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THE VIBRATIONAL SPECTRA OF MESITYLENECHROMIUM TRICARBONYL AND MESITYLENEMOLYBDENUM TRICARBONYL

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SUMMARY

The infrared (150–4000 cm^{-1}) and Raman spectra (50–3200 cm^{-1}) of [1,3,5-$C_6H_3(CH_3)_3$]$M(CO)_3$ were obtained, for M=Cr and Mo. The method of "local symmetry" was used to obtain a vibrational assignment. The results were largely in agreement with previous, incomplete, infrared studies of these and similar molecules.

INTRODUCTION

A considerable amount of work has been done on the infrared spectra of (arene)$M(CO)_3$ complexes (where M=Cr, Mo or W)[1-5]. All of these compounds are yellow, and experimental difficulties prevented the study of their Raman spectra. The development of Raman excitation sources using red radiation (chiefly the He–Ne laser) has greatly decreased these difficulties, and the complete vibrational spectrum is now accessible. At the present time, however, no Raman spectra of (arene)$M(CO)_3$ compounds have been reported, although two papers have been published which deal with the closely analogous $C_5H_5M(CO)_n$ system *i.e.* $C_5H_5Mn(CO)_3$[6] and $C_5H_5V(CO)_4$[7].

As there has been great interest in the structures of π-bonded organometallic complexes, and in the bonding in such systems, we were interested in obtaining as complete a picture as possible of the vibrational frequencies in [1,3,5-$C_6H_3(CH_3)_3$]$Cr(CO)_3$ and [1,3,5-$C_6H_3(CH_3)_3$]$Mo(CO)_3$.

EXPERIMENTAL

The compounds were prepared by refluxing the metal hexacarbonyls with mesitylene under an atmosphere of nitrogen[8-10]. Purification was carried out by sublimation of the product *in vacuo*. C and H analyses of the two compounds were satisfactory.

Infrared spectra were run on a Perkin–Elmer 521 (from 4000 to 300 cm^{-1}) and on a Beckman IR 11 (from 500 to 150 cm^{-1}). In the higher frequency region solid samples were run as KBr discs, and solutions in cyclohexane, CS_2 and CH_2Cl_2 were also used. The instrument was calibrated using peaks of CH_4, HBr, CO, H_2O and NH_3; the frequencies are all expected to be accurate to ± 2 cm^{-1}. For the IR 11

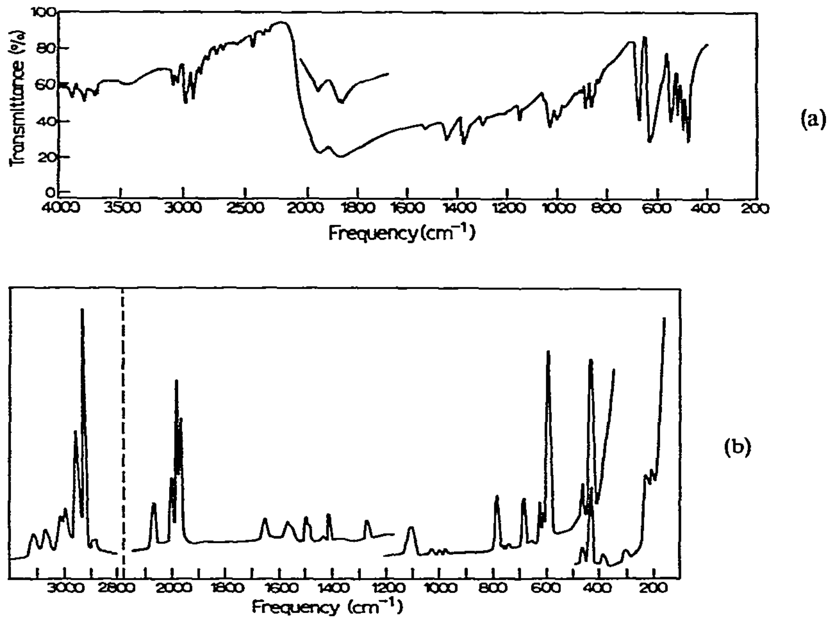

Fig. 1. (a). Infrared spectrum of solid $[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$ (KBr disc). (b). Raman spectrum of solid $[1,3,5\text{-}C_6H_3(CH_3)_3]$ $Cr(CO)_3$ (powder). (N.B. The bands at 2880 and 2910 cm^{-1} are spurious; that at 2930 cm^{-1} is partly spurious.)

