Journal of Organometallic Chemistry, 63 (1973) 381–388

RE-ASSIGNMENT OF THE VIBRATIONAL SPECTRA OF π-CYCLOPENTADIENYL- AND METHYL-π-CYCLOPENTADIENYL-MANGANESE TRICARBONYL

DAVID M ADAMS and ALAN SQUIRE

Department of Chemistry, University of Leicester, Leicester LE1 7RH (Great Britain)

(Received May 7th, 1973)

SUMMARY

The long-standing assignment by Hyams, Bailey and Lippincott[1] of the vibrational spectrum of $Mn(CO)_3(\pi\text{-}C_5H_5)$ is corrected: the $\pi\text{-}C_5H_5$ part of the spectrum cannot be assigned on the basis of C_{5v} "local" symmetry, and the a_1 (in C_{3v}) δ(MnCO) mode is at 668 cm^{-1}, not 543 cm^{-1} as previously claimed. New Raman data are given for $Mn(CO)_3(\pi\text{-}C_5H_4\text{–}CH_3)$ and assigned under C_s rules for the ring. C_{3v} symmetry is a good approximation for the $Mn(CO)_3$ moiety.

For many years the vibrational study of $Mn(CO)_3(\pi\text{-}C_5H_5)$ by Hyams, Bailey and Lippincott[1] (HBL) has stood as a point of reference for interpretation of other related molecular spectra. Their main conclusion was that the spectra could be interpreted on the basis of C_{5v} "local" symmetry for the ring, and C_{3v} "local" symmetry for the $M(CO)_3$ group. The concept of "local" symmetry has been widely, and often uncritically, applied to this and other systems despite much evidence to the contrary. We have re-investigated the spectra of this compound and conclude that C_{5v} "local" symmetry is *not* an adequate approximation. Further, the Raman polarisation data of HBL are partly in error: we give a corrected assignment for the $Mn(CO)_3$ group which is now consistent with our earlier work[2] on $Cr(CO)_3(\pi\text{-}C_6H_6)$.

No Raman data have been reported for $Mn(CO)_3(\pi\text{-}C_5H_4\text{–}CH_3)$: Parker and Stiddard[3] have studied the IR spectrum, but the theoretical basis of their assignment is wrong.

EXPERIMENTAL

Commercial samples of both complexes were purified by repeated sublimation $[Mn(CO)_3(\pi\text{-}C_5H_5)]$ or re-distillation *in vacuo*. IR spectra were obtained using PE-225 and Beckman-RIIC FS-620 instruments, with home-made cryostats. Raman spectra were recorded with a Coderg PHI instrument using 632.8 nm excitation. Liquid $Mn(CO)_3(\pi\text{-}C_5H_4\cdot CH_3)$ was distilled into a 1 cm Pyrex cell under vacuum and sealed off. It was studied as a solid by cooling a sealed capilliary in a "Cryocirc" cold cell. The Raman spectrum of liquid $Mn(CO)_3(\pi\text{-}C_5H_5)$ was obtained by heating the solid in vacuo in a 1 cm liquid cell mounted in a home-made thermostatted holder.

