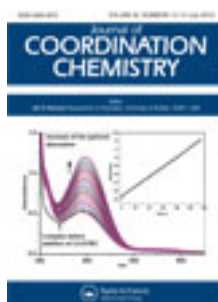


This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:36

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Heterocyclic thiocarboxylato complexes of iron: synthesis, characterization, electrochemistry, and reactions

Mohammad El-khateeb ^{a b}, Mousa Al-Noaimi ^c, Ala'a Al-Akhras ^b, Helmar Görls ^d & Wolfgang Weigand ^d

^a Chemistry Department, Faculty of Science and Arts at Alkamil Province, King Abdulaziz University, Alkamil 21931, Saudi Arabia

^b Chemistry Department, Faculty of Science, Jordan University of Science and Technology, Irbid 22110, Jordan

^c Chemistry Department, Hashemite University, Zarqa 13115, Jordan

^d Institut für Anorganische Chemie, Friedrich-Schiller-Universität Jena, Humboldtstrasse 8, Jena 07743, Germany

Accepted author version posted online: 29 May 2012. Published online: 13 Jun 2012.

To cite this article: Mohammad El-khateeb, Mousa Al-Noaimi, Ala'a Al-Akhras, Helmar Görls & Wolfgang Weigand (2012) Heterocyclic thiocarboxylato complexes of iron: synthesis, characterization, electrochemistry, and reactions, Journal of Coordination Chemistry, 65:14, 2510-2522, DOI: [10.1080/00958972.2012.698406](https://doi.org/10.1080/00958972.2012.698406)

To link to this article: <http://dx.doi.org/10.1080/00958972.2012.698406>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or

howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Heterocyclic thiocarboxylato complexes of iron: synthesis, characterization, electrochemistry, and reactions

MOHAMMAD EL-KHATEEB*^{†‡}, MOUSA AL-NOAIMI[§],
ALA'A AL-AKHRAS[‡], HELMAR GÖRLS[¶] and WOLFGANG WEIGAND[¶]

[†]Chemistry Department, Faculty of Science and Arts at Alkamil Province, King Abdulaziz University, Alkamil 21931, Saudi Arabia

[‡]Chemistry Department, Faculty of Science, Jordan University of Science and Technology, Irbid 22110, Jordan

[§]Chemistry Department, Hashemite University, Zarqa 13115, Jordan

[¶]Institut für Anorganische Chemie, Friedrich-Schiller-Universität Jena, Humboldtstrasse 8, Jena 07743, Germany

(Received 1 October 2011; in final form 24 April 2012)

Heterocyclic-thiocarboxylato complexes of iron, $\text{CpFe}(\text{CO})_2\text{SCO-het}$ (het = 2- $\text{C}_4\text{H}_3\text{O}$, 2- $\text{C}_4\text{H}_3\text{S}$, CH_2 -2- $\text{C}_4\text{H}_3\text{S}$), have been synthesized *via* the reaction of iron sulfides, (μ - S_x) [$\text{CpFe}(\text{CO})_2$]_x ($x = 3, 4$), with heterocyclic acid chlorides het-COCl. Photolytic substitutions of these complexes $\text{CpFe}(\text{CO})_2\text{SCO-het}$ with triphenylphosphine, triethylphosphite, triphenylarsine, and triphenylantimony [ER_3 (E = P, R = Ph, OC_2H_5 ; E = As, Sb, R = Ph)] exclusively gave the monosubstituted complexes $\text{CpFe}(\text{CO})(\text{ER}_3)\text{SCO-het}$ in good yields. The new complexes have been characterized by elemental analysis, UV-Vis, IR, ^1H , and ^{31}P NMR spectroscopies and by cyclic voltammetry for a representative family (**1**, **4a–d**). The solid state structures of $\text{CpFe}(\text{CO})_2\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**2**), $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5a**), $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5b**), and $\text{CpFe}(\text{CO})(\text{SbPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5c**) were determined by X-ray crystal structure analysis.

Keywords: Iron; Thiocarboxylates; Sulfur; Triphenylphosphine; Triphenylarsine; Triphenylantimony; Photolytic reactions; Complexes; Structures

1. Introduction

Thiocarboxylato ligands have two coordination sites; soft sulfur and hard oxygen enable them to coordinate to a variety of metal centers [1–3]. Their metal complexes are of continuing interest due to their bonding modes, reactivity, and use as metal sulfide or selenide precursors [4–7]. Biological studies on iron thiocarboxylates or selenocarboxylates showed antifungal activity on *Candida albicans* and antibacterial effects against *Bacillus subtilis* and *Staphylococcus aureus* [8]. Studies of the cytogenesis effects of $\text{CpFe}(\text{CO})_2\text{YCO}(\text{C}_6\text{H}_4)\text{COOH}$ (Y = S, Se) in cultured rat bone marrow cells proved that these two complexes altered cell division [9].

*Corresponding author. Email: kateeb@just.edu.jo

Organoiron thiocarboxylato complexes are accessible from the reaction of (μ -S_x) [Cp'Fe(CO)₂]₂ (Cp' = C₅H₅, Bu'^tC₅H₄, 1,3-(Bu'^t)₂C₅H₃; x = 1–4) with acid chlorides [10, 11]. These dicarbonyl thiocarboxylates undergo photolytic substitution reactions with EPh₃ (E = P, As, Sb) to produce mono-substituted complexes Cp'Fe(CO)(EPh₃)SCOR [12]. The di-substituted products (Cp'Fe(EPh₃)₂SCOR) were never obtained in these reactions due to electronic and steric factors [12]. However, analogous reactions with bis(diphenylphosphino)alkane ligands (Ph₂P(CH₂)_nPPh₂) gave either the monosubstituted complexes CpFe(CO)(κ P-Ph₂P(CH₂)_nPPh₂)SCOR for n = 1–6 and the di-substituted complexes CpFe(κ^2 P,P-Ph₂P(CH₂)_nPPh₂)SCOR only for n = 1 and 2 [13, 14].

Treatment of the sulfides (μ -S_x)[CpFe(CO)₂]₂ (x = 3, 4) with O-alkyl oxalyl chlorides gave the expected O-alkyl thiooxalato complexes CpFe(CO)₂SCOCO₂R [15]. In a similar way, the thiosulfonato complexes CpFe(CO)₂SSO₂R [16] were made from the same reagents and sulfonyl chlorides. Mono-, di-, or tri-thiocarbonato complexes CpFe(CO)₂SCY₂R (Y = O, S) were reported from the sulfides (μ -S_x)[CpFe(CO)₂]₂ and chloroformates (ROCOCl), chlorothionoformates (ROCSCl) or chlorodithioformates (RSCSCl), respectively [17–19].

In this article, we describe reactions of the iron sulfides (μ -S_x)[CpFe(CO)₂]₂ with acid chlorides bearing a heterocyclic group. The substitution reactions of the dicarbonyl iron complexes CpFe(CO)₂SCO-het with triphenylphosphine, triethylphosphite, triphenylarsine, and triphenylantimony are discussed.

2. Experimental

2.1. Materials and methods

All manipulations were performed using standard Schlenk techniques under nitrogen. Diethyl ether, hexane, tetrahydrofuran, and benzene were dried over sodium/benzophenone and were freshly distilled under nitrogen prior to use. Dichloromethane was heated under reflux over P₂O₅ and was freshly distilled under nitrogen prior to use. The compounds (μ -S_x)[CpFe(CO)₂]₂ (x = 3, 4) were prepared by previously published procedures [20]. The following chemicals were used as received (ACROS): iron dimer [CpFe(CO)₂]₂, 2-furan carbonyl chloride, 2-thiophene carbonyl chloride, 2-thiopheneacetyl chloride, triphenylphosphine, triethylphosphite, triphenylarsine, triphenylantimony, and elemental sulfur. Silica gel of particle size 0.063–0.200 mm (70–230 mesh) was dried at 110°C and employed for column chromatography.

