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INFRARED SPECTRA OF ^{13}CO-SUBSTITUTED METHYL- AND ACETYLMANGANESE PENTACARBONYLS*

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SUMMARY

Methyl- and acetylmanganese pentacarbonyl highly enriched with ^{13}CO either in *cis* or *trans* position and in the acetyl group are prepared and their carbonyl stretching frequencies assigned.

INTRODUCTION

In the course of a study on the mechanism of the reaction of methylmanganese pentacarbonyl with carbon monoxide and triphenylphosphine we have used the infrared spectra of ^{13}CO-monosubstituted methyl- and acetylmanganese pentacarbonyls to distinguish between radial and axial substitution products[1,2]. We wish now to discuss these spectra in more detail and justify our previous assignments. The study of the spectra of isotopically substituted metal carbonyls makes possible the calculation of the force constants of these molecules with fewer *a priori* assumptions than are needed with the ^{12}C-containing compounds alone. This method has very recently been used by Lewis and coworkers[3] on phosphine derivatives of manganese pentacarbonyl. They studied the weak absorption bands due to the presence of ^{13}C-substituted material in natural abundance ($\sim$1.1% of ^{13}C).

While this manuscript was being prepared two further papers on spectra of ^{13}C-substituted manganese carbonyls appeared. Kaesz and coworkers[4] studied randomly enriched metal pentacarbonyl halides while Cotton and coworkers[5] used the bands due to naturally abundant amounts of some ^{13}C-substituted manganese pentacarbonyl compounds to calculate vibrational force constants. None of these workers had, however, compounds available which were enriched at specific positions of the molecules, but only random mixtures of the several possible isomers. In the course of our investigation we have prepared the following compounds highly enriched at specific positions: $CH_3{}^{13}COMn(CO)_5$, *cis*-$CH_3Mn(CO)_4{}^{13}CO$ and less pure samples of *cis*-$CH_3COMn(CO)_4{}^{13}CO$ as well as mixtures of *cis*- and *trans*-$CH_3Mn(CO)_4{}^{13}CO$ (2:1) and *cis*- and *trans*-$CH_3COMn(CO)_4{}^{13}CO$ (2:1).

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* Paper given in part at the 9th European Congress on Molecular Spectroscopy, Madrid, September 1967, Abstracts p. 57.

EXPERIMENTAL

Preparations

$CH_3{}^{13}COMn(CO)_5$ enriched in the acetyl group was prepared starting from $Ba^{13}CO_3$ (obtained from Merck, Sharp & Dohme, Montreal, Canada) with 56% ^{13}C-enrichment and $NaMn(CO)_5$ by the following sequence of reactions:

$$Ba^{13}CO_3+H_2SO_4 \rightarrow {}^{13}CO_2+BaSO_4+H_2O$$

$$^{13}CO_2+CH_3MgI \rightarrow CH_3{}^{13}COOMgI \rightarrow CH_3{}^{13}COONa$$

$$CH_3{}^{13}COONa+C_6H_5COCl \rightarrow CH_3{}^{13}COCl+C_6H_5COONa$$

$$CH_3{}^{13}COCl+NaMn(CO)_5 \rightarrow CH_3{}^{13}COMn(CO)_5+NaCl$$

All the reactions and transfers of products were carried out in a vacuum manifold.

Seven mmoles of CH_3MgI in 15 ml ether were outgassed in a 50 ml flask containing a magnetic rod for stirring. ^{13}C-enriched CO_2 was prepared by dropping 8 ml conc. sulfuric acid into 700 mg enriched barium carbonate. The enriched CO_2 was condensed into the solution of the Grignard reagent and the mixture then slowly warmed-up to room temperature with stirring. The flask was removed from the vacuum line and 10 ml of ice-water added, followed by 7 ml of 20% NaOH solution. Finally 1.45 g (1.3 times the theoretical amount) of silver sulfate were added with vigorous stirring. Most of the water from the resulting slurry was distilled off *in vacuo* and to the residue 5 ml of phosphoric acid (85%) were added with cooling. Enriched acetic acid and water were distilled off, titrated with NaOH solution and evaporated to dryness. The yield at this point was 92%. To the dry $CH_3{}^{13}COONa$ were added 3 ml of freshly distilled benzoyl chloride, the mixture frozen with liquid nitrogen and put under vacuum. The flask was closed-off from the vacuum line and the mixture heated to reflux for a few minutes and then cooled in an ice bath. The acetyl chloride thus formed was distilled for only 1 min (not longer to avoid contamination with benzoyl chloride) into a flask cooled with liquid nitrogen. This whole procedure (refluxing and distillation) was repeated three times. To eliminate most of the HCl dissolved in the acetyl chloride, the latter was cooled with dry ice and the HCl pumped off for a few seconds. The remaining acetyl chloride was finally distilled into a solution of $NaMn(CO)_5$. This reaction mixture was slowly brought to room temperature under stirring and held there for a few minutes during which time sodium chloride precipitates. Nitrogen was admitted and the solution was quickly filtered from the NaCl and cooled again in dry ice. The acetylmanganese pentacarbonyl crystallised in about one hour and was filtered under nitrogen through a cooled fritted glass filter, dried in a nitrogen stream and weighed. Yield 269 mg (33% based on barium carbonate) of almost colourless crystals of ^{13}C-enriched acetylmanganese pentacarbonyl.

