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Half sandwich iron S-bonded mono-thiocarbonate complexes: structure of $CpFe(CO)_2SCO_2Et$

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Abstract

The synthesis and characterization of mononuclear iron complexes containing mono-thiocarbonate ligands are described. The new compounds of general formula $CpFe(CO)_2SCO_2R$ [R = Et (**1**), *iso*-Bu (**2**), Ph (**3**), 4-$C_6H_4NO_2$ (**4**), Me (**5**)] were prepared by reacting the iron sulfides (μ-S_x)$[CpFe(CO)_2]_2$ ($x = 2, 3$) with the corresponding chloroformates (ROCOCl). These new complexes have been characterized by elemental analyses and spectroscopic methods. The crystal structure of $CpFe(CO)_2SCO_2Et$, **1**, has been determined by single crystal X-ray diffraction analysis.

Keywords: Thiocarbonate complexes; Iron; X-ray structure; Carbonyl; Sulfur-ligands

1. Introduction

Thiocarbonate, dithiocarbonate and trithiocarbonate ligands provide a variety of transition and main group metal complexes [1–10]. These complexes were found to have important chemical [11] and biological [12] properties. Trithiocarbonate ligands, known as thioxanthates, are the most common ligands among all these carbonate ligands [6,13–18]. Complexes containing thioxanthate ligands are generally prepared by insertion of carbon disulfide into the metal–sulfur bond of metal–thiolate complexes [13–18]. Accordingly, the complexes $CpRu(PPh_3)S_2CSR$ [13,14], $CpW(CO)_2S_2CSR$ [6] and $(PPh_3)Pt(SR)(S_2CSR)$ [19] containing bidentate thioxanthate ligands were reported. Complexes with monodentate thioxanthate ligands, such as $(PP_3)RhS_2CSMe$ (PP_3 = tris(2-diphenylphosphino-ethyl)phosphine) [4] and $CpFe(CO)_2S_2CSR$ [20] were also reported in the literature. The later complexes, $CpFe(CO)_2S_2CSR$, were prepared from the reaction of the iron halide, $CpFe(CO)_2X$ (X = Cl, I) with the corresponding thioxanthate anions [20]. These iron thioxanthate complexes were reported to undergo CS_2 elimination to give the dimeric (μ-SR)$_2$[CpFe(CO)]$_2$ complexes [20].

Our studies on the synthesis and reactivities of iron–sulfur complexes have demonstrated that the iron sulfides, (μ-S_x)$[CpFe(CO)_2]_2$, can serve as precursors to a variety of iron complexes containing sulfur donor ligands [17–20]. Iron thiocarboxylate complexes $Cp'Fe(CO)_2SCOR$ ($Cp' = C_5H_5$, $Bu^tC_5H_4$, 1,3-$(Bu^t)_2C_5H_3$) were prepared from the corresponding iron sulfide precursors [21–24]. Recently, it has also been found that these iron sulfides react with sulfonyl chlorides to give the iron thiosulfonate complexes $CpFe(CO)_2SSO_2R$ [25].

Although, trithiocarbonate complexes are very common in the literature, mono-thiocarbonate complexes of transition metals are rare [26]. In this paper, the iron precursors (μ-S_x)$[CpFe(CO)_2]_2$ are used to prepare iron monothiocarbonate complexes. The preparation and characterization of $CpFe(CO)_2SCO_2R$ are discussed.

2. Results and discussion

2.1. Synthesis and characterization

A series of cyclopentadienyldicarbonyliron monothiocarbonate complexes, $CpFe(CO)_2SCO_2R$ (**1–5**),

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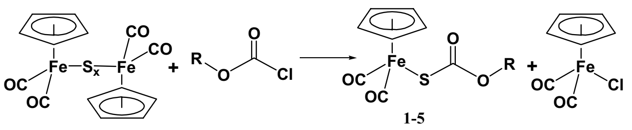
were prepared by the reaction of (μ-S_x)[$CpFe(CO)_2$]$_2$ with the corresponding chloroformates ROCOCl [R = Et (**1**), *iso*-Bu (**2**), Ph (**3**), 4-$C_6H_4NO_2$ (**4**), Me (**5**)] as shown in Eq. (1). The chloro-derivative $CpFe(CO)_2Cl$, was also obtained as a side product of Eq. (1). These two products were easily separated by column chromatography.



