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Synthesis and Reactivity of Mono-, Di-, and, Triiron Selenocarboxylate Complexes

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Abstract. Treatment of the iron selenide (μ-Se)[CpFe(CO)$_2$]$_2$ with one equivalent of 1,3,5-C$_6$H$_3$(COCl)$_3$ gave the organoiron selenocarboxylate complex CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$(COCl)$_2$ (**1**), which contains two free acid chloride groups. Complex **1** reacted with amines, thiols, and phenols to produce the corresponding amides CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$(CONR$_2$)$_2$ (**2**), thioesters CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$(COSR)$_2$ (**3**), and aromatic esters CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$(CO$_2$Ar)$_2$ (**4**), respectively. Complex **1** was converted into the diacid CpFe(CO)$_2$-SeCO-3,5-C$_6$H$_3$(COOH)$_2$ (**5**) or the diamide CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$(CONH$_2$)$_2$ (**6**) complexes by reactions with NaOH or NaNH$_2$, respectively. The bis(seleno)-1,3-(CpFe(CO)$_2$SeCO)$_2$-5-C$_6$H$_3$(COCl) (**7**) and tris(seleno)-carboxylate 1,3,5-(CpFe(CO)$_2$SeCO)$_3$C$_6$H$_3$ (**8**) complexes were also prepared by controlled reaction of 1,3,5-C$_6$H$_3$(COCl)$_3$ with the iron selenide (μ-Se)[CpFe(CO)$_2$]$_2$. Complexes **1**–**8** were characterized by spectroscopic techniques (IR, ^{1}H-NMR) and by elemental analysis as well. The X-ray structures of CpFe(CO)$_2$-SeCO-3,5-C$_6$H$_3$(COCl)$_2$ (**1**) and CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$-(COSCH$_2$Ph)$_2$ (**3b**) were determined.

Introduction

Monochalcogenocarboxylato metal complexes find extensive applications in catalysis and industry.[1,2] They are used as precursors for thin metal-chalcogenide films.[3,4] The chemistry of these complexes and their applications have been reviewed in journals[5,6] and advanced books as well.[7–9]

Selenocarboxylates of main group metals as well as their transition metal analogues have been thoroughly investigated.[10–13] Group 11 and 12 selenocarboxylato complexes, with different structural types and coordination modes of the ligand, were synthesized for single source precursors of thin films and nanoparticles.[14–16] On the other hand, transition metal selenocarboxylates have found application in catalysis and electronic industry.[17,18] *Cis*- and *trans*-four coordinate nickel, platinum, and palladium selenocarboxylates were reported and structurally characterized.[19,20]

Half-sandwich iron selenocarboxylato complexes were reported by our group. Treatment of the selenides (μ-Se)-[Cp′Fe(CO)$_2$]$_2$ [Cp′ = C$_5$H$_5$, *t*BuC$_5$H$_4$, 1,3-(*t*Bu)$_2$C$_5$H$_3$] with acid chlorides gave the corresponding selenocarboxylato complexes Cp′Fe(CO)$_2$SeCOR.[21] Reaction of the iron selenide with oxalyl chloride gave the bimetallic complex [CpFe(CO)$_2$-SeCO]$_2$, in which both acid chloride groups reacted with the iron species.[22] On the other hand, the reaction with terephthaloyl chloride produced either the mono- [CpFe(CO)$_2$SeCO-4-C$_6$H$_4$COCl] or the bimetallic complex {[CpFe(CO)$_2$SeCO]$_2$-4-C$_6$H$_4$} depending on the metal-to-ligand molar ratio.[23] The former underwent organic transformation reactions with amines, phenols, or thiols to give the corresponding acid derivatives. It was also reacted with (μ-E_x)[Cp′Fe(CO)$_2$]$_2$ (E = S; x = 3–5. E = Se; x = 1) to form the mixed chalcogen, mixed Cp′ bimetallic iron complexes.[23–25]

In this work, we further investigate the interaction of the iron selenide with tri-substituted acid chloride. Mono-, di- and tri-selenocarboxylato iron complexes were obtained. A second part of this work involves the transformation of the free acid chloride groups present in the monoiron complex, CpFe(CO)$_2$-SeCO-3,5-C$_6$H$_3$(COCl)$_2$, to other acid derivatives as amides, esters, and thioesters.

