108. *Dicyclopentadienyl-tin and -lead.*

By H. P. Fritz and E. O. Fischer.

The infrared spectra of dicyclopentadienyl-tin and -lead, in the range 2—40 μ, are recorded and compared with other published values. The results are consistent with previously suggested structures.

On the basis of the similarity of the infrared spectra, Fischer and his co-workers [1-3] postulated a sandwich structure, similar to that of ferrocene (I), for dicyclopentadienyl-tin [4] and -lead.[5] They further suggested that the dipole moments of these compounds indicated that the rings were at an angle to one another (II).[3,6] In view of criticism by Dave, Evans, and Wilkinson [7] we have now extended our earlier measurements of the

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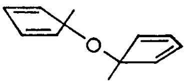
[1] Fischer and Piesbergen, *Z. Naturforsch.*, 1956, **11***b*, 758.
[2] Fischer, *Z. angew. Chem.*, 1957, **69**, 715.
[3] Fischer and Schreiner, *Chem. Ber.*, 1959, **92**, 938.
[4] Fischer and Grubert, *Z. Naturforsch.*, 1956, **11***b*, 423.
[5] Fischer and Grubert, *Z. anorg. Chem.*, 1956, **286**, 237.
[6] Weiss, *Z. anorg. Chem.*, 1956, **286**, 236.
[7] Dave, Evans, and Wilkinson, *J.*, 1959, 3684.

infrared spectra. It is well known that the influence of solvents on relatively unstable metal dicyclopentadienyls, which do not have a filled inert-gas configuration for the central atom, must not be overlooked. Thus, the nuclear magnetic resonance spectra of dicyclopentadienyl-mercury [8,7] or -beryllium [9] show only one proton line, although structures


(I)


(II)


(III)

involving σ-bonded cyclopentadienyl rings are probable on the basis of the infrared spectra. Dicyclopentadienyliron dicarbonyl shows only two proton signals,[10] one from the π-bonded and one from the σ-bonded ring. In each case a much more complicated nuclear magnetic resonance spectrum would be expected. In infrared spectroscopy, change of solvent sometimes causes remarkable changes in intensity and position of bands. The possibility of formation of addition compounds also must be considered, if the compounds show any donor or acceptor properties.*

For these and other reasons we regard infrared measurements on solutions of this special kind of polar metal dicyclopentadienyl as convenient though sometimes unreliable evidence.

Wilkinson and his co-workers [7] used tetrachloroethylene and carbon disulphide as solvents. The former is suitable when pure, but some important spectral regions cannot be investigated because of absorption by solvent. Carbon disulphide has good solvent properties too, but also, we find, a tendency to form addition compounds with the solute. We therefore conclude that infrared measurements of extremely sensitive and polar compounds are best carried out under the mild conditions of the Nujol or " Hostaflon " (fluorolube) mull technique or on halide discs, if air and moisture can be rigorously excluded. This is ensured in our laboratory, where sensitive substances are handled by means of Schlenk tubes and glove box.

Previously,[11] we listed, amongst others, infrared spectra of the tin and lead compounds in potassium bromide discs [12] and assigned some of the normal frequencies by analogy with ferrocene.[13] We now report the spectra of these two compounds, obtained from freshly resublimed samples as mulls in Nujol and " Hostaflon," respectively, in the range 2—40 μ. The measurements in the far-infrared region are part of an investigation of the position of the metal–ring frequencies of $M(C_5H_5)_2$-compounds.[14] In the Table we include the results reported by Wilkinson and his co-workers,[7] since they claimed that our results were " so much at variance with solution data " given earlier [15] and by them and therefore were " unreliable."

The relative similarity of these spectra with those of ferrocenes was emphasized earlier by Fischer and his co-workers.[1,3]

Clearly spectra of solutions can only be accepted with some reservation. Whilst our mull spectra show a definite difference between the tin and the lead compound, especially in the characteristic region of the CH-deformations,[13,11] the spectra recorded by Wilkinson and his co-workers give very similar values for the two compounds. One cannot explain this difference as that usual between spectra of solid and solution. It is rather the result of an equalizing effect of the solvents on those polar and weakly bonded compounds.

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* For recent results in this connexion see Strohmeier and von Hobe (*Z. Elektrochem.*, 1960, **64**, 945).

