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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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### Synthesis and Characterization of $\text{CpFe(CO)(EPh}_3\text{)SeSO}_2\text{R}$ (EP, As, Sb)

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**To cite this Article** El-khateeb, Mohammad , Obidate, Tara and Al-Noaimi, Mousa(2009) 'Synthesis and Characterization of  $\text{CpFe(CO)(EPh}_3\text{)SeSO}_2\text{R}$  (EP, As, Sb)', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 184: 3, 585 — 590

**To link to this Article:** DOI: 10.1080/10426500802233613

**URL:** <http://dx.doi.org/10.1080/10426500802233613>

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## Synthesis and Characterization of $\text{CpFe(CO)(EPh}_3\text{)SeSO}_2\text{R}$ ( $\text{E}=\text{P, As, Sb}$ )

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*Photolytic substitution reactions of the iron selenosulfonate complexes  $\text{CpFe(CO)}_2\text{SeSO}_2\text{R}$  with  $\text{EPh}_3$  produces the monosubstituted complexes  $\text{CpFe(CO)(EPh}_3\text{)SeSO}_2\text{R}$  [ $\text{E} = \text{P}$  (a), As (b), Sb (c);  $\text{R} = \text{C}_6\text{H}_5$  (1),  $4\text{-CH}_3\text{C}_6\text{H}_4$  (2),  $4\text{-CH}_3\text{OC}_6\text{H}_4$  (3)] in good yields. Complexes 1–3 were characterized by spectroscopic techniques and elemental analysis.*

**Keywords** Complexes; iron; selenium; selenosulfonate; substitution; triphenylarsine; triphenylphosphine; triphenylstibine

## INTRODUCTION

The substitution reactions of the iron complexes  $\text{Cp}'\text{Fe(CO)}_2\text{X}$  ( $\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5, \text{C}_5\text{H}_4\text{Bu}^t, \text{C}_5\text{H}_3(\text{Bu}^t)_2$ ;  $\text{X} = \text{alkyl, aryl, silyl, thiocarboxylate, selenocarboxylate}$ ) with  $\text{EPh}_3$  ( $\text{E}=\text{P, As, Sb}$ ) ligands have been investigated thoroughly.<sup>1–10</sup> These reactions were found to give a variety of products such as  $\text{CpFe(CO)(EPh}_3\text{)X}$ ,  $[\text{CpFe(CO)}_2(\text{EPh}_3)]\text{X}$ , or  $[\text{CpFe(EPh}_3)_3]\text{X}$  depending on the reaction conditions.<sup>1–10</sup>

Our research group has been interested in photolytic CO-substitution reactions of the iron thiocarboxylate complexes  $(\text{Cp}'\text{Fe(CO)}_2\text{SCOR})$ .<sup>7,11,12</sup> The reactions of the latter iron complexes with  $\text{EPh}_3$  ligands were reported to produce the monosubstituted complexes  $\text{Cp}'\text{Fe(CO)(EPh}_3\text{)SCOR}$ .<sup>7</sup> The disubstituted products  $(\text{Cp}'\text{Fe(EPh}_3)_2\text{SCOR})$  were never obtained in these reactions.<sup>7</sup>

Received 22 April 2008; accepted 27 May 2008.

We are grateful to the Deanship of Scientific Research, Jordan University of Science and Technology, for financial support (grant no. 106/2000).

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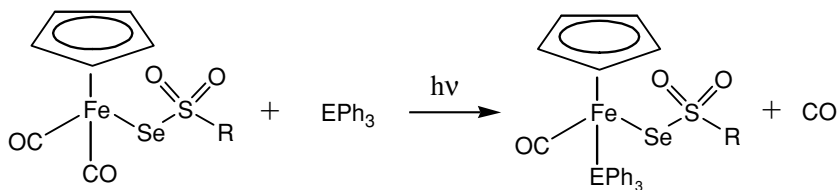
The effects of Cp-substituents, the R-group of the thiocarboxylate ligands, and the donor atom of the  $\text{EPh}_3$  ligands on the rate of these reactions have been reported.<sup>7</sup> However, the analogous reactions with bis(diphenylphosphino)alkane ligands ( $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ;  $n = 1-6$ ) gave the monosubstituted complexes  $\text{CpFe}(\text{CO})(\kappa P\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{SCOR}$  for  $n = 1-6$  and the disubstituted complexes  $\text{CpFe}(\kappa^2 P, P\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)\text{SCOR}$  only for  $n = 1$  and 2.<sup>11,12</sup> The reactions of the selenocarboxylate complexes  $\text{CpFe}(\text{CO})_2\text{SeCOR}$  with  $\text{EPh}_3$  have been also reported to give the mono-substituted complexes  $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeCOR}$ .<sup>[10]</sup>

