Vibrational Spectrum of π-Allylmanganese Tetracarbonyl

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The i.r. and Raman spectra of $(\pi\text{-}C_3H_5)Mn(CO)_4$ as a solid and in solution are reported and an assignment suggested. The vibrations of the allyl group are in good agreement with those in analogous molecules, and the vibrations of $Mn(CO)_4$ must be discussed in terms of C_s, not C_{4v} symmetry.

More or less complete vibrational spectra have now been reported and assigned for a number of π-complexes of the type (hydrocarbon)$M(CO)_n$. Most of these have been cyclopentadienyl or arene complexes, *e.g.*, $(C_5H_5)Mn(CO)_3$,[1] $(C_5H_5)V(CO)_4$,[2] (arene)$M(CO)_3$ (where arene = benzene, toluene, mesitylene, *etc.*; M = Cr, Mo, W),[3-5] although a few non-cyclic hydrocarbon ligands have also been studied, *e.g.*, (butadiene)$Fe(CO)_3$.[6]

The π-bonded allyl group, which occurs in the relatively stable $(\pi\text{-}C_3H_5)Mn(CO)_4$ and $(\pi\text{-}C_3H_5)Co(CO)_3$ complexes,[7,8] has not been studied in such detail. Indeed, the allyl group π-bonded to a transition metal has been strangely neglected by vibrational spectroscopists, despite its importance in modern organometallic chemistry. The only π-allyl complexes for which any detailed vibrational data are available are the dimeric species $[Pd(\pi\text{-}C_3H_5)X]_2$ and [Pd(π-2-methylallyl)X]$_2$ (where X = Cl, Br).[9,10]

In order to obtain further information on the vibrations of the π-allyl group, and on the mutual interactions of the π-allyl group and the carbonyl ligands, we have studied the i.r. and Raman spectra of $(\pi\text{-}C_3H_5)Mn(CO)_4$.

Selection Rules.—There have been no reports of *X*-ray

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[1] I. J. Hyams, R. T. Bailey, and E. R. Lippincott, *Spectrochim. Acta*, 1967, **23**, *A*, 273.

[2] J. R. Durig, A. L. Marston, R. B. King, and L. W. Houk, *J. Organometallic Chem.*, 1969, **16**, 425.

[3] G. Davidson and E. M. Riley, *J. Organometallic Chem.*, 1969, **19**, 101.

[4] D. M. Adams and A. Squire, *J. Chem. Soc.* (*A*), 1970, 814.

[5] G. Davidson and E. M. Riley, *Spectrochim. Acta*, in the press.

[6] G. Davidson, *Inorg. Chim. Acta*, 1969, **3**, 596.

[7] H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, 1960, **15*b***, 682.

[8] W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Amer. Chem. Soc.*, 1961, **83**, 1601.

[9] K. Shobatake and K. Nakamoto, *J. Amer. Chem. Soc.*, 1970, **92**, 3339.

[10] D. M. Adams and A. Squire, *J. Chem. Soc.* (*A*), 1970, 1808.

diffraction or other studies on the molecular structure of π-allylmanganese tetracarbonyl. We will consider the most symmetrical possibility, shown in Figure 1, with the $Mn(CO)_4$ fragment having a square pyramidal structure, and the plane defined by the C_3 skeleton of the allyl group parallel to the plane containing the four carbonyl carbon atoms.

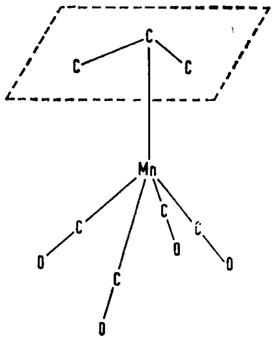

FIGURE 1 The molecular structure assumed for $(\pi\text{-}C_3H_5)Mn(CO)_4$

Very many investigations of the vibrational spectra of (hydrocarbon)–$M(CO)_n$ complexes have used the concept of ' local symmetry ' in the assignment and interpretation of spectra.[11] In the present example, the local symmetry of the allyl group would be C_s, and that of the $Mn(CO)_4$ portion would be C_{4v}. In a number of cases, however, the local symmetry approximation has been shown to be inadequate,[5,6] and one must consider the symmetry of the molecule as a whole. The overall symmetry of $(\pi\text{-}C_3H_5)Mn(CO)_4$ is C_s, and, as shown in Figure 2, the plane of symmetry may be derived from a σ_v plane of C_{4v} (a) or from a σ_d plane of C_{4v} (b).

