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Preparation and organic transformation reactions of $CpFe(CO)_2SCO–3\text{-}C_6H_4–SO_2Cl$

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Abstract

Treatment of the iron sulfides $(\mu\text{-}S_x)[CpFe(CO)_2]_2$ with $3\text{-}ClCOC_6H_4SO_2Cl$ gave the novel organoiron thiocarboxylate complex $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2Cl$ which contains a free sulfonyl chloride group. This complex reacts with nucleophiles such as R_2NH, ArOH and RSH to give stable complexes $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2NR_2$, $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2OAr$, and $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2SR$, respectively. The crystal structure of $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2N(CH_3)CH_2Ph$ has been determined: space group: $P2_1/c$, $a = 17.9594(5)$, $b = 9.2395(2)$, $c = 13.4341(4)$ Å, $\beta = 95.403(2)^\circ$, $V = 2219.26(10)$ Å^3 and $Z = 4$.

Keywords: Iron; Thiocarboxylate; Nucleophilic substitution; Structures; Sulfonates

1. Introduction

It has been demonstrated that organoiron sulfides and selenides, $(\mu\text{-}E_x)[CpFe(CO)_2]_2$ (E = S, Se, $x = 1–5$) react with acid chlorides to give the corresponding thio- or seleno-carboxylate complexes, $CpFe(CO)_2ECOR$ [1–5]. Recently, the reactions of these sulfides or selenides with sulfonyl chlorides were reported to give thio- or seleno-sulfonate complexes, $CpFe(CO)_2ESO_2R$ [6,7].

The organoiron thio- and seleno-terephthaloyl chloride complexes, $CpFe(CO)_2SCO–4\text{-}C_6H_4COCl$ have been prepared by the reaction of the corresponding sulfides or selenides complexes with terephthaloyl chloride [8]. These complexes have a reactive acyl chloride group, which is reactive toward nucleophiles [9–11]. Nucleophiles such as amines, phenols, thiols and organic acids were reported to react with these terephthaloyl chloride complexes and affords bifunctional complexes of the general formula $CpFe(CO)_2ECO–4\text{-}C_6H_4COY$ (Y = NR_2, OAr, SR, OCOR). Biological studies on these complexes showed that these systems have biological significance; selenium-containing complexes were found to have antifungal activity and antibacterial effects. Both sulfur and selenium derivatives showed mutagenic activity [12].

The reaction of the terephthaloyl chloride complexes $CpFe(CO)_2ECO–4\text{-}C_6H_4COCl$ with organoiron sulfides or selenides affords a large varity of homo bimetalic bischalcogeno terephthalate complexes of the formula $CpFe(CO)_2ECOC_6H_4COE'Fe(CO)_2Cp'$ ($Cp' = C_5H_5$, $Bu^tC_5H_4$, 1, 3-$Bu^t_2C_5H_3$) [8].

The important biological activity of sulfonyl-containing compounds [13–15] and our interest in organoiron sulfur complexes prompted us to prepare the iron thiocarboxylate complex, $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2Cl$. The reactions of this complex with amines, phenols and thiols are discussed in this paper.

2. Results and discussion

The organoiron sulfides $(\mu\text{-}S_x)[CpFe(CO)_2]_2$ react readily with 3-(chlorosulfonyl)benzoyl chloride in diethyl ether at room temperature to give $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2Cl$ (**1**), as a stable solid and $CpFe(CO)_2Cl$ which were separated by column chromatography (Scheme 1). The biiron complex $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2SFe(CO)_2Cp$, which may result from the reaction of the sulfonyl group with the iron sulfides, could not be obtained from this reaction

