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Reactions of Manganese Carbonyls with Quaternary Ammonium Halides

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Photolysis of $Mn_2(CO)_{10}$ in CH_2Cl_2 in the presence of a quaternary ammonium halide results in formation of $Mn(CO)_5^-$ and $Mn(CO)_4X_2^-$ (X = Cl or Br). Possible competing thermal reactions or reactions with solvent have been ruled out. The two anions are proposed to be formed as a result of cleavage of an intermediate, $Mn_2(CO)_9X^-$. The binuclear anion has been shown, independently, to give the same photolysis products.

Introduction

Reactions of halide ions with metal carbonyl complexes have been widely used to promote carbon monoxide substitution. Both thermal and photochemical means have been employed to promote the reactions and the proposed mechanisms vary from those involving dissociative loss of CO followed by halide ion capture to nucleophilic additions of halide ion to the metal or a carbonyl ligand [1].

Since the phase transfer route we have employed in the syntheses of allyl complexes [2] utilized quaternary ammonium halides in combination with various metal carbonyl halides, we have sought to determine the possible role of halide ions in the phase transfer reactions. Our studies have focused on reactions of manganese carbonyls and have included both thermal and photochemical processes in order to clarify the chemistry.

Phase transfer reactions involving aqueous base together with quaternary ammonium halides and $XMn(CO)_5$ (X = Cl, Br) lead to binuclear anions of the general type $Q^+Mn_2(CO)_9X^-$ [2a,c]. Compounds of this type had been reported previously [3] from photolyses of $Mn_2(CO)_{10}$ with Et_4NCl in $CHCl_3$ or CH_2Cl_2 solution. Both types of photolyses were reported to provide $Et_4N^+Mn_2(CO)_9Cl^-$ as a minor component. Photolysis of $Mn_2(CO)_{10}$ with KBr and dibenzo-18-crown-6 in CH_2Cl_2 was later reported [4] to provide the corresponding bromo anion (as the crown-K^+ salt) in somewhat better yield. We have tried to obtain samples of the binuclear anion by conducting photolyses of $Mn_2(CO)_{10}$ in $CHCl_3$ or CH_2Cl_2 with ϕCH_2NEt_3Cl and, indeed, a small amount of this product can be isolated from reaction conducted in CH_2Cl_2. However, there was no evidence for formation of $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$, the anion described by Levenson *et al.* [3] as the major product generated in either solvent. The μ-chloride was also reportedly [3] formed by irradiation of $Mn_2(CO)_9Cl^-$ in the presence of Et_4NCl, however our results indicate a different mode of reaction for $Mn_2(CO)_9X^-$. The thermal and photochemical behavior of $Mn_2(CO)_9X^-$ (X = Cl, Br), $Mn_2(CO)_{10}$ and related manganese carbonyls in the presence of quaternary ammonium halides is discussed below.

Results and Discussion

Photolyses of $Mn_2(CO)_{10}$ with ϕCH_2NEt_3Cl in the general manner** described by Levenson *et al.* [3], led to complete destruction of $Mn_2(CO)_{10}$ within a few minutes. Copious precipitation of a white solid began to occur shortly after photolysis was begun, but the solid exhibited no absorption in the carbonyl region of the IR. In a second photolysis, where a pyrex filter was used, a small amount of $ClMn(CO)_5$ was isolated, but the reaction again led mainly to non-carbonyl products. After these results, we adopted a less vigorous set of reaction conditions and conducted the remaining reactions in CH_2Cl_2.

The heat of the UV lamp used in our photochemical reactions raised the temperature of the solution to 35–40 °C; therefore, control experiments were performed in this temperature range to establish possible competing thermal reactions. There was no reaction of $Mn_2(CO)_{10}$ or *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ with Q^+X^- under these conditions and $Et_4N^+Mn_2(CO)_9Br^-$ is only slowly cleaved by Et_4NBr to equal portions of $Mn(CO)_4Br_2^-$ and $Mn(CO)_5^-$; $BrMn(CO)_5$

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**The photochemical conditions used by these workers were not specified precisely.