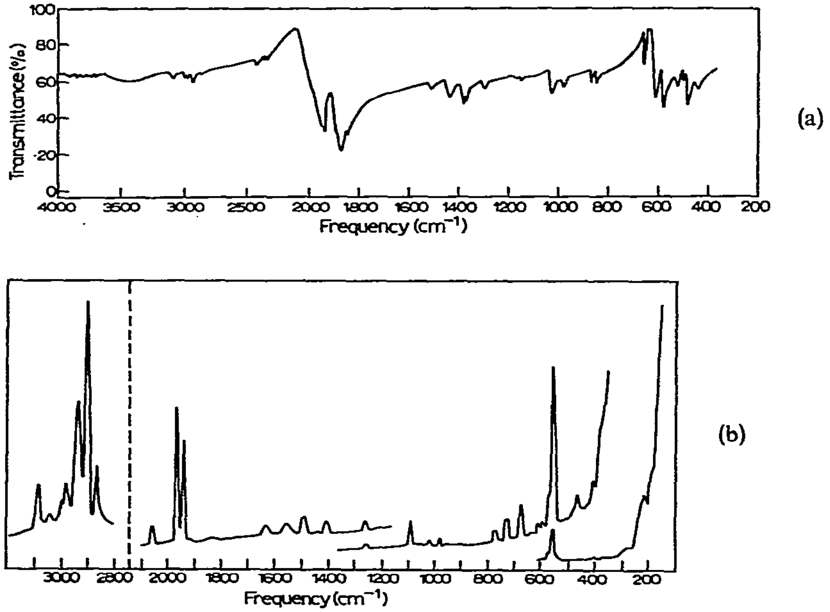

Fig. 2. (a) Infrared spectrum of solid $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$ (KBr disc). (b) Raman spectrum of solid $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$ (powder). [N.B. The spurious bands at 2900 cm^{-1} are described in Fig. 1(b).]

spectra, the solids only were examined, in nujol mulls between polythene discs.

Raman spectra were obtained using a Cary Model 81 spectrometer with a Spectra-Physics 125 He–Ne laser as exciting source (output approx. 60 mw at 632.8 nm). Solid state spectra were run, as well as solutions in benzene and CH_2Cl_2. There was no evidence of photodecomposition in any of the solid samples or solutions, but the solutions were slightly air-sensitive and were always used when freshly made up.

The infrared and Raman spectra of solid $[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$ and the analogous molybdenum compound are shown in Figs. 1 and 2 respectively.

RESULTS AND DISCUSSION

The infrared and Raman frequencies observed for $[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$ are listed in Table 1, together with the assignments of these frequencies which will be discussed below. The data for the molybdenum compound are treated similarly in Table 2.

(*continued p.* 106)

TABLE 1

INFRARED AND RAMAN SPECTRA AND ASSIGNMENT FOR $[1,3,5\text{-}C_6H_3(CH_3)_3]Cr(CO)_3$

Infrared			Raman			Assignment[c]
Solid (KBr disc)	Solution		Solid	Solution		
	CH_2Cl_2	CS_2		CH_2Cl_2	C_6H_6	
3908 vw						
3892 w						
3842 vw		3840 vw				
3795 w						
3710 w						
3691 vw						
3084 w		3084 vvw	3095 m			C–H stretch (A_1?)
3053 w			3049 m			
2985 m		2982 w	2987 sh			C–H stretch (E?)
2974 m		2961 w	2975 m			
2929 m	2924 m		2946 m		2927 m	CH_3 stretch (A_1)
2860 w	2868 w				p.	CH_3 stretch (E)
2808 vw						
2738 w			2745 w			
2680 vw						
2539 vvw						
2455 vw						
2433 w						
2349 vw						
2300 vvw						
2221 vvw						
1965 s 1946 sh	1960 vs	1963 vs 1968 s[b]	1949 s 1942 sh	1962 w	1961 m p.	C–O stretch (A_1)
1882 vs 1868 vs 1861 s 1852 s	1875	1889 vvs 1899 s[b]	1883 s 1867 vs 1854 vs	1880 s, dp.	1886 s dp.	C–O stretch (E)

TABLE 1 (*continued*)

