

## STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

### XII\*. THE VIBRATIONAL SPECTRA OF CYCLOPENTADIENYLTIN(IV) COMPOUNDS

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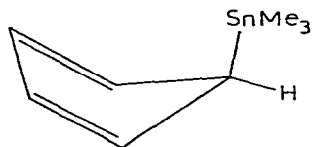
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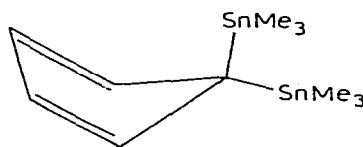
#### Summary

The vibrational spectra of  $\text{Me}_3\text{SnC}_5\text{H}_5$  and  $(\text{Me}_3\text{Sn})_2\text{C}_5\text{H}_4$  have been assigned in terms of the localised,  $\sigma$ -bonded structures inferred from electron diffraction data. The spectra of the product from the reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Sn}^{\text{II}}$  and diiron enneacarbonyl,  $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$ , is consistent with the presence of two inequivalent, *monohapto*-cyclopentadienyl rings bonded to each tin atom.

In our studies of cyclopentadienyltin(II) compounds [2], it has been apparent that, during the course of some reactions involving these compounds, the mode of bonding of the cyclopentadienyl rings to the tin changes drastically. The bonding phenomena of organotin(IV) cyclopentadienyl derivatives has been the subject of much investigation during the last few years because of the occurrence of facile metallotropic rearrangements. Electron diffraction data of both trimethylstannylcyclopentadiene [3] and bis(trimethylstannyl)cyclopentadiene [4] have been interpreted in terms of the *monohapto*- $\text{Me}_3\text{Sn-}\eta^1\text{-C}_5\text{H}_5$  and  $(5,5\text{-Me}_3\text{Sn})_2(\eta^1, \eta^1\text{-C}_5\text{H}_4)$  structures, I and II, respectively, in which the trimethylstannyl groups are associated with just one of the ring carbon



(I)

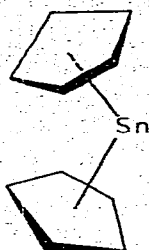


(II)

\* For Part XI see ref. 1.

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atoms. The best "fit" to the data was not, however, obtained with planar  $C_5$  rings but rather with puckered rings, in which the C(5) atom was somewhat out of the plane of the four olefinic ring carbon atoms. In sharp contrast to cyclopentadienyltin(IV) compounds, an electron diffraction study of dicyclopentadienyltin(II) [5] shows it to possess the angular sandwich *pentahapto* structure III, in which the tin is associated equally with all five ring carbon atoms. We have previously [6] measured the vibrational spectra of  $(\eta^5-C_5H_5)_2Sn$  and also



(III)

$(\eta^5-MeC_5H_4)_2Sn$  and have assigned them quite adequately on the basis of "local"  $C_{5v}$  and  $C_{2v}$  symmetry for the  $C_5H_5$  and  $MeC_5H_4$  groups, respectively. For a *pentahapto*-bonded cyclopentadienyl ring, only seven of the 24 normal vibrations of the  $C_5H_5$  unit are active in the infrared, whereas any lowering of the symmetry to  $C_s$  causes all 24 modes to become infrared active. Thus, the nature of the metal-ring bonding in cyclopentadienyltin compounds should be quite apparent from a careful interpretation of the infrared spectrum. In this paper we report the vibrational spectra of the model compounds,  $Me_3SnC_5H_5$  and  $(Me_3Sn)_2(C_5H_4)$ , and apply the bonding criteria to a product of a reaction involving dicyclopentadienyltin(II).

