REACTIONS OF SUBSTITUTED
MANGANESE CARBONYL RADICALS

BY

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I. INTRODUCTION

Until recently, radical intermediates were thought only to occur in group IV A metals. Radical intermediates in transition metal organometallic compounds are a current topic of research.

Flash photolysis studies of $\text{Mn}_2(\text{CO})_{10}$ have indicated the existence of a 17 electron radical species.$^1$

$$\text{Mn}_2(\text{CO})_{10} \rightarrow 2\text{Mn}(\text{CO})_5.$$  \hspace{1cm} (1)

The flash photolysis used light of wavelengths between 310 nm and 380 nm the electronic absorbance spectrum was monitored and a sharp decrease of absorbance at 342 nm was observed immediately after the flash followed by a regeneration of the absorbing species. The band at 342 nm has been assigned as the $\sigma \rightarrow \sigma^*$ transition in $\text{Mn}_2(\text{CO})_{10}$.\textsuperscript{2} Excitation at this wavelength leads to homolysis of the metal-metal bond. The process was proposed to be the recombination of two $\text{Mn}(\text{CO})_5$ radicals (Eq. 2).

$$2\text{Mn}(\text{CO})_5 \rightarrow \text{Mn}_2(\text{CO})_{10}$$  \hspace{1cm} (2)

This reaction occurs with a rate constant near the diffusion controlled limit. This rapid rate would be expected for $\text{Mn}(\text{CO})_5$. if the geometry of the radical is considered. Each metal in $\text{Mn}_2(\text{CO})_{10}$ is in octahedral geometry. Cleavage of the metal-metal bond produces two five coordinate 17 electron radicals which are also in octahedral geometry with the sixth coordination site occupied by the odd electron. Lack of steric hindrance about the metal in $\text{Mn}(\text{CO})_5$. facilitates
recombination to form the dimer. Replacement of CO by various ligands \( (L=\text{Bu}_3\text{P(OEt)}_3) \) shows a dramatic decrease in the rate of recombination.\(^3\)\(^4\) The radical of the general formula \( \text{Mn(CO)}_3L_2 \) are thought to have square pyramidal geometry about the metal with the ligands in the mutually trans basal positions. They are stable for days when stored in the absence of \( O_2 \).

Further studies of transition metal radicals found evidence of halogen abstraction reactions (Eq. 3). These reactions are well characterized for the main group radicals.

\[
\text{Mn}_2(\text{CO})_{10} \rightarrow 2\text{Mn(CO)}_5\text{Cl}
\]

This reaction consists of the homolytic cleavage of the metal-metal bond to form \( \text{Mn(CO)}_5 \), followed by the abstraction of a halogen atom from the solvent.\(^5\)

A reaction which is not observed for main group radicals but is present in many transition metal carbonyl radical pathways is substitution. Early studies could not determine if associative attack of the incoming ligand occurred or dissociation of CO followed by coordination of the ligand. The dissociative mechanism was supported by recent work such as the flash photolysis of \( \text{Mn}_2(\text{CO})_{10} \) in a degassed solution.\(^6\) Dramatically different behavior was observed in this system as compared to the experiments where no attempts to remove CO were made. There was a rapid decrease in absorbance followed by the continued increase beyond that characteristic of the initial \( \text{Mn}_2(\text{CO})_{10} \) solution. This suggested the formation of a species with similar absorbance characteristics. The fol-
The following mechanism was proposed:

**Scheme I**

\[ 2\text{Mn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_{10} \]
\[ \text{Mn(CO)}_5 \rightarrow \text{Mn(CO)}_4 + \text{CO} \]
\[ \text{Mn(CO)}_4 + \text{Mn(CO)}_4 \rightarrow \text{Mn}_2(\text{CO})_8 \]
\[ \text{Mn(CO)}_4 + \text{Mn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_9 \]
\[ \text{Mn}_2(\text{CO})_8 + \text{CO} \rightarrow \text{Mn}_2(\text{CO})_9 \]
\[ \text{Mn}_2(\text{CO})_9 + \text{CO} \rightarrow \text{Mn}_2(\text{CO})_{10} \]