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TABLE 1

VIBRATIONAL FREQUENCIES (in cm^{-1}) OF $Mn(CO)_3(\pi\text{-}C_5H_5)$

Raman[a]				*IR*				*Assignment*
Solid		*Solution*		*Solid*		*Solution*		
Ambient	*Cooled*	*Liquid*	CH_2Cl_2	*Ambient*	*Cooled*	CS_2	C_2Cl_4	
						4039 ms	4044 wm	$2\times\nu_{15}$
						3945 s	3951 m	$\nu_{15}+\nu_{21}$
						3860 ms	3868 wm	$2\times\nu_{21}$
3132 s	3140 ms							
3120 m	3122 m	3123 ms, P	3122 s, P[b]			3115 ms	3118 wm	ν_1
3108 m	3105 m	3101 w (sh), dp	3102 w, dp[b]					ν_9
3098 m	3095 wm							
(3068) w						3050 (sh)		
						3040 wm	3044 w	
						2837 w		$2\times\nu_8$
						2716 vw		$2\times\nu_{12}$
						2685 w	2685 vw	$\nu_{15}+\nu_{16}$
						2654 wm	2657 w	$\nu_{15}+\nu_{22}$
						2600 w		$\nu_{21}+\nu_{16}$
							2576} w	$\nu_{21}+\nu_{22}$
						2561 wm	2563}	$\nu_{15}+\nu_{23}$
						2509 wm	2512	$\nu_{15}+\nu_{17}$
						2479 wm	2480 w	$\nu_{21}+\nu_{23}$
						2428 m	2430 wm	$\nu_{21}+\nu_{17}$
		2032 w (sh), P						
		2016 m, P	2024 ms, P	2027 vs} (br)	2027 vs		2027 vvs	ν_{15}
2014 m	2016 m			2015 vs}	2015 vs			
					1956 sh			
1943 ms	1944 s	1925 ms (br), dp	1934 ms (br), dp	1943 vs	1942 vs		1942 vvs	ν_{21}
1921 s	1922 s				1926 w (sh)			
1914 m	1914 m			1906 (sh)	1910 w			
1428} wm	1430 wm	1427 m, dp	1427 w, dp[b]	1427} ms	1429 m	1423 ms	1425 ms	ν_8
1423}	1423 wm			1421}	1412 m			
1361 wm	1363 wm	1363 w, dp	1364 w, br[b]	1360 m	1362 m	1360 m[c]		ν_{12}
						1311 vw (sh)		

				1263 w (br)	1261 w (br)	1265 wm		ν_4
1219 w (br)	1223 vw (br)	1217 w P	1214 w, P	1204 vw (br)	1208 vw (br)	1200 w (br)		$\nu_{10\ a,b}$
1161 w	1163 vw (br)			1152 vw (br)	1157 vw (br)	1148 w		
1120 vs	1117 vs	1116 vs, P	1113 vs, P	1113 m	1114 wm	1114 wm		ν_3
1108 wm (sh)	1109 w							
1067 ms	1067 ms	1068 ms, P?	1065 ms, P?	1064 } m	1067 } wm	1060 wm		ν_{11}
1060 ms	1060 ms			1057 }	1058 }	1050 wm		
1014 w	1015 vw			1030 vw	1036 vw (br)			$\nu_{17}+\nu_{23}$
1006 wm	1008 w	1012 w, P?	1012 w, P?	1013 } m	1013 } m	1006 m	1007 m	ν_6
	1002 wm			1005 }	1006 }			
					1000 sh			
				959 vw (br)	960 vw (br)	981 (br, sh)		$\nu_{14}+\nu_{24}$
	946 vw			939 m	945 ms	956 (br, sh)		ν_{13}
933 w (br)	935 w	926 vw (br) dp	929 vw, dp					
		915 w, P	916 vw, P		915 vw (br)	917 } wm (br)		$\nu_{23}+\nu_{25}$
				903 w (br)	906 w (br)	903 }		
	865 vw	859 w (sh)		861 (sh)	866 m			$\nu_{24}+\nu_{25}$
	853 wm			849 } s	854 } s			
846 wm	848 w (sh)	839 m, P	839 m, P	845 }	847 }		842 wm (sh)	ν_2
	841 w (sh)				842 vw			
					840 vw			
835 wm	836 wm	827 w, dp		834 s	836 s	828 vs (br)	829 ms	ν_7
					833 s			
					740 w (br)	749 w		$2\times\nu_{25}$
					722 w	731 w		$\nu_{18}+\nu_{25}$
					695 w (br, sh)			$2\times\nu_{18}$
				669 } vs	669 } vs	669 sh	669 (sh)	
667 wm	670 vw	668 wm, P	670 w, P	663 }	664 }	663 vs	666 vs	ν_{16}
639 vw					638 } vs			
633 vw		640 vw, dp		633 vs	632 }	634 vs	634 vs	ν_{22}
610 wm	612 w	609 wm, P	609 w, P	608 ms	610 ms			ν_{14}
						589 vw (sh)		
545 m	548 wm				548 } s			
539 (sh)	541 wm	543 m, dp	543 m, dp	542 vs	544 }	537 s	539 s	ν_{23}
502 m	505 vs	499 vs, P	499 vs, P	500 wm	503 m			ν_{17}
489 wm	491 ms	491 ms, dp	491 m, dp	488 wm	491 } s	490 w		ν_{24}
					489 }			
387 wm	393 ms				391 vw			
		380 ms, dp	377 wm, dp				371 m (br)[d]	$\nu_{25a,b}$

