



Vinyl-thiocarboxylate complexes of iron: synthesis, characterization and reactions

MOHAMMAD EL-KHATEEB^{a,*}, KHALEEL J ASALI^a, BATOOL AL-JUNEIDI^a,
HASSAN ABUL-FUTOUH^b, HELMAR GÖRLS^c and WOLFGANG WEIGAND^c

^aChemistry Department, Jordan University of Science and Technology, Irbid 22110, Jordan

^bDepartment of Pharmacy, Al-Zaytoonah University of Jordan, P.O. Box 130, Amman 11733, Jordan

^cInstitut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Humboldt Str. 8, 07743 Jena, Germany

E-mail: kateeb@just.edu.jo

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Abstract. Half-sandwich iron thiocarboxylate complexes of the general formula $\text{CpFe}(\text{CO})_2\text{SCoCH}=\text{C}(\text{R}')(\text{R}'')$ ($\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$, $\text{R}' = \text{R}'' = \text{Me}$, $\text{R}' = \text{H}$, $\text{R}'' = \text{CH}=\text{CHMe}$) are obtained from the reaction of $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 1\text{--}5$) with the vinyl acid chlorides $\text{ClCOCH}=\text{C}(\text{R}')(\text{R}'')$. The substitution reaction of $\text{CpFe}(\text{CO})_2\text{SCoCH}=\text{C}(\text{R})\text{Me}$ with EPh_3 produced the monosubstituted complexes $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SCoCH}=\text{C}(\text{R})\text{Me}$ ($\text{R} = \text{Me}$, $\text{E} = \text{P}$, $\text{R} = \text{H}$, $\text{E} = \text{As}$, Sb). All the new complexes have been characterized by UV-Vis, IR, $^1\text{H-NMR}$, $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$, $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ spectroscopy and elemental analysis. The solid state structures and the cyclic voltammetric measurements of $\text{CpFe}(\text{CO})_2\text{SCoCH}=\text{CMe}_2$ and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCoCH}=\text{CMe}_2$ were determined.

Keywords. Iron; Vinyl thiocarboxylate; Substitution; Structures.

1. Introduction

Organometallic-sulfur complexes play a crucial role in the activity of metalloproteins in enzyme-based catalysis and also in the activity of these complexes as heterogeneous catalysts.^{1–4} The systematic search for models containing metal-sulfur bonds led to the discovery of interesting new structural chemistry due to different coordination modes of sulfur ligands.^{1–4} Iron-sulfur complexes are found in the active site of [FeFe]-hydrogenase enzymes that are responsible for hydrogen production.^{5,6} In biological systems, enzymes involve Fe-S bonds such as cytochromes, ferredoxins, rieske proteins and rubredoxins participate in electron transfer reactions.⁴

Thiocarboxylato complexes of the transition metals have been reported by us^{7–12} and others.^{13–15} The reactions of $(\mu\text{-S}_x)[\text{Cp}'\text{M}(\text{CO})_2]_2$ ($\text{M} = \text{Fe}$, Ru , $\text{Cp}' = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Bu}$, $1,3\text{-C}_5\text{H}_3(\text{Bu})_2$) with acid chlorides produced complexes of the type $\text{Cp}'\text{M}(\text{CO})_2\text{SCOR}$.^{7–9} The corresponding Mo and W complexes $\text{CpM}(\text{CO})_3\text{SCOR}$ ($\text{M} = \text{Mo}$, W) are accessible from the hydrosulfido complexes

$\text{CpM}(\text{CO})_3\text{SH}$ and the acid chlorides.^{9,10} In a similar reaction, the ruthenium thiocarboxylates $\text{CpRu}(\text{L})_2\text{SCOR}$ ($\text{L} = \text{PPh}_3$, CO , $\frac{1}{2} \text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\frac{1}{2} \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) are obtained from $\text{CpRu}(\text{L})_2\text{SH}$ and the acid chlorides.^{11–13} Thiocarboxylato derivatives of platinum group metals $\{(\text{L}_2\text{M}(\text{SCOR})_2, \text{M} = \text{Ni}$, Pd , Pt , $\text{L} = \text{PPh}_3$, PBu_3 , $\frac{1}{2} \text{Ph}_2\text{PCH}_2\text{PPh}_2$, $\frac{1}{2} \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\}$ are reported from the substitution reactions of the corresponding metal dichlorides by the thiocarboxylato anions.^{16–19}