Results and Discussion

CpFe(CO)$_2$SeCO-3,5-C$_6$H$_3$(COCl)$_2$ (1)

The reaction of the selenide complex (μ-Se)[CpFe(CO)$_2$]$_2$ with 1,3,5-benzenetricarboxylic acid chloride in a 1:1 metal-to-ligand molar ratio gave the organoiron complex CpFe(CO)$_2$-SeCO-3,5-C$_6$H$_3$(COCl)$_2$ (**1**), as shown in Scheme 1.

Carbonyl stretching absorptions of **1** appear as two strong bands at 2040 and 1994 cm^{-1} for the two terminal carbonyl ligands. The spectrum also shows the bands of the selenocarb-

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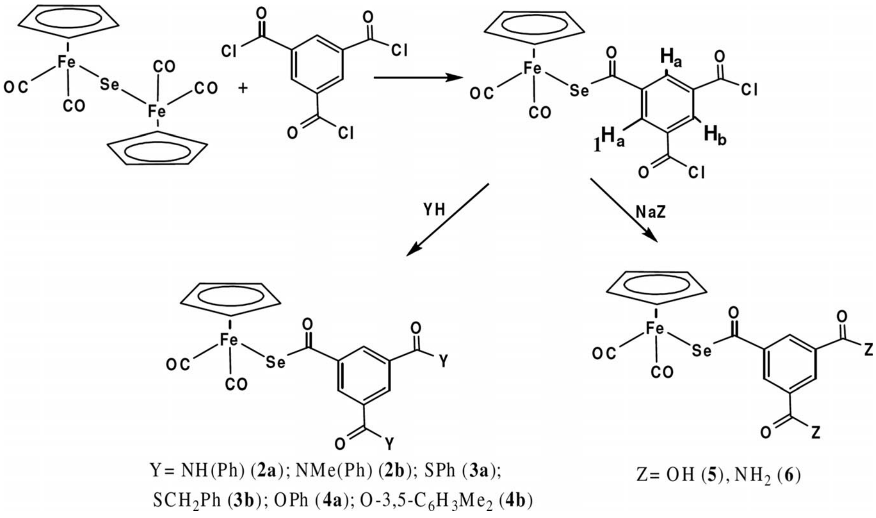


Scheme 1.

oxylate (SeC=O: 1631 cm^{-1}) and of the acid chloride (ClC=O: 1763 cm^{-1}). ^{1}H NMR spectrum of **1** displays a singlet signal at δ = 5.08 ppm due to the cyclopentadienyl ligand protons. These IR and ^{1}H NMR spectroscopic data are similar to those observed for $CpFe(CO)_2SeCOR$ and $CpFe(CO)_2Se$-4-C_6H_4COCl.[21,22] The molecular structure of **1** (Figure 1) shows the expected iron arrangement as a piano stool with the Cp ring as the base and the carbonyl groups and selenium containing ligand as the legs. The Fe–C(Cp) bond lengths, ranging between 2.071(6) to 2.091(7) Å, and Fe–C(O) bond lengths [1.772(7), 1.780(7) Å] are within the same range observed for similar systems.[21,26] The Fe–Se bond length in **1** of 2.3752(10) Å is slightly shorter than those of $CpFe(CO)_2$-Se*X* complexes {*X* = SO_2Ph [2.394(3) Å], CO_2Et [2.3829(8) Å], or C(S)O-4-C_6H_4Cl [2.3985(2) Å]}.[26–28] The C–O bond length of the ketone carbonyl group of the selenocarboxylate ligand [1.218(6) Å] is very comparable to those found in selenocarbonato complexes.[27,28] The corresponding bond length of the free acid chloride groups are different from each other [1.647(7), 1.187(7) Å], this difference is due to disorder of these carbonyl groups. The angles around the central iron atom (Se–Fe–C15, Se–Fe–C16, C15–Fe–C16) are around 90° showing disorder octahedral arrangement.

