

## Note

# The synthesis and structure of the thiosulfonato iron complexes $\text{CpFe}(\text{CO})_2\text{SS}(\text{O})_2\text{R}$

 Mohammad El-khateeb <sup>a</sup>, Alan Shaver <sup>b,\*</sup>, Anne-Marie Lebus <sup>b</sup>
<sup>a</sup> Department of Chemistry, Jordan University of Science and Technology, P.O. Box 3030, Irbid 22110, Jordan

<sup>b</sup> Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Que., Canada, H3A 2K6

Received 24 July 2000; received in revised form 28 August 2000

## Abstract

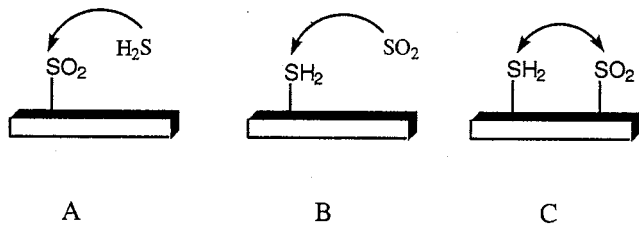
Treatment of the iron polysulfanes  $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$  ( $x = 3, 4$ ) with sulfonyl chlorides  $\text{RSO}_2\text{Cl}$  ( $\text{R} = \text{CF}_3$  (1),  $\text{CCl}_3$  (2),  $\text{C}_6\text{F}_5$  (3)) gave the corresponding iron thiosulfonato complexes  $\text{CpFe}(\text{CO})_2\text{SS}(\text{O})_2\text{R}$  in good yields. Crystal structure for 2:  $P_21/c$ ,  $a = 6.704(2)$ ,  $b = 8.933(2)$ ,  $c = 22.603(5)$  Å,  $\alpha = 90$ ,  $\beta = 92.82(2)$ ,  $\gamma = 90^\circ$ ,  $V = 1352.0(6)$  Å<sup>3</sup> and  $Z = 4$ . © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiosulfonato; Carbonyl; Claus process; Sulfur; Structure; Iron

## 1. Introduction

Sulfur in fossil fuels and natural gas must be removed to reduce air pollution. Sulfur is removed from petroleum by hydrodesulfurization (HDS) to give  $\text{H}_2\text{S}$  [1]. The  $\text{H}_2\text{S}$  is converted to elemental sulfur and water via the Claus process [2], the mechanism of which is poorly understood. Sulfur–sulfur bond formation and oxygen atom transfer are fundamental steps in this mechanism.

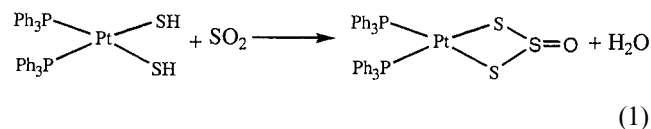
Conceptually, this heterogeneous reaction can be described by three models. Model A depicts the reaction of  $\text{H}_2\text{S}$  with adsorbed  $\text{SO}_2$ , model B involves the reaction of  $\text{SO}_2$  with adsorbed  $\text{H}_2\text{S}$  and in model C both adsorbed gases react.



\* Corresponding author. Tel.: +1-514-398 6999; fax: +1-514-398 3932.

E-mail address: shaver@artsci.lan.mcgill.ca (A. Shaver).

Organometallic analogs of these models are known [3]. As a simulation of model A, we reported the reaction of  $(\text{PPh}_3)_3\text{PtSO}_2$  with the alkylthiophthalimides to form *trans*- $(\text{PPh}_3)_2\text{Pt}(\text{phth})\text{S}(\text{O})_2\text{SR}$  (phth = phthalimide), complexes that contain the  $\text{SO}_2\text{SR}$  moiety [4]. Reactions of metal thiolato [3] and hydrosulfido [5] complexes with  $\text{SO}_2$  have been investigated as examples of model B. Accordingly, treatment of *cis*- $(\text{PPh}_3)_2\text{Pt}(\text{SH})_2$  with  $\text{SO}_2$  gave  $(\text{PPh}_3)_2\text{PtS}_3\text{O}$  and  $\text{H}_2\text{O}$  (Eq. (1)) [5]. No organometallic analog for model C has been reported. The demonstration that *cis*- $(\text{PPh}_3)_2\text{Pt}(\text{SH})_2$  is the first homogeneous catalyst of Claus chemistry has heightened our interest in model B. The product of Eq. (1) is also a catalyst and an intermediate in this Claus chemistry. It contains an oxygenated polysulfur ligand which is implicated in the sulfur–sulfur bond formation and oxygen transfer. The reaction of  $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$  with sulfonyl chlorides,  $\text{RSO}_2\text{Cl}$ , gave complexes containing the type of oxo-polysulfur ligand expected from model B.



