THE VIBRATIONAL SPECTRA OF CYCLOPENTADIENYLMETHYLTUNGSTEN TRICARBONYL

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SUMMARY

The infra-red (250–4000 cm^{-1}) and Raman spectra (50–3200 cm^{-1}) have been obtained for $(C_5H_5)W(CH_3)(CO)_3$ and the method of local symmetry was used as a basis for a vibrational assignment. The results differ somewhat from previous studies on similar molecules.

INTRODUCTION

Although there has been no X-ray study of the crystal structure of $(C_5H_5)W(CH_3)(CO)_3$, it is reasonable to assume that it is similar to that of the closely related complex $(C_5H_5)Mo(C_2H_5)(CO)_3$[1]. In this molecule the angle between the plane of the C_5 ring and the plane of the three carbonyl oxygen atoms was found to be 9.2°. The Mo–(CO) and C–O bond lengths respectively were found to be equal to well within experimental error, as were the five ring C–C distances. The Mo–(C_2H_5) bond length was found to be very close to the sum of the Mo and C atomic radii. This structure was compared with that of bis(cyclopentadienylmolybdenum tricarbonyl) published some years earlier by Wilson and Shoemaker[2], and it was found that the only significant structural change accompanying the replacement of an ethyl group by a $(C_5H_5)(CO)_3$Mo residue was a 7° distortion in the angle at which the group enters. Because of the similarities between these two structures it seems unlikely that the structure of the corresponding tungsten methyl complex will be radically different.

Both infra-red frequencies[3,4] and PMR shifts[4] for $(C_5H_5)W(CH_3)(CO)_3$ have been reported, but in neither case were structural inferences drawn.

At a later date Patil and Graham[5] published infra-red frequencies in the C–O stretching region from $(C_5H_5)W(CH_3)(CO)_3$ in solution in CCl_4 but only observed two distinct bands, 2019 and 1924 cm^{-1}. In 1969 King and Houk[6] reported the C–O stretching frequencies of several compounds of this type measured in solution in cyclohexane, and calculated some C–O stretching force constants. In all cases they observed three distinct bands in that region: for the tungsten methyl derivative the frequencies were 2015, 1939 and 1935 cm^{-1}, *i.e.* the lower two bands were split by 4 cm^{-1}. In the present work only two bands could be observed in that region, the lower frequency band being the broader of the two but having a symmetric appearance.

Faller *et al.*[7] discussed the possibility of pseudo-rotation in $(C_5H_5)WH(CO)_3$,

and showed that the structure undergoes a rapid intramolecular rearrangement in which the carbonyl and hydride coordination positions are interchanged, which would explain why only two bands were observed in cyclohexane solution of the hydride in the 2000 cm^{-1} region. In the present study, therefore, $(C_5H_5)W(CH_3)(CO)_3$ was taken to be a fluxional molecule[8].

Many spectral studies of π-bonded $C_5H_5^-$ have been reported[9,10]. Especially relevant are those dealing with ferrocene type complexes[11,12], and $(C_5H_5)Mn(CO)_3$ for which Hyams *et al.*[13] put forward a vibrational assignment in agreement with that for ferrocene[11] with respect to the hydrocarbon vibrations. Other studies on this molecule, with deuteriated[14,15] and substituted rings[16,17], are also in agreement with the assignment by Hyams of the C_5H_5 vibrations.

No complete assignment has yet been proposed for a complex of the type $(C_5H_5)MR(CO)_3$, where M = Cr, Mo, or W and R = H or alkyl, and so it was considered worthwhile to attempt as full a vibrational assignment as possible for (C_5H_5)-$W(CH_3)(CO)_3$.

EXPERIMENTAL

$(C_5H_5)W(CH_3)(CO)_3$ is a yellow, air-stable solid and it was prepared[18] by the action of methyl iodide on the sodium salt $Na^+[(C_5H_5)W(CO)_3]^-$. This salt was obtained by refluxing $W(CO)_6$ with C_5H_5Na in THF, and was used *in situ*. After allowing the CH_3I to react, the solvent was removed *in vacuo* and the yellow product was sublimed out of the residual solid at ca. 50° and 10^{-2} mmHg, and purified by resublimation. (Found: C, 31.14; H, 2.17. $C_9H_8O_3W$ calcd.: C, 30.86; H, 2.3%.)

