

trigonal bipyramidal. The contraction of average Mo-S distance from six- to five-coordinate complexes is not unexpected, even though the former contain weakly bound carboxylate groups as the sixth ligand.

The number of five-coordinate complexes of Mo(V) with cysteinato and thiolato ligands establishes this as a reasonable coordination mode of Mo(V) in enzymes, whether the active site complex is mono- or binuclear. Such a geometry provides ready access to the sixth coordination site by a potential substrate, without a prior ligand dissociation step.

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**Supplementary Material Available:** A listing of observed and calculated structure amplitudes (7 pages). Ordering information is given on any current masthead page.

## References and Notes

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- (37)  $R = \sum |F_o| - s |F_c| / \sum |F_o|$ ;  $R_w = (\sum w |F_o| - s |F_c|)^2 / \sum w |F_o|^2)^{1/2}$ .

# Photochemical Substitution Reactions of $Mn_2(CO)_{10}$ <sup>1</sup>

Dennis R. Kidd and Theodore L. Brown\*

Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801. Received November 4, 1977

**Abstract:**  $Mn_2(CO)_{10}$  undergoes photosubstitution by tributylphosphine,  $PBu_3$ , or triethyl phosphite,  $P(OEt)_3$ , in heptane, with 350-nm radiation, to yield mainly disubstituted dimer as initial product. In the absence of added CO, the quantum yields for disappearance of  $Mn_2(CO)_{10}$ ,  $\Phi_d$ , in both cases are on the order of 0.9. For  $[Mn_2(CO)_{10}] = 4 \times 10^{-4}$  M, and ligand concentrations in the range  $2-20 \times 10^{-3}$  M,  $\Phi_d$  is independent of the nature and concentration of ligand. Addition of  $10^{-2}$  M purified CO results in a lowered quantum yield, 0.6-0.7. The results can be accounted for most satisfactorily by assuming that  $Mn(CO)_5$  radicals undergo facile dissociative loss of CO. Substituted dimers,  $Mn_2(CO)_8L_2$ ,  $L = PBu_3$  or  $P(OEt)_3$ , undergo photosubstitution by CO to yield  $Mn_2(CO)_9L$  and  $Mn_2(CO)_{10}$ , with quantum yield for disappearance of starting carbonyl of about 0.2.  $Mn_2(CO)_8L_2$  compounds also undergo photosubstitution by  $L'$  to yield a complex array of products.

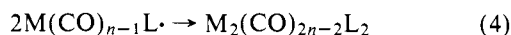
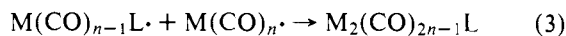
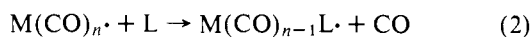
## Introduction

The chemical and physical properties of organometallic radicals, especially those derived from transition elements, are not as well understood as those of organic radicals. However, in recent years the importance of radical pathways in many organometallic reactions has become more widely appreciated.<sup>2-6</sup> There has thus been a considerable interest in the production and study of transition element organometallic radicals.<sup>7-12</sup>

We are concerned in the work reported here with the substitution characteristics of transition metal carbonyl radicals, of the form  $M(CO)_n^{\cdot}$  or  $M(CO)_mL_n^{\cdot}$ . These are formed under conditions suitable for study of their chemical characteristics mainly by thermal or photochemical homolysis of metal-metal bonds.

Formation of metal carbonyl radicals has been invoked to account for the kinetics and product distributions observed in the thermal substitution reactions of several metal carbonyl dimer species, including  $[Ru(CO)_4Si(CH_3)_3]_2$ ,<sup>13</sup>  $Mn(CO)_{10}$ ,<sup>14</sup>

and variously substituted carbonyl dimers,  $\text{Mn}_2(\text{CO})_8\text{L}_2$ ,<sup>15</sup>  $\text{Re}_2(\text{CO})_9\text{L}$ , and  $\text{Re}_2(\text{CO})_8\text{L}_2$ .<sup>16</sup> The overall reaction scheme involved is of the form



Certain important details, such as equilibria involving caged radical pairs, and the nature of the substitution process shown in eq 2, are omitted from the scheme. A rate-determining dissociation of CO,<sup>17</sup> associative interaction of L with the intact dimer, or metal migration<sup>22</sup> are alternative pathways for substitution of  $\text{M}_2(\text{CO})_{2n}$ .

Metal carbonyl radicals are conveniently generated by photolysis of metal carbonyl dimers. Following the initial assignment by Gray and co-workers of a band in the near UV spectrum of  $\text{M}_2(\text{CO})_{2n}$  compounds to a  $\sigma-\sigma^*$  transition,<sup>23</sup> a great deal of evidence has been amassed that irradiation at this wavelength leads to M-M bond homolysis with high quantum yield.<sup>24-27</sup>

The metal carbonyl radicals  $\text{M}(\text{CO})_n \cdot$  are one electron short of the stable 18-electron configuration about the metal atom. They may thus be expected to undergo reaction analogous to those observed for a typical organic radical, i.e., coupling, abstraction, or electron transfer. The rates of the second-order coupling reactions of  $\text{Mn}(\text{CO})_5$ ,<sup>26</sup> and  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3$ ,<sup>28</sup> have been measured; the rate constants approach the value expected for a diffusion-controlled process. Abstraction reactions are exemplified by formation of  $\text{M}(\text{CO})_n\text{Cl}$  in high quantum yield when  $\text{M}_2(\text{CO})_{2n}$  is photolyzed in  $\text{CH}_2\text{Cl}_2$  or  $\text{CCl}_4$ .<sup>24,29</sup> Electron transfer involving a metal carbonyl radical has been invoked to account for kinetics observations,<sup>30</sup> but the process has not yet been established for metal carbonyl radicals from independent physical studies. Analogous processes involving organic radicals are well established.<sup>31,32</sup>

A fourth mode of reaction, not typical of radicals centered on a main group element, is substitution, eq 2. A substantial body of evidence supports the contention that such substitution processes are facile: (a) Assuming that the thermal substitution reactions of the dimers are rate determined by the M-M bond homolysis, then substitution, eq 2, must be fast relative to radical recombination, for which the second-order rate constant is near the diffusion-controlled limit. (b)  $(\eta^5\text{-C}_5\text{H}_5)\text{-Mo}(\text{CO})_3$  undergoes loss of CO to form the dimer,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_4$ , in either a thermal<sup>33</sup> or photochemical<sup>34</sup> reaction. (c) Wrighton and Ginley observed ready photochemical substitution of  $\text{Mn}_2(\text{CO})_{10}$  in the presence of  $\text{PPh}_3$  to form mainly  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ .<sup>24</sup> Analogous observations were made for  $\text{Re}_2(\text{CO})_{10}$ .<sup>35</sup> (d) Substitution of  $\text{HRe}(\text{CO})_5$  by a radical chain process can be accounted for if it is assumed that  $\text{Re}(\text{CO})_5 \cdot$  is rapidly substituted by entering ligand.<sup>36</sup> (e) Facile loss of CO from  $\text{Re}(\text{CO})_5 \cdot$  has been invoked to account for the products of photochemical reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{H}_2$ .<sup>36</sup>

These various lines of evidence suggest that metal-centered carbonyl radicals are indeed labile toward substitution. However, it is not clear how the substitution occurs. Is the process shown in eq 2 associative in character, or is dissociation of CO from the radical rate determining? In what way does the substitution process depend on L? Are substituted radicals  $\text{M}(\text{CO})_m\text{L}_n \cdot$  also labile? Which ligand is lost preferentially? We report here a study of the photochemical substitution reactions of  $\text{Mn}_2(\text{CO})_{10}$ , conducted to answer some of these questions. We have concerned ourselves mainly with careful measurements of the quantum yields and product distributions for photochemical substitutions by tributylphosphine,  $\text{PBu}_3$ ,

or triethyl phosphite,  $\text{P}(\text{OEt})_3$ , and with the effects of added CO.

## Experimental Section

**Reagents.** Dimanganese decarbonyl [ $\text{Mn}_2(\text{CO})_{10}$ ] was obtained from Pressure Chemical Co. and sublimed before use. The sublimed material was stored in an inert atmosphere glove box.

