DOI: 10.1002/zaac.201200369

Ferrocenecarboselenoic Acid: Synthesis and Some Reactions

Toshinori Takahashi,[a] Osamu Niyomura,[b] Shinzi Kato,*[a,b,c] and Masahiro Ebihara[a]

Keywords: Ferrocenecarboselenoic acid; Acyl carbamoyl selenide; Acyl carbamothioyl selenide; Piperidinium ferrocenecarboselenoate; Diferrocenoyl selenide

Abstract. The first ferrocenecarboselenoic acid was synthesized and characterized. The existence of tautomeric equilibrium between the selenol (FcCOSeH) and selenoxo forms (FcCSeOH) in polar solvents was proven by ^{1}H-, ^{13}C- and ^{77}Se-NMR spectra. The selenoxo form exists predominantly in a polar solvent at low temperature below –70 °C. Treatment of this acid with lithium, sodium, and potassium hydrides and with rubidium and cesium fluorides gave the corresponding alkali metal ferrocenecarboselenoates in quantitative yields. Treatment with 4-methylphenyl isocyanate at room temperature led to ferrocenoyl 4-methylphenylcarbamoyl selenide $FcCOSeC(O)NHC_6H_4Me$-4 in high yield. A similar reaction with phenyl isothiocyanate formed a mixture of FcCOSeC(S)NHPh and FcCOSeC(SH)=NPh in moderate to good yield. The carboselenoic acid readily reacted with piperidine to give piperidinium ferrocenecarboselenoate in good yield. Air oxidation of this selenoic acid afforded diferrocenoyl selenide as a major product along with diferrocenoyl diselenide. The structures of the selenide $(FcCO)_2Se$ and diselenide $(FcCOSe)_2$ were examined by single-crystal X-ray analysis.

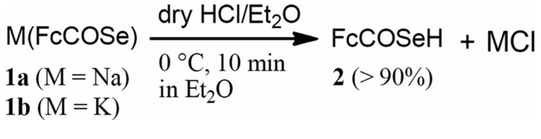
Introduction

Ferrocenecarboselenoic acid is one of the most important starting compounds for the synthesis of ferrocenecarboselenoic acid derivatives. In general, the most effective method for the synthesis of carbochalcogenoic acids ($RCEE'H$, R = alkyl, aryl; E, E' = O, S, Se, Te; E, $E' \neq$ O) may be acidolysis of their alkali and alkali earth metal salts or ammonium salts with hydrogen chloride under oxygen-free conditions. Previously, we reported the synthesis and isolation of a variety of alkali metal and secondary and tertiary ammonium carbothioates[1] and carbodithioates.[2] In addition, we have isolated ferrocenecarbo-thioic[3] and -dithioic acids,[4] and arenecarboselenoic acids,[5] and we succeeded in the preparation of alkali metal ferrocenecarboselenoates.[6] We describe herein the synthesis and some reactions of ferrocenecarboselenoic acid.

Results and Discussion

Synthesis

After we considered the synthesis of arenecarboselenoic acids,[5] acidolyses of sodium (**1a**) and potassium ferrocenecarboselenoates (**1b**) with hydrogen chloride were examined (Scheme 1). As a result, treatment of an excess of the salts **1** with hydrogen chloride led to the expected ferrocenecarboselenoic acid (**2**) in high yields. For example, a dry hydrogen chloride/ether solution was added to a suspension of the potassium salt **1b** in ether, and the mixture was stirred at 0 °C for 10 min. Filtration of the insoluble parts and removal of the solvent under reduced pressure gave ferrocenecarboselenoic acid **2** as a dark red oil in 95 % yield. Under conditions similar to those using the sodium salt **1a**, compound **2** was obtained in a yield of 92 %. *To avoid decomposition of the formed acid **2**, the use of excess salts **1** and oxygen-free conditions are required.*



$$\underset{\substack{\mathbf{1a}\ (M = Na)\\ \mathbf{1b}\ (M = K)}}{M(FcCOSe)} \xrightarrow[\substack{0\ ^{\circ}C,\ 10\ min\\ in\ Et_2O}]{dry\ HCl/Et_2O} \underset{\mathbf{2}\ (> 90\%)}{FcCOSeH} + MCl$$

Scheme 1.

The structure of the acid **2** was confirmed by IR and ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy, and by conversion into ferrocenoyl 4-methylphenylcarbamoyl (**5**) and phenylcarbamothioyl selenides (**6**) (see Scheme 6) and into piperidinium (**7**), rubidium (**8**), cesium (**9**) and lithium ferrocenecarboselenoates (**10**) (see Scheme 7). Thus, in the IR spectrum, characteristic absorption bands are observed at 2357 cm^{-1} and 1694 cm^{-1}, which can be ascribed to ν(SeH) and ν(C=O) stretching fre-

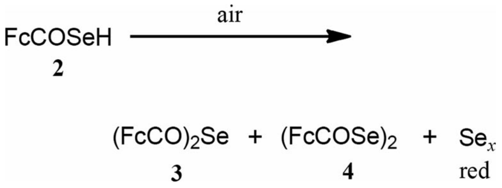
---

* Prof. Dr. S. Kato
Fax: 81-52-222-2442
E-Mail: kshinzi@nifty.com
[a] Faculty of Engineering
Department of Chemistry
Gifu University
Gifu, Japan
[b] Department of Applied Chemistry
School of Engineering
Chubu University
Aichi, Japan
[c] Present address:
Maruno-uchi 2–14–32
Lions-City Maruno-uchi 1105, Naka-ku
Nagoya 460–0002, Japan