Infra-red spectra were run on a Perkin–Elmer 521 (4000–250 cm^{-1}) spectrophotometer. Solid samples were in the form of KBr discs, and solutions in CH_2Cl_2 and cyclohexane were also used. The instrument was calibrated using known peaks of CH_4, CO, H_2O and NH_3. The frequencies are all expected to be accurate to ± 2 cm^{-1}.

Raman spectra were obtained using a Cary Model 81 spectrometer with a Spectra-Physics 125 He–Ne laser as excitation source (output approx. 50 mW at 632.8 nm). Solid state spectra were run, as well as solutions in CH_2Cl_2. There was no evidence for photodecomposition of solutions of the complex in less than a day, but there was slight discolouration of the solid samples after exposure to the laser beam for less than an hour, and so the sample was changed frequently during the running of a spectrum. Solution samples were contained in glass capillaries (1 mm, i.d.). Polarisation measurements were carried out by examining the spectrum with the incident light respectively parallel and perpendicular to the axis of a polaroid analyser. The depolarisation ratios so obtained were found to be proportional to the true values. The spectrum of a sample of liquid indene was used for calibration purposes, and again frequencies should be accurate to ± 2 cm^{-1}.

RESULTS AND DISCUSSION

The infra-red and Raman frequencies for $(C_5H_5)W(CH_3)(CO)_3$ are listed in Table 1, together with the assignments of these frequencies which will be discussed below.

TABLE 1

THE VIBRATIONAL SPECTRUM OF CYCLOPENTADIENYLMETHYLTUNGSTEN TRI-CARBONYL[a]

Infra-red		Raman		Approximate assignment
KBr disc	In CH_2Cl_2	Solid	In CH_2Cl_2	
3122 m		3130 m		Ring C–H stretch (A_1)
		3110 m		Ring C–H stretch (E_2)
2966 m				Ring C–H stretch (E_1)
2904 m				Methyl C–H stretch (E)
2829 w				Methyl C–H stretch (A_1)
2472 w				
2002 vs	2021 vs	2006 m	2017 w	C–O stretch (A_1)
	2015 m[b]			
1940 (sh) ⎱	1918 vs	1922 (sh) ⎫	1917 m	C–O stretch (E)
1890 vs ⎰	1930 s[b]	1903		
		1893 s ⎬		
		1872 w		
		1828 w		
		1431 m		Ring stretch (E_2)+ Methyl def. (E)
1418 m				Ring stretch (E_1)
1352 w		1358 w		Methyl def. (A_1)
1262 w				? CH i.p. def. (A_2)
1181 wm	1192 w	1182 w		CH i.p. def. (E_1)
1133 w				
1107 w		1111 s	1112 m, pol.	Ring stretch (A_1)
1061 w		1065 w		CH i.p. def. (E_2)
1030 w				Methyl rock (E)
1005 m	1012 w			CH o.o.p. def. (E_1)
969 w				
926 w				
917 w				
831 ms	830 m	838 w		CH o.o.p. def. (A_1+E_2)
772 (sh)				
617 w		614 vw		Ring i.p. def. (E_2)
585 ms	587 m	585 w		W–C–O def. (? E)
551 s	556 m			W–C–O def. (? E)
485 ms	489 m	487 m		W–C–O def. (? A_1)+ o.o.p. Ring def. (E_2)
462 m	464 m	470 vs	463 m, pol.	W–C stretch (A_1)
442 m		445 m		W–C stretch (E)
		430 m	430 w	? W–CH_3 stretch (A')
		387 (sh)		
364 wm		365 m	362 w	Ring tilt (E)
		333 m		Ring–W stretch (A_1)

[a] Frequencies in cm^{-1}. [b] Measured in cyclohexane solution.

π-Bonded organometallic complexes of tungsten seem to scatter much more weakly in the Raman spectrum than those of chromium. This trend was also noted for the mesitylene tricarbonyl complexes of Cr and Mo[19] and can be accounted for in terms of the ease of polarisability of the metal electrons. The result is that for (C_5H_5)-

W(CH$_3$)(CO)$_3$, solution data in the Raman spectrum are incomplete and polarisation measurements were only possible for the two strongest bands (see Table 1). The infra-red spectrum is also rather weak.