The importance of selenosulfonate group in organic synthesis<sup>13</sup> prompted us to make complexes containing this ligand, which are rare in the literature. The iron selenosulfonate complexes  $\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$  have been made by the reaction of  $(\mu\text{-Se})[\text{CpFe}(\text{CO})_2]_2$  with sulfonyl chlorides.<sup>14</sup> The tungsten analogues  $\text{CpW}(\text{CO})_3\text{SeSO}_2\text{R}$  were made by the reaction of the tungsten anions  $\text{CpW}(\text{CO})_3\text{Se}^-$  with sulfonyl chlorides.<sup>15</sup>

Here we report the synthesis of the substituted iron selenosulfonate complexes  $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeSO}_2\text{R}$  from the photolytic reaction of the parent dicarbonyl complexes ( $\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$ ) with  $\text{EPh}_3$  ligands.

## RESULTS AND DISCUSSION

The photolytic reaction of  $\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$  with triphenylphosphine, triphenylarsine, or triphenylstibine gave the corresponding CO-substituted complexes  $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeSO}_2\text{R}$  (**1-3**) as shown in Scheme 1.



R = Ph (**1**), 4- $\text{CH}_3\text{C}_6\text{H}_4$  (**2**), 4- $\text{CH}_3\text{OC}_6\text{H}_4$  (**3**)

E = P (**a**), As (**b**), Sb (**c**)

### SCHEME 1

The complexes **1-3** are stable in the solid state, but are sensitive in solution. Complexes **1-3** were characterized by IR and  $^1\text{H}$  NMR spectroscopy and by elemental analysis. The IR spectra of these

complexes exhibit one very strong band for the terminal carbonyl group in the range of 1955–1967  $\text{cm}^{-1}$ . These bands are at higher frequency than those reported for the corresponding selenocarboxylates  $\text{CpFe(CO)(EPh}_3\text{)SeCOR}$  (1941–1957  $\text{cm}^{-1}$ ).<sup>10</sup> This shift might be attributed to lower electron density around the iron atom in complexes **1–3** compared to the corresponding selenocarboxylate complexes. The IR bands appear at lower frequency than the corresponding bands for the parent dicarbonyl complexes, which exhibit two bands in the ranges of 2038–2043 and 1993–1999  $\text{cm}^{-1}$ .<sup>14</sup> A similar shift was observed for the thiocarboxylate system.<sup>7,16,17</sup> This shift may be due to the weak  $\pi$ -acceptor property of the incoming  $\text{EPh}_3$  ligand compared to that of the leaving CO ligand. The S=O stretching bands appear in the IR spectra of **1–3** as two strong bands in the ranges of 1260–1268 and 1110–1124  $\text{cm}^{-1}$ . These bands are in good agreement with those reported for  $\text{CpFe(CO)}_2\text{SeSO}_2\text{R}$ <sup>14</sup> and other complexes containing seleno- and thiosulfonate groups.<sup>15,18,19</sup>

In the  $^1\text{H}$  NMR spectra of **1–3** in  $\text{CDCl}_3$ , the protons of the cyclopentadienyl ligand appear as one singlet in the range of 4.62–4.88 ppm. This resonance is at higher field compared to that of the starting dicarbonyl complexes  $\text{CpFe(CO)}_2\text{SeSO}_2\text{R}$  (5.19–5.24 ppm).<sup>14</sup> This shift is consistent with an increase of the electron density around the Fe center by substitution of one carbonyl group by the  $\text{EPh}_3$  ligand. The proton chemical shift for the Cp substituent in **1–3** is similar to that observed for the corresponding selenocarboxylate complexes  $\text{CpFe(CO)(EPh}_3\text{)SeCOR}$  (4.61–4.87 ppm).<sup>10</sup> The  $^1\text{H}$  NMR signals of the R groups and the  $\text{EPh}_3$  ligands are present in the spectra with the expected multiplicity and integral ratio.

Table I shows the reaction times for the substitution reactions. The data indicate that the reaction time decreases in the order of  $\text{C}_6\text{H}_5 > \text{C}_6\text{H}_4\text{CH}_3 \geq \text{C}_6\text{H}_4\text{OCH}_3$ . The data also show that the reaction times for the reactions reported in this study are shorter than those for the

**TABLE I** Reaction Times for the Reaction of  $\text{CpFe(CO)}_2\text{SeSO}_2\text{R}$  with  $\text{EPh}_3$

E/R	Reaction times (min)		
	P	As	Sb
$\text{C}_6\text{H}_5$	80	85	70
4-Me $\text{C}_6\text{H}_4$	110	110	115
4-MeOC $_6\text{H}_4$	120	115	115

reactions of the selenocarboxylate complexes.<sup>10</sup> This is due to the weaker Fe-CO bond in  $\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$  compared to the analogous bond in the selenocarboxylate complexes.

