4550 *Inorg. Chem.* **1984**, *23*, 4550-4553

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Flash Photolytic Investigation of Photoinduced Carbon Monoxide Dissociation from Dinuclear Manganese Carbonyl Compounds

RICHARD S. HERRICK and THEODORE L. BROWN*

Received April 26, 1984

Flash photolytic studies of $Mn_2(CO)_8(PR_3)_2$ (R = *n*-Bu, *i*-Bu, *i*-Pr, O-*i*-Pr, Me or $(PR_3)_2 = Ph_2PCH_2CH_2PPh_2$) in hexane show the presence of a transient absorbance (λ_{max} centered near 530 nm) immediately following the flash. Kinetics investigations under Ar, CO, and mixed Ar/CO atmosphere show that decay of the transient absorbance follows the rate law $R = k'[M][CO]$, where M is a metal-containing transient. The proposed mechanism involves photoinduced loss of CO, forming the unsaturated dimer $Mn_2(CO)_7L_2$, which recombines with CO. Both the steric and electronic properties of the phosphine ligand control the magnitude of the rate constant. Comparisons of the recombination rate constants of $Mn_2(CO)_7L_2$ (L = CO, P(*i*-Bu)$_3$) with CO in hexane and perfluorohexane show no variation with solvent. This is attributed to rapid formation of a semibridging CO ligand in $Mn_2(CO)_7L_2$, to form the species that reacts with CO.

Introduction

It has been amply demonstrated that formation of metal-centered radicals from dinuclear metal carbonyl compounds (eq 1) is an efficient primary photoprocess. Cross-coupling[2]

$$(CO)_xM{-}M(CO)_x \underset{k_r}{\overset{h\nu}{\rightleftharpoons}} 2M(CO)_x\cdot \qquad (1)$$

and halogen atom abstraction[3] reactions during continuous photolysis are consistent with homolytic metal–metal bond cleavage, producing 17-electron metal-centered radicals. Time-resolved electronic spectra following flash photolysis permit direct observation of absorptions due to radicals between 700 and 900 nm. Rates of radical recombination are readily measured.[3-6] Pulse radiolysis experiments have also been used to measure recombination rates for $Mn(CO)_5\cdot$[7] and $Re(CO)_5\cdot$.[8]

It has long been recognized that dissociative CO loss (eq 2) is an alternative primary photoprocess. The presence of

$$(CO)_xM{-}M(CO)_x \underset{k'}{\overset{h\nu}{\rightleftharpoons}} (CO)_xM{-}M(CO)_{x-1} + CO \qquad (2)$$

$Co_2(CO)_7$ following photolysis of $Co_2(CO)_8$ in a low-temperature matrix has been deduced from infrared analysis.[9a] In addition flash photolysis experiments suggest the formation of $Cp_2Mo_2(CO)_5$ as well as $CpMo(CO)_3\cdot$ from $Cp_2Mo_2(CO)_6$,[3] $Cp_2Fe_2(CO)$ from $Cp_2Fe_2(CO)_2$,[9b] and $CpFeCo(CO)_5$ from $CpFe(CO)_2Co(CO)_4$.[9c] The analogous CO loss process has only recently been observed for $Mn_2(CO)_{10}$. In a flash photolysis study of $Mn_2(CO)_{10}$, Meyer and co-workers noted a relatively long-lived transient absorption.[4] Laser flash photolysis of an ethanol solution of $Mn_2(CO)_{10}$ produces a transient with λ_{max} = 480 nm, assigned to $Mn_2(CO)_9$ or an ethanol adduct of $Mn_2(CO)_9$.[10] Following flash photolysis of $Mn_2(CO)_{10}$ in cyclohexane a transient absorption with λ_{max} = 500 nm was also observed.[11] Decay of the species giving rise to the transient followed second-order kinetics, with $k'/\epsilon = 1.2 \times 10^2\ s^{-1}\ cm^{-1}$; the transient was attributed to $Mn_2(CO)_9$ and its decay to recombination with CO. Hepp and Wrighton have recently reported a study of irradiation of $Mn_2(CO)_{10}$ in a low-temperature matrix.[12a] Following irradiation, they observe the IR spectrum of a thermally unstable species, assigned as $Mn_2(CO)_9$. The IR data suggest that a CO group acts as a bridging ligand toward the coordinatively unsaturated metal center. Most recently, the bridged $Mn_2(CO)_9$ species has been observed with use of time-resolved IR spectroscopy in hydrocarbon solution.[12b] Together, these results constitute considerable evidence that dissociative CO loss occurs as an alternative primary process to metal–metal bond homolysis upon irradiation of $Mn_2(CO)_{10}$. However, the kinetics behavior of the presumed $Mn_2(CO)_9$ transient has not been well characterized.