Tri-*n*-butylphosphine ( $\text{PBu}_3$ ), obtained from Aldrich Chemical Co. (98%), was refluxed over  $\text{CaH}_2$  for 12 h, then distilled in an  $\text{N}_2$  atmosphere, under reduced pressure.

Triethyl phosphite [ $\text{P}(\text{OEt})_3$ ], Aldrich Chemical Co., was refluxed over  $\text{CaH}_2$  for 12 h, then distilled in an  $\text{N}_2$  atmosphere under reduced pressure.

Heptane ( $\text{C}_7\text{H}_{16}$ ) was purified using standard purification techniques. The solvent was stored over 4A molecular sieves until placed in a distillation apparatus; it was then distilled from sodium ketyl under an argon atmosphere just before use.

Xylene ( $\text{C}_8\text{H}_{10}$ ), certified reagent grade, Fischer, was dried over Na or 4A molecular sieves for several hours, then deaerated by bubbling  $\text{N}_2$  through the solvent for about 0.5 h before use.

All sample preparations were performed in a Vacuum Atmospheres glove box. The nitrogen atmosphere was purged of oxygen, water, and solvent as previously described.<sup>37,38</sup> The oxygen concentration in the box atmosphere was monitored by exposing a  $[\text{Cp}_2\text{TiCl}]_2\text{ZnCl}_2$  solution to the atmosphere.<sup>39</sup> The solution remained blue during evaporation of the THF, indicating that the oxygen content is well below 5 ppm.

**Preparations.** Dimanganese Octacarbonylbis(triethyl phosphite),  $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OEt})_3]_2$ .  $\text{Mn}_2(\text{CO})_{10}$  (0.500 g, 1.28 mmol) and  $\text{P}(\text{OEt})_3$  (0.65 mL, 3.84 mmol) were dissolved in 25 mL of dry,  $\text{N}_2$ -saturated xylene. The solution was heated for 7 h at 110 °C in the dark under nitrogen. The solvent was removed under reduced pressure, leaving a yellow residue. Upon recrystallization from hot methanol, yellow crystals were obtained. The electron impact mass spectrum showed the molecular ion peak at  $m/e$  666. No molecular ion peak was observed for  $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$ , but a trace amount of  $\text{Mn}_2(\text{CO})_9[\text{P}(\text{OEt})_3]$  was observed.

Anal. Calcd for  $[\text{Mn}_2\text{C}_{20}\text{H}_{30}\text{O}_{14}\text{P}_2]$ : Mn, 16.49; C, 36.05; H, 4.54; P, 9.30. Found: Mn, 16.55; C, 36.31; H, 4.61; P, 9.01. IR (hexane): 1996 (m), 1983 (sh), 1975 (sh), 1966 (s), 1946 (w), 1928  $\text{cm}^{-1}$  (w). Lit.<sup>40</sup> (cyclohexane): 2064 (vw), 1995 (m), 1983 (sh), 1945 (w), 1927  $\text{cm}^{-1}$  (w). UV (hexane): 350, 400 nm. The spectrum was not observed at wavelengths shorter than 300 nm.

**Dimanganese Heptacarbonyltris(triethyl phosphite)  $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$ .**  $\text{Mn}_2(\text{CO})_{10}$  (0.40 g, 1.0 mmol) and  $\text{P}(\text{OEt})_3$  (1.0 mL, 5.9 mmol) were dissolved in 60 mL of purified heptane and irradiated for 10 h under a nitrogen atmosphere with a 250-W General Electric sunlamp in a Pyrex flask. Solvent was removed under reduced pressure. The yellow residue was recrystallized from methanol at 0 °C. The mass spectrum showed the molecular ion peak at  $m/e$  804 and both monometallic fragments of the dimer, at  $m/e$  471 and 333 for  $\text{Mn}(\text{CO})_3[\text{P}(\text{OEt})_3]_2$  and  $\text{Mn}(\text{CO})_4\text{P}(\text{OEt})_3$ , respectively.

Anal. Calcd for  $[\text{Mn}_2\text{C}_{25}\text{H}_{45}\text{O}_{16}\text{P}_3]$ : Mn, 13.66; C, 37.33; H, 5.63. Found: Mn, 13.33; C, 37.88; H, 5.79. IR (hexane): 2046 (w), 1985 (w), 1959 (s), 1949 (s), 1925 (sh), 1897 (m), 1883  $\text{cm}^{-1}$  (m). UV (hexane): 363 nm. The spectrum was not observed at wavelengths shorter than 300 nm.

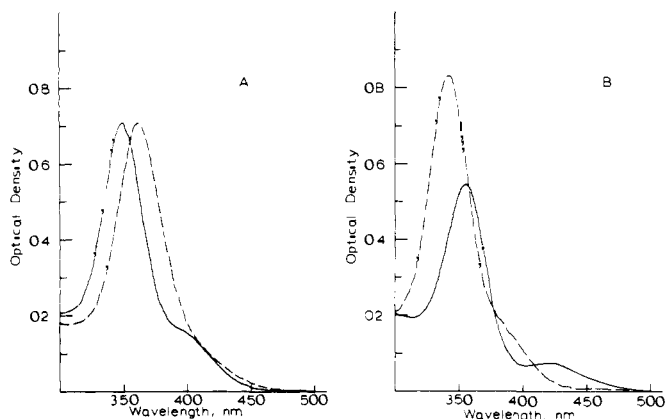
**Dimanganese Octacarbonylbis(tri-*n*-butylphosphine)  $[\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2]$ .**  $\text{Mn}_2(\text{CO})_{10}$  (0.39 g, 1.0 mmol) and  $\text{PBu}_3$  (0.50 mL, 2.1 mmol) were dissolved in 50 mL of heptane. The solution was irradiated for 12 h with a 250-W General Electric sunlamp in a Pyrex flask under a positive pressure of nitrogen. Solvent was removed under reduced pressure, leaving an orange residue. The residue was recrystallized from methanol at 0 °C, yielding yellow-orange platelets.

Anal. Calcd for  $[\text{Mn}_2\text{C}_{32}\text{H}_{54}\text{O}_8\text{P}_2]$ : Mn, 14.84; C, 52.04; H, 7.37. Found: Mn, 14.08; C, 52.48; H, 7.39. IR (hexane): 1973 (m), 1963 (sh), 1949 (vs), 1936  $\text{cm}^{-1}$  (w). Lit.<sup>40</sup> (cyclohexane): 2043 (vw), 1973 (m), 1964 (sh), 1949 (vs), 1935  $\text{cm}^{-1}$  (w). UV (hexane): 356, 422 nm. The spectrum was not observed at wavelengths shorter than 300 nm.

**Instrumentation.** All IR spectra were obtained using a Beckman IR7 spectrophotometer, frequency calibrated with water vapor.

Electronic spectra were recorded on a Cary Model 14 recording spectrophotometer using matched 1.0-cm quartz cells.

For photolysis experiments a 1000-W high-pressure xenon lamp



**Figure 1.** UV spectra of substituted manganese carbonyl compounds. In A,  $Mn_2(CO)_8[P(OEt)_3]_2$ , —;  $Mn_2(CO)_7[P(OEt)_3]_3$ , - - -. In B,  $Mn_2(CO)_8(PBu_3)_2$ , —;  $Mn_2(CO)_{10}$  - - -.

(X-1000-B, D and R Associates) in a Schoeffel lamp housing Model LH151N was used. A narrow band of radiation centered at 350-nm wavelength was obtained using an interference filter with 36.4% transmittance at  $\lambda_{max}$  and a 14-nm bandwidth at half-height. Neutral density filters were employed to vary the photon flux in various experiments.

For photochemical synthesis experiments in Pyrex glassware, either a 250-W General Electric sunlamp or a 600-W General Electric quartz-iodine lamp was used without a filter.

Mass spectral data were collected on a Varian CH5 mass spectrometer.

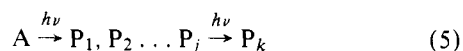
**Quantum Yield Measurements.** To minimize contamination with oxygen and other impurities, all solutions for quantum yield measurements were prepared in the dark in an inert atmosphere glove box. The reaction cell, fitted with a serum cap, was jacketed along its entire length. All photolyses for determination of quantum yields were conducted with the solutions at 8 °C. An atmosphere of argon, purified by passage through an activated manganese oxide column,<sup>37</sup> was maintained during photolysis. Continuous rapid stirring was maintained during irradiation. Samples for IR analysis were withdrawn using Hamilton gas-tight syringes, preflushed with purge gas.

