CARBON MONOXIDE INSERTION REACTIONS

IV. ROTATIONAL ISOMERISM IN ACYLMANGANESE PENTACARBONYLS AND RELATED COMPOUNDS*

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INTRODUCTION

We have recently reported[1] that compounds of the type $CH_3COMn(CO)_4L$ [$L = P(C_6H_5)_3$ or I^-], which can be obtained[1,2,3] by reaction (1), exist in solution as the two theoretically possible *cis-* and *trans-*isomers.

$$CH_3Mn(CO)_5 + L \rightleftharpoons CH_3COMn(CO)_4L \qquad (1)$$

The main evidence for the latter statement is the observation of two acetyl proton resonances between 7 and 8 τ (ppm from tetramethylsilane), and the relative intensity variation, observed between 10 and 50°, of two bands of the $[CH_3COMnI(CO)_4]^-$ anion at 1975 and 1967 cm^{-1}.

In addition to that, two infrared bands were observed in the ketonic CO stretching region at 1590 and 1566 cm^{-1} in the case of the $[CH_3COMnI(CO)_4]^-$ anion. The same is true for $CH_3COMn(CO)_4P(C_6H_5)_3$ which gives a broad band in tetrahydrofuran centered at about 1625 cm^{-1} clearly consisting of two bands separated by about 15 cm^{-1}. This anomalous behaviour in the ketonic CO stretching region was also attributed to the existence of the two geometrical isomers in solution.

It is the purpose of this paper to report some new observations dealing with high resolution infrared spectra, including measurements at different temperatures, of halogen substituted acylmanganese pentacarbonyls of the type $CXH_2COMn(CO)_5$ and $CX_2HCOMn(CO)_5$ ($X = F, Cl$). These compounds, for which geometrical isomers are not possible, also show in solution two bands in the ketonic CO stretching region, suggesting the existence of *rotational* isomers. The intensity ratio of these bands is strongly temperature dependent.

Since rotational isomers are possible for *cis-*$CH_3COMn(CO)_4L$ compounds, our previous observations[1] are extended to suggest that rotational isomerism phenomena may also be responsible for the complex pattern observed in these compounds in the ketonic CO stretching region.

All the compounds reported in the present paper are new.

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* For Part III, see Ref. 1.

EXPERIMENTAL

The infrared spectra were measured with a Perkin–Elmer Mod. 521 grating spectrophotometer. The spectral slit width with the employed slit schedule of 700 is about 1.2 cm^{-1} in the region of 2000 cm^{-1}. The grating order change was moved from 2000 to 2200 cm^{-1}. Each spectrum was recorded on expanded abscissa scale (10 cm^{-1}/ cm) and calibrated with CO. The limit of accuracy is believed to be ± 0.5 cm^{-1} for narrow bands.

The cool-cell for the measurements at temperatures below room temperature has been described elsewhere[4]. An improvement of the temperature control makes it now possible to maintain any temperature between +100° and —180° to ± 0.1° for any length of time. This modification consists of a selenoid valve in the nitrogen-exhaust line which is controlled by a photocell on the light spot of the mirror galvanometer connected with the thermocouple in the cool-cell.

The nuclear magnetic resonance spectra were measured with a Varian DP 60 A instrument at room temperature. Melting points (uncorr.) were measured in capillaries sealed under nitrogen. Diethyl ether and tetrahydrofuran were distilled over sodium and lithium tetrahydroaluminate and kept under nitrogen. Decacarbonyldimanganese was prepared by the procedure previously described[5]. Sodium pentacarbonylmanganate was obtained by reduction of $Mn_2(CO)_{10}$ with sodium sand in tetrahydrofuran.

TABLE 1

PREPARATION, ANALYTICAL DATA AND PROPERTIES OF ACYLMANGANESE PENTACARBONYLS

Compound	Yield %	Colour	M.p.[a] (dec.)	Analyses found (%) (calcd.)		
				C	H	Halogen
CFH$_2$COMn(CO)$_5$ (I)	50	white	67°–69°	33.31 (32.84)	1.26 (0.79)	6.80 (7.42)
CF$_2$HCOMn(CO)$_5$ (II)	61	yellow	32°–33°	30.88 (30.68)	0.71 (0.37)	13.68 (13.87)
CClH$_2$COMn(CO)$_5$ (III)	36	yellow	89°–91°	30.53 (30.36)	1.15 (0.74)	13.24 (13.01)
CClH$_2$CH$_2$COMn(CO)$_5$ (IV)	74	yellow	56°–58°	34.26 (33.54)	1.76 (1.41)	12.37 (12.37)

[a] The compounds melt with gas evolution. In the case of the fluoro derivatives, this corresponds to the formation of the alkyl compounds according to the equation: $RCOMn(CO)_5 \rightleftharpoons CO + RMn(CO)_5$.