We report here the results of flash photolysis studies of dinuclear manganese carbonyl compounds, $Mn_2(CO)_8L_2$, where L is a phosphine or carbon monoxide. We have observed the spectra of $Mn_2(CO)_7L_2$ as photoproducts and have measured the rate constants for recombination with CO. Variation of the concentration of CO in solution confirms the expected mixed second-order rate law. Use of different phosphine ligands has also permitted us to measure the effect of ligand substitution on the rate of recombination of $Mn_2(CO)_7L_2$ with CO. Finally, analysis of solvent effects on the rate of reaction with CO provides evidence that the formally unsaturated dimer $Mn_2(CO)_7L_2$ contains an unsymmetrically bridged CO, which acts as a 4-electron donor. This bridged species is apparently formed on a short time scale with respect to that for reaction with CO.

Experimental Section

Materials. Commercially acquired dimanganese decacarbonyl was sublimed before use. Phosphine ligands were obtained commercially and used without further purification. Hexane was purified for flash photolysis studies by consecutive treatment with H_2SO_4/H_2O/saturated aqueous $NaHCO_3/H_2O/MgSO_4$ prior to distillation from calcium hydride. Perfluorohexane was purchased from Aldrich and distilled from P_2O_5 in a carefully dried distillation apparatus with Teflon sleeves in place of silicone grease. Argon (NGC Industrial Gases, 99.998%) and carbon monoxide (Linde Research Grade, <5 ppm O_2) were used without further purification.

Syntheses. Phosphine-disubstituted manganese dinuclear compounds, $Mn_2(CO)_8(PR_3)_2$ (R = *n*-Bu, *i*-Bu, *i*-Pr, Ph, O-*i*-Pr, Me or

---

(1) Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

(2) Abrahamson, H. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 5510.

(3) Hughey, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

(4) Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49.

(5) Wegman, R. W.; Olsen, R. J.; Gard, O. R.; Faulkner, L. R.; Brown, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 6089.

(6) Walker, H. W.; Herrick, R. S.; Olsen, R. J.; Brown, T. L., to be submitted for publication.

(7) Waltz, W. L.; Hackelberg, O.; Dorfman, L. M.; Wojcicki, A. *J. Am. Chem. Soc.* **1978**, *100*, 7259.

(8) Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A. *J. Am. Chem. Soc.* **1982**, *104*, 1842.

(9) (a) Sweany, R. L.; Brown, T. L. *Inorg. Chem.* **1977**, *16*, 421. (b) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7794. (c) Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1984**, *268*, 259.

(10) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *J. Am. Chem. Soc.* **1982**, *104*, 3536.

(11) Yesaka, H.; Kobayashi, T.; Yasufuku, K.; Nagakuru, S. *J. Am. Chem. Soc.* **1983**, *105*, 6249.

(12) (a) Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5935. (b) Church, S. P.; Hermann, H.; Grevels, F.-W.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1984**, 785.