All reaction steps were monitored by thin layer chromatography. Infrared (IR) spectra were recorded on a JASCO FT-IR spectrometer. Electronic spectra were recorded on a Shimadzu 240-UV-Visible spectrophotometer. Electrochemical measurements were performed in 99.8% anhydrous acetonitrile (ALDRICH, HPLC grade) using a computer controlled Volta Lab model PGP201 with a platinum working electrode, a platinum wire auxiliary electrode, and silver wire pseudo-reference electrode. Ferrocene (0.665 V vs. normal hydrogen electrode) is used as an internal reference [21]. A Haake D8-G refrigerated bath and circulator was used to maintain the cell temperature at 25.0 ± 0.1°C. Tetrabutylammonium hexafluorophosphate, twice recrystallized and vacuum dried at 110°C, was used as the supporting

electrolyte (0.1 mol L⁻¹). Experimental solutions were degassed by bubbling with nitrogen gas. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-Avance 400 MHz spectrometer. Chemical shifts are given in ppm relative to TMS (¹H) at 0 ppm and to H₃PO₄ (³¹P). Elemental analyses of C, H, and S were carried out on a Eurovector E.A.3000 instrument using copper sample tubes. Melting points were reported on an electrothermal melting point apparatus and are uncorrected. Photolytic reactions were carried out using a low pressure mercury lamp bought from Herauios.

2.2. General procedure for preparation of CpFe(CO)₂SCO-het, 1–3

A 100 mL Schlenk flask was charged with iron sulfides (μ-S_x)[CpFe(CO)₂]₂ (2.83 mmol) and 50 mL of diethyl ether. The acid chloride (3.40 mmol) was added by syringe. The resulting mixture was stirred overnight at room temperature, solvent was removed under vacuum and the residue was dissolved in 2 mL of CH₂Cl₂. This solution was introduced to a silica gel column and was eluted with hexane to remove any unreacted acid chloride. Elution with a mixture of dichloromethane and hexane (1:1 volume ratio) gave an orange band which was collected and identified as CpFe(CO)₂SCO-het, followed by a red band which was also collected and identified as CpFe(CO)₂Cl. The CpFe(CO)₂SCO-het was recrystallized from CH₂Cl₂/hexane at -4°C.

2.2.1. CpFe(CO)₂SCO(2-C₄H₃O) (1). Orange (78%); m.p.: 127–128°C. IR (CH₂Cl₂, cm⁻¹): ν_{C=O} 2045, 1999 (s); ν_{SC=O} 1604 (m). ¹H-NMR (CDCl₃): δ 5.08 (s, 5H, C₅H₅); 6.42 (dd, 1H, H_b); 7.08 (d, 1H, H_c); 7.49 (d, 1H, H_a). UV-Vis in acetonitrile: λ_{max} (nm) (ε_{max}, (mol L⁻¹)⁻¹ cm⁻¹): 321 (8.00 × 10³). Anal. Calcd for C₁₂H₈FeO₄S (%): C, 47.40; H, 2.65; S, 10.54. Found (%): C, 47.07; H, 2.62; S, 11.07.

2.2.2. CpFe(CO)₂SCO(2-C₄H₃S) (2). Orange (82%); m.p.: 144–145°C. IR (CH₂Cl₂, cm⁻¹): ν_{C=O} 2045, 1999 (s); ν_{SC=O} 1590 (m). ¹H-NMR (CDCl₃): δ 5.06 (s, 5H, C₅H₅); 7.00 (dd, 1H, H_b, J_{HH} = 4.4 Hz); 7.39 (d, 1H, H_c, J_{HH} = 4.8 Hz); 7.74 (d, 1H, H_a, J_{HH} = 3.2 Hz). UV-Vis in acetonitrile: λ_{max} (nm) (ε_{max}, (mol L⁻¹)⁻¹ cm⁻¹): 328 (8.00 × 10³). Anal. Calcd for C₁₂H₈FeO₃S₂ (%): C, 45.02; H, 2.52; S, 20.03. Found (%): C, 45.00; H, 2.57; S, 20.13.

2.2.3. CpFe(CO)₂SCO(2-CH₂C₄H₃S) (3). Orange (85%); m.p.: 157–158°C. IR (CH₂Cl₂, cm⁻¹): ν_{C=O} 2044, 1997 (s); ν_{SC=O} 1606 (m). ¹H-NMR (CDCl₃): δ 4.14 (s, 2H, CH₂); 4.89 (s, 5H, C₅H₅); 6.96 (d, 1H, H_b); 7.25 (m, 2H, H_b and H_c). UV-Vis in acetonitrile: λ_{max} (nm) (ε_{max}, (mol L⁻¹)⁻¹ cm⁻¹): 327 (7.22 × 10³). Anal. Calcd for C₁₃H₁₀FeO₃S₂ (%): C, 46.72; H, 3.02; S, 19.19. Found (%): C, 46.50; H, 3.00; S, 19.25.

2.3. General procedure for preparation of CpFe(CO)(ER₃)SCO-het, 4–6

A THF solution of CpFe(CO)₂SCO-het (1.00 mmol) and ER₃ (1.20 mmol) was irradiated by UV-light at 0°C until disappearance of bands at 2044–2045 cm⁻¹ and 1997–1999 cm⁻¹ and the appearance of a single band at 1947–1968 cm⁻¹. The volatiles were removed under reduced pressure and the resulting solid was redissolved in 2 mL of

CH_2Cl_2 and transferred to a silica gel column made up in hexane. The column was first eluted with hexane to remove any unreacted ER_3 . Elution with hexane/diethyl ether solution (1:1 volume ratio) gave a dark red band of the products. The product was recrystallized from dichloromethane/hexane at -4°C .

2.3.1. $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{O})$ (4a). Orange (77%); m.p.: 188–189°C. IR (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1960 (s); $\nu_{\text{SC}=\text{O}}$ 1603 (m). $^1\text{H-NMR}$ (CDCl_3): δ 4.58 (s, 5H, C_5H_5); 6.34 (d, 1H, H_b , $J_{\text{HH}}=2.6$ Hz); 6.95 (d, 1H, H_c , $J_{\text{HH}}=2.6$ Hz); 7.26 (m, 1H, H_a , $J_{\text{HH}}=2.6$ Hz), 7.39 (m, 15H, PPh_3). $^{31}\text{P-NMR}$ (CDCl_3): δ 100. UV-Vis in acetonitrile: λ_{max} (nm) (ϵ_{max} , $(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$): 331 (8.20×10^3). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{FeO}_3\text{PS}$ (%): C, 64.70; H, 4.31; S, 5.96. Found (%): C, 63.94; H, 4.26; S, 6.01.

2.3.2. $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{O})$ (4b). Dark red (68%); m.p.: 162–163°C. IR (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1960 (s); $\nu_{\text{SC}=\text{O}}$ 1603 (m). $^1\text{H-NMR}$ (CDCl_3): δ 4.66 (s, 5H, C_5H_5); 6.34 (d, 1H, H_b , $J_{\text{HH}}=2.8$ Hz); 6.94 (d, 1H, H_c , $J_{\text{HH}}=2.8$ Hz); 7.27 (m, 2H, H_a , $J_{\text{HH}}=2.8$ Hz), 7.40 (m, 15H, AsPh_3). UV-Vis in acetonitrile: λ_{max} (nm) (ϵ_{max} , $(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$): 330 (8.10×10^3). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{FeO}_3\text{SAs} \cdot 0.25\text{CH}_2\text{Cl}_2$ (%): C, 58.21; H, 3.92; S, 5.31. Found (%): C, 57.98; H, 3.95; S, 5.52.