(continued)

TABLE 1 (*contd*)

Raman[a]				*IR*				*Assignment*
Solid		*Solution*		*Solid*		*Solution*		
Ambient	*Cooled*	*Liquid*	*CH_2Cl_2*	*Ambient*	*Cooled*	*CS_2*	*C_2Cl_4*	
					375 wm			
370 wm	371 ms				370 wm			
359 vvs	357 vvs	352 vvs, P	350 vs, P		358 w			ν_{18}
	149 wm							
	141 (sh)							
	139 m							
128 ms	128 m (sh)		132 w (sh) P?					$\nu_{19}{}^{e}$
120 s	124 vs	$\left.\begin{matrix}112\\104\end{matrix}\right\}$ vs, dp						
112 ms	114 vs		104 s, dp					$\nu_{26}{}^{e}$ Lattice modes
100 (sh)	101 s							
	73 vw							
49 w	60 m							
	34 wm							

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[a] P, polarised, dp. depolarised. [b] $CDCl_3$ solution, [c] Also at 1361 cm^{-1} (C_2HCl_3) and 1362 cm^{-1} (C_6H_6), [d] CH_2Cl_2 solution, [e] See text.

Depolarisation ratios were measured with a scrambler in the scattered beam and a half-wave plate in the incident beam: the maximum ratio is therefore 6/7.

SELECTION RULES

Selection rules for π-C_5H_5 systems have been quoted elsewhere[4]. For our purpose we need only note the numbers of bands predicted on the various symmetry approximations. They are: π-C_5H_5: C_{5v} $3a_1$ (IR, Ra) + a_2 + $4e_1$ (IR, Ra) + $6e_2$(Ra); C_s $13a' + 11a''$ (all IR + Ra), where activities are given in parentheses. The π-$C_5H_4 \cdot CH_3$ group can only be discussed on the basis of C_s symmetry, and not C_{2v} as has been done previously for reasons which elude us[5,6].

ASSIGNMENT AND DISCUSSION

Data are presented in Tables 1 and 2. Assignments follow logically both from this new evidence, and by comparison with the established assignments for ferrocene[7], ruthenocene[8], and $Cr(CO)_3(\pi$-$C_6H_6)$[2]. We discuss briefly the main points of difference from HBL: a fully argued account is given in ref. 9. Assignments are made using C_{5v} labels in order to emphasise the relation to ferrocene-like spectra, but are not to be taken literally, see below. The numbering system of Parker and Stiddard[3] is used.

π-C_5H_5 RING SPECTRA

A band count for both IR and Raman solution spectra shows (*i*) many more IR bands than predicted by C_{5v} "local" symmetry, (*ii*) eight, rather than the three C_{5v}-predicted, polarised Raman bands. Clearly, the effective symmetry is not C_{5v}. The point is well emphasised by comparing solution spectra of $Mn(CO)_3(\pi$-$C_5H_5)$ and ferrocene or ruthenocene: the simplicity of the latter is striking. The effect of the $Mn(CO)_3$ group is generally to cause e_2 species to become IR-active and/or Raman bands of e_1 and e_2 type to become partly polarised (due to an a' component in C_s), rather than to induce full splitting into a' and a'' components. It is this lack of pronounced splitting of e_1 and e_2 modes in solution that seems to have misled others into using the C_{5v} approximation. An analogous situation occurs in $Cr(CO)_3(\pi$-$C_6H_6)$: it has been clear ever since Fritz's original IR study[10] that the ring must be considered under C_{3v} rules, although the true reason was not then deduced.

THE π-$(C_5H_4$-$CH_3)$ RING SPECTRA

Assignments were made by analogy with unsubstituted π-C_5H_5 systems, having first accounted for modes due to the methyl group. The ring–methyl deformations are placed at 320 cm^{-1} (ν_{10b}) and 220 cm^{-1} (ν_{7a}): analogous modes in toluene are at 344 and 217 cm^{-1}. This assignment differs from those of Parker and Stiddard[5] for $Mn(CO)_3(\pi$-C_5H_4-$CH_3)$ and of Bailey and Lippincott[6] for $Fe(\pi$-C_6H_4-$CH_3)_2$ principally in its completeness.

