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Photochemical Reaction of Dinuclear Manganese Carbonyl Compounds with Tributyltin Hydride and with Silanes

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Abstract: The photochemical reactions of $Mn_2(CO)_8L_2$ (L = CO. PMe_3. P(n-Bu)$_3$. P(i-Pr)$_3$) with $HSnBu_3$ or $HSiEt_3$ in hexane solutions have been studied. using 366- or 313-nm irradiation. and under CO or Ar atmospheres. Under CO. 1.1–3.7 atm. the products of the reaction of $Mn_2(CO)_{10}$ with $HSnBu_3$ are $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$. Under Ar or low CO pressures. a third product. assigned as $HMn(CO)_4(SnBu_3)_2$. is formed at the expense of $Bu_3SnMn(CO)_5$. For a given photon flux. the reaction rate is inversely related to [CO]. The behavior of the system is consistent with a reaction pathway that involves oxidative addition of the hydride to the coordinatively unsaturated metal center formed upon CO loss. Analogous results are observed for the phosphine-substituted manganese carbonyl dimers. Reaction with $HSiEt_3$ proceeds much more slowly under equivalent conditions of irradiation. In the reaction with $Mn_2(CO)_{10}$. only $HMn(CO)_5$ is seen as a significant product. with trace amounts of $Et_3SiMn(CO)_5$ also observed. These results are also consistent with oxidative addition to the Co-loss product as the only pathway for the photochemical reaction. None of the manganese dimers undergo photochemical reaction with either fluorene or triphenylmethane. in spite of the comparatively low C–H bond energy in each case.

The photochemical properties of dinuclear metal carbonyl compounds have been the subject of intense study during the past 20 years. For compounds such as $Mn_2(CO)_{10}$. (η^5-C_5H_5)$_2$$Fe_2(CO)_4$ and their variously substituted analogues. there are two primary photochemical processes. homolysis of the metal–metal bond and CO loss.[1,2] The former process gives rise to 17-electron radicals which may undergo a variety of reactions. including atom transfer. recombination. electron transfer. and substitution.[3-5] Under appropriate conditions. these 17-electron species may add a 2-electron donor to become. at least formally. 19-electron in character.[6,7]

The focus for some years has been on the odd-electron products of photolysis of the dinuclear species. However. the chemical behavior of the dinuclear CO loss intermediates has taken on increased importance as interest has increased in the reactions of mononuclear coordinatively unsaturated species. such as (η^5-C_5H_5)Rh(CO).[8] (η^5-C_5H_5)Mn(CO)$_2$.[9] and $Cr(CO)_5$.[10] In the dinuclear compounds the coordinatively unsaturated molecule resulting from CO loss can engage in a form of "self-repair". e.g.. through formation of bridging ($Cp_2Fe_2(\mu_2$-$CO)_3$)[2,11] or semibridging ($Mn_2(CO)_9$)[12] CO linkages. Alternatively. or in addition to the rearrangements mentioned. the dinuclear CO-loss intermediate may subsequently react with other substrates.

In this and the following paper in this issue. we report on the results of studies of the photochemical reactions of dinuclear manganese carbonyl compounds $Mn_2(CO)_8L_2$ (L = CO or P(alkyl)$_3$) with tributyltin hydride. triethylsilane. and a few other selected molecules in which atom transfer or oxidative addition reactions to the metal center are possibilities. The present contribution concerns the results of continuous photolysis studies to determine the reaction products and to provide evidence regarding a plausible mechanism based on product distribution. The following paper deals with flash photolysis studies of intermediates. The flash photolysis results support the general mechanism proposed on the basis of the continuous photolysis results. They add to our understanding of the detailed course of the reaction. and shed important light on the lifetimes and relative stabilities of intermediates.

The interactions of main group element hydrides with unsaturated metal carbonyl fragments are well-established.[9,10a–c,13] A variety of mononuclear and dinuclear metal carbonyls have been employed as catalysts in hydrosilation.[13,14] For metal carbonyl dimers. both 17-electron metal carbonyl radicals and coordinatively unsaturated 16-electron species have been invoked as the active intermediates. The most widely accepted mechanism for the metal carbonyl catalyzed hydrosilation of olefins is that proposed by Chalk and Harrod for $Co_2(CO)_8$.[15] Because of its relatively high lability toward CO loss. $Co_2(CO)_8$ is effective as a catalyst under thermal reaction conditions. By contrast. $Mn_2(CO)_{10}$ is effective only under photochemical conditions. It has been proposed that the photochemical catalytic cycle is initiated through a hydrogen

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atom transfer to the $Mn(CO)_5^{\bullet}$ radical.[16] Given the relative bond energies. about 60–65 kcal mol^{-1} for $HMn(CO)_5$[17] and 90 kcal mol^{-1} for $HSi(C_2H_5)_3$.[18] such a pathway seems unlikely. Others have invoked a catalytic cycle similar to the Chalk–Harrod process.[19] In such a scheme, oxidative addition of the silane would occur to the coordinatively unsaturated metal center following CO loss. followed by reductive elimination of $HMn(CO)_5$. and forming $R_3SiMn(CO)_5$ after CO uptake.

Three pathways suggest themselves as possibilities for reaction of a main group element hydride with $Mn_2(CO)_8L_2$ (where L may be CO as well as a phosphine) under photochemical conditions. They involve reaction with either the radical formed via metal–metal bond homolysis or with the CO loss product.

1. Atom transfer to $Mn(CO)_4L^{\bullet}$:

$$Mn(CO)_4L^{\bullet} + HMR_3 \rightarrow HMn(CO)_4L + MR_3^{\bullet} \quad (1)$$

If atom transfer were the primary pathway for reaction. the products should consist of the metal carbonyl hydride and M_2R_6. Only small amounts. if any. of $R_3M-Mn(CO)_4L$ should be observed. This reaction must compete with other processes involving $Mn(CO)_4L^{\bullet}$. notably recombination to form the dimer. Atom transfer from $HSnBu_3$ to $Re(CO)_5^{\bullet}$ has been shown to compete effectively with recombination of the radicals.[20] Persistent manganese carbonyl radicals $Mn(CO)_3L_2^{\bullet}$. in which there is no competing radical recombination. undergo H atom transfer from $HSnBu_3$.[21] In the present case. given the comparatively low bond dissociation energy for the Mn–H bond. H atom abstraction by $Mn(CO)_4L^{\bullet}$ radicals may be endergonic to an extent that renders the reaction too slow to compete effectively with $Mn(CO)_4L^{\bullet}$ recombination.

2. Oxidative addition to $Mn(CO)_4L^{\bullet}$:

$$Mn(CO)_4L^{\bullet} + HMR_3 \rightarrow Mn(H)(MR_3)(CO)_3L^{\bullet} + CO \quad (2)$$

When the H atom transfer is energetically unfavorable. the high substitutional lability of the 17-electron radical may enable the hydride to react with the metal center via an oxidative addition reaction. The resulting 17-electron radical. being more electron rich. can then possibly undergo H atom transfer with a second molecule of hydride. followed by reductive elimination of H_2:

$$Mn(H)(MR_3)(CO)_3L^{\bullet} + HMR_3 \rightarrow Mn(H)_2(MR_3)(CO)_3L + MR_3^{\bullet} \quad (3)$$

$$Mn(H)_2(MR_3)(CO)_3L + CO \rightarrow H_2 + R_3MMn(CO)_4L \quad (4)$$

A mechanism of this type has been proposed for both thermal and photochemical reactions of some dinuclear carbonyl compounds with hydrides.[22] The products of the overall process are H_2 and the metal–metal bonded species $R_3M-Mn(CO)_4L$.