cis-$CH_3Mn(CO)_4{}^{13}CO$ was prepared by decarbonylation of $CH_3{}^{13}COMn(CO)_5$ by heating the solid or a heptane solution to 100° for 5 min[1].

cis-$CH_3COMn(CO)_4{}^{13}CO$ was prepared by carbonylation of $CH_3Mn(CO)_5$ with ^{13}CO (50% enriched, obtained from Merck, Sharp & Dohme, Montreal) by shaking an ether solution at atmospheric pressure and room temperature for several hours with ^{13}CO. The ether was evaporated on a water pump and the residue dissolved in heptane or pentane for the infrared spectra[1]. Under these conditions, the reaction was not complete and the solution contained unreacted methylmanganese pentacarbonyl.

cis-$Mn(CO)_4{}^{13}CO$ was carbonylated with ^{12}CO under pressure (50 atm) in ether solution to give a 2 : 1 mixture of *cis*- and *trans*-$CH_3COMn(CO)_4{}^{13}CO$ (ref. 1).

cis-$CH_3COMn(CO)_4{}^{13}CO$ was decarbonylated by heat to give a 2 : 1 mixture of *cis*- and *trans*-$CH_3Mn(CO)_4{}^{13}CO$ (ref. 1).

Spectra

The infrared spectra were taken in heptane or pentane solutions in 1.0 mm or 0.1 mm cells on a Perkin–Elmer Mod. 521 spectrophotometer. The abscissa scale was expanded 5 times (1 mm = 1 cm^{-1}). The slit programme 700 which gives a spectral slit width < 1.5 cm^{-1} over the range from 2200–1500 cm^{-1} was used. The scanning speed was 40 cm^{-1}/min. Each spectrum was calibrated with CO. The frequencies are accurate to ±1 cm^{-1}.

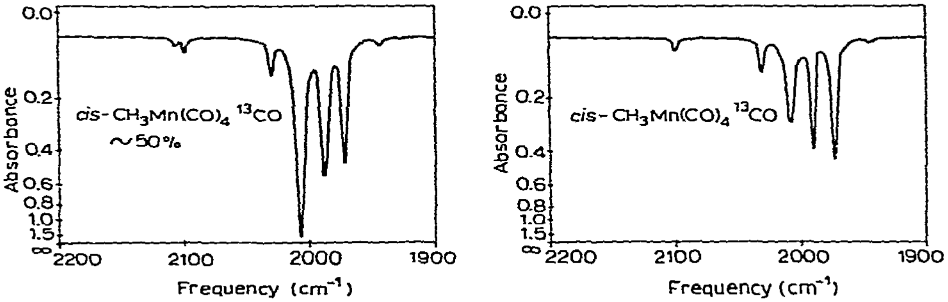

Fig. 1. Infrared spectrum of *cis*-$CH_3Mn(CO)_4{}^{13}CO$ in heptane solution: (a) 1 : 1 mixture with natural $CH_3Mn(CO)_5$, not compensated, (b) compensated with natural $CH_3Mn(CO)_5$.

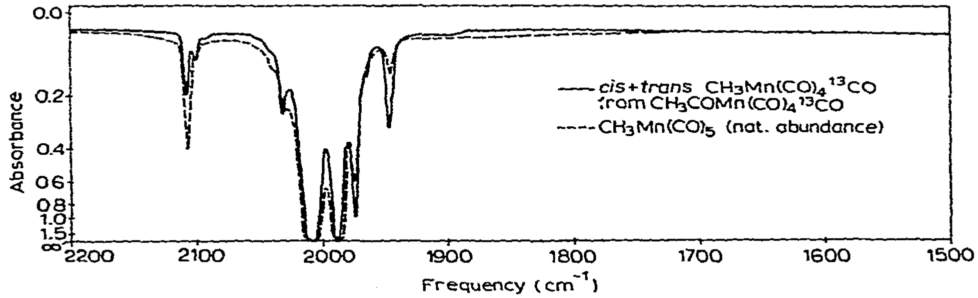

Fig. 2. Infrared spectrum of a 2 : 1 mixture of *cis*- and *trans*-$CH_3Mn(CO)_4{}^{13}CO$ and natural $CH_3Mn(CO)_5$ (——) natural $CH_3Mn(CO)_5$ alone (------).