The reactions of $\text{Cp}'\text{Fe}(\text{CO})_2\text{SCOR}$ ($\text{Cp}' = \text{C}_5\text{H}_5$, $\text{C}_5\text{H}_4\text{Bu}$, $1,3\text{-C}_5\text{H}_3(\text{Bu})_2$; $\text{R} = \text{alkyl}$, aryl , heterocycle) with EPh_3 ($\text{E} = \text{P}$, As , Sb) ligands were reported to produce the mono-substituted complexes $\text{Cp}'\text{Fe}(\text{CO})(\text{EPh}_3)\text{SCOR}$.²⁰ The kinetics of these reactions have been studied and the effects of Cp-substituents, the R-group of the thiocarboxylato ligands and the donor atom of the EPh_3 ligands on the rate of these reactions are reported.²¹ The phosphite ligands $\text{P}(\text{OEt})_3$ reacted photochemically with $\text{CpFe}(\text{CO})_2\text{SCOR}$ to give also the monosubstituted complexes $\text{CpFe}(\text{CO})(\text{P}(\text{OEt})_3)\text{SCOR}$.⁸ However, the analogous reactions of $\text{CpFe}(\text{CO})_2\text{SCOR}$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 1\text{--}6$) gave either the mono-

*For correspondence

substituted complexes $\text{CpFe}(\text{CO})(\kappa\text{P-Ph}_2\text{P}(\text{CH}_2)_n\text{-PPh}_2)\text{SCOR}$ for $n = 1\text{--}6$ and the di-substituted complexes $\text{CpFe}(\kappa^2\text{P,P-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{SCOR}$ only for $n = 1$ and 2.^{22,23}

In this contribution, we are investigating the reaction of iron sulfides with vinylic acid chlorides. The photolytic CO-substitution reactions of the produced vinyl thiocarboxylato complexes by EPH_3 ligands are demonstrated. The structures and cyclic voltammetric measurements of representative samples are also shown.

2. Experimental

2.1 Materials and methods

Reactions and manipulations were performed under dinitrogen atmosphere of standard Schlenk line techniques. Dichloromethane (P_2O_5), diethyl ether, tetrahydrofuran (Na/benzophenone) and hexane (Na) were dried following standard procedures. The iron sulfides $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 1\text{--}5$) were synthesized as reported in the literature.²⁴ 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, triphenylantimony. Silica gel of particle size 0.063–0.200 mm (70–230 mesh) was dried at 110 °C before used for column chromatography.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-Avance 400 MHz spectrometer ($^1\text{H-NMR}$), 161 MHz ($^{31}\text{P-NMR}$) and 100 MHz spectrometer ($^{13}\text{C-NMR}$). The chemical shifts are reported in ppm relative to CDCl_3 ($^1\text{H-}$, $^{13}\text{C-NMR}$) or H_3PO_4 ($^{31}\text{P-NMR}$). Infrared (IR) spectra were recorded on Bruker alpha FT-IR spectrometer equipped with ATR unit. UV-Vis spectra were recorded using Shimadzu instrument in dichloromethane at room temperature. Melting points were reported on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were done on CHNS and O Thermo Scientific 2000 instrument. The photolytic reactions were carried out by a medium pressure mercury lamp obtained from Heraios. Cyclic voltammetric measurements were conducted in three-electrode technique [glassy carbon disk ($d = 1.6$ mm) as working electrode, Ag/Ag^+ in MeCN as reference electrode, Pt wire as counter electrode] using a Reference 600 Potentiostat (Gamry Instruments). All experiments were performed in CH_2Cl_2 solutions containing 0.1 M $[n\text{-Bu}_4\text{N}][\text{BF}_4]$ at room temperature. The solutions were purged with N_2 and a stream of it was maintained over the solutions during the measurements. The vitreous carbon disk was polished on a felt tissue with alumina before each measurement. All potential values reported in this paper are referenced to the potential of the ferrocenium/ferrocene (Fc^+/Fc) couple.

Corrections for the iR drop were performed for all experiments.

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

The iron sulfides $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ (1.00 mmol) and the vinylic acid chloride (1.20 mmol) are dissolved in 150 mL diethyl ether. The resulting mixture was stirred overnight under nitrogen gas. The volatiles were removed under vacuum. The residual solid was re-dissolved in a minimum amount of CH_2Cl_2 and introduced to a silica gel column made up in hexane. The column was first eluted with hexane to remove the excess amount of acid chloride, then with a mixture of dichloromethane and hexane (1:1 volume ratio) to give an orange band which was collected and identified as the products, followed by a red band which was collected and identified as $\text{CpFe}(\text{CO})_2\text{Cl}$. The product was crystallized from CH_2Cl_2 /hexane at -4 °C.

2.2a $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CHMe}$, **1:** Orange (76%). M.p.: 111–112 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 2040, 1994 (s); $\nu_{\text{S}=\text{C}=\text{O}}$ 1702 (m); $\nu_{\text{C}=\text{C}}$ 1622 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 1.79 (d, 3H, CH_3 , J_{HH} = 6.4 Hz); 5.01 (s, 5H, C_5H_5); 6.41 (d, 1H, CH, J_{HH} = 15.2 Hz); 6.66 (td, 1H, CHMe, J_{HH} = 6.4, 15.2 Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 17.03 CH_3 , 75.09 Cp, 123.44 CH, 125.57 CH, 189.79 C=O, 201.87 C \equiv O. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 261, 324. DEI-MS: $m/z = 278$ $[\text{M}]^+$, 250 $[\text{M-CO}]^+$, 222 $[\text{M-2CO}]$. Anal. Calc. for $\text{C}_{11}\text{H}_{10}\text{FeO}_3\text{S}$: C, 47.51; H, 3.62; S, 11.53%. Found: C, 48.02; H, 3.64; S, 10.92%.