0020-1669/84/1323-4550$01.50/0 © 1984 American Chemical Society

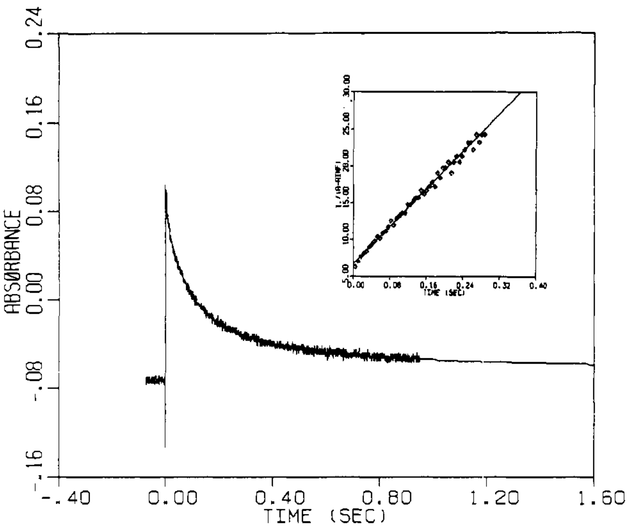


Figure 1. Change in absorbance vs. time at 510 nm on flash photolysis of a 2 × 10^{-5} M hexane solution of $Mn_2(CO)_{10}$ under an argon atmosphere. The line through the trace represents the second-order least-squares fit of the data for the disappearance of the transient. Insert: Linear least-squares fit of the data to a second-order rate law expression. Every 12th data point was employed out to 2.1 half-lives. A correlation coefficient of $R = 0.9962$ was determined.

$(PR_3)_2 = Ph_2PC_2H_4PPh_2)$, were prepared with use of previously described methods.[6] Satisfactory analyses were obtained for all derivatives prepared (C, H, Mn; University of Illinois microanalytical laboratory). CO stretching frequencies have been reported for all dimers except $Mn_2(CO)_8(PMe_3)_2$.[6,13] IR (hexane) ν(CO) for $Mn_2(CO)_8(PMe_3)_2$: 2040 (w), 1992 (m), 1954 (s), 1924 (sh), 1916 (m) cm^{-1}.

Flash Photolysis Studies. The flash photolysis apparatus has been described previously.[6] Samples were prepared in a drybox and loaded into cells fitted with a threaded Teflon stopcock. The 10^{-4}–10^{-5} M solutions were degassed by four freeze–pump–thaw cycles. Argon and/or CO was admitted as cover gas. When CO was used, the solution was allowed to remain at room temperature for 15 min with occasional agitation to ensure that an equilibrium of cover gas and dissolved gas had been reached.

Normally, the data from the first few flash cycles were not used in the analysis, because scavenging of impurities by the radicals can occur. After the first few flash cycles the solutions showed photochromic behavior; i.e., many traces could be obtained before substantial solute loss had occurred. Time-dependent absorbances following flash photolysis were analyzed by least-squares fits of absorbance vs. time or use of rate laws for reactions of appropriate orders. All 2048 data points taken were used in the fits of absorbance vs. time. Data through 2 or more half-lives were employed in fitting rate expressions. Reported rate constants are averages of three or more flash experiments, each producing a rate constant from data with linear least-squares correlation coefficients greater than 0.99.