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is readily converted to *cis*-$Mn(CO)_4Br_2^-$ in refluxing CH_2Cl_2, however. Authentic samples of Et_4N^+-$Mn(CO)_5^-$ (see Experimental) and *cis*-$Et_4N^+Mn(CO)_4$-Br_2^- [1c] were prepared and Beer's law plots, in the appropriate concentration range, were obtained for these anions and for $Et_4N^+Mn_2(CO)_9Br^-$ [2c] and $Mn_2(CO)_{10}$ in order to determine the amounts of such compounds in the product mixtures from photolysis.

Photochemical control experiments were also done; $Mn_2(CO)_{10}$ is inert during 2 hours of photolysis whereas $Et_4N^+Mn_2(CO)_9Br^-$ suffers about 30% conversion to products [mainly $Mn_2(CO)_{10}$ together with smaller amounts of $Mn(CO)_5^-$ and $Mn(CO)_4X_2^-$, [X = Cl or Br] after 1½ hours.

When photolyzed under our conditions for 2 hours in CH_2Cl_2 with approximately 2 molar equivalents of ϕCH_2NEt_3Cl, 2/3 of the $Mn_2(CO)_{10}$ was converted to approximately equimolar quantities of $Mn(CO)_5^-$ and *cis*-$Mn(CO)_4Cl_2^-$ together with a very small amount of $Mn_2(CO)_9Cl^-$. Believing that the binuclear anion might be an intermediate in this reaction, we examined the behavior of the related compound $Et_4N^+Mn_2(CO)_9Br^-$ toward photolysis in the presence of an equimolar quantity of Et_4-NBr. Indeed, $Mn(CO)_5^-$ and $Mn(CO)_4Br_2^-$ are rapidly formed in essentially equal amounts [together with a small amount of $Mn_2(CO)_{10}$].

Photolyses of *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ and Et_4N^+-$Mn(CO)_5^-$ together with equimolar quantities of Et_4-NBr were also conducted to probe for secondary reactions. The dihalo anion gives primarily non-carbonyl products whereas $Mn(CO)_5^-$ appears to be slowly converted to $HMn(CO)_5$. These reactions were not examined further.

After consideration of previous work on photochemical reactions of $Mn_2(CO)_{10}$ [5–7], the following sequences appear to account for the observed results:

$$Mn_2(CO)_{10} \rightleftarrows 2\,{\cdot}Mn(CO)_5 \quad (1)$$

$$\cdot Mn(CO)_5 + X^- \rightarrow \cdot Mn(CO)_4X^- + CO \quad (2)$$

$$\cdot Mn(CO)_5 + \cdot Mn(CO)_4X^- \rightarrow Mn_2(CO)_9X^- \quad (3)$$

$$Mn_2(CO)_9X^- + X^- \rightarrow Mn(CO)_5^- + Mn(CO)_4X_2^- \quad (4)$$

In reactions involving photochemical substitution by phosphines in $Mn_2(CO)_{10}$, Brown [5] has concluded that sequences analogous to (2) above take place by dissociative processes. Also, with phosphines, the formation of di- and tri-substituted manganese dimers is preferred over recombination of $\cdot Mn(CO)_5$ with the substitution radical [a sequence similar to (3)]. Although cleavage of the binuclear anion by halide ion does also take place thermally, the photochemical reaction appears to be faster. The mechanism of the photochemical cleavage, sequence (4), is not clear at this point; the observed formation of $Mn_2(CO)_{10}$ as a product suggests that $\cdot Mn(CO)_5$ may be formed initially.

We have not observed the μ-chloride described by Levenson *et al.*, [3] and it is not clear what reaction conditions are required to generate that product.