2.2b $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CMe}_2$, **2:** Orange (70%). M.p.: 116–118 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 2028, 1981 (s); $\nu_{\text{S}=\text{C}=\text{O}}$ 1702 (m); $\nu_{\text{C}=\text{C}}$ 1619 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 1.80 (s, 3H, CH_3); 2.06 (s, 3H, CH_3); 5.03 (s, 5H, C_5H_5); 6.43 (s, 1H, CH). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 20.17, 26.38 CH_3 , 84.84 Cp, 126.63 CHMe, 145.43 CH, 198.61 C=O, 213.35 C \equiv O. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 266, 323. DEI-MS: $m/z = 292$ $[\text{M}]^+$, 264 $[\text{M-CO}]^+$, 235 $[\text{M-2CO}]^+$, 276 $[\text{M-SCOCHCMe}_2]^+$. Anal. Calc. for $\text{C}_{12}\text{H}_{12}\text{FeO}_3\text{S}$: C, 49.34; H, 4.14, S, 10.97%. Found: C, 49.03; H, 4.06; S, 10.52%.

2.2c $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CHCH}=\text{CHMe}$, **3:** Orange (65%). M.p.: 136–137 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 2029, 1991 (s); $\nu_{\text{S}=\text{C}=\text{O}}$ 1713 (m); $\nu_{\text{C}=\text{C}}$ 1699 (m). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 1.82 (d, 3H, CH_3 , J_{HH} = 6.3 Hz); 5.02 (s, 5H, C_5H_5); 6.09 (m, 2H, CH); 6.38 (d, 1H, CH, J_{HH} = 14.8 Hz); 6.98 (td, 1H, CHMe, J_{HH} = 6.3, 14.8 Hz). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 18.80 CH_3 , 85.16 Cp, 129.87 CHMe, 130.07 CH, 136.50 CH; 138.42; 199.22 C=O, 211.91 C \equiv O. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 293, 336. DEI-MS: $m/z = 316$ $[\text{M}]^+$, 388 $[\text{M-CO}]^+$, 260 $[\text{M-2CO}]^+$, 176 $[\text{M-SCOR}]^+$. Anal. Calc. for $\text{C}_{13}\text{H}_{12}\text{FeO}_3\text{S}$: C, 51.34; H, 3.98, S, 10.54%. Found: C, 51.15; H, 3.81; S, 10.14%.

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

A solution of $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{C}(\text{R})\text{Me}$ (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 are removed under reduced pressure and the remaining solid was re-dissolved 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) gave a dark red band of the product. The product was recrystallized from dichloromethane/hexanes at -4 °C.

2.3a $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCOCH}=\text{CMe}_2$, **4a:** Orange (55%). M.p.: 130–131 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 1955 (s); $\nu_{\text{S}=\text{C}=\text{O}}$ 1720 (m); $\nu_{\text{C}=\text{C}}$ 1649 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.71 (s, 3H, CH_3); 2.05 (s, 3H, CH_3); 4.53 (s, 5H, C_5H_5); 6.37 (s, 1H, CH); 7.41 (m, 15H, PPh_3). $^{31}\text{P-NMR}$ (CDCl_3): δ 66.62. $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 20.19 CH_3 , 26.61 CH_2 , 84.10 Cp, 128.22–134.90 Ph, 135.33 CH, 142.46 CH, 202.10 $\text{C}=\text{O}$, 220.00 $\text{C}\equiv\text{O}$. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 263, 326. DEI-MS: $m/z = 526$ $[\text{M}]^+$, 264 $[\text{M-PPh}_3]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{27}\text{FeO}_2\text{PS}$: C, 66.17; H, 5.17; S, 6.09%. Found: C, 65.71; H, 5.13; S, 5.50%.

2.3b $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SCOCH}=\text{CHMe}$, **5b:** Brown (64%). M.p.: 125–126 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 1957 (s); $\nu_{\text{S}=\text{C}=\text{O}}$ 1692 (m); $\nu_{\text{C}=\text{C}}$ 1640 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.25 (d, 3H, CH_3); 4.51 (s, 5H, C_5H_5); 5.50 (m, 1H, CHMe); 6.36 (d, 1H CH); 7.33 (m, 15H, AsPh_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 17.11 CH_3 , 83.56 Cp, 127.32–131.08 Ph, 132.24 CH, 134.12 CH, 203.43 $\text{C}=\text{O}$, 217.13 $\text{C}\equiv\text{O}$. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 260, 328. DEI-MS: $m/z = 552$ $[\text{M}]^+$, 249 $[\text{M-AsPh}_3]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{27}\text{AsFeO}_2\text{S}$: C,

60.45; H, 4.53; S, 5.76%. Found: C, 60.83; H, 4.83; S, 5.80%.

