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DERIVATIVES OF DIVALENT GERMANIUM, TIN AND LEAD

II*. SPECTROSCOPIC INVESTIGATION OF DICYCLOPENTADIENYLTIN(II) AND ITS METHYLCYCLOPENTADIENYL ANALOGUE

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SUMMARY

The infra-red and Raman spectra of dicyclopentadienyltin(II) and its methylcyclopentadienyl analogue have been recorded and the observed bands assigned in terms of the "local" symmetry of the angular sandwich molecules. Proton magnetic resonance, mass and tin-119*m* Mössbauer spectra of bis(methylcyclopentadienyl)tin(II) are also reported.

INTRODUCTION

In sharp contrast to the vast preponderance of organotin(IV) compounds, known organic derivatives of divalent tin, for which spectroscopic, *i.e.* tin-119*m* Mössbauer isomer shift data, or structural confirmation is available, are as yet restricted to dicyclopentadienyltin[2,3] and its methylcyclopentadienyl analogue[3], their boron trifluoride adducts[4], monocyclopentadienyltin chloride and bromide[5], bis(phenylbarenyl)tin[6], and the unusual tin(II)–benzene complex, $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$[7]. Moreover, the properties of tin(II)–carbon bonded compounds are vastly different to the rather inert σ-bonded skeleton[1,8] characteristic of the higher oxidation state.

An electron diffraction study has corroborated the earlier suggestion based on infra-red[3,10,11] and dipole moment[12] data that dicyclopentadienyltin possesses an angular sandwich structure in which the planar C_5H_5 rings are centrally σ-bonded (pseudo π) to the central metal atom, which is approximately sp^2-hybridised. The lone pair of electrons therefore occupies an orbital with directional character, and this has been illustrated by its use as a ligand in complex formation[4]. This mode of bonding may be compared with the localised σ-bonding of the puckered, diene-type C_5 rings of tin(IV) cyclopentadienyls[13,14]. The infra-red spectra of dicyclopentadienyltin and -lead have been the subject of controversy[3,10,11]. In order to resolve this debate, we report in this paper the infra-red and Raman spectra of the former compound and its methylcyclopentadienyl analogue, together with related proton magnetic resonance, mass, and tin-119*m* Mössbauer spectral data.

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[*] For Part I see ref. 1.

EXPERIMENTAL

All manipulations were carried out under an atmosphere of dry argon or nitrogen. The organotin(II) compounds were prepared as described previously[1], and sublimed or distilled *in vacuo* just before use. Infra-red spectra were recorded as nujol or halocarbon oil mulls, and as a carbon tetrachloride solution or liquid film using a Perkin–Elmer 521 spectrometer calibrated with polystyrene film and water vapour. Raman spectra were recorded using a Cary 81 instrument equipped with a helium–neon laser. Proton magnetic resonance studies were performed using a Varian HA-100 instrument. Mass spectra were recorded at 70 eV by an AEI MS9 instrument.

RESULTS AND DISCUSSION

In this study we shall assume that the angular sandwich structure determined for dicyclopentadienyltin in the vapour phase[9] is preserved in both the solid and in carbon tetrachloride solution. Also we shall assume that bis(methylcyclopentadienyl)-tin possesses similar gross structural features. The highest possible overall symmetry for these molecules will therefore be C_{2v}.

Using the approximation of "local" symmetry the fundamental modes may be divided into two types: (*i*) ring vibrations, and (*ii*) vibrations associated with the tin atom. We shall consider first the vibrations associated with the cyclopentadienyl and methylcyclopentadienyl rings each in turn, and later the skeletal modes of both molecules which involve the metal atom.

Ring modes of the cyclopentadienyl ring

On the basis of C_{5v} "local" symmetry, the twenty-four normal vibrations of the isolated C_5H_5 unit are distributed as

$$3A_1+A_2+4E_1+6E_2$$

of which ten $(2A_1+A_2+3E_1+4E_2)$ will be in the plane of the ring and four $(A_1+E_1+2E_2)$ perpendicular. The description of these modes is given in Table 1.

The observed infra-red and Raman bands are listed in Table 2. No gross changes are apparent in going from the solid phase to a carbon tetrachloride solution. The assignment of the observed bands in this study are considerably aided by analogy with previous assignments of the spectra of π-cyclopentadienyl–metal carbonyl complexes[15,16] and ferrocene[17], which have been confirmed by deuteration studies.

The five CH stretching modes $[\nu_1(A_1), \nu_5(E_1), \nu_9(E_2)]$ are readily assigned to the two bands at ca. 3100 cm^{-1} in both the infra-red and the Raman. Polarisation studies of the similar two bands present in the Raman spectrum of π-cyclopentadienylmanganese tricarbonyl has unequivocally shown that the higher frequency band is the A_1 mode in that case[16]. In the present case, the intensity of the higher frequency band in the Raman is substantially greater than the band at lower energy, and so is also assigned to the totally symmetric A_1 mode, ν_1.

