

Synthesis and structural studies of 2-stannyl-substituted ferrocenylmethylamine and -phosphine derivatives $2\text{-Me}_2\text{RSnFcCH}_2\text{Y}$ ($\text{R} = \text{Me}, \text{Cl}; \text{Y} = \text{NMe}_2, \text{PPh}_2, \text{P}(\text{O})\text{Ph}_2; \text{Fc} = \text{C}_{10}\text{H}_8\text{Fe}$)

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Abstract

2-(Trimethylstannyl)ferrocenylmethylidiphosphine, $2\text{-Me}_3\text{SnFcCH}_2\text{PPh}_2$ (**2a**), was synthesized from $2\text{-Me}_3\text{SnFcCH}_2\text{NMe}_2$ (**1a**) and Ph_2PH . Compound **2a** is oxidized with H_2O_2 to $2\text{-Me}_3\text{SnFcCH}_2\text{P}(\text{O})\text{Ph}_2$ (**3a**). Halogenation of **1a** and **2a** with Me_2SnCl_2 and **3a** with HCl -diethyl ether yields the organotin monochlorides $2\text{-Me}_2(\text{Cl})\text{SnFcCH}_2\text{Y}$ (**1b**, $\text{Y} = \text{NMe}_2$; **2b**, $\text{Y} = \text{PPh}_2$; **3b**, $\text{Y} = \text{P}(\text{O})\text{Ph}_2$). Both crystal structure determinations and multinuclear magnetic resonance studies in solution reveal for **1b–3b** molecular structures in which the tin atom approaches a trigonal bipyramidal pentacoordination as a consequence of an intramolecular Y Sn interaction. The donor strength of Y increases in the order $\text{PPh}_2 < \text{NMe}_2 < \text{P}(\text{O})\text{Ph}_2$. In solution **1b** and **2b** undergo ligand-exchange processes.

Keywords: Organotin; Ferrocene; Pentacoordination; Crystal structure; NMR

1. Introduction

Organometallic compounds with C^\wedgeY -chelating substituents ($\text{Y} = \text{donor group}$) show significantly different structural and chemical behaviour to compounds bearing unsubstituted ligands [1,2]. In organotin chemistry, the following effects have been observed caused by intramolecular coordination: (i) stabilization of divalent organotin compounds in such a way that in some cases they are isolable as monomeric species [3–8]; (ii) first results indicate an enhanced reactivity of tin–carbon bonds in tetraorganotin compounds with C^\wedgeY built-in ligands, which is caused by intramolecular assistance of the potentially coordinating group Y ; this facilitates electrophilic substitutions and the transfer of organic groups from tin to various substrates [9–14]; and (iii) increase in the usually very low configurational stability

of the tin centre in triorganotin halides by intramolecular coordination of a C^\wedgeY ligand. In general, compounds of this type have a trigonal bipyramidal ligand polyhedron at the tin atom and are suitable model compounds to study both fluxional processes at stereogenic tin centres and inversion processes at the tin atom in $\text{S}_{\text{N}}2$ substitution reactions of triorganotin halides [2].

Besides the Lewis acidity of the tin atom and the donor strength of the group Y , the extent of the intramolecular coordination with C^\wedgeY ligands depends also on the nature of the organic bridge spanning the C atom and the Y group. In continuation of our studies on hypervalent organotin compounds, we became interested in using C^\wedgeY -chelating ligands with the ferrocenylene group spanning the two coordinating sites.

Although a number of investigations dealing with diorganoaminomethyl- and methoxymethylferrocenylstannanes have been reported [15,16], to the best of our knowledge an intramolecular coordination between the

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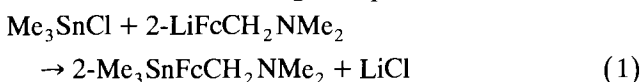
substituted ferrocenyl ligand and a tin atom is only known for $(2\text{-Me}_2\text{NCH}_2\text{Fc})_2\text{SnCl}_2$, in which the tin shows a distorted octahedral configuration [17].

We report here the synthesis, chemical behaviour and molecular structure of 2-organostannylferrocenylmethyldimethylamines **1a** and **1b**, diphenylphosphines **2a** and **2b** and diphenylphosphine oxides **3a** and **3b** (Scheme 1).

2. Results and discussion

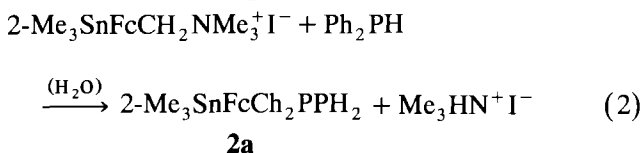
2.1. Preparative aspects

The starting substance for the synthesis of the title compounds is 2- $\text{Me}_3\text{SnFcCH}_2\text{NMe}_2$ (**1a**) ($\text{Fc} = \text{C}_{10}\text{H}_8\text{Fe}$) which is known from the literature [15] and can be obtained according to Eq. (1).

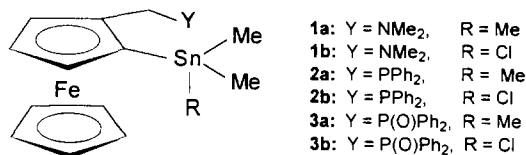


In order to achieve a higher yield, it is useful to isolate 2- $\text{LiFcCH}_2\text{NMe}_2$ before its reaction with Me_3SnCl . Compound **1a** is a distillable red oil.

$\text{FcCH}_2\text{PPh}_2$ is known to result from the reaction of $\text{FcCH}_2\text{NMe}_3^+ \text{I}^-$ with Ph_2PH [18]. However, its reaction with LiBu differs from its *N*-analogue in that it results mainly in metallation of the methylene group rather than in proton abstraction in *ortho* position [19]. The preparation of 2- $\text{Me}_3\text{SnFcCH}_2\text{PPh}_2$ (**2a**) was accomplished by reaction of 2- $\text{Me}_3\text{SnFcCH}_2\text{NMe}_3^+ \text{I}^-$ with an excess of Ph_2PH in boiling water (Eq. (2)).



The methiodide 2- $\text{Me}_3\text{SnFcCH}_2\text{NMe}_3^+ \text{I}^-$ was formed almost quantitatively by reaction of **1a** with MeI in

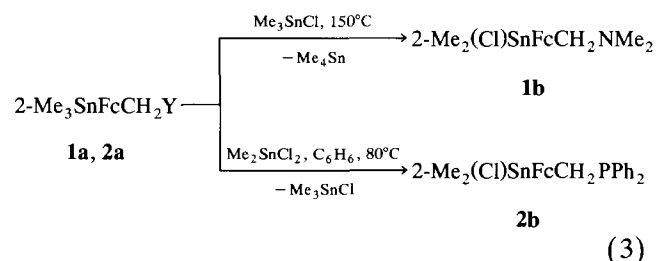


Scheme 1.

methanol–diethyl ether. The reaction mixture was buffered with $\text{NaH}_2\text{PO}_4\text{--Na}_2\text{HPO}_4$ in order to avoid acidic cleavage of tin–carbon bonds. After removal of excess Ph_2PH under high vacuum at 120°C , **2a** was obtained from ethanol as orange–red crystals. Compound **2a** is air-stable for some time and is soluble in benzene, diethyl ether and CH_2Cl_2 , but it is insoluble in hexane and alcohols.

The oxidation of **2a** with hydrogen peroxide in ethanol gives 2- $\text{Me}_3\text{SnFcCH}_2\text{P(O)Ph}_2$ (**3a**) as an orange–brown crystalline compound.