2.3c $\text{CpFe}(\text{CO})(\text{SbPh}_3)\text{SCOCH}=\text{CHMe}$, **5c:** Red (70%). M.p.: 109–111 °C. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{O}}$ 1943 (s); $\nu_{\text{S}=\text{C}=\text{O}}$ 1690 (m); $\nu_{\text{C}=\text{C}}$ 1642 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.15 (d, 3H, CH_3); 4.49 (s, 5H, C_5H_5); 5.29 (m, 1H, CHMe); 6.20 (d, 1H, CH); 7.18 (m, 15H, SbPh_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 17.21 CH_3 , 80.49 Cp, 128.50–132.29 Ph, 134.16 CH, 135.52 CH, 204.38 $\text{C}=\text{O}$, 218.06 $\text{C}\equiv\text{O}$. UV-Vis (CH_2Cl_2 , λ_{max} , nm) 265, 305. DEI-MS: $m/z = 664$ $[\text{M}]^+$, 312 $[\text{M-SbPh}_3]^+$. Anal. Calc. for $\text{C}_{29}\text{H}_{27}\text{FeO}_2\text{SbS}$: C, 55.76; H, 4.18; S, 5.32%. Found: C, 55.15; H, 3.96; S, 5.26%.

2.4 Crystal structure determination

The intensity data were collected on a Nonius KappaCCD 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.^{25–27}

The structures were solved by direct methods (SHELXS)²⁸ and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97).²⁸ The hydrogen atoms of compound **2** were located by difference Fourier synthesis and refined isotropically. The hydrogen atoms of **4a** were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.²⁸ XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

2.4a Crystal data for **2:** $\text{C}_{12}\text{H}_{12}\text{FeO}_3\text{S}$, $M_r = 292.13$ g mol^{-1} , brown prism, size $0.098 \times 0.082 \times 0.080$ mm^3 , monoclinic, space group $\text{P } 2_1/c$, $a = 7.1957(2)$, $b = 11.5181(3)$, $c = 15.2311(4)$ Å, $\beta = 101.558(2)^\circ$, $V = 1236.77(6)$ Å³, $T = -140$ °C, $Z = 4$, $\rho_{\text{calcd.}} = 1.569$ g cm^{-3} , μ (Mo- K_α) = 13.79 cm^{-1} , multi-scan, transmin: 0.6857, transmax: 0.7456, $F(000) = 600$, 6343 reflections in $h(-8/9)$, $k(-14/11)$, $l(-19/18)$, measured in the range $2.23^\circ \leq \Theta \leq 27.44^\circ$, completeness $\Theta_{\text{max}} = 96\%$, 2709 independent reflections, $R_{\text{int}} = 0.0418$, 2250 reflections with $F_o > 4\sigma(F_o)$, 202 parameters, 0 restraints, $R1_{\text{obs}} = 0.0405$, $wR2_{\text{obs}} = 0.0739$, $R1_{\text{all}} = 0.0539$, $wR2_{\text{all}} = 0.0833$, GOOF = 1.096, largest difference peak and hole: 0.488/−0.381 $\text{e} \text{ \AA}^{-3}$.

2.4b Crystal data for **4a:** $\text{C}_{30}\text{H}_{29}\text{Cl}_2\text{FeO}_2\text{PS}$, $M_r = 611.31$ g mol^{-1} , red-brown prism, size $0.092 \times 0.088 \times 0.084$ mm^3 , monoclinic, space group $\text{P } 2_1/n$, $a = 9.3705(2)$, $b = 17.9927(3)$, $c = 17.4733(4)$ Å, $\beta = 104.847(1)^\circ$, $V = 2847.65(10)$ Å³, $T = -140$ °C, $Z = 4$, $\rho_{\text{calcd.}} = 1.426$ g cm^{-3} , μ (Mo- K_α) = 8.73 cm^{-1} , multi-scan, transmin: 0.6591, transmax: 0.7456, $F(000) = 1264$, 20912 reflections in $h(-12/12)$, $k(-22/23)$, $l(-22/22)$, measured in the range $2.26^\circ \leq \Theta \leq 27.46^\circ$, completeness $\Theta_{\text{max}} = 99.6\%$, 6488 independent

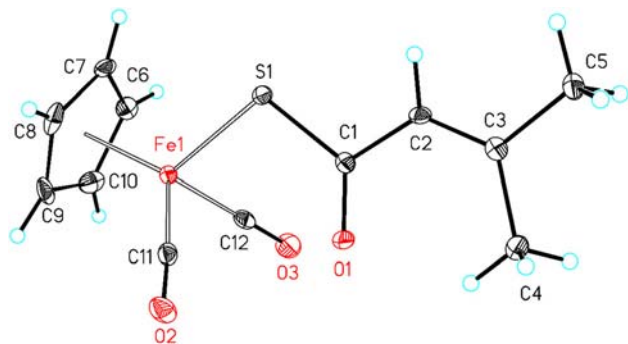


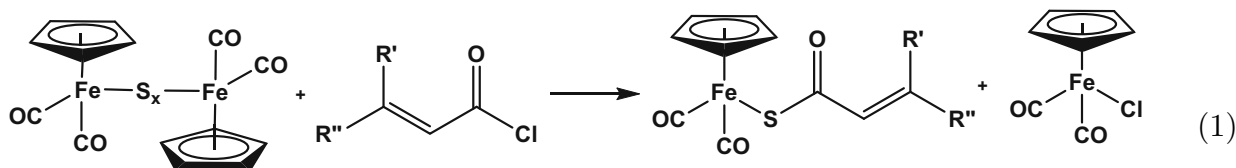
Figure 1. Molecular structure and numbering scheme of $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CMe}_2$ (**2**). The ellipsoids represent a probability of 30%. The hydrogen atoms are shown with arbitrary radii.