Infrared			Raman			Assignment[c]
Solid (KBr disc)	Solution		Solid	Solution		
	CH_2Cl_2	CS_2		CH_2Cl_2	C_6H_6	
1745 w						
1531 w	1539 m		1539 m	1542 w	1539 w	Ring stretch E
1450 ms	1454 ms		1455 ms		1455 w	Ring stretch (E)
			1440 sh		?p.	and CH_3 def. (E)
1385 m	1386 m	1382 m	1387 m	1389 w,	1388 w	CH_3 def. (A_1)
1379 ms		1382 m[b]	1381 w	p.	p.	
			1324 vw			
1302 m	1302 m	1303 m	1304 m	1301 w,	1304 m	C–C′ stretch (A_1)
1220 vw		1303 w[b]		p.	p.	? i.p. CH def. (A_2)
1156 w			1159 m			i.p. CH def. (E)
1149 w						
1048 vw		1035 m	1044 vw			CH_3 rock (E)
1032 m						
1001 m		1000 w	955	1001 m,		Ring stretch (A_1)
994 w				p.		
966 w						
920 vw			923 w	922 w	923 w	C–C′ stretch (E)
					? dp.	or o.o.p. CH def. (E).
901 vw						
888 mw			894 w	896 w		C–C′ stretch (E)
883 (sh)						or o.o.p. CH def. (E)
863 mw			874 w			
856 sh						
831 w	672 ms		835 w			o.o.p. CH def. (A_1)
	671 s	669 ms	673 ms	674 m	671 ms	Cr–C–O def. (A_1)
					? p.	and o.o.p. ring def. (A_1)
			659 sh			? Cr–C–O def. (A_2)
630 s	631 s	626 s	636 w	635 vw	631 w	Cr–C–O def. (E)
572 w			574 ms	576 ms,	576 ms	i.p. ring def. (A_1)
				p.	p.	
548 s	546 ms	543 m	549 w			Cr–C–O def. (E)
513 m	513 ms	514 m	514 ms	516 w,	516 m	i.p. ring def. (E)
				? dp.	? dp.	
499 ms	497 m	493 m	501 w	500 w	500 sh	Cr–C stretch (E)
		494 w[b]		(sh)		
483 s	482 ms	485 m	484 vs	484 s	483 vs	Cr–C stretch (A_1)
		476 w[b]		p.	p.	
357 ms[a]			354 ms	358 w	359 m	Ring tilt (E)
				dp.	dp.	
327 w[a]			325 vs	329 s	329 vs	Ring–Cr stretch (A_1)
				p.	p.	
				272 m	272 w	o.o.p. C–C′ def. (E)
196 m[a]			194 ms	195 m	185 m	o.o.p. C–C′ def. (A_1)
					p.	
			120			C–Cr–C def. (A_1)
			113 sh			C–Cr–C def. (E)
			97 s			Ring–Cr–$(CO)_3$ def. (E)

[a] Nujol mulls (IR 11 spectra). [b] In C_6H_{12} solution. [c] o.o.p. = out-of-plane; i.p. = in-plane.

TABLE 2

INFRARED AND RAMAN SPECTRA AND ASSIGNMENTS FOR $[1,3,5\text{-}C_6H_3(CH_3)_3]Mo(CO)_3$

Infrared			Raman			Assignment
Solid	Solution		Solid	solution		
(KBr disc)	CH_2Cl_2	C_6H_{12}		CH_2Cl_2	C_6H_6	
3895 w						
3798 w						
3784 vw						
3732 w						
3695 w						
3078 3040 vw			3084 w 3038 vw			C–H stretch (A_1 ?)
2985 m 2968 w			2995 w 2978 w			C–H stretch (E ?)
2922 w m			2945 m			CH_3 stretch (A_1)
2860 w						CH_3 stretch (E)
			2744 vw			
2421 w						
2409 vw						
2352 w						
2339 w						
1950 s 1943 vs	1960 s	1968 vs	1955 m 1950 sh	1960 w p.		C–O stretch (A_1)
1900 vw 1879 vs 1855 m	1876 s	1896 vs	1888 sh 1862 s 1842 s 1831 (sh)	1880 m dp.	1880 m dp.	C–O stretch (E)
			1820 vw			
1521 m 1508 (sh)			1528 w			Ring stretch (E)
1443 s			1451 w			CH_3 def. (E) and ring stretch (E)
1383 m 1376 ms			1386 s 1378 (sh)			CH_3 def. (A_1)
1298 m			1302 w		1304 vw	C–C′ stretch (A_1)
1170 vw 1153 w			1156 w			i.p. CH def. (E)
1033 s	1035 w					CH_3 rock (E)
986 m			990 ms	989 w p.		Ring stretch (A_1)
			918 w			C–C′ stretch (E) or o.o.p. CH def. (E)
873 m 870 (sh)			878 w			o.o.p. CH def. (E) or C–C′ stretch (E)
850 m 845 (sh)			858 vw			
821 ms			826 vw			o.o.p. CH def. (A_1)
663 ms			669 w			o.o.p. ring def. (A_1)
631 (sh) 613 s	617 w		625 m	620 vw ? dp.		Mo–C–O def. (E)
586 s	574 m		575 mw	572 w	572 m p.	Mo–C–O def. (A_1) and i.p. ring def. (A_1)

TABLE 2 (*continued*)

Infrared			Raman			Assignment
Solid	Solution		Solid	solution		
(KBr disc)	CH_2Cl_2	C_6H_{12}		CH_2Cl_2	C_6H_6	
527 m			535 vw			Mo–C–O def. (E)
504 m	503 w		507 w		508 vw	i.p. ring def. (E)
490 s 469 w	491 m		493 w 467 (sh)			Mo–C stretch (E)
451 m			453 vs	453 m p.	452 s p.	Mo–C stretch (A_1)
369 s[a] 360 ms[a]			360 m			Ring tilt (E)
306 s[a]			305 m		305 w	Ring stretch (A_1)
276 m[a]			275 m		286 w	o.o.p. C–C′ def. (E)
184 s[a]			175 m	172 w		o.o.p. C–C′ def. (A_1)
			121 (sh)			C–Mo–C def. (E)
			113 m			C–Mo–C def. (A_1)
			91 m			Ring–Mo–$(CO)_3$ def. (E)

[a] Nujol mull (IR 11 spectra).

