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Alkali Metal and Organo Group-14 Element Ferrocenecarboselenoates: Synthesis and Structures

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Abstract. Lithium, sodium, and potassium ferrocenecarboselenoates were synthesized in good yields by the reaction of ferrocenoyl chloride with the corresponding metal selenides. In air, the salts quickly oxidized to give diferrocenoyl diselenide. The salts readily reacted with alkyl and organo-germanium, -tin and -lead halides to give the corresponding *Se*-alkyl and *Se*-organo Group-14 element ferrocenecarboselenoates $[(FcCOSe)_xMPh_{4-x}$ (M = Ge, Sn, Pb; x = 1–3) in moderate to good yields. In contrast, the reaction of the sodium and potassium salts with trimethylsilyl chloride led to *O*-trimethylsilyl ferrocenecarboselenoate $FcCSeOSiMe_3$. Treatment of the *O*-silyl ester with RbF and CsF led to rubidium and cesium ferrocenecarboselenoates, respectively, in good yields. The structures of FcCOSe*t*Bu, $(FcCOSe)_2SnPh_2$, and $FcCOSePbPh_3$ were revealed by X-ray molecular structure analysis.

Introduction

Much attention has been paid recently to the chemistry of ferrocene derivatives, since the incorporation of a ferrocenyl group into organic and inorganic molecules gives an easy redox reaction. The synthesis of ferrocenecarbochalcogenoic acid derivatives has been limited to ferrocenecarbothioic[1] and -carbodithioic acid derivatives,[2] most likely due to the difficulty of purification. To the best of our knowledge, the synthesis of ferrocenecarboselenoic acid derivatives has been limited to only *Se*-aryl ferrocencarboselenoates via the reactions of ferrocenoyl chloride with areneselenolate ion prepared from diaryl diselenide and LiAlHSeH, diferrocenoyl selenide via the reaction of ferrocenoyl chloride with LiAlHSeH, and diferrocenoyl diselenide via the reaction of ferrocenoyl chloride with LiAlHSeH, followed by I_2/KI-oxidation, respectively,[3] Alkali metal carbochalcogenoates $M(RCEE')$ (M = alkali metal; E, E' = O, S, Se, Te; E, $E' \neq$ O) are the most important starting groups for the synthesis of their typical element and transition metal derivatives, etc.

We have developed methods for preparing a variety of alkali metal carbochalcogenoates.[4] As part of our studies on the synthesis of new carbochalcogenoic acid derivatives, we describe herein the synthesis of a series of alkali metal and *Se*-alkyl and *Se*-organo Group-14 element ferrocenecarboselenoates,[5] along with the X-ray molecular structures of *Se*-*tert*-butyl ferrocenecarboselenoate, *Se*-diphenyltin bis(ferrocenecarboselenoate), and *Se*-triphenyllead ferrocenecarboselenoate.

Results and Discussion

Synthesis

Alkali Metal Ferrocenecarboselenoates

After we considered previous papers,[6] the reaction conditions of ferrocenoyl chloride with alkali metal selenides were examined for the synthesis of lithium (**1**), sodium (**2**), and potassium ferrocenecarboselenoate (**3**) (Scheme 1). As a result, the reactions of ferrocenoyl chloride with an excess of alkali metal selenide in acetonitrile were found to give the corresponding salts **1**–**3** in good yields. For example, ferrocenoyl chloride was added dropwise to a suspension of freshly prepared sodium selenide (1.5 mol amount) in acetonitrile, and the mixture was stirred at 0 °C for 1 h. Filtration of the resulting precipitates (excess Na_2Se and NaCl) and evaporation of the solvent under reduced pressure afforded sodium ferrocenecarboselenoate (**2**) in 80 % yield as orange-brown micro crystals. Under similar conditions, the reactions with lithium and potas-

$$\mathrm{FcCOCl} \xrightarrow[\text{0 °C for 1 h, in MeCN}]{M_2Se} \mathrm{M(FcCOSe)} + \mathrm{MCl}$$

1 (M = Li)
2 (M = Na)
3 (M = K)

Scheme 1.

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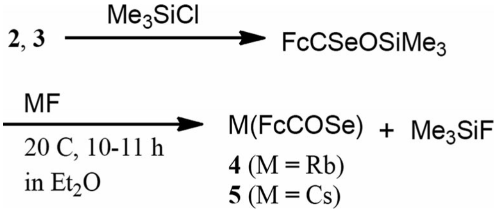
sium selenides gave the corresponding lithium (**1**) and potassium ferrocenecarboselenoates (**3**) in yields of 61 % and 80 % as orange to orange-brown micro crystals, respectively (Table 1).

Table 1. Reaction conditions and yields of lithium (**1**), sodium (**2**), potassium (**3**), rubidium (**4**), and cesium ferrocenecarboselenoates (**5**).

entry	starting material **I**	 **II**	mole ratio **I/II**	solvent	temp. [°C]	time [h]	product	yield [%]
1	FcCOCl	Li_2Se	1 : 1.1	MeCN	0	1	Li(FcCOSe) (**1**)	61
2		Na_2Se	1 : 1.1			1	Na(FcCOSe) (**2**)	80
3		K_2Se	1 : 1.1			1	K(FcCOSe) (**3**)	80
4	$FcCSeOSiMe_3$	RbF	1 : 1	Et_2O	20	11	Rb(FcCOSe) (**4**)	72
5		CsF	1 : 1			12	Cs(FcCOSe) (**5**)	68

On the other hand, rubidium (**4**) and cesium ferrocenecarboselenoates (**5**) were obtained as orange micro crystals in moderate yields of 72 % and 68 %, respectively, by the reaction of RbF and CsF with *O*-trimethylsilyl ferrocenecarboselenoate (**7a**),[6a–6c] prepared from the reaction of the sodium **2** and potassium salts **3** with trimethylsilyl chloride in acetonitrile, respectively (Scheme 2). The structures of these salts were characterized by their IR and ^1H, ^{13}C, and ^{77}Se NMR spectra and by conversion into the corresponding *Se*-alkyl ferrocenecarboselenoates (**6**) or *Se*-organo-germanium (**8**), -tin (**9**), and -lead carboselenoates (**10**), or by comparison of their IR spectra with those of authentic samples prepared by the reaction of ferrocencarboselenoic acid with the corresponding alkali metal hydrides or fluorides.[7]

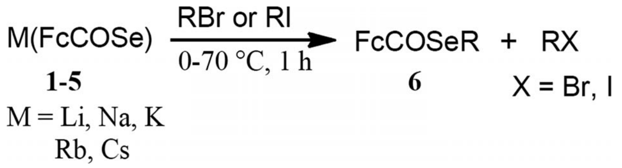


Scheme 2.

The salts **1**–**5** are orange-brown to red-brown micro crystals, which are stable thermally and toward oxygen. For example, when they were exposed to air at room temperature for over 2 h and below –15 °C for over one month, no appreciable change was observed. However, the lithium **1** and sodium salts **2** are hygroscopic (the lithium salt **1** appears to be more hygroscopic than **2**). Several attempts to obtain the water-free or solvent-free salts under reduced pressure or by recrystallization were unsuccessful.

Se-Alky Ferrocencarboselenoates 6

As expected, the lithium **1**, sodium **2**, and potassium salts **3** readily reacted with primary alkyl iodides and phenacyl bromide at 0 °C to afford the corresponding *Se*-alkyl ferrocenecarboselenoates (**6a**, **6b**, **6d**) in quantitative yields (Scheme 3, Table 2). The reaction with isopropyl iodide gave the expected selenoester **6c** in a low yield of 65 % (entry 8).



Scheme 3.

Table 2. Synthesis of *Se*-alkyl ferrocenecarboselenoates **6**.

entry	M(FcCOSe) M	alkyl halides	reaction conditions solvent	 temp. [°C]	product	yield[a] [%]
1	Li (**1**)	MeI	MeI	0	FcCOSeMe (**6a**)	95
2	Na (**2**)	MeI		0		83
3	K (**3**)	MeI		0		80
4	Rb (**4**)	MeI		0		67
5	Cs (**5**)	MeI		0		57
7		EtI	EtI	20	FcCOSeEt (**6b**)	97
8	K (**3**)	*iso*-PrI	*iso*-PrI	70	FcCOSePr-*iso* (**6c**)	65
9		*n*-BuI	*n*-BuI	20	FcCOSeBu-*n* (**6d**)	97
10		*tert*-BuI	*tert*-BuI	50	FcCOSeBu-*tert* (**6e**)	0
11		$PhCOCH_2Br$	Et_2O	0	$FcCOSeCH_2COPh$ (**6f**)	96

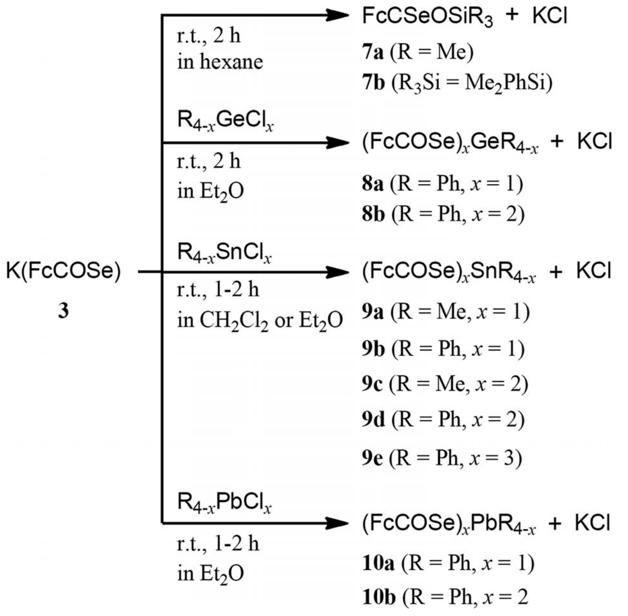
[a] Isolated yield.

No formation of *Se*-*tert*-butyl ferrocenecarboselenoate (**6e**) was detected from the reaction of **3** and *tert*-butyl iodide at 50 °C for over 10 h, due to their bulky alkyl groups. However, the ester **6e** was obtained by the reaction of ferrocenoyl chloride with lithium or sodium *tert*-butylselenolate in low yield. The rubidium **4** and cesium salts **5** appeared to be less reactive than the salts **2** and **3**, and under the same conditions they gave *Se*-methyl selenoester **6a** in respective yields of 67 % and 57 % (entries 4, 5). A similar trend was observed for the methylation of rubidium and cesium carbothio-.[8] and carbotelluroates.[9] The reaction of phenacyl bromide with an electron-withdrawing group proceeded more quickly to give the corresponding *Se*-phenacyl selenoester (**6f**) in quantitative yield.