Experimental

Except where otherwise indicated, all procedures were carried out under an atmosphere of prepurified nitrogen. Dichloromethane, chloroform and methanol were reagent grade and used directly. Hexane was distilled before use. THF was dried and deoxygenated by distillation from sodium benzophenone ketyl under nitrogen. The following compounds were prepared as described previously: $Q^+Mn_2(CO)_9X^-$ [Q = ϕCH_2NEt_3 or Et_4N; X = Cl, Br] [2a,c], $BrMn(CO)_5$ [8], $ClMn(CO)_5$ [6], *cis*-$Et_4N^+Mn(CO)_4$-X_2^- (X = Cl, Br) [1c]. Benzyltriethylammonium chloride and tetraethylammonium chloride and bromide were prepared according to literature procedures, recrystallized from ethanol/diethyl ether and then dried in a vacuum desiccator. High quality $Mn_2(CO)_{10}$ was obtained from Strem Chemical and used directly.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer and calibrated against polystyrene film. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of $Et_4N^+Mn(CO)_5^-$

Generation of $NaMn(CO)_5$ was done in the manner described previously [9] except that NaOH was used instead of sodium methoxide; the procedure was performed completely in an Ace-Burlitch inert atmosphere system with Schlenk techniques. The reaction was conducted in a 100 ml Schlenk reaction vessel fitted with a reflux condenser and a magnetic stirrer. After evacuating and then filling with purified nitrogen, the reaction vessel was charged with 2.0 g $Mn_2(CO)_{10}$ (5.1 mmol) and a solution obtained by dissolving 1 g (25 mmol) of NaOH in 25 ml of MeOH and 5 ml of H_2O. The reaction mixture was then heated for 30 minutes at 90 °C (oil bath temperature). During this process, the color of the solution changed from bright yellow to dark red, then to orange and finally to yellow green and a white precipitate was formed. The resulting greenish-yellow solution was cooled to room temperature and then, while stirring, was treated with a solution containing 2.30 g of Et_4NBr (11 mmol) in 20 ml of MeOH. After

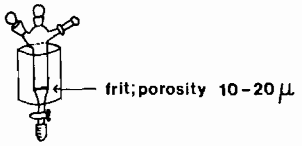

Fig. 1. Low-temperature crystallizer.

15 minutes, the reddish yellow solution was filtered and the filtrate was concentrated under vacuum to a small bulk (voluminous yellow solid separated out). This residue was dissolved with 60 ml of CH_2Cl_2 and transferred to a separatory funnel (with nitrogen inlet, Schlenk type); this solution was extracted with distilled water twice (20 ml each). After separation, the CH_2Cl_2 solution was dried over $MgSO_4$, filtered and solvent was removed under vacuum to yield an orange solid which was purified by recrystallization from CH_2Cl_2/hexane with a low-temperature crystallizer (Fig. 1) at −70 °C. Pale yellow crystals [1.98 g, 60% yield based on $Mn_2(CO)_{10}$] were obtained. The m.p. 199.5° (not reported previously), was taken under no-air conditions (see below). The IR (ν_{CO}) spectrum, in CH_2Cl_2, showed bands at 1903 (s) and 1862 (vs) cm^{-1} (taken under no-air conditions, see below) [lit. [10] (THF): 1902 and 1878 cm^{-1}]. *Anal.* Calcd for $C_{13}H_{20}O_5NMn$: C, 48.01; H, 6.20; N, 4.31. Found: C, 47.89; H, 6.38; N, 4.28. The analytical sample was prepared under nitrogen according to a published procedure [11].

