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Half-sandwich iron complexes bearing vinyl-selenocarboxylato ligands

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Abstract. Vinyl selenocarboxylato iron complexes of the formula $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{C}(\text{R}_1)(\text{R}_2)$ { $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{Me}$, $\text{R}_1 = \text{R}_2 = \text{Me}$, $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{CH}=\text{CHMe}$ } are synthesized by the reaction of $(\mu\text{-Se})[\text{CpFe}(\text{CO})_2]_2$ with the corresponding vinyl acid chlorides $\text{ClCOCH}=\text{C}(\text{R}_1)(\text{R}_2)$. Photolytic substitutions of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$ with EPh_3 gave the monosubstituted complexes $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeCOCH}=\text{CMe}_2$ ($\text{E} = \text{P}$, As , Sb) in good yields. The new complexes have been characterized by UV-Vis, IR, $^1\text{H-NMR}$, $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$, $^{77}\text{Se}\{^1\text{H}\}\text{-NMR}$, $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ spectroscopy and elemental analysis. The solid state structures of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$ and $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SeCOCH}=\text{CMe}_2$ were determined by X-ray crystallography. The cyclic voltammetric measurements of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$ were recorded.

Keywords. Iron; Vinyl selenocarboxylate; Substitution reactions; Structures.

1. Introduction

Selenoproteins are known since the 1970s and are involved in a range of mammals' biochemistry.¹⁻³ Selenoenzymes constitute important mammalian antioxidant enzymes which protect biomembranes and other cellular components from oxidative stress.⁴⁻⁶ Therefore, developments and design of new selenium chemistry have been attracting considerable attention due to their ability to mimic natural compounds with important biological properties.⁷⁻¹⁰ The butterfly $[\text{Fe}_2\text{Se}_2]$ complexes are widely investigated as models for the $[\text{FeFe}]$ -hydrogenase enzymes and found to catalyze hydrogen production from weak acids.¹¹⁻¹³ Cyclopentadienyl iron selenocarboxylates proved to have antifungal, antibacterial effects and are active substrates against cancer cells.^{14,15}

Half sandwich iron dicarbonyl complexes containing selenium ligands have been developed in our laboratory.¹⁶⁻²⁵ The selenide bridge-dimer

$(\mu\text{-Se})[\text{CpFe}(\text{CO})_2]_2$, generated from the insertion of elemental selenium into the Fe-Fe bond of the dimer $[\text{CpFe}(\text{CO})_2]_2$, is a great precursor for iron-selenium complexes. Its reactions with electrophiles such as acid chlorides, sulfonyl chlorides, *O*-alkyloxalyl chlorides or chloroformates produced complexes having the formula $\text{CpFe}(\text{CO})_2\text{SeQ}$ { $\text{Q} = \text{COR}$,¹⁶⁻¹⁸ SO_2R ,^{19,20} COCO_2R ,²¹ $\text{C}(\text{O})\text{OR}$,²² $\text{C}(\text{S})\text{OR}$,²³ $\text{C}(\text{O})\text{SR}$,²⁴ $\text{C}(\text{S})\text{SR}$ ¹⁵}. Among these complexes, the selenocarboxylato complexes are thoroughly investigated. Acid chlorides with one,^{16,17} two,^{18,26} or three,²⁷ functional groups are treated with the iron selenide forming the corresponding mono-, bi- or tri-functional iron selenocarboxylates. The organic transformation reactions of the selenocarboxylato complexes having one or more free acid chloride group produced several new complexes with amide, ester or thioester functionalities.^{26,27}

The selenium-containing dicarbonyl complexes $\text{CpFe}(\text{CO})_2\text{SeQ}$ are subjected to CO-substitution

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reactions by two-electron donor ligands. To that end, the iron selenocarboxylates ($\text{CpFe}(\text{CO})_2\text{SeCOR}$)^{28,29} and the iron selenosulfonates ($\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$)³⁰ reacted photochemically with EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) to produce the monosubstituted products $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeCOR}$ and $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeSO}_2\text{R}$, respectively. The selenocarboxylates are also reacted with the triphenylphosphite ligand forming the mixed $\text{CO}/\text{P}(\text{OEt})_3$ selenocarboxylates.²⁹

In this contribution, we describe the preparation of vinyl-selenocarboxylato iron complexes. The photolytic reactions of the latter complexes with PPh_3 , AsPh_3 , SbPh_3 are described. The X-ray structure determination and cyclic voltammetric measurements are presented for representative examples.

2. Experimental

2.1 General

All manipulations were performed under a dinitrogen atmosphere using standard Schlenk line techniques. Diethyl ether, hexane and tetrahydrofuran were dried over sodium and benzophenone. Dichloromethane was dried by using diphosphorus pentoxide (P_2O_5). The iron selenide ($\mu\text{-Se}[\text{CpFe}(\text{CO})_2]_2$) was prepared as reported elsewhere.³¹ The following chemicals were used as received (Sigma-Aldrich): cyclopentadienyl iron dicarbonyl dimer [$\text{CpFe}(\text{CO})_2$]₂, 3,3-dimethylacryloyl chloride, crotonoyl chloride, sorbic chloride, triphenylarsine, triphenylphosphine and triphenylantimony. Silica gel of particle size 0.063–0.200 mm (70–230 mesh) was dried at 110 °C before used for column chromatography.

