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Facile, Ambient Temperature, Double Sn–C Bond Cleavage: Synthesis, Structure, and Electrochemistry of Organotin and Organotellurium Ferrocenecarboxylates

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The reaction of organotin halides R_3SnCl (R = Me or benzyl) with ferrocenecarboxylic acid (FcCOOH) in the presence of triethylamine affords Me_3SnO_2CFc (**1**) or Bn_3SnO_2CFc (**2**) (Bn = benzyl). The latter undergoes a facile ambient temperature double Sn–C bond cleavage to give the monoorganostannoxane, $[BnSn(O)O_2CFc]_6$ (**3**). Compound **3** is also formed by a single Sn–C bond cleavage reaction in the reaction between Bn_2SnCl_2 and FcCOOH. In contrast, the reaction of Me_2SnCl_2 with FcCOOH affords $Me_2Sn(O_2CFc)_2$ (**4**), where the Sn–C bonds are robust. Organotellurium ferrocene carboxylates $[(4\text{-OMe-Ph})_2Te(O_2CFc)_2]$ (**5**) and $[(4\text{-NMe}_2\text{-Ph})_2\text{-}Te(O_2CFc)_2]$ (**6**) are obtained in the reaction of the corresponding diorganotellurium oxides/halides with FcCOOH. Whereas **1** is a zig-zag one-dimensional coordination polymer with a *square-wave* architecture, the structures of **3**–**6** are molecular. Compound **3** is a hexameric cage and possesses a *drum-type* structure, whereas **4** is mononuclear and contains a six-coordinate tin with a skewed trapezoidal geometry. In compounds **5** and **6** the lone pairs on tellurium are stereochemically active thereby conferring see-saw geometries. Compounds **1**, **2**, **4**, and **5** show single quasireversible peaks at +0.62, +0.72, +0.66, and +0.64 V, respectively with respect to the Ag/AgCl electrode. Compound **3**, which contains six ferrocene arms, shows a single redox event along with a stripping peak. Compound **6** shows quasireversible and irreversible redox events at +0.62 and +1.17 V, respectively. The latter is due to a ligand-centered oxidation.

Introduction

Multiferrocene compounds have been attracting considerable interest in recent years in view of their potential applications as multielectron reservoirs, electron-transfer mediators, and electrode modification materials.[1] Several electrode-modification methods have been developed for the preparation of these compounds, the majority of which involve tedious stepwise synthetic procedures.[2] In a departure from this we and others have developed a new paradigm where inorganic rings and cages can be utilized successfully to anchor multiple ferrocene units.[3] Utilizing this strategy we were also able to assemble hybrid macrocycles containing ferrocene and main group motifs.[4] Among the *inorganic strategies*, organostannoxane synthesis is very effective.[5] The process of building the organostannoxane framework simultaneously incorporates the ferrocene units in the molecule.[6] The nature of the organotin substrate modulates the type of organostannoxane, which in turn controls the number and orientation of the ferrocene groups.[3h,6] Such compounds have also attracted interest in surface chemistry. For example, organostannoxane-supported hexameric ferrocene assembly has been studied for its wetting behavior on silicon substrates.[7] Because of this continued interest and as part of our program on organostannoxanes, herein, we report the synthesis, structural characterization, and electrochemical studies of mono-, di-, and triorganotin ferrocenecarboxylates. During this study we discovered an unusual, ambient temperature, double Sn–C bond cleavage process that converts a tribenzyltin ferrocenecarboxylate into a monobenzyl derivative. Because of our recent interest[4,8] in organotellurium compounds, we also report the synthesis, structure, and electrochemistry of diorganotellurium ferrocenecarboxylates.

Results and Discussion

Synthetic Aspects

The reaction of FcCOOH (Fc = C_5H_4-Fe-C_5H_5) with organotin halides was carried out in the presence of hydrogen chloride scavengers such as triethylamine or potassium hydroxide (Scheme 1). Products **1**, **2**, and **4** were isolated in excellent yields. Remarkably, the tribenzyltin derivative Bn_3SnO_2CFc (Bn = benzyl; **2**) underwent ambient temperature double Sn–C bond cleavage to afford monoorganooxotin cage **3**. Although Sn–C bond cleavage is known among