Preparation and properties of acylmanganese pentacarbonyls

The manganese complexes were prepared from $NaMn(CO)_5$ and the corresponding acyl chloride in diethylether. The preparation of monofluoroacetyl-manganese pentacarbonyl (I) is here described in detail, the procedure being identical for all the other compounds. The 3-chloropropionylmanganese pentacarbonyl was prepared under an atmosphere of carbon monoxide.

Sodium pentacarbonylmanganate (2.71 g) was dissolved under nitrogen in diethylether (100 ml) and the solution cooled to —80°. After addition of monofluoroacetyl chloride (1.30 g) the temperature was slowly raised. Precipitation of sodium

chloride began at about $-10°$ and was complete in a few minutes. The reaction mixture was filtered at room temperature and the filtrate cooled to $-80°$. The crystalline colourless $CFH_2COMn(CO)_5$ was filtered and dried (1.59 g, 50 % yield). The mono-fluoroacetylmanganese pentacarbonyl is soluble in the common organic solvents. The solubility in bis(2-ethoxyethyl) ether is about 1 % (w/v).

Difluoroacetylmanganese pentacarbonyl (II), $CF_2HCOMn(CO)_5$, is readily soluble in CCl_4 and diethyl ether.

Monochloroacetylmanganese pentacarbonyl (III), $CClH_2COMn(CO)_5$, is poorly soluble in the common organic solvents. The solubility in bis(2-ethoxyethyl) ether is about 0.5 % (w/v).

3-Chloropropionylmanganese pentacarbonyl (IV), $CClH_2CH_2COMn(CO)_5$, is soluble in common organic solvents. The solubility in bis(2-ethoxyethyl) ether is about 2 % (w/v).

The fluoro derivatives are decarbonylated to the corresponding $CFH_2Mn(CO)_5$ and $CF_2HMn(CO)_5$, which have been isolated and characterised[6]. The decarbonylation is carried out at $120-140°$.

The chloro derivatives are decomposed by heating at about $80°$ to unidentified products and there is no indication of the formation of the corresponding chloro-alkylmanganese pentacarbonyls at that temperature.

All the compounds described are volatile. The fluoro derivatives can be sublimed at $60°/12$ mm Hg with little or no conversion to the corresponding alkyls. Sublimation of the chloro derivatives is not a convenient method of separation, because of their thermal lability.

RESULTS AND DISCUSSION

Rotational isomerism in compounds of the type $CXH_2COMn(CO)_5$ can arise from restricted rotation around the carbon–carbon bond of the CXH_2–CO–Mn grouping. The situation is illustrated in Fig. 1 where the group ClH_2–CO–Mn is drawn

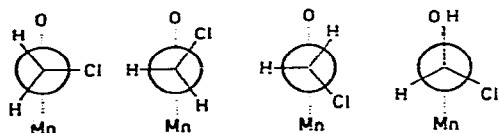
Fig. 1. Some possible rotational configurations of $CClH_2COMn(CO)_5$. The CO groups on the manganese atom are not shown.

in a representation of the Newman type. One eclipsed and three staggered forms are shown. By rotating the groups, many other configurations can be obtained. The main factor in determining the occurrence of rotational isomers is the steric repulsion between groups rotating against each other about a single bond[7].

It is of course difficult to predict from models only, which of the several possible arrangements have energy minima. The most important requirement for the stabilization of the rotamers is, in this particular case, the minimization of the repulsion between chlorine and manganese since these are the largest atoms [the single bond radius of manganese in these compounds is considered to be 1.46 Å, *i.e.* the same as that recently determined in $Mn_2(CO)_{10}$[8]]. It is, however, readily seen that a real *s-trans* configuration with the manganese and the chlorine atoms at 180° is probably not

the most stable because the oxygen and the chlorine would be in eclipsed positions. As an additional complication, the four equatorial CO groups on the manganese may also contribute to the steric hindrance.