[8] Strohmeier and Lemmon, *Z. Naturforsch.*, 1959, **14***a*, 109.
[9] Fischer and Hofmann, unpublished work.
[10] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.
[11] Fritz, *Chem. Ber.*, 1959, **92**, 780.
[12] Dr. O. Vohler, Anorg. Inst. T.H., München, kindly supplied these spectra.
[13] Lippincott and Nelson, *Spectrochim. Acta*, 1958, **10**, 307.
[14] Fritz and Schneider, *Chem. Ber.*, 1960, **93**, 1171.
[15] Lindstrom and Barusch, 131st Amer. Chem. Soc. Meeting, 1957, Abstr. 77, as cited in ref. 7.

Infrared spectra of dicyclopentadienyl-tin and -lead.

$Sn(C_5H_5)_2$				$Pb(C_5H_5)_2$			
KBr disc	Mull	Soln. C_2Cl_4 *	CS_2 *	KBr disc	Mull	Soln. C_2Cl_4 *	CS_2 *
		3100sh	3100sh			3090sh	3090sh
3061w	3065m	3094s	3094s		3021w	3082s	3082s
	2967sw						
	2924sw	2919w	2918w	2914w		2917w	2917w
	2882sw			2851sw	2890w		
	2778sw						
	2688sw	2695w	2695w		2632sw	2680w	
	2410sw						
	2356sw				2310sw		
	2262sw	2280w			2288sw	2278w	
	2195sw	2210w				2200w	
	2062sw	2085w			2088sw	2080w	
	1965sw						
	1894sw				1880sw		
	1754w	1750m	1750m				
1739w	1745w				1736w	1732m	1745m
					1721w		1720m
	1689sw				1706sw		
	1656sw						
	1642m						
1631w	1634m				1639w		
					1613w	1622m	
	1585sw						
	1565sw						
	1550w				1546sw		
	1529sw	1532m			1529sw		
	1515sw				1513sw	1515m	
	1504sw				1502sw		
		1482w			1493sw	1482w	
1424m	1428s	1426s				1427s	
				1418w	1416m		
1363m	1366sw		1360m	1382w			1351m
	1342w		1340m		1335sw		
	1258w	1260w	1260w		1263sw	1255w	1260w
		1228w	1228w			1228w	1228w
	1198sw		1193sw		1192sw		1190sw
	1167w		1156w		1164w		1156w
					1149sw		
1112m	1114s		1112s	1111w	1112m		1113s
	1094sw						1082sw
1059w	1060w	1055w	1055w	1057sw	1059w	1055w	1052w
1003s	1004s		1002s	1002m	1007s		1005s
959w	960sw				962sw		
	936sw				929sw		
914w	916sw			913sw	915sw		
890w	890w			898w	890sw		
					881sw		
					861sw		
837w	835w			836w	838w		
	818shw		805w				805w
792s	788shs		780m				780w
	770sh			769sh	766sh		
751s	758s		748ss	756s	752s		750ss
				744s	740s		
664w	663w	666w	666w	663w	662w	666w	666w
544sw	544swbr				588swbr		
	260mbr						

* Dave, Evans, and Wilkinson, ref. 7.
w = weak, m = medium, s = strong, sw = very weak, ss = very strong, sh = shoulder, and br = broad band.

Dave, Evans, and Wilkinson obviously did not consider this, and the question arises whether they measured the spectra of the pure compounds in their normal state at all.

Wilkinson and his co-workers[7] state, quite correctly, that it should be possible to distinguish theoretically between structures (I) [symmetry D_{5d} or D_{5h}] and (II) [symmetry

C_{2v}], and another structure (III), which could be angular [C_i, C_{2v} or other low symmetry].

Structure (III) can be excluded because of the types and low number of intensive bands observed in the infrared spectrum.

For structure (II), for example, with the two rings eclipsed, the selection rules would predict 44 of the 57 possible fundamentals to be active in the infrared region, 7 of which would belong to " skeletal " frequencies of the three-mass model YXY. The 37 ligand frequencies should appear mostly in the range covered by sodium chloride optics. Slight coupling being assumed between vibrations of the two rings, several frequencies will practically coincide, thus being observed as only one band. Nevertheless, more bands should still be observable than for structure (I). Wilkinson and his co-workers [7] state that fewer vibrations will be infrared-active for symmetry group D_{5d} than for D_{5h}, but this is incorrect for sandwich compounds. D_{5d} and D_{5h} symmetry would allow 7 ligand- and 3 " skeletal "-frequencies in the infrared region and 15 Raman-active vibrations for each point group.

