Multifunctional iron thiocarboxylate complexes: synthesis, reactivity and structure of $\text{CpFe}(\text{CO})_2\text{SCO}-3,5\text{-C}_6\text{H}_4(\text{COCl})_2$

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Abstract A controlled substitution reaction of the chlorine atoms of 1,3,5-benzenetricarbonyl trichloride by the organoiron fragment ($\text{CpFe}(\text{CO})_2\text{S}$) has been achieved. The complexes $\text{CpFe}(\text{CO})_2\text{SCO}-3,5\text{-C}_6\text{H}_3(\text{COCl})_2$ (**1**), 1,3- $[\text{CpFe}(\text{CO})_2\text{SCO}]_2-5\text{-C}_6\text{H}_3\text{COCl}$ (**2**) and 1,3,5- $[\text{CpFe}(\text{CO})_2\text{SCO}]_3\text{C}_6\text{H}_3$ (**3**) were prepared from the reaction of $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 3, 4$) with 1,3,5- $\text{C}_6\text{H}_3(\text{COCl})_3$ in a 1:1, 2:1, or 3:1 metal to ligand molar ratio. The reactions of (**1**) with amines, thiols, and carboxylic acids produce the trifunctional mono-iron complexes $\text{CpFe}(\text{CO})_2\text{SCO}-3,5\text{-C}_6\text{H}_3(\text{COY})_2$ [$\text{Y} = \text{NR}_2$ (**4**), SR (**5**), OCOR (**6**)]. The X-ray structure determination of (**1**) is reported.

Introduction

The chemistry of ligands containing sulfur, selenium, or tellurium has been actively pursued [1–3]. These ligands have high affinity to coordinate with transition metals in inorganic and organometallic complexes [2, 3]. The interest in such ligands is motivated by their bonding diversity, perspectives of reactivity, and relevance to bioinorganic chemistry [4–7].

The iron sulfide complexes $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 3, 4$), which are accessible through the insertion of elemental sulfur into the iron–iron bond of the dimer $[\text{CpFe}(\text{CO})_2]_2$ [8], were

found to be reactive toward electrophiles. Their reactions with mono-functional electrophiles such as acid chlorides [9, 10], sulfonyl chlorides [11], chloroformates [12], chlorothioformates [13], chlorodithioformates [14], and *O*-alkyloxalyl chlorides [15] produced the complexes $\text{CpFe}(\text{CO})_2\text{SZ}$ ($\text{Z} = \text{COR}, \text{SO}_2\text{R}, \text{CO}_2\text{R}, \text{C}(\text{S})\text{OR}, \text{CS}_2\text{R}, \text{COCO}_2\text{R}$) which contain one iron centre. The reaction of these iron sulfides with bi-functional acid chlorides, such as oxalyl chloride, gave $[\text{CpFe}(\text{CO})_2\text{SCO}]_2$ which contains two iron atoms [15]. On the other hand, their reaction with terephthaloyl chloride gave either the di-iron thioterephthalates $[\text{CpFe}(\text{CO})_2\text{SCO}]_2(4\text{-C}_6\text{H}_4)$ or the mono-iron complex $\text{CpFe}(\text{CO})_2\text{SCO}-4\text{-C}_6\text{H}_4\text{COCl}$, depending on the molar ratio of the reactants [16]. The latter complex was found to be reactive toward amines, phenols, carboxylic acids, and thiols to produce the bi-functional products $\text{CpFe}(\text{CO})_2\text{ECO}-4\text{-C}_6\text{H}_4\text{COY}$ ($\text{Y} = \text{NR}_2, \text{OR}, \text{OCOR}, \text{SR}$) [16–19]. The dimeric complexes containing two iron atoms with either homo- or hetero-bis(chalcogeno)-ligands were prepared by the reactions of $\text{CpFe}(\text{CO})_2\text{SCO}-4\text{-C}_6\text{H}_4\text{COCl}$ with the iron chalcogenides $(\mu\text{-E}_x)[\text{CpFe}(\text{CO})_2]_2$ ($\text{E} = \text{S}, \text{Se}$) [18, 19].