All reaction steps were followed by thin-layer chromatography (TLC). Infrared (IR) spectra were recorded on Bruker alpha FT-IR spectrometer equipped with ATR unit. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-Avance spectrometer (¹H-NMR: 400 MHz), (³¹P-NMR: 161 MHz) and (¹³C-NMR: 100 MHz). Chemical shifts are given in ppm relative to CDCl_3 : ¹H-, ¹³C-NMR, H_3PO_4 : ³¹P-NMR and to SeO_2 : ⁷⁷Se-NMR. UV-Vis spectra were recorded using Shimadzu instrument in dichloromethane at room temperature. Melting points were reported on an electrothermal melting point apparatus. Elemental analyses were performed on a CHNS and O Thermo Scientific 2000 instrument. The photolytic reactions were carried out by a medium pressure mercury lamp obtained from Heraios.

2.2 General procedure for the preparation of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{C}(\text{R}1)(\text{R}2)$ (**1–3**)

In 250 mL Schlenk flask, the acid chloride (4.21 mmol) was added to a reddish-brown solution (2.9 mmol) of ($\mu\text{-Se}[\text{CpFe}(\text{CO})_2]_2$) in diethyl ether (50 mL). The resulting

mixture was stirred overnight at room temperature under nitrogen gas. The volatiles were removed under vacuum and the residue was re-dissolved in a minimum amount of CH_2Cl_2 . This solution was introduced to a silica gel column made up in hexane and eluted with hexane to remove the excess amount of acid chloride. Elution with a mixture of dichloromethane and hexane (1:1 volume ratio) gave brown-orange band which was collected and identified as $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{C}(\text{R}1)(\text{R}2)$, followed by a red band which was collected and identified as the byproduct $\text{CpFe}(\text{CO})_2\text{Cl}$. The product was crystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$ at -4 °C.

2.2a $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CHMe}$, **1**: Brown (70%). M.p.: 106–107 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2029, 1984 (s); $\nu_{\text{SeC}=\text{O}}$ 1719 (m); $\nu_{\text{C}=\text{C}}$ 1648 (m). ¹H-NMR (400 MHz, CDCl_3): δ 1.75 (d, 3H, CH_3 , $J_{\text{HH}} = 6.8$ Hz); 5.01 (s, 5H, C_5H_5); 6.76 (d, 1H, CH, $J_{\text{HH}} = 15.2$ Hz); 6.73 (td, 1H, CHMe, $J_{\text{HH}} = 7.0, 15.2$ Hz). ¹³C-NMR (100 MHz, CDCl_3): δ 17.42 CH_3 , 84.48 Cp, 135.26, 135.82 C=C, 197.36 C=O, 212.69 $\text{C}\equiv\text{O}$. ⁷⁷Se-NMR (76 MHz, CDCl_3): δ 190.01. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 265, 329. DEI-MS: $m/z = 325$ [M]⁺, 297 [$\text{M}-\text{CO}$]⁺, 269 [$\text{M}-2\text{CO}$]⁺, 254 [$\text{M}-2\text{CO}-\text{Me}$]⁺. Anal. Calc. for $\text{C}_{11}\text{H}_{10}\text{FeO}_3\text{Se}$: C, 40.65; H, 3.10%. Found: C, 40.36; H, 3.01%.

2.2b $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$, **2**: Brown (75%). M.p.: 110–111 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2027, 1982 (s); $\nu_{\text{SeC}=\text{O}}$ 1715 (m); $\nu_{\text{C}=\text{C}}$ 1637 (m). ¹H-NMR (400 MHz, CDCl_3): δ 1.75 (s, 3H, CH_3); 2.00 (s, 3H, CH_3); 5.03 (s, 5H, C_5H_5); 6.53 (s, 1H, CH). ¹³C-NMR (100 MHz, CDCl_3): δ 21.01, 26.94 CH_3 , 84.75 Cp, 129.35, 145.70 C=C, 196.99 C=O, 213.17 $\text{C}\equiv\text{O}$. ⁷⁷Se-NMR (76 MHz, CDCl_3): δ 189.49. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 270, 343. DEI-MS: $m/z = 340$ [M]⁺, 312 [$\text{M}-\text{CO}$]⁺, 284 [$\text{M}-2\text{CO}$]⁺, 269 [$\text{M}-2\text{CO}-2\text{Me}$]⁺. Anal. Calc. for $\text{C}_{12}\text{H}_{12}\text{FeO}_3\text{Se}$: C, 42.51; H, 3.57%. Found: C, 42.43; H, 3.44%.

2.2c $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CHCH}=\text{CHMe}$, **3**: Brown (80%). M.p.: 110–111 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 2027, 1982 (s); $\nu_{\text{SeC}=\text{O}}$ 1712 (m); $\nu_{\text{C}=\text{C}}$ 1649 (m), 1612 (m). ¹H-NMR (400 MHz, CDCl_3): δ 1.80 (s, 3H, CH_3 , $J_{\text{HH}} = 6.0$ Hz); 5.02 (s, 5H, C_5H_5); 6.14 (m, 2H, CH); 6.37 (d, 1H, CH, $J_{\text{HH}} = 15.2$ Hz); 7.02 (td, 1H, CHMe, $J_{\text{HH}} = 4.8, 10.4$ Hz). ¹³C-NMR (100 MHz, CDCl_3): δ 18.98 CH_3 , 84.73 Cp, 130.11, 131.54, 136.46, 139.47 C=C; 197.67 C=O, 212.89 $\text{C}\equiv\text{O}$. ⁷⁷Se-NMR (76 MHz, CDCl_3): δ 188.70. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 270, 335. DEI-MS: $m/z = 351$ [M]⁺, 323 [$\text{M}-\text{CO}$]⁺, 295 [$\text{M}-2\text{CO}$]⁺, 280 [$\text{M}-2\text{CO}-\text{Me}$]⁺. Anal. Calc. for $\text{C}_{13}\text{H}_{12}\text{FeO}_3\text{Se}$: C, 44.48; H, 3.45%. Found: C, 44.21; H, 3.24%.