reflections, $R_{\text{int}} = 0.0474$, 5652 reflections with $F_o > 4\sigma(F_o)$, 336 parameters, 0 restraints, $R1_{\text{obs}} = 0.0398$, $wR2_{\text{obs}} = 0.0859$, $R1_{\text{all}} = 0.0484$, $wR2_{\text{all}} = 0.0902$, $\text{GOOF} = 1.081$, largest difference peak and hole: $0.470/-0.367 \text{ e } \text{\AA}^{-3}$.

3. Results and Discussion

3.1 Synthesis of complexes

Iron vinyl-thiocarboxylate complexes $\text{CpFe}(\text{CO})_2\text{-SCOCH}=\text{C}(\text{R}')(\text{R}'')$ ($\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$, $\text{R}' = \text{R}'' = \text{Me}$, $\text{R}' = \text{H}$, $\text{R}'' = \text{CH}=\text{CHMe}$) are readily synthesized by reaction of iron sulfides $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 1\text{--}5$) with the corresponding vinyl acid chlorides as shown in Equation 1. The organoiron chloride, $\text{CpFe}(\text{CO})_2\text{Cl}$ was obtained as a bi-product which was separated from the products by column chromatography.



$\text{R}' = \text{H}$, $\text{R}'' = \text{Me}$ (1); $\text{R}' = \text{R}'' = \text{Me}$ (2); $\text{R}' = \text{Me}$, $\text{R}'' = \text{CH}=\text{CHMe}$ (3);

The orange complexes (1–3) were recognized based on their MS, UV-Vis, IR, $^1\text{H-NMR}$, $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ spectroscopy, elemental analysis as well as X-ray structure determination of $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CMe}_2$ (2) (Figure 1). Their IR spectra show two bands for the terminal carbonyl groups in the ranges of 1981–1994 and

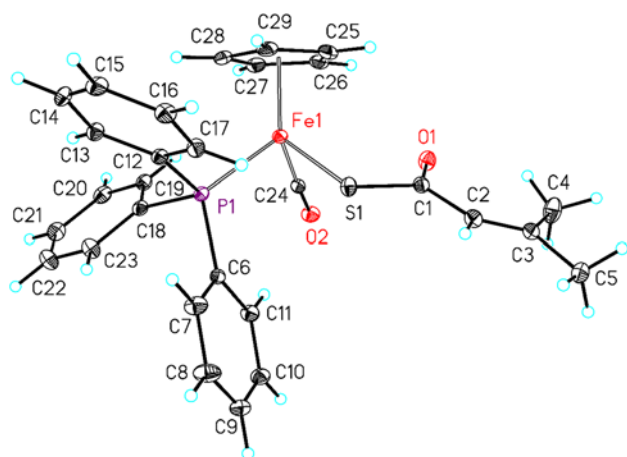
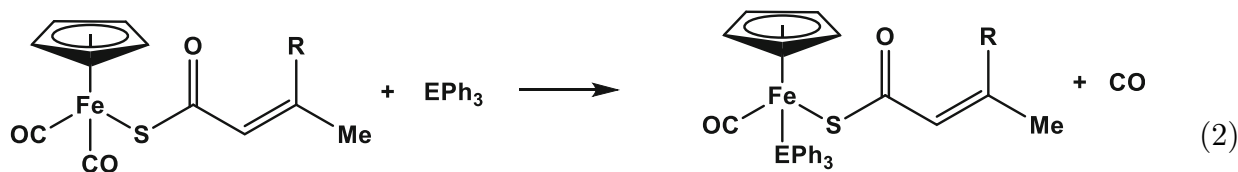


Figure 2. Molecular structure and numbering scheme of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCOCH}=\text{CMe}_2$ (4a). The ellipsoids represent a probability of 30%. The hydrogen atoms are shown with arbitrary radii.

