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MÖSSBAUER STUDIES ON FERROCENE COMPLEXES

XV *. STRUCTURE AND REACTIVITY OF TRIALKYL- AND TRIARYL-STANNYL FERROCENES

R.M.G. ROBERTS*, J. SILVER*,

Department of Chemistry, University of Essex, Wivenhoe Park, Colchester C04 3SQ, Essex (Great Britain)

and J. AZIZIAN

Shahid Chamran University, Ahwaz (Iran)

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Summary

^{57}Fe and ^{119}Sn Mössbauer data are reported for mono- and bis-triorganostannyl ferrocenes together with ^{119}Sn NMR chemical shifts. The reactions of bis-triphenylstannylferrocene $Fc(SnPh_3)_2$ with various electrophiles have been studied. Acid cleavage occurred with both Fc–Sn and Ph–Sn bond fission. In contrast, mercuridestannylation with $HgCl_2$ gave only $Fc(HgCl)_2$. Iodination gave a mixture of the mono- and bis-iodides $Fc(SnPh_3)(SnPh_2I)$ and $Fc(SnPh_2I)_2$ resulting from dominant Ph–Sn cleavage. Oxidation of $Fc(SnPh_3)_2$ by $FeCl_3$ required more than one equivalent of oxidant. The ^{57}Fe and ^{119}Sn Mössbauer spectra of the resultant ferrocinium ion was notable for the appearance of a measurable quadrupole splitting in both cases; this is discussed in terms of polar and steric effects.

Introduction

Metallated ferrocenes ($FcMX_n$) have been studied in some detail during the last two decades (e.g. M = Hg [2], Si [3], Ge [4]). The corresponding tin compounds, however, have received relatively little attention, and there are only a few reports [5–8].

Mono-triorganostannyl ferrocenes ($FcSnR_3$) are best prepared by using FcLi derived from FcBr, which avoids the problem of contamination by the bis product. The bis derivatives are conveniently prepared using $FcLi_2$-TMEDA, a method which gives almost exclusively the dilithiated intermediate [9]. Bitterwolf and Campbell-Ling

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[*] For part XIV see ref. 1.

[10] found a novel route to the mono-triorganotin derivatives involving reaction of diferrocenylmercury with hexaorganodistannanes at 190–230°C under reduced pressure. An interesting diferrocenyltin derivative has been prepared by Nesmeyanov et al. [11] from Fc_2Hg and $SnCl_2$; the structure [12] of the product, $FcSnCl_2Fc$, was notable in that the Sn–C bond was distorted 6.8° out of the plane of the cyclopentadienyl ring towards the iron atom, suggesting some interaction between the tin and iron atoms. Such an effect should be apparent from a Mössbauer and ^{119}Sn NMR study of these systems, and was one of the reasons we embarked on a detailed study of the structure of tin-substituted ferrocenes. Of particular interest to us was the possibility that oxidation to the corresponding ferricinium derivatives would provide a novel environment for the tin atom. Furthermore, very little work has been done on the reactivity of these derivatives, particularly with respect to cleavage of the Sn–C bonds by electrophiles such as $HgCl_2$, I_2, HX, etc.

A brief report [13] on some cleavage reactions of $FcSn(Ph)_2Fc$ [6] has appeared which indicates preferential cleavage of the Fc–Sn bond rather than the Sn–Ph bond. The ^{119}Sn and ^{57}Fe Mössbauer data have been reported for the oxidation product obtained by treatment of diferrocenyldichlorostannane with chlorine, and show a doublet (quadrupole splitting (QS) 2.65 mm s^{-1}) and a singlet respectively [14]. Recently the synthesis of a novel tin-bridged biferrocene was reported [15].

This paper considers the structure of some triorganostannylferrocenes on the basis of ^{119}Sn and ^{57}Fe Mössbauer and ^{119}Sn NMR spectroscopy, and reports a study of their reactions.