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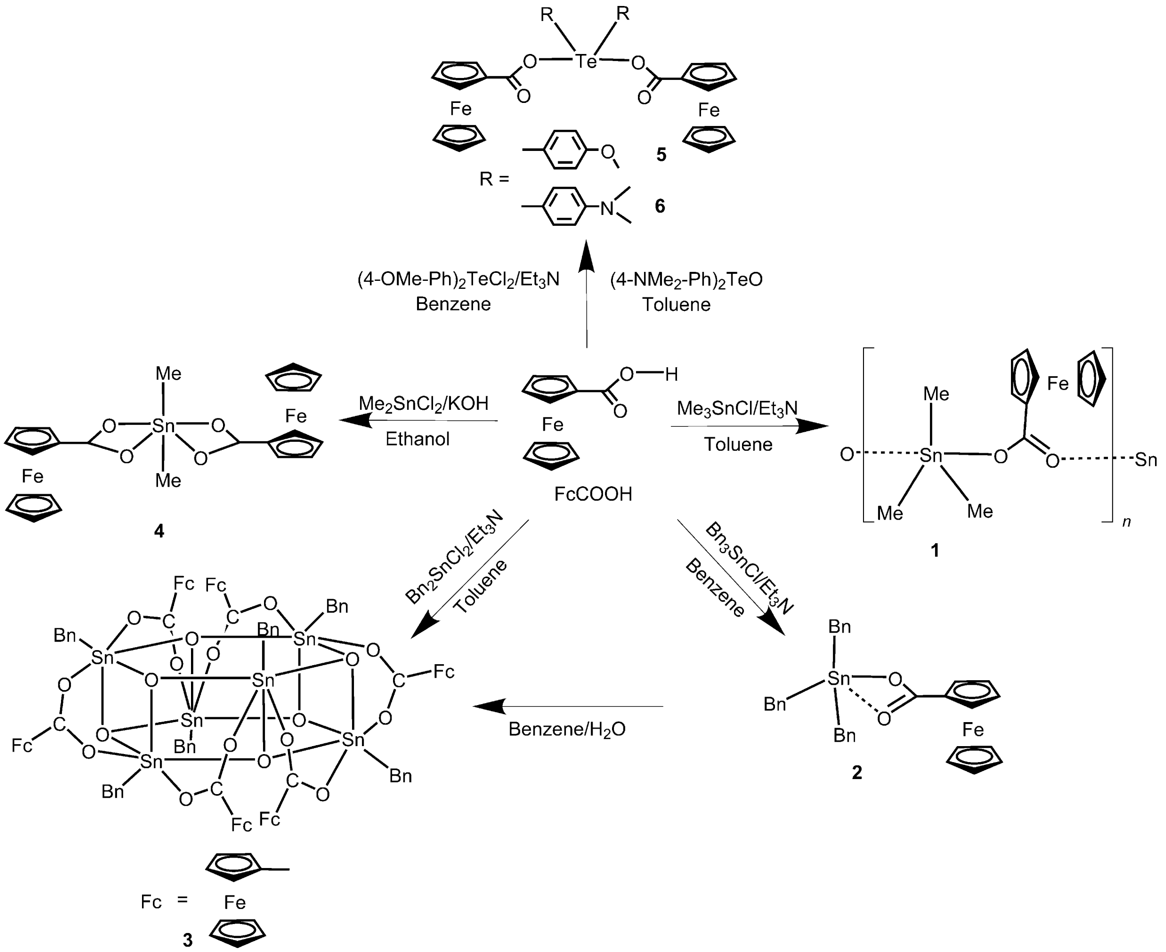

Scheme 1. Synthesis of mono-, di-, and triorganotin ferrocenecarboxylates.

benzyltin compounds, these usually occur at elevated temperatures.[9] Hexanuclear cage **3** is also obtained in a single Sn–C bond cleavage reaction involving Bn_2SnCl_2 and FcCOOH. In contrast to the facile Sn–C cleavage observed with benzyltin compounds, reactions with Me_3SnCl and Me_2SnCl_2 afford compounds **1** and **4**, where the Sn–C bonds are robust. Organotellurium ferrocenecarboxylates are prepared readily by the reaction of the corresponding organotellurium oxides/dichlorides with ferrocenecarboxylic acid by dynamic removal of water with the use of a Dean–Stark apparatus or by performing the reaction in the presence of triethylamine.

Compounds **1**–**4** show characteristic chemical shifts in their $^{119}Sn\{^1H\}$ NMR spectra (see Experimental Section). For example, the hexameric cage is characterized by the presence of a single peak at –524.2 ppm. Tellurium carboxylates **5** and **6** resonate at +957 and +984 ppm, respectively, in their $^{125}Te\{^1H\}$ NMR spectroscopy. ESI-MS studies of **1**, **2**, **4**, **5**, and **6** reveal that they retain their integrity in solution. The ESI-MS of **3** could not be recorded because of its insolubility in CH_3CN or CH_3OH.

The UV/Vis spectra of **1**–**6** recorded under similar concentration (10^{-3} M) conditions reveal the presence of a broad absorption band, and the value of λ_{max} varies between 444–448 nm. On the basis of literature precedents, this absorption is assigned to a d–d transition.[4,10] Increase in the number of ferrocenyl units leads to an increase in the value of ε. For example, **3**, which contains six ferrocene arms, has an ε value of 1537 L mol^{-1} cm^{-1} (see Figure S1).

The infrared spectra of **1**–**6** reveal the bidentate nature of binding by FcCOO in the case of **1**–**4**, as evidenced by the small difference between ν_{asym} and ν_{sym}; the $\Delta\nu$ value varies between 168 to 179 cm^{-1} in these compounds. In the case of **5** and **6**, however, the carboxylate ligand binds in a monodentate manner. This is reflected in the large $\Delta\nu$ values of 251 and 267 cm^{-1} in these compounds. The conclusions from the infrared spectra are borne out by the results obtained from X-ray crystallography.

X-ray Crystal Structures of 1, 3, 4, 5, and 6

The various structural diagrams of **1** and **3**–**6** are given in Figures 1–6 (see also Figures S2–S6). The bond parameters for these compounds are summarized in Table 1.

The X-ray crystal structure of **1** shows that it contains two independent ferrocene and trimethyltin units in its asymmetric unit. Compound **1** is a coordination polymer

Table 1. Selected bond lengths (Å) and bond angles (°) for compounds **1** and **3**–**6**.