## 2. Experimental

All experiments were performed under dinitrogen atmosphere using Schlenk techniques [6]. Benzene, diethylether and hexanes were distilled over sodium/benzophenone under nitrogen prior to use. Methylene chloride was distilled over phosphorus pentoxide. The reagents  $[\text{CpFe}(\text{CO})_2]_2$ , elemental sulfur and sulfonyl chlorides (Aldrich) were used as received. Iron sulfanes  $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$  were prepared as described [7].

Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL-270 spectrophotometer. Samples were prepared under nitrogen. Chemical shifts are in ppm relative to TMS at 0 ppm. Infrared spectra were recorded on a Nicolet 410 Impact FT-spectrophotometer. Elemental analyses were performed by Laboratoire d'Analyse Élémentaire, Université de Montréal, Montréal, QC, Canada. Melting points were measured on a Thomas Hoover Capillary melting point apparatus and are uncorrected.

### 2.1. General procedure for the preparation of $\text{CpFe}(\text{CO})_2\text{SS}(\text{O})_2\text{R}$

A 100 ml Schlenk flask was charged with the iron sulfanes  $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$  (0.45 g, 1.00 mmol) and 50 ml of diethylether. The sulfonyl chloride (1.20 mmol) was added by a syringe. The resulting mixture was stirred overnight. The solvent was removed under vacuum and the residue dissolved in a minimum amount of methylene chloride. This solution was introduced to a silica gel column and elution with hexanes removed any unreacted sulfonyl chloride. Elution with methylene chloride gave an orange band which was collected and identified as  $\text{CpFe}(\text{CO})_2\text{SS}(\text{O})_2\text{R}$ , followed by a red band which was also collected and identified as  $\text{CpFe}(\text{CO})_2\text{Cl}$  [7]. The  $\text{CpFe}(\text{CO})_2\text{SS}(\text{O})_2\text{R}$  was recrystallized from  $\text{CH}_2\text{Cl}_2$ –hexanes.

$\text{CpFe}(\text{CO})_2\text{SSO}_2\text{CCl}_3$  (**1**). Brown crystals. Yield 87%. M.p. 116–117°C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.26 ppm. IR (KBr):  $\nu_{(\text{CO})}$  2062 (s), 1997 (s)  $\text{cm}^{-1}$ ;  $\nu_{(\text{SO})}$  1122 (m), 1057 (m)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_8\text{H}_5\text{Cl}_3\text{FeO}_4\text{S}_2$ : C, 24.35; H, 1.29; S, 16.38. Found: C, 24.70; H, 1.03; S, 16.38%.

$\text{CpFe}(\text{CO})_2\text{SSO}_2\text{CF}_3$  (**2**). Yellow crystals. Yield 80%. M.p. 82–83°C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.21 ppm. IR (KBr):  $\nu_{(\text{CO})}$  2064 (s), 1998 (s)  $\text{cm}^{-1}$ ;  $\nu_{(\text{SO})}$  1180 (m), 1095 (m)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_8\text{H}_5\text{F}_3\text{FeO}_4\text{S}_2$ : C, 28.09; H, 1.47; S, 18.75. Found: C, 28.44; H, 1.32; S, 19.32%.

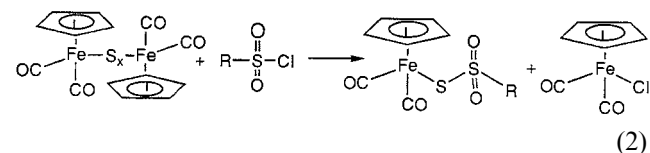
$\text{CpFe}(\text{CO})_2\text{SSO}_2\text{C}_6\text{F}_5$  (**3**). Yellowish-brown crystals. Yield 76%. M.p. 92–93°C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  5.28 ppm. IR (KBr):  $\nu_{(\text{CO})}$  2047 (s), 1991 (s)  $\text{cm}^{-1}$ ;  $\nu_{(\text{SO})}$  1131 (m), 1091 (m)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{13}\text{H}_5\text{F}_5\text{FeO}_4\text{S}_2$ : C, 35.47; H, 1.14; S, 14.57. Found: C, 34.88; H, 1.09; S, 14.48%.