Derivatization of $Mn(CO)_5^-$: Conversion to C_6H_5-$COMn(CO)_5$

The $Et_4N^+Mn(CO)_5^-$ was prepared from 2.0 g (5.1 mmol) of $Mn_2(CO)_{10}$ in the manner described above, however, at the last step of the preparation, instead of removing solvent under vacuum to isolate $Et_4N^+Mn(CO)_5^-$, the dried CH_2Cl_2 solution was allowed to react with a solution containing 1.2 ml (1.44 g, 10.4 mmol) of benzoyl chloride in 10 ml of CH_2Cl_2 (added dropwise during 10 minutes at 0 °C under an atmosphere of carbon monoxide). The resultant solution was stirred at 0 °C for another 4 hours under a CO atmosphere. The IR showed no more $Et_4N^+Mn(CO)_5^-$ was left and the reaction mixture was worked up without special precautions since the product, $C_6H_5COMn(CO)_5$, is not highly air sensitive. Thus, the reaction mixture was washed twice with distilled water (15 ml each) and then dried over $MgSO_4$. After filtration, solvent was removed on a rotary evaporator under reduced pressure to give a yellow crystalline solid which was purified by recrystallization from hexane at −20 °C; 2.5 g of pale yellow plates were obtained (82% based on $Mn_2(CO)_{10}$, m.p. 92–93 °C (lit. [12] 95–96°). The product had ν_{CO}(hexane); 2118(m), 2056(m), 2021(s), 2012(vs), 2002(s) cm^{-1} (lit. [13] 2114, 2055, 2021, 2010, 2002 cm^{-1}).

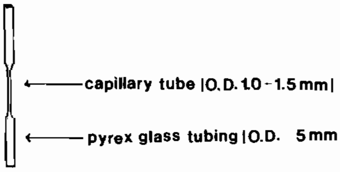

Fig. 2. An elongated tube for m.p. determination of an air sensitive compound.

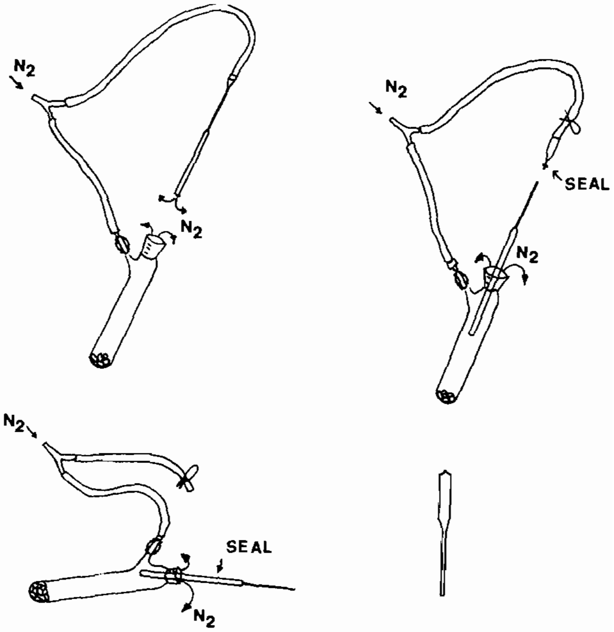

Fig. 3. Apparatus and procedures for melting point determination of an air sensitive compound. (1) After flushing the whole system with nitrogen, the elongated tube is inserted into the Schlenk storage tube. A positive N_2 flow should be present at all times. (2) Clamp the tygon tubing which is connected to the elongated tube and then seal off the elongated tube with a torch as indicated. The open end of the elongated tube should not be removed from the N_2 atmosphere of the Schlenk tube at anytime. (3) Insert the tube further into the storage tube to obtain some solid and tap the solid down to the sealed end of capillary tube. the tube is then withdrawn slightly from the storage tube and sealed off as indicated at the larger end. (4) A capillary m.p. tube sealed under N_2.

Inert Atmosphere Techniques

Melting point determination for air sensitive compounds

The melting point of an air sensitive compound can be taken by using a Schlenk storage tube containing the compound and a piece of glass tubing (O.D. 5 mm) elongated in the center to resemble a capillary

Fig. 4. A modified syringe barrel; a one ml glass syringe barrel which has been shortened to about 2 cm and into which a syringe needle has been inserted and glued using epoxy.

tube (Fig. 2). The stepwise procedures are shown in Fig. 3.