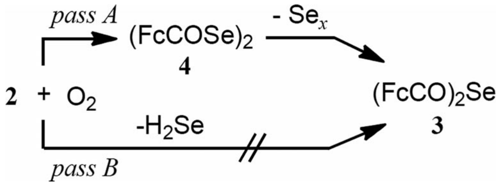
Supporting information for this article is available on the WWW under **http://dx.doi.org/10.1002/zaac.201200369** or from the author.

quencies, respectively. The ^{1}H, ^{13}C, and ^{77}Se NMR spectra show characteristic signals at δ = 2.93, δ = 190.6 and δ = 415.9, respectively, which can be ascribed to SeH proton, carbonyl carbon, and SeH selenium, respectively. These values were comparable to those of common arenecarboselenoic acids [ν(Se-H) = 2289–2320 cm^{-1}; ν(C=O) = 1682–1694 cm^{-1}, ^{1}H-Se: δ = 2.37–4.48, ^{13}C: δ = 187.6–193.4].[5a]

Ferrocenecarboselenoic acid (**2**) is labile toward oxygen and temperature. Upon exposure to air, compound **2** was quickly oxidized to give a mixture of diferrocenoyl selenide **3** and diselenide **4** along with a small amount of elemental selenium (Scheme 2). With regard to formation of the selenoic anhydride **3**, a possible route (Scheme 3, pass A) via deselenation of the diselenide **4** is considered because we did not detect any hydrogen selenide (Scheme 3, pass B).



Scheme 2.



Scheme 3.

We previously showed that carbochalcogenoic acids such as carbo-thioic, -selenoic, and -telluroic acids exist in a chalcogenoxo form *R*C*E*OH (*E* = S, Se, Te) at low temperature in polar solvents such as tetrahydrofuran (THF) and methanol.[5b] To confirm such equilibrium, variable low-temperature NMR spectra of ferrocenecarboselenoic acid (**2**) were measured in [D$_4$]MeOH (Figure 1).

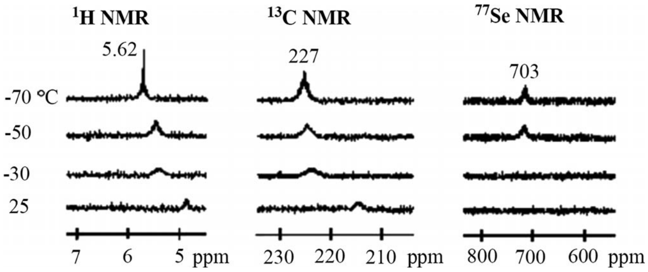
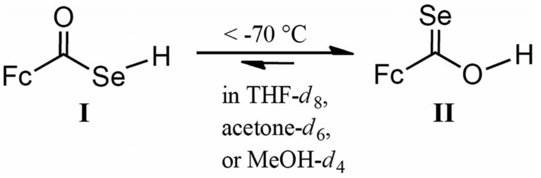
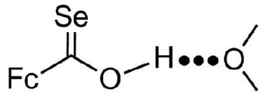


Figure 1. Variable low temperature NMR spectra of compound **2** in [D$_4$]MeOH.

As shown in Figure 1, broad signals ascribable to OH proton and ^{13}C=Se carbon appear near δ = 4.8 and 216, respectively, and are sharpened with a further decrease in temperature to –30 °C, –50 °C, and –70 °C. Signals due to carbonyl and selenocarbonyl carbon atoms were not observed at room temperature. The ^{77}Se=C NMR spectra near δ = 703 at –50 °C is sharpened with a further decrease in temperature to –70 °C. Similar trends of signals due to the OH protons and selenocarbonyl carbon and selenium atoms of compound **2** were observed in both [D$_8$]THF and [D$_6$]acetone (Figure S1a and b, Supporting Information). These spectroscopic data suggest that rapid equilibrium exists between the selenol form **I** and selenoxo form **II** in THF at room temperature. At low temperature, the selenoxo form **II** exists predominantly (Scheme 4), whereas the OH proton of **II** is presumed to form a hydrogen bond with the oxygen atoms of the polar solvent molecules (Scheme 5).



Scheme 4.



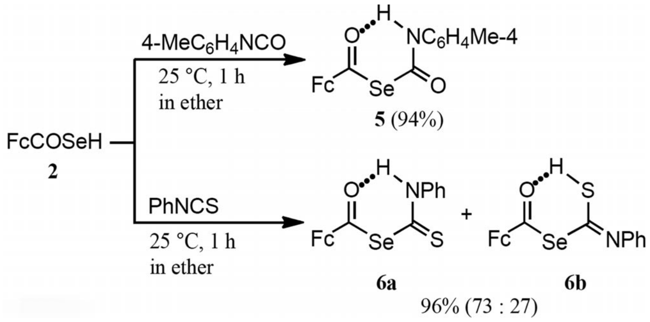
Scheme 5.

Reactions

With 4-Methylphenyl Isocyanate and Phenyl Isothiocyanate

Previously, we reported that arenecarbochalcogenoic acids (ArC*EE*′H, *E* = O, S; *E*′ = S, Se, Te) react with aryl isocyanates (Ar′NCO) to give the addition products ArC*EE*′C(O)NHAr′ (*E* = O, S; *E*′ = S, Se), the tautomer ArC*EE*′C(=NAr′)(OH), which can also be detected spectroscopically.[3,5,7a] In fact, ferrocenecarboselenoic acid (**2**) was found to readily react with 4-methylphenyl isocyanate in ether at 25 °C to give the expected (ferrocenoyl)(4-methylphenylcarbamoyl) selenide (**5**) in 94 % yield as red crystals, which showed two characteristic signals at δ = 198.9 and δ = 157.1 in the ^{13}C NMR spectrum, which can be ascribed to the carbonyl and carbamoyl carbon chemical shifts, respectively.