The flux of photons from the high-pressure xenon lamp used for irradiation was determined using potassium ferrioxalate actinometry.<sup>41</sup> Measurements were made both before and after irradiation of solutions of metal carbonyl. The flux of photons into the cell in most experiments was on the order of  $5 \times 10^{-8}$  einstein/min, but ranged in a few cases down to about  $7 \times 10^{-9}$  einstein/min.

## Results

**Interpretation of Photochemical Data.** A major concern in this work has been the determination of quantum yields for disappearance of  $Mn_2(CO)_{10}$  under irradiation, and the variation in quantum yields as a function of solution conditions. Interpretation of the data is complicated by the fact that the products of the photochemical substitution reactions possess absorption spectra very similar to that for  $Mn_2(CO)_{10}$ . Figure 1 shows the absorption spectra for  $Mn_2(CO)_{10}$ ,  $Mn_2(CO)_8(PBu_3)_2$ ,  $Mn_2(CO)_8[P(OEt)_3]_2$ , and  $Mn_2(CO)_7[P(OEt)_3]_3$  in the 300–500-nm region.<sup>42</sup> The wavelengths of absorption maxima and  $\epsilon_{max}$  values are summarized in Table I. The average values of  $\epsilon$  over the 14-nm interval corresponding to the half-height bandwidth of the filter used are also listed. In general, the substitution reaction products possess about the same absorption characteristics as the parent  $Mn_2(CO)_{10}$ , thus creating a strong internal filter effect. In addition, the possibility exists that the initial products undergo subsequent further substitution or other reaction.

The reaction system can be described as



**Table I.** Extinction Coefficients and Band Maxima of Manganese Carbonyl Dimers

Compd	$\lambda_{max}$ , nm	$\epsilon_{max}$ , $M^{-1} cm^{-1}$	$\epsilon_{av}$ , $M^{-1} cm^{-1}$ <sup>a</sup>
$Mn_2(CO)_{10}$	342	21 300	17 600
$Mn_2(CO)_8(PBu_3)_2$	355	18 600	16 600
$Mn_2(CO)_8[P(OEt)_3]_2$	350	21 300	20 200
$Mn_2(CO)_7[P(OEt)_3]_3$	362	23 900	19 200

<sup>a</sup> Averaged extinction coefficient over 14-nm interval centered at 350 nm.

where  $P_1, P_2 \dots P_j$  represent the initial products resulting from photon absorption, and the  $P_k$  represent secondary products. Let  $\sum_j \Phi_j$  represent the total quantum yield for formation of all initially formed products. One can then write

$$-\frac{d[A]}{dt} = \sum_j \Phi_j \left( \frac{I_0 S}{V} \right) \left( \frac{\epsilon_A [A]}{\sum_i \epsilon_i C_i} \right) \quad (6)$$

where  $(I_0 S/V)$  represents the flux of absorbed photons per unit volume. (We assume that total absorption occurs, a condition which is met under the experimental conditions.) The final term in parentheses on the right represents the fraction of all photons absorbed by the parent species A. The summation  $\sum_i \epsilon_i C_i$  represents the total absorption due to all absorbing species.

This expression yields a particularly simple result for the case in which the product species are formed in 1:1 ratio with the reactant, and when the  $\epsilon$  are all equal. The summation is then a constant, and the last term reduces to  $[A]/[A_0]$ . Equation 6 then has the form of a first-order differential equation, for which the integrated form is

$$\ln \left( \frac{A_0}{A} \right) = \kappa t \quad (7)$$

$$\kappa = \sum_j \Phi_j \left( \frac{I_0 S}{V} \right) \frac{1}{[A_0]} \quad (8)$$

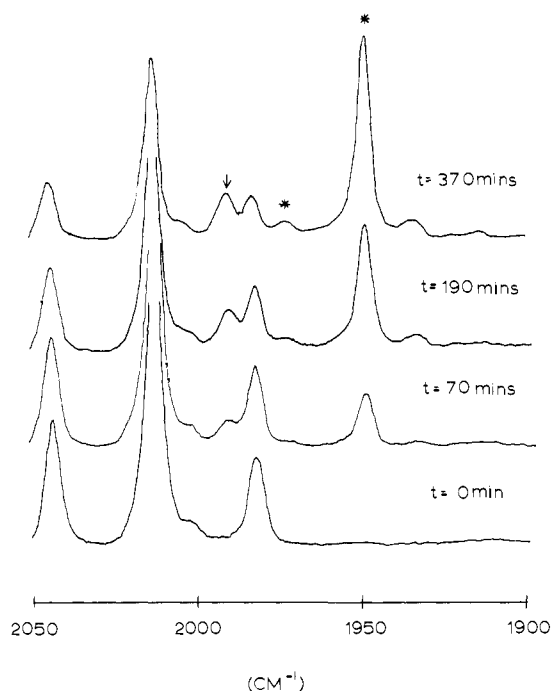
$$\Phi_d = \sum_j \Phi_j = \frac{\kappa [A_0]}{(I_0 S/V)} \quad (9)$$

where  $\Phi_d$  represents the total quantum yield for disappearance of parent species A. This relationship predicts that  $\ln(A_0/A)$  will vary linearly with time under irradiation, a condition which is met in practice (vide infra). From the slope, and with a knowledge of initial concentration  $[A_0]$  and photon flux per unit volume  $(I_0 S/V)$ , the quantum yield for disappearance of A can be determined.

It would appear from the data in Table I that the conditions outlined above are satisfied to within about 15%, and that the quantum yield might be obtained as outlined above. However, this procedure weights data obtained in the latter stages of the reaction rather heavily. It is just these data that reflect most seriously the departures of the real system from the model. In addition, there is an experimental problem in that the volume of solution,  $V$ , is substantially altered after a time by repeated withdrawals of samples for IR analysis.

Alternatively, quantum yields for disappearance of  $Mn_2(CO)_{10}$  can be obtained from measurements of the rate of disappearance of  $Mn_2(CO)_{10}$  in the early stages of the reaction, before more than about 10–15% of product formation has occurred. Under these conditions, no correction for the internal filter effect is made ( $\epsilon_A [A] / \sum_i \epsilon_i C_i \approx 1$ ). Then

$$\Phi_d = \sum_j \Phi_j = \frac{[A_0] - [A]}{I_0 S \Delta t / V} \quad (10)$$



**Figure 2.** IR spectrum of  $\text{Mn}_2(\text{CO})_{10} + \text{PBu}_3$  under irradiation in heptane. The absorptions assigned to  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$  are denoted \*. The absorption marked ↓ is assigned to  $\text{Mn}_2(\text{CO})_9\text{PBu}_3$ .

In practice we have found that quantum yields obtained from use of eq 10 are smaller by about 20% than those using eq 7. Only the former values are reported in what follows.

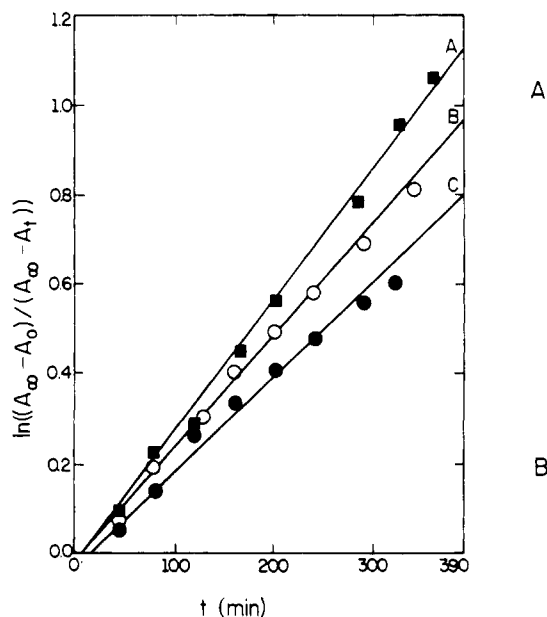
**Photosubstitution of  $\text{Mn}_2(\text{CO})_{10}$  by  $\text{PBu}_3$ .** When  $\text{Mn}_2(\text{CO})_{10}$  in heptane solution is photolyzed at 350 nm in the presence of  $\text{PBu}_3$ , the IR spectrum in the carbonyl stretching region changes as shown in Figure 2. The major product is diaxially substituted  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ ; lesser amounts of  $\text{Mn}_2(\text{CO})_9\text{PBu}_3$  are also observed.

