Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTRA OF ALKYL- AND ACYLMANGANESE PENTACARBONYLS

K. NOACK, U. SCHAERER AND F. CALDERAZZO
Cyanamid European Research Institute, 1223 Cologny/Geneva (Switzerland)

(Received October 1st, 1966)

In the course of our investigations[1-4] on the carbonylation of alkylmanganese pentacarbonyls, we have prepared some new alkyl- and acylmanganese pentacarbonyls (see Table 1), mainly in connection with studies of the kinetic dependence of the carbonylation reaction on the nature of the alkyl group[5]:

$$RMn(CO)_5 + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RCOMn(CO)_5 \qquad (1)$$

We report here on the properties of these compounds, in particular their high resolution infrared and proton resonance spectra. The spectra of several other alkyl- and acylmanganese pentacarbonyls are also reported, and compared with those obtained for the new compounds.

EXPERIMENTAL

The melting points are uncorrected. The specific rotations of the optically active compounds were measured with a ETL-NPL Bendix Type 143 A automatic polarimeter in 2.5 cm cells.

The infrared spectra were measured with a Perkin–Elmer spectrophotometer Mod. 521. The spectra were recorded on expanded abscissa scale and each spectrum calibrated with CO. The limit of accuracy for narrow bands is believed to be ±0.5 cm^{-1}. All the spectra in the carbonyl stretching region were measured in n-heptane which gives the narrowest bands and therefore the best resolution of close lying bands. The molar extinction coefficients given in Tables 3 and 4 are only approximate, the error being probably ±10%. The spectral slit width with the slit programme 700 is about 1 cm^{-1} in the region of the carbonyl stretching bands.

The nuclear magnetic resonance spectra were measured with a DP60A Varian instrument using tetramethylsilane as internal standard.

Decacarbonyldimanganese was prepared by a previously described[6] procedure. Sodium pentacarbonylmanganate was prepared by reduction of $Mn_2(CO)_{10}$ with sodium sand in tetrahydrofuran.

All the compounds reported in Table 1 are new. All the acylmanganese pentacarbonyls, except $CF_3COMn(CO)_5$, were prepared from $NaMn(CO)_5$ and acyl chlorides in diethyl ether at low temperature ($\sim -10°$). In the case of $CF_3COMn(CO)_5$, trifluoroacetic acid anhydride was used as acetylating agent[7]. All the fluorine containing acyl compounds were prepared in a nitrogen atmosphere. The other acyl

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF ACYL- AND ALKYLMANGANESE PENTACARBONYLS

Compound	*Colour*	*M.p.(°C)*[a]	*Analysis found (calcd.)(%)*	
			C	*H*
$(CH_3)_3CCOMn(CO)_5$ (I)	yellow	78-79	42.80 (42.88)	2.71 (3.24)
$CH_3CH_2CH_2COMn(CO)_5$ (II)	yellow	44–45	40.42 (40.62)	2.46 (2.65)
$(CH_3)_2CHCOMn(CO)_5$ (III)	yellow	57–58	40.30 (40.62)	2.85 (2.65)
$(+)C_6H_5CH_2CH(CH_3)COMn(CO)_5$ (IV)	yellow	46–47	52.35 (52.65)	3.33 (3.24)
$CH_3CH_2COMn(CO)_5$ (V)	pale yellow	58–59	37.66 (38.12)	2.17 (2.00)
$C_6H_5CH_2COMn(CO)_5$ (VI)	colourless	111–113	50.25 (49.71)	2.45 (2.25)
p-$CH_3OC_6H_4COMn(CO)_5$ (VII)	pale yellow	94–95	47.21 (47.30)	2.32 (2.14)
p-$FC_6H_4COMn(CO)_5$ (VIII)[b]	yellow	95–96	45.62 (45.31)	1.59 (1.27)
$CH_2FMn(CO)_5$ (IX)	yellow	86–87	31.65 (31.61)	0.97 (0.88)
$CHF_2Mn(CO)_5$ (X)	yellow	49–50	29.34 (29.29)	0.66 (0.41)

[a] The acyl derivatives melt with gas evolution. [b] Fluorine found 6.28%, calcd. 5.97%.

compounds were prepared under an atmosphere of carbon monoxide in order to prevent the reverse of reaction (1). After elimination of sodium chloride (or $NaOOCCF_3$) by filtration, the acyl derivatives were crystallized by cooling the filtered solution at about −80°.