## Results and discussion

$Me_3SnC_5H_5$  and  $(Me_3Sn)_2(C_5H_4)$  were prepared by the stannylation of cyclopentadiene using  $Me_3SnNEt_3$  in a 3:1 and 1:2 molar ratio of cyclopentadiene to stannylamine, respectively. The products were characterised by elemental analysis\* and mass spectra, which are briefly reported in Tables 1 and 2 together with suggested assignments. Infrared and Raman spectra of  $Me_3SnC_5H_5$  are presented in Table 3, together with those for  $(C_5H_5)_2Hg$  [7], a generally accepted model *monohapto*-cyclopentadienylmetal derivative. The spectra are readily rationalised in terms of non-interacting  $Me_3Sn$  and  $C_5H_5$  units, and additional Sn-C(5) stretching and C-Sn-C(5) angle deformation modes. The vibrations due to the methyl groups bonded to tin are easily identified at 2983,  $\nu(CH)E_1$ ; 2919,  $\nu(CH)A_1$ ; 1388,  $\delta(CH)E_1$ ; 1189,  $\delta(CH)A_1$ ; and 765,  $\rho(CH_3)cm^{-1}$ . The two bands at 531 and 509  $cm^{-1}$  are assigned as the antisymmetric and symmetric tin-carbon(methyl) stretching vibrations, respectively, on the

\* All compounds were analytically pure. Boiling points were:  $Me_3SnC_5H_5$  46° C/0.04 mmHg (lit. [9] 38° C/3 mmHg) and  $(Me_3Sn)_2(C_5H_4)$  65° C/0.05 mmHg (lit. [9] 80° C/3 mmHg).

TABLE 1  
MASS SPECTRAL DATA (70 eV) FOR  $\text{Me}_3\text{SnC}_5\text{H}_5$

<i>m/e</i>	Relative intensity	Assignment
229	20.5	$\text{Me}_3\text{SnC}_5\text{H}_5^+$
214	16.6	$\text{Me}_2\text{SnC}_5\text{H}_5^+$
199	2.0	$\text{MeSnC}_5\text{H}_5^+$
184	46.7	$\text{SnC}_5\text{H}_5^+$
164	100	$\text{Me}_3\text{Sn}^+$
149	11.8	$\text{Me}_2\text{Sn}^+$
134	18.0	$\text{MeSn}^+$
119	13.2	$\text{Sn}^+$

basis of Raman polarisation data. Since all the normal vibrations associated with the cyclopentadienyl ring will be expected to occur above  $600\text{ cm}^{-1}$ , the bands observed below  $500\text{ cm}^{-1}$  must be due to the Sn—C(5) stretching and C—Sn—C angle deformation modes. The band at  $332\text{mw cm}^{-1}$  in the infrared, which also occurs as a strong, polarised band in the Raman, is too high to be a skeletal deformation mode, and so is assigned as the Sn—C(5) stretching mode. The bands at 243, 186, and  $144\text{ cm}^{-1}$  are assigned as C—Sn—C angle deformation modes.

The remaining bands in the spectra also occur in the spectra of  $(\text{C}_5\text{H}_5)_2\text{Hg}$ , and are therefore considered to be associated with the  $\text{C}_5\text{H}_5$  fragment. The

TABLE 2  
MASS SPECTRAL DATA (70 eV) FOR  $(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)$

<i>m/e</i>	Relative intensity	Assignment
<i>Two-tin-containing fragments</i>		
392	5.7	$(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)^+$
377	15.0	$\text{Me}_3\text{SnC}_5\text{H}_4\text{SnMe}_2^+$
361	8.9	$\text{Me}_2\text{SnC}_5\text{H}_3\text{SnMe}_2^+$
347	11.3	$\text{Me}_2\text{SnC}_5\text{H}_4\text{SnMe}^+$
331	12.2	$\text{MeSnC}_5\text{H}_3\text{SnMe}^+$
317	6.5	$\text{MeSnC}_5\text{H}_4\text{Sn}^+$
302	4.5	$\text{SnC}_5\text{H}_4\text{Sn}^+$
281	3.1	$\text{MeSnCHSnMe}^+$
275	0.3	$\text{SnC}_3\text{HSn}^+$
267	0.7	$\text{MeSnCH}_2\text{Sn}^+$
253	1.7	$\text{MeSn}_2^+$
238	1.1	$\text{Sn}_2^+$
<i>Mono-tin-containing fragments</i>		
229	15.2	$\text{Me}_3\text{SnC}_5\text{H}_5^+$
213	12.7	$\text{Me}_2\text{SnC}_5\text{H}_4^+$
198	2.3	$\text{MeSnC}_5\text{H}_4^+$
184	32.7	$\text{SnC}_5\text{H}_5^+$
164	100	$\text{Me}_3\text{Sn}^+$
149	8.7	$\text{Me}_2\text{Sn}^+$
134	12.1	$\text{MeSn}^+$
119	9.8	$\text{Sn}^+$