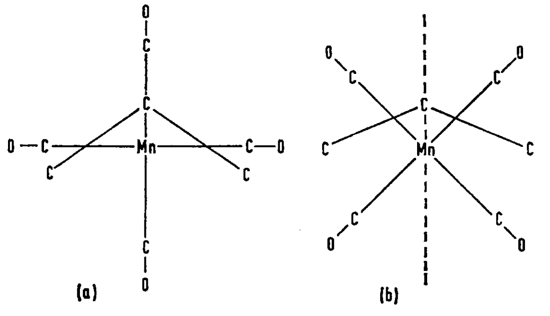

FIGURE 2 Two possible conformations of the $(\pi\text{-}C_3H_5)Mn(CO)_4$ molecule, symmetry plane derived from (a) σ_v of C_{4v}, (b) σ_d of C_{4v}

Table 1 lists the numbers and symmetry types of the normal modes of the allyl group and the Mn-(allyl) group in terms of C_s symmetry. Table 2 gives the corresponding information for the $Mn(CO)_4$ fragment, assuming C_{4v} symmetry and C_s symmetry (derived from σ_v *or* σ_d of C_{4v}). It will be seen that it should be possible to determine whether C_{4v} or C_s symmetry is necessary to explain the vibrations of $Mn(CO)_4$ from the number of i.r. and Raman bands observed, and also to distinguish between the different possibilities of C_s symmetry (from the number of polarised Raman bands). The Raman and i.r. frequencies for $(\pi\text{-}C_3H_5)Mn(CO)_4$ are listed in Table 3.

TABLE 1

Numbers and symmetries of normal modes for the allyl group and the Mn–(allyl) portion of $(\pi\text{-}C_3H_5)Mn(CO)_4$ (C_s symmetry)

ν(C–H)	A'
$\nu(CH_2)$	$2A' + 2A'$
$\delta(CH_2)$	$A' + A''$
π(C–H)	A'
δ(C–H)	A''
ν(C–C–C)	$A' + A'$
$\rho_t(CH_2)$	$A' + A''$
$\rho_w(CH_2)$	$A' + A''$
$\rho_r(CH_2)$	$A' + A'$
δ(C–C–C)	A'
ν[Mn–(allyl)]	$2A' + A'$
τ[Mn–(allyl)]	A''

All vibrations are i.r. and Raman active; A' vibrations will give polarised Raman scattering (ν = stretch; δ = in-plane deformation; π = out-of-plane deformation; ρ_t = twist; ρ_w = wag; ρ_r = rock; τ = torsion).

TABLE 2

Numbers and symmetries of $Mn(CO)_4$ vibrational modes

	C_{4v}	C_s (σ_v)	C_s (σ_d)
ν(Mn–C)	$A_1 + B_1 + E$	$3A' + A''$	$2A' + 2A''$
ν(C–O)	$A_1 + B_1 + E$	$3A' + A''$	$2A' + 2A'$
δ(C–Mn–C)	$A_1 + B_2 + E$	$2A' + 2A''$	$3A' + A''$
δ[(allyl)–Mn–$(CO)_4$]	$B_1 + E$	$2A' + A''$	$A' + 2A''$
δ(Mn–C–O)	$A_1 + A_2 + B_1 + B_2 + 2E$	$4A' + 4A'$	$4A' + 4A''$

All vibrations would be Raman-active (A', A_1 polarised), and all would also be i.r.-active except the B_1 and B_2 vibrations of C_{4v} symmetry.

RESULTS AND DISCUSSION

Assignment of Spectra.—This discussion can be subdivided conveniently into two parts: (*a*) internal vibrations of the allyl group and those involving Mn–(allyl), and (*b*) vibrations of $Mn(CO)_4$. We will deal with them in that order, as the former do not depend upon the problem of ' local ' *versus* ' overall ' symmetry (both are C_s). Data from solution spectra will be used wherever possible.