Step 5 involves the dissociative loss of CO forming the coordinatively unsaturated 15 electron species Mn(CO)_4. This can either recombine with a similar molecule or the 17 electron species Mn(CO)_5 to form the eight and nine coordinate species in steps 6 and 7. Reaction with CO in steps 8 and 9 form the initial dimer Mn_2(CO)_{10}. It was assumed that Mn_2(CO)_8 and Mn_2(CO)_9 were responsible for the extra absorbance in this experiment. The presence of these coordinatively unsaturated dimers suggested that the dissociative loss of CO was a major reaction pathway.

Following the loss of CO the coordination of a ligand to the coordinatively unsaturated species can occur. The mechanism for the reaction of Mn_2(CO)_{10} with a phosphine (L=PBU_3, P(OEt)_3) in the absence of added CO has been proposed (Eq. 10-14).

**Scheme II**

\[ \text{Mn}_2(\text{CO})_{10} \rightarrow 2\text{Mn(CO)}_5 \]
\[ \text{Mn(CO)}_5 \rightarrow \text{Mn(CO)}_4 + \text{CO} \]
\[ \text{Mn(CO)}_4 + \text{L} \rightarrow \text{Mn(CO)}_4\text{L} \]
\[ 2\text{Mn(CO)}_4\text{L} \rightarrow \text{Mn}_2(\text{CO})_9\text{L}_2 \]
\[ \text{Mn(CO)}_4\text{L} + \text{Mn(CO)}_5 \rightarrow \text{Mn}_2(\text{CO})_9 \]

Step 11 involves the dissociative loss of CO to form the coordinatively unsaturated 15 electron \( \text{Mn(CO)}_4 \). This reacts with the incoming ligand to form the 17 electron species in step 12. Recombination of the radicals forms the major product \( \text{Mn}_2(\text{CO})_9\text{L}_2 \) and trace amounts of \( \text{Mn}_2(\text{CO})_9\text{L} \). The substitution of \( \text{Mn(CO)}_5 \) is fast compared to the recombination of the radicals. The small amount of \( \text{Mn}_2(\text{CO})_9\text{L} \) present supports this fact. The overall limiting step therefore is the formation of the free radicals.

Photolysis of \( \text{Mn}_2(\text{CO})_9\text{L}_2 \) in the presence of excess ligand (L=P\( \text{Bu}_3 \), P(OEt)\( _3 \)) and with the removal of CO yields \( \text{Mn(CO)}_3\text{L}_2 \). (Scheme III).

**Scheme III**
\[ \text{Mn}_2(\text{CO})_9\text{L}_2 \rightarrow 2\text{Mn(CO)}_4\text{L} \]
\[ \text{Mn(CO)}_4\text{L} + \text{L} \rightarrow \text{Mn(CO)}_3\text{L}_2 + \text{CO} \]

Evidence is not conclusive to assign step 16 as either the associative attack of L or dissociative loss of CO. When attempts were not made to remove excess CO the reaction proceeded very slowly. 3

This study attempted to further characterize species of the general formula \( \text{Mn(CO)}_3\text{L}_2 \). It was hoped that values for the electrochemical oxidation and reduction of the radical could be obtained. This particular type of electrochemical
study on organometallic free radicals has no precedence in the
literature although the oxidation and reduction of mononuclear
and dinuclear metal carbonyls has been reported.\textsuperscript{8,9,10}