The optically active compound (IV) was obtained from $C_6H_5CH_2CH(CH_3)$-COCl* [$[\alpha]_D^{19} = +20.8°$, 2.12% solution in $CHCl_3$ (lit.[8] $[\alpha]_D^{20} = 26.28°$)] and $NaMn(CO)_5$ in diethyl ether. The manganesepentacarbonyl complex has $[\alpha]_D^{30} = 75.1°$ (1.027% solution in 2,2′-diethoxydiethyl ether).

The fluoroalkyl derivatives (IX), (X), and $CF_3Mn(CO)_5$[7] were prepared by repeated decarbonylation of the corresponding acyl compounds at 90–130° until disappearance of the ketonic CO stretching vibration band in the infrared spectrum. They were then purified by sublimation.

The benzyl derivative $C_6H_5CH_2Mn(CO)_5$ was prepared according to the procedure described by Closson, Kozikowski and Coffield[9], from benzyl chloride and $NaMn(CO)_5$ in diethyl ether. After elimination of NaCl by filtration, the filtrate was cooled to −80°. The crystalline yellow compound melted at 36–37° in a sealed capillary (lit.[9] 37.5–38.5°).

Methylmanganesepentacarbonyl was prepared from $NaMn(CO)_5$ and dimethyl sulphate in diethyl ether according to a previously described procedure[1].

Phenylmanganese pentacarbonyl was obtained by repeated decarbonylation[10] of $C_6H_5COMn(CO)_5$ at 80–90°, followed by sublimation at 95°/*ca.* 12 mm Hg (m.p. 50–52°, lit.[10] 52°).

---

* We thank Prof. RALPH L. DANNLEY, Western Reserve University, Cleveland, Ohio, for a generous sample of $(+)C_6H_5CH_2CH(CH_3)COOH$.

RESULTS AND DISCUSSION

A. Proton resonance spectra

The proton resonance data on the compounds reported in this paper are given in Table 2.

TABLE 2

PROTON RESONANCE DATA OF ACYL- AND ALKYLMANGANESE PENTACARBONYLS

$Mn(CO)_5$ compound	*Chemical shift*[a]	*Multiplicity*[b]	*J (c/s)*	*Assignment*	*Solvent*
$(CH_3)_3CCO$-	8.89	singlet		CH_3	CCl_4
$CH_3CH_2CH_2CO$-	7.15	triplet	6.5	α-CH_2	CCl_4
	8.15–9.25	approx. A_2B_3 spect.		$CH_3+\beta$-CH_2	
$(CH_3)_2CHCO$-	6.95	quintet	6.5	CH	CCl_4
	8.98	asym. doublet	6.5	CH_3	
	6.76	quintet	6.5	CH	CD_3COCD_3
	9.00	asym. doublet	6.5	CH_3	
CH_3CH_2CO-[c]	7.02	quartet	7	CH_2	CD_3COCD_3
	9.09	triplet	7	CH_3	
CH_3CO-[d]	7.42	singlet		CH_3	CCl_4
$C_6H_5CH_2CO$-	2.77	sing.; some struct.		C_6H_5	CD_3COCD_3
	5.76	singlet		CH_2	
p-$CH_3OC_6H_4CO$-	2.75	sym. pair of doub.	8	C_6H_5	CD_3COCD_3
	6.15	singlet		CH_3	
p-FC_6H_4CO-	2.28–2.93	seven peaks		C_6H_5	CD_3COCD_3
$ClCH_2CH_2CO$-[e]	6.60	approx. A_2B_2 spect.		α-$CH_2+\beta$-CH_2	CCl_4
$ClCH_2CO$-[e]	5.36	singlet		CH_2	CD_3COCD_3
CFH_2CO-[e]	5.80	doublet	50		CCl_4
CF_2HCO-[e]	5.15	triplet	59		CCl_4
CH_3-[f]	10.11	singlet			CCl_4
$C_6H_5CH_2$-	2.93	asym. peak		C_6H_5	CCl_4
	7.64	singlet		CH_2	
	2.84	asym. peak		C_6H_5	CD_3COCD_3
	7.58	singlet		CH_2	
C_6H_5-	2.33–3.03	complex band			CD_3COCD_3
CH_2F-	4.38	doublet	47.5		CCl_4
CHF_2-	2.77	triplet	48.5		CCl_4

[a] From tetramethylsilane (10τ) as internal standard. [b] Centres of symmetrical multiplets or positions of the peak maxima. [c] In ref. 15, resonances for CH_2 and CH_3 groups are given at 7.04 and 9.08 τ, respectively (CH_2Cl_2 solution). [d] The peak is at 7.40 τ in $CDCl_3$ and CD_3COCD_3 in ref. 2. [e] Taken from ref. 3. [f] Taken from ref. 2 and 15.

