

would have to be greater than that observed for the I_d mechanism actually followed by reaction with $P(OPh)_3$ (see data in Table II). The value of ΔH^\ddagger for the addition of $P(OPh)_3$ as in eq 5 would be small so the value of ΔH° for the reversible ring-opening step shown in eq 4 would also be ≥ 100 kJ mol $^{-1}$, and this is therefore a reasonable lower limit for the value of the Fe \rightarrow Fe bond strength. Similar values can be inferred from the activation parameters for reactions with $AsPh_3$ and $SbPh_3$ (Table II). The same analysis of the data⁷ for the I_d reactions of the analogous $Co(CO)_3$ complex suggests that the strength of the Fe \rightarrow Co bond has a similar, or slightly smaller, lower limit. These heteronuclear metal-metal bonds are therefore at worst only moderately weak and could be quite strong.

Acknowledgment. We thank Erindale College and the Natural Sciences and Engineering Research Council (NSERC), Ottawa, for support. R.A.J. thanks the NSERC for the award of a research fellowship, and acknowledgment is also gratefully made to NATO for a travel grant allowing collaboration with Professor Dr. H. Vahrenkamp of the University of Freiburg, Freiburg, West Germany.

Registry No. $(OC)_4Fe(\mu-AsMe_2)Fe(CO)_2(NO)$, 61951-19-7; $P(C_6H_{11})_3$, 2622-14-2; $P-n-Bu_3$, 998-40-3; $PPhEt_2$, 1605-53-4; PPh_2Et , 607-01-2; $P(OMe)_3$, 121-45-9; PPh_3 , 603-35-0; $P(OCH_2)_3CET$, 824-11-3; $P(OPh)_3$, 101-02-0; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1.

Supplementary Material Available: Tables of product IR spectra and observed rate constants (4 pages). Ordering information is given on any current masthead page.

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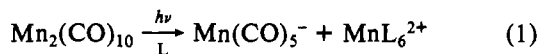
Mechanism of the Photochemical Disproportionation Reaction of $Mn_2(CO)_{10}$ with Nitrogen Donor Ligands

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The mechanism of the photochemical disproportionation of $Mn_2(CO)_{10}$ in the presence of the nitrogen donor ligands pyridine (py), triethylamine (NEt_3), trimethylethylenediamine (Me_3en), and diethylenetriamine (dien) was investigated. The disproportionation is proposed to follow a radical chain pathway: (1) $Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5$, (2) $Mn(CO)_5 + N \rightarrow Mn(CO)_4N + CO$, (3) $Mn(CO)_4N + N \rightarrow Mn(CO)_3N_2 + CO$, (4) $Mn(CO)_3N_2 + N \rightarrow Mn(CO)_3N_3$, (5) $Mn(CO)_3N_3 + Mn_2(CO)_{10} \rightarrow Mn(CO)_3N_3^+ + Mn_2(CO)_{10}^-$, (6) $Mn_2(CO)_{10}^- \rightarrow Mn(CO)_5 + Mn(CO)_5^-$. The quantum yields for the disproportionation are $\phi(py) = 0.1$, $\phi(NEt_3) = 0.1$, $\phi(Me_3en) = 1.2$, and $\phi(dien) = 6-19$. The key to the mechanism is the formation of the 19-electron intermediate $Mn(CO)_3N_3$. Evidence is presented for the formation of this intermediate. The intermediate $Mn_2(CO)_{10}^-$ was generated by reacting $Mn_2(CO)_{10}$ with Na; in the presence of ligand disproportionation occurred.

We recently showed that 19-electron species are key intermediates in the photochemical disproportionation reactions of $Cp_2Mo_2(CO)_6$.¹ In order to determine whether 19-electron intermediates were forming in the disproportionation reactions of other metal-metal-bonded carbonyl dimers, we studied the photochemical disproportionation of $Mn_2(CO)_{10}$ by amine ligands (eq 1).² This paper reports the results of quantum



yield measurements and electrochemical studies that strongly suggest that 19-electron intermediates are important in the photochemical disproportionation of $Mn_2(CO)_{10}$ by amines.

