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Triorganostannyl(IV) benzoates with pendulous framework appended with ferrocene scaffold☆

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ABSTRACT

A series of four new long chain triorganotin(IV) esters containing a diazenyl- and an imino-groups appended with ferrocene scaffold were designed and synthesized. Ferrocene based metallo pro-ligands H'HFcL^1 and H'HFcL^2 were obtained by reacting isomeric 3-/4-ferrocenylanilines with 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid, which upon reactions with appropriate triorganotin(IV) precursors yielded compounds namely, [nBu$_3$Sn(HFcL^1)] **1**, [Ph$_3$Sn(HFcL^1) **2**, [nBu$_3$Sn(HFcL^2)] **3** and [Ph$_3$Sn(HFcL^2) **4**. Compounds **1**–**4** have been characterized by elemental analysis and their spectroscopic properties were investigated using IR, UV-Vis and NMR spectroscopic techniques. The molecular structures of H'HFcL^1 and two representative heterobimetallic compounds **3** and **4** have been determined by X-ray crystallography. Compound **3** is a 1D polymer and **4** is a discrete molecule; their structural differences relative to those of H'HFcL^1 clearly indicate the influence of the binding of the tin cluster. The redox properties of the metallo pro-ligands and their compounds were also investigated by cyclic voltammetry.

1. Introduction

Bis(η^5-cyclopentadienyl)iron(II), ferrocene (Fc) and its derivatives have now attained a status of distinction in molecular chemistry and materials sciences owing to the ease in handling, robustness and the richness of its stereoelectronic properties. These properties have provided diverse applications such as in catalysis, nanomedicine, biological sensing including macromolecular, supramolecular and optoelectronics and are documented in excellent reviews [1–18]. Fc can be customized easily by both single electron oxidation and electrophilic substitution at the cyclopentadienyl rings, which results into functionalization of derivatives. Synthetic avenues for the preparation and reactivity of Fc derivatives with multi-variability of modification of compounds are also documented [19]. Fc derivatives containing organic fragments bearing heteroatoms such as sulphur [20], nitrogen [21], oxygen [22], phosphorous [23] and complexing behavior incorporating tin [24–26], have also achieved distinction. Among the Fc metallo ligands, metal complexes of Fc-derived Schiff base ligands have shown high activities towards ring opening of cyclic esters [27] and liquid crystalline properties (ferrocenomesogens) showing paramagnetism, etc [28,29]. Additionally, transition metal complexes of Fc metallo ligands, bridged by conjugated systems, are of prime importance because of the possible electronic communications between the metal centers [30,31]. Consequently, a large number of Fc pyridine Schiff base derivatives were explored as electrochemical sensors [32], homogenous catalysis [33], liquid crystals [34], non-linear optical materials [35], luminescent systems [36], novel bimetallic complexes with fascinating architectures [37,38], organometallic polymers [39] and conducting polymers [40] including cytotoxic- [8], antimicrobial- [41–45] and antiparasitic- [46] agents. Considering significant accomplishments of Fc-derived Schiff bases in various fields, new classes of compounds are also on record, which were synthesized by integrating Fc with 1,2-diphenyldiazene with the expectations of obtaining outstanding properties of both. Connecting the metal center and 1,2-

☆ Dedicated to Professor Armando José Latourrette de Oliveira Pombeiro.

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diphenyldiazene with an organic linker having suitable length and/or a π-conjugated system enables communication of the electronic states between the metal and the 1,2-diphenyldiazene groups. Accordingly, the Fc and 1,2-diphenyldiazene-based molecules have been suitably modified with a multitude of organic functionality and find state-of-the-art-applications in modern chemistry as chemosensor [47], colorimetric probe [48], ion recognitions [49], DNA detections [50,51], host-guest system [52,53], low molecular weight gelators [54], light driven molecular scissors [55,56], self-assembled monolayers [57–61], light driven molecular train [62], polyesters [63], polymers: with metallomesogens [64] and with flash memory behavior [65] and nano-sized high density memory devices [66].

On the other hand, Fc has been used as a scaffold for new ligands and coordination of Fc ligands with other metal centers to afford heterobimetallic compounds with varied geometries, oxidation states, and electronic properties are known to have biological action [8,9,24–26]. Although, heterobimetallic compounds of Fc and Sn have been known for quite some time [9], the extant literature on cytotoxic potential of structurally characterized Fc conjugated organotin(IV) carboxylates is scanty. To our knowledge, compounds of the types $[Ph_4Sn_2(\{OC(O)\}_2Fc')(OMe)]_2$, $[\{[nBu_2SnOC(O)Fc']_2O\}_2]$ and $[\{nBuSn(O)OC(O)Fc'\}_6]$ (Fc' = trifluoromethyl-5-ferrocenyl-pyrazol-1-yl-acetate) [67] and $[nBu_3SnOC(O)Fc]_n$, $[\{(\mu\text{-}nBu_2Sn)_2(\mu\text{-}nBu_2SnOC(O)Fc)_2(\mu_3\text{-}O)_2(\mu\text{-}OMe)_2\}]_2$, $[\{Ph_3SnOC(O)Fc(H_2O)\}(\text{-phen})]$, $[\{Ph_3SnOC(O)Fc\}(\mu\text{-}4,4'\text{-bipy})\{Fc(O)COSnPh_3\}]$ [68] were evaluated for their cytotoxic potentials against various cell lines and the observed results were found to be cell line specific. In agreement with these developments, a new series of heterobimetallic formulations of $[FcL^nSnPh_3]$, $[FcL^nSnBu_3]_n$, $[FcL^3SnCy_3]$ and $[FcL^3SnR_3(MeOH)]$ (R = Me, Et or Pr), where FcL^n (n = 1–3) refers to the isomeric 2/3/4-ferrocenylbenzoates, were synthesized and characterized [69]. Among these, $[FcL^1SnBu_3]_n$ demonstrated maximum inhibition in HepG2 cells with negligible effect on human peripheral blood mononuclear cells (PBMC) [69]. Recently, organotin(IV) carboxylates bearing imino-azo linkages have also shown promising cytotoxic properties against various cell lines [70,71]. In view of these, the present research is aimed at incorporating four key features in the ultimate compounds such as (i) a π-bonded iron(II) organometallic with an electro active center which is sensitive to the changes in the ligating branches such as conformation, coordination, donor-acceptor and Lewis acid-base interactions (ii) an aryl conjugated flexible linker with imino- and diazenyl-groups (iii) an adjustable carboxylic acid group that can bind with metal/organometal and (iv) incorporation of biologically active σ-bonded tin(IV) organometallics. In the present contribution, two metallo pro-ligands *viz*., 3- and 4-ferrocenyl benzoic acid derivatives, abbreviated as $H'HFcL^1$ and $H'HFcL^2$ ($H'HFcL^n$), respectively, have been synthesized and their triorganotin(IV) esters were prepared using appropriate triorganotin(IV) precursors (Scheme 1). Heterobimetallic compounds of compositions $[nBu_3Sn(HFcL^1)]$ **1**, $[Ph_3Sn(HFcL^1)]$ **2**, $[nBu_3Sn(HFcL^2)]$ **3** and $[Ph_3Sn(HFcL^2)]$ **4** were characterized by elemental analysis, spectroscopy, cyclic voltammetry and detailed structural information on representative metallo pro-ligand $H'HFcL^1$ and compounds **3** and **4** has been obtained through single-crystal X-ray diffraction.