	1		
Sn1–C12	2.126(10)	Sn2–C28	2.136(9)
Sn1–C13	2.089(10)	Sn1–O1	2.135(6)
Sn1–C14	2.121(10)	Sn1–O2	2.546(7)
Sn2–C26	2.115(8)	Sn2–O3	2.151(5)
Sn2–C27	2.107(8)	Sn2–O4	2.496(7)
C13–Sn1–C14	122.3(5)	C27–Sn2–C26	113.2(4)
C13–Sn1–C12	121.5(5)	C27–Sn2–C28	119.0(4)
C14–Sn1–C12	114.4(5)	C26–Sn2–C28	125.8(3)
C13–Sn1–O1	97.3(4)	C27–Sn2–O3	90.9(3)
C14–Sn1–O1	98.1(3)	C26–Sn2–O3	96.8(3)
C12–Sn1–O1	87.7(4)	C28–Sn2–O3	96.1(3)
C13–Sn1–O2	83.7(3)	C27–Sn2–O4	82.4(3)
C14–Sn1–O2	85.0(3)	C26–Sn2–O4	90.8(3)
C12–Sn1–O2	88.0(4)	C28–Sn2–O4	82.6(3)
O1–Sn1–O2	175.5(2)	O3–Sn2–O4	171.4(2)
	3		
Sn1–C12	2.178(6)	Sn1–O3	2.081(4)
Sn1–O1	2.119(5)	O1–C1	1.267(9)
Sn1–O2	2.133(5)		
O1–Sn1–O2	81.09(19)	O2–Sn1–O3	163.22(19)
O1–Sn1–O3	86.48(18)		
	4		
Sn1–C12	2.100(9)	Sn1–O4	2.514(6)
Sn1–C13	2.093(8)	C1–O1	1.246(9)
Sn1–O1	2.524(6)	C1–O2	1.309(9)
Sn1–O2	2.110(5)	C14–O3	1.286(10)
Sn1–O3	2.120(5)	C14–O4	1.235(10)
C13–Sn1–C12	146.9(4)	O2–Sn1–O4	139.3(2)
C13–Sn1–O2	103.0(3)	O3–Sn1–O4	55.4(2)
C12–Sn1–O2	102.2(3)	C13–Sn1–O1	88.7(3)
C13–Sn1–O3	103.2(3)	C12–Sn1–O1	88.4(3)
C12–Sn1–O3	100.5(3)	O2–Sn1–O1	55.0(2)
O2–Sn1–O3	83.9(2)	O3–Sn1–O1	138.9(2)
C13–Sn1–O4	87.2(3)	O4–Sn1–O1	165.6(1)
C12–Sn1–O4	87.6(3)		
	5		
Te1–C1	2.104(4)	O3–C15	1.303(6)
Te1–C8	2.103(5)	O4–C15	1.236(6)
Te1–O3	2.180(3)	O5–C26	1.299(6)
Te1–O5	2.137(3)	O6–C26	1.237(5)
C1–Te1–C8	100.87(11)	C8–Te1–O3	84.27(15)
C8–Te1–O5	83.22(16)	C1–Te1–O3	86.85(15)
C1–Te1–O5	87.20(11)	O3–Te1–O5	164.88(12)
	6		
Te1–C12	2.111(7)	O1–C1	1.230(8)
Te1–C20	2.115(7)	O2–C1	1.305(7)
Te1–O2	2.117(4)	O3–C28	1.331(8)
Te1–O3	2.182(4)	O4–C28	1.209(8)
C12–Te1–C20	100.1(3)	C20–Te1–O2	83.7(2)
C12–Te1–O3	87.2(3)	O3–Te1–O2	164.99(18)
C20–Te1–O3	83.9(2)	C1–O2–Te1	112.3(4)
C12–Te1–O2	86.5(2)	C28–O3–Te1	113.5(4)

formed as a result of an anisobidentate bridging coordination action of the ferrocenecarboxylate $(FcCOO)^-$ ligand, which connects successive trimethyltin units (Figure 1). The coordination geometry around each tin is trigonal bipyramidal with the equatorial positions occupied by the three carbon atoms. Two types of Sn–O distances are found [cf. Sn1–O1 2.135 (6); Sn1–O2, 2.546(7) Å]. The O1–Sn1–O2 bond angle is 175.5(2)° indicative of the regular trigonal bipyramidal geometry around tin. The solid-state organization of **1** leads to a one-dimensional zig-zag polymer in a *square-wave* architecture (Figure 2). Such architecture is quite unusual among triorganotin carboxylates.

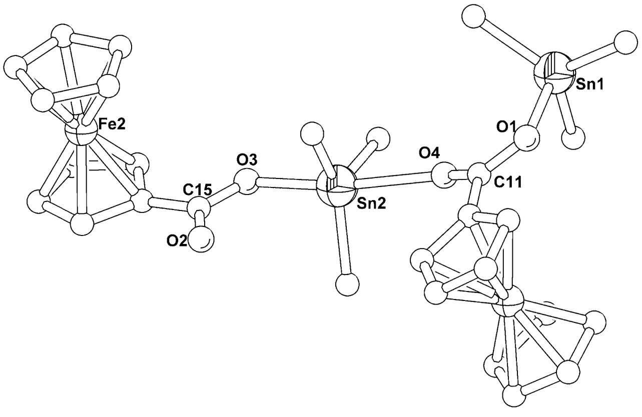

Figure 1. Structure of **1** showing the trimethyltin unit connected to ferrocenecarboxylate ligands (hydrogen atoms are omitted for clarity).

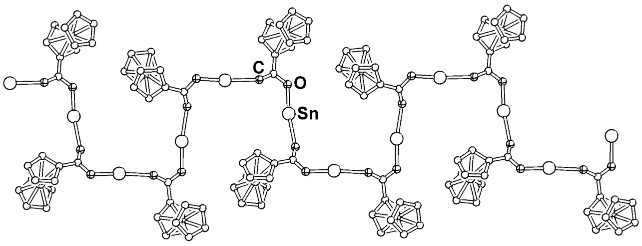

Figure 2. Coordination polymer of **1** showing the *square-wave*-type architecture (hydrogen atoms and methyl groups are omitted for clarity).

The molecular structure of **3** is shown in Figure 3. This structure belongs to the well-known family of *drum* compounds among organostannoxanes.[3h,3i,5a–5c,11] The structure of **3** comprises an Sn_6O_6 core. Alternate tin atoms are bridged by an isobidentate carboxylate ligand. The Sn_6O_6 core comprises two fused Sn_3O_3 rings giving rise to six Sn_2O_2 four-membered rings in the side. All the Sn–O bond lengths found in **3** are nearly similar (Table 1).