(i). Vibrational analysis

Previous studies[9,13,20] on π-bonded C$_5$H$_5^-$ indicate that it is valid to assume a local symmetry of C_{5v} for the C$_5$H$_5$ ring as a basis for vibrational analysis. Table 2 shows the modes predicted for C$_5$H$_5$ together with their spectroscopic activities according to C_{5v} symmetry.

TABLE 2

PREDICTED VIBRATIONS OF C$_5$H$_5$ IN C_{5v} SYMMETRY

C-H stretch	$A_1 + E_1 + E_2$	(3 R + 2 IR)
C-C stretch	$A_1 + E_1 + E_2$	(3 R + 2 IR)
i.p. CH deform.	$A_2 + E_1 + E_2$	(2 R + 1 IR)
o.o.p. CH deform.	$A_1 + E_1 + E_2$	(3 R + 2 IR)
i.p. ring deform.	E_2	(1 R)
o.o.p. ring deform.	E_2	(1 R)

As only two distinct bands are observed for this complex in solution in the 2000 cm^{-1} region, supporting the pseudo-rotation of the CH$_3$ and CO groups, the vibrations of the Ring–W–(CO)$_3$ and W(CO)$_3$ systems are discussed in terms of C_{3v}, which is the closest reasonable approximation. Table 3 shows the symmetries and activities of the vibrational modes thus predicted.

TABLE 3

PREDICTED NORMAL MODES FOR Ring–W–(CO)$_3$ IN C_{3v} SYMMETRY

C-O stretch	$A_1 + E$	(2 R + 2 IR)
W-C stretch	$A_1 + E$	(2 R + 2 IR)
Ring-W stretch	A_1	(R + IR)
W-C-O deform.	$A_1 + A_2 + 2 E$	(3 R + 3 IR)
Ring tilt	E	(R + IR)
Ring twist	A_2	(Inactive)
C-W-C deform.	$A_1 + E$	(2 R + 2 IR)
Ring-W-(CO)$_3$ deform.	E	(R + IR)

TABLE 4

PREDICTED NORMAL MODES INVOLVING THE METHYL GROUP IN INTERNAL C_{3v} SYMMETRY AND SKELETAL C_s SYMMETRY

C-H stretch	$A_1 + E$	(2 R + 2 IR)
Internal deform.	$A_1 + E$	(2 R + 2 IR)
Methyl rock	E	(R + IR)
Methyl torsion	A_2	(Inactive)
W-CH$_3$ stretch	A'	(R + IR)
Ring-W-CH$_3$ deform.	$A' + A''$	(2 R + 2 IR)

The internal modes of the methyl group seem to reflect local C_{3v} symmetry, i.e. the group appears to be rotating freely about the $W-CH_3$ bond. If pseudo-rotation is taking place, then the symmetry of the Ring–W–CH$_3$ system will be C_s, and the skeletal vibrations so predicted are shown in Table 4 together with the predicted internal methyl vibrations.

(ii). *Vibrational assignment*

The internal vibrations of the C_5H_5 ring will be discussed first, the main sources of reference being reviews by Fritz[9] and Davidson[10], and the paper by Hyams et al.[13] on the vibrational spectrum of $(C_5H_5)Mn(CO)_3$. Fritz noted that the frequencies of the seven infra-red active fundamental vibrations of the ring were remarkably constant throughout a series of π-complexes of this type. The assignment of the corresponding frequencies for $(C_5H_5)W(CH_3)(CO)_3$ should therefore be fairly straightforward.

For the C–H stretching region, only solid phase data are available in both the infra-red and Raman spectra. The ring C–H stretching frequencies are in general higher than the methyl C–H stretching frequencies. By analogy with $(C_5H_5)Mn-(CO)_3$[13], for which polarisation data are available, the highest frequency band is assigned to the totally symmetric ring C–H stretching mode (R, 3130 cm^{-1}; IR, 3122 cm^{-1}; both of medium intensity). A medium intensity Raman band at 3110 cm^{-1}, with no infra-red counterpart, is assigned to the ring C–H stretching mode of E_2 symmetry which is infra-red inactive. This leaves an infra-red band of medium intensity at 2966 cm^{-1} to be assigned to the corresponding mode of E_1 symmetry, there being no coincident feature in the Raman spectrum.