The tin monochlorides **1b** and **2b** were obtained by the well known redistribution reaction according to Eq. (3).



The monochlorination of **3a** to yield 2- $\text{Me}_2(\text{Cl})\text{SnFcCH}_2\text{P(O)Ph}_2$ (**3b**) was achieved with hydrogen chloride in ethanol (Eq. (4)).

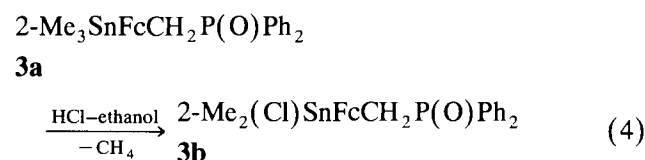


Table 1

Coordination $\text{Sn} \cdots \text{Y}$ and coordination polyhedra $(\text{Cl}/\text{Me}_{\text{axial}})\text{Sn}(\text{Me}_{\text{equatorial}})$ in transforming a tetrahedron to a trigonal bipyramid in the compound series **1b** to **3b**

Parameter	1b (Y = N)		2a (Y = P)		2b (Y = P)	3b (Y = O)
	Molecule (1)	Molecule (2)	Molecule (1)	Molecule (2)		
$d(\text{Sn} \cdots \text{Y})$ (Å)	2.559(9)	2.579(9)	4.038(2)	4.134(1)	3.349(2)	2.368(4)
$d(\text{Sn-Cl}/\text{Me}_{\text{ax}})$ (Å)	2.465(4)	2.523(5)	2.15(1)	2.14(1)	2.415(2)	2.504(2)
$d(\text{Sn-Me}_{\text{eq}})$ (Å)	2.15(1) ^a 2.07(9) ^a	2.30(2) ^a 2.13(1) ^a	2.16(1) 2.11(1)	2.07(1) 2.12(1)	2.12(1) 2.11(1)	2.13(1) 2.12(1)
$\theta(\text{Y-Sn-Cl}/\text{Me}_{\text{ax}})$ (°)	165.4(2)	168.3(2)	161.0(2)	161.9(3)	167.3(1)	176.7(2)
$\Sigma\theta_{\text{eq}}$ (°)	356.6	356.1	331.3	331.9	351.1	357.6
$\Sigma\theta_{\text{ax}}$ (°)	288.5	287.0	325.6	325.0	300.0	285.3
$\Sigma\theta_{\text{eq}} - \Sigma\theta_{\text{ax}}$ (°)	68.1	69.1	5.7	6.9	51.1	72.3
$\Delta(d(\text{Sn} \cdots \text{Y}) - d(\text{Sn-Y}))$ (Å) ^b	0.48	0.50	1.96	2.05	0.83	0.35
$\Delta\text{Sn (plane)}$ (Å)	0.22	0.22	0.68	0.66	0.37	0.19

^a All methyl groups at tin in **1b** are somewhat disordered (see experimental expansion).

^b $d(\text{Sn-P}) = 2.52$ (Å), $d(\text{Sn-O}) = 2.02$ (Å), $d(\text{Sn-N}) = 2.08$ (Å) [29].

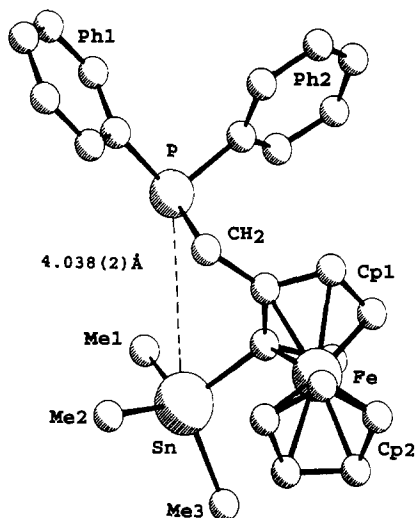


Fig. 1. Molecule (1) of **2a** with a tetrahedral Sn atom (no Sn \cdots P coordination). Labels of atoms and groups as given in Tables 1 and 4. Molecule (2) looks identical.

As described for other examples of intramolecular nucleophilic assistance in halodestannylation reactions [2,9,10], the intramolecular P=O \cdots Sn interaction in the transition state of this reaction is responsible for the change in the common cleavage sequence of tin–carbon bonds in electrophilic reactions. Thus, for **3a** the cleavage of the Sn–C bond to the methyl group is favoured over the cleavage of the Sn–C bond to the ferrocenyl ligand.

2.2. Molecular structures of **2a**, **1b**, **2b** and **3b**

The molecular structures of **2a** and **1b–3b** are shown in Figs. 1–4. The hydrogen atoms are omitted for clarity. All four molecules are pictured by means of PLUTO plots; the corresponding ORTEP plots look rather confusing. Selected bond lengths and bond angles are listed in Table 1. Crystallographic data, structure determination details and the final atomic coordinates are collected in Tables 3–6.

The structure of **2a** consists of two crystallographically independent molecules which hardly differ from each other. Fig. 1 shows molecule (1) with mean labelling for both molecules. The tin–phosphorus distances of 4.038(2) and 4.134(1) Å, respectively (the sum of the van der Waals radii is 4.05 Å [20]), show that there is no intramolecular Sn \cdots P interaction. Therefore, the bond angles at both tin and phosphorus reveal for the two atoms a tetrahedral ligand polyhedron. In the latter case the lone pair causes the expected decrease of the C–P–C angles in comparison with the ideal tetrahedral angle.

As for **2a**, the unit cell of **1b** contains two kinds of discrete but very similar molecules. The structure of molecule (1) with labelling for both molecules is shown

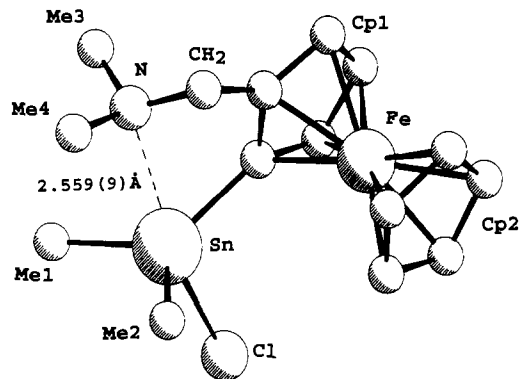


Fig. 2. Molecule (1) of **1b** with Sn \cdots N coordination. Labels of atoms and groups as given in Tables 1 and 5. Molecule (2) looks identical.

in Fig. 2. The main feature of the structure is the intramolecular coordination between tin and nitrogen with the consequence of a trigonal bipyramidal configuration of the former. The values of 2.559(9) Å in molecule (1) and 2.579(9) Å in molecule (2) for the Sn \cdots N distance are in the range observed for other pentacoordinated triorganotin halides with Sn \cdots N coordination [21–23]. As consequence of the Sn \cdots N interaction, the expected lengthening is observed of the Sn–Cl bonds to 2.465(9) Å in molecule (1) and 2.523(9) Å in molecule (2). This lengthening is of the same order of magnitude as observed for other hypervalent triorganotin chlorides [24,25].