### 2.2. Crystallographic analysis

Single crystals of **2** suitable for X-ray analysis were obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ –hexanes. The crystallographic data and structure refinement are as follows: empirical formula  $\text{C}_8\text{H}_5\text{Cl}_3\text{FeO}_4\text{S}_2$ , formula weight 391.44, monoclinic space group  $P_21/c$  with  $a = 6.704(2)$ ,  $b = 8.933(2)$ ,  $c = 22.603(5)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 92.82(2)$ ,  $\gamma = 90^\circ$ ,  $V = 1352.0(6)$  Å<sup>3</sup>,  $D_{\text{calc}} = 1.923$  g  $\text{cm}^{-3}$ ,  $Z = 4$ ,  $\mu = 2.016$   $\text{mm}^{-1}$ . The measurements were at 293(2) K on a Rigaku AFC65 diffractometer. An  $\omega$ – $2\theta$  data-collection method was used and a scan range of  $13 < 2\theta < 17.5^\circ$  was employed. There were 2657 independent reflections with 2085 observed reflections ( $I > 2\sigma(I)$ ). The structure was solved by direct method using SHELXS-96 [8]. All non-hydrogen atoms are anisotropic except minor orientation of disordered  $\text{CCl}_3$  group. Hydrogen atoms are isotropic. The refinement covered at  $R_1 = 0.0429$  (for significant reflections) and  $wR_1 = 0.0624$  (for all reflections).

## 3. Results and discussion

Treatment of the iron sulfanes  $(\mu\text{-S}_x)[\text{CpFe}(\text{CO})_2]_2$  ( $x = 3, 4$ ) [7] with sulfonyl chlorides  $\text{RSO}_2\text{Cl}$ , where  $\text{R} = \text{CF}_3$ ,  $\text{CCl}_3$  and  $\text{C}_6\text{F}_5$ , in diethylether at room temperature, gave the iron thiosulfonato complexes  $\text{CpFe}(\text{CO})_2\text{SS}(\text{O})_2\text{R}$  ( $\text{R} = \text{CF}_3$ , (**1**)  $\text{CCl}_3$  (**2**),  $\text{C}_6\text{F}_5$  (**3**)) in good yields (76–87%) and  $\text{CpFe}(\text{CO})_2\text{Cl}$  (Eq. (2)). These products were separated by column chromatography.



The thiosulfonato complexes **1–3** are air stable as solids and air sensitive in solution. They are soluble in common organic solvents but insoluble in hexanes. They were characterized by IR, NMR spectroscopy and elemental analysis. Their IR spectra contain the expected [9] two strong bands in the ranges 2030–2064 and 1991–1998  $\text{cm}^{-1}$  corresponding to the stretching frequencies of the two terminal carbonyl ligands. They contain two bands for the thiosulfonato ligand in the ranges 1122–1180 and 1057–1096  $\text{cm}^{-1}$ . These SO bands are similar to those obtained for complexes containing the sulfinato ( $\text{RSO}_2$ ) group [10]. The  $^1\text{H-NMR}$  spectra of **1–3** show a singlet due to the cyclopentadienyl ligand protons in the range 5.21–5.28 ppm, the same range observed for the analogous thio-carboxylate complexes  $\text{CpFe}(\text{CO})_2\text{SC}(\text{O})\text{R}$  [11].