3. Oxidative addition to $Mn_2(CO)_7L_2$:

$$Mn_2(CO)_7L_2 + HMR_3 \rightarrow (CO)_3L(H)(MR_3)Mn-Mn(CO)_4L \quad (5)$$

Following the oxidative addition step shown in eq 5. reductive elimination and uptake of CO would lead to $HMn(CO)_4L$ and $R_3MMn(CO)_4L$.

Our results. as described below. support oxidative addition to the CO-loss product as the only significant reaction pathway for reactions of the variously substituted dinuclear manganese compounds with $HSnBu_3$ and related compounds.

Experimental Section

Solvents. Hexane obtained from Burdich and Jackson Laboratories. Inc.. was purified by stirring over concentrated H_2SO_4 for at least 1 week. followed by washing with aqueous $NaHCO_3$ and then water. and predried with $CaCl_2$. It was then passed over freshly activated silica gel and refluxed over CaH_2 under N_2 for a minimum of 12 h prior to distillation. The distilled hexane was collected under an N_2 atmosphere. purged with Ar. freezed–pumped–thawed with Ar three times. and stored in an oven-dried amber bottle in the glovebox.

Tetrahydrofuran. THF. obtained from Fischer Scientific was purified by predrying a freshly opened bottle with KOH. followed by refluxing over $LiAlH_4$ under N_2 for at least 12 h prior to distillation. The distilled THF was collected under an N_2 atmosphere and freezed–pumped–thawed three times with Ar prior to use.

Benzene. obtained from Fischer Scientific. was purified by predrying with $CaCl_2$. followed by refluxing over CaH_2 under N_2 for at least 12 h prior to distillation. The distilled benzene was collected under N_2 and freezed–pumped–thawed three times with Ar prior to use.

Toluene was obtained from Fischer Scientific and was treated in the same manner as benzene.

Reagents. Manganese carbonyl $Mn_2(CO)_{10}$. obtained from Pressure Chemical Co.. was sublimed (50 °C. 0.3 mmHg) prior to use and stored in the refrigerator.

Phosphines were obtained from Strem Chemical Co. They were used as received and stored in the glovebox.

Tri-*n*-butyltin hydride. $HSnBu_3$. was obtained from Aldrich Chemical Co. It contained trace amounts of $ClSnBu_3$. which was removed by distillation over $LiAlH_4$ (65 °C. 0.3 mmHg). The purified $HSnBu_3$ was stored in a glass vial in the freezer under Ar.

Triethylsilane. $HSiEt_3$. obtained from Aldrich. was distilled from P_2O_5 under Ar prior to use and stored in the glovebox.

Fluorene was obtained from Lancaster Synthesis and was used as received.

Triphenylmethane. Ph_3CH. was obtained from Aldrich. It was recrystallized from ethanol prior to use (mp 93.4 °C).

Carbon tetrachloride. CCl_4. was obtained from Mallinckrodt. It was purified by washing with hot ethanolic KOH and then with H_2O. predried with $CaCl_2$. and then distilled from P_2O_5 under Ar.

Argon (research grade. minimum purity 99.9995%. <1 ppm O_2. <3 ppm H_2O) was obtained from Linde Speciality Gas Co. It was passed through a Drierite column prior to use.

Carbon monoxide. CO (Matheson purity grade. minimum purity 99.99%). was obtained from Matheson Gas Products. Inc. The IR spectra of CO-saturated hexane solutions revealed trace amounts of $Fe(CO)_5$. which is known to react photochemically with hydrides. and which interfered in our initial experiments. The $Fe(CO)_5$ was removed by passage through a copper tube 25 cm in length. 6 mm in diameter. packed with activated charcoal heated in a sand bath to 180 °C. followed by passage through a 1-m-long. 8-mm-diameter copper tube packed with activated charcoal cooled in a dry ice–ethanol bath. The CO was then passed through an O_2 trap obtained from American Scientific. The IR spectrum of a CO-saturated hexane solution showed no evidence of $Fe(CO)_5$ after passage of CO through the scrubbing system.

$Mn_2(CO)_8(PR_3)_2$ complexes ($PR_3 = PMe_3$. $P(n\text{-}Bu)_3$. and $P(i\text{-}Pr)_3$) were prepared by adding $Mn_2(CO)_{10}$ (typically 0.5–1 g) and 2 equiv of phosphine to a 100-mL round-bottom Schlenck flask containing 50 mL of dry. degassed hexane. The solution was photolyzed with stirring under argon for 12 h. after which the solvent was removed by evacuation. The crude reaction mixture was recrystallized from a mixture of methylene chloride and methanol. Crystals formed upon slow removal of the CH_2Cl_2 under vacuum. The complexes were stored in the refrigerator. All yielded satisfactory elemental analyses for C. H. Mn. and P and exhibited IR spectra in agreement with reported literature values.

$HMn(CO)_5$ was synthesized starting from $Mn_2(CO)_{10}$ using the standard literature preparation.[23] The product was characterized by ^1H NMR and IR. IR (hexane): 2016 cm^{-1} ($\epsilon = 2750$ mm^{-1} M^{-1}). 2008 ($\epsilon = 820$). 1984 ($\epsilon = 70$). ^1H NMR (benzene-d_6): −7.85 ppm (s).

***cis*-$HMn(CO)_4PMe_3$** was prepared in a similar method to that described by Atwood.[24] A solution of $Na^+Mn(CO)_4PMe_3^-$ was first prepared by stirring a THF solution of $Mn_2(CO)_8(PMe_3)_2$ over Na/Hg

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amalgam for 4 h under argon. The $Na^+Mn(CO)_4PMe_3^-$ solution was transferred under argon via a cannula to a 100-mL round-bottom Schlenck flask and acidified with glacial acetic acid. The THF was removed by vacuum, leaving a grey residue containing crude $HMn(CO)_4PMe_3$. The flask was transferred into the glovebox, and the residue was passed through a Fluorosil column using benzene as eluant. A yellow band containing $HMn(CO)_4PMe_3$ was collected. After removal of the solvent, the product was purified by trap-to-trap distillation over P_2O_5 and stored in the freezer in a glass vial under Ar. The product was characterized by ^{1}H NMR and IR. IR (hexane): 2062 cm^{-1} (ϵ = 200 mm^{-1} M^{-1}), 1984 (ϵ = 380), 1964 (ϵ = 1020), 1954 (ϵ = 690). ^{1}H NMR (benzene-d_6): 0.796 ppm (d, J_{H-P} = 9.1 Hz), −7.93 (d, J_{H-P} = 40.9 Hz).