Fig. 3 shows the molecular structure of **2b**. In contrast to **2a**, the Sn \cdots P distance of 3.349(2) Å in **2b** is shorter than the sum of the van der Waals radii (4.05 Å [20]) and indicates a weak Sn \cdots P interaction. The ligand polyhedron at tin can therefore be regarded as a monocoordinated tetrahedron. A comparison of **2b** with the

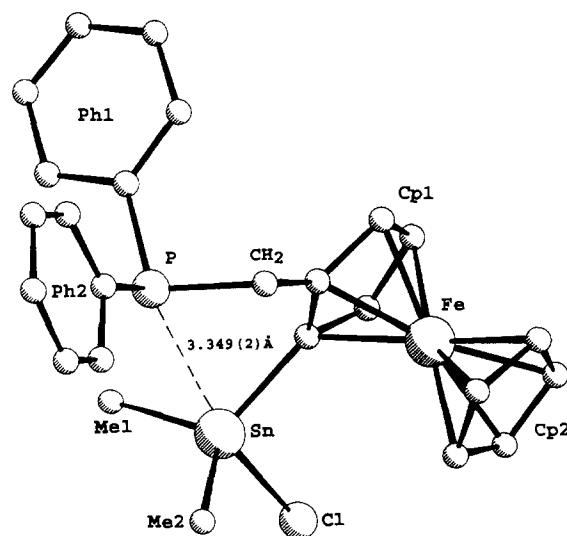


Fig. 3. Compound **2b** with Sn \cdots P coordination (five-membered chelate). Labels of atoms and groups as given in Tables 1 and 6.

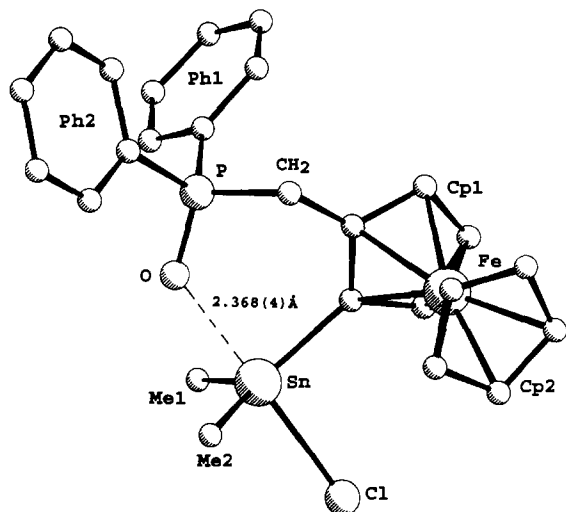


Fig. 4. Compound **3b** with Sn...O coordination (six-membered chelate). Labels of atoms and groups as given in Tables 1 and 6.

structure of $\text{Me}_2(\text{Cl})\text{SnCH}_2\text{CH}_2\text{CH}_2\text{PPh}^t\text{Bu}$ [24], ($\text{Sn} \cdots \text{P}$ 3.078 Å, $\text{Sn}-\text{Cl}$ 2.494 Å and $\text{Cl}-\text{Sn}-\text{P}$ 169.8°) shows that in the latter compound the intramolecular $\text{Sn} \cdots \text{P}$ interaction is stronger. This is due to the higher donor strength of the $^t\text{BuPhP}$ group and the greater flexibility of the five-membered chelate ring in this compound compared with **2b**.

Similarly to **1b**, the molecular structure of the P-oxide **3b** (Fig. 4) shows a strong intramolecular $\text{P}=\text{O} \cdots \text{Sn}$ coordination resulting in an only slightly distorted trigonal bipyramidal configuration about the tin atom. The $\text{Sn} \cdots \text{O}$ and the $\text{Sn}-\text{Cl}$ distances and also the other parameters describing the geometry at the tin atom in **3b** are in good agreement with other adducts between

triorganotin chlorides and tertiary phosphine oxides [10b,25,26].

The differences in the structures of **1b–3b** allow a comparison of the coordination tendency between the NMe_2 , PPh_2 and $\text{P}(\text{O})\text{Ph}_2$ groups. In Table 1 the following structure parameters are shown which characterize the extent of distortion of the structures of **1b–3b** on the pathway between the ideal tetrahedron and the ideal trigonal bipyramid as a result of increasing intramolecular coordination: (i) the difference $\Sigma\theta_{\text{eq}} - \Sigma\theta_{\text{ax}}$ (°) between the three equatorial C–Sn–C angles and the three axial C–Sn–Cl angles at tin, which is 90° for the trigonal bipyramid and 0° for the tetrahedron [27]; (ii) the deviation $\Delta\text{Sn}(\text{plane})$ (Å) of the tin atom from the plane through the three equatorial ligands in the tin polyhedron, which ranges from 0.71 Å for the tetrahedron to 0 Å for the trigonal bipyramid [28]; and (iii) the bond length differences $\Delta(d(\text{Sn} \cdots \text{Y}) - d(\text{Sn}-\text{Y}))$ (Å) ($\text{Y} = \text{N}, \text{P}, \text{O}$; $d(\text{Sn}-\text{N}) = 2.08$, $d(\text{Sn}-\text{P}) = 2.52$, $d(\text{Sn}-\text{O}) = 2.02$ Å), which decreases with increasing donor strength of the functional group Y [29].

All three parameters indicate an increase of the coordination tendency for the donor groups in **1b–3b** in the sequence $\text{Ph}_2\text{P} < \text{Me}_2\text{N} < \text{Ph}_2\text{P}(\text{O})$.

2.3. Structure of **1b–3b** in solution

The ^{119}Sn , ^{31}P and relevant ^1H NMR spectroscopic data for **1a–3a** and **1b–3b** are given in Table 2 (**1a** is known; its NMR data agree with those given in the literature [16]). To obtain information about the ligand geometry at tin in **1a–3a** and **1b–3b**, their ^{119}Sn chemical shifts and $^2J(^{119}\text{SnC}^1\text{H}_3)$ values, which depend on

Table 2
 ^{119}Sn , ^{31}P and selected ^1H NMR data for 2- $\text{Me}_3\text{SnC}_{10}\text{H}_8\text{FeCH}_2\text{Y}$ (**1a–3a**) and 2- $\text{Me}_2(\text{Cl})\text{SnC}_{10}\text{H}_8\text{FeCH}_2\text{Y}$ (**1b–3b**) (**1a**, **1b**: $\text{Y} = \text{NMe}_2$; **2a**, **2b**: $\text{Y} = \text{PPh}_2$; **3a**, **3b**: $\text{Y} = \text{P}(\text{O})\text{Ph}_2$)

Parameter ^a	1a	2a	3a	1b	2b	3b
$\delta_{^{119}\text{Sn}}$ (ppm)	–15.0	–12.0	–11.9	–3.6	43.1	–46.7
$\delta_{^{31}\text{P}}$ (ppm)		–12.7	24.6		–14.6	33.9
$^nJ(^{119}\text{Sn}, ^{31}\text{P})$ (Hz)		5.8 ^b	< 5.0 ^b		155.1 ^c	29.0 ^d
$\delta_{\text{H}}(\text{SnCH}_3)$ (ppm)	0.34 (s)	0.42 (d) ^e	0.26 (s)	0.65 (s) 0.89 (s)	0.95 (d) ^f	0.86 (s) 1.03 (d) ^g
$^2J(^{119}\text{SnC}^1\text{H}_3)$ (Hz)	54.5	54.4	55.0	66.0	63.3	72.3
$\delta_{\text{H}}(\text{NCH}_3)$ (ppm)	1.96 (s)			2.13 (s)		
$\delta_{\text{H}}(\text{CH}_2\text{Y})$ (ppm)		3.21 (m)	3.35 (m)	2.88 (d) ⁱ 3.91 (d) ⁱ	3.28 (m)	3.45 (m)
	2.65 (d) ^h 3.55 (d) ^h					

Solvent, CDCl_3 ; temperature, 27°C.

^a Me_3SnPh : $\delta_{^{119}\text{Sn}} = -28.6$ ppm; $^2J(^{119}\text{SnC}^1\text{H}_3) = 54.5$ Hz [31]. $\text{Me}_2(\text{Cl})\text{SnPh}$: $\delta_{^{119}\text{Sn}} = 48.3$ ppm; $^2J(^{119}\text{SnC}^1\text{H}_3) = 58.5$ Hz [10a].