Results and discussion

Reactivity of triorganostannylferrocenes

Cleavage of $Fc(SnPh_3)_2$ by CF_3CO_2H in CCl_4 was very rapid at room temperature, and gave a rather complex mixture of products resulting from the following reactions.

$$Fc(SnPh_3)_2 + HX \rightarrow FcSnPh_3 + Ph_3SnX \quad (1)$$

$$FcSnPh_3 + HX \rightarrow FcH + Ph_3SnX \quad (2)$$

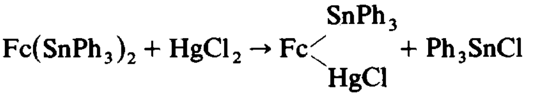
$$Fc(SnPh_3)_2 + HX \rightarrow Fc(SnPh_3)(SnPh_2X) + PhH \quad (3)$$

Thus using equimolar solutions of reactants (0.125 M), after 15 min at room temperature 37% starting material remained and the yields of $FcSnPh_3$, FcH and benzene were 36, 7 and 20%, respectively (57, 11 and 32% based on starting material consumed).

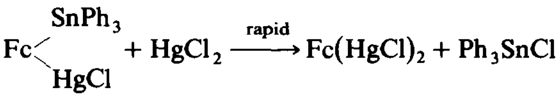
The significant amount of Sn–Ph bond fission is interesting, and reflects the difficulty of approach experienced by the incoming electrophile to the crowded carbon centres concerned.

Trifluoroacetic acid exists as dimers in CCl_4 [16] to the extent of about 80% at room temperature. There is some evidence that reactions involve the dimer in such media [17] and this seems to be the case here since the occurence of Sn–Ph cleavage suggests that a rather bulky electrophile is attacking. Unlike acid cleavage, mercuridestannylation proceeded with quantitative scission of the ferrocenyl–tin bond. When equimolar quantities of $HgCl_2$ were used and a solution of the latter in acetone was added slowly to $Fc(SnPh_3)_2$ in acetone, only $Fc(HgCl)_2$ was formed.

This indicates a more rapid cleavage of the second than of the first Sn–Fc bond.



$$Fc(SnPh_3)_2 + HgCl_2 \rightarrow Fc\begin{smallmatrix} SnPh_3 \\ HgCl \end{smallmatrix} + Ph_3SnCl \qquad (4)$$



$$Fc\begin{smallmatrix} SnPh_3 \\ HgCl \end{smallmatrix} + HgCl_2 \xrightarrow{\text{rapid}} Fc(HgCl)_2 + Ph_3SnCl \qquad (5)$$

This result is interesting in that $HgCl_2$ is unlikely to be appreciably dissociated in acetone, and is thus a rather bulky linear electrophile. As such it would have great difficulty in approaching $Fc(SnPh_3)_2$ between the cyclopentadienyl rings of the ferrocene moiety. The role of iron-bonded species as reactive intermediates has long been the subject of speculation but relatively little direct evidence has been forthcoming. Traylor [18] suggested that the direction of electrophilic attack in ferrocenes (*endo* from the Fe atom side, *exo* from above the Cp planes) is governed largely by the nature of the electrophile. Where the reagent is more electrophilic than the leaving group, *exo*-attack is preferred, with deprotonation occurring as a rapid second step with no observable isotope effect. In the case of weak electrophiles the reverse is true, and rapid attack occurs on the electron richer *endo* side with rate-determining proton transfer. This postulate is supported by results obtained for acylation [19] ($k_H/k_D = 1$) and mercuration [19] ($k_H/k_D = 3.2$) of ferrocene. In this treatment, however, steric effects are largely ignored. For ferrocene itself, attack by $HgCl_2$ takes place at the metal, to form an isolatable intermediate $FcH \cdot 7HgCl_2$, which is gradually oxidised to the ferricinium salt [20,21]. Such intermediates will involve appreciable ring tilt to accommodate the incoming mercury atom. Evidence for this is the absence of such complexes for ferrocenes with bulky substituents [22] and the enhanced stability of such complexes for [2]-ferrocenophanes [23] which have large tilt angles (~ 23°).

