

ON THE MECHANISM OF SUBSTITUTION OF HYDRIDOPENTACARBONYLMANGANESE(I)

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(Received July 13th, 1976)

Summary

The reaction of $\text{HMn}(\text{CO})_5$ with tributylphosphine, triphenylphosphine, triphenylarsine or CO has been studied in hexane solution. Difficulties in obtaining reproducible kinetics data were encountered due to contributions from a radical chain pathway caused by trace radical impurities. However, the substitution reactions appear to obey a rate law first order each in $\text{HMn}(\text{CO})_5$ and ligand. The reactivities of the ligands toward $\text{HMn}(\text{CO})_5$ vary in the order $\text{PBU}_3 > \text{PPh}_3 > \text{AsPh}_3 \sim \text{CO}$. Incorporation of ^{13}C into $\text{HMn}(\text{CO})_5$ via exchange was followed using changes in IR bands. The results of both substitution and exchange are consistent with the hydride migration mechanism, involving intermediate formation of a formyl species which undergoes rapid decarbonylation.

Introduction

The transition metal carbonyl hydrides occupy an important place in organometallic chemistry. Hydride species have been implicated as intermediates in many reactions in which transition metal carbonyl compounds act as catalysts [1–7]. Although the physical properties of some of the carbonyl hydrides have been thoroughly studied [7–11], there has been a surprising lack of mechanistic and kinetics work. Heck has studied the substitution of $\text{HCo}(\text{CO})_4$ [12]. The exchange of ^{14}C with $\text{HMn}(\text{CO})_5$ and with $\text{HFe}(\text{CO})_5^+$ was studied by Basolo and coworkers [13]. More recently exchange of ^{13}C with $\text{HMn}(\text{CO})_5$ [14] and $\text{HFe}(\text{CO})_5^+$ [15] has been observed. We recently reported studies of the substitution reactions of $\text{HRe}(\text{CO})_5$ [16]. Substitution of $\eta\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$ by phosphine has been studied by Green and coworkers [17].

Substitution at a metal carbonyl hydride might occur by (a) a CO dissociation pathway, (b) an associative displacement pathway, (c) a hydride migration, and (d) some other pathway such as a radical chain process. Whatever the pathway the general impression is that the carbonyl hydrides are quite labile toward sub-

stitution. Thus, for example, Heck found the substitution of $\text{HCo}(\text{CO})_4$ too rapid for convenient study, even at low temperatures [12]. The more recent ^{13}C exchange studies with $\text{HMn}(\text{CO})_5$ and $\text{HFe}(\text{CO})_5^+$ show that, while the exchange is slower than previously estimated, it is nevertheless rapid as compared with other substituted carbonyl compounds such as the carbonyl halides [18–20]. In rather striking contrast, $\text{HRe}(\text{CO})_5$ shows no observable tendency to undergo substitution other than by a radical chain process [16].

As pointed out sometime ago by Basolo and Pearson [21], the apparently anomalous lability of some carbonyl hydrides might be accounted for in terms of a hydride migration mechanism. This is a particularly attractive possibility in the case of $\text{HMn}(\text{CO})_5$, since the methyl migration pathway in the substitution reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ has been established [22]. However, although stable formyl species have been prepared [23,24], there is at present no well established example of hydride migration in a simple substitution process occurring in a metal carbonyl hydride. In an effort to define more precisely the nature of its substitution reactions, we have studied the reactions of $\text{HMn}(\text{CO})_5$ with various nucleophiles, including triphenylphosphine (PPh_3), triphenylarsine (AsPh_3), tributylphosphine (PBu_3) and ^{13}C O.