In general the NMR patterns observed in compounds containing non equivalent protons are in agreement with the expected electron coupled spin–spin interactions. The more complex NMR spectra are reported in Fig. 1 and 2. Thus, FC_6H_4-$COMn(CO)_5$ [Fig. 1(d)] gives a number of lines which approximates that observed in an A_2B_2X spectrum, for example, p-fluoroaniline[11].

The proton resonance spectrum of (p-methoxybenzoyl)manganese pentacarbonyl [see Fig. 1(c)] has four lines for the phenyl protons, resembling more an AB spectrum than an A_2B_2 one[12]. We believe this to be due to the low resolution which did not make the observation of the further splitting of the lines possible in this particular case. The alternative explanation of the coupling constants between opposite protons being zero appears less probable.

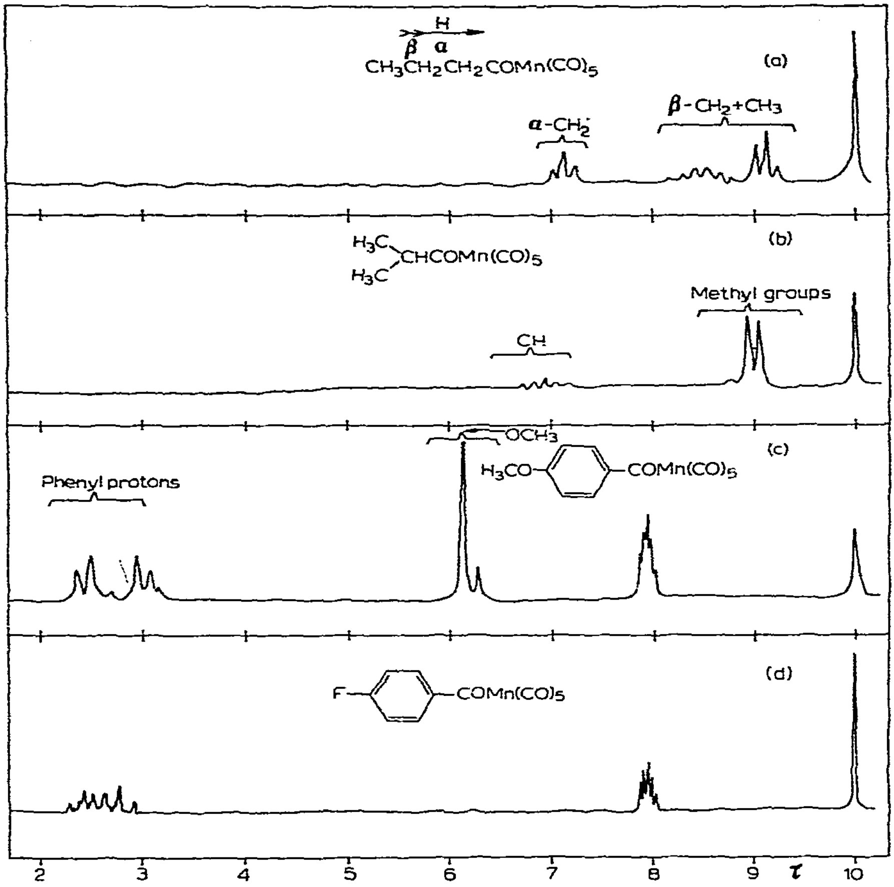

Fig. 1. Proton resonance spectra of some acylmanganese pentacarbonyls with tetramethylsilane as internal standard; (a) CCl_4 solution; (b) CCl_4 solution; (c) deuteroacetone solution [the additional low intensity peaks are due to small amounts of the decarbonylated compound, p-$CH_3OC_6H_4Mn(CO)_5$.]; (d) deuteroacetone solution. The band at about 8 τ in the deuteroacetone spectra is due to small amounts of partially deuterated acetone.

