

Transition Metal Alkyl Chemistry at Elevated Carbon Monoxide Pressures. An Infrared Spectroscopic Study of Systems Related to Catalytic Intermediates in Homogeneous Hydroformylation Reactions

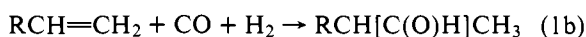
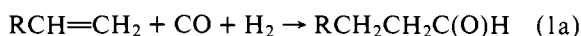
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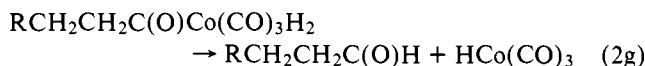
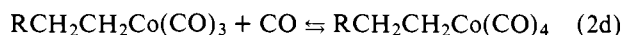
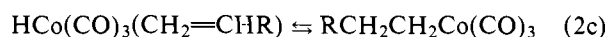
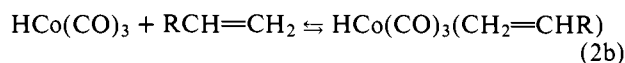
Abstract: Reactions of transition metal alkyls with CO at elevated pressures (~300 atm) in *n*-tetradecane solution have been followed by infrared spectroscopy under pressure using the $\nu(\text{CO})$ region to identify carbonyl intermediates. The manganese carbonyl derivative $\text{CH}_3\text{Mn}(\text{CO})_5$ reacts with CO to give $\text{CH}_3\text{COMn}(\text{CO})_5$ which in turn reacts with H_2 to give $\text{Mn}_2(\text{CO})_{10}$ and CH_3CHO . However, the substituted manganese carbonyl derivatives *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{PR}_3$ ($\text{R} = \text{C}_6\text{H}_5, \text{OC}_6\text{H}_5,$ and $\text{N}(\text{CH}_3)_2$) react with CO to give mixtures of $\text{CH}_3\text{COMn}(\text{CO})_5$, $\text{CH}_3\text{COMn}(\text{CO})_4\text{PR}_3$, and PR_3 which form no CH_3CHO upon treatment with H_2 . The rhenium carbonyl derivative $\text{CH}_3\text{Re}(\text{CO})_5$ forms $\text{Re}_2(\text{CO})_{10}$ rather than $\text{CH}_3\text{COPe}(\text{CO})_5$ upon heating with CO under pressure. The cyclopentadienyliron derivative $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ undergoes carbonylation to give $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$, but hydrogenolysis of this acyl produces no CH_3CHO . The alkyls $\text{RM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{M} = \text{Mo}, \text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2 = \text{CHCH}_2, \text{C}_6\text{H}_5\text{CH}_2,$ and CH_3SCH_2 ; $\text{M} = \text{W}, \text{R} = \text{CH}_3$) react with CO under pressure to form $\text{M}(\text{CO})_6$ without any evidence for the formation of the corresponding acyl derivatives $\text{RCOM}(\text{CO})_3\text{C}_5\text{H}_5$. In the case of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ the substituted cyclopentadienyl ring is liberated as the ketone $\text{CH}_3\text{COC}_5(\text{CH}_3)_5$ upon carbonylation. These results show that the presence of strong metal-alkyl bonds or easily displaced ligands prevent the carbonylation of alkyl-metal derivatives to the corresponding acyl-metal derivatives and the presence of weaker π acceptors than CO such as trivalent phosphorus or η^5 -cyclopentadienyl ligands prevent the hydrogenolysis of acyl-metal derivatives to the corresponding aldehydes. These results therefore provide some information on the types of transition metal systems likely to be the best candidates for hydroformylation catalysts. Details of an apparatus for obtaining infrared spectra at elevated pressures up to 500 atm are described.

Introduction

One of the important applications of carbon monoxide in organic synthesis is the hydroformylation of olefins to give the corresponding aldehydes according to the following overall reactions:²



These reactions are catalyzed by certain metal carbonyl derivatives, particularly those of the late transition metals such as cobalt,³ rhodium,⁴ and platinum.⁵ The mechanism of this reaction appears to involve metal alkyl intermediates as exemplified by the following cyclic sequence of eight reactions for the hydroformylation of olefins to give terminal aldehydes with $\text{HCo}(\text{CO})_4$ as the catalyst:⁶



This cyclic sequence involves the alternating production of 16- and 18-electron intermediates.⁶ An important intermediate in this cyclic sequence is a metal alkyl as exemplified by $\text{RCH}_2\text{CH}_2\text{Co}(\text{CO})_4$ produced in step 2d. Key reactions of such

metal alkyls in this type of catalytic sequence for olefin hydroformylation include CO insertion into the metal-alkyl bond to give the corresponding acyl-metal derivative (step 2e) and the subsequent hydrogenolysis of the acyl-metal bond to give the aldehyde with liberation of the metal carbonyl hydride (step 2g).

This paper describes a systematic study of the reactions of the important types of alkylmetal carbonyls with carbon monoxide and hydrogen at elevated pressures and temperatures using infrared spectroscopy in the $\nu(\text{CO})$ region to follow such reactions. Our ultimate objective in this work is to gain some insight into the types of transition metal systems most likely to be effective as catalysts for olefin hydroformylations by examining the reactivity of appropriate model compounds for the metal alkyl intermediates involved in hydroformylation reactions. In order to give us ample opportunity to observe any significant intermediates in our high-pressure infrared spectroscopy equipment, we have selected relatively stable metal alkyls of the types $\text{RM}(\text{CO})_5$ ($\text{M} = \text{Mn}$ and Re), $\text{RMn}(\text{CO})_4\text{L}$ ($\text{L} =$ tertiary phosphine or phosphite), $\text{RM}(\text{CO})_3\text{C}_5\text{R}'_5$ ($\text{M} = \text{Mo}, \text{R}' = \text{H}$ and CH_3 ; $\text{M} = \text{W}, \text{R}' = \text{H}$), and $\text{RFe}(\text{CO})_2\text{C}_5\text{H}_5$ for this study. The key features of the chemistry of such relatively stable metal alkyls can be extrapolated to the chemistry of the less stable metal alkyls such as $\text{RCo}(\text{CO})_4$ in the hydroformylation reaction sequence given above (reactions 2a-h) by realizing that the less stable metal alkyls will react much more rapidly and at significantly lower temperatures. Of particular interest are the effects of substitution of CO ligands with C_5H_5 or trivalent phosphorus ligands on the ease of insertion of CO into the metal-alkyl bond and, in cases where the corresponding acyl derivative can be detected, on the ease of hydrogenolysis of the metal-acyl bond. Our use of infrared spectroscopy to observe such carbonylation and hydrogenation reactions occurring at high pressures permits us to monitor such reactions continuously without perturbing the system. This allows us to obtain more direct and unambiguous information about the nature of the metal carbonyl species in

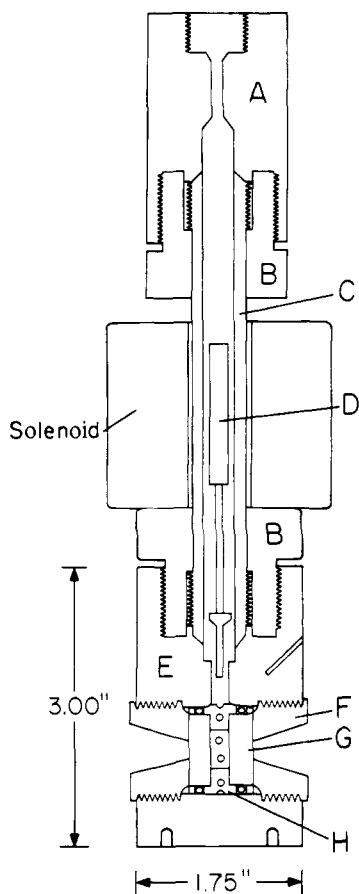


Figure 1. Lateral perspective of the assembled high-pressure optical cell and associated autoclave.

the system at any point in time. Experimental studies of this type were first carried out by Whyman and co-workers⁷ and have been used by his group at Imperial Chemical Industries for the study of numerous reactions of rhodium^{8,9} and iridium¹⁰⁻¹⁴ carbonyls, including their tertiary phosphine complexes, with carbon monoxide under pressure. However, modern advances in infrared spectrometer instrumentation and the availability of window materials with both high mechanical strengths and high transmittance in the $\nu(\text{CO})$ region (e.g., Irtran 1) now make such techniques for infrared spectroscopy at high CO pressures more suitable for routine experimental use.

