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Synthesis, structural characterization and electrochemistry of *C*,*N*-chelated organotin(IV) dicarboxylates with ferrocenyl substituents

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ABSTRACT

A set of C,N-chelated organotin(IV) ferrocenecarboxylates, $[L^{CN}(n-Bu)Sn(O_2CFc)_2]$ (1), $[(L^{CN})_2Sn(O_2CFc)_2]$ (2), $[L^{CN}(n-Bu)Sn(O_2CCH_2Fc)_2]$ (3), $[L^{CN}(n-Bu)Sn(O_2CCH_2Fc)_2]$ (4), $[L^{CN}(n-Bu)Sn(O_2CCH=CHFc)_2]$ (5), $[L^{CN}(n-Bu)Sn(O_2CfcPPh_2)_2]$ (6), $[(L^{CN})_2Sn(O_2CfcPPh_2)_2]$ (7), and $[L^{CN}(n-Bu)_2Sn(O_2CFc)]$ (8) $(L^{CN} = 2-(N,N-1))$ dimethylaminomethyl)phenyl, Fc = ferrocenyl and fc = ferrocene-1,1'-diyl) has been synthesized by metathesis of the respective organotin(IV) halides and carboxylate potassium salts and characterized by multinuclear NMR and IR spectroscopy. The spectral data indicated that the tin atoms in diorganotin(IV) dicarboxylates bearing one C,N-chelating ligand (1 and 3-6) are seven-coordinated with a distorted pentagonal bipyramidal environment around the tin constituted by the *n*-butyl group, the chelating L^{CN} ligand and bidentate carboxylate. Compounds 2 and 7 possessing two chelating L^{CN} ligands comprise octahedrally coordinated tin atoms and monodentate carboxylate donors, whereas compound 8 assumes a distorted trigonal bipyramidal geometry around tin with the carboxylate binding in unidentate fashion. The solid state structures determined for $1 \cdot C_6 D_6$ and **2** by single-crystal X-ray diffraction analysis are in agreement with spectroscopic data. Compounds 1, 3-5, and 8 were further studied by electrochemical methods. Whereas the oxidations of ferrocene units in bis(carboxylate) 2 and monocarboxylate 8 proceed in single steps, compound 1 undergoes two closely spaced one-electron redox waves due to two independently oxidized ferrocenyl groups. The spaced analogues of 2, compounds 3-5, again display only single waves corresponding to two-electron exchanged.

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1. Introduction

Current research in the chemistry of triorganotin(IV) carboxylates is focused mainly on structural studies as well as on catalytic and medicinal activity of these compounds [1–5]. The tin atom in simple triorganotin(IV) carboxylates is four- (Scheme 1A) or fivecoordinated in the solid state. Compounds with pentacoordinated tin atoms are particularly structurally variable because their carboxylate moieties can bind in asymmetric bidentate (Scheme 1, B), symmetric bidentate (Scheme 1, C) and bidentate-bridging fashions (Scheme 1D). Infinite polymeric networks, found in the solid state structures of compounds where the bidentate-bridging mode operates, often fragment into oligomeric or monomeric species in coordinating solvents [6].

The corresponding diorganotin (IV) carboxylates have also been extensively investigated over the last several decades, mainly due

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to their structural versatility. Depending on the nature of the carboxylic acid used and the stoichiometry of the reactants, several products such as monomers, dimers, tetramers, oligomeric ladders, and hexameric drum-like structures were isolated [7].

With our contributions to this field we have reported the preparation and structural characterization of triorganotin(IV) carboxylates resulting from 2-{[N-(2-oxo-2H-naphthalene-1-yliden)hydrazo]}benzoic acid. All these compounds were found to be monomeric in solution, featuring four-coordinated tin atoms [8]. Furthermore, a series of bis(triorganotin(IV)) esters of 4-ketopimelic acid was synthesized, structurally characterized and tested for fungicidal activity [9]. The structures and in vitro antifungal activity were also studied for some C,N-chelated azo dye organotin (IV) complexes [10]. All these C.N-chelated organotin(IV) carboxylates featured monodentate carboxylate units in solution and in the solid state. In other contributions, we focused on the preparation, structural characterization and catalytic activity of tri-, di- and monoorganotin(IV) trifluoroacetates bearing C,N-chelating ligand (s) [11], and also on the preparation and structures of organotin(IV) acetates [12] and ferrocenecarboxylates [13] bearing additional

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Scheme 1. Possible structural motifs for triorganotin(IV) esters of carboxylic acids.

phosphorus substituents in the carboxylate part. As an extension of our recent work, we report here on the reactivity of *C*,*N*-chelated tri- and diorganotin(IV) halides [14] towards potassium carboxylates *in situ* generated from simple and phosphine-substituted ferrocene carboxylic acids (Scheme 2).

2. Results and discussion

2.1. C,N-Chelated organotin(IV) dicarboxylates with simple ferrocenecarboxylic groups

The synthesis of C,N-chelated organotin(IV) carboxylates bearing ferrocenyl substituents (Scheme 2) proceeded in two steps. The first step involved the preparation of the corresponding potassium carboxylate using equimolar amounts of potassium t-butoxide and the respective carboxylic acid in anhydrous THF. Subsequent reaction of these salts with selected C,N-chelated organotin(IV) halides gave the desired products in satisfactory yields (isolated yields 58-81%, see Experimental). This reaction sequence appears to be the only proper synthetic strategy, since similar reactions between in situ generated lithium carboxylates failed to provide the desired products while the *n*-butyl containing monoorganotin(IV) drumlike hexamer [7d], resulting by a phenyl group migration process [14b,15], has been obtained from the reaction of L^{CN}(*n*-Bu)SnCl₂ $(L^{CN} = 2 - (N, N - dimethylaminomethyl) phenyl)$ with two equivalents of FcCOOLi. Likewise, the reactions of triorganotin(IV) hydrides (prepared by the reaction of the respective triorganotin(IV) chloride and K(BEt₃)H [16]) with FcCOOH did not reach completion, affording mixtures of the starting triorganotin(IV) hydride and the desired product in a molar ratio of ca. 1:2.

Compounds **1–7** are all air-stable and do not appreciably react with moisture. Their structures were established from multinuclear NMR (in solution) and IR spectra, and confirmed by elemental analysis. In addition, the solid-state structures of $1 \cdot C_6 D_6$ and 2 were determined by single-crystal X-ray diffraction analysis.

Reddish brown single crystals of solvate $1 \cdot C_6 D_6$ were obtained from a concentrated solution in C₆D₆. The crystal structure of this compound (Fig. 1) reveals seven-coordinated tin atom with a distorted pentagonal bipyramidal geometry. Two asymmetric bidentate carboxylate substituents (Sn1-O1 2.196(4) Å and Sn1-O2 2.495 (3) Å; Sn1-O3 2.189(3) Å and Sn1-O4 2.398(3) Å) are situated in the equatorial plane of the pentagonal bipyramid together with the nitrogen atom from the C,N-chelating ligand. Structural parameters indicate a relatively strong intramolecular $N \rightarrow Sn$ interaction (N1-Sn1 2.497(4) Å). Both tin-bound carbon atoms C1 (from the C,N-chelating ligand) and C10 occupy axial positions with the angle C1-Sn1-C10 being 165.3(2)°. The sum of the equatorial interatomic angles is 360.15°, which indicates with coplanar arrangement of the equatorial donor atoms. Both ferrocenyl moieties point in the same direction with respect to the equatorial plane. Their cyclopentadienyl rings are rotated from an eclipsed conformation by ca. 4° (Fe1) and 36° (Fe2), respectively, and show similar Fe-ring centroid distances (range 1.63-1.66 Å) and negligible tilting (4.0 $(5)^{\circ}$ for Fe1 and 2.9(3)° for Fe2).