^b $^4J(^{119}\text{SnCCC}^3\text{P})$.

^c $^1J(^{119}\text{Sn}^{31}\text{P}) + ^4J(^{119}\text{SnCCC}^3\text{P})$.

^d $^2J(^{119}\text{SnO}^{31}\text{P}) + ^4J(^{119}\text{SnCCC}^3\text{P})$.

^e $^6J(^{31}\text{PCCCSn}^1\text{H}_3) = 0.4$ Hz.

^f $^6J(^{31}\text{PCCCSn}^1\text{H}_3) + ^3J(^{31}\text{PSn}^1\text{H}_3) = 3.5$ Hz.

^g $^6J(^{31}\text{PCCCSn}^1\text{H}_3) + ^4J(^{31}\text{POSn}^1\text{H}_3) = 0.6$ Hz.

^h $^2J(\text{HCH}) = 12.3$ Hz.

ⁱ $^2J(\text{HCH}) = 13.5$ Hz.

the coordination number of tin [30–33] are compared with those of Me_3PhSn ($\delta^{119}\text{Sn} = -28.6$ ppm; $^2J(^{119}\text{SnC}^1\text{H}_3) = 54.5$ Hz [31]) and Me_2PhSnCl ($\delta^{119}\text{Sn} = 48.3$ ppm; $^2J(^{119}\text{SnC}^1\text{H}_3) = 58.5$ Hz [10a]) (note that in tetraorganotin compounds the substitution of a phenyl for a ferrocenyl group causes a downfield shift of $\delta^{119}\text{Sn}$ of about 20 ppm [16]).

The observed $\delta^{119}\text{Sn}$ and $^2J(^{119}\text{SnC}^1\text{H}_3)$ values suggest for **1a–3a** a tetrahedral geometry at tin, whereas **1b** and **3b** are unambiguously pentacoordinated. The $\delta^{119}\text{Sn}$

value of **2b** indicates only a small tendency for an increase in the coordination number of tin in this compound, but the $^2J(^{119}\text{SnC}^1\text{H}_3)$ of 63.3 Hz is in a range reported for pentacoordinated methyl-substituted triorganotin halides. This finding is strongly supported by the $^nJ(^{119}\text{Sn}, ^{31}\text{P})$ coupling constant of 155.1 Hz. The increase in this coupling compared with the $^4J(^{119}\text{SnCCC}^{31}\text{P})$ coupling in **2a** of only 5.8 Hz indicates that the coupling between phosphorus and tin in **2b** is the sum of $^4J(^{119}\text{SnCCC}^{31}\text{P})$ and $^1J(^{119}\text{Sn}^{31}\text{P})$.

Table 3
Crystallographic data and structure determination details for **2a** and **1b–3b**

Parameter	1b	2a	2b	3b
<i>Crystal data</i> ($Mo K\alpha_1$, $\lambda = 0.70926 \text{ \AA}$)				
Formula; M_r	$\text{C}_{15}\text{H}_{22}\text{NSnFeCl}$; 426.33	$\text{C}_{26}\text{H}_{29}\text{PSnFe}$; 547.03	$\text{C}_{25}\text{H}_{26}\text{PSnFeCl}$; 567.45	$\text{C}_{25}\text{H}_{26}\text{POSnFeCl}$; 583.45
Crystal habit	Block	Needles	Triangle fragment	Block
Dimensions	$0.45 \times 0.48 \times 1.40$ mm	$0.25 \times 0.45 \times 2.80$ mm	$0.20 \times 0.22 \times 0.45$ mm	$0.12 \times 0.28 \times 0.24$ mm
Faces (distance to a common origin) (mm)	011, 0–1–1, 01–1, 0–11 (0.225); 100, –100(0.7); 010, 0–10 (0.18)	110, –1–10, 1–10, –110 (1.3); 001, 00–1, 01–1, 0–11 (0.125); 011, 0–1–1 (0.15)	10–1, 010, 0–10 (0.10); 101 (0.13); –101 (0.18), 0–11 (0.05); –10–1 (0.06)	100, –100(0.06); 001, 010, 0–10 (0.12); 01–1, 0–11 (0.14)
Crystal colour	Orange	Orange	Orange	Orange
Crystal system; space group	Orthorhombic; $P2_12_12_1$ (No. 19)	Monoclinic; $P2_1/c$ (No. 14)	Triclinic; $P\bar{1}$ (No. 2)	Triclinic; $P\bar{1}$ (No. 2)
Unit cell dimensions determination	100 refl., $\theta = 26\text{--}29^\circ$	50 refl., $\theta = 24\text{--}29^\circ$	100 refl., $\theta = 20\text{--}24^\circ$	75 refl., $\theta = 19\text{--}21^\circ$
a ; α	13.294(2) \AA	11.101(1) \AA ;	8.904(1) \AA ; 80.73°	9.141(1) \AA ; $81.12(1)^\circ$
b ; β	14.520(1) \AA	20.029(2) \AA ; $103.19(1)^\circ$	9.435(1) \AA ; 78.74°	9.445(1) \AA ; $79.24(1)^\circ$
c ; γ	17.474(1) \AA	22.653(3) \AA ;	14.987 \AA ; 79.0°	14.574(2) \AA ; $78.47(1)^\circ$
V ; Z ; $F(000)$	3373(1) \AA^3 ; 8; 1695	4904(1) \AA^3 ; 8; 2208	1202(1) \AA^3 ; 2; 568	1202(1) \AA^3 ; 2; 584
D_{calc} ; D_{exp}	1.679 g cm^{-3}	1.482; 1.47 g cm^{-3}	1.568 g cm^{-3}	1.612 g cm^{-3}
<i>Intensity data collection</i> ($Mo K\alpha$, $\lambda = 0.71069 \text{ \AA}$, graphite monochromator)				
Temperature; scan; θ -range;	24°C; $\omega/2\theta$; $1.5\text{--}32^\circ$	24°C; $\omega/2\theta$; $1.5\text{--}29^\circ$	23°C; $\omega/2\theta$; $1.5\text{--}30^\circ$	24°C; $\omega/2\theta$; $1.5\text{--}30^\circ$
$\sin \theta_{\text{max}}/\lambda$	0.746 \AA^{-1}	0.682 \AA^{-1}	0.704 \AA^{-1}	0.704 \AA^{-1}
Range of h, k, l	+19, +21, +26	+15, +27, ± 30	+12, ± 13 , ± 21	+12, ± 13 , ± 20
No. of reflections	3, every 4000 s	3, every 4000 s	3 every 4000 s	3, every 4000 s
Loss of intensity, time; Correction	1%; 7 days; linear	2%; 12 days; linear	4%; 7 days; linear	8%; 9.5 days; linear
No. of reflections: meas., indep. (int. R)	6447, 6415	14005; 12992 (0.0370)	7416; 7002 (0.0115)	7363; 6961 (0.0147)
No. of reflections used, limit	4200 with $I > 3\sigma(I)$	8685 with $I > 3\sigma(I)$	4118 with $I > 2\sigma(I)$	4481 with $I > 2\sigma(I)$
μ (cm^{-1}); abs. corr.	23.57; numerical by face indices	15.87; numerical by face indices	17.23; numerical by face indices	17.27; numerical by face indices
Range of transmission	0.4943–0.3037	0.7221–0.6188	0.8307–0.7400	0.8260–0.6242
<i>Refinement</i>				
Choice of thermal parameters	Sn, Fe, Cl anisotropic; N, C isotropic; H isotropic fixed	Sn, Fe, P anisotropic; C isotropic; H isotropic fixed	Sn, Fe, P, Cl anisotropic, C isotropic; H isotropic fixed	Sn, Fe, P, Cl, O anisotropic, C isotropic; H isotropic fixed
Variables; ratio	172; 24.4	276; 31.5	148; 27.8	157; 28.5
2 $\sigma_{\text{refl.}}/\text{var.}$ last shifts	$< 0.5\sigma$ for unsubst. Cp ring	$< 0.013\sigma$; $< 0.056\sigma$ for stat. Cp ring	$< 0.07\sigma$; $< 0.125\sigma$ for U_{22} Sn	$< 0.012\sigma$; $< 0.083\sigma$ for stat. Cp ring
Final. R ; R_w	0.0602; 0.0959	0.0648; 0.1008	0.0640; 0.0719	0.0541; 0.0688
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.017414F^2$	$\sigma^2(F) + 0.007426F^2$	$\sigma^2(F) + 0.000819F^2$	$\sigma^2(F) + 0.001121F^2$
Final diff. Fourier maxima	3.6 e \AA^{-3} near Sn	1.88 e \AA^{-3} near Sn	1.39 e \AA^{-3} near phenyl	2.17 e \AA^{-3} near Sn