The ring breathing mode ν_3, also A_1, is easily identified as a strong band in both the infra-red and Raman at 1116 cm^{-1}. The remaining stretching vibrations to be assigned are the two CC stretching modes ν_8 of E_1 symmetry, which should be active in both the infra-red and Raman, and ν_{12} of E_2 symmetry which should exhibit

Raman activity only. The E_1 mode occurs as a strong band at 1430 cm^{-1} in both the infra-red and Raman. It would be tempting to assign the Raman band of medium intensity at 1354 cm^{-1} to the E_2 mode. However, by analogy with previous assignments[16,17], this vibration is expected to occur at higher energy than the E_1 mode, and the weak band at 1534 cm^{-1} in the infra-red appears to be the most likely candidate.

Six CH bending modes are expected for C_{5v} symmetry. Of these, three will be in the plane of the ring $[\nu_4(A_2), \nu_6(E_1), \nu_{10}(E_2)]$ and three perpendicular to the ring $[\nu_2(A_1), \nu_7(E_1), \nu_{11}(E_2)]$. Intense bands at 757 and 790 cm^{-1} in the infra-red and similar weak bands in the Raman are immediately identified as ν_2 and ν_7 respectively, although occurring to substantially lower energy of the same fundamentals in cyclopentadienylmetal carbonyl complexes[15,16]. The third out-of-plane CH bending mode is expected to occur at $\approx$1050 cm^{-1}, and is assigned to the weak infra-red and Raman active band at 1063 cm^{-1}. Of the three in-plane modes, only the E_1 mode (ν_6) is easily recognised, and is assigned as a strong infra-red and weak Raman band at ca. 1000 cm^{-1}. From previous studies[15–17] the two other in-plane CH bending modes are expected in the regions: A_2, 1200–1250 cm^{-1}, E_2 $\approx$1180 cm^{-1}. These modes may not

TABLE 1

DESCRIPTION OF RING MODES ON THE BASIS OF "LOCAL" SYMMETRY

C_5H_5 (C_{5v} "*local*" *symmetry*)			MeC_5H_4 (C_{2v} "*local*" *symmetry*)			*Description of mode*
Species	*Activity*	ν	*Species*	*Activity*	ν	
A_1	IR, R	1	A_1	IR, R	1	CH stretch
A_1	IR, R	2	B_2	IR, R	2	CH bend ⊥
A_1	IR, R	3	A_1	IR, R	3	Ring breathing
A_2	Inactive	4	B_1	IR, R	4	CH bend ‖
E_1	IR, R	5	A_1	IR, R	5a	CH stretch
			B_1	IR, R	5b	
E_1	IR, R	6	A_1	IR, R	6a	CH bend ‖
			B_1	IR, R	6b	
E_1	IR, R	7	A_2	R	7a	CH bend ⊥
			B_2	IR, R	7b[a]	
E_1	IR, R	8	A_1	IR, R	8a	CC stretch
			B_1	IR, R	8b	
E_2	R	9	A_1	IR, R	9a[b]	CH stretch
			B_1	IR, R	9b	
E_2	R	10	A_1	IR, R	10a	CH bend ‖
			B_1	IR, R	10b[c]	
E_2	R	11	A_2	R	11a	CH bend ⊥
			B_2	IR, R	11b	
E_2	R	12	A_1	IR, R	12a	CC stretch
			B_1	IR, R	12b	
E_2	R	13	A_1	IR, R	13a	CC bend ‖
			B_1	IR, R	13b	
E_2	R	14	A_2	R	14a	CC bend ⊥
			B_2	IR, R	14b	

[a] Becomes CMe out-of-plane bending mode. [b] Becomes CMe stretching mode. [c] Becomes CMe in-plane bending mode.

TABLE 2

OBSERVED VIBRATIONAL SPECTRA OF DICYCLOPENTADIENYLTIN AND ASSIGNMENTS[a]