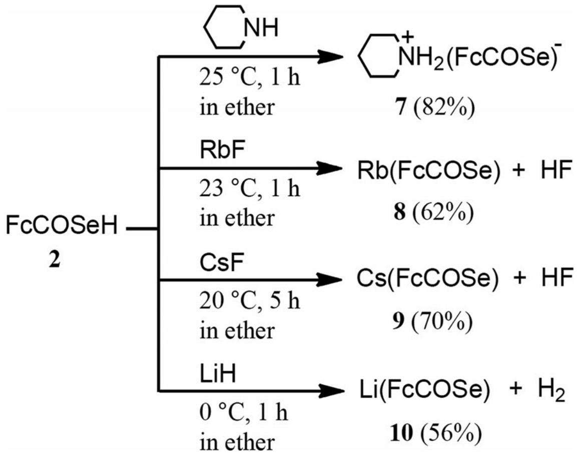
Under the same conditions, the reaction with phenyl isothiocyanate led to the corresponding adduct ferrocenoyl phenylcarbamothioyl selenide (**6**) in quantitative yield as red micro crystals. In contrast to the results with compound **5**, the ^{1}H NMR spectrum of this adduct showed two broad signals at δ = 10.2 and δ = 13.3, which can be ascribed to OH and SH protons, respectively. In the ^{13}C NMR spectrum, two small signals are seen at δ = 185.7 and δ = 202.6, which can be ascribed to the C=O and C=S groups, respectively, and two small signals are seen at δ = 187 and δ = 198.1, indicating the existence of C=O and C=N groups, respectively. In addition, the ^{77}Se NMR spectrum showed two signals at δ = 712.9 and δ = 698.5, which can be ascribed to *Se*C=S and *Se*C=N selenium, respectively. These results appear to indicate the existence of the tautomer **6b** of compound **6a**. The proton ratio of NH and SH in **6** was 73:27 (Scheme 6).



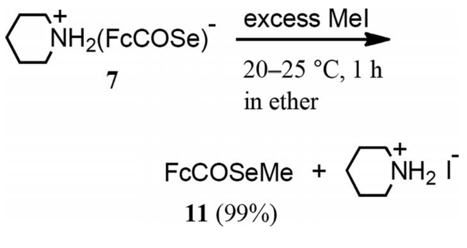
Scheme 6.

With Piperidine, RbF, CsF, and LiH or BuLi

Previously, we reported the synthesis of piperidinium arenecarbothioates[8] and -carbodithioates[9] from the corresponding carbothioic and carbodithioic acids with piperidine. As expected, the reaction of **2** with piperidine in ether readily proceeded at 25 °C to give piperidinium ferrocenecarboselenoate (**7**) in 82 % yield as orange crystals (Scheme 7). The salt **7** readily reacted with methyl iodide at room temperature to lead to *Se*-methyl ferrocenecarboselenoate (**11**) in quantitative yield (Scheme 8).



Scheme 7.



Scheme 8.

Under similar conditions, the reactions of the acid **2** with rubidium and cesium fluorides gave the corresponding rubidium (**8**) and cesium ferrocenecarboselenoates (**9**) in respective yields of 62 % and 70 %. Moreover, the reactions with lithium hydride and butyllithium led to lithium ferrocencarboselenoate in good yields, respectively.

X-ray Structural Analysis

Although several attempts to crystallize the acid **2** were unsuccessful, single crystals of compounds diferrocenoyl selenide **3** and diselenide **4** were obtained. The molecular structure of compound **3** is shown in Figure 2. Final atomic positional parameters are listed in Table 1. Selected bond lengths and angles are shown in Table 2.

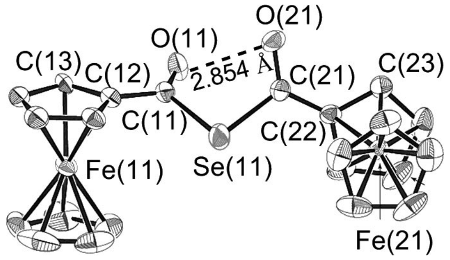


Figure 2. Ortep drawing of $(FcCO)_2Se$ (**3**). A black dotted line shows the intramolecular contact.

Table 1. Crystal data and data collection of $(FcCO)_2Se$ (**3**).

Empirical formula	$C_{22}H_{18}Fe_2O_2Se$
Formula weight	505.04
Color	red, prismatic
Crystal system	triclinic
Unit-cell dimensions	
a /Å	15.508(3)
b /Å	16.441(1)
c /Å	7.677(3)
β /°	96.85(2)
γ /°	85.05
Volume of unit cell /Å^3	1931.2(9)
Space group	$P\bar{1}$ (#2)
Z	4
D(calcd.) /g·cm^{-3}	1.737
Crystal size /mm	0.17 × 0.26 × 0.34
μ (Mo-K_α) /cm^{-1}	34
T /°C	23.0
λ (Mo-K_α) /Å	0.71069
2θ max /°	55.0
No. of measured reflections	9177
No. ofobservations [I>3 (I)]	3848
No. of variables	487
$R_2$$^{a)}$	0.047
$wR_2$$^{b)c)}$	0.124
Goodness-of-fit on F^2	1.005

a) $Rw = [(|F_o|–|F_c|)^2/\ w|F_o|^2]^{1/2}$. b) $w = [\sigma(F_o)+p^2(F_o)^2/4]^{-1}$. c) Large R-values appear to be most likely due to poor quality of single crystals.

The C=O and C–Se distances are comparable to those of common diaroyl diselenides[7b] and the reported $(FcCOSe)_2$[10] (Ortep drawing see Figure S2 and Tables S1 and S2, Supporting Information). The selenocarboxyl group and the substituted Cp ring plane are coplanar, which appears to be the general trend for ferrocenecarbochalcogenoic acid derivatives.[6,10]

The C(11)=O(11)···O(21)=C(21) distance is significantly short [2.854(4) Å], indicating an intramolecular interaction. The torsion angle O(11)–C(11)···C(21)–O(21) is 29.6°, which is comparable to that (30.6°) of bis(2-methoxybenzoyl) sulfide.[11]

Table 2. Selected bond lengths /Å, angles /°, and torsion angles /° of $(FcCO)_2Se_3$ (**3**).