## EXPERIMENTAL

Reactions and manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk line techniques. Tetrahydrofuran and hexane were dried over sodium/benzophenone and were distilled under nitrogen prior to use. Methylene chloride was distilled over  $\text{P}_2\text{O}_5$ . The complexes  $\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$  were prepared using a published method.<sup>14</sup> The reagents  $\text{EPh}_3$ ,  $[\text{CpFe}(\text{CO})_2]_2$ , the sulfonyl chlorides, and elemental selenium were obtained from Acros and were used as received.

NMR spectra were recorded with a Bruker 80 MHz spectrometer. Chemical shifts are in ppm relative to TMS as external standard. IR spectra were recorded on a Nicolet Nexus FT-IR spectrometer using NaCl solvent cells. Elemental analyses were performed in the Laboratoire d'Analyse Élémentaire, Université de Montréal, Montréal, Québec, Canada. Melting points were measured with an electrothermal melting point apparatus and are uncorrected. The photolytic reactions were carried out with a medium pressure mercury lamp (150 W) and a quartz immersion cell.

### General Procedure for the Preparation of $\text{CpFe}(\text{CO})(\text{EPh}_3)\text{SeSO}_2\text{R}$ (1–3)

A THF solution of  $\text{CpFe}(\text{CO})_2\text{SeSO}_2\text{R}$  (0.50 mmol) and  $\text{EPh}_3$  (0.51 mmol) is irradiated by UV light at  $0^\circ\text{C}$  until the disappearance of the bands in the range of  $2038\text{--}2043\text{ cm}^{-1}$  and  $1993\text{--}1999\text{ cm}^{-1}$  and the appearance of a single band in the range of  $1955\text{--}1967\text{ cm}^{-1}$ . The volatiles were removed under reduced pressure and the resulting solid was redissolved in a minimum amount of  $\text{CH}_2\text{Cl}_2$  and transferred to a silica gel column made up in hexane. The column was first eluted with hexane to remove any unreacted  $\text{EPh}_3$  ligand. Elution with hexane/dichloromethane solution (3:1) gives a dark red band of the products. The products were recrystallized from dichloromethane/hexane.

### ***CpFe(CO)(PPh<sub>3</sub>)SeSO<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (1a)***

Yield, 0.44 g, 55%. Mp  $126\text{--}128^\circ\text{C}$ . IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu = 1959$  (s) ( $\text{C}\equiv\text{O}$ ),  $1260$  (s),  $1119$  (s) ( $\text{SO}_2$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 4.65$  (s, 5H,  $\text{C}_5\text{H}_5$ ),  $7.83$  (m, 15H,  $\text{PPh}_3$ ),  $7.85$  (m, 5H,  $\text{C}_6\text{H}_5$ ). Anal. Calcd. for

$C_{30}H_{25}FeO_3PSSe$ : C, 57.07; H, 3.99; S, 5.08. Found: C, 56.58; H, 4.03; S, 5.23%.

**$CpFe(CO)(AsPh_3)SeSO_2C_6H_5$  (1b)**

Yield, 0.38 g, 45%. Mp 179–180°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1957$  (s) ( $C\equiv O$ ), 1261 (s), 1119 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 4.80$  (s, 5H,  $C_5H_5$ ), 7.80 (m, 15H,  $AsPh_3$ ), 7.87 (m, 5H,  $C_6H_5$ ). Anal. Calcd. for  $C_{30}H_{25}FeO_3AsSSe$ : C, 53.36; H, 3.73; S, 4.75. Found: C, 53.04; H, 3.86; S, 5.01%.

**$CpFe(CO)(SbPh_3)SeSO_2C_6H_5$  (1c)**

Yield, 0.51 g, 65%. Mp 146–148°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1957$  (s) ( $C\equiv O$ ), 1261 (s), 1119 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 4.85$  (s, 5H,  $C_5H_5$ ), 7.54 (m, 15H,  $SbPh_3$ ), 8.20 (m, 5H,  $C_6H_5$ ). Anal. Calcd. for  $C_{30}H_{25}FeO_3SbSSe$ : C, 49.90; H, 3.49; S, 4.44. Found: C, 48.95; H, 3.25; S, 5.09%.