Raman (solid)	*Infra-red*			*Assignment*
	KBr disc[b]	*Mull*	*CCl_4 solution*	
		3900 vw	3930 vw	
3101 s		3105 vvw	3100 m(sh)	ν_1, CH stretch A_1
3084 m	3061 w	3080 vvw(sh)	3090 m	ν_5, ν_9, CH stretches E_1, E_2
			2959 w	1534+1429=2963
			2922 w	3100−172=2928; 3090−172=2918
			2870 vw	2×1429=2858; 3100−242=2858
			2852 vw	3090−242=2848
			2700 vvw	1429+1263=2692
			2490 vvw	1534+961=2495
			2405 vvw	1429+961=2388
		2260 vvw	2265 vvw	1263+1011=2274
			2225 vvw	1429+790=2219; 2×1114=2228
			2198 vvw	1429+757=2186
			2120 vvw	1114+1011=2125
			2065 vvw	1114+961=2075; 1062+1011=2073
			1905 vvw	1114+790=1904
	1739 w	1745 vvw(br)	1754 vw(br)	961+790=1751
	1631 w	1640 vw(br)	1634 mw(br)	1114+544=1658?
			1534 vw(br)	ν_{12}, CC stretch E_2
1460 w			1465 vw(sh)	
1431 s	1424 m	1429 m	1429 vs	ν_8, CC stretch E_1
		1382 vw	1378 vw	
	1363 m	1369 vw	1365 vw	
1354 m			1358 vw	1114+242=1356
			1342 vw	1161+172=1333
			1294 vvw	1114+172=1286; 544+757=1301
			1263 vw	ν_4, CH bend $\parallel$ A_2
		1170 vvw	1161 vvw	ν_{10}, CH bend $\parallel$ E_2
1118 s	1112 m	1116 mw	1114 vs	ν_3, Ring breathing A_1
1063 w	1059 w	1064 vw	1062 w	ν_{11}, CH bend $\perp$ E_2
1005 w	1003 s	1005 s	1011 vs	ν_6, CH bend $\parallel$ E_1
	959 w		961 vw	790+172=962
	914 w			757+172=929
886 w	890 w	893 vvw	890 vw(sh)	ν_{13}, CC bend $\parallel$ E_2?
			870 vw(sh)	1114−242=872
	837 w	838 vw	841 w	
796 w	792 s	790 vvs		ν_3, CH bend $\perp$ E_1
738 w	751 s	757 vvs(br)		ν_2, CH bend $\perp$ A_1
			695 vvw	1263−544=719?
	664 w	664 vw	667 vw	1429−757=672
			649 vvw	1429−790=639
			600 vvw(br)	790−172=618; 757−172=585
	544 vw			ν_{14}, CC bend $\perp$ E_2?
242 s	260 m(br)	240 s		Asymm. metal–ring stretch
172 m				Symm. metal–ring stretch

[a] In cm^{-1}; w = weak, mw = medium weak, m = medium, ms = medium strong, s = strong, v = very, (sh) = shoulder, (br) = broad. [b] Ref. 11.

be assigned unequivocally, and strictly according to C_{5v} selection rules both should be inactive in the infra-red and only the E_2 mode should exhibit Raman activity. Weak bands at 1263 cm^{-1} (ν_4, A_2) and ≈ 1170 cm^{-1} (ν_{10}, E_2) appear to be the most probable choices.

The two remaining fundamentals to be assigned are ν_{13} and ν_{14}, the in-plane and out-of-plane CC bending vibrations respectively. Both these modes are of E_2 symmetry, and so are strictly forbidden in the infra-red. They have previously been assigned in the ranges 900–950 cm^{-1} and 480–620 cm^{-1} respectively[15-17]. Weak infra-red bands at 914 and 960 cm^{-1} may be assigned to the ν_{13} mode, however they may equally well be combination bands. The band at ca. 890 cm^{-1}, which is also present in the Raman, is preferred for this mode, although this also may be accounted for as a combination. The out-of-plane mode is tentatively assigned to the weak band observed previously by Fritz[10], but not by us, at 544 cm^{-1}. This band was assigned by Fritz as the antisymmetric metal–ring tilt mode, but this fundamental is to be expected at much lower energy[16]. A summary of the assignments for $(C_5H_5)_2Sn$ together with those for related compounds is given in Table 3.

TABLE 3

SUMMARY OF THE ASSIGNMENTS OF THE RING VIBRATIONS OF $(C_5H_5)_2Sn$ AND RELATED COMPOUNDS

Species	*Frequency No.*	$(C_5H_5)_2Sn^a$	$(C_5H_5)Mn(CO)_3^b$	$(C_5H_5)NiNO^c$	$(C_5H_5)_2Fe^d$
A_1	ν_1	3100	3126	3110	3099
	ν_2	757	849	807	810
	ν_3	1114	1113	1115	1108
A_2	ν_4	1263	1264	1240	1200–1260
E_1	ν_5	3090	3098	3058	3080
	ν_6	1011	1012	1004	1007
	ν_7	790	834	895	850
	ν_8	1429	1425	1425	1410
E_2	ν_9	3090	3098	3058	3085
	ν_{10}	1161	1152	1178	1180
	ν_{11}	1062	1062	1050	1050
	ν_{12}	1534	1520	1560	1560
	ν_{13}	886	934	880	900
	ν_{14}	544	487	500	500

[a] This work. [b] Ref. 16. [c] Ref. 18. [d] Ref. 17.

Ring modes of the methylcyclopentadienyl ring

Although the isolated methylcyclopentadienyl ring is nominally of the C_s molecular point group, if the methyl group is considered as a point mass, the symmetry is raised to C_{2v}. On this basis, the fourteen normal modes of the cyclopentadienyl ring become twenty-four normal modes, distributed among the symmetry species as:

$$9A_1+3A_2+8B_1+4B_2$$

as the degeneracy of the E_1 and E_2 modes under C_{5v} symmetry is removed. The description of the twenty-four normal modes is given in Table 1, which also indicates their origin to the fundamentals of the unsubstituted ring. The modes ν_{7b}, ν_{9a} and ν_{10b} then become the out-of-plane and in-plane CMe bending and CMe stretching vibrations respectively. In addition, there will be nine internal modes of vibration of the methyl group. These are described in Table 4.