The latter is the result of intramolecular P ··· Sn interaction. As previously described for Me₂(Cl)Sn(CH₂)₃PPh₂ [34], in solution of **2b** a fast equilibrium exists between tetracoordinated open-chain and pentacoordinated cyclic structures.

In the same manner the ${}^nJ(^{119}\text{Sn}, ^{31}\text{P})$ coupling in **3b** is the sum of ${}^4J(^{119}\text{SnCCC}^{31}\text{P})$ and ${}^2J(^{119}\text{SnO}^{31}\text{P})$. Furthermore, the intramolecular P = O ··· Sn interaction causes a bathochromic shift of the $\nu(\text{P}=\text{O})$ frequency to 1147 cm⁻¹ in the IR spectrum of **3b**. For **3a**, $\nu(\text{P}=\text{O})$ is 1195 cm⁻¹.

As a consequence of the asymmetry of 1,2-disubstituted ferrocenes and in the case of a rigid intramolecular donor–tin coordination and a stereochemically stable trigonal bipyramidal configuration at tin, the two tin methyl groups in **1b–3b** should be diastereotopic. Accordingly, the ¹H NMR spectra of **1b** and **3b** show two separate signals for these groups. Worth mentioning is

the coupling of phosphorus with the protons of only one methyl group at tin in **3b**.

In contrast to the non-equivalence of the methyl groups at tin, the *N*-methyl groups in **1b** are equivalent at room temperature. That means that an Sn ··· N dissociation–association with inversion at the nitrogen atom occurs, whereas the configuration at tin is stable. However, this process is slow on the ¹³C NMR time-scale at 233 K. Accordingly, two resonances of equal intensity are observed for the *N*-methyl carbon atoms (see Experimental section). These results are in agreement with fluxional processes of triorganotin bromides containing 2-dimethylaminomethyl-1-phenyl and 8-dimethylamino-1-naphthyl *C,N*-chelating ligands, which have been intensively studied by Jastrzebski and van Koten [2].

In agreement with the above-mentioned equilibrium between open-chain and cyclic species in solutions of

Table 4
Fractional atomic coordinates and equivalent isotropic thermal parameters for **2a** (monoclinic *P*2₁/*c*) (e.s.d.s in parentheses)

Group ^a	Molecule (1)					Molecule (2)				
	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b (Å ²)	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b (Å ²)
Sn	Sn(1)	0.32708(3)	0.12670(2)	0.11003(2)	0.0515(2)	Sn(2)	0.16845(4)	0.19361(2)	0.37391(2)	0.0570(2)
Fe	Fe(1)	0.63072(6)	0.18472(3)	0.08778(3)	0.0400(3)	Fe(2)	-0.13839(7)	0.13078(4)	0.38199(3)	0.0420(3)
P	P(1)	0.3767(1)	0.30745(7)	0.19126(7)	0.0474(7)	P(2)	0.1278(1)	0.01560(7)	0.27881(7)	0.0479(7)
Me1	C(11s)	0.1452(8)	0.1680(4)	0.1040(4)	0.084(2) *	C(21s)	0.1150(9)	0.2326(4)	0.2870(4)	0.104(2) *
Me2	C(12s)	0.3968(9)	0.0879(4)	0.1979(4)	0.097(2) *	C(22s)	0.3535(8)	0.1590(4)	0.3887(4)	0.085(2) *
Me3	C(13s)	0.3152(8)	0.0495(3)	0.0430(3)	0.085(2) *	C(23s)	0.1560(9)	0.2686(4)	0.4392(4)	0.097(2) *
Cp1	C(111)	0.5235(4)	0.2481(2)	0.1252(2)	0.043(1) *	C(211)	0.0477(5)	0.1158(2)	0.3885(2)	0.044(1) *
	C(112)	0.4476(4)	0.2011(2)	0.0875(2)	0.0414(9) *	C(212)	-0.0249(5)	0.0694(2)	0.3459(2)	0.045(1) *
	C(113)	0.4707(5)	0.2089(2)	0.0279(2)	0.052(1) *	C(213)	-0.0996(6)	0.0312(2)	0.3773(2)	0.056(1) *
	C(114)	0.5593(6)	0.2599(3)	0.0302(3)	0.063(1) *	C(214)	-0.0756(6)	0.0511(3)	0.4375(3)	0.063(1) *
	C(115)	0.5912(5)	0.2843(2)	0.0899(2)	0.054(1) *	C(215)	0.0147(6)	0.1029(3)	0.4458(2)	0.060(1) *
Cp2 ^c	C(121)	0.7258(6)	0.1233(3)	0.1534(2)	0.053(2) *	C(221)	-0.1740(5)	0.2293(2)	0.3651(3)	0.051(1) *
	C(122)	0.8073(6)	0.1693(3)	0.1349(2)	0.055(2) *	C(222)	-0.2325(5)	0.1909(2)	0.3139(3)	0.054(2) *
	C(123)	0.7985(6)	0.1601(3)	0.0719(2)	0.056(1) *	C(223)	-0.3152(5)	0.1457(2)	0.3324(3)	0.061(2) *
	C(124)	0.7115(6)	0.1083(3)	0.0515(2)	0.064(2) *	C(224)	-0.3079(5)	0.1562(2)	0.3952(3)	0.057(2) *
	C(125)	0.6666(6)	0.0856(3)	0.1018(2)	0.052(1) *	C(225)	-0.2206(5)	0.2079(2)	0.4154(3)	0.048(1) *
Cp2a ^c	C(131)	0.8198(12)	0.1740(6)	0.0953(7)	0.050(4) *	C(231)	-0.1907(12)	0.2234(6)	0.3424(7)	0.042(3) *
	C(132)	0.7516(12)	0.1311(6)	0.0499(7)	0.044(3) *	C(232)	-0.2653(12)	0.1713(6)	0.3108(7)	0.045(3) *
	C(133)	0.6800(12)	0.0876(6)	0.0778(7)	0.043(3) *	C(233)	-0.3242(12)	0.1386(6)	0.3522(7)	0.050(4) *
	C(134)	0.7039(12)	0.1037(6)	0.1404(7)	0.044(3) *	C(234)	-0.2860(12)	0.1705(6)	0.4094(7)	0.046(4) *
	C(135)	0.7903(12)	0.1571(6)	0.1513(7)	0.046(4) *	C(235)	-0.2035(12)	0.2229(6)	0.4033(7)	0.050(4) *
CH ₂	C(1p)	0.5244(5)	0.2634(2)	0.1907(2)	0.049(1) *	C(2p)	-0.0196(5)	0.0592(2)	0.2813(2)	0.048(1) *
Ph1	C(11p)	0.4070(5)	0.3423(2)	0.2676(2)	0.048(1) *	C(31p)	0.0932(5)	-0.0181(2)	0.2022(2)	0.047(1) *
	C(12p)	0.3262(6)	0.3924(3)	0.2784(3)	0.067(1) *	C(32p)	-0.0011(6)	0.0057(3)	0.1557(2)	0.059(1) *
	C(13p)	0.3362(8)	0.4184(4)	0.3350(3)	0.080(2) *	C(33p)	-0.0178(7)	-0.0181(3)	0.0973(3)	0.074(1) *
	C(14p)	0.4297(7)	0.3963(3)	0.3835(3)	0.079(1) *	C(34p)	0.0623(7)	-0.0671(3)	0.0833(3)	0.075(1) *
	C(15p)	0.5105(8)	0.3461(4)	0.3737(4)	0.082(2) *	C(35p)	0.1560(7)	-0.0902(3)	0.1278(3)	0.069(1) *
	C(16p)	0.4969(6)	0.3193(3)	0.3164(3)	0.061(1) *	C(36p)	0.1731(6)	-0.0665(3)	0.1874(3)	0.064(1) *
Ph2	C(21p)	0.3935(5)	0.3805(2)	0.1463(2)	0.051(1) *	C(41p)	0.1099(5)	-0.0572(2)	0.3246(2)	0.048(1) *
	C(22p)	0.4804(6)	0.4312(3)	0.1672(3)	0.068(1) *	C(42p)	0.0240(6)	-0.1077(3)	0.3045(3)	0.064(1) *
	C(23p)	0.4932(9)	0.4845(4)	0.1290(4)	0.091(2) *	C(43p)	0.0034(8)	-0.1572(4)	0.3443(3)	0.082(2) *
	C(24p)	0.4222(8)	0.4860(4)	0.0708(4)	0.090(2) *	C(44p)	0.0681(8)	-0.1552(4)	0.4050(3)	0.082(2) *
	C(25p)	0.3354(8)	0.4367(4)	0.0484(4)	0.085(2) *	C(45p)	0.1525(7)	-0.1088(3)	0.4242(3)	0.078(1) *
	C(26p)	0.3218(7)	0.3841(3)	0.0875(3)	0.085(2) *	C(46p)	0.1750(6)	-0.0590(3)	0.3842(2)	0.062(1) *