2.3 General procedure for the preparation of $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeCOCH}=\text{CMe}_2$, **4a–c**

A solution of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$ (0.34 g, 1.00 mmol) and EPh_3 (1.20 mmol) in 100 mL THF is irradiated by UV-light at 0 °C until the disappearance of the

bands near 2029, 1985 cm^{-1} and the appearance of a single one at around 1950 cm^{-1} . The volatiles were removed under reduced pressure and the remaining solid was redissolved in a minimum amount of CH_2Cl_2 and introduced to a column made up in hexane. The column was eluted with hexane to remove any unreacted ligand. Elution with hexane/diethyl ether solution (1:1) gives a dark red band of the product. The product was recrystallized from dichloromethane/hexanes at -4°C .

2.3a *CpFe(CO)(PPh₃)SeCOCH=CMe₂*, **4a**: Orange (85%). M.p.: 130–131 $^\circ\text{C}$. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1949 (s); $\nu_{\text{SeC=O}}$ 1726 (m); $\nu_{\text{C=C}}$ 1649 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.57 (s, 3H, CH₃); 1.91 (s, 3H, CH₃); 4.47 (s, 5H, C₅H₅); 6.43 (s, 1H, CH); 7.31 (m, 6H, PPh₃); 7.65 (m, 9H, PPh₃). $^{31}\text{P-NMR}$ (CDCl_3): δ 71.20. $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 20.73 CH₃, 26.69 CH₂, 83.63 Cp, 128.16–132.38 Ph, 135.26, 135.69 C=C, 200.16 C=O, 220.96 C \equiv O. $^{77}\text{Se-NMR}$ (76 MHz, CDCl_3): δ 237.70. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 272, 360. DEI-MS: $m/z = 573$ [M]⁺, 311 [M-PPh₃]⁺. Anal. Calc. for C₂₉H₂₇FeO₂PSe: C, 60.72; H, 4.75%. Found: C, 60.51; H, 4.52%.

2.3b *CpFe(CO)(AsPh₃)SeCOCH=CMe₂*, **4b**: Brown (81%). M.p.: 125–126 $^\circ\text{C}$. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1948 (s); $\nu_{\text{SeC=O}}$ 1713 (m); $\nu_{\text{C=C}}$ 1640 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.65 (s, 3H, CH₃); 1.97 (s, 3H, CH₃); 4.62 (s, 5H, C₅H₅); 6.53 (s, 1H, CH); 7.39 (m, 6H, AsPh₃); 7.45 (m, 9H, AsPh₃). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 20.73 CH₃, 26.68 CH₃, 81.37 Cp, 128.46–133.73 Ph, 135.54, 136.00 C=C, 199.39 C=O, 220.10 C \equiv O. $^{77}\text{Se-NMR}$ (76 MHz, CDCl_3): δ 203.47. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 275, 330. DEI-MS: $m/z = 617$ [M]⁺, 312 [M-AsPh₃]⁺. Anal. Calc. for C₂₉H₂₇AsFeO₂Se: C, 56.43; H, 4.41%. Found: C, 56.14; H, 4.30%.

2.3c *CpFe(CO)(SbPh₃)SeCOCH=CMe₂*, **4c**: Brown (70%). M.p.: 88–89 $^\circ\text{C}$. IR (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1940 (s); $\nu_{\text{SeC=O}}$ 1710 (m); $\nu_{\text{C=C}}$ 1642 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.70 (s, 3H, CH₃); 1.92 (s, 3H, CH₃); 4.50 (s, 5H, C₅H₅); 6.48 (s, 1H, CH); 7.11 (m, 6H, SbPh₃); 7.43 (m, 9H, SbPh₃). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 19.23 CH₃, 26.22 CH₃, 83.80 Cp, 127.91–132.67 Ph, 135.62, 142.54 C=C, 199.92 C=O, 219.34 C \equiv O. $^{77}\text{Se-NMR}$ (76 MHz, CDCl_3): δ 195.64. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 280, 340. DEI-MS: $m/z = 664$ [M]⁺, 312 [M-SbPh₃]⁺. Anal. Calc. for C₂₉H₂₇FeO₂SbSe: C, 52.45; H, 4.50%. Found: C, 52.20; H, 4.12%.

2.4 X-ray structure analysis

The intensity data were collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-

empirical basis using multiple-scans.^{32–34} The structures were solved by direct methods (SHELXS)³⁵ and refined by full-matrix least squares techniques against Fo² (SHELXL-97).³⁵ The hydrogen atoms of compound **2** were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms of compound **4b** were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.³⁵ XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

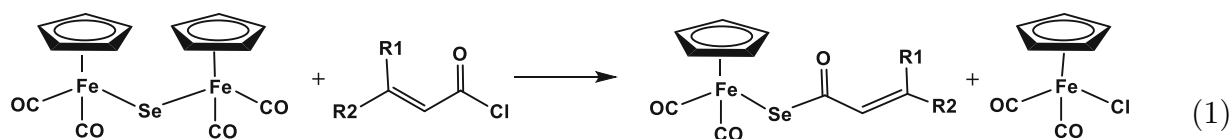
2.4a Crystal data for 2: C₁₂H₁₂FeO₃Se, Mr = 339.03 g mol⁻¹, brown prism, size 0.102 × 0.102 × 0.048 mm³, monoclinic, space group P 2₁/c, a = 7.3006(2), b = 11.6659(3), c = 15.2097(5) Å, $\beta = 101.645(2)^\circ$, V = 1268.72(6) Å³, T = -140°C , Z = 4, $\rho_{\text{calcd.}} = 1.775 \text{ g cm}^{-3}$, μ (Mo-K α) = 40.49 cm⁻¹, multi-scan, transmin: 0.5425, transmax: 0.7456, F(000) = 672, 14354 reflections in h(–9/9), k(–15/15), l(–19/19), measured in the range $2.73^\circ \leq \Theta \leq 27.48^\circ$, completeness $\Theta_{\text{max}} = 99.5\%$, 2897 independent reflections, R_{int} = 0.0359, 2550 reflections with F_o > 4 σ (F_o), 202 parameters, 0 restraints, R_{1,obs} = 0.0281, wR_{2,obs}² = 0.0521, R_{1,all} = 0.0355, wR_{2,all}² = 0.0548, GOOF = 1.098, largest difference peak and hole: 0.433/–0.345 e Å⁻³.