For the mercuridestannylation of both $Fc(SnBu_3)_2$ and $Fc(SnPh_3)_2$, attack would be expected to be on the *exo* side both from the point of view of the Traylor hypothesis ($HgCl_2$ is a stronger electrophile than Ph_3SnCl) and because of the large steric inhibition for *endo* approach. However such a transition state would involve severe steric strain between the leaving group and the lower Cp ring.

In view of the smaller bulk of $HgCl_2$ than of R_3Sn we favour the view that the reaction occurs via *endo* attack by $HgCl_2$, albeit with appreciable ring tilt in the ferrocene structure. The observation that the second R_3Sn group is cleaved off much more readily than the first is not readily explained. It could be argued that replacement of R_3Sn by HgCl reduces the steric interactions of the leaving group. However, the two Cp rings are free to rotate through at least 120°, and so such compressions can be alleviated fairly easily.

Bromination of $Fc(SnPh_3)_2$) resulted in appreciable oxidation to the ferricinium derivative. The remaining reaction products were the result of Sn–Ph rather than Sn–Fc bond fission. This was demonstrated quite conclusively for iodination reactions, in which oxidation was minimal. $Fc(SnPh_3)_2$ reacted rapidly with two equivalents of iodine to give a mixture of the mono- and bis-iodides (1.4/1), $Fc(SnPh_3)(SnPh_2I)$ and $(C_5H_4SnPh_2I)_2Fc$. The mono derivative showed two ^{119}Sn resonances in the ^{119}Sn NMR spectrum at −90 and −116 ppm due to the two different tin environments (cf. $\delta(^{119}Sn)$ −105 for $Fc(SnPh_3)_2$, −114 for Ph_3SnI and

~ −140 ppm for Ph_4Sn). The bis-iodide showed a single resonance at −90 ppm. Thus cleavage of the Ph–Sn bonds is preferred in iodination reactions. The reasons for this difference between iodination and mercuration is not clear, but may be due to subtle differences in steric effects between $HgCl_2$ and I_2.

Oxidation of $Fc(SnR_3)_2$ derivatives requires more than one equivalent of oxidant (here $FeCl_3$ or $AgOSO_2CF_3$). The resulting ferricinium derivatives seem to be very much more susceptible to reduction than the unsubstituted ferricinium salts. This effect has been noted previously for 1,1′-bis-(triphenylsilyl)ferricinium tetrachloroferrate, which can be reduced by simply adding water to an acetone solution of the salt [24]. The structure of the ferricinium salt is discussed below.

NMR and Mössbauer spectroscopy

The ^{119}Sn NMR and ^{119}Sn, ^{57}Fe Mössbauer data appear in Table 1. It is likely that $Fc(SnPh_3)_2$ exists as the *trans* isomer with the bulky $SnPh_3$ groups as far apart as possible. Molecular models clearly indicate a considerable barrier to mutual rotation of the Cp rings. The $\delta(^{119}Sn)$ for $Fc(SnPh_3)_2$ (−105.2) lies considerably downfield from that of Ph_4Sn (≃ ~ 140 [25]), which suggests significant electron release by the Fc moiety. However, ^{13}C studies of aryl ferrocenes [26] indicate that Fc and Ph have almost identical electronic effects in these systems. A more likely explanation is that the bulky Fc ligand causes distortion from tetrahedral geometry about the tin [27,28]. Thus Fc_2SnCl_2 has a tin shift of +68.4 ppm, whereas that of Ph_2SnCl_2 −32 ppm, the former shift indicating displacement of the tin atom towards the iron centre.