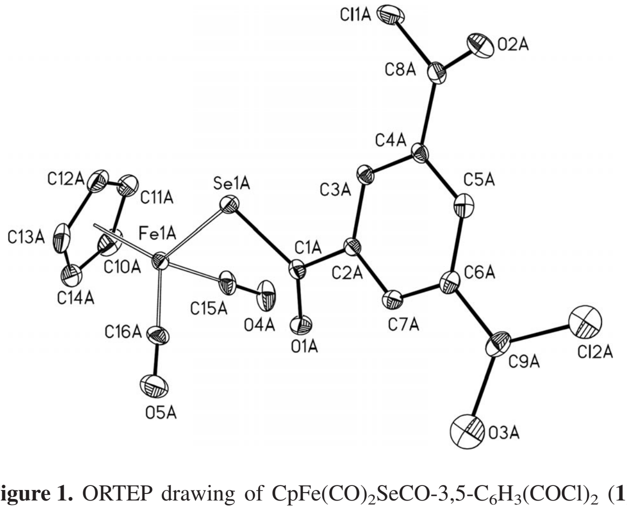


Figure 1. ORTEP drawing of $CpFe(CO)_2SeCO$-3,5-$C_6H_3(COCl)_2$ (**1**) at the 50 % probability level (hydrogen atoms are omitted for clarity).

Reactions of 1 with Nucleophiles

Complex **1** has two reactive acid chloride groups, which can be replaced by several nucleophiles facilitating the synthesis of several tri-functional iron complexes. The reaction of **1** with amines, thiols, or phenols gives the corresponding iron functionalized complexes as shown in Scheme 1. Complexes **2**–**4** were characterized by elemental analysis, IR, and ^{1}H NMR spectroscopy, and the results are in agreement with the suggested structures. The IR spectra of these complexes exhibit two stretching frequencies in the ranges of 2026–2035 and 1980–1987 cm^{-1} consistent with the two terminal carbonyl groups. These values are similar to those reported for $CpFe(CO)_2SeCO$-4-C_6H_4COY (*Y* = NR_2, OAr, S*R*, OCO*R*) systems.[22,23] The C=O of selenocarboxylate group appears as a medium band in the range 1590–1629 cm^{-1}. The spectra also contain another ketone carbonyl frequency in the ranges of 1646–1653, 1662–1675, and 1707–1710 cm^{-1} for **2**, **3**, and **4**, respectively. These values are consistent with the inductive effect of the nitrogen, sulfur, and oxygen atoms next to the carbonyl group. The ^{1}H NMR spectra of **2**–**4** exhibit singlet peak for the Cp protons in the ranges of 5.00–5.05, 5.07–5.09, and 5.30–5.31 ppm, respectively. These regions reflect the electron-withdrawing ability of the amide-, thiolate-, and thioester groups. The aromatic protons of the selenocarboxylate group and those of the substituents (*Y*) are shown in the spectra with the expected multiplicity and chemical shift regions.

The X-ray structure analysis reveals the proposed structure of **3b** as shown in Scheme 1. Its ORTEP-drawing with atomic numbering scheme is shown in Figure 2. Selected bond lengths and angles are given in Table 1. The structure shows that the iron atom is in a distorted octahedral environment as indicated from the bond angles of the iron atom, which are around 90°. The Cp ring is bonded to the iron atom in a η^5-fashion with

Fe–C bond lengths ranging from 2.061 to 2.076 Å. The Fe–C(O) bond lengths are 1.750(7) and 1.762(7) Å. These Fe–C bond lengths are shorter than those reported for **1** indicating stronger π back donation from iron orbital to *anti*-bonding CO orbital for **3b** compared to **1**. This suggestion is also supported by a longer Fe–Se bond length of **3b** [2.3974(10) Å] compared to that of **1**. This implies that the acid chloride groups of **1** make the selenocarboxylate moiety a better π acceptor ligand compared to the thioester substituted one. The C=O bond lengths of the selenocarboxylate and amide functionalities are shorter than the corresponding ones of **1**.

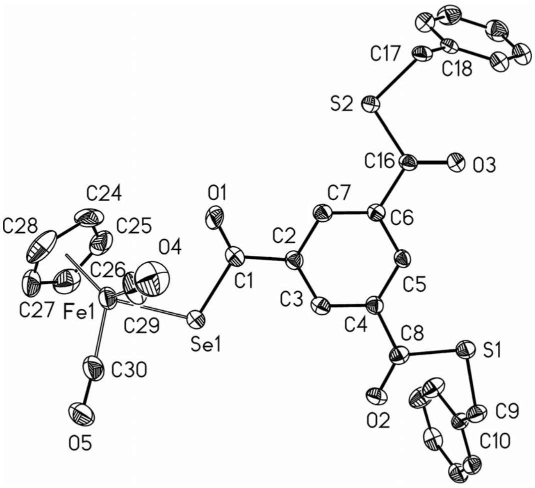


Figure 2. ORTEP drawing of $CpFe(CO)_2SeCO\text{-}3,5\text{-}C_6H_3(COSCH_2Ph)_2$ (**3b**) at the 50 % probability level (hydrogen atoms are omitted for clarity).

