(OPPh_3)_2$, 22578-21-8.

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Photochemical Reaction of $Mn_2(CO)_{10}$ with Pyridine: Evidence for a Radical Pathway[1a]

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The photochemical reaction of $Mn_2(CO)_{10}$ with pyridine and several alkyl- and halogen-substituted pyridines as neat solvents has been studied. Initial products of the reaction are $Mn_2(CO)_9py$ and $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$, formed concurrently in roughly comparable amounts. Continued photolysis leads eventually to $[Mn(py)_6^{2+}][Mn(CO)_5^-]_2$ as final product. Addition of CO results in a shift in initial product distribution toward the nonionic product. Addition of galvinoxyl results in a slower rate of conversion of $Mn_2(CO)_{10}$ to products. The rate of conversion of $Mn_2(CO)_{10}$ to products is increased slightly for 4-alkyl-substituted pyridines and decreased markedly for 3-chloro- or 3-bromopyridine. In addition, the relative amount of ionic product is slightly higher for the alkylpyridines and markedly lower for the halogen-substituted compounds. The results support a mechanism involving a homolytic cleavage of the metal–metal bond, followed by rapid pyridine substitution into the $Mn(CO)_5$· radical. There follows an electron transfer, probably from $Mn(CO)_3(py)_2$·, to $Mn_2(CO)_{10}$, leading to the formation of $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$.

Introduction

In recent years there has been a growing interest in the formation and reactivity of metal-centered radicals. One widely employed means of producing transition-metal carbonyl radicals involves photolysis of a dinuclear metal carbonyl compound.[2] Gray and co-workers have assigned the strong absorption in the UV spectrum of $M_2(CO)_{2n}$ complexes as a $\sigma \rightarrow \sigma^*$ transition characteristic of the metal–metal bond.[3]

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[1] (a) This research was supported by the National Science Foundation through Research Grant CHE76-17570. (b) Eli Lilly Fellowship, 1977–1978; Sohio Fellowship, 1980–1981.

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Photolysis at or near this absorption results in efficient metal–metal bond homolysis. Other means of formation of metal carbonyl radicals include oxidation–reduction processes[4] and atom-abstraction reactions.[5,6]

Photochemical reaction of $M_2(CO)_{10}$ (M = Mn, Re) with phosphorus bases leads to the formation of $M_2(CO)_8L_2$ (L = PR_3, $P(OR)_3$) compounds as primary products.[2,7] The overall mechanism proposed, eq 1–4, involves efficient substitution

$$M_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} 2M(CO)_5\cdot \qquad (1)$$

$$M(CO)_5\cdot + L \xrightarrow{k_2} M(CO)_4L\cdot + CO \qquad (2)$$

$$M(CO)_4L\cdot + M(CO)_5\cdot \xrightarrow{k_3} M_2(CO)_9L \qquad (3)$$

$$2M(CO)_4L\cdot \xrightarrow{k_4} M_2(CO)_8L_2 \qquad (4)$$

of a $M(CO)_5\cdot$ species. Substitution into the radical may occur via dissociative loss of CO followed by coordination of L,[7] or by an associative substitution mechanism.[7,8]

Electron transfer from a metal carbonyl radical[9-12] to an acceptor species has been proposed as a mode of reaction. For example, the thermal reaction of $Co_2(CO)_8$ and tri-*n*-butylphosphine leads to $[Co(CO)_3(PBu_3)_2^+][Co(CO)_4^-]$ (Bu = *n*-butyl) as the product.[10,11] The reaction has been proposed to occur by a radical chain process involving electron transfer from a substituted cobalt carbonyl radical to $Co_2(CO)_8$.

The photochemical reaction of $Mn_2(CO)_{10}$ in donor solvents has been reported to form $[Mn(B)_6^{2+}][Mn(CO)_5^-]_2$ (B = donor solvent) as the final product.[13] It was suggested that the primary photoprocess is heterolysis of the metal–metal bond. However, as noted above, photolysis of $M_2(CO)_{2n}$ involves homolysis of the metal–metal bond as the primary photoprocess. It does not seem likely that the presence of a polar donor solvent, which does not result in a substantial alteration in the UV–visible spectrum, alters the character of the primary photoprocess. The observed product distribution suggests that the reaction in a polar medium may involve homolytic metal–metal bond rupture, followed by substitution and then electron transfer, to finally form an ionic product. In an attempt to more clearly delineate the mechanism of photolysis in donor solvents, we report here a study of the photochemical reaction of $Mn_2(CO)_{10}$ with pyridine or a substituted pyridine in neat bases as solvents.