Experimental Section

$Mn_2(CO)_{10}$ was obtained from Strem Chemical Co. and sublimed before use. $[Mn(CO)_3(py)_3][PF_6]$ (py = pyridine) and $[Mn(C-$

$O)_3(CH_3CN)_3][PF_6]$ were synthesized by literature methods.³ It was necessary to recrystallize $[Mn(CO)_3(py)_3][PF_6]$ several times from acetone/ether to obtain material free of $[Mn(CO)_3(py)_2(CH_3CN)][PF_6]$. $LiClO_4$ was obtained from Aldrich, recrystallized from water, and dried in an oven for 3 days at 180 °C. THF (Gold Label) was obtained from Aldrich and used as received. Pyridine and triethylamine were purchased from MCB, stirred over calcium hydride, and distilled under argon.⁴ Spectral grade acetonitrile and benzene were purchased from Fisher and used as received. Sodium powder, suspended in mineral oil (40% by weight), trimethylethylenediamine, and diethylenetriamine were purchased from Aldrich and used without further purification.

All photochemical reactions were carried out under anaerobic conditions as previously described.⁵ Irradiations were performed with an Oriol 200-W high-pressure mercury lamp or a Tensor high-intensity incandescent lamp. Lamp intensities were determined by using ferrioxalate actinometry.⁶ Typical lamp intensities were 5×10^{-6} einstein/min for the mercury lamp and 1×10^{-9} einstein/min for the incandescent lamp. Radiation of 366-nm wavelength was isolated with a Corning 7-83 narrow band-pass glass filter. The quantum yields were measured for the disappearance of $Mn_2(CO)_{10}$. With the monodentate and bidentate ligands at low concentrations, substitution products as well as the ionic disproportionation products form. Thus, in these cases, the reported quantum yields are upper limits for the true quantum yield of disproportionation.

(1) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032.

(2) The photochemical disproportionation reaction of $Mn_2(CO)_{10}$ in neat pyridine solvent was recently studied by McCullen and Brown: McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528-3533. They proposed a radical chain mechanism initiated by photochemical homolytic cleavage of the metal-metal bond but not involving 19-electron intermediates. Note that the $Mn(I)$ complex $Mn(CO)_3N_3^+$ is the expected product of the disproportionation. Using infrared spectroscopy, McCullen and Brown observed the transitory species $Mn(CO)_3(py)_3^+$ during the irradiation. They independently synthesized the $Mn(CO)_3(py)_3^+$ complex and showed that irradiation of this complex in pyridine produced $Mn(py)_6^{2+}$ and small amounts of $Mn(CO)_5^-$:



This reaction is thus the source of the $Mn(II)$ product.

(3) Drew, D.; Darenbourg, D. J.; Darenbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579-1584.

(4) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

(5) Tyler, D. R. *Inorg. Chem.* **1981**, *20*, 2257-2261.

(6) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966.

Table I. Quantum Yields of Disappearance for $\text{Mn}_2(\text{CO})_{10}$ in the Disproportionation of $\text{Mn}_2(\text{CO})_{10}^a$ with Various Ligands upon Irradiation at 366 nm

ligand	concn ^b	ϕ^c
pyridine	neat (≈ 12 M)	0.10, 0.10
$\text{N}(\text{CH}_2\text{CH}_3)_3$	neat (≈ 7 M)	0.11, 0.10, 0.20
$(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{H})(\text{CH}_3)$	neat (≈ 8 M)	1.2
	2.0 M	0.17, 0.28
$\text{NH}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$	0.1 M	6.3, 7.8
	0.2 M	10.7, 19.1

^a The concentration of $\text{Mn}_2(\text{CO})_{10}$ is 1.4×10^{-4} M. The disappearance of $\text{Mn}_2(\text{CO})_{10}$ was monitored at 343 nm. ^b In benzene solution. ^c Each number represents an independent determination of the quantum yield. The error for each measurement is approximately 10%.