**$CpFe(CO)(PPh_3)SeSO_2(4-MeC_6H_4)$  (2a)**

Yield, 0.35 g, 45%. Mp 84–85°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1967$  (s) ( $C\equiv O$ ), 1264 (s), 1124 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 2.46$  (s, 3H,  $CH_3$ ), 4.62 (s, 5H,  $C_5H_5$ ), 7.76 (m, 15H,  $PPh_3$ ), 7.79 (m, 4H,  $C_6H_4$ ). Anal. Calcd. for  $C_{31}H_{27}FeO_3PSSe$ : C, 57.69; H, 4.22; S, 4.97. Found: C, 57.13; H, 4.05; S, 5.09%.

**$CpFe(CO)(AsPh_3)SeSO_2(4-MeC_6H_4)$  (2b)**

Yield, 0.42 g, 50%. Mp 61–62°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1965$  (s) ( $C\equiv O$ ), 1265 (s), 1117 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 2.39$  (s, 3H,  $CH_3$ ), 4.86 (s, 5H,  $C_5H_5$ ), 7.43 (m, 15H,  $AsPh_3$ ), 7.84 (m, 4H,  $C_6H_4$ ). Anal. Calcd. for  $C_{31}H_{27}FeO_3AsSSe$ : C, 54.01; H, 3.95; S, 4.65. Found: C, 53.67; H, 3.95; S, 5.11%.

**$CpFe(CO)(SbPh_3)SeSO_2(4-MeC_6H_4)$  (2c)**

Yield, 0.58 g, 65%. M.p. 64–65°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1955$  (s) ( $C\equiv O$ ), 1261 (s), 1110 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 2.39$  (s, 3H,  $CH_3$ ), 4.88 (s, 5H,  $C_5H_5$ ), 7.79 (m, 15H,  $SbPh_3$ ), 8.84 (m, 5H,  $C_6H_5$ ). Anal. Calcd. for  $C_{31}H_{27}FeO_3SbSSe$ : C, 50.58; H, 3.70; S, 4.36. Found: C, 49.81; H, 3.52; S, 4.48%.

**$CpFe(CO)(PPh_3)SeSO_2(4-MeOC_6H_4)$  (3a)**

Yield, 0.36 g, 47%. Mp 72–73°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1967$  (s) ( $C\equiv O$ ), 1267 (s), 1119 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 2.46$  (s, 3H,  $CH_3$ ), 4.62 (s, 5H,  $C_5H_5$ ), 7.76 (m, 15H,  $PPh_3$ ), 7.79 (m, 4H,  $C_6H_4$ ). Anal.

Calcd. for  $C_{31}H_{27}FeO_4PSSe$ : C, 56.30; H, 4.11; S, 4.85. Found: C, 56.14; H, 4.00; S, 4.26%.

***CpFe(CO)(AsPh<sub>3</sub>)SeSO<sub>2</sub>(4-MeOC<sub>6</sub>H<sub>4</sub>) (3b)***

Yield, 0.45 g, 54%. Mp 84–86°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1966$  (s) ( $C\equiv O$ ), 1268 (s), 1117 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 2.39$  (s, 3H,  $CH_3$ ), 4.66 (s, 5H,  $C_5H_5$ ), 7.43 (m, 15H,  $AsPh_3$ ), 7.84 (m, 4H,  $C_6H_4$ ). Anal. Calcd. for  $C_{31}H_{27}FeO_4AsSSe$ : C, 52.79; H, 3.86; S, 4.55. Found: C, 52.52; H, 3.45; S, 4.12%.

***CpFe(CO)(SbPh<sub>3</sub>)SeSO<sub>2</sub>4-MeOC<sub>6</sub>H<sub>4</sub>) (3c)***

Yield, 0.60 g, 68%. Mp 66–67°C. IR ( $CH_2Cl_2$ ,  $cm^{-1}$ ):  $\nu = 1957$  (s) ( $C\equiv O$ ), 1267 (s), 1119 (s) ( $SO_2$ ).  $^1H$  NMR ( $CDCl_3$ ):  $\delta = 2.43$  (s, 3H,  $CH_3$ ), 4.70 (s, 5H,  $C_5H_5$ ), 7.81 (m, 15H,  $SbPh_3$ ), 8.84 (m, 5H,  $C_6H_5$ ). Anal. Calcd. for  $C_{31}H_{27}FeO_4SbSSe$ : C, 49.50; H, 3.62; S, 4.26. Found: C, 49.61; H, 3.42; S, 3.88%.

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