Experimental Section

Material. $Mn_2(CO)_{10}$ was obtained from Pressure Chemical and sublimed before use. $[(C_6H_5)_6P_2N^+]Cl^-$ was obtained from Alfa Products. Galvinoxyl (2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-*p*-tolyloxy) was obtained from Aldrich Chemical Co. and was used without further purification. Reagent grade pyridine (Mallinckrodt) and derivatives 3-chloropyridine, 3-bromopyridine, 4-methylpyridine, 4-ethylpyridine, and 4-*tert*-butylpyridine were all distilled under Ar from CaH_2 and stored over activated 3A molecular sieves. The solvents were degassed in three freeze–pump–thaw cycles and stored in a glovebox under a continuously purified N_2 atmosphere.

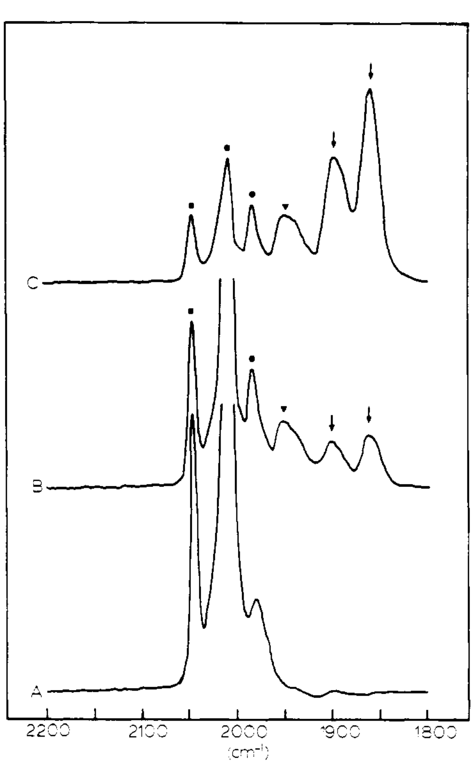

Figure 1. IR spectrum of $Mn_2(CO)_{10}$ + pyridine following continuous irradiation: A, initial; B, 120 min; C, 320 min. Assignment of absorptions: ■, $Mn_2(CO)_{10}$; ●, $Mn_2(CO)_9py$; ▼, $[Mn(CO)_3(py)_3^+]$; ↓, $[Mn(CO)_5^-]$.

(Pyridine)nonacarbonyldimanganese, $Mn_2(CO)_9(C_5H_5N)$, was prepared via a reported method.[14]

Tricarbonyltris(pyridine)manganese(I) tetrafluoroborate, $[Mn(CO)_3(C_5H_5N)_3^+]BF_4^-$, was prepared via a reported method.[15]

Bis(triphenylphosphin)iminium pentacarbonylmanganate, $[[(C_6H_5)_3P]_2N^+][Mn(CO)_5^-]$, was prepared via a reported method.[16]

Instrumentation. All IR spectra were obtained by using a Beckman Model 4240 spectrophotometer. Electronic spectra were recorded on solutions in matched 1.0-cm quartz cells, with use of a Cary Model 14 spectrophotometer. The EPR spectra were obtained on a Varian Model 9 X-band spectrometer. High-resolution field-desorption mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029).

Photolysis Experiments. The photolyses of $Mn_2(CO)_{10}$ in pyridine solvents were performed under continuous- or flash-photolysis conditions. For continuous-photolysis experiments a 250-W General Electric sunlamp with Pyrex filter or an Ace Hanovia (Model 2825-32) medium-pressure mercury lamp was used. A narrow band of radiation centered at 366 nm was obtained by using a $CaSO_4$–$NiSO_4$ filter solution.[17] The reactions were carried out in Pyrex flasks or quartz tubes fitted with rubber septum caps.

Flash-photolysis experiments were performed in CaF_2 IR cells with use of a Sunpac 322 electronic flash as light source. Flash duration was varied from 0.30 to 0.77 ms. The effective temperature of the source during the flash is 5500 K. So that contamination with oxygen and water might be minimized, all solutions were prepared in an inert-atmosphere glove box. Samples for IR analysis were withdrawn from Pyrex sample vials fitted with septum caps by using a Hamilton gastight syringe that had been flushed with Ar.