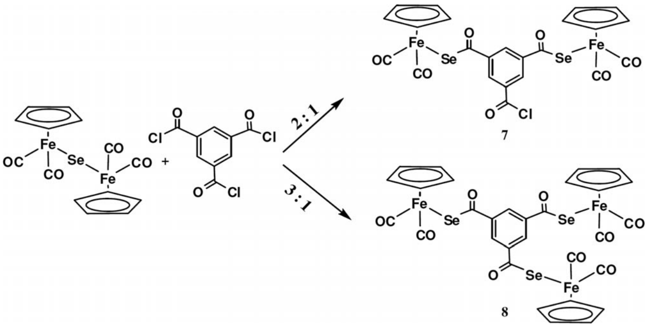
Table 1. Selected bond lengths /Å and bond angles /° of $CpFe(CO)_2\text{-}3,5\text{-}C_6H_3(COCl)_2$ (**1**), and $CpFe(CO)_2\text{-}3,5\text{-}C_6H_3(COSCH_2Ph)_2$ (**3b**).

1		**3b**	
Fe–C16	1.772(7)	Fe–C29	1.750(7)
Fe–C15	1.780(7)	Fe–C30	1.762(7)
Fe–C14	2.071(6)	Fe–C26	2.061(6)
Fe–C11	2.083(7)	Fe–C28	2.062(7)
Fe–C12	2.089(6)	Fe–C27	2.065(6)
Fe–C10	1.078(7)	Fe–C24	2.074(7)
Fe–C13	1.091(7)	Fe–C25	2.076(6)
Fe–Se	2.3752(16)	Fe–Se	2.3974(10)
Se–C1	1.891(6)	Se–C1	1.909(5)
C1–O1	1.218(6)	O1–C1	1.164(6)
C16–Fe–C15	94.8(3)	C29–Fe–C30	96.9(3)
C16–Fe–Se	93.0(2)	C29–Fe–Se	88.4(2)
C15–Fe–Se	91.26(19)	C30–Fe–Se	105.4(3)
O1–C1–Se	125.5 (4)	O1–C1–Se	121.9(4)
C1–Se–Fe	104.27(17)	C1–Se–Fe	101.88(18)

Complex **1** was also reacted with NaOH or $NaNH_2$ to form the diacid $CpFe(CO)_2SeCO\text{-}3,5\text{-}C_6H_3(COOH)_2$ (**5**) or the diamide $CpFe(CO)_2SeCO\text{-}3,5\text{-}C_6H_3(CONH_2)_2$ (**6**) (Scheme 1). The IR spectra of **5** and **6** exhibit two strong bands (**5**: 2030, 1982 cm^{-1}, **6**: 2034, 1990 cm^{-1}) due to the stretching of the carbonyl ligands. The stretching band of the selenocarboxylate (SeC=O) moiety for **5** appears at 1604 cm^{-1}, which is lower than that of **6** (1623 cm^{-1}). The bands at 1693 cm^{-1} for **5** and at 1714 cm^{-1} for **6** are assigned for the stretching of the (C=O) of the acid and amide moieties. The O–H and N–H frequencies are present in the spectra at 3615 and 3122 cm^{-1}, respectively. These IR data proved the increase electron richness around the central iron atom in **5** or **6** compared to that of **1**. The ^1H NMR spectra for complexes **5** and **6** show a singlet signal due to the five cyclopentadienyl ligand protons in the range 5.29–5.31 ppm. The signal of the N–H protons of **5** is observed at $\delta = 8.85$ ppm.

