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DERIVATIVES OF DIVALENT GERMANIUM, TIN AND LEAD

IV. SYNTHESIS AND INFRARED SPECTRUM OF THE NOVEL ALUMINIUM–TIN BONDED COMPLEX: BIS(METHYLCYCLOPENTADIENYL)TIN–ALUMINIUM TRICHLORIDE. A COMMENT ON THE STRUCTURE OF BIS(METHYLCYCLOPENTADIENYL)LEAD

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SUMMARY

The novel aluminium–tin bonded complex, bis(methylcyclopentadienyl)tin–aluminium trichloride has been synthesised from its two components. Its infrared spectrum has been recorded and normal modes assigned by comparison with bis(methylcyclopentadienyl)tin. A structure for the complex is proposed in which the angular "sandwich" nature of the free ligand is preserved. From the infrared spectrum of the bis(methylcyclopentadienyl)lead, it is deduced that this compound is isostructural with the analogous tin compound.

INTRODUCTION

The structure and nature of the bonding in Group IV cyclopentadienyls has aroused much interest[1–5]. Initially it was suggested that the cyclopentadienyl rings in tin(IV) cyclopentadienyl compounds are π-bonded[6,7]. However infrared[2], NMR[2] and structural[8,9] evidence has shown that these compounds possess a fluxional, σ-bonded diene-type ring, around which the metal migrates via 1,2- or 1,3-metallotropic shifts. The cyclopentadienyls of tin in its lower oxidation state are also the subject of much investigation, since they account for the majority of known organotin(II) derivatives. Electron diffraction[10] has shown that dicyclopentadienyltin has an angular "sandwich" structure in the vapour phase, in which the rings are centrally σ- (pseudo π-) bonded. In an earlier report[1] we showed that the vibrational spectra of this compound are consistent with the preservation of the angular "sandwich" structure in both the solid and solution phases. This formulation, with a bond angle at tin of ca. 120° [10], indicates sp^2 hybridisation for the tin valence electrons. The lone pair of electrons will therefore reside in an orbital possessing directional character*[,11]. This has been confirmed by the formation of the donor–acceptor complex, $(C_5H_5)_2$-$Sn \cdot BF_3$, in which the tin atom acts as a Lewis base[5]. Bis(methylcyclopentadienyl)tin

* *Cf.* $SnCl_3^-$, in which the ClSnCl angles are ca. 90°, and the lone pair is located in the tin 5*s* orbital.

exhibits similar properties, and this paper reports the preparation and infrared spectrum of its adduct with aluminium trichloride. The infrared spectrum of bis-(methylcyclopentadienyl)lead[12] is also reported.

EXPERIMENTAL

All manipulations were carried out under an atmosphere of dry argon. Bis-(methylcyclopentadienyl)tin was prepared as described previously[13]. Bis(methyl-cyclopentadienyl)lead was prepared similarly from lead acetate. Aluminium trichloride was sublimed immediately before use. Infrared measurements were carried out using a Perkin–Elmer 521 instrument calibrated with polystyrene and water vapour.

Bis(methylcyclopentadienyl)tin–aluminium trichloride adduct

Bis(methylcyclopentadienyl)tin (4.23 g, 15.3 mmol) in anhydrous benzene (5 ml) was added dropwise to a suspension of freshly sublimed aluminium trichloride (2.09 g, 15.7 mmol) in benzene (10 ml). After vigorous stirring for 20 min, all the aluminium trichloride had dissolved, and two liquid layers had formed. The lower layer was removed, and the solvent removed *in vacuo* to yield the adduct as a viscous, golden oil. (Found: C, 34.7; H, 3.5. $C_{12}H_{14}AlCl_3Sn$ calcd.: C, 35.1; H, 3.4%.)

RESULTS AND DISCUSSION

Bis(methylcyclopentadienyl)tin (I) reacts readily with anhydrous aluminium trichloride in dry benzene to form a 1/1 adduct (II) as a viscous, golden oil [eqn. (1)].

$$\underset{\text{(I)}}{(MeC_5H_4)_2Sn:} + AlCl_3 \rightarrow \underset{\text{(II)}}{(MeC_5H_4)_2Sn:\rightarrow AlCl_3} \quad (1)$$

The similarity of the tin-119*m* Mössbauer parameters of the boron trifluoride adducts of dicyclopentadienyltin[5] and (I)[14] and the ligands themselves has led us previously to suggest that the angular "sandwich" structure of the free ligands is preserved in the complexes[5]. Although Mössbauer evidence is not available in the present case, the complex (II) readily reduces mercury(II) chloride to mercury, and so is postulated to have a similar structure (Fig. 1), in which the coordination numbers of the tin and aluminium are three and four respectively. As such it is, as far as we are aware, the first example of a coordinate tin→aluminium bond. Like the free ligand, the complex (II) is both moisture- and oxygen-sensitive.