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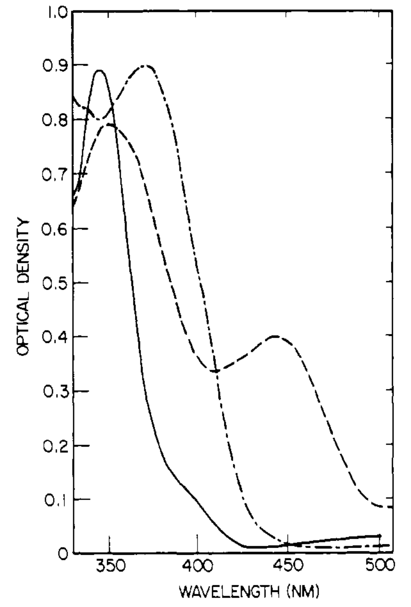

Figure 2. UV spectra of manganese carbonyl compounds in pyridine: (—) $Mn_2(CO)_{10}$; (---) $Mn_2(CO)_9py$; (-·-) $[Mn(CO)_3(py)_3^+]BF_4^-$.

Results

Photolysis of $Mn_2(CO)_{10}$. Photolysis of $Mn_2(CO)_{10}$ in neat pyridine at 366 nm was monitored by observing IR spectra in the CO stretching region. At intermediate stages of the reaction several new bands appeared in the IR spectrum (Figure 1). These absorbances were due to formation of $Mn_2(CO)_9py$ and $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$ (py = C_5H_5N), which are formed concurrently. On the basis of comparative IR intensities, the anion and cation are formed initially in equivalent amounts. Identification of the monosubstituted dimer and ionic product was made by isolation of the compounds from the reaction mixture and comparison with the IR of authentic samples.[14,15] Field-desorption mass spectra were also obtained. At the completion of the photolysis the only IR bands present in the carbonyl stretching region, at 1890 and 1855 cm^{-1}, are due to $[Mn(CO)_5^-]$. Although it has not been possible to isolate and obtain a satisfactory elemental analysis for the final product, we propose it to be $[Mn(py)_6^{2+}][Mn(CO)_5^-]_2$ on the basis of the above data and EPR results described below.

The photolysis of $Mn_2(CO)_{10}$ in pyridine with purified CO (1 atm) was monitored in the IR and visible spectral regions. The presence of CO increases the amount of $Mn_2(CO)_9py$ and decreases the amount of $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$. The rate of $Mn_2(CO)_{10}$ loss was comparable to that observed in the absence of CO.

Photolysis of $Mn_2(CO)_9py$. When $Mn_2(CO)_9py$ in pyridine was flash photolyzed, several new bands in the IR spectra were observed at 2045, 1950, 1890, and 1855 cm^{-1}. The initial products, $Mn_2(CO)_{10}$ and $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$, both react at later stages of the reaction. When $Mn_2(CO)_9py$ is photolyzed with CCl_4 in pyridine, $Mn(CO)_5Cl$[18] and $Mn(CO)_3(py)_2Cl$[19] are formed in approximately 1:3 ratio. The products were identified by the appearance of new absorbances in the IR spectrum at 2050, 2030, 1935, and 1905 cm^{-1} during photolysis.

The UV-visible spectrum of $Mn_2(CO)_9py$ in pyridine is shown in Figure 2. The strong absorbance at 345 nm is assigned to a $\sigma \rightarrow \sigma^*$ transition of the M-M bond in analogy with $Mn_2(CO)_{10}$.

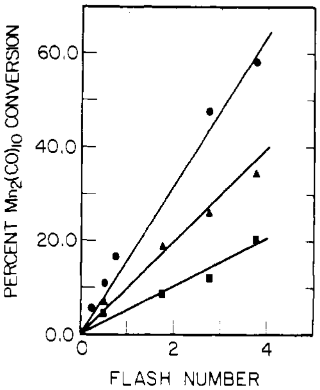

Figure 3. Percent conversion of $Mn_2(CO)_{10}$ in pyridine in the presence of varying concentrations of galvinoxyl: ●, 0; ▲, 3.3×10^{-3} M; ■, 7.1×10^{-3} M.