In this article, we describe the reaction of the iron sulfides $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ with 1,3,5-benzenetricarbonyl trichloride, which contains three acid chloride groups as an extension to our efforts in this area. The reactions of the mono-iron complex $\text{CpFe}(\text{CO})_2\text{SCO}-3,5\text{-C}_6\text{H}_3(\text{COCl})_2$ with amines, thiols, or carboxylic acids are discussed.

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Experimental

General considerations

All reactions and manipulations were carried out under a dinitrogen atmosphere by using standard Schlenk line

techniques. The use of dry solvents is necessary. The starting materials $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 3, 4$) were prepared according to the literature method [8], while 1,3,5- $\text{C}_6\text{H}_3(\text{COCl})_3$, amines, thiols, and carboxylic acids were obtained commercially (Acros) and were used without further purification. Infrared (i.r.) spectra were recorded on a Nicolet-Impact 410 FT-IR spectrometer. ^1H -NMR spectra were recorded on a Bruker-Avance-400 MHz spectrometer. Chemical shifts are given in ppm relative to TMS at 0 ppm. Elemental analyses were carried out on a Perkin-Elmer 2400 Series II CHN-analyzer.

Preparation of $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{COCl})_2$ (**1**)

A solution of $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 3, 4$) (2.00 mmol) in diethyl ether (50 cm^3) was dropwise added, over a period of 30 min, to a solution of 1,3,5- $\text{C}_6\text{H}_3(\text{COCl})_3$ (0.67 g, 2.5 mmol) in diethyl ether (10 cm^3). The resulting mixture was stirred for 2 h at room temperature. The volatiles were removed under vacuum and re-dissolved in a minimum amount of CH_2Cl_2 . This solution was introduced to a silica gel column made up in hexane. Elution with a mixture of diethyl ether and hexane (7:3 volume ratio) gave an orange band which was collected and identified as $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{COCl})_2$, followed by a red band which was identified as $\text{CpFe}(\text{CO})_2\text{Cl}$. The title complex was re-crystallized from CH_2Cl_2 /hexane. Yield = 0.54 g, 62%. M.p = 193–195 °C. I.r. (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ = 2047 (vs); 2003 (vs); $\nu_{\text{C}=\text{O}}$ = 1764 (s); $\nu_{\text{SC}=\text{O}}$ = 1612 (m). ^1H -NMR (CDCl_3): δ 9.10 (d, 2H, H_a); 8.84 (t, 1H, H_b); 5.09 (s, 5H, Cp). $\text{C}_{16}\text{H}_8\text{FeO}_5\text{SCl}_2$ calcd.: C, 43.8; H, 1.8; S, 7.3%. Found: C, 43.4; H, 2.1; S, 6.9%.

Preparation of 1,3- $[\text{CpFe}(\text{CO})_2\text{SCO}]_2\text{-5-}\text{C}_6\text{H}_3\text{COCl}$ (**2**)

A solution of 1,3,5- $\text{C}_6\text{H}_3(\text{COCl})_3$ (0.26 g, 1 mmol) in diethyl ether (150 cm^3) was added to a solution (2.00 mmol) of $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ ($x = 3, 4$) (2.00 mmol) in diethyl ether (50 cm^3) under dinitrogen atmosphere. The resulting mixture was stirred for 3 h at room temperature. The volatiles were removed under vacuum and re-dissolved in a minimum amount of CH_2Cl_2 . This solution was introduced to a silica gel column made up in hexane. Elution with THF/hexane gave an orange band which was discarded. Elution with THF gave an orange band which was collected and identified as 1,3- $[\text{CpFe}(\text{CO})_2\text{SCO}]_2\text{-5-}\text{C}_6\text{H}_3\text{COCl}$ and was re-crystallized from CH_2Cl_2 /hexane. Yield = 0.17 g, 29%. M.p = 213–214 °C. I.r. (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ = 2046 (vs); 2001 (vs); $\nu_{\text{C}=\text{O}}$ = 1761 (w); $\nu_{\text{SC}=\text{O}}$ = 1610 (m). ^1H -NMR (CDCl_3): δ 9.18 (bs, 1H, H_a); 8.86 (bs, 2H, H_b); 5.06 (s, 10H, Cp). $\text{C}_{23}\text{H}_{13}\text{Fe}_2\text{O}_7\text{S}_2\text{Cl}$ calcd.: C, 45.1; H, 2.1; S, 10.5%. Found: C, 44.9; H, 2.0; S, 9.8%.