2. Experimental

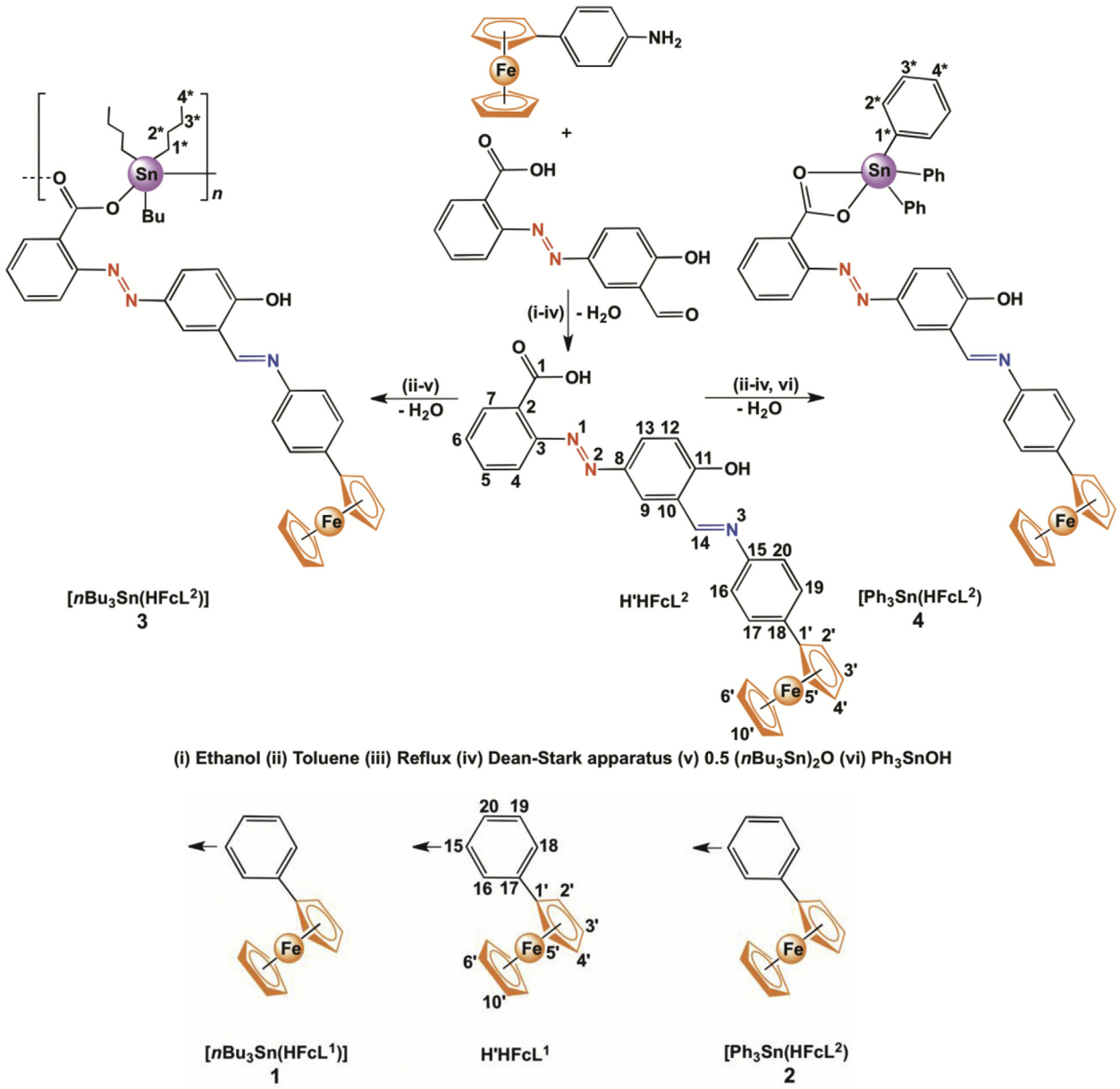
2.1. Materials and physical measurements

All chemicals were used as purchased without purification: anthranilic acid (Sigma-Aldrich), salicylaldehyde, 3-nitroaniline, 4-nitroaniline, cetyltrimethyl ammonium bromide (Sisco), Ph_3SnOH (Fluka) and $(nBu_3Sn)_2O$ (Merck). Solvents used in the reactions were AR grade and dried using standard literature procedures. Melting points were measured using a Büchi M-560 melting point apparatus and are uncorrected. Elemental analyses were performed using a Perkin Elmer 2400 series II instrument. IR spectra in the range 4000-400 cm^{-1} were obtained on a Perkin Elmer Spectrum BX series FT-IR spectrophotometer with samples investigated as KBr discs. Absorption measurements were carried out on a Perkin-Elmer Lambda25 spectrophotometer at ambient temperature in freshly prepared DMSO solution (Fig. S1). The ^1H, ^{13}C, ^{15}N and ^{119}Sn NMR spectra of the pro-ligands and triorganotin(IV) compounds **1**–**4** (Figs. S2–S23) were recorded on a Bruker Avance III HD 400 spectrometer and measured at 400.13 MHz, 100.62 MHz, 40.55 MHz and 149.12 MHz, respectively, in $CDCl_3$ using 5 mm tunable PRODIGY cryo probe. The ^1H and ^{13}C chemical shifts were referenced to internal Me_4Si ($\delta = 0.00$ ppm) while ^{15}N and ^{119}Sn chemical shifts were referenced to external neat CH_3NO_2 and external neat Me_4Sn, respectively, in a co-axial capillary ($\delta = 0.00$ ppm). All 2D experiments, gradient-selected (gs)-correlation spectroscopy (COSY), total correlation spectroscopy (TOCSY), heteronuclear multiple-quantum correlation (HMQC), HMQC-RELAY, HMQC-TOCSY, heteronuclear multiple bond correlation (HMBC) were performed using manufacturer's software (TOPSHIM 3.5). After NMR measurements of compounds **1**–**4** in $CDCl_3$, the solvent was evaporated and ^1H, ^{13}C, and ^{119}Sn NMR spectra were recorded in DMSO-d_6. The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface and by using a three electrode cell with a platinum-disc working electrode (0.5 mm diameter) whose potential was controlled *vs*. a Luggin capillary connected to a silver wire pseudo reference electrode; a platinum auxiliary electrode was employed. Cyclic voltammograms of the metallo pro-ligands $H'HFcL^n$ and of their triorganotin(IV) compounds **1**–**4** were obtained in 0.2 M $[^nBu_4N][BF_4]$/DMSO solutions at ambient temperature. The redox potential values of the compounds are quoted relative to saturated calomel electrode (SCE); they were measured by cyclic voltammetry at a scan rate of 200 mVs^{-1} in the presence of acetylferrocene as the internal standard ($E^{ox}_{1/2}$ = 0.67 V *vs*. SCE in DMSO, whose potential value was measured using ferrocene as internal standard) (*Note*: The $E^{ox}_{1/2}$ redox potential value for ferrocene was measured at 200 mVs^{-1} in a $[^nBu_4N][BF_4]$ 0.1 M DMSO solution and using the saturated calomel electrode (SCE) as reference; the $E^{ox}_{1/2}$ redox potential value for acetylferrocene was measured under the same experimental conditions and using ferrocene as internal standard). Conversion to the normal hydrogen electrode (NHE) was done by addition of 0.24 V to the values quoted relative to SCE [72].

