

CARBON MONOXIDE INSERTION REACTIONS V. THE CARBONYLATION OF METHYLMANGANESE PENTACARBONYL WITH ^{13}CO

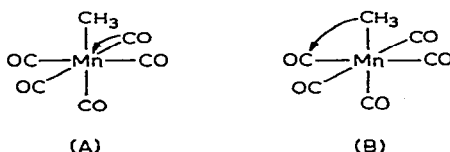
K. NOACK AND F. CALDERAZZO

Cyanamid European Research Institute, 1223 Cologny/Geneva (Switzerland)

(Received March 6th, 1967)

Mechanistic studies on carbonylations of alkyl manganese pentacarbonyls promoted by carbon monoxide¹, triphenylphosphine^{2,3}, phosphites^{3,4}, primary amines³ and iodide ion⁵ have recently been published.

Two main mechanisms have been proposed for the carbonylation of $\text{CH}_3\text{Mn}(\text{CO})_5$: the carbonyl insertion (A) and the methyl migration (B).



No experimental evidence in favour of either mechanism can be found in the literature. A recent paper by Mawby, Basolo and Pearson⁶ dealing with the decarbonylation of $\text{CH}_3\text{CO Mn}(\text{CO})_4\text{PPh}_3$ cannot be taken as evidence for mechanism (B) because of isomerisations later found^{7,8} to take place during the formation of $\text{CH}_3\text{COMn}(\text{CO})_4\text{PPh}_3$.

We wish now to report on some investigations of the system $\text{CH}_3\text{Mn}(\text{CO})_5 + \text{CO} \rightleftharpoons \text{CH}_3\text{COMn}(\text{CO})_5$ using ^{13}CO as carbonylating agent. We will show that by carbonylation of $\text{CH}_3\text{Mn}(\text{CO})_5$ with ^{13}CO , no ^{13}CO is found in the acetyl group, which confirms the yet unpublished experiment by Coffield⁹ with ^{14}CO . Further, by studying the stereochemical changes in this and other reactions we could gather conclusive evidence that the carbonylation occurs by methyl migration rather than by carbonyl insertion.

The reaction products were examined by infrared spectroscopy. Molecules of the type $\text{LMn}(\text{CO})_5$ ($\text{L}=\text{CH}_3, \text{CH}_3\text{CO}$) with C_{4v} symmetry have three infrared active stretching vibrations due to the terminal CO groups¹⁰⁻¹². In the acetyl derivative also the stretching vibration of the acetyl CO is observed. In the spectra of the compounds containing the naturally abundant amount of ^{13}C , bands due to ^{13}CO stretching vibrations are observed as weak shoulders. In Table 1 we report the three ^{12}CO stretching vibrations of $\text{CH}_3\text{Mn}(\text{CO})_5$ and $\text{CH}_3\text{COMn}(\text{CO})_5$ and some of the ^{13}CO bands which are of interest to us for the discussion of the experimental results. Apart from a small degree of mixing the A_1 band at high wavenumber and the E and A' bands are due to vibrations of the radial CO groups (*cis* with

TABLE 1

CARBONYL STRETCHING BANDS OF LMn(CO)₅^a

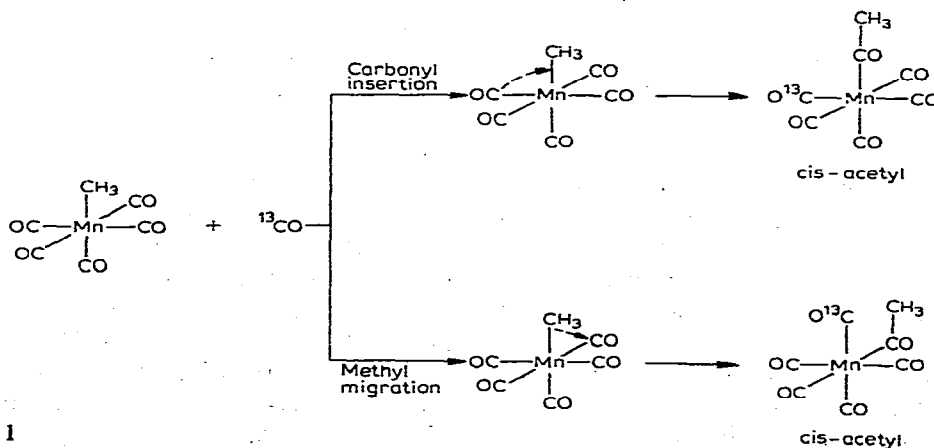
L	ν(CO) (cm ⁻¹)				
	Radial CO groups			Axial CO groups	Acetyl CO
	A ₁	E	A'	A ₁	
CH ₃	2110	2012	(1976) ^b	1991 (1949)	
CH ₃ CO	2115	2011	(1970) ^b	2003 (1963)	1664 (1625)

^a Numbers in parentheses denote bands of the ¹³CO satellites (all the other ¹³CO stretching vibrations which are not relevant to the present work are omitted). ^b This is an infrared active vibration of *cis*-LMn(CO)₄¹³CO (C_s symmetry).

respect to L); the A₁ band at lower wavenumber is due to the single axial group (trans to L). When ¹³CO enters the axial or one of the radial positions, the intensity of the corresponding ¹³CO band will be increased. Intensity measurements will therefore make it possible to determine stereochemical changes¹³. Assignments and symmetry changes consequent to ¹³CO substitution will be discussed in detail in a forthcoming publication¹⁴, in which also the preparations of the labelled compounds will be reported.