2.3.3. $\text{CpFe}(\text{CO})(\text{SbPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{O})$ (4c). Black red (60%); m.p.: 128–130°C. IR (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1951 (s); $\nu_{\text{SC}=\text{O}}$ 1607 (m). $^1\text{H-NMR}$ (CDCl_3): δ 4.74 (s, 5H, C_5H_5); 6.26 (dd, 1H, H_b , $J_{\text{HH}}=2.6, 3.4$ Hz); 6.78 (d, 1H, H_c , $J_{\text{HH}}=2.6$ Hz); 7.26 (m, 2H, H_a , $J_{\text{HH}}=3.4$ Hz); 7.39 (m, 9H, SbPh_3); 7.54 (m, 6H, SbPh_3). UV-Vis in acetonitrile: λ_{max} (nm) (ϵ_{max} , $(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$): 334 (8.00×10^3). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{FeO}_3\text{SSb}$ (%): C, 55.36; H, 3.68; S, 5.10. Found (%): C, 54.92; H, 3.63; S, 5.34.

2.3.4. $\text{CpFe}(\text{CO})(\text{P}(\text{OEt})_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{O})$ (4d). Red (78%); m.p.: 128–129°C. IR (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1968 (s); $\nu_{\text{SC}=\text{O}}$ 1595 (m). $^1\text{H-NMR}$ (CDCl_3): δ 1.29 (m, 9H, CH_3); 4.00 (m, 6H, CH_2); 4.79 (s, 5H, C_5H_5); 6.39 (d, 1H, H_b , $J_{\text{HH}}=3.4$ Hz); 7.03 (d, 1H, H_c , $J_{\text{HH}}=3.4$ Hz); 7.45 (m, 1H, H_a , $J_{\text{HH}}=3.4$ Hz). $^{31}\text{P-NMR}$ (CDCl_3): δ 239. UV-Vis in acetonitrile: λ_{max} (nm) (ϵ_{max} , $(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$): 335 (7.85×10^3). Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{FeO}_6\text{PS}$ (%): C, 46.17; H, 5.24; S, 7.25. Found (%): C, 45.63; H, 5.21; S, 7.62.

2.3.5. $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (5a). Orange (80%); m.p.: 174–175°C. IR (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1959 (s); $\nu_{\text{SC}=\text{O}}$ 1604 (m). $^1\text{H-NMR}$ (CDCl_3): δ 4.61 (s, 5H, C_5H_5); 6.95 (dd, 1H, H_b , $J_{\text{HH}}=3.9, 4.1$ Hz); 7.32 (d, 1H, H_c , $J_{\text{HH}}=4.1$ Hz); 7.45 (m, 1H, H_a , $J_{\text{HH}}=3.9$ Hz), 7.37 (m, 15H, PPh_3). $^{31}\text{P-NMR}$ (CDCl_3): δ 101. UV-Vis in acetonitrile: λ_{max} (nm) (ϵ_{max} , $(\text{mol L}^{-1})^{-1}\text{cm}^{-1}$): 349 (7.61×10^3). Anal. Calcd for $\text{C}_{29}\text{H}_{23}\text{FeO}_2\text{PS}_2$ (%): C, 62.82; H, 4.18; S, 11.57. Found (%): C, 62.71; H, 4.22; S, 10.92.

2.3.6. $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (5b). Dark red (70%); m.p.: 155–156°C. IR (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ 1959 (s); $\nu_{\text{SC}=\text{O}}$ 1603 (m). $^1\text{H-NMR}$ (CDCl_3): δ 4.67 (s, 5H, C_5H_5); 6.93 (d, 1H, H_b , $J_{\text{HH}}=4.8$ Hz); 7.31 (d, 1H, H_c , $J_{\text{HH}}=3.1$ Hz); 7.42 (m, 1H, H_a , $J_{\text{HH}}=4.8$ Hz), 7.39 (m, 15H, AsPh_3). UV-Vis in acetonitrile: λ_{max} (nm)

(ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 355 (7.92 × 10³). Anal. Calcd for C₂₉H₂₃FeO₂S₂As (%): C, 58.21; H, 3.87; S, 10.72. Found (%): C, 58.10; H, 3.77; S, 10.32.

2.3.7. CpFe(CO)(SbPh₃)SCO(2-C₄H₃S) (5c). Black red (60%); m.p.: 158–160°C. IR (CH₂Cl₂, cm⁻¹): $\nu_{\text{C=O}}$ 1949 (s); $\nu_{\text{SC=O}}$ 1603 (m). ¹H-NMR (CDCl₃): δ 4.75 (s, 5H, C₅H₅); 6.86 (dd, 1H, H_b, $J_{\text{HH}} = 4.2, 4.3$ Hz); 7.25 (d, 1H, H_c, $J_{\text{HH}} = 4.2$ Hz); 7.35 (m, 9H, SbPh₃); 7.44 (m, 1H, H_a, $J_{\text{HH}} = 4.3$ Hz); 7.55 (m, 6H, SbPh₃). UV-Vis in acetonitrile: λ_{\max} (nm) (ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 357 (8.46 × 10³). Anal. Calcd for C₂₉H₂₃FeO₂S₂Sb (%): C, 53.98; H, 3.59; S, 9.94. Found (%): C, 53.43; H, 3.60; S, 9.42.

2.3.8. CpFe(CO)(P(OEt)₃)SCO(2-C₄H₃S) (5d). Red (82%); m.p.: 100–101°C. IR (CH₂Cl₂, cm⁻¹): $\nu_{\text{C=O}}$ 1968 (s); $\nu_{\text{SC=O}}$ 1603 (m). ¹H-NMR (CDCl₃): δ 1.29 (m, 9H, CH₃); 4.02 (m, 6H, CH₂); 4.80 (s, 5H, C₅H₅); 7.00 (d, 1H, H_b, $J_{\text{HH}} = 4.4, 4.2$ Hz); 7.03 (d, 1H, H_c, $J_{\text{HH}} = 4.2$ Hz); 7.45 (m, 1H, H_a, $J_{\text{HH}} = 4.3$ Hz). ³¹P-NMR (CDCl₃): δ 238. UV-Vis in acetonitrile: λ_{\max} (nm) (ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 360 (7.50 × 10³). Anal. Calcd for C₁₇H₂₃FeO₃PS₂ (%): C, 44.55; H, 5.06; S, 13.99. Found (%): C, 43.81; H, 5.19; S, 13.34.

2.3.9. CpFe(CO)(PPh₃)SCO(2-CH₂C₄H₃S) (6a). Orange (76%); m.p.: 158–159°C. IR (CH₂Cl₂, cm⁻¹): $\nu_{\text{C=O}}$ 1958 (s); $\nu_{\text{SC=O}}$ 1617 (m). ¹H-NMR (CDCl₃): δ 4.05 (s, 2H, CH₂); 4.52 (s, 5H, C₅H₅); 6.82 (dd, 1H, H_b, $J_{\text{HH}} = 4.0, 4.1$ Hz); 6.90 (d, 1H, H_c, $J_{\text{HH}} = 4.0$ Hz); 7.13 (d, 1H, H_a, $J_{\text{HH}} = 4.1$ Hz); 7.38 (m, 15H, PPh₃). ³¹P-NMR (CDCl₃): δ 98. UV-Vis in acetonitrile: λ_{\max} (nm) (ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 397 (7.26 × 10³). Anal. Calcd for C₃₀H₂₅FeO₂PS₂ (%): C, 63.39; H, 4.43; S, 11.28. Found (%): C, 62.97; H, 4.40; S, 11.63.