All infrared spectra were taken on a Perkin-Elmer 621 spectrophotometer using CaF_2 solution cells. Silicon wafers were taped over the windows of the IR cells to prevent photolysis by the instrument beam.

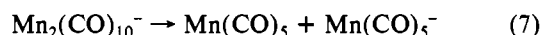
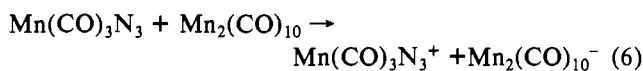
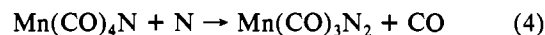
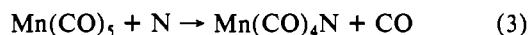
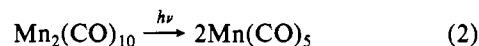
Cyclic voltammograms were recorded with a PAR 173/176 potentiostat driven by a PAR 175 Universal Programmer. Voltammograms were recorded with a normal X-Y recorder with a sweep rate of 100 mV s^{-1} . The experiments were done in THF solvent with 0.2 M LiClO_4 as the electrolyte. A Pt working electrode was used in conjunction with a Ag/Ag^+ reference electrode. Ferrocene was used as an internal standard.⁷

Results and Discussion

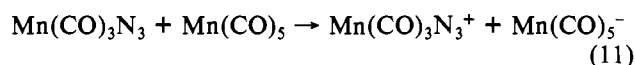
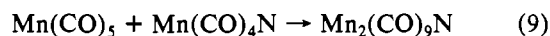
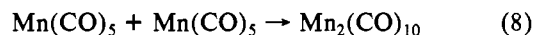
It is generally recognized that the primary photoprocess resulting from low-energy ($\lambda > 320 \text{ nm}$) excitation of the $\text{Mn}_2(\text{CO})_{10}$ complex is homolytic cleavage of the Mn–Mn bond.⁸ However, in early work on the disproportionation reaction of $\text{Mn}_2(\text{CO})_{10}$, it was proposed that direct heterolytic cleavage of the metal–metal bond occurred in polar solvents.⁹ Presumably, photochemical heterolysis was induced by the polarity of the solvent just as solvent polarity was proposed to be responsible for thermal heterolysis.¹⁰ It is an easy matter to show that the disproportionation of $\text{Mn}_2(\text{CO})_{10}$ is not brought about by any special bulk properties of the solvent. This conclusion follows from our observation that disproportionation occurs when $\text{Mn}_2(\text{CO})_{10}$ (7×10^{-2} M) is irradiated ($\lambda = 366 \text{ nm}$) in hexane solution containing 2×10^{-2} M pyridine. That disproportionation occurs is evidenced by the appearance of product peaks in the infrared spectrum at 1902 and 1859 cm^{-1} and 2045 and 1941 cm^{-1} attributable to $\text{Mn}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_3(\text{py})_3^+$, respectively.^{3,9} With such a small concentration of pyridine present in the hexane, it is unlikely that the molar polarizability of the solvent is changed much from that of pure hexane. Thus, the purpose of pyridine, Me_2SO , or other “polar” solvents in the disproportionation reactions is not to change the primary photoprocess. Rather, these solvents are acting as ligands, inducing disproportionation by their ability to coordinate to the metal.

