protons with the ^{103}Rh nucleus ($I = 1/2$, 100% abundance). Strong interaction between these protons and the rhodium nucleus in the $H_2C_2S_2M$ chelate ring is indicated by the relatively high value of this J(Rh–H) coupling constant.[30]

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AF-AFOSR-1211-67.

[30] For comparison the J(Rh–H) coupling constant in $C_5H_5Rh(CO)_2$ is only 0.5 cps.

CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

Carbon Monoxide Insertion Reactions. VI. The Mechanisms of the Reactions of Methylmanganese Pentacarbonyl and Acetylmanganese Pentacarbonyl with Triphenylphosphine

BY K. NOACK, M. RUCH, AND F. CALDERAZZO

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The reaction of methylmanganese pentacarbonyl with triphenylphosphine yields the isomeric mixture of $CH_3COMn(CO)_4P(C_6H_5)_3$ (I). The *cis* and *trans* isomers, which give two distinct acetyl proton peaks in nmr spectra, have been separated by chromatography on silica and the infrared spectra of enriched chromatographic fractions were measured. The number of infrared C–O stretching vibrations is that expected for local C_s and C_{4v} symmetries for the *cis* and the *trans* isomers, respectively. The *cis* isomer is the initial product of the reaction. The rate of isomerization *cis* $\overset{k_i}{\rightleftharpoons}$ *trans* follows a first-order kinetic equation with $k_i = 2.5 \times 10^{-4}$ sec^{-1} at 30° in acetone. A dissociative intermolecular mechanism involving $\{CH_3COMn(CO)_4\}$ is proposed for the isomerization. This is confirmed by the finding that an isomeric mixture of $CH_3COMn(CO)_4P(C_6H_5)_3$ exchanges the phosphine ligand with $P(C_6D_5)_3$. The infrared study of the reaction between $CH_3{}^{13}COMn(CO)_5$ and triphenylphosphine has shown that the final product is the isomeric mixture of $CH_3{}^{13}COMn(CO)_4P(C_6H_5)_3$ with retention of ^{13}C labeling at the acetyl position. A dissociative mechanism is proposed for this reaction.

Introduction

The kinetics of the reactions

$$CH_3Mn(CO)_5 + P(C_6H_5)_3 \longrightarrow CH_3COMn(CO)_4P(C_6H_5)_3 \quad (1)$$

$$CH_3COMn(CO)_5 + P(C_6H_5)_3 \longrightarrow CH_3COMn(CO)_4P(C_6H_5)_3 + CO \quad (2)$$

have been studied[1,2] and it was found that both reactions are first order in the metal complex and independent of triphenylphosphine concentration in ether solvents.

Acetylmanganese tetracarbonyltriphenylphosphine (I) exists in solution as an equilibrium mixture of the *cis* and *trans* isomers, according to nmr measurements,[3,4] showing the presence of two peaks of unequal intensities between τ 7 and 8. Kraihanzel and Maples[4] suggested that the high-field peak was due to the *trans* isomer, whereas we did not specify any assignment.

By studying the reaction of $CH_3Mn(CO)_5$ with ^{13}CO we have shown[5] that *cis*-$CH_3COMn(CO)_4{}^{13}CO$ is formed by a mechanism of methyl migration.

From a mechanistic point of view, it is important to determine which geometrical isomer of $CH_3COMn(CO)_4P(C_6H_5)_3$ is formed initially in the course of reaction 1. Furthermore, two mechanisms, both consistent with the kinetic data,[1,2] have been proposed[6] for reaction 2. The first one involves the coordinately unsaturated intermediate $\{CH_3COMn(CO)_4\}$, while the second considers the slow preequilibrium of $CH_3COMn(CO)_5$ to $CH_3Mn(CO)_5$. Since previous work[6] had not distinguished between the two possibilities, it appeared interesting in this connection to investigate the reaction of $CH_3{}^{13}COMn(CO)_5$ with triphenylphosphine.