Results and Discussion

Photolytic CO Dissociation in $Mn_2(CO)_{10}$. In agreement with earlier observations,[10,11] flash photolysis of $Mn_2(CO)_{10}$ in hexane leads to a transient absorption in the region 460–600 nm, $\lambda_{max} = 510$ nm, that decays steadily following the flash. In the absence of added CO (using argon as cover gas) the decay of the absorbance follows second-order kinetics with a typical half-life on the order of 0.1 s. Second-order kinetics plots of $1/(A - A_\infty)$ vs. t are linear (Figure 1) with a slope of 37 ± 8 s^{-1} at 26 °C. When the solutions is saturated with 1 atm of carbon monoxide, the decay is much more rapid, with a typical half-life of 0.2 ms, and follows first-order kinetics. The pseudo-first-order rate constant at 26 °C is (2.9 ± 0.5) × 10^3 s^{-1}. When the atmosphere over the solution consists of 10% CO/90% argon, the observed pseudo-first-order rate constant for decay is (2.7 ± 0.6) × 10^2 s^{-1} at 26 °C, in excellent agreement with the value reported by Church et al.[12b] Assuming that Henry's Law applies, these results suggest that decay of the transient involves a process that is first order in CO. Thus the overall rate law has the form k'[Mn][CO]. A process that satisfactorily accounts for these observations is recombination of CO with $Mn_2(CO)_9$. Assuming that the concentration of CO in hexane under 1 atm pressure is 1 × 10^{-2} M,[14] the bimolecular rate constant for recombination with CO is (2.9 ± 0.6) × 10^5 M^{-1} s^{-1}. From the slope, m, of the second-order plot, the path length, b (10 cm), and the second-order rate constant, k', the extinction coefficient, ϵ, for the transient at 510 nm can be calculated: $\epsilon = k'/mb$. The extinction coefficient of the absorbing transient is calculated to be 800 ± 300 M^{-1} cm^{-1}. This value is close to the value of less than 1000 M^{-1} cm^{-1} estimated previously.[11]

Table I. Values of λ_{max} for $Mn_2(CO)_7L_2$ Transients Determined by Measuring $A_0 - A_\infty$ vs. Wavelength

$Mn_2(CO)_7L_2$	λ_{max}, nm[a]	$Mn_2(CO)_7L_2$	λ_{max}, nm[a]
$Mn_2(CO)_9$	510	$Mn_2(CO)_7(dppe)$	500
$Mn_2(CO)_7(PMe_3)_2$	500	$Mn_2(CO)_7[P(i\text{-}Bu)_3]_2$	560
$Mn_2(CO)_7[P(O\text{-}i\text{-}Pr)_3]_2$	510	$Mn_2(CO)_7[P(i\text{-}Pr)_3]_2$	550
$Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$	530		

[a] ±10 nm.

Our experiments allow us to estimate that following flash photolysis roughly 70% of the primary photochemical product is due to Mn–Mn cleavage, while the remaining 30% involves CO dissociation. This is essentially the same ratio previously calculated.[12a]

Photolytic CO Loss from $Mn_2(CO)_8(PR_3)_2$. Flash photolysis studies were extended to disubstituted phosphine derivatives of $Mn_2(CO)_{10}$ to examine the dependence of the rate constant for recombination of $Mn_2(CO)_7L_2$ with CO on steric and electronic parameters of the ligands. With the exception of $Mn_2(CO)_8(PMe_3)_2$, each of these dimers has been prepared and characterized previously. The other monodentate phosphine compounds are known to have a 1,2-diaxial geometry.[13,15] $Mn_2(CO)_8(PMe_3)_2$ has IR ν(CO) stretching frequencies characteristic of a 1,2-diequatorially substituted dimer; five bands of varying intensities are observed between 1900 and 2100 cm^{-1}, as contrasted with one intense band at ~1950 cm^{-1} and one weak band at ~1980 cm^{-1} observed for 1,2-*ax*,*ax*-$Mn_2(CO)_8(PR_3)_2$. The infrared spectrum strongly resembles the pattern observed for 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$[16] and 1,2-*eq*,*eq*-$Mn_2(CO)_8(AsMe_2Ph)_2$,[17] both of which have a diequatorial geometry, as determined by X-ray crystallography of the latter compound.[18]

Hexane solutions of $Mn_2(CO)_8L_2$ compounds, saturated with CO, were examined for the appearance of a transient absorption in the range 450–650 nm. The maximum absorbance, determined by measuring $A_0 - A_\infty$ as a function of wavelength, lies between 500 and 560 nm (Table I). A typical transient electronic spectrum obtained in this manner is shown in Figure 2. The nature of the transition giving rise to the absorbance is unknown. $Mn_2(CO)_{10-x}L_x$ compounds show a relatively weak band in this region at slightly lower wavelength assigned to a d$\pi \rightarrow \sigma^*$ transition.[19] The transient band may be due to the same transition, but there is a possibility of large

---

(13) Olsen, R. J. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1981.