Infrared spectra

As shown by the data of Table 2 and by the spectra of Fig. 2, rotational isomers in halogen-substituted acylmanganese pentacarbonyls are evidenced by two C–O stretching vibrations in the region characteristic of the ketonic group at about 1650 cm^{-1} in compounds (I), (II) and (III). Rotational isomers have been detected by

TABLE 2

INFRARED SPECTRA OF ACYLMANGANESE PENTACARBONYLS[a]

Compound	$\nu_{C\equiv O}$ (cm^{-1})				$\nu_{C=O}$ (cm^{-1})	Solvent
	A_1	B_1	E	A_1		
(I)	2121 (500)	2056 (300)	2021 (6700)[c]		1667 (300)	THF[b]
					1632 (700)	
	2121 (600)	2057 (300)	2027 (12000)	2010 (5000)	1677 (100)	heptane
					1642 (1500)	
(II)	2125 (500)	2062 (250)	2036 (8000)	2015 (5000)	1658 (350)	heptane
			2028 (8000)		1643 (350)	
(III)	2120 (650)	2057 (600)	2024 (5000)	2008 (4000)	1680 (200)	heptane
			2020 (5600)		1644 (230)	
	2119	2000 (very broad)			1651	nujol mull
					1620 vw	
(IV)	2117 (800)	2055 (1000)	2014 (9000)	2007 (7000)	1654 (900)	heptane

[a] Figures in parentheses are the approximate molecular extinction coefficients. [b] THF = tetrahydrofuran. [c] This peak is very asymmetrical, a second component at about 2000 cm^{-1} is hidden underneath the wing.
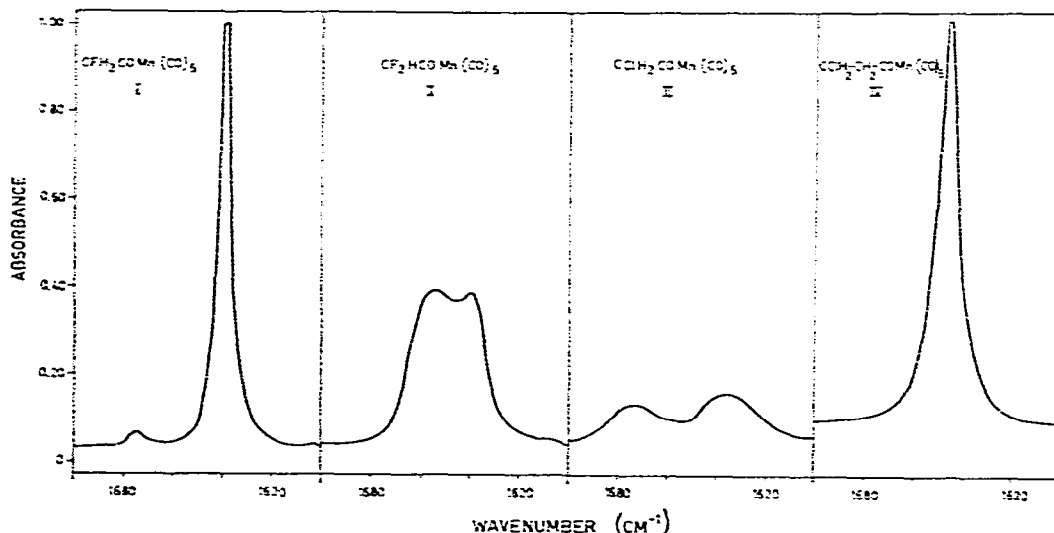

Fig. 2. Infrared spectra of halogen-substituted acylmanganese pentacarbonyls in the 1700–1600 cm^{-1} region. Heptane solutions. The values of $1/c \times l$ are approximately: (I): 1500; (II): 1000; (III): 2500; (IV): 1000 with 0.1 or 1.0 mm cells according to the solubility.

infrared measurements for instance in chloroacetone[9], 1,3-dichloroacetone[10] and ortho-substituted acetophenones[11] and unsaturated ketones[12]. In most cases two carbonyl stretching bands are observed. An exception is diethylketone where the different forms have the same carbonyl frequency[13]. Compound (IV) has also only one band in the ketonic carbonyl stretching region. This does not necessarily mean that it consists of one form only; more probably the different isomers have the same carbonyl absorption as in the case of diethyl ketone[13].

Since there will always be an energy difference between the two (or more) rotational isomers, their population must be temperature dependent. It is often observed that in the crystalline solid only one of the forms persists.

