



Preparation and structural characterization of simple and donor-substituted triorganostannyl 1'-(diphenylphosphino)-1-ferrocenecarboxylates and their P-chalcogenide derivatives

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ABSTRACT

Triorganotin chlorides Me_3SnCl and $(\text{L}^{\text{NC}})\text{Me}_2\text{SnCl}$ ($\text{L}^{\text{NC}} = 2\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyl}$) reacted with potassium 1'-(diphenylphosphino)-1-ferrocenecarboxylate to give the respective carboxylates, $\text{Ph}_2\text{PfcCO}_2\text{SnMe}_3$ (**1**) and $\text{Ph}_2\text{PfcCO}_2\text{SnMe}_2(\text{L}^{\text{NC}})$ (**2**; fc = ferrocene-1,1'-diyl), while the analogous triphenylstannyl derivative **3** resulted by condensation of Ph_3SnOH with 1'-(diphenylphosphino)-1-ferrocenecarboxylic acid (Hdpf). Compounds **1** and **2** were smoothly oxidized with hydrogen peroxide or elemental sulfur to afford the corresponding P-chalcogen derivatives (P-oxides **1a** and **2a**; P-sulfides **1b** and **2b**). All compounds were characterized by multinuclear NMR, IR and mass spectroscopy, and the solid-state structures of **1**, **1a**, **2**, **2a** and **2b** were determined by single-crystal X-ray diffraction. In the crystal structures of **1** and **1a**, the tin atoms were found with distorted trigonal bipyramidal coordination environments completed by the C=O or P=O oxygens, respectively, from adjacent molecules, which in turn resulted in the formation of infinite linear assemblies. Tin atoms in **2**, **2a**, and **2b** were found with trigonal bipyramidal surrounding as well, though with the donor substituent L^{NC} assuming one of the axial donor sites. Compounds **2** and **2a** crystallized as stoichiometric hydrates (**2**·1/2H₂O, **2a**·H₂O), in which the water molecules served as hydrogen bond donors for the polar groups (C=O and P=O) and thus aided the formation of closed H-bonded assemblies; the structure of **2b** was essentially molecular.

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1. Introduction

Organotin(IV) carboxylates attracted considerable attention in both academia and industry because of their massive use as PVC stabilizers, biocides, catalysts, and also due to their newly discovered biological activity [1]. Apart from numerous application-directed studies, considerable attention has been devoted also to their structures that were shown to change broadly from simple discrete species to complicated supramolecular networks depending on the nature of tin and carboxylate substituents, tin-to-carboxylate stoichiometry, and with the presence of additional components such as donors or solvent of crystallization [2].

Stimulated by the seminal work of Ng and Zuckerman dealing with triorganostannyl esters of phosphorus-substituted acetic acids, $\text{Ph}_2\text{P}(\text{E})\text{CH}_2\text{CO}_2\text{SnR}_3$ (E/R = O/alkyls and Ph, S/Ph) and $(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CO}_2)_2\text{SnR}_2$ (R = Me, Ph) [3], their related phosphonium salts $[\text{Ph}_3\text{P}(\text{CH}_2)_2\text{CO}_2\text{SnR}_3]\text{X}$ (R = Me and Ph; X = various anions) [4], and also by the work of Cross et al. reporting the synthesis of $[\text{CH}_3\text{CH}(\text{P}(\text{O})\text{Ph}_2)\text{CO}_2]_{4-n}\text{SnR}_n$ (R = Me, Ph; n = 2, 3) [5,6], we have

recently prepared trimethylstannyl (diphenylphosphino)acetate and studied this compound in reactions with transition metal precursors leading to phosphinocarboxylate complexes [7]. Later, we expanded our study towards the synthesis and structural characterization of the related compounds possessing donor-functionalized $(\text{L}^{\text{NC}})\text{R}_2\text{Sn}$ groups (R = Me and Ph; $\text{L}^{\text{NC}} = 2\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyl}$) [8]. This follow-up study extends our previous work, reporting on the preparation and structural characterization of simple $(\text{SnR}_3, \text{R} = \text{Me and Ph})$ and $(\text{L}^{\text{NC}})\text{Me}_2\text{Sn}$ triorganotin carboxylates prepared from an organometallic carboxylic acid, viz 1'-(diphenylphosphino)-1-ferrocenecarboxylic acid (Hdpf) [9,10], and their P-chalcogenide derivatives (P=O and P=S).

2. Results and discussion

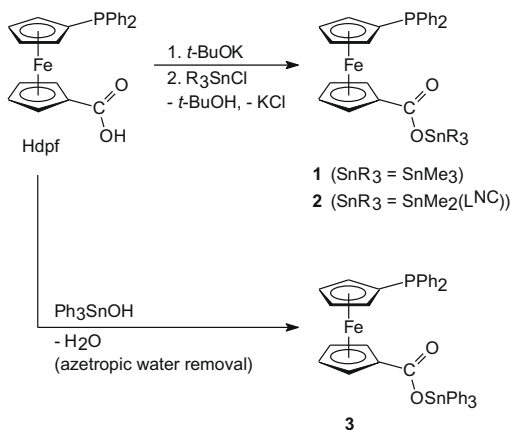
2.1. Syntheses and spectroscopic characterization

Metathesis reaction between stoichiometric amounts of triorganotin chloride and potassium 1'-(diphenylphosphino)-1-ferrocenecarboxylate, which was generated *in situ* from 1'-(diphenylphosphino)-1-ferrocenecarboxylic acid (Hdpf) and potassium *tert*-butoxide, followed by a removal of the formed

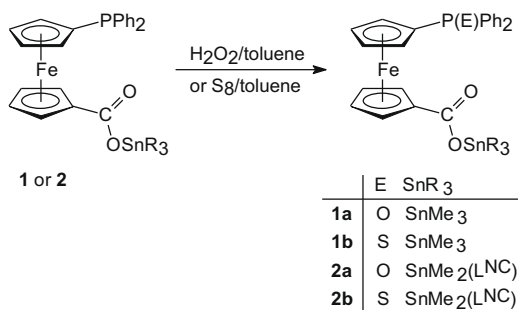
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KCl cleanly afforded the respective stannyl esters. The reaction proceeded equally well with trimethyltin chloride to give the simple ester **1** as well as with dimethyl[2-((dimethylamino)methyl)phenyl]tin chloride to provide the donor-functionalized carboxylate **2** (Scheme 1). Analogous triphenyltin ester **3** was conveniently prepared by condensation of Hdpf with triphenyltin hydroxide under azeotropic conditions (Scheme 1; see Refs. [3,11]). All compounds were isolated essentially pure and in excellent yields simply by evaporation. However, if appropriate, their further purification could be effected by crystallization, albeit with a considerable loss of the materials owing to a high solubility and general reluctance to crystallize.



Scheme 1. Preparation of stannyl esters **1–3** ($\text{L}^{\text{NC}} = 2\text{-}[(\text{dimethylamino})\text{methyl}]\text{phenyl}$).



Scheme 2. Preparation of P-chalcogenide derivatives from **1** and **2**.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **1** displayed signals typical for phosphinoferocecyl moiety, while the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum confirmed the presence of an uncoordinated phosphine group ($\delta_{\text{P}} -17.6$, cf. $\delta_{\text{P}} -17.6$ for Hdpf [9]). The trimethylstannyl moiety gave rise to singlets in both H-1 and C-13 spectra, flanked with diagnostic ^{117}Sn and ^{119}Sn satellites. Ratios of the observed spin-spin coupling constants, $^2J(^{119}\text{Sn}, ^1\text{H})/^2J(^{117}\text{Sn}, ^1\text{H}) = 1.04$ and $^1J(^{119}\text{Sn}, ^{13}\text{C})/^1J(^{117}\text{Sn}, ^{13}\text{C}) = 1.05$, were very close to the theoretical value determined by the ratio of magnetogyric factors ($\gamma(^{119}\text{Sn})/\gamma(^{117}\text{Sn}) = 1.05$). The $^{119}\text{Sn}\{^1\text{H}\}$ spectrum of **1** showed a single broad resonance at $\delta_{\text{Sn}} = +130$, thus suggesting the tin atom to remain tetracoordinate in the solution (cf. $\text{MeCO}_2\text{SnMe}_3$ in CDCl_3 : $\delta_{\text{Sn}} = 129$ [12]; see also Ref. [13]). NMR spectra of ester **3** were also not unexpected, indicating the presence of free phosphine group and tetracoordinate tin centers (cf. $\text{MeCO}_2\text{SnPh}_3$ in CDCl_3 : $\delta_{\text{Sn}} = -121$ [12]). Likewise, NMR spectra of **2** fully supported the formulation, showing additional bands due to the L^{NC} substituent, while the P-31 and Sn-119 NMR spectra suggested the presence of uncoordinated phosphine group ($\delta_{\text{P}} = -16.7$) and pentacoordinate tin centers ($\delta_{\text{Sn}} = -79$) in the solution [14]. In IR spectra, esters **1** and **3** displayed characteristic carboxylate bands (ν_{as}) at 1579 and 1535 cm^{-1} , respectively (cf. $\nu_{\text{C=O}}$ 1666 cm^{-1} for Hdpf, and 1710 cm^{-1} for its methyl ester [9]). The corresponding $\text{Sn}(\text{L}^{\text{NC}})\text{Me}_2$ ester showed the same vibration as a strong composite band at 1612/1601/1583 cm^{-1} .