Obtaining solution infrared spectra under inert atmosphere conditions

The infrared spectrum of an air sensitive compound in solution is taken by using a Schlenk reaction vessel, two modified syringes (Fig. 4) and two pieces of polyethylene tubing (I.D. 0.76 mm, O.D. 1.2 mm). The set-up and stepwise procedures are shown in Fig. 5. A similar procedure was reported recently [14], however, we believe that the method presented here is somewhat better since the IR cell is fully deaerated before being filled.

Beer's Law Plots and Molar Extinction Coefficients

Beer's law plots were used to calculate the percentages of reactants and products in the thermal and photochemical reaction mixtures; linear plots were obtained in the appropriate concentration range for $Et_4N^+Mn(CO)_5^-$, $Et_4N^+Mn_2(CO)_9Br^-$, *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ and $Mn_2(CO)_{10}$. The molar extinction coefficients, ϵ, for these compounds in CH_2Cl_2 are as follows:

$Et_4N^+Mn(CO)_5^-$:*
$\epsilon_{1903} = 3600\ M^{-1}\ cm^{-1}$, $\epsilon_{1862} = 4640\ M^{-1}\ cm^{-1}$.

$Et_4N^+Mn_2(CO)_9Br^-$:
$\epsilon_{2080} = 576\ M^{-1}\ cm^{-1}$, $\epsilon_{2010} = 4540\ M^{-1}\ cm^{-1}$,
$\epsilon_{1980} = 7580\ M^{-1}\ cm^{-1}$, $\epsilon_{1902} = 1300\ M^{-1}\ cm^{-1}$.

cis-$Et_4N^+Mn(CO)_4Br_2^-$:
$\epsilon_{2090} = 335\ M^{-1}\ cm^{-1}$, $\epsilon_{1985} = 1220\ M^{-1}\ cm^{-1}$,
$\epsilon_{1940} = 2080\ M^{-1}\ cm^{-1}$.

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*The reported ϵ value [15] for the analogous compound, $Me_4N^+Mn(CO)_5^-$, in THF was $3870\ M^{-1}\ cm^{-1}$ at $1903\ cm^{-1}$.