Results and discussion

Reaction of $\text{HMn}(\text{CO})_5$ with nucleophiles leads to substitution of CO and formation of *cis*- $\text{HMn}(\text{CO})_4\text{L}$ [25–27]. Continued exposure to the more nucleophilic ligands such as PBu_3 leads, at a slower rate, to disubstitution. Because $\text{HMn}(\text{CO})_5$ is quite air sensitive, it is necessary to carry out all reactions under an inert atmosphere, and in thoroughly degassed solvents. Using the apparatus shown in Fig. 1 it is possible to carry out the reactions under an inert atmosphere with intermittent withdraw of samples for IR analysis. Because the infrared cell chamber and the reaction vessel were thermostated to the same temperature, it was possible to observe the progress of reaction by maintaining the reaction solution in the infrared cell with continuous monitoring, or by intermittent withdrawal of samples from the reaction vessel for infrared cell analysis. However it became obvious that these two methods of obtaining data did not yield the same results. For solutions of the same concentration, maintained at the same temperature, reaction was invariably faster in those maintained in the infrared cell as compared with those contained in the upper reaction chamber. An example of this IR cell catalysis effect is shown in Fig. 2. By blocking the IR beam except for short periods of absorption measurements, it was determined that the faster reaction was not due to irradiation from the source. Furthermore, even after exercising the greatest care, we were not able to obtain highly reproducible kinetics results. The behavior of $\text{HMn}(\text{CO})_5$ in substitution reactions is in many respects similar to that of $\text{HRe}(\text{CO})_5$ [16]. It seems likely that substitution in $\text{HMn}(\text{CO})_5$ occurs via an efficient radical chain process when there is even a trace concentration of initiating radicals present. Solutions of $\text{HMn}(\text{CO})_5$ are likely to be more susceptible to substitution via a radical chain pathway than $\text{HRe}(\text{CO})_5$, since $\text{HRe}(\text{CO})_5$ in solution is stable to O_2 , and traces of O_2 retard the radical chain process. In solutions of $\text{HMn}(\text{CO})_5$, on the other hand any traces of O_2 are scavenged by reaction with the hydride, so that this source of inhibition of the

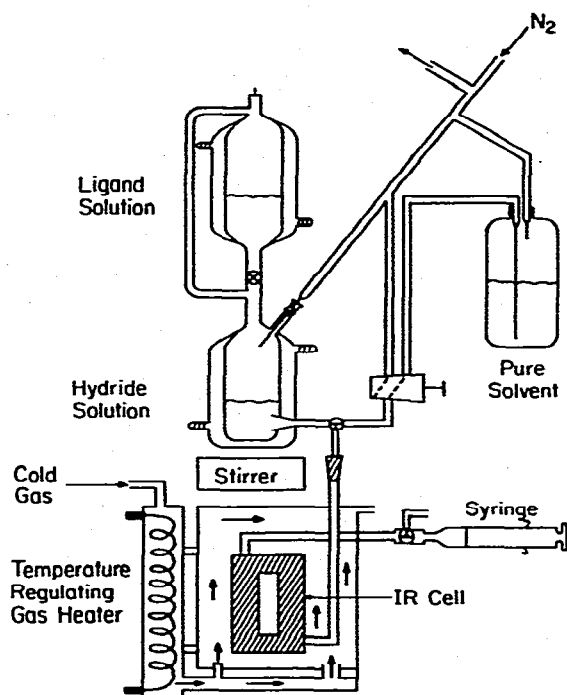


Fig. 1. Apparatus for study of substitution reactions.

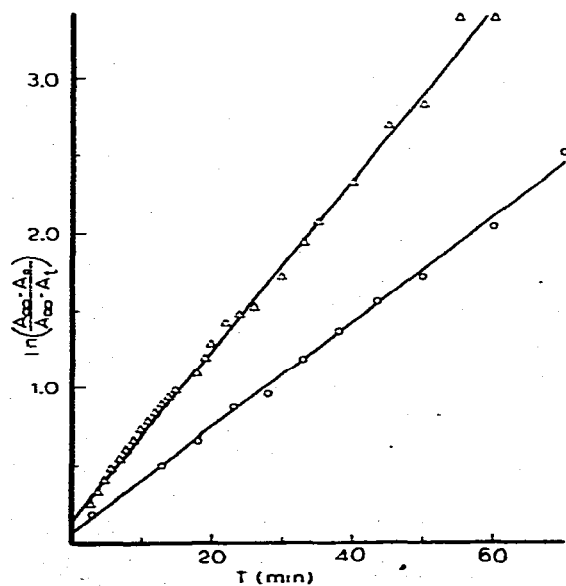


Fig. 2. Example of first-order plots of absorbance changes with time for $HMn(CO)_5$ reaction with PPh_3 in hexane. The upper line corresponds to data for a solution maintained in the IR cell; the lower line to data for a solution maintained in the glass reaction vessel during reaction.

radical chain process is virtually absent. In what follows we describe the results of experiments in which every possible attempt was made to avoid a contribution from a radical chain process. Reactions were maintained in the upper glass reaction vessel; samples were withdrawn under isothermal conditions for infrared sample analysis immediately prior to acquisition of the data.