Oxidations of phosphinocarboxylic esters **1** and **2** with aqueous hydrogen peroxide or sulfur cleanly produced the respective P-chalcogen derivatives (Scheme 2). Whereas the former reaction was advantageously performed in the biphasic toluene–hydrogen peroxide system, from which the product precipitated in essentially pure form, the sulfidation was accomplished by heating the stoichiometric amounts of the respective phosphine–ester with elemental sulfur in toluene.

NMR spectra of the chalcogenide derivatives confirmed the oxidation to affect only the phosphine moiety. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals appeared shifted to lower fields (**1a/2a**: $\delta_{\text{P}} 29.4/29.6$ and **1b/2b**: $\delta_{\text{P}} 41.5/41.9$) to positions similar to the corresponding Hdpf derivatives (HdpfO: $\delta_{\text{P}} 32.9$ [9] and HdpfS: $\delta_{\text{P}} 41.3$ [15]). Besides, the oxidation was manifested also in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, namely by shifts of the signals due to carbon atoms within the phosphorus-substituted rings and, particularly, by an increase in the J_{PC} coupling constants [16]. On the other hand, the $^{119}\text{Sn}\{^1\text{H}\}$ NMR response did not change much, indicating that the environments of the tin atoms remained unaltered upon oxidation. The carboxylate bands in IR spectra of the trimethylstannyl derivatives were observed slightly shifted when compared to parent **1** ($\nu_{\text{C=O}}$: **1a** > **1** > **1b**) and were composite. By contrast, the $\nu_{\text{C=O}}$ bands in

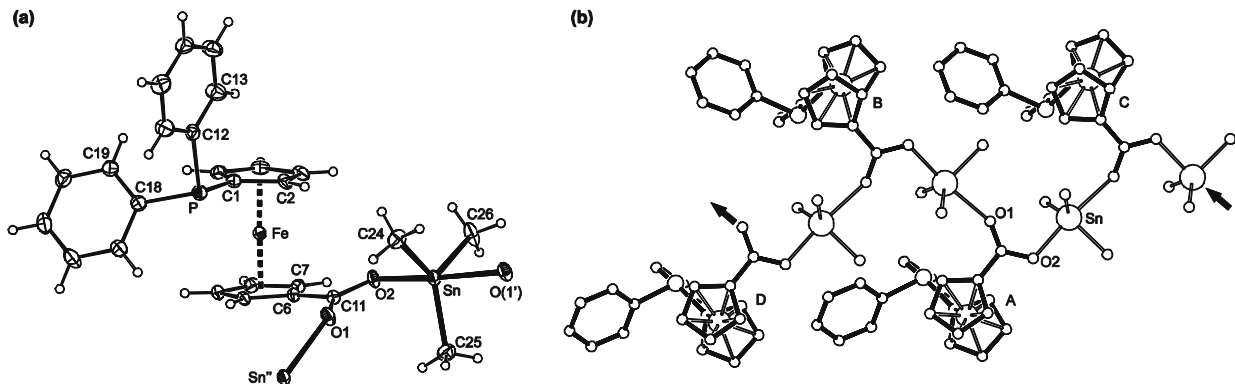


Fig. 1. (a) A view of the repeating unit in the structure of **1** showing the atom labeling scheme (displacement ellipsoids at the 30% probability level). (b) Section of the infinite chain in the structure of **1**. Symmetry operations: $A = (x, y, z)$, $B = (x, 1/2 - y, 1/2 + z)$, $C = (x, 1/2 - y, -1/2 + z)$, $D = (x, y, 1 + z)$. The arrows indicate the propagation of the molecular assembly.

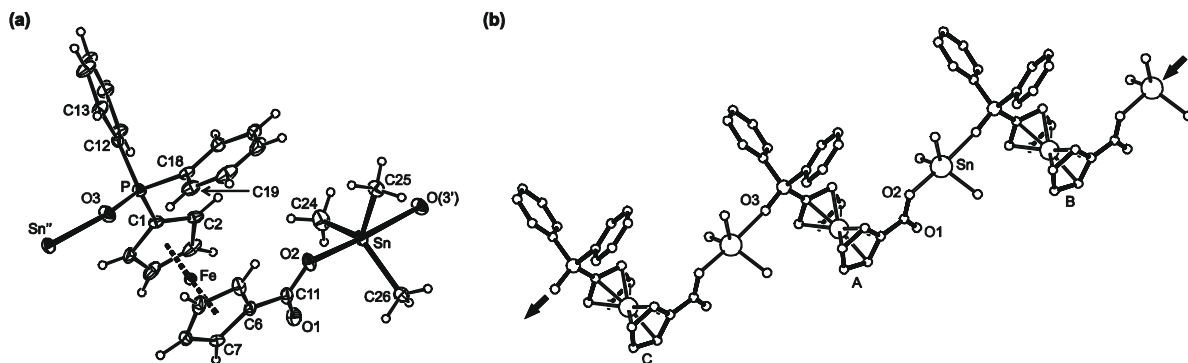


Fig. 2. (a) A view of the repeating unit in the crystal structure of **1a**. Displacement ellipsoids correspond to the 30% probability level. (b) Section of the infinite chain in the structure of **1a**. Symmetry operations: $A = (x, y, z)$, $B = (x - 1, y, z)$, and $C = (x + 1, y, z)$.

the spectra of P-chalcogenides obtained from **2** were not split (only shoulders being seen) and showed a different trend ($2a > 2b > 2$).

The solid-state structures of **1**, **1a**, **2**, **2a**, and **2b** have been established by single-crystal X-ray diffraction analysis. X-ray quality crystals were all obtained by crystallization from ethyl acetate/hexane. Attempted crystallization of **1b** afforded only few crystals of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{P}(\text{S})\text{Ph}_2)(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})]$ [15] as a product of accidental O–Sn bond cleavage.

2.2. Crystal structures of trimethylstannyl esters **1** and **1a**

Solid-state structures of esters **1** and **1a** are depicted in Figs. 1 and 2. Pertinent geometric data for both compounds are summarized in Table 1. In the structure of **1**, the tin atom is found with trigonal bipyramidal environment, made up from the covalently bonded methyl groups and carboxylate oxygen O2, and completed

by the C=O oxygen (O1') from a molecule related by the crystallographic glide plane. The bridging carboxylate is situated between the zig-zag distributed SnMe_3 units, whereas the phosphinoferrrocenyl moieties are located at the exterior of the infinite coordination chain (Fig. 1). It should be noted that such bridging coordination of the carboxylate moiety that coordinatively saturates the tin centers and simultaneously leads to a formation of supramolecular aggregates is relatively common among simple triorganotin carboxylates. The polymeric trimethyltin acetate [17] and 2-methoxybenzoate [18] may serve as representative examples.

The trigonal bipyramid around tin in **1** is severely distorted as evidenced by the structural descriptor introduced by Addison, Reedijk et al. being 0.77° [19], which can be accounted for by a protrusion of the non-bonded carboxylate oxygen atom into the coordination sphere of tin ($\text{Sn}\cdots\text{O}1$ 3.133(2) Å) [20]. The carboxyl plane is practically perpendicular to the plane defined by the tin-bound methyl carbons (the dihedral angle of the C(24–26) and {C11, O1, O2} planes being $86.8(3)^\circ$) and is directed in between the Sn–C24 and Sn–C25 bonds, bisecting the C24–Sn–C25 angle (N.B. As a consequence, the C26–Sn–O2 angle is more acute than the C(24/25)–Sn–O2 angles). In contrast, the three C(24–26)–Sn–O1' angles differ considerably less (by ca. 2°) and the 'axial' angle O2–Sn–O1' (ca. 174°) does not depart much from the ideal 180° . Whereas the Sn–C bond lengths in **1** vary only negligibly, the two Sn–O distances differ by as much as 0.25 Å in accordance with the different nature of the Sn ← O interactions. Accordingly, the tin is displaced by 0.124(1) Å from the plane of its bonding methyl groups towards the covalently attached O2.

Oxidation at phosphorus brings in another good donor atom into the structure of **1a**, which replaces the C=O oxygen in the coordination sphere of tin [21]. Thus, individual molecules in the crystal of **1a** assemble into infinite chains featuring pentacoordinate tin atoms but via coordination of the phosphoryl oxygen O3 from the molecule related by elemental translation. In this regard, the structures of **1** and **1a** parallel hydrogen bonding patterns observed for Hdpf and its phosphine oxide in case of which the oxidation at phosphorus resulted into the breakage of the ordinary carboxylic dimers and formation of infinite chains via $\text{O}-\text{H}\cdots\text{O}=\text{P}$ hydrogen bonds [9].