TABLE 4

DESCRIPTION OF INTERNAL VIBRATIONS OF THE METHYL GROUP OF THE MeC_5H_4 RING

Species	*Activity*	*m*[a]	*Description of mode*
A_1	IR, R	1	CH stretch
		2	HCH bend
A_2	R	3	Me torsion
B_1	IR, R	4	CH stretch
		5	HCH bend
		6	CMe wag ∥
B_2	IR, R	7	CH stretch
		8	HCH bend
		9	CMe wag ⊥

[a] Frequency number.

The observed infra-red and Raman bands together with polarisation data are listed in Table 5. The most profitable approach to the assignment of the fundamental modes of the MeC_5H_4 rings of bis(methylcyclopentadienyl)tin is to use the assignments for the unsubstituted ring, utilizing the inequality rule of Whiffen and Steele[19]. The assignment of the vibrational spectra of dimethylferrocene[20] and some (methylcyclopentadienyl)metal[21] carbonyl complexes have been assigned in a similar way. It is worthwhile mentioning here that, since no vibration of the rigid methyl group is attributable to an A_2 species, the inequality rule may not be applied to this species, and the observed frequency for $(MeC_5H_4)_2Sn$ should resemble corresponding frequencies in $(C_5H_5)_2Sn$.

First of all we shall consider vibrations associated with the methyl group, described in Table 4. The three CH stretching modes $(A_1+B_1+B_2)$ may be immediately assigned to the two bands in the infra-red at 2965 and 2925 cm^{-1}. The latter band occurs as a polarised band in the Raman and so is assigned as the A_1 mode, m_1. Parker and Stiddard[21] have similarly assigned the lower frequency band to the A_1 mode by analogy with dimethylferrocene and toluene. The three HCH bending modes $(A_1+B_1+B_2)$ should occur in the region 1370–1500 cm^{-1}. A suitable candidate for the A_1 mode is the weak band at ca. 1380 cm^{-1} which is polarised in the Raman. The B_1 and B_2 modes, m_5 and m_8, are to be expected at higher frequency. In dimethylferrocene and $MeC_5H_4Mn(CO)_3$ these modes have been assigned to bands at ca. 1460 cm^{-1} and ca. 1480 cm^{-1} respectively. Of the bands available in this region, the infra-red and depolarised Raman band at 1482 cm^{-1} is assigned to the B_2 mode, m_8, on account of its greater intensity than the weak shoulder at 1492 cm^{-1}. The choice for the B_1 mode lies between weak bands at 1458 cm^{-1} and 1448 cm^{-1}. The latter may be assigned to the higher frequency band. Three methyl bands remain to be assigned: the in-plane and out-of-plane CMe wagging modes, m_6 (B_1) and m_9 (B_2), and the Me torsion

TABLE 5

OBSERVED VIBRATIONAL SPECTRA OF BIS(METHYLCYCLOPENTADIENYL)TIN[a]

Raman (liquid)	*Infra-red (liquid film)*	*Assignment*
	3920 w	
3102 p	3100 w	CH stretch A_1 ; ν_1, ν_{5a}
3080 dp	3080 w	CH stretch B_1 ; ν_{5b}, ν_{9b}
	2965 w	CH stretch B_1, B_2 ; m_4, m_7
2927 p	2925 m	CH stretch A_1, m_1
	2897 mw	
2860	2860 w	
	2632 vvw	
	1735 vvw(br)	
	1680 vvw(vbr)	
	1620 vw(br)	
	1607 vw	CC stretch A_1, ν_{12a}
	1571 vw(br)	
	1526 vw	CC stretch B_1, ν_{12b}
	1492 w(sh)	
1483 w dp	1482 m	HCH bend B_2, m_8
	1458 w(sh)	HCH bend B_1, m_5
	1448 w	CC stretch A_1, ν_{8a}
1406 vw dp	1408 vw	CC stretch B_1, ν_{8b}
1383 w p	1378 w	HCH bend A_1, m_2
	1358 vw	
	1332 vvw(sh)	
	1294 vvw	
1260 vw dp?	1260 vvw(br)	CH bend B_1, ν_4?
	1236 vw(sh)	
1230 s p	1229 m w	CMe stretch A_1, ν_{9a}
	1163 vvw	
1114 w p	1117 vvw	CH bend ǁ A_1, ν_{10a}
1062 w dp	1062 w	CH bend ǁ B_1, ν_{6b}
1043 m p	1042 m	Ring breathing A_1, ν_3
	1026 m	{ CMe wag ǁ B_1, m_6 CMe wag ⊥ B_2, m_9
	1010 w(sh)	CH bend ⊥ A_2, ν_{11a}?
	976 vvw	CH bend ⊥ B_2, ν_{11b}?
	939 vw(sh)	
930 w p	928 m w	CH bend ǁ A_1, ν_{6a}
	898 w } 885 w }	CC bend ǁ B_1, ν_{13b}
	847 w(sh)	CC bend ⊥ A_1, ν_{13a}
813 vw	813 vs	CH bend ǁ A_2, ν_{7a}
773 w dp	767 vvs(br)	CH bend ǁ B_2, ν_2
	688 vvw(sh)	
	673 w	
634 w p	630 vvw	
606 vw	610 w	CC bend B_2, ν_{14b}
	585 vw(br)	
563 vw	561 w	CC bend A_2, ν_{14a}
	368 vvw	Ring tilt?
320 w dp	319 mw	CMe bend B_1, ν_{10b}
	295 m(sh)	Ring tilt?
237 s dp		Antisymm. tin–ring stretch B_2
171 w p		Symm. tin–ring stretch A_1
113 m dp		Ring–tin–ring def. B_1

