PREPARATION, STRUCTURE AND REACTIVITY OF (η^6-1-TRIPHENYLSTANNYLBENZENE)(η^5-CYCLOPENTADIENYL)IRON(II) HEXAFLUOROPHOSPHATE

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Summary

A novel organotin compound containing a $C_5H_5Fe^+C_6H_5$ ligand has been synthesised. (η^6-Triphenylstannylbenzene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate was prepared by treating Ph_3SnLi with (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate in THF at room temperature. ^1H, ^{13}C and ^{119}Sn NMR shifts are reported. The ^{119}Sn shift of -132 ppm is very close to that of Ph_4Sn indicating that the $C_5H_5Fe^+C_6H_5$ ligand has only a small effect. ^{57}Fe and ^{119}Sn Mössbauer data are also given. The ^{57}Fe data show a reduced quadrupole splitting compared with the parent benzene complex, indicative of electron withdrawal by the Ph_3Sn moiety. The ^{119}Sn data are notable for the appearance of a small quadrupole splitting (0.49 mms^{-1}); this splitting is probably due to a combination of steric and polar effects.

The complex reacted with $HgCl_2$ in acetone to give PhHgCl. Quenching the residual filtrate in KI gave the new complex (η^6-diphenyliodostannylbenzene)(η^5-cyclopentadienyl)iron(II) tetraiodomercurate. Reaction with iodine also resulted in displacement of the non-complexed phenyl groups.

We describe the preparation and structure of a novel stannylated arene(cyclopentadienyl)iron(II) complex. During the last five years we have carried out systematic structural studies on ferrocene derivatives using ^{57}Fe Mössbauer spectroscopy in conjunction with ^1H and ^{13}C NMR spectroscopy [1]. As a result we have been able to correlate Mössbauer quadrupole splittings (QS) with the electronic properties of substituents on the ferrocene nucleus using both oxidation potentials and Hammett substituent constants [2]. Very recently we have been able to observe similar effects in η^6-benzene-η^5-cyclopentadienyliron(II) compounds [3], hereafter referred to as arene complexes. We have also recently reported on the effect of

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bulky ligands on Mössbauer parameters of some tetraorganotin derivatives [4]. In particular, tetraadamantyltin was shown to have a large QS of 2.7 mms^{-1}. This was the first example of a symmetrically substituted R_4Sn derivative showing quadrupole splitting.

These studies in tin and iron chemistry led us to prepare the title compound with the aim of creating a novel environment for the tin atom.

Results and discussion

Areneiron complexes of the type described above have long been known to possess useful properties [5]. Of particular relevance here is the relative ease with which aryl halide complexes undergo nucleophilic substitutions [6]. This is due to the strong activation by the Fe^+Cp moiety. We have used this property to synthesise the novel organotin derivative reported here *.
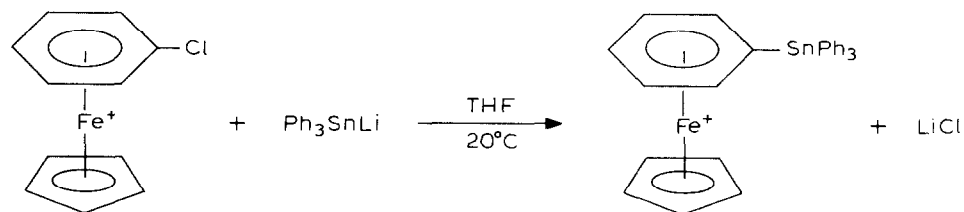
The reaction proceeded smoothly at room temperature to give a 46% yield of the stannylated arene complex. The ^1H, ^{13}C and ^{119}Sn NMR data appear in Table 1. The ^1H NMR spectrum shows the usual upfield shift for the complexed aromatic protons (~ 1.2 ppm) compared with that for uncomplexed arene protons and a corresponding downfield shift for the Cp protons relative to ferrocene [7] (~ 0.25 ppm). There are similar, though more marked changes in the ^{13}C NMR spectrum [8]. The individual assignment of the ^{13}C resonance of the complexed phenyl ring was accomplished using the reported additivity factors for the Ph_3Sn group [9] (modified to take account of complexation, see Experimental) in conjunction with the value of the shift for the parent benzene complex. The agreement is good for C(3) and C(4) but there are discrepancies for C(1) and, to a lesser extent, C(2) though not significant enough to invalidate the assignment of the latter. The assignments of the uncomplexed phenyl substituents were made by reference to values recently reported for Ph_4Sn [10]. Only the C(1') values differ, as is to be expected since these are closest to the perturbing influence of the $CpFe^+C_6H_5$ group, already seen to cause an anomalous shift at C(1). The ^{119}Sn shift of -132.2 ppm (DMSO-d_6) is interesting in that the molecule can be regarded as a $CpFe^+$ complex of tetraphenyltin which has a shift of -128.1 in $CDCl_3$ at room temperature. Allowance for a solvent shift of about -2 ppm for a change from $CDCl_3$ to DMSO, brings the $\delta(Ph_4Sn)$ very close to that of the arene complex. The $CpFe^+$ moiety therefore has very little effect on the ^{119}Sn shift.