The ^{57}Fe Mössbauer data for $Fc(SnPh_3)_2$, $Fc(SnBu_3)_2$ and $Fc(SiMe_3)_2$ all have quadrupole splittings (*QS*) smaller than that of ferrocene. This indicates that the Sn and Si atoms are withdrawing electron density from the Cp rings of the ferrocene moiety [29], and also that these molecules are more difficult to oxidise than ferrocene itself [21]. The latter point may well be relevant to the different modes of reaction of $Fc(SnPh_3)_2$ and ferrocene with $HgCl_2$.

The compound Fc_2SnCl_2 is of known structure, the Sn atom having a distorted tetrahedral coordination. Bakii et al. [12] suggest that there is a weak Fe–Sn interaction since the relevant interatomic distance is 3.54 Å. The ^{57}Fe *QS* is 2.33 mm

TABLE 1

^{57}Fe AND ^{119}Sn MÖSSBAUER PARAMETERS (isomer shift, *IS*; quadrupole splitting, *QS*, and line width, *LW*, are in mm s^{-1}) AND ^{119}Sn CHEMICAL SHIFTS ($\delta(^{119}Sn)$ in ppm rel. Me_4Sn) FOR SOME FERROCENYL TIN COMPOUNDS AND RELATED SPECIES

Compound	^{57}Fe			^{119}Sn			$\delta(^{119}Sn)$
	IS	*QS*	*LW*	*IS*	*QS*	*LW*	
$Fc(SnPh_3)_2$	0.54(1)	2.34(1)	0.31(2)	1.11(1)	0.00	0.96(3)	−105.2
$Fc(SnBu_3)_2$	0.54(1)	2.32(1)	0.35(2)	1.14	0.00	1.13(3)	−0.03
$\overset{+}{Fc}(SnPh_3)_2$ PF_6^-	0.52(1)	0.56(1)	0.50(2)	1.11(2)	0.00	1.34(6)	–
BF_4^-	0.52(1)	0.00	0.69(4)	1.21(1)	0.66(3)	1.09(3)	–
$Fc(SiMe_3)_2$	0.52(1)	2.30(1)	0.25(2)	–	–	–	–
$FcCPh_3$	0.51(1)	2.40(1)	0.35(1)	–	–	–	
$Fc(SnPh_3)$	–	–	–	–	–	–	−104.5
Fc_2SnCl_2	0.52(1)	2.33(1)	0.30(1)	1.26(2)	2.50(3)	1.07(7)	+68.4

s^{-1}; this is similar to values recorded for the other spectra, and would be in accord with donation of electron density from the Cp rings to the Sn atom. Thus there is no evidence from the ^{57}Fe Mössbauer parameters to support the presence of a Sn–Fe interaction, especially when it is recalled that Fe–Hg [21], Fe–H [30] and Fe–C [29] interactions always produce *QS* values larger than that of ferrocene itself.

The $Fc(SnPh_3)_2^+$ cation gives a ^{57}Fe *QS* value of 0.56 mm s^{-1} for its PF_6^- salt and a wide line (suggestive of an unresolved *QS*) for its BF_4^- salt. The ferrocinium cation itself shows no *QS*. We have previously explained that for an oxidised ferrocene species to display a *QS* the moiety must have gained electron density [31]. The only atoms that could donate this electron density are the two tin atoms. Thus when oxidation takes place the Sn atoms now act as electron donors, in contrast to their role in unoxidised parent. Evidence to support this postulate comes from the ^{119}Sn Mössbauer data for the parent $FcSn(Ph_3)_2$ and its oxidised BF_4^- salt. In the former a singlet spectrum is observed, whereas in the latter a small value of *QS* (0.66(3) mm s^{-1}) is seen. The PF_6^- derivative shows a wide line indicative of an unresolved *QS*. This *QS* is unusual in tetraorganotin(IV) species and previously we have shown that they arise from severe distortion of the tetrahedral coordination at tin by steric effects of bulky ligands [32].

Quadrupole splitting can also be generated if there is a large electronegativity difference between the organic substituents in unsymmetrical tetraorganotin derivatives ($Me_3SnC_6F_5$ has a *QS* of 1.31 mm s^{-1}) [33].