Preparation of 1,3,5- $[\text{CpFe}(\text{CO})_2\text{SCO}]_3\text{C}_6\text{H}_3$ (**3**)

A solution of 1,3,5- $\text{C}_6\text{H}_3(\text{COCl})_3$ (0.18 g, 0.67 mmol) in diethyl ether (100 cm^3) was added slowly over a period of 1 h to a solution of $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$ (2.00 mmol) ($x = 3, 4$) in diethyl ether (50 cm^3) under dinitrogen atmosphere. The resulting mixture was stirred for 3 h at room temperature. The volatiles were removed under vacuum and re-dissolved in a minimum amount of CH_2Cl_2 . This solution was introduced to a silica gel column made up in hexane. Elution with 1:1 volume ratio of THF/hexane gave an orange band, which was discarded. Elution with THF gave an orange band which was collected and recrystallized from CH_2Cl_2 /hexane. Yield = 0.24 g, 48%. M.p = 227–228 °C. I.r. (CH_2Cl_2 , cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ = 2044 (vs); 2000 (vs); $\nu_{\text{SC}=\text{O}}$ = 1606 (m). ^1H -NMR (CDCl_3): δ 8.91 (s, 3H, Ar-H); 5.03 (s, 15H, Cp). $\text{C}_{30}\text{H}_{18}\text{Fe}_3\text{O}_9\text{S}_3$ calcd.: C, 45.8; H, 2.3; S, 12.2%. Found: C, 45.3; H, 2.3; S, 12.4%.

Preparation of $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{CONR}^1\text{R}^2)_2$ (**4**)

A THF solution (60 cm^3) containing the amine (2.3 mmol) and (**1**) (0.5 g, 1.14 mmol) was refluxed. The volatiles were removed under vacuum and the residue was re-dissolved in CH_2Cl_2 and transferred to a chromatographic column made up in hexane. An orange band was eluted with CH_2Cl_2 /diethyl ether (9:1 volume ratio). This band was collected and identified as $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{CONR}^1\text{R}^2)_2$ and re-crystallized from CH_2Cl_2 /hexane.

$\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{CONHPh})_2$ (**4a**)

Yield = 0.42 g, 67%. M.p = 220–221 °C. Reflux time = 2 h. I.r. (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ = 2036 (vs); 1987 (v), $\nu_{\text{NC}=\text{O}}$ = 1647 (s); $\nu_{\text{SC}=\text{O}}$ = 1601 (m). ^1H -NMR (CDCl_3): δ 8.63 (s, 2H, H_a); 8.39 (s, 1H, H_b); 8.29 (bs, 2H, NH); 7.70 (d, 4H, Ar-H); 7.37 (t, 4H, Ar-H); 7.16 (t, 2H, Ar-H); 5.00 (s, 5H, Cp). $\text{C}_{28}\text{H}_{21}\text{FeO}_5\text{SN}_2\cdot 2\text{CH}_2\text{Cl}_2$ calcd.: C, 54.6; H, 3.5; S, 5.0; N, 4.4%. Found: C, 54.2; H, 3.5; S, 4.7; N, 4.3%.

$\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{CON}(\text{CH}_3)\text{Ph})_2$ (**4b**)

Yield = 0.37 g, 56%. M.p = 180–181 °C. Reflux time = 3 h. I.r. (KBr, cm^{-1}): $\nu_{\text{C}\equiv\text{O}}$ = 2041 (vs); 1991 (vs), $\nu_{\text{NC}=\text{O}}$ = 1648 (s); $\nu_{\text{SC}=\text{O}}$ = 1601 (m). ^1H -NMR (CDCl_3): δ 7.91 (bs, 2H, H_a); 7.29 (bs, 1H, H_b); 7.19 (t, 4H, Ph); 7.11 (t, 2H, Ph); 6.88 (d, 4H, Ph); 4.98 (s, 5H, Cp); 3.38 (s, 6H, CH_3). $\text{C}_{28}\text{H}_{24}\text{FeO}_5\text{SN}_2\cdot 0.5\text{CH}_2\text{Cl}_2$ calcd.: C, 58.8; H, 4.1; S, 5.2; N, 4.5%. Found: C, 58.4; H, 3.9; S, 4.9; N, 4.4%.