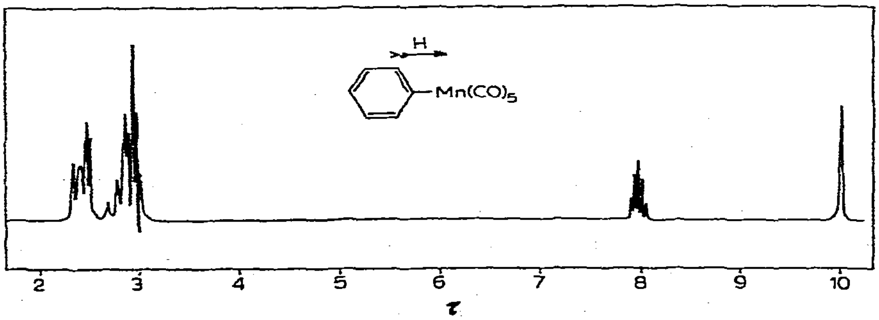

Fig. 2. Proton resonance spectrum of $C_6H_5Mn(CO)_5$ in deuteroacetone solution.

In Fig. 2 the proton magnetic resonance spectrum of $C_6H_5Mn(CO)_5$ is shown. This is believed to be the first detailed proton resonance spectrum of a phenyl group σ-bonded to a metal carbonyl residue to be reported in the literature. King and Bisnette[13] mentioned that the phenyl protons of $C_6H_5FeC_5H_5(CO)_2$ absorb at 2.74 and 3.22 τ (multiplets), but no further details were given by these authors.

The chemical shifts of alkyl- and acylmanganese pentacarbonyls containing equivalent protons are of particular interest. Let us consider the proton resonances of the alkyl derivatives first. Unfortunately, the number of stable alkylmanganese pentacarbonyls containing a saturated aliphatic chain is rather limited. Their stability appears to decrease drastically with increasing size of the alkyl residue. The methyl derivative, $CH_3Mn(CO)_5$, is very stable provided it is kept in the absence of carbon monoxide. A relatively easy conversion into the corresponding acetyl derivative, $CH_3COMn(CO)_5$, takes place in the presence of carbon monoxide. The corresponding conversion of the ethyl derivative into $C_2H_5COMn(CO)_5$ was calculated[5] to occur with a rate constant roughly thirteen times larger than for $CH_3Mn(CO)_5$. The ethyl derivative was prepared by Green and Nagy[14] and by Davison, McCleverty and Wilkinson[15] and its nuclear magnetic resonance spectrum measured. The compound, however, rearranges very rapidly to the corresponding propionyl derivative even in an atmosphere of nitrogen[16,17].

Alkylmanganese pentacarbonyls containing fluorine atoms on the α-carbon atom, such as $CF_2HMn(CO)_5$ and $CFH_2Mn(CO)_5$ are, on the other hand, kinetically rather inert with respect to their conversion into the corresponding acyl derivatives. Their nuclear magnetic resonance spectra could therefore be measured without difficulty.

From the NMR data obtained on alkylmanganese pentacarbonyls, it can be

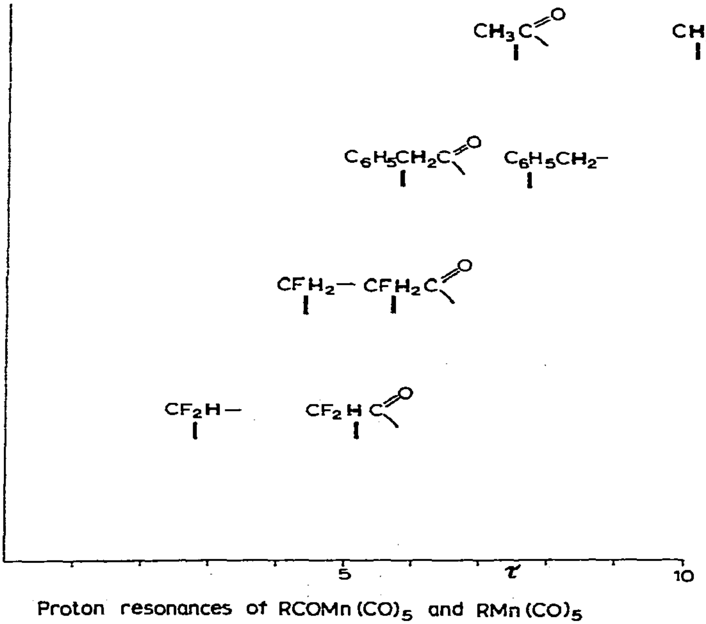

Fig. 3. Proton chemical shifts of some acyl- and alkylmanganese pentacarbonyls. The protons to which the τ values refer are in bold-face type. All the values refer to measurements done in CCl_4 solutions.