This study also investigated the reaction of \textit{Mn}(\textit{CO})_{3}\textit{L}_{2}.
(\textit{L}=\textit{P}(\textit{i-Pr})_{3}) with \textit{HSnBu}_{3}. The photolysis of \textit{Co}_{2}(\textit{CO})_{6}\textit{L}_{2} (\textit{L}=
\textit{PBu}_{3}) and \textit{HSnBu}_{3} has been reported to yield \textit{Bu}_{3}\textit{SnCo}(\textit{CO})_{3}\textit{L}.\textsuperscript{6} It was thought that the presence of two bulky ligands on the
manganese radical may prevent the oxidative addition of \textit{HSnBu}_{3}
to the radical and \textit{HMn}(\textit{CO})_{3}\textit{L}_{2} would instead be formed via hy-
dride abstraction from \textit{HSnBu}_{3}. Hydride abstraction has been
reported for metal carbonyl radicals and their analogous met-
metal carbonyl hydride.\textsuperscript{11,12}

II. EXPERIMENTAL

All reagents, solvents and compounds were stored in the
inert atmosphere glove box. All sample preparation was done
in the glove box.

A. REAGENTS

Dimanganese decacarbonyl (\textit{Mn}_{2}(\textit{CO})_{10}) was obtained from
Pressure Chemical Co. and sublimed at 50-70\textdegree C and 0.5mm. The
yellow-orange crystals were stored in a refrigerator until use.

Tri-\textit{n}-butylphosphine (\textit{PBU}_{3}) was obtained from Aldrich
Chemical Co. This air sensitive compound was distilled over
\textit{CaH}_{2} under reduced pressure in a \textit{N}_{2} atmosphere.

Tri-\textit{iso}-propylphosphine [(\textit{P}(\textit{i-Pr})_{3}]] was obtained from
Strem Chemicals, Inc. This extremely air sensitive compound
was distilled over CaH₂ under reduced pressure in a N₂ atmosphere.

B. SOLVENT PURIFICATIONS

Hexane (C₆H₁₄) was purified by passing it through a column of silica to remove the olefins present then degassing it with N₂.

Propylene carbonate (C₄H₆O₃) was purified by heating it with Na₂CO₃ and KMnO₄ (both 10 g/liter) for two hours before vacuum distillation.

1-methyl-2-pyrrolidone (C₅H₉NO) was purified by heating over KMnO₄ for 30 minutes at 70°C followed by a vacuum fractional distillation. The solvent was stored over activated 4Å molecular sieves.

C. PREPARATION OF COMPOUNDS

Dimanganese octacarbonylbis(tri-n-butylphosphine) [Mn₂-(CO)₈(PBu₃)₂] was prepared by a literature method. Mn₂(CO)₁₀ (1 mmol) and PBu₃ (2.1 mmol) were dissolved in approximately 50 ml of degassed hexane. This solution was photolyzed under a N₂ atmosphere with a 275 watt General Electric sunlamp in a pyrex Schlenk flask. The flask was fitted with a rubber septum so that the reaction could be followed by syringing out a sample for analysis by IR. The solution was stirred and cooled by a fan during photolysis to discourage any thermal reaction. Photolysis time was approximately 12 hours. The solvent was removed under reduced pressure and the resulting orange residue was recrystallized from methanol.
yielding yellow-orange crystals. The IR obtained for \( \text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2 \) in hexane is shown in figure 1.

IR (hexane); 1967 (m), 1942 (vs), 1928 (m).

Dimanganese octacarbonylbis(tri-iso-propylphosphine) \([\text{Mn}_2(\text{CO})_8(\text{P}[i-\text{Pr}]_3)_2]\) was prepared following the procedure used for \( \text{Mn}_2(\text{CO})_8(\text{PBu}_3) \) with the exception of photolysis time being extended to 22 hours. The IR obtained for \( \text{Mn}_2(\text{CO})_8[\text{P}(i-\text{Pr})_3)_2 \) is shown in figure 1.

IR (hexane); 1978 (m), 1952 (vs), 1937 (m).