The molecular structure of **4** (Figure 4) shows a hexacoordinate tin present in a skewed trapezoidal coordination bound by two chelating anisobidentate ferrocenecarboxylate ligands. The two ferrocene ligands present in **4** are oriented in a *trans* manner. Two types of Sn–O bond lengths are present: a short distance [cf. Sn1–O2 2.110(5) Å] and a long distance [cf. Sn1–O1 2.524(6) Å; Table 1].

Organotellurium ferrocenecarboxylates **5** and **6** are present in a see-saw geometry as a result of the stereochemically

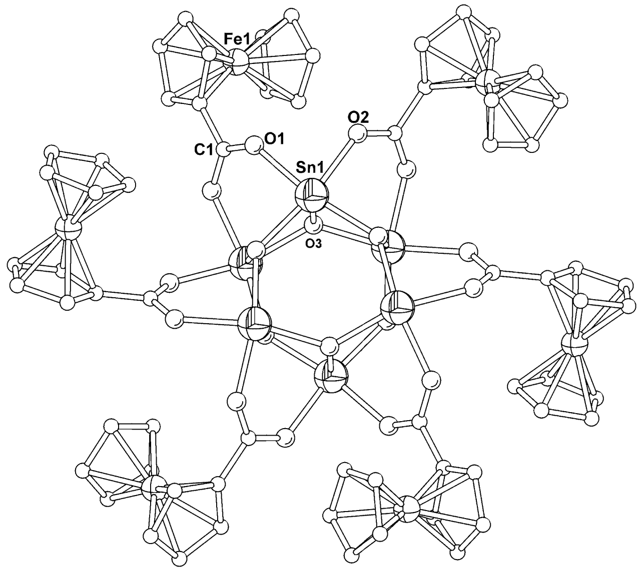

Figure 3. Molecular structure of **3** (hydrogen atoms and benzyl groups are omitted for clarity).

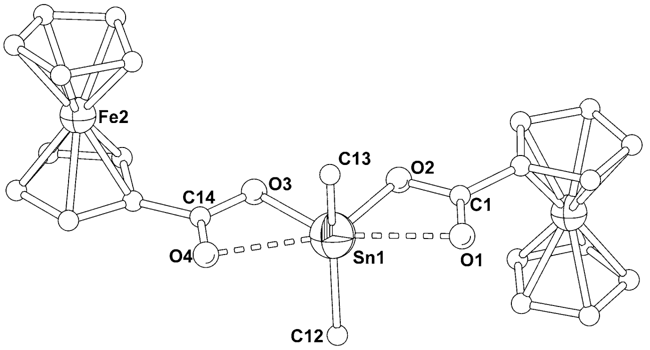

Figure 4. Molecular structure of **4** (hydrogen atoms are omitted for clarity).

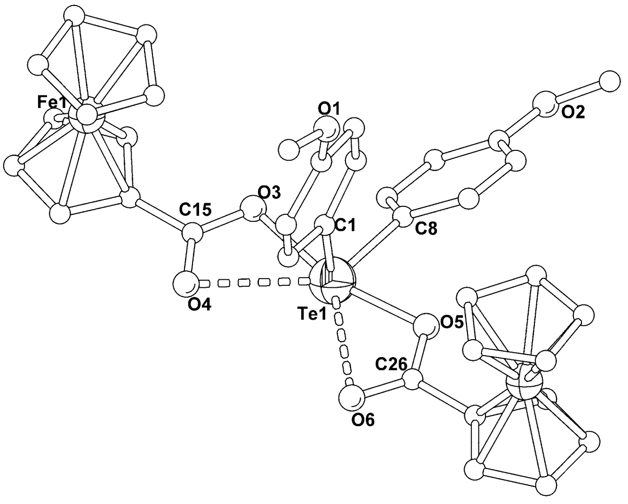

Figure 5. Molecular structure of **5** (hydrogen atoms are omitted for clarity).

active lone pair present on tellurium (Figures 5 and 6). In both compounds the ferrocene ligands are present in a *cis* orientation. The Te–O bond length in **5** is 2.159(3) Å (av.), whereas in **6** it is 2.150(4) Å. In both these compounds the O–Te–O angles deviate considerably from the ideal angle of 180° [in **5** the O5–Te1–O3 angle is 164.88 (12)°, whereas in **6** the O3–Te1–O2 angle is 164.99 (18)°].

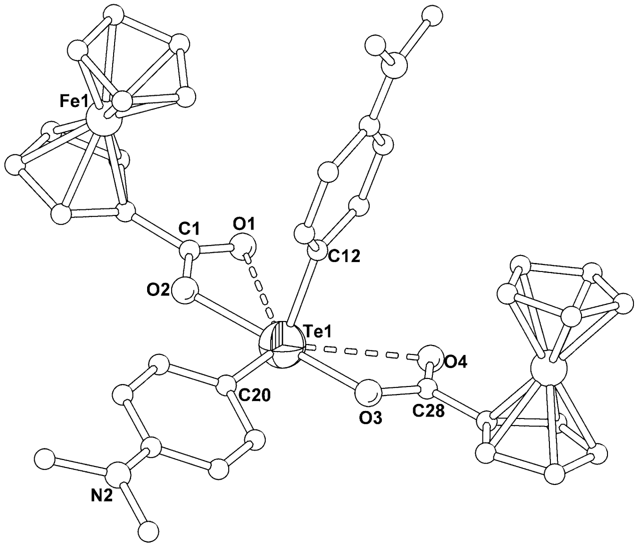

Figure 6. Molecular structure of **6** (hydrogen atoms are omitted for clarity).

