DERIVATIVES OF BIVALENT GERMANIUM, TIN AND LEAD

XIV*. THE REACTIONS OF CYCLOPENTADIENYLTIN(II) COMPOUNDS WITH SOME MAIN GROUP LEWIS ACIDS

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Summary

The reactions of dicyclopentadienyltin and bis(methylcyclopentadienyl)tin with some boron and aluminium trihalides give complexes of composition $R_2Sn:MX_3$ ($R = C_5H_5$, $MX_3 = BF_3$, BBr_3, $AlCl_3$, $AlBr_3$; $R = MeC_5H_4$, $MX_3 = AlCl_3$). With BCl_3, $SnBr_4$, and $FeCl_3$, exchange of cyclopentadienyl groups for halogen takes place. Cyclopentadienyltin chloride and $AlCl_3$ yield the complex $C_5H_5SnAlCl_4$. Redistribution of organic groups occurs between cyclohexyl-magnesium bromide and dicyclopentadienyltin producing cyclopentadienyl-magnesium bromide etherate. Reaction of allyl or trimethylsilyl halides with $(C_5H_5)_2Sn:AlX_3$ yields $C_5H_5SnAlX_4$ complexes. The structures of the complexes have been investigated by infrared and tin-119m Mössbauer spectroscopy.
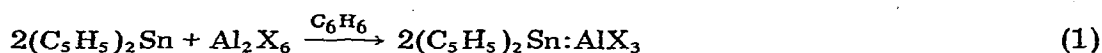
Introduction

The angular sandwich structure of dicyclopentadienyltin [2] suggests that the lone pair resides in a sp^2 hybrid orbital, and therefore should be available for complex formation with Lewis acids. The recently communicated crystal structure of cyclopentadienyltin chloride shows that this compound too has a bent structure, again suggesting a stereochemically-active lone pair [3]. We have previously reported briefly the formation of the complexes $(C_5H_5)_2Sn:BF_3$ [4], $(MeC_5H_4)_2Sn:AlCl_3$ [5], and $(C_5H_5)_2Sn:M(CO)_5$ (M = Cr, Mo, W) [6], in this paper we give a more detailed account of the reactions of cyclopentadienyltin(II) compounds with Main Group Lewis acids.

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Results and discussion

Similar to the reaction of aluminium trichloride dimer with $(MeC_5H_4)_2Sn$ the addition of a benzene solution of $(C_5H_5)_2Sn$ to either Al_2Cl_6 or Al_2Br_6 in benzene yields the 1/1 complexes as white air-sensitive solids (eq. 1). Reaction with Al_2Cl_6 is heterogeneous and slower than the immediate reaction observed with Al_2Br_6. The similar reactions of $(C_5H_5)_2Sn$ and $(MeC_5H_4)_2Sn$ with BCl_3

$$2(C_5H_5)_2Sn + Al_2X_6 \xrightarrow{C_6H_6} 2(C_5H_5)_2Sn:AlX_3 \tag{1}$$

X = Cl, Br

$$R_2Sn + BX_3 \rightarrow SnX_2 + (R_2BX) \tag{2}$$

R = C_5H_5, MeC_5H_4 ; X = Cl, Br

or BBr_3 in benzene, despite stringent purification of the boron trihalides, gave the corresponding tin(II) halide as the only isolated product, presumably as a result of facile ligand exchange (eq. 2). Reaction of freshly prepared and re-crystallised BI_3 with $(C_5H_5)_2Sn$ in benzene gave the immediate formation of an amorphous yellow solid, which analysed as the complex $(C_5H_5)_2Sn:BI_3$. However the tin-119m Mössbauer spectrum of the solid showed a single line with a higher isomer shift than the other complexes, and the infrared spectrum was not comparable with those of the other Group III complexes. It would appear therefore that in this case both exchange and complexation occur giving the complex $I_2Sn:B(C_5H_5)_2I$. The BBr_3 complex of $(C_5H_5)_2Sn$ could be obtained via the boron tribromide etherate formed in situ prior to the addition of the stannocene (eq. 3). The attempted preparation of the BCl_3 complex by the same route

$$(C_5H_5)_2Sn + BBr_3 \cdot O(C_2H_5)_2 \rightarrow (C_5H_5)_2Sn:BBr_3 + (C_2H_5)_2O \tag{3}$$
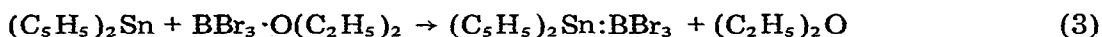
again resulted in ligand exchange and the formation of tin(II) chloride, although we have previously obtained $(C_5H_5)_2Sn:BF_3$ from $BF_3 \cdot O(C_2H_5)_2$ [4].

The tin-119m Mössbauer spectra of the Group III metal trihalide complexes all consist of broad single resonances in the range 3.71—3.83 mm s^{-1} (Table 1), with the exception of the product from the BI_3 reaction. These values are very similar to the isomer shift values of the free stannocenes, $(C_5H_5)_2Sn$ (3.74 mm s^{-1}) [7] and $(MeC_5H_4)_2Sn$ (3.83 mm s^{-1}) [8], confirming the divalent nature of the tin in these complexes, and excluding the possibility of insertion of the stannylene into the Group III metal—halogen bond to form a tetravalent tin derivative. The rather large line-widths (Γ = 1.24—2.08 mm s^{-1}) suggest the presence of unresolved quadrupole splittings (cf. the resolved splitting of 0.90 mm s^{-1} observed for $(C_5H_5)_2Sn:BF_3$ [4]) and the similarities of the spectra with those of the parent stannocenes indicates negligible change in the electronic environment of the tin and suggesting the retention of the hybridisation state at the tin on complexation.