The tin spectrum for $Fc(SnPh_3)_2$ itself shows line-broadening comparable to that of Ph_4Sn [32]. This is probably the result of distortion from tetrahedral geometry, and this is supported by the ^{119}Sn NMR data discussed above. On oxidation such distortions will remain. However $Fc^+(SnPh_3)_2\ BF_4^-$ has a quadrupole splitting indicating that additional factors are now operating. The electronic effects of Fc are not greatly different from those of phenyl groups [26]. However oxidation to Fc^+ effectively reverses the inductive effect of the ferrocenyl moiety, thus causing an observable *QS*. The ^{57}Fe and ^{119}Sn Mössbauer data are therefore complementary.

The ^{119}Sn isomer shifts for both $Fc(SnPh_3)_2$ and $Fc(SnBu)_2$ are both less than those for $SnPh_4$ (1.30 mm s^{-1}, ref. 34) and $SnBu_4$ (1.35 mm s^{-1}, ref. 35), indicating that the Cp rings bonded to the Sn atoms are poorer electron donors than the Ph rings, although, as shown by the ^{57}Fe Mössbauer data, they are still net electron donors.

The increase in the ^{119}Sn isomer shift on oxidation of $Fc(SnPh_3)_2$ indicates that the appearance of the *QS* of 0.66 mm s^{-1} is linked to a redistribution of the Sn *s* and *p* electrons. When the $SnPh_3$ moiety acts as an electron donor less *s* electron density is used in the bonding, suggesting a concomitant increase in *p* electron involvement.

The ^{119}Sn isomer shift and *QS* for Fe_2SnCl_2 are typical of tetrahedral tin(IV) diorganotin dihalides [36]. The bulky ferrocene ligands must encourage tetrahedral geometry similar to that envisaged for $[(SiMe_3)_2CH)]_2MeSnX$ (X = Cl, Br, I) [37] and $(C_6H_5)_3SnBr$ [38]; the structure of the latter is known [39]. Therefore the ^{119}Sn Mössbauer data, like the ^{57}Fe Mössbauer data, provide no obvious evidence for Fe–Sn interaction. Indeed, Fe–Sn interactions are usually manifest in ^{119}Sn Mössbauer by the presence of much higher isomer shifts ($\sim$ 1.7–2.0 mm s^{-1}).

Experimental

1,1'-Bis(trimethylsilyl)ferrocene [40], tritylferrocene [41] and diferrocenyldichlorotin [11] were prepared by published procedures.

Preparation of 1,1'-bis(triphenylstannyl)ferrocene (nc) and 1,1'-bis(tri-n-butylstannyl)ferrocene

Dilithioferrocene was made by the published method [9] from n-BuLi (93.2 ml, 1.5 *M* in hexane 0.14 mol), TMEDA (22.2 ml, 0.15 mol) in dry hexane (20 ml), and a slurry of ferrocene (11.2 g, 0.06 mol) in dry hexane (150 ml). The mixture was refluxed for 2 h then solid triphenyltin chloride (92.5 g, 0.24 mol) added in portions. The mixture was stirred for 18 h at room temperature then poured into saturated aqueous KF to remove the excess of Ph_3SnCl. The organic phase was separated after filtration and evaporated to give the crude product. This was purified by chromatography using neutral alumina. The first elution, with petroleum ether (40–60°C), removed any unreacted ferrocene. Elution with CH_2Cl_2/ethylacetate (10/1) then yielded mainly 1,1'-bis(triphenylstannyl)ferrocene contaminated with about 5% of the mono derivative. The latter was removed by washing with dry ether, to give 34.5 g (65%) of the desired product.

A small sample was recrystallised from ethanol (m.p. 179°C). ^1H NMR ($CDCl_3$) 4.18 (br.s, 8H), 7.2–8.2 ppm (m, 30H). ^{13}C NMR ($CDCl_3$) 66.31, 71.84, 74.88, 128.60, 129.08, 137.09, 138.87 ppm. $\delta(^{119}Sn)$ ($CDCl_3$) -105.2 ppm.