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[a] In cm^{-1}; w = weak, mw = medium weak, = medium, ms = medium strong, s = strong, v = very, (sh) = shoulder, (br) = broad, p = polarised, dp = depolarised.

mode (A_2). This latter mode, strictly inactive in the infra-red for C_{2v} symmetry, is expected to occur at a frequency below 250 cm^{-1}, outside the range of this study, although the Raman band at 113 cm^{-1} cannot be ruled out. Bands at 1062 w, 1042 m, 1026 m and 1010 w(sh) cm^{-1} in the infra-red may be considered for m_6 and m_9. A single band at 1046 cm^{-1} has been assigned to both modes in $MeC_5H_4Mn(CO)_3$[21], whilst for dimethylferrocene[20] bands at 1037 cm^{-1} and 1053 cm^{-1} have been assigned as the B_1 and B_2 modes respectively. The band at 1043 cm^{-1} is polarized in the Raman and hence is assigned to the ring breathing mode (A_1) ν_3. The very weak shoulder at 1010 cm^{-1} is probably too low for a wagging mode, whilst the weak infra-red and depolarised Raman band at 1062 cm^{-1} is probably the ring in-plane CH bend, ν_{6b}. The CMe wagging modes are therefore assigned to the medium intensity band at 1026 cm^{-1}.

Three of the ring modes, ν_{7b}, ν_{9a} and ν_{10b}, are associated with the rigid methyl group. The CMe stretch, ν_{9a} (A_1), is assigned to the strong band at 1229 cm^{-1}, which also occurs as a strong polarised Raman line, consistent with previous assignments[21]. The band at ca. 320 cm^{-1} in both the infra-red and Raman, absent in the spectra of $(C_5H_5)_2Sn$ has similarly been assigned to the in-plane CMe bending mode, ν_{10b}. The out-of-plane bend, ν_{7b}, has been assigned to a band at 217 cm^{-1} in toluene[21], and is not assigned in this present work.

The remaining ring fundamentals may be assigned using the assignments for $(C_5H_5)_2Sn$ and utilizing the inequality rule. The ring CH stretching modes, $2A_1+2B_1$ (ν_1, ν_{5a}, ν_{5b}, ν_{9b}) are assigned to the two bands observed in both the infra-red and Raman at 3080 and 3100 cm^{-1}. The assignment by previous authors[21] of the higher frequency band to the A_1 modes is confirmed in the present case by the polarisation properties of the bands.

As stated above, the ring breathing mode, ν_3, is readily assigned to the infra-red and polarised Raman band at 1042 cm^{-1}. This is significantly lower than that in the unsubstituted ring, indicating appreciable interaction between this mode and the CMe stretching vibration. Two other CC stretching vibrations, ν_8 and ν_{12}, need to be assigned. These modes, originally E_1 and E_2 modes respectively in $(C_5H_5)_2Sn$, become split into A_1 and B_1 compounds under C_{2v} symmetry. For ν_8, the inequality rule predicts the range 1534–1429 cm^{-1} for the A_1 species, and 1429–1263 cm^{-1} for the B_1 species. Of the band of the higher range, only the weak features at 1492 (sh) and 1448 cm^{-1} remain unassigned. In the lower range, a band at 1408 cm^{-1}, which is also present as a depolarised Raman line, seems to be the obvious choice for the B_1 mode. This would then make the band at 1448 cm^{-1} the most suitable candidate for the A_1 mode. The ν_{12} mode was assigned to the band at 1534 cm^{-1} in $(C_5H_5)_2Sn$. The inequality rule therefore predicts the ranges 3090–1534 and 1534–1429 cm^{-1} for the A_1 and B_1 respectively. Bands at 1609 and 1558 cm^{-1} have been assigned to these modes in dimethylferrocene[20], whilst in $MeC_5H_4Mn(CO)_3$[21], bands attributable to these modes have not been observed but have been estimated to occur at 1600 and 1500 cm^{-1} respectively. Of the several bands available in the spectrum of $(MeC_5H_4)_2Sn$, those at 1607 and 1526 cm^{-1} have been assigned to the A_1 and B_1 modes by comparison with dimethylferrocene[20].

