Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

VIBRATIONAL SPECTRA OF σ-ALLYLMANGANESE PENTACARBONYL

HENRY L. CLARKE and NOEL J. FITZPATRICK
Department of Chemistry, University College, Dublin 4 (Ireland)

(Received March 1st, 1972)

SUMMARY

The vibrational spectra of σ-$(C_3H_5)Mn(CO)_5$ are reported. Assignment of bands is made and carbonyl force constants are calculated. The results indicate that the $Mn(CO)_5$ moiety has C_{4v} symmetry. The calculated angle between the axial and equatorial carbonyl groups is approximately 95°. The bonding in this compound is very similar to that in $(CH_3)Mn(CO)_5$.

In the far-infrared region, seven bands are expected in C_{4v} symmetry ($3A_1+4E$), and all are observed.

INTRODUCTION

Partial infrared studies of $LMn(CO)_5$ have been reported. $HMn(CO)_5$ has been studied in the carbonyl stretching region by Kaesz and co-workers[1,2]. Complexes with L other than H have been considered by various researchers in the same spectral region[3-6]. Recently other regions of the infrared spectrum have been reported. Cattrall and Clark[7] have studied the spectra of $LMn(CO)_5$ in the 700–200 cm^{-1} frequency region. Adams and Squire[8] have also considered the spectra of $LMn(CO)_5$ in the far infrared region. $HMn(CO)_5$ in the middle and low frequency range has been reported[9]. However, σ-allylmetal carbonyl systems have been little investigated. Both McClellan and co-workers[10] and King and co-workers[11] give some infrared frequencies for σ-$(C_3H_5)Mn(CO)_5$ but full assignments were not made.

RESULTS AND DISCUSSION

σ-$(C_3H_5)Mn(CO)_5$, carbonyl stretching region

The vibrations of the $Mn(CO)_5$ moiety are treated by the method of localised symmetry. They can be described approximately as CO stretching modes (≈2000 cm^{-1}), metal–carbon–oxygen bending modes (≈600 cm^{-1}), metal–carbon stretching modes (≈400 cm^{-1}) and carbon–metal–carbon bending modes (≈100 cm^{-1}). In this section the carbonyl stretching vibrations are discussed.

The 2200–1900 cm^{-1} region of the IR spectrum of σ-$(C_3H_5)Mn(CO)_5$ in cyclohexane and the Raman spectrum in benzene in the same region are given in Table 1, along with the symmetry modes and force constants. The latter are non-

TABLE 1

σ-(C_3H_5)Mn(CO)$_5$, CARBONYL REGION

Band (cm^{-1})		*C_{4v} symmetry mode*	*Force constants*		*Parameters of Manning and Miller*[14]
IR (cyclohexane)	*Raman (benzene)*		*Cotton–Kraihanzel*[12]	*Bor*[13]	
2109 m	2111 m	A_1(eq)	k_{ax} 15.92	16.43	$p=1.945$
2047 m	2047 m	B_1	k_{eq} 16.91	16.78	$\rho=0.242$
2014 vs	2020 m	E	k_i 0.26	0.197 (eq)	$\theta=95.3°$
1992 s	1991 m	A_1(ax)		0.254 (ax)	

rigorous and were calculated by the Cotton–Kraihanzel[12] and Bor[13] methods. In this Table p and ρ values, as defined by Manning and Miller[14], are given, which were used to calculate the angle (θ) between the axial and equatorial carbonyls in C_{4v} symmetry. In these calculations the Cotton–Kraihanzel force constants were used.

The positions of the bands agree excellently with those reported by Kaesz and co-workers[11] (in tetrachloroethylene). However, this group reports an additional very weak band at 1926 cm^{-1}. In the carbonyl region of LMn(CO)$_5$ a band corresponding to 1926 cm^{-1} is not given[3], as the lowest reported band is at 1949 cm^{-1}.

The assignments of the bands were made bearing in mind that mixing occurs and that therefore the separation into two A_1 modes is not strictly correct. The possible symmetries of the Mn(CO)$_5$ moiety are C_{4v}, C_{2v} and C_s. In C_{4v} the allyl group if it perturbs the equatorial carbonyl groups does so in a symmetrical manner. In C_{2v} symmetry pairs of equatorial carbonyls are perturbed and in C_s symmetry only one equatorial group is perturbed.