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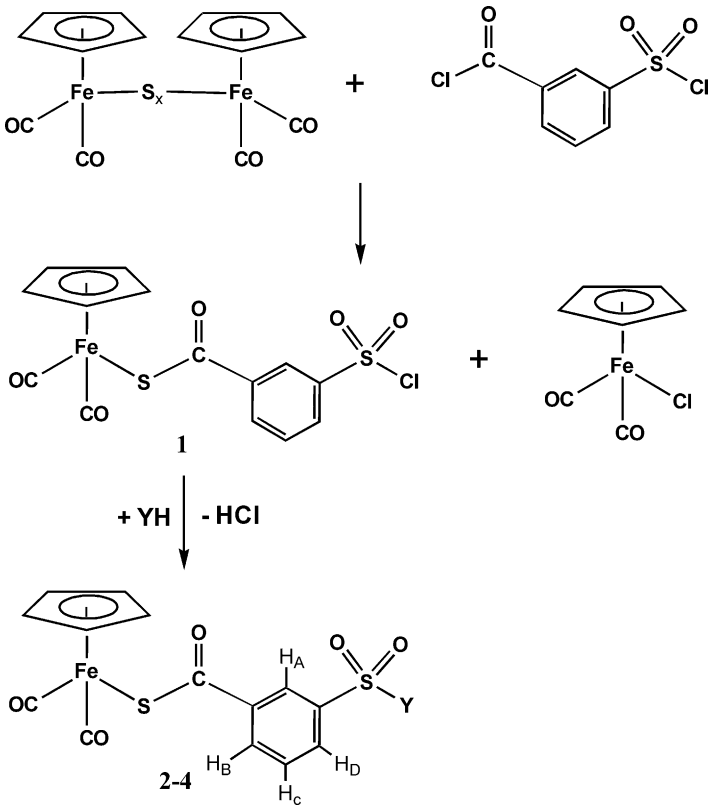

Scheme 1. Y = NRR′:R, R′ = H, CH_2Ph; H, 4-C_6H_4Cl; H, 4-$C_6H_4NO_2$; CH_3, CH_2Ph; C_2H_5, C_2H_5; Ph, CH_2Ph; Ph, Ph (**2**), OAr: Ar = 4-$C_6H_4NO_2$, 4-C_6H_4Cl, 2,4-$C_6H_3Cl_2$ (**3**), SR: R = C_2H_5, Ph, $C(CH_3)_3$ (**4**).

even when excess of the iron sulfide was added. This result is in agreement with our earlier finding that only strongly electrophilic sulfonyl chlorides react with the iron sulfides [6].

The IR spectrum of **1** shows two strong terminal carbonyl bands at 2046, 2001 cm^{-1}, a medium band at 1605 cm^{-1} for the thiocarboxylate group and two bands at 1253, 1156 cm^{-1} for the sulfonyl group. These bands are similar to those obtained for comparable systems [1,6,16]. The ^{1}H-NMR spectrum of **1** shows a singlet peak at 5.07 ppm for the Cp-protons. The aromatic protons appear as four peaks with the expected splitting and chemical shifts.

Complex **1** has a sulfonyl chloride group which is reactive with nucleophiles. The reactions of **1** with primary amines, secondary amines, phenols and thiols gave $CpFe(CO)_2SCO$–3-$C_6H_4SO_2NRR'$ (R, R′ = H, CH_2Ph; H, 4-C_6H_4Cl; H, 4-$C_6H_4NO_2$, CH_3, CH_2Ph; C_2H_5, C_2H_5; Ph, CH_2Ph; Ph, Ph) (**2**), $CpFe(CO)_2SCO$–3-$C_6H_4SO_2OAr$ (Ar = 4-$C_6H_4NO_2$, 4-C_6H_4Cl, 2,4-$C_6H_3Cl_2$) (**3**), $CpFe(CO)_2SCO$–3-$C_6H_4SO_2SR$ (R = C_2H_5, Ph, $C(CH_3)_3$ (**4**), respectively, as shown in Scheme 1.

Complexes **2**–**4** were characterized by elemental analysis, IR and ^{1}H-NMR spectroscopy, and the results are in agreement with the suggested structures. In particular, the ^{1}H-NMR spectra of all these complexes exhibited Cp-protons in the range 5.06–5.14 ppm, suggesting similar environment around the Fe-centre. These Cp-resonances agree well with the reported data for $CpFe(CO)_2SCOR$ complexes [1,2]. The aromatic protons and the protons for the sulfonyl-substituents are shown in the spectra with the expected multiplicity and chemical shift regions [6,14].