Experimental Section

Methylmanganese pentacarbonyl was prepared according to a method described previously.[7] Labeled acetylmanganese pentacarbonyl, $CH_3{}^{13}COMn(CO)_5$, was prepared from $NaMn(CO)_5$ and $CH_3{}^{13}COCl$; details of this preparation will be given in a forthcoming publication.[8] All of the reactions were carried out in an atmosphere of prepurified nitrogen. Fully deuterated triphenylphosphine was prepared by allowing phenyl-d_5-magnesium bromide to react with phosphorous trichloride. Benzene-d_6 was brominated with a solution obtained from bromine and silver nitrate in nitric acid according to a known procedure.[9]

The infrared spectra were measured with a Perkin-Elmer Model 521 spectrophotometer, modified in such a way that the grating order change was at 2200 cm^{-1} rather than at 2000 cm^{-1}. The spectral slit width in the 2200–1500-cm^{-1} region was between 1.0 and 1.4 cm^{-1} (slit program 700). The spectra were measured on an expanded abscissa scale (1 cm = 10 wavenumbers with scan speed 40 cm^{-1}/min).

The infrared measurements of the carbon monoxide evolved

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[1] F. Calderazzo and F. A. Cotton, *Chim. Ind.* (Milan), **46**, 1165 (1964).

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[5] K. Noack and F. Calderazzo, *J. Organometal. Chem.* (Amsterdam), **10**, 101 (1967).

[6] F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

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during the reactions of ^{13}C-enriched samples of acetylmanganese pentacarbonyl were carried out in a special wedge-shaped gas cell (capacity 22 ml, path length 10 cm). The cell was evacuated and the reaction mixture placed in a vessel connected to a side arm of the gas cell. Samples containing 0.1 mmol of the manganese complex were generally used. For the gas-phase spectra the instrument was programmed as follows: slit program 500 (spectral slit width about 0.7 cm^{-1}), chart display 1 cm = 2.5 wavenumbers, scan speed 3 cm^{-1}/min. Under these conditions and with the amounts of sample used, naturally abundant ^{13}CO could be detected satisfactorily.

For the chromatographic separation of *cis*- and *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$, preliminary tests were done on thin layers of silica gel, using iodine vapor as detector. The preparative separation was carried out in a column 250 × 12 mm, packed with SiO_2. Each filling required about 30 g of SiO_2 (Merck, 0.05–0.2-mm particle size); methylene chloride or alcohol-free chloroform was used as solvent and eluent. The zones in the chromatographic column were made visible by irradiation with a mercury lamp equipped with a filter to eliminate the visible light. The *cis* isomer was eluted first. The eluates were collected at $-20°$ in order to minimize both the isomerization and the decarbonylation to $CH_3Mn(CO)_4P(C_6H_5)_3$. The solvent was then evaporated *in vacuo* and the solid residue redissolved in heptane for measuring the infrared spectra and in benzene-d_6 or acetone-d_6 for the nmr spectra.

Since the isomerization at room temperature is rather fast ($\tau_{1/2}$ is about 26 min in acetone at 30°), the infrared spectral assignments were done by comparing consecutive fractions of chromatography and by compensating with dilute solutions enriched in the other isomer.

The nmr spectra were measured with a DP60A Varian spectrometer, using tetramethylsilane as internal reference. The temperature of the probe was measured and found to attain equilibrium (30.0 ± 0.5°) within 3 min.

Results and Discussion

In order to answer the question concerning the initial formation of one of the two isomers obtained by reaction 1, we separated the isomers by chromatography. Any success would of course depend on the rate of isomerization and the time needed for the separation and the measurement of the spectra. We succeeded in obtaining chromatographic fractions highly enriched in either one of the two isomers. During the chromatographic separation the product of decarbonylation, $CH_3Mn(CO)_4P(C_6H_5)_3$, was eluted from the column rapidly and was therefore mostly discarded with the first fractions. It is perhaps surprising that *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ is eluted before the *trans* isomer but this is consistent with the findings of Jolly and Stone,[10] who also found that *cis*-$MnBr(CO)_4P(C_6H_5)_3$ is eluted before the *trans* isomer. Although completely pure samples of the geometrical isomers of $CH_3COMn(CO)_4P(C_6H_5)_3$ could not be obtained because of the relatively fast isomerization, we could measure the infrared spectra and assign the bands in the C–O stretching region by making use of the compensation technique indicated below. *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ (Ia), of local symmetry C_s, should have four C–O stretching vibrations ($3A' + A''$), whereas the *trans* isomer (Ib), of local symmetry C_{4v}, should have two infrared-active C–O stretching vibrations ($A_1 + E$). The observed spectra agree with these expectations (see Figure 1 and Table I). It is worth pointing out that the two bands of the *trans* form coincide with two of the bands of the *cis* form. This made the determination of the infrared spectra rather difficult and only by compensating the solution of the enriched *cis* or *trans* isomers with each other or with the equilibrium mixture, was unequivocal assignment of the bands possible.