C_{4v}	C_{2v}	C_s
$2A_1+E+B_1$	$3A_1+B_1+B_2$	$4A'+A''$

C_{4v} symmetry is adequate to explain the observed spectrum of σ-(C_3H_5)-Mn(CO)$_5$ reported in Table 1. Whether a perturbation produces C_{2v} or C_s symmetry cannot be determined from the infrared spectrum, since in both cases five allowed bands are expected. Assignment of the vibrational modes is aided by utilising the symmetry coordinates below, where r_5 corresponds to stretching of the axial carbonyl.

$$S_{A_1}(\text{eq})=\tfrac{1}{2}(r_1+r_2+r_3+r_4)$$

$$S_{A_1}(\text{ax})=r_5$$

$$S_E=\frac{1}{\sqrt{2}}(r_1-r_3);\quad \frac{1}{\sqrt{2}}(r_2-r_4)$$

$$S_B=\tfrac{1}{2}(r_1-r_2+r_3-r_4)$$

The most intense band in the infra-red corresponds to the E mode[15]. Orgel[16] notes that using an idealised system, this vibration accounts for approximately 80% of the absorption. The two A_1 vibrations consist of the vibration of the axial carbonyl and the symmetrical breathing mode of the equatorial groups. Assuming an ideal situation the former would account for the remaining 20% of the absorption. The weaker A_1 band is expected to have the highest frequency, as four carbonyls are being stretched simultaneously. Thus the IR band at 2109 cm^{-1} corresponds to the A_1(eq) mode. Cotton and Kraihanzel[12] assume that $k_{eq} > k_{ax}$ and $k_i > 0$, thus the A_1(eq) assignment is justified as the A_1 band with higher frequency. The lowest frequency band is assigned to the A_1(ax) mode as only one carbonyl is being stretched. The B_1 band is forbidden in the infrared in C_{4v} symmetry, however its appearance is indicative of a slight perturbation. A small mechanical coupling of the carbonyls and the allyl group would enable the B_1 to gain intensity without splitting the E mode[12]. The B_1 band is allowed in the Raman.

The assignments in Table 1 are in accord with those of other authors for $LM(CO)_5$[1-3]. In $LMn(CO)_5$, with L=H, Cl the B_1 band was not seen in the IR. However with L=Br, I the band was observed[1,3]. Thus steric factors influence the appearance of the B_1 mode. A comparison of the spectrum with that reported[3] for $CH_3Mn(CO)_5$ (also in cyclohexane) is of interest, since the positions of the A_1 and E bands are almost identical, differing by less than 3 cm^{-1}, yet the B_1 band is not seen in the more symmetrical methyl compound. Therefore the bonding in σ-(C_3H_5)-$Mn(CO)_5$ and $CH_3Mn(CO)_5$ is approximately the same, with the allyl perturbing the C_{4v} symmetry of the $Mn(CO)_5$ moiety more than the methyl group.

The force constants using the Cotton–Kraihanzel method are as expected and do not differ greatly from those reported for $HMn(CO)_5$[2], where the k_{eq} and k_i values differ least (16.93 *vs.* 16.91 and 0.25 *vs.* 0.26); however the k_{ax} values differ to a greater extent (16.47 *vs.* 15.92). As the axial carbonyl is affected more than the equatorial ones in changing from $HMn(CO)_5$ to σ-$(C_3H_5)Mn(CO)_5$ a greater change in the values of k_{ax} is predicted. Also as extra approximations are required to calculate k_{ax}, it is less reliable than k_{eq}.

Cotton[17] notes that the increase in frequencies and of k_{eq} and k_{ax} in changing from $CH_3Mn(CO)_5$ to $C_2F_5Mn(CO)_5$ is due to the stronger inductive effect of the fluorinated ligand, as π interactions are excluded. Thus as the allyl- and methylmanganese pentacarbonyls agree in frequencies[3,17], and in force constants[17], the bonding in both is similar and the inductive effects of the CH_3 and allyl groups are almost identical. The very slight increase in frequency, in changing from $L=CH_3$ to $L=\sigma$-(C_3H_5) in $LMn(CO)_5$, of the A_1(ax) mode (1990 *vs.* 1992 cm^{-1}) indicates that, if the difference is significant, the inductive effect of the allyl is slightly greater than that of the methyl group.

The force constants using Bor's[13] method are also given in Table 1. Again $k_{eq} > k_{ax}$, as expected, indicating the relative ease in stretching the axial carbonyl. Since the allyl is not a strong π acceptor the bond order in the axial CO is predicted to be less than in the equatorial carbonyl. Bor calculated force constants in $LM(CO)_5$ and found $k_{eq} > k_{ax}$, in agreement with the above results and with the generally accepted picture. Using Bor's method two interaction constants are calculated corresponding to interactions between equatorial carbonyls and the interaction between the axial carbonyl with an equatorial one. The Cotton–Kraihanzel method calculates one interaction constants are the same. Using the force constants from Bor's method $\nu(B_1)$ is calculated as 2038 cm^{-1}, which is in reasonable agreement with the experimental value of 2047 cm^{-1}.