Table I. Effects of Pyridine Ring Substituents on $Mn_2(CO)_{10}$ Photolysis

solvent	σ	$10^4 \times$ $(-\Delta M(Mn_2(CO)_{10})/$ flash)	$\Delta[Mn(CO)_5^-]/$ $\Delta[Mn_2(CO)_{10}]$
py		6.1 ± 0.3	0.73 ± 0.03
4-CH_3-py	−0.17	6.3 ± 0.2	0.73 ± 0.02
4-CH_3CH_2-py	−0.15	6.5 ± 0.0	0.76 ± 0.03
4-$(CH_3)_3C$-py	−0.20	7.4 ± 0.0	0.77 ± 0.03
3-Cl-py	0.37	1.9 ± 0.1	0.47 ± 0.03
3-Br-py	0.39	2.1 ± 0.1	0.34 ± 0.02

Photolysis of $[Mn(CO)_3(py)_3^+]X^-$ (X^- = BF_4^-, $Mn(CO)_5^-$). Flash photolysis of $[Mn(CO)_3(py)_3^+]X^-$ in neat pyridine results in several changes in the IR spectrum. The major product was $Mn(py)_6^{2+}$; minor amounts of $Mn(CO)_5^-$ were also seen. In analogy with $W(CO)_5py$, the photosubstitution of CO in $Mn(CO)_3(py)_3^+$ is most likely due to excitation of a high-energy ligand field state.[20] The UV-visible spectrum of $[Mn(CO)_3(py)_3^+]BF_4^-$ is shown in Figure 2.

Effect of Galvinoxyl. When $Mn_2(CO)_{10}$ is photolyzed in pyridine, the presence of galvinoxyl has no effect on the distribution of products. However, the rate of $Mn_2(CO)_{10}$ conversion, as monitored by observing changes in the IR spectrum, decreases with increasing concentration of galvinoxyl, as illustrated in Figure 3.

Effect of Pyridine Ring Substituents. $Mn_2(CO)_{10}$ was flash photolyzed in several alkyl- or halogen-substituted pyridine solvents. The rate of $Mn_2(CO)_{10}$ loss and the relative amount of $[Mn(CO)_3(py\text{-}R)_3^+][Mn(CO)_5^-]$ produced were monitored by recording changes in the IR spectrum as a function of the number of flashes during the first 15–20% conversion of $Mn_2(CO)_{10}$. The amount of ionic product formed was determined from the absorption bands of $Mn(CO)_5^-$, because they are not obscured by absorbances of other species in solution and have large extinction coefficients. The results are presented in Table I. In general the halogen-substituted pyridines exhibit a slower rate of $Mn_2(CO)_{10}$ conversion. In addition less ionic product is observed for a given amount of $Mn_2(CO)_{10}$ conversion, as compared with pyridine or the alkyl-substituted derivatives.

Effect of Water. In certain experiments a band at 2340 cm^{-1} due to CO_2 appeared in the course of steady-state photolysis or flash photolysis of $Mn_2(CO)_{10}$ in pyridine. Formation of CO_2 proved to be due to traces of water in the solvent. Reactions of manganese carbonyl species with water or hydroxide ion have been known for some time,[21-25] as for example in eq

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5. In a basic medium such as pyridine, any manganese hydrido species formed as a result of such a reaction would be likely to be deprotonated. Thus $Mn(CO)_5^-$ and CO_2 are the likely products of such a reaction in pyridine. To determine whether a significant fraction of the $Mn(CO)_5^-$ formed in the photochemical reaction originates in such a reaction, we carried out several flash photolysis experiments in which the activity of the hydroxide ion in pyridine was altered, by varying the concentration of added water. Addition of water results in a modest increase in the amount of $Mn(CO)_5^-$ formed, along with formation of CO_2. However, the amount of additional $Mn(CO)_5^-$ is small relative to the total quantity formed under dry solvent conditions, when no CO_2 evolution is observed.

$$Mn(CO)_6^+ + OH^- \rightarrow HMn(CO)_5 + CO_2 \qquad (5)$$

EPR Spectra. Photolysis of $Mn_2(CO)_{10}$ in very dry pyridine at 366 nm produced a broad EPR signal with a g value of 2.019 and a manganese hyperfine coupling constant of 70 G (Figure 4). The center portion of the spectrum is very similar to that reported for the photolysis of $Mn_2(CO)_{10}$ in donor solvents other than THF.[26] The authors proposed $Mn(B)_6^{2+}$ (B = donor solvent) to be responsible for the EPR signal. In analogy to this assignment we believe the signal in Figure 4 is due to $Mn(py)_6^{2+}$.