2029–2040 cm^{-1} , which are comparable to those reported for the corresponding thiocarboxylates $\text{CpFe}(\text{CO})_2\text{-SCOR}$.^{8–10} The spectra also show two medium bands in the ranges of 1700–1702 and 1641–1658 cm^{-1} for the carbonyl group and the carbon-carbon double bond of the thiocarboxylato moiety, respectively. The carbonyl bands are found at higher wave numbers compared to similar systems due to less conjugated with the sulfur lone pairs or the C=C bond due to geometric factors. The $^1\text{H-NMR}$ spectra of complexes 1–3 display a singlet peak for the five equivalent Cp-protons in the 5.01–5.05 ppm range. This range is similar to those reported for thiocarboxylato complexes indicating similar electron density around the iron.^{8–10} The methyl groups of 1 and 3 are present in the spectra as doublet at 1.79 and 1.82 ppm, respectively. The spectrum of $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CMe}_2$ shows two singlet peaks at 1.80 and 2.06 ppm indicating two magnetically different methyl groups. The vinylic pro-

tons are also present in the spectra in the range of 6.09–6.98 ppm with the expected multiplicity. In the $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ spectra of 1–3; the peak in the 75.09–85.16 ppm range is due to the Cp-carbons while the ranges 201.87–211.91 and 199.22–189.79 ppm are due to the terminal and the ketonic carbonyl carbons, respectively. The vinylic carbons display their presence in the spectra in the range of 123.44–145.43 ppm and the number of peaks are equal to the number of vinylic carbons in each molecule. The methyl carbons for $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CMe}_2$ complex have two peaks at 20.17 ppm and 26.38 ppm indicating two magnetically different environments as proved by the $^1\text{H-NMR}$ spectrum of the same complex (*vide supra*). On the other hand, the methyl group of $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CHMe}$ is shown at 17.03 ppm and for $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{CH}=\text{CHMe}$ is at 18.80 ppm. The mass spectra of complexes 1–3 showed the molecular ion peak for all complexes followed by two peaks resulted from losing the two carbonyl groups consequently.

The photolytic CO-substitution reactions of the $\text{CpFe}(\text{CO})_2\text{SCOCH}=\text{C}(\text{R})(\text{Me})$ with EPh_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}$) produce mono-substituted complexes $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{-SCOCH}=\text{C}(\text{R})(\text{Me})$ in good yields (Equation 2).



R = Me; E = P (**4a**). R = H, E = As (**5b**), E = Sb (**5c**).

Complexes **4a** and **5b–c** were characterized by UV-Vis, IR, $^1\text{H-NMR}$ spectroscopy, elemental analysis and structure determination of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{-SCoCH=CMe}_2$. Their IR spectra contain a strong band in the range $1943\text{--}1955\text{ cm}^{-1}$ corresponding to the stretching frequency of the terminal carbonyl ligand. This band is shifted to a lower value compared to those of the starting complexes **1** and **2**. This shift might be caused by weak π -accepting properties of EPh_3 as reported for analogous systems.^{8,20} The spectra also contain a band in the range $1690\text{--}1700\text{ cm}^{-1}$ for the ketonic carbonyl group of the thiocarboxylato ligand, comparable to those of **1** and **2** and higher than those of the thiocarboxylato analogues ($1595\text{--}1618\text{ cm}^{-1}$).^{8,20} The vinylic groups ($\text{C}=\text{C}$) of thiocarboxylato ligand exhibit medium band in the $1575\text{--}1585\text{ cm}^{-1}$ range which are shifted to lower wave number compared to that of **1** and **2**. The cyclopentadienyl protons of **4a**, **5b** and **5c** show a singlet peak in the $4.49\text{--}4.53\text{ ppm}$ range in their $^1\text{H-NMR}$ spectra. This range is lower than that reported for the starting materials (**1**, **2**). This shift might be due to an increasing electron density at the iron center after one CO is substituted by EPh_3 ligands. The phenyl protons of the EPh_3 ligands are observed as multiplet peaks in the range $7.38\text{--}7.48\text{ ppm}$. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of these complexes show a peak in the $80.49\text{--}84.10\text{ ppm}$ range for the Cp-carbons. The carbon resonances of the terminal carbonyl group and the ketonic carbonyl of the thiocarboxylato ligands are displayed in the ranges $217.13\text{--}220.00\text{ ppm}$ and $202.10\text{--}204.38\text{ ppm}$, respectively. While the vinylic carbons are shown in the range of $132.24\text{--}142.46\text{ ppm}$. The peaks in the range $128.22\text{--}135.33\text{ ppm}$ are due to the phenyl carbons of EPh_3 . The methyl carbons for **4a** have two peaks at 20.19 ppm and 26.61 ppm indicating two magnetically different environments while the methyl groups of **5b** and **5c** are shown at 17.11 and 17.21 ppm , respectively. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **4a** shows a strong peak at 66.62 ppm for the phosphorus atom of the PPh_3 ligand.