RESULTS

The spectra of the *cis*- and *trans*-$CH_3Mn(CO)_4{}^{13}CO$ are shown in Figs. 1 and 2. For comparison the spectra of the compounds containing ^{13}C in natural abundance are also given at relatively high concentration. The frequencies and approximate extinction coefficients are listed in Tables 1 and 2.

TABLE 1

CARBONYL FREQUENCIES AND ASSIGNMENTS OF METHYLMANGANESE PENTACARBONYLS[a]

All-^{12}C–$CH_3Mn(CO)_5$		*trans*-$CH_3Mn(CO)_4{}^{13}CO$		*cis*-$CH_3Mn(CO)_4{}^{13}CO$	
2110 (350)	A_1	2110	A_1	2102 (600)	A'
2011 (26000)	E	2011	E	2033 (1600)	A'
1990 (5600)	A_1			2011 (5000)	A''
				1992 (7000)	A'
		1949	A_1	1975 (9000)	A'

[a] Heptane solution; molar extinction coefficients in brackets.

TABLE 2

CARBONYL FREQUENCIES AND ASSIGNMENTS OF ACETYLMANGANESE PENTACARBONYLS[a]

All-^{12}C–$CH_3COMn(CO)_5$		Bands enhanced on ^{13}C substitution	
2115 (700)	A_1		
2051 (900)	B_1	2044	A' of *cis*
2011 (10000)	E		
2003 (7000)	A_1	1969	A' of *cis* (one component from E)
1661 (1500)	Acetyl CO	1962 1626	A_1 of *trans* Acetyl CO

[a] Heptane solution, molar extinction coefficients in brackets.

DISCUSSION

Methylmanganese pentacarbonyls

The spectrum of the all-^{12}C containing compound (I) has been published and amply discussed[6,7] and is in excellent agreement with the selection rules for a C_{4v}-structure. This implies that the methyl group either rotates freely or does not influence the fourfold axis of the manganese coordination. The bands and assignments are listed in Table 1 for comparison with the ^{13}C substituted products.

cis-$CH_3Mn(CO)_4{}^{13}CO$ *(II)*. This compound was only contaminated with slightly more than the naturally abundant amount of the corresponding *trans* ^{13}CO compound. It is of course mixed with about 50% of the all-^{12}CO compound. Its spectrum can be easily deduced by subtracting that of the all-^{12}C compound. This can be done either numerically or, preferably, by compensating with solutions of known concentration of the ^{12}C compound (see Fig. 1).

TABLE 3

SELECTION RULES

	$CH_3Mn(CO)_5$ and *trans*-$CH_3Mn(CO)_4{}^{13}CO$			*cis*-$CH_3Mn(CO)_4{}^{13}CO$	
Symmetry:	C_{4v}		$\longrightarrow$	C_s	
Vibrations:	$2A_1$	IR+Ra	$\longrightarrow$	$2A'$	all IR+Ra
	E	IR+Ra	$\longrightarrow$	$A'+A''$	
	B_1	Ra	$\longrightarrow$	A'	

The compound exhibits 5 carbonyl stretching bands, which are listed in Table 1. The symmetry is C_s. The selection rules for C_s symmetry predict the presence of five infrared active bands ($4A'$, A''). Table 3 shows the correlations with the corresponding all-^{12}C compound of C_{4v} symmetry. If we compare the spectrum with the one of natural methylmanganese pentacarbonyl the following observations can be made: The A_1 band at high frequency, mainly due to the vibration of the 4 radial CO groups in (I) is slightly shifted from 2110 to 2102 cm^{-1} ($\Delta = 8$ cm^{-1}). The new band in (II) belongs to the class A' (see Table 3). The E band of (I) is expected to split into $A' + A''$. The in plane A' mode is much more affected by the ^{13}CO substitution than the out of plane A'' mode. We assign therefore the pair at 2011 cm^{-1} [unshifted from (I)] and 1975 cm^{-1} (shifted by 36 cm^{-1}) to the A'' and A' part respectively. The A_1 band of (I) at low frequency attributed mainly to the vibration of the single axial CO group is expected to be only slightly influenced. It is found at 1992 cm^{-1} in (II). Finally we are left with the band at 2033 cm^{-1} which should be of the class A' and corresponds therefore to the infrared inactive B_1 mode of (I).

trans-$CH_3Mn(CO)_4{}^{13}CO$ (III). (Fig. 2). This compound could not be obtained pure, but only in a mixture with (II). The only significant difference of the spectrum of this mixture as compared with that of (II) is the large increase of the band at 1949 cm^{-1} relative to that at 1975 cm^{-1} of the *cis* compound. This 1949 cm^{-1} band is clearly the ^{13}CO satellite of the band at 1991 cm^{-1} in (I) (A_1, attributed mainly to the single trans CO group).