Organo Group 14 Element Ferrocenecarboselenoates 7–10

We previously reported the reactions of alkali metal carbochalcogenoates [*M*(*R*CO*E*) (*M* = Li, Na, K, Rb, Cs; *E* = S, Se, Te) with trimethylsilyl halides to give the corresponding *O*-trimethylsilyl carbochalcogenoates [$RC(=E)OSiMe_3$],[10] while the reactions with organo-germanium, -tin, and -lead halides $R_{4-x}M'X_x$ (M' = Ge, Sn, Pb) produce the *E*-organo Group 14 element carbochalcogenoates [$(RCOE)_xM'R'_{4-x}$, *R*, *R'* = alkyl, aryl; *M'* = Ge, Sn, Pb; *E* = S, Se, Te].[4a,4f]

By referring to these reaction conditions, we next examined the reactions of potassium ferrocenecarboselenoate (**3**) with a variety of organo Group-14 element chlorides (Scheme 4). The reaction conditions and yields are shown in Table 3. For example, when excess trimethylsilyl chloride was added to a suspension of potassium salt **3** in hexane, the color of the suspension rapidly changed from orange to dark red. The mixture was stirred at 23–25 °C for 1 h. Filtration of the resulting precipitates and removal of the solvent under reduced pressure gave *O*-trimethylsilyl ferrocenecarboselenoate (**7a**) as a reddish purple oil. Similarly, the reaction with dimethylphenylsilyl chloride led to a reddish purple oil of the corresponding *O*-organosilyl selenoester (**7b**).

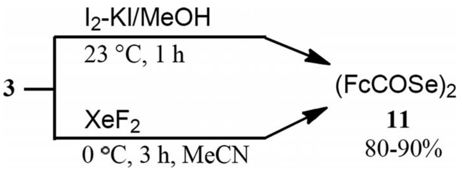


Scheme 4.

In the ^{13}C NMR spectra, these compounds show a sharp signal near $\delta = 225$, which can be ascribed to their selenocarbonyl carbon. Moreover, the ^{77}Se chemical shifts at $\delta = 887$ for **7a** and $\delta = 912$ for **7b** with coupling constants [J(C-Se)] of 218 Hz support the formation of a C=Se group. In addition, treatment of these purple oils with RbF and CsF led to the formation of rubidium **4** and cesium ferrocenecarboselenoates **5** in high yields, respectively. Under similar conditions, the stoichiometric reactions of **3** with organo-germanium, -tin and -lead chlorides proceeded quantitatively to afford the corresponding *Se*-organo-Group 14 element ferrocenecarboselenoates **8**–**10** in good yields as red to red-brown crystals.

*Oxidation of Alkali Metal Ferrocenecarboselenoates **1**–**5** leading to Diferrocenoyl Diselenide*

It is well known that alkali metal and ammonium carbothioates.[4,11] –selenoates,[12] and -telluroates[13a] are readily oxidized by I_2-KI ethanol solution or XeF_2[13b] to give the corresponding diacyl dichalcogenides in quantitative yields. In fact, the potassium salt **3** was readily oxidized by these oxidizing agents at 0 °C to give diferrocenoyl diselenide (**11**) in quantitative yield as red crystals (Scheme 5).



Scheme 5.

In general, ferrocenecarboselenoic acid derivatives, except for *Se*-organyl selenoester derivatives FcCOSe*R* (*R* = alkyl, aryl), are micro crystals or very thin plates, and are unsuitable for X-ray crystallography. There have been only two examples of an X-ray structure analysis for diferrocenoyl diselenide and *Se*-1-(2-methylnaphthyl) ferrocenecarboselenoate.[3] After several disappointing attempts to obtain single crystals of the ferrocenecarboselenoates **1**–**10**, single crystals of *Se*-*tert*-butyl ferrocenecarboselenoate (**6e**),[14] *Se*-diphenyltin bis(ferrocenecarboselenoate) (**9d**), and *Se*-triphenyllead ferrocenecarboselenoate (**10a**) were obtained from mixed solvents such as diethyl ether/hexane or dichloromethane/ether/hexane. ORTEP drawings and selected bond lengths and angles are shown in Figure 1. Final atomic positional parameters are listed in Table 4. Selected bond lengths, angles and torsion angles are shown in Table 5. As shown in Figure 1(a) and Figure 2(a) in the structure of *Se*-*tert*-butyl ferrocenecarboselenoate (**6e**), the ethyl carbon atoms of the *tert*-butyl group, the selenocarboxyl group, and the substituted cyclopentadienyl (hereafter called Cp) ring plane are coplanar [Figure 1(a)]. The C(11)–O(11), C(11)–Se(11), and C(21)–Se(11) distances are 1.207(4), 1.943(4), and 1.992(3) Å, respectively. These values indicate C=O double and C–Se single bonds, respectively. Intermolecular weak hydrogen bonding [2.649(2) Å] is observed between the carbonyl oxygen atoms and the Cp ring hydrogen atoms (Figure S1a, Supporting Information)]. In addition, weak C···H [2.774(2) Å] (a weak CH-π-bond[15]) and H···H contacts [2.27–2.38 (1) Å] are noted between the Cp ring car-

Table 3. Synthesis of *Se*-organo Group-14 element ferrocenecarboselenoates **7**–**10**.

entry	M(FcCOSe) M	RX	mole ratio **3**/RX	solvent	temp. [°C]	time [h]	product	yield[a] [%]
1	K (**3**)	Me_3SiCl	1 : 1.5	hexane	25	2	$FcCSeOSiMe_3$ (**7a**)	82
2		$Me_2PhSiCl$	1 : 1	hexane		2	$FcCSeO_2SiPhMe_2$ (**7b**)	90
3		Ph_3GeCl	1 : 1	Et_2O	23	2	$FcCOSeGePh_3$ (**8a**)	94
4		Ph_2GeCl_2	1 : 2	Et_2O		2	$(FcCOSe)_2GeMe_2$ (**8b**)	78
5		Me_3SnCl	1 : 1	Et_2O	0	2	$FcCOSeSnMe_3$ (**9a**)	93
6		Ph_3SnCl	1 : 1	CH_2Cl_2		1	$FcCOSeSnPh_3$ (**9b**)	81
7		Me_2SnCl_2	1 : 2	Et_2O		1	$(FcCOSe)_2SnMe_2$ (**9c**)	89
8		Ph_2SnCl_2	1 : 2	CH_2Cl_2		1	$(FcCOSe)_2SnPh_2$ (**9d**)	90
9		$PhSnCl_3$	1 : 3	CH_2Cl_2		2	$(FcCOSe)_3SnPh$ (**9d**)	94
10		Ph_3PbCl	1 : 1	Et_2O	23	1	$FcCOSePbPh_3$ (**10a**)	96
11		Ph_2PbCl_2	1 : 2	Et_2O	25	2	$(FcCOSe)_2PbPh_2$ (**10b**)	93

[a] Isolated yields.

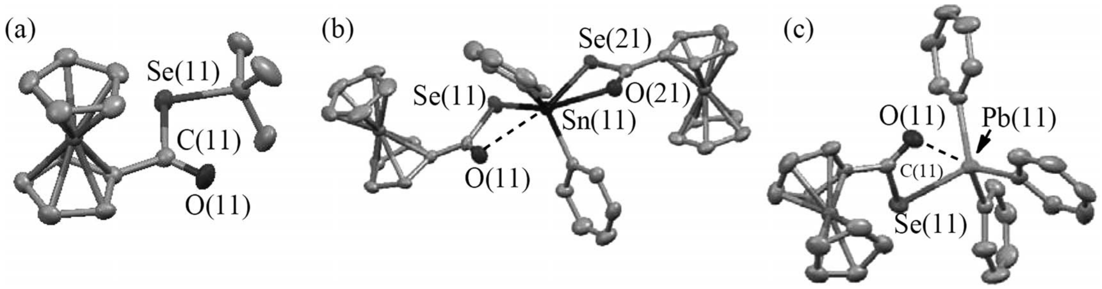
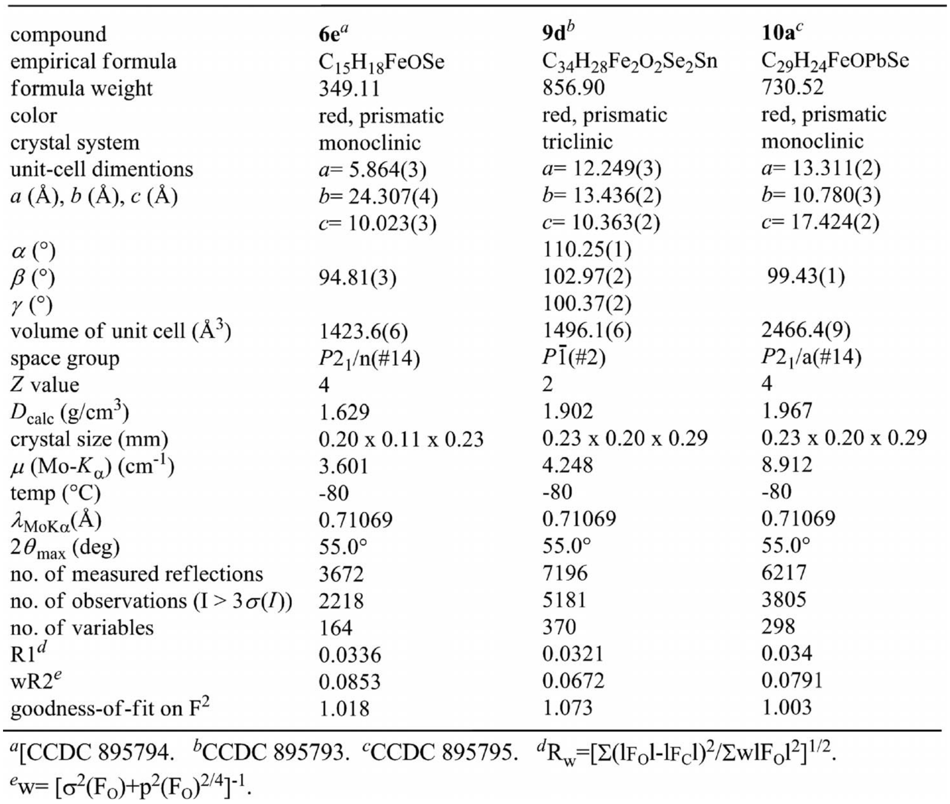


Figure 1. Structures of (a) *Se-tert*-butyl ferrocenecarboselenoate (**6e**), (b) *Se*-diphenyltin bis(ferrocenecarboselenoate) (**9d**), and (c) *Se*-triphenyllead ferrocenecarboselenoate (**10a**). Short intramolecular contacts are shown in black dotted lines. Thermal ellipsoids are 50 % propability revel. All hydrogen atoms are omitted for clarity.