3.2 Crystal structure of **2** and **4a**

X-ray quality crystals of the two complexes are obtained from a mixed solvent ($\text{CH}_2\text{Cl}_2/\text{hexane}$) and are shown in Figures 1 and 2, respectively. Both complexes display a three-legged piano-stool configuration at Fe in which the Cp-ring is bonded to iron in η^5 -mode. The Fe-C(Cp) bond distances {**2**: average = 2.095 \AA , **4a**: average = 2.104 \AA } are similar to the corresponding lengths of analogous complexes.^{8,20} The Fe-C(CO) bond distances of **2** ($1.773(3)$ and $1.778(3)\text{ \AA}$) are similar to the corresponding lengths of analogous complexes^{8,20,29–33} and are longer than that of **4a** ($1.754(2)\text{ \AA}$). This might be due to more π -back bonding to CO of **4a** resulted from the electron richness imposed by the presence of PPh_3 ligand. The Fe-S bond length (**2**: $2.2672(8)\text{ \AA}$, **4a**: $2.2674(6)\text{ \AA}$) is comparable to each other and to the values observed in another $\text{CpFe}(\text{CO})_2\text{SX}$ complexes (X = C(S)O-4- $\text{C}_6\text{H}_4\text{Cl}$: $2.2765(5)\text{ \AA}$, COCO_2Me : $2.2677(4)\text{ \AA}$, $\text{SO}_2\text{-CCl}_3$: $2.2803(13)\text{ \AA}$).^{29–33} The CO bond distance of thiocarboxylato carbonyl ligand of **2** ($1.224(3)\text{ \AA}$) and of **4a** ($1.230(3)\text{ \AA}$) are similar to those of $\text{CpFe}(\text{CO})_2\text{SCO-2-C}_4\text{H}_3\text{S}$ and $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SCO-2-C}_4\text{H}_3\text{S}$ complexes ($1.225(3)\text{--}1.234(4)\text{ \AA}$).⁸ The C=C bond length of thiocarboxylato ligand (**2**: $1.338(4)$, **4a**: $1.337(3)\text{ \AA}$) are of the normal C=C bond length indicating no resonances with the adjacent carbonyl group as proved by the IR data (Table 1). The angles around the iron-center (around 90°) showing pseudo octahedral geometry. The Fe-S-C1 angles {**2**: 106.92 , **4a**: 106.88° } indicate that the sulfur atoms have an sp^3 hybridization in these complexes. The thiocarboxylato group is almost planar as shown from the S-C-O, O-C-C and S-C-C bond angles which are all close to 120° .

3.3 UV-Visible spectroscopy of complexes **1–3**, **4a**, **5b** and **5c**

The electronic absorption spectra of complexes **1–3** were reported using dichloromethane solvent. Figure 3 presents the spectra of complexes **2** and **4a**. The spectra of **1–3** illustrate two absorption bands in the

Table 1. Selected bond length (Å) and selected bond angles (°) of CpFe(CO)₂SCOCH=CMe₂ (**2**) and CpFe(CO)(PPh₃)SCOCH=CMe₂ (**4d**).

2		4d	
Fe-C6	2.100(3)	Fe-C24	1.754(2)
Fe-C7	2.111(3)	Fe-P	2.2159(6)
Fe-C8	2.097(3)	Fe-C25	2.107(2)
Fe-C9	2.090(3)	Fe-C26	2.108(2)
Fe-C10	2.077(3)	Fe-C27	2.109(2)
Fe-C11	1.778(3)	Fe-C28	2.093(2)
Fe-C12	1.773(3)	Fe-C29	2.102(2)
Fe-S	2.2672(8)	Fe-S	2.2674(6)
S-C1	1.758(3)	S-C1	2.2674(6)
C1-O1	1.224(3)	C1-O1	1.230(2)
C1-C2	1.478(4)	C1-C2	1.482(3)
C2-C3	1.338(4)	C2-C3	1.337(3)
C11-Fe-C12	94.37(14)	C24-Fe-P	95.50(7)
C11-Fe-S	91.88(10)	C24-Fe-S	91.21 (7)
C12-Fe-S	91.50(10)	S-Fe-P	89.56(2)
Fe-S-C1	106.92(10)	Fe-S-C1	106.88(8)
S-C1-O1	123.2(2)	S-C1-O1	123.92(17)
O1-C1-C2	124.7(3)	O1-C1-C2	124.2(2)
C1-C2-C3	127.7(3)	C1-C2-C3	127.2(2)
S-C1-C2	112.1(2)	S-C1-C2	111.82(16)

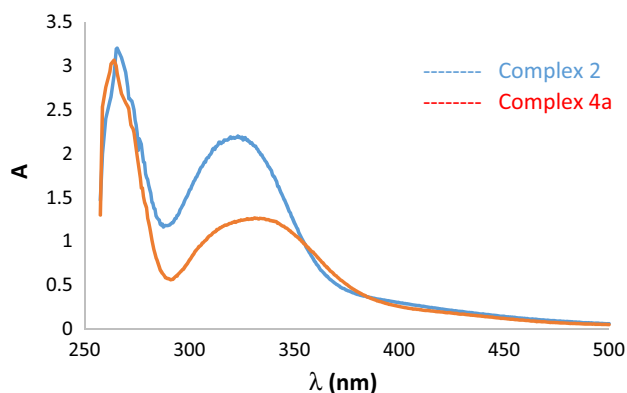


Figure 3. UV-Vis spectra of complexes **2** and **4a**.