The ring C–C stretching modes will now be considered. That belonging to the E_1 symmetry class is expected to occur[9] around 1420 cm^{-1}, and a medium intensity infra-red band is observed in the solid phase spectrum at 1418 cm^{-1}, with no Raman counterpart. The ring stretching mode of E_2 symmetry is assigned to a solid-phase Raman band[13] (no infra-red counterpart) at 1431 cm^{-1}, and is thought to be accidentally degenerate with the anti-symmetric methyl internal deformation mode. The totally symmetric (ring-breathing) mode is readily assigned to a sharp, intense Raman band (1111 cm^{-1} solid-phase; 1112 cm^{-1} in solution in CH_2Cl_2), which has a weak infra-red counterpart at 1107 cm^{-1} (solid-phase only). This assignment agrees well with those for ferrocene[11,12], and with that for $(C_5H_5)Mn(CO)_3$[13].

The assignment of the CH deformation modes is not so straightforward. Two in-plane modes are predicted to be Raman active (E_1+E_2) and one to be infra-red active (E_1). Three out-of-plane modes are predicted to be Raman active $(A_1+E_1+E_2)$ and two to be infra-red active (A_1+E_1). Vibrational assignments by Hartley and Ware[12] for $(C_5H_5)_2Fe$ and $(C_5H_5)_2Co^+$ agree with assignments by Lippincott and Nelson[11] for $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ru$ which are backed up by normal coordinate analyses[11,21]. The assignment by Hyams et al. for $(C_5H_5)Mn(CO)_3$[13] is made on the same basis. If the present assignment for $(C_5H_5)W(CH_3)(CO)_3$ followed those of previous workers, a band occurring in the infra-red solution spectrum at 1192 cm^{-1} (1182 cm^{-1}, Raman and infra-red solid-phase spectra) would be attributed to the CH in-plane deformation of E_2 symmetry. The feature observed in the infra-red solution spectrum at 1012 cm^{-1} (solid-phase IR at 1005 cm^{-1}, absent in the Raman spectrum) would be ascribed to an in-plane CH deformation of E_1 symmetry, while

a band observed only in the solid-phase (R, 1065 cm^{-1}; IR, 1061 cm^{-1}) would be assigned as the out-of-plane CH deformation belonging to the E_2 symmetry species. These assignments were based on comparisons with the vibrational spectra of benzene and the tropylium ion $(C_7H_7^+)^{21}$, and also the types of motion occurring in comparable normal modes of different molecules or ions were considered. Normal coordinate analyses for $(C_5H_5)_2Fe$ and $(C_5H_5)_2Ru$ were necessarily approximate as sufficient vibrational frequencies were available for the inclusion of only one interaction constant in the calculation. Another disturbing fact is the assignment of an infra-red solution frequency to a mode of E_2 symmetry, as such modes should be infra-red inactive, although they may be observable in solid-phase spectra. Also, for the free[22] and complexed[23] benzene molecule, all CH in-plane deformation modes occur at higher frequencies than the out-of-plane CH deformation modes.

In the light of the above discussion the following alternative assignments of these modes are tentatively put forward.