TABLE 3

CARBONYL AND AROMATIC C=C STRETCHING FREQUENCIES AND MOLAR EXTINCTION COEFFICIENTS OF ACYLMAGANESE PENTACARBONYLS[a]

$Mn(CO)_5$ compound	$\nu(CO)_{carbonyl}$ (cm^{-1}) A_1	B_1	E	A_1	^{13}CO	$\nu(CO)_{acyl}$ (cm^{-1})	$\nu(C{=}C)$ (cm^{-1})
$(CH_3)_3CCO$-	2111 (800)	2045 (2500)	2013 (8400) 2006 (9000)	1994 (4500)	1948[b] (600)	1651 (390) 1619 (180)	
$CH_3CH_2CH_2CO$-	2112 (700)	2046 (1000)	2010 sh (7000) 2006 (8000)	2000 (7500)	1983 sh (200) 1968 (200) 1962 (150)	1651 (500)	
$(CH_3)_2CHCO$-	2112 (900)	2048 (1300)	2010 sh (7500) 2006 (8500)	2000 (7000)	1983 sh (300) 1968 (200) 1961 (120)	1663 (650) 1630 (150)	
(+)$C_6H_5CH_2$-$CH(CH_3)CO$-	2112 (600)	2050 (900) 2044 (1000)	2013 (6500) 2006 sh (4500)	1999 (4800)	1983 (500) 1966 (150) 1956 (70)	1652 sh[c]	1644 (300)
CH_3CH_2CO	2111 (650)	2046 (800)	2005 (8300)	1999 (7000)	1968 (200) 1960 (120)	1656 (750)	
$C_6H_5CH_2CO$-	2114 (1200)	2053 (1200)	2014 (10000) 2000 (5500)	1991 (1200)		1650 (500)	[d]
p-$CH_3OC_6H_4CO$-	2116 (1200)	2055 (800)	2010 (6200)	2003 (5200)	1985 (200) 1974 (150) 1966 (150)	1653 (100)	1614 (300) 1586 (250)
p-FC_6H_4CO-	2116 (1500)	2055 (1300)	2010 (8000)	2003 (6600)	1975 (200) 1967 (200) 1958 (100)	1656 (100)	1616 (350) 1586 (250)

[a] Heptane solutions. Numbers in parenthesis are molar extinction coefficients. [b] Another band is present at 1983 cm^{-1} with a molar extinction coefficient of 2000. The origin of this band is unknown. [c] The ketonic CO stretching vibration appears as a shoulder of a stronger band due to the carbon-carbon stretching of the phenyl ring. [d] The C=C stretching vibration is of low intensity and it was not observed at the concentration used for the other bands.

seen that the proton resonances for alkyl groups bonded to manganese range from 10.11 τ [$CH_3Mn(CO)_5$] to 2.77 τ [$CF_2HMn(CO)_5$] (see Table 2 and Fig. 3). The electronegativity of the fluorine atoms is certainly important in determining the extent of the diamagnetic current and consequently the decreased shielding of the protons. This is not, however, the only cause of the very low values of chemical shifts observed in $CH_2FMn(CO)_5$ and $CHF_2Mn(CO)_5$. That this is so is shown by the fact that the proton magnetic resonances of the corresponding acyl derivatives are contained in a much narrower range, from 7.40 τ [$CH_3COMn(CO)_5$] to 5.15 τ [$CF_2HCOMn(CO)_5$]. This corresponds roughly to the chemical shift difference found between CH_3COCl (7.33 τ in $CHCl_3$) and CF_2HCOCl (4.09 τ as 2.5% CCl_4 solution). We believe that the large chemical shift difference observed in the series of alkylmanganese pentacarbonyls is caused by an abnormally high magnetic deshielding in the case of the fluorine substituted compounds. From this arises the most interesting peculiarity observed in the nuclear magnetic resonance spectra of these compounds. As shown in Fig. 3 in a schematic manner, the proton resonances of the acyl derivatives not containing fluorine are at lower fields compared with the corresponding alkyl compounds, whilst in the fluorine-substituted derivatives the situation is reversed. Although a metal proximity effect is intuitively responsible for this, the precise interpretation of the abnormally low chemical shifts would require a very elaborate treatment of the particular case, which is beyond the scope of the present paper. We can, however, tentatively suggest that our proton magnetic resonance data for the fluorine substituted alkylmanganese pentacarbonyls could be correlated with an increased metal–carbon bond order. There is considerable agreement on the fact that the metal–carbon bond in certain perfluoroalkyl metal complexes is stronger than in the corresponding alkyl metal complexes[18]. In the case of $CF_3Mn(CO)_5$, withdrawing of electrons from the filled *d*-orbitals of manganese to C–F antibonding orbitals was suggested to occur[18]. It is worth mentioning that Pritcher, Buckingham and Stone[19] have also observed large ^{19}F chemical shifts to low field for the CF_2 groups in the α-position in a number of completely fluorinated alkyl metal carbonyls. To the best of our knowledge this is the first time that proton resonance spectra of partially fluorinated alkyl metal carbonyls are reported in the literature.