In the presence of excess PPh_3 , the rate law for reaction is nearly pseudo-first-order. Frequently the graphs of $\ln[A_\infty - A_0]/(A_\infty - A_t)$ vs. time showed a linear segment of higher slope in the early stages of the reaction, suggesting a higher pseudo-first-order rate constant during the first portion of the reaction. We have accepted only those data for reaction solutions in which the nonlinearity is absent, or in which the initial linear portion persists through at least two half lives.

In hexane solutions containing $2 \times 10^{-3} M$ $\text{HMn}(\text{CO})_5$, and with varying PPh_3 concentration, the pseudo-first-order rate constant for reaction to yield the *cis*-monosubstituted hydride was found to increase linearly with phosphine concentration. The rate data for a typical series of experiments is shown in Table 1. The second order rate constant derived from the slope of a graph of k_1 vs. $[\text{PPh}_3]$ is $0.047 M^{-1} \text{sec}^{-1}$. Although the variation of k_1 with ligand concentration is reasonably linear in any given series of experiments, the observed second-order rate constants were found to vary from one run to another. The second series of rate constants shown in Table 1, involving a test of reproducibility with fixed PPh_3 concentration, yielded the lowest second-order rate constant we observed, $0.014 \pm 0.005 M^{-1} \text{sec}^{-1}$. We take this as our best estimate. The rate of substitution by AsPh_3 at 28°C was also found to vary with ligand concentration. In this case also nonlinearity in the kinetics plots was usually observed, and it was not possible to obtain a very good value for the bimolecular rate constant. From the data in Table 1 we estimate a value on an order of $3 \times 10^{-4} M^{-1} \text{sec}^{-1}$ at 28°C . Reaction of $1 \times 10^{-3} M$ solution of $\text{HMn}(\text{CO})_5$ with PBu_3 at $10^{-2} M$ proceeded rapidly at 25°C ; reaction to give a *cis*-monosubstituted product was complete after about 5 min. These results taken together, though lacking in quantitative

TABLE 1
RATE CONSTANTS FOR SUBSTITUTION OF CO IN $\text{HMn}(\text{CO})_5$, 20°C IN HEXANE

Ligand conc. ($\times 10^2 M$)	$k_1(\text{obs}) (10^{-4} \text{sec}^{-1})$
<i>PPh</i> ₃ (series 1) ^a	
1.28	4.5
1.45	5.3
1.7	7.4
2.40	9.9
2.70	12
<i>PPh</i> ₃ (series 2) ^b	
3.69	5.7
3.69	4.3
3.69	5.5
3.69	4.8
<i>AsPh</i> ₃ ^c	
2.1	0.05
2.85	0.10













^a $[\text{HMn}(\text{CO})_5] = 2 \times 10^{-3} M$. ^b $[\text{HMn}(\text{CO})_5] = 3.2 \times 10^{-3} M$. ^c $[\text{HMn}(\text{CO})_5] = 1 \times 10^{-3} M$, 28°C .

precision, suggest that substitution at $\text{HMn}(\text{CO})_5$ obeys a second-order rate law, and that the rate constant is strongly dependent on the nucleophilicity of the attacking ligand.

In an attempt to clarify further the mechanism of substitution in $\text{HMn}(\text{CO})_5$ we carried out a detailed infrared study of the exchange with ^{13}CO . A preliminary study of this exchange reaction was reported earlier [14].

Using the carbonyl stretching parameters obtained by Kaesz and coworkers [28], based upon an approximate force field, the carbonyl stretching frequencies for each of the 12 ^{13}CO labeled isomers of $\text{HMn}(\text{CO})_5$ and $\text{DMn}(\text{CO})_5$ were calculated. Substitution of deuterium for hydrogen has little effect on the carbonyl stretching absorptions. The data for the isotopically labeled species of $\text{DMn}(\text{CO})_5$ are shown in Table 2. The rates of exchange of ^{13}CO with $\text{DMn}(\text{CO})_5$ were followed by observ-

TABLE 2
CALCULATED IR FREQUENCIES IN THE CARBONYL STRETCHING REGION FOR THE TWELVE POSSIBLE ISOTOPIC SPECIES OF $\text{DMn}(\text{CO})_5$ ENRICHED WITH ^{13}CO .