Experimental Section

Design and Construction of the High-Pressure Infrared Spectroscopic Equipment. The infrared spectra recorded in these studies were obtained with a Perkin-Elmer Model 281 spectrometer. This instrument is modular in design with separate units for the optics and for the recorder. The optical unit, which contains the sample area, was mounted behind a $\frac{3}{8}$ in. aluminum shield along with all other high-pressure components of the system for reasons of safety. All spectra were recorded using a normal slit program which provides a resolution of approximately 3 cm^{-1} in the spectral region of interest ($2500\text{--}2000\text{ cm}^{-1}$).

A lateral perspective of the assembled high-pressure optical cell and associated autoclave is shown in Figure 1. The body of the autoclave (C) consists of a 5-in. section of $\frac{9}{16}$ in. o.d. \times $\frac{5}{16}$ in. i.d. 316 stainless steel tubing which is coned to fit a standard Aminco $\frac{1}{4}$ HP- $\frac{1}{4}$ HP straightway coupling (A) at the top. It is joined to the body of the optical cell by a standard $\frac{9}{16}$ HP connection using the appropriate gland nut (B) and sleeve which can be obtained from commercial sources. The body of the optical cell (E) consists of a $1.58 \times 1.75 \times 3.00$ in. block of 316 stainless steel through which a 1.00 in. diameter hole has been bored to form a central cavity which accommodates the windows (G), spacer (H), and the "O" ring seal between

the windows and cell proper. The interior surface of this bored section is polished to an 8- $\mu\text{in.}$ finish to ensure a good seal with the "O" ring packing mounted around each window.

The windows (G) are 0.75 in. diameter by 6 mm thick cylindrical optical flats composed of Irtran 1. This material transmits infrared radiation in the $3000\text{--}1500\text{-cm}^{-1}$ range and yet has a high modulus of rupture (21 800 psi at 25°C)¹⁵ which is of obvious importance for its application in this work. This choice of window material is, of course, not unique to this cell and other members of the Irtran series having lower moduli of rupture can be used with this cell at correspondingly lower pressures.

The bending stress S caused by the load W provided by a pressure P over the face of an edge-supported circular plate of radius r and thickness t can be calculated using the following equation:¹⁶

$$S = \frac{0.39W}{t^2} = 1.2 \frac{Pr^2}{t^2} \quad (3)$$

A safety factor of 4 is desirable in situations where a brittle material such as these windows is to be loaded over an unsupported area, i.e., the maximum allowable stress should be limited to $\frac{1}{4}$ of the modulus of rupture. In the cell shown in Figure 1, the threaded plugs (F) which support the windows have an unsupported optical aperture 1 cm in diameter at the surface of contact with the windows. Thus eq 3 predicts that the desired safety factor of 4 will be maintained at pressures in excess of 500 atm when the Irtran 1 windows described above are used in this high-pressure optical cell.^{17,18}

The windows of this cell are an integral part of the seal which contains the pressure within the cell in that two of the three elements of the packing (the "O" ring and Teflon backup ring) are supported by the window itself. The third element of each packing, a brass ring having a triangular cross section, is supported by the threaded plug (F). This modified Poulter seal was devised by Robertson and Hughes¹⁹ and has proven to be very dependable in optical studies at high pressures. The choice of "O" ring composition is very important, however, and care must be exercised in selecting an "O" ring which is not subject to chemical attack by the solvent. Viton "O" rings have proven to be resistant to attack by tetradecane, the solvent used in these studies, at temperatures in excess of 200°C .

The length of the optical path between the windows (G) is determined by the thickness of the spacer (H). Interchangeable spacers with thicknesses ranging from 5 to 0.1 mm can be used with this cell. While a 5-mm spacer is shown in Figure 1 for the sake of clarity, much thinner spacers are used for infrared studies. When spacers having a thickness of 1 mm or less are used, supporting plugs (F) having a longer extension into the cell cavity are used in order to compensate for the decreased space taken up by the spacer and two windows. The spectra reported in this paper were all taken using a 0.2-mm optical path length.

The complete unit for observing infrared spectra at elevated pressures in the high-pressure optical cell and associated autoclave is conveniently called a "spectraclave".

General Procedure for Obtaining Infrared Spectra at High Pressures. All of the infrared spectra at high pressures reported in this paper were obtained by the same general method (Figure 1). The cell and autoclave reservoir (C) were assembled and the desired solution was introduced into the reservoir. An agitator constructed from iron (D) was then inserted and an air-cooled solenoid coil was lowered over the body of the autoclave (C). The coupling (A) was then joined to the autoclave and the completed assembly placed in a miniature pyrophyllite oven mounted on a Perkin-Elmer $4 \times$ beam condenser assembly as depicted in Figure 2. The gas pressurization system was then connected by means of a standard Aminco $\frac{1}{4}$ HP fitting to the top of coupling (A) and compressed CO was introduced into the autoclave-cell assembly. The temperature of the cell interior was monitored throughout each experiment with a type T thermocouple which was inserted into the thermocouple well shown in Figure 1. An electronic timer mechanism was used to periodically activate the solenoid so that the solution was agitated throughout the experiment by the periodic rise and fall of the agitator D.

All spectra reported here were taken using Eastman Highest Purity Grade n -tetradecane as the solvent. n -Tetradecane was found to have an advantage over many other high-boiling nonpolar solvents by having exceptionally good optical transmission in the vicinity of the critical 2000-cm^{-1} region. Furthermore, the solubility of free CO in n -tetradecane is relatively low. This minimizes infrared absorption arising from free CO in solution and the resulting intensity of the band

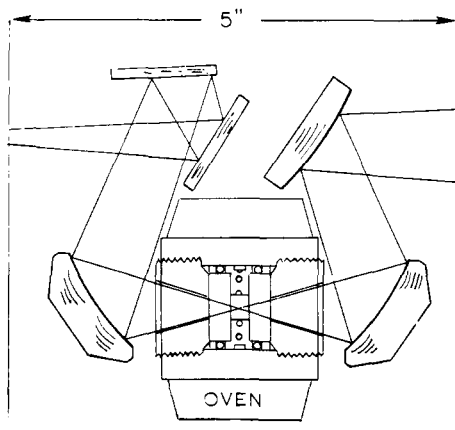


Figure 2. Location of the optical cell (Figure 1) and the 4X beam condenser in the beam of the infrared spectrometer.

at $\sim 2135\text{ cm}^{-1}$ arising from the free CO. Representative spectra at high pressures of CO and/or H_2 obtained by this technique are depicted in Figures 3–8.