Manganese tricarbonylbis(tri-n-butylphosphine) radical \([\text{Mn}(\text{CO})_3(\text{PBu}_3)_2\cdot]\) was prepared following a literature method.\(^3\) \( \text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2 \) (10\(^{-2}\) M) and \( \text{PBu}_3 \) (2 x 10\(^{-2}\) M) were dissolved in approximately 15 ml of degassed hexane. The reaction vessel illustrated in figure 2 was attached to a high vacuum line and the solution was degassed by three freeze-pump-thaw cycles. A 275 watt General Electric sunlamp was used to photolyze the solution under reduced pressure in the quartz sample chamber. Approximately every 90 minutes the sample chamber was degassed by a freeze-pump-thaw cycle to remove CO. The initial solution was yellow but after photolysis turned green indicating the existence of \( \text{Mn}(\text{CO})_3(\text{PBu}_3)_2\cdot \). This radical was stable for many days when stored under an \( \text{O}_2 \) free atmosphere. The UV-near IR spectrum of the radical showed the characteristic absorbance at 750 nm. The IR of \( \text{Mn}(\text{CO})_3(\text{PBu}_3)_2\cdot \) in hexane is illustrated in figure 3.

IR (hexane); 1867 (sh), 1858 (m).
Figure 1. Infrared spectra in the carbonyl stretching region for $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ (A) and $\text{Mn}_2(\text{CO})_8[\text{P}(\text{i-Pr})_3]_2$ (B) in hexane.
Figure 2. Reaction vessel used for photolyzing $\text{Mn}_2(\text{CO})_8L_2$ and $L$ at reduced pressure.
Figure 3. Infrared spectra in the carbonyl stretching region for $\text{Mn(CO)}_3\text{P(Bu)}_3\text{P}_2$ in hexane.
Manganese tricarbonylbis(tri-iso-propylphosphine) radical [Mn(CO)$_3$(P[i-Pr]$_3$)$_2$] was prepared using the procedure for Mn(CO)$_3$(PBU$_3$)$_2$. Mn$_2$(CO)$_8$[P(i-Pr)$_3$]$_2$ was found to be less soluble in hexane than Mn$_2$(CO)$_8$(PBU$_3$)$_2$. The solution was photolyzed for approximately 14 hours. This solution also changed from yellow to green after photolysis. The IR in hexane is shown in figure 4.

IR (hexane): 1860 (m), 1853 (m).

D. INERT ATMOSPHERE GLOVE BOX

All sample preparations were made in a Vacuum Atmospheres model Dri-Lab HE-43-2 glove box. The box atmosphere was purified of oxygen by circulation of the atmosphere through a manganese oxalate column. The atmosphere was purified of solvents by circulation through a column of 4A and 13X molecular sieves. The oxygen concentration of the box atmosphere was tested by exposing a THF solution of [Cp$_2$TiCl]$_2$ZnCl$_2$ to the atmosphere. The maintenance of the initial blue color throughout the evaporation of the solvent indicates the oxygen concentration to be below 5 ppm.

E. REACTION VESSEL

The reaction vessel shown in figure 2 was used for the reactions of Mn$_2$(CO)$_8$L$_2$ (L=PBU$_3$,P(i-Pr)$_3$) with L. These reactions are inhibited by very low levels of CO so the reaction vessel was attached to a high vacuum line and evacuated period-
Figure 4. Infrared spectra in the carbonyl stretching region for Mn(CO)$_3$[P(i-Pr)$_3$)$_2$ in hexane.
ically. Tube A is the quartz reaction chamber and tube B is the quartz UV sample cell with 0.2 cm pathlength. UV spectra can be obtained without opening the chamber to the air by opening stopcock A and transferring solution to the sample cell. Samples for IR analysis were obtained by taking the sample chamber into the box and syringing out some of the solution through stopcock A.

F. INSTRUMENTATION

All IR spectra were obtained on a Beckman IR 4240 spectrophotometer. Matched solution IR cells of either 1 mm or 0.2 mm pathlength and NaCl windows were used.

Electronic spectra were obtained on a Cary Model 14 Recording Spectrophotometer using matched 0.2 cm quartz cells.

Gas chromatography was done on F and M Laboratory Chromatograph Model 700. The column contained 11% Carbowax 20M on Chromasorb W-AW. The carrier gas was argon.