Synthesis of $1,3\text{-}(CpFe(CO)_2SeCO)_2\text{-}5\text{-}C_6H_3COCl$ (7) and $1,3,5\text{-}C_6H_3(CpFe(CO)_2SeCO)_3$ (8)

The reaction of the selenide complex $(\mu\text{–}Se)[CpFe(CO)_2]_2$ with $1,3,5\text{-}C_6H_3(COCl)_3$ in a 2:1 or 3:1 metal-to-ligand molar ratio gives the di- or tri-substituted iron selenocarboxylate complexes $1,3\text{-}(CpFe(CO)_2SeCO)_2\text{-}5\text{-}C_6H_3COCl$ (**7**), $1,3,5\text{-}(CpFe(CO)_2SeCO)_3C_6H_3$ (**8**), and slight amount of complex **1** (Scheme 2).



Scheme 2.

The IR spectrum of **7** and **8** exhibit the two strong bands for the terminal carbonyl ligands. The stretching band of the selenocarboxylate (SeC=O) moiety appears at 1619 cm^{-1} and at 1617 cm^{-1} for complex **7** and **8**, respectively. The stretching band (ClC=O) of the acid chloride appears at 1756 cm^{-1} for complex **7**. The ^1H-NMR spectra for complexes **7** and **8** exhibit a singlet due to the five cyclopentadienyl ligand protons at δ = 5.32 ppm and 5.30 ppm, respectively. These values are higher than that reported for **1**.

Experimental Section

General Comments: All experiments were done using standard Schlenk or vacuum line techniques in a nitrogen atmosphere. Hexane, diethyl ether, and tetrahydrofuran were dried and distilled over sodium and benzophenone. Dichloromethane was dried and distilled over P_2O_5. The selenide $(\mu\text{-}Se)[CpFe(CO)_2]_2$ was synthesized according to the literature.[21] All chemicals: $[CpFe(CO)_2]_2$, 1,3,5-benzentricarboxylic acid chloride, aniline, *N*-methylaniline, thiophenol, α-thiophenol, phenol, 3,5-dimethylphenol, sodium hydroxide, sodium amide, and elemental selenium were used as received from Acros or Aldrich. Silica gel of particle size 0.063–0.200 mm (70–230 mesh) was employed for column chromatography.

Reaction steps were monitored by thin layer chromatography (TLC): Merck F60 silica plates with fluorescence indicator. Infrared spectra were recorded with a JASCO FT-IR spectrometer. ^{1}H NMR spectra were recorded with a Bruker-Avance 400 MHz spectrometry, in deuterated solvents and referenced to TMS. Elemental analyses were performed with a Perkin–Elmer 240C elemental analyzer.

Preparation of $CpFe(CO)_2SeCO$-3,5-$C_6H_3(COCl)_2$ (1)

A reddish-brown solution (0.70 g, 1.60 mmol) of (μ-Se)$[CpFe(CO)_2]_2$ in diethyl ether (50 mL) was added dropwise at room temperature to a solution of 1,3,5-benzenetricarboxylic acid chloride (0.43 g, 1.60 mmol) in diethyl ether (25 mL). The resulting mixture was stirred for 3 h at room temperature. The volatiles were removed in vacuum and the residue was re-dissolved in a minimum amount of CH_2Cl_2 and transferred into a silica gel column made up in hexane. Elution with a mixture of dichloromethane and hexane (6:4 volume ratio) gave brown-orange band, which was collected and identified as $CpFe(CO)_2$-SeCO-3,5-$C_6H_3(COCl)_2$, followed by a red band which was collected and identified as $CpFe(CO)_2Cl$. Color: Orange. Yield 0.43 g (48 %), M.p = 145–147 °C. Elemental analysis $C_{16}H_8FeO_5SeCl_2$ (485.94): calcd. C 39.55, H 1.66 %; found: C 39.57, H 1.75 %. **IR** (CH_2Cl_2): $\nu_{C\equiv O}$ 2040 (vs), 1994 (vs); $\nu_{ClC=O}$ 1763 (vs); $\nu_{SeC=O}$ 1631 (m); ν_{C-Se} 844 (m) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 9.07 (d, 2 H, H_a); 8.88 (t, 1 H, H_b); 5.08 (s, 5 H, Cp) ppm.