Sources of Compounds Used in This Study. The metal carbonyl derivatives $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}$ and W ; Pressure Chemical Co., Pittsburgh, Pa.), $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ (Ethyl Corp., New York, N.Y.), $\text{Fe}(\text{CO})_5$ (GAF Corp., New York, N.Y.), and $\text{Re}_2(\text{CO})_{10}$ (Pressure Chemical Co., Pittsburgh, Pa.) were purchased from the indicated commercial sources. The $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ was converted to $\text{Mn}_2(\text{CO})_{10}$ by the standard published method.²⁰ The $\text{Mn}_2(\text{CO})_{10}$, in turn, was converted to $\text{CH}_3\text{Mn}(\text{CO})_5$ by treatment with sodium hydroxide followed by addition of methyl iodide.²¹ Reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ with triphenylphosphine and with triphenyl phosphite according to published procedures²² gave *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$, *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$, and *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{OC}_6\text{H}_5)_3$. The *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}[\text{N}(\text{CH}_3)_2]_3$ was a sample remaining from the original work²³ on this compound. The $\text{CH}_3\text{Re}(\text{CO})_5$ was obtained from $\text{Re}_2(\text{CO})_{10}$ by reaction with sodium amalgam in tetrahydrofuran followed by addition of excess methyl iodide.²⁴ The $\text{CF}_3\text{Mn}(\text{CO})_5$ was obtained by reaction of $\text{NaMn}(\text{CO})_5$ with trifluoroacetic anhydride followed by thermal decarbonylation of the intermediate $\text{CF}_3\text{COMn}(\text{CO})_5$.²⁵ The $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ was obtained from the thermal reaction of $\text{Mo}(\text{CO})_6$ with acetylpentamethylcyclopentadiene.²⁶ The alkyl derivatives of cyclopentadienylmetal carbonyls $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ ²⁷ and $\text{RM}(\text{CO})_3\text{C}_5\text{H}_5$ ($\text{R} = \text{CH}_3$,²⁷ C_2H_5 ,²⁷ $\text{C}_6\text{H}_5\text{CH}_2$,²⁸ $\text{CH}_2=\text{CHCH}_2$,²⁹ and CH_3SCH_2 ,³⁰ $\text{M} = \text{Mo}$; $\text{R} = \text{CH}_3$,²⁷ $\text{M} = \text{W}$) were prepared by the reaction of the corresponding cyclopentadienylmetal carbonyl anion with the corresponding alkyl halide. All of the alkylmetal carbonyls used in this work were identified by comparison of their $\nu(\text{CO})$ frequencies and their melting or decomposition points with those given in the cited literature.

Results

1. Manganese Carbonyl Derivatives. (a) $\text{CH}_3\text{Mn}(\text{CO})_5$. This was the only metal alkyl where both the carbonylation to the corresponding metal acyl and the subsequent hydrogenolysis of this metal acyl to the corresponding aldehyde (i.e., steps 2d–g in the $\text{HCo}(\text{CO})_4$ hydroformylation mechanism) could be observed in the spectracleve.

A solution of $\text{CH}_3\text{Mn}(\text{CO})_5$ in tetradecane ($\nu(\text{CO})$ 2108 w, 2005 vs, 1988 vs, 1975 m, 1946 cm^{-1} vw) was found to react with CO at 320 atm pressure and 67 °C to give $\text{CH}_3\text{COMn}(\text{CO})_5$ identified by its acetyl $\nu(\text{CO})$ band at 1661 cm^{-1} (literature value³¹ 1661 cm^{-1}) (Figure 3). Although the formation of $\text{CH}_3\text{COMn}(\text{CO})_5$ started at 46 °C, the reaction was only complete at 67 °C. Thus keeping the temperature between 46 and 51 °C at 320 atm of CO for more than 30 min did not increase the formation of $\text{CH}_3\text{COMn}(\text{CO})_5$ from $\text{CH}_3\text{Mn}(\text{CO})_5$ to an appreciable extent. However, $\text{CH}_3\text{COMn}(\text{CO})_5$ was found to remain in solution after formation at 67 °C even when the temperature was dropped to

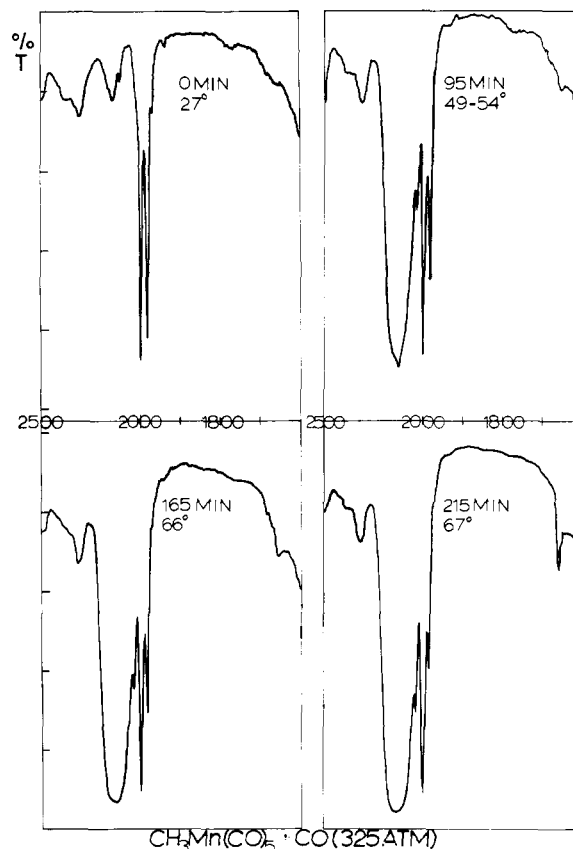
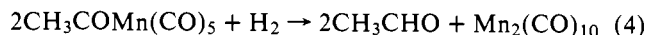


Figure 3. Infrared spectra obtained upon heating $\text{CH}_3\text{Mn}(\text{CO})_5$ under CO pressure.

37 °C at atmospheric pressure in accord with the stability of $\text{CH}_3\text{COMn}(\text{CO})_5$ under ambient conditions.

A solution of $\text{CH}_3\text{COMn}(\text{CO})_5$ formed in the above manner was pressurized with 313 atm of H_2 (Figure 4) after releasing the CO pressure. Upon heating at 95 °C the 1661- cm^{-1} acetyl $\nu(\text{CO})$ band decreased in intensity with the concurrent appearance of a new $\nu(\text{CO})$ band at 1738 cm^{-1} . This 1738- cm^{-1} $\nu(\text{CO})$ frequency was assigned to acetaldehyde by comparison with the reported³² $\nu(\text{CO})$ frequency of 1740 cm^{-1} and by comparison with the infrared spectrum of an authentic sample of acetaldehyde in tetradecane (1738 cm^{-1}). In addition, acetaldehyde was detected in a sample of the reaction solution by vapor phase chromatography. In addition to the formation of the 1738- cm^{-1} $\nu(\text{CO})$ frequency assigned to acetaldehyde a much weaker $\nu(\text{CO})$ frequency appeared at 1700 cm^{-1} which was assigned to formaldehyde (literature $\nu(\text{CO})$ frequencies for formaldehyde³³ 1700–1705 and 1760 cm^{-1}). Observation of the 1760- cm^{-1} band expected for formaldehyde was clearly prevented by overlap with the much stronger 1738- cm^{-1} band assigned to acetaldehyde. When the formation of acetaldehyde from $\text{CH}_3\text{COMn}(\text{CO})_5$ and H_2 was complete the manganese carbonyl derivative present in the solution appeared to be $\text{Mn}_2(\text{CO})_{10}$ rather than $\text{HMn}(\text{CO})_5$ as indicated by $\nu(\text{CO})$ frequencies at 2042 s, 2012 s, and 1981 ms cm^{-1} which correspond to those of an authentic sample of $\text{Mn}_2(\text{CO})_{10}$ in tetradecane. The overall reaction for the hydrogenolysis of $\text{CH}_3\text{COMn}(\text{CO})_5$ can therefore be represented by the following scheme:



The side reaction leading to the apparent formation of formaldehyde is less clear, but the weakness of the $\nu(\text{CO})$ frequencies assignable to formaldehyde suggests that this side reaction is rather unfavorable.