The infrared spectra of the complexes $(C_5H_5)_2Sn:AlX_3$ (X = Cl, Br) and $(C_5H_5)_2Sn:BBr_3$ are given in Table 2, and as can be seen from these have many similarities with the spectrum of $(C_5H_5)_2Sn$ itself in the range 3500—700 cm^{-1} [8]. The ring modes of the complexes are in the majority of cases very similar

TABLE 1

THE MÖSSBAUER PARAMETERS FOR THE GROUP III TRIHALIDE COMPLEXES OF $(C_5H_5)_2$Sn AND $(MeC_5H_4)_2$Sn AND RELATED COMPOUNDS (mm s^{-1})

Compound	I.S.	Q.S.	Γ_1	Γ_2
$(MeC_5H_4)_2$Sn [a]	3.83	0.78	—	—
$(MeC_5H_4)_2$Sn:$AlCl_3$ [b]	3.71	—	1.50	—
$(C_5H_5)_2$Sn [c]	3.74	0.86	—	—
$(C_5H_5)_2$Sn:$AlCl_3$ [b]	3.71	—	1.46	—
$(C_5H_5)_2$Sn:$AlBr_3$ [b]	3.83	—	1.24	—
$(C_5H_5)_2$Sn:BBr_3 [b]	3.77	—	2.08	—
$(C_5H_5)_2$Sn:BF_3 [c]	3.79	0.90	—	—
I_2Sn:$B(C_5H_5)_2I$ [b]	4.03	—	0.85	—
C_5H_5SnCl [b]	3.71	1.04	0.99	0.76
C_5H_5SnAlCl$_4$ [b]	3.73	—	1.19	—
C_5H_5SnAlBr$_4 \cdot \frac{1}{2}C_6H_6$ [b]	3.75	—	0.91	—
SnCl$_2$ [d]	4.07	—	—	—
SnBr$_2$ [d]	3.93	—	—	—
SnI$_2$ [d]	3.85	—	—	—
(C_6H_6)Sn$(AlCl_4)_2 \cdot C_6H_6$ [e]	3.42	—	—	—

[a] Ref. 8. [b] This work. [c] Ref. 4. [d] Ref. 21. [e] Ref. 14.

indicating "local" C_{5v} symmetry for the cyclopentadienyl rings, however the two C—H deformation modes ν_2 and ν_7 are raised in energy by 20—30 cm^{-1} on complexation. On the basis of C_{3v} "local" symmetry, two Al—X stretching $(A_1 + E)$ and two XAlX deformation $(A_1 + E)$ modes are expected for a pyramidal AlX$_3$ residue from group-theoretical predictions. In the complex $(C_5H_5)_2$Sn:$AlCl_3$, the two Al—Cl stretching modes are found at 485 (E) and 428 (A_1) cm^{-1}, and the two ClAlCl deformation modes at 294 (A_1) and 274 (E) cm^{-1}, although the latter absorption may correspond to the antisymmetric tin—ring stretch which is found at 240 cm^{-1} in $(C_5H_5)_2$Sn and 237 cm^{-1} in $(MeC_5H_4)_2$Sn [8]. These vibrations are similar to those found in the complexes Me$_3$N:AlCl$_3$ [9], ν(Al—Cl)(E) 545, ν(Al—Cl)(A_1) 416 and δ(Al—Cl)(A_1) 313 cm^{-1}, and $(MeC_5H_4)_2$Sn:$AlCl_3$ [5], ν(Al—Cl)(E) 493, ν(Al—Cl)(A_1) 442 and δ(Al—Cl)(A_1) 327 cm^{-1}. The Al—Br stretching frequencies for the complex $(C_5H_5)_2$Sn:$AlBr_3$ are assigned to bands at 391 (E) and 331 (A_1) cm^{-1} in comparison to the Me$_3$N:AlBr$_3$ [9], ν(Al—Br)(E) 450, ν(Al—Br)(A_1) 375 and δ(Al—Br)(A_1) 227 cm^{-1}. The spectra of both aluminium trihalide complexes exhibit additional bands in the region 600—700 cm^{-1}, which cannot be assigned as either ring or skeletal fundamentals although similar bands were observed in the spectrum of $(MeC_5H_4)_2$Sn:$AlCl_3$ which were attributed to interactions between the C—H(out-of-plane) bending motions of the ring and the AlCl$_3$ residue [5]. Assignments of the amine adducts of boron tribromide [10] place the stretching modes for the pyramidal BBr$_3$ unit within the ranges δ(B—Br)(A_1) 275—267 cm^{-1} and ν(B—Br)(E) 709—674 cm^{-1} with the two deformation modes occurring below the limits of the present study. Thus, in the spectrum of $(C_5H_5)_2$Sn:BBr_3, the δ(B—Br)(A_1) mode is assigned to the band at 289 cm^{-1} whilst the (E) stretching mode probably coincides with the out-of-plane bending vibration ν_2 at 763 cm^{-1}.