The four in-plane CH bending modes belong to the symmetry species $2A_1$-(ν_{6a}, ν_{10a})+$2B_1$(ν_4, ν_{6b}). Application of the inequality rule would place the A_1 modes, ν_{10a} and ν_{6a}, in the ranges 1161–1114 cm^{-1} and 1011–886 cm^{-1} respectively. In these ranges, only two polarised Raman bands, 1114 and 980 cm^{-1}, have not yet been assigned, the polarised band at 1043 cm^{-1} having been assigned to the ring breathing mode ν_3. These bands are therefore assigned to the modes ν_{10a} and ν_{6a} respectively. The B_1 modes are, however, not so easily assigned. The inequality rule predicts the ranges 1161–1011 cm^{-1} for ν_{6b} and 1263–1161 cm^{-1} for ν_4. In the former range, only the weak infra-red band at 1062 cm^{-1}, depolarised in the Raman, is unassigned, and so is assigned as ν_{6b}. Bands in the latter range occur at 1260, 1236, 1229 and 1163 cm^{-1}. The band at 1229 cm^{-1} has already been assigned as the CMe stretching mode ν_{9a}. The band at 1260 cm^{-1} also occurs as a depolarised line in the Raman, and so is the preferred assignment for ν_4.

The remaining in-plane vibration to be assigned is the CC in-plane bending mode, ν_{13}. In C_{2v} symmetry, this mode becomes split into $A_1(\nu_{13a})$ and $B_1(\nu_{13b})$ components, for which the inequality rule predicts that ν_{13a} should fall below 886 cm^{-1} and ν_{13b} should lie in the range 1011–886 cm^{-1}. Bands at 851 cm^{-1} (A_1) and 892 cm^{-1} (B_1) have been assigned to these modes in dimethylferrocene, corresponding to the 885 cm^{-1} band in ferrocene itself[20]. In the present case, the choice appears to lie between the three weak features in the infra-red at 847, 885 and 898 cm^{-1}, the low frequency band being assigned as ν_{13a}.

Bending vibrations perpendicular to the ring belong to the symmetry species A_2 and B_2. As noted above, the inequality rule does not apply for the A_2 modes, and those fundamentals should closely resemble those in the unsubstituted ring. Thus the out-of-plane CH bending mode ν_{7a} is readily located as a strong infra-red and weak Raman band at 813 cm^{-1}. The A_2 modes should strictly be inactive in the infra-red and the intensity of this band may indicate some lowering of the symmetry of the ring from C_{2v}. The other out-of-plane CH bending mode of A_2 symmetry ν_{11a} should occur at ca. 1062 cm^{-1}, the position of ν_{11} in $(C_5H_5)_2Sn$. The weak infra-red and Raman band at 1062 cm^{-1} in the spectra of $(MeC_5H_4)_2Sn$ has already been assigned as the in-plane mode ν_{6b}, but it is conceivable that both modes occur at this frequency. However in MeC_5H_4NiNO[22] and dimethylferrocene[20], this mode has been assigned to bands at 967 and 1002 cm^{-1} respectively, and so the weak feature at 1010 cm^{-1} is not unreasonable in the present case. Of the two remaining out-of-plane CH bending modes, both B_2, the mode ν_2 is immediately assigned as the intense infra-red band at 767 cm^{-1}, whilst the inequality rule places the position of ν_{11b} in the range 790–1062 cm^{-1}. In this range, only weak features at 976, 939(sh) cm^{-1} and one of the two bands at 898 and 885 cm^{-1} (the other already having been assigned to ν_{13b}) remain unassigned. In several (methylcyclopentadienyl)metal carbonyl complexes, this mode was thought[21] to occur in the range 989–982 cm^{-1}. In the present case, the assignment of ν_{11b} is at best tentative, the best candidate probably being the band at 976 cm^{-1}.