The sulfonamide protons of complexes **2a**–**c** were clearly observed in the IR and ^{1}H-NMR spectra of these complexes. The IR spectra of **2a**–**c** show the N–H band in the range 3150–3097 cm^{-1} as a weak band, similar to those observed for organic sulfonamides (3200–3050 cm^{-1}) [17–22]. The reactivity of primary amines with **1** is greater than that of secondary amines.

The IR spectra of **2**–**4** exhibited two absorbances in the regions 2046–2043 and 2001–1997 (vs) cm^{-1} consistant with the two terminal carbonyl groups bonded to the iron centre. These absorbances are similar to those reported for $CpFe(CO)_2SCO$–4-C_6H_4COY (Y = NR_2, OAr, SR, OCOR) systems (2045–2051, 2000–1998 cm^{-1}) [8,9]. The spectra contain also a medium band in the range 1606–1599 cm^{-1} for the C–O of the thiocarboxylate group. The sulfonyl group reveals its presence through a strong absorptions at 1261–1249 and 1172–1146 cm^{-1} for the symmetric and asymmeric S–O stretching bands. These peaks are within the range for the sulfonyl groups observed for

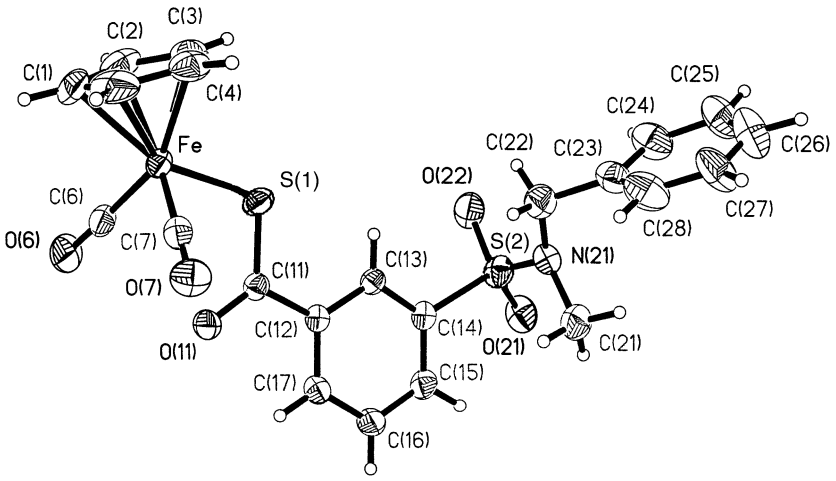

Fig. 1. ORTEP drawing of $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2N(CH_3)CH_2Ph$ (**2d**). Selected bond length (Å) and angles (°): Fe–C1 = 2.060(4), Fe–C2 = 2.100(4), Fe–C3 = 2.114(4), Fe–C4 = 2.086(4), Fe–C5 = 2.065(4), Fe–C6 = 1.780(4), Fe–C7 = 1.774(4), Fe–S1 = 2.2714(9), S–C11 = 1.740(3), C11–O11 = 1.224 (6), S2–O22 = 1.417(3), S2–O21 = 1.426(3), S2–N21 = 1.617(3), C7–Fe–S1 = 90.36(11), C6–Fe–S1 = 93.75(12), C6–Fe–C7 = 93.94(16), C11–S1–Fe = 107.16(11), O22–S2–O21 = 119.28(19), O22–S2–N21 = 108.73(19), O21–S2–N21 = 107.16(17).

$CpFe(CO)_2SSO_2R$ and $CpRu(PP)SSO_2R$ ($PP = 2PPh_3$, dppm, dppe) [6,16] and for those observed for organic sulfonamides [17–21].