Table I

Carbonyl Stretching Frequencies for *trans*- and *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$[a]

	← ν_{CO}, cm^{-1} →		Assignment
trans-$CH_3COMn(CO)_4P(C_6H_5)_3$	2067	(0.12)	A_1
	1957	(1.0)	E
	1925	(0.02)	^{13}CO
	1646	(0.18)	Acetyl CO
cis-$CH_3COMn(CO)_4P(C_6H_5)_3$	2067	(0.27)	A′
	1994	(0.70)	A′
	1964 1957	(1.0)	A′, A″
	1925	(0.02)	^{13}CO
	1625[b]	(0.05)	Acetyl CO

[a] In heptane solutions. Numbers in parentheses are relative intensities, referred to the strongest band in each spectrum. [b] Broad.

In addition, the two isomers have acetyl stretching bands in the region between 1650 and 1620 cm^{-1}. The acetyl stretching band of the *trans* isomer is sharp, whereas the one of the *cis* isomer is rather broad. This is in agreement with an earlier prediction[11] that, in the case of compounds of type *cis*-$CH_3COMn(CO)_4L$, rotational isomerism can occur, because of restricted rotation around the carbon–metal bond when L is a bulky group such as I^- or $P(C_6H_5)_3$.

Based on the infrared results, the acetyl proton peaks of the nmr spectra have been assigned as follows (in acetone-d_6, chemical shifts in ppm from tetramethylsilane = τ 10): Ia (*cis* isomer), τ 7.68 (+139 cps); Ib (*trans* isomer), τ 7.37 (+158 cps). The high-field peak (τ 7.68, +139 cps) is therefore due to the *cis* isomer, contrary to the previous assignment by Kraihanzel and Maples.[4]

Reaction 1 was followed in the nmr spectrometer and the peak at τ 7.68 was found to appear first. In a slower reaction the *cis* isomer was then converted into the *trans* isomer until the equilibrium mixture of Ia and Ib was obtained. In the solvent used for this experiment (acetone-d_6), reaction 1 is reasonably fast. By using high concentrations of $CH_3Mn(CO)_5$ in a 2:1 molar ratio to triphenylphosphine, it was possible to form Ia in high initial concentrations and to follow its conversion to the equilibrium concentration

$$cis\text{-}CH_3COMn(CO)_4P(C_6H_5)_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} trans\text{-}CH_3COMn(CO)_4P(C_6H_5)_3 \quad (3)$$

The conversion of *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ into the *trans* isomer follows a first-order equation for over three half-times with an approximate rate constant $k_3 = 2.5 \times 10^{-4}$ sec^{-1} at 30°. Equilibrium 3 is solvent dependent, as indicated by the data of Table II.

Reaction 2 was followed by nmr in benzene-d_6. Acetone-d_6 could not be used because of overlapping of the

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(10) P. W. Jolly and F. G. A. Stone, *J. Chem. Soc.*, 5259 (1965).

(11) K. Noack, U. Schaerer, and F. Calderazzo, *J. Organometal. Chem.* (Amsterdam), **6**, 265 (1966).