Isotope	Geometry	Frequencies (cm^{-1})				
1		2117.5	2042.9	2015.0	2015.0	2005.7
2		2110.2	2037.0	2015.0	1982.1	2006.4
3		2113.3	2042.9	2015.0	2015.0	1965.0
4		2105.6	2036.9	2015.0	1985.2	1963.1
5		2101.5	2032.8	1980.0	1984.0	2007.1
6		2102.8	2019.8	2015.0	1970.2	1997.5
7		2096.2	2032.8	1989.5	1980.0	1961.9
8		2097.9	2014.7	2015.0	1970.2	1962.6
9		2092.0	2018.6	1981.5	1970.2	1997.5
10		2079.0	1997.5	1970.2	1970.2	1997.5
11		2086.0	2014.7	1982.6	1970.2	1961.5
12		2070.4	1997.5	1970.2	1970.2	1961.1

ing the absorbances at 1964, 1982 and 1970 cm^{-1} . These absorbances correspond respectively to substitution of ^{13}C O into the axial position, a mono-radial substitution, and a *trans*-diradial substitution.

From Table 2 it can be seen that not all vibrations due to a similar mode occur at the same frequency. For example, the absorption at 1982 cm^{-1} for the mono-radial ^{13}C O labeled species shifts by 3 cm^{-1} when a ^{13}C O ligand is also present in the axial position. Thus the observed peak is broadened and the major absorbance at a particular wave number may not accurately represent the concentration of the species involved. Figure 3 shows the time-dependent IR spectra in the car-

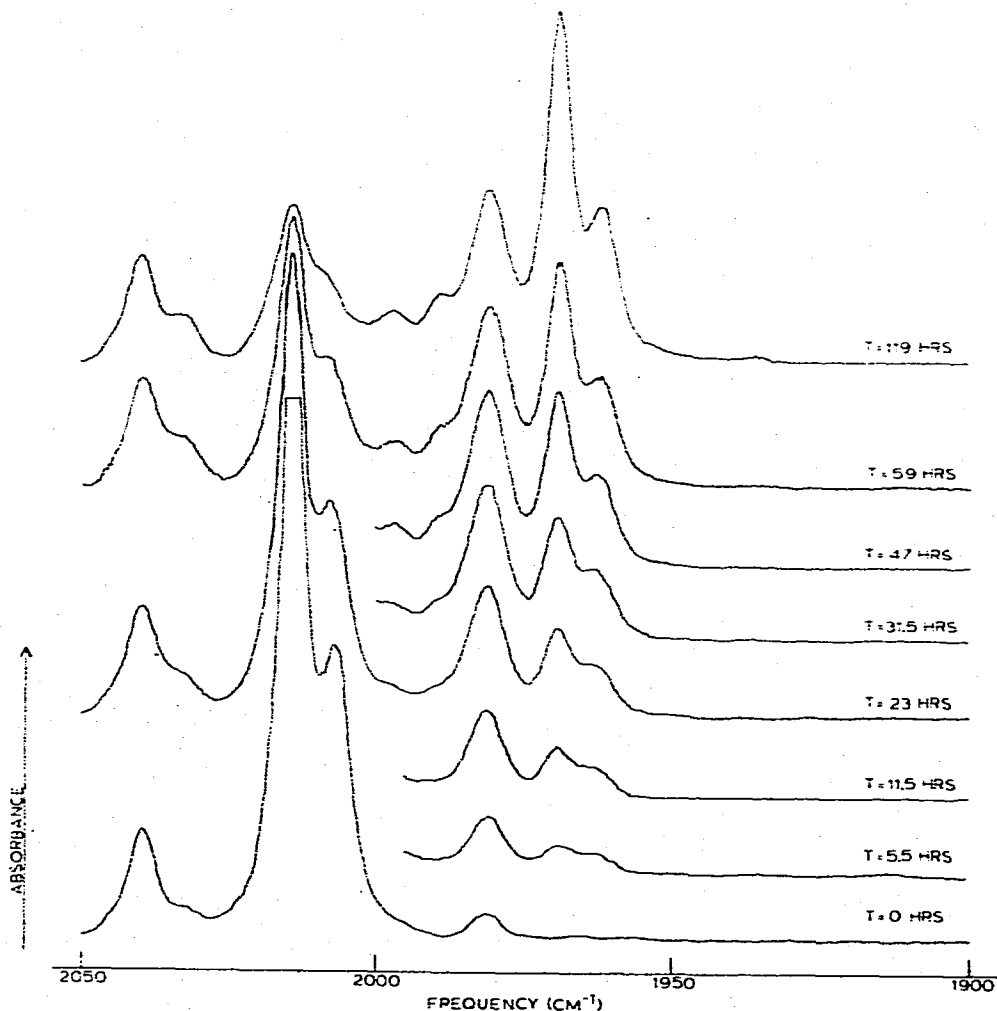


Fig. 3. Variation in IR spectra of $\text{DMn}(\text{CO})_5$ in hexane as a function of time, in presence of ^{13}C . The absorbance at 2042 cm^{-1} is due to a component of unknown composition; it undergoes no change during reaction.