Bond lengths	
Se(11)–C(11)	1.981(2)
Se(11)–C(21)	1.980(3)
C(11)–O(11)	1.175(2)
C(21)–O(21)	1.191(2)
O(11)···O(21)	2.854(4)
Angles	
C(11)–Se(11)–C(21)	95.3(1)
O(11)–C(11)–Se(11)	121.5(2)
O(21)–C(21)–Se(11)	118.5(2)
Torsion angles	
O(11)–C(11)–Se(11)–C(21)	29.6(2)
O(21)–C(21)–Se(11)–C(11)	35.3(2)
O(12)–C(11)–C(12)–C(13)	20.1(3)
O(21)–C(21)–C(22)–C(23)	10.7(3)
Se(11)–C(11)–C(12)–C(13)	23.1(4)
Se(11)–C(21)–C(21)–O(21)	17.3(2)
C(13)–C(12)–C(22)–C(23)	66.0(3)

Intermolecular hydrogen bonding between carbonyl oxygen atoms and the hydrogen atoms of neighboring molecules, and weak CH-π-bonding and H···H short contacts are observed between the Cp ring carbon atoms and the Cp ring hydrogen atoms of neighboring molecules and between Cp ring-hydrogen atoms[13], respectively [Figure 3(a)]. For Figure 3(b), a linear molecular chain formed by both O···H hydrogen bond and CH-π-bonding is shown. In addition, two-dimensional sheet [Figure 3(c)] and three-dimensional arrangements [Figure 3(d)] are formed by both the C=O···H hydrogen bonding and H···H short contacts, where small columns (7.2 × 7.8 Å) such as (A) are formed.

Diferrocenoyl Diselenide 4

In addition to the two structural features of compound **4** reported by *Singh* et al. [intramolecular contacts between the carbonyl oxygen and the opposite selenocarboxyl selenium atom, C(11)=O(11)···Se(21) 3.179(3) Å and C(21)=O(21) ···Se(11) 3.189(3) Å, and intermolecular hydrogen bonding between the carbonyl oxygen and Cp ring hydrogen atoms],[10] weak intermolecular CH-π-bonding and H···H short contacts are observed between the Cp ring carbon and the Cp ring hydrogen atoms of neighboring molecules and between Cp ring-hydrogen atoms, respectively[13] (see Figure S3, Supporting Information).

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 JNM-α-400 instruments at 399.7 and 100.4 MHz, respectively, with tetramethylsilane as an internal standard. The ^{77}Se NMR (76 MHz) spectra were obtained with 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–

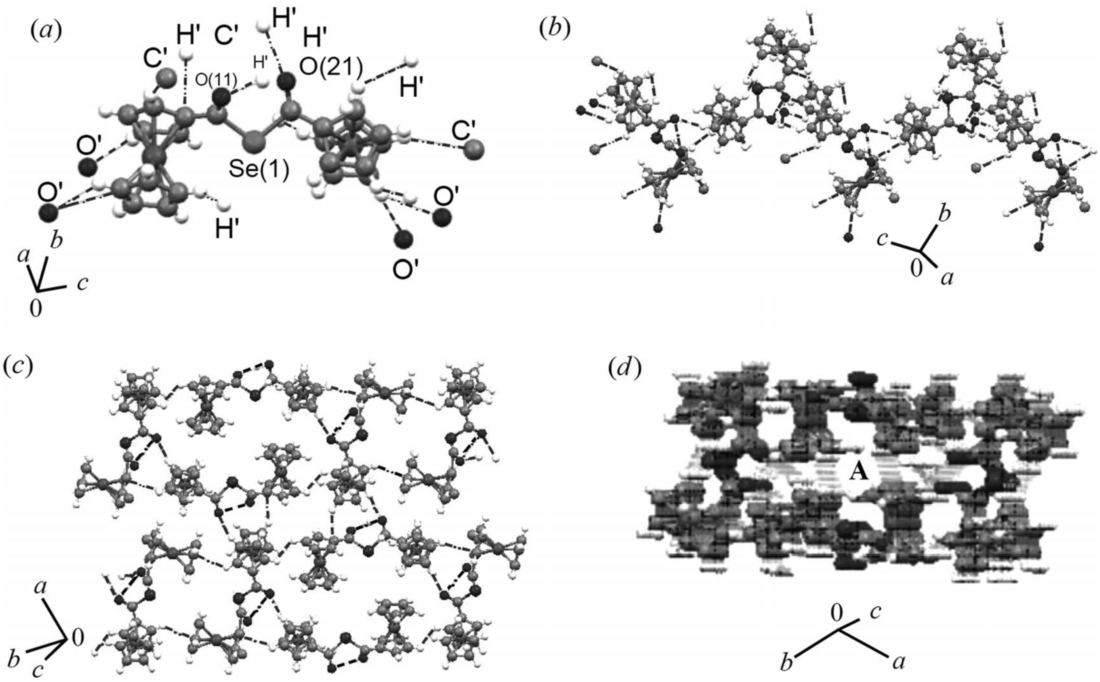


Figure 3. Intermolecular short contacts and molecular arrangement of $(FcCO)_2Se$ (**3**). (a) Dashed numbering atoms show ones of neighboring molecules (distances in Å) (b) Linear chain. (c) 2D Sheet formed by intermolecular short contact of these linear chains (the opposite molecule of the pairs is omitted for clarity). (d) 3D Networks formed by stacking of these sheets and the central (A) is one of the large holes of 9.21 × 5.53 Å).