(14) Atwood, J. D. Ph.D. Dissertation, University of Illinois, Urbana, IL, 1976.

(15) (a) Lewis, J.; Manning, A. R.; Miller, J. R. *J. Chem. Soc. A* **1966**, 845. (b) Bennett, M. J.; Mason, R. *J. Chem. Soc. A* **1968**, 75.

(16) Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 6340.

(17) Reimann, R. H.; Singleton, E. *J. Chem. Soc., Dalton Trans.* **1976**, 2109.

(18) Laing, M.; Ashworth, T.; Sommerville, P.; Singleton, E.; Reimann, R. H. *J. Chem. Soc., Chem. Commun.* **1972**, 1251.

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

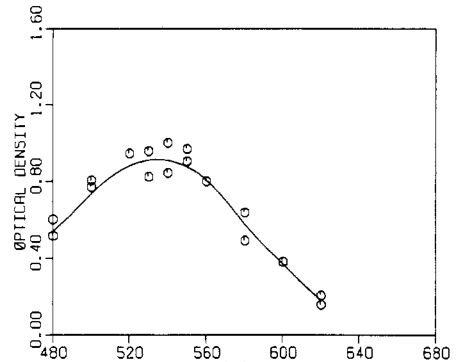


Figure 2. Absorbance spectrum of $Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$ reported as a plot of $A_0 - A_\infty$ vs. wavelength.

Table II. Pseudo-First-Order Rate Constants for the Recombination of CO with $Mn_2(CO)_7L_2$ under 1 atm of CO and under 1 atm of CO Mixed with Argon

$Mn_2(CO)_7L_2$	10^3[CO], M^{13}	k'_{obsd}, s^{-1}	10^3[CO], M	k'_{obsd}, s^{-1}
$Mn_2(CO)_9$	10	$2.9 \times 10^{3\,a}$	1	270^b
$Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$	10	91^c	3.3	27^d
$Mn_2(CO)_7(dppe)$	10	62^c	1.3	6.7^d
$Mn_2(CO)_7[P(i\text{-}Bu)_3]_2$	10	23^c	2.0	4.4^d

[a] $\pm 0.5 \times 10^3\ s^{-1}$. [b] $\pm 0.6 \times 10^2\ s^{-1}$. [c] ±5%. [d] ±10%.

Table III. Bimolecular Rate Constants for the Recombination of $Mn_2(CO)_7L_2$ with CO in Hexane at 25 °C

$Mn_2(CO)_7L_2$	k', $M^{-1}\ s^{-1\,a}$	θ, deg^b	ν, $cm^{-1\,c}$
$Mn_2(CO)_9$	2.9×10^5		
$Mn_2(CO)_7(PMe_3)_2$	4.7×10^4	118	2064.1
$Mn_2(CO)_7[P(O\text{-}i\text{-}Pr)_3]_2$	4.0×10^4	130	2076.1
$Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$	9.1×10^3	132	2060.3
$Mn_2(CO)_7(dppe)$	6.2×10^3	$(140)^d$	$(2066.7)^d$
$Mn_2(CO)_7[P(i\text{-}Bu)_3]_2$	2.3×10^3	143	2060.3
$Mn_2(CO)_7[P(i\text{-}Pr)_3]_2$	1.4×10^2	160	2059.2

[a] ±5%. [b] Phosphine cone angle, from ref 13. [c] Phosphine electronic parameter, from ref 13. [d] Parameters for PPh_2Et.

electronic and geometric changes accompanying the loss of CO.

The absorbance observed following photolysis of the CO-saturated solutions decays following first-order kinetics. A typical time-dependent absorbance is shown in Figure 3. Several derivatives were flash photolyzed in hexane solution under 1 atm of CO/Ar mixtures. In each case the pseudo-first-order rate constant decreases in proportion to a decrease in CO concentration (Table II). This confirms again the rate law proposed above. Therefore we presume that the observed photoprocess in each case is loss of CO from $Mn_2(CO)_8L_2$, followed by recombination of the coordinatively unsaturated dimer with CO (eq 2).