The quantum yields of disproportionation of $\text{Mn}_2(\text{CO})_{10}$ with various amine ligands are shown in Table I. The data in Table I show that disproportionation is inefficient with monodentate amines, slightly more efficient with the bidentate amine $\text{Me}_3\text{en}^{11}$ (especially when the Me_3en is concentrated),

and very efficient with the tridentate amine dien (even at very low concentrations). We propose that these data are consistent with the radical chain mechanism



The following are termination steps:



This reaction scheme is quite similar to the one we proposed for the disproportionation reactions of $\text{Cp}_2\text{Mo}_2(\text{CO})_6$.¹ The key feature is the 19-electron intermediate $\text{Mn}(\text{CO})_3\text{N}_3$. Based on the requirement that this intermediate form, it is easy to explain the inefficiency of the disproportionation chain reaction with the monodentate and bidentate amine ligands. The inefficiency arises because the $\text{Mn}(\text{CO})_5$ fragment must be substituted twice (eq 3 and 4) and form an adduct (eq 5) in order for the $\text{Mn}(\text{CO})_3\text{N}_3$ complex to form. The coupling reactions of the 17-electron fragments (eq 8–10) compete with these substitution/adduct formation reactions. Because the coupling reactions are chain-terminating steps, they impede the efficiency of the chain reaction. Obviously, anything that increases the efficiency of the substitution/adduct formation steps will increase the efficiency of the disproportionation chain process. The increased quantum yield with the en ligand as compared to those with the monodentate ligands can be attributed to the increased rate of the second substitution reaction (eq 4) (this step is now a ring-closure step; such steps are usually quite fast¹³). But because a second en ligand must still coordinate to form the 19-electron species (eq 5), the chain process is still relatively inefficient. The chain process only becomes efficient with a tridentate ligand (e.g. dien). A tridentate ligand greatly enhances the efficiency of the dis-

(7) Bernhard, J.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748.

(8) Geoffroy, G. L.; Wrighton, M. S. “Organometallic Photochemistry”; Academic Press: New York, 1979; p 61.

(9) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q. *J. Chem. Soc., Dalton Trans.* **1976**, 1189–1193.

(10) Hieber, W.; Beck, W.; Zeitler, G. *Angew. Chem.* **1961**, *73*, 364–368.

(11) An infrared spectrum from the photoreaction of 2 M trimethylethylenediamine and $\text{Mn}_2(\text{CO})_{10}$ in benzene shows the emergence of a broad intense band between 1831 and 1910 cm^{-1} upon 366-nm irradiation. This broad band is found to be composed of two bands associated with $\text{Mn}(\text{CO})_5^-$ ($\nu(\text{CO}) = 1899, 1860 \text{ cm}^{-1}$) and two bands associated with $\text{Mn}_2(\text{CO})_8(\text{NN})$ ($\nu(\text{CO}) = 1912$ and 1876 cm^{-1} ; see ref 12).

(12) The mono- and disubstituted products are identified by their infrared spectra. The disubstituted dimer $\text{Mn}_2(\text{CO})_8(\text{NN})$ (NN = trimethylethylenediamine) is identified by comparison to the infrared spectrum of the known compound $\text{Mn}_2(\text{CO})_8(\text{phen})$ (phen = 1,10-phenanthroline). $\text{Mn}_2(\text{CO})_8(\text{phen})$ has two low-energy bands at 1953 (s) and 1908 (m, s) cm^{-1} . The bands in $\text{Mn}_2(\text{CO})_8(\text{NN})$ have the same relative intensities and similar separations compared to the bands in $\text{Mn}_2(\text{CO})_8(\text{phen})$, but they are shifted to lower energy as would be expected with amines that are stronger σ donors (Hieber, W.; Schropp, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1960**, *15B*, 271–276). $\text{Mn}_2(\text{CO})_8\text{L}$ (L = pyridine) has a known infrared spectrum with characteristic low-energy bands at 1978 (vs) and 1960 (m) cm^{-1} . Irradiation of $\text{Mn}_2(\text{CO})_{10}$ in benzenes with a low concentration of NEt_3 produces analogous bands at 1973 (s) and 1956 (m) cm^{-1} that we assign to $\text{Mn}_2(\text{CO})_8(\text{NEt}_3)$.

(13) Basolo, F.; Pearson, R. G. “Mechanisms of Inorganic Chemistry”, 2nd ed.; Wiley: New York, 1967; p 223. Recent work suggests that the substitution reactions of 17-electron fragments are associatively activated¹⁴ so it is not necessary to wait for CO to dissociate from the complex before the second nitrogen atom bonds to the Mn atom.