^a Labelling as given in Fig. 1 and used in Table 1.

^b *U*_{eq} = one third of the trace of the isotropic *U*_{ij} tensor; asterisks indicate isotropic *U*.

^c These two Cp groups are statistically ordered with sof for Cp(2) 0.70 and sof for Cp(2a) 0.30.

2b, the two methyl groups at tin are equivalent at room temperature. The temperature and concentration dependence of this process have not been investigated.

Summarizing the results of the NMR studies, it can be established that (i) as in the solid state **1b–3b** show in solution intramolecular donor–tin interactions and (ii) the coordination tendency of the donor groups is the same as in the solid state, namely $\text{Ph}_2\text{P} < \text{Me}_2\text{N} < \text{Ph}_2\text{P}(\text{O})$.

3. Experimental details

3.1. General comments

Where necessary, the reactions were carried out under an atmosphere of dry argon by using the Schlenk tube technique. The solvents were dried by standard methods and freshly distilled before use. The NMR spectra were recorded on Bruker AC 80, WP 80/DS and WP 200 spectrometers with respect to TMS (^1H , ^{13}C), 85% H_3PO_4 (^{31}P) and Me_4Sn (^{119}Sn). Low-field shifts are positive. Compound **1a** was synthesized from 2-LiFcCH₂NMe₂ and Me₃SnCl as described in the literature [15]. For a higher yield, 2-LiFcCH₂NMe₂ was isolated before its reaction with Me₃SnCl.

3.2. Synthesis of 2-(CH₃)₃SnC₁₀H₈FeCH₂N(CH₃)₃⁺ I⁻

To a solution of 8.6 g (20 mmol) of **1a** in 30 ml of dry methanol at 0°C, 4.3 g (30 mmol) of CH₃I in 10 ml

of methanol were added. After boiling the mixture for 5 min and cooling to room temperature, 50 ml of diethyl ether were added to precipitate the methiodide of **1a**: yield 9.5 g (87%); m.p. 197°C (decomp.). Anal. Found: C, 37.56; H, 5.25; I, 24.08. C₁₇H₂₈NiFeSn Calc.: C, 37.27; H, 5.15; I, 23.16%.

3.3. Synthesis of 2-(CH₃)₃SnC₁₀H₈FeCH₂P(C₆H₅)₂ (**2a**)

A mixture of 33.6 g (61 mmol) of 2-Me₃Sn-C₁₀H₈FeCH₂NMe₃⁺I⁻ and 22.8 g (122 mmol) of Ph₂PH in 600 ml of oxygen-free water buffered with 77 mmol Na₂HPO₄–NaH₂PO₄ was refluxed for 18 h. The aqueous solution was extracted with diethyl ether and the organic phase was dried over Na₂SO₄, filtered and evaporated. The remaining oil was heated at 120°C and 10⁻³ mmHg in a Kugelrohr distillation apparatus to remove the excess of Ph₂PH. After addition of ethanol the residue crystallizes. Recrystallization from ethanol yields 14 g (42%) of **2a** as orange crystals; m.p. 104°C. Anal. Found: C, 56.79; H, 5.43. C₂₆H₂₉PFeSn Calc.: C, 57.08; H, 5.34%.

3.4. Synthesis of 2-(CH₃)₃SnC₁₀H₈FeCH₂P(O)(C₆H₅)₂ (**3a**)

To 3.2 g (5.8 mmol) of **2a** in 50 ml of ethanol, 0.8 ml (7.7 mmol) of H₂O₂ (30%) were added. After heating the solution at 50–60°C for 30 min, the solvent was removed. Recrystallization from hexane yields 2.1

Table 5
Fractional atomic coordinates and equivalent isotropic thermal parameters for **1b** (orthorhombic $P2_12_12_1$) (e.s.d.s in parentheses)