(*i*). *Vibrational analysis*

We may consider first the isolated $[1,3,5\text{-}C_6H_3(CH_3)_3]M(CO)_3$ molecule. The overall symmetry of the molecule could be as high as C_{3v}, if the methyl groups and the carbonyl groups are eclipsed. It is more likely, however, that they will be staggered as shown in the crystal structure of $[C_6(CH_3)_6]Cr(CO)_3$[11], and if this is so the threefold axes and vertical planes of symmetry will be lost and the overall point group will be C_1. However, the use of the concept of "local symmetry" is well established for this type of molecule[6,7,12], and so the mesitylene ligand and the $M(CO)_3$ fragment can be treated separately, and both have effective C_{3v} symmetry.

In the mesitylene portion, it is convenient to subdivide the vibrations once again into methyl vibrations and those of the $C_6H_3C'_3$ portion. If the 3 methyl groups do not couple to any significant extent, then we would expect to find the following: C–H stretches, A_1+E; CH_3 deformations, A_1+E; CH_3 rock, E and C–X stretch, A_1 (included in ring vibrations). For the rest of the mesitylene molecule, the following modes are predicted:

(*a*) Stretching vibrations of the C_6 ring: A_1+A_2+2E.
(*b*) In-plane ring deformations: A_1+E.
(*c*) Out-of-plane ring deformations: A_1+E.
(*d*) C–H stretches: A_1+E.
(*e*) C–C′ stretches: A_1+E.
(*f*) In-plane CH deformations: A_2+E.
(*g*) Out-of-plane CH deformations: A_1+E.
(*h*) In-plane CC′ deformations: A_2+E.
(*i*) Out-of-plane CC′ deformations: A_1+E.

(It must be remembered that in systems of C_{3v} symmetry A_1 modes are infrared- and Raman-active, giving polarised bands in the latter; that A_2 modes are totally inactive, and that E modes are infrared and Raman-active, giving depolarised Raman lines.)

For the $M(CO)_3$ fragment, there will be 15 vibrations, which can be classified as follows:
(*a*) M–C stretch: A_1+E.
(*b*) C–O stretch: A_1+E.
(*c*) M–C–O deformation: A_1+A_2+2E.
(*d*) C–M–C deformation: A_1+E.
Inclusion of the vibrations involving the whole (arene)–M–$(CO)_3$ unit adds another six (A_1+A_2+2E):
(*a*) Ring–M stretch: A_1.
(*b*) Ring twist: A_2.
(*c*) Ring tilt: E.
(*d*) Ring–M–$(CO)_3$ deformation: E.
Thus we have a total of 78 fundamental vibrations (57 from the mesitylene ligand), and a complete and unambiguous assignment of frequencies to all of these would be a formidable task, even with the help of infrared and Raman spectra (complete with polarisation data). Some question marks will undoubtedly remain.

All that has been said so far relates to the free molecules, which exist, to a reasonable approximation, in solution. The spectra of the solid compounds are very much more complex than can be accounted for even in terms of 78 fundamental frequencies. Unfortunately, no crystal structures have been determined for the two molecules with which we are concerned, but some inferences can be drawn from the results on $C_6H_6Cr(CO)_3$[13] and $[C_6(CH_3)_6]Cr(CO)_3$[11]. The former has two, the latter no less than eight, molecules per unit cell, and their space groups are respectively $P2_1/m$ (C_{2h}^2) and $Pbca$ (D_{2h}^{15}). The local symmetries for the mesitylene complexes could not be sub-groups of either of these, and hence the site-symmetry would be C_1. Thus the vibrations of the molecule would all be infrared- and Raman-active, and also all the degenerate vibrations of the free molecule would be split. In addition, the possible presence of several molecules per unit cell could give rise to extensive correlation splitting. It will be seen from the tables of frequencies that in many cases in the solid spectra there are considerable differences in frequency between the Raman and infrared features corresponding to the same vibration of the free molecule.

In the absence of crystal structure data, a detailed assignment of the solid frequencies will in general not be possible, but useful information may sometimes be gained from the behaviour of bands upon passing from solution to solid.

(*ii*). *Assignment of frequencies*

The chromium compound was found to be much more soluble in convenient solvents than the molybdenum compound, and so much more reliable polarisation data etc. could be obtained for the former. Consequently, in the following discussion, the chromium compound will always be the first to be discussed, and in greater detail.

The vibrations of the mesitylene will be dealt with first, in the order in which they were listed above. The chief source of information on the vibrational spectrum of mesitylene itself is the paper by Pitzer and Scott[14], with assignments modified as suggested by Mair and Hornig[15].

Let us consider first the methyl vibrations. A band at 1025 cm^{-1} is assigned as a methyl rocking vibration for free mesitylene[14], and in the Cr complex bands are found at 1035 (IR, CS_2 solution) and 1044 cm^{-1} (Raman, solid only), which can be similarly assigned. In the Mo compound, no Raman band is found in this region, but an IR absorption at 1035 cm^{-1} (in CH_2Cl_2 solution) is observed.