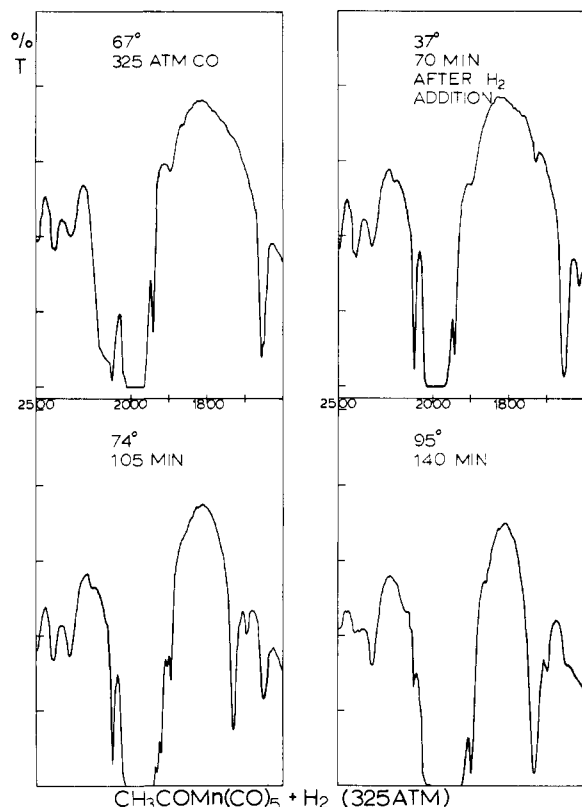


Figure 4. Infrared spectra obtained upon heating $\text{CH}_3\text{COMn}(\text{CO})_5$ under H_2 pressure. The solution used for this experiment is more concentrated than that used for the experiment depicted in Figure 3.

In other experiments the reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ with hydrogen at elevated temperatures and pressures were also investigated. The methyl derivative $\text{CH}_3\text{Mn}(\text{CO})_5$ was found to react with 320 atm of H_2 at 100 °C to form $\text{Mn}_2(\text{CO})_{10}$ as the final product as indicated by $\nu(\text{CO})$ frequencies at 2042 s, 2012 vs, and 1981 cm^{-1} ms. Upon heating above 195 °C and at 320 atm of H_2 the $\text{Mn}_2(\text{CO})_{10}$ began to react further to give $\text{HMn}(\text{CO})_5$ indicated by a new broad band at 2017 cm^{-1} ms (the only reported³⁴ strong $\nu(\text{CO})$ frequency for $\text{HMn}(\text{CO})_5$ occurs at 2017 cm^{-1}). Upon cooling this solution to 30 °C and allowing it to stand in solution overnight this $\text{HMn}(\text{CO})_5$ reverted to $\text{Mn}_2(\text{CO})_{10}$ as indicated by the presence of only the bands at 2042 s, 2012 vs, and 1981 cm^{-1} ms. In another experiment $\text{Mn}_2(\text{CO})_{10}$ was found to react with 300 atm of H_2 at 168–200 °C to form $\text{HMn}(\text{CO})_5$ indicated again by the very strong band at 2017 cm^{-1} .

The thermal stability of $\text{CH}_3\text{Mn}(\text{CO})_5$ in the absence of other reactants was also checked in the spectracleve. Thus heating $\text{CH}_3\text{Mn}(\text{CO})_5$ in the high-pressure cell in the presence of N_2 resulted in no change at 100 °C and in the formation of $\text{Mn}_2(\text{CO})_{10}$ only at temperatures above 158 °C.

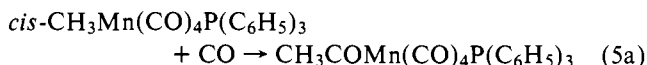
(b) $\text{CF}_3\text{Mn}(\text{CO})_5$. Treatment of $\text{CF}_3\text{Mn}(\text{CO})_5$ in tetradecane solution with 333 atm of CO at temperatures up to 200 °C failed to give any evidence for the formation of the known²⁵ acyl $\text{CF}_3\text{COMn}(\text{CO})_5$. However, under these conditions the $\text{CF}_3\text{Mn}(\text{CO})_5$ thermally decomposed to give $\text{Mn}_2(\text{CO})_{10}$, again identified by its $\nu(\text{CO})$ frequencies.

(c) $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}[\text{N}(\text{CH}_3)_2]_3$. A tetradecane solution of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}[\text{N}(\text{CH}_3)_2]_3$ ($\nu(\text{CO})$ 2048 m, 1998 s, 1974 sh, 1955 vs, 1934 sh, 1928 cm^{-1} s) was found to react with 315 atm of CO at 81 °C to give $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}[\text{N}(\text{CH}_3)_2]_3$ identified by its $\nu(\text{CO})$ frequencies at 2015 w, 2000 vs, 1968 w, and 1659 cm^{-1} m. Release of the CO pressure followed by treatment of this $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}[\text{N}(\text{CH}_3)_2]_3$ with 300 atm of H_2 at 72 °C gave $\text{Mn}_2(\text{CO})_{10}$ identified by its

$\nu(\text{CO})$ frequencies at 2042 s, 2012 vs, and 1981 cm^{-1} ms. The 1600–1750- cm^{-1} region of these spectra was clear indicating no appreciable formation of acetaldehyde or formaldehyde. Also no $\nu(\text{CO})$ frequencies were observed that could be assigned to the known²³ bimetallic complex $\{[(\text{CH}_3)_2\text{N}]_3\text{PMn}(\text{CO})_4\}_2$.

(d) $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$. A tetradecane solution of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ ($\nu(\text{CO})$ 2053 ms, 1979 s, 1963 s, 1941 cm^{-1} m) was subjected to 300 atm of CO in the spectracleve. A reaction started at approximately 50 °C but went to completion only at 95 °C under 300 atm of CO. New $\nu(\text{CO})$ frequencies appeared at 2005 s, 1995 sh, 1989 sh, 1959 w, 1661 m, and 1631 cm^{-1} vw. The bands at 2005 s, 1989 sh, and 1661 cm^{-1} m were assigned to $\text{CH}_3\text{COMn}(\text{CO})_5$. The relatively weak bands at 1995, 1959, and 1631 cm^{-1} were assigned to small amounts of $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ also formed during the reaction.

Upon cooling the solution to 24 °C the intensities of the 1995- and 1959- cm^{-1} bands were found to increase during a 15-h period while held under 1 atm of CO. These observations can be explained by the following sequence:



Reaction 5b slowly reverses upon standing at room temperature after releasing the CO pressure.

The mixture of $\text{CH}_3\text{COMn}(\text{CO})_5$ and $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ obtained by carbonylation of $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ as described above reacted with 313 atm of H_2 at 65 °C to give a mixture of $\text{Mn}_2(\text{CO})_{10}$ and $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$. Upon further heating to 75–81 °C two new bands appeared at 2085 and 1993 cm^{-1} but these bands disappeared upon heating to 159 °C. Further heating up to 186 °C still under 313 atm of H_2 did not affect the $\nu(\text{CO})$ frequencies assigned to $\text{Mn}_2(\text{CO})_{10}$ and $\text{CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ but led to the gradual growth of a strong 1954- cm^{-1} band. This band is assigned to $[(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4]_2$ (literature³⁵ $\nu(\text{CO})$ frequencies in CHCl_3 at 1980 w and 1956 cm^{-1} vs). The expected 1980 cm^{-1} w band from $[(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4]_2$ would be obscured by the stronger 1981 cm^{-1} s band from the $\text{Mn}_2(\text{CO})_{10}$ present in the solution. This $[(\text{C}_6\text{H}_5)_3\text{PMn}(\text{CO})_4]_2$ might be formed by reaction of $\text{Mn}_2(\text{CO})_{10}$ with some of the triphenylphosphine present in the solution from the earlier reaction of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ with carbon monoxide.

At no time during the reaction of the $\text{CH}_3\text{COMn}(\text{CO})_5$ / $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ mixture with H_2 was any evidence obtained for the formation of acetaldehyde or formaldehyde. Presumably the excess triphenylphosphine present in the solution inhibited the hydrogenolysis of $\text{CH}_3\text{COMn}(\text{CO})_5$ to give acetaldehyde.