Comparison of the radical recombination rates of $Mn(CO)_4PR_3\cdot$ with the electronic and steric parameters of the phosphine[20] clearly shows that the size of the phosphine affects recombination rates.[6] A similar analysis can be made for the rate of recombination of $Mn_2(CO)_7L_2$ intermediates with CO. The rate constants and size-related parameters for the compounds studied are compiled in Table III. The rate constants for the phosphine-substituted dimers are up to 10^3 times smaller than the value of $2.9 \times 10^5\ M^{-1}\ s^{-1}$ measured for $Mn_2(CO)_9$. As the cone angle, θ, a measure of the steric bulk of the ligand, increases, the rate of recombination with CO decreases. Comparison of the $P(O\text{-}i\text{-}Pr)_3$ and $P(n\text{-}Bu)_3$ derivatives shows a slight discrepancy between rate constants and cone angles. The rate constant of the phosphite derivative is 4 times larger than the value for the $P(n\text{-}Bu)_3$ derivative despite a difference of merely 2° in the cone angles. The unexpectedly high value for the phosphite can be explained in terms of the weaker electron-donating ability of the phosphite compared to that of the alkyl phosphines, as reflected in the frequency of the A_1 symmetry stretching mode, ν, of $Ni(CO)_3PR_3$ compounds, listed in Table II.[20] A weaker electron-donating ligand should produce a lower degree of stabilization of the metal center in the coordinatively unsaturated intermediate. Thus the unsaturated dimer will recombine with CO more rapidly. The dependence of the rate constants for recombination of $Mn_2(CO)_7L_2$ on both the steric and electronic parameters of the phosphorus ligand contrasts with the effects of these ligands on the recombination of $Mn(CO)_4L\cdot$ radicals, which showed only a dependence on size.[6]

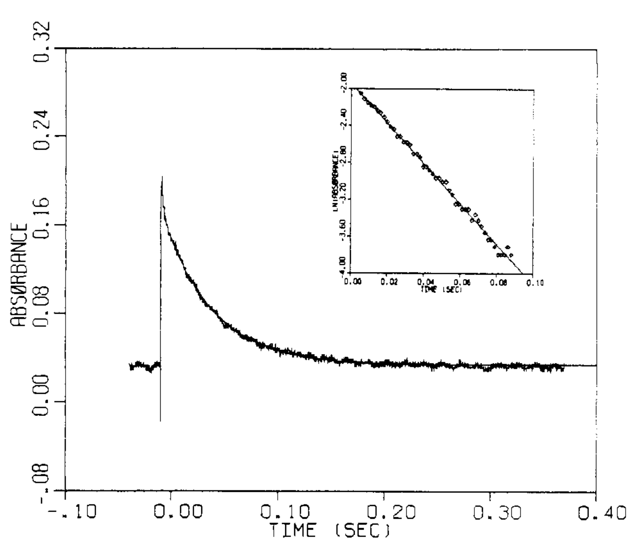


Figure 3. Change in absorbance vs. time at 540 nm on flash photolysis of a 1.1×10^{-4} M hexane solution of $Mn_2(CO)_7[P(i\text{-}Pr)_3]_2$ under 1 atm of CO. The line through the trace represents the first-order least-squares fit of the data for the disappearance of the transient. Insert: Linear least-squares fit of the data to a pseudo-first-order rate expression. Every tenth data point was utilized out to 2.6 half-lives. A correlation coefficient of $R = 0.9982$ was determined.

Finally, the CO-loss photoprocess and concomitant recombination were studied for $Mn_2(CO)_8(PMe_3)_2$ and $Mn_2(CO)_8dppe$ (dppe = 1,2-bis(diphenylphosphino)ethane). Each of these dimers is diequatorially substituted, and the latter compound has a bridging phosphine ligand. Measured rate constants are listed in Table III. The steric and electronic parameters for PPh_2Et[20] are used as approximations of the values for dppe. The rate constant for $Mn_2(CO)_7(dppe)$ recombination falls in the expected range for a derivative with the electronic and steric parameters of diphenylethylphosphine. The recombination rate constant for $Mn_2(CO)_7(PMe_3)_2$ is a factor of 5 larger than the rate constant measured for $Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$, consistent with the assignment of a smaller cone angle for PMe_3. These data indicate that though there may be an effect of the equatorial or axial placement of the phosphine ligands on the recombination rate constant of the unsaturated dimer, the dominant factors are the electronic and steric parameters of the phosphines.