ranges of 261–293 nm and 323–336 nm which is corresponding to ligand-ligand charge transfer (LLCT) band and to Fe (II) → CO (MLCT) transitions, respectively. These values are similar to those reported earlier.^{8,34} The analogous EPh₃ substituted complexes CpFe(CO)(EPh₃)SCOCH=C(R)(Me) **4a** and **5b,c** also show similar bands which are shifted to higher ranges (261–265 nm and 306–328 nm, respectively) compared to complexes **1–3**. This shift might be attributed to stabilization of the π*-LUMO orbital by coordination of the more electron donor EPh₃ ligand which reduces the energy of electronic transition resulting in red shift of the wave number.³⁵

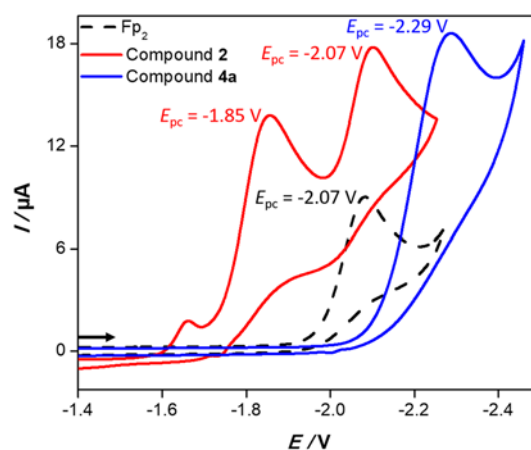


Figure 4. Cyclic voltammetry of 1.0 mM of **2** (red), **4a** (blue) and 0.05 M of **Fp₂** in CH₂Cl₂-[*n*-Bu₄N][BF₄] (0.1 M) at 0.2 V s⁻¹ scan rate. Glassy carbon disk (*d* = 1.6 mm). The arrow indicates the scan direction. The potential *E* is given in V and referenced to the Fc⁺/Fc couple.

3.4 Electrochemistry

The electrochemical behaviour of complexes **2** and **4a** has been analyzed in CH₂Cl₂-[*n*-Bu₄N][BF₄] (0.1 M) solutions at 0.2 V s⁻¹ scan rate as representative examples (Figure 4). Moreover, the electrochemistry of the iron dimer [CpFe(CO)₂]₂, **Fp₂**, was re-investigated to allow comparison with complexes **2** and **4a**. On initiating the electrochemical scan in the cathodic direction, two cathodic peaks at *E*_{pc} = -1.85 and -2.07 V were observed for complex **2**. On the other hand, the cyclic voltammogram of complex **4a** displays only one irreversible reduction event at *E*_{pc} = -2.29 V (Figure 4). Such behavior is similar to that reported for CpFe(CO)₂SeC(O)S^{*i*}Pr.³⁶ Therefore, the first reduction event (*E*_{pc} = -1.85 V) of complex **2** is attributed to the dissociation of the anion [SC(O)CH=CMe₂]⁻ and generated the radical intermediate [CpFe(CO)₂][•] (Fp[•]) species. The latter is then dimerized to give the iron dimer, **Fp₂**, which reduce at *E*_{pc} = -2.07 V accounting for the second reduction event in the cyclic voltammogram of **2**. In order to confirm the formation of **Fp₂** upon reduction of complex **2**, we have additionally performed an independent cyclic voltammetry of **Fp₂** and determined its reduction potential to be -2.07 V under the same conditions as shown in Figure 4 (black line).

It is evident from Figure 4 that the reduction event at *E*_{pc} = -2.29 V of complex **4a** is shifted about 440 mV to more negative potential compared to its parent complex **2**. This can be explained in terms of increasing the electron density at the iron atom due to weaker π-accepting properties of PPh₃ ligand compared to that of CO. This change in the electron

density can be also noted from the IR data of **2** compared to **4a**. This reduction event ($E_{pc} = -2.29$ V) may be attributed to the chemical processes, such as M–PPh₃ bond elongation or dissociation.

4. Conclusions

In summary, three iron complexes bearing vinyl-thiocarboxylato moieties have been successfully obtained and fully characterized. The CO-substitution reactions of representative examples by EPh₃ ligand produced the expected mono-substituted complexes. It is noteworthy that the replacement of one carbonyl group by EPh₃ leads to a shift in the terminal carbonyl frequencies to lower values and the peak of the Cp-protons to lower chemical shift values consistent with an increase of electron density around iron upon substitution. The X-ray structural analysis exhibits that both **2** and **4a** are piano-stool structures with approximately similar bond lengths. The UV-Vis spectra prove that the wave numbers of the substituted complexes are red-shifted compared to that of the parent dicarbonyl complexes. The CV of the dicarbonyl complexes showed two-irreversible peaks which are replaced by one peak, shifted to more negative values, upon substitution. The IR and X-ray data show that there are minimum resonances between the sulfur lone pairs, the C=O and C=C double bonds within the thiocarboxylato moieties.

Supplementary Information (SI)

Crystallographic data deposited at the Cambridge Crystallographic Data Centre under CCDC-1946639 for **2**, and CCDC-1946640 for **4a** 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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