Vibrations of the Allyl Group and of Mn–(*allyl*).—Table 1 shows that an allyl group with an effective symmetry of C_s should give rise to 18 vibrational modes ($10A' + 8A''$), all allowed in both the i.r. and Raman, with 10 polarised Raman bands. The vibrational spectrum of the free $C_3H_5^-$ ion (C_{2v}) has not been investigated thoroughly, although some i.r. data are available for $Na^+C_3H_5^-$.[12] Consequently the assignment must be based largely upon the published assignments for $[(\pi\text{-}C_3H_5)PdX]_2$,[9,10] it being borne in mind that the carbonyl ligands present in $(\pi\text{-}C_3H_5)Mn(CO)_4$ are very different electronically from the halogens in these molecules.

C–H *Stretching vibrations.* In the region 2900—3100 cm^{-1}, the Raman spectrum (in CCl_4 or CS_2 solution) shows 6 bands, the i.r. 5. The highest-frequency band,

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[11] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

[12] E. J. Lanpher, *J. Amer. Chem. Soc.*, 1957, **79**, 5578.

TABLE 3

Observed vibrational frequencies (cm^{-1}) of (π-C_3H_5)Mn(CO)$_4$

Raman			I.r.			Approximate assignment
Solid	CS_2	CCl_4	Solid	CS_2	CCl_4	
					3980w	
				3920vw	3928m	
					3902w	
3082	3078w,dp	3078w,dp	3078w	3073m	3079m	$A''\ \nu(\mathrm{CH_2})$
3037w	3020w,pol	3025w,pol		3018m	3022m	$A'\ \nu(\mathrm{CH})$
	2973w,pol	2973w,pol		2972w		$A'\ \nu(\mathrm{CH_2})$
	2963vw	2964vw		2962m	2962m	$A''\ \nu(\mathrm{CH_2})$
	2949w,pol	2948w,pol		2946w		$A'\ \nu(\mathrm{CH_2})$
	2903wm,pol	2901wm,pol				$2 \times A'\ \delta(\mathrm{CH_2})_{\mathrm{sym.}}$
				2888vw	2888vw	
				2850vvw	2855vvw	
					2740vw	
			2720w	2706w	2710w	
				2626w		
				2556w	2555w	
				2500w	2502w	
				2480w	2478w	
				2443w	2440w	
				2406w	2405w	
				2389w	2390w	
					2380w	
					2330w	
					2181m	
2077s	2070m,pol	2071m,pol	2070s	2068s	2064s	$A'\ \nu(\mathrm{C{-}O})$
				2046w	2046w	
				2022vw	2014vw	
1994s	1991m,pol	1993m,pol	1991vs	1989vs	1981vs	$A'\ \nu(\mathrm{C{-}O})$
1967s	1970w,?dp	1974w,?dp	1970vs	1974vs	1971vs	$A''\ \nu(\mathrm{C{-}O})$
1953s	1955m,pol	1957m,pol	1952vs	1958s	1955s	$A'\ \nu(\mathrm{C{-}O})$
				1940w		
				1919w		
				1847w	1846w	
				1810w	1808w	
				1774w	1770w	
1505m	1503w,dp	1503w,dp	1500m		1499s	$A''\ \delta(\mathrm{CH_2})_{\mathrm{asym.}}$
1469w	1469w,pol	1462w,pol			1464s	$A'\ \delta(\mathrm{CH_2})_{\mathrm{sym.}}$
1403m	1397w,dp	1397w,dp		1397m	1394m	$A''\ \nu(\mathrm{C{-}C{-}C})_{\mathrm{asym.}}$
			1305w		1305w	
			1258w	1257m	1255m	
1221m	1218w,pol	1214w,pol	1212m	1215s	1211s	$A'\ \pi(\mathrm{C{-}H})$
			1155m,br	1150w	1143w	$A''\ \delta(\mathrm{C{-}H})$
				1120w		
				1097m	1095m	
			1059w	1058m	1057m	
1013m	1019w,pol	1017w,pol	1020m	1020m	1016m	$A'\ \nu(\mathrm{C{-}C{-}C})_{\mathrm{sym.}}$
	1008w,pol	1007w,pol		1009m	1005s	$A'\ \rho_t(\mathrm{CH_2})_{\mathrm{sym.}}$
970w			985vw	980w	977w	$A''\ \rho_t(\mathrm{CH_2})_{\mathrm{asym.}}$
				960w		
921m	923w,pol	920w,pol	929m	922m	919w	$A'\ \rho_w(\mathrm{CH_2})_{\mathrm{sym.}}$
				907w	903vw	
			880w	886m	883m	$A''\ \rho_w(\mathrm{CH_2})_{\mathrm{asym.}}$
			788w	785m		$A''\ \rho_r(\mathrm{CH_2})_{\mathrm{asym.}}$
775vw		774w,pol	770w	773w		$A'\ \rho_r(\mathrm{CH_2})_{\mathrm{sym.}}$
		669vw,pol	670s	662vs	669vs	$A'\ \delta(\mathrm{Mn{-}C{-}O})$
		640vw,pol	638s	637vs	638vs	$A' + ?A''\ \delta(\mathrm{Mn{-}C{-}O})$
			572m	575w		$A' + A''\ \delta(\mathrm{Mn{-}C{-}O})$
565w	560m,pol	561m,pol	562m	561s	560s	$A' + ?A''\ \delta(\mathrm{Mn{-}C{-}O})$
	521w,pol		523w	523w	520w	$A'\ \delta(\mathrm{C{-}C{-}C})$
479m	478m,pol		486s	482s	480s	$A'\ \nu(\mathrm{Mn{-}CO})$
			460m	456m	454m	$A' + A''\ \nu(\mathrm{Mn{-}CO})$
	430w,pol		436m	433m	430m	$A'\ \nu(\mathrm{Mn{-}CO})$
417m	411m,dp	412m,dp	414w			$A''\ \nu(\mathrm{Mn{-}allyl})_{\mathrm{asym.}}$
389m	385s,pol	387s,pol	379w			$A'\ \nu(\mathrm{Mn{-}allyl})_{\mathrm{asym.}}$
331s	327s,pol		330m			$A'\ \nu(\mathrm{Mn{-}allyl})_{\mathrm{sym.}}$
158vw		159m,?dp				$A'' + ?A'\ \delta(\mathrm{C{-}Mn{-}C})$