From the ether extract, a small quantity of triphenylstannyltin ferrocene was obtained, m.p. 154°C (lit. 156°C [10]), $\delta(^{119}Sn)$ -104.5 ppm. Analysis: Found: C, 62.5; N, 4.4. $C_{28}H_{24}FeSn$ calcd.: C, 62.50; H, 4.33%.

Using the same procedure, bis(tri-n-butylstannyl)ferrocene [5] was prepared in 59% yield.

^1H NMR (CCl_4) 0.7–2.2 (m, 54H), 3.98 (br.s, 4H) 4.25 ppm (br.s, 4H). ^{13}C NMR ($CDCl_3$) 10.32, 13.71, 27.45, 29.27, 68.74, 70.48, 74.22 ppm. $\delta(^{119}Sn)$($CDCl_3$) -0.03 ppm.

Cleavage reactions

(i) With trifluoroacetic acid

An 0.25 *M* solution (0.5 ml) of CF_3CO_2H (0.125 mmol) in CCl_4) was added slowly during 10 min to a solution of $Fc(SnPh_3)_2$ (0.5 ml, 0.25 *M*, 0.125 mmol in CCl_4) at room temperature. After 15 min, TLC revealed the presence of traces of ferrocene (R_F 0.70, elution with petroleum ether (40–60°C)) and roughly equally intense spots for $Fc(SnPh_3)_2$ (R_F 0.23) and $FcSnPh_3$ (R_F 0.11). In addition a pale blue spot remained at the origin ($FcSnPh_3SnPh_2OCOCF_3$). ^1H NMR spectroscopy revealed that all the acid had reacted. The mixture was quenched with a few drops of saturated aqueous KF and filtered, and the filtrate was analysed by HPLC. Isocratic elution was employed using 70/30 $MeCN/H_2O$ on a Novapak RP C_{18} analytical column at a flow rate of 1 ml/min. The instrument comprised two Waters Model 510 pumps controlled by a Waters Automated Gradient Controller. Detection was carried out at 254 nm using a Waters 481 LC absorption spectrophotometer. Samples were prepared in Spectrograde CCl_4. 20 μl aliquots of the filtrate after KF treatment were diluted with 1 ml CCl_4, filtered and 5 μl injections made. Benzene, ferrocene and $Fc(SnPh_3)_2$ had retention times of 2, 3.6, and 7.7 min, respectively. $FcSnPh_3$ could not be detected under these conditions, and the starting material $Fc(SnPh_3)_2$ gave a rather unsymmetrical trace of low intensity. By comparison with a series of standard solutions, yields of 20 and 9% were found for benzene and ferrocene, respectively. Using this data it was then possible to calculate the concentration of $Fc(SnPh_3)_2$ and $FcSnPh_3$ from the ^1H NMR spectra of the reaction solution, and this revealed yields of 36 and 35% respectively, in the final reaction mixture.

(ii) With mercuric chloride

A stirred solution of $Fc(SnPh_3)_2$ (0.22 g, 0.25 mmol) in acetone AR (4 ml) was treated dropwise at room temperature with $HgCl_2$ (0.07 g, 0.25 mmol) in acetone AR (4 ml). A yellow precipitate appeared immediately. After completion of the addition the precipitate was filtered off and dried, to give 0.08 g $Fc(HgCl)_2$, as identified by its infrared spectrum. The yield was almost quantitative.

Reaction with $Fc(SnBu_3)_2$ was very similar. $Fc(SiMe_3)_2$ however reacted much more slowly, only 2% yield being obtained after 24 h.