The crystal structure of $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2N(CH_3)CH_2Ph$ (**2d**), was determined and is shown in Fig. 1. The cyclopentadienyl ring is bonded to the Fe atom in an η^5-fashion with Fe–C bond distances ranging between 2.060(4) and 2.114(4) Å which are similar to those of $CpFe(CO)_2SCO–2\text{-}C_6H_4NO_2$ [1] and $CpFe(CO)_2SSO_2CCl_3$ [7]. The compound has an Fe–S bond length of 2.2714(9) Å, is also similar to those of $CpFe(CO)_2SCO–2\text{-}C_6H_4NO_2$, [1] and $CpFe(CO)_2S\text{-}SO_2CCl_3$ [7]. The C–O bond length (of thiocarboxylate) is 1.224(4) Å is longer than the corresponding C–O of $CpFe(CO)_2SCO–2\text{-}C_6H_4NO_2$ [1] (1.209(5) Å). This might be due to the important withdrawing effect of the *ortho* nitro group related to *meta* sulfonyl group. The S–O bonds are similar to those of organic sulfonamides [19]. The S2 atom shows a distorted tetrahedral arrangement. The largest angle is the O22–S2–O21 angle (119.28(19)°) and the smallest is O21–S2–C14 (106.15(17)°).

3. Experimental

All experiments were performed under N_2 atmosphere using Schlenk techniques [23]. Benzene, Et_2O, THF and C_6H_{14} were distilled over sodium/benzophenone under N_2 prior to use. Methylene chloride was distilled over P_2O_5. The reagents, $[CpFe(CO)_2]_2$, suflur 3-(chlorosulfonyl)benzoyl chloride, amines, alcohols and thiols (Acros or Aldrich) were used as received. Iron sulfides $(\mu\text{-}S_x)[CpFe(CO)_2]_2$ were prepared as described in the literature [24].

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-300 spectrophotometer. Samples were prepared under nitrogen. Chemical shifts are in ppm relative to Me_4Si at 0 ppm. Infrared (IR) spectra were recorded on a Nicolate 410-Impact Fourier-Transform spectrophotometer. Elemental analyses were performed by Laboratoire d'Analyse Élémentaire, University of Montréal, Montréal, Québec, Canada. Melting points were measured on an Electrothermal melting point apparatus and are uncorrected.

3.1. Preparation of $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2Cl$ (*1*)

A solution of the acid chloride $3\text{-}ClCOC_6H_4SO_2Cl$ (0.86 g, 3.61 mmol) in Et_2O (10 ml) was added at room temperature (r.t.) to a reddish–brown solution (2.82 mmol) of $(\mu\text{-}S_x)[CpFe(CO)_2]_2$ ($x = 3$ or 4) in Et_2O (60 ml). The resulting mixture was stirred overnight at r.t. The volatiles were removed under vacuum and the residue was redissolved in a minimum amount of methylene chloride and introduced to a silica gel column made up in C_6H_{14}. Elution with a mixture of CH_2Cl_2 and C_6H_{14} (1:1 volume ratio) gave a brownish–orange band which was collected and identified as $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2Cl$, followed by a red band which was identified as $CpFe(CO)_2Cl$. The title complex was re-crystallized from $CH_2Cl_2–C_6H_{14}$.

3.1.1. $CpFe(CO)_2SCO–3\text{-}C_6H_4SO_2Cl$ (*1*)

Yield: 1.29 g (78%). M.p. = 105–107 °C. IR (cm^{-1}, CH_2Cl_2) 2046, 2001 (ν_{CO}), 1605 ($\nu_{C=O}$), 1253, 1156 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 5.07 (s, 5H, Cp), 7.60 (bt, $1H_C$, Ar–H), 8.06 (m, $1H_D$, Ar–H), 8.41 (m, $1H_B$, Ar–H), 8.78 (s, $1H_A$, Ar–H). Anal. Calc. for $C_{14}H_9ClFeO_5S_2$: C, 40.73; H, 2.20; S, 15.51. Found: C, 41.08; H, 2.00; S, 15.61%.