Discussion

Our observations indicate that the photochemical reaction of $Mn_2(CO)_{10}$ in pyridine proceeds via a free-radical pathway. The appearance of $Mn_2(CO)_9py$ is consistent with a metal–metal bond homolysis as the primary photochemical step, followed by efficient CO substitution by pyridine. The observation that added galvinoxyl results in some inhibition suggests that the reaction possesses radical character.[9] The scheme given in eq 6–14 is consistent with the observations.

$$Mn_2(CO)_{10} \underset{k_{-6}}{\overset{h\nu}{\rightleftharpoons}} 2Mn(CO)_5\cdot \qquad (6)$$

$$Mn(CO)_5\cdot \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Mn(CO)_4 + CO \qquad (7)$$

$$Mn(CO)_4 + N \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} Mn(CO)_4N\cdot \qquad (8)$$

$$Mn(CO)_4N\cdot \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} Mn(CO)_3N + CO \qquad (9)$$

$$Mn(CO)_3N + N \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} Mn(CO)_3N_2\cdot \qquad (10)$$

$$Mn(CO)_3N_2\cdot + Mn_2(CO)_{10} \xrightarrow{k_{11}} Mn(CO)_3N_2^+ + Mn_2(CO)_{10}^-\cdot \qquad (11)$$

$$Mn_2(CO)_{10}^-\cdot \xrightarrow{k_{12}} Mn(CO)_5\cdot + Mn(CO)_5^- \qquad (12)$$

$$Mn(CO)_3N_2^+ + N \xrightarrow{k_{13}} Mn(CO)_3N_3^+ \qquad (13)$$

$$Mn(CO)_4N\cdot + Mn(CO)_5\cdot \xrightarrow{k_{14}} Mn_2(CO)_9N \qquad (14)$$

The symbol N represents a nitrogen base such as pyridine. We have denoted $Mn(CO)_3N_2\cdot$ as the species involved in the electron-transfer reaction. The rate of electron transfer should be increased upon substitution of a σ-donor ligand such as pyridine for CO at the metal, because the energy of the orbital containing the odd electron should be increased by such a substitution. Replacement of a second CO by a pyridine should enhance the rate of electron transfer still further.[27,28]

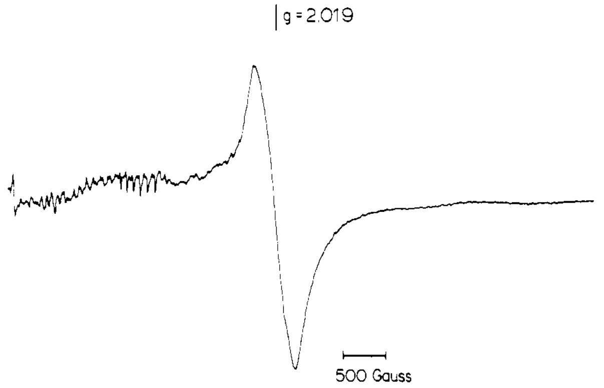

Figure 4. EPR spectrum of $Mn_2(CO)_{10}$ in pyridine following irradiation.

The effect of added CO is to increase the relative amount of $Mn_2(CO)_9py$ as product, at the expense of the ionic product. Once $Mn(CO)_4py\cdot$ is formed, formation of a carbonyl radical species more highly substituted than $Mn(CO)_4py\cdot$ may be inhibited by added CO. Steric interactions could result in a barrier to incorporation of a second pyridine, so that added CO could effectively compete for addition to the 15-electron $Mn(CO)_3py$ intermediate. Thus a larger fraction of a manganese species forming $Mn(CO)_4py\cdot$ would end up in formation of $Mn_2(CO)_9py$.

The reaction scheme as written is a chain process. However, the fact that $Mn_2(CO)_9py$ is formed along with $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$ indicates that the chain-terminating step, eq 14, is of comparable importance with the reactions that result in electron transfer. The overall rate of formation of ionic products may be limited by the rate of formation of substituted radical species that undergo the electron transfer or by the rate of electron transfer itself. Computer-modeling studies of chain processes similar in character to that proposed here suggest that the fractionation between the chain-propagating (electron-transfer) step and the chain-terminating (radical-recombination) step is likely to be very critically dependent on the relative magnitudes of the electron-transfer and radical-recombination rate constants when formation of the radical that undergoes the electron transfer is not rate limiting.[29]

On the other hand, if the important electron-transfer rate process involves a more highly substituted radical, then the competition between the electron-transfer route that leads to an ionic product and the recombination that leads to $Mn_2(CO)_9py$ are likely to be determined by the rate at which the more highly substituted species is formed. The fact that comparable amounts of ionic and nonionic products are seen, even when the system is subjected to variation in the form of pyridine ring substitution, is an indication that the latter interpretation is correct.