2.2. Synthesis of the metallo pro-ligands

2.2.1. Synthesis of 3-ferrocenyl-2-((E)-(4-hydroxy-3-((E)-(phenylimino)methyl)phenyl)diazenyl)benzoic acid ($H'HFcL^1$)

An ethanolic solution (15 ml) of 3-ferrocenylaniline (0.51 g, 1.85 mmol) was added to a hot toluene solution (30 ml) containing 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (0.50 g, 1.85 mmol). The reaction mixture was heated to reflux for 5 h using a Dean-Stark apparatus and filtered while hot. The filtrate was evaporated to dryness using a rotary evaporator, which upon standing at room temperature deposited orange material. The orange residue was boiled with hexane (3 × 5 ml), filtered and dried *in vacuo*. The product was then recrystallized from methanol/benzene (2:1) to afford orange crystalline material. Yield: 0.80 g, 79%. M.p.: 118–120 °C. Anal. Found. C, 57.66; H, 3.60; N, 6.28. Calc. for $C_{31}H_{24}Cl_3FeN_3O_3$: C, 57.39; H, 3.73; N, 6.48%. IR (cm^{-1}): 1733, 1617,



Scheme 1. Schematic representation of the synthetic methodologies for preparation of H'HFcL^2 and triorganotin(IV) esters (**3** and **4**) with atom numbering protocol used for NMR assignment along with bonding interactions as found in the solid state. The ligands difference in H'HFcL^1 and triorganotin(IV) esters (**1** and **2**) is the *para*- and *meta*-relationship of ferrocenyl and the arylimine groups, where arrow refers to the continuity of the rest of the molecules.

1602, 1516, 1495, 1412, 1393, 1370, 1278, 1237, 1221, 1155, 1108, 1086, 1010, 884, 823, 793, 763, 730, 685, 652, 592, 486. Electronic absorption data in DMSO λ_{max}, nm; (ε [M^{-1}]): 327 (8600), 492sh (1,300).

2.2.2. Synthesis of 4-ferrocenyl-2-((E)-(4-hydroxy-3-((E)-(phenylimino)methyl)phenyl)diazenyl)benzoic acid (H'HFcL^2)

An analogous method to that used for the preparation of H'HFcL^1 was followed except that 3-ferrocenylaniline was replaced by 4-ferrocenylaniline. The product was crystallized from ethanol, giving dark-red crystals of H'HFcL^2. Yield: 0.83 g, 82%. M.p.: 206–208 °C. Anal. Found. C, 68.35; H, 4.54; N, 8.04. Calc. for $C_{30}H_{23}FeN_3O_3$: C, 68.07; H, 4.38; N, 7.94%. IR (cm^{-1}): 1731, 1619, 1594, 1521, 1493, 1437, 1405, 1347, 1279, 1238, 1154, 1111, 1084, 888, 828, 763, 686, 685, 651, 613, 536, 496. Electronic absorption data in DMSO λ_{max}, nm; (ε [M^{-1}]): 346 (11,000), 482sh (2,100).

2.3. Synthesis of the triorganotin(IV) compounds *1*–*4*

A general method was followed for the synthesis of ferrocene appended tri-*n*-butyltin compounds **1** and **3**. In a typical procedure, a mixture of (nBu$_3$Sn)$_2$O and the appropriate metallo pro-ligands H′HFcL^n in a 1:2 stoichiometric ratio was heated to reflux in anhydrous toluene (50 ml) for 8 h in a round bottom flask equipped with a Dean-Stark apparatus and a water-cooled condenser. The reaction mixture was filtered while hot and the solvent was removed using a rotary evaporator. The residue was washed with cold hexane to give a loose powder and dried *in vacuo*. The solid was recrystallized using appropriate solvent(s) to yield the desired product. An analogous procedure was followed for the synthesis of the triphenyltin(IV) compounds **2** and **4**, but using Ph$_3$SnOH with H′HFcL^n in a 1:1 stoichiometric ratio. The crude products of **2** and **4** were boiled with hexane and dried *in vacuo*. The dried mass was

dissolved in benzene and filtered to remove any suspended particles. The clear filtrate was concentrated and precipitated twice with hexane to afford the desired solid material. The specific details pertaining to reactants, analytical and characterization data for the complexes are given below.

*2.3.1. Synthesis of [nBu$_3$Sn(HFcL^1)] (**1**)*

(*n*Bu$_3$Sn)$_2$O (0.22 g, 0.38 mmol); H'HFcL^1 (0.40 g, 0.75 mmol). Recrystallized from methanol to give an orange microcrystalline product. Yield: 0.48 g, 77%. M.p.: 90–92 °C. Anal. Found. C, 62.14; H, 5.83; N, 5.10%. Calc. for $C_{42}H_{49}FeN_3O_3Sn$: C, 61.64; H, 6.03; N, 5.13%. IR (cm^{-1}): 1618 ν_{asym}(OCO), 1598, 1582, 1567, 1491, 1463, 1396, 1343, 1286, 1183, 1144, 1106, 1089, 1033, 1018, 864, 831, 807, 793, 766, 690, 674, 664, 584, 517, 497. Electronic absorption data in DMSO λ_{max}, nm; (ε [M^{-1}]): 326 (7900), 502sh (900).