The Sn–O3' bond length in **1a** is similar to those reported for, e.g., the polymeric carboxylate $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CO}_2\text{SnPh}_3$ (Sn–O 2.397(3) Å) [22], or molecular adducts $2\text{-}[\text{C}_6\text{H}_5\text{C}(\text{O})\text{C}_6\text{H}_4\text{CO}_2\text{SnPh}_3\cdot\text{Ph}_3\text{PO}$ (Sn–O 2.402(3) Å) [23] and $1,2,3,4\text{-F}_4\text{C}_6\text{HCO}_2\text{SnPh}_3\cdot\text{Ph}_3\text{PO}$ (Sn–O 2.386(3) Å) [24]. On the other hand, both Sn–O bond in **1a** are somewhat shorter than those in **1** (by ca. 0.05 Å for the carboxylate oxygen O2 and by ca. 0.04 Å for the other oxygen atom (O1'/O3)), indicating a better donating ability of the phosphoryl oxygen or a reduced steric congestion (the structural descriptor mentioned above being 0.87). Similarly to **1**, the tin

Table 1
Selected geometric data for trimethylstannyl esters **1** and **1a** (in Å and $^\circ$).^a

Parameter	1 (E = O1)	1a (E = O3)
Sn–O2	2.183(2)	2.135(2)
Sn–E ^b	2.436(2)	2.397(2)
Sn–C24	2.123(3)	2.121(3)
Sn–C25	2.115(3)	2.127(3)
Sn–C26	2.117(3)	2.113(3)
O2–Sn–E ^c	174.04(6)	175.68(8)
C–Sn–C ^d	113.9(1)–127.7(1)	116.2(1)–123.2(1)
O2–Sn–C ^e	88.72(9)–95.31(9)	90.5(1)–98.4(1)
E–Sn–C ^f	85.32(9)–87.41(9)	84.3(1)–85.3(1)
Fe–Cg1	1.644(1)	1.639(1)
Fe–Cg2	1.655(1)	1.644(2)
$\angle\text{Cp}1, \text{Cp}2$	3.0(1)	4.4(2)
τ^g	85	124
P–C1	1.820(2)	1.766(3)
P–C12	1.834(3)	1.799(3)
P–C18	1.835(3)	1.807(3)
P–O3	n.a.	1.500(2)
C6–C11	1.475(3)	1.490(5)
C11–O1	1.248(3)	1.234(4)
C11–O2	1.290(3)	1.301(4)
O1–C11–O2	122.6(2)	125.1(3)
C11–O2–Sn	118.7(1)	118.4(2)
φ^h	19.7(3)	6.4(4)

^a The ring planes are defined as follows: Cp1 = C(1–5), Cp2 = C(6–10); Cg1 and Cg2 are the respective ring centroids.

^b Sn–O1' distance for **1a**: $i = (x, 1/2 - y, z - 1/2)$ and $ii = (x - 1, y, z)$.

^c O2–Sn–O1' angle for **1** and O2–Sn–O3ⁱⁱ angle for **1a**.

^d The range of C24–Sn–C(25, 26) and C25–Sn–C26 angles.

^e The range of O2–Sn–C(24–26) angles.

^f The range of O1'–Sn–C(24–26) angles for **1**, the range of O3ⁱⁱ–Sn–C(24–26) angles for **1a**.

^g Torsion angle C1–Cg1–Cg2–C6.

^h Dihedral angle of the Cp2 and {C11, O1, O2} planes.

atom in **1a** is moved out of the plane of the methyl groups towards O2 (by 0.196(1) Å) and the carboxyl plane is nearly perpendicular to the equatorial plane (dihedral angle 86.5(3)°), pointing into the C24–Sn–C26 wedge (cf. the trend in the O2–Sn–C(24–26) angles: C26 ≈ C24 > C25; the O3'–Sn–C(24–26) angles differ by only 1°).

The ferrocene units in the structures of **1** and **1a** do not exert any unexpected features when compared with the structures of the parent acids [9]. The carboxyl group in **1a** retains some localized bond character ($\Delta = 0.067$ Å), whereas the bridging coordination in the case of **1** ensues in a partial leveling of the C–O bond lengths ($\Delta = 0.042$ Å; cf. 0.129 Å for Hdpf methyl ester [9], and <0.001 Å for $[(\eta^5\text{-C}_5\text{HMe}_4)_2\text{Ti}(\text{dpf}-\kappa^2\text{O},\text{O}')] [25]$). Finally, the ferrocene moiety in **1a** assumes a more opened conformation than that in **1** (cf. $\tau = 85^\circ$ for **1**, and 124° for **1a**), which brings the attached donor moieties into a position more appropriate for linear propagation of the coordination array.

2.3. Crystal structures of the dimethyl[2-((dimethylamino)methyl)phenyl]stannyl esters **2a**, and **2b**

Views of the molecular structures of **2a**, and **2b** are presented in Figs. 3–5 and the selected geometric data are given in Table 2.

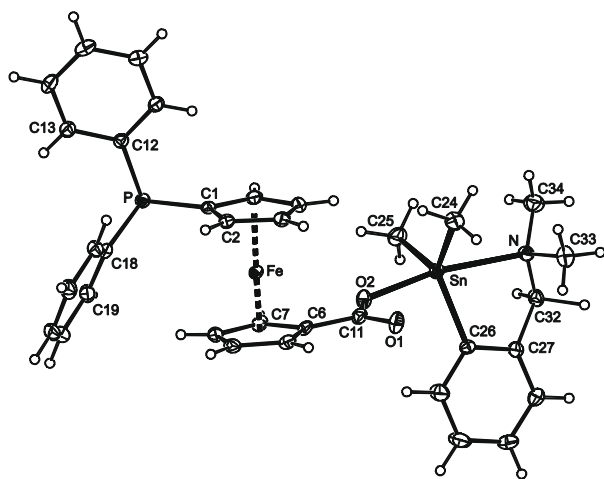


Fig. 3. A view of the molecular structure of **2** showing the atom labeling scheme. Displacement ellipsoids enclose the 30% probability level. For clarity, only one orientation of the disordered CH_2NMe_2 arm is shown (see Section 4).

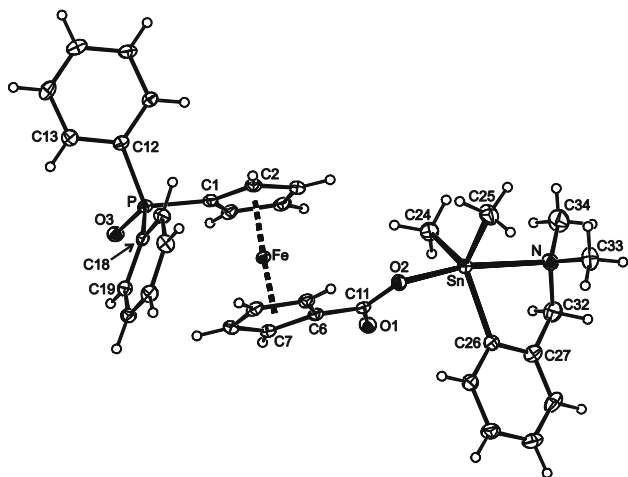


Fig. 4. A view of the molecular structure of **2a** at the 30% probability level.

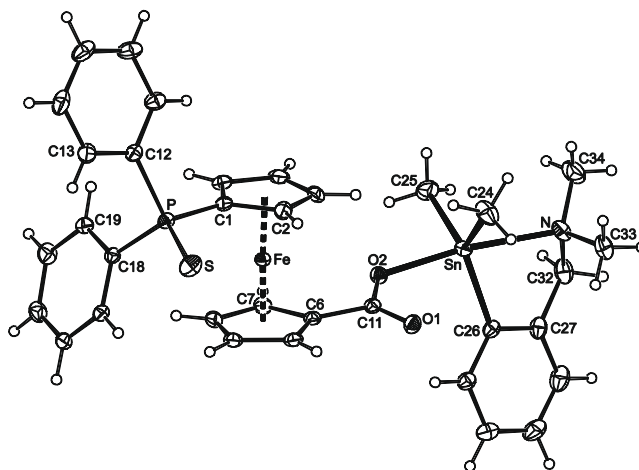


Fig. 5. A view of the molecular structure of **2b** at the 30% probability level.

Table 2

Selected geometric data for **2a** and **2b** (in Å and °).^a

Parameter	2 (E = void)	2a (E = O3)	2b (E = S)
Sn–O2	2.142(2)	2.147(3)	2.135(2)
Sn–N	2.515(3)	2.508(3)	2.498(3)
Sn–C24	2.121(3)	2.115(4)	2.121(3)
Sn–C25	2.128(4)	2.127(4)	2.126(4)
Sn–C26	2.139(3)	2.135(4)	2.140(3)
O2–Sn–N	170.29(8)	167.86(9)	169.41(8)
O2–Sn–C ^b	90.4(1)–96.5(1)	88.4(1)–99.8(2)	87.9(1)–99.4(1)
N–Sn–C ^c	75.32(9)–93.7(1)	74.7(1)–91.5(2)	74.90(9)–91.5(1)
C–Sn–C ^d	112.5(1)–128.8(1)	114.6(2)–122.0(2)	115.2(2)–125.7(1)
Fe–Cg1	1.642(1)	1.644(2)	1.643(1)
Fe–Cg2	1.649(1)	1.648(2)	1.642(1)
∠Cp1, Cp2	2.8(2)	3.5(2)	2.6(2)
τ^e	143	169	160
P–C1	1.812(3)	1.780(4)	1.795(3)
P–C12	1.841(3)	1.806(4)	1.817(3)
P–C18	1.833(4)	1.808(3)	1.817(3)
P–E	n.a.	1.497(3)	1.953(1)
C6–C11	1.475(4)	1.476(5)	1.486(4)
C11–O1	1.234(3)	1.231(5)	1.232(3)
C11–O2	1.297(4)	1.302(4)	1.299(3)
O1–C11–O2	124.4(3)	123.4(3)	124.1(2)
C11–O2–Sn	121.8(2)	115.1(2)	116.8(2)
ϕ^f	5.2(4)	11.3(4)	12.2(3)

^a The ring planes are defined as follows: Cp1 = C(1–5), Cp2 = C(6–10); Cg1 and Cg2 denote the respective ring centroids.