The structure of **1** in solution was studied by multinuclear NMR spectroscopy (in C_6D_6). Both multiplicity and integral intensity of signals in the ¹H NMR spectrum are in agreement with the formulation. The coupling constant ³J(¹¹⁹Sn, ¹H) of the satellites observed

$$L^{CN}RSnX_{2} + 2 R'COOK \xrightarrow{\text{THF}} L^{CN}RSn(OC(O)R')_{2}$$
$$X = Cl \text{ or } Br$$

R	R'	
<i>n</i> -Bu	Fc	1
L^{CN}	Fc	2
<i>n</i> -Bu	CH_2Fc	3
<i>n</i> -Bu	CH ₂ CH ₂ Fc	4
<i>n</i> -Bu	(E)-CH=CHFc	5
<i>n</i> -Bu	dpf	6
L^{CN}	dpf	7
<i>2n-</i> Bu	Fc	8

Scheme 2. Preparation and numbering of compounds 1-8 ($L^{CN} = 2-(N,N-dimethyl)$ aminomethyl)phenyl, Fc = ferrocenyl, dpf = 1'-(diphenylphosphino)-1-ferrocenecarboxylate).

for the doublet due to aromatic H(6') (δ (¹H) = 8.48 ppm; see Scheme 3) is 98.5 Hz, which is within the range reported previously for other *C*,*N*-chelated diorganotin(IV) compounds [14b,17]. Unfortunately, the only ¹H NMR resonance observable for the CH₂NMe₂ pendant arm is the signal of the methyl groups at δ (¹H) = 2.33 ppm, the signal of the methylene group being obscured by the relatively broad resonance assigned to protons of the Cp' rings.

In the ¹³C{¹H} NMR spectrum, a relatively broad, diagnostic signal of the carboxyl group is seen at 183.1 ppm. This signal is accompanied by the resonances due to ferrocene CH and C_{ipso} . Whereas the resonance of $C_{ipso}(Cp)$ is clearly seen at 73.5 ppm, the CH resonances are



Fig. 1. Molecular structure of $1 \cdot C_6 D_6$. ORTEP view (50% probability level); benzene molecule and hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-N1 2.497(4), Sn1-O1 2.196(4), Sn1-O2 2.495(3), Sn1-O3 2.189 (3), Sn1-O4 2.398(3), Sn1-C1 2.113(5), Sn1-C10 2.123(6), O1-C14 1.283(5), O2-C14 1.252 (6), O3-C25 1.278(6), O4-C25 1.261(6), N1-Sn1-O1 144.80(12), N1-Sn1-O2 90.37(12), N1-Sn1-O3 133.65(13), N1-Sn1-O4 77.53(13), N1-Sn1-C10 90.71(18), C1-Sn1-C10 165.3 (2), O1-Sn1-O2 55.51(11), O1-C14-O2 120.5(4), O1-Sn1-O3 79.88(12), O2-Sn1-O4 167.75(11), O3-Sn1-O4 56.86(13), O3-C25-O4 119.4(4).



Scheme 3. General NMR numbering of organic substituents.

presumably overlapped, resulting in one broad signal at 71.7 ppm. In the ¹¹⁹Sn{¹H} spectrum, there is a single resonance at -386.0 ppm, confirming the presence of only one tin-containing species in benzene solution. The chemical shift value is typical for seven-coordinated tin atoms bearing one *C*,*N*-chelating ligand and one *n*-Bu substituent. Compared to the starting $[L^{CN}(n-Bu)SnCl_2](\delta$ (¹¹⁹Sn) ~ -107 ppm), the ¹¹⁹Sn resonance of **1** appears shifted to lower frequencies, which again implicates an increase of the coordination number of the tin atom from five to seven [18]. From the data collected, it follows that both carboxylate ligands are bonded in bidentate fashion both in the solid state and in solution. IR spectra [19] are in agreement with this observation, showing the carboxylate bands for neat **1** at 1544 and 1360 cm⁻¹, which again indicates bidentate coordination of the carboxylate moieties [8,9].

As mentioned above compound **1** is air-stable and does not react with water. This was proven simply by adding few drops of D_2O to the NMR tube containing benzene-d6 solution of **1**. The spectra recorded after mixing for 5 min were identical with those of **1**.

The reaction of $[(L^{CN})_2SnBr_2]$ with two equivalents of FcCOOK as described above produced $[(L^{CN})_2Sn(OC(O)Fc)_2]$ (**2**), which was isolated as an orange crystalline solid in a 71% isolated yield. Single crystals suitable for the X-ray diffraction analysis were grown from a THF solution at -30 °C. The crystal structure (Fig. 2) reveals the central tin atom in **2** to be six-coordinated with highly distorted octahedral environment around tin and two carbon atoms of the L^{CN} ligands located *trans* to each other. The N atoms of each L^{CN} ligand



Fig. 2. Molecular structure of 2. ORTEP plot at 50% probability level; hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Sn1-N1 2.544 (4), Sn1-N2 2.613(5), Sn1-01 2.072(3), Sn1-02 3.252(3), Sn1-03 2.059(4), Sn1-04 3.290(4), Sn1-C1 2.123(4), Sn1-C10 2.126(5), O1-C19 1.298(6), O2-C19 1.216(6), O3-C30 1.290(6), O4-C30 1.218(6), N1-Sn1-O3 164.79(12), N2-Sn1-O1 165.64(13), C1-Sn1-C10 155.77(19), N1-Sn1-N2 102.70(12), O1-Sn1-O3 99.82(13), O1-Sn1-N1 80.08(12), O3-Sn1-N2 81.22(14).

are cis to one carboxylate groups and trans to another. The interatomic distances Sn1-N1 (2.544(4) Å) and Sn1-N2 (2.613(5) Å) slightly differ from each other but still are within the range expected for intramolecular N \rightarrow Sn interactions [8–10,12–14] In comparison with 1, where both carboxylic moieties coordinated in anisobidentate manner, the carboxylate moieties in 2 are bonded in monodentate fashion (Sn1-O1 2.072(3) Å and Sn1-O2 3.252(3) Å: Sn1-O3 2.059(4) Å and Sn1-O4 3.290(4) Å, respectively: see Scheme 1). A possible bidentate coordination is prevented by the two bidentate C,N-chelating ligands at the tin atom (Sn1-N1 2.544 (4) Å, Sn1-N2 2.613(5) Å, Sn1-C1 2.123(4) Å a Sn1-C10 2.126(5)Å). The tin atom in 2 thus reveals a geometry similar to that found previously for $[(L^{CN})_2 Sn(OC(O)CF_3)_2]$ [11] and $[(L^{CN})_2 SnX_2]$ (X = F, Cl, Br, I) [14b,20]. Ferrocene cyclopentadienyls in 2 assume intermediate conformations, departing by ca. 2 (Fe2) and 12° (Fe1) from an ideal eclipsed conformation. The ferrocene units exert negligible tilts (max. 2.3(3)°) and similar Fe-ring centroid distances (1.643(3) and 1.652(3) Å for Fe1, 1.631(2) and 1.630(2) Å for Fe2).