CpFe(CO)₂SCO-3,5-C₆H₃(CON(CH₃)CH₂Ph)₂ (**4c**)

Yield = 0.52 g, 75%. M.p = 118–120 °C. Reflux time = 3 h. I.r. (KBr, cm⁻¹): $\nu_{C\equiv O}$ = 2038 (vs); 1985 (vs), $\nu_{NC=O}$ = 1648 (s); $\nu_{SC=O}$ = 1590 (m). ¹H-NMR (CDCl₃): δ 8.25 (s, 2H, H_a); 7.65 (s, 1H, H_b); 7.36 (m, 8H, Ph); 7.14 (m, 2H, Ph); 5.05 (s, 5H, Cp); 4.51 (s, 4H, CH₂); 3.03 (s, 6H, CH₃). C₃₂H₂₈FeO₅SN₂·0.5CH₂Cl₂ calcd.: C, 60.0; H, 4.5; S, 4.9; N, 4.3%. Found: C, 59.6; H, 4.3; S, 4.7; N, 3.9%.

Preparation of CpFe(CO)₂SCO-3,5-C₆H₃(COSR)₂ (**5**)

A THF solution (50 cm³) containing 2.50 mmol of thiol and (**1**) (0.50 g, 1.14 mmol) was refluxed for 6 h. The solvent was removed under vacuum and the residue was re-dissolved in a minimum amount of CH₂Cl₂ and transferred to a silica gel column made up in hexane. An orange band was eluted by a mixture of CH₂Cl₂/diethylether (6:4 volume ratio). The collected products were recrystallized from CH₂Cl₂/hexane.

CpFe(CO)₂SCO-3,5-C₆H₃(COSR)₂ (**5a**)

Yield = 0.53 g, 77%. M.p = 152–153 °C. I.r. (KBr, cm⁻¹): $\nu_{C\equiv O}$ = 2040 (vs); 1991 (vs), $\nu_{C=O}$ = 1661 (s); $\nu_{SC=O}$ = 1611 (m). ¹H-NMR (CDCl₃): δ 9.01 (d, 2H, H_a); 8.67 (t, 1H, H_b); 7.56 (m, 4H, Ph); 7.45 (m, 6H, Ph); 5.13 (s, 5H, Cp). C₂₈H₁₈FeO₅S₃·0.5CH₂Cl₂ calcd.: C, 54.4; H, 3.0; S, 15.3%. Found: C, 54.4; H, 2.9; S, 14.6%.

CpFe(CO)₂SCO-3,5-C₆H₃(COSCH₂Ph)₂ (**5b**)

Yield = 0.62 g, 89%. M.p = 139–141 °C. I.r. (KBr, cm⁻¹): $\nu_{C\equiv O}$ = 2038 (vs); 1987 (vs), $\nu_{C=O}$ = 1658 (s); $\nu_{SC=O}$ = 1608 (m). ¹H-NMR (CDCl₃): δ 8.91 (d, 2H, H_a); 8.72 (t, 1H, H_b); 7.37–7.53 (m, 10H, Ph); 5.08 (s, 5H, Cp); 4.36 (s, 4H, CH₂). C₃₀H₂₂FeO₅S₃·0.5CH₂Cl₂ calcd.: C, 55.7; H, 3.5; S, 14.6%. Found: C, 55.2; H, 3.4; S, 13.8%.

Preparation of CpFe(CO)₂SCO-3,5-C₆H₃(C₂O₃R)₂ (**6**)

A THF solution (50 cm³) containing 2.60 mmol of carboxylic acid and (**1**) (0.50 g, 1.14 mmol) was refluxed for 12 h. The solvent was removed under vacuum and the residue was re-dissolved in a minimum amount of THF and transferred to a silica gel column made up in hexane. An orange band was eluted by a mixture of THF/hexane (8:2 volume ratio), the collected products were re-crystallized from THF/hexane.