The Mössbauer data for the title compound I are presented in Table 2, together with those of other relevant materials. The QS for the iron site is reduced compared

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* Ligand exchange reactions [5] using ferrocene and phenyltin derivatives e.g. $PhSnBu_3$ were unsuccessful.

TABLE 1

^{1}H ^{a}, ^{13}C ^{b} AND ^{119}Sn ^{c} NMR DATA FOR [CpFeC$_6$H$_5$SnPh$_3$]$^+$ PF$_6^-$

	Cp	complexed C$_6$H$_5$				Uncomplexed C$_6$H$_5$			
^{1}H	4.43(s)	6.00 br.s				6.8 – 7.7 m			
^{13}C	75.1	C(1)	C(2)	C(3)	C(4)	C(1)	C(2)	C(3)	C(4)
		115.6	92.9	87.9	87.0	135.0	136.0	128.2	129.0
		(120.7)	(94.7) ^{d}	(88.0) ^{d}	(87.0) ^{d}	(138.0) ^{e}	(137.2) ^{e}	(128.6) ^{e}	(129.1) ^{e}

^{119}Sn – 132.2
(– 128.1) ^{e}

^{a} Acetone-d_6, ppm from ext. TMS. ^{b} DMSO-d_6, ppm from TMS. ^{c} DMSO-d_6, ppm from Me$_4$Sn (negative values indicates upfield shift). ^{d} Calculated values based on additivity factors derived from data in ref. 8,9 (see text). ^{e} Values for Ph$_4$Sn [10].

with that of the parent benzene complex. This suggests that the SnPh$_3$ group is withdrawing electron density from the arene ring. Electron-withdrawing groups are known to cause marked decreases in QS for these systems [12]. Comparison of the ^{119}Sn Mössbauer data for I and Ph$_4$Sn reveal some interesting features. The IS is lower for I, indicating that there is less s electron density at the nucleus and more used in bonding. The linewidth of I, fitted as a singlet, is large compared with that of a sample of Ph$_4$Sn which had been slowly cooled [4]. Better fits of the data for I are obtained when the spectrum is treated as a narrow doublet, or two singlets. This we take as evidence for a QS of about 0.5 mm s^{-1}. Such a QS can be explained in three ways (or a combination of them): (i) the QS is caused only by the steric bulk of the arene moiety; (ii) it is caused by the phenyl ring in the arene moiety donating less electron density to the tin than the other three phenyl groups; or (iii) it results from a change in the electric field gradient caused by the nearby positive charge.