*2.3.2. Synthesis of [Ph$_3$Sn(HFcL^1)] (**2**)*

Ph$_3$SnOH (0.20 g, 0.55 mmol); H'HFcL^1 (0.30 g, 0.56 mmol). Recrystallized from benzene to give an orange microcrystalline product. Yield: 0.36 g, 70%. M.p.: 130–132 °C. Anal. Found. C, 65.93; H, 4.22; N, 4.80%. Calc. for $C_{48}H_{37}FeN_3O_3Sn$: C, 65.63; H, 4.25; N, 4.78%. IR (cm^{-1}): 1619 ν_{asym}(OCO), 1599, 1574, 1480, 1430, 1332, 1285, 1260, 1180, 1145, 1107, 1076, 1022, 997, 864, 820, 763, 730, 696, 496. Electronic absorption data in DMSO λ_{max}, nm; (ε [M^{-1}]): 332 (7400), 496sh (1,500).

*2.3.3. Synthesis of [nBu$_3$Sn(HFcL^2)] (**3**)*

(*n*Bu$_3$Sn)$_2$O (0.22 g, 0.38 mmol); H'HFcL^2 (0.40 g, 0.75 mmol). Recrystallized from ethanol/benzene (1:1) mixture to give red microcrystalline product. Yield: 0.49 g, 80%. M.p.: 138–140 °C. Anal. Found. C, 61.78; H, 5.83; N, 5.03%. Calc. for $C_{42}H_{49}FeN_3O_3Sn$: C, 61.64; H, 6.034; N, 5.134%. IR (cm^{-1}): 1615 ν_{asym}(OCO), 1583, 1547, 1522, 1490, 1460, 1394, 1347, 1284, 1189, 1107, 1091, 1030, 890, 874, 834, 815, 764, 670, 609, 536, 495. Electronic absorption data in DMSO λ_{max}, nm; (ε [M^{-1}]): 343 (9900), 490sh (1,800).

*2.3.4. Synthesis of [Ph$_3$Sn(HFcL^2)] (**4**)*

Ph$_3$SnOH (0.20 g, 0.55 mmol); H'HFcL^2 (0.30 g, 0.56 mmol). Recrystallized from chloroform/benzene (2:1) mixture to give orange-red microcrystalline product. Yield: 0.38 g, 76%. M.p.: 214–216 °C. Anal. Found. C, 65.30; H, 4.23; N, 5.11%. Calc. for $C_{48}H_{37}FeN_3O_3Sn$: C, 65.63; H, 4.25; N, 4.78%. IR (cm^{-1}): 1618 ν_{asym}(OCO), 1597, 1576, 1521, 1430, 1384, 1354, 1329, 1281, 1247, 1191, 1145, 1135, 1106, 1077, 887, 815, 762, 730, 697, 677, 601, 542, 501. Electronic absorption data in DMSO λ_{max}, nm; (ε [M^{-1}]): 344 (12,000), 485sh (2,100).

2.4. Single-crystal X-ray diffraction analysis

Single crystals suitable for an X-ray crystal structure determination were obtained from chloroform/methanol/benzene (2:2:1, v/v) (H'HFcL^1), ethanol/benzene (1:1, v/v) (**3**) and chloroform/benzene (2:1, v/v) (**4**) solutions of the respective compounds by slow evaporation of the solvent(s) at room temperature. Diffraction data were recorded at low temperature (150 K) on a Bruker AXS-KAPPA APEX II Photon 100 detector diffractometer using Mo Kα radiation (λ = 0.71073 Å). Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART [73] software and refined using Bruker SAINT [73] on all the observed reflections. Absorption corrections were applied using SADABS [74].

Structures were solved by direct methods by using SIR-97 [75] and refined with SHELXL–2014 [76]. Calculations were performed using the WinGX-Version 2014.01 [77]. All non-hydrogen atoms were found from the difference Fourier syntheses. The hydrogen atoms attached to carbon atoms were placed at geometrically calculated positions and included in the refinement using the riding-model approximation; U_{iso}(H) were defined as 1.2 U_{eq} of the parent carbon atoms for phenyl and methylene residues and 1.5 U_{eq} of the parent carbon atoms for the methyl groups. The data collection and refinement parameters are given in Table 1.

3. Results and discussion

*3.1. Synthesis and spectroscopic characterization of **1**–**4***

Two metallo pro-ligands H'HFcL^1 and H'HFcL^2 were synthesized by reacting 2-[(*E*)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid with 3-ferrocenylaniline and 4-ferrocenylaniline, respectively, in toluene/ethanol mixture. Ferrocenyl appended tri-*n*-butyltin(IV) compounds **1** and **3** were synthesized by reacting (*n*Bu$_3$Sn)$_2$O and respective H′HFcL^n in a 1:2 stoichiometric ratio while triphenyltin(IV) analogues **2** and **4** were accomplished from the reactions of an equimolar amounts of Ph$_3$SnOH and appropriate H′HFcL^n, in refluxing toluene. Synthetic methodologies are detailed in Scheme 1. The compounds were isolated as air stable coloured crystalline solids and they are soluble in common polar and non-polar organic solvents. The metallo pro-ligands H′HFcL^n were characterized by IR, ^{1}H and ^{13}C NMR spectroscopic techniques, while additionally ^{119}Sn NMR spectroscopy was used to confirm the coordination behavior of compounds **1**–**4** in solution. The asymmetric stretching vibrations for the carboxylate groups, ν_{asym}(OCO), for compounds **1**–**4** were detected at around 1615 cm^{-1}, which is ~110 cm^{-1} lower than the value measured for the metallo pro-ligands H′HFcL^n (~1730 cm^{-1}), indicating coordination of the carboxylate group to the triorganotin fragments [78]. A band due to ν_{sym}(OCO) was detected in the range 1330–1355 cm^{-1} (refer to the experimental section for specific values). The observed differences, i.e. $\Delta(\nu_{asym} - \nu_{sym})$ in compounds **1**–**4** are 275, 287, 265 and 264 cm^{-1}, respectively, which are in the lower limit of both unidentate and bidentate coordination (Δ range from 107 to 565 cm^{-1} for unidentate and 45-299 cm^{-1} for bidentate bridging mode) as correlated by Watkinson et al. [79]. The results of single crystal X-ray diffractions data for compounds **3** and **4**, resolved the

Table 1
Crystal data, data collection parameters and convergence results for **3** and **4**.