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: Sodium ferrocenecarboselenoates (**1a**) and potassium ferrocenecarboselenoates (**1b**) were prepared by the reaction of ferrocenoyl chloride with the corresponding alkali metal selenides as described in the literature.[6] Rubidium and cesium fluorides, 4-methylphenyl isocyanate, phenyl isothiocyanate, and piperidine were purchased from Kanto Kagaku Co. Ltd. and used without further purification. Silica gel used on column chromatography was run on silica gel 60 of Kanto Chemical Co., Ltd. Diethyl ether was distilled from sodium/benzophenone ketyl prior to use. Hexane and petroleum ether (bp: 40–60 °C) were distilled from sodium metal. Acetonitrile, dichloromethane, and chloroform were distilled from phosphorus pentoxide. Methanol was distilled from magnesium powder. The distillation of these solvents was carried in a nitrogen atmosphere. All air sensitive compounds were prepared and handled in an argon atmosphere. $[D_4]$Methanol, $[D_6]$acetone, and $[D_8]$THF were purchased from Aldrich.

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 crystal of compound **4** was 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[14]) were also applied. The structures were solved by direct method using SHELXS-86[15] and expanded using DIRDIF94.[16] Scattering factors for neutral atoms were from Cromer and Waber[17] and anomalous dispersion[18] 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 final least-square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom.

Preparation of Single Crystals of Diferrocenoyl Selenide (3) and Diferrocenoyl Diselenide (4): Diferrocenoyl selenide (**3**) (250 mg) was dissolved in chloroform (8 mL), and ether (3 mL) was added dropwise. The solution was allowed to stand at 20 °C for 2 h to give red needles of compound **3**. One of the single needles was cut to the size of 0.17 × 0.26 × 0.34 mm.

Diferrocenoyl diselenide (**4**) (184 mg) was dissolved in chloroform (14 mL), and ether (2 mL) was added dropwise. The solution was allowed to stand at 20 °C for 2 d to give red needles of compound **4**. One of the single needles was cut to the size of 0.17 × 0.09 × 0.20 mm.

Ferrocenecarboselenoic Acid (2): The preparation procedures using potassium ferrocenecarboselenoate (**1b**) are described in detail.[19]

From Sodium Ferrocenecarboselenoate: The reaction of hydrogen chloride (1.30 mmol) in a dry diethyl ether solution (1.0 mL) and freshly prepared sodium ferrocenecarboselenoate (**1a**) (460 mg, 1.46 mmol) in diethyl ether (20 mL) at 0 °C for 10 min gave ferrocenecarboselenoic acid (**2**) (269 mg) [92 %, purity >95 % by ^{1}H-NMR of (ferrocenoyl)(4-methylphenylcarbamoyl) selenide and (ferrocenoyl) (phenylcarbamothioyl) selenide]

From Potassium Ferrocenecarboselenoate. An dry ether solution of hydrogen chloride (1.0 M, 1.3 mL, 1.3 mmol) was added to a suspension of freshly prepared potassium ferrocenecarboselenoate (**1b**) (461 mg, 1.39 mmol) in dry ether (15 mL) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The color of the suspension rapidly changed from orange to dark red. The mixture was stirred at the same temperature for 10 min. The insoluble part (KCl and an excess of **1b**) were filtered off. Removal of the solvent under reduced pressure (20 °C/0.2 Torr) gave 361 mg (95 %) of ferrocenecarboselenoic acid (**2**) as dark purple oil. The IR, ^{1}H, and ^{13}C NMR spectra of **2** were consistent with those of the authentic compound prepared by similar acidolysis of sodium ferrocenecarboselenoates (**1b**) with hydrogen chloride and was identified by conversion into ferrocenoyl 4-methylbenzenecarbamoyl selenide (**5**) (described later). **IR** (KBr, neat): ṽ = 2357 (Se–H), 1715, 1694 (C=O), 1682, 1434, 1240, 1107, 1044, 1027, 1002, 933, 821, 774, 722, 676, 534, 486 cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 2.68 (br. s, 1 H, SeH), 4.21 (s, 5 H, Cp), 4.46 (t, J = 1.8 Hz, 2 H, Cp meta), 4.68 (t, J = 1.8 Hz, 2 H, Cp_{ortho}) ppm. **^{13}C NMR** ($CDCl_3$): δ = 70.7 (Cp_{ortho}), 70.9 (Cp), 71.2 (Cp_{meta}), 81.5 (Cp_{ipso}), 190.7 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 415.9 ppm.

Air Oxidation of Ferrocenecarboselenoic Acid (2): Ferrocenecarboselenoic acid (**2**) (306 mg), freshly prepared by HCl acidolysis of potassium ferrocencarboselenoate (**1b**) was stirred in THF (5 mL) at 21–25 °C for 24 h. Removal of the solvent and fractional crystallization of the resulting residue from dichloromethane and hexane gave diferrocenoyl selenide (**3**) (188 mg, 62 %) and a mixture (32 mg) of diferrocenoyl diselenide (**4**) and elemental selenium (brown red). The structures of **3** and **4** were confirmed by IR, ^{13}C, and ^{77}Se NMR spectra with those of the authentic examples.