Two CH_3 deformation frequencies should be seen, of symmetry A_1 and E respectively. The former can be assigned to a Raman band (Cr) at 1388 cm^{-1}, which is polarised, and which has an infrared counterpart at 1386 cm^{-1} (both CH_2Cl_2 solution). Both the infrared and Raman bands appear to be split in the solid, which could indicate that another mode might be accidentally degenerate with this in the solution. In the Mo compound, no bands are found in solution in this region, but, in the solid phase, a Raman band at 1386 cm^{-1} (shoulder at 1378 cm^{-1}) and an infrared band at 1383 cm^{-1} (shoulder at 1376 cm^{-1}) probably represent the same mode. The CH_3 deformation of symmetry class E normally occurs at a higher frequency than the symmetric mode[16]; in the Cr compound a Raman band of uncertain polarisation is found at 1455 cm^{-1} (in benzene solution), with an infrared band at 1454 cm^{-1} (CH_2Cl_2) which can be assigned to this mode. For the Mo analogue again, bands are only seen in the solid-phase spectra, at 1443 (IR) and 1451 cm^{-1} (Raman).

The methyl C–H stretches are expected to occur between 2860 and 2950 cm^{-1}. A polarised feature at 2927 cm^{-1} in the Cr complex (benzene solution) is assigned as the A_1 stretch (IR band at 2924 cm^{-1} in CH_2Cl_2), while the E mode is assigned to the IR band at 2868 cm^{-1} (CH_2Cl_2 solution). No Raman counterpart to the latter is seen. For the Mo compound, only solid phase data are again available; the most likely candidate for the E mode is an infrared band at 2860 cm^{-1} (no Raman), while the A_1 mode is assigned to a Raman band at 2945 cm^{-1}, and an infrared band at 2922 cm^{-1}. [This frequency difference must be attributed to correlation splitting; in the Cr compound a similar effect is found in the solid spectra, the Raman band at 2927 cm^{-1} (solution) shifting to 2946 cm^{-1} in the solid.]

The remaining vibrations of the mesitylene ligand are those of $C_6H_3C'_3$, where C′ now represents the methyl group considered as a point mass. The vibrations were classified above into nine types (which must of course be approximations, as in many cases extensive coupling between modes will occur). The first were the stretching vibrations of the C_6 ring (A_1+A_2+2E). The totally symmetric (ring-breathing) mode gives rise to a strong band in the Raman spectrum. This is found, in the Cr compound, to give a polarised band at 1001 cm^{-1} (CH_2Cl_2 solution) with an infrared band at 1000 cm^{-1} (CS_2 solution). For the Mo compound, á polarised band is found at 989 cm^{-1}, with an infrared counterpart at 986 cm^{-1} (solid only).

The two ring stretching E modes in benzene are found[15] at 1596 and 1478 cm^{-1}. In mesitylene itself, the analogous bands are found[2] at 1620 and 1515 cm^{-1}, and Humphrey has suggested[2] that both are decreased in frequency in the (mesitylene) $Cr(CO)_3$, with infra-red bands at 1545 and 1465 cm^{-1}. The present results confirm this finding; in the infrared (CH_2Cl_2 solution) bands are found at 1539 and 1454 cm^{-1}, while in the Raman spectrum (CH_2Cl_2 solution) a band is seen at 1542 cm^{-1}, and in benzene solution bands occur at 1539 and 1455 cm^{-1} (all of uncertain polarisation). These are, therefore, assigned to the E class ring stretching modes (the lower frequency band has also been assigned to a CH_3 deformation, *vide sup.*). In the Mo compound, infrared bands are found at 1521 and 1443 cm^{-1}, Raman bands at 1528 and 1451 cm^{-1} (all in the solid).

The second class of ring vibrations are the in-plane deformations (A_1+E). In benzene these occur at 1010 and 606 cm^{-1}, but in free mesitylene they are assigned to strong bands in the Raman spectrum at 575 (pol, A_1) and 515 cm^{-1} (depol, E) respectively. It seems that there is very little shift in frequency for these modes on going from the free molecule to the Cr complex; a strong, polarised Raman band is found at 576 cm^{-1} (CH_2Cl_2 and benzene solution) with a weak infrared band at 572 cm^{-1} (solid), and a medium intensity Raman band is found at 516 cm^{-1} (probably depolarised) with an infrared band at 513 cm^{-1} (infrared and Raman frequencies for a CH_2Cl_2 solution). The higher frequency band is assigned as the A_1 mode, the lower as the E mode. In the Mo compound the E mode is assigned to a Raman band at 508 cm^{-1} (benzene solution), while the A_1 mode is thought to be accidentally degenerate with an Mo–C–O deformation mode at 572 cm^{-1} (benzene and CH_2Cl_2 solutions). The corresponding infrared absorptions are at 503 (CH_2Cl_2 solution) and 574 cm^{-1} (CH_2Cl_2 solution).