Wilkinson and his co-workers deduced that their spectra are consistent with the lower symmetry because of the increased number of bands compared with ferrocene; but their comparison was with a ferrocene spectrum of unknown concentration in carbon tetrachloride [13] and their assignments were incomplete. Hence, their argument is rather speculative.

There are, of course, more efficient methods to prove the absence of structure (I), one being an analysis of the combination bands. The spectra show some weak bands, which (allowing for deviations due to anharmonicity) can be explained as binary combinations of fundamental frequencies, indicating that a D_{5d} or D_{5h} structure is probably absent.

In the far-infrared region we found only one band, which can be assigned with some certainty to a fundamental frequency, for the tin compound and none for the lead compound.

If the structure of the molecules, which we assume to be analogous, were linear (I), only the doubly degenerate, asymmetric ring-tilt and the asymmetric metal–ring stretching vibration would be observable in the range to 40 μ, the doubly degenerate ring–metal–ring deformation lying at much lower frequencies.[13]

If the structure is angular (II) there would be two asymmetric ring-tilt and one metal–ring stretching vibrations within the same range, and the results obtained with ferrocene and ruthenocene [13] suggest that the remaining fundamentals of the YXY model active in the infrared region would probably lie at lower frequencies.

Since the asymmetric ring-tilt vibration does not occur lower than 400 cm.$^{-1}$ in all other metal dicyclopentadienyls [14] the corresponding frequencies of the tin and the lead compound will be tentatively assigned to the very weak bands at 544 and 588 cm.$^{-1}$, respectively, although deformation frequencies are likely to occur in the same range. Their broad contour might be due to splitting, caused by removal of the degeneracy.

Only the 260 cm.$^{-1}$ band of the tin compound can be assigned reasonably securely to asymmetric metal–ring stretching. In tin tetrabromide the Sn–Br stretching frequency occurs at 279 cm.$^{-1}$, so our assignment to metal–ring stretching can be regarded as plausible.

It is now possible to refine Fischer's earlier concept. Accepting the structure to be angular (II), we can assume a non-linear configuration YXY for the molecules if one cyclopentadienyl ligand is regarded as one point of mass Y in an approximation used for dicyclopentadienyl-iron and -ruthenium.[13] The force constant of the metal–ring bond being taken as approximately the same as in other metal dicyclopentadienyls of comparable sensitivity,[14] that is *ca.* $1{\cdot}5 \times 10^5$ dynes/cm., an angle of *ca.* 108° between the two axes perpendicular to the planes of the rings is obtained.[16] The assumption of a sp^2-hybridisation for the tin atom, which Wilkinson *et al.* discuss too, seems to be in good accord with

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[16] Calculated by using an approximate formula given by Herzberg, "Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand Corp., Inc., Princeton, 1956, p. 169.

this value, if the deviation from 120° is considered as due to an increase of *p*-character for the bonding orbitals and an increase of *s*-character for the third sp^2 hybrid orbital, which should contain the remaining two electrons as a lone pair. Dave, Evans, and Wilkinson agree with our concept of predominantly σ-bonding with some additional π-bonding between metal atoms and rings in dicyclopentadienyltin and probably also in the lead compound.

EXPERIMENTAL

Pure samples of dicyclopentadienyl-tin [4] and -lead [5] were resublimed and immediately used for infrared spectral measurements. The Nujol had been heated for some hours in a high vacuum and was cooled in an atmosphere of purified nitrogen. The " Hostaflon " (fluorolube) was treated similarly. The infrared measurements were made on a Perkin-Elmer spectrophotometer model 21 with sodium chloride and cæsium bromide optics. In order to reduce stray light and water absorption in the far-infrared region, a " reststrahlen " filter was used, and the spectrometer and its sample compartment were flushed with dry nitrogen. The mulls were placed between sealed sodium chloride or cæsium bromide windows. The spectra of potassium bromide discs were obtained on a different spectrometer of the same model with sodium chloride optics.[12]

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