2.3.10. CpFe(CO)(AsPh₃)SCO(2-CH₂C₄H₃S) (6b). Dark red (72%); m.p.: 115–116°C. IR (CH₂Cl₂, cm⁻¹): $\nu_{\text{C=O}}$ 1959 (s); $\nu_{\text{SC=O}}$ 1618 (m). ¹H-NMR (CDCl₃): δ 4.02 (s, 2H, CH₂); 4.58 (s, 5H, C₅H₅); 6.77 (d, 1H, H_b, $J_{\text{HH}} = 4.8$ Hz); 6.96 (d, 1H, H_c, $J_{\text{HH}} = 3.3$ Hz); 7.11 (m, 1H, H_a, $J_{\text{HH}} = 4.8$ Hz); 7.37 (m, 15H, AsPh₃). UV-Vis in acetonitrile: λ_{\max} (nm) (ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 408 (8.00 × 10³). Anal. Calcd for C₃₀H₂₅FeO₂S₂As · 0.5CH₂Cl₂ (%): C, 55.94; H, 4.00; S, 9.79. Found (%): C, 55.65; H, 4.12; S, 10.27.

2.3.11. CpFe(CO)(SbPh₃)SCO(2-CH₂C₄H₃S) (6c). Black red (55%); m.p.: 129–130°C. IR (CH₂Cl₂, cm⁻¹): $\nu_{\text{C=O}}$ 1947 (s); $\nu_{\text{SC=O}}$ 1603 (m). ¹H-NMR (CDCl₃): δ 3.72 (dd, 2H, CH₂, $J_{\text{HH}} = 15.7, 4.0$); 4.67 (s, 5H, C₅H₅); 5.59 (dd, 1H, H_b, $J_{\text{HH}} = 4.3, 3.7$ Hz); 7.09 (d, 1H, H_c, $J_{\text{HH}} = 4.3$ Hz); 7.35 (m, 1H, H_a, $J_{\text{HH}} = 3.7$ Hz); 7.38 (m, 9H, SbPh₃); 7.50 (m, 6H, SbPh₃). UV-Vis in acetonitrile: λ_{\max} (nm) (ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 401 (7.40 × 10³). Anal. Calcd for C₃₀H₂₅FeO₂S₂Sb (%): C, 54.66; H, 3.82; S, 9.73. Found (%): C, 54.07; H, 3.79; S, 9.73.

2.3.12. CpFe(CO)(P(OEt)₃)SCO(2-CH₂C₄H₃S) (6d). Red (80%); m.p.: 111–112°C. IR (CH₂Cl₂, cm⁻¹): $\nu_{\text{C=O}}$ 1967 (s); $\nu_{\text{SC=O}}$ 1607 (m). ¹H-NMR (CDCl₃): δ 1.25 (m, 9H, CH₃); 4.01 (m, 6H, CH₂); 4.13 (s, 2H, CH₂); 4.54 (s, 5H, C₅H₅); 6.86 (d, 1H, H_b, $J_{\text{HH}} = 4.0, 4.0$ Hz); 7.09 (d, 1H, H_c, $J_{\text{HH}} = 4.0$ Hz); 7.25 (m, 1H, H_a, $J_{\text{HH}} = 4.0$ Hz). ³¹P-

NMR (CDCl₃): δ 236. UV-Vis in acetonitrile: λ_{\max} (nm) (ϵ_{\max} , (mol L⁻¹)⁻¹ cm⁻¹): 388 (7.22 × 10³). Anal. Calcd for C₁₈H₂₅FeO₅PS₂ (%): C, 44.55; H, 5.06; S, 13.99. Found (%): C, 43.81; H, 5.19; S, 13.34.

2.4. Crystallographic analysis of CpFe(CO)₂SCO(2-C₄H₃S) (2), CpFe(CO)(PPh₃)SCO(2-C₄H₃S) (5a), CpFe(CO)(AsPh₃)SCO(2-C₄H₃S) (5b), and CpFe(CO)(SbPh₃)SCO(2-C₄H₃S) (5c)

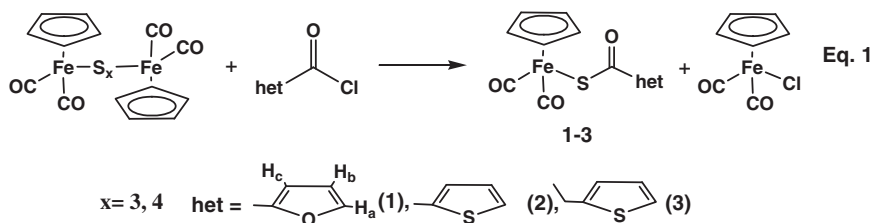
Single-crystals suitable for X-ray structure analysis of **2**, **5a**, **5b**, and **5c** were obtained by recrystallization from CH₂Cl₂/hexane. The X-ray diffraction intensity data for these compounds were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects [22, 23]. Crystallographic data as well as structure solution and refinement details are summarized in table 1.

The structures were solved by direct methods (SHELXS [23]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97 [24]). All hydrogen positions were included at calculated positions with fixed thermal parameters. All non-disordered non-hydrogen atoms were refined anisotropically [24]. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

3. Results and discussion

3.1. Synthesis of complexes

Heterocyclic thiocarboxylato complexes of iron CpFe(CO)₂SCO-het, **1–3** are readily synthesized by reaction of iron sulfides (μ -S_x)[CpFe(CO)₂]₂ with the corresponding heterocyclic acid chlorides as shown in equation 1.



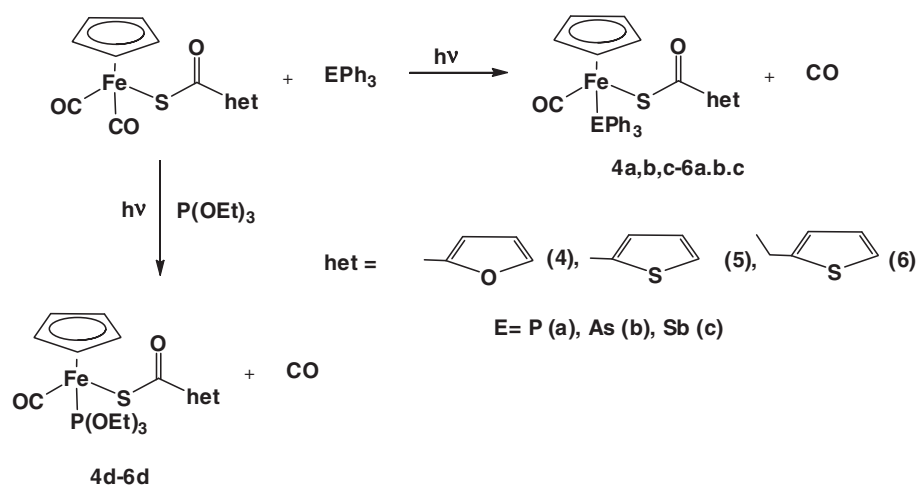
Complexes **1–3** are orange crystals, stable to air as solids and are identified based on spectroscopy, elemental analysis, and X-ray structure determination for **2**. IR spectra of **1–3** show two strong CO-stretching bands at 2044–2045 and 1997–1999 cm⁻¹, within the range observed for alkyl or aryl thiocarboxylato analogs CpFe(CO)₂SCOR (2027–2060 and 1984–1998 cm⁻¹) [10, 11]. The spectra also contain a band of medium intensity at 1590–1606 cm⁻¹ for ketonic carbonyl of the thiocarboxylate, which is also comparable to those reported for the corresponding alkyl or aryl thiocarboxylates CpFe(CO)₂SCOR (1595–1613 cm⁻¹) [10, 11].