The rate of photosubstitution was monitored quantitatively by following the decrease in absorbance at  $2045 \text{ cm}^{-1}$  due to  $\text{Mn}_2(\text{CO})_{10}$ . Under constant flux of photons a pseudo-first-order rate law was observed; examples are shown in Figure 3. Quantum yield measurements were made following photolysis for 40 and 80 min, with various concentrations of  $\text{PBu}_3$ , in both the absence and presence of added CO. The results are listed in Table II.

**Photosubstitution of  $\text{Mn}_2(\text{CO})_{10}$  by  $\text{P}(\text{OEt})_3$ .** Photosubstitution of  $\text{Mn}_2(\text{CO})_{10}$  by  $\text{P}(\text{OEt})_3$  in heptane upon irradiation at 350 nm was monitored by observing the IR spectra in the CO stretching region. The major products are  $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OEt})_3]_2$  and  $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$ ; small amounts of  $\text{Mn}_2(\text{CO})_9\text{P}(\text{OEt})_3$  are also seen. Identification of the di- and trisubstituted dimers was made by reference to the IR spectra of authentic isolated samples. The absorption assigned to  $\text{Mn}_2(\text{CO})_9\text{P}(\text{OEt})_3$  is based on analogy with spectra of other monosubstituted compounds.

Under constant photon flux the disappearance of  $\text{Mn}_2(\text{CO})_{10}$  follows a pseudo-first-order rate law, as illustrated for two cases in Figure 4. Quantum yield measurements were made for several reaction conditions; the results are listed in Table III. It should be noted that the CO used in these experiments was taken from the tank without further purification.

**Photosubstitution of  $\text{Mn}_2(\text{CO})_8\text{L}_2$  by CO.** Heptane solutions of  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$  or  $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OEt})_3]_2$ ,  $\sim 4.3 \times 10^{-4} \text{ M}$ , were equilibrated with gaseous CO at atmospheric pressure. Experiments were performed with CO directly from the tank, and with CO purified by passage through a column of



**Figure 3.** Pseudo-first-order rate law for disappearance of  $\text{Mn}_2(\text{CO})_{10}$  ( $4.5 \times 10^{-4} \text{ M}$ ) under irradiation in heptane in presence of  $\text{PBu}_3$  ( $2.2 \times 10^{-3} \text{ M}$ ): A, without added CO; B, with nonpurified CO; C, with purified CO.

**Table II.** Quantum Yields for Photosubstitution of  $\text{Mn}_2(\text{CO})_{10}$  by  $\text{PBu}_3$ , with 350-nm Radiation

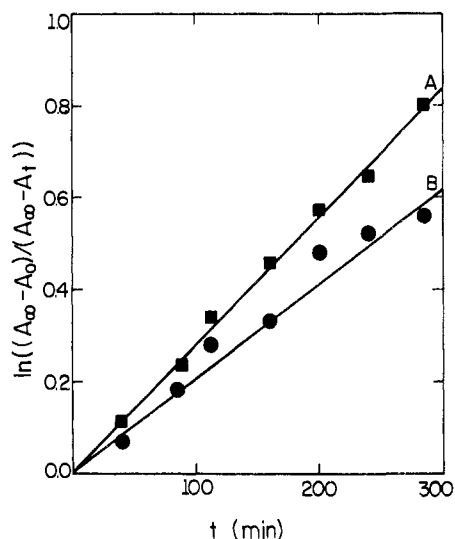
$[\text{Mn}_2(\text{CO})_{10}] \times 10^4, \text{ M}$	$[\text{PBu}_3] \times 10^3, \text{ M}$	$[\text{CO}] \times 10^2, \text{ M}$	Irradiation time, min	$\Phi_d$	$\Phi_d(\text{av})$
5.14	22.5		40	0.84	
4.57	22.5		40	0.92	0.89
4.57	22.5		80	0.91	
4.51	4.50		40	0.81	0.84
4.51	4.50		80	0.88	
4.71	2.22		40	0.85	
4.48	2.22		40	0.88	
4.40	2.22	1.3	40	0.73	
4.63	2.22	1.3 <sup>a</sup>	44	0.68	0.66
4.63	2.22	1.3 <sup>a</sup>	80	0.63	

<sup>a</sup> Purified by passage over manganese oxide column.

activated manganese oxide. The solutions were then irradiated with 350-nm light. The quantum yields for disappearance of the disubstituted dimers are listed in Table IV. It is evident from the data obtained with  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$  that the quantum yield for disappearance of the disubstituted dimer is larger when nonpurified CO is employed. The difference is ascribed to traces of  $\text{O}_2$  in the nonpurified CO. Linde CP grade CO can contain up to 800 ppm  $\text{O}_2$ . There is evidence that  $\text{O}_2$  reacts with the carbonyl radicals formed upon homolysis of the Mn-Mn bond.<sup>43</sup>

Aside from the difference in quantum yields, the removal of  $\text{O}_2$  from the CO has an important effect on the product distribution.  $\text{Mn}_2(\text{CO})_9\text{PBu}_3$  is seen as product when oxygen-free CO is employed, whereas it is absent when nonpurified CO is used. This result can be explained by assuming that there is some selectivity in the reactions of  $\text{O}_2$  with the carbonyl radicals, and that  $\text{O}_2$  reacts preferentially with  $\text{Mn}(\text{CO})_4\text{PBu}_3$ , as compared with  $\text{Mn}(\text{CO})_5$ .<sup>44</sup>

**Photosubstitution of  $\text{Mn}_2(\text{CO})_8\text{L}_2$  by  $\text{L}'$ .** Quantum yields for the photochemical reaction of  $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OEt})_3]_2$  with  $\text{PBu}_3$  at various concentrations were measured. One major



**Figure 4.** Pseudo-first-order rate law for disappearance of  $Mn_2(CO)_{10}$  ( $4.5 \times 10^{-4}$  M) under irradiation in heptane in presence of  $P(OEt)_3$  ( $1 \times 10^{-3}$  M): A, without added CO; B, with nonpurified CO.

**Table III.** Quantum Yield Measurements for Photosubstitution of  $Mn_2(CO)_{10}$  by  $P(OEt)_3$  in Heptane, with 350-nm Radiation

$[Mn_2(CO)_{10}] \times 10^4, M$	$[P(OEt)_3] \times 10^3, M$	$[CO] \times 10^2, M$	Irradiation time, min	$\Phi_d$	$\Phi_d(av)$
4.48	9.8		41	0.86	0.90
4.48	9.8		61	0.94	
4.80	2.0		40	0.80	0.83
4.80	2.0		80	0.87	
4.62	1.9	1.3	40	0.80	0.76
4.62	1.9	1.3	80	0.71	
4.74	1.0		40	0.90	0.85
4.74	1.0		85	0.81	
4.91	1.0	1.3	40	0.59	0.67
4.91	1.0	1.3	80	0.75	

product was identified as  $Mn_2(CO)_8(PBu_3)_2$ ; other products not specifically identified exhibited IR bands at 1936, 1922, and 1909  $cm^{-1}$ . These are probably due to mixed, polysubstituted dimers, possibly also monomers. The quantum yield for disappearance of  $Mn_2(CO)_8[P(OEt)_3]_2$  is dependent on the concentration of  $PBu_3$ , as illustrated by the data in Table V.

A  $4.14 \times 10^{-4}$  M heptane solution of  $Mn_2(CO)_8[P(OEt)_3]_2$  was saturated with air and irradiated at 350 nm. The quantum yield for disappearance of starting compound was observed to be 0.89. No products of the reaction were identified.