Table 4. Crystal data and data collection of $FcCOSeCMe_3$ (**6e**), $(FcCOSe)_2SnPh_2$ (**9d**), and $FcCOSePbPh_3$ (**10a**).



compound	**6e**[a]	**9d**[b]	**10a**[c]
empirical formula	$C_{15}H_{18}FeOSe$	$C_{34}H_{28}Fe_2O_2Se_2Sn$	$C_{29}H_{24}FeOPbSe$
formula weight	349.11	856.90	730.52
color	red, prismatic	red, prismatic	red, prismatic
crystal system	monoclinic	triclinic	monoclinic
unit-cell dimentions	*a*= 5.864(3)	*a*= 12.249(3)	*a*= 13.311(2)
a (Å), *b* (Å), *c* (Å)	*b*= 24.307(4)	*b*= 13.436(2)	*b*= 10.780(3)
	c= 10.023(3)	*c*= 10.363(2)	*c*= 17.424(2)
α (°)		110.25(1)	
β (°)	94.81(3)	102.97(2)	99.43(1)
γ (°)		100.37(2)	
volume of unit cell (Å^3)	1423.6(6)	1496.1(6)	2466.4(9)
space group	$P2_1/n$(#14)	$P\bar{1}$(#2)	$P2_1/a$(#14)
Z value	4	2	4
D_{calc} (g/cm^3)	1.629	1.902	1.967
crystal size (mm)	0.20 x 0.11 x 0.23	0.23 x 0.20 x 0.29	0.23 x 0.20 x 0.29
μ (Mo-K_α) (cm^{-1})	3.601	4.248	8.912
temp (°C)	-80	-80	-80
$\lambda_{MoK\alpha}$(Å)	0.71069	0.71069	0.71069
$2\theta_{max}$ (deg)	55.0°	55.0°	55.0°
no. of measured reflections	3672	7196	6217
no. of observations ($I > 3\sigma(I)$)	2218	5181	3805
no. of variables	164	370	298
R1[d]	0.0336	0.0321	0.034
wR2[e]	0.0853	0.0672	0.0791
goodness-of-fit on F^2	1.018	1.073	1.003

[a] [CCDC 895794. [b] CCDC 895793. [c] CCDC 895795. [d] $R_w=[\Sigma(|F_O|-|F_C|)^2/\Sigma w|F_O|^2]^{1/2}$.
[e] $w= [\sigma^2(F_O)+p^2(F_O)^{2/4}]^{-1}$.

bon and the methyl or the cyclopentadienyl ring-hydrogen atoms and between the Cp ring hydrogen atoms.

A linear molecular chain formed by O···H hydrogen bonding is shown [Figure 2(a)]. A two-dimensional sheet is formed by both short O···H hydrogen bonding and H···H contacts between cyclopentadienyl ring-hydrogen atoms [Figure 2(b)]. A three-dimensional arrangement is formed by the short contacts O···H and H···H [Figure 2(c)].

In the case of diphenyltin bis(ferrocenecarboselenoate) (**9d**), the two –COSe– groups, the substituted two Cp ring planes and the central tin atom have a nearly coplanar arrangement [torsion angles [Sn(11)–Se(11)–C(11)–O(11) = 8.3(1)°; Sn(11)–Se(21)–C(21)–O(21) = 2.8(2)°; O(11)–C(11)–C(13)–C(14) = 6.0(3); O(21)–C(21)–C(23)–C(24) = 4.5(2)°], with their two C=O moieties pointing in the same direction [Figure 1(b)]. The two C=O distances [C(11)–O(11) = 1.226(4) Å; C(21)–O(21) = 1.209(4) Å] are different.[16] The C=O(11) ···Sn(11) and C=O(21)···Sn(11) distances are 2.744(4) Å and 2.837(4) Å, respectively, and thus shorter than the sum of the van der Waals radii of oxygen and tin atoms (3.70 Å),[17] indicating that both of the carbonyl oxygen atoms intramolecularly contact the central tin atom. The bond angle C(31)–Sn(11)–C(41) of the two phenyl groups is 117.8(2)°. Thus, compound **9d** is considered to have a strained bipyramidal structure. Weak hydrogen bonding is observed between the carbonyl oxygen and Cp ring hydrogen atom, and weak CH-π-bonding is seen between the Cp ring carbon and Cp ring hydrogen of neighboring molecules[15] (Figure S1b, Supporting Information). A linear molecular chain is formed by C···H and H···H short contacts between the phenyl or cyclopentadienyl ring-

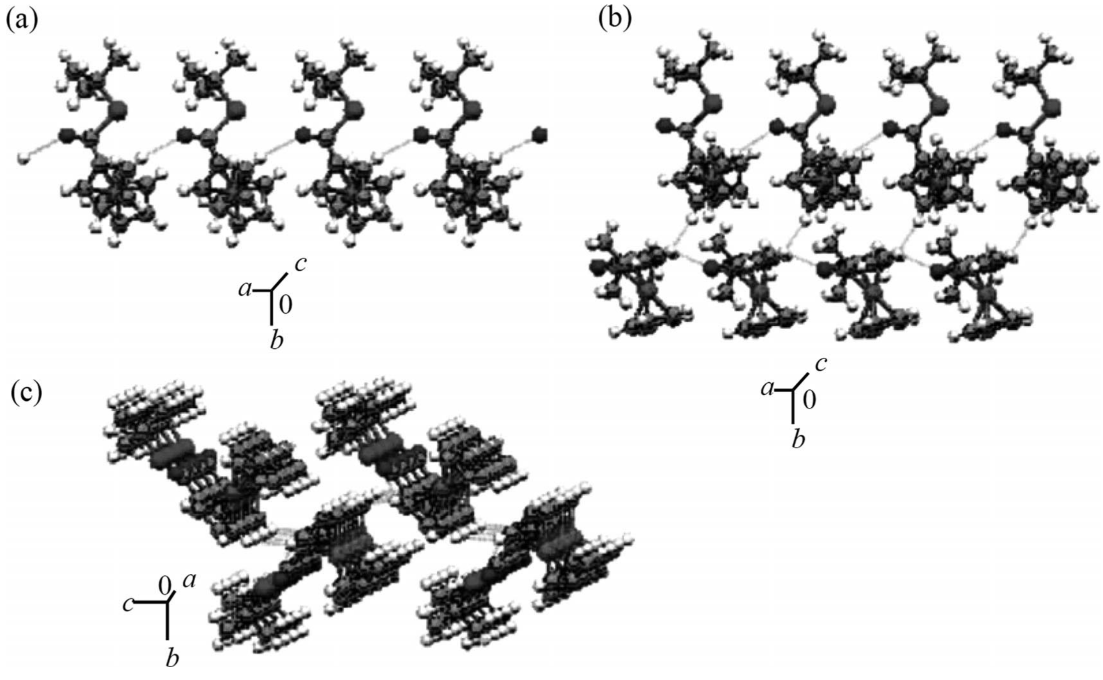


Figure 2. Molecular arrangements (a–c) of FcCOSeBu-*t* (**6e**). Short intermolecular contacts are shown as dotted lines. (a) One-dimensional linear chain formed by the O···H hydrogen bonding between cyclpentadienyl ring-hydrogen and carbonyl-oxygen atoms is shown. (b) Two-dimensional sheet formed by hydrogen bonding interactions and H···H short contacts between cyclopentadienyl ring-hydrogen atoms. (c) 3D Network formed by stacking of these sheets.

Table 5. Selected bond distances /Å, angles /°, and torsion angles /° of $FcCOSeCMe_3$ (**6e**), $(FcCOSe)_2SnPh_2$ (**9d**), and $FcCOSePbPh_3$ (**10a**).

$FcCOSeCMe_3$ (**6e**)							
Bond lengths				Angles			
O(11)–C(11)	1.207(4)	O(11)···Se(11)	4.943(4)	C(11)–C(11)–Se(11)	122.6(2)	O(11)–C(11)–Se(11)	122.4(3)
C(11)–Se(11)	1.943(4)	O(21)···O(22)	2.651(4)	C(11)–Se(11)–C(21)	102.0(1)	O(11)–C(11)–C(21)	123.7(4)
C(21)–Se(11)	1.992(3)						
Torsion angles							
O(11)–C(11)–Se(11)-C(21)	0.0(2)	O(11)–C(11)–C(12)–C(13)	9.0(3)				
Se(11)-C(11)-C(12)-C(13)	171.2(3)						
$(FcCOSe)_2SnPh_2$ (**9d**)							
Bond lengths				Angles			
Se(11)–C(11)	1.922(3)	Sn(11)···O(11)	2.744(4)	C(11)–Se(11)–Sn(11)	84.9(1)	C(23)–Sn(11)–C(29)	117.9(1)
Se(11)–C(21)	1.805(2)	Sn(11)···O(21)	2.837(4)	C(12)–Se(12)–Sn(11)	87.5(2)	Se(11)–Sn(11)–Se(12)	91.7(2)
C(11)–O(11)	1.226(4)	Sn(11)–Se(21)	2.5613(7)	O(11)–Sn(11)–Se(11)	60.6(2)		
C(21)–O(21)	1.209(4)	Sn(11)–Se(11)	2.5679(7)	O(12)–Sn(11)–Se(12)	61.9(1)		
Torsion angles							
C(11)–Se(11)–Sn(11)–O(11)	8.2(2)	Se(11)–C(11)–C(15)–C(16)	1.3(2)	O(11)-C(11)-C(13)-C(14)	6.0(3)		
C(21)–Se(21)–Sn(11)–O(21)	0.8(1)	Se(21)–C(21)–C21)–C(22)	2.0(3)	O(21)-C(21)-C(23)-C(24)	4.5(2)		
O(11)-C(11)-C(13)-C(14)	6.0(2)	Sn(11)–Se(11)–C(11)–C(12)	169.3(2)				
O(21)-C(21)-C(23)-C(24)	4.5(2)	Sn(11)–Se(21)–C(21)–C(23)	178.0(3)				
$FcCOSePbPhe_3$ (**10a**)							
Bond lengths				Angles			
Pb(11)–Se(11)	2.629(2)	C(11)–O(11)	1.214(2)	C(11)–Se(11)–Pb(11)	94.6(1)	O(11)–C(11)–C(12)	124.7(2)
Se(11)–C(11)	1.941(3)	O(11)···Pb(11)	3.217(4)	O(11)–C(11)–Se(11)	121.5(2)		
Torsion angles							
O(11)–C(11)–Se(11)–Pb11)	8.2(2)	O(11)–C(11)–C(12)–C(13)	6.9(2)				

carbon atom and the phenyl ring-hydrogen atoms [Figure 3(a)]. A two-dimensional sheet [Figure 3(b)] and three-dimensional arrangement [Figure 3(c)] are formed both by the Se···H hydrogen bonding and by C···H and/or H···H short contacts.