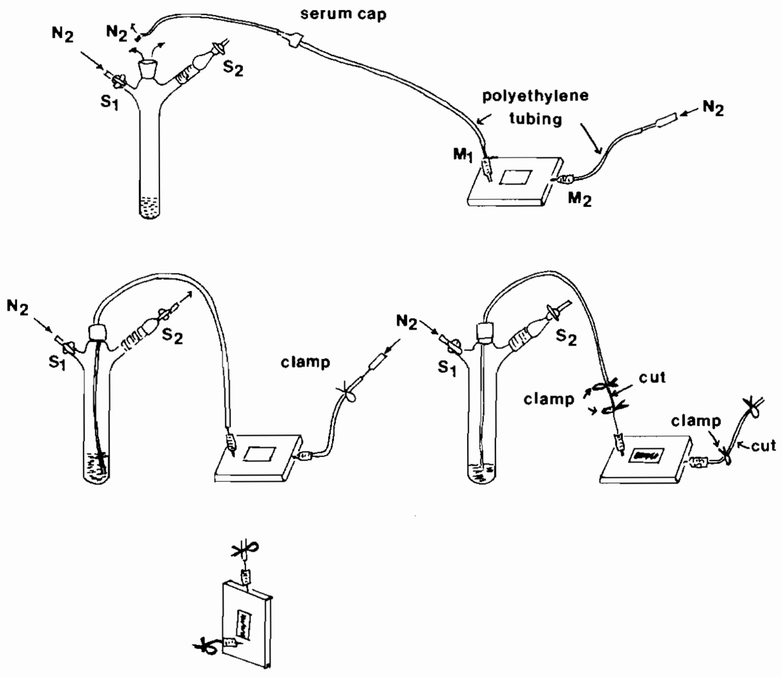

Fig. 5. Apparatus and procedures for obtaining an inert atmosphere liquid IR spectrum (for convenience, only the front of the IR cell holder is shown). (1) Using standard Schlenkware techniques, load solids into the Schlenk reaction vessel and dissolve them in a suitable solvent; with stopcock S_2 closed, continue flushing the system with N_2 through stopcock S_1. (2) Flush the IR cell with N_2 through modified syringes M and insert the polyethylene tubing into the center joint of the reaction vessel. (3) Open stopcock S_2 and then secure the serum cap in place (tubing should be immersed into the solution) and then turn off the N_2 on the IR cell and clamp the tubing as indicated. (4) Close S_2 and simultaneously turn off N_2 entering S_1. By slowly turning the N_2 back on, the solution is forced up through the tubing and into the IR cell. Clamp the tubing and cut each of them as indicated. (5) Final air-free IR set-up.

$Mn_2(CO)_{10}$:
$\epsilon_{2040} = 8960\,M^{-1}\,cm^{-1}$, $\epsilon_{2010} = 19090\,M^{-1}\,cm^{-1}$, $\epsilon_{1976} = 2580\,M^{-1}\,cm^{-1}$.

Thermal Reactions

Attempted reaction of $Mn_2(CO)_{10}$ with ϕCH_2NEt_3Cl

The $Mn_2(CO)_{10}$ (0.2 g, 0.51 mmol) and ϕCH_2NEt_3Cl (0.21 g, 0.95 mmol) were dissolved in 20 ml of CH_2Cl_2 and stirred at 40–45 °C for 2 hours. Infrared spectra indicated no evidence of reaction.

Attempted reaction of cis-*$Et_4N^+Mn(CO)_4Br_2^-$ with Et_4NBr*

The *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ (0.23 g, 0.5 mmol) and Et_4NBr (0.11 g, 0.5 mmol) were dissolved in 20 ml of CH_2Cl_2 and stirred at 40–45 °C for 2 hours. Infrared spectra indicated no evidence of reaction.

Reaction of $Et_4N^+Mn_2(CO)_9Br^-$ with Et_4NBr

The $Et_4N^+Mn_2(CO)_9Br^-$(0.28 g, 0.5 mmol) and 0.11 g (0.5 mmol) of Et_4NBr were refluxed in 20 ml of CH_2Cl_2. The reaction was monitored by observing the changes in the infrared spectra of samples taken from the reaction mixture; $Et_4N^+Mn(CO)_5^-$ and *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ were slowly formed (after an hour, the relative molar percentages for $Mn_2(CO)_9Br^-$, *cis*-$Mn(CO)_4Br_2^-$ and $Mn(CO)_5^-$ were 70:17:13 as determined by IR from the Beer's law plots of these compounds). A small amount of $HMn(CO)_5$ also appeared to be present (by IR).

Photochemical Reactions

Photolysis of $Mn_2(CO)_{10}$ with ϕCH_2NEt_3Cl in $CHCl_3$

Procedure (1): Photolysis of $Mn_2(CO)_{10}$ and ϕCH_2NEt_3Cl in $CHCl_3$ was performed in a manner similar to the procedure described by Levenson *et al.* [3]. Thus, 1.95 g (5.0 mmol) of $Mn_2(CO)_{10}$ and 1.65 g (7.2 mmol) of benzyltriethylammonium chloride were dissolved in 280 ml of $CHCl_3$ (purged with nitrogen immediately prior to use) in a 300 ml photo reaction vessel (Ace Glassware) and irradiated under nitrogen with an Ace-Hanovia 450 W medium pressure quartz mercury vapor lamp which was cooled by circulating water through a quartz immersion well. The photolysis was monitored by IR. After 15 minutes, a substantial amount of white solid had formed and the IR of the solution showed the following bands at 2132(w), 2060(s), 2039(s), 2017(s) and 1945(m) cm^{-1} in the carbonyl absorption region, but all of these absorptions disappeared after another 15 minutes of photolysis. The white solid was collected by filtration; it showed no carbonyl absorption and did not melt below 260 °C. There was no evidence* for the formation of $\phi CH_2N^+Et_3Mn_2(CO)_6(\mu\text{-}Cl)_3^-$.