The band seen in the infra-red solution spectrum of $(C_5H_5)W(CH_3)(CO)_3$ at 1192 cm^{-1} is assigned as the CH in-plane deformation of E_1 symmetry, leaving the other band observed in solution in the infra-red in this region (at 1012 cm^{-1}) to be attributed to the out-of-plane CH deformation of E_1 symmetry. A feature appearing only in solid-phase spectra, at 1061 (IR), 1065 (R), is assigned to the E_2 CH in-plane deformation, while a weak infra-red band at 1262 cm^{-1} with no Raman counterpart is possibly due to the corresponding A_2 deformation which is formally totally inactive. The remaining out-of-plane deformation modes $(A_1 + E_2)$ are thought to be accidentally degenerate, or almost so. For $(C_5H_5)_2Fe^{11,12}$ and $(C_5H_5)Mn(CO)_3^{13}$ the A_1 and E_1 modes are assigned to bands only separated by a few wavenumbers, in the frequency region 820–840 cm^{-1}. In the infra-red spectrum of $(C_5H_5)W(CH_3)(CO)_3$, a medium to strong band is observed in the solid-phase at 831 cm^{-1} which is present in solution at 830 cm^{-1}, and this band probably arises from the totally symmetric out-of-plane CH deformation. A solid-phase Raman band at 838 cm^{-1} may also be due to this mode, or possibly to the corresponding one of E_2 symmetry. A comparable phenomenon is also noted for ferrocene by Hartley and Ware[12]. The above assignment of frequencies to CH deformations for $C_5H_5^-$ in C_{5v} symmetry differs significantly from earlier ones on what are considered to be reasonable grounds.

Only one each of the in-plane and out-of-plane ring deformation modes are spectroscopically active. Both of these belong to the E_2 symmetry species and should ideally give rise to bands in the Raman spectrum while being absent in the infra-red. Hyams[13] assigns the in-plane mode to a strong solid-phase infra-red band at 934 cm^{-1}, which has no Raman counterpart, in $(C_5H_5)Mn(CO)_3$. This is 150 cm^{-1} higher than the highest frequency assigned to an in-plane ring deformation in the toluene-chromium tricarbonyl complex[24]; however, a planar C_5 ring is under greater steric strain than a planar C_6 ring, so such modes might be expected to give rise to somewhat higher frequencies. Pitzer and Scott[22] assign the related mode in free benzene, of E_{1g} symmetry, to a frequency of 606 cm^{-1} and it is assigned to a frequency close to this in $(C_6H_6)Cr(CO)_3^{24,25}$. The degenerate in-plane ring deformation is assigned to a frequency of 947 cm^{-1} (solid-phase, very weak) for $[(C_5H_5)_2Co]Br_3^{12}$, but it was not observed for ferrocene or $[(C_5H_5)_2Co]Cl^{12}$. However, Hartley and Ware[12] noted that while most of the ring fundamentals were similar, the out-of-plane CH deformation frequencies were markedly higher for the cobalticinium cation than for the ferrocene

molecule, and so such a trend would not be surprising for the ring deformations. In the present work, therefore, the E_2 in-plane ring deformation is cautiously assigned to a weak band at 617 cm^{-1} (IR) and 614 cm^{-1} (R), both solid-phase frequencies.

The E_2 out-of-plane ring deformation mode corresponds to a mode of E_{2u} symmetry for free benzene, which should be totally inactive under the selection rules for the D_{6h} point group. It has, however, been attributed by Pitzer and Scott[22] to a weak Raman feature at 404 cm^{-1} for free benzene, and in benzene chromium tricarbonyl, where this mode has E symmetry and is therefore active, to a frequency of 426 cm^{-1} [25]. It might therefore be expected to give rise to a weak band of somewhat higher frequency for $(C_5H_5)W(CH_3)(CO)_3$. Hyams, for $(C_5H_5)Mn(CO)_3$[13], has assigned the out-of-plane ring deformation to a weak feature at 487 cm^{-1}, i.e. accidentally degenerate with the asymmetric W-(CO) stretching mode. A medium to strong band is observed in the solid-phase infra-red spectrum at 485 cm^{-1} (in solution at 489 cm^{-1}) which is assigned to a W-C-O deformation mode (vide infra). Its Raman counterpart at 487 cm^{-1} (solid-phase only) is comparatively more intense than has been observed for M-C-O deformations in other π-bonded (Hydrocarbon)M(CO)$_n$ complexes[19,24,25], and this is accounted for by also assigning the out-of-plane ring deformation mode to the frequency of 487 cm^{-1} (solid-phase).

This completes the proposed assignment for the C_5H_5 moiety and a summary of the frequencies and their corresponding modes is presented in Table 5.