^b The range of O2–Sn–C(24–26) angles.

^c The range of N–Sn–C(24–26) angles.

^d The range of C24–Sn–C(25, 26) and C25–Sn–C26 angles.

^e Torsion angle C1–Cg1–Cg2–C6.

^f Dihedral angle of the Cp2 and {C11, O1, O2} planes.

Whereas compound **2b** resulted unsolvated, forming an essentially molecular crystal assembly [26], its corresponding phosphine and phosphine oxide separated as defined hydrates, **2**·1/2H₂O and **2a**·H₂O [27]. In the case of **2**·1/2H₂O, the water molecules are disordered over two equally populated sites lying across the crystallographic inversion centers and form a closed hydrogen-bonded array with carbonyl oxygens from two inversion-related molecules of the ester (Fig. 6a) [28]. The crystal assembly of **2a**·H₂O (Fig. 6b) is rather similar. However, it is generated through interactions between the phosphoryl oxygen atoms and two molecules of solvating water [29].

Molecular parameters of **2a**, and **2b** do not depart much from those of the (diphenylphosphino)acetate derivatives studied earlier [8]. The tin atoms are found with distorted trigonal bipyramidal environments, showing unlike Sn–donor bond lengths (Sn–N ≈ Sn–C ≫ Sn–O) and pronounced angular deformation due to

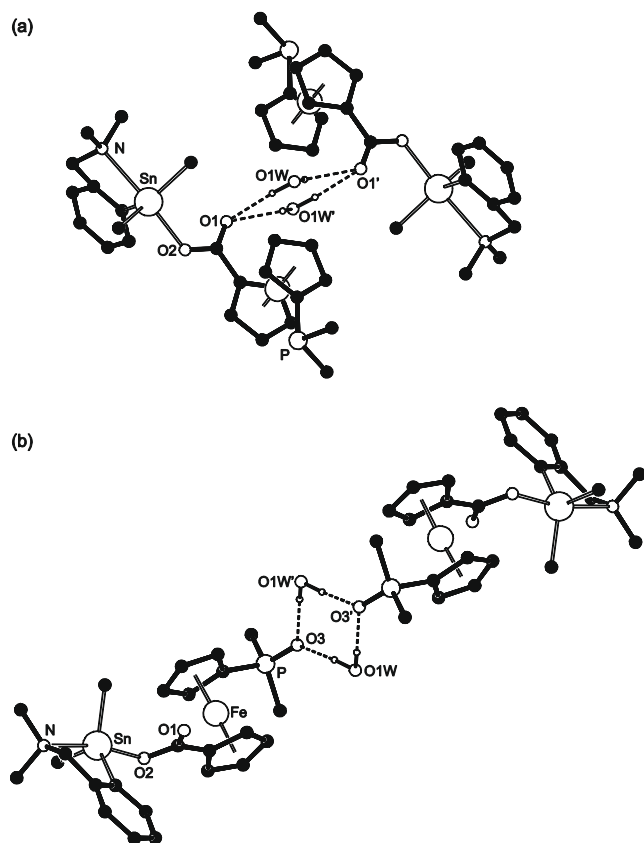


Fig. 6. The basic hydrogen-bonded assemblies in the crystal structures of (a) phosphine-ester **2** and (b) phosphine oxide-ester **2a**. Irrelevant hydrogens and some phenyl ring carbons atoms were omitted for clarity. Hydrogen bond parameters for **2**: O1W–H1W...O1', O1W...O1' = 2.808(7) Å, angle at H1W = 156(10)°; O1W–H2W...O1, O1W...O1 = 2.891(7) Å, angle at H2W = 128(7)°. Hydrogen bond parameters for **2a**: O1W–H1W...O3, O1W...O3 = 2.806(4) Å, angle at H1W = 164°; O1W–H2W...O3', O1W...O3' = 2.887(4) Å, angle at H2W = 162°. Prime-labeled atoms related by crystallographic inversion operations.

an interference of the second carboxylate oxygen (Sn...O1 3.0–3.2 Å in the series) and, *mainly*, the small size of the (L^{NC})Sn ring. The aforementioned structural descriptor [19] takes the values 0.69, 0.76, and 0.73 for **2**, **2a**, and **2b**, respectively. In all cases, the nitrogen atom deviates from the axis of the trigonal bipyramid around tin, being inclined towards the metallacycle (cf. N–Sn–O2 angles in Table 2, and the angles subtended by the Sn–O2/Sn–N vectors: 9.71(6)° for **2**, 12.15(7)° for **2a**, and 10.59(6)° for **2b**). Similarly to simple esters, the tin atoms are displaced from the planes of their bonding carbon atoms (C24–C26) towards O2 (by 0.154(1) Å for **2**, 0.167(1) Å for **2a**, and 0.172(1) Å for **2b**), which indeed corresponds with the bond strengths (Sn–O vs. Sn–N). The metallacycles assume approximate envelope conformation with the methylene carbon C32 projecting out of the plane of the remaining ring atoms. The C(26–31) phenyl ring is directed away from the ferrocene unit and almost perpendicular to the Cp2 plane (the dihedral angles of the C(26–31) and Cp2 ring planes being 87.8(2), 83.0(2), and 78.9(2) for **2**, **2a**, and **2b**, respectively).

The ferrocenyl moieties adopt regular geometries with negligible tilts (below 4°) and exert practically identical Fe–ring centroid distances. The overall geometries compare well with those of Hdpf and its respective P-chalcogenides [9,15]. In all cases, the carboxyl groups deviate slightly from coplanarity with the planes of their parent cyclopentadienyl ring (**2** < **2a** ≈ **2b**; dihedral angle max. ca. 12°). The phosphorus substituents, not interacting with the organotin residue, are rotated away from the carboxyl groups to assume an ideal anti-eclipsed conformation in **2** and even more

opened intermediate conformations in the P-chalcogenides **2a** and **2b** that possess the bulkier phosphorus substituents.

3. Conclusions

Triorganostannyl 1'-(diphenylphosphino)-1-ferrocenecarboxylates, Ph₂PfcCO₂SnR₃, are readily accessible via salt metathesis between potassium 1'-(diphenylphosphino)-1-ferrocenecarboxylate and the corresponding triorganotin chloride or, alternatively, from condensation of a triorganotin hydroxide with 1'-(diphenylphosphino)-1-ferrocenecarboxylic acid. Subsequent oxidation of the phosphine moiety affords the corresponding phosphine-oxides and sulfides. Compounds with simple ester groups (R = Me and Ph) are monomeric in solution featuring tetracoordinate tin centers whereas, in the solid state, they aggregate to increase the coordination number of tin via interactions with donor atoms from adjacent molecules (see the crystal structures of **1** and **1a**). On the other hand, compounds bearing the L^{NC} substituent at tin remain penta-coordinate in both solution and the solid state. Their uncoordinated polar atoms, however, may draw water molecules into their crystals, with which they form hydrogen-bonded assemblies.

4. Experimental

4.1. Materials and methods

The preparations of **1–3** were carried out under argon atmosphere. Other syntheses (oxidations) were performed in the air. Solvents used for the syntheses were dried over the appropriate drying agents (CH₂Cl₂: anhydrous potassium carbonate and toluene: potassium metal) and distilled under argon. Solvents utilized during the work-up and in crystallizations were used without any purification. Hdpf [9], dimethyl[2-((dimethylamino)methyl)phenyl]tin chloride [30], and triphenyltin hydroxide [31] were prepared as described elsewhere. Other chemicals were used as received (Fluka, Aldrich; solvents from Lach-ner).

NMR spectra were recorded with a Varian Unity Inova 400 spectrometer at 25 °C (¹H, 399.95; ¹³C, 100.58; ³¹P, 161.90; and ¹¹⁹Sn, 149.14 MHz). Proton decoupled tin-119 NMR spectra were recorded in inverse gated broadband decoupling mode. Chemical shifts (δ/ppm) are given relative to internal SiMe₄ (¹³C and ¹H), to external 85% aqueous H₃PO₄ (³¹P), or to external neat SnMe₄ (¹¹⁹Sn). In addition to the standard notation of the signal multiplicity, vt and vq are used to distinguish virtual multiplets arising from the spin systems of the substituted cyclopentadienyl rings (AA'BB' for C₅H₄CO₂ and AA'BB'X for C₅H₄PPh₂); fc = ferrocene-1,1'-diyl. (Note: Tin satellites in the ¹³C{¹H} NMR spectra of SnMe₂(L^{NC}) esters could not be all unequivocally identified and, hence, the J_{SnC} coupling constants are not given.) IR spectra were measured with an FT-IR Nicolet Magna 650 spectrometer in the range 4000–400 cm⁻¹. Electron impact (EI) and electrospray (ESI) mass spectra were recorded with a GCT Premier (Waters) and a LTQ Orbitrap XL (Thermo Fisher Scientific) instruments, respectively. Samples for ESI measurements were dissolved in methanol. Composition of the fragment ions was confirmed by a comparison of the experimental isotopic distributions with the calculated patterns.