3.2. General procedure for the preparation of $CpFe(CO)_2SCO$–3-$C_6H_4SO_2Y$

A THF solution (70 ml) containing YH (1.45 mmol) and $CpFe(CO)_2SCO$–3-$C_6H_4SO_2Cl$ (0.30 g, 0.72 mmol) was refluxed. The volatiles were removed under vacuum and the residue was redissolved in CH_2Cl_2 and transferred to a chromatographic column made up in C_6H_{14}. An orange band was eluted with Et_2O–C_6H_{14}. This band was collected and identified as $CpFe(CO)_2SCO$–3-$C_6H_4SO_2Y$, and re-crystallized from CH_2Cl_2–C_6H_{14}.

3.2.1. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2NHCH_2Ph$ (**2a**)

Yield: 0.26 g (76%). M.p. = 117–118 °C. Reflux time = 4 h. IR (cm^{-1}, CH_2Cl_2) 2044, 1999 (ν_{CO}), 1605 ($\nu_{C=O}$), 1252, 1153 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 4.15 (m, 2H, CH_2), 4.75 (t, 1H, NH), 5.09 (s, 5H, Cp), 7.35 (m, 5H, Ph), 7.52 (bt, $1H_C$, Ar–H), 8.10–8.57 (m, 2H, Ar–H), 8.65 (s, $1H_A$, Ar–H). Anal. Calc. for $C_{21}H_{17}FeO_5S_2N$: C, 52.18; H, 3.54; N, 2.95. Found: C, 52.52; H, 3.62; N, 3.22%.

3.2.2. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2NH$–4-C_6H_4Cl (**2b**)

Yield: 0.23 g (64%). M.p. = 122–123 °C. Reflux time = 5 h. IR (cm^{-1}, CH_2Cl_2) 2045, 2001 (ν_{CO}), 1604 ($\nu_{C=O}$), 1253, 1156 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 4.82 (s, 1H, NH), 5.07 (s, 5H, Cp), 7.25–7.89 (m, 4H, Ar–H), 8.12–8.79 (m, 4H, Ar–H). Anal. Calc. for $C_{20}H_{14}ClFeO_5S_2N$: C, 47.59; H, 2.79; N, 2.77. Found: C, 47.59; H, 2.78; N, 2.72%.

3.2.3. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2NH$–4-$C_6H_4NO_2$ (**2c**)

Yield: 0.29 g (78%). M.p. = 115–116 °C. Reflux time = 4.5 h. IR (cm^{-1}, CH_2Cl_2) 2045, 2000 (ν_{CO}), 1601 ($\nu_{C=O}$), 1253, 1157 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 2.68 (br, 1H, NH), 5.08 (s, 5H, Cp), 7.26–7.85 (m, 4H, Ar–H), 8.13–8.73 (m, 4H, Ar–H). Anal. Calc. for $C_{20}H_{14}FeO_7S_2N_2$: C, 46.71; H, 2.74; N, 5.45. Found: C, 46.65; H, 3.06; N, 5.15%.

3.2.4. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2N(CH_3)CH_2Ph$ (**2d**)

Yield: 0.28 g (78%). M.p. = 121–124 °C. Reflux time = 6 h. IR (cm^{-1}, CH_2Cl_2) 2044, 1999 (ν_{CO}), 1605 ($\nu_{C=O}$), 1249, 1155 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 2.55 (s, 3H, Me), 4.24 (m, 2H, CH_2Ph), 5.09 (s, 5H, Cp), 7.37 (m, 5H, Ph), 7.53 (bt, $1H_C$, Ar–H), 8.28–8.51 (m, 2H, Ar–H); 8.75 (s, $1H_A$, Ar–H). Anal. Calc. for $C_{22}H_{15}FeO_5S_2N$: C, 53.13; H, 3.85; N, 2.85. Found: C, 52.31; H, 3.79; N, 2.66%.