Out-of-plane ring deformations (A_1+E for C_{3v}) occur in benzene at 703 and 405 cm^{-1} respectively; the former is shifted to 690 cm^{-1} in mesitylene, while the latter does not give an observable band. In the Cr complex, there is no band which can reasonably be assigned as the E mode, while the expected position of the A_1 mode coincides with the region of the spectrum where Cr–C–O deformations might be found[5]. It is probably accidentally degenerate with the 671 cm^{-1} carbonyl deformation mode. In the Mo compound, the carbonyl deformations have been assigned to lower frequencies[5], and the band at 669 (Raman, solid), and 663 cm^{-1} (infrared, solid) can be assigned as the A_1 out-of-plane ring deformation. Once again, no feature attributable to the E mode was seen.

It proved to be impossible to find a solvent for the two complexes which would given Raman bands for the "aromatic" C–H stretching region of sufficient intensity to be observed (It should be noticed that the sensitivity of the Cary 81 over 3000 cm^{-1} from 632.8 nm on the Stokes side is rather low.). Hence the unambiguous assignment of frequencies for the A_1 and E modes is difficult. A pair of bands at 2970–2985 cm^{-1} is found in the infrared and the Raman of the solid Cr compound, and another pair at 3050–3080 cm^{-1}. A tentative assignment of the higher frequency region to the A_1 mode, and the lower to the E mode can be made on the basis of Fritz and Manchot's results for $C_6H_6Cr(CO)_3$[3]. They would presumably be split by both site symmetry and factor group effects, but there appear to be two bands in the infrared CS_2 solution spectrum at 2982 and 2961 cm^{-1}. Further studies on this region will be necessary to clarify the position. The situation in the Mo compound is exactly similar, although here solid phase frequencies only are available.

Two C–C′ stretches are also expected (A_1+E), and the frequencies assigned to them by Pitzer and Scott for free mesitylene[14] are 1300 (Raman pol; A_1) and 930 cm^{-1} (Raman, uncertain polarisation, and infrared; E). The former clearly corresponds to the polarised Raman band found for the Cr complex at 1301 cm^{-1} (CH_2Cl_2 solution), with an infrared band at 1302 cm^{-1} (CH_2Cl_2 solution). An assignment of the E mode is much more difficult; three bands are found in the region 860–925 cm^{-1} which could be chosen (an out-of-plane C–H deformation is expected in the same region). On present evidence no choice can be made between the bands (Raman) at 874, 894 and 923 cm^{-1}. For the lower frequency features, the infrared counterpart is split into two components.

In the Mo compound, the A_1 mode gives a Raman line at 1304 cm^{-1} with an infrared band at 1298 cm^{-1}. One can pick values for the two expected fundamentals (E mode C–C′ stretch and out-of-plane CH deformation) from three frequencies in the 850–925 cm^{-1} region.

In-plane C–H deformations give rise to an A_2 (inactive) mode and an E mode. The latter appears at 1160 cm^{-1} in free mesitylene[14], and can be assigned, in the Cr compound, to a band at 1159 cm^{-1} (Raman, solid) and an infrared band at 1156 cm^{-1} (solid, shoulder at 1149 cm^{-1}). A value of 1220 cm^{-1} is predicted for the A_2 mode, and the only feature which could be assigned to this is a very weak infrared band (solid) at exactly 1220 cm^{-1} in the Cr compound. In the Mo compound, the E mode is assigned to a Raman band at 1156 cm^{-1} (solid) and an infrared band at 1153 cm^{-1} (solid, possible second component at 1170 cm^{-1}).

Two out-of-plane C–H deformations are expected; the E mode has been discussed above in connection with the C–C′ stretching frequency. The A_1 mode is expected to appear at about 840 cm^{-1} [14] and is tentatively assigned to the band in the Cr compound at 835 cm^{-1} (Raman, solid) and 831 cm^{-1} (infrared, solid). Similarly, in the Mo compound, a weak band at 826 (Raman, solid) and 821 cm^{-1} (infrared, solid) can be so assigned.

TABLE 3

SUMMARY OF VIBRATIONS ASSOCIATED WITH THE MESITYLENE LIGAND IN $[1,3,5\text{-}C_6H_3(CH_3)_3]M(CO)_3$
Figures in brackets refer to solid phase frequencies. All frequencies are in cm^{-1}.

Mode	Vibration	M=Cr	M=Mo
A_1	C–H stretch	(~3060)	(~3060)
	CH_3 stretch	2927	(2945)
	C–C′ stretch	1302	1301
	Ring stretch	1001	989
	CH_3 def.	1387	(1385)
	i.p. ring def.	576	572
	o.o.p. ring def.	671	(666)
	o.o.p. CH def.	(833)	(824)
	o.o.p. C–C′ def.	185	172
A_2	Ring stretch		
	i.p. C–H def.	(1220)	
	i.p. C–C′ def.		
E	C–H stretch	~2970	(~2975)
	CH_3 stretch	2886	(2860)
	C–C′ stretch	~880 or ~920	~860 or ~920
	Ring stretch	1540	(1521)
	Ring stretch	1455	(1447)
	CH_3 def.	1455	(1447)
	i.p. ring def.	515	503
	o.o.p. ring def.		
	i.p. C–H def.	(1158)	(1155)
	o.o.p. C–H def.	~860 or ~920	~850 or ~920
	i.p. C–C′ def.		
	o.o.p. C–C′ def.	272	286
	CH_3 rock	1035	1035