bonyl stretching region for ^{13}CO exchange in $\text{DMn}(\text{CO})_5$ in hexane at 26°C . It is evident that substantial overlap of bands occurs, especially between 1964 and 1970 cm^{-1} . Because the ^{13}C enrichment in the CO employed is 90%, a major portion of the hydride molecules are eventually substituted with the more than one ^{13}CO . As a result, the absorbance at 1982 cm^{-1} , corresponding to a mono-radial substituted species, reaches a maximum and then gradually decreases. This effect is evident in Fig. 4, which shows a graph of absorbance of the 1982 and 1964 cm^{-1} bands as a function of time. In determining the rate constants for substitution at the axial and radial positions it is necessary to take account of this effect, since it is not possible directly to obtain a value for A_∞ . However, by assuming that the exchange reaction is pseudo-first-order, the changes in absorbances at 1964 cm^{-1} and 1982 cm^{-1} as a function of time could be fitted to an optimal value for A_∞ . In the case of the 1964 cm^{-1} absorbance this optimal value is not very much different from the observed value of A_∞ . However, because the mono-radial species is extensively replaced by species that are more highly substituted in the radial positions, the optimal value of A_∞ is significantly larger than the observed final value of absorbance at this frequency. Using those values of A_∞ which maximize the R -coefficient in the least-squares analysis of the rate data during the first half life, the values of specific rate constant of substitution in the radial and axial positions were respectively, $k_{\text{rad}} = 1.98 \pm 0.11 \times 10^{-6}\text{ sec}^{-1}$ and $k_{\text{ax}} = 4.1 \pm 0.13 \times 10^{-6}\text{ sec}^{-1}$.

The overall pseudo-first-order rate constant for exchange, $4k_{\text{rad}} + k_{\text{ax}}$, of $1.2 \times 10^{-5}\text{ sec}^{-1}$ compares reasonably well with the value of $4.6 \times 10^{-5}\text{ sec}^{-1}$ obtained in the earlier study at 40°C [14].

The absorbance at 1970 cm^{-1} , corresponding to products with *trans*-diradially substituted CO groups (Table 2), becomes at equilibrium the most intense absorption in the spectrum. No pronounced induction period in growth of this absorption was noted. However, it is apparent from inspection of Fig. 3 that the 1970 cm^{-1} absorbance grows in initially more slowly than the one at 1984 cm^{-1} , despite its higher final intensity. Thus, although this absorption did not afford

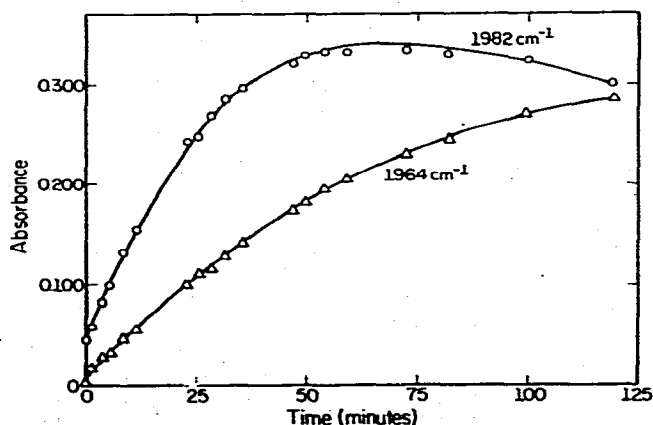


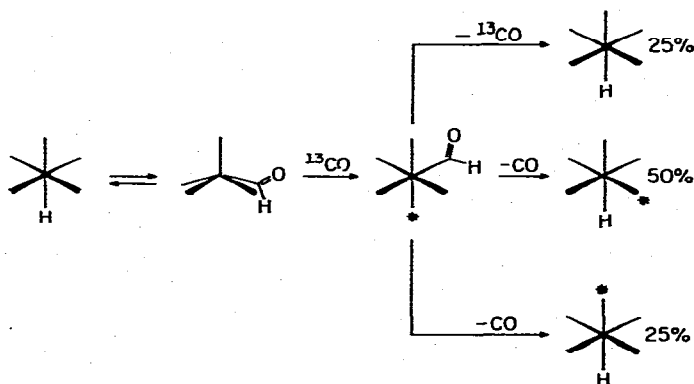
Fig. 4. Variation in absorbances at 1964 and 1982 cm^{-1} with time in reaction of ^{13}CO with $\text{DMn}(\text{CO})_5$.

useful kinetics results, the time dependence of absorption at 1970 cm^{-1} seems roughly consistent with a slow initial rate of growth, and more rapid growth at longer times.