CpFe(CO)₂SCO-3,5-C₆H₃(C₂O₃CF₃)₂ (**6a**)

Yield = 0.38 g, 56%. M.p = 176–178 °C. I.r. (KBr, cm⁻¹): $\nu_{C\equiv O}$ = 2037 (vs); 1996 (vs), $\nu_{C=O}$ = 1728 (s); 1696 (s); $\nu_{SC=O}$ = 1608 (m). ¹H-NMR (Acetone-*d*₆): δ 8.95 (d, 2H, H_a); 8.77 (t, 1H, H_b); 5.34 (s, 5H, Cp). C₂₀H₈FeO₉SF₆·2THF calcd.: C, 45.0; H, 3.3; S, 4.3%. Found: C, 44.9; H, 3.2; S, 4.1%.

CpFe(CO)₂SCO-3,5-C₆H₃(C₂O₃CCl₃)₂ (**6b**)

Yield = 0.31 g, 39%. M.p = 187–189 °C. I.r. (KBr, cm⁻¹): $\nu_{C\equiv O}$ = 2036 (vs); 1995 (vs), $\nu_{C=O}$ = 1728 (s); 1697 (s); $\nu_{SC=O}$ = 1607 (m). ¹H-NMR (Acetone-*d*₆): δ 8.94 (d, 2H, H_a); 8.75 (t, 1H, H_b); 5.33 (s, 5H, Cp). C₂₀H₈FeO₉ SCl₆·2THF calcd.: C, 40.2; H, 2.9; S, 3.8%. Found: C, 40.0; H, 2.8; S, 3.6%.

Crystallographic analysis of CpFe(CO)₂SCO-3,5-C₆H₃(COCl)₂, (**1**)

A single crystal suitable for X-ray structure determination of (**1**) was obtained by recrystallization from CH₂Cl₂/hexane mixture. Crystallographic data were as follows: C₁₆H₈Cl₂FeO₅S, formula weight: 439.03, space group P2(1)/n with $a = 6.9492(4)$ Å, $b = 20.7699(14)$ Å, $c = 11.9657$ Å, $\beta = 102.280^\circ$, $V = 1687.45(16)$ Å³, $\rho_{\text{calc}} = 1.728$ g/cm³ and $Z = 4$. The measurements were collected at 183(2) K on a Kappa CCD diffractometer with a graphite monochromator ($\lambda = 0.71073$ Å). There were 11154 independent reflections with 3834 observed reflections ($>2\sigma(I)$). The structure was solved by direct methods using SHELXS97 (Sheldrick, 1997) [20] and difmap synthesis using SHELXTL96 (Sheldrick, 1996) [21]. All non-hydrogen atoms were fully refined with anisotropic thermal parameters. The refinement coverage to $R_I = 0.0635$ and $wR_2 = 0.1527$.

Results and discussion

Synthesis and characterization

The reaction of (μ -S_x)[CpFe(CO)₂]₂ with the trifunctional acid chloride 1,3,5-C₆H₃(COCl)₃ can be controlled to give either the mono-, bi- or tri-iron complexes shown in Scheme 1. The organo-iron chloride, CpFe(CO)₂Cl was obtained as a byproduct of these reactions, separated from the products by column chromatography and identified.

Complexes (**1**), (**2**), and (**3**) are stable as solids and are also stable in solution. The structures of these complexes were identified by spectroscopic techniques (i.r. and ¹H-NMR) as well as by elemental analysis. Their i.r. spectra show 2 bands for the terminal carbonyl groups in

Scheme 1 Preparation of $\text{CpFe(CO)}_2\text{SCO-3,5-C}_6\text{H}_3(\text{COCl})_2$ (**1**), $[\text{CpFe(CO)}_2\text{SCO}]_2\text{-5-C}_6\text{H}_3\text{COCl}$ (**2**) and $1,3,5\text{-}[\text{CpFe(CO)}_2\text{SCO}]_3$ (**3**)