4.2. Preparation of trimethylstannyl 1'-(diphenylphosphino)-1-ferrocenecarboxylate (**1**)

Potassium *tert*-butoxide (224 mg, 2.0 mmol) was added to a solution of 1'-(diphenylphosphino)-1-ferrocenecarboxylic acid (Hdpf; 828 mg, 2.0 mmol) in dry dichloromethane (30 mL). The mixture was stirred at room temperature for 30 min, whereupon it deposited potassium salt of Hdpf as a yellow orange precipitate.

Then, a solution of trimethyltin chloride (400 mg, 2.0 mmol) in dichloromethane (10 mL) was introduced. The most of the precipitated salt quickly dissolved and some fine precipitate (KCl) began to form. After stirring overnight, the reaction mixture was diluted with pentane (30 mL), allowed to stand for 30 min, and filtered through a pad of diatomaceous earth (Celite). Subsequent evaporation afforded **1** as a rusty orange-brown solid. Yield: 1.078 g (93%). The product is essentially pure. However, if necessary, it can be crystallized from hot heptane or from ethyl acetate–hexane.

^1H NMR (CDCl_3): δ 0.59 (s with tin satellites: $^2J(^{119}\text{Sn}, \text{H}) = 58.4$, $^2J(^{117}\text{Sn}, \text{H}) = 56.0$ Hz; 9H, SnMe_3), 4.12 (vt, $J' = 1.8$ Hz, 2H), 4.21 (vt, $J' = 1.9$ Hz, 2H), 4.35 (vt, $J' = 1.8$ Hz, 2H), 4.67 (vt, $J' = 1.9$ Hz, 2H) (fc); 7.28–7.39 (m, 10H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ –2.09 (s with tin satellites: $^1J(^{119}\text{Sn}, \text{C}) = 400$, $^2J(^{117}\text{Sn}, \text{H}) = 382$ Hz; SnMe_3), 71.51 (s), 72.45 (d, $J_{\text{PC}} \approx 2$ Hz), 73.04 (d, $J_{\text{PC}} = 4$ Hz) (CH of fc); 73.29 (C–CO of fc), 74.04 (d, $J_{\text{PC}} = 14$ Hz, CH of fc), 77.49 (d, $J_{\text{PC}} = 8$ Hz, C– PPh_2 of fc), 128.16 (d, $J_{\text{PC}} = 7$ Hz), 128.53 (s), 133.45 (d, $J_{\text{PC}} = 20$ Hz) (CH of PPh_2); 138.68 (d, $J_{\text{PC}} = 10$ Hz, C_{ipso} of PPh_2), 176.28 (s, C=O). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ –17.6 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ 130.0 (s). IR (Nujol): ν 1579 vs (with a shoulder), 1337 s, 1183 s, 1159 m, 1093 w, 1068 w, 1027 s, 998 w, 921 w, 889 w, 834 m, 826 m, 786 br s, 753 m, 738 m, 702 w, 695 s, 633 w, 610 m, 594 w, 575 m, 552 m, 525 m, 511 w, 502 m, 487 s, 457 w, 449 cm^{-1} . MS (ESI+): 579 ($[\text{M}+\text{H}]^+$), 601 ($[\text{M}+\text{Na}]^+$), 617 ($[\text{M}+\text{K}]^+$), 741 ($[\text{M}+\text{SnMe}_3]^+$). HR MS (ESI+) calc. for $\text{C}_{26}\text{H}_{28}^{56}\text{FeO}_2\text{P}^{120}\text{Sn}$ ($[\text{M}+\text{H}]^+$): 579.0193, found: 579.0194. Anal. Calc. for $\text{C}_{26}\text{H}_{27}\text{FeO}_2\text{PSn}$: C, 54.12; H, 4.72. Found: C, 54.15; H, 4.73%.

4.3. Preparation of dimethyl[2-((dimethylamino)methyl)phenyl]stannyl 1'-(diphenylphosphino)-1-ferrocenecarboxylate (**2**)

Potassium *tert*-butoxide (112 mg, 1.0 mmol) was added to a solution of Hdpf (414 mg, 1.0 mmol) in dry dichloromethane (15 mL). The resulting mixture was sonicated for 5 min and then stirred for 30 min. To the suspension of the *in situ* formed carboxylate salt (Kdpf), a solution of dimethyl[2-((dimethylamino)methyl)phenyl]tin chloride (319 mg, 1.0 mmol) in dichloromethane (10 mL) was introduced. The precipitated salt dissolved to give a cloudy orange solution, which was stirred for 20 h at room temperature and then diluted with pentane (25 mL). The resulting mixture was allowed to stand for 30 min and filtered through diatomaceous earth (Celite). The filtrate was evaporated and the residue dried under vacuum to afford **2** as an orange glassy solid. Yield: 0.632 g (91%).

^1H NMR (CDCl_3): δ 0.69 (s with tin satellites: $^2J(^{119}\text{Sn}, \text{H}) = 67.1$, $^2J(^{117}\text{Sn}, \text{H}) = 62.9$ Hz; 6H, SnMe_2), 2.30 (s, 6H, NMe_2), 3.61 (s with unresolved tin satellites, 2H, NCH_2), 4.14–4.17 (m, 4H), 4.41 (vt, $J' = 1.8$ Hz, 2H), 4.71 (vt, $J' = 1.8$ Hz, 2H) (fc); 7.08–8.17 (m, 14 H, $\text{C}_6\text{H}_4 + \text{PPh}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ –2.91 (s with tin satellites: $^1J(^{119}\text{Sn}, \text{C}) = 541$, $^2J(^{117}\text{Sn}, \text{H}) = 513$ Hz; SnMe_2), 45.27 (s, NMe_2), 65.05 (s, NCH_2), 71.27 (s), 71.74 (s), 73.05 (d, $J_{\text{PC}} = 4$ Hz), 73.81 (d, $J_{\text{PC}} = 15$ Hz) (CH of fc); 126.66 (s, CH of C_6H_4), 127.81 (s, CH of C_6H_4), 128.10 (d, $J_{\text{PC}} = 7$ Hz, CH of PPh_2), 128.42 (s, CH of PPh_2), 129.08 (CH of C_6H_4), 133.46 (d, $J_{\text{PC}} = 20$ Hz, CH of PPh_2), 137.58 (CH of C_6H_4), 139.03 (d, $J_{\text{PC}} = 10$ Hz, C_{ipso} of PPh_2), 141.70 (s, C_{ipso} of C_6H_4), 142.50 (s, C_{ipso} of C_6H_4), 175.26 (s, C=O). The C_{ipso} of fc were not found. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ –16.7 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ –79.0 (s). IR (Nujol): ν 3520 w, 1707 w, 1612 s, 1601 s, 1583 m, 1349 m, 1326 vs, 1180 m, 1158 m, 1096 w, 1031 m, 1025 m, 1008 w, 979 w, 918 w, 832 s, 798 s, 774 s, 746 vs, 700vs, 633w, 609 w, 578 m, 543 m, 517 m, 508 s, 491 s, 467 m, 450 m, 421 w cm^{-1} . MS (EI+): m/z (relative abundance) 713 ($[\text{M}+\text{O}]^+$), 697 (20, M^+), 682 (40, $[\text{M}-\text{Me}]^+$), 654 (7), 414 (19, Hdpf^+), 284 (100, $[\text{SnMe}_2(\text{L}^{\text{NC}})]^+$). HR MS (EI+) calc. for $\text{C}_{34}\text{H}_{36}^{56}\text{FeNO}_2\text{P}^{120}\text{Sn}$ (M^+): 697.0855, found: 697.0859.

4.4. Preparation of triphenylstannyl 1'-(diphenylphosphino)-1-ferrocenecarboxylate (**3**)

Triphenylstannyl hydroxide (367 mg, 1.0 mmol) and Hdpf (414 mg, 1.0 mmol) were suspended in dry toluene (20 mL) and the mixture was heated under Dean-Stark trap, yielding quickly a clear solution. After refluxing for 3 h, the reaction mixture was cooled, filtered and evaporated under vacuum to give ester **3** in quantitative yield. The product is essentially pure but has a strong tendency to hold the reaction solvent.