(e) $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{OC}_6\text{H}_5)_3$. A solution of $\text{cis-CH}_3\text{Mn}(\text{CO})_4\text{P}(\text{OC}_6\text{H}_5)_3$ in tetradecane was heated slowly under 310 atm of CO. At 99 °C evidence for the formation of $\text{CH}_3\text{COMn}(\text{CO})_5$ was obtained as indicated by the appearance of $\nu(\text{CO})$ frequencies at 2045 m, 2005 s, 1989 ms, and 1661 cm^{-1} m as compared with the $\nu(\text{CO})$ frequencies of 2108 w, 2045 m, 2005 s, 1989 ms, and 1661 cm^{-1} m observed for authentic $\text{CH}_3\text{COMn}(\text{CO})_5$ generated from $\text{CH}_3\text{Mn}(\text{CO})_5$ and CO in tetradecane as described above. (The expected band at 2108 cm^{-1} for $\text{CH}_3\text{COMn}(\text{CO})_5$ was masked by the strong band due to free CO.) Some $\nu(\text{CO})$ frequencies at 2066 w, 1995 m, 1969 ms, and 1590 cm^{-1} w were also observed indicative of the formation of relatively small amounts of $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{OC}_6\text{H}_5)_3$. Upon heating this solution under 313 atm of CO above 160 °C the formation of

$\text{Mn}_2(\text{CO})_{10}$ occurred as indicated by infrared $\nu(\text{CO})$ frequencies at 2042 vs, 2012 s, and 1981 cm^{-1} vs. In addition a strong band at 1596 cm^{-1} was observed of unknown origin. However, the persistence of this 1596- cm^{-1} band upon treatment with 320 atm of H_2 at temperatures up to 198 °C under conditions where even a relatively unreactive acylmetal derivative would be expected to form the corresponding aldehyde suggests that this 1596- cm^{-1} band does not arise from an acylmetal derivative but possibly from the phenyl groups in triphenyl phosphite.

2. The Rhenium Carbonyl Derivative $\text{CH}_3\text{Re}(\text{CO})_5$. A tetradecane solution of $\text{CH}_3\text{Re}(\text{CO})_5$ ($\nu(\text{CO})$ 2128 vs, 2043 m, 2013 vs, 1982 cm^{-1} s) was heated slowly under 320 atm of CO. No change in the infrared $\nu(\text{CO})$ frequencies occurred up to 140 °C. However, upon further heating to 200 °C the $\text{CH}_3\text{Re}(\text{CO})_5$ was partially converted to $\text{Re}_2(\text{CO})_{10}$ as indicated by the appearance of new $\nu(\text{CO})$ frequencies at 2068 s, 2012 vs, 1975 vs, 1957 m, and 1939 cm^{-1} m similar to the $\nu(\text{CO})$ frequencies observed in the infrared spectrum of a tetradecane solution of authentic $\text{Re}_2(\text{CO})_{10}$. Even at 200 °C and 320 atm of CO about half of the $\text{CH}_3\text{Re}(\text{CO})_5$ remained unchanged indicating the stability under CO pressure of this rhenium derivative as compared to the corresponding manganese derivative $\text{CH}_3\text{Mn}(\text{CO})_5$ discussed above.

The failure of $\text{CH}_3\text{Re}(\text{CO})_5$ to form $\text{CH}_3\text{COPe}(\text{CO})_5$ by treatment with CO under pressure at elevated temperatures is not a consequence of the instability of $\text{CH}_3\text{COPe}(\text{CO})_5$, which has been prepared²⁴ as a stable compound by the reaction of $\text{NaRe}(\text{CO})_5$ with acetyl chloride.

3. The Cyclopentadienyliron Carbonyl Derivative $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ (Figure 5). A tetradecane solution of $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ ($\nu(\text{CO})$ 1998 vs, 1952 cm^{-1} vs) reacted with 325 atm of CO at 97 °C to form $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ ($\nu(\text{CO})$ 2009 s, 1961 s, 1667 cm^{-1} m) identified by comparison of the $\nu(\text{CO})$ frequencies with those of authentic $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ prepared³⁶ according to the published method. The formation of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ is relatively easy and begins even at 26 °C. However, the reaction is slow at this temperature and goes to completion at 97 °C.

During this reaction rather large amounts of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ were also formed at 97 °C and 325 atm of CO. The presence of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ was confirmed by comparing the spectrum with that of an authentic sample taken in tetradecane ($\nu(\text{CO})$ 2001 s, 1958 vs, 1790 cm^{-1} ms). Furthermore, crystals of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, mp 192–193 °C (lit.³⁷ mp 194 °C dec), were obtained from the solution in the high-pressure infrared cell.

Treatment of a tetradecane solution of $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ with 313 atm of H_2 at 155 °C resulted in removal of the acetyl group to give $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ identified by its $\nu(\text{CO})$ frequencies at 2001 s, 1958 vs, and 1790 cm^{-1} ms. No infrared bands were observed in the range 1600–1780 cm^{-1} indicating the absence of acetaldehyde. Cooling the solution to 31 °C while maintaining the H_2 pressure gave in addition to the above bands from $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ additional $\nu(\text{CO})$ frequencies at 1998 vs and 1952 cm^{-1} sh which can be assigned to $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$.

4. Cyclopentadienylmolybdenum Carbonyl Derivatives. (a) $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$. A rather concentrated solution of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ in tetradecane ($\nu(\text{CO})$ 2020 s, 1937 cm^{-1} vs) was heated under 316 atm of CO. No change was observed up to 52 °C. At 55 °C a shoulder appeared at 1985 cm^{-1} which developed into a stronger band upon further heating to 153 °C along with the disappearance of the 2020- and 1937- cm^{-1} $\nu(\text{CO})$ frequencies of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$. The bands at 1985 vs and 1954 cm^{-1} vw were the only $\nu(\text{CO})$ frequencies which appeared during this reaction and can be assigned to $\text{Mo}(\text{CO})_6$ formed by cleavage of the cyclopentadienyl ring and methyl groups from $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ with the CO under pressure.

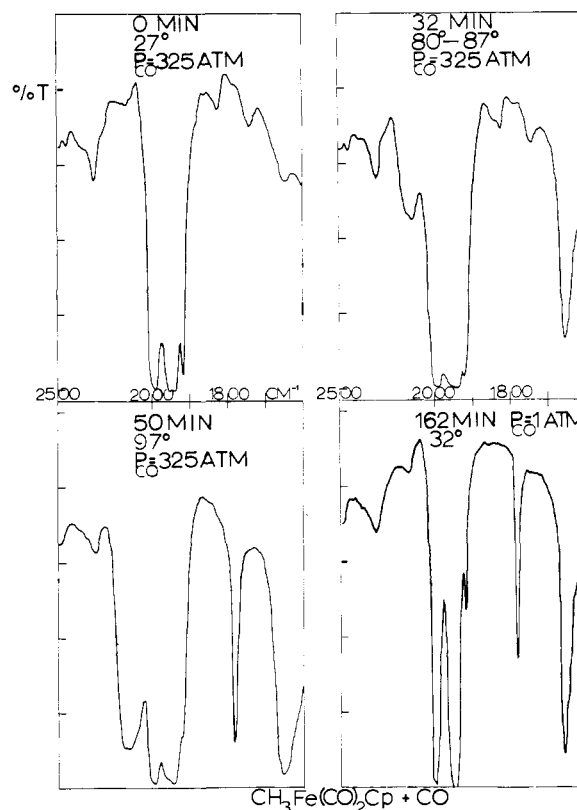


Figure 5. Infrared spectra obtained upon heating $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ under CO pressure.

This reaction was irreversible as indicated by no change in the infrared $\nu(\text{CO})$ frequencies after cooling the solution from 153 °C to room temperature. No evidence for the formation of the bimetallic complex $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ was observed at any time during this reaction of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ with CO.