TABLE 3

VIBRATIONAL SPECTRA ( $\text{cm}^{-1}$ ) OF  $\text{Me}_3\text{SnC}_5\text{H}_5$ 

$(\text{C}_5\text{H}_5)_2\text{Hg}^a$		$\text{Me}_3\text{SnC}_5\text{H}_5$		Assignment
Raman	Infrared	Raman	Infrared <sup>b</sup>	
	3090s	3100w (dp)	3101(sh)	$\nu(\text{C-H})$
	3088s		3092ms	$\nu(\text{C-H})$
	3076(sh)	3066w (dp)	3078(sh)	$\nu(\text{C-H})$
	3040(sh)	3039w (dp)	3052w	$\nu(\text{C-H})$
	2970w			$\nu(\text{C-H})$
		2977w (br) (dp)	2983vs	$\nu(\text{C-H})E_1, \text{Me-Sn}$
		2911m (p)	2919vs	$\nu(\text{C-H})A_1, \text{Me-Sn}$
			2354w	} Combination bands and overtones
			2140w	
			1929vw	
	1808w		1717w (br)	
	1630w		1697w (br)	
1530w	1530w		1616w (br)	$\nu(\text{C=C})?$
1445m				
1420m	1427m	1427w (dp)		
			1410w	
		1390w (dp)	1388m	$\delta(\text{C-H})E_1, \text{Me-Sn}$
1384m	1383m		1367mw	$\delta(\text{C-H})$
1300w	1296m		1300w	$\delta(\text{C-H}) + \text{Ring def.}$
			1261vw	
1230w	1234m		1236w	$\delta(\text{C-H}) + \text{Ring def.}$
		1198m (p)	1189s	$\delta(\text{C-H})A_1, \text{Me-Sn}$
			1132w	
1109m	1109m	1111w (p)	1116w	Ring def.
1080w	1084m	1085w (dp)	1087ms	$\delta(\text{C-H})$
1033w	1026m	1037w (dp)	1032m	$\pi(\text{C-H})$
	985w		991m	$\delta(\text{C-C}(5)\text{-H})$
	955w	970w (dp)	973s	Ring def. + $\delta(\text{C-H})$
	905w		915mw (sh)	$\delta(\text{C-H})$
	874s	875w (dp)	873vs (br)	Ring def.
	815s	824w (p?)	825m (sh)	Ring def.
			765vvs	$\rho(\text{CH}_3), \text{Me-Sn}$
			735vs	$\pi(\text{C-H})$
	748vs			
	720w			
639s	646s	639m (p)	665m	509 + 144
	575w		638s	$\delta(\text{C-H})$
			580vw	
		529m (dp)	531vs	$\nu(\text{Sn-C})E_1$
		508s (p)	509ms	$\nu(\text{Sn-C})A_1$
			379w	
		333s (p)	332mw	$\nu(\text{Sn-C}(5))$
		305w (p)		825-509 = 316?
		243w (p)		} $\delta(\text{C-C}(5)\text{Sn})$
		186w (dp)		
		144m (dp)		

<sup>a</sup> Ref. 7. <sup>b</sup> Liquid film.

assignments of the ring fundamentals are those given by Maslowsky and Nakamoto [7] for  $(\text{C}_5\text{H}_5)_2\text{Hg}$ . Only four of the expected five ring C-H stretching modes are observed at 3101, 3092, 3078, and 3052  $\text{cm}^{-1}$ , the fifth, which occurs at 2970  $\text{cm}^{-1}$  in  $(\text{C}_5\text{H}_5)_2\text{Hg}$ , being masked by the strong C-H(methyl) stretching mode at 2983  $\text{cm}^{-1}$ . The two predominantly C=C stretching modes of the ring occur at 1498 and 1590  $\text{cm}^{-1}$  in cyclopentadiene, but only a single



of the 5,5-isomer. Thus, any attempt to assign the vibrational spectra of  $(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)$  should allow for the possible observation of bands due to the 2,5-isomer IIb, although the spectra should be largely attributable to the 5,5-isomer IIa.