Electrochemical Studies

Cyclic voltammetry of compounds **1**–**6** were carried out in dichloromethane solutions at a scan rate of 100 mV s^{-1}. The cyclic voltammograms are shown in Figures 7 and 8. Compounds **1**, **2**, **4**, and **5** show single quasireversible peaks at +0.62, +0.72, +0.66, and +0.64 V, respectively, with respect to the Ag/AgCl electrode (see Table 2). The observation of a single oxidation peak for **4** and **5**, which contain

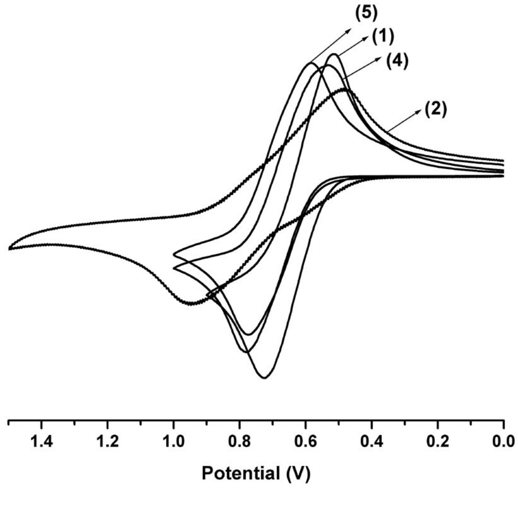

Figure 7. Cyclic voltammograms of **1**, **2**, **4**, and **5**.

two ferrocene units indicates very weak (or no) interaction between ferrocene moieties.[3h,3i,4,6,12] Compound **3**, which contains six ferrocene arms, shows a single redox event along with a stripping peak. The appearance of the stripping peak indicates that upon oxidation the solubility of **3** decreases leading to precipitation at the electrode surface. During the reverse scan the reduction event resolubilizes the compound. Accordingly, in the more soluble ferrocene drum [*n*BuSn(O)O_2CFc]$_6$ such a stripping peak is absent.[3h] Interestingly, **6** shows quasireversible and irreversible redox events at +0.62 and +1.17 V, respectively. We conjectured that the latter might be due to ligand-centered oxidation. This was proved by recording the cyclic voltammogram of bis(*p*-dimethylaminophenyl)telluroxide, which showed an irreversible oxidation at +1.09 V (Table 2; see also Figure S7).

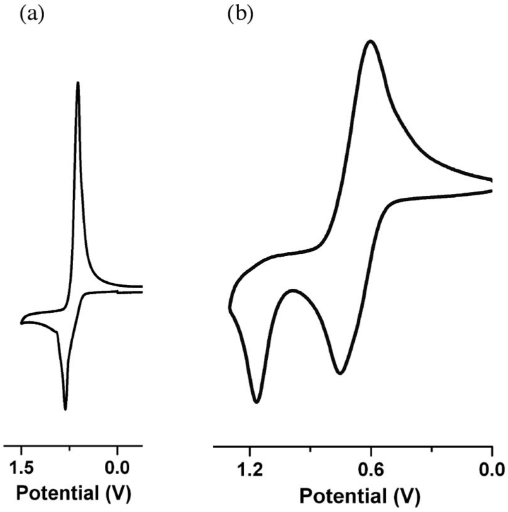

Figure 8. Cyclic voltammograms of (a) **3** and (b) **6**. For **3** note the presence of a stripping peak. For **6** the second irreversible oxidation is ligand centered.

Table 2. Electrochemical data for compounds **1**–**6**.[a]

Compound	$E_{1/2}$[b] (ΔE_p)	Compound	$E_{1/2}$[b] (ΔE_p)
1	0.62 (210)	**5**	0.64 (213)
2	0.72 (463)	**6**	0.62 (268), 1.17[c]
3	0.74 (147)	(4-$NMe_2Ph)_2$TeO	1.09[c]
4	0.66 (249)		

[a] Measured in CH_2Cl_2 containing 0.2 M [*n*Bu_4N][PF_6] at a scan rate of 100 mV s^{-1}. [b] $E_{1/2} = (E_{pc} + E_{pa})/2$. [c] Irreversible peak.

Conclusions

We report a facile synthetic methodology for the preparation of new mono-, di-, and triorganotin ferrocenecarboxylates and diorganotellurium ferrocenecarboxylates. We have observed an interesting ambient temperature double Sn–C bond cleavage reaction, which leads to the conversion of Bn_3SnO_2CFc into [BnSn(O)O_2CFc]$_6$. Electrochemical studies on these main-group element ferrocenecarboxylates reveal the occurrence of primarily quasireversible oxidation events.

Experimental Section

Reagents and General Procedures Solvents were purified by conventional methods and were freshly distilled under a nitrogen atmosphere prior to use according to the standard procedures.[13] Ferrocenecarboxylic acid, dimethyltin dichloride, and trimethyltin chloride were purchased from Aldrich Chemical Co. (USA) and were used as received. Dibenzyltin dichloride, tribenzyltin chloride, bis(4-methoxyphenyl)tellurium dichloride, and bis(*p*-dimethylaminophenyl)telluroxide were prepared according to literature procedures.[14] Potassium hydroxide (RANKEM) was purchased from RFCL Limited, New Delhi, India and was used as such. Triethylamine was purchased from s.d. Fine. Chem. Ltd., Mumbai, India and purified by well-known procedures.[13]