(b) $\text{C}_2\text{H}_5\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$. A tetradecane solution of $\text{C}_2\text{H}_5\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ ($\nu(\text{CO})$ 2005 vs, 1928 cm^{-1} s) reacted with 300 atm of CO at 82 °C to form $\text{Mo}(\text{CO})_6$. No indications for the formation of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ were obtained.

(c) $\text{C}_6\text{H}_5\text{CH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ (Figure 6). A tetradecane solution of $\text{C}_6\text{H}_5\text{CH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ ($\nu(\text{CO})$ 2010 s, 1929 cm^{-1} vs) reacted with 320 atm of CO at 100 °C to form $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ ($\nu(\text{CO})$ 1961 vs, 1917 s, 1910 cm^{-1} sh) and $\text{Mo}(\text{CO})_6$ ($\nu(\text{CO})$ 1985 cm^{-1} vs). Upon keeping the solution at 175 °C for 15 min under the CO pressure the bands at 1961, 1917, and 1910 cm^{-1} disappeared and the 1985- cm^{-1} band became stronger indicating total conversion of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ to $\text{Mo}(\text{CO})_6$.

(d) $\text{CH}_2=\text{CHCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ (Figure 7). Reaction of $\text{CH}_2=\text{CHCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ ($\nu(\text{CO})$ 2015 s, 1930 cm^{-1} vs) with 300 atm of CO in tetradecane solution at 31 °C for 8 h led to the gradual formation of $\text{Mo}(\text{CO})_6$ as indicated by gradual appearance of a weak band at 1985 cm^{-1} . No evidence for the formation of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ was observed in this room temperature experiment possibly because of the insolubility of $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ in tetradecane at room temperature.

Heating a tetradecane solution of $\text{CH}_2=\text{CHCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ to 60 °C under 313 atm of CO resulted in the development not only of the 1985- cm^{-1} band of $\text{Mo}(\text{CO})_6$ but also of a pair of bands at 1961 and 1881 cm^{-1} which can be assigned to one of the stereoisomers³⁸ of the trihapto allyl derivative $(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_2\text{C}_5\text{H}_5$. Upon raising the temperature to 91 °C bands were observed at 1985 s, 1961 w, 1917 w, 1896 w, and 1881 cm^{-1} w. Further heating to 120 °C led to the further development of $\nu(\text{CO})$ frequencies at 1985, 1961,

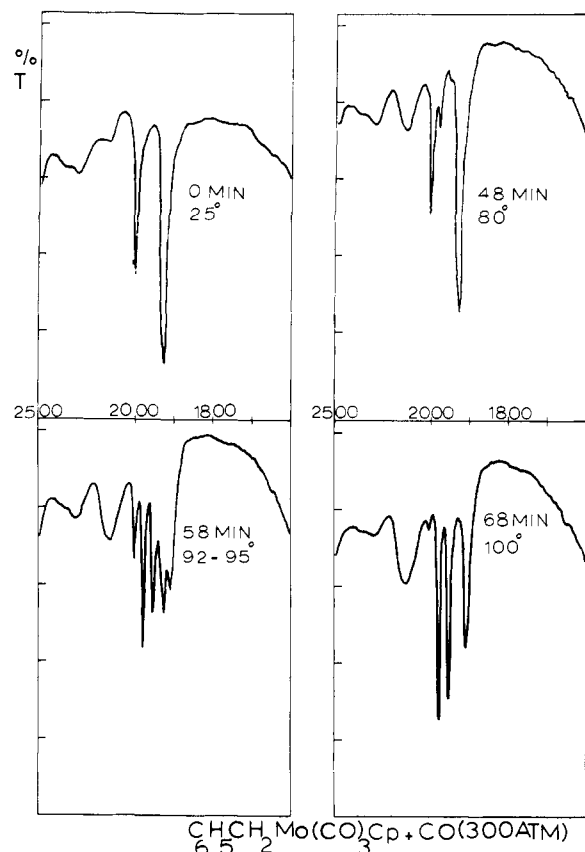


Figure 6. Infrared spectra obtained upon heating $C_6H_5CH_2Mo(CO)_3C_5H_5$ under CO pressure.

1956, 1917, 1911, 1896, and 1881 cm^{-1} but weak $\nu(CO)$ frequencies at 2015 and 1930 cm^{-1} from the original $CH_2=CHCH_2Mo(CO)_3C_5H_5$ starting material were still present. However, at 159°C and 300 atm of CO the $CH_2=CHCH_2Mo(CO)_3C_5H_5$ had reacted completely to give $Mo(CO)_6$ (1985 cm^{-1} vs), $[C_5H_5Mo(CO)_3]_2$ (1961 vs, 1917 s, 1911 cm^{-1} w sh), and both stereoisomers of $C_3H_5Mo(CO)_2C_5H_5$ (1964 sh, 1956 s, 1896 s, 1881 cm^{-1} s). Cooling this solution to room temperature under CO pressure resulted in no significant changes in any of the $\nu(CO)$ frequencies except for decreases in the intensities of the $\nu(CO)$ frequencies assigned to $[C_5H_5Mo(CO)_3]_2$ owing to the limited solubility of this compound in tetradecane at room temperature.

(e) $CH_3SCH_2Mo(CO)_3C_5H_5$. A fairly concentrated tetradecane solution of $CH_3SCH_2Mo(CO)_3C_5H_5$ was heated under 300 atm of CO. At 50°C new $\nu(CO)$ frequencies appeared at 1942 and 1858 cm^{-1} which can be assigned to the dicarbonyl³⁰ $CH_3SCH_2Mo(CO)_2C_5H_5$. Upon further heating to 106°C these $\nu(CO)$ bands became rather strong. Still further heating to 146°C resulted in apparent decomposition of $CH_3SCH_2Mo(CO)_2C_5H_5$ to give $Mo(CO)_6$, identified by its characteristic strong $\nu(CO)$ frequency at 1985 cm^{-1} . At this point further heating was discontinued. Cooling the resulting solution to room temperature under CO pressure resulted in reappearance of the bands assigned to $CH_3SCH_2Mo(CO)_2C_5H_5$. It thus appears that CO at high pressures does not prevent the reported³⁰ thermal decarbonylation of $CH_3SCH_2Mo(CO)_3C_5H_5$ to $CH_3SCH_2Mo(CO)_2C_5H_5$.

5. Pentamethylcyclopentadienylmolybdenum Carbonyl Derivatives. The reactions of cyclopentadienylmolybdenum carbonyl derivatives with carbon monoxide at elevated pressures and temperatures discussed above ultimately result in cleavage of the metal-cyclopentadienyl bond to form $Mo(CO)_6$. In order to obtain a better idea of the fate of the cyclopentadienyl rings some experiments were done with

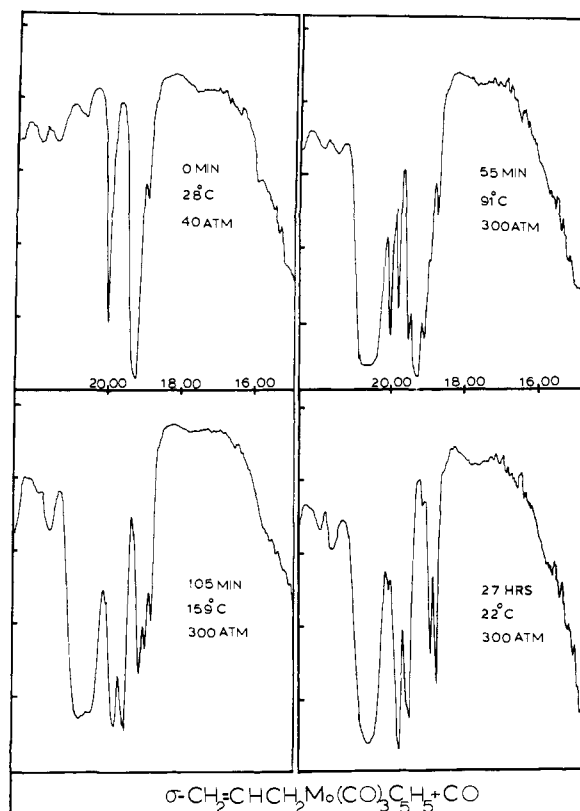
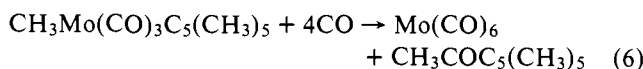


Figure 7. Infrared spectra obtained upon heating $CH_2=CHCH_2Mo(CO)_3C_5H_5$ under CO pressure.