at 3078 cm^{-1}, is definitely depolarised, and can be assigned to the A'' CH_2 stretch. Most of the other assignments follow those of Adams and Squire[10] quite closely, thus: 3020 cm^{-1} (pol.), A' CH stretch; 2973 cm^{-1} (pol.), A' CH_2 stretch; 2949 cm^{-1} (pol.), A' CH_2 stretch. It should be noticed that all of these occur at a *lower* frequency than in the Pd complexes. The remaining fundamental expected in this region (an A'' CH_2 stretch), not detected by previous workers corresponds to a very weak Raman band, of uncertain polarisation, at 2963 cm^{-1} (with an i.r. counterpart of medium intensity). The last feature in this part of the spectrum is a weak- to medium-intensity Raman band (polarised) at 2903 cm^{-1}. This is rather low in frequency to be a C–H stretching fundamental and, following Adams and Squire,[10] we assign it as $2 \times \delta(CH_2)$ sym. ($= 2928$ cm^{-1}) in this case lowered in frequency by a Fermi resonance interaction with the A' CH_2 stretching fundamental found at 2949 cm^{-1}.

Deformation and skeletal stretching vibrations. All of these vibrations are expected to occur in the region 500—1600 cm^{-1}, and here the assignment is much less clear-cut than for the C–H stretches. The chief reason for this is that there are a number of vibrations of the same symmetry species within a fairly restricted frequency range, resulting in an extensive coupling of modes. Thus a description such as 'in-plane CH_2 deformation' for a particular frequency will be an approximation.