3.2.5. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2N(C_2H_5)_2$ (**2e**)

Yield: 0.27 g (85%). M.p. = 128–130 °C. Reflux time = 7 h. IR (cm^{-1}, CH_2Cl_2) 2043, 1997 (ν_{CO}), 1605 ($\nu_{C=O}$), 1251, 1146 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 1.23 (t, 6H, CH_2CH_3), 3.22 (q, 4H, CH_2CH_3); 5.09 (s, 5H, Cp), 7.95 (bt, $1H_C$, Ar–H), 8.22–8.49 (m, 2H, Ar–H), 8.56 (s, $1H_A$, Ar–H). Anal. Calc. for $C_{18}H_{19}FeO_5S_2N$: C, 50.79; H, 3.14; N, 3.12. Found: C, 50.85; H, 3.07; N, 2.98%.

3.2.6. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2N(Ph)CH_2Ph$ (**2f**)

Yield: 0.30 g (75%). M.p. = 126–129 °C. Reflux time = 7 h. IR (cm^{-1}, CH_2Cl_2) 2044, 1999 (ν_{CO}), 1604 ($\nu_{C=O}$), 1252, 1155 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 4.75 (s, 2H, CH_2), 5.08 (s, 5H, Cp), 7.21–7.54 (m, 10H, 2Ph), 7.67–8.48 (m, 4H, Ar–H). Anal. Calc. for $C_{27}H_{21}FeO_5S_2N$: C, 57.97; H, 3.78; N, 2.50. Found: C, 57.80; H, 3.76; N, 2.45%.

3.2.7. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2NPh_2$ (**2g**)

Yield: 0.23 g (58%). M.p. = 95–97 °C. Reflux time = 6 h. IR (cm^{-1}, CH_2Cl_2) 2045, 1999 (ν_{CO}), 1604 ($\nu_{C=O}$), 1253, 1159 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 5.14 (s, 5H, Cp), 7.32–7.67 (m, 10H, 2Ph), 7.81–8.65 (m, 4H, Ar–H). Anal. Calc. for $C_{26}H_{19}FeO_5S_2N$: C, 57.26; H, 3.51; N, 2.57. Found: C, 57.51; H, 2.96; N, 2.25%.

3.2.8. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2O$–4-$C_6H_4NO_2$ (**3a**)

Yield: 0.19 g (51%). Reflux time = 12 h. M.p. = 99–102 °C. IR (cm^{-1}, CH_2Cl_2) 2046, 2001 (ν_{CO}), 1599 ($\nu_{C=O}$), 1261, 1164 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 5.12 (s, 5H, Cp), 7.26–7.73 (m, 4H, Ar–H), 7.80–8.87 (m, 4H, Ar–H). Anal. Calc. for $C_{20}H_{13}FeO_8S_2N$: C, 46.62; H, 2.54; N, 2.72. Found: C, 47.55; H, 3.31; N, 2.62%.

3.2.9. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2O$–4-C_6H_4Cl (**3b**)

Yield: 0.18 g (49%). Reflux time = 12 h. M.p. = 94–96 °C. IR (cm^{-1}, CH_2Cl_2) 2045, 2000 (ν_{CO}), 1604 ($\nu_{C=O}$), 1246, 1157 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 5.10 (s, 5H, Cp), 7.26–7.51 (m, 4H, Ar–H), 7.75–8.90 (m, 4H, Ar–H). Anal. Calc. for $C_{20}H_{13}FeO_6S_2Cl$: C, 47.59; H, 2.59. Found: C, 47.50; H, 3.02%.

3.2.10. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2O$–2,4-$C_6H_3Cl_2$ (**3c**)

Yield: 0.19 g (50%). Reflux time = 12 h. M.p. = 101–103 °C. IR (cm^{-1}, CH_2Cl_2) 2046, 2001 (ν_{CO}), 1605 ($\nu_{C=O}$), 1245, 1162 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 5.11 (s, 5H, Cp), 7.26–7.75 (m, 3H, Ar–H), 7.84–8.89 (m, 4H, Ar–H). Anal. Calc. for $C_{20}H_{12}Cl_2FeO_6S_2$: C, 44.55; H, 2.24. Found: C, 44.73; H, 2.17%.