Both the Mössbauer and infrared data for the Group III trihalide complexes

are consistent with the formation of a Lewis base—Lewis acid complex with a structure retaining the geometry of the $(C_5H_5)_2Sn$ residue whilst forming a σ donor tin—metal bond(I).
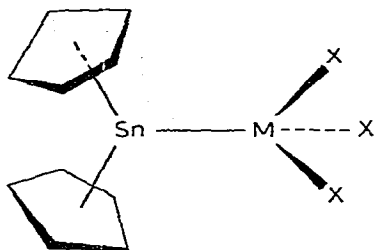

(I)

On mixing THF solutions of $(C_5H_5)_2Sn$ and $SnCl_2$, rapid and facile ligand exchange takes place yielding cyclopentadienyltin chloride in high yield as a creamy white crystalline solid [11]. The infrared spectrum of the solid in the range 3500—250 cm^{-1} is listed in Table 3. Again the spectrum can be assigned in terms of "local" C_{5v} geometry for the cyclopentadienyl ring. Neither of the two expected C—H stretching modes could be observed. The bands observed at 282 and 269 cm^{-1} are assigned as the Sn—Cl stretching and antisymmetric metal—ring stretching vibrations, respectively, although some degree of mixing of these modes is to be expected. The crystal structure of C_5H_5SnCl, however, shows that, although the cyclopentadienyl ring is planar and regular, it is tilted with respect to the tin such that two carbon atoms are closer to the tin than the others [3]. It would appear, therefore, that the infrared spectra are rather insensitive to the exact orientation of the rings with respect to the metal (cf. the spectral changes between η^5 and η^1 cyclopentadienylmetal complexes [12]).

Cyclopentadienyltin chloride also forms a 1 : 1 complex with aluminium chloride, for which several structures are possible. The compound, which is a white crystalline air-sensitive solid, may have a similar structure to those proposed for the similar $(C_5H_5)_2Sn$ derivatives, i.e. with a dative tin aluminium σ-bond (IV). Alternatively, structures involving $AlCl_4$ units either as discrete ionic species (V) or covalently bonded to the tin by a chlorine bridge (VI) may occur.
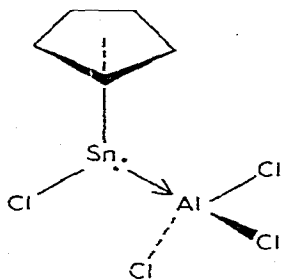
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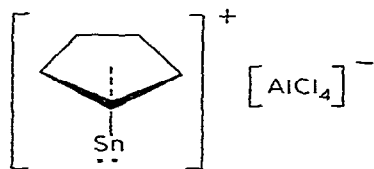
(V)
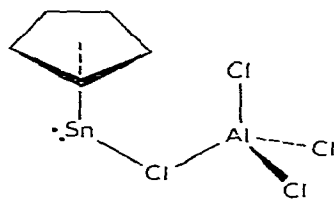
(VI)

TABLE 2

THE INFRARED SPECTRA OF THE GROUP III TRIHALIDE COMPLEXES OF $(C_5H_5)_2Sn$ IN THE SOLID STATE [a]

$(C_5H_5)_2Sn$ [b]	$(C_5H_5)_2-$ SnAlCl$_3$	$(C_5H_5)_2-$ SnAlBr$_3$	$(C_5H_5)_2-$ SnBBr$_3$	Assignment [c]
3105 vvw	3103 vw	3112 w	—	ν_1(C—H) stretch (A_1)
3080 vvw	3051 vw	3060 vw	—	ν_5, ν_9(C—H) stretches (E_1, E_2)
2260 vvw	2264 vvw	—	—	Combin. band ($\nu_4 + \nu_6$)
1745 vvw				
1640 vw	1632 vw	1619 vw	1641 vvw	Combin. band ($\nu_{14} + \nu_3$)
	1478 w		1548 vvw	ν_{12}(C—C) stretch (E_2)?
1429 m	1423 mw	1424 ms	1427 s	ν_8(C—C) stretch (E_1)
1382 vw		1404 mw		
1369 vw	1367 w	1369 vw (sh)		
	1262 vvw	1265 vvw		ν_4(C—H) bend i.p. (A_2)
1170 vvw	1170 vvw	1169 vvw		ν_{10}(C—H) bend i.p. (E_2)
	1151 vvw	1156 vvw	1157 vvw	
1116 mw	1110 m	1111 m	1112 s	ν_3 Ring breathing (A_1)
1064 vw	1060 vw	1072 w	1065 w	ν_{11}(C—H) bend o.p. (E_2)
	1035 vw	1060 vw		
1005 s	1006 m	1004 ms	1002 vs	ν_6(C—H) bend i.p. (E_1)
		978 m		
	962 vvw	960 vvw		
	916 vw	916 vvw		
893 vvw	892 mw	896 vw (sh)	892 vw (sh)	ν_{13}(C—C) bend i.p. (E_2)
		891 w	872	
838 vw		838 ms (sh)		
790 vvs	809 ms	813 vvs	801 vvs	ν_7(C—H) bend o.p. (E_1)
757 vvs (br)	783 ms	782 vvs	763 vvs	ν_2(C—H) bend o.p. (A_1)
		753 m (sh)		
		737 w (sh)		
	722 w (br)	723 w (sh)		
	674 mw	674 mw		
664 vw	663 mw	663 ms		Combin. band ($\nu_8-\nu_2$)
		654 ms		
	564 w			ν_{14}(C—C) bend ?
		489 w	487 vw	
	485 s (br)			ν(Al—Cl) stretch (E)
	428 m (sh)			ν(Al—Cl) stretch (A_1)
		430 ms (sh)		
		415 s (sh)		
		391 vvs		ν(Al—Br) stretch (E)
	349 vvw			
		333 m		ν(Al—Br) stretch (A_1)
	294 vs (sh)			δ(Al—Cl) deform. (A_2)
			289 vs	ν(B—Br) stretch (A_1)
	274 w (br)			δ(Al—Cl) deform. (E)
240 s				Asymm. metal—ring stretch