Instrumentation: Melting points were measured by using a JSGW melting point apparatus and are uncorrected. Elemental analyses of the compounds were obtained from Thermoquest CE instruments CHNS-O, EA/110 model. The analyses of compounds were carried out on fully dried samples. Electronic spectra were recorded with a Perkin–Elmer-Lambda 20 UV/Vis spectrometer and with a Shimadzu UV-160 spectrometer by using dichloromethane as the solvent. IR spectra were recorded as KBr pellets with a Bruker Vector 22 FTIR spectrophotometer operating from 4000–400 cm^{-1}. Electrospray ionization mass spectra were recorded with a WATERS – HAB213 spectrometer by using capillary 2.7 kV. ^{1}H, ^{119}Sn{^{1}H}, and ^{125}Te NMR spectra were recorded with a JEOL JNM LAMBDA 400 model spectrometer or a JEOL JNM DELTA 500 model spectrometer. Electrochemistry was performed with a BAS Epsilon electrochemical workstation. The working electrode was a BAS Pt disk electrode, and the auxiliary electrode was a Pt wire. The electrochemistry of the complexes was studied by cyclic voltammetry (CV) in dichloromethane solutions containing 0.20 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Typically the concentration of the complexes was in the range of ≈10^{-2} M. The CV scans were carried out against Ag/AgCl with a scan rate of 100 mV s^{-1}.

X-ray Crystallography: Crystallographic parameters are given in Tables 3 and 4. Single crystals suitable for X-ray crystallographic analyses for **1** and **4** were obtained by slow evaporation/diffusion of *n*-hexane solutions. Compounds **3**, **5**, and **6** were obtained by slow evaporation of dichloromethane, benzene, and toluene solutions, respectively.

For compounds **1** and **4**, the data were collected at room temperature but for the remaining compounds data were collected at 100 or 153 K (Tables 3 and 4). Single-crystal data for compounds **1**, **3**, **4**, and **5** were collected with a Bruker Smart Apex Diffractometer. Data for compound **6** were collected with a Multiwire proportional. In compound **1**, C1 and C2 are disordered over two positions. Also a Q peak with a height of 2.09 e Å^{-3} was observed near the iron center. The latter may due to absorption by X-rays. Similarly, in compound **3**–**5** carbon atoms of the benzyl [C17, C18 (**3**)], ferrocene [C20, C21, and C24 (**4**)], and methoxy group [C7, C14 (**5**)] are disordered over two positions. These were treated satisfactorily. All the structures were solved by direct methods by using the program SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[15] Hydrogen atoms were fixed at calculated positions and their positions were refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Table 3. Crystallographic data and structure refinement details for compound **1**, **3**, and **4**.

	1	**3**	**4**
Empirical formula	$C_{28}H_{36}Fe_2O_4Sn_2$	$C_{108}H_{102}Fe_6O_{21}Sn_6$	$C_{25}H_{28}Fe_2O_5Sn$
Formula weight	785.65	2783.14	638.86
Temperature (K)	273(2)	100(2)	273(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	trigonal	triclinic
Space group	*Pnab*	$R\bar{3}$	$P\bar{1}$
a (Å)	12.889(3)	17.5654(15)	9.345(2)
b (Å)	15.233(3)	17.5654(15)	10.871(2)
c (Å)	34.855(7)	28.643(3)	12.311(3)
α (°)	90	90	95.867(4)
β (°)	90	90	101.042(4)
γ (°)	90	120	97.968(4)
V (Å^3)	6844(2)	7653.5(12)	1204.9(4)
Z	8	3	2
Crystal size (mm)	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.1
$D_{calcd.}$ (g cm^{-3})	1.525	1.812	1.761
μ (mm^{-1})	2.300	2.336	2.250
F(000)	3104	4122	640
θ Range (°)	4.15–25.03	1.95–25.49	2.38–28.35
Limiting indices	$-15 \le h \le 12$ $-17 \le k \le 18$ $-41 \le l \le 40$	$-21 \le h \le 21$ $-21 \le k \le 17$ $-33 \le l \le 34$	$-9 \le h \le 12$ $-14 \le k \le 14$ $-13 \le l \le 16$
Reflections collected	33516	13809	7970
Independent reflections	6010 [R(int) = 0.0795]	3169 [R(int) = 0.0532]	5727 [R(int) = 0.0264]
Data/restraints/parameters	6010/0/324	3169/0/221	5727/0/297
Goodness-of-fit on F^2	1.055	1.135	1.086
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0645, wR_2 = 0.1697	R_1 = 0.0521, wR_2 = 0.1496	R_1 = 0.0617, wR_2 = 0.1511
R indices (all data)	R_1 = 0.0923, wR_2 = 0.1909	R_1 = 0.0642, wR_2 = 0.1563	R_1 = 0.0908, wR_2 = 0.2091

Table 4. Crystallographic data and structure refinement details for compounds **5** and **6**.

	5	**6**
Empirical formula	$C_{36}H_{32}Fe_2O_6Te$	$C_{45}H_{46}Fe_2N_2O_4Te$
Formula weight	799.92	918.14
Temperature (K)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.4190(10)	10.0938(3)
b (Å)	11.6740(11)	11.7072(3)
c (Å)	13.9197(13)	17.9541(5)
α (°)	73.170(2)	97.319(2)
β (°)	69.575(2)	92.951(2)
γ (°)	65.250(2)	108.750(3)
V (Å^3)	1556.6(2)	1983.00(10)
Z	2	2
Crystal size (mm)	0.2 × 0.1 × 0.1	0.3 × 0.3 × 0.2
$D_{calcd.}$ (g cm^{-3})	1.707	1.538
μ (mm^{-1})	1.898	1.498
F(000)	800	932
θ Range (°)	2.27–26.37	2.14–25.00
Limiting indices	$-13 \le h \le 14$ $-13 \le k \le 14$ $-17 \le l \le 16$	$-11 \le h \le 11$ $-13 \le k \le 13$ $-13 \le l \le 21$
Reflections collected	9174	12124
Independent reflections	6218 [R(int) = 0.0260]	6858 [R(int) = 0.0948]
Data/restraints/parameters	6218/0/404	6858/0/492
Goodness-of-fit on F^2	1.057	0.886
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0446 wR_2 = 0.0970	R_1 = 0.0579 wR_2 = 0.1286
R indices (all data)	R_1 = 0.0543 wR_2 = 0.1057	R_1 = 0.0891 wR_2 = 0.1387

CCDC-690136 (for **1**), -690137 (for **3**), -690138 (for **4**), -690139 (for **5**), and -690140 (for **6**) 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.