2.4b Crystal data for 4b: C₂₉H₂₇AsFeO₂Se, Mr = 617.24 g mol⁻¹, red-brown prism, size 0.088 × 0.082 × 0.080 mm³, triclinic, space group P $\bar{1}$, a = 10.1444(2), b = 10.4060(3), c = 13.3699(4) Å, $\alpha = 91.631(1)^\circ$, $\beta = 91.568(2)^\circ$, $\gamma = 112.155(2)^\circ$, V = 1305.52(6) Å³, T = -140°C , Z = 2, $\rho_{\text{calcd.}} = 1.570 \text{ g cm}^{-3}$, μ (Mo-K α) = 32.53 cm⁻¹, multi-scan, transmin: 0.6349, transmax: 0.7456, F(000) = 620, 10986 reflections in h(–13/13), k(–13/13), l(–17/17), measured in the range $2.11^\circ \leq \Theta \leq 27.48^\circ$, completeness $\Theta_{\text{max}} = 99\%$, 5929 independent reflections, R_{int} = 0.0312, 5095 reflections with F_o > 4 σ (F_o), 309 parameters, 0 restraints, R_{1,obs} = 0.0395, wR_{2,obs}² = 0.0824, R_{1,all} = 0.0496, wR_{2,all}² = 0.0884, GOOF = 1.016, largest difference peak and hole: 1.348/–0.364 e Å⁻³.

3. Results and Discussion

3.1 Synthesis of complexes

In a typical reaction, (μ -Se)[CpFe(CO)₂]₂ reacted with the vinyl acid chlorides in diethyl ether at room temperature forming the desired vinyl selenocarboxylato complexes CpFe(CO)₂SeCOCH=C(R1)(R2) {R1 = H, R2 = Me (**1**), R1 = R2 = Me (**2**), R1 = H, R2 = CH=CHMe (**3**)} as shown in Equation 1. The reaction produces also the iron chloride CpFe(CO)₂Cl which is separated from the products by column chromatography.

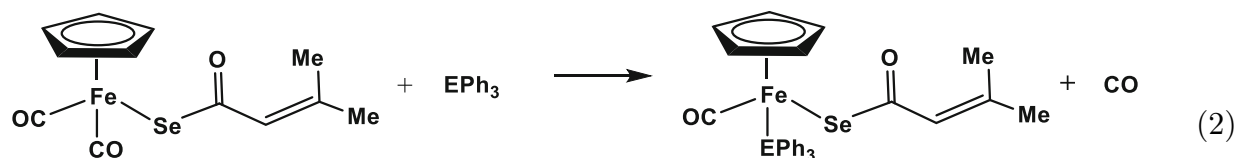


R¹ = H, R² = Me (**1**); R¹ = R² = Me (**2**); R¹ = H, R² = CH=CHMe (**3**)

Complexes **1–3** are fairly stable to air as solids but decompose upon exposure to air in solution. The identity of these complexes is determined based on their IR, MS, ¹H-, ⁷⁷Se- ¹³C-NMR spectroscopic data, elemental analysis and X-ray structure determination for **2**. The infrared spectra of **1–3** displayed two strong bands in the ranges of 2027–2029 and 1982–1984 cm⁻¹ assigned to the stretching frequencies of the two terminal carbonyl groups bonded to the iron center. These bands are a bit lower than those observed for the heterocyclic selenocarbonylato analogues CpFe(CO)₂SeCO-het (2035–2040 and 1985–1990 cm⁻¹).¹⁸ The spectra contain another CO-band in the range of 1712–1719 cm⁻¹ with medium intensity for the carbonyl group of the selenocarbonylato ligand. This band is much higher than the corresponding frequency of heterocyclic selenocarbonylato CpFe(CO)₂SeCO-het (1610–1617 cm⁻¹)¹⁸ and also higher than that of the selenocarbonates CpFe(CO)₂SeCO₂R (1655–1678 cm⁻¹).¹¹ This shift might be due to fewer resonances between the lone pairs on selenium and the carbon-carbon double bond with the carbonyl group. The C=C frequency discloses its presence in the spectra of complexes **1–3** as a medium band in the range of 1637–1649 cm⁻¹.

around the iron center.^{11–13} The methyl group-protons appear as a doublet (**1**: 1.75 ppm and **3**: 1.80 ppm) and two singlets of **2** (1.75, 2.00 ppm). Moreover, the vinylic protons of the selenocarbonylato moiety of **1–3** are present in the range of 6.53–6.76 ppm with the expected multiplicities. The ¹³C{¹H}-NMR spectra of **1–3** reveal the resonances of the carbon atoms of the Cp-ring in the range of 84.48–84.75 ppm. The carbonyl group of the selenocarbonylato and that of the terminal one are found in the ranges 197.36–197.99 ppm and 212.69–213.17 ppm, respectively. The methyl carbons of **1–3** are also present in the spectra in the range of 17.42–26.94 ppm. The chemical shift of the ⁷⁷Se atom of **1–3** (188.70–190.01 ppm) are at a higher value compared to the heterocyclic selenocarbonylato complexes.¹⁸ The molecular ion peak, together with peaks resulted from losing one or two carbonyl groups, are demonstrated in the mass spectra (DEI) of complexes **1–3**.