A single sample was studied to observe the quantum yield for photosubstitution of  $Mn_2(CO)_8(PBu_3)_2$  by  $P(OEt)_3$ ,  $4.9 \times 10^{-2}$  M. The quantum yield for disappearance of starting compound was found to be 0.58 and 0.53, for two sample withdrawals. The IR spectrum of the reaction solution showed no evidences of absorption above the 1949- $cm^{-1}$  absorption of  $Mn_2(CO)_8(PBu_3)_2$ , where either  $Mn_2(CO)_8[P(OEt)_3]_2$  or  $Mn_2(CO)_8(PBu_3)P(OEt)_3$  might be expected to absorb. A single product absorption at 1940  $cm^{-1}$  was observed.

**Reaction of  $Mn(CO)_5^-$  with Triphenylcyclopropenium Cation,  $C_3Ph_3^+$ .** A solution of  $NaMn(CO)_5$  in carefully purified THF was prepared using previously reported procedures.<sup>45</sup> Upon addition of  $PPh_3$ , there was no evidence of reaction as determined from IR spectra, after 13 days. However, immediately upon addition of  $C_3Ph_3BF_4$  there was gas evolution.

**Table IV.** Quantum Yields for Photosubstitution of  $Mn_2(CO)_8L_2$  Compounds by CO

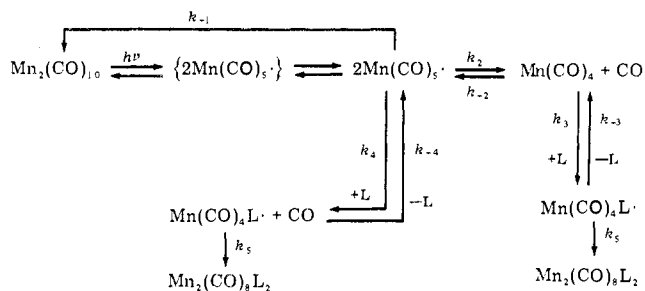
$[Mn_2(CO)_8L_2] \times 10^4, M$	Irradiation time, min	$\Phi_d$	$\Phi_d(av)$
$Mn_2(CO)_8(PBu)_2$			
4.85 <sup>a</sup>	66	0.78	
4.85 <sup>a</sup>	125	0.75	0.71
4.79 <sup>a</sup>	60	0.71	
4.79 <sup>a</sup>	130	0.61	
$Mn_2(CO)_8[P(OEt)_3]_2$			
2.62	40	0.17	0.18
2.62	80	0.19	
4.38	146	0.24	
4.38	355	0.22	0.22
4.17	40	0.21	
4.17	85	0.20	

<sup>a</sup> Nonpurified CO.

**Table V.** Quantum Yields for Photosubstitution of  $Mn_2(CO)_8[P(OEt)_3]_2$  by  $PBu_3$

$Mn_2(CO)_8[P(OEt)_3]_2 \times 10^4, M$	$PBu_3 \times 10^3, M$	Irradiation time, min	$\Phi_d$	$\Phi_d(av)$
3.80	5.0	40	0.28	0.28
3.80	5.0	80	0.29	
4.06	10.0	120	0.41	0.46
4.06	10.0	260	0.51	
3.66	25.0	20	0.82	0.82
3.66	25.0	40	0.83	

Scheme I



The color of the solution changed from light green to red-orange over a 30-min period. The IR spectrum of the solution revealed that  $Mn_2(CO)_8(PPh_3)_2$  is the major product, with traces of  $Mn_2(CO)_9PPh_3$  and  $Mn_2(CO)_{10}$ . The same result was observed when  $[(CH_3)_2N=CH_2]Br$  was employed in place of  $C_3Ph_3BF_4$ . However, no reaction was observed with  $C_3Ph_3Cl$ .

## Discussion

The photosubstitution studies with  $PBu_3$  and  $P(OEt)_3$  reveal several important generalities: (a) In the absence of added CO, the quantum yields for disappearance of  $Mn_2(CO)_{10}$  are high, and independent of the nature or concentration of L. (b) The disubstituted complex,  $Mn_2(CO)_8L_2$ , is a major product of the photosubstitution in both cases. (c) When purified CO is added to the solution at a concentration greater than that of L, a significant reduction in quantum yield is observed.

A general model for photosubstitution of  $Mn_2(CO)_{10}$  by L is diagrammed in Scheme I. Photodissociation of  $Mn_2(CO)_{10}$ , with quantum yield  $\Phi_r$ , results in formation of caged radical pairs,<sup>46,47</sup> denoted by brackets. These radical pairs may sep-

arate as a result of the excess energy that remains following photodissociation, or by thermal diffusion to form solvent-separated radicals. Geminate recombination of the radicals within the solvent cage is assumed to occur with a fractional probability  $G$  related mainly to the solvent and energy of irradiation, but—at the concentration levels employed in this study—not to the concentration of substituting ligand  $L$ . Diffusive recombination consumes a fraction  $k_{-1}[\text{Mn}\cdot]^2/N$  of solvent-separated radicals, where  $N$  is the total number of radicals formed per unit time,  $2\Phi_r[\text{Mn}_2(\text{CO})_{10}]I_0S/C_0V$ , and  $[\text{Mn}\cdot]$  represents the concentration of  $\text{Mn}(\text{CO})_5\cdot$ . Thus, the quantum yield for disappearance of  $\text{Mn}_2(\text{CO})_{10}$ ,  $\Phi_d$ , is given by

$$\Phi_d = \Phi_r - G - \frac{2k_{-1}[\text{Mn}\cdot]^2}{N} \quad (11)$$

Assuming that an identifiable set of products is formed,  $\Phi_d$  can also be expressed in terms of the rate of product formation. Assuming, as shown in Scheme I, that  $\text{Mn}_2(\text{CO})_8\text{L}_2$  is the sole product,  $\Phi_d = (2/N)d[\text{Mn}_2(\text{CO})_8\text{L}_2]/dt$ .

Since high quantum yields are observed for the overall photosubstitution process, it is evident that a large fraction of  $\text{Mn}(\text{CO})_5\cdot$  radicals formed undergoes substitution. The question remains of whether the substitution process follows the dissociative or associative pathway.

If substitution is governed by a rate-determining dissociation of  $\text{CO}$  from  $\text{Mn}(\text{CO})_5\cdot$ , and if loss of  $L$  from  $\text{Mn}(\text{CO})_4\text{L}\cdot$  can be ignored, then

$$\frac{d[\text{Mn}_2(\text{CO})_8\text{L}_2]}{dt} = \frac{1}{2} k_3[\text{Mn}(\text{CO})_4][L] \quad (12)$$

Employing a steady-state expression for  $[\text{Mn}(\text{CO})_4]$ ,

$$[\text{Mn}(\text{CO})_4] = k_2[\text{Mn}\cdot]/\{k_3[L] + k_{-2}[\text{CO}]\} \quad (13)$$

one obtains

$$\Phi_d = \frac{2}{N} \frac{d[\text{Mn}_2(\text{CO})_8\text{L}_2]}{dt} = \frac{k_3 k_2 [\text{Mn}\cdot][L]}{N\{k_3[L] + k_{-2}[\text{CO}]\}} \quad (14)$$

Based on this expression, when  $[L] \gg [\text{CO}]$ ,  $\Phi_d$  will be independent of the nature and concentration of  $L$ , as observed. In effect, every  $\text{Mn}(\text{CO})_4$  intermediate formed by loss of  $\text{CO}$  from  $\text{Mn}(\text{CO})_5\cdot$  is captured by  $L$  and converted to product. Because  $\text{Mn}(\text{CO})_4$  is a coordinatively unsaturated species, reaction with either  $L$  or  $\text{CO}$  should be rapid. Thus, both  $k_{-2}$  and  $k_3$  should be large, perhaps  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  or larger.<sup>48</sup> Assuming that  $k_{-2} \sim k_3$ , the quantum yield for product formation should decrease when  $[\text{CO}]$  is on the order of, or greater than,  $[L]$ , again in accord with observations when  $L$  is either  $\text{PBu}_3$  or  $\text{P}(\text{OEt})_3$ . Under these conditions, it is possible also that the loss of  $L$  from  $\text{Mn}(\text{CO})_4\text{L}\cdot$ , with capture of  $\text{Mn}(\text{CO})_4$  by  $\text{CO}$ , is also important in reducing the quantum yield (vide infra).