$[Me_3SnO_2CFc]_n$ (1): Ferrocenecarboxylic acid (0.31 g, 1.35 mmol) was taken up in toluene (80 mL) and to this was added triethylamine (0.14 g, 1.39 mmol). To the resultant clear solution was added trimethyltin chloride (0.27 g, 1.35 mmol) in small portions. The reaction mixture was heated under reflux for 3 h, cooled, and filtered. Removal of the solvent from the filtrate afforded a solid that was recrystallized from hot *n*-hexane to afford red crystals of **1**. Yield: 0.52 g (98 %). M.p. 142 °C (decomp.). UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 444 (230) nm. IR (KBr): $\tilde{\nu}$ = 1563 [s, ν_{asym}COO], 1385 [s, ν_{sym}COO] cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 4.57–4.55 (m, 2 H, Cp), 3.65 (s, 5 H, Cp), 3.63–3.61 (m, 2 H, Cp), 0.07 (s, 9 H, CH_3) ppm. ^{119}Sn NMR (149 MHz, C_6D_6): δ = 115.91 (s) ppm. ESI-MS: *m*/*z* (%) = 165.0080 (87) $[Me_3Sn]^+$, 344.9584 (32) $[(Me_3Sn)_2OH]^+$, 393.9751 (27) $[Me_3SnO_2CFc]$, 556.9326 (100) $[(Me_3Sn)_2O_2CFc]^+$. $C_{14}H_{18}FeO_2Sn$ (392.83): calcd. C 42.80, H 4.62; found C 42.43, H 4.52.

$[Bn_3SnO_2CFc]$ (2): To a clear solution of ferrocenecarboxylic acid (0.16 g, 0.70 mmol) and triethylamine (0.07 g, 0.70 mmol) in benzene (60 mL) was added tribenzyltin chloride (0.30 g, 0.70 mmol). The reaction mixture was stirred at room temperature for 24 h and then filtered, and the solvent was removed from the filtrate in vacuo. A light-sensitive compound identified as **2** was obtained. Yield: 0.42 g (96 %). M.p. >300 °C (decomp.). UV/Vis (CH_2Cl_2): λ (ε, L mol^{-1} cm^{-1}) = 446 (271) nm. IR (KBr): $\tilde{\nu}$ = 1556 [s, ν_{asym}COO], 1383 [s, ν_{sym}COO] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51–6.77 (m, 15 H, Ph), 4.70 (s, 2 H, Cp), 4.48 (s, 2 H, Cp), 3.79 (s, 5

H, Cp), 2.31 (s, 6 H, CH_2) ppm. ^{119}Sn NMR (149 MHz, C_6D_6): δ = –18.15 (s) ppm. ESI-MS: *m*/*z* (%) = 393.0617 (100) $[Bn_3Sn]^+$, 1013.1147 (19) $[(Bn_3Sn)_2SnO_2CFc]^+$, 623.0690 (7) $[Bn_3SnO_2CFcH]^+$. $C_{32}H_{30}FeO_2Sn$ (621.12): calcd. C 61.88, H 4.87; found C 61.57, H 4.73.

$[BnSn(O)O_2CFc]_6$ (3)

Method A: Compound **2** (0.3 g, 0.48 mmol) was dissolved in a benzene/water mixture (99:1, 20 mL) and then filtered, and the filtrate was kept in the dark for slow evaporation. Red crystals, identified as **3**, were obtained over a period of time. These were further washed with methanol and dried. Yield: (0.092 g, 42%).

Method B: To a clear solution of ferrocenecarboxylic acid (0.06 g, 0.26 mmol) and triethylamine (0.06 g, 0.59 mmol) in toluene (50 mL) was added dibenzyltin dichloride (0.10 g, 0.27 mmol). The reaction mixture was heated under reflux for 3 h, cooled, and then filtered, and the solvent was stripped off the filtrate in vacuo. The oily residue that was obtained was washed with diethyl ether/water (9:1, 10 mL). The residue was dissolved in dichloromethane and layered with *n*-hexane and kept for crystallization in the refrigerator. The orange solid obtained was filtered and crystallized from hot dichloromethane to afford **3**. Compound **3** was soluble only in hot dichloromethane. Yield: 0.042 g (34%). M.p. >300 °C. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 445 (1537) nm. IR (KBr): $\tilde{\nu}$ = 1561 [s, ν_{asym}COO], 1393 [s, ν_{sym}COO] cm^{-1}. ^{119}Sn NMR (149 MHz, CD_2Cl_2): δ = –524.21 (s) ppm. $C_{108}H_{96}Fe_6O_{18}Sn_6$ (2729.16): calcd. C 47.53, H 3.55; found C 47.26, H 3.46.