The substitution reactions of complex **2** by EPh₃ ligand is investigated to see if one or two carbonyl groups can be substituted. Equation 2 represents these photolytic reactions which resulted in one carbonyl substitution leading to the mono-substituted complexes.



E = P (**4a**); As (**4b**); Sb (**4c**)

The ¹H-NMR spectra of complexes **1–3** display several peaks for the different protons present in these molecules. The singlet in the range of 5.01–5.03 ppm is assigned to the five equivalent cyclopentadienyl protons. This range of chemical shift is similar to that observed for the reported selenocarbonylato (4.95–5.05 ppm) and selenocarbonates (4.95–5.08 ppm) indicating similar electron density

The higher electron density at the iron center of **4**, resulted from substitution of CO by weaker π-acceptor EPh₃ ligands, shifts the carbonyl stretching band to lower values (1940–1949 cm⁻¹) compared to that of **2**. This is due to more back-bonding into the π*-orbital of the CO ligand upon substitution. A similar shift was also observed in the corresponding alkyl or aryl selenocarbonylato systems.^{15,16} The C=O frequency of

the selenocarboxylato ligands appears in the 1710–1726 cm^{-1} range and that of the C=C frequency is found in the 1640–1649 cm^{-1} range.

The ^1H -NMR data for **4a–c** are consistent with their formulations, their cyclopentadienyl ring protons are shown in the 4.47–4.62 ppm range. This range is found at higher field compared to that of the starting dicarbonyl complex **2**. This shift is consistent with an increase of the electron density around the Fe center upon substitution of one carbonyl group by the EPh_3 ligand. The methyl group-protons show two singlets (1.57–1.70 and 1.91–1.97 ppm) indicating magnetically different groups. The vinyl protons of complexes **4a–c** are shown as a singlet in the range of 6.43–6.53 ppm. The phenyl protons of the EPh_3 ligands are observed in the aromatic range as two multiplets with 2:3 proton integration ratio. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of **4a–c** reveals the resonances of the carbon atoms of the Cp-ring in the range of 81.37–83.80 ppm. The carbonyl group of the selenocarboxylate group (199.36–200.16 ppm) and that of the terminal one (219.34–220.96 ppm) are found in the spectra. The methyl carbons are present as two different peaks in the ranges 19.23–20.73 and 26.22–26.69 ppm proving the magnetically different environment. The ^{77}Se -NMR spectra of these complexes show a peak in the range of 195.64–237.70 ppm which is higher than the reported value for **2**. The molecular ion peaks of each of complexes **4a–c** is present in its mass spectrum followed by peaks resulted from losing the EPh_3 ligand first followed by losing the CO ligand.

3.2 Crystal structures of **2** and **4b**

The molecular structures of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$ (**2**) and $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SeCOCH}=\text{CMe}_2$ (**4b**) are shown in Figures 1 and 2, respectively. Selected bond distances and angles of these two complexes are shown in Table 1. Both complexes adopt a piano stool structure with the Cp ring as the base and the carbonyls, triphenylarsine and selenium-containing ligand as the legs.

The cyclopentadienyl ligand is bonded to iron in η^5 -fashion. The Fe-C(Cp) average bond distances of **2** (2.091 Å) and of **4b** (2.087 Å) are equivalent to the analogous bonds reported for similar complexes.^{16–24} In addition, the Fe-Cp(central) distance (**2**: 1.720 Å, **4b**: 1.709 Å) is longer than that reported for the corresponding distance of ferrocene (1.651 Å).³⁶ The Fe-C(CO) distances of **2** (1.769(2) and 1.773(3) Å) are similar to that of **4b** (1.757(4) Å). The Fe-Se bond

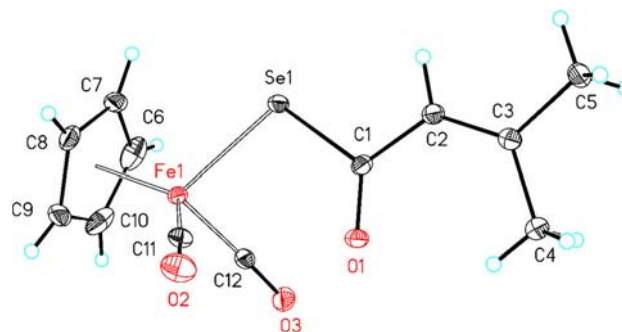


Figure 1. Molecular structure and numbering scheme of $\text{CpFe}(\text{CO})_2\text{SeCOCH}=\text{CMe}_2$ (**2**). The ellipsoids represent a probability of 30%. The hydrogen atoms are shown with arbitrary radii.

distance of **2** (2.3844(4) Å) and of **4b** (2.3851(6) Å) are comparable to each other and to those observed for analogous complexes $\text{CpFe}(\text{CO})_2\text{SQ}$.^{16–24} The C=O and C=C bond lengths of the selenocarboxylato ligand (**2**: 1.217(3), 1.343(3) Å, **4b**: 1.225(5), 1.340(6) Å) are within the normal C=O and C=C lengths. This indicates that there is very little if any, electron delocalization between the π -electron in these bonds. This result is supported by the high IR frequencies of both the C=O and C=C bonds compared to analogous complexes (*Vide supra*).^{11,13,18} The angles around the iron center (Se-Fe-C, Se-Fe-As, C-Fe-C(As)) are around 90° indicating a distorted octahedral geometry. The selenium atoms in these complexes have sp^3 hybridization as predicted from the Fe-Se-C1 angle of $104.12(7)^\circ$ or $104.03(12)^\circ$.