Not unexpectedly, the vibrational spectrum of  $(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)$  is qualitatively similar to that of  $\text{Me}_3\text{SnC}_5\text{H}_5$ . Only one set of bands ascribable to vibrations of the  $\text{Me}_3\text{Sn}$  group is observed at 2985,  $\nu(\text{CH}) E_1$ ; 2919,  $\nu(\text{CH}) A_1$ ; 1386,  $\delta(\text{CH}) E_1$ ; 1190,  $\delta(\text{CH}) A_1$ ; 766,  $\rho(\text{CH}_3)$ ; 531,  $\nu(\text{Sn}-\text{C}) E_1$ ; and 510,  $\nu(\text{Sn}-\text{C}) A_1 \text{ cm}^{-1}$ . The bands at 378vs and 332vw  $\text{cm}^{-1}$  in the infrared are assigned as the antisymmetric and symmetric stretching vibrations of the  $\text{Sn}-\text{C}(5)-\text{Sn}$  three-atom linkage of the 5,5-isomer, IIa. The bands at 249 and 149  $\text{cm}^{-1}$ , as in the spectra of  $\text{Me}_3\text{SnC}_5\text{H}_5$ , are ascribed to  $\text{C}-\text{Sn}-\text{C}$  angle deformation modes.

The introduction of a second  $\text{Me}_3\text{Sn}$  group should result in a decrease in the number of ring modes involving motion of the ring hydrogen atoms. Thus, whereas all three ring deformation modes observed in the spectrum of  $\text{Me}_3\text{SnC}_5\text{H}_5$  are retained in the spectrum of  $(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)$  (at 1119, 871 and 829  $\text{cm}^{-1}$ ), only three  $\text{C}-\text{H}$  stretching modes are observed at 3092, 3081 and 3063  $\text{cm}^{-1}$ , the fourth expected band as before being masked by the strong methyl  $\text{C}-\text{H}$  stretching mode at 2985  $\text{cm}^{-1}$ . Similarly, only four ring  $\delta(\text{CH})$  modes are observed at 1410, 1367, 1063 and 633  $\text{cm}^{-1}$ , the  $\pi(\text{CH})$  modes occurring at 1030 and 712  $\text{cm}^{-1}$ ; and only two of the three bands due to coupling of  $\delta(\text{CH})$

TABLE 5  
INFRARED SPECTRUM ( $\text{cm}^{-1}$ ) OF  $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2^a$

Assignment		Assignment	
3102(sh)	$\nu(\text{C}-\text{H})$	1027mw	} $\pi(\text{C}-\text{H})$
3082vw	$\nu(\text{C}-\text{H})$	1020ms	
3063vww	$\nu(\text{C}-\text{H})$	999w	} $\delta(\text{C}-\text{C}(5)-\text{H})$
2025vvs	$\nu(\text{CO})$	990w	
1985vvs	$\nu(\text{CO})$	969m	} Ring def. + $\delta(\text{C}-\text{H})$
1963(sh)		962mw (sh)	
1952(sh)		914vs	} $\delta(\text{C}-\text{H})$
1937(sh)		903(sh)	
1797vww		890(sh)	} Ring def.
1625w		877vvs	
1535vw	} $\nu(\text{C}=\text{C})$	818s	} Ring def.
1525mw			
1438ms	} $\delta(\text{C}-\text{H})$	742vvs	} $(\text{C}-\text{H})$
1429s			
1361w	$\delta(\text{C}-\text{H})$	639s	} $\delta(\text{C}-\text{H})$
1297vw	} $\delta(\text{C}-\text{H}) + \text{Ring def.}$	598vvs (br)	
1290vw			560s
1234w	$\delta(\text{C}-\text{H}) + \text{Ring def.}$	537ms	
1220mw			505mw
1143vww	}	466w	} $\nu(\text{Fe}-\text{C})$
1123vww			
1111vw	} Ring def.	424(sh)	
1104w			407w
1081vs	$\delta(\text{C}-\text{H})$	309s	} $\nu(\text{Sn}-\text{C}(5))$
		301ms (sh)	