Procedure (2): A second photolysis was performed in the same manner except that a pyrex filter was placed between the lamp and the reaction vessel. After photolyzing the mixture for 10 minutes, a large amount of white solid was again formed and the IR of the solution was essentially the same as that obtained after 15 minutes of photolysis without using a pyrex filter (see above). The photolysis was stopped after 15 minutes; the white solid was collected by filtration and again showed no carbonyl absorption in the IR. A trace amount of pale yellow solid was obtained after removing the solvent from the filtrate and was identified as $Mn(CO)_5Cl$. Again, there was no evidence for the formation of $\phi CH_2N^+Et_3Mn_2(CO)_6(\mu\text{-}Cl)_3^-$.

For the photolyses described below, the same general procedure was followed: Photolyses were carried out in a 100 ml pyrex three-necked round bottom flask by placing a 100 W (G.E. AH-4) mercury vapor lamp 4 inches from the flask. The average temperature in the reaction mixture was about 35–40 °C due to the heat of lamp. The progress of each reaction was monitored by IR.

Photolysis of $Mn_2(CO)_{10}$

The $Mn_2(CO)_{10}$ (0.2 g, 0.51 mmol) was dissolved in 20 ml of CH_2Cl_2 and the solution was photolyzed for 2 hours. Infrared spectra indicated no evidence of reaction.

Photolysis of $Mn_2(CO)_{10}$ with ϕCH_2NEt_3Cl

The $Mn_2(CO)_{10}$ (0.2 g, 0.51 mmol) and ϕCH_2NEt_3Cl (0.21 g, 0.95 mmol) were dissolved in 20 ml of CH_2Cl_2 and the solution was photolyzed for 2 hours; 67% of $Mn_2(CO)_{10}$ had been consumed after this time and the reaction mixture contained about equal amounts of $\phi CH_2N^+Et_3Mn(CO)_5^-$ and *cis*-$\phi CH_2N^+Et_3Mn(CO)_4Cl_2^-$ and a small amount of $\phi CH_2N^+Et_3Mn_2(CO)_9Cl^-$ (based on IR data and Beer's law plots). Addition of 50 ml of hexane to the filtered solution gave a reddish oil which was isolated by decanting the yellow solution followed by washing with 10 ml of hexane. Solvent was removed from the decanted yellow solution under reduced pressure to give a yellow solid which was identified as unreacted $Mn_2(CO)_{10}$. The reddish oil described above was dissolved in 20 ml of CH_2Cl_2 and then extracted with distilled water twice (15 ml each). The organic layer was dried over $MgSO_4$ and then concentrated to a small bulk (~5 ml). Hexane was then added into it (to the cloud point) and the mixture was cooled at –20 °C for several days; a small quantity of reddish yellow solid was obtained

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*The IR ν_{CO} bands reported (ref. 3) for $Mn_2(CO)_6(\mu\text{-}Cl)_3^-$ in $CHCl_3$ were 2029(s) and 1928(vs) cm^{-1}.

which was identified as $\phi CH_2N^+Et_3Mn_2(CO)_9Cl^-$ by IR and m.p. determination [2a].

Photolysis of $Et_4N^+Mn_2(CO)_9Br^-$

The $Et_4N^+Mn_2(CO)_9Br^-$ (0.14 g, 0.25 mmol) was dissolved in 10 ml of CH_2Cl_2 and the solution was photolyzed for 1½ hours. IR spectra indicated that 30% of the starting material had been converted to products, mainly $Mn_2(CO)_{10}$ together with smaller quantities of $Mn(CO)_5^-$ and $Mn(CO)_4X_2^-$ (X = Br or Cl).