¹H-NMR spectra of **1–3** exhibit a singlet at 4.89–5.08 ppm for the Cp. This chemical shift range is similar to that observed for alkyl or aryl thiocarboxylate (5.00–5.13 ppm)

Table 1. Crystallographic data and refinement details for CpFe(CO)₂SCO(2-C₄H₃S) (2), CpFe(CO)(PPh₃)SCO(2-C₄H₃S) (5a), CpFe(CO)(AsPh₃)SCO(2-C₄H₃S) (5b), and CpFe(CO)(SbPh₃)SCO(2-C₄H₃S) (5c).

	2	5a	5b	5c
CCDC No.	806381	806382	806383	806384
Empirical formula	C ₁₂ H ₈ FeO ₅ S ₂	C ₂₀ H ₁₂ FeO ₅ PS ₂	C ₂₀ H ₁₂ FeO ₅ AsS ₂	C ₂₀ H ₁₂ FeO ₅ SbS ₂
Formula weight (g mol ⁻¹)	320.15	554.41	598.36	645.19
Temperature (K)	183(2)	183(2)	183(2)	183(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1
Unit cell dimensions (Å, °)				
<i>a</i>	9.3113(3)	10.5782(4)	10.4881(4)	8.0694(3)
<i>b</i>	10.7475(5)	14.1678(7)	14.3191(6)	9.3480(3)
<i>c</i>	13.2069(6)	17.1817(9)	17.5130(7)	18.2986(6)
α	90	90	90	98.960(2)
β	106.487(2)	98.402(3)	99.488(3)	91.526(2)
γ	90	90	90	107.705(2)
Volume (Å ³), <i>Z</i>	1267.32(9), 4	2547.4(2), 4	2594.13(18), 4	1294.87(8), 2
Calculated density (Mg m ⁻³)	1.678	1.446	1.532	1.655
Absorption coefficient (mm ⁻¹)	1.513	0.844	2.033	1.790
<i>F</i> (000)	486	1144	1216	644
Crystal size (mm ³)	0.05 × 0.05 × 0.04	0.04 × 0.04 × 0.04	0.04 × 0.04 × 0.04	0.04 × 0.04 × 0.04
θ range for data collection (°)	2.97–27.49	2.43–27.47	2.75–27.47	2.93–27.43
Limiting indices	-12 ≤ <i>h</i> ≤ 11; -12 ≤ <i>k</i> ≤ 13; -15 ≤ <i>l</i> ≤ 17	-13 ≤ <i>h</i> ≤ 13; -18 ≤ <i>k</i> ≤ 14; -22 ≤ <i>l</i> ≤ 21	-13 ≤ <i>h</i> ≤ 13; -18 ≤ <i>k</i> ≤ 17; -22 ≤ <i>l</i> ≤ 22	-10 ≤ <i>h</i> ≤ 8; -12 ≤ <i>k</i> ≤ 12; -23 ≤ <i>l</i> ≤ 22
Reflections collected	8307	16,830	18,106	8834
Independent reflections	2880 [<i>R</i> (int) = 0.0370]	5731 [<i>R</i> (int) = 0.0782]	5948 [<i>R</i> (int) = 0.0559]	5845 [<i>R</i> (int) = 0.0291]
Completeness to $\theta = 27.50$ (%)	99.3	98.4	99.8	98.7
Data/restraints/parameters	2880/0/163	5731/0/335	5948/0/329	5845/0/329
Goodness-of-fit on <i>F</i> ² ^b	1.009	0.937	0.973	0.987
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0323, <i>wR</i> ₂ = 0.0751	<i>R</i> ₁ = 0.0444, <i>wR</i> ₂ = 0.0834	<i>R</i> ₁ = 0.0381, <i>wR</i> ₂ = 0.0767	<i>R</i> ₁ = 0.0361, <i>wR</i> ₂ = 0.0746
<i>R</i> indices (all) ^a	<i>R</i> ₁ = 0.0477, <i>wR</i> ₂ = 0.0815	<i>R</i> ₁ = 0.1062, <i>wR</i> ₂ = 0.1012	<i>R</i> ₁ = 0.0774, <i>wR</i> ₂ = 0.0890	<i>R</i> ₁ = 0.0571, <i>wR</i> ₂ = 0.0829
Largest difference peak and hole (e.Å ⁻³)	0.389 and -0.409	0.315 and -0.344	0.419 and -0.462	0.826 and -0.745
Absorption method	None	None	None	None

^a*R*₁ = $(\sum |F_o| - |F_c|) / \sum |F_o|$; *wR*₂ = $(\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2 + F_c^2)])^{1/2}$; *w*⁻¹ = $\sigma^2(F_o^2) + (aP)^2 + bP$; *P* = $[2F_o^2 + \text{Max}(F_o^2)]/3$.
^b*S*₂ = $(\sum [w(F_o^2 - F_c^2)^2] / (N_o - N_p))^{1/2}$.



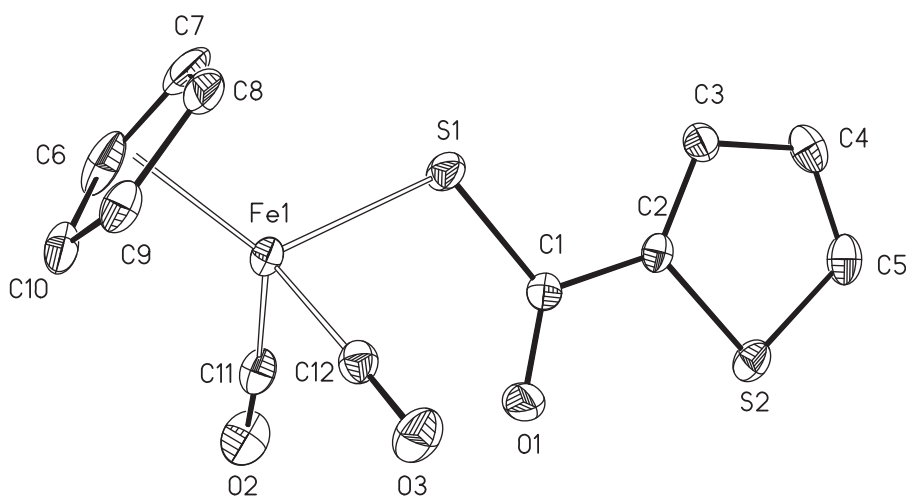
Scheme 1. Synthesis of the substituted complexes 4–6.

[10, 11] and thiocarbonate (4.98–5.12 ppm) analogs [17]. Resonances of the protons of the heterocycle of **1** and **2** appear as two doublets at 7.48–7.74 ppm for H_a and 7.07–7.39 ppm for H_c and as a doublet of doublets at 6.42–7.00 ppm for H_b (equation (1)). For **3** resonances of the protons of heterocycle are a doublet at 6.96 ppm for H_c and a multiplet at 7.25 for H_b and H_a . These chemical shifts are similar to those observed for heterocyclic-thiolato ruthenium complexes $\text{CpRu}(\text{PPh}_3)_2(\text{SC}_4\text{H}_3\text{E})$ ($\text{E} = \text{O}$ or S) [25].