	3	4
Empirical formula	$C_{42}H_{49}FeN_3O_3Sn$	$C_{48}H_{37}FeN_3O_3Sn$
Formula weight	818.38	878.34
Temperature (K)	150	150
Crystal system	orthorhombic	monoclinic
Space group	P b c a	P 2$_1$/c
a (Å)	10.5826(11)	21.607(3)
b (Å)	24.476(2)	23.955(3)
c (Å)	28.978(3)	7.5711(11)
α (°)	90	90
β (°)	90	93.770(5)
γ (°)	90	90
V (Å^3)	7505.7(12)	3910.3(9)
Z	8	4
D_{calc} (g/cm^3)	1.448	1.492
F000	3376	1784
μ (mm^{-1})	1.095	1.057
Reflections measured	152657	53894
Independent reflections	6863	7129
Reflection with I > 2σ(I)	5384	6173
Number of parameters	457	509
R_{int}	0.0878	0.0641
$R(F)$ ($I \geq 2\sigma$)	0.0341	0.0949
wR (F^2) (all data)	0.0982	0.2413
GOF (F^2)	0.952	0.989

ambiguity of the coordination modes of carboxylate to the tin atom (bridging bidentate and chelate, respectively; see X-ray discussion). Proton NMR spectra were assigned using gs-COSY. Carbons bearing protons were assigned by gs-HMQC and quaternary carbons were assigned by gs-HMBC. The most important correlations were as follows: protons C(7) H with COOH resp. COOSn carbons and quaternary C(17) (compounds **1** and **2**) resp. C(18) (compounds **3** and **4**) carbons with −C-CH protons of substituted cyclopentadiene ring via ^{3}J(C, H) differentiating closer CH from more distant CH groups of substituted cyclopentadiene ring. The second non-substituted cyclopentadiene ring provided only one signal both in ^{1}H and ^{13}C NMR spectra on the NMR time scale. There are minor changes of the signals in the ^{1}H and ^{13}C NMR spectra upon complex formation, for example, the carbonyl group C(1), however, the most important information which could be extracted from the results of ^{1}J(Sn-C) coupling constants are discussed below. The assignment of other proton and carbon resonances was relatively straightforward. gs-HMBC technique was used to measure ^{1}H-^{15}N correlations, experiment being optimized for coupling constants of 4 Hz. ^{3}J(^{15}N, ^{1}H) coupling constants are mainly responsible for formation of appropriate cross-peaks. Compounds **1**–**4** exhibit a single sharp resonance in ^{119}Sn NMR spectra. NMR data of pro-ligands H′HFcL^{n} and four triorganotin(IV) esters **1**–**4**, measured in $CDCl_3$, are given in Table S1 while ^{1}H, ^{13}C and ^{119}Sn chemical shifts and ^{n}J(^{119}Sn, ^{13}C) coupling constants in triorganotin(IV) moieties of compounds **1**–**4** in $CDCl_3$ and DMSO-d_6 are collected in Table 2. The tin atom in both tri-*n*-butyltin(IV)- (**1** and **3**) and triphenyltin(IV) (**2** and **4**) esters measured in $CDCl_3$ are four-coordinated as reflected from their ^{119}Sn chemical shifts and ^{n}J(^{119}Sn, ^{13}C) coupling constants values [80,81]. Taking into consideration the solid-state X-ray diffraction studies (see below), these results suggest a rupture of the polymeric structure of **3** in solution and the break of the chelation mode of carboxylate in **4**. Coordination number five of tin atom is retained when spectra of **1**–**4** were measured in DMSO-d_6 [82,83]. An upfield shift of ~150 ppm is typical of such a change as well as an increase of ^{1}J(^{119}Sn, ^{13}C) coupling constant values were noted [84,85]. Although an estimate of C-Sn-C angle can be analyzed by Lockhert equation but is applicable only for methyltin compounds [86]. However, for the tributyltin(IV) compounds, ^{1}J(^{119}Sn, ^{13}C) coupling constants values were used for estimations of C-Sn-C angles using the proposed following equations [87].

$$|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})| = (9.99 \pm 0.73)\theta - (746 \pm 100)$$

A linear dependence of $|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})|$ in *n*-butyltin(IV) compounds on the C-Sn-C angles θ obtained from X-ray analysis was found:

$$746 + 355 = 9.99\ \theta\ \theta = 110.2 \text{ (calculated for compound } \mathbf{1})$$

$$746 + 481 = 9.99\ \theta\ \theta = 122.8 \text{ (calculated for compound } \mathbf{2})$$

Analogously, equation for phenyltin(IV) derivatives is also known [88]:

$$|^{1}J(^{119}\mathrm{Sn},^{13}\mathrm{C})| = (15.56 \pm 0.84)\theta - (1160 \pm 101)$$

$$1160 + 646 = 15.56\ \theta\ \theta = 116.1 \text{ (calculated for compound } \mathbf{3})$$

$$1160 + 832 = 15.56\ \theta\ \theta = 128.0 \text{ (calculated for compound } \mathbf{4})$$

Using these equations, angles θ in compounds **1** and **3** in $CDCl_3$ were found to be 110.2° (nearly ideal trigonal arrangement) while 122.8° (nearly ideal arrangement of butyl groups in a plane around tin atom, i.e. close 120°) in DMSO-d_6. The corresponding calculated θ values for compounds **2** and **4** are 116.1° in $CDCl_3$ and 128.0° in DMSO-d_6. The relatively considerable increase of angle in **2** and **4** is very likely due to steric reasons caused by more bulky phenyl groups in comparison with smaller *n*-butyl analogues.

Metallo pro-ligands H′HFcL^{n} display ^{15}N chemical shifts for all the nitrogen atoms. However, in all triorganotin(IV) compounds **1**–**4**, signal due to one of the diazenyl nitrogen atom (N1) is not observed in spite of measuring several times under different experimental conditions and appears to be a typical of these set of compounds (Table 3).

3.2. Electrochemistry

The redox properties of the metallo pro-ligands H′HFcL^{n} and their triorganotin(IV) derivatives **1**–**4** were studied by cyclic voltammetry at a Pt electrode ($d = 0.5$ mm), in 0.2 M [^{n}Bu$_4$N][BF$_4$]/DMSO. Fig. 1 exemplifies the type of cyclic voltammograms obtained, and the redox potential values (vs. SCE) of the compounds are shown in Table 4. The H′HFcL^{n} and compounds **1**–**4** exhibit a one-electron reversible anodic wave (I^{ox}) at $E^{ox}_{1/2}$ values of 0.41–0.48 V *vs.* SCE assigned to the Fe(II) → Fe(III) oxidation process and the values are close to that of ferrocene (0.44 V *vs.* SCE) [89] but lower than that of the value reported for acetylferrocene. Moreover, compounds **1**–**4** are rather insensitive to the presence and the disparity of the triorganotin(IV) moiety as reported earlier

Table 3
^{15}N chemical shifts in metallo pro-ligands H'HFcL^{1} and H'HFcL^{2} and triorganotin(IV) compounds[a] **1**–**4** in $CDCl_3$.