On the other hand, the structure of *Se*-triphenyllead ferrocenecarboselenoate (**10a**) shows that the –COSePb– moiety and the substituted cyclophentadiene ring plane are nearly coplanar [Figure 1(c)]. The C(11)–O(11) [1.214(2) Å] and

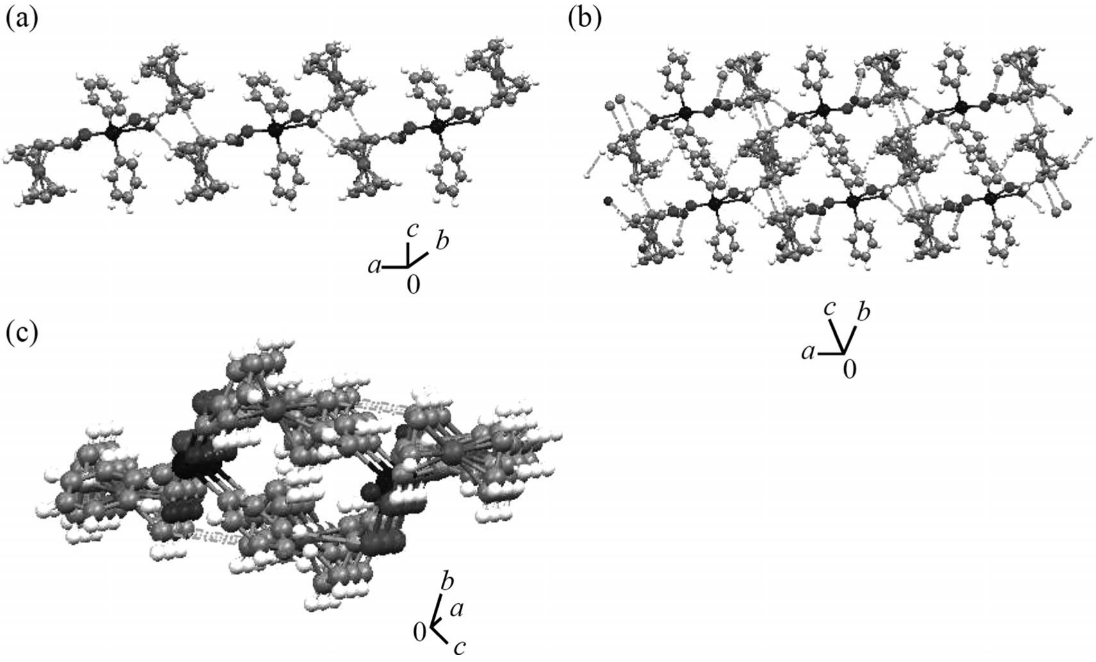


Figure 3. Molecular arrangements (a–c) of $(FcCOSe)_2SnPh_2$ (**10d**). Dotted lines show intermolecular short contacts. (a) One-dimensional linear chain formed by C···H and H···H short contacts between phenyl ring- or cyclopentadienyl ring-carbon atoms and phenyl ring-hydrogen atoms. (b), Two-dimensional sheet formed by Se···H hydrogen bonding and by C···H and H···H short contacts. (c) 3D Network formed by stacking of these sheets.

C(11)–Se(11) distances [1.941(4) Å] of the selenocarboxyl group indicate a double and single bond, respectively, and the three phenyl rings on the lead atom have a propeller-like arrangement. The Pb(11)–Se(11) distance [2.629(4) Å] also indicates a single bond. The distance between Pb(11) and O(11) is 3.217(4) Å, which is shorter than the sum of the van der Waals radii of both atoms (3.54 Å),[16] which indicates intramolecular coordination of the carbonyl oxygen to the lead atom. The structure around the lead atom appears to be a strained trigonal bipyramidal with one selenium, one oxygen, and three phenyl carbon atoms around the lead atom, similar to that of the sulfur and selenium isologues $4\text{-MeC}_6H_4COEPbPh_3$ (E = S[17]; E = Se[18]). As expected, the carbonyl oxygen or selenium atom forms a weak intermolecular hydrogen bond with the benzene ring hydrogen atom of the neighboring molecule. In addition, the distances between the benzene ring carbon and hydrogen atoms of neighboring molecules are relatively short (2.813–2.900 Å), indicating a weak CH-π-bond.[15] (Figure S1c, Supporting Information). A linear molecular chain is formed by C···H and H···H short contacts between the phenyl-ring or cyclopentadienyl-carbon atom and the phenyl ring-hydrogen atoms (Figure 4(a)]. The two-dimensional sheet [(Figure 4(b)] and three-dimensional arrangement [(Figure 4(c)] are formed by Se···H hydrogen bonding and by C···H and H···H short contacts.

Spectra

The spectroscopic data of alkali metal ferrocenecarboselenoates **1**–**5** along with those of *Se*-alkyl **6** and *Se*-triphenyl Group-14 element derivatives (**8a**, **9b**, **10a**) are shown in Table 6. The carbonyl stretching frequencies of the salts **1**–**5** appear at 1520 cm^{-1}, except for that of the lithium salt **1**.[19] The carbonyl carbon chemical shifts appear near δ = 215, which reflects the slight influence of alkali metal cations. The ^{77}Se NMR spectra were observed in the range δ = 343–361, and showed a tendency for downfield shifts with an increase in the atomic number of the alkali metal ions, except for the lithium salt **1**. These absorption bands are comparable to those of common alkali metal arenecarboselenoates [ν(C=O): 1519–1558 cm^{-1}; ^{13}C=O: δ213–222; ^{77}Se: δ = 330–517].[6b–6e] Both the ^{13}C (C=O) and ^{77}Se NMR chemical shifts for *Se*-alkyl selenoesters **6** show downfield shifts in the order R=C_2H_5, *iso*-C_3H_7 and *tert*-C_4H_9, indicating hyperconjugation of the methyl group. The carbonyl stretching frequencies of *Se*-triphenyl Group-14 element ferrocenecarboselenoates **8a**, **9b**, and **10a** appear in the range1637–1668 cm^{-1} and exhibit a shift to low-frequency regions in going from germanium to tin and lead. The ^{13}C (C=O) chemical shifts, which are observed in the range of δ = 191–195, show a trend in downfield shifts in the order: M = Ge, Sn, and Pb. The ^{77}Se NMR spectra do not show a general shifting tendency.

Conclusions

We have described the synthesis of a series of alkali metal ferrocenecarboselenoates M(FcCOSe) (M = Li, Na, K, Rb, Cs), which readily react with alkyl halides and organo-germanium, -tin, and -lead halides at room temperature to give the corresponding *Se*-organyl FcCOSeR (R = alkyl) and Group-14 element derivatives $(FcCOSe)_xMPh_{4-x}$ (M = Ge, Sn, Pb; x = 1–2) in moderate to good yields. X-ray molecular structure

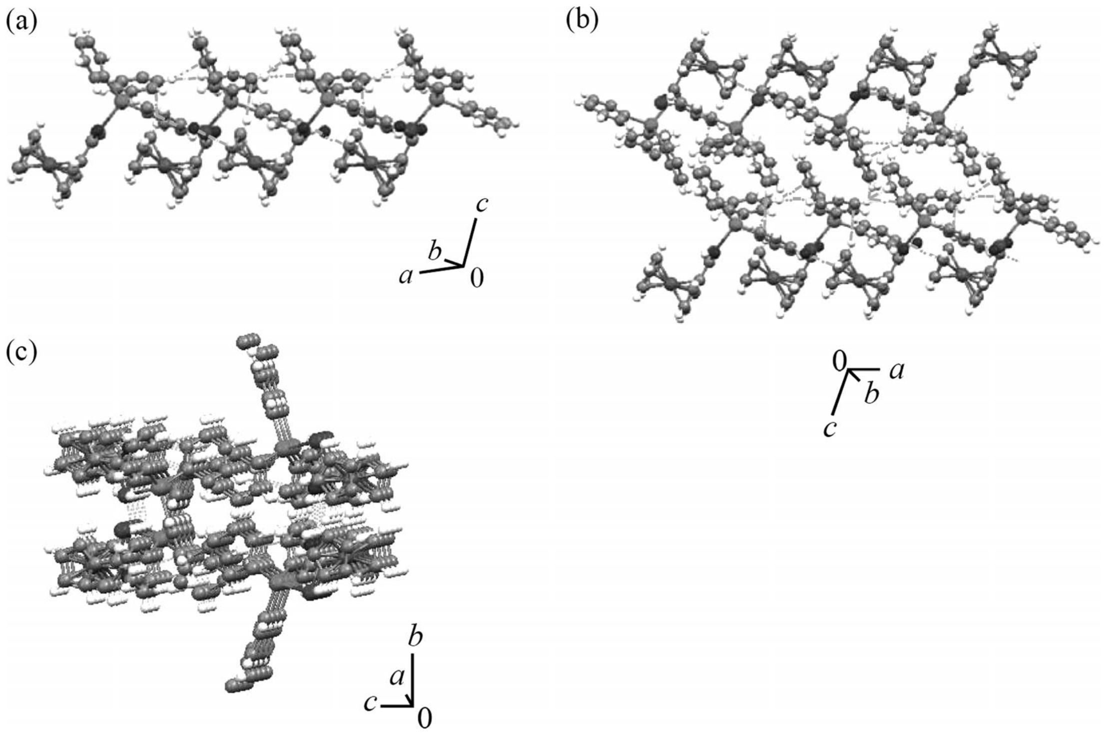


Figure 4. Molecular arrangements (a–c) of $FcCOSePbPh_3$ (**10a**). Short intermolecular contacts are shown as dotted lines. (a) One-dimensional linear chain formed by C···H short contacts between cyclopentadienyl carbon and hydrogen atoms and by H···H short short contacts between cyclpentadienyl ring hydrogen atoms. (b) Two-dimensional sheet formed by C···H short contacts between cyclopentadienyl ring-carbon and phenyl ring-hydrogen atoms and H···H short contacts between phenyl and cyclopentadienyl ring hydrogen atoms. (c) 3D Network formed by stacking of these sheets.

Table 6. Spectral data of alkali metal (**1**–**5**), *Se*-alkyl (**6**), and *Se*-triphenyl Group-14 element ferrocenecarboselenoates (**7**–**10**).