[a] Spectra recorded as nujol and halocarbon mulls, and listed as cm^{-1}. [b] Data quoted in Ref. 8. [c] Ring modes labelled in terms of 14 fundamental vibrations predicted by group theory for C_{5v} "local" symmetry for a more detailed treatise, see Ref. 8.

The solid-state infrared spectrum (Table 3) of the adduct exhibits bands similar to the cyclopentadienyl ring modes of C_5H_5SnCl and $(C_5H_5)_2Sn$, and is therefore consistent with the retention of a *pentahapto*-C_5 ring on complexation; however the two out-of-plane C—H deformation modes (ν_7 and ν_2) are increased in energy significantly from C_5H_5SnCl. Unlike the aluminium trihalide

TABLE 3

THE INFRARED SPECTRA OF CYCLOPENTADIENYLTIN(II) CHLORIDE AND ITS ALUMINIUM TRICHLORIDE COMPLEX IN THE SOLID STATE [a]

$(C_5H_5)SnCl$	$(C_5H_5)SnClAlCl_3$	Assignment
	3108 m	$\nu_1(C-H)$ stretch (A_1)
1783 vvw (br)	1809 vvw (br)	
1752 vvw (br)	1724 vvw (br)	
1664 vvw (br)		
1633 vvw (br)	1630 vw (sh)	
1544 vvw (br)	1512 vw (sh)	$\nu_{12}(C-C)$ stretch (E_2)?
	1494 mw	
1437 vvw (sh)		
1428 mw	1427 s	$\nu_8(C-C)$ stretch (E_1)
1424 w	1422 ms (sh)	
1364 vw (br)		
	1308 vvw (br)	
1259 vvw	1272 vw	$\nu_4(C-H)$ bend i.p. (A_2)
1169 vvw (br)	1172 vvw (br)	$\nu_{10}(C-H)$ bend i.p. (E_2)
1151 vvw (br)	1151 vvw (br)	
1113 ms	1113 s	ν_3 Ring breathing (A_1)
1106 w (sh)	1107 vw (sh)	
1067 w		$\nu_{11}(C-H)$ bend o.p. (E_2)
	1034 vvw (sh)	
1003 vs	1010 s	$\nu_6(C-H)$ bend i.p. (E_1)
962 vw (sh)		
938 vvw		
915 vvw	922 vvw (br)	
891 vw		$\nu_{13}(C-C)$ bend i.p. (E_2)
861 vw (sh)		
791 vvw	828 vvs (sh)	$\nu_7(C-H)$ bend o.p. (E_1)
760 vvs	819 vvs	$\nu_2(C-H)$ bend o.p. (A_1)
	723 w	
	700 ms	
	696 ms	
	692 ms	
	678	
663 w		Combin. band $(\nu_8-\nu_2)$
578 vw	572 vw	
537 vw (br)		$\nu_{14}(C-C)$ bend ?
	496 vvs	$\nu(Al-Cl)$ stretch (E)
414 vvw		
	391 vvw (br)	
	350 vvw (br)	
	293 ms	$\delta(Al-Cl)$ deform. $(A_1 + E)$
282 mw (sh)	287 ms (sh)	Metal—chlorine stretch
269 m	255 w	Asymm. metal—ring stretch

[a] Spectra recorded as nujol and halocarbon mulls, and listed in cm^{-1}.

complexes of the stannocenes which exhibit two Al—X stretching modes, $C_5H_5SnCl \cdot AlCl_3$ exhibits a single band at 496 cm^{-1} in the Al—Cl stretching region and additional bands at ca. 290 cm^{-1}. The single Al—Cl stretching frequency is compatible with the existence of tetrahedral $AlCl_4$ moieties, which generally give rise to a single stretching frequency at ca. 495 cm^{-1} [13]. A solid state structure involving isolated $[(C_5H_5)Sn]^+$ cations such as in structure V is unlikely since the electron density at the tin would be expected to be very high giving a correspondingly very high Mössbauer isomer shift. However, the isomer

shift value of the complex (3.75 mm s^{-1}) is similar to that of C$_5$H$_5$SnCl (3.71 mm s^{-1}). The structure VI involving a tin—chlorine—aluminium bridge does however fit the available data, although it is possible that the AlCl$_4$ units bridge adjacent tin atoms as they do in the arene complexes (C$_6$H$_6$)Sn(AlCl$_4$)$_2$ · C$_6$H$_6$ [14] and [ArSnCl(AlCl$_4$)]$_2$ (Ar = C$_6$H$_6$, MeC$_6$H$_4$Me-p) [15].