The most important observation of the ^{13}C O exchange studies is that incorporation of the labeled CO occurs in both radial and axial positions concurrently, with no evidence for an induction period at either site (Fig. 4). This suggests that $\text{HMn}(\text{CO})_5$ is not an example of *cis*-labilization [20] in which the hydrido ligand preferentially labilizes the *cis* CO ligand towards dissociative loss. A CO loss process preferentially from the *cis* position would result in appearance of labelled CO in the axial period only after a significant induction period, assuming that the five-coordinate $\text{HMn}(\text{CO})_4$ intermediate is fluxional during its lifetime, and assuming that $\text{HMn}(\text{CO})_5$ does not undergo intramolecular rearrangement on the time scale of the experiment [29]. In any case, a dissociative pathway for the exchange is rendered unlikely by the observation that the substitution reactions with other ligands are second order, whereas a substitution mechanism which depended upon CO loss in the rate-determining step would yield a rate law independent of attacking ligand concentration. Furthermore, it seems very unlikely that a ligand of such low nucleophilicity as CO would substitute at a six-coordinate metal carbonyl center via an associative pathway. Assuming that substitution by ^{13}C O follows the same mechanism as reactions with other ligands, the most likely mechanism is a hydride migration pathway.

The expectations for the stereochemistry of ^{13}C O incorporation in an exchange reaction which proceeds via hydride migration are outlined in Scheme 1. In this

SCHEME 1. OUTLINE OF ^{13}C O EXCHANGE VIA A HYDRIDE MIGRATION PATHWAY, ASSUMING NO SCRAMBLING OF ^{13}C O IN DECARBOXYLATION PROCESS.

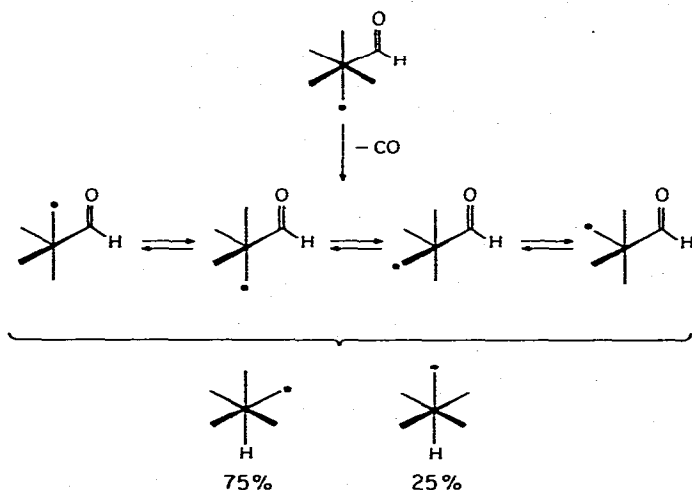


scheme it is assumed that there is no intramolecular exchange of CO groups within the formyl species at any stage of the decarbonylation. The formyl species postulated as an intermediate is not observed; it is presumed to undergo decomposition via a decarbonylation reaction with equal a priori probability at any of the four positions *cis* to the formyl group itself. Of those isomers which retain label after decarbonylation, the *cis* isomer should be twice as abundant as the *trans*. However, in terms of specific rate constants, this means that the specific rate constant for substitution in a radial position is half as large as that for sub-

stitution at the *trans* position. This is true because if the specific rate constants for substitution for all positions were equal, the *cis* isomer would be four times as abundant as the *trans*.

An alternative to part of the proposal just outlined is diagrammed in Scheme 2.

SCHEME 2. OUTLINE OF PROCESS BY WHICH THE ^{13}CO GROUP IS SCRAMBLED IN THE COURSE OF DECARBONYLATION.