The ¹H NMR spectrum of **2** in a CDCl₃ solution displays only one set of signals due to the CH₂N (δ (¹H) = 3.59 ppm) and N(CH₃)₂ (δ $(^{1}H) = 2.09 \text{ ppm}$) moieties, which indicates their equivalency in the solution. This observation is in contrast with the previously discussed ¹H NMR spectra of doubly C,N-chelated organotin(IV) halides and related compounds, where an AX pattern is typically seen for the CH_2N protons and a broad signal found for the $N(CH_3)_2$ groups [14b]. On the other hand, we have found that $[(L^{CN})_2Sn(OC$ $(O)CF_3)_2$ has a different ¹H NMR response since only one signal is detected for the CH₂N fragment (δ (¹H) = 3.73 ppm in THF-d8) and two broad resonances are observed for non-equivalent $N(CH_3)_2$ groups [11]. The expected doublet of H(6') (δ (¹H) = 8.42 ppm) in the spectrum of 2 is somewhat broadened but still exhibits tin satellites with coupling constant ${}^{3}I({}^{119}Sn, {}^{1}H)$ of ca. 87 Hz, which is a typical value for diorganotin(IV) compounds bearing C,N-chelating ligand (s). There are also three expected resonances due to protons in the equivalent ferrocenyl moieties. The resonance at 4.19 ppm was assigned to protons of unsubstituted Cp' rings while the other two signals at 4.24 and 4.77 ppm were attributed to protons at the substituted ring. A relatively broad signal of the OC(O) fragment at 174.2 ppm in the ¹³C{¹H} NMR spectrum suggests the presence of two equivalent monodentate carboxylates (bidentate carboxylic substituents exhibit this signal shifted to about 180 ppm) [8,9,11]. Neither the resonance of the C1' carbon [21] nor the signal attributable to Cipso(Cp) could be indentified owing to their low intensity or overlaps.

A single resonance observed in the ¹¹⁹Sn{¹H} NMR spectrum of **2** at -375.2 ppm ultimately confirms the existence of one tincontaining species in the solution. This chemical shift is typical for the six-coordinated tin bearing two *C*,*N*-chelating ligands [11,14b], which in turn indicates that the monodentate coordination of the FcCO₂ units as observed in the solid state is maintained even in the solution. The IR spectrum (Nujol mull) of **2** exhibits two strong carboxylate bands at 1655 cm⁻¹ (v_{as}(COO)) and 1316 cm⁻¹ (v_s(COO)). The difference between the v_{as}(COO) and v_s(COO) vibrations (>300 cm⁻¹) is in agreement with monodentate coordination of the carboxylate moieties and thus corresponds with the X-ray structure and NMR data.

In analogy to compound **2**, another three *C*,*N*-chelated diorganotin(IV) carboxylates were prepared from ferrocenecarboxylic acids having a hydrocarbon spacer inserted between the ferrocenyl and carboxyl groups (compounds **3**–**5** in Scheme 2), and isolated in good yields as very viscous oils or microcrystalline solids.

NMR data of **3-5** as obtained in benzene-d6 solutions corresponded with the formulated structures. The ¹H NMR spectrum of **3** showed broad unresolved signals in both the aromatic and

aliphatic regions. Nevertheless, all signals of the *C*,*N*-chelating ligand (δ (¹H) = 8.21, 7.17 and 6.85 ppm for the phenyl ring; δ (¹H) = 3.28 and 2.18 ppm, for CH₂N and N(CH₃)₂ moieties, respectively), the butyl group and the carboxylate ligands were identified. The single resonance at 183.1 ppm in the ¹³C NMR spectrum suggests bidentate coordination and equivalency of the carboxylate moieties. Together with the only ¹¹⁹Sn NMR signal at –388.3 ppm, this indicates that the tin atom in **3** has the same coordination geometry as in **1** (i.e., a distorted pentagonal bipyramid). The IR spectrum of neat **3** also corroborates the presence of bidentate carboxylate donors.

The NMR response of reddish brown oily $[L^{CN}(n-Bu)Sn(OC(O) CH_2CH_2Fc)_2]$ (**4**) is similar to that of **1** and **3**, the important distinguishing features being the presence of resonances due to the CH₂CH₂ linkers ($\delta(^{1}H) = 2.74$ and $\delta(^{13}C) = 30.1$ ppm for FcCH₂ and $\delta(^{1}H) = 2.61$ and $\delta(^{13}C) = 36.4$ ppm for CH₂CO₂). Similarly to **1** and **3**, the position of the carboxylate signal ($\delta(^{13}C) = 184.8$ ppm) and the ¹¹⁹Sn NMR signal ($\delta(^{119}Sn) = -390.0$ ppm) suggest bidentate coordination of the carboxylate donors, which is in line with the IR spectrum.

Contrary to **3** and **4**, the ¹H NMR spectrum of [L^{CN}(*n*-Bu)Sn (O₂CCH=CHFc)₂] (**5**) displays narrow, nicely resolved signals, allowing for a complete interpretation. The value of ³*J*(¹¹⁹Sn, ¹H) = 98.8 Hz for tin-satellites flanking the doublet of the aromatic H(6') (δ (¹H) = 8.41 ppm) is within the range reported previously for *C*,*N*-chelated diorganotin(IV) compounds [14b,17]. A typical pattern is found also for the CH=CH group, namely a pair of doublets (δ (¹H) = 7.87 ppm for CH = *CH*Fc, δ (¹H) = 6.32 ppm for O₂CCH = CH) with ³*J*(¹H, ¹H) coupling constant of 15.7 Hz, which corroborates (*E*)-geometry at the double bond. The resonance of the CH₂N fragment was not identified, probably due to overlaps with the relatively broad resonance due to Cp' protons. On the other hand, the signal of the N(CH₃)₂ moiety was clearly seen at 2.37 ppm together with a typical pattern of the *n*-Bu substituent in the aliphatic region of the ¹H NMR spectrum.

The ¹³C NMR spectrum of **5** displays the C=O signal at 178.1 ppm, shifted to lower frequencies when compared to the corresponding resonances in **3** or **4** due to conjugation. Signals of the double bond carbons are seen at 145.8 ppm (CH=CHFc) and 117.1 ppm (O₂CCH=CH). The ¹¹⁹Sn NMR signal at -391.0 ppm suggests a seven-coordinated tin species to be present in solution.