$Bu_3SnMn(CO)_5$ and $Bu_3SnMn(CO)_4PR_3$ complexes were prepared by adding an equivalent amount of $ClSnBu_3$ to a THF solution of $Na^+Mn(CO)_4L$ (L = CO or PR_3) under Ar. After stirring for several hours, the solvent was removed and the product was crudely purified by column chromatography using hexane as the solvent. The product was recrystallized from hexane in the cases of L = PMe_3 and $P(C_6H_{11})_3$ and sublimed in the cases of L = CO and $P(n\text{-}Bu)_3$. The complexes were characterized by IR and microanalysis.

$Bu_3SnMn(CO)_5$. Anal. Calcd for $C_{17}H_{27}MnO_5Sn$: C, 42.10; H, 5.61; Mn, 11.33; Sn, 24.47. Found: C, 41.92, H, 5.62; Mn, 11.36; Sn, 24.40. IR (hexane): 2085 cm^{-1} (ϵ = 217 mm^{-1} M^{-1}), 1989 (ϵ = 1747).

***cis*-$Bu_3SnMn(CO)_4PMe_3$.** Anal. Calcd for $C_{19}H_{36}MnO_4PSn$: C, 42.81; H, 6.81; Mn, 10.31; P, 5.81; Sn, 22.26. Found: C, 42.96; H, 6.92; Mn, 10.14; P, 5.72; Sn, 21.91. IR (hexane): 2033 cm^{-1} (ϵ = 220 mm^{-1} M^{-1}), 1940 (ϵ = 1540). Mp: 38–41 °C.

***trans*-$Bu_3SnMn(CO)_4P(C_6H_{11})_3$.** Anal. Calcd for $C_{34}H_{60}MnO_4PSn$: C, 55.38; H, 8.20; Mn, 7.45; P, 4.20; Sn, 16.09. Found: C, 55.60; H, 8.25; Mn, 7.60; P, 4.29; Sn, 15.86. IR (hexane; relative intensities): 1956 cm^{-1} (1), 1933 (60), 1921 (44), 1904 (1.7). Mp: 113–4 °C.

***trans*-$Bu_3SnMn(CO)_4P(n\text{-}Bu)_3$.** IR (hexane): 2029 cm^{-1} (1.2), 1958 (1.3), 1935 (49), 1905 (1).

$PPN^+Mn(CO)_5^-$ was prepared as described by Wrighton.[25] Anal. Calcd for $C_{14}H_{30}MnNO_5P_2$: C, 66.15; H, 4.12; N, 1.91; Mn, 7.49; P, 8.44. Found: C, 67.05; H, 4.30; N, 1.87; Mn, 7.40; P, 8.38. IR (THF): 2010 cm^{-1} (1), 1893 (77, sh), 1859 (186).

$PPN^+Mn(CO)_4(SnBu_3)_2^-$ has not been reported in the literature. It was prepared using the method employed in the synthesis of the analogous compound $PPN^+Mn(CO)_4(SnPh_3)_2^-$.[25] An FAB mass spectrum of $PPN^+Mn(CO)_4(SnBu_3)_2^-$ showed good agreement between the experimental and theoretical isotopic abundance patterns in the molecular ion at *m/e* 747. Anal. Calcd for $C_{64}H_{84}MnNO_4P_2Sn_2$: C, 59.79: H, 6.59; N, 1.09; Mn, 4.23. Found: C, 60.54; H, 6.97; N, 1.76; Mn, 4.29. IR (THF): 1971 cm^{-1}, 1880. IR (CH_3CN): 1967 cm^{-1}, 1874.

Instrumentation. IR spectroscopy was performed on either a Perkin-Elmer Model 1710 or 1750 FTIR or a Beckman IR-4240 dispersive mode spectrophotometer. The model 1710 was interfaced to an AST Premium/286 computer. The data was saved on the hard disk or on a floppy disk by the program 17DX provided by Perkin-Elmer. KCl cells of 1-mm path length were used for most IR spectra.

^{1}H NMR spectra were recorded on a varian XL-200 (200 MHz), Nicolet NT360 (360 MHz), or General Electric QE300 (300 MHz) NMR spectrometer.

Mass Spectra. All mass spectra were obtained in the Mass Spectrometry Laboratory of the School of Chemical Sciences. Field desorption (FD) mass spectra were obtained on a Finnegan-MAT, model 731. Fast atom bombardment (FAB) spectra were obtained on a VG ZAB-SE.

Light Sources. A 275-W General Electric sunlamp (predominantly 366-nm radiation) was used for most of the syntheses and for some of the continuous photolysis reaction studies.

Radiation of 313- or 366-nm wavelengths was obtained by isolation of the appropriate mercury emission line from a Hanovia 200-W medium-pressure mercury lamp, using a two-chambered jacketed lamp housing of quartz. The 313-nm Hg emission line was isolated by filling the inner chamber with approximately 1 L of aqueous 1.5 M $CoSO_4\cdot7H_2O$ solution[26] (path length 1 cm) and the outer chamber with a 2-L aqueous mixture of 1.25 M K_2CrO_4 and 0.45 M $NiSO_4\cdot6H_2O$[27] (path length 2 cm). The 366-nm Hg emission was isolated as described by Knoesel.[28] The inner chamber was filled with approximately 500 mL of 0.013 M I_2 in CCl_4 (path length 0.6 cm), and the outer chamber was filled with approximately 2 L of 3.5 × 10^{-4} M 2,3-diphenylindenone in hexane (path length 2.2 cm).

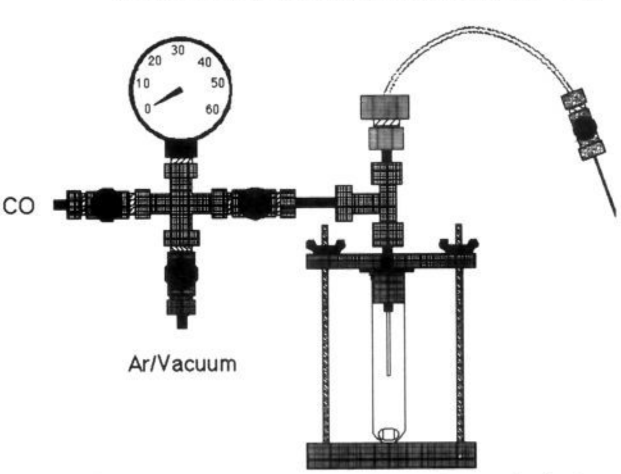

Figure 1. Photochemical reactor employed in continuous photolysis reactions with periodic withdrawal of samples.

Glovebox. All samples for photolysis were prepared in a Vacuum Atmospheres glovebox, with an Ar atmosphere. The purification system has been described elsewhere.[29]

Photolysis Procedures. A description of the experimental procedure will be given only for the continuous photolysis reaction of $Mn_2(CO)_{10}$ with $HSnBu_3$ in hexane. The same procedure was followed for other systems.