Diferrocenoyl Selenide (3): Ferrocenoyl chloride (168 mg, 0.68 mmol) was added to a suspension of potassium ferrocenecarboselenoate (**1b**) (236 mg, 0.71 mmol) in diethyl ether (10 mL) at 20 °C. The color of the suspension rapidly changed from orange to red brown. The mixture was stirred at the same temperature for 1 h. Dichloromethane (5 mL) was added and the precipitates (KCl) were filtered off. Removal of the solvent under reduced pressure (20 °C, 0.2 Torr) gave 260 mg (76 %) of diferrocenoyl selenide (**3**) as red orange solid. Recrystallization of this solid (290 mg) from a mixed solvent (12 mL) of dichloromethane/hexane (2:10) at 0 °C for 30 min gave 68 mg (11 %) of chemically pure **3** as red needles. Mp. 181–183 °C. $C_{22}H_{18}Fe_2O_2Se$ (505.02): C 52.33 (calcd. 52.32), H 3.70 (3.59) %. **IR** (KBr): ṽ = 3102, 1708 (C=O), 1687, 1655, 1433, 1372, 1333, 1236, 1106, 1038, 1002, 932, 832, 804, 763, 684, 671, 592, 553. 534, 492 cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 4.34 (s, 10 H, Cp), 4.58 (t, J = 1.96 Hz, 4 H, Cp_{meta}), 4.86 (t, J = 1.96 Hz, 4 H, Cp_{ortho}) ppm. **^{13}C NMR** ($CDCl_3$): δ = 70.0 (Cp_{ortho}), 70.8 (Cp), 72.8 (Cp_{meta}), 81.8 (Cp_{ipso}), 187.8 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 764.5 ppm.

I_2-KI Oxidation of Potassium Ferrocenecarboselenoate (1b): A methanol solution (3 mL) containing I_2-KI (82 mg, 0.32 mmol) was added to a solution of potassium ferrocenecarboselenoate (**1b**) (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. 5 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 diferrocenoyl diselenide (**4**) as red micro crystals. Mp: 170–172 °C (dec.) (163–165 °C[10]). $C_{22}H_{18}Fe_2O_2Se_2$ (583.99): C 44.68 (calcd. 45.25), 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.

Ferrocenoyl 4-Methylbenzenecarbamoyl Selenide (5): A solution of 4-methylphenyl isocyanate (86 mg, 0.65 mmol) in diethyl ether (1 mL) was added to a solution of ferrocenecarboselenoic acid (**2**) (188 mg, 0.64 mmol) in the same solvent (10 mL) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The mixture was stirred at room temperature (25 °C) for 1 h. Removal of the solvent under reduced pressure (25 °C, 0.2 Torr) followed by recrystallization of the resulting residue from a mixed solvent (26 mL) of dichloromethane/hexane (1:25) at 0 °C gave 256 mg (94 %) of ferrocenoyl 4-methylbenzenecarbamoyl selenide (**5**) as orange micro crystals. Mp: 107–113 °C (dec.). $C_{19}H_{17}FeNO_2Se$: C 53.38 (calcd. 53.55), H 4.02 (4.18) %. **IR** (KBr, neat): $\tilde{\nu}$ = 3038, 1704 (C=O), 1645 (NC=O), 1602, 1542, 1514, 1432, 1372, 1330, 1310, 1293, 1246, 1153, 1108, 1047, 1030, 1010, 934, 866, 825, 808, 790, 740, 674, 616, 550, 508, 497 cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 4.31 (s, SH, Cp), 4.68 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$), 4.89 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$), 7.16 (δ, J = 8.4 Hz, 2 H, Ph), 7.48 (δ, J = 8.4 Hz, 2 H, Ph), 10.34 (br. s, 1 H, NH) ppm. **^{13}C NMR** ($CDC1_3$): δ = 21.0 (CH_3), 69.3 (Cp$_{ortho}$), 71.4 (Cp), 73.5 (Cp$_{meta}$), 79.8 (Cp$_{ipso}$), 119.9, 129.7, 1345, 134.9 (Ph), 157.1 (N*C*=O), 198.9 (Se*C*=O) ppm. **^{77}Se NMR** ($CDC1_3$): δ = 633.9 ppm.

Ferrocenoyl Phenylcarbamothioyl Selenide (6): A solution of phenyl isothiocyanate (157 mg, 1.16 mmol) in diethyl ether (5 mL) was added to a solution of ferrocenecarboselenoic acid (**2**) (342 mg, 1.17 mmol) in the same solvent (9 mL) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The mixture was stirred at room temperature (30 °C) for 2 h. Removal of the solvent under reduced pressure (30 °C, 0.2 Torr), followed by recrystallization of the resulting residue from a mixed solvent (13 mL) of dichloromethane/hexane (3:10) at 0 °C gave 479 mg (96 %) of ferrocenoyl phenylcarbamothioyl selenide (**6**) as orange micro crystals. The IR and ^{1}H and ^{13}C NMR spectra were exactly consistent with those of the authentic sample obtained by the reaction of ferrocencarboselenoic acid (prepared from acidolysis of sodium ferrocencarboselenoate with hydrogen chloride) with phenyl isothiocyanate. **IR** (KBr, neat): $\tilde{\nu}$ = 3630, 3483, 3097, 2966, 2346, 1684 (C=O), 1655, 1595, 1545, 1493, 1436, 1387, 1332, 1285, 1248, 1157, 1106, 1047, 1029, 1002, 933, 824, 798, 775, 690, 675, 547, 495 cm^{-1}. **^{1}H NMR** ($CDCl_3$) (a = **6a**, b = **6b**): δ = 4.19 (s, SH, Cp)^{a}, 4.21 (s, SH, Cp)^{b}, 4.48 (s, 2 H, Cp$_{meta}$)^{b}, 4.57 (t, J = 1.95 Hz, 2 H, Cp$_{meta}$^{a}, 4.74 (t, J = 1.95 Hz, 2 H, Cp$_{ortho}$)^{a}, 4.81 (s, 2 H, Cp$_{ortho}$)^{b}, 7.07–7.83 (m, 5 H, Ph), 12.22 (br., 1 H, NH)^{a}, 13.31 (br. s, 1 H, SH)^{b} ppm. **^{13}CNMR** ($CDCl_3$): δ = 68.6 (Cp$_{ortho}$)^{a}, 68.8 (Cp$_{ortho}$)^{b}, 71.1 (Cp)^{b}, 71.2 (Cp)^{a}, 73.7 (Cp$_{meta}$)^{a}, 73.8 (Cp$_{meta}$)^{b}, 78.2 (Cp$_{ipso}$)^{a}, 78.3 (Cp$_{ipso}$)^{b}, 122.3, 123.2, 125.5, 126.1, 128.7, 129.3, 138.4, 138.9 (Ph), 185.7 (C=O)^{a}, 187.5 (C=O)^{b}, 198.1 (C=N)^{b}, 202.6 (C = S)^{a} ppm. **^{77}Se NMR** ($CDCl_3$): δ = 698.5^{b}, 712.9^{a} ppm. **HRMS** (20 eV): calcd. for $C_{18}H_{14}FeNOSSe$: m/z 427.93153 (calcd. 427.93107).