III. RESULTS AND DISCUSSION

With the initial intent to study the electrochemical reduction of manganese carbonyl radicals by cyclic voltammetry, I set out to form Mn(CO)$_3$(PBu$_3$)$_2$. in a solvent suitable for electrochemical work. Acetonitrile, although a common solvent of choice, was found to be unsuitable due to the coordination of the solvent with the radicals.$^{13}$

Propylene carbonate was tried because it does not coor-
dinate to organometallic free radicals. Also this solvent has a high dielectric constant needed for an electrochemical study. The ligand (PBU$_3$) was found to be immiscible in this solvent and Mn$_2$(CO)$_8$(PBU$_3$)$_2$ was only slightly soluble. I was unable to generate Mn(CO)$_3$(PBU$_3$)$_2$. in propylene carbonate.

The solvent 1-methyl-2-pyrroldione was tried next. The solution was photolyzed for 12 hours after which time there seemed to be a darkening of the orange solution but no distinguishable green color was present. The UV-near IR spectrum showed no absorbance near 750 nm. The IR of the solution, illustrated in figure 5, gave broadened peaks. Other than the starting material peaks at 1967 cm$^{-1}$ and 1937 cm$^{-1}$, an intense peak occurred at 1882 cm$^{-1}$. This was believed to be HMn(CO)$_3$(PBU$_3$) based on the assignment for this species at 1896 cm$^{-1}$ in hexane.$^3$ There were no visible peaks in the 1845 cm$^{-1}$ range that would indicate Mn(CO)$_3$(PBU$_3$)$_2$. 

In order to determine if a radical of the type Mn(CO)$_3$L$_2$. could exist in a 1-methyl-2-pyrroldione solution, hexane solutions of Mn(CO)$_3$L$_2$. (L=PBU$_3$, P(i-Pr)$_3$) were mixed with an equal amount of 1-methyl-2-pyrroldione. The two solvents were immiscible though it was visibly evident that some of the green species was extracted into the 1-methyl-2-pyrroldione layer. An IR was taken of this layer with a reference solution which was similarly extracted from a mixture of equal amounts of the two solvents. A peak at 1848 cm$^{-1}$ for L=PBU$_3$ and 1845 cm$^{-1}$ for L P(i-Pr)$_3$ was seen in this solvent. This was assigned
Figure 5. Infrared spectra in the carbonyl stretching region for product of photolysis of $\text{Mn}_2(\text{CO})_8(\text{PBu}_3)_2$ with excess $\text{PBu}_3$ in 1-methyl-2-pyrrolidone.
to Mn(CO)$_3$L$_2$. based on the disappearance of this peak after exposure to air. The diminished size of the peaks were thought to be due to the dilution factor or some reaction of the radical with 1-methyl-2-pyrrolidone (figure 6).

This evidence suggested that Mn(CO)$_3$L$_2$. ($i$=PBU$_3$, P(i-Pr)$_3$) can exist in 1-methyl-2-pyrrolidone but cannot be generated in this solvent by photolysis. The questionable behavior of the radical in this solvent discouraged further attempts of an electrochemical study in this solvent.

The inability to form Mn(CO)$_3$(PBU)$_2$. in 1-methyl-2-pyrrolidone may be attributed to the hydrogen bond strength of the solvent. After photolysis of Mn$_2$(CO)$_8$(PBU$_3$)$_2$ with excess (PBU$_3$) in 1-methyl-2-pyrrolidone a peak at 1882 cm$^{-1}$ occurred which was assumed to be HMn(CO)$_3$(PBU$_3$)$_2$. Assuming the hydrogen was abstracted from a solvent molecule, we can assign hydrogen bond strengths to the solvents by crude comparisons to similar molecules to help understand this behavior. The carbon-hydrogen bond strength of xane can be assumed to be similar to propane which is 98 ± 1 kcal mol$^{-1}$. The carbon-hydrogen bond strength of the methyl hydrogen in 1-methyl-2-pyrrolidone, if compared to H-CH$_2$NH$_2$, is 94.6 ± 2.0 kcal mol$^{-1}$ and the strength of the ring carbon-hydrogen bonds, if compared to cyclopropane, is 94.5 ± 1.14 The lower carbon-hydrogen bond strength in 1-methyl-2-pyrrolidone may be the cause for the inability to form Mn(CO)$_3$L$_2$. in this solvent.