Solvent Effects on Recombination Rates. Laser flash photolysis studies of $Cr(CO)_6$ in solution demonstrate that the rate of recombination of $Cr(CO)_5$ with CO varies considerably with solvent:[21] $k' = 3.1 \times 10^6\ M^{-1}\ s^{-1}$ in cyclohexane, $3 \times 10^9\ M^{-1}\ s^{-1}$ in perfluorocarbon solvent. In the latter solvent, which can

---

[20] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

[21] Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1220.

Table IV. Bimolecular Rate Constants for the Radical Recombination of $Mn(CO)_4L\cdot$, k_r, and Recombination of $Mn_2(CO)_7L_2$ with CO, k', in Hexane and Perfluorohexane at 25 °C

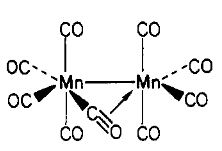
L	solvent	k_r, M^{-1} s^{-1} [a]	k', M^{-1} s^{-1} [a]
CO	C_6H_{14}	9×10^8	2.9×10^5
CO	C_6F_{14}	1×10^9	3.2×10^5
$P(i\text{-}Bu)_3$	C_6H_{14}	2×10^7	2.3×10^3
$P(i\text{-}Bu)_3$	C_6F_{14}	2×10^7	4.5×10^3

[a] ±5%.

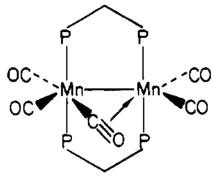
be taken to be noninteracting with the $Cr(CO)_5$ intermediate, the rate of recombination with CO approaches the diffusion-controlled limit, as do the recombination rates observed for such weak nucleophiles as N_2, $Cr(CO)_6$, and cyclohexane. These facts are of interest in considering the significance of the measured rate of recombination of $Mn_2(CO)_7L_2$ with CO.

Flash photolysis experiments on $Mn_2(CO)_8L_2$ (L = CO, $P(i\text{-}Bu)_3$) in perfluorohexane under a CO atmosphere were conducted to determine the magnitude of the solvent effect. Absorptions were observed in the electronic spectral regions associated with the radical and the unsaturated dimer. The transients decayed as expected following second- and first-order rate laws, respectively. Rate constants measured for radical recombination and unsaturated dimer recombination with CO in hexane and perfluorohexane are organized in Table IV. Radical recombination rates are independent of solvent. Since the rate constants approach a diffusion-controlled limit, the only expected dependence might arise from relatively minor viscosity differences. The rate constants for recombination of $Mn_2(CO)_7L_2$ with CO are also essentially unchanged by the nature of the solvent. Neither intermediate shows the factor of 10^3 differential in the rate constants between alkane and perfluoroalkane solvents observed for $Cr(CO)_5$. Furthermore, neither intermediate has a recombination rate that approaches a diffusion-controlled limit in perfluorohexane. We conclude that hexane molecules are not involved in stabilization of the dimer intermediate. However, there must be some other mode of stabilization of the intermediate; if there were not, it would display a diffusion-limited rate of reaction with CO in perfluoroalkane.