3.3 Cyclic voltammetric measurements of **2**

Cyclic voltammetry of complex **2** in CH_2Cl_2 (Figure 3) at scan rate, v , of 0.2 V s^{-1} shows two reduction waves at $E_{\text{pc}} = -1.85 \text{ V}$ and -2.08 V , vs. ferrocenium/ferrocene (Fc^+/Fc). Reversing the cathodic scan at -1.98 V (dashed curve in Figure 3a) shows that not only the second reduction event ($E_{\text{pc}} = -2.08 \text{ V}$) is irreversible, but also the first one. Moreover, the reversibility of the two reduction events does not enhance even at higher scan rate. However, this behaviour is similar to those of corresponding model complexes reported in the literature.^{18,24} Therefore, the first reduction event is attributed to the dissociation of the $[\text{SeCOCH}=\text{CMe}_2]^-$ ligand and generated the radical species, $[\text{CpFe}(\text{CO})_2]^\cdot$ (Fp^\cdot), which then dimerized to give the iron dimer (Fp_2) that reduce at $E_{\text{pc}} = -2.08 \text{ V}$ accounting for the second reduction event in the cyclic voltammogram of **2**.

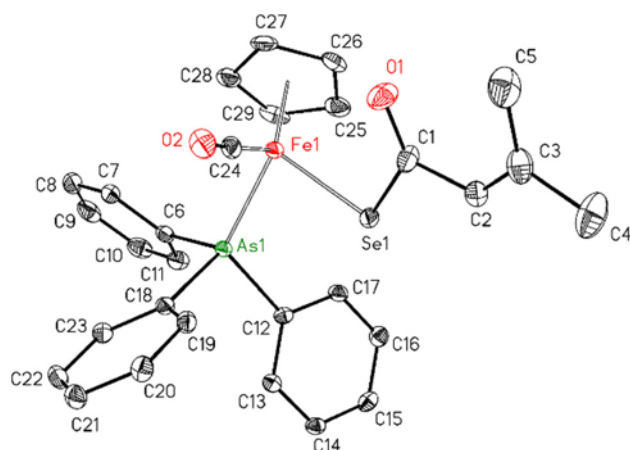


Figure 2. Molecular structure and numbering scheme of CpFe(CO)(AsPh₃)SeCOCH=CMe₂ (**4b**). The ellipsoids represent a probability of 30%. The hydrogen atoms are neglected for clarity reasons.

Table 1. Selected bond length (Å) and selected bond angles (°) of CpFe(CO)₂SeCOCH=CMe₂ (**2**) and CpFe(CO)(AsPh₃)SeCOCH=CMe₂ (**4b**).

2		4b	
Fe-C6	2.095(3)	Fe-C25	2.098(4)
Fe-C7	2.108(2)	Fe-C26	2.075(4)
Fe-C8	2.092(2)	Fe-C27	2.071(4)
Fe-C9	2.080(3)	Fe-C28	2.081(4)
Fe-C10	2.082(3)	Fe-C29	2.108(4)
Fe-C11	1.773(3)	Fe-C24	1.757(4)
Fe-C12	1.769(2)	Fe-As	2.3101(6)
Fe-Se	2.3844(4)	Fe-Se	2.3951(6)
Se-C1	1.922(2)	Se-C1	1.942(4)
C1-O1	1.217(3)	C1-O1	1.225(5)
C2-C3	1.343(3)	C2-C3	1.340(6)
C1-C2	1.472(3)	C1-C2	1.467(5)
C11-Fe-C12	94.34(11)	C24-Fe-As	88.78(12)
C11-Fe-Se	90.90(8)	C24-Fe-Se	90.25(12)
C12-Fe-Se	91.34(7)	C24-Fe-As	95.75(2)
Fe-Se-C1	104.12(7)	Fe-Se-C1	104.03(11)
Se-C1-O1	122.53(18)	Se-C1-O1	122.6(3)
O1-C1-C2	126.1(2)	O1-C1-C2	125.2(3)
Se-C1-C2	111.36(11)	Se-C1-C2	111.43(3)

3.4 UV-Visible spectra of **1–3** and **4** complexes

The electronic absorption spectra of **1–3** and **4** were recorded in dichloromethane in order to identify the metal to ligand charge transfer and π - π^* absorption bands. Figure 4 showed representative UV-Vis spectra of **2** and **4b**. The UV-Vis spectra of these complexes showed two absorption bands; one band is observed in the range of (265–270 nm) and is assigned to a ligand-ligand charge transfer (LLCT) type which is comparable to those reported for analogous systems.^{18,37}

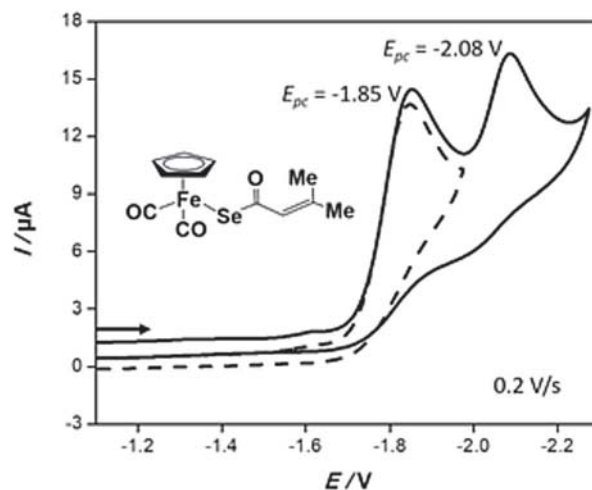


Figure 3. Cyclic voltammetry of 1.0 mm of **2** in CH₂Cl₂-[*n*-Bu₄N][BF₄] (0.1 M) at $\nu = 0.2 \text{ V s}^{-1}$. Glassy carbon disk ($d = 1.6 \text{ mm}$). The arrow indicates the scan direction. The potential E is given in V and referenced to the Fc⁺/Fc couple.