No.	M(FcCOSe) M	IR[a] [cm^{-1}] νC=O	NMR[b] [δ] ^{13}C=O[c]	^{77}Se[d]
1	Li	1454	215.9	351.1
2	Na	1520	215.7	343.9
3	K	1520	215.7	346.2
4	Rb	1520	215.2	351.2
5	Cs	1520	215.3	361.2
	FcCOSeR R			
6a	Me	1652[e]	194.5	429.2
6b	Et	1668[f]	194.5	547.6
6c	*iso*-Pr	1656[f]	195.4	637.3
6e	*tert*-Bu[g]	1646[e]	196.7	690.0
8a	$GePh_3$	1657[e]	191.5	352.2
9b	$SnPh_3$	1643[e]	194.3	344.5
10a	$PbPh_3$	1637[e]	195.0	418.6

[a] Nujol. [b] CD_3OD. [c] Standard: Me_4Si. [d] Standard: Me_2Se. [e] KBr. [f] Neat. [g] Prepared from the reaction of FcCOCl and Me_3CSeLi in ether (see Experimental section).

analysis revealed shortening of the C=O···Sn distances in $(FcCOSe)_2SnPh_2$ as $4\text{-}MeC_6H_4COSeSnPh_3$.[18]

Experimental Section

Instrumentation: The melting points were measured with a Yanagimoto micro melting point apparatus and uncorrected. The IR spectra were measured with a PERKIN ELMER FT-IR 1640 and a JASCO grating IR spectrophotometer IR-G. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a JNM-α400 instruments at 399.7 and 100.4 MHz, respectively with tetramethylsilane as an internal standard. The ^{77}Se NMR (76 MHz) spectra were obtained from a JEOL *α*-400 spectrometer, and ^{77}Se chemical shifts are expressed in *δ* values deshielded with respect to neat Me_2Se as an external standard. All spectra were acquired in the proton-decoupled mode; generally 0.05–0.3 mmol solutions in $CDCl_3$ (0.4 mL) were used. Electron spectra were measured with a JASCO U-Best 55. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Materials: Diethyl ether was distilled from sodium/benzophenone ketyl prior to use. Hexane was distilled from sodium metal. Acetonitrile and dichloromethane were distilled from phosphorus pentoxide. Petroleum ether (bp: 40–60 °C) was distilled. Methanol was distilled from magnesium powder. Lithium selenide,[6d] sodium selenide,[20] and potassium selenide[20] were prepared according to the literature. Iodine, iodomethane, -ethane, -1-methylethane and -1-butane and phenacyl bromide, cesium fluoride, sodium metal, and tin tetrachloride were purchased from Nacalai Tesque Inc. Dimethyltin dichloride, trimethyltin chloride and triphenyltin chloride were purchased from Tokyo Kasei Industrial Co., Ltd. Diphenyllead dichloride was purchased from Alfa. Lithium, sodium, and potassium hydrides were purchased from Wako Pure Chemical Ind. Ltd. Dimethylphenylsilyl chloride, dimethylsilyl dichloride, and trimethylsilyl chloride were purchased from

Shin-Etsu Chem. Co. Ltd. Diphenylgermanium dichloride, diphenyltin dichloride, ferrocenecarboxylic acid, 1.0 M hydrogen chloride/ether, rubidium fluoride, triphenylgermanium chloride, and triphenyllead chloride, were purchased from Aldrich. Xenon difluoride was purchased from Fluka. These reagents all are chemical grade and used without further purification. Ferrocenoyl chloride was prepared according to the literature.[21] Silica gel used on column chromatography was run on silica gel 60 of Kanto Chemical Co., Ltd.

X-ray Measurements: The measurement was carried out with a Rigaku AFC7R four-circle diffract meter with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). All of the structures were solved and refined using the teXsan crystallographic software package on an IRIS Indigo computer. The crystals were coated with an epoxy resin and mounted on a glass fiber. The cell dimensions were determined from a least-squares refinement of the setting diffract-meter angles for 25 automatically centered reflections. Lorentz and polarization corrections were applied to the data, and empirical absorption corrections (ψ-scans)[22] were also applied. The structures were solved by direct method using SHELXS-86[23] and expanded using DIRDIF92.[24] Scattering factors for neutral atoms were from Cromer and Waber[25] and anomalous dispersion[26] was used. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, and the weighting scheme employed was $w = [\sigma^2(F_o)+p^2(F_o)^2/4]^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The structures were solved by direct methods using SIR97[22] and refined by using SHELXL97.[23] The final full-matrix least-squares cycle included non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were placed in idealized positions and treated as riding atoms with C–H distances in the range 0.93–0.98 Å.

Single Crystals of Compounds 6e, 9d, and 10a: *Se*-1,1-Dimethyl ferrocenecarboselenoate (**6f**) (21 mg) was dissolved in diethyl ether (0.25 mL) in a glass tube (Ø = 6 mm) and hexane (0.5 mL) was slowly added. The glass tube with a rubber septum was allowed to stand at room temperature (ca. 20 °C) for 2 d. Decantation of the solvents gave red plate single crystals of **6e**. *Se*-Diphenyltin bis(ferrocenecarboselenoate) (**9d**) (96 mg) was dissolved in dichloromethane (2 mL). The insoluble parts were filtered off. Diethyl ether (2 mL) and hexane (6 mL) were slowly added to the filtrate in this order. The glass tube with a rubber septum was allowed to stand at room temperature (ca. 20 °C) for 14 d. Decantation of the solvent gave red columnar crystals of **9d**. *Se*-Triphenyllead ferrocenecarboselenoate (**10a**) (20 mg) was dissolved in dichloromethane (0.5 mL) and hexane (0.5 mL) was slowly added. The tube with a rubber septum was allowed to stand at 20 °C for 12 d. Decantation of the solvents gave red plate crystals of **10a**.

Alkali Metal Salts (1–5)[27]

Lithium Ferrocenecarboselenoate (1): Ferrocenoyl chloride (700 mg, 2.80 mmol) was added to a suspension of lithium selenide (390 mg, 4.20 mmol) in acetonitrile (20 mL). The color of the suspension rapidly changed from brown to orange brown. The mixture was stirred at 20 °C for 1 h. Filtration of the insoluble part and removal of the solvent under reduced pressure (20 °C, 0.2 Torr). Washing the resulting precipitates with diethyl ether (10 mL), followed by removal of the diethyl ether in vacuo gave 510 mg [61 %, purity: > 90 % on the basis of conversion into *Se*-methyl ferrocenecarboselenoate (**6a**)] of lithium ferrocenecarboselenoate (**1**) as orange micro crystals the IR spectrum shows broad peaks at the range of 3400–3900 cm^{-1}, indicating the presence of OH groups of water molecule. The structure was confirmed by comparison of the IR spectrum with that of the authentic sample prepared by the reaction of ferrocenecarboselenoic acid[7] with lithium hydride and conversion into *Se*-methyl ferrocenecarboselenoate. The IR and ^{13}C NMR spectra were exactly consistent with those of the authentic compound prepared from the reactions of ferrocencarboselenoic acid with lithium hydride (see a part of lithium ferrocencarboselenoate in the Experimental Section). **IR** (nujol, neat): $\tilde{\nu}$ = 3850, 2976, 2880, 2839, 1708, 1678, 1454 (C=O), 1424, 1376, 1330, 1232, 1104, 1040, 1002, 955, 932, 872, 844, 825, 776, 673, 594, 557, 495) cm^{-1}. **^{1}H NMR** (CD$_3$OD): δ = 4.18 (s, 5 H, Cp), 4.37 (s, 2 H, Cp$_{meta}$), 4.87 (s, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CD$_3$OD): δ = 71.1 (Cp), 71.5 (Cp$_{ortho}$), 71.8 (Cp$_{meta}$), 90.9 (Cp$_{ipso}$), 215.9 (COSe) ppm. **^{77}Se NMR** (CD$_3$OD): δ = 351.1 ppm.

Sodium Ferrocenecarboselenoate (2). Ferrocenoyl chloride (840 mg, 3.38 mmol) was added to a suspension of sodium selenide (585 mg, 4.68 mmol) in acetonitrile (20 mL) at 0 °C in an argon atmosphere. The color of the suspension rapidly changed from pale yellow to orange brown. The mixture was stirred at the same temperature for 1 h. The precipitates (NaCl, excess of Na$_2$Se and red selenium) were filtered off. Removal of the solvent under reduced pressure (23 °C, 0.2 Torr), followed by washing the resulting residue with diethyl ether (20 mL) gave 852 mg [80 %, purity: >98 % on the basis of conversion into *Se*-methyl ferrocenecarboselenoate (**6a**)] of sodium ferrocenecarboselenoate (**2**) as orange brown micro crystals containing a small amount of water. The IR and ^{13}C NMR spectra were exactly consistent with those of the authentic compound prepared from the reaction of ferrocencarboselenoic acid with sodium hydride. **IR** (nujol, neat): $\tilde{\nu}$ = 2975, 2881, 2842, 1714, 1684, 1682, 1615, 1574, 1520 (C=O), 1464, 1377, 1240, 1154, 1104, 1041, 1001, 946, 870, 837, 817, 723, 694, 550, 497) cm^{-1}. **^{1}H NMR** (CD$_3$OD): δ = 4.16 (s, 5 H, Cp), 4.34 (t, *J* = 1.95 Hz, 2 H, Cp$_{meta}$), 4.86 (t, *J* = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CD$_3$OD): δ = 71.1 (Cp$_{ortho}$), 71.4 (Cp), 71.6 (Cp$_{meta}$), 90.9 (Cp$_{ipso}$), 215.7 (C=O) ppm. **^{77}Se NMR** (CD$_3$OD): δ = 343.9 ppm.

Potassium Ferrocenecarboselenoate (3). Ferrocenoyl chloride (731 mg, 2.94 mmol) was added to a suspension of potassium selenide (650 mg, 4.14 mmol) in acetonitrile (17 mL) at 0 °C in an argon atmosphere. The color of the suspension rapidly changed from pale yellow to orange brown. The mixture was stirred at the same temperature for 1 h. The brown precipitates (KCl, excess of K$_2$Se and red selenium) were filtered off. Removal of the solvent from the filtrate under reduced pressure (23 °C, 0.2 Torr), followed by washing with diethyl ether (20 mL) gave 778 mg [80 %, purity: >98 % on the basis of conversion into *Se*-alkyl selenoesters (**6a**)] of potassium ferrocenecarboselenoate (**3**) as orange brown micro crystals. The IR spectrum was exactly consistent with that of the authentic sample prepared by the reaction of ferrocenecarboselenoic acid with potassium hydride.[7] **IR** (nujol, neat): $\tilde{\nu}$ = 2979, 2881, 2838, 1652, 1531, 1520 (C=O), 1505, 1470, 1456, 1378, 1235, 1105, 1037, 1024, 943, 813, 694, 547, 496) cm^{-1}. **^{1}H NMR** (CD$_3$OD): δ = 4.16 (s, 5 H, Cp), 4.33 (t, *J* = 1.95 Hz, 2 H, Cp$_{meta}$), 4.84 (t, *J* = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CD$_3$OD): δ = 71.2 (Cp$_{ortho}$), 71.5 (Cp), 71.7 (Cp$_{meta}$), 91.1 (Cp$_{ipso}$), 215.7 (C=O) ppm. **^{77}Se NMR** (CD$_3$OD): δ = 346.2 ppm.