Solutions were prepared by placing enough $Mn_2(CO)_{10}$ in a 25-mL volumetric flask to make a (2–3) × 10^{-3} M solution. The flask was sealed with a serum stopper, purged with Ar, and transferred into the glovebox. In the glovebox, the $Mn_2(CO)_{10}$ was dissolved in hexane. In experiments where the $HSnBu_3$ concentration was varied at constant CO pressure, 1 mL of $Mn_2(CO)_{10}$ stock solution was pipetted into a 10-mL volumetric flask containing $HSnBu_3$ dispensed via a gas-tight syringe. The final $Mn_2(CO)_{10}$ concentration was adjusted to (2–3) × 10^{-4} M by diluting to the mark with hexane. In experiments where the CO pressure was varied at a constant $HSnBu_3$ concentration, 10 mL of $Mn_2(CO)_{10}$ stock solution was placed in a 100-mL volumetric flask containing a known quantity of $HSnBu_3$. The $Mn_2(CO)_{10}$ concentration was adjusted to (2–3) × 10^{-4} M by dilution to the mark with hexane. In all of these experiments, the $HSnBu_3$ concentration was present in at least a 10-fold excess. After the solutions were prepared, they were transferred to a Schlenk vessel and stopped with a serum stopper. The solutions were stored in the refrigerator until needed.

The photochemical reactor used in these experiments, shown in Figure 1, is based on the Fisher–Porter design. In a typical experiment performed under CO, the pressure manifold and the reaction vessel were made anaerobic by a series of pumps/flushes with the argon/vacuum manifold. After the pump/flush cycles were complete, the reaction vessel was evacuated and then charged with CO; 10 mL of sample was then transferred into the reaction vessel anaerobically via a 30-mL gas-tight syringe equipped with a 20-gauge needle, 28 cm in length. After the reaction vessel was charged with sample, the Teflon needle equipped with a high-pressure miniature valve was then pushed through the septum into the reaction chamber with the valve open in order to flush the air out of the line. The septum retaining nut was then tightened to prevent leakage and the miniature valve closed. The CO pressure was then adjusted to the desired level and the solution equilibrated by stirring for 45 min. The reaction vessel was covered with foil to protect the solution from room light. Progress of the reaction was monitored by IR. The solution was stirred continuously during irradiation. Stirring was stopped during removal of sample and resumed after an aliquot of sample had been removed. A sample was transferred anaerobically to an Ar-purged 1-mm IR cell.

When the reaction was performed under 1 atm of Ar, the same procedures were followed except that the sample was removed via a stainless steel cannula.

Results and Discussion

Photolysis of $HSnBu_3$ and $Mn_2(CO)_{10}$. The photochemical reaction between $HSnBu_3$ and $Mn_2(CO)_{10}$ in hexane was carried out under 1 atm of Ar or CO pressures in the range 1.1–3.7 atm. The $Mn_2(CO)_{10}$ concentration was generally in the range of (1–3) × 10^{-4} M, with $HSnBu_3$ in 10-fold or greater excess. The light

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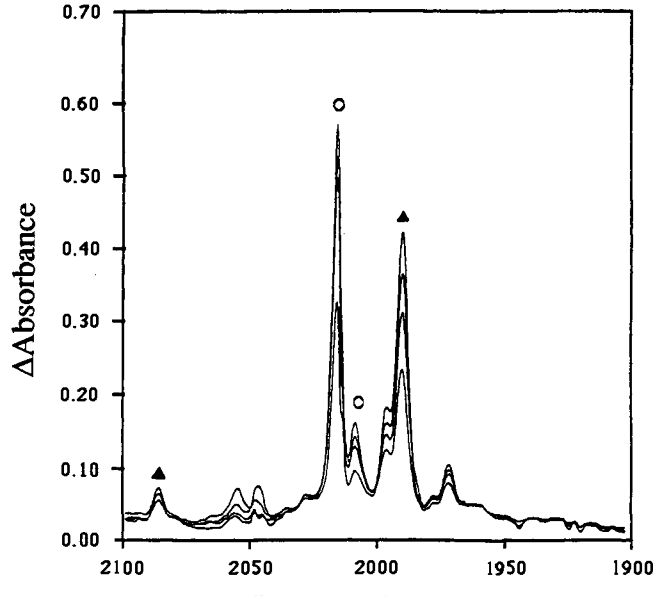

Figure 2. Difference FTIR spectra of products formed upon continuous photolysis of $Mn_2(CO)_{10}$ and $HSnBu_3$ in hexane. under 1.4 atm of CO. Absorbances due to $Mn_2(CO)_{10}$ have been subtracted. The bands at 2085 and 1989 cm^{-1}. labeled ▲. are assigned to $Bu_3SnMn(CO)_5$: those at 2015 and 2008 cm^{-1}. labeled ○. are assigned to $HMn(CO)_5$.

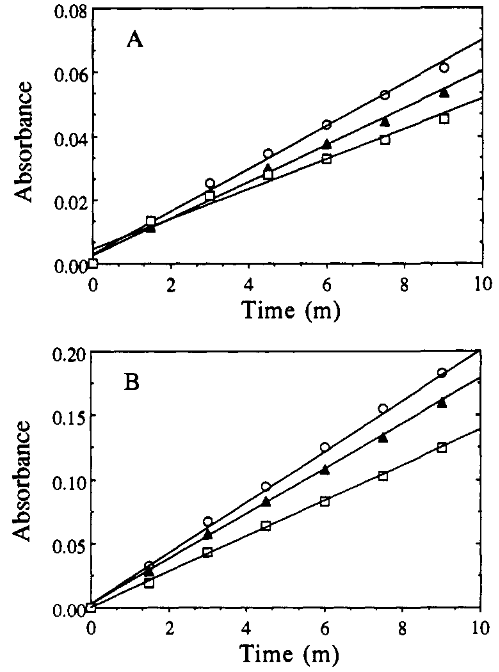

Figure 3. Rate of growth in absorbances upon continuous photolysis. as a function of CO pressure: ○. 1.7 atm: ▲. 2.1 atm: □. 2.5 atm. (a) 2008-cm^{-1} absorbance due to $HMn(CO)_5$: (b) 1989-cm^{-1} absorbance due to $Bu_3SnMn(CO)_5$.

source was either a 250-W GE sunlamp. consisting predominantly of 366-nm radiation. or a 200-W medium-pressure Hg lamp. from which either the 366- or 313-nm line was selected by use of chemical filter solutions. The reactions were typically carried to about 10% completion. with removal of samples at intervals for FTIR analysis.

As the reaction proceeds. IR bands at 2045. 2015. and 1984 cm^{-1}. due to $Mn_2(CO)_{10}$. disappear. A set of difference IR spectra from which absorptions due to $Mn_2(CO)_{10}$ have been removed is shown in Figure 2. New IR bands at 2085 and 1989 cm^{-1}. due to $Bu_3SnMn(CO)_5$. and at 2016 and 2008. assignable to $HMn(CO)_5$. are seen. The origin of an additional low-intensity absorbance at 1969 cm^{-1} is discussed below. From the absorbance measurements on authentic samples. it was determined that the two major products appear in a nearly 1:1 molar ratio. and in a 1:1 molar ratio with loss of $Mn_2(CO)_{10}$.