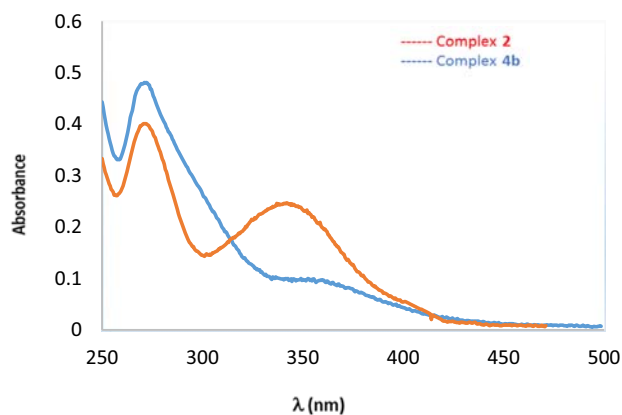


Figure 4. UV-Vis absorption spectra of **2** and **4a** in dichloromethane.

Another band is observed in the range of (329–340 nm) and is assigned to Fe→Cp metal to ligand charge transfer (MLCT) transition.^{18,37}

4. Conclusions

In summary, we reported here the synthesis and characterization of selenocarboxylato complexes of the iron-bearing vinylic moiety. The CO-substitution reactions of one complex (**2**) by EPh₃ (E = P, As, Sb) is demonstrated and produced only the monosubstituted complexes. The crystal structures, IR and NMR spectroscopic data confirm that the electron density around the iron is enhanced by replacing the CO group by less π -accepting EPh₃ ligand. The cyclic voltammetry of **2** showed two irreversible reduction bands.

The spectroscopic data proved that there is a minimum resonance between the selenium lone pair, C=O and C=C bonds.

Supplementary Information (SI)

Tables S1–S4 and Figures S1–S15 are available at www.ias.ac.in/chemsci. Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-1949366 for **2**, and CCDC-1949367 for **4b** contain the supplementary crystallographic data excluding structure factors; this data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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References

- Labunsky Y M, Hatfield D and Gladyshev V N 2014 Selenoproteins: molecular pathways and physiological roles *Physiol. Rev.* **94** 739
- Lobo V, Patil A, Phatak A and Chandra N 2010 Free radicals, antioxidants and functional foods: impact on human health *Pharmacogn. Rev.* **4** 118
- Rahal A, Kumar A, Singh V, Yadav B, Tiwari R, Chakraborty S and Dhama K 2014 Oxidative stress, prooxidants, and antioxidants: the interplay *Bio. Med. Res. Int.* <https://doi.org/10.1155/2014/761264>
- Xia L, Nordman T, Olsson J M, Damdimopoulos A, Björkhem-Bergman L, Nalvarte I, Eriksson L C, Arner E S J, Spyrou G and Björnstedt M 2003 The mammalian cytosolic selenoenzyme thioredoxin reductase reduces ubiquinone: a novel mechanism for defense against oxidative stress *J. Bio. Chem.* **278** 2141
- Zoidis E, Seremelis I, Kontopoulos N and Danezis G P 2018 Selenium-dependent antioxidant enzymes: actions and properties of selenoproteins *Antioxidant* **7** 66
- Alberto E E, do Nascimento V and Braga A L 2010 Catalytic application of selenium and tellurium compounds as glutathione peroxidase enzyme mimetics *J. Braz. Chem. Soc.* **21** 2032
- Dresch L C, de Araújo B B, Casagrande Jr O L and Stieler R 2016 A novel class of nickel(II) complexes containing selenium-based bidentate ligands applied in ethylene oligomerization *Dalton Trans.* **6** 104338
- Harb M K, Alshurafa H, El-khateeb M, Al-Zuheiri A, Görls H, Abul-Futouh H and Weigand W 2018 [FeFe]-hydrogenase models containing long diselenolato linkers *ChemSelect* **3** 8867
- Elsherbini M S, Hamama W S and Zoorob H H 2019 Recent advances in the chemistry of selenium-containing heterocycles: five-membered ring systems *Coord. Chem. Rev.* **312** 149
- Laitinen R S, Oilunkaniemi R and Chivers T 2019 Introduction of selenium and tellurium into reaction systems *Phys. Sci. Rev.* **4** <https://doi.org/10.1515/psr-2018-0059>
- Abul-Futouh H, El-khateeb M, Görls H, Asali K and Weigand W 2017 Selenium makes the difference: protonation of [FeFe]-hydrogenase mimics with diselenolato ligands *Dalton Trans.* **46** 2937
- Harb M K, Görls H, Sakamoto T, Feltin G A N, Evans D H, Glass R S, Lichtenberger D L, El-khateeb M and Weigand W 2018 Synthesis and characterization of [FeFe]-hydrogenase models with bridging moieties containing (S, Se) and (S, Te) *Eur. J. Inorg. Chem.* **25** 3976
- Abul-Futouh H, Zagranyski Y, Müller C, Schulz M, Kupfer S, Görls H, El-khateeb M, Gräfe S, Dietzek B, Peneva K and Weigand W 2017 [FeFe]-Hydrogenase H-cluster mimics mediated by naphthalene monoimide derivatives of peri-substituted dichalcogenides *Dalton Trans.* **46** 11180
- Maslat A, Jibril I, Abusaud M, Abed-Alhadi A and Hamadeh Z 2002 Synthesis and biological study of a new series of bifunctional organoiron thio- and selenoterephthalate derivatives (C₅H₅)Fe(CO)₂ECO(C₆H₄)-COX (E = S, X = R₂N, RNH, NH₂, OH, Cl; E = Se, X = RNH, RS, RCOO, NH₂, OH, Cl) *Appl. Organomet. Chem.* **16** 44
- Maslat A, Jibril I and Mizyed S 2010 Antimutagenic activities of two suspected anticarcinogenic bifunctional organoiron seleno-terephthalate derivatives *Drug Chem. Toxicol.* **33** 254
- Jibril I and Abu-Nimreh O 1996 Organoiron selenium complexes. Synthesis and characterization of tert-butyl substituted cyclopentadienyldicarbonylselenocarboxylate iron complexes Cp'Fe(CO)₂SeCOR (Cp' = C₅H₅, t-BuC₅H₄, 1,3-t-Bu₂C₅H₃) *Synth. React. Inorg. Met. Org. Chem.* **26** 1409
- El-khateeb M, Al-Noaimi M, Al-Rejjal N, Abul-Futouh H, Görls H and Weigand W 2013 Mono- and bi-iron chalcogenocarboxylate complexes *Trans. Met. Chem.* **38** 529
- El-khateeb M, Abul-Futouh H, Görls H, Weigand W and Almazahreh L R 2016 Synthesis, characterization and electrochemical investigations of heterocyclic-selenocarboxylate iron complexes *Inorg. Chim. Acta* **449** 14
- El-khateeb M and Obidate T 2001 The first selenosulfonate complexes CpFe(CO)₂SeSO₂R: preparation and structure of CpFe(CO)₂SeSO₂C₆H₅ *Polyhedron* **20** 239
- El-khateeb M, Asali K, Al-Noaimi M, Al-Rabaei E, Awwadi F, Taher D and Lang H 2014 Thio- and selenosulfonate complexes of iron bearing aromatic and heterocyclic groups *Inorg. Chim. Acta* **421** 553
- El-khateeb M, Görls H and Weigand W 2007 O-Alkylthio- and O-alkylselenooxalate iron complexes: structures of CpFe(CO)₂ECOCO₂Me and [CpFe(CO)₂-ECO]₂ *Inorg. Chim. Acta* **360** 705
- El-khateeb M 2004 Iron Se-bonded mono-selenocarbonates CpFe(CO)₂SeCO₂R: the first selenocarbonates complexes *Inorg. Chim. Acta* **357** 4341