The relevance of these nuclear magnetic resonance data for the interpretation of the kinetics of reaction (1) will be discussed in a forthcoming publication.

B. Infrared spectra

The frequencies and maximum molecular extinction coefficients of the carbonyl stretching bands are given in Tables 3 and 4.

The compounds studied can be divided into two groups:

1. Acylmanganese pentacarbonyls, $RCOMn(CO)_5$ (Table 3)
2. Alkylmanganese pentacarbonyls, $RMn(CO)_5$ (Table 4)

Both groups fall into the category of monosubstituted pentacarbonyls with approximate octahedral configuration. Several papers have recently appeared on the infrared spectra of compounds of this symmetry[20–23].

If the $Mn(CO)_5$ grouping has C_{4v} symmetry, one should observe three infrared active carbonyl stretching vibrations ($E+2A_1$). When the overall symmetry is lowered by the substituent, the degeneracy of the E vibration may be suppressed and the B_1 vibration may become infrared active. In the first group of compounds the

TABLE 4

CARBONYL AND AROMATIC C=C STRETCHING FREQUENCIES AND MOLAR EXTINCTION COEFFICIENTS OF ALKYLMANGANESE PENTACARBONYLS[a]

$Mn(CO)_5$	*$\nu(CO)$ (cm^{-1})*					*$\nu(C=C)_{arom.}$*[d]
compound	*A_1*	*B_1*	*E*	*A_1*	^{13}CO	(cm^{-1})
CH_3-[b]	2110 (350)		2012.5 (26000)	1991 (5600)	1976 (600)	
CH_2F-	2119 (300)	2053 (450) 2045 (350)	2019 (6300)	2000 (5200)	1983, 1980 (200) 1960 (100)	
CHF_2-	2127 (300)	2062 (400) 2044 sh (600)	2029 (12000)	2010 (6000)	1982 (300) 1968 (50)	
CF_3-[c]	2136 (200)	2068 sh (150)	2044 (21000)	2019 (5000)	2007 (500) 1977 (80)	
$C_6H_5CH_2$-	2106 (1300)	2041 (300)	2015 (9200) 2007 (9000)	1990 (5700)	1973 (300) 1949 (150)	1599 (90) 1578 (20)
C_6H_5-	2114 (1000)	2043 (300)	2019 (12500)	1997 (6000)	1984 (500) 1954 (100)	1570 (150) 1566 sh
p-FC_6H_4-	2116 (1100)		2021 (12000)	2000 (6000)	1986 (300) 1959 (100)	1605 (50) 1587 (50) 1573 (90)

[a] Heptane solutions. Numbers in parenthesis are molar extinction coefficients. [b] Spectrum reported also in ref. 23. [c] Spectrum reported also in ref. 7. [d] C_2Cl_4 solutions.

acyl residue alters the symmetry of the molecule so much that the B_1 vibration becomes infrared active and in most cases a splitting of the E vibration can be detected. The assignments follow those given by Orgel[20] or by Wilford and Stone[23]. The highest band at about 2110 cm^{-1} with an extinction coefficient of about 500 to 1000 is the breathing vibration of the four carbon monoxide groups (A_1); the other A_1 band lies at about 2000 cm^{-1} and has a much higher intensity ($\varepsilon \sim 5000$–7000). The E mode consists clearly of the two components at about 2010 cm^{-1} with the highest intensity of all. The splitting of the E mode is between zero and 14 cm^{-1} depending on the nature of the R group of $RCOMn(CO)_5$. The B_1 band has again a rather low intensity of about 1000 and is situated around 2050 cm^{-1}. The magnitude of the splitting between the components of the E mode and the intensity of the B_1 mode seem to be rather independent, since the latter is present with almost the same intensity in all the acyl compounds. For the simplest compound of this type, $CH_3COMn(CO)_5$, our data in heptane solution are: 2115 cm^{-1} ($\varepsilon = 700$), 2051 (900), 2011 (10,000), 2003 (7000), 1971 ($\sim$200), 1664 (1500). These frequencies agree very well with those given by Beck, Hieber and Tengler[7]. In this case, there is no splitting of the E band observed, but the B_1 band appears with the same intensity as in all the other acyl pentacarbonyls.