Group ^a	Molecule (1)					Molecule (2)				
	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b (Å ²)	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} ^b (Å ²)
Sn	Sn(1)	0.24521(6)	0.53133(6)	0.05117(5)	0.0338(4)	Sn(2)	0.25475(6)	-0.03154(6)	0.44919(5)	0.0350(4)
Fe	Fe(1)	0.1438(1)	0.4234(1)	0.2277(1)	0.036(1)	Fe(2)	0.3531(1)	0.0761(1)	0.2710(1)	0.0367(9)
Cl	Cl(1)	0.3349(2)	0.3870(2)	0.0219(2)	0.057(1)	Cl(2)	0.1622(3)	0.1165(3)	0.4765(2)	0.076(2)
N	N(1)	0.1699(6)	0.6739(6)	0.1154(4)	0.035(1) *	N(2)	0.3461(6)	-0.1726(6)	0.3162(5)	0.035(1) *
Me1	C(11s)	0.3456(7)	0.6226(6)	-0.0083(5)	0.037(2) *	C(21s)	0.4019(11)	-0.0055(11)	0.5146(10)	0.087(5) *
Me2	C(12s)	0.1172(6)	0.5030(5)	-0.0124(4)	0.034(1) *	C(22s)	0.1413(9)	-0.1130(8)	0.5023(6)	0.051(3) *
Me3	C(13n)	0.2419(7)	0.7333(8)	0.1421(8)	0.055(3) *	C(23n)	0.2593(7)	-0.2372(8)	0.3614(7)	0.050(3) *
Me4	C(14n)	0.0942(8)	0.7217(8)	0.0551(7)	0.044(2) *	C(24n)	0.4041(10)	-0.2299(10)	0.4336(9)	0.062(3) *
Cp1	C(111)	0.2406(7)	0.5080(6)	0.1686(6)	0.028(2) *	C(211)	0.2570(9)	-0.0100(9)	0.3272(8)	0.041(2) *
	C(112)	0.1737(7)	0.5613(8)	0.2138(6)	0.033(2) *	C(212)	0.3300(10)	-0.0615(11)	0.2853(8)	0.052(3) *
	C(113)	0.1691(9)	0.5412(7)	0.2919(6)	0.046(2) *	C(213)	0.3048(7)	-0.0319(6)	0.2062(5)	0.038(1) *
	C(114)	0.2460(10)	0.4754(9)	0.2991(8)	0.059(3) *	C(214)	0.2333(7)	0.0358(6)	0.2050(6)	0.039(2) *
	C(115)	0.2943(7)	0.4559(7)	0.2269(5)	0.037(2) *	C(215)	0.2008(7)	0.0571(6)	0.2834(5)	0.035(2) *
Cp2	C(121)	0.0755(6)	0.3389(7)	0.1556(4)	0.050(2) *	C(221)	0.4245(6)	0.1599(7)	0.3528(4)	0.052(3) *
	C(122)	0.0039(6)	0.3946(7)	0.1942(4)	0.059(4) *	C(222)	0.4965(6)	0.1039(7)	0.3149(4)	0.049(3) *
	C(123)	0.0134(6)	0.3779(7)	0.2739(4)	0.063(3) *	C(223)	0.4917(6)	0.1239(7)	0.2354(4)	0.058(3) *
	C(124)	0.0910(6)	0.3119(7)	0.2846(4)	0.056(3) *	C(224)	0.4168(6)	0.1923(7)	0.2242(4)	0.054(2) *
	C(125)	0.1293(6)	0.2878(7)	0.2114(4)	0.045(2) *	C(225)	0.3752(6)	0.2145(7)	0.2968(4)	0.061(4) *
CH ₂	C(1n)	0.0961(7)	0.6317(6)	0.1675(5)	0.039(2) *	C(2n)	0.3876(6)	-0.1314(6)	0.3162(5)	0.035(1) *

^a Labelling as given in Fig. 2 and used in Table 1.

^b *U*_{eq} = one third of the trace of the isotropic *U*_{*ij*} tensor; asterisks indicate isotropic *U*.

g (64%) of **3a** as orange crystals; m.p. 142°C. IR (cm^{-1} , KBr), 1195 ($\nu_{\text{P}=\text{O}}$). Anal. Found: C, 55.42; H, 5.23. $\text{C}_{26}\text{H}_{29}\text{OPFeSn}$ Calc.: C, 55.47; H, 5.19%.

3.5. Synthesis of $2\text{-(CH}_3)_2\text{(Cl)SnC}_{10}\text{H}_8\text{FeCH}_2\text{N(CH}_3)_2$ (**1b**)

A 7.5 g (18.5 mmol) amount of **1a** and 3.7 g (18.6 mmol) of Me_3SnCl were slowly heated without solvent to 150°C and kept at this temperature for 2 h. The reaction product was dissolved in boiling diethyl ether and the solution filtered off. Evaporation of the solvent gives **1b** as orange–brown crystals: yield 5.2 g (66%); m.p. 122–125°C. Anal. Found: C, 42.12; H, 5.14; Cl, 8.22. $\text{C}_{15}\text{H}_{22}\text{NClFeSn}$ Calc.: C, 42.26; H, 5.20; Cl,

8.31%. NMR: ^{13}C (CDCl_3 , room temperature), δ 0.5 (s, SnCH_3), 45.3 (s, NCH_3), 60.2 (s, NCH_2), 69.4 (s, C_5H_5), 68.7, 69.7, 73.0, 75.0, 90.2 (s, C_5H_3). ^{13}C (CD_2Cl_2 , 233 K), δ 0.6 (s, SnCH_3), 44.1, 46.2 (s, NCH_3), 59.9 (s, NCH_2), 69.4 (s, C_5H_5), 68.5, 69.7, 72.6, 74.9, 90.0 (s, C_5H_3).

3.6. Synthesis of $(\text{CH}_3)_2\text{(Cl)SnC}_{10}\text{H}_8\text{FeCH}_2\text{P(C}_6\text{H}_5)_2$ (**2b**)

A solution of 2 g (3.5 mmol) of **2a** and an equimolar amount of Me_2SnCl_2 (0.77 g) in 50 ml of benzene was refluxed for 18 h. After evaporation of benzene and Me_3SnCl under high vacuum, the solid orange residue of **2b** was recrystallized from CH_2Cl_2 –hexane: yield 1.3 g (65%); m.p. 182°C. Anal. Found: C, 52.88; H,

Table 6
Fractional atomic coordinates and equivalent isotropic thermal parameters for **2b** and **3b** (triclinic *P*1) (e.s.d.s in parentheses)