An instructive example of the results of such a mixing of modes occurs in the vibrational spectrum of Zeise's salt, $K[PtCl_3(C_2H_4)],H_2O$. Earlier workers assigned the $\nu(C=C)$ vibration to a band at *ca.* 1515 cm^{-1}, but Hiraishi[13] preferred an assignment of 1243 cm^{-1}, suggesting that the strength of the $Pt–(C_2H_4)$ band supported this. Sheppard, however, has shown by a study of Zeise's salt and its tetramethyl analogue[14] that the confusion has arisen because of the strong coupling between the $\nu(C=C)$ and $\delta(CH_2)_{sym.}$ (in-plane, 'scissors', deformation). This gives two bands, *ca.* 1515 cm^{-1} and *ca.* 1240 cm^{-1}, each of which is intermediate in character between the $\nu(C=C)$ and the $\delta(CH_2)_{sym.}$ vibrational modes. In all of the subsequent discussions, the approximate nature of the descriptions of modes must always be kept in mind.

The only previous attempted assignments for $(\pi\text{-}C_3H_5)Mn(CO)_4$ were made by McClellan *et al.*[8] who suggested tentatively that a strong (i.r.) band at 1500 cm^{-1} corresponded to the $\nu(C–C–C)_{asym.}$ vibration. That vibration in $C_3H_5^-$, however, is believed to occur at 1535 cm^{-1} (ref. 12), and so this assignment implies only a weak perturbation of the bonding in the allyl group by the attachment of the $Mn(CO)_4$ unit. The Mn–(allyl) band appears to be quite strong, however (see below), and so this is not very plausible. In addition, this assignment would leave no reasonable frequencies to be assigned to the $\delta(CH_2)_{asym.}$ vibration. It is therefore suggested that the band found at 1503 cm^{-1} (depol., Raman) and 1499 cm^{-1} (i.r.) should be assigned to $\delta(CH_2)_{asym.}$, with $\nu(C–C–C)_{asym.}$ assigned to the depolarised Raman band of next-highest frequency, at 1397 cm^{-1} (with a coincident i.r. band).

By comparing the spectra of $[Pd(\pi\text{-}CH_2–CH–CH_2)X]_2$ and of $[Pd(\pi\text{-}CH_2–CMe–CH_2)X]_2$, Adams and Squire[10] were able to assign the two CH deformation modes as follows: $\pi(CH)$ (out-of-plane, A'), 1225 cm^{-1}; $\delta(CH)$ (in-plane, A''), 1197 cm^{-1}. A weak, polarised Raman and strong i.r. band at 1215 cm^{-1} in $(\pi\text{-}C_3H_5)Mn(CO)_4$ can be assigned to the A' out-of-plane deformation, but the $\delta(CH)$, A'', must be considerably shifted. The next likely candidate is a weak i.r. band at 1150 cm^{-1}, with no observable Raman counterpart.

The antisymmetric skeletal stretch was assigned, above, to a band at 1397 cm^{-1}. A polarised Raman band at 1019 cm^{-1} (with a corresponding i.r. band) can be assigned to $\nu(C–C–C)_{sym.}$. This is in agreement with previous assignments.[9,10]

The remaining deformations of the CH_2 group are those (out-of-plane) which involve twisting (ρ_t) and wagging (ρ_w) of the group, together with the (in-plane) CH_2 rocking vibration (ρ_r). The first two types should give rise to bands in the 900—1100 cm^{-1} region, the last to bands between 700 and 800 cm^{-1}.[15] There are 6 vibrations of these types ($A' + A''$ for each of the three subdivisions), and they can be assigned as follows: $\rho_t(CH_2)_{sym.}$ (A'), 1008 (pol.); $\rho_t(CH_2)_{asym.}$ (A''), 980 (i.r. only); $\rho_w(CH_2)_{sym.}$ (A'), 923 (pol.); $\rho_w(CH_2)_{asym.}$ (A''), 886 (i.r. only); $\rho_r(CH_2)_{asym.}$ (A''), 785 (i.r. only); $\rho_r(CH_2)_{sym.}$ (A'), 774 (pol.) (all figures in cm^{-1}).