We have therefore measured the spectra of one of the compounds, CF_2HCOMn $(CO)_5$, in heptane solution over a temperature range from $+26°$ to $-32°$. The results are given in Fig. 3. The intensity of the two bands due to the absorption of the ketonic
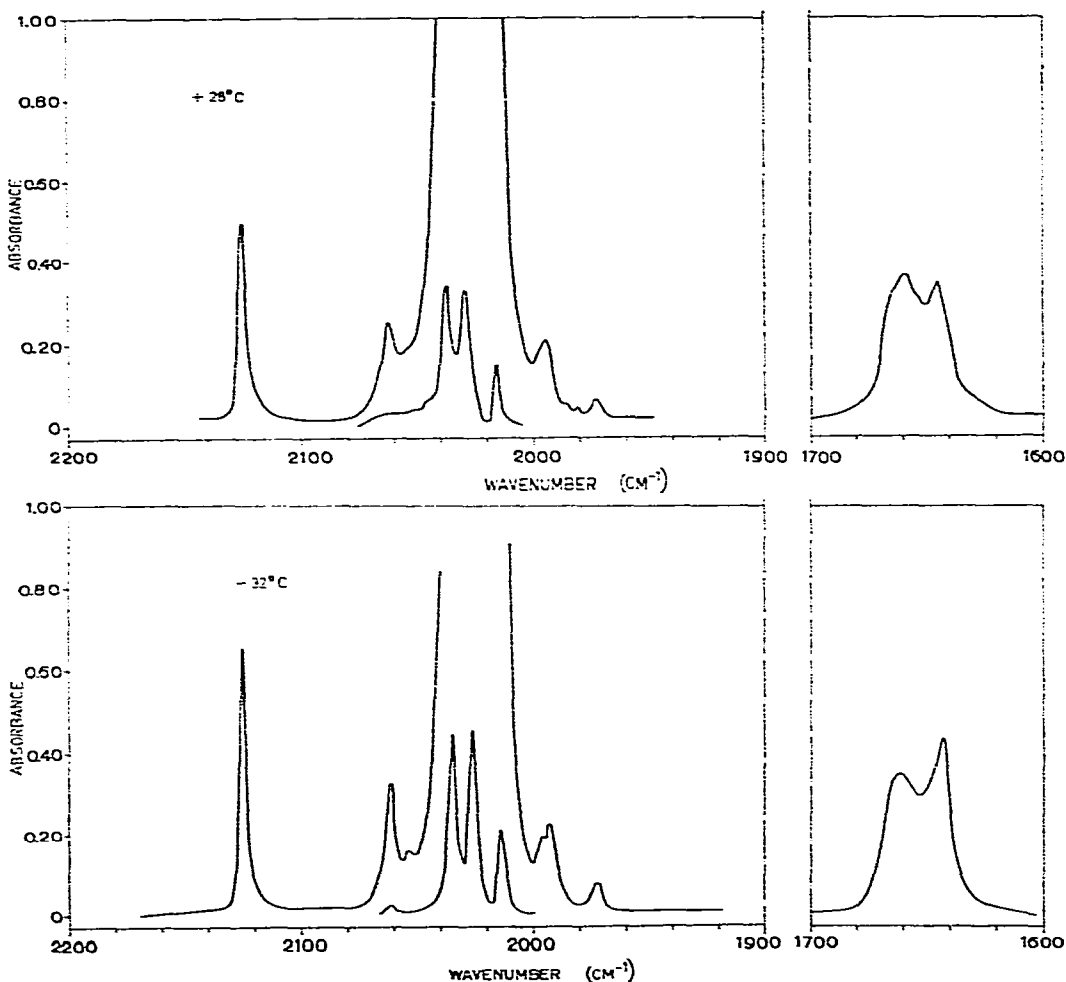

Fig. 3. Infrared spectra in the CO stretching region of $CF_2HCOMn(CO)_5$ at different temperatures (heptane solutions).

carbonyls changes considerably with temperature. In the solid (KBr) only one band persists and is shifted to 1620 cm^{-1}. The terminal CO stretching vibrations are, as expected, not affected by this temperature change.