^1H NMR (CDCl_3): δ 4.00 (vt, $J' = 1.8$ Hz, 2H), 4.13 (br vt, 2H), 4.24 (vt, $J' = 2.0$ Hz, 2H), 4.77 (vt, $J' = 2.0$ Hz, 2H) (fc); 7.27–7.92 (m, 25H, PPh_2 and SnPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 71.89 (s), 72.87 (d, $J_{\text{PC}} \approx 1$ Hz), 73.03 (d, $J_{\text{PC}} = 4$ Hz), 74.05 (d, $J_{\text{PC}} = 14$ Hz) (CH of fc); 77.53 (d, $J_{\text{PC}} = 9$ Hz, C– PPh_2 of fc), 128.13 (d, $J_{\text{PC}} = 7$ Hz, CH of PPh_2), 128.52 (s, CH of PPh_2), 128.84 (s with Sn satellites: $J_{\text{SnC}} = 64$ Hz, CH of SnPh_3), 130.06 (s with Sn satellites: $J_{\text{SnC}} = 13$ Hz, CH of SnPh_3), 133.41 (d, $J_{\text{PC}} = 20$ Hz, CH of PPh_2), 136.97 (s with Sn satellites: $J_{\text{SnC}} = 48$ Hz, CH of SnPh_3), 138.64 (d, $J_{\text{PC}} = 10$ Hz, C_{ipso} of PPh_2), 138.64 (s, C_{ipso} of SnPh_3 ; Sn satellites not found), 177.78 (br s, C=O). The resonance due C–CO of fc was not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ –17.3 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ –115.0 (s). IR (Nujol): ν 1535 s br, 1317 s br, 1193 m, 1160 s, 1096 w, 1076 m, 1026 s, 997 m, 922 m, 834 m, 817 m, 788 m, 729 vs, 696 vs, 679 w, 568 w, 503 s br, 449 cm^{-1} . MS (EI+): m/z (relative abundance) 764 (28, M^+), 735 (36), 687 (19, $[\text{M}-\text{Ph}]^+$), 659 (100, $[\text{M}-\text{Ph}-\text{CO}]^+$), 414 (97, Hdpf^+), 370 (27, FcPPh_2^+), 321 (59, $[\text{Ph}_2\text{PC}_3\text{H}_4\text{FeO}]^+$). HR MS (EI+) calc. for $\text{C}_{41}\text{H}_{33}^{56}\text{FeO}_2\text{P}^{120}\text{Sn}$ (M^+): 764.0590, found: 764.0599.

4.5. Preparation of trimethylstannyl 1'-(diphenylphosphinoyl)-1-ferrocenecarboxylate (**1a**)

Compound **1** (57.5 mg, 0.10 mmol) was dissolved in warm toluene (5 mL). After cooling to room temperature, 30% aqueous hydrogen peroxide (3 drops) was added and the heterogeneous mixture was vigorously stirred for 2 days. The precipitated product was filtered off, washed with water and pentane, and dried under vacuum to give **1a** as an orange solid. Yield: 48 mg (81%).

^1H NMR (CDCl_3): δ 0.58 (s with tin satellites: $^2J(^{119}\text{Sn}, \text{H}) = 58.7$, $^2J(^{117}\text{Sn}, \text{H}) = 56.3$ Hz; 9H, SnMe_3), 4.42 (m, 4H), 4.45 (br m, 2H), 4.73 (br s, 2H) (fc); 7.42–7.71 (m, 10 H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ –2.03 (s, SnMe_3), 71.95 (s), 73.00 (s), 73.38 (d, $J_{\text{PC}} = 12$ Hz), 74.20 (d, $J_{\text{PC}} = 10$ Hz) (CH of fc); 128.28 (d, $J_{\text{PC}} = 13$ Hz), 131.41 (d, $J_{\text{PC}} = 10$ Hz), 131.65 (d, $J_{\text{PC}} = 2$ Hz) (CH of $\text{P}(\text{O})\text{Ph}_2$); 133.98 (br d, $J_{\text{PC}} \approx 110$ Hz, C_{ipso} of $\text{P}(\text{O})\text{Ph}_2$), 175.8 (br s, C=O). Resonances due to ferrocene C_{ipso} were not found due to overlaps or broadening. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 29.4 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ 132.1 (s). IR (Nujol): ν 3524 br w, 3200 br w, 1614 vs, 1590 vs, 1331 vs, 1308 m, 1197 s, 1183 vs, 1165 vs, 1119 m, 1100 m, 1071 w, 1058 w, 1040 w, 1028 s, 997 w, 922 w, 935 m, 824 m, 800 m, 777 s, 754 m, 740 m, 724 s, 704 s, 696 m, 633 w, 617 w, 569 vs, 546 m, 529 s, 508 s, 501 m, 484 m, 448 cm^{-1} . MS (ESI+): 595 ($[\text{M}+\text{H}]^+$), 617 ($[\text{M}+\text{Na}]^+$), 757 ($[\text{M}+\text{SnMe}_3]^+$). HR MS (ESI+) calc. for $\text{C}_{26}\text{H}_{27}^{56}\text{FeO}_3\text{P}^{120}\text{SnNa}$ ($[\text{M}+\text{Na}]^+$): 616.9961, found: 616.9971.

4.6. Preparation of trimethylstannyl 1'-(diphenylthiophosphoryl)-1-ferrocenecarboxylate (**1b**)

Compound **1** (57.5 mg, 0.10 mmol) and elemental sulfur (3.5 mg, 0.11 mmol) were dissolved in dry toluene (5 mL). The mixture was heated at reflux for 3 h and then allowed to stand at room temperature for 24 h. The reaction solution was treated with a little charcoal, filtered, and evaporated under vacuum to afford **1b** as an orange solid. Yield: 60 mg (81%).

^1H NMR (CDCl_3): δ 0.59 (s with tin satellites: $^2J(^{119}\text{Sn}, \text{H}) = 57.0$, $^2J(^{117}\text{Sn}, \text{H}) = 55.9$ Hz; 9H, SnMe_3), 4.36 (vt, $J' = 2.0$ Hz, 2H), 4.45 (vq, $J' = 1.8$ Hz, 2H), 4.49 (vq, $J' = 2.0$ Hz, 2H), 4.67 (vt, $J' = 2.0$ Hz, 2H) (fc); 7.39–7.75 (m, 10 H, PPh_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ –2.17 (s, SnMe_3), 72.12 (s), 73.64 (s), 74.00 (d, $J_{\text{PC}} = 12$ Hz), 74.27 (d, $J_{\text{PC}} = 10$ Hz) (CH of fc); 128.24 (d, $J_{\text{PC}} = 12$ Hz), 131.29 (d, $J_{\text{PC}} = 3$ Hz), 131.59 (d, $J_{\text{PC}} = 11$ Hz) (CH of $\text{P}(\text{S})\text{Ph}_2$); 134.35 (d, $J_{\text{PC}} = 87$ Hz, C_{ipso} of $\text{P}(\text{S})\text{Ph}_2$), 175.72 (s, $\text{C}=\text{O}$). The signals due to ferrocene C_{ipso} were not found. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ +41.5 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ 133.9 (s). IR (Nujol): ν 1572 vs, 1557 vs, 1339 vs, 1187 m, 1171 s, 1101 s, 1073 w, 1055 w, 1027 s, 921 w, 834 m, 795 m, 774 m, 758 m, 745 m, 719 vs, 698 m, 659 s, 615 w, 602 w, 573 m, 550 w, 540 s, 520 m, 503 s, 485 m, 458 w, 451 w cm^{-1} . MS (EI+): m/z (relative abundance) 610 (100, M^+), 595 (53, $[\text{M}-\text{Me}]^+$), 518 (30, $[\text{M}-\text{C}_5\text{H}_4\text{CO}]^+$), 503 (59, $[\text{M}-\text{C}_5\text{H}_4\text{CO}-\text{Me}]^+$), 473 (30, $[\text{M}-\text{C}_5\text{H}_4\text{CO}-3\text{Me}]^+$), 466 (29, $[\text{HdpfS}^+]$), 354 (33), 337 (72, $[\text{Ph}_2\text{PC}_5\text{H}_4\text{FeS}]^+$), 321 (65, $[\text{Ph}_2\text{PC}_5\text{H}_4\text{FeO}]^+$). HR MS (ESI+) calc. for $\text{C}_{26}\text{H}_{27}^{56}\text{FeO}_2\text{PS}^{120}\text{Sn}$ (M^+): 609.9841, found: 609.9837.

4.7. Preparation of dimethyl[2-((dimethylamino)methyl)phenyl]stannyll 1'-(diphenylphosphinoyl)-1-ferrocenecarboxylate (**2a**)

Aqueous hydrogen peroxide (3 drops of 30% solution) was added to a solution of ester **2** (70 mg, 0.10 mmol) in toluene (3 mL), and the resulting mixture was vigorously stirred overnight. The separated product was filtered off, washed thoroughly with diethyl ether and pentane, and dried under vacuum to give **2a** as a fine ochre brown solid. Yield: 59 mg (83%).