On reaction of anhydrous tin(IV) bromide and (MeC$_5$H$_4$)$_2$Sn in a 1 : 1 molar ratio in benzene, tin(II) bromide and a waxy solid of composition SnBr$_4$ · 2(MeC$_5$H$_4$)$_2$Sn were obtained. The Mössbauer spectrum of the latter solid consisted of three resonances, a singlet at 4.00 mm s^{-1}, and a doublet in the tetravalent tin region with isomer shift 1.51 mm s^{-1} and quadrupole splitting 1.82 mm s^{-1}, the two signals being in an approximately 1 : 1 ratio. The high value of the tin(II) resonance serves to exclude a stannocene complex, and the material appears to be a mixture of tin(II) bromide (*I.S.* 3.93 mm s^{-1}) and (MeC$_5$H$_4$)$_2$-SnBr$_2$ (cf. (C$_5$H$_5$)$_2$SnCl$_2$: *I.S.* 1.51, *Q.S.* 1.83 mm s^{-1}) [16], resulting from ligand exchange.

The addition of an ether solution of anhydrous iron(III) chloride to a similar solution of dicyclopentadienyltin in the molar ratio 1 : 3 leads to a rapid ligand exchange and redox to yield three products, ferrocene, tin(II) chloride and dicyclopentadienyltin(IV) dichloride (eq. 4). The two tin products coprecipitate as a creamy white powder, which exhibits a Mössbauer spectrum com-

$$Fe_2Cl_6 + 3(C_5H_5)_2Sn \rightarrow 2\,SnCl_2 + (C_5H_5)_2SnCl_2 + 2(C_5H_5)_2Fe \qquad (4)$$

patible with a mixture of products, with a tin(II) singlet (*I.S.* 3.97 mm s^{-1}) and a tin(IV) doublet (approximate parameters: *I.S.* 1.6, *Q.S.* 2.0 mm s^{-1}). Reaction of Fe$_2$Cl$_6$ and (C$_5$H$_5$)$_2$Sn in a 1:2 molar ratio in ether leads to the formation of a grey powder, which has a tin-119m Mössbauer spectrum similar to that of the white solid obtained above; however it also contains iron (iron-57 Mössbauer). Ferrocene is again a product of the reaction. Repetition of the reaction in THF gave on concentration a white crystalline solid which exhibited both an iron and tin Mössbauer resonances, although when removed from solution the solid rapidly powdered and became a grey colour. No identification was therefore possible.

We reported previously that both (C$_5$H$_5$)$_2$Sn and (MeC$_5$H$_4$)$_2$Sn take part in a pseudo-carbenoid insertion into the magnesium—carbon bond of phenylmagnesium bromide forming the tetravalent tin species R$_2$PhSnMgBr (R = C$_5$H$_5$, MeC$_5$H$_4$) rather than the formation of a complex [17]. With cyclohexylmagnesium bromide in ether, (C$_5$H$_5$)$_2$Sn reacts rapidly at ambient temperatures to deposit colourless crystals which were shown to contain no tin (Mössbauer spectrum), and were identified by microanalysis and ^{1}H NMR as the Grignard reagent etherate, (C$_5$H$_5$)MgBr · O(C$_2$H$_5$)$_2$, illustrating that a facile redistribution of organic groups between the magnesium and tin centres occurs in this case. The tin-containing residue of the reaction remained in solution and could not be identified, although its tetravalent nature was demonstrated from a Mössbauer spectrum of the solution.

The reactions of alkyl halides with (C$_5$H$_5$)$_2$Sn have been examined by Noltes [18], and reactions with a 1 : 1 stoichiometry eventually yield tin(IV) species by carbenoid insertion of the stannylene into the carbon—halogen bond, but the presence of other tin(II) intermediates indicates that the mechanism is more complex than is initially obvious. The reaction is reported to proceed read-

ily for methyl iodide, allyl bromide and benzyl bromide. Contrary to expectation, cyclohexyl bromide and $(C_5H_5)_2Sn$ did not react even in boiling benzene. The addition of allyl bromide or chloride to the freshly prepared complexes $(C_5H_5)_2Sn:AlX_3$ (where X = Br or Cl, respectively) under benzene resulted in the rapid dissolution of the insoluble complexes to form two layer systems, which within minutes crystallised to form white solids. The infrared spectrum of the oxygen- and moisture-sensitive solid from the reaction of allyl chloride and $(C_5H_5)_2Sn:AlCl_3$ is identical to that of the complex $C_5H_5SnCl \cdot AlCl_3$ obtained from C_5H_5SnCl and $AlCl_3$, and thus indicates the presence of *pentahapto*-cyclopentadienyl rings and (approximately) tetrahedral $AlCl_4$ units. The infrared spectrum of the solid product from the reaction of $(C_5H_5)_2Sn:AlBr_3$ and allyl bromide contains features characteristic of *pentahapto* rings and also a strong band at 397 cm^{-1} assigned to a $AlBr_4$ moiety (cf. $NMe_4^+AlBr_4^-$ which exhibits bands at 405 and 118 cm^{-1} in the infrared) [13]. Microanalysis and additional features in the infrared spectrum indicate the presence of molecular benzene in the bromide complex, which has the composition $(C_5H_5)Sn \cdot AlBr_4 \cdot \frac{1}{2}C_6H_6$. Lattice molecular benzene also occurs in the arene complex (C_6H_6)-$Sn(AlCl_4)_2 \cdot C_6H_6$ in addition to coordinated benzene and bridging $AlCl_4$ units which render the structure polymeric [14]. The mass spectra of the two products $(C_5H_5)SnClAlCl_3$ and $(C_5H_5)SnBrAlBr_3 \cdot \frac{1}{2}C_6H_6$ are complex containing multiple tin-containing fragments, indicating that these compounds are also polymeric with structures similar to the arene complexes reported by Amma [14,15]. Mixing cyclohexyl or isopropyl bromide with $(C_5H_5)_2Sn:AlBr_3$ in benzene failed to produce any reaction even after 5 days at ambient temperature; however, cyclohexyl bromide reacts readily in boiling benzene to yield the solvated complex $(C_5H_5)SnBrAlBr_3 \cdot \frac{1}{2}C_6H_6$. The complex $(C_5H_5)SnClAlCl_3$ is also rapidly formed on addition of a benzene solution of Me_3SiCl to $(C_5H_5)_2Sn:AlCl_3$, although the infrared spectrum showed slight contamination of the product by some trimethylsilyl species. Concentration in vacuo of the reaction medium after removal of the complex yielded a green oil which solidified slowly over several days and could not be identified. The most likely second product of the reaction, $Me_3SiC_5H_5$, is however, known to be unstable and readily decomposes via polymerisation processes.