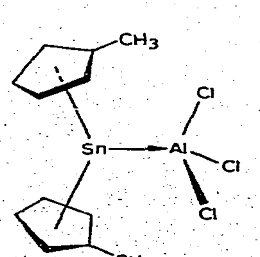

Fig. 1. Proposed structure of $(MeC_5H_4)_2Sn\cdot AlCl_3$.

TABLE 1

OBSERVED INFRARED BANDS OF $(MeC_5H_4)_2Sn \cdot AlCl_3$, $(MeC_5H_4)_2Sn$ AND $(MeC_5H_4)_2Pb$ (cm^{-1})

$(MeC_5H_4)_2Sn \cdot AlCl_3$[a]	*$(MeC_5H_4)_2Sn$*[a,b]	*$(MeC_5H_4)_2Pb$*[a]	*Assignment*
3975 vw	3920 w	3920 vvw	
	3100 w		CH str. A_1; ν_1, ν_{5a}
3112 m		3085 w	
	3080 w		CH str. B_1; ν_{5b}, ν_{9b}
3050			
2972 m	2965 w	2965 w	CH str. B_1, B_2; m_4, m_7
2930 m	2925 m	2925 w	CH str. A_1; m_1
2880 w(sh)		2870 w	
2755 vw		2735 vvw	
1825 vw(br)			Combination bands
		1740 vw(vbr)	
1660 w(vbr)		1685 vw(vbr)	
1640 w(vbr)			
	1607 vw	1610 vw	CC str. A_1; ν_{12a}
1521 m	1526 vw		CC str. B_1; ν_{12b}
1507 m(sh)			
1481 vs	1482 m	1485 mw	HCH bend, B_2; m_8
1456 vs	1458 w	1460 w	HCH bend, B_1; m_5
1448 vs(sh)	1448 w(sh)	1450 w	CC str., A_1; ν_{8a}
1418 m(sh)	1408 vw	1409 vw	CC str., B_1; ν_{8b}
1383 m			
1369 m	1378 w	1378 w	HCH bend, A_1; m_2
1346 w		1355 vw(sh)	
		1335 vw(sh)	
1319 vw			
1265 w	1260 vvw(br)	1265 mw	CH bend, B_1; ν_4
1238 w(sh)			
1229 s	1229 s	1230 w	CMe str., A_1, ν_{9a}
1180 vw		1180 vw(br)	
1112 vw(sh)	1117 vvw	1118 mw	CH bend, A_1; ν_{10a}
1065 m	1062 w	1065 m	CH bend, B_1; ν_{6b}
1045 s	1042 m	1044 ms	Ring breathing, A_1; ν_3
1029 vw	1026 m	1028 ms	CMe wag, B_2; m_9
			CMe wag, B_1; m_6
1003 m	1010 w(sh)	1010 w(sh)	CH bend, A_2; ν_{11a}
978 w(sh)	976 vvw	977 vvw	CH bend, A_1; ν_{6a}
	898 w	901 vw(sh)	CC bend, B_1; ν_{13b}
	885 w		
	847 w(sh)	848 mw	CC bend, A_1; ν_{13a}
847 vvs(sh)	813 vs	811 vs	CH bend, A_2; ν_{7a}
803 vvs(vbr)	767 vvs(br)	750 vvs(br)	CH bend, B_2; ν_2
685 s		680 vvw	
647 s		637 vvw	
629 s			
609 s	610 w	612 mw	CC bend, B_2; ν_{14b}
566 m	561 w	565 vw	CC bend, A_2; ν_{14a}
		523 vw	
493 vvs(br)			AlCl str. E
442 vs			AlCl str. A_1
327 s	319 mw		CMe bend, B_1; ν_{10b}: AlCl bend A_1
265 vs			Antisymm. tin–ring str.

[a] Taken as liquid film. [b] Ref. 1.

TABLE 2

SKELETAL MODES OF (II) AND RELATED COMPLEXES (cm^{-1})

$(MeC_5H_4)_2Sn \cdot AlCl_3$	$(MeC_5H_4)_2Sn$[a]	$(C_5H_5)_2Sn$[a]	$AlCl_3 \cdot NMe_3$[b]	$AlCl_3 \cdot OEt_2$[c]	$AlCl_3 \cdot SEt_2$[c]	*Assignment*
493			545	535	540	AlCl str. E
442			416	408	418	AlCl str. A_1
327			313			AlCl bend A_1
265	237	241				Antisymm. tin–ring str.

[a] Ref. 1. [b] Ref. 17. [c] Ref. 16.

The observed infrared spectrum of the complex, taken as a liquid film, is listed in Table 1, together with the previously measured spectrum of (I)[1]. The assignment of the normal modes of the latter was accomplished by the application of the inequality rule of Whiffen and Steele[15] to the spectrum of the unsubstituted compound, dicyclopentadienyltin, together with Raman polarisation data[1]. In the present case, the complex fluoresced strongly in the laser beam, and a Raman spectrum could not be obtained. However, direct comparison with the spectrum of (I) using the principal of "local" symmetry greatly simplifies the assignment of the spectrum of (II).