An attempt was made to measure the rate of disappearance
Figure 6. Infrared spectra in the carbonyl stretching region of extraction of Mn(CO)$_3$L$_2$. (with L=PBu$_3$ in A and L=P(i-Pr)$_3$ in B) from a hexane solution into 1-methyl-2-pyrrolidone.
of Mn(CO)$_3$[P(i-Pr)$_3$]$_2$· and probable formation of HMn(CO)$_3$[P(i-Pr)$_3$]$_2$ in 1-methyl-2-pyrrolidone. An extraction of the green species into the 1-methyl-2-pyrrolidone was made and the absorbance at 1845 cm$^{-1}$ was monitored. The absorbance decreased by only 10% after one hour and there was no increase in any other peak. No further attempts were made to measure the kinetics of Mn(CO)$_3$[P(i-Pr)$_3$]$_2$· in this solvent.

The reaction kinetics of Mn(CO)$_3$L$_2$· with other hydrogen donors was also studied. Tri-n-butyltin hydride, which is a good hydrogen donor, was added to a hexane solution of Mn(CO)$_3$[P(i-Pr)$_3$]$_2$·. The IR of the solution in the carbonyl stretching frequency range was monitored and is illustrated in figure 7. Over a period of 20 minutes a measurable decrease in intensity of the peak at 1852 cm$^{-1}$ occurred accompanied by the large increase in intensity of the peak at 1891 cm$^{-1}$ and a weak new peak at 1870 cm$^{-1}$. The substance which was growing in was thought to be HMn(CO)$_3$[P(i-Pr)$_3$]$_2$ and/or Bu$_3$SnMn(CO)$_3$[P(i-Pr)$_3$]$_2$.

To distinguish the two possible products H$_2$ evolution was measured by gas chromatography. In order to assure that any absence of H$_2$ in a gc experiment was not due to the insensitivity of the machine to small concentrations of H$_2$ rather than the actual absence of gas, samples were run with the estimated amount of H$_2$ present. Calculations were made to determine the amount of H$_2$ which would be present in the headspace of a reaction vessel. A 10 ml flask with 7 ml of the
Figure 7. Infrared spectra in the carbonyl stretching region for the reaction of Mn(CO)$_3$[P(i-Pr)$_3$]$_2$ with HSnBu$_3$ at $t=0$ (A) and $t=20$ minutes (B).
hexane solution of \( \text{Mn(CO)}_3[\text{P(i-Pr)}_3]_2 \) was used. Due to the large amount of unreacted \( \text{Mn}_2(\text{CO})_8[\text{P(i-Pr)}_3]_2 \) in solution, the concentration of radical was based on only a 12% yield. The headspace in the reaction vessel contained argon, the gas present in the inert atmosphere box at the time. If all of the radical present was converted to \( \text{Bu}_3\text{SnMn(CO)}_3[\text{P(i-Pr)}_3]_2 \) then the 3 ml of headspace in the reaction vessel would contain a \( \text{H}_2 \) concentration of approximately \( 8.75 \times 10^{-6} \) M.

A gc of the atmosphere of the box showed a peak which was thought to be hydrogen. Small amounts of hydrogen can be expected to be present in the box since it is used in the regeneration of the manganese oxalate columns. Oxygen was found to have the same retention time as hydrogen under the conditions of this experiment so this peak may have been from oxygen contamination in the reaction vessel. Assuming the peak to be \( \text{H}_2 \), the concentration of \( \text{H}_2 \) in the box can be estimated from the peak height and is calculated to be \( 5.36 \times 10^{-6} \) M.