Piperidinium Ferrocenecarboselenoate (7)[20]: A solution of piperidine (41 mg, 0.48 mmol) in diethyl ether (1 mL) was added to a solution of ferrocenecarboselenoic acid (**2**) (140 mg, 0.48 mmol) in the same solvent (19 mL) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The mixture was stirred at room temperature (25 °C) for l h. Filtration of the resulting precipitates gave 128 mg (82 %) of piperidinium ferrocenecarboselenoate (**7**) as orange micro crystals. The IR, and ^{1}H, ^{13}C and ^{77}Se NMR spectra were exactly consistent with those of the authentic sample obtained from the reaction of ferrocencarboselenoic acid (prepared by acidolysis of sodium ferrocencarboselenoate with hydrogen chloride) with phenyl isothiocyanate. In addition, the structure was identified by conversion into *Se*-methyl ferrocenecarboselenoate (see a part of the reaction with iodomethane in the Experimental Section below). **IR** (nujol, neat): $\tilde{\nu}$ = 3079, 3058, 2925, 2860, 2763 (N-H), 2364, 2344, 1654, 1598, 1507 (C=O), 1455, 1430, 1407, 1380, 1330, 1290, 1274, 1230, 1205, 1156, 1103, 1039, 1026, 998, 943, 869, 839, 828, 815, 694, 670, 568, 558, 549, 449, 482 cm^{-1}. **^{1}H NMR** ($CDC1_3$): δ = 1.56 (quint, J = 5.7 Hz, 2 H, $NCH_2CH_2CH_2$), 1.81 (quint, J = 5.7 Hz, 4 H, NCH_2CH_2), 3.18 (t, J = 5.6 Hz, 4 H, $NCCH_2CH_2$), 4.12 (s, 5 H, Cp), 4.31 (t, J = 1.6 Hz, 2 H, Cp$_{meta}$), 4.85 (t, J = 1.6 Hz, 2 H, Cp$_{ortho}$), 9.09 (br. s, 2 H, NH_2) ppm. **^{13}C NMR** ($CDCl_3$): δ = 22.4 ($NCCH_2CH_2CH_2$), 22.6 ($NCCH_2CH_2$), 44.5 ($NCCH_2$), 70.8 (Cp$_{ortho}$), 70.9 (Cp$_{meta}$), 89.5 (Cp$_{ipso}$), 215.4 (C=O) ppm. **^{77}Se NMR** ($CDCl_3$): δ = 399.5 ppm.

Reaction of Piperidinium Ferrocenecarboselenoate (7) with Iodomethane: Iodomethane (2 mL, 32 mmol) and piperidinium ferrocenecarboselenoate **7** (66 mg, 0.18 mmol) were stirred at 20 °C for 1 h in an argon atmosphere and diethyl ether (10 mL) was added. Filtration of insoluble part (piperidinium iodide) and removal of the solvent and excess of methyl iodide under reduced pressure (25 °C, 0.2 Torr) gave 53 mg (99 %) of *Se*-methyl ferrocenecarboselenoate as orange micro crystals. The IR and ^{1}H NMR spectra of the *Se*-methyl ester were exactly consistent with that of the authentic sample obtained from the reaction of potassium ferrocenecarboselenoate (**1b**) with iodomethane.

Rubidium Ferrocenecarboselenoate (8): Rubidium fluoride (77 mg, 0.74 mmol) was added to a solution of ferrocenecarboselenoic acid (**2**) (219 mg, 0.75 mmol) in diethyl ether (15 mL) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The mixture was stirred at room temperature (23 °C) for 11 h. Orange solid was gradually deposited. Filtration of the solid gave 146 mg (52 %) of rubidium ferrocenecarboselenoate (**8**) as orange micro crystals. The IR, and ^{1}H, ^{13}C and ^{77}Se NMR spectra of compound **8** were exactly consistent with those of the authentic sample prepared from the reaction of *O*-trimethylsilyl ferocenecarboselenoate with RbF.[6] **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 (9): Cesium fluoride (65 mg, 0.43 mmol) was added to a solution of ferrocenecarboselenoic acid (**2**) (123 mg, 0.42 mmol) in diethyl ether (8 mL) in a 20 mL two necked round-bottomed flask at 0 °C in an argon atmosphere. The mixture was stirred at room temperature (20 °C) for 5 h. Orange solid was gradually deposited. Filtration of the solid gave 125.2 mg (70 %) of cesium ferrocenecarboselenoate (**9**) as orange micro crystals. The structure was determined by comparison of the IR, and ^{1}H, ^{13}C and ^{77}Se NMR spectra with those of the authentic sample prepared from the reaction of *O*-trimethylsilyl ferocenecarboselenoate with CsF.[6] **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.