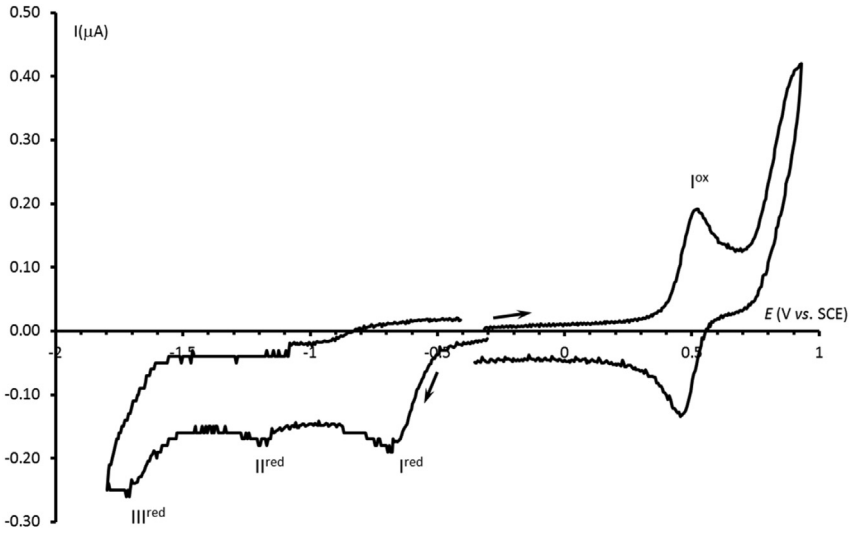
N No.	H'HFcL^{1}	H'HFcL^{1}	1	2	3	4
N1	49.0	48.4	[b]	[b]	[b]	[b]
N2	112.8	112.3	122.7	124.1	123.0	125.1
N3	−91.3	−93.2	−86.2	−87.0	−87.7	−89.1

[a] Refer to Scheme 1 for N numbering protocol used for assignment.
[b] Not observed.

Table 2
^{1}H, ^{13}C and ^{119}Sn chemical shifts and ^{n}J(^{119}Sn, ^{13}C) coupling constants (in parentheses, Hz, ± 0.5 Hz) in triorganotin(IV) moiety of compounds[a] **1**–**4** in $CDCl_3$ and DMSO-d_6.

Compound	Solvent	1*		2*		3*		4*		δ(^{119}Sn)
		^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	
1	$CDCl_3$	1.34	16.7 (355.1)	1.62	27.8 (20.2)	1.34	27.1 (65.6)	0.87	13.6 (2.5)	117.3
	DMSO-d_6	1.09	18.6 (481.5)	1.53	27.7 (27.1)	1.23	26.5 (76.5)	0.83	13.6 (3.6)	−22.4
2	$CDCl_3$	–	138.1 (646.0)	7.74	136.9 (49.0)	7.37	128.9 (64.6)	7.37	130.1 (13.4)	−106.6
	DMSO- d_6	–	143.0 (832.2)	7.89	136.2 (46.3)	7.39	128.1 (69.3)	7.39	128.8 (14.8)	−259.9
3	$CDCl_3$	1.31	16.6 (355.5)	1.63	27.8 (20.2)	1.31	27.1 (66.8)	0.87	13.6 (2.5)	117.3
	DMSO- d_6	1.09	18.8 (480.1)	1.54	27.4 (27.4)	1.24	26.5 (78.4)	0.78	13.6 (3.4)	−23.6
4	$CDCl_3$	–	138.1 (646.2)	7.74	136.9 (49.3)	7.40	128.9 (64.7)	7.40	130.1 (13.4)	−106.6
	DMSO- d_6	–	143.0 (831.2)	7.89	136.2 (46.1)	7.41	128.2 (69.4)	7.41	128.8 (14.8)	−259.9

[a] Refer to Scheme 1 for H/C numbering protocol used for assignment.



(a)

Fig. 1(a). Cyclic voltammogram for the H'HFcL^2 (5.2×10^{-4} M) in [NBu_4][BF_4] 0.2 M in DMSO at a platinum disc working electrode ($d = 0.5$ mm) and at a scan rate of 0.2 V s^{-1}. The arrows indicate the initial anodic or cathodic scans.

Table 4
Cyclic voltammetric data[a] for metallo pro-ligands H'HFcL^1 and H'HFcL^2 and triorganotin(IV) compounds **1**–**4**.

Compound	R group in $\{SnR_3\}^+$	Oxidation, $^{I}E^{ox}_{1/2}$	Reduction		
			$^{I}E^{red}_{p}$	$^{II}E^{red}_{p}$	$^{III}E^{red}_{p}$
H'HFcL^1	–	0.47	−0.63	−0.97	−1.70
1	*n*Bu	0.48	−0.72	−1.00	−1.72
2	Ph	0.48	−0.67	−1.22	−1.74
H'HFcL^2	–	0.48	−0.70	−1.16	−1.74
3	nBu	0.41	–	–	–
4	Ph	0.48	–	−0.98	–

[a] Potential values (in Volt ± 0.02) relative to SCE, measured by CV at a Pt electrode in DMSO/0.2 M [^{n}Bu$_4$N][BF_4] at 0.2 V s^{-1}.

for other Fc-containing complexes [69,89], although on comparing H'HFcL^2 and **3** a redox potential change of 70 mV was measured upon the binding of the $\{SnBu_3\}^+$ moiety. Therefore, the Cp substituents in the compounds of present investigation are weaker net electron-donors (**3** is the exception) than the H-substituent but they are better than the acetyl group. In addition, the oxidation potential values in the compounds of present study are slightly lower than the related ferrocenyl benzoic acids or triorganotin(IV) ferrocenyl benzoate analogues [69], indicating a stronger electron-acceptor character of the carboxylic (or carboxylate) group in the latter compounds in comparison with the imine substituents in the former.

The compounds H′HFcL^n, as well as **1** and **2**, show ligand centred cathodic processes (Fig. 1) at potential values in the ranges −0.63 to −0.72 (wave I^{red}), −0.97 to −1.22 (wave II^{red}) and −1.70 to −1.74 V *vs.* SCE (wave III^{red}). No cathodic processes were detected in **3**, and in **4** only wave II^{red} could be identified.