The atmosphere above the solution in the reaction vessel gave a peak with the same retention time and a peak height corresponding to a concentration of \( 7.77 \times 10^{-6} \) M. An increase of \( \text{H}_2 \) concentration of approximately \( 2.41 \times 10^{-6} \) M was detected but this is substantially less than the estimated concentration of \( 8.75 \times 10^{-6} \) M. The increase of the peak was probably not due to solvent molecules present in the atmosphere above my reaction since hexane would be expected to have a very long retention time on this column.\(^{15} \)
The absorbance at 1852 cm\(^{-1}\) which decreased in intensity in the reaction of Mn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) with HSnBu\(_3\) has been assigned to Mn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\)^•. The absorbance at 1891 cm\(^{-1}\) which increased in intensity can be partially assigned by comparison to a similar experiment. Reaction of Mn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\)^• with CCl\(_4\) produced a peak at 1890 cm\(^{-1}\) which was assigned to ClMn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\).\(^{16}\) A similar absorbance value would be expected for HMeN(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) so the 1891 cm\(^{-1}\) absorbance in figure 7 is partially the result of the hydride. This suggests HMeN(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) is among the products of this reaction. My preliminary gas chromatography experiments of the atmosphere above the reaction solution showed possible H\(_2\) evolution suggesting the formation of Bu\(_3\)SnMn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\). Without actual absorbance values assigned to HMeN(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) or Bu\(_3\)SnMn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) accurate assignment of the 1891 cm\(^{-1}\) peak cannot be made. The possibility that the two substances have the same absorbance values also exists.

The experimental evidence is not conclusive enough to predict the products of the reaction. Mechanisms can be proposed for the formation of either HMeN(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) and/or Bu\(_3\)SnMn(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) and further experiments to verify the identity of the products may be possible.

A mechanism for the formation of HMeN(CO)\(_3\)[P(i-Pr)\(_3\)]\(_2\) is proposed in Scheme IV.

Scheme IV

\[
\text{Mn(CO)}_3\text{L}_2^\cdot + \text{HSnBu}_3 \rightarrow \text{HMeN(CO)}_3\text{L}_2 + \text{SnBu}_3^\cdot
\]
This mechanism involves the hydrogen abstraction from HSnBu$_3$ to form HMn(CO)$_3$L$_2$.

A mechanism for the formation of Bu$_3$SnCo(CO)$_3$L complexes has been proposed. A similar mechanism may be proposed for the reaction of Mn(CO)$_3$L$_2^+$ and HSnBu$_3$ (L=P(i-Pr)$_3$) (Scheme V).

\[
\text{Scheme V} \\
\text{Mn(CO)$_3$L$_2^+$} \rightarrow \text{Mn(CO)$_2$L$_2$ + CO} \\
\text{Mn(CO)$_2$L$_2$ + HSnBu$_3$} \rightarrow \text{Mn(H)(SnBu$_3$)(CO)$_2$L$_2$} \\
\text{Mn(H)(SnBu$_3$)(CO)$_2$L$_2$ + HSnBu$_3$} \rightarrow \text{Mn(H)$_2$(SnBu$_3$)(CO)$_2$L$_2$ + SnBu$_3$} \\
\text{Mn(H)$_2$(SnBu$_3$)(CO)$_2$L$_2$ + CO} \rightarrow \text{Mn(SnBu$_3$)(CO)$_3$L$_2$ + H$_2$}
\]

Step 17 is the dissociation of CO to give the coordinatively unsaturated 15 electron intermediate. Oxidative addition of HSnBu$_3$ results in Mn(H)(SnBu$_3$)(CO)$_2$L$_2$ which abstracts a hydrogen from a second molecule of HSnBu$_3$ in step 19. In step 20, H$_2$ is reductively eliminated followed by CO coordination to obtain the final products of Bu$_3$SnMn(CO)$_3$L$_2$ and H$_2$(g). If both HMn(CO)$_3$L$_2$ and Bu$_3$SnMn(CO)$_3$L$_2$ are identified as products then Scheme IV and Scheme V may be occurring simultaneously or another mechanism may exist with both substances as products.