The general appearance of the spectra of acylmanganese pentacarbonyls is very similar and the frequencies of the terminal CO stretching vibrations are rather insensitive to the nature of the R group. An exception to this is represented by the halogen substituted acylmanganese pentacarbonyls[3], where all the terminal CO stretching vibrations are shifted to higher frequencies. The shift is due to the lowering of the electron density on manganese by the inductive effect of the halogens. It is interesting to note that this effect operates even if the fluoroalkyl group is separated from the metal by the acyl group. As will be shown later, however, the shift is almost twice as big for the fluoroalkyl than for the (fluoroacyl)manganese pentacarbonyls.

The two acyl derivatives, p-$CH_3OC_6H_4COMn(CO)_5$ and p-$FC_6H_4COMn(CO)_5$, are readily decarbonylated in solution. Their infrared spectra always contained some bands due to the decarbonylated products. These extra bands were, however, easily recognised by their increasing intensity with time.

It is interesting to note that in most of the compounds the ^{13}CO bands corresponding to the E and the lower A_1 mode are clearly observed. In Table 3 three bands are reported as ^{13}CO stretchings for some of the compounds. Probably only two of them are genuine ^{13}CO stretching vibrations. The origin of the third band is unknown.

In the region of the ketonic CO stretching vibration one single band is observed in $CH_3CH_2CH_2COMn(CO)_5$ and $CH_3CH_2COMn(CO)_5$. In $(CH_3)_3CCOMn(CO)_5$ and $(CH_3)_2CHCOMn(CO)_5$, there are, however, two distinct bands. Their relative intensities in heptane solution are reversed in nujol or KBr. It has not been investigated whether the two ketonic bands are due to rotational isomers. This was previously shown[3] to be the case for $CH_2FCOMn(CO)_5$, $CHF_2COMn(CO)_5$ and $CH_2ClCOMn(CO)_5$. However, it seems difficult to imagine for $(CH_3)_3CCOMn(CO)_5$ the possibility of rotational isomerism. Fermi resonance with the first harmonic of the strong band observed at 860 cm^{-1} could be operative in this particular case. In the four compounds containing aromatic substituents some of the bands around 1600 cm^{-1} are due to the C=C stretching modes of the aromatic ring. These vibrations can interact with the ketonic C=O stretching vibration. This could account for the rather low intensity of the latter in some of the compounds. The C=C stretching bands on the other hand are stronger in aroyl- than in arylmanganese pentacarbonyls (see Table 4).

In the second group of compounds, $RMn(CO)_5$, the alkyl group is directly bonded to manganese. The same symmetry considerations as before apply also to these compounds. In all but two of the compounds investigated, the C_{4v} symmetry is so much distorted that the B_1 mode becomes infrared active. The E mode splits only in the case of $C_6H_5CH_2Mn(CO)_5$. The origin of the weak band or shoulder at 2044 cm^{-1} in $CH_2FMn(CO)_5$ and $CHF_2Mn(CO)_5$ is not known.

To distinguish more clearly the influence of the fluorine atoms on the stretching vibrations of the terminal CO groups, the spectra of fluorine-substituted alkylmanganese pentacarbonyls should be compared with those of $CH_3Mn(CO)_5$ (see Table 4). Each additional fluorine increases all the frequencies by about 10 cm^{-1}. This is due, as discussed above in the case of the fluorine substituted acetylmanganese pentacarbonyls, to the inductive effect of the fluorine atoms. The magnitude of the shift is almost twice that of the (fluoroacyl)manganese pentacarbonyls: the total shift of the highest A_1 band from methyl- to (trifluoromethyl)manganese pentacarbonyl is 26 cm^{-1}, from acetyl- to (trifluoroacetyl)manganese pentacarbonyl 15 cm^{-1}.