2.2. C,N-Chelated organotin(IV) dicarboxylates bearing 1'-(diphenylphosphino)ferrocen-1-yl moieties

In addition to simple carboxylates, two C,N-chelated diorganotin (IV) carboxylatates 6 and 7 (Scheme 2) were prepared from 1'-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) [22]. Compound $[L^{CN}(n-Bu)Sn(O_2CfcPPh_2)_2]$ (**6**; fc = ferrocene-1,1'-diyl) was isolated as an orange crystalline solid. Its ¹H NMR spectrum is similar to that of 1. However, the presence of the PPh₂ moieties leads to a differentiation of all cyclopentadienyl protons and appearance of a broad multiplet near 7.40 ppm, which overlaps with the signals of the C,N-chelating ligand. The presence of the phosphorus substituent is clearly manifested in the ³¹P NMR spectrum, showing a singlet at $\delta(^{31}P) = -16.8$ ppm, which is close to Hdpf itself [22a]. Likewise 1, the position of the resonance due to the carboxyl group in 6 (182.7 ppm) indicates its bidentate coordination while the ¹¹⁹Sn NMR spectrum suggest the presence of seven-coordinated tin species in solution ($\delta(119 \text{ Sn}) = -388.2 \text{ ppm}$). The IR spectrum supports the formulation, showing two carboxylate bands with $v_{as}(COO) - v_s(COO) < 200 \text{ cm}^{-1}$.

Compound $[(L^{CN})_2Sn(O_2CfcPPh_2)_2]$ (7) was isolated as reddish brown microcrystalline solid in 79% yield. The NMR resonances attributed to protons at the *C*,*N*-chelating ligands constitute

a pattern similar to those of **2**. The doublet of the H(6') (δ $(^{1}H) = 8.66 \text{ ppm})$ is broadened but still exhibits clearly discernible tin satellites with ${}^{3}J({}^{119}Sn, {}^{1}H) \approx 90$ Hz. Signals of the remaining C_6H_4 protons are overlapped by the resonance of the PPh₂ moieties. Signals of the CH₂NMe₂ pendant arm (NCH₂: 3.12 ppm, NMe₂: 1.74 ppm) and the cyclopentadienyl protons are found within the expected range. More importantly, the position of the carboxylate signal (δ (¹³C) = 173.2 ppm) indicates monodentate coordination and equivalency of the carboxylic substituents, whilst the single ³¹P NMR resonance observed at $\delta(^{31}P) = -17.9$ ppm clearly suggests the phosphorus groups to remain uncoordinated. The presence of only one tin-containing species in solution is proven by the ¹¹⁹Sn NMR spectrum, showing one resonance at $\delta(^{119}\text{Sn}) = -370.0$ ppm, which is close to that of compound 2. Based on the NMR data, one can suggest a pseudo-octahedral coordination environment around the tin atom for 7, similar to that described for compound 2. The presence of monodentate carboxylates is confirmed by IR spectroscopy, showing $v_{as}(COO)$ and $v_s(COO)$ bands separated by more than 300 cm^{-1} .

2.3. The related C,N-chelated organotin(IV) monocarboxylate 8

Triorganotin(IV) carboxylate $[L^{CN}(n-Bu)_2Sn(O_2CFc)]$ (**8**) was synthesized similarly to compounds mentioned above by reacting $[L^{CN}(n-Bu)_2SnCl]$ with one equivalent of FcCOOK and was isolated as a reddish brown oily product in a 73% yield.

According to NMR spectra one can assume that the central tin atom in **8** is five-coordinated (in benzene-d6) and has a distorted trigonal bipyramidal geometry as found previously for *C*,*N*-chelated triorganotin(IV) compounds [L^{CN}R₂SnX], where R = *n*-Bu or Ph, and X = F, Cl, Br, OCOCF₃ [11,23]. The ¹H NMR spectrum of **8** displays the expected signals of the L^{CN} and butyl groups. However, the ¹H chemical shifts of CH₂N protons (δ (¹H) = 3.12 ppm) differs greatly from that of **1** (δ (CH₂N) = 4.24 ppm) and a similar trend is seen also for the signal of NMe₂ group (δ (¹H) = 1.80 ppm; for **1**: δ (¹H) = 2.31 ppm). The coupling constant ³*J*(¹¹⁹Sn, ¹H) = 53.5 Hz observed for the satellites around the H(6') signal is characteristic for *C*,*N*-chelated triorganotin(IV) compounds [17a,23a].

The position of the signal of the carboxyl fragment (δ (^{13}C) = 175.2 ppm in C₆D₆) implies monodentate coordination of the carboxylato ligand, which is in accordance with the position of the carboxylate bands in the IR spectrum ($\nu_{as}(COO) = 1636 \text{ cm}^{-1}$ and $\nu_{s}(COO) = 1321 \text{ cm}^{-1}$; difference > 300 cm⁻¹). Finally, the ¹¹⁹Sn NMR spectrum suggests the presence of five-coordinated tin centre, showing a single resonance at δ (¹¹⁹Sn) = -92.2 ppm. The ¹¹⁹Sn NMR signals of **8** appears shifted by ca. 45 ppm to lower frequencies compared to the starting [L^{CN}(*n*-Bu)₂SnCl] (δ (¹¹⁹Sn) = -48.5 ppm in C₆D₆), which is a trend already noted for other, chemically related *C*,*N*-chelated organotin(IV) carboxylates [12].

Table 1Summary of electrochemical data for 1, 3–5, and 8.ª

Compound	<i>E</i> [V] ^b	$\Delta E_{\rm p} \ [{\rm mV}]^{\rm c}$
1	$E_{\rm pa} = 0.250, E_{\rm pc} = 0.110$	d
2	$\dot{E^{\circ'}} = 0.075$	85
3	$E^{\circ'} = 0.035$	ca. 125
4	$E^{\circ'} = 0.050$	85
5	$E^{\circ'} = 0.110$	90
8	$E^{\circ'} = 0.080$	75

^a In 1,2-dichloroethane in the presence of 0.1 M Bu₄N[PF₆] supporting electrolyte. Values versus ferrocene/ferrocenium reference (see Experimental).

 $^{\rm b}$ $E_{\rm pa}/E_{\rm pc}$ are anodic/cathodic peak potentials. $E^{\circ\prime}=\mathcal{V}_2(E_{\rm pa}+E_{\rm pc});$ scan rate = 200 mV s^{-1}.

^c $\Delta E_{\rm p} = E_{\rm p} - E_{\rm pc}$.

^d Two convoluted waves.



Fig. 3. Cyclic voltammograms of compounds **1**, **4**, **5**, and **8** as recorded in 1,2-dichloroethane on a platinum disc electrode at scan rate 0.20 V s^{-1} . The potentials are given relative to ferrocene/ferrocenium. For details, see Experimental.

2.4. Electrochemistry

Compounds $[L^{CN}(n-Bu)Sn(O_2C-Y-Fc)_2]$ (**1**, Y = none; **3**, Y = CH₂; **4**, Y = CH₂CH₂; and **5**, Y = (*E*)-CH=CH), $[(L^{CN})_2Sn(O_2CFc)_2]$ (**2**) and the monocarboxylate $[L^{CN}(n-Bu)_2Sn(O_2CFc)]$ (**8**) have been studied by cyclic and differential pulse voltammetry on platinum disc electrode in 1,2-dichloroethane. Because of the presence of the redox active ferrocenyl groups, attention was paid mainly to anodic region, where the oxidation of the ferrocene units takes place. The pertinent data are summarized in Table 1; selected voltammograms are presented in Figs. 3 and 4.