In discussing the relative intensities of the A_1 modes Manning and Miller[14] introduce the parameters ρ and p. These authors note that the intensity of the A_1(eq) band is due to coupling of the motions of the carbonyls and distortions of the equatorial carbonyls from the plane perpendicular to the axial carbonyls. Large ρ values suggest a coupling mechanism, where A_1(eq) is really a stretching of all carbonyls. However, even though ρ is large for $HMn(CO)_5$ the intensity of the A_1(eq) band is small, indicating that distortions (or other factors) are also important in discussing the intensity of the A_1(eq) band. Using the Cotton–Kraihanzel force constants the ρ value of σ-$(C_3H_5)Mn(CO)_5$ is between those of $HMn(CO)_5$ and $IMn(CO)_5$, and is greater than those of the other halogens. This suggests that the coupling of the carbonyl vibrations is greater in σ-$(C_3H_5)Mn(CO)_5$ than in $XMn(CO)_5$ (X = halogen). However $HMn(CO)_5$ has greater coupling. The angle between the axial and equatorial carbonyls in σ-$(C_3H_5)Mn(CO)_5$ is calculated as 95.3°, using the Cotton–Kraihanzel force constants. This value compares with the average value of 97° in $HMn(CO)_5$[18]. The angle is decreased in the allyl compound, partially because of the steric repulsions of the more bulky allyl group. Manning and Miller[14] note that θ-values greater than 90° have been observed in other molecules. The large value of θ is indicative of back-bonding, which gives partial double bonding between the metal and the carbonyls.

σ-$(C_3H_5)Mn(CO)_5$, 700–300 cm^{-1} region

In Table 2 the spectrum of σ-$(C_3H_5)Mn(CO)_5$ in the ν(M–C) and δ(MCO) frequency region is shown, along with proposed assignments.

TABLE 2

σ-$(C_3H_5)Mn(CO)_5$, 700–300 cm^{-1} REGION.

Band (cm^{-1})			*C_{4v} symmetry mode*
Raman (benzene)	*IR*		
	KBr cell (CCl_4)	*Polyethylene cell (benzene)*	
676 m	664 vs		A_1 δ(MCO) out of plane (E?)
650 w	647 vvs		E δ(MCO)
608 w	609 vvs		E δ(MCO)
564 m		556 w	E δ(MCO) axial and in plane
		537 w	E ν(M–C) planar (A_1?)
479 ms	456 vs	453 vs	A_1 ν(M–C) axial (E?)
400 s	396 m	396 m	A_1 ν(M–C) equatorial
392 s			

In C_{4v} symmetry the ν(M–C) vibrations are distributed, as are the ν(CO) vibrations, into $2A_1+B_1+E$. The distribution of the normal modes of the type δ(MCO) is $A_1+A_2+B_1+B_2+3E$, and that of ω(CMC) is $A_1+B_1+2E+B_2$. With 33 Cartesian coordinates, in $Mn(CO)_5$, and 27 internal degrees of freedom, simple group theory shows that:

$$IDF = 6A_1+A_2+4B_1+2B_2+7E$$

The ν(CO) modes have been assigned. It remains to assign bands to the remaining symmetry modes, bearing in mind that the A_1 and E alone are infrared active. Edgell and co-workers'[9] study of $HMn(CO)_5$ aids in the assignments. In the 700–300 cm^{-1} region, seven IR bands are expected approximately corresponding to the three A_1 and four E modes of the M–C stretches and MCO bends. From Table 2 it is seen that seven infrared bands are observed. There is extensive mixing of modes of the same symmetry in this region due to the small frequency differences between the fundamentals. Therefore the assignment of the bands is not simple[19]. δ(MCO) modes generally fall between 700 and 250 cm^{-1} depending on the environment while ν-(M–C) bands fall in the region 500–300 cm^{-1}. However, bending modes are generally more intense in the infrared than are M–C stretching modes. Thus it seems reasonable to make the following assignments of the infrared bands in CCl_4:

δ(MCO) 664, 647, 609
ν(M–C) 456, 396

The 664 cm^{-1} band is the least intense of the above bending modes, thus A_1 is suggested, corresponding to the MCO out-of-plane bend. In the 650–600 cm^{-1} region Edgell and Cengel note two infrared bands, assigned to A_1 and E modes, in the spectra of $XMn(CO)_5$, X = Br, Cl. However Adams and Squire[8], in the 700–600 cm^{-1} region using infrared and Raman spectra observed three E bands. Thus the band at 664 cm^{-1} may be an E band. The 647 cm^{-1} and 609 cm^{-1} bands are in E modes.