Compounds of the type $CH_3COMn(CO)_4L$, where L is a bulky group such as iodide or triphenylphosphine, can in principle also give rise to rotational isomers. Of the two possible geometrical isomers, the *cis*-form can in fact consist of different "rotamers" because of the hindered rotation of the $COCH_3$ group around the manganese–carbon bond. The detection of rotational isomers in compounds of the
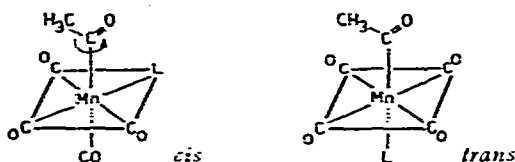
cis   *trans*

type $CH_3COMn(CO)_4L$ would be rather difficult because of the simultaneous presence of the geometrical isomers. However, by studying the infrared spectra at low temperature where the *cis* $\rightleftharpoons$ *trans* equilibrium should be frozen, all the variations observed in the ketonic CO stretching region should be attributed to rotational isomerism phenomena. The check should be given by the invariance of the terminal CO region throughout the cooling process. It is hoped to report in the future about temperature dependence studies of this kind on *cis*- and *trans*-mixtures of $CH_3COMn(CO)_4P(C_6H_5)_3$.

In the region of the terminal CO stretching vibrations all the compounds reported have four or five main bands. For a molecule $LMn(CO)_5$ of C_{4v} symmetry only three infrared active C–O stretching vibrations are predicted from group theory ($2A_1$ and E). However, Wilford and Stone[14] have already pointed out that lower symmetry than C_3 of the alkyl or the acyl groups of alkyl- and acylmanganese pentacarbonyls causes the normally infrared inactive B_1 stretching vibration mode to become infrared active, and the E mode to split into two components. Our assignment in Table 2 follows the one given by Wilford and Stone[14] for similar cases.

Proton magnetic resonance spectra

The pertinent data are shown in Table 3. In all four compounds the observed pattern is the one expected. In each case, only one molecular species is shown in the NMR spectrum, the observed multiplicity being that expected for the coupling of the protons with fluorine [(I), (II)] or with non equivalent protons [(IV)]. In the latter case the observed pattern approximates that expected for an A_2B_2 system.

TABLE 3

PROTON RESONANCE SPECTRA OF ACYLMANGANESE PENTACARBONYLS

Compound	Chemical shift[a]	Multiplicity	J (c/s)	Solvent
$CFH_2COMn(CO)_5$ (I)	5.80[b]	doublet	50	CCl_4
$CF_2HCOMn(CO)_5$ (II)	5.15[b]	triplet	59	CCl_4
$CCIH_2COMn(CO)_5$ (III)	5.36	singlet		CD_3COCD_3
$CCIH_2CH_2COMn(CO)_5$ (IV)	6.60[b]	[c]		CCl_4

[a] In ppm from tetramethylsilane as internal standard expressed in $\tau = 10 - \delta$. [b] Centres of multiplets. [c] This is a spectrum of approximately the A_2B_2 type. The A and B portions of the spectrum are symmetrical with respect to a line at 6.60 τ. Another peak of low intensity at about 8.78 τ is also present, due to some unknown impurities.

In principle the screening constants for the protons of the rotational isomers are different. We should therefore observe the resonances of all the rotamers. This is however only true if the interconversion of one form into the other is relatively slow. If the interconversion is rapid, then the protons are averaged over all possible positions and only an average chemical shift is observed[15]. The fact that we observe only one resonance proves therefore that the interconversion is very rapid in all the four compounds studied, at least at room temperature, where the NMR spectra have been measured. The fact that rotational isomers of the $CXH_2COMn(CO)_5$ are not observed in the NMR spectrum strengthens our previous suggestions[1] that the two proton resonances observed for $CH_3COMn(CO)_4L$ between 7 and 8 τ are due to geometrical isomers*.

SUMMARY

Infrared data in the ketonic CO stretching region including measurements over a wide temperature range show the presence of rotational isomers in acylmanganese pentacarbonyls of the type $CXH_2COMn(CO)_5$, $CX_2HCOMn(CO)_5$ (X = F, Cl). The rate of interconversion between different rotational isomers is high, as indicated by the fact that one single molecular species is shown in the nuclear magnetic resonance spectra of $CXH_2COMn(CO)_5$ and $CX_2HCOMn(CO)_5$. This is taken as further evidence that the two proton resonances observed between 7 and 8 τ in substituted acylmanganese pentacarbonyls of the type $CH_3COMn(CO)_4L$ have to be attributed to the presence of geometrical isomers.

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* Shortly after the appearance of our previous paper[1], Kraihanzel and Maples[16] also reported the presence of two proton resonances between 7 and 8 τ in the NMR spectrum of CH_3COMn-$(CO)_4PPh_3$. The high field peak was assigned by these authors to the trans-isomer.