(14) (a) Fox, A.; Malito, J.; Poe, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (b) Shi, Q.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032–4034. (c) McCullen, S. B.; Walker, H. W.; Brown, T. L. *Ibid.* **1982**, *104*, 4007–4008.

proportionation reaction because the second substitution (eq 4) and the adduct formation (eq 5) are very fast (both are ring-closure steps with a tridentate ligand). The point is that with a tridentate ligand the formation of the $\text{Mn}(\text{CO})_3\text{N}_3$ complex (eq 3–5) is competitive with the chain-terminating coupling reactions (eq 8–10).

The following observation is consistent with our proposal of a 19-electron intermediate. When $\text{Mn}_2(\text{CO})_{10}$ is photochemically disproportionated with the monodentate ligands or with the bidentate Me_3en ligand, we observe the formation of substituted dimer products of the types $\text{Mn}_2(\text{CO})_9\text{N}$ and $\text{Mn}_2(\text{CO})_8(\text{NN})$.¹² At low ligand concentrations the quantity of these products formed is high as is expected from the mechanism (eq 9 and 10); at higher ligand concentrations few or none of the substituted dimer products are formed, only the ionic disproportionation products. With the tridentate ligand dien, however, no substitution products are ever observed, even at very low dien concentrations. The ionic disproportionation products are the only products formed. Our interpretation of these results is that once one nitrogen of the dien ligand is coordinated to the Mn atom, the occurrence of electron transfer is virtually ensured because the other nitrogen atoms quickly coordinate and the coupling reactions are prevented. On the other hand, with the bidentate or monodentate ligands, more than one ligand is required to form the 19-electron intermediate so the coupling reactions still occur at low ligand concentrations.

Note in eq 6 of the proposed mechanism that the 19-electron intermediate reduces the $\text{Mn}_2(\text{CO})_{10}$ complex. Obviously, a strong reductant is required to form $\text{Mn}_2(\text{CO})_{10}^-$ because the reduction potential of $\text{Mn}_2(\text{CO})_{10}$ is -1.7 V.^{15,16} Cyclic voltammetry experiments confirm that the 19-electron intermediates are powerful reducing agents. A 10^{-3} M THF solution of $\text{Mn}(\text{CO})_3(\text{py})_3^+$ was scanned from $+0.5$ to -3.0 V (vs. a standard Ag^+/Ag reference electrode). The $\text{Mn}(\text{CO})_3(\text{py})_3^+$ complex could not be reduced. From this result we conclude that the $\text{Mn}(\text{CO})_3(\text{py})_3$ complex (and related $\text{Mn}(\text{CO})_3(\text{amine})_3$ complexes) is capable of reducing the $\text{Mn}_2(\text{CO})_{10}$ complex. (Scanning potentials lower than about 3 V were unattainable because THF begins to reduce at this potential.)

We also note that 19-electron intermediates have been proposed before. Wrighton has shown they are involved in certain photochemical substitution reactions;¹⁷ they have been proposed in several thermal reactions,¹⁸ and we have shown they are involved in the photochemical disproportionation reactions of the $\text{Cp}_2\text{Mo}_2(\text{CO})_6$ complex.¹

The $\text{Mn}_2(\text{CO})_{10}^-$ complex is another key intermediate in the chain pathway for disproportionation. We devised the following experiment to test for the intermediacy of this dimer anion. With the rigorous exclusion of all light, 10 mL of