Monocarboxylate **8** expectedly undergoes a single reversible, one-electron oxidation attributable to the ferrocene/ferrocenium couple. A similar behavior is observed for compound **2**, which displays one reversible redox wave attributable to simultaneous oxidation of both ferrocenyl units at a potential very similar to that of **8** (Table 1). In contrast, the oxidation of compound **1** proceeds in two closely spaced one-electron steps (see Figs. 3 and 4). The fact that the chemically equivalent ferrocene units of **1** are oxidized in



Fig. 4. Differential pulse voltammograms of **1**, **4**, **5**, and **8** as recorded in 1,2-dichloroethane on a platinum disc electrode with a 5 mV step and modulation amplitude of 50 mV. The potentials are given relative to ferrocene/ferrocenium. For details, see Experimental.

stepwise manner indicates their electronic communication (probably through-space). An introduction of a spacer unit between the ferrocenyl moiety and the carboxylate group in type-1 compounds (i.e., in carboxylates **3-5**) changes this redox response so that it limits to the case of identical non-communicating redox centres (such in **2**) and, hence, a standard redox wave with an intensity corresponding to an overall two-electron exchange is observed. Besides, the spacer unit causes the ferrocene/ferrocenium redox wave to shift along the potential axis depending on its electronic influence (E° : **5** >> **3** > **4**).

3. Conclusion

Potassium carboxylates prepared in situ from ferrocenecarboxvlic acid and its analogues bearing a spacer between the carboxyl group and the ferrocene unit react smoothly with $[L^{CN}(n-Bu)SnX_2]$ or $[(L^{CN})_2 SnX_2]$ (X = Cl or Br) to afford the respective bis-carboxylates 1–5. Structures of these compounds (particularly the coordination environment around tin) changes with the number of the C,N-chelating organic groups (L^{CN}): Compounds bearing only one L^{CN} moiety feature seven-coordinated tin centres and bidentate carboxylate ligands while that with two L^{CN} groups (compound **2**) comprises a six-coordinated tin atom. Similar situation was observed for compounds prepared from Hdpf (compounds 6 and 7) as the phosphorus groups do not coordinate the tin centres in either intra- or intermolecular fashion. The related triorganotin(IV) monocarboxylate 8 assumes trigonal bipyramidal geometry with monodentate carboxylate ligand. The redox properties of the compounds depend on the overall structure and the nature of the spacer group which separates the redox active ferrocenyl units from the tin bonded carboxylate. The spacer not only influences the value of the redox potential of the ferrocene/ferrocenium couple but also a possible communication in compounds possessing two equivalent redox-active pendants.

4. Experimental

4.1. Materials and methods

All reactions were carried out under argon using standard Schlenk techniques if not described otherwise. $[L^{CN}(n-Bu)_2SnCl]$ [24], $[L^{CN}(n-Bu)SnCl_2]$ [24], $[(L^{CN})_2SnBr_2]$ [14b], Hdpf [22a], FcCH₂COOH [25], FcCH₂CH₂COOH [26] and (*E*)-FcCH = CHCOOH [27] were prepared according to published procedures. *t*-BuOK (97%), FcCOOH (97%) and all solvents were obtained from commercial sources (Sigma–Aldrich). THF was dried by distillation from sodium-potassium alloy, degassed and stored over a potassium mirror.

Solution NMR spectra (see Scheme 3) were recorded with a Bruker Avance 500 spectrometer at 500.13 MHz (¹H), 125.76 MHz (¹³C{¹H}), 202.45 MHz (³¹P{¹H}), and 186.50 MHz (¹¹⁹Sn{¹H}) at ambient temperature. The solutions were obtained by dissolving of approximately 40 mg of the analyzed compound in 0.6 ml of deuterated solvent. Chemical shifts in the ¹H and ¹³C NMR spectra are given relative to residual signals of the solvent (CDCl₃: 7.27 ppm for ¹H and 77.2 ppm for ¹³C; benzene-d6: 7.16 ppm for ¹H and 128.4 ppm for ¹³C). ³¹P and ¹¹⁹Sn NMR data are referenced to external H₃PO₄ (δ (³¹P) = 0.0 ppm), respectively. The ¹¹⁹Sn NMR spectra were measured in the inverse gated-decoupling mode. IR spectra were recorded with a Nicolet 7600 FT IR spectrometer. Melting points were determined on a Kofler block and are uncorrected.

Electrochemical measurements were performed with a computer-controlled potentiostat μ AUTOLAB III (Eco Chemie, Netherlands) at room temperature using a standard Metrohm

three-electrode cell equipped with a platinum disc electrode (AUTOLAB RDE, 3 mm diameter) as the working electrode, platinum sheet auxiliary electrode, and saturated calomel reference electrode (SCE), which was separated from the analyzed solution by a salt-bridge (0.1 M Bu₄N[PF₆] in 1,2-dichloroethane). The analyzed compounds were dissolved in 1.2-dichloroethane (anhydrous, Sigma–Aldrich) to give a solution containing ca. 7.5×10^{-4} M of the analyzed compound and 0.1 M Bu₄N[PF₆] (Fluka, purissimum for electrochemistry) as the supporting electrolyte. The solutions were degassed with argon before the measurement and then kept under an argon blanket. The redox potentials were internally referenced to decamethylferrocene/decamethylferrocenium [28] and the values then converted to the conventional ferrocene/ferrocenium scale by subtracting 0.548 V, which as the redox potential of decamethylferrocene/decamethylferrocenium vs. ferrocene/ferrocenium [29].

4.2. Preparation of $[L^{CN}(n-Bu)Sn(O_2CFc)_2]$ (1)

A suspension of t-BuOK (201 mg, 1.74 mmol) in THF (20 ml) was added to a solution of FcCO₂H (413 mg, 1.74 mmol) in THF (20 ml). The reaction mixture was stirred for 1 h to complete precipitation of FcCO₂K. Then, a solution of [L^{CN}(*n*-Bu)SnCl₂] (331 mg, 0.87 mmol) in THF was introduced in one portion, whereupon the color of the reaction mixture changed rapidly from orange to reddish brown. The following operations were performed in the air. The precipitated KCl was filtered off and the filtrate was evaporated to drvness *in vacuo* giving **1** as a reddish brown crystalline solid. Further purification was not necessary. Yield: 540 mg (81%). M.p. 189-191 °C. ¹H NMR (C₆D₆, 295 K, ppm): 8.48 (d, 1H, H(6'), ³/(¹H) $(5'), {}^{1}H(6') = 7.0 \text{ Hz}, {}^{3}J({}^{119}\text{Sn}, {}^{1}\text{H}) = 98.5 \text{ Hz}); 7.20 (m, 1H, H(5'));$ 7.11 (t, 1H, H(4')); 6.88 (d, 1H, H(3'), 3 /(1 H(4'), 1 H(3')) = 7.4 Hz)); 5.02 (br d, 4H, H(Cp)); 4.02 (br, 6H, CH₂N and H(Cp)); 3.93 (br, 10H, H (Cp')); 2.33 (s, 6H, N(CH₃)₂); 1.99 (m, 2H, H(1)); 1.86 (m, 2H, H(2)); 1.37 (m, 2H, H(3)); 0.83 (t, 3H, H(4)). ¹³C NMR (C₆D₆, 295 K, ppm): 183.1 (br, OC(O)); 147.3 (C2'); 141.1 (C1'); 135.0 (C6'); 130.0 (C4'); 129.0 (C5'); 127.3 (C3'); 73.5 (br, C_{ipso}(Cp)); 71.7 (br, Cp); 70.3 (Cp'); 64.1 (CH₂N); 46.5 (N(CH₃)₂); 28.9 (C2); 28.7(C3); 27.2 (C1); 14.2 (C4). ¹¹⁹Sn NMR (C₆D₆, 295 K, ppm): –386.0. IR (Nujol mull, cm⁻¹): 1544 (vs, v_{as}(COO)); 1360 (s, v_s(COO)). Elemental analysis (%): found C, 55.0; H, 5.4; N, 1.7. Calcd. for C₃₅H₃₉Fe₂NO₄Sn (768.09): C, 54.73; H, 5.12; N, 1.82.