Photolytic CO-substitution of **1–3** with excess triphenylphosphine, triethylphosphite, triphenylarsine, or triphenylantimony gave exclusively the mono-substituted complexes $\text{CpFe}(\text{CO})(\text{ER}_3)\text{SCO-het}$ in good yields (scheme 1).

IR spectra of **4–6** contain a strong band at $1947\text{--}1968\text{ cm}^{-1}$ corresponding to terminal carbonyl. This band is shifted to lower wavenumber compared to that of **1–3**. This shift might be attributed to weaker π -acid character of ER_3 compared to that of CO. A similar shift was also observed in the corresponding alkyl or aryl thiocarboxylate systems [26]. The stretching frequency of the carbonyl-thiocarboxylato ligands are at $1595\text{--}1618\text{ cm}^{-1}$, similar to that observed for $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SCOR}$ ($1558\text{--}1610\text{ cm}^{-1}$). The CO stretching frequency of the terminal carbonyl for the triethylphosphite complexes (**4d–6d**) is higher than those of **4a–c** to **6a–c**, in accord with the π -accepting properties of $\text{P}(\text{OEt})_3$. The CO stretching frequencies for these complexes are almost equal for PPh_3 and AsPh_3 adducts but are higher for the corresponding SbPh_3 derivatives.

$^1\text{H-NMR}$ spectra of **4–6** show a singlet due to cyclopentadienyl at 4.52–4.80 ppm. This range is upfield compared to that of the starting dicarbonyl complexes $\text{CpFe}(\text{CO})_2\text{SCO-het}$ (4.89–5.08 ppm). This shift may reflect an increase in electron density at Fe following substitution of one carbonyl by ER_3 . The phenyl protons of EPh_3 are at 7.35–7.55 ppm as one ($\text{E} = \text{P}, \text{As}$) or two multiplets ($\text{E} = \text{Sb}$). The CH_2CH_3 protons of $\text{P}(\text{OEt})_3$ complexes appeared as two multiplets, one (4.00–4.02 ppm) for the CH_2 and one (1.25–1.29 ppm) for methyl. These chemical shifts are lower than those observed for dithiocarbonate complexes $\text{CpFe}(\text{CO})(\text{P}(\text{OEt})_3)\text{SCSOR}$ (1.52 (CH_3); 4.35 (CH_2)) [27]. The $^{31}\text{P-NMR}$ spectra of **4a–6a** show a singlet at 98–101 ppm whereas those

Figure 1. Molecular structure of CpFe(CO)₂SCO(2-C₄H₃S) (**2**).Table 2. Selected bond lengths (Å) and angles (°) of **2**, **5a**, **5b**, and **5c**.

2		5a		5b		5c	
Fe–S1	2.2691(6)	Fe–S	2.2708(8)	Fe–S	2.2734(8)	Fe–S	2.2665(10)
Fe–C11	1.777(2)	Fe–P	2.2284(9)	Fe–As	2.3258(5)	Fe–Sb	2.4777(5)
Fe–C12	1.773(2)	Fe–C11	1.752(3)	Fe–C11	1.749(3)	Fe–C11	1.751(4)
Fe–C6	2.091(3)	Fe–C6	2.100(3)	Fe–C6	2.080(3)	Fe–C6	2.093(3)
Fe–C7	2.090(3)	Fe–C7	2.092(3)	Fe–C7	2.089(3)	Fe–C7	2.084(3)
Fe–C8	2.091(2)	Fe–C8	2.105(3)	Fe–C8	2.096(3)	Fe–C8	2.099(3)
Fe–C9	2.091(2)	Fe–C9	2.115(3)	Fe–C9	2.110(3)	Fe–C9	2.114(4)
Fe–C10	2.085(2)	Fe–C10	2.102(3)	Fe–C10	2.086(3)	Fe–C10	2.109(4)
S1–C1	1.737(2)	S–C1	1.742(3)	S–C1	1.740(3)	S–C1	1.739(3)
C1–O1	1.225(3)	O1–C1	1.225(3)	O1–C1	1.226(4)	O1–C1	1.234(4)
C1–S–Fe	107.79(8)	Fe–S–C1	107.86(10)	Fe–S–C1	107.87(10)	Fe–S–C1	109.67(12)
C11–Fe–S	94.27(8)	C11–Fe–S	93.60(9)	C11–Fe–S	92.36(10)	C11–Fe–S	88.72(12)
C12–Fe–S	92.05(7)	P–Fe–S	87.27(3)	As–Fe–S	86.46(2)	Sb–Fe–S	93.10(3)
C11–Fe–C12	94.00(10)	P–Fe–C11	94.09(10)	As–Fe–C11	94.63(10)	Sb–Fe–C11	91.87(10)
S–C1–O1	125.13(17)	S–C1–O1	126.1(2)	S–C1–O1	125.8(2)	S–C1–O1	124.7(3)

of **4d–6d** exhibit a similar singlet at 236–239 ppm for the phosphine or phosphite. These data are comparable to those observed for cyclopentadienyl iron complexes containing phosphine or phosphite ligands [28–30].

3.2. Crystal structures of **2** and **5a–c**

Crystal structure of CpFe(CO)₂SCO(2-C₄H₃S), **2**, is shown in figure 1 and selected bond lengths and angles of this complex are listed in table 2. The complex displayed a three legged piano-stool configuration at Fe with η⁵-cyclopentadienyl. The Fe–C(Cp) (average = 2.09 Å) and Fe–C(O) (1.777(2), 1.773(2) Å) bond lengths of **2** are similar to those found in other CpFe(CO)₂-containing complexes [17–19]. The Fe–S bond distance of **2** (2.2691(6) Å) and C–O bond length of the ketonic carbonyl group of the

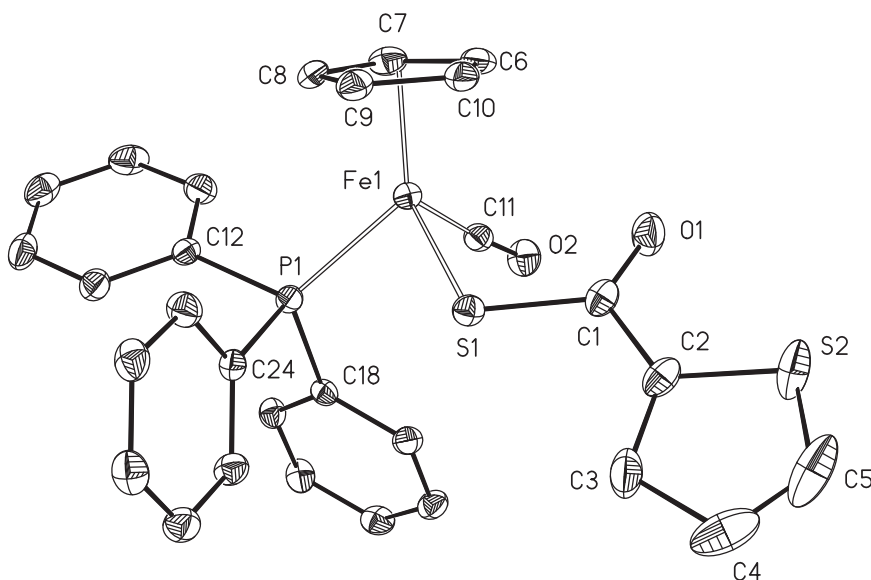


Figure 2. Molecular structure of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5a**).

thiocarboxylato ligand ($1.225(3)\text{ \AA}$) are also comparable to those found in $\text{CpFe}(\text{CO})_2\text{SC}(=\text{O})\text{X}$ complexes. Angles around iron (S1-Fe-C11 , S1-Fe-C12 , and C11-Fe-C12) are about 90° . The Fe-S-C1 angle of $107.79(8)^\circ$ is consistent with sp^3 hybridization of sulfur.