One of the more interesting aspects of the reaction is that no $Mn_2(CO)_8(py)_2$ is observed among the products. It is noteworthy that, whereas equatorially bissubstituted $Re_2(CO)_8(py)_2$ can be readily formed from thermal reaction of $Re_2(CO)_{10}$ and py, with use of $(CH_3)_3NO$ to promote the substitution reaction,[30] $Mn_2(CO)_8(py)_2$ cannot be similarly

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formed. It would appear that there is a large barrier, no doubt steric in origin, to formation of the disubstituted product.[31] A σ-donor ligand such as pyridine can be expected to preferentially occupy a basal position in a square-pyramidal five-coordinate radical species. If the steric impediment to recombination of two such basally substituted species is large, then the recombination rate constant for formation of $Mn_2(CO)_8(py)_2$ will be small. We suggest that, in keeping with the behavior observed in many other contexts for the 17-electron radical species, substitution of $Mn(CO)_5\cdot$ to form $Mn(CO)_4py\cdot$ is rapid. Such substitution is, however, not irreversible. As CO accumulates in solution, some reverse reaction is possible, so that the concentration of $Mn(CO)_5$; though small, need not be insignificant. The existence of facile equilibria involving both CO and pyridine in the case of $Re_2(CO)_{10}$ is evident from the observation that photolysis of $Re_2(CO)_8(py)_2$ in THF results in formation of $Re_2(CO)_{10}$ in 40% yield, along with several other products suggestive of lability of the metal center with respect to loss of either CO or pyridine.[30] Thus, if the rate constant for recombination of two $Mn(CO)_4py\cdot$ radicals to form $Mn_2(CO)_8(py)_2$ is relatively very small, formation of $Mn_2(CO)_9py$ will predominate.

Homolysis of the metal–metal bond of $Mn_2(CO)_9py$ leads to the same radical species involved in the reaction scheme of eq 6–14. The results of photolysis of $Mn_2(CO)_9py$ in pyridine support the proposed mechanism; the initial products are $Mn_2(CO)_{10}$ and $[Mn(CO)_3(py)_3{}^+][Mn(CO)_5{}^-]$.

Evidence regarding the intermediacy of $Mn(CO)_4py\cdot$ in the photochemical reaction is obtained from photolysis of $Mn_2(CO)_9py$ in the presence of 3 M CCl_4 in pyridine. The products, $Mn(CO)_5Cl$ and $Mn(CO)_3(py)_2Cl$, are indicative of halogen abstraction as the major reaction pathway for the radicals formed in the photolysis as outlined in eq 15–19.[2,19]

$$Mn_2(CO)_9py \underset{}{\overset{h\nu}{\rightleftharpoons}} Mn(CO)_5\cdot + Mn(CO)_4py\cdot \quad (15)$$

$$Mn(CO)_5\cdot + CCl_4 \rightarrow Mn(CO)_5Cl + \cdot CCl_3 \quad (16)$$

$$Mn(CO)_4py\cdot + CCl_4 \rightarrow Mn(CO)_4pyCl + \cdot CCl_3 \quad (17)$$

$$Mn(CO)_4pyCl + py \rightarrow Mn(CO)_3(py)_2Cl + CO \quad (18)$$

$$Mn(CO)_5Cl + 2py \rightarrow Mn(CO)_3(py)_2Cl + 2CO \quad (19)$$

The thermal reaction of $Mn(CO)_5Cl$ with py has been studied.[19] It occurs too slowly under the conditions of the photochemical experiment to account for the large excess of $Mn(CO)_3(py)_2Cl$ observed. The observations indicate that a large fraction of the $Mn(CO)_5\cdot$ radicals formed in the metal–metal bond homolysis undergo substitution by py *before* halogen abstraction. Such halogen-abstraction reactions are known to be rapid;[2,32-36] thus, the results provide another indication of lability of the $Mn(CO)_5\cdot$ radical toward substitution. Incidentally, $Mn(CO)_4pyCl$ is not observed as a substitution product because the second pyridine substitutes at a faster rate than the first, as a result of the cis-labilizing effect of the pyridine.[37,38]