4.3. Preparation of $[(L^{CN})_2 Sn(O_2 CFc)_2]$ (2)

The synthesis of **2** was carried out as described above starting with FcCO₂H (510 mg, 2.16 mmol), *t*-BuOK (249 mg, 2.16 mmol) and [(L^{CN})₂SnBr₂] (588 mg, 1.08 mmol). Orange crystalline product was obtained. Yield: 648 mg (71%). M.p. > 220 °C (dec.). ¹H NMR (CDCl₃, 295 K, ppm): 8.42 (br, 2H, H(6'), ³J(¹¹⁹Sn, ¹H) \approx 87 Hz); 7.46 (m, 2H, H(5')); 7.34 (t, 2H, H(4')); 7.13 (d, 2H, H(3'), ³J(¹H(4'), ¹H (3')) = 7.5 Hz), ⁴J(¹¹⁹Sn, ¹H) = 39.9 Hz); 4.77 (s, 4H, H(Cp)); 4.24 (s, 4H, H(Cp)); 4.19 (s, 10H, H(Cp')); 3.59 (s, 4H, CH₂N); 2.09 (s, 12H, N (CH₃)₂). ¹³C NMR (CDCl₃, 295 K, ppm): 174.2 (OC(O)); 141.4 (C2'); 136.9 (C6'); 129.7 (C4'); 128.3 (C5'); 127.6 (C3'); 70.7 (Cp); 70.3 (Cp); 69.7 (Cp'); 64.9 (CH₂N); 46.4 (N(CH₃)₂); the resonances for the C1' and C_{ipso}(Cp) atoms were not found. ¹¹⁹Sn NMR (CDCl₃, 295 K, ppm): -375.2. IR (Nujol mull, cm⁻¹): 1655 (s, v_{as}(COO)); 1316 (s, v_s(COO)). Elemental analysis (%): found C, 57.1; H, 5.2; N, 3.2. Calcd. for C₄₀H₄₂Fe₂N₂O₄Sn (845.18): C, 56.85; H, 5.01; N, 3.31.

4.4. Preparation of $[L^{CN}(n-Bu)Sn(O_2CCH_2Fc)_2]$ (3)

Compound **3** was prepared analogously from FcCH₂COOH (156 mg, 0.64 mmol), *t*-BuOK (74 mg, 0.64 mmol) and [L^{CN}(*n*-Bu)

SnCl₂] (122 mg, 0.32 mmol). Reddish oily product was obtained. Yield: 147 mg (58%). ¹H NMR (C_6D_6 , 295 K, ppm): 8.21 (br, 1H, H (6')); 7.17 (br, 2H, L^{CN}); 6.85 (br, 1H, H(3')); 4.15 (br, 2H, H(Cp)); 3.91 (br, 14H, H(Cp and Cp')); 3.57 (br, 4H, OC(O)CH₂); 3.28 (br, 2H, CH₂N); 2.18 (br, 6H, N(CH₃)₂); 1.83 (br, 2H, H(1)); 1.71 (br, 2H, H(2)); 1.42 (br, 2H, H(3)); 0.95 (br, 3H, H(4)). ¹³C NMR (C_6D_6 , 295 K, ppm): 183.1 (OC(O)); 146.7 (C2'); 140.6 (C1'); 134.5 (C6'); 129.6 (C4'); 127.0 (C3'); 82.2 ($C_{ipso}(Cp)$); 69.0 (br, Cp and Cp'); 67.9 (br, Cp'); 63.9 (CH₂N); 46.0 (N(CH₃)₂); 36.0 (OC(O)CH₂); 28.0 (C2); 26.8 (C3); 25.9 (C1); 14.2 (C4); the signal of C5' is overlapped by the resonance of benzene-d6. ¹¹⁹Sn NMR (C_6D_6 , 295 K, ppm): –388.3. IR (neat, cm⁻¹): 1563 (vs, v_{as}(COO)); 1360 (m, v_s(COO)). Elemental analysis (%): found C, 56.2; H, 5.8; N, 1.5. Calcd. for C₃₇H₄₃Fe₂NO₄Sn (796.14): C, 55.82; H, 5.44; N, 1.76.

4.5. Preparation of $[L^{CN}(n-Bu)Sn(O_2CCH_2CH_2Fc)_2]$ (4)

The synthesis was carried out as above with FcCH₂CH₂COOH (315 mg, 1.22 mmol), *t*-BuOK (141 mg, 1.22 mmol) and [L^{CN}(*n*-Bu) SnCl₂] (232 mg, 0.61 mmol). Reddish brown oily product was obtained. Yield: 347 mg (69%). ¹H NMR (C₆D₆, 295 K, ppm): 8.29 (d, 1H, H(6'), ³J(¹H(5'), ¹H(6')) = 5.5 Hz), ³J(¹¹⁹Sn, ¹H) \approx 90 Hz)); 7.22 (br, 2H, L^{CN}); 6.95 (d, 1H, H(3'), ³J(¹H(4'), ¹H(3')) = 7.1 Hz)); 4.01 (br, 10H, H(Cp')); 3.95 (br, 8H, H(Cp)); 3.57 (br, 2H, CH₂N); 2.74 (br, 4H, CH₂CH₂Fc); 2.61 (br, 4H, OC(O)CH₂CH₂); 2.32 (br, 6H, N(CH₃)₂); 1.88 (br, 2H, H(1)); 1.42 (br, 2H, H(2)); 1.24 (br, 2H, H(3)); 1.04 (br, 3H, H (4)). ¹³C NMR (C₆D₆, 295 K, ppm): 184.8 (OC(O)); 146.5 (C2'); 140.5 (C1'); 134.4 (C6'); 129.4 (C4'); 126.9 (C3'); 88.4 (C_{ipso}(Cp)); 68.7 (Cp'); 68.3 (Cp); 67.5 (Cp); 63.7 (CH₂N); 46.0 (N(CH₃)₂; 36.4 (OC(O)CH₂); 30.1 (CH₂Fc); 27.9 (C2); 26.8 (C3); 25.8 (C1); 14.1 (C4); the signal of C5' is overlapped by the resonance of benzene-d6. ¹¹⁹Sn NMR (C₆D₆, 295 K, ppm): -390.0. IR (Nujol mull, cm⁻¹): 1557 (vs, v_{as}(COO)); 1362 (m, v_s(COO)). Elemental analysis (%): found C, 57.1; H, 6.0; N, 1.6. Calcd. for C₃₉H₄₇Fe₂NO₄Sn (824.20): C, 56.84; H, 5.75; N, 1.70.