Rubidium Ferrocenecarboselenoate (4). Rubidium fluoride (85 mg, 0.81 mmol) was added to a solution of *O*-trimethylsilyl ferrocenecarboselenoate (**8a**) (315 mg, 0.86 mmol) in diethyl ether (10 mL) at 25 °C. The mixture was stirred at the same temperature for 11 h. Orange solid was gradually deposited. Filtration of the precipitates gave 221 mg (72 %, purity: >98 % on the basis of conversion into *Se*-methyl ferrocenecarboselenoate) of rubidium ferrocenecarboselenoate (**4**) as orange microcrystalline solid. The IR and ^{13}C NMR spectra were exactly consistent with those of the authentic compound obtained by ferrocencarboselenoic acid with rubidium fluoride. **IR** (nujol, neat): $\tilde{\nu}$ = 3090, 2925, 2854, 2658, 2026, 1833, 1686, 1537, 1520 (C=O), 1460, 1429, 1368, 1335, 1233, 1104, 1038, 1029, 1010, 942, 854, 844, 834, 813, 695, 546, 505, 486) cm^{-1}. **^{1}H NMR** (CD_3OD): δ = 4.18 (s, 5 H, Cp), 4.35 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.86 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CD_3OD): δ = 71.2 (Cp), 71.5 (Cp$_{ortho}$), 71.6 (Cp$_{meta}$), 91.0 (Cp$_{ipso}$), 215.2 (C=O) ppm. **^{77}Se NMR** (CD_3OD): δ = 351.2 ppm.

Cesium Ferrocenecarboselenoate (5). A solution of freshly prepared *O*-trimethylsilyl ferrocenecarboselenoate (**8a**) (203 mg, 0.56 mmol) in diethyl ether (1 mL) was added to a suspension of cesium fluoride (79 mg, 0.52 mmol) in the same solvent (4 mL) at 22 °C in an argon atmosphere. The mixture was stirred at the same temperature for 12 h. Orange solid was gradually deposited. Filtration of the precipitates gave 150 mg (68 %, purity: >98 % on the basis of conversion into *Se*-methyl ferrocenecarboselenoate) of cesium ferrocenecarboselenoate (**5**) as orange micro crystals. The IR and ^{13}C NMR spectra were exactly consistent with thse of the authentic compound obtained by ferrocencarboselenoic acid with cesium fluoride. **IR** (nujol, neat): $\tilde{\nu}$ = 2984, 2833, 1998, 1537, 1520 (C=O), 1471, 1431, 1231, 1104, 1036, 1011, 940, 891, 853, 843, 813, 723, 695, 595, 545, 504, 485) cm^{-1}. **^{1}H NMR** (CD_3OD): δ = 4.18 (s, 5 H, Cp), 4.35 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.86 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CD_3OD): δ = 71.1 (Cp), 71.5 (Cp$_{ortho}$, Cp$_{meta}$), 90.8 (Cp$_{ipso}$), 215.3 (C=O) ppm. **^{77}Se NMR** (CD_3OD): δ = 361.2 ppm.

Typical Procedure for the Synthesis of Se-alkyl 6 and Se-Group-14 Element Ferrocencarboselenoates 7–10

***Se*-Methyl Ferrocenecarboselenoate (6a) from Potassium Ferrocenecarboselenoate (3):** Iodomethane (10 mL, 160 mmol) was added to potassium ferrocenecarboselenoate (**3**) (395 mg, 1.19 mmol) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The mixture was stirred at the same temperature for 1 h. Diethyl ether (10 mL) was added and the white precipitates (KI) were filtered off. Removal of the solvent under reduced pressure (23 °C, 0.2 Torr) and recrystallization from a mixed solvent (35 mL) of ether/hexane (5:30) at 0 °C gave 292.2 mg (80 %, purity: >98 % on the basis of conversion into *Se*-methyl ferrocenecarboselenoate) of *Se*-methyl ferrocenecarboselenoate (**6a**) as red needles. Mp: 67–69 °C. $C_{12}H_{12}FeOSe$ (307.03): C 46.92 (calcd. 46.94), H 4.10 (3.94)%. **IR** (KBr, neat): $\tilde{\nu}$ = 3852, 2359, 1774, 1652 (C=O), 1441, 1408, 1371, 1338, 1237, 1104, 1049, 1023, 1001, 945, 866, 828, 796, 679, 591, 551, 497, 473) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 4.23 (s, 5 H, Cp), 4.49 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.84 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** ($CDCl_3$): δ = 4.3 ($^1J_{C\text{–}Se}$ = 59.5 Hz, CH_3), 68.8 (Cp$_{ortho}$), 70.7 (Cp), 71.8 (Cp$_{meta}$), 81.6 (Cp$_{ipso}$), 194.5 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 429.3 ppm.

***Se*-Ethyl Ferrocenecarboselenoate (6b):** Chromatographic purification on silica gel column (ether/hexane = 1:5, R_f = 0.64) gave 103 mg (52 %, 0.32 mmol). Red oil. $C_{13}H_{14}FeOSe$ (321.06): C 48.77 (calcd. 48.63), H 4.48 (4.40)%. **IR** (KBr, neat): $\tilde{\nu}$ = 3098, 2961, 2923, 2867, 2346, 1736, 1668 (C=O), 1560, 1542, 1508, 1439, 1412, 1396, 1373, 1337, 1231, 1107, 1044, 1026, 1002, 963, 939, 824, 799, 680, 546, 495 cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 1.41 (t, J = 7.4 Hz, 3 H, CH_3), 2.94 (q, J = 7.5 Hz, 2 H, CH_2), 4.14 (s, 5 H, Cp), 4.39 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.74 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** ($CDCl_3$): δ = 16.4 (CH_3), 18.6 (1JC-Se = 57.5 Hz, CH_2), 68.7 (Cp$_{ortho}$), 70.6 (Cp), 71.7 (Cp$_{meta}$), 81.7 (Cp$_{ipso}$), 194.5 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 547.6 ppm.

***Se*-1-Methylethyl Ferrocenecarboselenoate (6c).** Chromatographic purification on silica gel column (developing solvent: ether/hexane = 1:5, R_f = 0.64). Red brown oil. $C_{14}H_{16}FeOSe$ (335.08): C 50.39 (calcd. C 50.18); H 4.86 (4.81)%. **IR** (KBr, neat): $\tilde{\nu}$ = 3099, 2956, 1735, 1656 (C=O), 1592, 1560, 1508, 1460, 1439, 1411, 1372, 1336, 1248, 1214, 1156, 1106, 1046, 1027, 1002, 943, 827, 812, 800, 678, 593, 559, 542, 498, 483, 474 cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 1.47 (d, J = 7.1 Hz, 6 H, CH_3), 3.74 (hept, J = 7.0 Hz, 1 H, CH), 4.14 (s, 5 H, Cp), 4.39 (t, J = 2.0 Hz, 2 H, Cp$_{meta}$), 4.72 (t, J = 2.0 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** ($CDCl_3$): δ = 24.6 (CH_3), 32.7 (CH), 68.8 (Cp$_{ortho}$), 70.7 (Cp$_{meta}$), 71.7 (Cp), 82.1 (Cp$_{ipso}$), 195.4 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 637.3 ppm.

***Se*-*n*-Butyl Ferrocenecarboselenoate (6d).** Chromatographic purification on silica gel column (developing solvent: ether/hexane = 1:5, R_f = 0.59). Red oil. $C_{15}H_{18}FeOSe$ (349.11): C 51.73 (calcd. C 51.61), H 5.25 (5.20)%. **IR** (KBr, neat): $\tilde{\nu}$ = 3098, 2958, 2930, 2872, 1668 (C=O), 1439, 1412, 1374, 1337, 1237, 1208, 1107, 1043, 1026, 1002, 940, 823, 799, 688, 545, 495) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 0.95 (t, J = 7.4 Hz, 3 H, CH_3), 1.45 (sex, J = 7.8 Hz, 2 H, CH_3CH_2), 1.72 (quint, J = 7.6 Hz, 2 H, $CH_3CH_2CH_2$), 3.03 (t, J = 7.3 Hz, 2 H, $SeCH_2$), 4.22 (s, 5 H, Cp), 4.48 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.83 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** ($CDCl_3$): δ = 13.6 (CH_3), 23.1 (CH_3CH_2), 24.7 ($CH_3CH_2CH_2$), 33.0 ($SeCH_2$), 68.9 (Cp$_{ortho}$), 70.8, (Cp) 71.8 (Cp$_{meta}$), 81.9 (Cp$_{ipso}$), 194.8 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 513.6 ppm.

***Se*-*tert*-Butyl Ferrocenecarboselenoate (6e).** Selenium (168 mg, 2.13 mmol) was added to a pentane solution of 1.6 M *tert*-butyllithium (1.3 mL, 2.08 mmol) in diethyl ether (10 mL) at 0 °C. After stirring at the same temperature for 10 min, ferrocenoyl chloride (515 mg, 2.07 mmol) was added to the solution. The color of the solution rapidly changed from pale yellow to orange. The mixture was stirred at the same temperature for 1 h. The reaction mixture was extracted with diethyl ether (35 mL). The organic layer was washed with water (ca. 30 mL for 5 times), dried with $MgSO_4$ (ca. 2 g) for 15 min. Removal of the solvent under reduced pressure (30 °C, 0.2 Torr), followed by chromatographic purification of the resulting residue on silica gel (ether/hexane = 1:5, R_f = 0.64) gave 210 mg (29 %) of chemically pure *Se*-*tert*-butyl ferrocenecarboselenoate (**6e**) as orange plate crystals. Mp: 106–108 °C. $C_{15}H_{18}FeOSe$ (349.11): C 51.11 (calcd. 51.61), H 5.14 (5.20)%. **IR** (KBr): $\tilde{\nu}$ = 3854, 2966, 1735, 1686, 1646 (C=O), 1560, 1543, 1508, 1474, 1458, 1438, 1410, 1372, 1361, 1248, 1236, 1153, 1106, 1045, 1028, 1002, 937, 838, 821, 800, 682, 552, 522, 500, 486) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 1.59 (s, 9 H, CCH_3), 4.15 (s, 5 H, Cp), 4.37 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.71 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** ($CDCl_3$): δ = 31.7 (CCH_3), 47.5 (CCH_3), 68.7 (Cp$_{ortho}$), 70.6 (Cp), 71.6 (Cp$_{meta}$), 82.6 (Cp$_{ipso}$), 196.7 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 690.0 ppm.