The reactivity of the metal sulfanes toward sulfonyl chlorides may be attributed to the presence of electron-

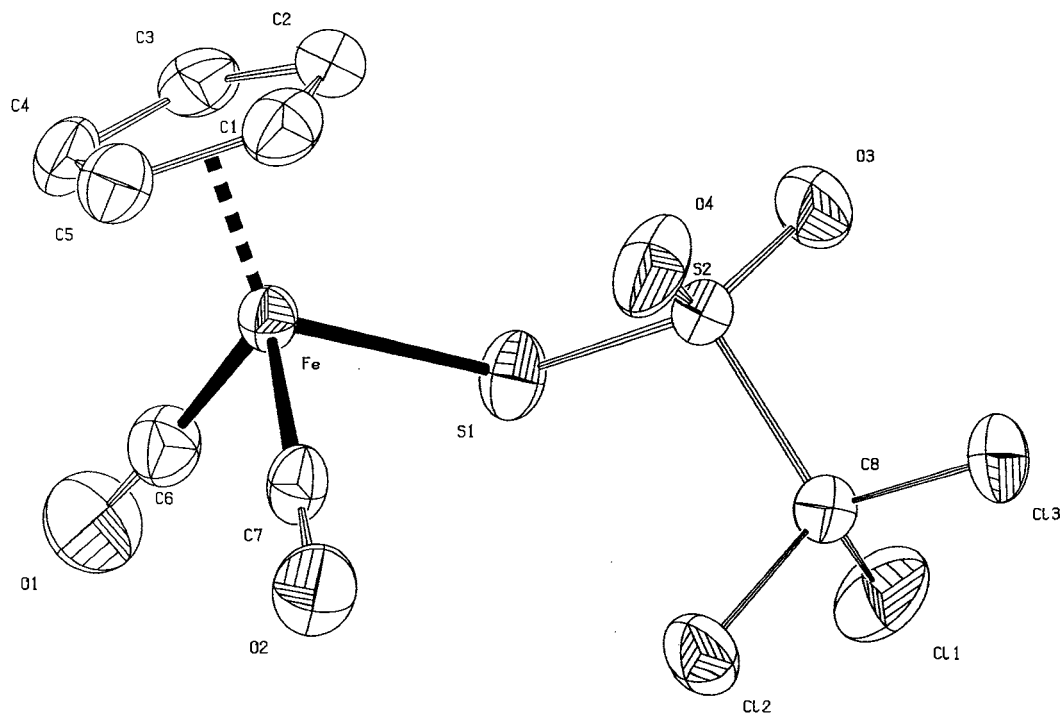


Fig. 1. An ORTEP view of **2** (major orientation). Ellipsoids are drawn at 40% probability level and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Fe–S 2.2803(13), Fe–C(6) 1.777(5), Fe–C(7) 1.783(4), S–S 2.022(2), S–O(4) 1.423(4), S–O(3) 1.432(4), C(6)–Fe–C(7) 94.4(2), S–S–Fe 109.43(6), O(4)–S–O(3) 119.5(3).

rich sulfur atoms in the sulfide bridge. Sulfonyl chlorides with no electron-withdrawing groups ( $R = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_4\text{CH}_3$ ) or even with moderate electron withdrawing groups (2,5-( $\text{NO}_2$ ) $_2\text{C}_6\text{H}_3$ , 4- $\text{NO}_2\text{C}_6\text{H}_4$ ) did not react with the sulfanes. This may be due to the weak electrophilic behavior of the sulfonyl chlorides.

The structure of **2** was determined and is shown in Fig. 1. This compound has a Fe–S bond length of 2.2803(13) Å which is longer than that observed for  $\text{CpFe}(\text{CO})_2\text{SC}(\text{O})\text{-}2\text{-NO}_2\text{C}_6\text{H}_4$  (2.266(1) Å) [11]. The S–S bond length (2.022(2) Å) and the S–O bond lengths (1.432(4) and 1.432(4) Å) are similar to those observed in complexes of the type  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{E}$  where  $\text{E} = \text{SS}(\text{O})\text{CH}_2\text{Ph}$ ,  $\text{SS}(\text{O})\text{CHMe}_2$  and  $\text{SS}(\text{O})_2\text{-}4\text{-C}_6\text{H}_4\text{Me}$  [12].

While complexes containing sulfonato ligands,  $\text{RSO}_2^-$ , are well known [13], thiosulfonato ligands are rare. We are aware of only one example, namely  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS}(\text{O})_2\text{R}$ , which was the product of an oxygen atom disproportionation reaction of  $\text{CpRu}(\text{PPh}_3)(\text{CO})\text{SS}(\text{O})\text{R}$  [12b]. The reaction reported here is the first direct synthesis of this class of ligands. The mechanism of this reaction is probably similar to that proposed for the preparation of  $\text{CpFe}(\text{CO})_2\text{SCOR}$  [11].