(1)

The thiocarbonate complexes (**1–5**) are air stable as solids and are air sensitive in solutions. They are soluble in most common polar organic solvents but insoluble in hydrocarbons. The structures of these complexes were established by elemental analysis, IR and ^1H NMR spectroscopy. The IR spectra of **1–5** showed two strong bands in the ranges 2044–2045 and 1997–1999 cm^{-1} attributed to the stretching frequencies of the two terminal carbonyl groups bonded to the iron center. These bands are within the same range observed for the thiocarboxylate analogues $CpFe(CO)_2SCOR$ (2027–2060 and 1998–1984 cm^{-1}) [22] and lower than those of thiosulfonates, $CpFe(CO)_2SSO_2R$ (2047–2064 and 1991–1998 cm^{-1}) [25]. The spectra also contain a band with medium intensity in the range 1655–1677 cm^{-1} for the ketonic carbonyl group of the thiocarbonate ligand. This band is lower than that observed for $Ph_2Ge(SCO_2R)_2$ and Ph_3GeSCO_2R (1691–1702 cm^{-1}) [26]. This shift is due to higher electron density on iron in **1–5** compared to that of germanium. The frequency of this ketonic band is also higher than that of the corresponding thiocarboxylate complexes (1595–1605 cm^{-1}) [22], which may be attributed to more π-bond character in the S–C bond compared to that of the C–OR bond (vide infra) [26,27]. The ^1H NMR data of these new complexes are collected in Section 3 and exhibit a singlet peak for the five Cp-protons in the range 4.98–5.12 ppm. These peaks are similar to those observed for the thiocarboxylates, $CpFe(CO)_2SCOR$ (4.98–5.13 ppm) and lower than those observed for the thiosulfonate complexes, $CpFe(CO)_2SSO_2R$ (5.21–5.28 ppm) [25]. The IR and NMR data reflect a relatively higher electron density around the iron-center in complexes **1–5** compared to those of the thiosulfonates and similar to those of the thiocarboxylates. The chemical shifts for the protons of the thiocarbonate ligands are observed in the expected ranges and the signals have the expected multiplicity.

The reactivity of the iron sulfides toward the chloroformates is due to the presence of lone pairs of electrons on the sulfur atoms of the sulfide-bridge ligand. In contrast to the sulfonyl chlorides [25], all chloroformates used in this study reacted with the iron sulfides to give mono-thiocarbonate complexes. Although thioxanthate ligands are excellent bidentate ligands, the monothiocarbonate ligands are not. All attempts to prepare the bidentate complexes $CpFe(CO)SCO_2R$, in which the thiocarbonate ligands is bonded to the iron through both S and O-atoms, were unsuccessful. Irradiating of a THF solution of the complexes **1–5** with UV-light or heating of these solutions under reflux resulted in excessive decomposition of the starting complexes.

2.2. Crystal structure

The molecular structure of $CpFe(CO)_2SCO_2Et$, **1**, and the atom numbering scheme are shown in Fig. 1. It can be seen that the thiocarbonate ligand is bonded to the iron atom in a monodentate fashion through the sulfur atom. Compound **1** possesses a Fe–S bond distance of 2.2675(10) Å, which is similar to that observed for $CpFe(CO)_2SCO$-2-$C_6H_4NO_2$ (2.266(1) Å) [22], and a Fe–S–C(1) angle of 108.25(12)°. The C(1)–O(1) bond length of 1.197(4) Å is also similar to that obtained for $CpFe(CO)_2SCO$-2-$C_6H_4NO_2$ (1.209(5) Å) [22]. The S–C(1)–O(2) bond angle of 108.2(2)° is smaller than the S–CO–R bond in $CpFe(CO)_2SCO$-2-$C_6H_4NO_2$ (114.7(3)°) and similar to those obtained for $Ph_2Ge(SCO_2R)_2$ and Ph_3GeSCO_2R (average 107°). The C(1)–O(2)–C(3) angle (116.7(3)°) is consistent with less π-bond character in the C–O bond involved in the C(1)–O(2)–C(3) connection compared to the S–C(1)–O(1) core, in accordance with reported systems [26].

3. Experimental

3.1. General

Manipulations were performed under a nitrogen atmosphere using Schlenk techniques. Diethyl ether, hexane and benzene were purified by reflux over sodium and distillation under nitrogen. Dichloromethane was heated under reflux over P_2O_5 and distilled under nitrogen. Chloroformates, iron dimer, elemental sulfur were obtained from Acros and were used as received. The iron sulfides were prepared using literature procedures [28].