One further observation is worth mentioning. In the spectra of heptane solutions of methylmanganese pentacarbonyl and of (p-fluorophenyl)manganese pentacarbonyl, the B_1 band is clearly absent or better, if it is present, its extinction coefficient is smaller than 50. But in diethoxydiethyl ether, bands at 2044 cm^{-1} ($\varepsilon = 300$) and at 2055 cm^{-1} ($\varepsilon = 500$), respectively, are observed in the two compounds. This would indicate that diethoxydiethyl ether interacts strongly with these complexes, altering the symmetry enough to bring about the appearance of the otherwise inactive B_1 mode. No systematic investigation has been made to test the generality of this observation.

SUMMARY

Several new acyl- and alkylmanganese pentacarbonyls of general formula $XMn(CO)_5$ [$X = (CH_3)_3CCO$, $CH_3CH_2CH_2CO$, $(CH_3)_2CHCO$, $C_6H_5CH_2CH(CH_3)CO$, CH_3CH_2CO, $C_6H_5CH_2CO$, p-$CH_3OC_6H_4CO$, p-FC_6H_4CO, CH_2F and CHF_2] are described. The proton magnetic resonance and infrared spectra of these and other compounds of the same class are also reported. The fluorine-substituted alkylmanganese pentacarbonyls ($X = CH_2F$ and CHF_2) show chemical shifts to low field considerably larger than expected for the electronegativity of the fluorine atoms. The large chemical shift to lower fields can be tentatively regarded as an evidence for the presence of a metal–carbon bond order higher than one in the fluorine substituted compounds.

The number and the intensity of the observed infrared carbonyl stretching vibrations are in agreement with a slightly distorted C_{4v} symmetry for the compounds.

REFERENCES

1 F. CALDERAZZO AND F. A. COTTON, *Inorg. Chem.*, 1 (1962) 30.
2 F. CALDERAZZO AND K. NOACK, *J. Organometal. Chem.*, 4 (1965) 250.
3 F. CALDERAZZO, K. NOACK AND U. SCHAERER, *J. Organometal. Chem.*, 6 (1966) 265
4 F. CALDERAZZO AND K. NOACK, *Organometal. Chem. Rev.*, 1 (1966) 118.
5 F. CALDERAZZO AND F. A. COTTON, *Proc. 7th ICCC*, Stockholm and Upssala, June 25–29, 1962, p. 296.
6 F. CALDERAZZO, *Inorg. Chem.*, 4 (1965) 293.
7 W. BECK, W. HIEBER AND H. TENGLER, *Chem. Ber.*, 94 (1961) 862.
8 R. H. PICKARD AND J. YATES, *J. Chem. Soc.*, (1909) 1011.
9 R. D. CLOSSON, J. KOZIKOWSKI AND T. H. COFFIELD, *J. Org. Chem.*, 22 (1957) 598.
10 T. H. COFFIELD, J. KOZIKOWSKI AND R. D. CLOSSON, *J. Org. Chem.*, 22 (1957) 598.
11 R. E. RICHARDS AND T. SCHAEFER, *Proc. Roy. Soc.*, A 246 (1958) 429.
12 R. E. RICHARDS AND T. P. SCHAEFER, *Trans. Faraday Soc.*, 54 (1958) 1280.
13 R. B. KING AND M. B. BISNETTE, *J. Organometal. Chem.*, 2 (1964) 15.
14 M. L. H. GREEN AND P. L. I. NAGY, *J. Organometal. Chem.*, 1 (1963) 58.
15 A. DAVISON, J. A. MCCLEVERTY AND G. WILKINSON, *J. Chem. Soc.*, (1963) 1133.
16 F. CALDERAZZO, unpublished observation.
17 W. HIEBER, G. BRAUN AND W. BECK, *Chem. Ber.*, 93 (1960) 901.
18 F. A. COTTON AND J. A. MCCLEVERTY, *J. Organometal. Chem.*, 4 (1965) 490 and references therein.
19 E. PITCHER, A. D. BUCKINGHAM AND F. G. A. STONE, *J. Chem. Phys.*, 36 (1962) 124.
20 L. E. ORGEL, *Inorg. Chem.*, 1 (1962) 25.
21 M. A. EL-SAYED AND H. D. KAESZ, *J. Mol. Spectry.*, 9 (1962) 310.
22 F. A. COTTON, *Inorg. Chem.*, 3 (1964) 702.
23 J. B. WILFORD AND F. G. A. STONE, *Inorg. Chem.*, 4 (1965) 389.