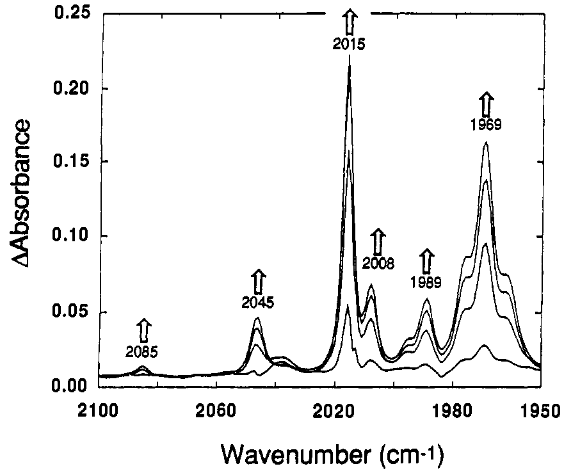

Figure 4. Difference FTIR spectra of products formed upon continuous photolysis of $Mn_2(CO)_{10}$ in hexane under Ar. Absorbances due to $Mn_2(CO)_{10}$ have been subtracted. Bands due to the third product **1** occur at 2045 and 1969 cm^{-1}.

Under identical conditions of irradiation. the rate of loss of $Mn_2(CO)_{10}$ is inversely dependent on CO pressure. as illustrated in Figure 3. The existence of an inverse CO pressure dependence rules out pathway 1 as the dominant process for the reaction: the reactivity of the 17-electron radical toward H atom transfer should not be diminished by the presence of CO. This pathway is further ruled out by the product distribution. For $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ to appear in a 1:1 molar ratio via mechanism 1, all the $Bu_3Sn^•$ radicals formed would have to combine with metal carbonyl radicals. to the exclusion of reaction with another $Bu_3Sn^•$ radical.

The observed product distribution contrasts with those observed in reactions of $HSnBu_3$ with $Co_2(CO)_6[P(n\text{-}Bu)_3]_2$ and $Cp_2M_2(CO)_6$ (M = Mo. W), presumed to proceed via mechanism 2. in which only the heterodinuclear products $Bu_3SnCo(CO)_3P(n\text{-}Bu)_3$ and $CpM(CO)_3SnBu_3$. respectively. are observed. Thus, in the present case. oxidative addition at the radical center does not appear to be the operative reaction pathway.

The observed products and the dependence of their rates of formation on CO pressure are accounted for in terms of Scheme 1. This mechanism requires formation of $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ in a 1:1 molar ratio. and accounts for CO inhibition. via recombination of CO with $Mn_2(CO)_9$.

Scheme I

$$Mn_2(CO)_{10} \xrightarrow{h\nu} Mn_2(CO)_9 + CO \tag{6}$$

$$Mn_2(CO)_9 + CO \xrightarrow{k_2} Mn_2(CO)_{10} \tag{7}$$

$$Mn_2(CO)_9 + HSnBu_3 \xrightarrow{k_3} (CO)_5Mn\text{-}Mn(CO)_4(H)(SnBu_3) \tag{8}$$

$$(CO)_5Mn\text{-}Mn(CO)_4(H)(SnBu_3) \xrightarrow{k_4} HMn(CO)_5 + Bu_3SnMn(CO)_4 \tag{9}$$

$$Bu_3SnMn(CO)_4 + CO \xrightarrow{k_5} Bu_3SnMn(CO)_5 \tag{10}$$

The proposed mechanism is also consistent with the dramatically different course of the reaction under an Ar atmosphere. as revealed by the IR spectra (Figure 4). Under Ar the overall rate of loss of $Mn_2(CO)_{10}$ for equivalent conditions of irradiation is much faster than under CO. A third product. **1**. absorbing at 1969 and 2045 cm^{-1} in the IR. is formed. apparently at the expense of $Bu_3SnMn(CO)_5$. This new product is also formed in the photochemical reaction of $Bu_3SnMn(CO)_5$ with $HSnBu_3$ in hexane under 1 atm of Ar. The rate of reaction is about 1 order of magnitude slower than observed for reaction of $HSnBu_3$ with $Mn_2(CO)_{10}$; further, the reaction is inhibited by addition of CO. The fact that the reaction with $Bu_3SnMn(CO)_5$ is so much slower than reaction with $Mn_2(CO)_{10}$ rules out the possibility that **1** is a secondary photolysis product derived from $Bu_3SnMn(CO)_5$. The likelihood of this being the case is further reduced by the consideration that $Bu_3SnMn(CO)_5$ has a low extinction coefficient at 366 nm, whereas $Mn_2(CO)_{10}$ absorbs significantly at this wavelength. The presence of $Mn_2(CO)_{10}$ thus precludes the photochemical reaction of $Bu_3SnMn(CO)_5$ by exerting an overwhelming internal filter effect.

From Scheme I it appears that **1** is formed via oxidative addition of $HSnBu_3$ to $Bu_3SnMn(CO)_4$:

$$HSnBu_3 + Bu_3SnMn(CO)_4 \xrightarrow{k_6} HMn(CO)_4(SnBu_3)_2 \quad (11)$$

Under an Ar atmosphere, this oxidative addition can compete effectively with recombination with CO, to yield the seven-coordinate hydride $HMn(CO)_4(SnBu_3)_2$. Although **1** has not previously been reported, several precedents exist for this type of reaction. A particularly pertinent example, from the work of Wrighton and Anderson, involves photolysis of $Et_3SiCo(CO)_4$ in a frozen 3-methylpentane glass containing $HSiEt_3$.[30] Upon warming, a species postulated to be $HCo(CO)_3(SiEt_3)_2$ is formed.

We have also observed that **1** is formed as a sole product upon photolysis of $HMn(CO)_5$ and $HSnBu_3$ in hexane solution under Ar. The reaction probably proceeds as shown in Scheme II.

Scheme II

$$HMn(CO)_5 \xrightarrow{h\nu} HMn(CO)_4 + CO \quad (12)$$

$$HMn(CO)_4 + HSnBu_3 \rightarrow (H)_2Mn(CO)_4SnBu_3 \quad (13)$$

$$(H)_2Mn(CO)_4SnBu_3 \rightarrow H_2 + Mn(CO)_4SnBu_3 \quad (14)$$

$$Mn(CO)_4SnBu_3 + HSnBu_3 \rightarrow HMn(CO)_4(SnBu_3)_2 \quad (15)$$

Various attempts, all unsuccessful, were made to isolate **1**. Several forms of chromatographic separation were also attempted without success. It is likely that the instability of **1** has its origins in the reversibility of the oxidative reaction by which it is formed: **1** is moderately stable only when excess $HSnBu_3$ is present. However, solutions containing primarily **1** as solute were obtained by extended photolysis of $Mn_2(CO)_{10}$ with $HSnBu_3$, followed by removal of solvent and $HMn(CO)_5$ by evacuation. IR spectra in the CO stretching region of the yellow oil remaining showed only minor amounts of $Bu_3SnMn(CO)_5$ and other unidentified components absorbing at 1936 and 1905 cm^{-1}. The FD mass spectrum consisted of a series of isotopic clusters. The most intense of these, centered at *m/e* 748, corresponds to the molecular mass of $HMn(CO)_4(SnBu_3)_2$. Figure 5 shows the experimental and calculated isotopic distribution of masses in the cluster centered at *m/e* 748. The calculated distribution is based on the formula $HMn(CO)_4(SnBu_3)_2$.