By analogy with $XMn(CO)_5$[8,9], the 456 cm^{-1} band (in CCl_4) may be assigned to the A_1 mode corresponding to the Mn–C axial stretch; however, its intensity suggests that it may be due to an E vibration while the 396 cm^{-1} mode is probably the A_1 Mn–C equatorial stretch. The weak band at 556 cm^{-1} is due to MCO axial and in-plane bends of E symmetry, and the lower frequency (537 cm^{-1}) is the E planar or the A_1(eq) Mn–C stretching mode.

The ω(CMC) are at even lower frequencies ($\approx$ 100 cm^{-1}) than those measured. The above assignments account for the seven observed infrared bands in the 700–300 cm^{-1} region. Three bands are assigned to the allowed $2A_1+E$ stretches and four to the allowed A_1+3E bends.

σ-$(C_3H_5)Mn(CO)_5$, *allyl vibrations*

In Table 3 are shown the 4000–700 cm^{-1} IR bands of σ-$(C_3H_5)Mn(CO)_5$ in a film and in solution, the Raman bands and possible assignments. Some bands in σ-$(C_3H_5)Mn(CO)_5$ have previously been reported and assignments proposed[10].

Assuming C_s local symmetry for the allyl group the symmetry species of the σ-allyl vibrational modes were calculated in the standard way: $IDF = 12A' + 6A''$ (A', A'' infrared active). The symmetry coordinates are given in Table 4.

In the allyl moiety the vibrations can be described approximately as C–H stretches ($\approx$3000 cm^{-1}), a C=C stretch ($\approx$1600 cm^{-1}), a C–C stretch ($\approx$900 cm^{-1}), C–H bending modes ($\approx$1400–900 cm^{-1}) and a C–C=C bend ($\approx$500 cm^{-1}). The terminal C–H bonds are most difficult to stretch, thus ν_1 and ν_2 are predicted to be the modes of highest frequency. ν_3 is expected at lower frequencies than ν_1 and ν_2.

1-Propene has the C=C stretch of 1647 cm^{-1}. The bonding in σ-$(C_3H_5)Mn(CO)_5$ lowers this frequency to 1617 cm^{-1} in the IR and 1614 cm^{-1} in the Raman. This assignment is in agreement with that reported previously (1620 cm^{-1})[10]. ν(C–C)

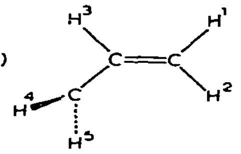
TABLE 3

σ-$(C_3H_5)Mn(CO)_5$, 4000–700 cm^{-1} REGION

Film (*NaCl 0.2 mm, 457*)	*Raman*	*CCl_4 soln.* (*KBr 0.1 mm, 457*)	*Assignments*
3085		3085	ν_1
3025		3000	ν_2
3000		2975	ν_3
2975			
2955 w			
2945			
2933		2934	ν_5
2865		2865	ν_4
1617 s	1614	1617	ν_6
1465		1465	
1448		1448	
1400 w	1400	1405	ν_9–ν_{13}
1382		1382	
1295	1295	1297	
1204 ms	1221	1204	
1079 m	1082	1080	
1032 w		1032	
1016		1017	ν_{14}–ν_{18}
988 m	993	989	
920 w	934	920	
882 s		883	
752 w			ν_7 (?)

TABLE 4

SYMMETRY COORDINATES[20] OF σ-(C_3H_5)



ν(C–H)	$S_1(A')=r_1$	ν_1
	$S_2(A')=r_2$	ν_2
	$S_3(A')=r_3$	ν_3
	$S_4(A')=(r_4+r_5)/\sqrt{2}$	ν_4
	$S_5(A'')=(r_4-r_5)/\sqrt{2}$	ν_5
ν(C=C)	A'	ν_6
ν(C–C)	A'	ν_7
δ(C–C=C)	$S_6(A')=\delta_6$	ν_8
δ(H–C=C)	$S_7(A')=\delta_3$	ν_9
δ(C=C–H)	$S_8(A')=\delta_1$	ν_{10}
	$S_9(A')=\delta_2$	ν_{11}
δ(H–C–C)	$S_{10}(A')=(\delta_4+\delta_5)/\sqrt{2}$	ν_{12}
	$S_{11}(A'')=(\delta_4-\delta_5)/\sqrt{2}$	ν_{13}
ξ(CH in C–C=C plane)	$S_{12}(A'')=\xi_1$	ν_{14}
	$S_{13}(A'')=\xi_2$	ν_{15}
	$S_{14}(A'')=\xi_3$	ν_{16}
ξ(CH in H^4CH^5 plane)	$S_{15}(A')=(\xi_4+\xi_5)/\sqrt{2}$	ν_{17}
	$S_{16}(A'')=(\xi_4-\xi_5)/\sqrt{2}$	ν_{18}