#### 4. Supplementary material

Crystallographic data for **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 147214. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

#### Acknowledgements

We thank the Natural Science and Engineering Research Council of Canada and the Quebec Department of Education for financial support. ME thanks the Dean of Research, Jordan University of Science and Technology for financial support, Grant No. 70/99.

#### References

- [1] (a) C.N. Satterfield, in: *Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, New York, 2nd edn., 1991, pp. 378–384.  
(b) B.C. Gates, J.R. Katzer, G.C.R. Schuit, in: *Chemistry of*

- Catalytic Processes, McGraw Hill, New York, 1979, pp. 390–445. (c) D.V. Vivic, W.D. Jones, *Organometallics* 18 (1999) 134. (d) D.V. Vivic, W.D. Jones, *Organometallics* 17 (1998) 3411.
- [2] (a) P. Grancher, *Hydrocarbon Process* 57 (1978) 155. (b) P. Grancher, *Hydrocarbon Process* 57 (1978) 257. (c) Z.M. George, *Can. Chem. Eng.* 63 (1985) 612.
- [3] (a) A. Shaver, P.-Y. Plouffe, *Inorg. Chem.* 31 (1992) 1823. (b) W.A. Schenk, E. Dombrowski, I. Reuther, T.Z. Sturr, *Z. Naturforsch. Teil B* 47 (1992) 732. (c) M.Y. Darensbourg, T. Tuntulani, J.H. Reibenspies, *Inorg. Chem.* 33 (1994) 611. (d) G.J. Kubas, *Inorg. Chem.* 18 (1979) 182. (e) G.J. Kubas, R.R. Ryan, *Inorg. Chem.* 23 (1984) 3181. (f) G.J. Kubas, R.R. Ryan, K.A. Kubar-Martin, *J. Am. Chem. Soc.* 111 (1989) 1910. (g) K.Yamanari, M. Mori, S. Dogi, A. Fuyuhiko, *Inorg. Chem.* 33 (1994) 4807. (h) A. Toupadakis, G.J. Kubas, C. Bruns, *Inorg. Chem.* 31 (1992) 1380.
- [4] A. Shaver, H. Boily, A.-M. Lebuis, *Inorg. Chem.* 35 (1996) 6356.
- [5] A. Shaver, M. El-khateeb, A.-M. Lebuis, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 2362.
- [6] D. Shriver, M. Drezdson, in: *The Manipulation of Air Sensitive Compounds*, Wiley Interscience, Toronto, 2nd edn., 1986.
- [7] M.A. El-Hinnawi, A.A. Aruffo, B.D. Santarsiero, D.B. McAlister, V. Shomaker, *Inorg. Chem.* 22 (1983) 1585.
- [8] G.M. Sheldrick, SHELXL-96, Program for Structure Analysis, University of Göttingen, Germany, 1996.
- [9] T.S. Piper, G.J. Wilkinson, *J. Inorg. Nucl. Chem.* 3 (1956) 104.
- [10] (a) W.A. Schenk, J. Frisch, W. Adam, F. Prechtel, *Inorg. Chem.* 31 (1992) 3329. (b) S.L. Miles, D.L. Miles, R. Bau, T.C. Flood, *J. Am. Chem. Soc.* 100 (1976) 7279. (c) T.C. Flood, F.J. Disanti, D.L. Miles, *Inorg. Chem.* 15 (1976) 1910.
- [11] (a) M.A. El-Hinnawi, A.M. Al-Ajlouni, *J. Organomet. Chem.* 332 (1987) 321. (b) M.A. El-Hinnawi, A.M. Al-Ajlouni, J.S. Abu-Nasser, A.K. Powell, H. Vahrenkamp, *J. Organomet. Chem.* 359 (1989) 79.
- [12] (a) A. Shaver, P.-Y. Plouffe, *Inorg. Chem.* 33 (1992) 4327. (b) A. Shaver, P.-Y. Plouffe, *J. Am. Chem. Soc.* 113 (1991) 7780.
- [13] (a) J.P. Bibler, A. Wojcicki, *J. Am. Chem. Soc.* 88 (1966) 4862. (b) S.E. Jacobson, A. Wojcicki, *J. Am. Chem. Soc.* 95 (1973) 6962.