Experimental

All manipulations were performed under dry nitrogen or argon. Dicyclopentadienyltin and bis(methylcyclopentadienyl)tin were prepared from tin(II) chloride and lithium cyclopentadienide in THF. Boron and aluminium trihalides were distilled or sublimed at least twice immediately prior to use. Iron(III) chloride was dried using thionyl chloride. All solvents were dried and freed from dissolved oxygen by standard methods also immediately before use.

Infrared spectra were recorded using Perkin—Elmer 457 and 521 instruments. NMR spectra were recorded using a Varian HA-100 spectrometer with TMS as an internal standard and lock signal. Mossbauer spectra were recorded at 77 K using a Harwell instrument equipped with a 256 multichannel analyser. ^{57}Fe and ^{119}Sn spectra were obtained against ^{57}Co/Pd and $Ba^{119m}SnO_3$ sources, respectively. ^{57}Fe isomer shifts are quoted with respect to iron metal and ^{119}Sn shifts

with respect to SnO_2. Data reduction to Lorentzian line shapes was effected by usual least-squares methods. Maximum estimated standard deviations are ±0.05 (*I.S.*) and ±0.10 mm s⁻¹ (*Q.S.*).

(a) Reaction of dicyclopentadienyltin with aluminium tribromide dimer

Al_2Br_3 (0.707 g, 1.33 mmol) in benzene (10 ml) was treated dropwise with a benzene solution (6 ml) of $(C_5H_5)_2Sn$ (0.660 g, 2.65 mmol) with the immediate formation of a white solid, which was filtered off and dried in vacuo to give dicyclopentadienyltin—aluminium tribromide (1.11 g, 81%) as an air- and moisture-sensitive white solid. Found: C, 23.07; H, 1.91. $C_{10}H_{10}Br_3AlSn$ calcd.: C, 23.30; H, 1.96%.

(b) Reaction of dicyclopentadienyltin with aluminium trichloride dimer

$(C_5H_5)_2Sn$ (0.689 g, 2.77 mmol) and Al_2Cl_6 (0.370 g, 1.39 mmol) were brought into reaction in benzene as in (a) to give dicyclopentadienyltin—aluminium trichloride as a white solid. Found: C, 31.74; H, 2.73. $C_{10}H_{10}Cl_3AlSn$ calcd.: C, 31.24; H, 2.64%.

(c) Reaction of bis(methylcyclopentadienyl)tin with aluminium trichloride dimer

$(MeC_5H_4)_2Sn$ (3.74 g, 13.5 mmol) and Al_2Cl_6 (1.80 g, 6.75 mmol) were mixed in benzene (16 ml) whereupon the insoluble chloride dissolved and a two-layer system formed. The heavy layer was removed to another vessel, and excess solvent removed in vacuo to yield bis(methylcyclopentadienyl)tin—aluminium trichloride as a viscous golden brown oil. Found: C, 34.7; H, 3.5. $C_{12}H_{14}Cl_3AlSn$ calcd.: C, 35.1; H, 3.4%.

(d) Reaction of boron tribromide with dicyclopentadienyltin

$(C_5H_5)_2Sn$ (1.26 g, 5.06 mmol) in benzene (10 ml) was added dropwise with stirring to a benzene solution of BBr_3 (1.42 g, 5.67 mmol) with the immediate formation of a white precipitate identified as tin(II) bromide from its Mössbauer spectrum (*I.S.* 4.03, *Q.S.* 0, Γ 1.21 mm s⁻¹).

(e) Reaction of boron tribromide with bis(methylcyclopentadienyl)tin

$(MeC_5H_4)_2Sn$ (2.01 g, 7.26 mmol) and BBr_3 (1.82 g, 7.26 mmol) were brought into reaction as in (d) to yield tin(II) bromide (*I.S.* 4.03, *Q.S.* 0, Γ 1.45 mm s⁻¹).

(f) Reaction of boron trichloride with bis(methylcyclopentadienyl)tin

$(MeC_5H_4)_2Sn$ (2.29 g, 8.27 mmol) and BCl_3 (0.97 g, 8.27 mmol) were brought into reaction as in (d) to yield tin(II) chloride (*I.S.* 4.15, *Q.S.* 0, Γ 1.45 mm s⁻¹) as the only identified product.