The 300-MHz ^1H NMR spectrum of a sample consisting mainly of **1** in C_6D_6 shows the presence of several peaks in the -5 to -20 ppm region. The most intense line, rather broad and centered at -7.5 ppm, is most likely due to **1**, but the assignment is uncertain. A variable-temperature ^1H 360-MHz NMR study in toluene-d_8 revealed that the broad resonance sharpens upon cooling to -35 °C, but not sufficiently to reveal evidence of coupling to Sn nuclei. The broadness could be the result of proximity to the quadrupolar ^{55}Mn nucleus ($I = {}^5/_2$).

To provide additional confirmation of the identity of **1**, attempts were made to synthesize the hydride by an independent pathway. The anion $Mn(CO)_4(SnBu_3)_2^-$ was formed using a procedure similar to that outlined by Faltynek and Wrighton.[25] Attempts were made to form the corresponding hydride by protonation of the PPN^+ or Na^+ salts with a variety of acids and under varying solvent conditions, but none of these yielded the hydride. Several other related synthetic approaches also failed to yield the hydride.

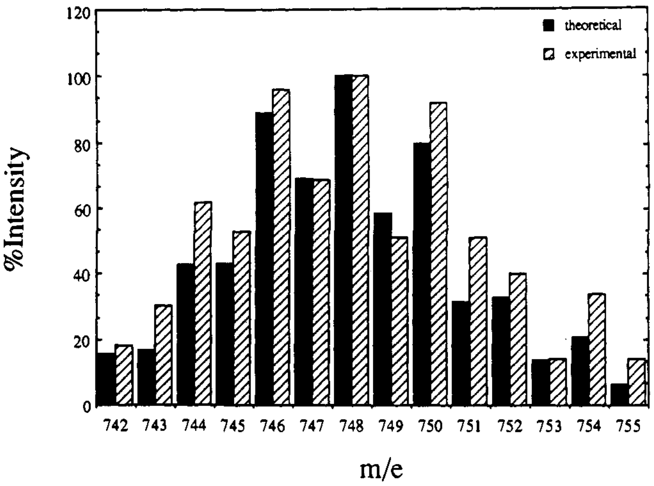

Figure 5. Comparison of experimental and calculated abundances of masses in the cluster corresponding to the molecular ion of $HMn(CO)_4(SnBu_3)_2$.

Having failed to form the hydride by an independent route, we undertook to deprotonate **1**, to compare the IR spectrum of the resulting anion with that of the independently synthesized anion. Addition of NEt_3 to a THF solution of **1** resulted in loss of IR bands ascribed to **1**, and appearance of IR bands identical to those of an authentic sample of $[PPN][Mn(CO)_4(SnBu_3)_2]$. Similar results were obtained when *n*-BuLi was employed as base.

Additional evidence for the proposed mechanism was obtained from low-temperature irradiations of 3-methylpentane glasses containing 3×10^{-3} M $Mn_2(CO)_{10}$, with a 20-fold molar excess of $HSnBu_3$. Irradiation of such glasses at 77 K resulted in the appearance of pale yellow color, ascribable to the CO loss product $Mn_2(CO)_9$.[12b] Radicals formed via Mn–Mn bond homolysis should remain trapped in the same solvent cage, and readily recombine. Several solutions were irradiated for periods of time ranging from 5 to 15 min and then allowed to thaw. Upon warming, they flashed orange in color and then turned yellow. IR analysis of the reaction mixtures revealed that $HMn(CO)_5$ and **1** were the major products: only minor amounts of $Bu_3SnMn(CO)_5$ were observed. The amount of product formed increased with photolysis time.

To test for the possible role of radicals in this experiment, a 3×10^{-3} M solution of $Mn_2(CO)_{10}$ in 3-methylpentane, with a 20-fold excess of CCl_4 was similarly irradiated at 77 K. Only trace amounts of $ClMn(CO)_5$ were seen after warming, and the amount formed did not increase in proportion to the time of irradiation. We conclude that only $Mn_2(CO)_9$ is significantly active in such experiments. Thus, the observed products can be traced to reaction with $Mn_2(CO)_9$, consistent with the proposed mechanism.

The overall mechanism for photochemical reaction of $Mn_2(CO)_{10}$ with $HSnBu_3$ is thus as shown in Scheme I, with the addition of reaction 11. It is worth pointing out that the experimental evidence supports the reductive elimination of $HMn(CO)_5$ in step 9, rather than the alternative reductive elimination of $Bu_3SnMn(CO)_5$. If the latter were operative, formation of $HMn(CO)_5$ would decline under an Ar atmosphere, whereas it is formation of $Bu_3SnMn(CO)_5$ that is reduced in favor of formation of the hydride **1**.

Kinetic Aspects of the Photochemical Reaction. It is possible to obtain from the rate of appearance of products under continuous photolysis an estimate of k_3, the rate of oxidative addition of $HSnBu_3$ to $Mn_2(CO)_9$, eq 8. We have

$$d[HMn(CO)_5]/dt = k_4[Mn_2(CO)_9(H)(SnBu_3)] \quad (16)$$

Assuming a steady-state approximation for the concentrations of $Mn_2(CO)_9(H)(SnBu_3)$ and $Mn_2(CO)_9$, we obtain

$$R = \frac{d[HMn(CO)_5]}{dt} = \frac{I_a\Phi k_3[HSnBu_3]}{k_2[CO] + k_3[HSnBu_3]} \quad (17)$$

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(30) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995.

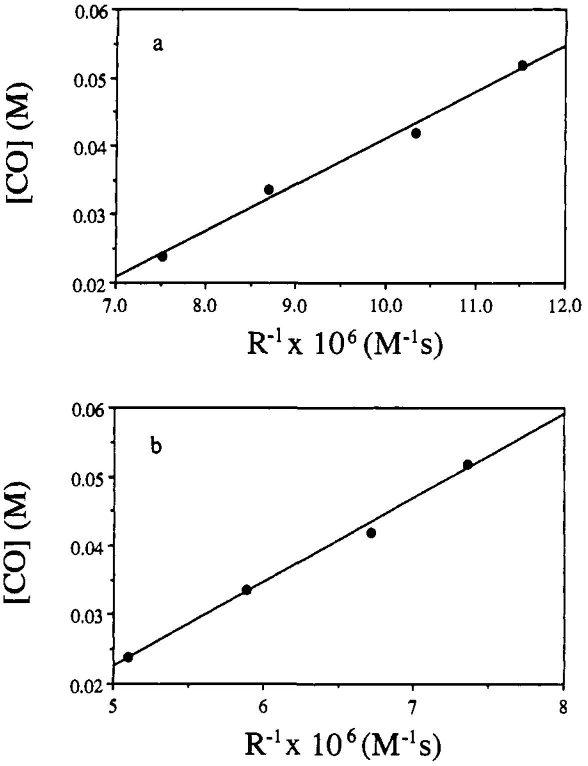

Figure 6. [CO] vs R^{-1} for (a) appearance of $HMn(CO)_5$ and (b) appearance of $Bu_3SnMn(CO)_5$.

where I_a is the total photon flux into the sample and Φ is the quantum yield for reaction 6. Rearranging, we obtain

$$[CO] = \frac{k_3 I_a \Phi [HSnBu_3] R^{-1}}{k_2} - \frac{k_3[HSnBu_3]}{k_2} \qquad (18)$$

At constant $[HSnBu_3]$, a plot of [CO] vs R^{-1} should yield a straight line: k_3 is obtainable from both the slope and intercept, provided the other quantities are known. The rate of reaction, R, can also be evaluated by measuring the appearance of $Bu_3SnMn(CO)_5$ when [CO] is sufficiently high to effectively quench formation of **1**, as is the case for CO pressures over 1 atm.