Finally, the out-of-plane CC bending modes need to be assigned. This mode, ν_{14}, was tentatively assigned to a band at 544 cm^{-1} in $(C_5H_5)_2Sn$. In $(MeC_5H_4)_2Sn$ this mode becomes split into two components of the symmetry species A_2 and B_2. In dimethylferrocene these have been assigned to 597 and 632 cm^{-1} respectively, whilst in toluene they occur at 408 and 464 cm^{-1}[21]. The A_2 mode should occur near 544 cm^{-1}, and is assigned as the weak infra-red and Raman band at 561 cm^{-1}. The choice for the B_2 mode lies between the infra-red bands at 585, 610 and 630 cm^{-1}, the two latter bands also occurring in the Raman. The 630 cm^{-1} band is probably too high to be associated with a band at 544 cm^{-1}, and so ν_{14b} is assigned to the band at

TABLE 6

SUMMARY OF THE ASSIGNMENTS OF THE RING VIBRATIONS OF $(MeC_5H_4)_2Sn$ AND RELATED COMPOUNDS

Species	$(MeC_5H_4)_2Sn$	MeC_5H_4NiNO[a]	$(MeC_5H_4)_2Fe$[b]
A_1	3100	3090	3087
	3100	3090	3087
	1607	1610	1609
	1448	1452	1440
	1229	1225	1229
	1117		1106
	1042	1042	1025
	928	928	919
	847	849	851
ν(Me)	2925	2911	2922
δ(Me)	1380	1385	1384
B_1	3080	3106	3087
	3080	3106	3087
	1526	(1560)	1558
	1408	1385	1373
	1260	1237	1207
	1062	1025	1115
	898 or 885	888	892
	319	344	328
ν(Me)	2965	2941	2950
δ(Me)	1458	1460	1464
δ(Me)	1026	1056	1037
B_2	976	975	975
	767	802	811
	610	624	632
	–	354	(217)
νMe	2965	2973	2966
δMe	1482	1481	1478
δMe	1026	1056	1053
A_2	1010	967	1002
	813	819	833
	561	780 or 639	597

[a] Ref. 22. [b] Ref. 20.

610 cm^{-1}. A summary of the assignments of $(MeC_5H_4)_2Sn$ is given in Table 6, together with those of the related molecules MeC_5H_4NiNO[22] and dimethylferrocene[20].

Non-ring skeletal modes

Assuming the C_5 rings to be rigid, nine skeletal modes $(3A_1+2A_2+2B_1+2B_2)$ involving the tin atom will be expected for angular dicyclopentadienylmetal compounds under C_{2v} symmetry. The description of these modes is given in Table 7.

Bands attributable to the ring tilting modes $(2A_1+B_1+B_2)$ have not been observed in $(C_5H_5)_2Sn$. However, in $(MeC_5H_4)_2Sn$, the bands at 368 vvw and 295 m(sh) cm^{-1} in the infra-red could belong to such vibrations. In the analogous ferrocenes, the

TABLE 7

DESCRIPTION OF THE NON-RING SKELETAL MODES FOR ANGULAR DICYCLOPENTADIENYLMETAL COMPOUNDS

Under C_{2v} symmetry.

Description of mode	*Species*	*Activity*	*Frequency No.*
Symmetric metal–ring stretch	A_1	IR, R	R_1
Torsion	A_2	R	R_2
Antisymm. metal–ring stretch	B_2	IR, R	R_3
Torsion	A_2	R	R_4
Symmetric ring tilt	$\{B_2$	IR, R	R_5
	$\{A_1$	IR, R	R_6
Antisymm. ring tilt	$\{B_1$	IR, R	R_7
	$\{A_1$	IR, R	R_8
Ring–metal–ring def.	B_1	IR, R	R_9

symmetric and antisymmetric modes have been reported to occur at ca. 380 cm^{-1} and ca. 495 cm^{-1} respectively; and C_5H_5NiNO and MeC_5H_4NiNO the ring tilting mode occurs at 252 and 298 cm^{-1} respectively.

In the Raman spectra of both compounds two bands at ca. 240 s cm^{-1} and ca. 170 w–m cm^{-1} were observed. The higher frequency band was also observed in the infra-red spectra, but an accurate measurement was not possible, since it occurred on the very limit of this study. Polarisation studies for $(MeC_5H_4)_2Sn$ show that the band at 171 cm^{-1} belongs to the A_1 symmetry class, whilst the 240 cm^{-1} band is depolarised. These bands are therefore assigned as the antisymmetric and symmetric metal–ring stretching modes, R_2 and R_1. These assignments are much lower than the similar assignments for analogous sandwich molecules (Table 8), but are quite reasonable in view of the greater mass of the tin atom. Fritz, who observed a strong band in the infra-red of $(C_5H_5)_2Sn$ at 260 cm^{-1}, presumably the same as our 242 cm^{-1} Raman band, has compared the tin–C_5H_5 ring stretching mode with the tin–bromine stretch, since both ligands are of comparable mass[11]. This vibration may be found in the range 170–280 cm^{-1} in tin(IV) complexes[23–26], and in the range 182–205 cm^{-1} in tin(II) derivatives[27]. The metal–ring stretching vibration may also be likened to the Whiffen *t*-mode in phenyltin compounds. This mode describes what is for the most part the Sn–Ph stretching vibration, and usually occurs as a strong band in the infra-red[26] at ca. 220 cm^{-1}.