IR and ^1H NMR spectra were recorded on a Nicolat-Impact 410 FT-IR spectrometer and a Bruker AS-200 MHz spectrometer, respectively. Elemental analyses were done in the Laboratoire D'Analyse Élementaire Universite de Montréal, Montréal, Québec, Canada. Melting points were reported on a Staurt Melting point apparatus (SMP3) and are uncorrected.

3.2. General procedure for the preparation of $CpFe(CO)_2SCO_2R$, **1–5**

A 100 ml Schlenk flask was charged with the iron sulfides (μ-S_x)[$CpFe(CO)_2$]$_2$ (0.45 g, 1.00 mmol) and 50

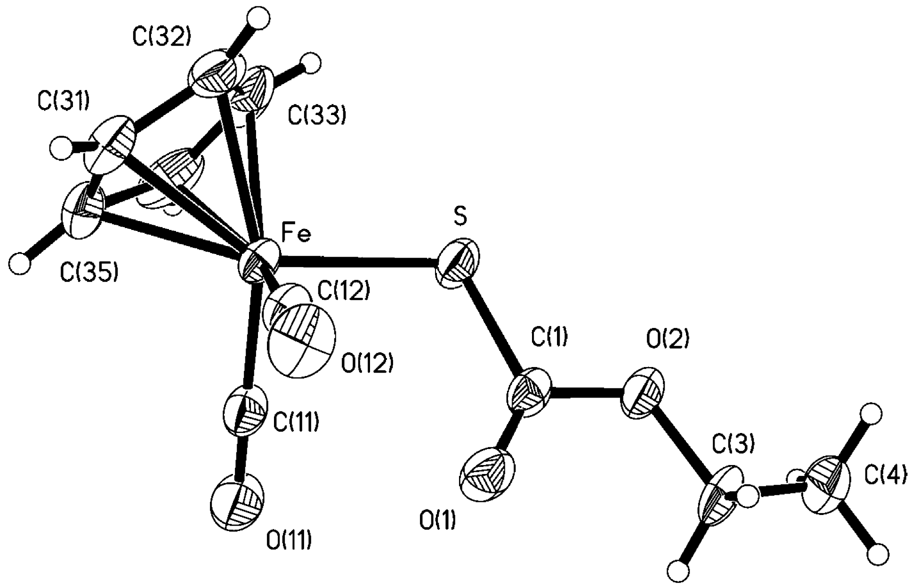


Fig. 1. ORTEP drawing of $CpFe(CO)_2SCO_2Et$ (**1**). Selected bond lengths (Å) and angles (°): Fe–S = 2.2675(10), Fe–C11 = 1.768(4), Fe–C12 = 1.780(4), Fe–C31 = 2.081(4), Fe–C32 = 2.088(4), Fe–C33 = 2.103(4), Fe–C34 = 2.092(4), Fe–C35 = 2.090(4), S–C1 = 1.748(3), C1–O1 = 1.97(4), C1–O2 = 1.346(4), C11–O11 = 1.137(4), C12–O12 = 1.125(4), C11–Fe–C12 = 93.80(17), C11–Fe–S = 89.83(12), C12–Fe–S = 93.55(11), C1–S–Fe = 108.25(12), O1–C1–O2 = 123.8(3), O1–C1–S = 123.8(3), O2–C1–S = 108.2(2), C1–O2–C3 = 116.7(3).

ml of diethyl ether. The chloroformate (1.20 mmol) was added via syringe. The resulting solution was stirred overnight. The volatiles were removed under vacuum and the resulting solid was redissolved in a minimum amount of dichloromethane and introduced to a silica gel column made up in hexane. Elution with hexane eliminated the unreacted chloroformates. Elution with hexane/dichloromethane solution (1:1 v:v ratio) gave an orange band which was collected and identified as $CpFe(CO)_2SCO_2R$, followed by a red band which was also collected and identified as $CpFe(CO)_2Cl$. The $CpFe(CO)_2SCO_2R$ were recrystallized from dichloromethane/hexane.

3.2.1. *$CpFe(CO)_2SCO_2Et$ (**1**)*

Yield, 75%. M.p., 109–110 °C. *Anal.* Found: C, 42.35; H, 3.33; S, 11.95. Required for $C_{10}H_{10}FeO_4S$: C, 42.58; H, 3.57; S, 11.37%. IR (CH_2Cl_2, cm^{-1}): 2044 s, 1997 s ($\nu C\equiv O$), 1655 w ($\nu C=O$). ^1H NMR ($CDCl_3$, δ ppm): 1.15 (t, 3H, CH_3), 4.12 (q, 2H, CH_2), 5.05 (s, 5H, C_5H_5).