This leaves just one vibrational mode, the skeletal deformation, $\delta(C–C–C)$ (A'), which is assigned to a band which is weak in both the i.r. (523 cm^{-1}) and Raman (521 cm^{-1}, pol.). This assignment is made by elimination after assigning the Mn–CO stretches, and Mn–C–O deformations which are also found in that region.

The vibrations of the Mn–(*allyl*) *portion.* Table 1 indicates perhaps the most realistic way of describing the 4 modes which are associated with this: three Mn–(allyl) stretches [$2A' + A''$; these could alternatively be described as the Mn–(allyl) stretch, A', and two non-degenerate allyl tilting vibrations, $A' + A''$] and one torsional motion of the allyl group. Such torsional vibrations usually give very weak i.r. and Raman bands, and no feature which can be so assigned was seen.

In the $(hydrocarbon)M(CO)_n$ systems hitherto investigated, the M–(hydrocarbon) stretches were found between 300 and 400 cm^{-1}.[1-6,10,13] In this region in $(\pi\text{-}C_3H_5)Mn(CO)_4$ three bands are seen, both in the i.r. and the Raman. Two, at 327 and 385 cm^{-1}, give strong, polarised Raman bands; these are assigned as the A' symmetric (327) and antisymmetric (385) Mn–(allyl) stretches. The third band, at 411 cm^{-1}, is depolarised, and it is assigned to the A'' antisymmetric Mn–(allyl) stretch.

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[13] J. Hiraishi, *Spectrochim. Acta*, 1969, **25**, *A*, 749.

[14] N. Sheppard, unpublished observations, reported at the 2nd International Conference on Raman Spectroscopy, Oxford, England, Sept. 1970.

[15] N. Sheppard and D. M. Simpson, *Quart. Rev.*, 1953, **7**, 19.

The only remaining vibrations which involve the allyl group are the (allyl)–Mn–$(CO)_4$ deformations, which will be discussed together with the Mn–$(CO)_4$ vibrations.

Vibrations of the $Mn(CO)_4$ *Group*.—The assignment of observed bands to the different types of vibration listed in Table 2 can be carried out quite simply by analogy with known carbonyl systems. The main point of interest is whether the effective symmetry for $Mn(CO)_4$ is C_{4v} (local symmetry) or C_s (overall symmetry) and, if the latter appears to be more likely, whether the symmetry plane is derived from a σ_v or a σ_d plane or C_{4v}.

Considering first the C–O stretches, C_{4v} predicts a total of 3 bands ($A_1 + B_1 + E$), only 2 of which are i.r. active ($A_1 + E$), and only one of which (A_1) should give a polarised Raman band. C_s on the other hand predicts four bands, all i.r. and Raman active, but the two possible C_s structures [Figures 2(a) and (b)] would give different numbers of polarised bands. If the symmetry plane is a σ_v plane of C_{4v} [Figure 2(a)] there should be $3A' + A''$, *i.e.*, *three* polarised Raman bands, but if the plane is a σ_d plane of C_{4v} [Figure 2(b)] there should be $2A' + A''$, *i.e.*, *two* polarised Raman bands. Both the i.r. and Raman solution spectra of $(\pi\text{-}C_3H_5)Mn(CO)_4$ show four bands in the C–O stretching region, and therefore effective C_s symmetry must be assumed. Further, *three* of them are polarised in the Raman spectrum (2070, 1991, and 1955 cm^{-1}), and only one is depolarised (1974 cm^{-1}); it therefore seems that the selection rules for the structure in Figure 2(a) are being obeyed.

It is unlikely that we will get such unequivocal information from the remaining vibrations, since the C–O stretches are the strongest and sharpest features in the $Mn(CO)_4$ spectrum. The Mn–(CO) stretches, however, do give three i.r. bands, at 433, 456, and 482 cm^{-1}, and two polarised Raman bands (430, 478 cm^{-1}). These observations are not consistent with C_{4v} symmetry, although they do not permit a distinction to be made between the C_s possibilities. The best assignment that can be made therefore, in agreement with the C–O stretching assignments, is as follows: 478 cm^{-1}, A' (A_1 for C_{4v}); 456 cm^{-1}, $A' + A''$ (E for C_{4v}); 430 cm^{-1}, A' (B_1 for C_{4v}). The last two assignments follow (*a*) by analogy with $(\pi\text{-}C_5H_5)V(CO)_4$, where the V–(CO) stretch of E symmetry is not observed in the Raman spectrum [2] (the 456 cm^{-1} band is seen only in the i.r.), and (*b*) from the C–O stretching assignments, since the B_1 modes of C_{4v} will correlate with A' of C_s, and the Raman band at 430 cm^{-1} is definitely polarised.