Formation of $[Mn(CO)_3(py)_3{}^+][Mn(CO)_5{}^-]$ is best accounted for in terms of an electron-transfer reaction between a substituted radical and $Mn_2(CO)_{10}$. We have attempted to test at least certain aspects of the assumed pathway by observing the effects of substituted pyridines on the reaction product distribution. The rate of electron transfer will depend on the energy of the unpaired electron in the radical. As the energy of the orbital containing this electron is raised, the electron-transfer rate should increase. Ring substituents on pyridine in the 3- or 4-position can alter the donor characteristics of the nitrogen base and thus alter the energy levels in the substituted metal carbonyl radical. Introduction of electron-withdrawing substituents such as halogen should have the effect of producing a lower relative yield of ionic product. On the other hand, more electron-releasing substituents such as alkyl groups should result in relatively more ionic product. The results, listed in Table I, are in reasonable accord with these expectations. The effect of 4-alkyl substitution is not marked, but there is some indication of a slight increase in the ratio of ionic to nonionic product with increasing electron release. 3-Halogen substitution results in a marked decrease in this ratio, as expected from the positive Hammett substituent parameter for 3-Cl or 3-Br.[39,40]

A less obvious aspect of the results is that the overall rate of conversion of $Mn_2(CO)_{10}$ is lower when the halogen-substituted pyridines are employed. Much of this lower conversion rate is ascribable to the fact that the electron-transfer step itself, eq 11, consumes an additional molecule of $Mn_2(CO)_{10}$. Thus, when the electron-transfer process is slowed, the total rate of conversion of $Mn_2(CO)_{10}$ is reduced. In addition, the process encompassed in eq 6–14 has some chain character. The chain length cannot be very long, because if it were there would be little or no nonionic product formed. In addition, the quantum yield for overall conversion of $Mn_2(CO)_{10}$ to product was not observed in any case to exceed about 0.40. Nevertheless, insofar as there is some chain character involved in formation of the ionic product, the consumption of $Mn_2(CO)_{10}$ is increased as the electron-transfer step gains importance. Thus, the effect of ring substituents on both the overall rate of conversion of $Mn_2(CO)_{10}$ to products and the relative amounts of ionic and nonionic products are accounted for very well by the proposed mechanism.

The EPR spectrum of the solution containing the final products of the photolysis is very similar to that reported by others following photolysis of $Mn_2(CO)_{10}$ in solvents other than THF. On the basis of both EPR and IR data the products have been formulated as $[Mn(N)_6]^{2+}[Mn(CO)_5{}^-]_2$.[26,41,42] We believe that $Mn(CO)_3(py)_3{}^+$ undergoes photolysis to eventually yield $Mn(py)_6{}^{2+}$. The mechanism given by eq 20–22 is proposed for the reaction.

$$Mn(CO)_3(py)_3{}^+ + py \xrightarrow{h\nu} Mn(CO)_2(py)_4{}^+ + CO \quad (20)$$

$$Mn(CO)_2(py)_4{}^+ + 2py \rightarrow Mn(py)_6{}^+ + 2CO \quad (21)$$

$$Mn(py)_6{}^+ \rightarrow Mn(py)_6{}^{2+} + e^- \quad (22)$$

The minor amounts of $Mn(CO)_5{}^-$ that we observed upon photolysis of $[Mn(CO)_3(py)_3{}^+]BF_4{}^-$ could be formed in a reaction of the type

$$3Mn(CO)_3(py)_3{}^+ + 3py \rightarrow 2Mn(py)_6{}^{2+} + Mn(CO)_5{}^- + 4CO \quad (23)$$

However, the relative amounts of $Mn(py)_6{}^{2+}$ and $Mn(CO)_5{}^-$ formed, as deduced from IR intensity measurements, are not in accord with this overall reaction.