Here it is assumed that a discrete five-coordinate species is formed following dissociation of CO from the labelled formyl compound, and that this intermediate undergoes complete scrambling of CO groups before hydride migration occurs. Regardless of whether the five-coordinate intermediate is assumed to be trigonal bipyramidal with the formyl in an axial position, or square-pyramidal with formyl in a basal position [20], the model predicts that the *cis/trans* ratio will be 3 : 1, corresponding to $k_{\text{rad}}/k_{\text{ax}} = 0.75$. Thus, the hydride migration mechanism involving a formyl intermediate leads to the prediction that there should be no induction period for incorporation of label in either *cis* or *trans* position, and that the ratio of specific rate constants, $k_{\text{rad}}/k_{\text{ax}}$ is either 0.50 or 0.75. These predictions are in accord with the results obtained from analysis of the IR spectra in the present experiments. The observed ratio $k_{\text{rad}}/k_{\text{ax}} = 0.48$ is perhaps fortuitously close to the theoretically predicted value of 0.50 for the scheme outlined in Scheme 1. However, given the uncertainties in analysis of the IR data resulting from the inability to actually measure A_{∞} values, and from overlapping of bands, the possibility that the formyl intermediate is fluxional cannot be excluded.

An overall pseudo-first-order rate constant for exchange, $4k_{\text{rad}} + k_{\text{ax}}$, is about $1.2 \times 10^{-5} \text{ sec}^{-1}$ at 26°C . Assuming $[\text{CO}]$ to be about 0.01 M , the second-order rate constant for substitution is $1.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at 26°C . This is to be compared with the value of $9 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at 30°C for incorporation of ^{13}CO into $\text{CH}_3\text{Mn}(\text{CO})_5$, [30], a process for which a CH_3 group migration is strongly indicated [22]. Thus, assuming that both reactions proceed by a ligand migration process, the propensity for migration of hydride and methyl groups attached to

Mn do not appear to be greatly different. However, it must be noted that the $\text{CH}_3\text{Mn}(\text{CO})_5$ substitution study was carried out in ether, a solvent of some nucleophilic character; in these circumstances there may be solvent assistance of the ligand migration process. Such a solvent role is indicated by the fact that substitution reaction is independent of entering ligand, whereas in the present case substitution is first-order in ligand, indicating a prior equilibrium as shown in Scheme 1.

The present results, which indicate that hydride migration is involved in the substitution of $\text{HMn}(\text{CO})_5$, stand in strong contrast to the results obtained for substitution of $\text{HRe}(\text{CO})_5$ [16]. Orbital analysis of the transition state in a hydride migration pathway suggests a loss of bond order relative to ground state. [31] This in turn would suggest that the stronger the M—H bond, the higher the activation barrier for the hydride migration pathway. Recent thermochemical studies of $\text{CH}_3\text{Re}(\text{CO})_5$ and $\text{CH}_3\text{Mn}(\text{CO})_5$ indicate that the C—Re bond in $\text{CH}_3\text{Re}(\text{CO})_5$ has a significantly higher bond energy than the C—Mn bond in $\text{CH}_3\text{Mn}(\text{CO})_5$ [32]. Thermochemical data are not available for the hydrido species, but it is reasonable to suppose that the H—Re bond is stronger than the H—Mn bond, as suggested by the kinetics results. Although the IR stretching frequencies of H—M bonds are a rather poor indication of relative bond energies it is noteworthy that the M—H stretching frequency is higher in $\text{HRe}(\text{CO})_5$ (1822 cm^{-1}) than in $\text{HMn}(\text{CO})_5$ (1776 cm^{-1}). [28].

Assuming for the moment that hydride migration is operative, the question arises as to the role of incoming ligand in promoting migration. In a non-coordinating solvent, incoming ligand may assist in the hydride migration. Such an assistance gives rise to the same form of rate law as observed for the reaction pathway outlined in Scheme 1, in which no ligand assistance is assumed. The present results shed little light on the matter. It is noteworthy that the overall rate constant for ^{13}CO exchange is apparently larger than for substitution by AsPh_3 , even after making reasonable allowance for the six degree temperature difference. Variations of this order of magnitude in apparent overall rate could arise from the competitive dissociation of the ligand from the formyl species. That is AsPh_3 may dissociate in preference to CO. In light of these uncertainties, additional experimental work is needed to more clearly define the role of the incoming ligand in the transition state.

Experimental

Materials

Triphenylphosphine, PPh_3 , Aldrich Chemical Company (99%), was recrystallized at least twice from methanol and stored in the inert atmosphere glove box. Tri-*n*-butylphosphine, PBu_3 , Aldrich Chemical Company (98%), was fractionally distilled under 50 mm of N_2 , and stored in an amber bottle in the glove box. Triphenylarsine, AsPh_3 , Aldrich Chemical Company (97%), was used without further purification.