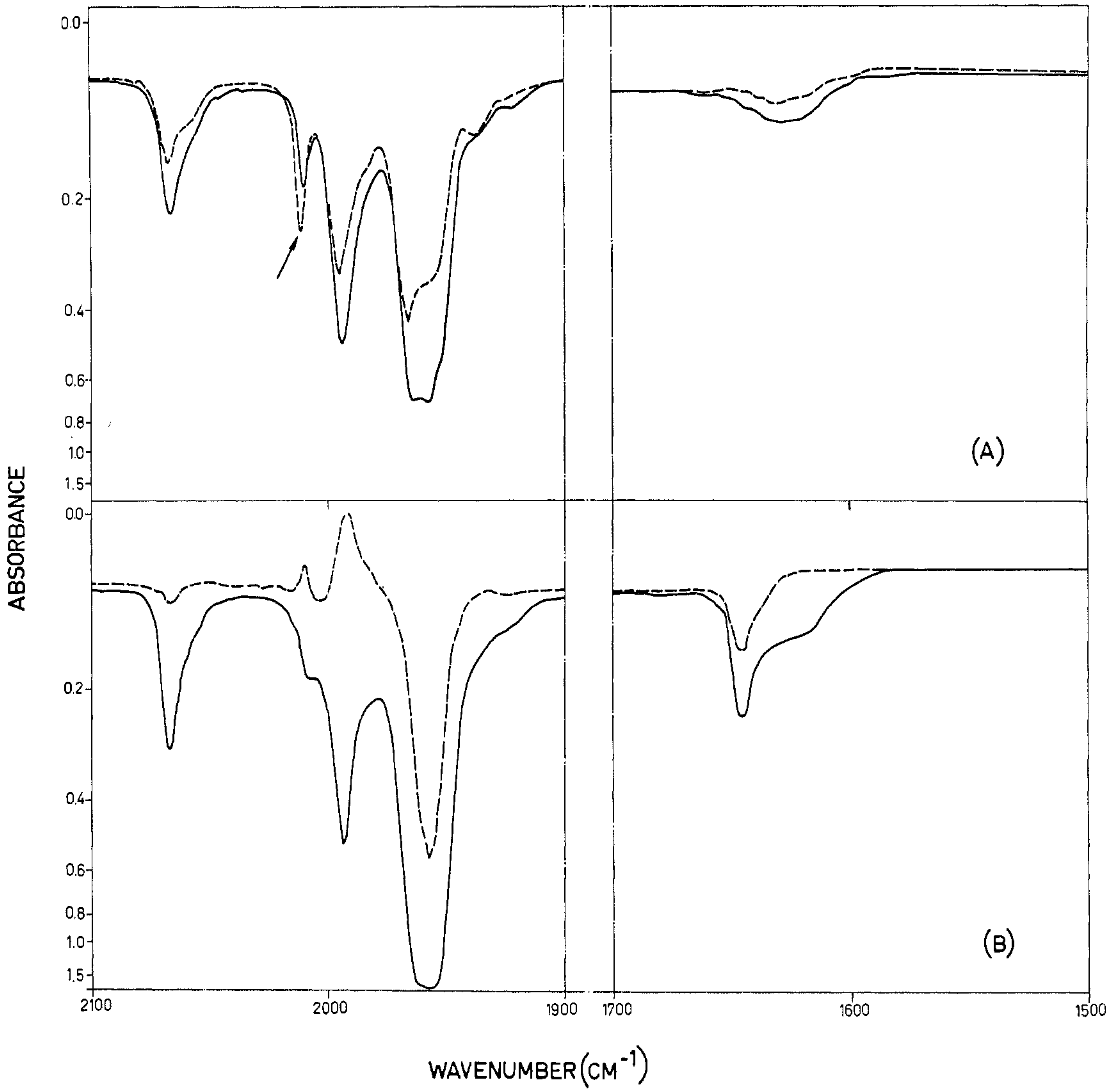

Figure 1.—Chromatographic separation of *cis*- and *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$. Infrared spectra of enriched fractions of the two isomers; heptane solutions in a 1-mm cell. (A): ———, solution of the *cis* isomer (Ia) containing small amounts of the *trans* isomer; - - - - -, the same solution compensated with a dilute enriched solution of the *trans* isomer. The band with the arrow is due to $CH_3Mn(CO)_5$ whose concentration increases during the measurement because of radiative heating. (B): ———, solution of the *trans* isomer (Ib) containing small amounts of the *cis* isomer; - - - -, compensation with an equilibrium mixture of the two isomers. Although the solution is overcompensated at 1994 cm^{-1}, the band at 2067 cm^{-1} still persists which shows the latter to be due to the *trans* isomer. The overcompensation at 2011 cm^{-1} is due to some $CH_3Mn(CO)_5$ in the reference beam.

TABLE II

SOLVENT EFFECT ON THE RELATIVE AMOUNTS OF *cis*- AND *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$ AT EQUILIBRIUM AT 30°[a]

Solvent	% *trans*	% *cis*
CS_2	23	77
C_6D_6	30	70
$CDCl_3$	35	65
CD_3COCD_3	56	44

[a] From the integrated areas of the acetyl proton peaks in the nmr spectra.

acetyl proton peak of *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$ with that of $CH_3COMn(CO)_5$. The reaction is rather slow and this makes the conclusions concerning the initially formed isomer rather uncertain (*vide infra*).