4.6. Preparation of $[L^{CN}(n-Bu)Sn(O_2CCH=CHFc)_2]$ (5)

Compound 5 was obtained similarly form (E)-FcCH=CHCOOH (270 mg, 1.05 mmol), *t*-BuOK (122 mg, 1.05 mmol) and [L^{CN}(*n*-Bu) SnCl₂] (201 mg, 0.53 mmol). Reddish brown crystalline product was obtained. Yield: 250 mg (58%). M.p. 88–90 °C. ¹H NMR (C₆D₆, 295 K, ppm): 8.41 (d, 1H, H(6'), ${}^{3}J({}^{1}H(5'), {}^{1}H(6')) = 7.3$ Hz), ${}^{3}J({}^{119}Sn, {}^{1}H) = 98.8$ Hz)); 7.87 (d, 2H, CH=CHFc, ${}^{3}J({}^{1}H, {}^{1}H) = 15.7$ Hz); 7.16 (m, 1H, H(5')); 7.07 (t, 1H, H(4')); 6.85 (d, 1H, H(3'), ³J(¹H(4'), ¹H $(3') = 7.4 \text{ Hz}); 6.32 (d, 2H, OC(0)CH=CH, {}^{3}J({}^{1}H, {}^{1}H) = 15.7 \text{ Hz}); 4.11$ (s, 4H, H(Cp)); 3.97 (s, 4H, H(Cp)); 3.80 (br, 12H, H(Cp') and CH₂N); 2.37 (s, 6H, N(CH₃)₂); 2.06 (m, 2H, H(1)); 1.91 (m, 2H, H(2)); 1.46 (m, 2H, H(3)); 0.93 (t, 3H, H(4)). ¹³C NMR (C₆D₆, 295 K, ppm): 178.1 (OC (O)); 147.1 (C2'); 145.8 (CH=CHFc); 140.5 (C1'); 134.4 (C6'); 129.2 (C4'); 126.9 (C3'); 117.1 (OC(O)CH=CH); 79.5 (C_{ipso}(Cp)); 70.7 (Cp); 69.8 (Cp'); 68.7 (Cp); 64.0 (CH₂N); 46.1 (N(CH₃)₂; 30.1 (C2); 28.3(C3); 28.1 (C1); 14.2 (C4); the signal of C5' is overlapped by the resonance of the solvent. ¹¹⁹Sn NMR (C_6D_6 , 295 K, ppm): -391.0. IR (Nujol mull, cm⁻¹): 1636 (vs, v_{as} (COO)); the band of v_s (COO) is obscured by Nujol bands. Elemental analysis (%): found C, 57.4; H, 5.5; N, 1.6. Calcd. for C₃₉H₄₃Fe₂NO₄Sn (820.17): C, 57.11; H, 5.28; N, 1.71.

4.7. Preparation of $[L^{CN}(n-Bu)Sn(O_2CfcPPh_2)_2]$ (6)

Starting with Hdpf (240 mg, 0.58 mmol), *t*-BuOK (68 mg, 0.58 mmol) and [$L^{CN}(n$ -Bu)SnCl₂] (110 mg, 0.29 mmol), the procedure described in detail for **1** afforded compound **6** as an orange crystalline solid. Yield: 202 mg (61%). M.p. 81–83 °C. ¹H NMR (C₆D₆, 295 K, ppm): 8.44 (d, 1H, H(6'), ³*J*(¹H(5'), ¹H(6')) = 7.0 Hz), ³*J*(¹¹⁹Sn, ¹H) = 98.7 Hz); 7.40 (br d, 8H, PPh₂); 7.16–7.05 (m, 8H, PPh₂ and

 $\begin{array}{l} L^{CN}; \ 7.02 \ (m, 6H, PPh_2 \ and \ L^{CN}); \ 6.74 \ (d, 1H, \ H(3'), \ {}^3J(^1H(4'), \ {}^1H(3')) = 7.3 \ Hz); \ 4.98 \ (br \ d, 4H, \ H(Cp)); \ 4.17 \ (br, 2H, \ H(Cp')); \ 4.09 \ (br, 2H, \ H(Cp')); \ 4.02 \ (br, 6H, \ H(Cp \ and \ Cp')); \ 3.79 \ (s, 2H, \ H(Cp')); \ 4.09 \ (br, 2H, \ H(Cp')); \ 4.02 \ (br, 6H, \ H(Cp \ and \ Cp')); \ 3.79 \ (s, 2H, \ H(Cp')); \ 4.09 \ (br, 2H, \ H(Cp')); \ 4.02 \ (br, 6H, \ H(Cp \ and \ Cp')); \ 3.79 \ (s, 2H, \ H(Cp')); \ 4.09 \ (br, 2H, \ H(2p')); \ 4.02 \ (br, 6H, \ H(Cp \ and \ Cp')); \ 3.79 \ (s, 2H, \ H(Cp')); \ 4.09 \ (br, 2H, \ H(2p')); \ 4.02 \ (br, 6H, \ H(Cp \ and \ Cp')); \ 3.79 \ (s, 2H, \ H(Cp')); \ 4.09 \ (br, 2H, \ H(2p')); \ 4.02 \ (br, 6H, \ H(Cp \ and \ Cp')); \ 3.79 \ (s, 2H, \ H(Cp')); \ 3.62 \ (s, 2Ph, H(2p)); \ 3.62 \ (s, 2Ph, H(1)); \ 1.83 \ (m, 2H, \ H(2p)); \ 3.62 \ (s, 2Ph, \ H(1)); \ 1.83 \ (m, 2H, \ H(2p)); \ 3.62 \ (s, 2Ph, \ H(1)); \ 1.83 \ (m, 2H, \ H(2p)); \ 3.62 \ (s, 2Ph, \ H(1)); \ 1.83 \ (m, 2H, \ H(2p)); \ 1.82 \ (m,$