From the observation that the values for  $\Phi_d$  are large, it is reasonable to assume that  $k_2 \gg k_{-1}[\text{Mn}\cdot]$ . The value of  $k_{-1}$  has been measured to be about  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  under conditions closely similar to those employed here.<sup>26</sup> An upper limit for the concentration of  $\text{Mn}(\text{CO})_5\cdot$  can be obtained by calculating its steady-state concentration in the absence of substitution:

$$[\text{Mn}\cdot] = \left[ \frac{k_{\text{obsd}}[\text{Mn}_2(\text{CO})_{10}]}{k_{-1}} \right]^{1/2} \quad (15)$$

where  $k_{\text{obsd}}$  is the pseudo-first-order rate constant for disappearance of  $\text{Mn}_2(\text{CO})_{10}$  under irradiation when  $L$  is present in excess, typically about  $5 \times 10^{-5} \text{ s}^{-1}$ . For  $[\text{Mn}_2(\text{CO})_{10}] \sim 5 \times 10^{-4} \text{ M}$ ,  $[\text{Mn}\cdot] = 2 \times 10^{-9} \text{ M}$ . This in turn means that if

the dissociative pathway is the mode of substitution,  $k_2 \gg 10 \text{ s}^{-1}$ .

Assuming that substitution occurs via the associative pathway, the rate of appearance of product can be written as

$$\frac{d[\text{Mn}_2(\text{CO})_8\text{L}_2]}{dt} = k_5[\text{Mn}(\text{CO})_4\text{L}]^2 \quad (16)$$

Substituting the steady-state concentration expression for one of the  $\text{Mn}(\text{CO})_4\text{L}$  on the right,

$$[\text{Mn}(\text{CO})_4\text{L}] = \frac{k_4[\text{Mn}\cdot][L]}{k_{-4}[\text{CO}] + 2k_5[\text{Mn}(\text{CO})_4\text{L}]} \quad (17)$$

$$\frac{d[\text{Mn}_2(\text{CO})_8\text{L}_2]}{dt} = \frac{k_4 k_5 [\text{Mn}(\text{CO})_4\text{L}][\text{Mn}\cdot][L]}{k_{-4}[\text{CO}] + 2k_5[\text{Mn}(\text{CO})_4\text{L}]} \quad (18)$$

When  $k_5[\text{Mn}(\text{CO})_4\text{L}] \gg k_{-4}[\text{CO}]$ ,

$$\Phi_d = \frac{2}{N} \frac{d[\text{Mn}_2(\text{CO})_8\text{L}_2]}{dt} = k_4[\text{Mn}\cdot][L]/N \quad (19)$$

This expression appears to predict a first-order dependence of the quantum yield on  $L$ . However, in the associative process, the steady-state concentration of  $\text{Mn}(\text{CO})_5\cdot$  is itself dependent on  $L$ :

$$\frac{d[\text{Mn}\cdot]}{dt} = N' + k_{-4}[\text{Mn}(\text{CO})_4\text{L}\cdot][\text{CO}] - 2k_{-1}[\text{Mn}\cdot]^2 - k_4[\text{Mn}\cdot][L] \approx 0 \quad (20)$$

$$[\text{Mn}\cdot] = \frac{N' + k_{-4}[\text{Mn}(\text{CO})_4\text{L}\cdot][\text{CO}]}{2k_{-1}[\text{Mn}\cdot] + k_4[L]} \quad (21)$$

where  $N' = 2(\Phi_r - G)[\text{Mn}_2(\text{CO})_{10}]I_0S/C_0V$ . We neglect the second term in the numerator in eq 21 to be consistent with neglect of this process in deriving eq 19. Then, substituting into eq 19,

$$\Phi_d = \frac{k_4 N' [L]}{\{2k_{-1}[\text{Mn}\cdot] + k_4[L]\}N} \quad (22)$$

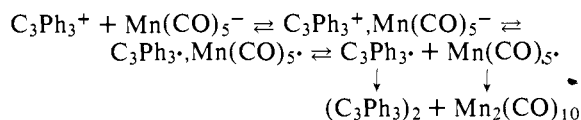
Thus, under the conditions  $[L] \gg [\text{CO}]$  and  $k_4[L] \gg k_{-1}[\text{Mn}\cdot]$ , the observed value of  $\Phi_d$  could be independent of the nature and concentration of  $L$ . The latter condition requires, for  $L \sim 2 \times 10^{-3} \text{ M}$ , that  $k_4 \gg 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , assuming that  $[\text{Mn}\cdot] \sim 4 \times 10^{-10} \text{ M}$  (20% of the calculated upper limit steady state concentration), and using the experimentally determined value of  $k_{-1} = 4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

If the associative process is operative, a decrease in quantum yield in the presence of excess  $\text{CO}$  in solution can arise only through a process in which  $L$  is displaced from  $\text{Mn}(\text{CO})_4\text{L}$  by  $\text{CO}$ , with rate constant  $k_{-4}$ . For such a process to be effective,  $k_{-4}$  must be on the same order of magnitude as  $k_4$ . This in turn implies that the bimolecular rate constants are relatively insensitive to the nature of the attacking nucleophile.

The observations regarding  $\Phi_d$  can in a general sense be accounted for in terms of either the dissociative or associative process. However, the values required for the rate constants involved in the associative pathway are not very appealing. The radical intermediates,  $\text{Mn}(\text{CO})_5\cdot$  or  $\text{Mn}(\text{CO})_4\text{L}\cdot$ , possess 17 electrons in the valence shell orbitals of the metal. The transition state in the associative pathway would involve 19 electrons in the metal orbitals. The large value required for the bimolecular rate constant,  $k_4$ , corresponds to a  $\Delta G^\ddagger$  value of 50 kJ or less. It seems highly unlikely that an associative transition state, involving the incorporation of antibonding metal orbitals, should be so accessible. Furthermore, the requirement that  $k_4$  and  $k_{-4}$  be of comparable magnitude is also not in accord with the general observations regarding dependences of second-order rate constants on ligand nucleophilicities in associative processes;  $\text{CO}$  is ordinarily a considerably weaker nucleophile than phosphine ligands.

The enthalpy of dissociation of the Mn–Mn bond in  $Mn_2(CO)_{10}$  has been variously estimated from physical studies to be from 80 to 145 kJ/mol.<sup>49,50</sup> By contrast, the energy of photons of 350-nm wavelength is 342 kJ/mol. Thus the possibility exists that the apparently high lability of the  $Mn(CO)_5\cdot$  radicals produced photochemically is due to excess energy present following bond homolysis. It is significant that in the thermal substitution reactions of  $Mn_2(CO)_{10}$ , the monosubstituted species  $Mn_2(CO)_9L$  is formed to a large extent.<sup>14b,51</sup> The extent to which the thermal substitution proceeds via metal–metal bond homolysis, as opposed to CO dissociation from  $Mn_2(CO)_{10}$ , is not entirely clear. The situation is complicated by the fact that the relative proportion of geminate pairs and solvent-separated radicals is likely to be much different in the two cases.<sup>52</sup> The excess energy present in the system following photochemical bond homolysis should occasion a substantial kinetic energy in the metal carbonyl radical fragments, and result in a large degree of solvent separation of radicals. Indeed, that this is so is evident from the very high observed quantum yields. Because of all these complexities, the photochemical results alone do not rule out photochemically induced CO loss from  $Mn(CO)_5$  as an important process.

The reaction of  $Mn(CO)_5^-$  with triphenylcyclopropenium ion, first observed by Olander,<sup>53</sup> provides a means of generating  $Mn(CO)_5\cdot$  by chemical means. The reaction presumably involves a one-electron oxidation–reduction process between the ions in an intimate ion pair:

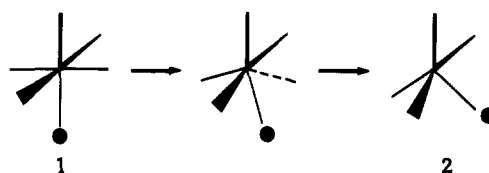


Any species capable of acting as a one-electron acceptor toward  $Mn(CO)_5^-$  should be capable of the same reaction, with  $Mn_2(CO)_{10}$  as a major product. Because of solubility limitations, the reaction was studied in THF as solvent. This might cause complications, in that THF is moderately nucleophilic. However, the parent ion,  $Mn(CO)_5^-$ , is, in the absence of an electron acceptor, stable indefinitely in THF, even in the presence of  $PPh_3$ .