$CH_3Mo(CO)_3C_5(CH_3)_5$ hoping that the liberated permethylated cyclopentadienyl ring would form a more stable and therefore isolable or detectable product.

A solution of $CH_3Mo(CO)_3C_5(CH_3)_5$ in tetradecane was heated under 300 atm of CO (Figure 8). The 1985-cm^{-1} band indicating the formation of $Mo(CO)_6$ began to appear at 82°C . At 110°C a new band at 1704 cm^{-1} also began to appear. At 137°C the 1704-cm^{-1} band became fairly strong and stopped growing further. Upon cooling the solution the 1704-cm^{-1} band persisted. The CO was then vented from the system and 320 atm of H_2 added. Heating to 212°C failed to affect the 1704-cm^{-1} band. The relative intensity of the 1704-cm^{-1} band seemed to be independent of the only $\nu(CO)$ frequency at 1985 cm^{-1} assigned to $Mo(CO)_6$. Vapor phase chromatography of the solution obtained from the infrared cell after the conclusion of this experiment indicated the presence of acetylpentamethylcyclopentadiene.³⁹ Furthermore, an authentic sample of acetylpentamethylcyclopentadiene³⁹ exhibited a $\nu(CO)$ frequency at 1704 cm^{-1} in tetradecane solution.

These observations indicate that $CH_3Mo(CO)_3C_5(CH_3)_5$ reacts with CO under pressure according to the following equation:



Equation 6 is exactly the reverse of the reaction for the preparation of $CH_3Mo(CO)_3C_5(CH_3)_5$ by heating $Mo(CO)_6$ with acetylpentamethylcyclopentadiene.²⁶

6. The Cyclopentadienyltungsten Carbonyl Derivative $CH_3W(CO)_3C_5H_5$. A tetradecane solution of $CH_3W(CO)_3C_5H_5$ was heated under 316 atm of CO pressure. No change in the infrared spectrum was observed upon heating to 143°C and even after standing for 4 h at this temperature. At 157°C a new infrared band began to appear at 1980 cm^{-1} . At the same time the intensities of the bands at 2015 and 1928 cm^{-1}

arising from $\text{CH}_3\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ began to decrease. However, under 316 atm of CO the reaction was complete only at 210 °C when the infrared bands from $\text{CH}_3\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ completely disappeared with the formation of a strong 1980-cm^{-1} $\nu(\text{CO})$ frequency assigned to $\text{W}(\text{CO})_6$ by comparison with the infrared spectrum of an authentic sample in tetradecane solution.

Discussion

For a transition metal alkyl to be an effective intermediate in the metal-catalyzed hydroformylation of olefins it must be capable of undergoing the following two reactions in sequence:



In reactions 7a and 7b the designation [M] is taken to represent the transition metal with all associated carbonyl, cyclopentadienyl, and/or trivalent phosphorus ligands. Reactions 7a (corresponding to reaction 2d and 2e in the $\text{HCo}(\text{CO})_4$ hydroformylation scheme above) and 7b (corresponding to reactions 2f and 2g in the $\text{HCo}(\text{CO})_4$ hydroformylation scheme above) can only be part of a catalytic sequence similar to 2a–h above if the R group contains a β -hydrogen atom thereby allowing the metal alkyl to be generated from the metal hydride [M]H and an olefin. In this work the more readily available and handled methyl-transition metal derivatives were frequently used as models for the reactivities of the corresponding transition metal derivatives containing alkyl groups with β -hydrogen atoms.

In this work the only metal alkyl found to undergo both reactions 7a and 7b is $\text{CH}_3\text{Mn}(\text{CO})_5$. The iron alkyl $\text{CH}_3\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5$ undergoes carbonylation (reaction 7a) to give $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ but attempts to hydrogenolyze $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ to give CH_3CHO instead lead only to the formation of $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$. The phosphine-substituted derivatives *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4\text{PR}_3$ (R = C_6H_5 , OC_6H_5 , and $\text{N}(\text{CH}_3)_2$) appear to form the corresponding acetyls $\text{CH}_3\text{COMn}(\text{CO})_4\text{PR}_3$ with CO but only under conditions where the CO also displaces the trivalent phosphorus ligand to form large amounts of $\text{CH}_3\text{COMn}(\text{CO})_5$. Hydrogenolysis of these mixtures of $\text{CH}_3\text{COMn}(\text{CO})_5$, $\text{CH}_3\text{COMn}(\text{CO})_4\text{PR}_3$, and free R_3P do not give any acetaldehyde. No evidence was obtained for the carbonylation of the alkyls $\text{CH}_3\text{Re}(\text{CO})_5$ and $\text{RM}(\text{CO})_3\text{C}_5\text{R}'_5$ (M = Mo, R' = H and CH_3 ; M = W, R' = H) to the corresponding acyls $\text{CH}_3\text{CORe}(\text{CO})_5$ and $\text{RCOM}(\text{CO})_3\text{C}_5\text{R}'_5$ under any accessible conditions. Under forcing conditions these alkyls instead form $\text{Re}_2(\text{CO})_{10}$ and $\text{M}(\text{CO})_6$, respectively.

A reasonable hypothesis to account for these observations and consistent with present mechanistic understanding that the carbonylation step 7a (which really involves alkyl migration⁴⁰) requires the metal-alkyl bond to be labile relative to the bonds between the metal and the other ligands. Furthermore, the hydrogenolysis step 7b requires relatively labile metal-carbonyl bonds to allow the required loss of one CO group before H_2 oxidative addition (e.g., steps 2e and 2f in the $\text{HCo}(\text{CO})_4$ -catalyzed hydroformylation mechanism). Thus the failure of $\text{CH}_3\text{Re}(\text{CO})_5$ to undergo carbonylation to $\text{CH}_3\text{CORe}(\text{CO})_5$ under conditions far more vigorous than those required to convert $\text{CH}_3\text{Mn}(\text{CO})_5$ to $\text{CH}_3\text{COMn}(\text{CO})_5$ can be attributed to the much greater stability of metal-alkyl σ bonds involving 5d transition metals in comparison to corresponding metal-alkyl σ bonds involving 3d transition metals as indicated, for example, in the much greater stability of $\text{CH}_3\text{W}(\text{CO})_3\text{C}_5\text{H}_5$ relative to $\text{CH}_3\text{Cr}(\text{CO})_3\text{C}_5\text{H}_5$. Similarly, the failure of $\text{CH}_3\text{COMn}(\text{CO})_4\text{PR}_3$ (R = C_6H_5 , OC_6H_5 , and $\text{N}(\text{CH}_3)_2$) and $\text{CH}_3\text{COFe}(\text{CO})_2\text{C}_5\text{H}_5$ to undergo hydroge-