Upon conversion to the NHE scale by adding +0.24 V, the measured reversible oxidation potentials for the compounds were applied to calculate the electrochemical E_L ligand parameter [90] for the substituted cyclopentadienyl ligands, and thus predict the net electron-donor character of the ligand (the stronger is this character, the lower the E_L). With this purpose, the linear relationship (1) was applied; which was proposed by Lever [91] and is valid for mixed sandwich complexes of the type used in the present work, *viz.* H'HFcL^1. This expression assumes an additive contribution to the redox potential [$E^o(Fe^{III}/Fe^{II})$] of the non-substituted (Cp) and the substituted (Cp^s) cyclopentadienyl ligands.

$$E^o(Fe^{III}/Fe^{II}) = E_L(Cp^s) + E_L(Cp) \quad (1)$$

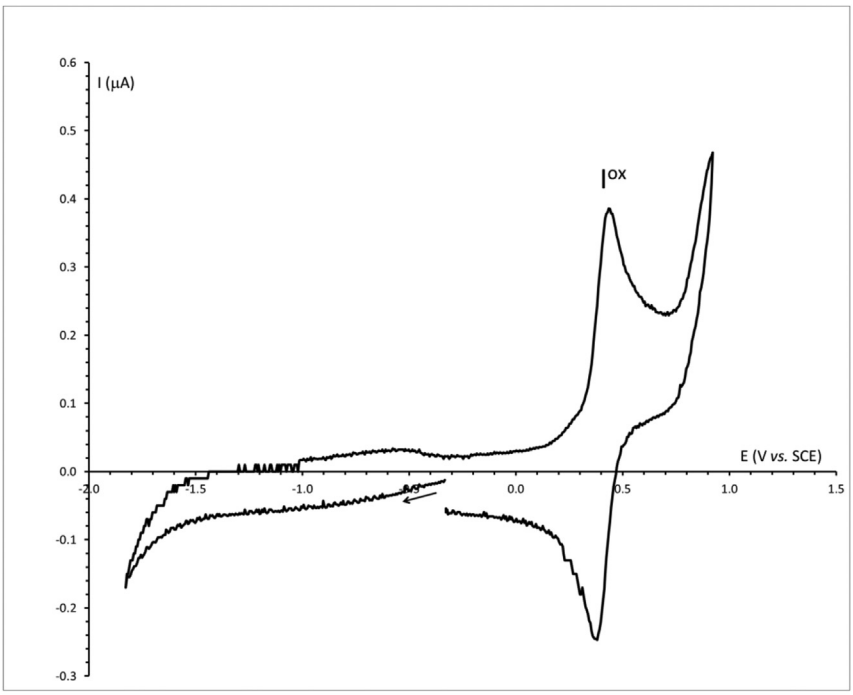
Thus, knowing the redox potential of the compound (E^o) and the E_L parameter for Cp (0.33 V *vs.* NHE) [90], the values of 0.38 and 0.39 V *vs.* NHE were obtained for the E_L ligand parameter of the substituted cyclopentadienyl ligand in H'HFcL^1 and H'HFcL^2, respectively, indicating identical electron-donor properties. The obtained values are in the range found for ferrocenyl benzoic acids [69].

3.3. Description of the X-ray crystal structures

The heterobimetallic compounds **3** and **4** were characterized by single crystal X-ray diffraction. The perspective views of their molecular structures are shown in Fig. 2, while a comparison of selected bond distances and angles are presented in Table 5. Despite the low quality of the molecular structure of H'HFcL^1, some comments are worth to be taken to compare its structures (Fig. S24 and Table S2) with those of the heteronuclear complexes **3** and **4**, regardless of their holding a different ligand (HFcL^2).

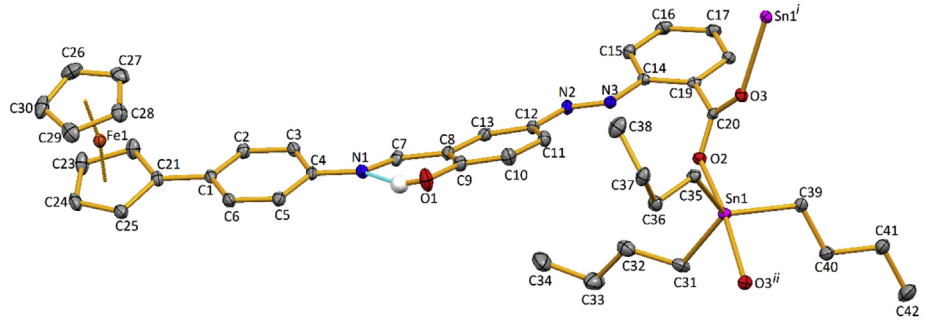
The metallo pro-ligand H'HFcL^1 consists of discrete mononuclear entities and crystallized with chloroform molecules. The cyclopentadienyl rings of the ferrocene moiety (see Fig. S25) are in the eclipse form in H'HFcL^1, contrasting with the staggered conformation found in **3** and the intermediate situation met in **4**. In H'HFcL^1, the distance between the perpendicular projection of the iron cation on the least-square plane of this ring and its centroid (*ring slippage*) is of 0.043 Å, differing considerably from the value in the non-substituted Cp (0.000 Å, Table 5) and confirming the influence of the organic substituent on such parameter; the presence of the Sn moieties in **3** and **4** affected the ring slippage in both Cp. The planarity of organic substituent in the cyclopentadienyl ring is highly dependent on the compound (see Fig. S26 and Table S3).

Besides the intramolecular H-bond interaction conecting the hydroxide and the N_{imine} atoms in H'HFcL^1, with the typical $S^1_1(6)$ graph set [92] (Fig. S24), the molecules of H'HFcL^1 are coupled by

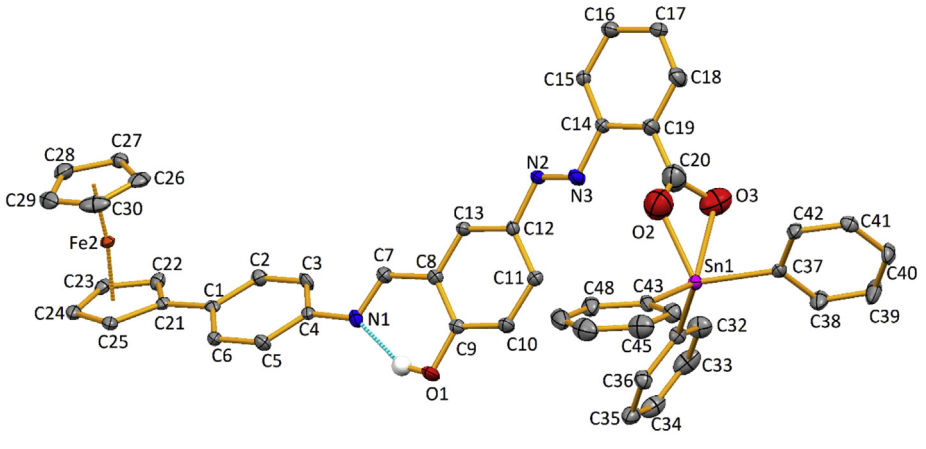


(b)

Fig. 1(b). Cyclic voltammogram for compound **3** (5.7×10^4 M) in $[NBu_4][BF_4]$ 0,2 M in DMSO at a platinum disc working electrode ($d = 0.5$ mm) and at a scan rate of 0.2 V s^{-1}. The arrow indicates the initial cathodic scan.