23. El-khateeb M 2006 Selenothiocarbonate complexes of iron: structure of $\text{CpFe}(\text{CO})_2\text{SeC}(\text{S})\text{O}-4-\text{C}_6\text{H}_4\text{Cl}$ *Polyhedron* **25** 1386
24. El-khateeb M, Abul-Futouh H, Görls H and Weigand W 2019 Towards the synthesis of piano-stool iron complexes mediated by *S*-alkylselenothiocarbonate ligands and their substitution reactions *Monatsh. Chem.* **150** 1461
25. El-khateeb M and Roller A 2007 Synthesis and structures of $\text{CpFe}(\text{CO})_2(\kappa E\text{-ECS}_2\text{Ph})$ and $[\text{CpFe}(\text{CO})(\kappa^2\text{S}, E\text{-ECS}_2\text{Ph})]$ (E=S, Se) *Polyhedron* **26** 3920
26. Jibril I, Abd-Alhadi E H and Hamadeh Z 2000 Imide and anhydride bridged organoiron dinuclear homo and hetero dichalcogeno carboxylate complexes $[\text{CpFe}(\text{CO})_2\text{ECO}(\text{C}_6\text{H}_4)\text{CO}]_2\text{NH}$ and $[\text{CpFe}(\text{CO})_2\text{ECO}(\text{C}_6\text{H}_4)\text{CO}]_2\text{O}$; E = S, Se *Trans. Met. Chem.* **25** 407
27. El-khateeb M, Asali K J, Jibril I, Abuseni A, Görls H and Weigand W 2009 Multifunctional iron thiocarboxylate complexes: synthesis, reactivity and structure of $\text{CpFe}(\text{CO})_2\text{SCOO}-3,5-\text{C}_6\text{H}_4(\text{COCl})_2$ *Trans. Met. Chem.* **34** 419
28. El-khateeb M, Lataifeh A and Jibril I 2003 Substituted iron selenocarboxylate complexes $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{-SeCOR}$ (E = P, As, Sb) *Trans. Met. Chem.* **28** 85
29. El-khateeb M 2016 Preparation, characterization and structure determination of $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeCO}$ -het complexes *J. Mol. Struct.* **1123** 300
30. El-khateeb M and Obidate T 2009 Synthesis and characterization of $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeSO}_2\text{R}$ (E = P, As, Sb) *Phos. Sul. Sil. Rel. Elem.* **184** 585
31. Herman W A, Rohrmann J and Hecht H 1985 Mehrfachbindungen zwischen hauptgruppenelementen und übergangsmetallen: XVII. Selen- und tellurbrücken in organometallkomplexen: AUFBAU, protonierung und methylierung *J. Organomet. Chem.* **290** 53
32. Nonius BV COLLECT, Data Collection Software; Netherlands, **1998**
33. Otwinowski Z and Minor W 1997 Processing of X-ray diffraction data collected in oscillation mode *Methods Enzymol.* **276** 307
34. SADABS 2.10, Bruker-AXS inc, 2002, Madison, WI, USA
35. Sheldrick G M 2008 *Acta Cryst.* **A64** 112
36. XP, Siemens Analytical X-ray Instruments Inc., 1990, Karlsruhe, Germany; 1994; Madison, WI, USA
37. Dunitz J D, Orgel L E and Rice A 1956 The crystal structure of ferrocene *Acta Cryst.* **9** 373
38. Belmont J and Wrighton W 1986 Photochemical conversion of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ and related complexes to ferrocene and related derivatives: reactivity of the monocarbonyl intermediate *Organometallics* **5** 1421