Hepp and Wrighton[12a] recently reported that, following photolysis of $Mn_2(CO)_{10}$ in a cyclohexane matrix, the low-temperature IR spectrum exhibits a band at 1760 cm^{-1}. The intermediate in the matrix was proposed to contain a bridging CO (I). Church et al. have also assigned this absorption, seen as a transient in the time-resolved IR spectrum, to a bridging species.[12b] The proposed structure of the intermediate is based on the crystal structure of $Mn_2(CO)_5(dppm)_2$ (dppm = 1,2-bis(diphenylphosphino)methane) (II).[22] The bridging CO is apparently not present in 2-methyltetrahydrofuran, a donor solvent. Similar low-temperature matrix experiments yield the same results for $Cp_2Mo_2(CO)_6$.[23]



I



II

Our results indicate that the $Mn_2(CO)_7L_2$ intermediates in solution contain an analogous bridge. Through a bridging CO interaction at the coordinatively unsaturated metal center, bringing the electron count at each metal to 18, stabilization by interaction with solvent molecules is precluded. The present results show that the semibridging CO structure is formed rapidly in solution, i.e. on a short time scale with respect to CO recombination, consistent with the time-resolved IR results.[12b]

Acknowledgment. The authors gratefully acknowledge financial support for this research from National Science Foundation Grants CHE 83-12331 and CHE 81-19525.

Registry No. $Mn_2(CO)_8(P(n\text{-}Bu)_3)_2$, 15609-33-3; $Mn_2(CO)_8(P(i\text{-}Bu)_3)_2$, 83634-21-3; $Mn_2(CO)_8(P(i\text{-}Pr)_3)_2$, 75847-41-5; $Mn_2(CO)_8(P(O\text{-}i\text{-}Pr)_3)_2$, 75862-69-0; $Mn_2(CO)_8(PMe_3)_2$, 93503-87-8; $Mn_2(CO)_8dppe$, 75847-46-0; $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)_9$, 86633-01-4; $Mn_2(CO)_7(PMe_3)_2$, 93503-88-9; $Mn_2(CO)_7[P(O\text{-}i\text{-}Pr)_3]_2$, 93503-93-6; $Mn_2(CO)_7[P(n\text{-}Bu)_3]_2$, 93503-92-5; $Mn_2(CO)_7(dppe)$, 93503-89-0; $Mn_2(CO)_7[P(i\text{-}Bu)_3]_2$, 93503-91-4; $Mn_2(CO)_7[P(i\text{-}Pr)_3]_2$, 93503-90-3; CO, 630-08-0.

---

(22) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663.
(23) Hooker, R. H.; Mahmoud, K. A.; Rest, A. J. *J. Organomet. Chem.* **1983**, *254*, C25.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Study of *trans*-Dichlorobis(ethylenediamine)nickel(III) in Zeolite Y

HANFAN LIU, WENXIA SHEN, WILLIAM H. QUAYLE, and JACK H. LUNSFORD*

Received November 2, 1983

At temperatures as low as −40 °C $[Ni^{II}(en)_2]^{2+}$ (en = ethylenediamine) in zeolite Y is oxidized with molecular chlorine to a complex that contains nickel(III) in a low-spin state. The EPR spectrum indicates that the d^7 ion is in D_{4h} symmetry with two equivalent chlorine atoms along the symmetry axis. The paramagnetic species is attributed to the $[Ni^{III}(en)_2Cl_2]^+$ complex that is formed within the large cavities of the zeolite. At 25 °C this complex decays with a half-life of ca. 30 h.

Introduction

Intracrystalline cavities of zeolites provide an interesting environment for carrying out redox chemistry involving transition-metal ions. In previous work $[Ru^{II}(bpy)_3]^{2+}$ (bpy = bipyridine) in zeolite Y was oxidized with Cl_2 to the corresponding Ru(III) complex and reduced back to Ru(II) with water.[1] Although no O_2 was produced from the water, a small amount of CO_2 was observed in which the oxygen was derived from the water. In the present study a nickel(III) complex has been formed, again by oxidation with molecular chlorine, and in this case the resulting chloride ions enter the first coordination sphere.

The chemistry of Ni(III) is described in two reviews.[2,3] A number of Ni(III) complexes have been reported in which the

---

(1) Quayle, W. H.; Lunsford, J. H. *Inorg. Chem.* **1982**, *21*, 97.
(2) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87.
(3) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.