TABLE 2

^{57}Fe AND ^{119}Sn MÖSSBAUER DATA (isomer shifts (IS), quadrupole splitting (QS) and linewidth (Γ) all in mm s^{-1})

Compound	T(K)	^{57}Fe			^{119}Sn		
		IS	QS	Γ	IS	QS	Γ
Ph$_4$Sn	193	–	–	–	1.20(2)	0.0	0.88
	80	–	–	–	1.24(3)	0.0	0.82 ^{a}
	80	–	–	–	1.18(3)	0.52	0.79 ^{a}
	80	–	–	–	1.22(2)	0.0	1.60 ^{b}
[CpFe$^+$ C$_6$H$_6$] PF$_6^-$	80	0.52 ^{c}	1.67 ^{c}	–	–	–	–
[CpFe$^+$ C$_6$H$_5$SnPh$_3$] PF$_6^-$	80	0.523(4)	1.583(6)	0.307(9)	1.16(1)	0.49(2)	0.84(4) ^{d}
					1.16	0.48	0.80(5) ^{e} 0.84(5)
					1.20(10)	0.49(10)	0.71(12) ^{f} 0.92(7)
					1.163(10)	0.00	1.184(19) ^{g}

^{a} First fit ref. 4. ^{b} Second fit ref. 4. ^{c} Data from ref. 12. ^{d} Fitted as a doublet. ^{e} Fitted as two singlets in fixed positions. ^{f} Fitted as two singlets free to move. ^{g} Fitted as one singlet.

Factor (ii) appears to contribute, since the QS in the ^{57}Fe spectrum is reduced. Molecular models indicate that steric effects in I and Ph$_4$Sn are very similar. Such steric effects have been invoked to explain the appearance of a small QS (0.52 mm s^{-1}) on quench cooling a sample of Ph$_4$Sn. Recently we have synthesised a series of stannylated NN-dimethylbenzylamines [13]. The Mössbauer spectra of these show broad lines both for the amine and quaternary ammonium salts. Thus the adjacent positive charge does not appear to have much effect. We therefore conclude that the observed QS in I is due to a combination of polar and steric effects. Both metal atoms find themselves outside ideal environments, and compete for a greater share in the available electron density.

Compound I can be cleaved with HgCl$_2$ in acetone to give a 71% yield of PhHgCl and upon treatment with KI a 45% yield of the CpFeC$_6$H$_5$Sn(C$_6$H$_5$)$_2$I complex, which was isolated as its HgI$_4^{2-}$ salt.

Ph-SnPh$_3$ + HgCl$_2$ ⟶ Ph-SnPh$_2$Cl + PhHgCl

Fe$^+$cp   Fe$^+$cp

(I)   (II)
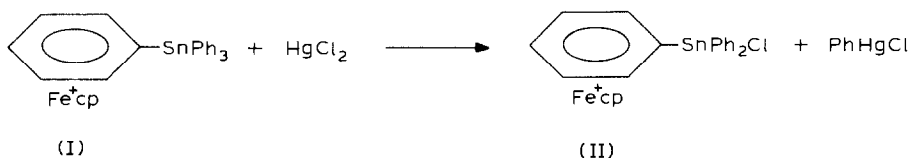
This result demonstrates the low activity of the complex towards electrophilic attack at C(1) caused by the strong withdrawal of electron density by the FeCp moiety. Attack proceeds exclusively at the C(1′) carbons, which are much less affected by the complexing group.

Reaction with iodine gave a 42% yield of [CpFeC$_6$H$_5$Sn(C$_6$H$_5$)$_2$I]$^+$I$^-$. The fate of the PF$_6$ anion in this reaction is unkown, though it is possible that the species I$^+$ PF$_6^-$ is produced which may be soluble in the medium used for crystallisation (acetone/ether) or may dissociate into IF and PF$_5$. This selective reactivity opens up possibilities for the synthesis of novel derivatives of II, an aspect which we are now investigating.