Structures of $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5a**), $\text{CpFe}(\text{CO})(\text{AsPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5b**), and $\text{CpFe}(\text{CO})(\text{SbPh}_3)\text{SCO}(2\text{-C}_4\text{H}_3\text{S})$ (**5c**) are shown in figures 2–4, respectively. Relevant bond parameters are listed in table 2. These complexes also adopt a three legged piano-stool with $\eta^5\text{-Cp}$ as the seat. The $\text{Fe-C}(\text{O})$ bond distances in these molecules are comparable, $1.749\text{--}1.752\text{ \AA}$, moderately shorter than the corresponding lengths in **2** (average = 1.775 \AA). This is due to stronger σ -donor ability and weaker π -accepting ability of ER_3 compared to carbonyl. The Fe-S bond distances in **5a**, **5b**, and **5c** of $2.2708(8)$, $2.2734(8)\text{ \AA}$, and $2.2665(10)\text{ \AA}$, respectively, are similar. However, those of **5a** and **5b** are longer than that of **2** but the corresponding bond of **5c** is close to that of **2** (2.2691 \AA). The C-O bond lengths of the ketonic carbonyl group attached to sulfur are comparable to those found in $\text{CpFe}(\text{CO})_2\text{SCOZ}$ [$\text{Z} = 2\text{-O}_2\text{NC}_6\text{H}_4$ ($1.209(5)\text{ \AA}$), $3\text{-C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{Ph}$ ($1.224(6)\text{ \AA}$), $3,5\text{-C}_6\text{H}_3(\text{COCl})_2$ ($1.216(6)\text{ \AA}$)] [9, 31, 32]. A noticeable increase in the E-Fe-S bond angle is observed going from $\text{E}=\text{P}$ to $\text{E}=\text{Sb}$ in accord with the size of the E-atom and is accompanied by a decrease in $\text{S-Fe-C}(\text{O})$ bond angle in the same order.

3.3. Electrochemistry

Cyclic voltammograms are reported for **1** and **4a-d** (table 3). Complex **4a**, as a representative example (Supplementary material), displayed a quasi-reversible oxidation at 0.79 V attributed to metal-centered $\text{Fe}(\text{III}/\text{II})$ couple [33]. This couple is affected by the electron-donor ability of ER_3 . However, the half-wave potential of

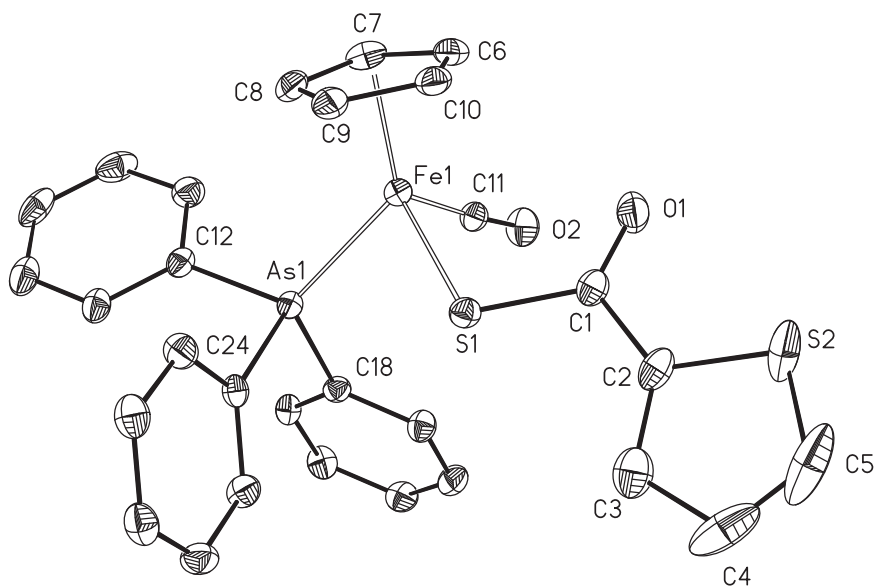


Figure 3. Molecular structure of $\text{CpFe(CO)(AsPh}_3\text{)SCO(2-C}_4\text{H}_3\text{S)}$ (**5b**).

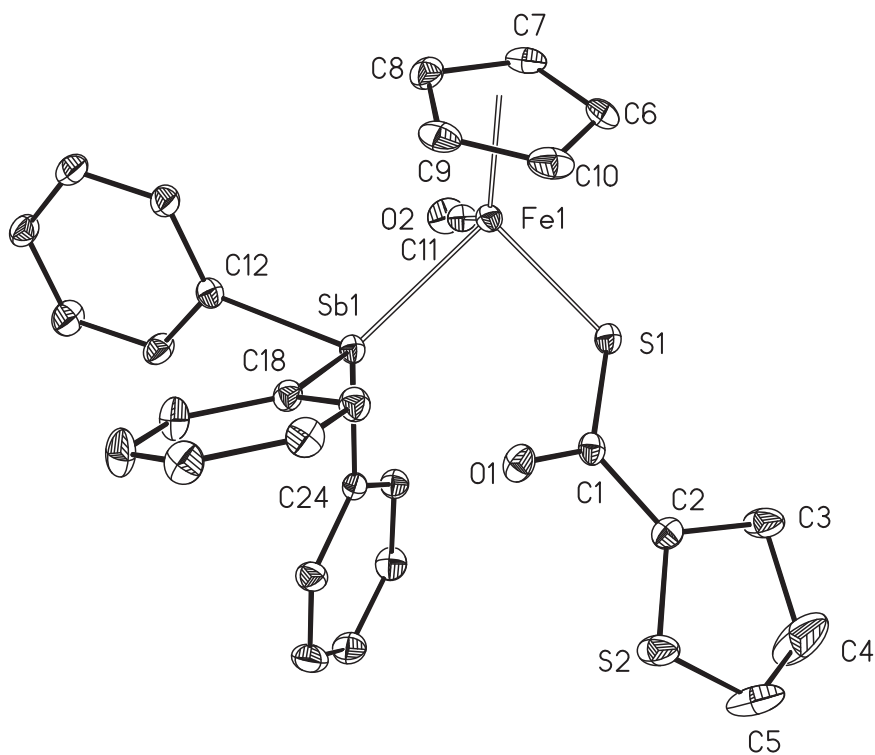


Figure 4. Molecular structure of $\text{CpFe(CO)(SbPh}_3\text{)SCO(2-C}_4\text{H}_3\text{S)}$ (**5c**).

Table 3. Cyclic voltammetric and electronic spectroscopic data of **1** and **4a–d**.

Complex	$(E_{1/2}^0, \text{V})^{\text{a,b}}$	Electronic spectra λ_{max} (nm)
1	1.14	321
4a	0.79	331
4b	0.83	330
4c	0.71	334
4d	0.83	335

^aSolvent: MeCN, supporting electrolyte: Bu₄NPF₆ (0.1 mol L⁻¹), scan rate: 0.1 V s, Pt-disc working electrode, Pt-wire auxiliary electrode, reference electrode Ag at 25°C.

^b $E_{1/2}^0 \text{ M} = (E_{\text{pa}}^0 + E_{\text{pc}}^0)/2$.