We return finally to the question of whether the primary photochemical step is heterolytic. A reaction scheme to ac-

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count for the observed products in terms of a heterolytic metal–metal bond scission can be written as shown in eq 24–28. Reaction of $Mn(CO)_5py^+$ in neat pyridine to form

$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} Mn(CO)_5^+ + Mn(CO)_5^- \quad (24)$$

$$Mn(CO)_5^+ + py \rightarrow Mn(CO)_5py^+ \quad (25)$$

$$Mn(CO)_5py^+ \rightarrow Mn(CO)_4py^+ + CO \quad (26)$$

$$Mn(CO)_4py^+ + Mn(CO)_5^- \rightarrow Mn_2(CO)_9py \quad (27)$$

$$Mn(CO)_5py^+ + 2py \rightarrow Mn(CO)_3(py)_3^+ + 2CO \quad (28)$$

$Mn(CO)_3(py)_3^+$ is very rapid at room temperature.[15] To form $Mn_2(CO)_9py$ in significant amounts would therefore require an overall very rapid rate for processes 26 and 27. We have studied the reaction of $[Mn(CO)_5py^+]BF_4^-$ with $[(C_6H_5)_6P_2N^+][Mn(CO)_5^-]$ in pyridine. The sole product observed is $[Mn(CO)_3(py)_3^+][Mn(CO)_5^-]$; no evidence for $Mn_2(CO)_9py$ was seen in the IR spectra of the reaction mixture. Further evidence of homolysis of the metal–metal bond in the photochemical reaction comes from the results obtained when CCl_4 is present upon photolysis of $Mn_2(CO)_9py$, as described above. It is difficult to see how the observed products could be accounted for on the basis of a heterolytic cleavage of the metal–metal bond.

The mechanism we have presented here is applicable to the disproportionation reactions of other dinuclear metal carbonyl compounds in donor solvents such as THF, amines, and so forth[41–47] and may apply also the photochemical reactions of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ with halides and phosphines, in which ionic products are observed.[48–50]

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Synthesis and Reactivity of an Anionic Tetrairon Nitrido Cluster. Crystal and Molecular Structure of $PPN[Fe_4N(CO)_{12}]$

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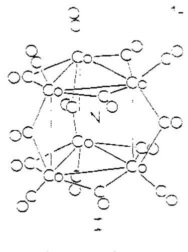
The reaction of $PPN[Fe(CO)_3(NO)]$ (PPN = bis(triphenylphosphin)iminium cation) with $Fe_3(CO)_{12}$ produces the nitrido cluster $PPN[Fe_4N(CO)_{12}]$. The structure was determined by single-crystal X-ray crystallography [$P\bar{1}$ space group, Z = 2, a = 10.700 (2) Å, b = 14.146 (3) Å, c = 16.249 (3) Å, α = 91.15 (1)°, β = 94.55 (2)°, γ = 97.52 (2)°] and found to contain a butterfly arrangement of iron atoms with the nitrogen situated in the center of the cluster. $[Fe_4N(CO)_{12}]^-$ reacts with acids giving several products, of which $Fe_4N(CO)_{12}H$ is the major derivative. The remaining products, apparently formed when excess acid and free carbon monoxide are present, are $Fe_4N(CO)_{11}(NO)$, $Fe_3(NH)(CO)_{10}$, and $Fe_3(NH)_2(CO)_9$. The last two imido clusters have been characterized by comparison to existing related compounds. The structure of $Fe_4N(CO)_{11}(NO)$ likely contains the same Fe_4N moiety as $[Fe_4N(CO)_{12}]^-$, although other structures are possible. The reaction of $NOPF_6$ with $PPN[Fe_4N(CO)_{12}]$ produces $Fe_4N(CO)_{11}(NO)$ in 62% yield.

Introduction

The ability of metal clusters to bind, stabilize, and/or activate small molecules has led to several fascinating discoveries. The synthesis and characterization of new functional groups such as C_2,[1] η^2-CH,[2] and η^2-CO,[3] as well as cluster-bound atomic species of C,[4] P,[5] S,[6] and N,[7–9] are providing some insight into the chemistry that occurs on metal surfaces. Nitrido clusters are a recent development in this area.[7–9] Martinengo and co-workers[7] prepared the first example of nitrido clusters with low valent metals using the reaction of $NOBF_4$ with $[Co_6(CO)_{15}]^{2-}$ forming $[Co_6N(CO)_{15}]^-$ (I) in



40–50% yield. Muetterties and co-workers[8] utilized this nitrosonium ion approach and conducted the reaction of $NOBF_4$ with a mixture of $[Fe_2(CO)_8]^{2-}$ and $Fe(CO)_5$ at 130 °C for 1 h. The tetrairon nitride $[Fe_4N(CO)_{12}]^-$ was isolated from

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