the ranges of $2047\text{--}2044$ and $2003\text{--}2000\text{ cm}^{-1}$, which are comparable to those reported for the corresponding thiocarboxylates $\text{CpFe(CO)}_2\text{SCOR}$ [9, 10]. The bands are shifted to lower wave-numbers as the number of the iron fragment increases, consistent with increasing electron density around the metal centre. The spectra show also a medium band in the range of $1606\text{--}1612\text{ cm}^{-1}$ for the thiocarboxylate-carbonyl group. For (**1**) and (**2**) the presence of the acid chloride group is confirmed by the presence a band at $1764\text{--}1761\text{ cm}^{-1}$ [16]. The $^1\text{H-NMR}$ spectra of (**1**)–(**3**) exhibit a singlet in the range of $5.03\text{--}5.09\text{ ppm}$ for the Cp-protons. This chemical shift range is similar to that observed for the thiocarboxylate ($4.98\text{--}5.13\text{ ppm}$) [9, 10] and thiocarbonate ($4.98\text{--}5.12\text{ ppm}$) analogues [12]. The protons of the phenyl ring appear as two sets for (**1**) (doublet and triplet) and for (**2**) (two broad singlets) and as one singlet for (**3**).

Complex (**1**) was reacted with amines, thiols, and carboxylic acids to give the substituted complexes $\text{CpFe(CO)}_2\text{SCO-3,5-C}_6\text{H}_3(\text{CONR}^1\text{R}^2)_2$ (**4**), $\text{CpFe(CO)}_2\text{SCO-3,5-C}_6\text{H}_3(\text{COSR})_2$ (**5**), or $\text{CpFe(CO)}_2\text{SCO-3,5-C}_6\text{H}_3(\text{CO}_2\text{COR})_2$ (**6**) respectively as shown in Scheme 2.

Compounds (**4**), (**5**), and (**6**) were characterized by i.r., $^1\text{H-NMR}$ spectroscopy and elemental analysis. The i.r. spectra of each of these complexes exhibit two strong bands in the ranges of $2040\text{--}2036\text{ cm}^{-1}$ and $1996\text{--}1985\text{ cm}^{-1}$ for the terminal carbonyl group coordinated to the iron centre. These ranges are shifted to lower wave-

numbers compared to the starting complex (**1**). The spectra contain a medium band in the range of $1611\text{--}1590\text{ cm}^{-1}$ for the thiocarboxylate-carbonyl ligands. Additionally, the carbonyl group of the amide or thio-ester groups appears as a medium band in the ranges of $1647\text{--}1680\text{ cm}^{-1}$ or $1608\text{--}1611\text{ cm}^{-1}$, respectively. The corresponding carboxylato ligands show two bands in the range of $1697\text{--}1696$ and at 1728 cm^{-1} . These ranges are found in accordance to the electronegativity of the $\text{N(R}^1\text{)R}^2$, SR or OCOR groups. $^1\text{H-NMR}$ spectra of (**4**), (**5**), and (**6**) show singlet peak in the range of $4.90\text{--}5.34\text{ ppm}$ for the cyclopentadienyl protons and the expected patterns of the aromatic protons.

Crystal structure of (**1**)

The molecular structure of $\text{CpFe(CO)}_2\text{SCO-3,5-C}_6\text{H}_3(\text{COCl})_2$ (**1**) is shown in Fig. 1. Selected bond distances and the bond angles of (**1**) are shown in Table 1. The structure of (**1**) is a typical piano stool with three legs in which the cyclopentadienyl ligand is bonded to iron in an η^5 -fashion. The Fe-C(Cp) (average = $2.093\text{ \AA}$) and Fe-C(CO) ($1.764(7)$, $1.786(6)\text{ \AA}$) bond lengths of (**1**) are similar to those found in CpFe(CO)_2 -containing complexes [8–14]. The Fe-S bond distance in (**1**) of $2.2529(14)\text{ \AA}$ is comparable to that found in $\text{CpFe(CO)}_2\text{SX}$ complexes [$\text{X} = \text{SO}_2\text{CCl}_3$ ($2.2803(13)\text{ \AA}$), CO_2Et ($2.2675(10)\text{ \AA}$), $\text{CO-2-C}_6\text{H}_4\text{NO}_2$ ($2.266(1)\text{ \AA}$), $\text{C(S)O-C}_6\text{H}_4\text{Cl}$ ($2.2765(5)\text{ \AA}$)] [9–12]. The C–O bond lengths of the ketonic carbonyl group of the

Scheme 2 Reactions of $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{COCl})_2$ (**1**) with amines, thiols or carboxylic acids