$[Me_2Sn(O_2CFc)_2]$ (4): To a mixture of ethanol (100 mL) and potassium hydroxide (0.09 g, 1.60 mmol) was added ferrocenecarboxylic acid (0.36 g, 1.56 mmol), and the mixture was stirred for 10 min to get a clear solution. To this was added dimethyltin dichloride (0.17 g, 0.78 mmol). The reaction mixture was heated under reflux for 3 h, cooled, and filtered, and the solvent was removed from the filtrate to afford an orange residue. This was dissolved in a dichloromethane/methanol mixture. Slow diffusion of *n*-hexane allowed the formation of orange crystals of **4**. Yield: 0.46 g (98%). M.p. >202 °C. UV/Vis (CH_2Cl_2) λ (ε, $L\,mol^{-1}\,cm^{-1}$): 448 (633) nm. IR (KBr): $\tilde{\nu}$ = 1561 [s, ν_{asym}COO] and 1382 [s, ν_{sym}COO] cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6): δ = 4.65 (s, 4 H, Cp), 3.72 (s, 14 H, Cp), 0.70 (s, 6 H, Me) ppm. ^{119}Sn NMR (186.5 MHz, C_6D_6): δ = –130.64 (s) ppm. ESI-MS: *m*/*z* (%) = 230.0272 (26) $[FcCO_2H]$, 274.9928 (100) $[(C_5H_4COOH)_2Fe + H]^+$, 378.9508 (38) $[Me_2SnO_2CFc]^+$, 607.9413 (40) $[(Me)_2Sn(O_2CFc)_2]$. $C_{24}H_{24}Fe_2O_4Sn$ (606.84): calcd. C 47.50, H 3.99; found C 47.25, H 3.90.

$[(4\text{-}OMePh)_2Te(O_2CFc)_2]$ (5): To a clear solution of ferrocenecarboxylic acid (0.1 g, 0.43 mmol) and triethylamine (0.04 g, 0.40 mmol) in benzene (10 mL) was added bis(4-methoxyphenyl)tellurium dichloride (0.09 g, 0.22 mmol), and the mixture was stirred for 24 h. Filtration followed by slow evaporation of solvent from the filtrate afforded red crystals of **5**. Yield: 0.16 g (92%). M.p. 125–126 °C. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 446 (549) nm. IR (KBr): $\tilde{\nu}$ = 1627 [s, ν_{asym}COO], 1376 [s, ν_{sym}COO] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.55 Hz, 4 H, Ph), 7.07 (d, *J* = 7.79 Hz, 4 H, Ph), 4.70 (s, 4 H, Cp), 4.30 (s, 4 H, Cp), 4.03 (s, 10 H, Cp), 3.84 (s, 6 H, methoxy) ppm. ^{125}Te NMR (157.8 MHz, $CDCl_3$): δ = 957 (s) ppm. ESI-MS: *m*/*z* (%) = 361.0052 (42) $[(4\text{-}OMe\text{-}Ph)_2Te(OH)]^+$, 375.0125 (100) $[(4\text{-}OMe\text{-}Ph)_2Te(OMe)]^+$, 572.9966 (24) $[(4\text{-}OMe\text{-}Ph)_2Te(O_2CFc)]^+$, 604.0182 (3) $[(4\text{-}OMe\text{-}Ph)_2Te(CH_3O)(O_2CFc)]$, 731.0170 (11) $[\{(4\text{-}OMe\text{-}Ph)_2Te\}_2(O)(CH_3O)]^+$, 928.9952 (12) $[\{(4\text{-}OMe\text{-}Ph)_2Te(O_2CFc)_2\} + 4\ CH_3OH]$. $C_{36}H_{32}Fe_2O_6Te$ (799.94): calcd. C 54.05, H 4.03; found C 53.87, H 3.96.

$[(4\text{-}NMe_2\text{-}Ph)_2Te(O_2CFc)_2]$ (6): Ferrocenecarboxylic acid (0.12 g, 0.52 mmol) was taken up in toluene (25 mL) and to this was added bis(*p*-dimethylaminophenyl)telluroxide (0.10 g, 0.26 mmol). The reaction mixture was heated under reflux with the use of a Dean–Stark apparatus for 1 h. Cooling the reaction mixture afforded dark-red crystals of **6**. Yield: 0.21 g (98%). M.p. 180–181 °C. UV/Vis (CH_2Cl_2): λ (ε, $L\,mol^{-1}\,cm^{-1}$) = 446 (488) nm. IR (KBr): $\tilde{\nu}$ = 1634 [s, ν_{asym}COO], 1367 [s, ν_{sym}COO] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.99 Hz, 4 H, Ph), 6.80 (d, *J* = 9.03 Hz, 4 H, Ph), 4.70 (s, 4 H, Cp), 4.27 (s, 4 H, Cp), 4.04 (s, 10 H, Cp), 2.99 (s, 12 H, NMe_2) ppm. ^{125}Te NMR (157.8 MHz, $CDCl_3$): δ = 984 (s) ppm. ESI-MS: *m*/*z* (%) = 387.0273 (34) $[(4\text{-}NMe_2\text{-}Ph)_2Te(OH)]^+$, 401.0887 (100) $[(4\text{-}NMe_2\text{-}Ph)_2Te(CH_3O)]^+$, 599.0647 (17) $[(4\text{-}NMe_2\text{-}Ph)_2Te(O_2CFc)]^+$, 783.1462 (22) $[\{(4\text{-}NMe_2\text{-}Ph)_2Te\}_2(O)(CH_3O)]^+$, 1027.1625 (7) $[\{(4\text{-}NMe_2\text{-}Ph)_2Te(O_2CFc)_2\} + 3\ CH_3COOH + OH_3]^+$. $C_{38}H_{38}Fe_2N_2O_4Te$ (826.02): calcd. C 55.25, H 4.64, N 3.39; found C 55.02, H 4.55, N, 3.27.

Supporting Information (see footnote on the first page of this article): Electronic spectra of **1**–**6**; ORTEP diagrams of **1**, **3**–**6**; CV of bis(*p*-dimethylaminophenyl)telluroxide.

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