The dependence of the rate on [CO] was examined for CO pressures in the range 1.6–3.7 atm, using either the filtered 366-nm line from a medium-pressure Hg lamp, or the unfiltered output of a sunlamp, consisting mainly of 366-nm radiation. The rates were estimated from the slopes of the linear time vs IR absorbance plots for both $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ during the initial stages of the reaction. Figure 6 shows graphs of [CO] vs R^{-1} for the appearances of both $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ for one set of experiments. The solutibility of CO in hexane was taken to be 0.014 M for 1 atm of CO:[31] Henry's law was assumed to apply.

From the intercepts of a total of five such experiments, we estimate a value for k_3 of 3.0 (±0.5) × 10^6 M^{-1} s^{-1}, assuming a value of 2.9 × 10^5 M^{-1} s^{-1} for k_2.[32]

Experiments in which the concentration of $HSnBu_3$ is varied at constant CO concentration provide an additional basis for estimating k_3. Rearranging eq 17, we have

$$[HSnBu_3]^{-1} = \frac{I_a \Phi k_3 R^{-1}}{k_2[CO]} - \frac{k_3}{k_2[CO]} \qquad (19)$$

The initial rates of formation of both $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ were observed under sunlamp irradiation, for solutions under 1.7 atm of CO and with $HSnBu_3$ concentrations in the range 5 × 10^{-4} to 2.6 × 10^{-3} M. Figure 7 shows plots of $[HSnBu_3]^{-1}$ vs R^{-1} for formation of both $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$. Assuming that CO in hexane obeys Henry's law, and that [CO] = 1.4 × 10^{-2} M for 1 atm of CO pressure, and assuming as before a value of 2.9 × 10^5 M^{-1} s^{-1} for k_2, the intercepts of the $HMn(CO)_5$ and $Bu_3SnMn(CO)_5$ plots yield k_3 values of 2.9 × 10^6 and 3.5 × 10^6 M^{-1} s^{-1}, respectively.

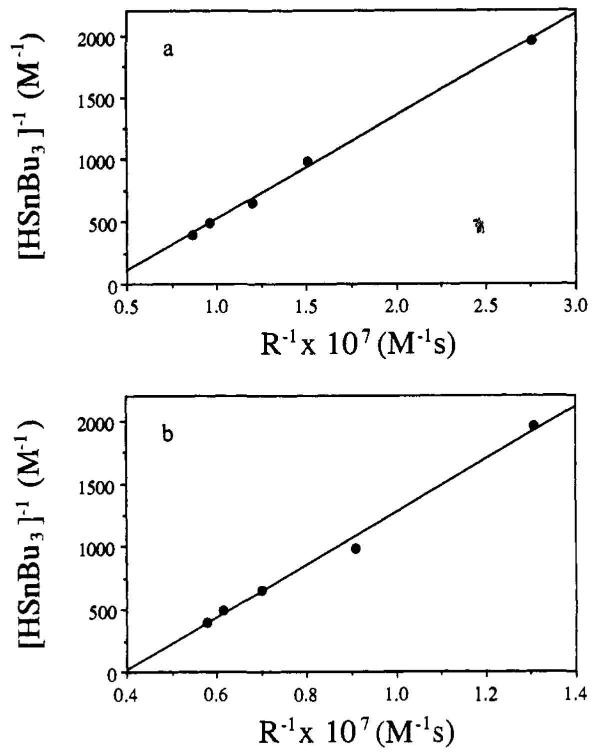

Figure 7. $[HSnBu_3]^{-1}$ vs R^{-1} for formation of (a) $HMn(CO)_5$ and (b) $Bu_3SnMn(CO)_5$.

It is interesting to note that the rate constant for oxidative addition of $HSnBu_3$ is even larger than that for recombination of $Mn_2(CO)_9$ with CO. The system is in fact somewhat more complex than suggested by the model outlined in Scheme I and eq 11, as revealed by the flash photolysis results described in the following paper in this issue. Nevertheless, it remains true that the barrier to oxidative addition is low. The reaction system described by Scheme I and eq 11 was simulated by numerical integration of the rate expression, using the HAVCHM program.[33] By evaluating the manner in which the ratio $[Bu_3SnMn(CO)_5]/[HMn(CO)_4(SnBu_3)_2]$ in the products varies with relative CO and $HSnBu_3$ concentrations, in comparison with experimental results such as those illustrated in Figure 4, it was possible to estimate that the ratio of rate constants k_5/k_6 is about 1. Here again, oxidative addition and CO recombination possess about the same free energy barrier.

Photochemical Reactions of $Mn_2(CO)_8(PR_3)_2$ with $HSnBu_3$. We have shown that photochemical reaction of $Mn_2(CO)_{10}$ with $HSnBu_3$ proceeds via oxidative addition of the hydride to $Mn_2(CO)_9$. There is no evidence of participation of the $Mn(CO)_5^{\bullet}$ radical in the process: direct H atom transfer is presumably too slow because the reaction is substantially endergonic. The situation may be different in the case of the phosphine-substituted dimers. Increased crowding around the metal may slow the oxidative addition and radical recombinations relative to H atom transfer. Furthermore, phosphine substitution leads to a stronger Mn–H bond,[34] so the direct H atom transfer process should be less endergonic. To test the generality of the oxidative addition mech-

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(31) *Solubility Data Series*; Gorgill, R. W., Ed.; Pergamon Press: Oxford, 1990; Vol. 43.

(32) Herrick, R. S.; Brown, T. L. *Inorg. Chem.* **1984**, *23*, 4450.

(33) (a) Stabler, R. N.; Chesick, J. P. *Int. J. Chem. Kinet.* **1978**, *10*, 461. (b) Chesick, J. P. *J. Chem. Educ.* **1988**, *65*, 599.

(34) The effect of phosphine substitution is actually a matter of current dispute.[17c,35] Our view is based on activation enthalpies measured for atom-transfer reactions of substituted manganese radicals,[3b,21] which leads straightforwardly to the conclusion of an increased Mn–H bond energy upon phosphine substitution.

(35) (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711. (b) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34.

anism. the photochemical reactions of $Mn_2(CO)_8(PR_3)_2$ (R = CH_3. *n*-C_4H_9. or *i*-C_3H_7) were studied.

The photochemical reaction of $Mn_2(CO)_8(PMe_3)_2$ with $HSnBu_3$ in hexane was studied under Ar or CO. in the same manner as described above for $Mn_2(CO)_{10}$. The FTIR spectra of solutions drawn from the reaction mixture show loss of $Mn_2(CO)_8(PMe_3)_2$. with concomitant growth of absorptions at 2062. 2033. 1991. 1984. 1964. 1954. and 1940 cm^{-1}. The absorptions at 2062. 1984. 1964. and 1954 cm^{-1} are assigned to *cis*-$HMn(CO)_4PMe_3$: those at 2033 and 1940 cm^{-1} are assigned to $Bu_3SnMn(CO)_4PMe_3$. In both cases the assignments are based on comparisons with the IR spectra of authentic. separately synthesized samples. A low-intensity absorption at 1991 cm^{-1} is assigned to $Mn_2(CO)_9PMe_3$ on the basis of the spectrum reported in the literature. This minor product probably results from substitution of CO for PMe_3 in the radical. followed by recombination with a $Mn(CO)_4PMe_3^{\bullet}$ radical.