(g) Reaction of boron tribromide etherate with dicyclopentadienyltin

$(C_5H_5)_2Sn$ (1.17 g, 4.70 mmol) in benzene (10 ml) was added dropwise with stirring to a solution of boron tribromide (1.22 g, 4.87 mmol) in ether (15 ml) with the formation of a creamy white solid, which was filtered off and dried in vacuo to give dicyclopentadienyltin—boron tribromide. Found: C, 23.76; H, 2.03. $C_{10}H_{10}Br_3BSn$ calcd.: C, 24.05; H, 2.02%.

(h) Reaction of boron trichloride etherate with dicyclopentadienyltin

$(C_5H_5)_2Sn$ (1.49 g, 5.99 mmol) and BCl_3 (0.702 g, 5.99 mmol) were brought into reaction as in (g) to yield tin(II) chloride (*I.S.* 4.16, *Q.S.* 0, Γ 1.52 mm s^{-1}).

(i) Reaction of boron triiodide with dicyclopentadienyltin

BI_3 (2.94 g, 7.51 mmol) (prepared from the reaction of lithium iodide and boron tribromide at $120°C$ and the crude BI_3 recrystallised from benzene in the presence of mercury metal [19]) and $(C_5H_5)_2Sn$ (1.87 g, 7.51 mmol) were brought into reaction as described in (d) to yield a brown solid. Found: C, 17.79; H, 1.40. $C_{10}H_{10}BI_3Sn$ calcd.: C, 18.76; H, 1.57%.

(j) Reaction of aluminium trichloride dimer with cyclopentadienyltin chloride

A slurry of C_5H_5SnCl (1.07 g, 4.88 mmol) (prepared from mixing $SnCl_2$ and $(C_5H_5)_2Sn$ in THF as described by Noltes [18]) in benzene (12 ml) was added with stirring to Al_2Cl_6 (0.651 g, 2.44 mmol) under benzene (30 ml), whereupon both reactants dissolved to form a two-layer system. The layers were separated, and the heavier component dried in vacuo to yield a solid which was washed further with pentane to give cyclopentadienyltin tetrachloraluminate (0.61 g, 36%) as a pale brown solid. Found: C, 16.26; H, 1.64. $C_5H_5Cl_4AlSn$ calcd.: C, 17.03; H, 1.43%.

(k) Reaction of tin(IV) bromide with bis(methylcyclopentadienyl)tin

$(MeC_5H_4)_2Sn$ (1.48 g, 5.34 mmol) in benzene (4 ml) was added dropwise with stirring to a benzene solution (40 ml) of $SnBr_4$ (2.34 g, 5.34 mmol) with the immediate formation of a white solid, which contained a negligible amount of carbon and hydrogen, and was identified as tin(II) bromide by its Mössbauer spectrum (*I.S.* 4.05 mm s^{-1}, *Q.S.* 0). Evaporation of the filtrate in vacuo afforded a brown oil, which solidified within a few days to a waxy solid. Found: C, 27.29; H, 3.11%. Mössbauer parameters: two tin environments. *I.S.*(1) = 4.00 *Q.S.*(1) = 0, Γ(1) 1.39 mm s^{-1} and *I.S.*(2) 1.51, *Q.S.*(2) 1.82, Γ_1(2) 1.06, Γ_2(2) 1.06 mm s^{-1}.

(l) Reaction of iron(III) chloride dimer with dicyclopentadienyltin

(i) 1 : 2 reaction in ether. Fe_2Cl_6 (1.72 g, 5.30 mmol) in ether (40 ml) was added rapidly to an ether solution (30 ml) of $(C_5H_5)_2Sn$ (2.64 g, 10.60 mmol) with the immediate formation of a blue-grey solid, which was filtered off, washed with ether and dried in vacuo. Found: C, 24.61; H, 3.73. Mössbauer parameters: ^{57}Fe: *I.S.* 1.07, *Q.S.* 1.77, Γ_1 0.96, 1.00 mm s^{-1}; ^{119}Sn: *I.S.*(1) 4.14, *Q.S.*(1) 0, Γ_1 1.48 mm s^{-1}, *I.S.*(2) ca. 1.6, *Q.S.* ca. 2.0 mm s^{-1}. The solid rapidly hydrolysed on exposure to the atmosphere. The products were not investigated further.

(ii) 1 : 2 reaction in THF. Fe_2Cl_6 (1.32 g, 4.07 mmol) in THF (15 ml) was added dropwise with stirring to a THF solution (20 ml) of $(C_5H_5)_2Sn$ (2.21 g, 8.88 mmol), whereupon the iron(III) chloride solution was immediately decolourised to give an orange-brown solution in an exothermic reaction. Addition of pentane and subsequent refrigeration produced creamy white crystals which were filtered off, but began to disintegrate on removal of the solvent. Mössbauer parameters: ^{119}Sn: *I.S.* 4.14, *Q.S.* 0 mm s^{-1}. Other products were not identified.

(iii) 1 : 3 reaction in ether. Fe_2Cl_6 (0.376 g, 0.72 mmol) in ether was added

dropwise to an ether solution of $(C_5H_5)_2Sn$ (0.88 g, 1.77 mmol) with the formation of a blue-grey solid which on shaking disappeared leaving a white solid under an orange solution. The white solid was filtered off and washed several times with ether and dried in vacuo. The Mössbauer spectrum of the white solid gave no [57]Fe signal, but indicated two tin environments: $I.S.(1)$ ca. 3.97, $Q.S.(1)$ 0, $I.S.(2)$ ca. 1.6, $Q.S.(2)$ ca. 2.0 mm s^{-1}. Evaporation of the filtrate gave an orange solid, which was recrystallised from pentane to give ferrocene. Found: C, 64.36; H, 5.13. $C_{10}H_{10}Fe$ calcd.: C, 64.56; H, 5.42%. $I.S.$ 0.53; $Q.S.$ 2.42 mm s^{-1} (lit. [20]: $I.S.$ 0.53; $Q.S.$ 2.37 mm s^{-1}).