The symmetry of (III) and (I) are the same, therefore, the same selection rules apply and bands and assignments are given in Table 1. Only the low frequency A_1 band is shifted with respect to (I). Due to the strong overlapping of the bands of (II) the spectrum of (III) is less well established than those of (I) and (II). It is however remarkable that no shoulder on the low frequency side of the high frequency A_1 band of (I) can be detected. This would mean that the high frequency A_1 band is virtually unshifted by axial ^{13}CO substitution and that there is only negligible coupling between the two A_1 modes in this molecule.

Our results agree within the limits of experimental error with those of Cotton and coworkers[5], who, by the use of the naturally abundant amount of ^{13}C compound present, made assignments of the *cis*- and *trans*-$CH_3Mn(CO)_4{}^{13}CO$ and calculated the force constants.

Acetylmanganese pentacarbonyls

$CH_3{}^{13}COMn(CO)_5$. This compound labelled in the acetyl group shows in the region of the terminal CO absorptions a spectrum which is identical with the non-labelled compound. This demonstrates that the coupling of the acetyl-CO and the terminal-CO vibrations is negligible. The acetyl band shows the expected shift and is found at 1626 cm^{-1} ($\Delta = 35$ cm^{-1}).

$CH_3COMn(CO)_4{}^{13}CO$. The species enriched at the terminal CO groups were unfortunately always contaminated with the corresponding natural and enriched methylmanganese pentacarbonyls, because of some decarbonylation in solution, and also because the carbonylation reaction of $CH_3Mn(CO)_5$ with ^{13}CO was not complete under the reaction conditions employed. Therefore the spectra are less well defined than in the case of the methyl compounds. Nevertheless, by comparison with the naturally abundant compound and using the results from the methylmanganese

pentacarbonyl, reasonable assignments can be made. For sake of completeness, the frequencies of the all-^{12}C compound are again given in Table 2, together with some bands of the substitution products. The following observations can be made.

The symmetry of the *cis* compound is C_s, the one of the *trans* compound can be approximated by C_{4v} (see below).

In the *cis* compound the band which is present very weakly in the natural acetylmanganese pentacarbonyl at 1969 cm^{-1} is strongly enhanced. This is the A'' band and corresponds to one component of the E band of the all-^{12}C compound. Other bands in the spectrum of the *cis* compound are masked by the methylmanganese pentacarbonyl bands.

In the *trans* compound (obtained only as *cis*+*trans* mixture) also the band at 1662 cm^{-1} is enhanced. This is the A_1 mode, mainly due to vibration of the axial CO group.

By ^{13}CO substitution the band at 2051 cm^{-1} is broadened and shows two maxima at 2050 and 2044 cm^{-1}; the new band is probably the A' mode of the *cis*-substituted compound corresponding to the B_1 mode of the all-^{12}C compound. The fact that in the all-^{12}C compound the band at 2051 cm^{-1} is observed (assigned as B_1 in C_{4v}) shows that the influence of the acetyl group on the total symmetry of the molecule is such that the selection rules for C_s-symmetry have to be applied in a rigorous treatment.

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REFERENCES

1 K. NOACK AND F. CALDERAZZO, *J. Organometal. Chem.*, 10 (1967) 101.
2 K. NOACK, M. RUCH AND F. CALDERAZZO, *Inorg. Chem.*, in press.
3 J. LEWIS, A. R. MANNING AND J. R. MILLER, *J. Chem. Soc., A*, (1966) 845.
4 H. D. KAESZ, R. BAU, D. HENDRICKSON AND J. M. SMITH, *J. Amer. Chem. Soc.*, 89 (1967) 2844.
5 F. A. COTTON, A. MUSCO AND G. YAGUPSKY, *Inorg. Chem.*, 6 (1967) 1357.
6 K. NOACK, U. SCHAERER AND F. CALDERAZZO, *J. Organometal. Chem.*, 8 (1967) 516.
7 F. A. COTTON, *Inorg. Chem.*, 3 (1964) 702.