in 1-propene is at 919 cm^{-1}. Thus the IR band at 920 cm^{-1} (934 cm^{-1} in the Raman) or the strong band at 882–883 cm^{-1} is the C–C stretch, ν_7.

In-plane bending modes have higher frequencies than out-of-plane modes[20]. The bands between 1500 and 1200 cm^{-1} are, therefore, expected to be in-plane bends and those in the 1100–900 cm^{-1} are due to out-of-plane vibrations.

Some of the vibrations reported in Table 3 are presumably due to overtone and allyl–manganese vibrations.

EXPERIMENTAL

The synthesis of the compound has been described previously[10,11]. In the 4000–400 cm^{-1} region spectra of liquid films, carbon tetrachloride and petroleum ether solutions were obtained in KBr 0.1 mm cells and in the 4000–600 cm^{-1} region in NaCl 0.2 mm cells. In the 2200–1900 cm^{-1} region the spectra of cyclohexane solutions were obtained in KBr 0.1 mm cells. In the 600–250 cm^{-1} region benzene and dichloromethane were used as solvents in 1 mm polyethylene cells. IR spectrometers used were PE 337 with a Hitachi PE recorder readout and a PE 457. The spectra were calibrated using polystyrene, deuterium chloride and indene. Accuracy is expected to be ± 1 cm^{-1} at and above 700 cm^{-1} and ± 2 cm^{-1} below 700 cm^{-1}.

σ-$(C_3H_5)Mn(CO)_5$ is air sensitive, though not markedly so. Therefore a sample was exposed for 30 min to air and the liquid film spectrum then taken was found to be the same as the spectra of unexposed samples. The Raman spectra of the liquid, σ-$(C_3H_5)Mn(CO)_5$ in benzene were obtained with a Coderg PH1 instrument using 637.8 nm excitation.

ACKNOWLEDGEMENTS

We wish to thank Professor D. A. Brown and Dr. A. R. Manning of this Department and Dr. D. M. Adams of the Department of Chemistry, Leicester, for their help and Miss J. Gardner of the Department of Chemistry, Leicester, for running the Raman spectra.

REFERENCES

1 P. S. Braterman, R. W. Harrill and H. D. Kaesz, *J. Amer. Chem. Soc.*, 89 (1967) 2851.
2 D. K. Huggins and H. D. Kaesz, *J. Amer. Chem. Soc.*, 86 (1964) 2734.
3 H. D. Kaesz, R. Bau and J. M. Smith, *J. Amer. Chem. Soc.*, 89 (1967) 2844.
4 F. A. Cotton, *Inorg. Chem.*, 3 (1964) 702.
5 J. C. Hileman, D. K. Huggins and H. D. Kaesz, *Inorg. Chem.*, 1 (1962) 933.
6 J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 4 (1965) 389.
7 R. W. Cattrall and R. J. H. Clark, *J. Organometal. Chem.*, 6 (1966) 167.
8 D. M. Adams and A. Squire, *J. Chem. Soc. A*, (1968) 2817.
9 W. F. Edgell, J. W. Fisher, G. Asato and W. M. Risen, *Inorg. Chem.*, 8 (1969) 1103.
10 W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Amer. Chem. Soc.*, 83 (1961) 1601.
11 H. D. Kaesz, R. B. King and F. G. A. Stone, *Z. Naturforsch. B*, 15 (1960) 682.
12 F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84 (1962) 4432.
13 G. Bor, *Inorg. Chim. Acta*, 1 (1967) 81.
14 A. R. Manning and J. R. Miller, *J. Chem. Soc. A*, (1966) 1521.

15 W. Beck, A. Melnikoff and R. Stahl, *Chem. Ber.*, 99 (1966) 3721.
16 L. E. Orgel, *Inorg. Chem.*, 1 (1962) 25.
17 F. A. Cotton, *Inorg. Chem.*, 3 (1964) 702.
18 S. J. LaPlaca, W. C. Hamilton and J. A. Ibers, *Inorg. Chem.*, 3 (1964) 1491.
19 A. R. Manning, *J. Chem. Soc. A*, (1971) 106.
20 G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, 1945.