CpFe(CO)₂SCO(2-C₄H₃O) (**1**) was shifted anodically by ~300 mV compared to those observed for **4a–d**. This anodic shift can be explained by the difference in electron density added to the metal center by the presence of the σ -donor (ER₃) relative to CO. Based on the data provided in table 3, the largest shift of the Fe(III/II) redox couple relative to **1** is observed for **4c** (SbPh₃) followed by **4a** (PPh₃) with **4b** (AsPh₃) and **4d** (P(OEt)₃) being essentially equal. The shift for Fe(III/II) couples is **4b** = **4d** < **4a** < **4c** from a balance between σ - and π -contributions of the (ER₃) ligands [34, 35].

3.4. Absorption spectra

The optical absorption spectra of **1–6** were recorded in acetonitrile in order to identify the metal-to-ligand charge transfer (MLCT) and π - π^* absorption bands expected. The UV-Vis spectra of **1** and **4a** are provided in “Supplementary material.” Electronic spectra of all the compounds showed two intense absorptions in the UV region. Bands at $\lambda = 290$ – 300 nm are assigned as ligand-to-ligand charge transfer and bands at 321–408 nm are assigned to Fe(II) \rightarrow L(Cp) MLCT transition [36]. The replacement of a CO of **1** with a poorer π -acceptor ER₃ leads to a 10–15 nm increase in λ_{max} for **4a–d**, consistent with the corresponding decrease in the energy separation between the highest occupied molecular orbital and lowest unoccupied molecular orbital for these compounds. However, λ_{max} is not very sensitive to the type of ER₃ ligand.

4. Conclusion

Substitution of one CO by ER₃ resulted in an increase in electron density near iron. This is shown by stretching frequencies of the terminal carbonyl group, the Fe–C(O) bond lengths determined from the X-ray data, and the Fe(II/III)-oxidation potentials obtained from CV measurements. The stretching frequencies of terminal carbonyls is in the order CpFe(CO)₂SCO-het > CpFe(CO)(P(OEt)₃)SCO-het > CpFe(CO)(PPh₃)SCO-het = CpFe(CO)(AsPh₃)SCO-het > CpFe(CO)(SbPh₃)SCO-het. The Fe–S bond distances for **5a–5c** are 2.2665(10) Å in **5c** to 2.2734(8) Å in **5b**. The Fe(III/II) redox couple increases in the order **4b** = **4d** < **4a** < **4c**.

Supplementary material

CCDC-806381, 806382, 806383, and 806384 for **2**, **5a**, **5b**, and **5c**, respectively, contain supplementary crystal data. These data can be obtained free of charge on application to The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Deanship of Research, Jordan University of Science and Technology for financial support (grant no. 82/2009).

References

- [1] S. Kato, O. Niyomura. *Top. Curr. Chem.*, **251**, 15 (2005).
- [2] S. Dey, V.K. Jain. *Platinum Met. Rev.*, **5**, 16 (2004).
- [3] J.J. Vittal, D.T. Ng. *Acc. Chem. Res.*, **39**, 869 (2006).
- [4] M.D. Santana, M. Sáez-Ayala, L. García, J. Pérez, G. García. *Eur. J. Inorg. Chem.*, 4628 (2007).
- [5] S. Singh, J. Chaturvedi, S. Bhattacharya, H. Nöth. *Polyhedron*, **30**, 93 (2010).
- [6] M.S. Cartese, A.B. Caplan, R.L. Crawford. *BMC Evolutionary Biol.*, **2**, 8 (2002).
- [7] J.T. Sampanthar, J.J. Vittal, P.A.W. Dean. *J. Chem. Soc., Dalton Trans.*, 3153 (1999).
- [8] A.O. Maslat, I. Jibril, M. Abussaud, E.H. Abd-Alhadi, Z. Hamadh. *Appl. Organomet. Chem.*, **16**, 44 (2001).
- [9] J. Jacob, A. Khalil, A.O. Maslat. *J. Carcinogenesis*, **3**, 1477 (2004).
- [10] M.A. El-Hinnawi, A. Al-Ajlouui, J. AbuNasser. *J. Organomet. Chem.*, **359**, 79 (1989).
- [11] M.A. El-Hinnawi, A. Al-Ajlouni. *J. Organomet. Chem.*, **332**, 329 (1987).
- [12] M.A. El-Hinnawi, M. El-khateeb, I. Jibril, S.T. Abu-Orabi. *Synth. React. Inorg. Met-Org. Chem.*, **19**, 809 (1989).
- [13] I. Jibril, M. El-khateeb, H. Barakat, G. Rheinwald, H. Lang. *Inorg. Chim. Acta*, **333**, 1 (2002).
- [14] M. El-khateeb, H. Jibril, H. Barakat, G. Rheinwald, H. Lang. *Polyhedron*, **22**, 3445 (2003).
- [15] M. El-khateeb, H. Görls, W. Weigand. *Inorg. Chim. Acta*, **360**, 705 (2007).
- [16] M. El-khateeb, A. Shaver, A.-M. Lebuis. *J. Organomet. Chem.*, **622**, 293 (2001).
- [17] M. El-khateeb, K.J. Asali, A. Lataifeh. *Polyhedron*, **25**, 1695 (2006).
- [18] M. El-khateeb, K.J. Asali, A. Lataifeh. *Polyhedron*, **22**, 3105 (2003).
- [19] M. El-khateeb, A. Roller. *Polyhedron*, **26**, 3920 (2007).
- [20] M.A. El-Hinnawi, B.D. Santasiero, D.R. McAlister, V. Shomaker. *Inorg. Chem.*, **22**, 1585 (1983).
- [21] X-D.F. Gennett, M. Milner, J. Weaver. *J. Phys. Chem.*, **89**, 2787 (1985).
- [22] COLLECT, *Data Collection Software*, Nonius B.V., The Netherlands (1998).
- [23] Z. Otwinowski, W. Minor. In *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*, C.W. Carter, R.M. Sweet (Eds), pp. 307–326, Academic Press, New York (1997).
- [24] G.M. Sheldrick. *Acta Cryst.*, **A46**, 112 (2008).
- [25] M. El-khateeb, M. Al-Noaimi, Z. Al-Amawi, A. Roller, S. Shova. *Inorg. Chim. Acta*, **361**, 2957 (2008).
- [26] I. Jibril, M.A. El-Hinnawi, M. El-khateeb. *Polyhedron*, **10**, 2095 (1991).
- [27] M. Morán, I. Cuadrado, J.R. Masaguer, J. Losada, C. Foces-Poces, F. Cano. *Inorg. Chim. Acta*, **143**, 59 (1988).
- [28] G. Consinglio, F. Morandini. *Inorg. Chim. Acta*, **127**, 79 (1987).
- [29] D. White, L. Carlton, N. Coville. *J. Organomet. Chem.*, **440**, 15 (1992).
- [30] G. Carriedo, A. Arancibia, C. Diaz-Valenzuela, N. Yutronic, E. Perez-Carreno, S. Garcia-Granda. *J. Organomet. Chem.*, **508**, 23 (1996).
- [31] M. El-khateeb, K.J. Asali, I. Jibril, A. Abuseni, H. Görls, W. Weigand. *Trans. Met. Chem.*, **34**, 419 (2009).
- [32] M. El-khateeb, A. Younis. *J. Organomet. Chem.*, **664**, 228 (2002).
- [33] N. Kuznik, O.F. Wendt. *J. Chem. Soc., Dalton Trans.*, 3074 (2002).
- [34] G.M. Bodner, M.P. May, L.E. McKinney. *Inorg. Chem.*, **19**, 1951 (1980).
- [35] S.K. Sharma, V.K. Srivastava, P.H. Pandya, R.V. Jasra. *Catal. Commun.*, **6**, 205 (2005).
- [36] J. Belmont, M. Wrighton. *Organometallics*, **5**, 1421 (1986).