$Mn(CO)_3$ SPECTRA

In the $\nu(CO)$ region $Mn(CO)_3(\pi$-$C_5H_5)$ shows the two bands expected for a

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TABLE 2

THE VIBRATIONAL FREQUENCIES (In cm^{-1}) OF $\mathrm{Mn(CO)_3(\pi\text{-}C_5H_4\text{-}CH_3)}$[a,b]

Raman		*IR*		*Assignment*
Solid (cooled)	*Liquid*	*Solid (cooled)*	*Liquid*	
			4030 m	$2\times\nu_{15}$
			3934 ms	$\nu_{15}+\nu_{21}$
			3840 m	$2\times\nu_{21}$
3128 w				
3120 wm	3119 s, P	3118 w	3116 m	ν_1
3106 w	3100 m, dp	3104 w		$\nu_{5a\,b,9a}$
2990 vvw (br)	2989 w (sh), dp		2983 m	$\nu(\mathrm{CH_3})_{as}$
2976 vw (br)	2971 wm, dp		2965 m	
2943 w	2936 s, P		2934 m	$\nu(\mathrm{CH_3})_s$
2938 w		2925 w (br)		
	2908 wm, P		2905 m	$2\times\nu(\mathrm{CH_3})_{as}$
			2743 w	$2\times\nu(\mathrm{CH_3})_s$
			2687 w	$\nu_{15}+\nu_{16}$
			2653 w	$\nu_{15}+\nu_{22}$
			2558 wm	$\nu_{15}+\nu_{23}$
			2509 wm	$\nu_{15}+\nu_{17}$
			2455 (sh)	$\nu_{21}+\nu_{23}$
			2415 wm	$\nu_{15}+\nu_{25}$
			2365 w (br)	$\nu_{15}+\nu_{18}$
			2302 vw (sh)	$\nu_{21}+\nu_{25}$
			2276 wm	$\nu_{9a}+\nu_3$
	2027 (sh), P	2021 s	2030 (sh)	
2006 wm	2012 m, P	2011 (sh)	2017 vs	ν_{15}
		1988 (sh)		
1942 w		1958 (sh)	1942 (sh) (br)	
	1919 ms (br), dp	1920 s	1917 vs	ν_{21}
1912 m				
1910 (sh)				
1905 m		1897 (sh)		
1884 w		1880 m		
		1682 w	1673 wm (br)	
1487 w	1487 wm (0.57)	1486 m	1485 m	ν_{8a}, ν_{8b}?
1466 w (br)	1461 wm (0 75)	1458 (sh)	1459 m	$\delta\,(\mathrm{CH_3})_{as}$
1454	1454 (0 8)	1456 m		
		1450 m	1450 (sh)	
		1433 w	1427 (sh)	ν_{8b}?
		1421 w		
1398 wm	1396 wm (br) (0 5)	1397 m	1392 wm	$\nu_{12a,b}$
1377 w	1380 w (0 72)	1377 m	1379 m	$\delta\,(\mathrm{CH_3})_s$
			1353 wm	
		1313 w		
			1266 w	
1232 ms	1233 s (0.07)	1231 w	1235 wm	ν_{9b}
			1206 w	
			1158 w	
1117 wm	1118 m (≈ 0)		1121 w	ν_{10a}

(Continued)

TABLE 2 (*contd*)