In all respects this system behaves analogously to the $Mn_2(CO)_{10}$ case: At a CO pressure of 1 atm or above. the two major products are formed in a 1:1 molar ratio: formation of both primary products is inhibited by increased CO pressure. and graphs of [CO] vs the inverse of the rate are linear. From the intercepts of such plots. and employing a value of 4.7×10^4 M^{-1} s^{-1} for the analogue of k_2.[32] an average value of 2.41 (±0.5) × 10^5 M^{-1} s^{-1} is obtained for k_3. the analogous oxidative addition step.

In further analogy to the $Mn_2(CO)_{10}$ case. when irradiation is carried out under Ar. reaction proceeds much faster. While *cis*-$HMn(CO)_4PMe_3$ is formed as before. the bands due to $Bu_3SnMn(CO)_4PMe_3$ are absent. and a new band is observed at 1919 cm^{-1}. Irradiation of $Bu_3SnMn(CO)_4PMe_3$ with $HSnBu_3$ in hexane under Ar gives rise to IR absorptions at 1919 and 1990 cm^{-1}. assigned to $HMn(CO)_3(SnBu_3)_2PMe_3$ by analogy to the experiment involving $Bu_3SnMn(CO)_5$. No further efforts were made to characterize the hydride.

Irradiation of hexane solutions of $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$ and $HSnBu_3$ gives rise to analogous results. The IR bands ascribed to $Mn_2(CO)_8[P(n\text{-}Bu)_3]_2$ disappear. and new IR absorptions at 2057. 1980. and 1960 cm^{-1}. ascribed to *cis*-$HMn(CO)_4P(n\text{-}Bu)_3$. and at 1940 cm^{-1}. assigned to $Bu_3SnMn(CO)_4P(n\text{-}Bu)_3$. grow in. No detailed quantitative studies were carried out on this reaction.

Photochemical reaction of $Mn_2(CO)_8[P(i\text{-}Pr)_3]_2$ with $HSnBu_3$ in hexane was carried out under 1.3 atm of CO and 1 atm of Ar. Under CO. loss of the starting carbonyl is accompanied by the growth of IR absorptions at 2056. 1978. and 1959 cm^{-1}. due to *cis*-$HMn(CO)_4P(i\text{-}Pr)_3$. and at 1930 cm^{-1} due to $Bu_3SnMn(CO)_4P(i\text{-}Pr)_3$. Although the latter compound was not isolated. its IR spectrum is closely analogous to that for *trans*-$Bu_3SnMn(CO)_4P(C_6H_{11})_3$. which was fully characterized (see Experimental Section). Bands ascribed to $Mn_2(CO)_9P(i\text{-}Pr)_3$ were also observed. Irradiation under Ar resulted in much more rapid reaction. The major product of the reaction is *cis*-$HMn(CO)_4P(i\text{-}Pr)_3$: only trace amounts of $Bu_3SnMn(CO)_4P(i\text{-}Pr)_3$ were observed. A low-intensity absorbance at 1905 cm^{-1} may be due to the hydride $HMn(CO)_3(SnBu_3)_2P(i\text{-}Pr)_3$. These results suggest that even for fairly hindered disubstituted dinuclear compounds the principal pathway for reaction is oxidative addition of $HSnBu_3$ at the coordinatively unsaturated metal center.

Reactions with $HSiEt_3$ and Other Potential H Atom Donors. Photolysis of hexane solutions of $Mn_2(CO)_{10}$ (3×10^{-4} M) and $HSiEt_3$ (9×10^{-1} M) under 1.1 or 3.7 atm of CO resulted in slow formation over several hours of $HMn(CO)_5$ as the major product. and only very minor amounts of $Et_3SiMn(CO)_5$. The reaction proceeds somewhat slowly under the higher CO pressure. The photochemical reaction of $Mn_2(CO)_8(PMe_3)_2$ with $HSiEt_3$ was studied under CO at pressures between 1.1 and 3.7 atm. and under Ar. Under CO the reaction proceeded slowly to yield mainly *cis*-$HMn(CO)_4PMe_3$. and lesser amounts of $HMn(CO)_5$ and $Mn_2(CO)_9PMe_3$. Under Ar the reaction proceeded to completion within about 1.5 h. with *cis*-$HMn(CO)_4PMe_3$ as the major product. These results suggest that photochemical reactions of the dinuclear species with $HSiEt_3$ also proceed via oxidative addition. but with much lower quantum yields. The longer irradiation times are in all likelihood responsible for the comparatively lower net yield of the heterodinuclear reaction product.

The photochemical reactions of $Mn_2(CO)_8(PMe_3)_2$ with the organic H atom donors fluorene or triphenylmethane were studied under 1.1 atm of CO. These organic donors contain relatively weak C–H bonds (80 kcal mol^{-1} for fluorene. 81 kcal mol^{-1} for Ph_3CH).[36] However. sunlamp irradiation with either donor for up to 19 h provided no conclusive evidence for either *cis*-$HMn(CO)_4PMe_3$ or $HMn(CO)_5$ formation, only small amounts of $Mn_2(CO)_9PMe_3$. It is thus evident that even these comparatively good H atom donors fail to react with $Mn(CO)_4L^{\bullet}$ radicals because of the overall endergonic character of the reaction. and perhaps also because of steric impediments. They also fail to undergo oxidative addition with $Mn_2(CO)_7(PMe_3)_2$, because of unfavorable steric or overall energetic factors. or both.

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Registry No. $Mn_2(CO)_{10}$. 10170-69-1: $HSnBu_3$. 688-73-3: $HSiEt_3$. 617-86-7: Ph_3CH. 519-73-3: $Mn_2(CO)_8(PMe_3)_2$. 93503-87-8: $Mn_2(CO)_8(P(n\text{-}Bu)_3)_2$. 15609-33-3: $Mn_2(CO)_8(P(i\text{-}Pr)_3)_2$. 75847-41-5: $HMn(CO)_5$. 16972-33-1: *cis*-$HMn(CO)_4PMe_3$. 136735-35-8: $Bu_3SnMn(CO)_5$. 54966-76-6: *cis*-$Bu_3SnMn(CO)_4PMe_3$. 136660-31-6: *trans*-$Bu_3SnMn(CO)_4P(C_6H_{11})_3$. 136660-32-7: *trans*-$Bu_3SnMn(CO)_4P(n\text{-}Bu)_3$. 136660-33-8: $PPN^+Mn(CO)_5^-$. 52542-59-3: $PPN^+Mn(CO)_4(SnBu_3)_2^-$. 136660-35-0: $HMn(CO)_4(SnBu_3)_2$. 136660-36-1: fluorene. 86-73-7.

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