Further information about the mechanism of reaction 2 was obtained by allowing 50% enriched $CH_3{}^{13}COMn(CO)_5$ to react with $P(C_6H_5)_3$. It was found by infrared analysis that the evolved gas contained ^{12}CO with only the naturally abundant amount of ^{13}CO, thus suggesting that all of the ^{13}CO is retained in the reaction product. This is true both in heptane and in 2,2′-dimethoxydiethyl ether. The product of the reaction does not show any appreciable change in the terminal C–O stretching region as compared with a *cis–trans* mixture of naturally abundant $CH_3COMn(CO)_4P(C_6H_5)_3$. Finally, the infrared region where the acetyl C–O groups absorb contains two broad bands of equal intensity centered at 1626 and 1592 cm^{-1}, thus showing that the original 50% enrichment in ^{13}C has been retained in the acetyl groups of the reaction products.[12] The observed separation between the two bands—each of them containing the acetyl bands of both *cis*

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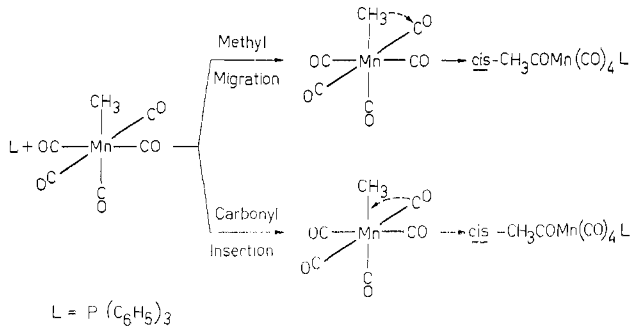
(12) Interfering absorption of triphenylphosphine was compensated.

and *trans* isomers—is that expected for the isotopic frequency ratio.

The results presented here can be explained as follows. Since the *cis* isomer is the first product of reaction 1, the mechanism can be either methyl migration or carbonyl insertion[5]



The reaction of $CH_3Mn(CO)_5$ with CO was shown[5] to occur by methyl migration. Although one would tend to consider a similar mechanism for the triphenylphosphine reaction, this is not unequivocally proved by the experimental data. It is worth mentioning that the carbonylation of $CH_3Mn(CO)_5$ with CO follows second-order kinetics[7] ($k(30.0°) = 8.99 \times 10^{-3}$ sec^{-1} l. mole^{-1}), whereas reaction 1 in the same solvent is independent of triphenylphosphine concentration[1] with $k = 6.6 \times 10^{-4}$ sec^{-1} at 30.5° in the same solvent. It has been suggested[2] that this change of reaction order could be due to the low concentration of carbon monoxide since the kinetic measurements were carried out at atmospheric or subatmospheric pressure. We have verified this suggestion and found that the rate of carbonylation of $CH_3Mn(CO)_5$ becomes independent of carbon monoxide concentration above 15 atm. Details of this study will be given in a forthcoming paper. It is conceivable that a similar change of reaction order could be found at sufficiently low concentrations of triphenylphosphine. In any case, the stereospecificity of reaction 1 to give initially *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ suggests that we are dealing with a concerted mechanism in which a solvent molecule attacks the metal in a position *cis* with respect to the methyl group, probably by direct displacement of the methyl group (methyl migration) or less likely by displacement of an adjacent carbon monoxide group (carbonyl insertion). The intermediate of this reaction can therefore be represented as $\{CH_3COMn(CO)_4\}_A$. The latter is most probably a solvated hexacoordinate species from which *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ can be obtained stereospecifically by solvent displacement and addition of triphenylphosphine before rearrangement of the ligands can take place (*vide infra*). The initial formation of *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ is in agreement with the similar observation by Green and Wood[13] for the reaction of $CH_3Mn(CO)_5$ with $P(OCH_2)_3CCH_3$, but contrasts with another indication contained in the literature.[14]