3.2.11. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2SC_2H_5$ (**4a**)

Yield: 0.19 g (62%). Reflux time = 8 h. M.p. = 111–114 °C. IR (cm^{-1}, CH_2Cl_2) 2045, 2000 (ν_{CO}), 1606 ($\nu_{C=O}$), 1254, 1172 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 1.32 (t, 3H, CH_2CH_3), 4.20 (q, 2H, CH_2CH_3), 5.09 (s, 5H, Cp), 7.89–8.79 (m, 4H, Ar–H). Anal. Calc. for

$C_{16}H_{14}FeO_6S_3$: C, 43.84; H, 3.22. Found: C, 43.40; H, 3.11%.

3.2.12. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2SPh$ (**4b**)

Yield: 0.16 g (45%). Reflux time = 9 h. M.p. = 122–124 °C. IR (cm^{-1}, CH_2Cl_2) 2044, 1999 (ν_{CO}), 1601 ($\nu_{C=O}$), 1251, 1160 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 5.06 (s, 5H, Cp), 7.25–7.79 (m, 5H, Ph), 7.85–8.92 (m, 4H, Ar–H). Anal. Calc. for $C_{20}H_{14}FeO_5S_3$: C, 49.39; H, 2.90. Found: C, 49.45; H, 2.85%.

3.2.13. $CpFe(CO)_2SCO$–3-$C_6H_4SO_2SC(CH_3)_3$ (**4c**)

Yield: 0.19 g (57%). Reflux time = 9 h. M.p. = 128–131 °C. IR (cm^{-1}, CH_2Cl_2) 2045, 2002 (ν_{CO}), 1605 ($\nu_{C=O}$), 1251, 1160 (ν_{SO}). ^{1}H-NMR ($CDCl_3$): δ 2.23 (m, 9H, ^{t}Bu), 5.09 (s, 5H, Cp), 7.25 (bt, $1H_C$, Ar–H), 8.14–8.57 (m, 2H, Ar–H), 8.81 (s, $1H_A$, Ar–H). Anal. Calc. for $C_{18}H_{18}FeO_5S_3$: C, 46.36; H, 2.90. Found: C, 46.27; H, 2.97%.

3.3. Crystallographic analysis of $CpFe(CO)_2SCO$–$C_6H_4SO_2N(CH_3)CH_2Ph$ (**2d**)

Crystals suitable for the X-ray study were obtained by re-crystallization of **2d**, from CH_2Cl_2–hexane mixture. The crystallographic data are presented in Table 1 and were obtained on a Bruker AXS SMART 2K/platform diffractometre. The structure was solved by use of the program SHELXS-97 (Sheldrick, 1997) by direct methods, and difmap synthesis using SHELXS-96 (Sheldrick, 1996) [25,26]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in the calculated positions.

Table 1
Selected crystal data and refinement parameters for $CpFe(CO)_2SCO$–3-$C_6H_4SO_2N(CH_3)CH_2Ph$ (**2d**)

Empirical formula	$C_{22}H_{19}FeO_5S_2N$
Formula weight	497.352
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	17.9594(5)
b (Å)	9.2395(2)
c (Å)	13.4341(4)
β (°)	95.403(2)
Volume (Å^3)	2219.29(10)
Radiation type	Cu–K_α
Density (Mg m^{-3})	1.4885
μ (mm^{-1})	7.502
λ (Å)	1.54178
Crystal size (mm)	0.30 × 0.13 × 0.02
Index ranges	$-22 < h < 22$, $-11 < k < 11$, $-16 < l < 15$
θ Range (°)	5.39–72.57
$R[F^2 > 2\sigma(F^2)]$	0.0472
$\omega R(F^2)$ [a]	0.1322

[a] $\omega = 1/[\sigma^2(F^2) + (0.0802P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