<sup>a</sup> Nujol/halocarbon mull.

and ring deformation modes are preserved at 1288 and 973  $\text{cm}^{-1}$ . The  $\delta(\text{C}-\text{C}(5)-\text{H})$  mode which occurred at 991  $\text{cm}^{-1}$  in  $\text{Me}_3\text{SnC}_5\text{H}_5$  is also missing from the spectrum of  $(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)$ . The two ring C=C stretching bands are observed as very weak features at 1516 and 1620  $\text{cm}^{-1}$ , although the latter may be a combination band. Additional bands at 1133 and 805  $\text{cm}^{-1}$  are probably due to the presence of the 2,5 isomer.

Thus, the vibrational spectra of both  $\text{Me}_3\text{SnC}_5\text{H}_5$  and  $(\text{Me}_3\text{Sn})_2(\text{C}_5\text{H}_4)$  are consistent with, and may be adequately interpreted in terms of, the *monohapto*, localised  $\sigma$ -bonded structures deduced by electron-diffraction methods. For  $\text{Me}_3\text{SnC}_5\text{H}_5$ , nineteen of the expected 24 of the ring fundamentals have been observed, and hence the spectrum of this compound may be employed as a model for *monohapto*-cyclopentadienyl rings bonded to tin, as that of  $(\text{C}_5\text{H}_5)_2\text{Sn}$  may be used as a model for *pentahapto*-bound species. As a test of this criterion, we have measured the infrared spectrum of the product of the reaction between  $(\eta^5-\text{C}_5\text{H}_5)_2\text{Sn}$  and diiron enneacarbonyl, which has the composition  $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$ . Preservation of the *pentahapto* bonding of  $(\eta^5-\text{C}_5\text{H}_5)_2\text{Sn}$  during the reaction would give a relatively simple spectrum composed of the characteristic bands due to  $\eta^5-\text{C}_5\text{H}_5$  rings and  $\text{Fe}(\text{CO})_4$  groups. It is immediately apparent that the spectrum of  $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$  listed in Table 5, is far too complex to be consistent with an  $\eta^5-\text{C}_5\text{H}_5$  structure, but, on close examination, not only are all the ring vibrations observed for  $\text{Me}_3\text{SnC}_5\text{H}_5$  present, but the majority are duplicated. In addition, two Sn—C(5) stretching bands are observed at 301 and 309  $\text{cm}^{-1}$ . Thus, it is apparent that not only has the mode of attachment of the cyclopentadienyl rings to the tin changed from *pentahapto* to *monohapto* during the reaction with diiron enneacarbonyl, but that in  $[(\text{C}_5\text{H}_5)_2\text{SnFe}(\text{CO})_4]_2$ , the two *monohapto*-cyclopentadienyl rings are inequivalent.

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### References

- 1 P.G. Harrison and R.C. Phillips, *J. Organometal. Chem.*, **99** (1975) 79.
- 2 P.G. Harrison, T.J. King and J.A. Richards, *J. Chem. Soc. Dalton*, (1975) 2097.
- 3 N.N. Veniaminov, Y.A. Ustynyuk, N.V. Alekseev, I.A. Ronova and Y.T. Struchkov, *Doklady Chem.*, **199** (1971) 577.
- 4 N.N. Veniaminov, Y.A. Ustynyuk, N.V. Alekseev, I.A. Ronova and Y.T. Struchkov, *J. Struct. Chem. (USSR)*, **12** (1971) 879.
- 5 A. Alm nningen, A. Haaland and T. Motzfeldt, *J. Organometal. Chem.*, **7** (1967) 97.
- 6 P.G. Harrison and M.A. Healy, *J. Organometal. Chem.*, **51** (1973) 113.
- 7 E. Maslowsky and K. Nakamoto, *Inorg. Chem.*, **8** (1969) 1108.
- 8 Y.A. Ustynyuk, A.V. Kisin and A.A. Zenkin, *J. Organometal. Chem.*, **37** (1972) 101.
- 9 I.M. Pribytlova, A.V. Kisin, Y.N. Luzikov, N.P. Makoveyeva, V.N. Torocheshnikov and Y.A. Ustynyuk, *J. Organometal. Chem.*, **30** (1971) C57.