Only four Mn–C–O deformation frequencies are observed (only 3 in the Raman spectrum), and so no distinction between C_{4v} and C_s symmetry can be made on the basis of these (6 predicted for C_{4v}, 8 for C_s). As expected,[16] they lie in the region 550—700 cm^{-1} and they are much stronger in the i.r. than in the Raman region. Their assignment is by no means definite, but the following fits all of the known facts: 669 cm^{-1} (R., pol., i.r.), A'; 640 cm^{-1} (R., ?pol., i.r.), $A' + ?A''$; 575 cm^{-1} (i.r. only), $A' + A''$; 560 cm^{-1} (R., pol., i.r.), $A' + ?A''$.

The remaining vibrations constitute the least satisfactory part of the whole analysis. It proved to be very difficult to obtain good crystalline solid samples of $(\pi\text{-}C_3H_5)Mn(CO)_4$ to study the Raman spectrum below 150 cm^{-1} (solution spectra below *ca.* 150 cm^{-1} are very difficult to obtain). The only band seen which could be assigned as a C–Mn–C deformation was found at 159 cm^{-1} (medium intensity, depolarised) in the Raman spectrum of a CCl_4 solution. The remaining C–Mn–C deformations and also the deformations of the whole (allyl)–Mn–$(CO)_4$ unit (expected to lie below 100 cm^{-1}) must, therefore, be left unassigned.

Conclusions.—A full assignment has been obtained for the vibrations of the allyl group in $(\pi\text{-}C_3H_5)Mn(CO)_4$, in accord with previous work on analogous systems. The assignment of the $Mn(CO)_4$ group was incomplete in that the low-frequency deformation modes were not properly characterised, but it was possible to show that C_{4v} symmetry is inadequate to explain the observed spectra and to make a tentative suggestion as to the equilibrium conformation of the molecule.

EXPERIMENTAL

π-Allylmanganese tetracarbonyl was prepared by the method of Kaesz *et al.*[7] The product was purified by sublimation at 25 °C/15 mmHg (Found: C, 40·4; H, 2·7. Calc. for $C_7H_5MnO_4$: C, 40·4; H, 2·4%).

The Raman spectra of solid samples of $(\pi\text{-}C_3H_5)Mn(CO)_4$, and also of solutions in CS_2 and CCl_4 (contained in capillary cells, *ca.* 1·5 mm i.d.) were obtained with a Cary Model 81 Raman spectrophotometer (the solutions were stable for at least one week). The excitation source was a Spectra-Physics Model 125 He–Ne laser, having an output of *ca.* 60 mW at 632·8 nm. Spectra were calibrated with known indene peaks, and depolarisation ratios (for solutions) were determined by observing the spectrum with the plane of the polarised incident light parallel and perpendicular, respectively, to the axis of the polaroid analyser. Such a technique, with capillary cells, does not give exact values of depolarisation ratio, ρ, but the sample cell was calibrated with accurately known standards.

The i.r. spectra (4000—250 cm^{-1}) were run on a Perkin-Elmer 521 spectrometer, with the $(\pi\text{-}C_3H_5)Mn(CO)_4$ present as a mull in Nujol or halogenocarbon oil, or as a solution in CS_2 or CCl_4. Spectra were calibrated with known absorptions of water vapour, NH_3, and CO.

All of the frequencies quoted, with the exception of a few very weak and/or broad features, are accurate to ± 2 cm^{-1} for both the i.r. and Raman spectra.

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[16] D. M. Adams, *J. Chem. Soc.*, 1964, 1771.