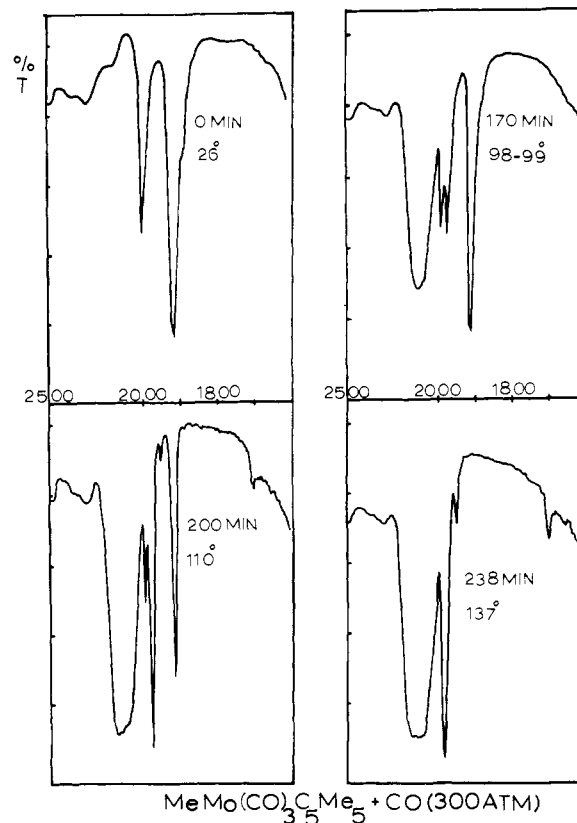
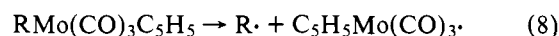


Figure 8. Infrared spectra obtained upon heating $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ under CO pressure.

nolysis to CH_3CHO under conditions where $\text{CH}_3\text{COMn}(\text{CO})_5$ forms CH_3CHO can be attributed to the stabilization of the remaining metal-carbonyl bonds when one or more carbonyl groups are replaced by the weaker π acceptor trivalent phosphorus or η^5 -cyclopentadienyl ligands.⁴¹

Several specific aspects of the carbonylation of the alkyls $\text{RMO}(\text{CO})_3\text{C}_5\text{R}'_5$ are of interest. For example, the alkyls $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$, and $\text{C}_2\text{H}_5\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ react with CO to form directly $\text{Mo}(\text{CO})_6$ without any evidence for the formation of intermediate $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ whereas the alkyls $\text{CH}_2=\text{CHCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, $\text{C}_6\text{H}_5\text{CH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$, and $\text{CH}_3\text{SCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ form $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$ as an intermediate in their reactions with CO. This appears to be a consequence of the ease of homolytic cleavage of the $\text{RMO}(\text{CO})_3\text{C}_5\text{H}_5$ alkyls according to



The liberated $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\cdot$ radicals can easily dimerize to form $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$. The ease of reaction 8 is much greater for the alkyls $\text{CH}_2=\text{CHCH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ where the corresponding R· radicals are resonance stabilized⁴² than for the alkyls $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ and $\text{C}_2\text{H}_5\text{Mo}(\text{CO})_3\text{C}_5\text{H}_5$ where the corresponding R· radicals methyl and ethyl, respectively, are not resonance stabilized. In the exhaustive carbonylation of $\text{RM}(\text{CO})_3\text{C}_5\text{R}'_5$ to $\text{M}(\text{CO})_6$ there is some evidence that the R group couples with the five-membered ring before its removal since in the carbonylation of $\text{CH}_3\text{Mo}(\text{CO})_3\text{C}_5(\text{CH}_3)_5$ to $\text{Mo}(\text{CO})_6$ the five-membered ring is converted to acetylpentamethylcyclopentadiene. A stable product analogous to acetylpentamethylcyclopentadiene is not possible from the carbonylation of the derivatives $\text{RM}(\text{CO})_3\text{C}_5\text{H}_5$ containing unsubstituted cyclopentadienyl rings because of the possibility of enolization involving one of the ring hydrogens.

The hydrogenolysis of $\text{CH}_3\text{COMn}(\text{CO})_5$ was studied in some detail, since this was the only example of the hydrogenolysis of a metal-acyl to the corresponding aldehyde found in this work. In apparent contradiction to eq 7b is the concurrent formation of $\text{Mn}_2(\text{CO})_{10}$ rather than $\text{HMn}(\text{CO})_5$ with the hydrogenolysis of the metal-acyl bond to acetaldehyde. However, a sequence of reactions for manganese carbonyl catalyzed hydroformylation analogous to eq 2a-h would produce the coordinatively unsaturated intermediate $\text{HMn}(\text{CO})_4$ rather than the coordinatively saturated $\text{HMn}(\text{CO})_5$ in the hydrogenolysis step corresponding to 2g. The greater ease of dimerization of an $\text{HMn}(\text{CO})_4$ unit as compared with co addition to form $\text{HMn}(\text{CO})_5$ is sufficient to account for the formation of $\text{Mn}_2(\text{CO})_{10}$ rather than $\text{HMn}(\text{CO})_5$ from the hydrogenolysis of $\text{CH}_3\text{COMn}(\text{CO})_5$. Facile dimerization of an $\text{HMn}(\text{CO})_4$ unit is not unreasonable since the resulting dimer $\text{H}_2\text{Mn}_2(\text{CO})_8$ would be isoelectronic with the known⁴³ anion $[\text{H}_2\text{W}_2(\text{CO})_8]^{2-}$. Furthermore, carbonylation of the coordinatively unsaturated $\text{H}_2\text{Mn}_2(\text{CO})_8$ to $\text{Mn}_2(\text{CO})_{10}$ with H_2 evolution is also likely to be a facile process. The formation of $\text{Mn}_2(\text{CO})_{10}$ rather than $\text{HMn}(\text{CO})_5$ from the hydrogenolysis of $\text{CH}_3\text{COMn}(\text{CO})_5$ at 313 atm and 95 °C suggests difficulty in obtaining a catalytic cycle for olefin hydroformylation based on manganese carbonyl derivatives without the use of considerably more vigorous conditions (e.g., 195 °C and 320 atm) where $\text{Mn}_2(\text{CO})_{10}$ reacts with H_2 to form $\text{HMn}(\text{CO})_5$.

Summary

This work indicates several difficulties in searching for new alkylmetal systems capable of catalyzing the hydroformylation of olefins. Thus the presence of weak π -acceptor ligands such as tertiary phosphines and η^5 -cyclopentadienyl leading to strong metal-carbonyl bonds, the presence of ligands displaced by CO under the reaction conditions, and/or the use of metals, particularly 5d transition metals, forming particularly strong metal-alkyl bonds can lead to systems incapable of undergoing all of the reactions required for the hydroformylation catalytic cycle. Even in the case of the manganese carbonyl system, the only system studied in this work found to undergo both the required carbonylation and hydrogenolysis steps, the hydrogenolysis step gives a transition metal derivative (e.g., $\text{Mn}_2(\text{CO})_{10}$ rather than $\text{HMn}(\text{CO})_5$) which creates some difficulties in generating a complete catalytic cycle.

This work also suggests reasons for the high activity of rhodium derivatives as hydroformylation catalysts.⁴⁴ Rhodium, as a 4d transition metal, would be expected to form weaker chemical bonds with carbon ligands such as alkyl groups and carbon monoxide (e.g., the comparative chemistry of the metal hexacarbonyls⁴⁵ $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{and W}$)) than corresponding 3d and 5d transition metals. Thus rhodium alkyls should undergo insertion reactions more readily than corresponding cobalt and iridium alkyls. Furthermore, the stabilities of both 16-electron rhodium(I) intermediates and 18-electron rhodium(III) intermediates make it relatively easy to form all of the catalytic intermediates required for a cycle analogous to reactions 2a-h.

Finally, this work illustrates the value of modern techniques

for measuring infrared spectra at high carbon monoxide pressures in the study of intermediates in catalytic reactions of carbon monoxide. We are in the process of extending our work with the equipment described in this paper to the study of other important catalytic reactions of carbon monoxide including the water gas shift and Fischer-Tropsch reactions.

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References and Notes

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