Carbonylation reactions were run in diethyl ether to assure reasonable rates but at the end of the reaction diethyl ether was replaced by heptane in order to increase the resolution of the infrared bands. Decarbonylations were done thermally in the solid state or in heptane solutions.

(1) CH₃Mn(CO)₅ was carbonylated with 50% enriched ¹³CO for about 15 h. Intensity measurements on the obtained acetyl manganese pentacarbonyl as compared to the compound with ¹³C in natural abundance (statistically distributed) gave the following results. Only the 1970 cm⁻¹ band involving radial or *cis*-CO groups increased in intensity, whereas the band at 1963 cm⁻¹ of the axial or *trans*-CO group and the ¹³C-acetyl band at 1625 cm⁻¹ did not show any significant change. This shows that: (a) the incoming ¹³CO is not directly inserted from the gas phase in between the metal-carbon bond; (b) the newly formed acetyl and terminal ¹³CO groups are mutually in a *cis* position; (c) no significant isomerisation, which would

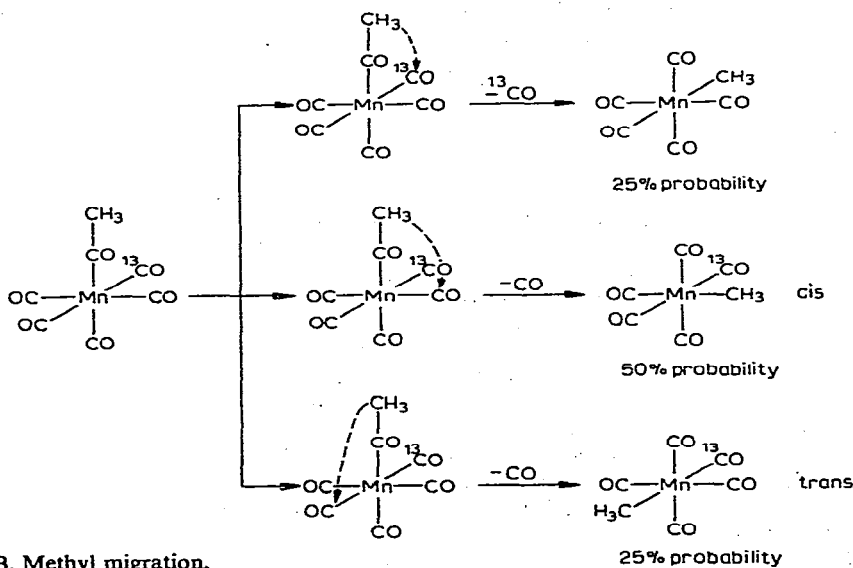
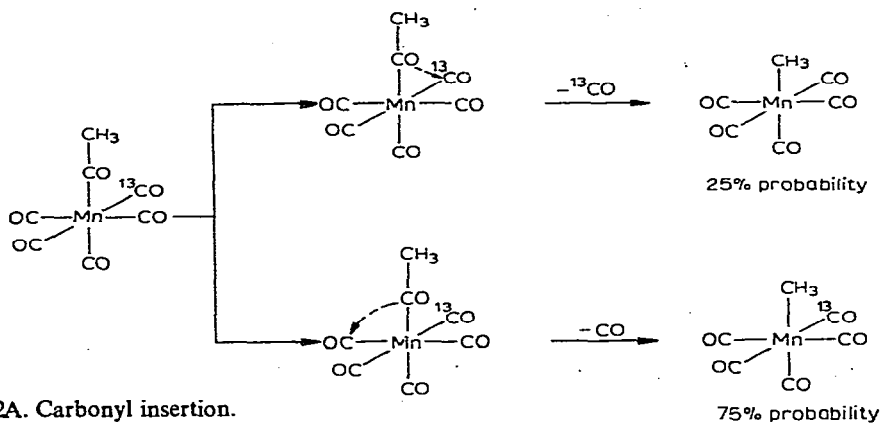


Scheme 1

have led to a statistical distribution of the ^{13}C has taken place under the reaction conditions. It is worth mentioning that point (a) definitely supports one of the two mechanisms, (A) or (B). From this experiment, no decision can, however, be taken between these two mechanisms since both would lead to the same observed stereochemical distribution. This is shown in Scheme 1. In this scheme the incoming ^{13}C is assumed to approach the metal at the coordination position of the ligand to be displaced [the methyl group in mechanism (B) or one of the radial CO groups in mechanism (A)].