3.2.2. *$CpFe(CO)_2SCO_2CH_2CH(CH_3)_2$ (**2**)*

Yield, 65%. M.p., 69–70 °C. *Anal.* Found: C, 45.95; H, 4.64; S, 10.51. Required for $C_{12}H_{14}FeO_4S$: C, 46.49; H, 4.55; S, 10.34%. IR (CH_2Cl_2, cm^{-1}): 2044 s, 1997 s ($\nu C\equiv O$), 1657 w ($\nu C=O$). ^1H NMR ($CDCl_3$, δ ppm): 0.95 (d, 6H, CH_3), 1.90 (m, 1H, CH), 3.80 (d, 2H, CH_2), 4.98 (s, 5H, C_5H_5).

3.2.3. *$CpFe(CO)_2SCO_2Ph$ (**3**)*

Yield, 72%. M.p., 98–99 °C. *Anal.* Found: C, 50.28; H, 3.17; S, 10.19. Required for $C_{14}H_{10}FeO_4S$: C, 50.94; H, 3.05; S, 9.71%. IR (CH_2Cl_2, cm^{-1}): 2045 s, 1999 s ($\nu C\equiv O$), 1677 w ($\nu C=O$). ^1H NMR ($CDCl_3$, δ ppm): 5.12 (s, 5H, C_5H_5), 7.22 (m, 3H, C_6H_5), 7.41 (m, 2H, C_6H_5).

3.2.4. *$CpFe(CO)_2SCO_2$-4-$C_6H_4NO_2$ (**4**)*

Yield, 80%. M.p., 59–60 °C. *Anal.* Found: C, 43.90; H, 2.35; S, 7.85, N, 3.51. Required for $C_{14}H_9FeNO_6S$: C, 44.80; H, 2.42; S, 8.55; N, 3.73%. IR (CH_2Cl_2, cm^{-1}): 2044 s, 1998 s ($\nu C\equiv O$), 1670 w ($\nu C=O$). ^1H NMR ($CDCl_3$, δ ppm): 5.08 (s, 5H, C_5H_5), 6.94 (d, 2H, C_6H_4), 8.22 (d, 2H, C_6H_4).

3.2.5. *$CpFe(CO)_2SCO_2Me$ (**5**)*

Yield, 65%. M.p., 101–102 °C. *Anal.* Found: C, 39.51; H, 2.48; S, 11.19. Required for $C_9H_8FeO_4S$: C, 40.33; H, 3.10; S, 11.96%. IR (CH_2Cl_2, cm^{-1}): 2044 s, 1999 s ($\nu C\equiv O$), 1662 w ($\nu C=O$). ^1H NMR ($CDCl_3$, δ ppm): 3.73 (s, 3H, CH_3), 5.00 (s, 5H, C_5H_5).

3.3. *Crystallographic analysis*

Single crystals suitable for X-ray were obtained by recrystallization of **1** from dichloromethane/hexane mixture. The crystallographic data are shown in Table 1. Cell parameters were determined from 7978 reflections ($2.92° < \theta < 72.88°$). There were 2277 independent reflections with 1638 observed reflections ($>2\sigma(I)$). The structure was solved by direct methods using SHELXS-97 [29] and DIFMAP synthesis using SHELXL-96 [30]. All non-hydrogen atoms are anisotropic. Hydrogen atoms are isotropic.

Table 1
Selected crystal data and refinement parameters for $CpFe(CO)_2SCO_2Et$ (**1**)

Empirical formula	$C_{10}H_{10}FeO_4S$
Formula weight	282.09
Crystal size (mm)	$0.60 \times 0.14 \times 0.10$
Crystal system	orthorhombic
Space group	Pb_{ca}
Unit cell dimension	
a (Å)	13.5049(3)
b (Å)	11.3748(3)
c (Å)	15.1179(3)
V (Å^3)	2322.34(9)
Z	8
Index ranges	$-16 < h < 15$, $-13 < k < 12$, $-17 < l < 17$
D_{calc} (Mg m^{-3})	1.614
Radiation type	Cu Kα
μ (mm^{-1})	12.088
λ (Å)	1.54178
θ Range (°)	2.92–72.88
$R[F^2 > 2\sigma(F^2)]$	0.0395
$\omega R(F^2)^a$	0.1166

[a] $\omega = 1/[\sigma^2(F_o^2) + (0.0693P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

4. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 208084. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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