4. Supplementary material

Further details of the structure determination may be obtained from Cambridge Crystallographic Data Centre, CCDC no. 187632. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] M.A. El-Hinnawi, A.M. Al-Ajlouni, J. Organomet. Chem. 332 (1987) 321.
[2] M.A. El-Hinnawi, A.M. Al-Ajlouni, J.S. Abu-Nasser, A.K. Powell, H. Vahrenkamp, J. Organomet. Chem. 359 (1989) 79.
[3] M.A. El-Hinnawi, M. El-khateeb, I. Jibril, S.T. Obu-Orabi, Synth. React. Inorg. Met.-Org. Chem. 19 (1989) 809.
[4] I. Jibril, O. Abu-Nimreh, Synth. React. Inorg. Met.-Org. Chem. 26 (1996) 1409.
[5] I. Jibril, M.A. El-Hinnawi, M. El-khateeb, Polyhedron 10 (1991) 2095.
[6] M. El-khateeb, A. Shaver, A.-M. Labius, J. Organomet. Chem. 622 (2001) 293.
[7] M. El-khateeb, T. Obidate, Polyhedron 20 (2001) 2393.
[8] I. Jibril, A.K. Ali, Ind. J. Chem. Sect. A 36 (1997) 987.
[9] I. Jibril, A.K. Ali, J.T. Omar, Polyhedron 16 (1997) 3327.
[10] I. Jibril, E.H. Abd-Alhadi, Ind. J. Chem. Sect. A 39 (2000) 1055.
[11] I. Jibril, E.H. Abd-Alhadi, Z. Hamadh, Trans. Met. Chem. 25 (2000) 407.
[12] A.O. Maslat, I. Jibril, M. Abussaud, E. Abd-Alhadi, Z. Hamadh, Appl. Organomet. Chem. 16 (2001) 44.
[13] M.A. Letavic, M.Z. Axt, J.T. Barberia, T.J. Carty, D.E. Danley, K.E. Geoghegan, N.S. Halim, L.R. Hotn, A.V. Kamath, E.R. Laird, Bioorg. Med. Chem. Lett. 12 (2002) 1387.
[14] T.M. Schwartz, G.L. Bundy, J.W. Strohbach, S. Thaisrivongs, P.D. Johnson, H.I. Slculnick, P.K. Tomich, J.C. Lynn, K.T. Chomg, R.R. Hinshaw, T.J. Raub, G.E. Padary, L.N. Toth, Bioorg. Med. Chem. Lett. 7 (1997) 399.
[15] I. Bertini, H.B. Gray, S.T. Lippard, J.S. Valentine, Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994.
[16] M. El-khateeb, B. Wolfsberger, W.A. Schenk, J. Organomet. Chem. 612 (2000) 14.
[17] A. Garcia-Raso, J.J. Fiol, G. Martorell, A. Lopez-Zafra, M. Quiros, Polyhedron 16 (1997) 613.
[18] B. Macias, I. Garcia, M.V. Villa, J. Borras, A. Castineiras, F. Sanz, Polyhedron 21 (2002) 1229.
[19] J.C. Pedregosa, J. Casanova, G. Alzuet, J. Borras, S. Garcia-Granda, M.R. Diaz, A. Gutierrz-Rodriguez, Inorg. Chim. Acta 232 (1995) 117.
[20] N. Ergenc, N.S. Gunay, R. Demirdamar, Eur. J. Med. Chem. 33 (1998) 143.

[21] R. Silverstein, G. Bassler, T. Morrill, Spectroscopic Identification of Organic Compounds, 4th ed., Wiley, New York, 1981.
[22] B.F. Senkal, U. Tunca, N. Bicak, Eur. Polym. J. 37 (2001) 2429.
[23] D. Shriver, M. Drezdzon, The Manipulation of Air Sensitive Compounds, 2nd ed., Wiley Interscience, Toronto, 1986.
[24] M.A. El-Hinnawi, A.A. Aruffo, B.D. Santarsiero, D.R McAlister, V. Shomaker, Inorg. Chem. 22 (1983) 1585.
[25] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.
[26] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.