3



4

Fig. 2. Ortep structures (drawn at 30% probability lever) of compounds **3** and **4** with atom labeling scheme. Intramolecular H-bond interactions are represented in light blue colour.: O1–H1o•••N1, d(D · A) = 2.599(4) Å, ∠(D–H · A) 151(3)° (**3**); O1–H1o · N1, d(D · A) = 2.613(13) Å, ∠(D–H · A) 152(10)° (**4**). Hydrogen atoms not involved in such interactions are omitted for clarity. Symmetry operations to generate equivalent atoms in **3**: *i*) −1/2 + x,y,1/2-z; *ii*) 1/2 + x,y,1/2-z. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 5
Selected bond distances (Å) and angles (°) for H'HFcL[1], **3** and **4**.

	H'HFcL[1]	**3**	**4**
Fe ··· Cg1 (subst. Cp)	1.6627(7)	1.6407(18)	1.642(5)
(ring slippage, Å)	(0.043)	(0.018)	(0.032)
Fe ··· Cg2 (ring slippage)	1.680(9)	1.658(2)	1.646(6)
	(0.000)	(0.029)	(0.010)
∠Cg1 ··· Fe ··· Cg2	177.8(5)	179.1(3)	177.9(3)
$C_{aromatic}-N_{imine}$	1.431(16)	1.424(4)	1.424(13)
$N_{imine}=C_{imine}$	1.339(15)	1.266(4)	1.297(14)
$N_{azo}=N_{azo}$	1.309(14)	1.256(4)	1.230(13)
Sn-O	–	2.214(2)	2.121(16)
		2.391(2)	2.65(1)
Sn-C (range)	–	2.134(4) – 2.143	2.127–2.129
Sn coordination parameter (τ_5)	–	0.84	0.44
Fe ··· Sn (*intra*molecular)	–	17.052	16.643
Fe ··· Fe (*inter*molecular)	5.942	7.134	6.323
Sn ··· Sn (*inter*molecular)	–	5.446	7.571

means of H-bond contacts involving the phenolic OH groups of adjacent molecules and forming $R_2^2(24)$ graph sets.

The asymmetric unit of the heterometallic compound **3** comprises the $HFcL^2$ fragment binding the Sn^nBu_3 unit through the deprotonated carboxylate group. Symmetry expansion reveals the compound as polymeric (Fig. 2) spreading along the crystallographic *a* axis (Fig. S27) by means of bridging bidentate *syn-anti* carboxylates, with the ferrocene branches on the same side of the $\{Sn\text{-}OCO\}_n$ chain. The iron-containing branches, however, are not aligned on the same plane but alternately disposed (Fig. S28). The Sn cations present trigonal bipyramid coordination spheres ($\tau_5 = 0.84$) [93] made of the C_{butyl} atoms in the equatorial positions and the $O_{carboxylate}$ atoms from two symmetry related ligands in the axial sites. The Sn–O and Sn–C bond distances (Table 5) are in the range of those found in other tin(IV) complexes [94].

The asymmetric unit of **4** includes one discrite molecule of the compound with the $HFcL^2$ ligand bridging to the $\{SnPh_3\}^+$ cation through the chelating carboxylate group. The tin cation presents a five-coordinate geometry ($\tau_5 = 0.44$) made of three C_{phenyl}- and two $O_{carboxylate}$-atoms. The Sn-O lengths are quite dissimilar (Table 5), the longer one (2.61(1) Å) including the oxygen atom involved in the longest $CO_{carboxylate}$ bond (1.38(2) Å); the remaining $CO_{carboxylate}$ is considerably shorter (1.13(2) Å) and clearly shows a double bond character. The SnC distances in **4** are shorter than the ones in **3** (Table 5), which is probably related to the greater electron-donor character of the butyl groups relative to the phenyl ones.

In view of the folding of $HFcL^2$ in **4** (see Fig. S26 and Table S3) its intramolecular Fe···Sn distance in shorter than in **3** (16.643 against 17.052 Å). Probably as a result of steric constraints, the shortest intermolecular Sn···Sn distance in **4** (7.571 Å) is more than 2 Å greater than that in **3** (5.446 Å). The presence of the Sn(IV) clusters in the heterobimetallic compounds also increased the intermolecular Fe···Fe distances (Table 5).

4. Conclusion

In summary, a series of four new triorganotin(IV) esters [nBu$_3$Sn($HFcL^1$)] **1**, [Ph$_3$Sn($HFcL^1$)] **2**, [nBu$_3$Sn($HFcL^2$)] **3** and [Ph$_3$Sn($HFcL^2$)] **4** containing a diazenyl- and an imino-groups was synthesized from ferrocene supported metallo pro-ligands $H'HFcL^1$ and $H'HFcL^2$. The molecular frameworks in solution were characterized by the use of ^{1}H, ^{13}C, ^{15}N and ^{119}Sn chemical shifts together with 2D experiments such as gs-COSY, TOCSY, HMQC, HMQC-RELAY, HMQC-TOCSY and HMBC. The molecular structures of $H'HFcL^1$ and two representative heterobimetallic compounds **3** and **4** have been determined by X-ray crystallography, revealing that **4** is a discrete molecules while **3** is polymeric. The binding of the tin clusters to the carboxylate groups in **3** and in **4**, although influencing the Cps ring slippages, on the planarity of $HFcL^n$, the twisting of the carboxylate group and on the double bond characters of the C=N and the N=N groups, had no effect on the redox potential values of the compounds. The solid-state five coordinate polymeric structure of **3** and the carboxylate chelating mode of **4** are not retained in $CDCl_3$ solution, as revealed from ^{119}Sn chemical shifts and $^nJ(^{119}Sn, ^{13}C)$ coupling constants values. Coordination number of tin atoms is five when spectra of **1**–**4** were measured in DMSO-d_6. The present study discovered triorganotin carboxylates in which the carboxylate moiety contains a ferrocene substituent, which may find application in cancer chemotherapeutics and related work are underway in our laboratory.

Conflicts of interest

The authors declare that they have no conflicts of interest with the contents of this article.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.12.009.

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