Using standard purification techniques [33], spectranalyzed "Hexanes" from Fisher Scientific Company was treated with concentrated sulfuric acid. The solvent was then washed repeatedly with deionized water, dried with anhydrous magnesium sulfate, and fractionally distilled. The mainrun was collected in clean,

oven-baked amber bottles, deaerated by bubbling N_2 through the solution for about one-half hour and stored over sodium wire in the glove box. The hexane used for the exchange study was further purified by distillation in the glove box prior to use.

Hydridopentacarbonylmanganese(I), $HMn(CO)_5$, was prepared using a standard preparation [34]. The compound was stored at $5^\circ C$, and distilled on a vacuum manifold before use. Traces of oxygen gradually decomposed some of the hydride to $Mn_2(CO)_{10}$, as evidenced by the appearance of a pale yellow color. To ensure high purity, the hydride was redistilled through P_4O_{10} at frequent intervals.

IR bands (hexane): 2117, 2043, 2014.5, 2007.5, 1981, 1966 cm^{-1} (Lit. [28] (cyclohexane): 2116.7, 2042.0, 2014.5, 2006.7, 1981.8, 1965.4 cm^{-1}).

The deuteride, $DMn(CO)_5$, was prepared in an analogous manner using D_3PO_4 .

Sample preparation and handling

Since $HMn(CO)_5$ is air sensitive, most sample preparations were carried out in a Vacuum Atmospheres glove box with a circulating, continuously purified N_2 atmosphere.

Stock solutions of solid compounds were prepared by weighing samples in volumetric flasks. Solutions of $HMn(CO)_5$ were prepared by distilling the neat liquid on a vacuum manifold into small pyrex flasks containing degassed purified hexane. After transfer to the glove box, solutions were diluted to the desired concentrations and stored behind black plastic in the box. The two glass sections of the reaction apparatus (Fig. 1) were filled with aliquots from the appropriate stock solutions and connected together in the glove box. After the reaction apparatus was assembled, thermal equilibrium was obtained (approximately 0.5 h allowed) before commencing the reaction.

The apparatus and technique for the ^{13}CO exchange reaction with $DMn(CO)_5$ have been described elsewhere [19,20]. The complete apparatus was set up and used in the glove box at ambient temperature. Several layers of black plastic were used to exclude light.

All kinetics data were obtained from IR spectra, obtained on a Beckman IR-7 spectrophotometer, frequency-calibrated using water vapor.

Reaction vessel

To study the substitution reactions of $HMn(CO)_5$, it was necessary to be able to combine the hydride and ligand solutions, and shortly thereafter monitor the infrared spectrum at short intervals. A glass-metal system, shown in Fig. 1, was built to meet these requirements. The two glass sections containing the ligand (upper) and hydride (lower) solutions were filled and assembled in the glove box. They were then connected to the IR cell via a 10/30 standard taper joint, a vycor seal, 15 gauge stainless steel tubing, and a threaded header screwed into the lower opening in the IR cell. A gas-tight syringe was similarly connected to the upper opening in the IR cell, except a metal stopcock was used to connect the syringe to the stainless steel tubing. The IR cell is placed in a brass box insulated with asbestos. The window in the brass box facing the Nernst glower infrared source was covered with an infrared-pass filter, thereby reducing the possibility of photochemical reaction. The other window consisted of a sodium chloride plate.

The temperature of the IR cell was regulated by a thermocouple attached to the IR cell and connected to a constant temperature regulator. Liquid N₂ boil-off passes through the heating tower up into the brass box through holes in the bottom of the box. By controlling the temperature of the incoming N₂, the temperature of the IR cell could be thermostated ($\pm 0.1^\circ\text{C}$). The solution vessels were water jacketed and thermostated using a constant temperature circulating bath.

To maintain an inert atmosphere throughout the system, a positive pressure of N₂ was maintained in the reaction vessel and solvent bottle by inserting a syringe needle through rubber serum caps. The N₂ line was also connected in such a manner that the stainless steel tubing and IR cell could be flushed before each new sample was withdrawn. Through the use of two 2-way stopcocks, the cell could be flushed with N₂, filled with sample, or rinsed with pure solvent—all fluids passing out through the syringe.

Acknowledgement

We are grateful to Professor Charles P. Casey for helpful comments.

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