(2) About 50% enriched $\text{CH}_3^{13}\text{COMn}(\text{CO})_5$ was prepared from $\text{CH}_3^{13}\text{COCl}$ and $\text{NaMn}(\text{CO})_5$. This was decarbonylated and gave *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4^{13}\text{CO}$ exclusively. This shows that the decarbonylation occurs by the same mechanism as the carbonylation, in agreement with the principle of microscopic reversibility¹⁵.

(3) *cis*- $\text{CH}_3\text{COMn}(\text{CO})_4^{13}\text{CO}$ obtained in (1) was decarbonylated and gave *trans* and *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4^{13}\text{CO}$ in the ratio 1:2, as inferred from the intensities of the bands at 1976 and 1949 cm^{-1} . This is only in agreement with the methyl migra-

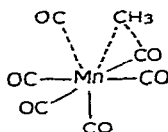


tion mechanism, since by carbonyl insertion no *trans* product would have been produced (see schemes 2A and 2B).

(4) The *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4^{13}\text{CO}$ obtained in (2) was carbonylated with naturally abundant CO. Acetylmanganese pentacarbonyl which contained the *cis*, the *trans* and the $^{13}\text{COCH}_3$ products in the ratio 2:1:1 was obtained. Carbonyl insertion would have given the *cis* and $^{13}\text{COCH}_3$ products in ratios 3:1 and no *trans* isomer. The observed ratio of products is just the one expected for the mechanism (B) of methyl migration.

(5) When the 1:2 mixture of *trans*- $\text{CH}_3\text{Mn}(\text{CO})_4^{13}\text{CO}$ and *cis*- $\text{CH}_3\text{Mn}(\text{CO})_4^{13}\text{CO}$ as obtained in (3) was recarbonylated with naturally abundant CO, *cis*- and *trans*- $\text{CH}_3\text{COMn}(\text{CO})_4^{13}\text{CO}$ and $\text{CH}_3^{13}\text{COMn}(\text{CO})_5$ were obtained in the ratio 4:1:1. This is again only in agreement with the mechanism of methyl migration. For carbonyl insertion one would expect a *cis/trans*/ $^{13}\text{COCH}_3$ ratio of 3:2:1, which is largely different from the experimental value.

In conclusion, the mechanism by which $\text{CH}_3\text{Mn}(\text{CO})_5$ is converted into $\text{CH}_3\text{COMn}(\text{CO})_5$ by carbon monoxide is most probably a direct displacement of the methyl group by the incoming nucleophile followed by or simultaneous to a methyl migration to one of the adjacent carbon monoxide groups as shown below.



SUMMARY

The reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with ^{13}CO and the decarbonylation of $\text{CH}_3^{13}\text{COMn}(\text{CO})_5$ have been investigated by infrared spectroscopy. The results previously obtained by Coffield and coworkers with ^{14}CO have been confirmed. Furthermore, by use of ^{13}CO the stereochemical changes occurring during the carbonylation reaction have been studied. The results are in agreement with a mechanism of methyl migration for the conversion of methyl manganese pentacarbonyl into acetyl manganese pentacarbonyl by carbon monoxide.

REFERENCES

- 1 F. CALDERAZZO AND F. A. COTTON, *Inorg. Chem.*, 1 (1962) 30.
- 2 F. CALDERAZZO AND F. A. COTTON, *Chim. Ind. (Milan)*, 46 (1964) 1165.
- 3 R. J. MAWBY, F. BASOLO AND R. G. PEARSON, *J. Am. Chem. Soc.*, 86 (1964) 3994.
- 4 M. GREEN AND D. C. WOOD, *J. Am. Chem. Soc.*, 88 (1966) 4106.
- 5 F. CALDERAZZO AND K. NOACK, *Coord. Chem. Rev.*, 1 (1966) 118.
- 6 R. J. MAWBY, F. BASOLO AND R. G. PEARSON, *J. Am. Chem. Soc.*, 86 (1964) 5043.
- 7 F. CALDERAZZO AND K. NOACK, *J. Organometal. Chem.*, 4 (1965) 250.
- 8 C. S. KRAIHANZEL AND P. K. MAPLES, *J. Am. Chem. Soc.*, 87 (1965) 5267.
- 9 T. H. COFFIELD, J. KOZIKOWSKI AND R. D. CLOSSON, *Abstr. Papers, Intern. Conf. Coord. Chem.*, London, 1959, Paper No. 26; C. W. BIRD, *Chem. Rev.*, 62 (1962) 283.
- 10 L. E. ORGEL, *Inorg. Chem.*, 1 (1962) 25.
- 11 M. A. EL-SAYED AND H. D. KAESZ, *J. Mol. Spectry.*, 9 (1962) 310.
- 12 K. NOACK, U. SCHAEERER AND F. CALDERAZZO, *J. Organometal. Chem.*, in the press.
- 13 R. W. HARRILL AND H. D. KAESZ, *Inorg. Nucl. Chem. Letters*, 2 (1966) 69.
- 14 K. NOACK, in preparation.
- 15 R. M. KRUPKA, H. KAPLAN AND K. J. LAIDLER, *Trans. Faraday Soc.*, 62 (1966) 2754.