degassed benzene was added to 0.06 g of $\text{Mn}_2(\text{CO})_{10}$. To this solution was added 0.02 mL of dien, and the combined solutions were mixed. An aliquot of this solution was withdrawn by syringe and used to fill an infrared cell. This cell served as the control experiment. A silicon wafer was taped to the window of the cell to prevent photolysis by stray light or by the infrared spectrometer beam. To the remaining portion of the solution was added 0.2 mL of sodium dispersed in mineral oil (40% Na by weight). After several seconds of mixing, an aliquot was withdrawn by syringe and injected into a second infrared cell. (This cell also had silicon wafers taped to its windows.) The infrared spectrum of the sodium-treated solution was run immediately (within 2 min of adding the sodium), and it showed that disproportionation (but no substitution) had occurred. No disproportionation occurred in the sodium-free control cell. (Note that disproportionation did occur when the Si wafers were removed; the visible light in the IR beam is sufficient to photolyze the solution.) Further control experiments showed that the ligand, in this case dien, must be present in order for reaction to occur. When the sodium dispersion was added to a benzene solution containing only $\text{Mn}_2(\text{CO})_{10}$, only a very small amount of $\text{Mn}(\text{CO})_5^-$ was detected by IR methods.

Our interpretation of the experiments above is as follows. We propose that sodium is reducing the $\text{Mn}_2(\text{CO})_{10}$ complex and generating the $\text{Mn}_2(\text{CO})_{10}^-$ anion. Once the $\text{Mn}_2(\text{CO})_{10}^-$ anion is generated, it decomposes according to eq 7, and the disproportionation chain reaction is started. The control experiments show that sodium is not just simply reducing the $\text{Mn}_2(\text{CO})_{10}$ dimer. If this were the case, no cation would form.

In conclusion, the radical chain mechanism that arises from homolytic cleavage of the metal–metal bond adequately explains the disproportionation reactions undergone by $\text{Mn}_2(\text{CO})_{10}$.¹⁹ We have been able to add support to this mechanism by the independent generation of one of the crucial intermediates—the $\text{Mn}_2(\text{CO})_{10}^-$ dimer. The product distribution as a function of ligand concentration that we observed is also consistent with the proposed mechanism.

It is with the requirement of a 19-electron “supersaturated” intermediate to generate the reduced intermediate $\text{Mn}_2(\text{CO})_{10}^-$ that our mechanism differs from those previously proposed.² The quantum yield data for bi- and tridentate ligands and the strong ligand dependence of the overall reaction argue strongly for the necessity of such an intermediate.

The possibility that these “supersaturated” 19-electron complexes could become important in a wide variety of electron-transfer and electrochemical reactions is a subject of much interest in our group, and research is ongoing in an effort to trap and stabilize such complexes.

Acknowledgment. We thank Professor T. L. Brown for a helpful discussion and Uday Maitra for help with the electrochemistry experiments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.

(15) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117–5121.

(16) Our experiments also give a value of -1.7 V.

(17) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 5238–5241.

(18) (a) Astruc, D.; Roman, E.; Hamon, J. R.; Batail, P. *J. Am. Chem. Soc.* **1979**, *101*, 2240–2242. (b) Astruc, D.; Hamon, J. R.; Althoff, G.; Roman, E.; Batail, P.; Michaud, P.; Mariot, J. P.; Varret, F.; Cozak, D. *Ibid.* **1979**, *101*, 5445–5447. (c) Baker, P. K.; Connelly, N. G.; Jones, B. M. R.; Maher, J. P.; Somers, K. R. *J. Chem. Soc., Dalton Trans.* **1980**, 579–585.

(19) It is possible to measure the stoichiometry of the disproportionation reaction by using CH_3CN as the ligand/solvent. The $\text{Mn}(\text{CO})_3(\text{CH}_3\text{CN})_3^+$ that forms in the disproportionation of $\text{Mn}_2(\text{CO})_{10}$ does not photochemically disproportionate to give $\text{Mn}(\text{CO})_5^-$. Thus, any $\text{Mn}(\text{CO})_5^-$ that does form is formed only by the disproportionation of $\text{Mn}_2(\text{CO})_{10}$. Experiments show that one $\text{Mn}(\text{CO})_5^-$ molecule is formed for every $\text{Mn}_2(\text{CO})_{10}$ molecule consumed.