^1H NMR (CDCl_3): δ 0.67 (s with tin satellites: $^2J(^{119}\text{Sn}, \text{H}) = 68.6$, $^2J(^{117}\text{Sn}, \text{H}) = 65.6$ Hz; 6H, SnMe_2), 2.30 (s, 6H, NMe_2), 3.61 (s with unresolved tin satellites, 2H, NCH_2), 4.36 (vt, $J' = 1.9$ Hz, 2H), 4.45 (vt, $J' = 1.8$ Hz, 2H), 4.49 (vt, $J' = 1.8$ Hz, 2H), 4.76 (vt, $J' = 1.9$ Hz, 2H) (fc); 7.08–8.09 (m, 14H, $\text{C}_6\text{H}_4 + \text{PPh}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ –2.96 (s, SnMe_2), 45.28 (s, NMe_2), 65.04 (s, NCH_2), 71.76 (s,

72.31 (s), 73.04 (d, $J_{\text{PC}} = 13$ Hz) ($3 \times \text{CH}$ of fc); 73.28 (d, $J_{\text{PC}} = 117$ Hz, $\text{C}-\text{PPh}_2$ of fc), 74.17 (d, $J_{\text{PC}} = 10$ Hz, CH of fc), 77.74 ($\text{C}-\text{CO}$ of fc), 126.71 (s, CH of C_6H_4), 127.84 (s, CH of C_6H_4), 128.22 (d, $J_{\text{PC}} = 12$ Hz, CH of $\text{P}(\text{O})\text{Ph}_2$), 129.16 (CH of C_6H_4), 131.42 (d, $J_{\text{PC}} = 10$ Hz, CH of $\text{P}(\text{O})\text{Ph}_2$), 131.54 (d, $J_{\text{PC}} = 2$ Hz, CH of $\text{P}(\text{O})\text{Ph}_2$), 134.16 (d, $J_{\text{PC}} = 107$ Hz, C_{ipso} of $\text{P}(\text{O})\text{Ph}_2$), 137.42 (CH of C_6H_4), 141.54 (s, C_{ipso} of C_6H_4), 142.47 (s, C_{ipso} of C_6H_4), 174.79 (s, $\text{C}=\text{O}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 29.6 (s). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (CDCl_3): δ –78.5 (s). IR (Nujol): ν 3510 m, 3435 w, 1715 w, 1629 vs, 1321 vs, 1184 s, 1177 s, 1156 s, 1122 m, 1101 m, 1075 w, 1031 m, 1010 w, 839 m, 789 m, 753 s, 726 s, 708 s, 697 m, 570 s, 550 w, 527 s, 507 s, 488 m, 478 w cm^{-1} . MS (ESI+): m/z 736 ($[\text{M}+\text{Na}]^+$), 714 ($[\text{M}+\text{H}]^+$), 453 ($[\text{HdpfO}+\text{Na}]^+$), 284 ($\text{Me}_2\text{L}^{\text{NCsn}^+}$). HR MS (ESI) calc. for $\text{C}_{34}\text{H}_{36}^{56}\text{FeNO}_3\text{P}^{120}\text{Sn}$ ($[\text{M}+\text{Na}]^+$): 736.0696, found: 736.0720.

4.8. Preparation of dimethyl[2-((dimethylamino)methyl)phenyl]stannyll 1'-(diphenylthiophosphoryl)-1-ferrocenecarboxylate (**2b**)

Ester **2** (70 mg, 0.10 mmol) and sulfur (3.5 mg, 0.11 mmol) were dissolved in toluene (5 mL) and the solution was heated to 75 °C for 18 h (temperature in bath). After cooling to room temperature, the solution was treated with little charcoal, filtered and evaporated under vacuum, leaving **2b** as a microcrystalline, rusty orange solid. Yield: 68 mg (96%).

^1H NMR (CDCl_3): δ 0.67 (s with tin satellites: $^2J(^{119}\text{Sn}, \text{H}) = 68.6$, $^2J(^{117}\text{Sn}, \text{H}) = 65.7$ Hz; 6H, SnMe_2), 2.30 (s, 6H, NMe_2), 3.61 (s with unresolved tin satellites, 2H, NCH_2), 4.34 (vt, $J' = 1.9$ Hz, 2H), 4.49–4.53 (m, 4H), 4.70 (vt, $J' = 1.9$ Hz, 2H) (fc); 7.09–8.10 (m, 14H, $\text{C}_6\text{H}_4 + \text{PPh}_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ –2.94 (s, SnMe_2), 45.27 (s, NMe_2), 65.03 (s, NCH_2), 71.84 (s), 73.07 (s), 73.67 (d, $J_{\text{PC}} = 12$ Hz), 74.36 (d, $J_{\text{PC}} = 10$ Hz) (CH of fc); 75.53 (d, $J_{\text{PC}} = 98$ Hz, $\text{C}-\text{PPh}_2$ of fc), 77.68 ($\text{C}-\text{CO}$ of fc), 126.70 (s, CH of C_6H_4), 127.85 (s, CH of C_6H_4), 128.20 (d, $J_{\text{PC}} = 12$ Hz, CH of $\text{P}(\text{S})\text{Ph}_2$), 129.15 (CH of C_6H_4), 131.18 (d, $J_{\text{PC}} = 3$ Hz, CH of $\text{P}(\text{S})\text{Ph}_2$), 131.60 (d, $J_{\text{PC}} = 10$ Hz, CH of

Table 3
Crystallographic data, data collection and structure refinement parameters for **1**, **1a**, **2**, **2a** and **2b**.^a

Compound	1	1a	2	2a	2b
Formula	$\text{C}_{28}\text{H}_{31}\text{FeO}_3\text{PSn}^f$	$\text{C}_{26}\text{H}_{27}\text{FeO}_3\text{PSn}$	$\text{C}_{34}\text{H}_{37}\text{FeNO}_{2.5}\text{PSn}^h$	$\text{C}_{34}\text{H}_{36}\text{FeNO}_4\text{PSn}^i$	$\text{C}_{34}\text{H}_{36}\text{FeNO}_2\text{PSSn}$
M (g mol^{-1})	621.04	592.99	705.16	730.16	728.21
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19) ^g	$P1$ (no. 2)	$P1$ (no. 2)	$P1$ (no. 2)
a (Å)	12.3700(2)	10.8321(2)	8.5686(3)	9.3792(4)	9.1011(2)
b (Å)	24.3300(4)	13.3435(2)	13.4231(3)	12.0247(3)	12.3486(3)
c (Å)	9.9635(2)	17.4506(2)	13.4231(3)	15.4844(7)	15.3094(3)
α (°)			83.596(2)	67.789(2)	71.704(1)
β (°)	101.633(1)		85.593(2)	78.636(2)	79.589(1)
γ (°)			73.454(2)	79.076(2)	78.762(2)
V (Å ³)	2937.04(9)	2522.28(7)	1541.02(8)	1572.3(1)	1589.01(6)
Z	4	4	2	2	2
D_{calc} (g mL^{-1})	1.404	1.562	1.520	1.542	1.522
μ ($\text{Mo K}\alpha$) [mm^{-1}]	1.423	1.653	1.366	1.345	1.390
T-range ^b	0.549–0.680	0.636–0.858	0.714–0.899	0.835–0.961	0.781–0.904
Diffractions total	41 294	43 744	31 654	26 147	29 102
R_{int} (%)	5.06	3.83	5.65	6.09	5.14
Unique diffractions	6722	5779	7101	6183	7030
Observed diffractions ^d	5634	5506	5553	4783	5535
R (Observed diffractions) ^{d,e} (%)	3.11	2.54	3.54	3.71	3.36
R_w (all diffractions) ^e (%)	4.19, 7.80	2.82, 5.17	5.84, 7.63	6.09, 7.89	5.26, 7.74
$\Delta\rho$ (e Å^{-3})	0.89, –0.63	0.30, –0.52	0.93, –1.00	0.56, –0.78	0.91, –0.79

^a Common details: $T = 150(2)$ K.

^b The range of transmission coefficients.

^c $R_{\text{int}} = \sum |F_o^2 - F_c^2(\text{mean})| / \sum F_o^2$, where $F_c^2(\text{mean})$ is the average intensity for symmetry-equivalent diffractions.

^d Diffractions with $I_o > 2\sigma(I_o)$.

^e $R = \sum \|F_o - |F_c|\| / \sum F_o$, $wR = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum w(F_o^2)^2]^{1/2}$.

^f $\text{C}_{25}\text{H}_{27}\text{FeO}_2\text{PSn} \cdot 1/2\text{C}_4\text{H}_8\text{O}_2$ (see Section 4).

^g Flack's enantiomorph parameter: –0.01(2).

^h $\text{C}_{34}\text{H}_{36}\text{FeNO}_2\text{PSn} \cdot 1/2\text{H}_2\text{O}$.

ⁱ $\text{C}_{34}\text{H}_{36}\text{FeNO}_3\text{PSn} \cdot \text{H}_2\text{O}$.

P(S)Ph₂), 134.55 (d, ¹J_{PC} = 87 Hz, C_{ipso} of P(S)Ph₂), 137.50 (CH of C₆H₄), 141.53 (s, C_{ipso} of C₆H₄), 142.46 (s, C_{ipso} of C₆H₄), 174.67 (s, C=O). ³¹P{¹H} NMR (CDCl₃): δ 41.9 (s). ¹¹⁹Sn{¹H} NMR (CDCl₃): δ –78.4 (s). IR (Nujol): ν 1624 vs, 1323 vs, 1171 s, 1103 s, 1051 w, 1024 m, 1010 w, 977 w, 920 w, 824 m, 805 w, 788 m, 750 s, 716 s, 699 m, 695 m, 653 s, 628 w, 615 w, 571 w, 543 s, 514 s, 503 m, 485 s, 467 w, 456 w, 427 w, 415 w cm⁻¹. MS (ESI⁺): *m/z* 752 ([M+Na]⁺), 469 ([HdpfS+Na]⁺), 284 (Me₂L^{NC}Sn⁺). HR MS (ESI) calc. for C₃₄H₃₆⁵⁶FeNO₂PS¹²⁰Sn ([M+Na]⁺): 752.0468, found: 752.0492.