Preparation of $CpFe(CO)_2SeCO$-3,5-$C_6H_3(COY)_2$ [Y = NH(Ph) (2a), N(Me)(Ph) (2b); SPh (3a); SCH_2Ph (3b); OPh (4a); $OC_6H_3Me_2$ (4b); OH (5), NH_2 (6)]

A THF solution (50 mL) containing the nucleophile (1.00 mmol) and **1** (0.25 g, 0.50 mmol) in the presence of few drops of pyridine, was heated to reflux for several hours. The volatiles were removed under vacuum and the residue was re-dissolved in CH_2Cl_2 and introduced to a silica gel column made up in hexane. Brown-orange band was eluted with THF/hexane (2:3 volume ratio), collected, dried, and recrystallized from CH_2Cl_2/hexane.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3[CONH(Ph)]_2$ (2a): Reflux time: 1.5 h. Yield 0.13 g (43 %). M.p = 168–170 °C. Color: Orange. Elemental analysis $C_{28}H_{20}FeO_5SeN_2{\cdot}CH_2Cl_2$ (599.27): calcd. C 50.91, H 3.24, N 4.09 %; found: C 50.03, H 3.58, N 3.80. **IR** (KBr): $\nu_{C\equiv O}$ 2032 (vs), 1981 (vs); $\nu_{NC=O}$ 1653 (m); $\nu_{SeC=O}$ 1599 (m); ν_{C-Se} 845 (w) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.73 (br. s, 2 H, H_a); 8.64 (br. s, 1 H, H_b); 8.59 (br. s, 2 H, NH); 7.69 (t, 2 H, C_6H_5); 7.42 (d, 4 H, C_6H_5); 7.21 (d, 4 H, C_6H_5); 5.05 (s, 5 H, Cp) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3[CON(Me)(Ph)]_2$ (2b): Reflux time: 1.5 h. Yield 0.21 g (67 %). M.p = 180–182 °C. Color: Orange. Elemental analysis $C_{30}H_{24}FeO_5SeN_2$ (627.33 + $0.5CH_2Cl_2$): calcd. C 54.69, H 3.76, N 4.18 %; found: C 55.81, H 4.05, N 4.59 %. **IR** (KBr): $\nu_{C\equiv O}$ 2031(vs), 1980 (vs); $\nu_{NC=O}$ 1646 (s); $\nu_{SeC=O}$ 1590 (m); ν_{C-Se} 845 (w) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.88 (br. s, 2 H, H_a); 7.39 (br. s, 1 H, H_b); 7.23 (d, 4 H, C_6H_5); 7.17 (t, 2 H, C_6H_5); 6.92 (d, 4 H, C_6H_5); 5.00 (s, 5 H, Cp); 3.42 (s, 6 H, CH_3) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3(COSPh)_2$ (3a): Reflux time: 4.0 h. Yield 0.24 g (73 %). M.p = 120–122 °C. Color: Brown. Elemental analysis $C_{28}H_{18}FeO_5SeS_2$ (633.37): calcd. C 53.10, H 2.86, S 10.13 %; found: C 53.00, H 3.01, S 9.83 %. **IR** (KBr): $\nu_{C\equiv O}$ 2032 (vs), 1987 (vs); $\nu_{SC=O}$ 1675 (s); $\nu_{SeC=O}$ 1617 (m); ν_{C-Se} 835 (w) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.95 (d, 2 H, H_a); 8.69 (t, 1 H, H_b); 7.53 (m, 4 H, C_6H_5); 7.48 (m, 6 H, C_6H_5); 5.09 (s, 5 H, Cp) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3(COSCH_2Ph)_2$ (3b): Reflux time: 4.0 h. Yield 0.22 g (65 %). M.p = 132–134 °C. Color: brown. Elemental analysis $C_{30}H_{22}FeO_5SeS_2$ (661.43): calcd. C 54.48, H 3.35, S 9.70 %; found: C 53.96, H 3.39, S 9.32 %. **IR** (KBr): $\nu_{C\equiv O}$ 2026 (vs), 1980 (vs); $\nu_{SC=O}$ 1662 (s); $\nu_{SeC=O}$ 1619 (m); ν_{C-Se} 839 (w) cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.84 (d, 2 H, H_a); 8.62 (t, 1 H, H_b); 7.37 (d, 4 H, C_6H_5); 7.32 (t, 6 H, C_6H_5); 5.07 (s, 5 H, Cp); 4.35 (s, 4 H, CH_2) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3(CO_2Ph)_2$ (4a): Reflux time: 3.0 h. Yield 0.20 g (64 %). M.p = 205–207 °C. Color: Orange. Elemental analysis $C_{28}H_{18}FeO_7Se$ (601.24): calcd. C 50.76, H 2.94 %; found: C 50.06, H 3.06 %. **IR** (KBr): $\nu_{C\equiv O}$ 2035 (vs), 1986 (vs); $\nu_{OC=O}$ 1707 (s); $\nu_{SeC=O}$1629 (m); ν_{C-Se} 841 (w) cm^{-1}. **^{1}H NMR** ([D_6]acetone): δ = 8.96 (d, 2 H, H_a); 8.91 (t, 1 H, H_b); 7.51 (d, 4 H, C_6H_5); 7.39 (t, 6 H, C_6H_5); 5.30 (s, 5 H, Cp) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3(CO_2$-3,5-$C_6H_3Me_2)_2$ (4b): Reflux time: 3.0 h. Yield 0.21 g (61 %), M.p = 214–216 °C. Color: Orange. Elemental analysis $C_{32}H_{26}FeO_7Se$ (657.35): calcd.: C 55.78, H 3.89 %; found: C 56.18, H 3.89 %. **IR** (KBr): $\nu_{C\equiv O}$ 2033 (vs), 1987 (vs); $\nu_{OC=O}$ 1710 (s); $\nu_{SeC=O}$ 1617 (m); ν_{C-Se} 844 (w) cm^{-1}. **^{1}H NMR** ([D_6]acetone): δ = 8.96 (d, 2 H, H_a); 8.93 (t, 1 H, H_b); 6.97 (br. s, 6 H, C_6H_3); 5.31 (s, 5 H, Cp); 2.35 (s, 12 H, CH_3) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3(COOH)_2$ (5): Color: Brown. Reflux time: 6.0 h. Yield 0.14 g (42 %). M.p = 172–174 °C. Elemental analysis $C_{18}H_{10}FeO_7Se$.THF (449.05 + THF): calcd.: C 46.09, H 3.48 %; found: C 46.94, H 3.78 %. **IR** (KBr): $\nu_{C\equiv O}$ 2030 (vs), 1982 (vs); $\nu_{C=O}$ 1693(s), $\nu_{SeC=O}$ 1604 (m), ν_{C-Se} 853 (w) cm^{-1}. **^{1}H NMR** ([D_6]acetone): δ = 8.91 (d, 2 H, H_a); 8.81 (t, 1 H, H_b); 5.31 (s, 5 H, Cp) ppm.