Raman		*IR*		*Assignment*
Solid (cooled)	*Liquid*	*Solid (cooled)*	*Liquid*	
1072 ms	1069 ms (0 39)	1069 (sh)		ν_{11a}
		1065 m	1065 wm	ν_{11b}
		1061 (sh)		
1045 ms	1048 vs (< 0.1)	1042 m	1045 m	ν_3
		1035 wm		$\rho(CH_3)$
1032 wm	1033 (sh) ?	1029 m	1030 m	
983 w	985 w (0 85)		984 w (br)	$\nu_{13a,b}$ or ν_{6b}
			959 vw	
932 m	931 s (0.08)	931 wm	929 wm	ν_{6a}
921 vw	918 vvw, dp			
			906 vw (br)	
882 w (br)	881 vvvw, dp	876 w		$\nu_{13a,b}$?
857 wm	851 wm, dp	852 ms	848 (sh)	ν_{7b}
847 w	841 wm, P	844 m		ν_2
		835 wm	835 m	
			740 vw	
			706 vw (br)	
675 w	671 wm (0.18)	675 s	669 s	ν_{16}
		669 (sh)		
654 wm				
644 w	641 wm	646 (sh)		
		639 s	634 s (br)	ν_{22}
630 wm	629 m (0 26)	629 (sh)		ν_{14a}
623 w	613 w (sh)	620 w	617 (sh)	ν_{14b}
612 w		610 vw		
546 wm	543 wm (0.73)	547 ms	539 s	ν_{23}
		543 (sh)		
		537 (sh)		
509 m		506 wm		
504 m	500 s, P	501 wm		ν_{17}
498 m	493 ms, dp		495 wm	ν_{24}
494		491 wm		
405 m				
398	398 ms (0 65)		394 wm	ν_{25}
370 vs	362 vvs, P		356 vw	ν_{18}
361 (sh)				
326 wm	322 w (0 87)		318 wm	ν_{10b}
238 wm				
220 wm	222 wm (0 5)		217 wm	ν_{7a}
150 w				
127 s				
114 wm	112 vs (0 88)			$\nu_{26,27}$
102 vs	104			
85 wm				
60 w				

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[a] Figures in brackets are the approximate band depolarisation ratios Maximum value is 0.86. [b] For $Mn(CO)_3(\pi\text{-}C_5H_4\text{-}CH_3)$ ν_{9a}, ν_{10b} and ν_{7a} become $\nu(C\text{-}CH_3)$, $\delta(C\text{-}CH_3)$ and $\pi(C\text{-}CH_3)$ respectively. In addition $2a' + a''$ components are expected for each of the modes $\nu(CH_3)$, $\delta(CH_3)$ and $\rho_r(CH_3)$

C_{3v} top. The more complex solid state spectra are in accord with factor group predictions. HBL considered that the additional complexity of the solid state spectra upon cooling is due to a phase change. This is not so: we could not detect any specific heat anomaly down to 175 K using a differential scanning calorimeter. This complex crystallises in the monoclinic group C_{2h}^5 with a tetramolecular cell[11]. Thus, the a_1 ν(CO) modes couple around the cell giving a vector[12] $A_g+B_g+A_u+B_u$: the IR bands at 2027 and 2015 cm^{-1} are therefore the A_u+B_u modes and the 2016 cm^{-1} Raman band is either A_g or B_g. The e ν(CO) mode, after coupling, gives $2(A_g+B_g+A_u+B_u)$, most of which we observed.

Below 700 cm^{-1} the Raman polarisation data and the IR/Raman coincidences lead to an assignment for the ν(M-C), δ(MCO) region which is in close agreement with that established earlier for $Cr(CO)_3(\pi\text{-}C_6H_6)$[2]. Contrary to the report of HBL that the 543 cm^{-1} band is polarised (and hence a_1 in C_{3v}) we find it to be depolarised. We were able to see the weak 668 cm^{-1} band for the first time in solution. It is definitely polarised. The situation is summarised in Table 3.

TABLE 3

VIBRATIONAL FREQUENCIES (in cm^{-1}) AND ASSIGNMENT FOR THE $M(CO)_3$ GROUP (C_{3v})

$Cr(CO)_3(\pi\text{-}C_6H_6)$[a]	$Mn(CO)_3(\pi\text{-}C_5H_5)$	Assignment	
1980	2027	a_1	ν(CO)
653	666		δ(MCO)
483	499		ν(M–C)
301	350		ν(M–Ring)
1908	1942	e	ν(CO)
624	634		δ(MCO)
531	539		δ(MCO)
476	491		ν(M–C)
338	377		Ring tilt

ACKNOWLEDGEMENT

We thank the S.R.C. for a maintenance grant to A.S.

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