Photolysis of $Et_4N^+Mn_2(CO)_9Br^-$ with Et_4NBr

The $Et_4N^+Mn_2(CO)_9Br^-$ (0.57 g, 1.0 mmol) and Et_4NBr (0.21 g, 1.0 mmol) were dissolved in 40 ml of CH_2Cl_2 and the solution was photolyzed. After 30 minutes, the reaction mixture contained 39% (molar %) unreacted $Et_4N^+Mn_2(CO)_9Br^-$, 31% *cis*-$Et_4N^+Mn(CO)_4Br_2^-$, 28% $Et_4N^+Mn(CO)_5^-$ and 2% $Mn_2(CO)_{10}$ as calculated from the IR spectral data based on the Beer's law plots of these compounds (see above). After an hour photolysis was stopped and the reaction mixture contained 24% of unreacted $Et_4N^+Mn_2(CO)_9Br^-$, 39% *cis*-$Et_4N^+Mn(CO)_4Br_2^-$, 35% $Et_4N^+Mn(CO)_5^-$ and 3% $Mn_2(CO)_{10}$.

Photolysis of cis-*$Et_4N^+Mn(CO)_4Br_2^-$ with Et_4NBr*

The *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ (0.23 g, 0.5 mmol) and Et_4NBr (0.11 g, 0.5 mmol) were dissolved in 20 ml of CH_2Cl_2 and the solution was photolyzed for 1 hour. By this time, the IR showed that 68% of $Et_4N^+Mn(CO)_4Br_2^-$ had been consumed and some pale yellow solids were also formed; the solids were collected by filtration but showed no IR absorption in the carbonyl region. Additional solid obtained by evaporation of solvent from the filtrate appeared to be a mixture containing unreacted *cis*-$Et_4N^+Mn(CO)_4Br_2^-$ together with a small amount of an unknown compound [$\nu_{CO}(CH_2Cl_2)$: 2020, 1985, 1918 cm^{-1}].

Photolysis of $Mn(CO)_5Cl$ with ϕCH_2NEt_3Cl

The $Mn(CO)_5Cl$ (0.2 g, 0.87 mmol) and ϕCH_2NEt_3Cl (0.2 g, 0.95 mmol) were dissolved in 20 ml of CH_2Cl_2 and the solution was photolyzed. The *cis*-$Mn(CO)_4Cl_2^-$ was immediately formed (15 minutes, based on the IR spectrum) and reached its highest concentration after 30 minutes of photolysis; $Mn_2(CO)_{10}$ was also formed during this time. The rate of consumption of $Mn(CO)_5Cl$ in this reaction [about 1/3 of the $Mn(CO)_5Cl$ remained after 30 minutes as estimated from IR] was slightly slower than in the preapration of *cis*-$\phi CH_2N^+Et_3Mn(CO)_4Cl_2^-$ (in which $Mn(CO)_5Cl$ was essentially consumed after 30 minutes in refluxing CH_2Cl_2).

Photolysis of $Et_4N^+Mn(CO)_5^-$ with Et_4NBr

The $Et_4N^+Mn(CO)_5^-$ (0.4 g , 1.2 mmol) and Et_4NBr (0.25 g, 1.2 mmol) were dissolved in 20 ml of CH_2Cl_2 and the solution was photolyzed for 3½ hours. Based on IR data, $Mn(CO)_5H$ was slowly formed, however it was not stable under the reaction conditions and started to disappear after 2 hours of photolysis. The rate of consumption of $Et_4N^+Mn(CO)_5^-$, determined by IR using the Beer's law plot, was as follows:

Reaction time (h)	% consumed
½	31
1	55
1½	70
2	82
2½	88
3½	100

During the photolysis some white solid formed, however it showed no IR carbonyl absorption. The IR spectrum of the reaction mixture at the end of photolysis was very complex, the products were not identified.

Acknowledgments

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