Experimental

Preparation of (η^6-triphenylstannylbenzene)(η^5-cyclopentadienyl) hexafluorophosphate (I)

A solution of Ph$_3$SnLi [14] was prepared by stirring a mixture of Ph$_3$SnCl (5.1 g, 13.2 mmol), Li shavings (0.3 g, 43 mg-atom), and sodium 0.15 g (6 mg-atom) in dry THF (150 ml) under N$_2$ for 16 h. This solution was added via a syringe to a slurry of [CpFeC$_6$H$_5$Cl]$^+$ PF$_6^-$ [7] (5 g, 13.2 mmol) in dry THF (20 ml) at −78°C under N$_2$. The mixture was allowed to warm to room temperature and left for 60 h with stirring. The purple solution was quenched with a saturated solution of NH$_4$PF$_6$ at 0°C. The THF was evaporated off and the residue extracted with acetone. The extract was evaporated and the residue recrystallised from methanol to give yellow-brown crystals, M.p. 274°C. Yield 4.2 g, 45.7%. Analysis: found: C, 50.55; H, 3.60. C$_{29}$H$_{25}$F$_6$FePSn calcd.: C, 50.26; H, 3.63%. The ^{1}H, ^{13}C and ^{119}Sn NMR data appear in Table 1.

Assignments of the ^{13}C NMR spectrum

Plots of additivity factors $\Delta(= \delta^{C_n}_{arene} - \delta_{benzene})$ for the complexed (c) [8] and

uncomplexed (uc) [15] arenes were reasonably linear for C(1), C(2) and C(4) carbons, and generated equations from which new additivity factors for the arene complexes could be calculated:

$$\Delta^c C(1) = 1.17\Delta^{uc}C(1) + 10.1(r = 0.95 \; 12 \; \text{points})$$

$$\Delta^c C(2) = 1.05\Delta^{uc}C(2) - 1.8 \; (r = 0.90 \; 12 \; \text{points})$$

$$\Delta^c C(4) = 0.57\Delta^{uc}C(4) - 0.3 \; (r = 0.97 \; 12 \; \text{points})$$

The additivity factors for C(3) were small and similar for complexed and uncomplexed arenes. Values for the additivity effect of the Ph_3Sn group were obtained by substituting the Δ^{uc} values [9] in the above equations.

Reaction of I with HgCl₂

A solution of I (0.69 g, 1 mmol) in acetone (10 ml) was added dropwise to a solution of $HgCl_2$ (0.54 g, 2 mmol) in acetone (5 ml). The mixture was subsequently refluxed briefly then cooled to $-5°C$, whereupon crystals appeared. These were filtered off and were shown to be PhHgCl from the melting point and infrared spectrum (0.22 g, 71%). The filtrate was added to a solution of KI (2.0 g in 25 ml H_2O) to remove the excess $HgCl_2$ as HgI_4^{2-}, and the resulting pale brown precipitate was filtered off to give 0.42 g of a tan coloured solid, m.p. 198–199°C. The infrared spectrum showed the absence of the strong bands due to the PF_6^- group at 830 cm^{-1}, and it was concluded that the complex formed was the tetraiodomercurate rather than the hexafluorophosphate and that chloride–iodide exchange had occurred at tin. Yield, 45%. Analysis: Found: C, 29.6; H, 2.1. $C_{46}H_{40}Fe_2Sn_2HgI_6$ calcd.: C, 29.0; H, 2.1%.

Reaction of I with I₂

A solution of I (0.69 g, 1 mmol) in acetone (10 ml) was added dropwise to a solution of iodine (0.54 g, 2 mmol) in acetone (5 ml). The mixture was refluxed for 5 min than cooled and added to dry ether (75 ml). The resultant yellow-brown solid (0.3 g, 42%) was filtered off and air dried. M.p. 160°C. The infrared spectrum showed the absence of the intense broad resonance at 830 cm^{-1} due to $\nu(P-F)$, indicating that the iodide had been formed rather then the hexafluorophosphate. Analysis: Found: C, 37.4; H, 2.8. $C_{23}H_{20}FeI_2Sn$ calcd.: C, 38.11; H, 2.78%. ^1H NMR (DMSO-d_6) 4.67s (5H), 6.0–6.4m (5H), 7.0–7.7 ppm (10H).

Apparatus

^1H NMR spectra were recorded with a Varian EM 360 spectrometer. ^{13}C and ^{119}Sn NMR spectra were recorded with a Bruker WP 80 FT spectrometer. Cracac was added to solutions for recording of the tin spectra.

Mössbauer spectra were run and fitted as previously described [1].

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