$CpFe(CO)_2SeCO$-3,5-$C_6H_3(CONH_2)_2$ (6): Color: Orange. Reflux time: 2.0 h. Yield: 0.12 g (54 %). M.p. 182–184 °C, Elemental analysis $C_{16}H_{12}FeO_5SeN_2.0.5CH_2Cl_2$ (447.08 + $0.5CH_2Cl_2$): calcd. C 40.48, H 2.68, N 5.72 %; found: C 39.73, H 3.50, N 5.01 %. **IR** (KBr): $\nu_{C\equiv O}$ 2034 (vs), 1990 (vs), $\nu_{NC=O}$ 1714 (vs), $\nu_{SeC=O}$ 1623 (m), ν_{C-Se} 849 (w) cm^{-1}. **^{1}H NMR** ([D_6]acetone): δ = 8.98 (m, 3 H, C_6H_3); 8.85 (s, 4 H, NH_2); 5.29 (s, 5 H, Cp) ppm.

Preparation of 1,3-$(CpFe(CO)_2SeCO)_2$-5-C_6H_3COCl (7)

A solution of 1,3,5-benzenetricarboxylic acid chloride (0.25 g, 0.90 mmol) in diethyl ether (100 mL) was added slowly over a period of 1 h to a reddish-brown solution of (μ–Se)$[CpFe(CO)_2]_2$ (1.8 mmol) in diethyl ether (50 mL). The resulting mixture was stirred for 4 h at room temperature. The volatiles were removed under vacuum and re-dissolved in a minimum amount of CH_2Cl_2 and transferred to a silica gel column made up in hexane. Elution with CH_2Cl_2/hexane (9:1 volume ratio) gave two brown-orange bands; both were collected dried and analyzed. The first is found to be **1** and the second is 1,3-$C_6H_3(CpFe(CO)_2$-$SeCO)_2$-5-COCl, (**7**), which was recrystallized from a CH_2Cl_2/hexane mixture. Yield 0.15 g (23 %). M.p = 163–165 °C. Color: Brown. Elemental analysis $C_{23}H_{13}Fe_2O_7Se_2Cl$ (708.42): calcd. C 38.88, H 2.41 %; found: C 39.05, H 2.22 %. **IR** (KBr): $\nu_{C\equiv O}$ 2033 (vs), 1985 (vs); $\nu_{ClC=O}$ 1756 (m); $\nu_{SeC=O}$ 1619 (m); ν_{C-Se} 840 (m) cm^{-1}. **^{1}H NMR** ([D_6]acetone): δ = 9.15 (t, 1 H, H_a); 8.84 (d, 2 H, H_b); 5.32 (s, 10 H, Cp) ppm.