***Se*-Phenacyl Ferrocenecarboselenoate (6f).** Similar procedure to the synthesis of compound **6d**. Recrystallization solvent: a mixed solvent (25 mL) of ether/hexane (10:15) at –20 °C for 2 d. Orange micro crystals. Mp: 74–76 °C. $C_{19}H_{16}FeO_2Se$ (411.97): C 55.38 (calcd. 55.51), H 4.00 (3.92)%. **IR** (KBr): $\tilde{\nu}$ = 3104, 2367, 1669 (C=O), 1662 (C=O), 1596, 1560, 1446, 1408, 1374, 1277, 1250, 1104, 1054, 1032, 1008, 940, 838, 817, 803, 731, 712, 687, 606, 550, 500, 486) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 4.16 (s, 5 H, Cp), 4.42 (s, 2 H, CH_2), 4.50 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.81 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$), 7.24–8.03 (m, 5 H, Ph) ppm. **^{13}C NMR** ($CDCl_3$): δ = 29.4 ($^1J_{C\text{–}Se}$ = 66.3 Hz, CH_2), 68.7 (Cp$_{ortho}$), 70.6 (Cp), 72.2 (Cp$_{meta}$), 79.9 (Cp$_{ipso}$), 128.3, 128.4, 133.1, 135.1 (Ph), 191.5 ($^1J_{C\text{–}Se}$ = 139.4 Hz, SeC=O), 195.3 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 526.3 ppm.

***O*-Trimethylsilyl Ferrocenecarboselenoate (7a):** Trimethylsilyl chloride (0.15 mL, 1.2 mmol) was added to a suspension of potassium ferrocenecarboselenoate (**3**) (304 mg, 0.92 mmol) in hexane (10 mL) at 24 °C. The mixture was stirred at the same temperature for 2 h. The color of the suspension slowly changed from orange to red. The precipitates (KCl) were filtered off. Removal of the solvent under reduced pressure (24 °C, 0.2 Torr) gave 259 mg (77 %) of *O*-trimethylsilyl ferrocenecarboselenoate (**7a**) as dark red oil, which was identified by conversion into cesium ferrocenecarboselenoate (**5**). **IR** (KBr, neat): $\tilde{\nu}$ = 3097, 2957, 2361, 1687, 1441, 1399, 1374, 1337, 1291, 1237, 1200, 1107, 1047, 1028, 1003, 972, 847 (C = Se), 760, 723, 675, 494) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 0.46 (s, 9 H, CH$_3$), 4.09 (s, 5 H, Cp), 4.50 (t, J = 1.96 Hz, 2 H, Cp$_{meta}$), 4.90 (t, J = 1.96 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CDCl$_3$): δ = 1.0 (CH$_3$), 71.4, (Cp$_{ortho)}$ 71.5 (Cp), 73.2 (Cp$_{meta}$), 89.1 (Cp$_{ipso}$), 225.2 (C = Se, $^{1}J_{C\text{–}Se}$ = 218 Hz) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 887.1 ppm.

***O*-Dimethyl(phenyl)silyl Ferrocenecarboselenoate (7b):** Red purple oil. Identification: conversion into cesium ferrocenecarboselenoate (**5**). **IR** (KBr, neat): $\tilde{\nu}$ = 3070, 2959, 2365, 1687, 1428, 1290, 1256, 1200, 1120, 1047, 830 (C = Se), 793, 727, 700, 650, 471) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 0.73 (s, 6 H, CH$_3$), 4.00 (s, 5 H, Cp), 4.45 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.90 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$), 7.26–7.64 (m, 5 H, Ph) ppm. **^{13}C NMR** (CDCl$_3$): δ = 2.1 (CH$_3$), 69.7, (Cp$_{ortho)}$ 71.5 (Cp), 73.3 (Cp$_{meta}$), 89.0 (Cp$_{ipso}$), 128.0, 130.3, 133.0, 133.6 (Ph), 224.6 (C = Se, $^{1}J_{C\text{–}Se}$ = 218 Hz) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 911.6. **MS**(CI) *m/z*: 427 [M^{+} + 1]. **HRMS** (*m/z*) (EI, 20 eV): $C_{19}H_{20}OFeSeSi$: 427.97992; calcd. 427.97981.

***Se*-Triphenylgermanium Ferrocenecarboselenoate (8a):** Triphenylgermanium chloride (149 mg, 0.44 mmol) was added to a suspension of potassium ferrocenecarboselenoate (**3**) (147 mg, 0.44 mmol) in diethyl ether (17 mL) at 23 °C. The mixture was stirred at the same temperature for 2 h. The color of the suspension slowly changed from orange to reddish orange. Filtration of the precipitates (KCl) and removal of the solvent under reduced pressure (23 °C, 0.2 Torr), followed by recrystallization of the resulting residue from a mixed solvent (10 mL) of dichloromethane/ether/hexane (1:3:6) at –10 °C gave 247 mg (94 %) of *Se*-triphenylgermanium ferrocenecarboselenoate (**8a**) as red plate crystals. Mp: 157–159 °C. $C_{29}H_{24}FeGeOSe$ (595.95): C 58.41 (calcd. 58.45); H 4.08 (4.06)%. **IR** (KBr): $\tilde{\nu}$ = 3651, 3630, 1719, 1680, 1661 (C=O), 1650, 1543, 1508, 1483, 1431, 1262, 1090, 1043, 1027, 792, 735, 697, 492, 456) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 4.12 (s, 5 H, Fc), 4.45 (t, J = 2.1 Hz, 2 H, Fc), 4.80 (t, J = 2.0 Hz, 2 H, Fc), 7.39–7.71 (m, 15 H, Ph) ppm. **^{13}C NMR** (CDCl$_3$): δ = 70.2, 70.6, 72.3, 82.8 (Fc), 128.4, 129.7, 134.9, 135.7 (Ph), 191.9 (C=O) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 352.4 ppm.

***Se*-Diphenylgermanium Bis(ferrocenecarboselenoate) (8b):** Recrystallization solvent: a mixed solvent (21 mL) of dichloromethane/hexane (1:20). Red micro crystals. Mp: 154–156 °C. **IR** (KBr): $\tilde{\nu}$ = 1718, 1663 (C=O), 1484, 1435, 1397, 1372, 1338, 1246, 1106, 1089, 1042, 1003, 938, 871, 834, 819, 787, 734, 694, 676, 546, 495, 458) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 4.12 (s, 10 H, Cp), 4.45 (t, J = 1.95 Hz, 4 H, Cp$_{meta}$), 4.78 (t, J = 1.95 Hz, 4 H, Cp$_{ortho}$), 7.41–7.94 (m, 10 H, Ph) ppm. **^{13}C NMR** (CDCl$_3$): δ = 70.2 (Cp$_{ortho}$), 70.7 (Cp), 72.4 (Cp$_{meta}$), 82.1 (Cp$_{ipso}$), 128.4, 130.2, 134.2, 135.7 (Ph), 192.1 (C=O) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 395.4.

***Se*-Trimethyltin Ferrocenecarboselenoate (9a):** Red micro crystals. Mp: 188–190 °C. **IR** (KBr): $\tilde{\nu}$ 3854, 2346, 1719, 1702, 1686, 1654, 1630 (C=O), 1560, 1542, 1508, 1459, 1432, 1238, 1106, 1026, 937, 824, 800, 532, 498) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 0.54 (s, 9 H, CH$_3$), 4.16 (s, 5 H, Cp), 4.40 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.75 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CDCl$_3$): δ = –4.2 ($^{1}J_{13C\text{–}117Sn}$ = 339, $^{1}J_{13C\text{–}119Sn}$ = 354 Hz, CH$_3$), 70.3 (Cp$_{ortho}$), 70.7 (Cp), 72.1 (Cp$_{meta}$), 83.3 (Cp$_{ipso}$), 195.9 (C=O) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 327.5 ppm) ppm. **^{119}Sn NMR** (CDCl$_3$): δ = 49.8 ($^{1}J_{119Sn\text{–}13C}$ = 354, $^{1}J_{119Sn\text{–}77Se}$ = 779 Hz) ppm.

***Se*-Triphenyltin Ferrocenecarboselenoate (9b):** Recrystallization solvent: a mixed solvent of dichloromethane/ether/hexane (2:3:6) at –10 °C. Red micro crystals. Mp: 146–148 °C. $C_{29}H_{24}FeOSeSn$ (643.94): C 54.10 (calcd. 54.25), H 3.85 (3.77)%. **IR** (KBr): $\tilde{\nu}$ 1686, 1643 (C=O), 1560, 1543, 1508, 1479, 1458, 1430, 1244, 1107, 1074, 1041, 938, 819, 795, 730, 697, 544, 493) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 4.10 (s, 5 H, Cp), 4.45 (t, J = 1.95 Hz, 2 H, Cp$_{meta)}$, 4.80 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$), 7.39–7.72 (m, 15 H, Ph) ppm. **^{13}C NMR** (CDCl$_3$): δ = 69.7 (Cp$_{ortho}$), 70.7 (Cp), 72.5 (Cp$_{meta}$), 82.6 (Cp$_{ipso}$), 128.7, 129.6, 136.9, 138.4 (Ph), 194.3 (C = $^{1}J_{77Se\text{–}117Sn}$ = 854, $^{1}J_{77Se\text{–}119Sn}$ = 891 Hz) ppm. **^{117}Sn NMR** (CDCl$_3$): δ = –104.0 ($^{1}J_{119Sn\text{–}13C}$ = 564 Hz) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 344.5 ($^{1}J_{\ 119Sn\text{–}77Se}$ = 894 Hz) ppm.