When the reaction of  $Mn(CO)_5^-$  with an electron acceptor is carried out in the presence of  $PPh_3$ ,  $Mn_2(CO)_8[PPh_3]_2$  is a principal product, along with traces of  $Mn(CO)_9PPh_3$  and  $Mn_2(CO)_{10}$ . This result implies that the substitution of  $Mn(CO)_5\cdot$  occurs rapidly with respect to the rate of recombination of radicals to form the dinuclear metal carbonyl species. Thus, even in the absence of any excess energy imparted to the radicals via the photochemical process, they undergo a facile substitution.

The experimental facts to this point are thus that the  $Mn(CO)_5\cdot$  radical, however generated, is subject to remarkably facile substitution. A similar behavior is evident for  $Re(CO)_5\cdot$ .<sup>35,36,54</sup> In both cases the evidence, while incomplete, suggests that substitution occurs via dissociative loss of CO. While a rapid loss of ligand from metal via a dissociative (D) or dissociative interchange ( $I_d$ ) process is not uncommon in complexes of transition metal ions, there is no precedent in the behavior of the spin-paired ground state metal carbonyls for a *rapid* dissociative loss of carbonyl. (It should be noted, however, that the dissociative loss of ligand, although slow, is the observed mode of substitution into the mononuclear metal carbonyls of the first transition row metals,  $Cr(CO)_6$ ,  $Fe(CO)_5$ , or  $Ni(CO)_4$ .)<sup>55</sup> It is thus not entirely clear why the barrier to dissociative loss of CO from a five-coordinate carbonyl radical such as  $Mn(CO)_5\cdot$  should be so low. The explanation would seem to lie in the fact that the resulting four-coordinate species,  $Mn(CO)_4$ , has relatively high stability. The

Scheme II



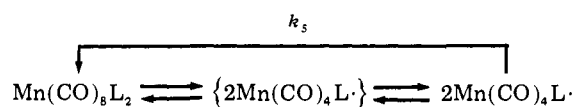
simple MO calculations carried out by Elian and Hoffmann<sup>56</sup> and by Burdett<sup>57</sup> suggest that  $Mn(CO)_4$  should have a  $C_{2v}$  geometry, **2**. Thus the formation of  $Mn(CO)_4$  from  $Mn(CO)_5\cdot$  can be visualized as occurring along the reaction coordinate shown in Scheme II. The  $Mn(CO)_5\cdot$  radical has  $C_{4v}$  geometry.<sup>56</sup> It is likely to have a structure closely similar to the well-characterized  $Co(CN)_5^{3-}$  ion, a radical species with 17 electrons in the valence shell orbitals of the metal.<sup>59</sup> The unpaired electron in these species appears to occupy a stereochemically active orbital. One can thus think of  $Mn(CO)_5\cdot$  as a six-coordinate species, with the unpaired electron as a sixth “ligand”. Looked at from this point of view, the unpaired electron can be classified as a ligand that stabilizes the radical toward dissociative loss of CO. It is reasonable to suppose that it is a cis-labilizing ligand, inasmuch as it lacks the characteristics expected for a ligand that could stabilize the trans CO.<sup>60</sup> In general, non- $\pi$ -bonding ligands such as amines, or others that are weak  $\sigma$  donors as well, are observed to be strongly cis stabilizing. However, the unpaired electron lacks the orbital characteristics that appear from a molecular orbital analysis<sup>61</sup> to be important in determining the cis stabilizing tendency of halide, nitrate, or similar ligands. Thus, the origin of the remarkable lability of the five-coordinate radicals is not clear.

**Photosubstitution of  $Mn_2Co_8L_2$ .** Analysis of the photosubstitution of  $Mn_2(CO)_8L_2$  substances is complicated by the number of obtainable products. In addition, and depending on the identity of the entering ligand  $L'$ , the ability of the radicals to couple becomes an important consideration. The synthesis and general characteristics of substituted manganese carbonyl radicals are discussed in the following paper.<sup>62</sup> We need only note here that species of the form  $Mn(CO)_3LL'$ , where  $L$  and  $L'$  are both phosphorus ligands, usually possess sufficient steric requirements to preclude stable dimer formation. Because of these added complexities we do not attempt to analyze in detail the dependences of quantum yield on ligand concentrations. Nevertheless, several useful observations have been made.

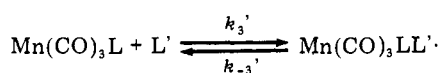
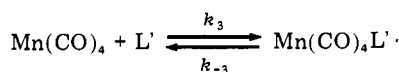
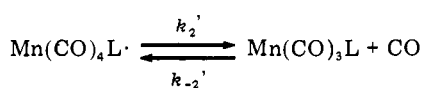
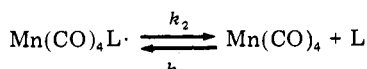
An outline of the photosubstitution of  $Mn_2(CO)_8L_2$  compound that includes the steps likely to be most important is depicted in Scheme III. Both dissociative and associative modes of substitution are shown as alternatives. An important consideration in evaluating the photochemical observations is that, *when  $L$  and  $L'$  are both moderately bulky ligands such as phosphine or phosphite, all the radical dimerization steps are expected to be much slower than for  $Mn(CO)_5\cdot$ .* That is, all the  $k_5$  rate constants are likely to be several orders of magnitude smaller than the rate constant for recombination observed for  $Mn(CO)_5\cdot$ .<sup>26</sup> (This matter is discussed in more detail in the following paper.<sup>62</sup>) As a result, the substitution process involving the substituted radicals, whether dissociative or associative, can be considerably slower than for  $Mn(CO)_5\cdot$  and still lead to a high quantum yield for photosubstitution.

The quantum yield for disappearance of either  $Mn_2(CO)_8[PBu_3]_2$  or  $Mn_2(CO)_8[P(OEt)_3]_2$  upon photosubstitution by CO is 0.2. A value of 0.7 is obtained for  $\Phi_d$  when nonpurified CO is employed. The  $O_2$  present in the solution under these conditions is presumed to scavenge solvent-separated  $Mn(CO)_4L\cdot$  radicals. The lower value of 0.2 for  $\Phi_d$  when purified CO is employed suggests that only a fraction of the  $Mn(CO)_4L\cdot$  radicals formed undergoes substitution of  $L$ .

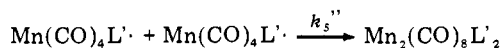
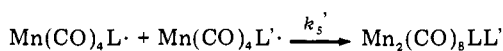
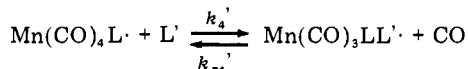
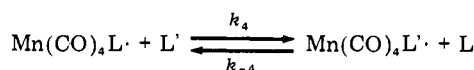
## Scheme III



## Dissociative mode



## Associative mode



These observations suggest that substitution of the phosphorus ligand from  $\text{Mn}(\text{CO})_4\text{L}$  is much slower than loss of CO from  $\text{Mn}(\text{CO})_5\cdot$ . This follows from the expectation that formation of either  $\text{Mn}_2(\text{CO})_9\text{L}$  or  $\text{Mn}_2(\text{CO})_{10}$  following loss of L from  $\text{Mn}(\text{CO})_4\text{L}\cdot$  and replacement by CO should be relatively much faster than re-formation of  $\text{Mn}_2(\text{CO})_8\text{L}_2$ . There should thus be a considerably longer time during which the  $\text{Mn}(\text{CO})_4\text{L}\cdot$  radicals can undergo substitution of L by CO.