(iii) With iodine and bromine

$Fc(SnPh_3)_2$ (3.0 g, 3.4 mmol) was dissolved in CS_2 (15 ml) and a solution of iodine (1.7 g, 6.7 mmol) in CS_2 (15 ml) was added dropwise. The iodine colour was discharged rapidly. The mixture was allowed to stand for a 2 h and a small quantity (0.4 g) of black solid ($Fc^+(SnPh_3)_2I_3$) was filtered off. The solvent was removed to give a red oil which smelled strongly of iodobenzene – subsequently identified by IR spectroscopy. This was removed by heating for 0.5 h at 100°C at 0.5 mmHg. The product (1.4 g) was a sticky solid whose ^1H NMR spectrum indicated a mixture of mono- and di-iodinated products, $Fc(SnPh_3)(SnPh_2I)$ (**A**), $Fc(SnPh_2I)_2$ (**B**). Attempts to separate these by column chromatography failed.

Analysis: Found: C, 47.1; H, 3.2; I, 18.2. 1.44/1 **A**/**B** calcd.: C, 47.3; H, 3.28; I, 18.6%. The ^{119}Sn spectrum of the mixture showed peaks at -90.1, -91.0 and -166.2 ppm, with the latter two having equal intensities, each being approximately one half as intense as the first peak. The chemical shifts are fairly close to that of Ph_3SnI (-114.5 ppm) [42]. We assign the large singlet at -90.1 to $Fc(SnPh_2I)_2$, the resonance at -91.0 to the iodine bearing tin in **A**, and the peak at -116.2 to the $SnPh_3$ group in **A**. These assignments were confirmed by the downfield shifts caused by substitution by one iodine atom, $\Delta\delta = \delta(Ph_4Sn) - \delta(Ph_3SnI) = \sim 26$ ppm; an almost identical $\Delta\delta$ value of 25 ppm is found for **A**. The reaction with bromine was more complex, there being considerably more oxidation. Sn–C bond fission again appeared to occur predominatingly in the Sn–Ph bonds. Complications arise from electrophilic attack at the free Cp positions.

$Fc(SiMe_3)_2$ reacted with I_2 to give almost exclusively oxidation products. Thus when $Fc(SiMe_3)_2$ (0.22 g, 0.67 mmol) in CS_2 (3 ml) was treated with I_2 (0.28 g, 1.10 mmol) in CS_2 (3 ml) an immediate black precipitate occurred. This was filtered off to give 0.41 g (86%) of $Fc^+(SiMe_3)_2I_3^-$, showing a γ(CH) band at 860 cm^{-1} characteristic of ferrocinium ions.

Oxidation

A solution of $FeCl_3$(3 g, 18.5 mmol) in dry AR acetone (30 ml) was filtered and a solution of $Fc(SnPh_3)_2$ (3.1 g, 3.5 mmol) in dry AR acetone (30 ml) was added. An immediate green colour developed. After 1 h, the solvent was removed and the green oil washed thoroughly with dry ether to remove the excess of $FeCl_3$. The residue was taken up in acetone and the solution filtered into saturated aqueous NH_4PF_6. The resultant green-blue precipitate was filtered off and dried. Yield 1.4 g (39%).

Analysis: Found: C, 54.6; H, 3.7; Sn, 22.4. $C_{46}H_{38}F_6FePSn_2$ calcd.: C, 53.7; H, 3.7; Sn, 23.1%.

Use of equimolar quantities of $Fc(SnPh_3)_2$ and $FeCl_3$ resulted in incomplete oxidation, yielding a species which analysed as a 1/1 complex of the ferricinium salt with the starting material.

NMR spectroscopy

^1H NMR spectra were recorded with a Varian EM 360 instrument housed in a constant temperature room. The ^{13}C and ^{119}Sn spectra were recorded with a Bruker WP 80 FT spectrometer.

Chemical shifts are in ppm from TMS for ^1H and ^{13}C. The tin shifts are relative to Me_4Sn, a negative sign indicating a resonance upfield from the reference.

Mössbauer spectroscopy

Mössbauer spectra were obtained and fitted as described previously [43].

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