Although the overall symmetry for the molecule will be C_2, using "local" symmetry, the rings, assumed to a first approximation to be equivalent, will belong to the C_{2v} point group if the methyl group be treated as a point mass. To a large extent, the assignment of the ring fundamentals follows directly from those of (I) and requires no further comment. The frequency numbers (ν, m) noted in Table 1 refer to those used previously for the assignment of (I)[1].

Assuming "local" C_{3v} symmetry for the $AlCl_3$ moiety, four normal modes $(2A_1+2E)$ are expected from group theoretical considerations. Of these, two (A_1+E) will refer to Al–Cl stretching and two to Al–Cl bending modes. The two stretching modes are readily identified as very strong, broad bands at 493 and 442 cm^{-1}. The strong band at 327 cm^{-1} is probably largely the A_1 bending mode, although a ring CMe in-plane bending mode is expected to occur in a similar position. The E_1 Al–Cl bending mode occurs below 250 cm^{-1}, outside the range of this study, as do most of the skeletal modes involving the tin atom. However, the very strong band at 265 cm^{-1} may be assigned to the antisymmetric tin–ring stretching mode. This mode occurs at 237 cm^{-1} in (I), and its shift to high frequency is probably indicative of coupling between the tin–ring fundamentals and the Al–Cl stretching modes, which also differ significantly from those in complexes of aluminium trichloride with oxygen, sulphur[16] and nitrogen[17] donor ligands. In Table 2 are listed the skeletal modes of (II) together with the analogous vibrations in similar compounds.

No information concerning the position of the Al–Sn stretching vibration is available. However, it should occur close to the Si–Sn stretching vibration, which in (trimethylsilyl)trimethyltin is located at 322 cm^{-1} [18]. In (II), the metal–metal stretching vibration is probably masked by the Al–Cl bending mode at 327 cm^{-1}.

In the region 620–700 cm^{-1} there occur three bands of significantly intensity which can be assigned to neither ring modes nor skeletal modes of the $Ring_2Sn \cdot AlCl_3$ framework. Parker and Stiddard[19] observed similar extra bands in the spectrum of

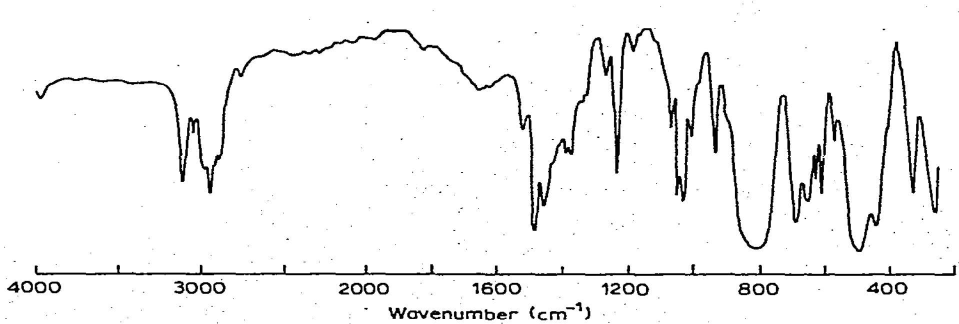

Fig. 2. The infrared spectrum (4000–250 cm^{-1}) of $(MeC_5H_4)_2Sn \cdot AlCl_3$.

$[MeC_5H_4Fe(CO)_3]_2$. Since they disappeared in solution, they were not assigned as fundamentals, and were rationalised as either (*i*) combination bands involving modes of the $[Fe(CO)_2]_2$ moiety or Ring–Fe stretching vibrations, or (*ii*) bands resulting from interaction between the CH out-of-plane bending motions of the ring and the rest of the molecule. In view of the bulkiness of the $AlCl_3$ residue, the latter explanation is quite reasonable in the present case.

The infrared spectrum of the adduct (II) is, therefore, consistent with the structure formulated in Fig. 1, in which the "sandwich", centrally σ-bonded character of the methylcyclopentadienyl rings is retained. Investigations into the chemistry of this novel aluminium–tin bonded compound are continuing in this laboratory.

Also listed in Table 1 are the observed infrared bands of bis(methylcyclopentadienyl)lead[12] as a liquid film. The obvious similarity of the spectra of this compound and (I) leads us to conclude that the two compounds are isostructural in the liquid phase. Dicyclopentadienyllead on the other hand, although known to possess the angular "sandwich" structure in the vapour phase[10], in the condensed phase (crystal) has a structure consisting of zig-zag chains in which the lead atoms alternate with cyclopentadienyl rings, equidistant from two lead atoms [r(Pb–C) 3.06 Å]. Each lead atom is further bonded to a third cyclopentadienyl ring at a closer distance [r(Pb–C) 2.76 Å]. In the solid therefore, the coordination number of each lead atom is raised to three[20].

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