A mechanism which would produce both HMn(CO)$_3$L$_2$ and Bu$_3$SnMn(CO)$_3$L$_2$ as products is presented in Scheme VI.

\[
\text{Scheme VI} \\
\text{Mn(CO)$_3$L$_2^+$ + HSnBu$_3$} \rightarrow \text{HMn(CO)$_3$L$_2$ + SnBu$_3^+$.} \\
\text{HMn(CO)$_3$L$_2$ + HSnBu$_3$} \rightarrow \text{HMn(CO)$_2$L$_2$ + CO} \\
\text{HMn(CO)$_2$L$_2$ + HSnBu$_3$} \rightarrow \text{(H)$_2$Mn(SnBu$_3$)(CO)$_2$L$_2$}
\]
\[(\text{H})_2\text{Mn(SnBu}_3\text{)}(\text{CO})_2\text{L}_2 + \text{CO} \rightarrow \text{H}_2 + \text{Mn(SnBu}_3\text{)}(\text{CO})_3\text{L}_2\]

A hydride abstraction occurs in step 21 followed by the loss of CO from \(\text{H}_2\text{Mn(CO)}_3\text{L}_2\) in step 22. Oxidative addition of \(\text{H}_2\text{SnBu}_3\) occurs in step 23 followed by replacement of \(\text{H}_2\) by CO.

This mechanism must have step 22 lay far to the left in order to yield \(\text{H}_2\text{Mn(CO)}_3\text{L}_2\) as a product in addition to \(\text{Mn(SnBu}_3\text{)}(\text{CO})_3\text{L}_2\). The loss of CO from the 16 electron \(\text{H}_2\text{Mn(CO)}_3\text{L}_2\) in step 22 seems improbable although the bulkiness of the ligand or the presence of \(\text{H}_2\text{SnBu}_3\) may in some way facilitate CO loss.

The formation of \(\text{Mn(CO)}_3\text{L}_2\) involves the dissociation of the CO groups from \(\text{Mn(CO)}_5\). This dissociation takes place only after diligent efforts to remove free CO were included.

The mechanism in Scheme V involves a third CO dissociation from \(\text{Mn(CO)}_5\text{L}_2\) to form \(\text{Mn(CO)}_2\text{L}_2\). It seems improbable that a third CO would dissociate from \(\text{Mn(CO)}_3\text{L}_2\) under the conditions which this experiment was run. The formation of \(\text{Bu}_3\text{SnMn(CO)}_5\text{L}_2\) by the mechanism in Scheme V seems improbable at this time.

Further studies are needed to understand the reaction of \(\text{H}_2\text{SnBu}_3\) and \(\text{Mn(CO)}_3\text{L}_2\). Identification of the products of the reaction should be made by NMR analysis and electron impact or field absorption mass spectrometry.

Additional studies may be done on the \(\text{Mn(CO)}_3\text{L}_2\) species after the exact identification of products has been made. The kinetics of the reaction with \(\text{H}_2\text{SnBu}_3\) can be followed on a conventional IR spectrometer since the reaction takes place over
a period of approximately 30 minutes for Mn(CO)$_3$[P(i-Pr)$_3$]. The long reaction time is thought to be a result of the bulky P(i-Pr)$_3$ ligand blocking incoming reactants.

The reaction of HSnBu$_3$ with Mn(CO)$_3$L$_2$. with L being some other ligand could be analyzed. Determination of the products should first be made to find if they are the same as for the P(i-Pr)$_3$ case. A less bulky ligand may yield a different product. The kinetics of the reactions with less bulky ligands (i.e. PBu$_3$) could prove to be faster. Stop-flow techniques may be needed to follow these reactions.

The original goal of this thesis was to study the electrochemistry of Mn(CO)$_3$L$_2$. Although time did not allow for this, it may be possible to study the electrochemistry of this species in 1-methyl-2-pyrroldione since the radical was able to be extracted into this solvent.
IV. BIBLIOGRAPHY

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