The only remaining mesitylene vibrations are these associated with in-plane and out-of-plane C–C′ deformations, of low frequency. An A_1 out-of-plane mode is assigned for the Cr complex to the polarised Raman band at 185 cm^{-1} (benzene solution), which has an infrared counterpart at 196 cm^{-1} (solid). This agrees quite well with the figure of 183 cm^{-1} for the analogous vibration in free mesitylene[17,18]. Two E modes should be seen, one in-plane and one out-of-plane C–C′ deformation, which are found at 230 and 275 cm^{-1} respectively, in mesitylene[14,17,18]. The latter band is found at 272 cm^{-1} in the Raman spectrum of the Cr compound (benzene solution) but nothing corresponding to the in-plane mode is seen, unless it has shifted into accidental degeneracy with one of the out-of-plane modes. In the Mo compound a band at 172 (Raman CH_2Cl_2 solution) and 184 cm^{-1} (infrared, solid) corresponds to the A_1 in-plane deformation, while a band at 286 (Raman, benzene solution) and 276 cm^{-1} (infrared, solid) corresponds to the E mode. There is again no sign of the E class in-plane deformation or (for either compound) of the A_2 mode.

A summary of the proposed assignments is given in Table 3.

It will now be possible to consider the vibrations of the $M(CO)_3$ fragment and those involving the whole Ring–M–$(CO)_3$ system.

A very useful set of general observations on the assignments of transition metal carbonyl frequencies has been published by Durig *et al.*[7]. These were of considerable assistance in interpreting the present data.

The C–O stretching region is the one which has been the most extensively studied for all transition-metal carbonyl systems, and so there is a great deal of evidence upon which to base an assignment. For a C_{3v} $M(CO)_3$ arrangement, two C–O stretches (A_1+E) are expected. For both the complexes, two bands are found in the 1800–2000 cm^{-1} region, which can be assigned to these two modes. A medium intensity, polarised Raman band at 1962 cm^{-1} (benzene solution) in the Cr complex must be due to the A_1 mode (an infrared absorption is found at 1968 cm^{-1} in cyclohexane solution). A strong depolarised Raman band at 1886 cm^{-1} (benzene solution) in the Cr complex, with an infrared band at 1899 cm^{-1} (cyclohexane solution) corresponds to the E mode. In the Raman spectrum of the Mo complex the analogous band is found (depolarised) at 1880 cm^{-1} (CH_2Cl_2 and benzene solutions), and in the infrared at 1896 cm^{-1} (cyclohexane solution).

In the solid-phase spectra, this simplicity disappears, and a very complex array of bands is seen; this is due to both site symmetry and to factor group splitting effects. That the latter are important can be seen from the splitting of the A_1 mode in the solid spectrum of both complexes *e.g.* in the solid Raman spectra of the Cr complex, two bands are seen, at 1949 cm^{-1} and 1942 cm^{-1} while in the infrared of the solid two bands occur at 1965 and 1946 cm^{-1}.

For all of the subsequent normal modes, the conventional descriptions are clearly only approximate, as extensive mixing of the different modes will undoubtedly occur.

M–C stretches should give two modes (A_1+E) and there has been some disagreement among previous authors about the assignment of these modes in $C_6H_6Cr(CO)_3$. Fritz and Manchot suggested that the A_1 mode is situated at 535 cm^{-1}, with the E mode at 306 cm^{-1}, whereas Adams[5] and Bailey and Lippincott[19] favour 483 cm^{-1} for the A_1 mode and 306 cm^{-1} for the E mode. This low value for the degenerate M–C stretch is not, however, repeated in other, similar systems. In $C_5H_5Mn(CO)_3$, Hyams *et al.*[6] assign this mode to a frequency of 480 cm^{-1} (*cf.* A_1 mode 500 cm^{-1}) and in $C_5H_5V(CO)_4$[7], the A_1 mode is assigned to the lowest frequency (432 cm^{-1}) with both the B_1 (456 cm^{-1}) and E modes (495 cm^{-1}) higher. The present investigation seems to indicate a similar situation for the two mesitylene complexes. In the Cr complex a very strong, polarised, Raman band at 483 cm^{-1} (CH_2Cl_2 and benzene solutions) must belong to the A_1 mode, but the most likely candidate for the E mode is a weak Raman band at 500 cm^{-1}. Both of these have infrared counterparts; the former at 482 cm^{-1} (CH_2Cl_2 solution), the latter at 497 cm^{-1} (medium strong, CH_2Cl_2 solution). In the Mo complex, a strong, polarised Raman band at 452 cm^{-1} (CH_2Cl_2 and benzene solutions) corresponds to the A_1 stretch (infrared at 451 cm^{-1} solid phase), while a strong infrared band at 491 cm^{-1} (CH_2Cl_2) can be assigned to the E mode (weak Raman band at 493 cm^{-1}—solid only).