Lithium Ferrocenecarboselenoate (10): A solution of ferrocenecarboselenoic acid (**2**) (219 mg, 0.75 mmol) in diethyl ether (10 mL) was added to a suspension of lithium hydride (6.3 mg, 0.79 mmol) in diethyl ether (10 mL) at 0 °C in an argon atmosphere. The mixture was stirred at 23 °C for 1 h. Filtration of the resulting precipitates gave 133 mg (56 %) of lithium ferrocenecarboselenoate (**10**) as orange micro crystals. The structure was determined by comparison of the IR, and ^{1}H, ^{13}C and ^{77}Se NMR spectra of the authentic sample prepared from the reaction of lithium selenide with ferrocenoyl chloride[6] and by conversion into *Se*-methyl ferrocenecarboselenoate. **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_3OD): 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_3OD): δ = 71.1 (Cp), 71.5 (Cp_{ortho}), 71.8 (Cp_{meta}), 90.9 (Cp_{ipso}), 215.9 (COSe) ppm. **^{77}Se NMR** (CD_3OD): δ = 351.1 ppm.

Crystallographic data (excluding structure factors) for the structure 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 number CCDC-895791 (**3**) (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): Additional tables and figures of the compounds.

Acknowledgements

This work was supported by the Grant-in-Aids for Scientific Research (B) and on Priority Areas provided by the Ministry of Education, Science, Sport and Culture, Japan. *S. K.* thanks *Professor Takashi Kawamura* of Gifu University for X-ray structure analyses.

References

[1] S. Kato, O. Niyomura, *Top. Curr. Chem.* **2005**, *251*, 13–85.

[2] N. Kano, T. Kawashima, *Top. Curr. Chem.* **2005**, *251*, 141–180.

[3] T. Katada, M. Nishida, S. Kato, M. Mizuta, *J. Organomet. Chem.* **1977**, *129*, 189–196.

[4] S. Kato, M. Wakamatsu, M. Mizuta, *J. Organomet. Chem.* **1974**, *78*, 405–414.

[5] a) H. Kageyama, T. Murai, T. Kanda, S. Kato, *J. Am. Chem. Soc.* **1994**, *116*, 2195–2196; b) S. Kato, Y. Kawahara, H. Kageyama, R. Yamada, O. Niyomura, T. Murai, T. Kanda, *J. Am. Chem. Soc.* **1996**, *118*, 1262–1267.

[6] T. Takahashi, O. Niyomura, S. Kato, M. Ebihara, *Z. Anorg. Allg. Chem.* **2013**, published online, DOI:10.1002/zaac.201200368.

[7] a) H. Kageyama, K. Tani, S. Kato, T. Kanda, *Heteroat. Chem.* **2001**, *12*, 250–258; b) O. Niyomura, K. Tani, S. Kato, *Heteroat. Chem.* **1999**, *10*, 373–379.

[8] S. Kato, W. Akada, M. Mizuta, *Int. J. Sulfur Chem. Sect. A* **1972**, *2*, 279–282.

[9] S. Kato, W. Akada, M. Mizuta, *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3492; S. Kato, M. Akada, M. Mizuta, *Int. J. Sulfur Chem. Sect. A* **1973**, *8*, 359.

[10] S. Kumar, S. K. Tripathi, H. B. Singh, G. J. Wolmershauser, *J. Organomet. Chem.* **2004**, *689*, 3046–3055.

[11] O. Niyomura, Y. Kito, M. Ishida, M. Ebihara, S. Hayashi, W. Nakanishi, *Z. Anorg. Allg. Chem.* **2012**, *638*, 2508–2520.

[12] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[13] M. Nishio, *The CH/π Interaction. Evidence, Nature and Consequences*, Wiley-VCH, New York, **1998**; M. Nishio, *CrystEngComm* **2004**, *6*, 138–158; O. Takahashi, Y. Kohno, M. Nishio, *Chem. Rev.* **2010**, *110*, 6049–6076.

[14] A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351–359.

[15] G. M. Sheldrick, in: *Crystallographic Computing 3*, (Eds.: G. M. Sheldrick, C. Kruger, R. Goddard), Oxford University Press, **1985**, pp.175–189.

[16] The DIRDIF-94 program system was used: P. T. Beukskens, G. Admiraal, G. Beurskiens, W. P. Bosman, R. de Gelder, R. Israel, J. M. M. Smits, in: *Technical Report of the Crystallography Laboratory*; University of Nijmegen; The Netherlands, **1994**.

[17] D. T. Cromer, J. T. Waber, in: *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, **1974**; vol. IV, Table 2.2A.

[18] D. C. Creagh, W. J. McAuley, in: *International Tables for X-ray Crystallography*; (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Boston, **1992**, vol. C, Table 4.2.6.8, pp. 219–222.

[19] In general, chalcogenocarboxylic acids are very labile thermally and sensitive towards oxygen. In fact, ferrocencarboselenoic acid (**2**) was too labile to isolate. Its high resolution mass spectroscopy did not show any mother peak. Therefore, the acid **2** was characterized by ^{1}H, ^{13}C, and ^{77}Se NMR and IR spectra and by conversion into more stable (ferrocenoyl)(4-methylphenylcarbamoyl) selenide (**5**) and (ferrocenoyl)phenylcarbamothioyl selenide (**6**), which were quantitatively obtained by addition reaction to 4-methylphenyl isocyante and phenyl iosthiocyanate, respectively.

[20] Piperidinium ferrocenecarboselenoate (**7**) similar to alkali metal ferrocencarboselenoates was hygroscopic and too sensitive towards oxygen to isolate and in addition, its high resolution mass spectroscopy (HRMS) also did not show any mother peaks. The structure of compound **7**, therefore, was charcterized by its IR, and ^{1}H, ^{13}C and ^{77}Se NMR spectra and by conversion into *Se*-methyl ferrocenecarboselenoate.

Received: August 15, 2012
Published Online: December 20, 2012