***Se*-Dimethyltin Bis(ferrocenecarboselenoate) (9c):** Recrystallization solvent: a mixed solvent of dichloromethane/ether/hexane (1:2:4) at –10 °C. Orange micro crystals. $C_{24}H_{24}Fe_2O_2Se_2Sn$ (732.77): C 39.88 (calcd. 39.34), H 3.25 (3.30)%. Mp: 185–187 °C. **IR** (KBr): $\tilde{\nu}$ 1616 (C=O), 1600, 1432, 1373, 1336, 1251, 1240, 1108, 1045, 1027, 1003, 940, 838, 804, 682, 546, 501, 486) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 1.17 (s, 6 H, CH$_3$), 4.19 (s, 10 H, Cp), 4.46 (t, J = 2.0 Hz, 4 H, Cp$_{meta}$), 4.76 (t, J = 2.0 Hz, 4 H, Cp$_{ortho}$) ppm. **^{13}C NMR** (CDCl$_3$): δ = 3.36 (CH$_3$), 70.6 (Cp$_{ortho}$), 71.0 (Cp), 72.7 (Cp$_{meta}$), 82.5 (Cp$_{ipso}$), 199.1 (C=O) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 397.0 ($^{1}J_{77Se\text{–}117Sn}$ = 690, $^{1}J_{77Se\text{–}119Sn}$ = 726 Hz) ppm. **^{119}Sn NMR** (CDCl$_3$): δ = –65.2 ($^{1}J_{119Sn\text{–}77Se}$ = 719 Hz) ppm.

***Se*-Diphenyltin Bis(ferrocenecarboselenoate) (9d):** Diphenyltin dichloride (151 mg, 0.44 mmol) was added to a suspension of potassium ferrocenecarboselenoate (**3**) (295 mg, 0.89 mmol) in dichloromethane (12 mL) at 0 °C. The color of the suspension rapidly changed from orange to red brown. The mixture was stirred at the same temperature for 1 h. Filtration of the precipitates (KCl) and removal of the solvent under reduced pressure (29 °C, 0.2 Torr), followed by recrystallization of the resulting residue from a mixed solvent of dichloromethane/ether/hexane (2:1:11) at –10 °C for 5 d, gave 339 mg (90 %) of *Se*-diphenyltin bis(ferrocenecarboselenoate) (**9d**) as red micro crystals. Mp: 188–190 °C. $C_{34}H_{28}Fe_2O_2Se_2Sn$ (856.90): C 47.36 (calcd. 47.66), H 3.31 (3.29)%. **IR** (KBr): $\tilde{\nu}$ 3065, 2963, 2346, 1736, 1718, 1686, 1654, 1624 (C=O), 1592, 1534, 1479, 1459, 1432, 1339, 1373, 1340, 1250, 1108, 1072, 1046, 1031, 942, 870, 797, 729, 695, 678, 548, 494, 453) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 4.12 (s, 10 H, Cp), 4.48 (t, J = 1.95 Hz, 4 H, Cp$_{meta}$), 4.79 (t, J = 1.95 Hz, 4 H, Cp$_{ortho}$), 7.39–7.98 (m, 10 H, Ph) ppm. **^{13}C NMR** (CDCl$_3$): δ = 70.4 (Cp$_{ortho}$), 70.8 (Cp), 72.7 (Cp$_{meta}$), 82.2 (Cp$_{ipso}$), 128.8, 129.9, 135.9, 139.2 (Ph), 196.8 (C=O) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 394.2 ($^{1}J_{77Se\text{–}117Sn}$ = 812, $^{1}J_{77Se\text{–}119Sn}$ = 843 Hz) ppm. **^{119}Sn NMR** (CDCl$_3$): δ = –168.9 ($^{1}J_{119Sn\text{–}77Se}$ = 842 Hz) ppm.

***Se*-Phenyltin Tris(ferrocenecarboselenoate) (9e):** Recrystallization solvent: a mixed solvent of dichloromethane/hexane (4:15) at 26 °C. Red plate crystals. Mp: 187–188 °C. $C_{39}H_{32}Fe_2O_3Se_3Sn$ (1019.76): C 46.05 (calcd. C, 46.11), H 3.25 (3.17)%. **IR** (KBr): $\tilde{\nu}$ 1638 (C=O), 1431, 1371, 1244, 1106, 1041, 937, 822, 791, 732, 677, 545, 495) cm^{-1}. **^{1}H NMR** (CDCl$_3$): δ = 4.28 (s, 15 H, Cp), 4.52 (t, J = 1.95 Hz, 6 H, Cp$_{meta}$), 4.86 (t, J = 1.95 Hz, 6 H, Cp$_{ortho}$), 7.39–8.01 (m, 5 H, Ph) ppm. **^{13}C NMR** (CDCl$_3$): δ = 70.7 (Cp$_{ortho}$), 71.1 (Cp), 72.8 (Cp$_{meta}$), 82.0 (Cp$_{ipso}$), 128.9, 130.3, 134.8, 140.7 (Ph), 196.2 (C=O) ppm. **^{77}Se NMR** (CDCl$_3$): δ = 463.0 ($^{1}J_{77Se\text{–}117Sn}$ = 1056, $^{1}J_{77Se\text{–}119Sn}$ = 1099 Hz) ppm. **^{119}Sn NMR** (CDCl$_3$): δ = –204.1 ($^{1}J_{119Sn\text{–}77Se}$ = 1104 Hz) ppm.

***Se*-Triphenyllead Ferrocenecarboselenoate (10a):** Triphenyllead chloride (282 mg, 0.60 mmol) was added to a suspension of potassium ferrocenecarboselenoate (**3**) (199 mg, 0.60 mmol) in diethyl ether (17 mL) at 23 °C. The mixture was stirred at the same temperature for 1 h. The color of the suspension slowly changed from orange to reddish orange. Filtration of the precipitates (KCl) and removal of the solvent under reduced pressure (23 °C, 0.2 Torr) and recrystallization of the resulting residue from a mixed solvent of dichloromethane/ether/hexane (2:2:5) at –10 °C for 2 d gave 410 mg (94 %) of *Se*-triphenyllead ferrocenecarboselenoate (**10a**) as red plate crystals. Mp: 144–146 °C. $C_{29}H_{24}FeOPbSe$ (730.51): C 47.40 (calcd. 47.68), H 3.44 (3.31)%. **IR** (KBr): ṽ 3062, 2360, 1639 (C=O), 1569, 1474, 1430, 1370, 1336, 1242, 1231, 1156, 1106, 1060, 1039, 1027, 1016, 995, 936, 862, 834, 818, 793, 726, 718, 692, 676, 542, 492, 479, 466) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 4.10 (s, 5 H, Cp), 4.43 (t, J = 1.95 Hz, 2 H, Cp_{meta}), 4.82 (t, J = 1.95 Hz, 2 H, Cp_{ortho}), 7.32–7.77 (m, 15 H, Ph) ppm. **^{13}C NMR** ($CDCl_3$): δ = 70.6 (Cp_{ortho}), 70.8 (Cp), 72.2 (Cp_{meta}), 83.2 (Cp_{ipso}), 129.1, 129.8, 137.1 (Ph), 152.9 ($^1J_{13C-207Pb}$ = 504 Hz, Ph), 195.0 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 418.6 ($^1J_{77Se-207Pb}$ = 1141 Hz) ppm.

***Se*-Diphenyllead Bis(ferrocenecarboselenoate) (10b):** Recrystallization solvent: a mixed solvent of dichloromethane/hexane (6:10) at 0 °C. Red micro crystals. Mp: 160–162 °C. $C_{34}H_{28}Fe_2O_2PbSe_2$ (945.39): C 42.80 (calcd. 43.20), H 3.09 (2.99)%. **IR** (KBr): ṽ 1624 (C=O), 1567, 1474, 1434, 1371, 1339, 1245, 1108, 1045, 1028, 1013, 994, 939, 866, 817, 792, 732, 721, 690, 676, 546, 477) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 4.12 (s, 10 H, Cp), 4.47 (t, J = 1.8 Hz, 4 H, Cp_{meta}), 4.82 (t, J = 1.8 Hz, 4 H, Cp_{ortho}), 7.33–8.16 (m, 10 H, Ph) ppm. **^{13}C NMR** ($CDCl_3$): δ = 70.7 (Cp_{ortho}), 70.7 (Cp), 72.4 (Cp_{meta}), 83.0 (Cp_{ipso}), 129.7, 130.0, 135.6, 155.0 (Ph), 198.0 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 481.8 ($^1J_{77Se-207Pb}$ = 934 Hz) ppm.

Diferrocenoyl Diselenide (11)

Oxidation of the Potassium Salt 3 with I_2-KI: A methanol solution (3 mL) containing I_2-KI (82 mg, 0.32 mmol) was added to a solution of potassium ferrocenecarboselenoate (**3**) (188 mg, 0.57 mmol) in methanol (10 mL) at 0 °C and the mixture was stirred for l h. Aqueous sodium thiosulfate (ca. 5 %, 20 mL) was added and extracted with dichloromethane (25 mL). The organic layer was washed with water (ca. 30 mL × 5) and dried with Na_2SO_4 (ca. 2 g) for 15 min. Removal of the solvent under reduced pressure (20 °C, 0.2 Torr), followed by recrystallization from dichloromethane/hexane (1:5) at –20 °C for 4 h gave 136 mg (87 %) of compound **11** as red micro crystals. Mp: 170–172 °C (dec.) (163–165 °C[5]) $C_{22}H_{18}Fe_2O_2Se_2$ (583.99): C 44.68 (calcd. 44.75), H 3.05 (3.11)%. **IR** (KBr): ṽ 3630, 2361, 2344, 1718, 1680 (C=O), 1654, 1560, 1542, 1508, 1459, 1431, 1367, 1262, 1239, 1106, 1038, 932, 822, 774, 670, 544, 492) cm^{-1}. **^{1}H NMR** ($CDC1_3$): δ = 4.32 (s, 10 H, Cp), 4.53 (t, J = 1.95 Hz, 4 H, Cp_{meta}), 4.88 (t, J = 1.95 Hz, 4 H, Cp_{ortho}) ppm. **^{13}C NMR** ($CDC1_3$): δ = 69.7 (Cp_{ortho}), 71.2 (Cp), 72.7 (Cp_{meta}), 785 (Cp_{ipso}), 186.7 (C=O) ppm. **^{77}Se NMR** ($CDCI_3$): δ = 581.7 ppm.

Oxidation with XeF_2: Xenon difluoride (115 mg, 0.68 mmol) was added to a solution of potassium ferrocenecarboselenoate (**3**) (226 mg, 0.68 mmol) in acetonitrile (10 mL) at 0 °C and the mixture was stirred for 10 min. The solvent was evaporated under reduced pressure. Dichloromethane (25 mL) was added followed by stirring for 30 min. Evaporation of the dichloromethane under reduced pressure gave chemically pure compound **12** in 82 % (153 mg).

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-895794 (**6e**), CCDC-895793 (**9d**), and CCDC-895795 (**10a**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Details of the synthesis and additional figures.

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