Preparation of 1,3,5-$C_6H_3(CpFe(CO)_2SeCO)_3$ (8)

A solution of 1,3,5-benzenetricarboxylic acid chloride (0.16 g, 0.60 mmol) in diethyl ether (25 mL) was added dropwise to a red-brown solution of (μ-Se)$[CpFe(CO)_2]_2$ (2.0 mmol) in diethyl ether (50 mL). The resulting mixture was stirred for 4 h at room temperature. The volatiles were removed under vacuum and re-dissolved in a minimum amount of CH_2Cl_2 and transferred to a silica gel column made up in hexane. Elution with THF/hexane (3:7 volume ratio) gave two brown-orange bands, both were collected dried and analyzed. The first was a mixture of **1** and **7**, the second was 1,3,5-$C_6H_3(CpFe(CO)_2$-$SeCO)_3$ (**8**), which was recrystallized from CH_2Cl_2/hexane. Yield 0.12 g (22 %), M.p = 185–187 °C. Color: Brown. Elemental analysis $C_{30}H_{18}Fe_3O_9Se_3$ (928.89): calcd.: C 39.28, H 2.87 %; found: C 39.05, H 2.45 %. **FTIR** (KBr): $\nu_{C\equiv O}$ 2036 (vs), 1990 (vs); $\nu_{SeC=O}$ 1617 (m); ν_{C-Se} 844 (w) cm^{-1}. **^1H NMR** ([D_6]acetone): δ = 8.86 (s, 3 H, C_6H_3); 5.30 (s, 15 H, Cp) ppm.

X-ray Structure Analysis of $CpFe(CO)_2SeCO$-3,5-$C_6H_3(COCl)_2$ (1) and $CpFe(CO)_2SeCO$-3,5-$C_6H_3(COSCH_2Ph)_2$ (3b)

The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[29,30]

The structures were solved by direct methods (SHELXS[29]) and refined by full-matrix least-squares techniques against Fo^2 (SHELXL-97[30]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically[31]. Crystallographic data as well as structure solution and refinement details are summarized in Table 2. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

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-800771 for **1** and CCDC-800772 for **3b** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Table 2. Crystal data and refinement details for the X-ray structure determinations of **1** and **3b**.

	1	**3b**
Formula	$C_{16}H_8Cl_2FeO_5Se$	$C_{30}H_{22}FeO_5S_2Se$
Fw /g·mol^{-1}	485.93	661.41
T /K	–90(2)	–90(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a /Å	7.0787(4)	6.5279(5)
b /Å	12.2734(6)	15.0929(9)
c /Å	20.9064(8)	15.9657(9)
α /°	84.141(3)	110.913(4)
β /°	80.716(3)	101.330(5)
γ /°	74.732(2)	100.789(5)
V /Å^3	1725.89(14)	1382.73(16)
Z	4	2
ρ /g·cm^{-3}	1.870	1.589
μ /mm^{-1}	33.16	20.52
Measured data	11387	9997
Data with $I > 2\sigma(I)$	5114	3300
Unique data (R_{int})	7653/0.0457	6295/0.0496
wR_2 (all data, on F^2)$^{a)}$	0.1291	0.1589
R_1 [$I > 2\sigma(I)$]$^{a)}$	0.0555	0.0606
S $^{b)}$	1.007	0.999
Res. dens./e·Å^{-3}	1.251/–1.143	0.726/–0.633
Absorpt method	NONE	NONE

a) Definition of the R indices: $R_1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$. b) $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

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Synthesis and Reactivity of Mono-, Di-, and, Triiron Selenocarboxylate Complexes