(m) Reaction of cyclohexylmagnesium bromide with dicyclopentadienyltin

Freshly distilled $C_6H_{11}Br$ (1.35 g, 8.28 mmol) in ether (10 ml) was added dropwise and slowly to iodine-activated magnesium (0.222 g, 9.11 mmol) in dry ether (30 ml) and the reaction mixture was refluxed for two hours after the initial reaction had subsided. The reaction mixture was filtered and added dropwise to a solution of $(C_5H_5)_2Sn$ (1.65 g, 6.63 mmol) in ether (10 ml), whereupon the reaction mixture became orange-brown, and colourless crystals formed. These crystals, which gave no Mössbauer resonance, and readily powdered on removal from the reaction solution, were identified as cyclopentadienylmagnesium bromide etherate. Found: C, 44.77; H, 6.99%. $C_9H_{15}BrMgO$ calcd.: C, 44.40; H, 6.21%. ^1H NMR (degassed $CDCl_3$): δ_1 5.85, δ_2 (quartet) 3.53, δ_3 (triplet) 1.00, J ca. 7 Hz.

(n) Reaction of allyl bromide with $(C_5H_5)_2Sn:AlBr_3$

Allyl bromide (0.805 g, 6.65 mmol) (freshly distilled under nitrogen) in benzene (4 ml) was added dropwise to freshly prepared $(C_5H_5)_2Sn:AlBr_3$ (3.43 g, 6.65 mmol) under benzene (12 ml) with stirring, whereupon the complex dissolved to form a two-layer system which solidified within a few minutes forming a white solid. This was filtered off, washed with benzene, and dried in vacuo to give cyclopentadienyltin tetrabromoaluminate hemi(benzene) (2.92 g, 77%). Found: C, 16.92; H, 1.50%. $C_8H_8Br_4AlSn$ calcd.: C, 16.87; H, 1.42%.

(o) Reaction of allyl chloride with $(C_5H_5)_2Sn:AlCl_3$

Allyl chloride (0.19 g, 2.48 mmol) and $(C_5H_5)_2Sn:AlCl_3$ (0.937 g, 2.45 mmol) were brought into reaction as in (n) to give cyclopentadienyltin tetrachloraluminate (0.59 g, 68%) as a white crystalline solid. Found: C, 17.87; H, 1.84%. $C_5H_5AlCl_4Sn$ calcd.: C, 17.03; H, 1.43%.

(p) Reaction of cyclohexyl bromide with $(C_5H_5)_2Sn:AlBr_3$

Freshly distilled cyclohexyl bromide (0.784 g, 4.81 mmol) in benzene (6 ml) was added to $(C_5H_5)_2Sn:AlBr_3$ (2.48 g, 4.81 mmol) in benzene (15 ml) with no apparent initial reaction. The reaction mixture was refluxed for 1 h, whereupon a two-layer system formed, and on cooling a white solid crystallised out. The solid was filtered off and dried in vacuo to give cyclopentadienyltin tetrabromoaluminate hemi(benzene) (2.29 g, 84%). Found: C, 16.69; H, 1.63%. $C_8H_8AlBr_4Sn$ calcd.: C, 16.87; H, 1.42%.

(q) Reaction of allyl bromide with $(C_5H_5)_2Sn:AlBr_3$ in a 1 : 3 ratio

Allyl bromide (0.07 g, 0.58 mmol) in benzene (6 ml) was added to $(C_5H_5)_2$-Sn:AlBr$_3$ (0.89 g, 1.73 mmol) in benzene with no apparent sign of reaction. This mixture was stirred for 48 h, after which the solid was filtered off, washed with benzene and dried in vacuo to give the starting material $(C_5H_5)_2Sn:AlBr_3$. Found: C, 23.21; H, 2.16. $C_{10}H_{10}AlBr_3Sn$ calcd.: C, 23.30; H, 1.96%. On concentration of the reaction filtrate, colourless platelets crystallised out, which were filtered off and dried to afford cyclopentadienyltin tetrabromoaluminate hemi(benzene). Found: C, 16.22; H, 1.53. $C_8H_8AlBr_4Sn$ calcd.: C, 16.87; H, 1.42%.

(r) Reaction of trimethylchlorosilane with $(C_5H_5)_2Sn:AlCl_3$

Trimethylchlorosilane (0.690 g, 6.35 mmol) in benzene (4 ml) was added dropwise to $(C_5H_5)_2Sn:AlCl_3$ (2.43 g, 6.36 mmol) in benzene (23 ml) dissolving the complex to form a two-layer system, which was filtered. Addition of pentane to the two layers precipitated a white solid, which was filtered off, washed and dried in vacuo to give cyclopentadienyltin tetrachloraluminate (1.86 g, 83%). Found: C, 17.53; H, 1.99. $C_5H_5AlCl_4Sn$ calcd.: C, 17.03; H, 1.43%.

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