Since isomerization reaction 3 follows a first-order kinetic law, it seems reasonable to assume an intermolecular dissociative mechanism of the type suggested by Basolo and co-workers[15] for the isomerization of phosphine-disubstituted manganese carbonyl derivatives

$$cis\text{-}CH_3COMn(CO)_4L \underset{+L\ (fast)}{\overset{-L\ (slow)}{\rightleftharpoons}} \{CH_3COMn(CO)_4\}_A \rightleftharpoons$$
$$\{CH_3COMn(CO)_4\}_B \underset{-L\ (slow)}{\overset{+L\ (fast)}{\rightleftharpoons}} trans\text{-}CH_3COMn(CO)_4L$$

(scheme for reaction 3)

$\{CH_3COMn(CO)_4\}_A$ and $\{CH_3COMn(CO)_4\}_B$ are energetically and structurally different. In coordinating solvents they probably exist as solvated species and they can be represented as *cis*-$\{CH_3COMn(CO)_4(\text{solvent})\}$ and *trans*-$\{CH_3COMn(CO)_4(\text{solvent})\}$, respectively. The corresponding unsolvated species could be depicted as a tetragonal pyramid and a trigonal bipyramid,[16] the former being converted into the latter with the expenditure of some energy.[17] An alternative intermediate of reaction 3 could be $\{CH_3COMn(CO)_3P(C_6H_5)_3\}$. In order to distinguish between the two possibilities we treated an isomeric mixture of $CH_3COMn(CO)_4P(C_6H_5)_3$ with triphenylphosphine-d_{15}. The phosphine-exchange reaction in acetone-d_6

$$CH_3COMn(CO)_4P(C_6H_5)_3 + P(C_6D_5)_3 \rightleftharpoons CH_3COMn(CO)_4P(C_6D_5)_3 + P(C_6H_5)_3 \quad (4)$$

was found to occur as evidenced by the appearance of free triphenylphosphine in solution (phenyl protons at 443.5 cps, τ 2.61) and the simultaneous decrease of bonded triphenylphosphine (*cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$, 450.5 cps, τ 2.49; *trans*-$CH_3COMn(CO)_4P(C_6H_5)_3$, 455 cps, τ 2.42. Although not exactly measured, the rate of exchange was comparable to that of reaction 3. We therefore conclude by saying that the intermediates of reaction 3 are those indicated in the scheme for reaction 3. That no methyl movement is involved in the isomerization of $CH_3COMn(CO)_4P(C_6H_5)_3$ is shown by the fact that $CH_3{}^{13}COMn(CO)_4P(C_6H_5)_3$ obtained from $CH_3{}^{13}COMn(CO)_5$ and triphenylphosphine still contained all the ^{13}C in the acetyl position and yet this is an *equilibrium* mixture of *cis* and *trans* isomers. This retention of acetyl ^{13}C suggests that the reaction occurs *via* the dissociative mechanism

$$CH_3{}^{13}COMn(CO)_5 \underset{+CO\ (fast)}{\overset{-CO\ (slow)}{\rightleftharpoons}} \{CH_3{}^{13}COMn(CO)_4\} \underset{-L\ (slow)}{\overset{+L\ (fast)}{\rightleftharpoons}} CH_3{}^{13}COMn(CO)_4L$$

(scheme for reaction 2)

In view of our previous studies on decarbonylations of $CH_3{}^{13}COMn(CO)_5$[5] and (+)-$C_6H_5CH_2CH(CH_3)COMn(CO)_5$,[6] we prefer to regard the formation of the intermediate $\{CH_3{}^{13}COMn(CO)_4\}$ as occurring *via* the dissociation of a CO group *cis* with respect to the acetyl group. The intermediate can then be identical, apart from the ^{13}C enrichment, with $\{CH_3COMn(CO)_4\}_A$ pre-

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(15) R. J. Angelici, F. Basolo, and A. J. Poë, *ibid.*, **85**, 2215 (1963).

(16) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 215 ff.

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viously postulated for reaction 1 or with $\{CH_3COMn(CO)_4\}_B$, if rearrangement has occurred. In the first case *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ would be formed initially whereas $\{CH_3COMn(CO)_4\}_B$ would lead to the equilibrium mixture of the two isomers. The choice will depend on the energy required to rearrange $\{CH_3COMn(CO)_4\}_A$ relative to that required to form it. As mentioned earlier, this point could not be ascertained because of an unfavorable kinetic situation in benzene-d_6.