4.8. Preparation of $[(L^{CN})_2Sn(O_2CfcPPh_2)_2]$ (7)

Using the procedure described above, Hdpf (257 mg, 0.62 mmol), t-BuOK (97%, 72 mg, 0.62 mmol) and [(L^{CN})₂SnBr₂] (170 mg, 0.31 mmol) afforded **7** as a reddish brown crystalline solid. Yield: 289 mg (79%). M.p. 92–94 °C. ¹H NMR (C₆D₆, 295 K, ppm): 8.66 (br, 2H, H(6'), ${}^{3}J({}^{119}Sn, {}^{1}H) \approx 90$ Hz); 7.50 (br, 8H, PPh₂); 7.37 (br, 2H, L^{CN}); 7.16–7.05 (m, 10H, PPh₂ and L^{CN}); 6.56 (d, 2H, H(3'), ³] $({}^{1}H(4'), {}^{1}H(3')) = 7.1 \text{ Hz}$; 4.89 (s, 4H, H(Cp)); 4.78 (br, 4H, H(Cp')); 4.31 (br, 4H, H(Cp)); 4.09 (s, 4H, Cp'); 3.12 (br, 4H, CH₂N); 1.74 (very broad, 12H, N(CH₃)₂). ¹³C NMR (C₆D₆, 295 K, ppm): 173.2 (OC(O)); 142.4 (C2'); 142.1 (C1'); 140.4 (d, $C_{ipso}(Ph)$, ${}^{1}J({}^{31}P, {}^{13}C_{ipso}) = 10.7$ Hz); 138.0 (C6'); 134.3 (d, $C_{ortho}(Ph)$, ${}^{2}J({}^{31}P, {}^{13}C_{ortho}) = 19.1$ Hz); 129.9 (C4'); 78.0 ($C_{ipso}(Cp)$); 77.6 (d, $C_{ipso}(Cp')$, ${}^{1}J({}^{31}P, {}^{13}C_{ipso}) = 8.0$ Hz); 74.8 (br, Cp'); 74.5 (Cp); 72.5 (Cp'); 72.2 (Cp); 65.0 (CH₂N); 46.3 (N (CH₃)₂); the signals of C5', C3', C_{meta}(Ph) and C_{para}(Ph) atoms are overlapped by the resonance of benzene-d6. ³¹P NMR (C₆D₆, 295 K, ppm): -17.9 (s, PPh₂). ¹¹⁹Sn NMR (C₆D₆, 295 K, ppm): -370.0. IR (Nujol mull, cm⁻¹): 1654 (vs, $v_{as}(COO)$); 1316 (vs, $v_{s}(COO)$). Elemental analysis (%): found C, 57.1; H, 5.2; N, 3.2. Calcd. for C40H42Fe2N2O4Sn (845.18): C, 56.85; H, 5.01; N, 3.31.

4.9. Preparation of $[L^{CN}(n-Bu)_2Sn(O_2CFc)]$ (8)

Compound 8 was obtained in an analogous manner using FcCO₂H (309 mg, 1.30 mmol), t-BuOK (151 mg, 1.30 mmol) and [L^{CN}(*n*-Bu)₂SnCl] (525 mg, 1.30 mmol). Reddish brown oily product was obtained. Yield: 567 mg (73%). ¹H NMR (C₆D₆, 295 K, ppm): 8.61 (d, 1H, H(6'), ${}^{3}J({}^{1}H(5'), {}^{1}H(6')) = 6.7$ Hz), ${}^{3}J({}^{119}Sn,$ 1 H) = 53.5 Hz); 7.38 (t, 1H, H(5')); 7.25 (m, 1H, H(4')); 6.99 (d, 1H, H $(3'), {}^{3}J({}^{1}H(4'), {}^{1}H(3')) = 7.4 \text{ Hz}); 5.21 (s, 2H, H(Cp)); 4.33 (s, 5H, H)$ (Cp')); 4.22 (s, 2H, H(Cp)); 3.12 (s, 2H, CH₂N); 1.98 (m, 4H, H(1)); 1.80 (s, 6H, N(CH₃)₂); 1.55 (m, 4H, H(2)); 1.42 (m, 4H, H(3)); 1.02 (t, 3H, H(4)). ¹³C NMR (C₆D₆, 295 K, ppm): 175.2 (OC(0)); 143.3 (C2'); 142.8 (C1'); 138.5 (C6'); 129.1 (C4'); 127.1 (C3'); 77.7 (C_{ipso}(Cp)); 71.2 (Cp); 70.3 (Cp); 69.8 (Cp'); 65.5 (CH₂N); 45.1 (N(CH₃)₂); 28.6 (C2); 27.5 (C3); 17.0 (C1); 14.0 (C4); the resonance of C5' is overlapped by the solvent signal. ¹¹⁹Sn NMR (C_6D_6 , 295 K, ppm): -92.2. IR (neat, cm^{-1}): 1636 (vs, $v_{as}(COO)$); 1321 (vs, $v_s(OC(O))$). Elemental analysis (%): found C, 56.7; H, 6.7; N, 2.2. Calcd. for C₂₈H₃₉FeNO₂Sn (596.17): C, 56.41; H, 6.59; N, 2.35.

4.10. X-Ray crystallography

Single crystals of **1** grew overnight directly in the NMR tube containing a concentrated solution of the compound in benzened6. Single crystals of **2** were obtained from a THF solution of the compound at -30 °C. The diffraction data were obtained at 150 K using Oxford Cryostream low-temperature device and a Nonius KappaCCD diffractometer using graphite-monochromatized MoKa radiation ($\lambda = 0.71073$ Å). Data reductions were performed with DENZO-SMN [30] and the data were corrected for absorption by integration methods [31]. The structures were solved by direct methods (Sir-92) [32] and refined by full matrix least-squares based on F^2 (SHELXL97) [33]. Hydrogen atoms were mostly localized on a difference Fourier maps. However to ensure uniformity in the treatment of the crystal structures, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.5U_{eq}(pivotal atom)$ for methyl groups and $1.2U_{eq}$ for all other with C–H = 0.96, 0.97, and 0.93 Å for methyl, methylene and aromatic hydrogen atoms, respectively, and 0.82 Å for N–H and O–H protons. The molecule of $1 \cdot C_6 D_6$ reveals a disordered *n*-butyl group. The disorder was treated using constraint and restraint options available in SHELXL-97 software. Besides, one of the unsubstituted Cp rings in each 1 and 2 of are disordered and were refined with planar aromatic arrangements.

Crystallographic data for $1 \cdot C_6 D_6$, $C_{41}H_{45}Fe_2NO_4Sn$, M = 846.17, monoclinic, P21/c, a = 11.1430(12), b = 12.6761(10), c = 28.1690(14)Å, $\alpha = 90$, $\beta = 111.124(7)$, $\gamma = 90^\circ$, Z = 4, V = 3711.5(5)Å³, $D_c = 1.514$ g cm⁻³, $\mu = 1.481$ mm⁻¹, $T_{min} = 0.633$, $T_{max} = 0.846$; 51851 reflections measured ($\theta_{max} = 24.0^\circ$), 5815 independent ($R_{int} = 0.0426$), 5070 with $I > 2\sigma(I)$, 390 parameters, S = 1.072, R1(obs. data) = 0.0426, wR2(all data) = 0.0973; max, min residual electron density = 1.925, -1.140 eÅ⁻³.

Crystallographic data for **2**; $C_{40}H_{42}Fe_2N_2O_4Sn$, M = 845.15, monoclinic, Cc, a = 12.2571(12), b = 18.6440(9), c = 15.6719(7) Å, $\alpha = 90$, $\beta = 95.571(13)$, $\gamma = 90^{\circ}$, Z = 4, V = 3564.4(1) Å³, $D_c = 1.575$ g cm⁻³, $\mu = 1.543$ mm⁻¹, $T_{min} = 0.668$, $T_{max} = 0.788$; 14272 reflections measured ($\theta_{max} = 27.5^{\circ}$), 7318 independent ($R_{int} = 0.0350$), 6798 with $I > 2\sigma(I)$, 398 parameters, S = 1.074, R1(obs. data) = 0.0350, $wR2(all \ data) = 0.0703$; max, min residual electron density = 1.121, -0.67 eÅ⁻³.

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Appendix A. Supplementary information

CCDC 807996 and CCDC 807995 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.

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