TABLE 8

SKELETAL MODES IN SOME "SANDWICH" MOLECULES

Mode	$(C_5H_5)_2Sn$	$(MeC_5H_4)_2Sn$	$(C_5H_5)_2Fe$[a]	$C_5H_5Mn(CO)$[b]	$(C_6H_6)_2Cr$[c]	C_5H_5NiNO[d]
Antisymm. RMR str.	242	237	478	350	279	322
Sym. RMR str.	172	171	303		415	
Ring tilt		368, 295?	388, 492	375	333, 466	252
RMR def.		113	170	100 or 120	144	153

Ref. 17. [b] Ref. 16. [c] Ref. 28. [d] Ref. 18.

The medium intensity depolarised line at 113 cm^{-1} in the Raman spectrum of $(MeC_5H_4)_2Sn$ could be assigned to either of the torsion modes R_2 or R_4, or the ring–metal–ring deformation mode R_9. Although the torsion modes cannot be ruled out, the deformation mode R_9 is preferred. The corresponding vibration in ferrocene is found at 170 cm^{-1}, whilst the similar deformation modes in $C_5H_5Mn(CO)_3$, $(C_6H_6)_2Cr$ and C_5H_5NiNO fall in the range 100–150 cm^{-1}.

It is clear that the vibrational spectra of $(C_5H_5)_2Sn$ and $(MeC_5H_4)_2Sn$ are quite adequately described in terms of the "local" symmetries for the angular sandwich molecules.

Further information concerning their structural similarity comes from the mass spectra of the two compounds (Table 9). The most prominent feature in both spectra is the polyisotopic monoring–tin fragment, with only a weak parent ion. Monocyclopentadienyltin chloride is reported to behave similarly[5]. Ferrocene on the other hand exhibits the parent ion as the strongest peak. Fragments analogous to the cyclopropeniumtin and alkynyltin species observed for $(C_5H_5)_2Sn$ could not be detected in the methylcyclopentadienyl compound.

TABLE 9

MASS SPECTRA OF DICYCLOPENTADIENYLTIN AND BIS(METHYLCYCLOPENTADIENYL)-TIN

$(C_5H_5)_2Sn$[a]	$(CH_3C_5H_4)_2Sn$	*Assignment*
	277 (2.3)	$(CH_3C_5H_4)_2Sn^+$
249 (4.6)		$(C_5H_5)_2Sn^+$
	198 (100)	$CH_3C_5H_4Sn^+$
184 (100)		
158 (3.7)		$C_3H_3Sn^+$
144 (3.0)		HC_2Sn^+
119 (13)	119 (17)	Sn^+

[a] Ref. 8.

TABLE 10

TIN-119m MÖSSBAUER DATA FOR ORGANOTIN(II) DERIVATIVES

Compound	*IS (mm/s)*	*QS (mm/s)*
$(C_5H_5)_2Sn$[a]	3.74±0.06	0.86±0.12
$(MeC_5H_4)_2Sn$[b]	3.83±0.06	0.78±0.12
$(C_5H_5)_2Sn{:}BF_3$[c]	3.79±0.06	0.90±0.12

[a] Ref. 8. [b] Ref. 30. [c] Ref. 4.

The tin-119*m* Mössbauer spectral data of both compounds and $(C_5H_5)_2Sn \cdot BF_3$ is listed in Table 10. The isomer shift and quadrupole splitting parameters are all identical within experimental error, indicating that the valence electrons experience no significant perturbation as the groups about the tin atom are varied.

The proton magnetic resonance spectrum of $(MeC_5H_4)_2Sn$ at ambient tempera-

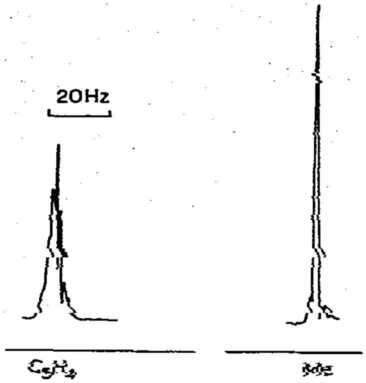

Fig. 1. Proton magnetic resonance spectrum of $(MeC_5H_4)_2Sn$ in the regions τ 4.30 and τ 8.0.

tures exhibits two resonances at ca. τ 4.30 and τ 7.97 (Fig. 1) [*cf.* $Me_3SnC_5H_4Me$: τ 4.34, 4.47 (C_5H_4); τ 7.96 ($Cp{-}CH_3$)][29]. The low field resonance consists of a partially resolved AA'BB' pattern for the ring protons, whilst the resonance due to the methyl group consists of a sharp single line. Spin–spin coupling between the metal atom and the methyl protons was not observed, however partially resolved tin satellites could be seen on the low field resonance with $J(Sn{-}H) \approx 10$ Hz [*cf.* $(C_5H_5)_2Sn$, J 15.9 Hz][8]. This is to be compared with $Me_3SnC_5H_4Me$ where coupling was observed between tin and the methyl protons (J 10.5 Hz) but not the ring protons[29].

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