The proposed mechanism for reaction 2 is in agreement with the previously reported[6] experiment with (+)-$C_6H_5CH_2CH(CH_3)COMn(CO)_5$ showing retention of sign of rotation during its reaction with I^- in 2,2′-diethoxydiethyl ether. The alternative explanation[6] of a stereospecific slow preequilibrium of $RCOMn(CO)_5$ to $RMn(CO)_5$ must be ruled out on the basis of the present data.

No important isomerizations, with consequent statistical redistribution of ^{13}CO, were observed,[5] within the time of the experiment, during the reaction of $CH_3Mn(CO)_5$ with ^{13}CO, whereas isomerization occurs with $CH_3COMn(CO)_4P(C_6H_5)_3$. This can be explained on kinetic terms by considering that $CH_3COMn(CO)_5$ can exchange its CO groups with CO in the gas phase only *via* decarbonylation to $CH_3Mn(CO)_5$ or, in other words, through the intermediate $\{CH_3COMn(CO)_4\}_A$ (k ranging from 2.46×10^{-5} to 1.99×10^{-6} sec^{-1} at 30° depending on the solvent[7]). The decarbonylation of $CH_3COMn(CO)_5$ is therefore a slow process compared to its formation from $CH_3Mn(CO)_5$. On the other hand, the initially formed *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ reverts to the *trans* isomer at a rate which is relatively fast ($k = 2.5 \times 10^{-4}$ sec^{-1} at 30° in acetone).

We can conclude by saying that the experimental facts contained in this paper and probably most of those reported in previous papers[1-3,5-7] can be explained by assuming the *preliminary* formation of intermediates obtained from changes taking place at a position *cis* with respect to the alkyl or the acyl group.

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY, DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

The Crystal and Molecular Structure of Dimeric Azulenetricarbonylmethylmolybdenum

BY PETER H. BIRD AND MELVYN R. CHURCHILL

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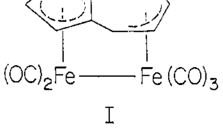
Dimeric azulenetricarbonylmethylmolybdenum, $[C_{10}H_8Mo(CO)_3CH_3]_2$, crystallizes in the triclinic space group $P\bar{1}$ (C_i^1; No. 2) with cell parameters $a = 10.02 \pm 0.02$ Å, $b = 8.36 \pm 0.02$ Å, $c = 8.19 \pm 0.02$ Å, $\alpha = 107.3 \pm 0.2°$, $\beta = 89.3 \pm 0.2°$, $\gamma = 100.4 \pm 0.2°$, $Z = 1$. Observed and calculated densities are, respectively, 1.68 ± 0.02 and 1.667 g cm^{-3}. A single-crystal X-ray structural analysis, based on complete three-dimensional data ($\sin \theta_{max} = 0.38$, Mo Kα radiation) collected with a Buerger automated diffractometer, has been completed. Patterson, Fourier, and least-squares refinement techniques have led to the accurate location of all atoms other than the methyl hydrogens. The final discrepancy index, R_F, is 5.82% for 1438 independent nonzero reflections. The crystal consists of discrete molecular units of $[C_{10}H_8Mo(CO)_3CH_3]_2$ separated by normal van der Waals forces. The molecule possesses a crystallographic center of symmetry, two azulene residues being linked *via ortho–ortho* (4,4′) carbon–carbon coupling. An $Mo(CO)_3CH_3$ moiety is bonded to each five-membered ring of the resulting diazulene ligand. The Mo–CH_3 bond length is 2.383 ± 0.010 Å and the mean Mo–CO distance is 1.996 ± 0.012 Å.

Introduction

Although azulene–metal–carbonyl complexes have been known for some time,[1-5] only recently have the structures of any of these complexes been unambiguously established. Crystallographic studies of azulenediiron pentacarbonyl[6,7] (I) and azulenedimolybdenum hexacarbonyl[8,9] (II) show them to have a metal atom associated with each ring. There are, however, some azulene–metal–carbonyl complexes in which the azulene-to-metal ratio is 1:1, *viz*, $[C_{10}H_8V(CO)_4]_2$,[4] $[C_{10}H_8$-



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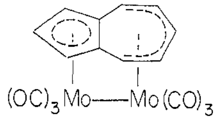

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