5. X-ray crystallography

Crystals used for single-crystal X-ray diffraction analysis were all grown by crystallization from ethyl acetate-hexane (**1**: orange-brown prism, 0.16 × 0.50 × 0.62 mm³, **1a**: orange-brown plate, 0.08 × 0.25 × 0.25 mm³; **2**: orange-brown plate, 0.13 × 0.23 × 0.28 mm³; **2a**: orange plate, 0.03 × 0.10 × 0.15 mm³; **2b**: orange-brown prism, 0.10 × 0.18 × 0.18 mm³). Full-set diffraction data (±h ±k ±l, 2θ ≤ 52–55°) were collected with a Nonius KapkaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The data were analyzed with HKL program package [32] and corrected for absorption by conventional methods included in the diffractometer software. The ranges of the transmission factors are given in Table 3.

The structures were solved by direct methods (SIR97, Ref. [33]) and refined by full-matrix least-squares procedure on F² (SHELXL97, Ref. [34]). The non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in their calculated positions and refined as riding atoms with U_{iso}(H) set to a multiple of U_{eq}(C) of their bonding carbon atom. Particular details on structure solution and treatment are as follows.

The crystals of **1** contained disordered molecules of ethyl acetate. Contribution of the solvent molecules to the scattering was numerically removed by SQUEEZE routine as incorporated in the PLATON program [35]. Within the 2 × 372 Å³ of void space per the unit cell, a total of 162 electrons were calculated, compared to the 176 electrons predicted for the presence of two molecules of ethyl acetate. In the crystal of **2**, the methyl and methylene groups in the CH₂NMe₂ arm adopt two positions while the phenyl ring (C(26–31)) and the nitrogen atoms act as pivots (statistic disorder). The disordered methyl and methyl groups were refined over two positions with the same occupancies (50:50) and anisotropic displacement parameters.

Relevant crystallographic data are given in Table 3. Geometric parameters and structural drawings were obtained by using a recent version of the PLATON program [35]. All values are presented relative to their estimated standard deviations given with one decimal. Those concerning atoms in constrained positions (hydrogens) are given without estimated standard deviations.

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Appendix A. Supplementary data

CCDC 742131, 742132, 742133, 742134 and 742135 contain the supplementary crystallographic data for this paper. These data can

be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.09.042](https://doi.org/10.1016/j.jorganchem.2009.09.042).

References

- [1] (a) A.W. Davies, *Organotin Chemistry*, Wiley, Weinheim, 2004 (Chapters 13 and 23); (b) M. Gielen, E.R.T. Tiekink, in: M. Gielen, E.R.T. Tiekink (Eds.), *Metallotherapeutic Drugs and Metal-Based Diagnostic Agents*, Wiley, New York, 2005 (Chapter 22); (c) S.K. Hadjikakou, N. Hadjiliadis, *Coord. Chem. Rev.* 253 (2009) 235.
- [2] (a) E.R.T. Tiekink, *Appl. Organomet. Chem.* 5 (1991) 1; (b) V. Chandrasekhar, S. Nagendran, V. Baskar, *Coord. Chem. Rev.* 235 (2002) 1; (c) R.C. Mehrotra, R. Bohra, *Metal Carboxylates*, Academic Press, London, 1983 (Chapter 4.1).
- [3] S.-W. Ng, J.J. Zuckerman, *Organometallics* 1 (1982) 714.
- [4] S.-W. Ng, J.J. Zuckerman, *J. Organomet. Chem.* 234 (1982) 257.
- [5] R.J. Cross, L.J. Farrugia, P.D. Newnam, R.D. Peacock, D. Stirling, *J. Chem. Soc., Dalton Trans.* (1996) 1087.
- [6] (a) For recent examples of organotin(IV) phosphinocarboxylates, see: R.J. Bowen, J. Caddy, M.A. Fernandes, M. Layh, M.A. Mamo, R. Meijboon, *J. Organomet. Chem.* 691 (2006) 717; (b) P.P. Phadnis, S. Dey, V.J. Jain, M. Nethaji, R.J. Butcher, *Polyhedron* 25 (2006) 87.
- [7] P. Zoufalá, R. Gyepes, P. Štěpnička, *J. Organomet. Chem.* 689 (2004) 3556.
- [8] P. Zoufalá, I. Císařová, A. Růžička, P. Štěpnička, *Appl. Organomet. Chem.* 19 (2005) 118.
- [9] J. Podlaha, P. Štěpnička, I. Císařová, J. Ludvík, *Organometallics* 15 (1996) 543.
- [10] (a) P. Štěpnička, *Eur. J. Inorg. Chem.* (2005) 3787; (b) P. Štěpnička, in: P. Štěpnička (Ed.), *Ferrocenes: Ligands, Materials and Biomolecules*, Wiley, Chichester, 2008 (Chapter 5).
- [11] For a recent example of an organometallic triphenylstannyl carboxylate, [Co(η⁴-C₄Ph₄)(η¹-C₅H₄CO₂SnPh₃)], prepared similarly from (Ph₃Sn)₂O and the respective acid, see: M.S. Kumar, S. Upreti, H.P. Gupta, A.J. Elias, *J. Organomet. Chem.* 691 (2006) 4708.
- [12] (a) P.J. Smith, A.P. Tupčiauskas, *Ann. Rep. NMR Spectrosc.* 8 (1978) 291; (b) B. Wrackmeyer, *Ann. Rep. NMR Spectrosc.* 16 (1985) 73.
- [13] J. Chalupa, K. Handlíř, I. Císařová, R. Jirásko, J. Brus, A. Lyčka, A. Růžička, J. Holeček, *J. Organomet. Chem.* 691 (2006) 2631, and references cited therein.
- [14] J. Chalupa, K. Handlíř, Z. Padělková, M. Vejcová, V. Buchta, R. Jirásko, A. Růžička, *Appl. Organomet. Chem.* 22 (2008) 308.
- [15] P. Štěpnička, J. Schulz, I. Císařová, K. Fejfarová, *Collect. Czech. Chem. Commun.* 72 (2007) 453.
- [16] H.-O. Kalinowski, S. Berger, S. Braun, ¹³C-NMR-Spektroskopie, Thieme, Stuttgart, 1984 (Chapter 4).
- [17] (a) D.R. Smith, E.R.T. Tiekink, *Z. Kristallogr.* 213 (1998) 605 (Sn–O 2.203(4), Sn–O 2.381(4) Å at 200 K); (b) H. Chih, B.R. Penfold, *J. Cryst. Mol. Struct.* 3 (1973) 285 (Sn–O 2.205(3), Sn–O 2.391(4) Å at room temperature).
- [18] P.J. Smith, R.O. Day, V. Chandrasekhar, J.M. Holmes, R.R. Holmes, *Inorg. Chem.* 25 (1986) 2495 (at 23 °C).
- [19] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, *J. Chem. Soc., Dalton Trans.* (1984) 1349 (the parameter takes 1.00 for ideal trigonal bipyramid and 0.00 for ideal square pyramid).
- [20] The C–O and C=O distances observed for **1** and **1a** correspond well with those reported for the related esters obtained from non-functionalized ferrocenecarboxylic acid, FcCO₂Sn(CH₂C₆H₄X-2)₃ (Fc = ferrocenyl, X = Cl and Br; refcodes TAFNYI and ADUSIC in the Cambridge Structural Database). However, these reference structures display distinctly shorter Sn–O and Sn···O distances (ca. 2.07 and 2.68 Å, respectively).
- [21] The 'liberated' C=O oxygen in **1a** takes part in a soft intramolecular hydrogen bonding (C20–H20···O1': C20···O1' = 3.365(5) Å, angle at H20 = 157°; symmetry operation: 1 – x, 1/2 + y, 1/2 – z).
- [22] S.W. Ng, V.G.K. Das, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 52 (1996) 1373.
- [23] C.A.K. Diop, A. Touré, L. Diop, R. Welter, *Acta Crystallogr., Sect. E: Struct. Rep. Online* 62 (2006) m3338.
- [24] C. Ma, J. Sun, R. Zhang, *J. Organomet. Chem.* 691 (2006) 5873.
- [25] K. Mach, J. Kubišta, I. Císařová, P. Štěpnička, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 58 (2002) m116.
- [26] An intermolecular C19–H19···O1 contact with C19···O1 being 3.288(4) Å between molecules related by elemental translation along x-axis was detected.
- [27] Crystallisation from dry solvents was unsuccessful starting only when some adventitious water was present.
- [28] A supportive C14–H14···O1 contact between molecules relating by translation along the a-axis (C14···O1 = 3.473(4) Å) was detected.
- [29] An additional C23–H23···O1 contact between molecules relating by translation along the a-axis (C23···O1 = 3.242(5) Å) was detected.
- [30] A. Růžička, R. Jambor, J. Brus, I. Císařová, J. Holeček, *Inorg. Chim. Acta* 323 (2001) 163.
- [31] B. Kushlfsky, I. Simmons, A. Ross, *Inorg. Chem.* 2 (1963) 187.

- [32] Z. Otwinowski, W. Minor, H.K.L. Denzo, Scalepack Program Package, Nonius BV, Delft, The Netherlands [For a reference, see: Z. Otwinowski, W. Minor, *Meth. Enzymol.* 276 (1997) 307].
- [33] A. Altomare, M.C. Burla, M. Camalli, G.L. Casciaro, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [34] G.M. Sheldrick, SHELXL97. Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Göttingen, 1997.
- [35] A.L. Spek, *J. Appl. Crystallogr.* 36 (2003) 7.