TABLE 5

SUMMARY OF VIBRATIONAL FREQUENCIES FOR C_5H_5[a]

A_1	C-H stretch	(3126)
	C-C stretch	1112
	CH o.o.p. deform	830
A_2	CH i.p. deform.	? (1262)
E_1	C-H stretch	(2966)
	C-C stretch	(1418)
	CH i.p. deform.	1192
	CH o.o.p. deform.	1012
E_2	C-H stretch	(3110)
	C-C stretch	(1431)
	CH i.p. deform.	(1063)
	CH o.o.p. deform.	(ca. 838)
	Ring i.p. deform.	? (616)
	Ring o.o.p. deform.	(487)

[a] In cm^{-1}; figures in brackets refer to solid-phase frequencies.

The internal and external vibrations of the methyl group will now be discussed. The spectroscopic data indicate free rotation of the methyl group about the W-CH$_3$ bond, and so the internal modes are assigned on the basis of C_{3v} local symmetry. The C-H stretching modes are readily assigned to solid-phase infra-red frequencies at 2904 and 2829 cm^{-1}. The antisymmetric mode usually occurs at a higher frequency than the symmetric mode and is generally more intense. The present assignments are

based on this generalisation[26] in the absence of polarisation data. These frequencies are rather lower than the corresponding ones in toluene[22] and (toluene)$Cr(CO)_3$[24].

The only frequency assignable to the degenerate methyl internal deformation mode occurs in the solid-phase Raman spectrum at 1431 cm^{-1}, which is also assigned as a ring stretching mode (*vide supra*). The corresponding symmetric deformation is assigned to a weak band with a frequency of 1352 (IR), 1358 cm^{-1} (R), (solid-phase only).

The degenerate rocking mode is assigned with rather less confidence to a solid-phase infra-red band of low intensity at 1030 cm^{-1}. Such modes are mass-sensitive and variable in position due to interaction with skeletal stretching modes (which should not be too significant for this molecule); they are usually weak, and occur[26] in the range 900–1100 cm^{-1}. This assignment is therefore reasonable but by no means certain.

The W–CH_3 stretching mode (of A' symmetry) is assigned to a medium intensity Raman band occurring at 430 cm^{-1} in both solid-phase and solution spectra. This assignment must be regarded as very tentative, by analogy with frequencies of the Cr–(CH_3) stretching modes in $Li_4Cr_2(CH_3)_8 \cdot 4 C_4H_8O$ quoted by Krausse et al.[27] (480, 450, and 430 cm^{-1}). No more certain assignment of this mode can be made without the study of a series of similar compounds. Only incomplete spectral data are available for e.g. the $(C_5H_5)WH(CO)_3$ complex.

No bands attributable to the Ring–W–CH_3 or CH_3–W–$(CO)_3$ deformation modes were observed (all expected to occur below ca. 150 cm^{-1}).

A summary of the frequencies assigned to modes involving the methyl group is given in Table 6.

TABLE 6

SUMMARY OF VIBRATIONAL FREQUENCIES FOR THE METHYL GROUP[a]

A_1	C–H stretch	(2829)
	Internal deform.	(1356)
E	C–H stretch	(2904)
	Internal deform.	(1431)
	Rock	(1030)
A'	W–CH_3 stretch	430
	Ring–W–CH_3 deform. (i.p.)	
A''	Ring–W–CH_3 deform. (o.o.p.)	

[a] In cm^{-1}; figures in brackets refer to solid-phase frequencies.

As mentioned above, the vibrations of the Ring–$M(CO)_3$ system are discussed in terms of local symmetry of C_{3v} for the carbonyl ligands. Those of highest frequency are the C–O stretching modes, of which only two are observed in solution spectra, indicating that the selection rules of the C_{3v} point group prevail. The A_1 mode is assigned by analogy with previous work[13], where polarisation data are available, to the higher frequency band which occurs at 2021 (IR), 2017 (R) in solution in CH_2Cl_2 and at 2015 (IR) in solution in cyclohexane. This mode is not split in the solid-phase

spectra. The degenerate mode (E) is assigned to a frequency of 1918 (IR), 1917 (R) in CH_2Cl_2 and 1930 cm^{-1} (IR) in cyclohexane. This band is split in both solid-phase infra-red and Raman spectra, but cannot be resolved in solution in cyclohexane, showing that C_{3v} symmetry is a valid approximation for the discussion of the W–$(CO)_3$ vibrations.