The M–C–O deformations have been previously assigned on the basis of infrared results by Adams[5]. In the Cr complex, Adams gives the frequencies 673, 632 and 543 cm^{-1}, and in the Mo complex 614, 587 and 528 cm^{-1} (all frequencies for solid-phase spectra). In the present work similar infrared frequencies are found in solution for both complexes (except for the lowest frequency mode of Mo). Corresponding Raman frequencies are also seen. No very conclusive polarisation data were obtained, but there were indications that in the Cr complex the highest frequency (670 cm^{-1}) band was polarised and hence probably the A_1 mode. For the Mo complex, however, the highest frequency band appeared to be depolarised, while that at approximately 575 cm^{-1} was certainly polarised. The latter is not such good evidence as it might appear to be, however, as this band is coincident with the A_1 in-plane ring deformation (*vide sup.*). Finally, a weak Raman band is seen in the solid spectrum of the Cr complex at 659 cm^{-1}. This could be the formally forbidden A_2 deformation.

The C–M–C deformations are generally agreed to occur around 100 cm^{-1}. In the present investigation, infrared facilities in this region were not available, and only solid-phase Raman spectra were obtained. Two deformation bands are expected (A_1+E), and also in this region the Ring–M–$(CO)_3$ bend (E). Three bands are seen for each complex, and without further evidence a definite assignment cannot be made. It is suggested that the A_1 C–M–C deformation is represented by the strong band at 120 cm^{-1} (Cr) and the medium intensity band at 113 cm^{-1} (Mo), while the E C–M–C deformation is assigned to the shoulders at 113 cm^{-1} (Cr) and 121 cm^{-1} (Mo). This assumes that the stronger band in each case corresponds to the totally symmetric mode. The Ring–M–$(CO)_3$ deformation is then assigned to the one remaining band at 97 cm^{-1} (Cr) and 91 cm^{-1} (Mo).

Three normal modes now remain, the ring–M stretch (A_1) the ring tilt (E) and the ring twist (A_2). The last is inactive and no observed frequency can reasonably be assigned to it. The ring–Cr stretch is assigned to a strong, polarised, Raman band at 329 cm^{-1} (CH_2Cl_2 and benzene solutions), with an infrared band at 327 cm^{-1}; the ring–Mo stretch is assigned to a band at 305 cm^{-1} in the Raman spectrum (uncertain polarisation in benzene solution) which has an infrared analogue at 306 cm^{-1} (solid). Finally, the ring-tilt can be assigned to the medium intensity, depolarised Raman band at 359 cm^{-1} (Cr, CH_2Cl_2 and benzene solutions) and a medium strong band at 357 cm^{-1} (infrared, solid). For the Mo complex, a band is observed at 360 cm^{-1} in the Raman spectrum of the solid, and at 360 cm^{-1} (with a shoulder at 369 cm^{-1}) in the infrared spectrum; this is clearly the E class ring tilt vibration.

TABLE 4

SUMMARY OF VIBRATIONS ASSOCIATED WITH THE $M(CO)_3$ FRAGMENT AND WITH THE RING–M–$(CO)_3$ SYSTEM IN $[1,3,5\text{-}C_6H_3(CH_3)_3]M(CO)_3$

Figures in brackets refer to solid phase frequencies. All frequencies in cm^{-1}.

Mode	Vibration	M=Cr	M=Mo
A_1	C–O stretch	1968	1968
	M–C stretch	484	452
	M–Ring stretch	329	305
	M–C–O def.	671	572
	M–C–M def.	(120)	(113)
A_2	M–Co–O def.	(659)?	
	Ring twist		
E	C–O stretch	1899	1896
	M–C stretch	494	492
	M–C–O def.	633	620
	M–C–O	(547)	(530)
	Ring tilt	385	(360)
	C–M–C def.	(113)	(121)
	Ring–M–$(CO)_3$ def.	(97)	(91)

A summary of the proposed assignments for the Ring–M–$(CO)_3$ vibrations is given in Table 4.

In addition to the above frequencies which have all been assigned as fundamentals, a large number of other bands (all weak to very weak in intensity) must be assigned as combinations and or overtones. We felt that it would not be a profitable exercise to attempt assignments for all these. Most are observed only in the solid-phase spectra, and our knowledge of the state of the molecules in the solid is insufficient to attempt other than a very superficial analysis. It appears, however, that in no case is it necessary to invoke combination between a vibration of the mesitylene ligand and one involving the rest of the complexes.

CONCLUSION

An almost complete vibrational assignment for the molecules $[1,3,5\text{-}C_6H_3(CH_3)]M(CO)_3$ (where M=Cr and Mo) has been achieved. Removal of ambiguities and gaps in the assignment must await an analysis of many more complexes of similar type. The results are generally in agreement with previously reported work on these and similar systems, although the assignment of metal–carbon stretching frequencies is closer to those reported $C_5H_5M(CO)_n$ systems than that for $C_6H_6Cr(CO)_3$.

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