When  $\text{Mn}_2(\text{CO})_8[\text{P}(\text{OEt})_3]_2$  is irradiated with  $\text{PBu}_3$  as substituting ligand,  $\Phi_d$  is found to increase with the concentration of  $\text{PBu}_3$ , as shown in Table V. While  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$  is a major product in this reaction, other unidentified products are formed. The higher quantum yields observed in this reaction as compared with  $\text{L}' = \text{CO}$  can be ascribed at least in part to the replacement of CO in  $\text{Mn}(\text{CO})_4\text{P}(\text{OEt})_3\cdot$  by  $\text{PBu}_3$ . The observation that  $\Phi_d$  increases with concentration of  $\text{PBu}_3$  could be accounted for in terms of an associative step for substitution. Such a process is made more plausible by the longer lifetimes of the  $\text{Mn}(\text{CO})_4\text{L}\cdot$  radical following formation. However, the relative rates of recombination of the radical monomers can be expected to vary widely. When  $\text{L} = \text{P}(\text{OEt})_3$  and  $\text{L}' = \text{PBu}_3$ , the recombination rates shown in Scheme III should vary in the order  $k_5 > k_5' > k_5''$ ; that is, the rate constants for recombination should decrease in the order of increasing steric requirement of substituting ligand. A considerably more detailed study will be required to sort out the details of these more complex systems.

Finally, it should be noted that when  $\text{Mn}_2(\text{CO})_8[\text{PBu}_3]_2$  is photolyzed in the presence of  $\text{P}(\text{OEt})_3$ , no evidence is seen in the IR spectra for  $\text{Mn}(\text{CO})_8[\text{P}(\text{OEt})_3]_2$  or  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)\text{P}(\text{OEt})_3$ . This observation provides further evidence that loss of  $\text{PBu}_3$  from  $\text{Mn}(\text{CO})_4\text{PBu}_3\cdot$  is slow.

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## Formation and Properties of Substituted Manganese Carbonyl Radicals<sup>1</sup>

Dennis R. Kidd, C. P. Cheng, and Theodore L. Brown\*

Contribution from the School of Chemical Sciences and Materials Research Laboratory, University of Illinois—Urbana, Urbana, Illinois 61801. Received November 4, 1977

**Abstract:** Extended photolysis of bis(tributylphosphine)dimanganese octacarbonyl,  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ , in the presence of excess  $\text{PBu}_3$ , or of tris(triethyl phosphite)dimanganese heptacarbonyl,  $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$ , in heptane, with periodic removal of CO, results in formation of paramagnetic species. The frozen solution containing  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2 + \text{PBu}_3$  exhibits an ESR spectrum consistent with a square-pyramidal  $\text{Mn}(\text{CO})_3(\text{PBu}_3)_2$  radical, with mutually trans  $\text{PBu}_3$  groups in basal positions. An analogous, but less well-resolved, ESR spectrum is obtained for the frozen  $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3 + \text{P}(\text{OEt})_3$  solution following irradiation. The radicals formed are apparently prevented from recombining by steric repulsions due to the phosphorus ligands. The  $\text{Mn}(\text{CO})_3\text{L}_2$  radicals slowly abstract hydrogen from solvents; with xylene the reaction is relatively rapid.

The substitution reactions of the group 7 dinuclear metal carbonyl compounds have been the subjects of several reports. In general, mono- or disubstitution of  $\text{Mn}_2(\text{CO})_{10}$  by a monodentate phosphorus ligand occurs in the axial<sup>2</sup> or 9,10 positions.<sup>3–13</sup> Ligands of relatively small steric requirement have been found to substitute into the equatorial positions.<sup>14,15</sup> There have been few reports of well-characterized dimers of the type  $\text{Mn}_2(\text{CO})_7\text{L}_3$ , where L is a monodentate ligand;<sup>8,16,17</sup> three cases of the type  $\text{Mn}_2(\text{CO})_6(\text{L}-\text{L})_2$  are known, in which L-L is a bidentate ligand;<sup>18–20</sup> for L-L = diphenylphosphinomethane, the ligands are bonded in the 1,5 and 3,7 positions.<sup>21,22</sup>

The relative paucity of examples of the more highly substituted derivatives of  $\text{Mn}_2(\text{CO})_{10}$  is related to the fact that the metal-metal bond is not stable. There are several reports in the literature of monomeric, paramagnetic metal carbonyl species  $\text{Mn}(\text{CO})_{5-n}\text{L}_n$  or  $\text{Mn}(\text{CO})_{5-2n}(\text{L}-\text{L})_n$ ; these prior evidences are summarized in Table I. Analogous species have been formulated for rhenium.<sup>30,31</sup>

While reports of the formation of substituted metal carbonyl radicals are numerous, these species have not, in general, been well characterized. In fact, current evidence suggests that in most cases, the supposed manganese(0) radical species have not been observed. It appears from relatively recent studies,<sup>11,32</sup> and on the basis of our own work, that, while radicals may have been formed in the systems investigated, the physical observations made were of the corresponding hydride, e.g.,  $\text{Mn}(\text{CO})_{5-n}\text{L}_n\text{H}$ . The only radical species for which a solid-state crystal structure determination has been carried out is  $\text{Mn}(\text{CO})(\text{C}_4\text{H}_6)_2$ .<sup>28</sup>

In this contribution we report the results of exhaustive photosubstitution of  $\text{Mn}_2(\text{CO})_{10}$  by either tributylphosphine,  $\text{PBu}_3$ , or triethyl phosphite,  $\text{P}(\text{OEt})_3$ , including evidence for formation of moderately stable radical species.

### Experimental Section

Solvents, techniques for handling of materials, and instrumentation are described in the previous paper.<sup>17</sup> The photochemical substitution

reactions of  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$  or  $\text{Mn}_2(\text{CO})_7[\text{P}(\text{OEt})_3]_3$  were carried out in a Pyrex solution chamber that could be attached to a vacuum line for degassing and repeated removing of CO during photolysis. The photolyses were carried out on thoroughly degassed solutions, using a 650-W GE type DVY tungsten-halogen lamp, with 3400 K temperature. The UV-visible or ESR spectra of the photolyzed solutions were recorded without opening the chamber, by transferring a portion of the solution to an attached side arm fitted with an appropriate cell. Samples for IR analysis were obtained by removal of a sample from the chamber in an inert atmosphere box, using a gas-tight syringe. The photolysis solutions proved to be extremely sensitive to traces of oxygen; only with the most diligent efforts was it possible to obtain reproducible results.

The ESR spectra were obtained on a Varian Model 9 X-band spectrometer.

The hydrides  $\text{HMn}(\text{CO})_3(\text{PBu}_3)_2$  and  $\text{HMn}(\text{CO})_3[\text{P}(\text{OEt})_3]_2$  were formed in a thermal reaction by refluxing  $\text{Mn}_2(\text{CO})_{10}$  or the appropriate  $\text{Mn}_2(\text{CO})_8\text{L}_2$  compound plus L in reagent grade xylene at atmospheric pressure under  $\text{N}_2$  for 80 h.<sup>33</sup> The hydrides were not isolated but their formulations as  $\text{HMn}(\text{CO})_3\text{L}_2$  were established in each case from the <sup>1</sup>H NMR spectra in benzene. The spectrum for  $\text{HMn}(\text{CO})_3(\text{PBu}_3)_2$  was centered at  $\tau$  18.76 with  $J(\text{H}-\text{P}) = 33$  Hz. For  $\text{HMn}(\text{CO})_3[\text{P}(\text{OEt})_3]_2$  the triplet is centered at  $\tau$  17.93,  $J(\text{H}-\text{P}) = 43$  Hz. The IR spectrum of  $\text{HMn}(\text{CO})_3(\text{PBu}_3)_2$  exhibited a single CO stretching mode in heptane at  $1896\text{ cm}^{-1}$ .<sup>34</sup> Bands were observed for  $\text{HMn}(\text{CO})_3[\text{P}(\text{OEt})_3]_2$  at 1945 and  $1924\text{ cm}^{-1}$ .

### Results

**Photolysis of  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ .** A heptane solution of  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ ,  $10^{-2}$  M, with  $2 \times 10^{-2}$  M  $\text{PBu}_3$ , was irradiated with repeated degassing to remove any CO formed. Over a period of several hours the color of the solution changes from an orange to green. After continued photolysis without degassing it changes to pale yellow. The green color during the intermediate stages of the reaction results from the absorption at 355 nm due to  $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ , and a broad absorption at about 750 nm due to an intermediate product.

The green solution yields an ESR signal at room temperature, as shown in Figure 1. A frozen solution spectrum, taken at 83 K, is shown in Figure 2. This spectrum was simulated by