Group ^a	2b					3b				
	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^b (\AA^2)	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^b (\AA^2)
Sn	Sn(1)	−0.15089(6)	0.85359(5)	0.72970(5)	0.0741(4)	Sn(1)	−0.17123(4)	0.85378(4)	0.74879(3)	0.0444(2)
Fe	Fe(1)	−0.3144(1)	0.66466(8)	0.57770(6)	0.0424(4)	Fe(1)	−0.3120(1)	0.66668(8)	0.57509(5)	0.0404(4)
P	P(1)	−0.5260(1)	0.9187(1)	0.8251(1)	0.0441(8)	P(1)	−0.5621(1)	0.9177(1)	0.8234(1)	0.0351(6)
Cl	Cl(1)	0.1013(2)	0.7670(3)	0.6454(2)	0.137(2)	Cl(1)	0.0882(2)	0.7427(2)	0.6755(2)	0.088(1)
O						O(1)	−0.4114(4)	0.9563(4)	0.8265(3)	0.046(2)
Me1	C(1s)	−0.1020(13)	0.8185(13)	0.8653(7)	0.125(3) *	C(1s)	−0.1237(9)	0.7987(8)	0.8891(5)	0.071(1) *
Me2	C(2s)	−0.1896(11)	1.0711(10)	0.6662(7)	0.100(2) *	C(2s)	−0.1679(9)	1.0651(8)	0.6754(5)	0.074(2) *
Cp1	C(11)	−0.2743(6)	0.7019(6)	0.7016(4)	0.043(1) *	C(11)	−0.2827(5)	0.7056(5)	0.7053(3)	0.035(1) *
	C(12)	−0.4365(6)	0.7207(5)	0.7004(3)	0.039(1) *	C(12)	−0.4396(5)	0.7198(5)	0.6992(3)	0.0319(9) *
	C(13)	−0.4717(7)	0.5863(6)	0.6835(4)	0.053(1) *	C(13)	−0.4676(6)	0.5857(5)	0.6780(4)	0.041(1) *
	C(14)	−0.3338(7)	0.4868(7)	0.6731(4)	0.053(1) *	C(14)	−0.3287(6)	0.4876(6)	0.6706(4)	0.047(1) *
	C(15)	−0.2112(7)	0.5556(6)	0.6844(4)	0.048(1) *	C(15)	−0.2136(6)	0.5593(6)	0.6867(4)	0.043(1) *
Cp2 ^c	C(21)	−0.2503(11)	0.8250(7)	0.4770(5)	0.068(2) *	C(21)	−0.2485(10)	0.8288(7)	0.4743(5)	0.069(2) *
	C(22)	−0.4045(11)	0.8067(7)	0.4758(5)	0.059(2) *	C(22)	−0.3960(10)	0.8079(7)	0.4687(5)	0.059(2) *
	C(23)	−0.4007(11)	0.6611(7)	0.4610(5)	0.064(2) *	C(23)	−0.3860(10)	0.6622(7)	0.4513(5)	0.064(2) *
	C(24)	−0.2441(11)	0.5894(7)	0.4530(5)	0.065(2) *	C(24)	−0.2323(10)	0.5930(7)	0.4461(5)	0.070(2) *
	C(25)	−0.1512(11)	0.6907(7)	0.4629(5)	0.073(2) *	C(25)	−0.1473(10)	0.6960(7)	0.4604(5)	0.076(2) *
Cp2a ^c	C(31)	−0.3316(36)	0.8413(18)	0.4771(16)	0.028(5) *	C(31)	−0.3193(27)	0.8442(15)	0.4746(15)	0.025(4) *
	C(32)	−0.4178(36)	0.7384(18)	0.4614(16)	0.098(14) *	C(32)	−0.4030(27)	0.7433(15)	0.4559(15)	0.092(13) *
	C(33)	−0.3146(36)	0.6053(18)	0.4502(16)	0.054(8) *	C(33)	−0.3026(27)	0.6093(15)	0.4445(15)	0.037(5) *
	C(34)	−0.1645(36)	0.6260(18)	0.4589(16)	0.055(8) *	C(34)	−0.1569(27)	0.6274(15)	0.4561(15)	0.041(5) *
	C(35)	−0.1750(36)	0.7718(18)	0.4755(16)	0.079(11) *	C(35)	−0.1672(27)	0.7725(15)	0.4748(15)	0.064(8) *
CH ₂	C(01p)	−0.5531(6)	0.8563(6)	0.7194(4)	0.044(1) *	C(01p)	−0.5583(5)	0.8550(5)	0.7121(3)	0.036(1) *
	C(11p)	−0.5927(6)	0.7827(6)	0.9165(4)	0.046(1) *	C(11p)	−0.6124(6)	0.7808(5)	0.9167(3)	0.038(1) *
	C(12p)	−0.6768(7)	0.6779(7)	0.9070(4)	0.056(1) *	C(12p)	−0.6917(6)	0.6750(6)	0.9052(4)	0.044(1) *
	C(13p)	−0.7200(8)	0.5747(8)	0.9813(5)	0.070(2) *	C(13p)	−0.7261(8)	0.5689(7)	0.9782(4)	0.057(1) *
	C(14p)	−0.6820(9)	0.5770(8)	1.0646(5)	0.075(2) *	C(14p)	−0.6815(8)	0.5860(7)	1.0651(5)	0.060(1) *
Ph2	C(15p)	−0.6015(9)	0.6768(9)	1.0763(6)	0.081(2) *	C(15p)	−0.6072(9)	0.6731(8)	1.0778(5)	0.069(1) *
	C(16p)	−0.5534(8)	0.7815(8)	1.0030(5)	0.068(1) *	C(16p)	−0.5711(7)	0.7807(7)	1.0038(4)	0.056(1) *
	C(21p)	−0.6829(6)	1.0737(5)	0.8348(4)	0.041(1) *	C(21p)	−0.7080(5)	1.0759(5)	0.8314(3)	0.037(1) *
	C(22p)	−0.6639(9)	1.2037(8)	0.7828(5)	0.069(1) *	C(22p)	−0.6729(7)	1.2107(7)	0.7951(4)	0.055(1) *
	C(23p)	−0.7808(9)	1.3254(9)	0.7867(5)	0.075(2) *	C(23p)	−0.7842(8)	1.3347(8)	0.7975(5)	0.067(1) *
	C(24p)	−0.9161(8)	1.3196(8)	0.8422(5)	0.065(1) *	C(24p)	−0.9294(8)	1.3232(8)	0.8368(5)	0.062(1) *
	C(25p)	−0.9394(10)	1.1893(9)	0.8966(6)	0.086(2) *	C(25p)	−0.9669(9)	1.1874(8)	0.8749(5)	0.073(2) *
C(26p)	−0.8232(9)	1.0692(9)	0.8930(5)	0.075(2) *	C(26p)	−0.8560(8)	1.0655(7)	0.8733(5)	0.060(1) *	

^a Labelling as given in Figs. 3 and 4 and used in Table 1.

^b U_{eq} = one third of the trace of the isotropic U_{ij} tensor; asterisks indicate isotropic U .

^c These two Cp groups are statistically ordered with sof for Cp2 0.80 and sof for Cp2a 0.20.

4.68; Cl, 6.33. $C_{25}H_{26}PClFeSn$ Calc.: C, 52.92; H, 4.68; Cl, 6.33%.

3.7. Synthesis of $(CH_3)_2(Cl)SnC_{10}H_8FeCH_2P(O)(C_6H_5)_2$ (**3b**)

A solution of 0.15 g (4.1 mmol) of hydrogen chloride in diethyl ether was added dropwise at room temperature to 1.8 g (3.2 mmol) of **3a** in 30 ml of methanol. After heating at 50°C for 30 min, the solvent was removed and the residue dissolved in CH_2Cl_2 . Addition of hexane causes the crystallization of **3b**. Recrystallization from CH_2Cl_2 -hexane yields 1.3 g (70%) orange crystals of **3b**; m.p. 207°C (decomp.). IR (cm^{-1} , KBr), 1147 ($\nu_{P=O}$). Anal. Found: C, 51.34; H, 4.62; Cl, 6.53. $C_{25}H_{26}OPClFeSnP$ Calc.: C, 51.46; H, 4.49; Cl, 6.08%.

3.8. Crystal structure determinations

Crystal data and details of intensity data collections and refinements are given in Table 3.

The crystals were obtained from several solvents: **1b** from toluene, **2a** from CH_2Cl_2 -hexane, **2b** from ethanol and **3b** from $CHCl_3$. They were fixed with glue and sealed in small glass capillaries. The quality and symmetry of the crystals were examined by Weissenberg exposures. Integrated intensities were measured on a CAD4 diffractometer (Enraf-Nonius).

The structures were solved by Patterson syntheses (Sn, Fe) and completed by Fourier syntheses (P, N, O, Cl, C). After weighted difference Fourier syntheses, a second unsubstituted Cp ring appeared for **2a** (site occupation factors (sof) 70:30) and for **2b** and **3b** (sof 80:20). The unsubstituted Cp ring in **1b** is only slightly disordered; relevant additional maxima could not be fully resolved (likewise additional maxima near to the methyl groups at Sn could not be resolved). All these unsubstituted Cp rings were fixed as regular pentagons. Hydrogen atoms are considered as riding on carbon atoms.

The refinements came out with good convergences and even distributions of the variances. Besides several locally written routines, local versions of SHELX-76 and SHELX-86 were used for the calculations (VAX-cluster at the Zentrum für Datenverarbeitung, Universität Mainz). Tables 4–6 give the final parameters.

4. Supplementary material

Tables of anisotropic thermal parameters and hydrogen atom coordinates, complete bond lengths, angles and torsion angles (7 pages for **1b**, 20 pages for **2a**, 11 pages for **2b**, 11 pages for **3b**) are available from M.D.

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