The remaining vibrations of the Ring–W–$(CO)_3$ system are expected to have frequencies below 700 cm^{-1}, those of highest frequency being the W–C–O deformation modes, of which three should be active $(A_1 + 2E)$. For this type of molecule such vibrations usually give rise to strong infra-red bands with somewhat weaker, or even absent, Raman counterparts. Three such bands are observed in the infra-red spectrum of both the solid-phase and the solution of the complex. In the absence of polarisation data, the lowest frequency mode of the three is assigned as belonging to the totally symmetric species, by analogy with $(C_5H_5)Mn(CO)_3$[13] where polarisation data are available. This occurs at 485 (IR, solid), 489 (IR, solution) and 487 cm^{-1} (R, solid). This band is also thought to contain the out-of-plane ring deformation (vide supra). The features occurring at 551 (IR, solid-phase), 556 (IR, solution) and 585 (IR, solid), 587 (IR, solution), 585 (R, solid-phase) (all frequencies in cm^{-1}) are assigned as the two W–C–O deformation modes of E symmetry.

Two W–(CO) stretching modes $(A_1 + E)$ are expected at lower frequencies than the W–C–O deformation modes. The A_1 stretching mode is characteristically a very intense, polarised Raman band and is therefore assigned to such a feature at 470 (R, solid-phase), 463 (R, solution) 462 (IR, solid-phase) 464 cm^{-1} (IR, solution).

For the π-bonded (Hydrocarbon)M$(CO)_3$ complexes, the degenerate M–(CO) stretching mode generally occurs at a higher frequency than the corresponding symmetric vibration[20,23–25]. However, for $(C_5H_5)W(CH_3)(CO)_3$ this order seems to be reversed, and the degenerate mode is assigned to solid-phase infra-red and Raman bands of medium intensity at 442 and 445 cm^{-1} respectively. This order of frequencies is in agreement with the assignment proposed by Hyams[13] for $(C_5H_5)Mn(CO)_3$.

TABLE 7

SUMMARY OF THE VIBRATIONAL FREQUENCIES FOR Ring–W–$(CO)_3$[a]

A_1	C–O stretch	2015
	W–C stretch	463
	Ring–W stretch	(333)
	W–C–O deform.	? 489
	C–W–C deform.	
A_2	W–C–O deform.	
	Ring twist	
E	C–O stretch	1930
	W–C stretch	(444)
	W–C–O deform.	? 587
	W–C–O deform.	? 556
	Ring tilt	362
	C–W–C deform.	
	Ring–W–$(CO)_3$ deform.	

[a] In cm^{-1}; figures in brackets refer to solid-phase frequencies.

The degenerate ring-tilting mode is generally agreed to occur at a somewhat higher frequency than the corresponding ring–metal stretching mode, and in most cases bands attributed to these modes of vibration are observable. The ring tilt is assigned to a frequency of 364 cm^{-1} (IR, solid-phase) with a Raman counterpart at 365 (solid-phase), 362 cm^{-1} (solution), which is a little higher than the frequency of 352 cm^{-1} assigned by Fritz[9] to this vibration. The ring–metal stretch, which is often strong in the Raman spectrum, is assigned to a band of medium intensity at 333 cm^{-1} (R, solid-phase only). These frequencies are considerably higher than the comparable ones in (mesitylene)$W(CO)_3$[23], which could indicate stronger bonding between a Group VI transition metal atom and a $C_5H_5^-$ ring than such a metal atom and a C_6H_6 ring.

The only modes remaining to be assigned are the skeletal deformations i.e. of the Ring–W–$(CO)_3$ system and of the C–W–C angles. These are usually expected below 150 cm^{-1}, but examination of this region in both the far infrared and Raman spectra yielded no data.

A summary of the assignments of the Ring–W–$(CO)_3$ vibrations is given in Table 7.

Several weak bands are observed in the spectrum of this complex, especially in the infrared from a sample in the solid-phase, which arise from overtones and combinations. No analysis of these frequencies is attempted.

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