Fig. 1 ORTEP drawing of $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{COCl})_2$ (**1**) at 30% probability

thiocarboxylate ligand (1.216(2) Å) are very comparable to those found in thiocarboxylate complexes [9, 10]. The corresponding bond lengths of the free acid chloride groups are somewhat different from each other (1.391(8), 1.181(7)). This might be due to some disorder of one of these groups. The angles around the iron center (S–Fe–C15, S–Fe–C16, C16–Fe–C15) are around 90°, consistent with a pseudo-octahedral structure. The sulfur atom in this complex has a sp^3 hybridization as predicted from the Fe–S–C1 angle.

Table 1 Selected bond length (Å) and angles (°) of $\text{CpFe}(\text{CO})_2\text{SCO-3,5-}\text{C}_6\text{H}_3(\text{COCl})_2$ (**1**)

Fe–S	2.2529(14)	C1–S–Fe	109.89(18)
Fe–C15	1.764(7)	C15–Fe–S	93.94(18)
Fe–C16	1.786(6)	C16–Fe–S	94.92(5)
Fe–C10	2.093(6)	C15–Fe–C16	94.42(3)
Fe–C11	2.096(6)	C8–O3–C9	120.75(12)
Fe–C12	2.091(6)	C2–C1–S	114.6(4)
Fe–C13	2.093(6)	O1–C1–S	125.5(4)
Fe–C14	2.091(6)	O3–C9–C6	129.8(6)
S1–C1	1.731(5)	O3–C9–C12	114.3(4)
C1–O1	1.216(6)	C6–C9–C12	115.7(5)
C8–O2	1.181(7)	O2–C8–C11	118.0(5)
C9–O3	1.391(8)	O2–C8–C11	126.9(5)
C15–O4	1.153(7)	C4–C8–C11	115.1(4)
C16–O5	1.148(7)		

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References

1. Patai S, Rappoport Z (eds) (1986/1987) The chemistry of organic selenium and tellurium compounds, vols 1 and 2. Wiley, New York
2. Murray SG, Hartley FR (1981) *Chem Rev* 81:365
3. Gysling HJ (1982) *Coord Chem Rev* 42:133
4. Ng MT, Vittal JJ (2006) *Inorg Chem* 45:10247
5. Jacob JH, Khalil AM, Muslat AO (2004) *J Carcinog* 3:1477
6. Muslat AO, Jibril I, Abussaud M, Abd-Alhadi E, Hamadeh Z (2002) *J Appl Organomet Chem* 16:44
7. Delgado JE, Donnadiou B, Hernandez E, Zamora PF (2004) *J Organomet Chem* 689:552
8. El-Hinnawi MA, Aruffo AA, Santarsiero BD, McAlister DR, Shomaker V (1983) *Inorg Chem* 22:1585
9. El-Hinnawi MA, Ajlouni A (1987) *J Organomet Chem* 332:321
10. El-Hinnawi MA, Ajlouni A, Abu-Nasser JS, Powell AK, Wahrenkamp H (1989) *J Organomet Chem* 359:79
11. El-khateeb M, Obidate T (2001) *Polyhedron* 20:2393
12. El-khateeb M, Asali KJ, Lataifeh A (2003) *Polyhedron* 22:3105
13. El-khateeb M, Asali KJ, Lataifeh A (2006) *Polyhedron* 25:1605
14. El-khateeb M, Roller A (2007) *Polyhedron* 26:3920
15. El-khateeb M, Goerls H, Weigand W (2006) *Inorg Chim Acta* 360:705
16. Jibril I, Ali AK (1997) *Indian J Chem* 36A:987
17. Jibril I, Ali AK, Omar JT (1997) *Polyhedron* 16:3327
18. Jibril I, Abd-Alhadi EH (2000) *Indian J Chem* 39A:1055
19. Jibril I, Abd-Alhadi EH, Hamadeh Z (2000) *Trans Met Chem* 25:407
20. Sheldrick GM (1997) SHELXS-97, program for the solution of crystal structures. University of Göttingen, Germany
21. Sheldrick GM (1996) SHELXL-96, program for the refinement of crystal structures. University of Göttingen, Germany