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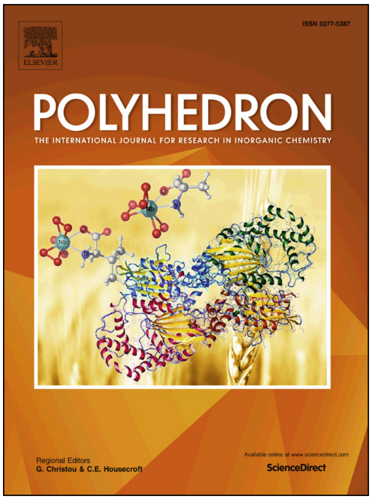

PII: S0277-5387(17)30352-2
DOI: http://dx.doi.org/10.1016/j.poly.2017.05.016
Reference: POLY 12635

To appear in: *Polyhedron*

Received Date: 25 April 2017
Accepted Date: 9 May 2017

Please cite this article as: M. El-khateeb, A. Mansor, I. Jibril, T. Rüffer, H. Lang, Substitution Reactions of Mono-, Di- and Tri-thiocarbonato Complexes of Iron, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly.2017.05.016

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Substitution Reactions of Mono-, Di- and Tri-thiocarbonato Complexes of Iron

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Abstract

The photolytic reactions of iron thiocarbonato complexes $CpFe(CO)_2SC(Y)Y'R$ [Y= Y'= O; R= 2-C_6H_4Cl (**1**), 4-C_6H_4Cl (**2**); Y= S, Y'= O; R= C_6H_4F (**3**), Y= Y' = S; R= Ph (**4**)] with EPh_3 (E = P, As, Sb) are performed. Monosubstituted complexes of the general formula $CpFe(CO)(EPh_3)SC(Y)Y'R$ [Y= Y'= O; R= 2-C_6H_4Cl (**5**), 4-C_6H_4Cl (**6**); Y= S, Y'= O; R= C_6H_4F (**7**), Y= Y' = S; R= Ph (**8**); E= P (**a**), As (**b**), Sb (**c**)] have been isolated and characterized by spectroscopic analysis (UV-Vis, IR, ^{1}H-, ^{31}P-NMR) and elemental analysis. The molecular structures of $CpFe(CO)(PPh_3)SCO_2$-2-C_6H_4Cl (**5a**) and its dicarbonyl parent $CpFe(CO)_2SCO_2$-2-C_6H_4Cl (**1**) have been determined by single crystal X-ray crystallographic studies.

Keywords: Iron, Thiocarbonate, Substitution, Sulfur, Complexes, Structures.

1. Introduction

Iron carbonyl complexes undergo smooth substitution of one or more CO groups generating a number of different products [1-10]. Reactions of $CpFe(CO)_2X$ (X= SPh, $SiMe_3$, $SnMe_3$, $SnPh_3$) with PMe_3 gave the mono-substituted $CpFe(CO)(PMe_3)X$ and the di-substituted $CpFe(PMe_3)_2X$ products [1]. The reaction of $CpFe(CO)_2Me$ with PMe_3 gave either the inserted product $CpFe(CO)(PMe_3)COMe$ or the di-substituted one $CpFe(PMe_3)_2Me$ depending on the reaction conditions [2]. On the other hand, the photolytic reaction of the ethyl derivative $CpFe(CO)_2Et$ with L (= $P(OMe)_3$, PMe_3) gave the mono and the disubstituted

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complexes in addition to the hydrides $CpFe(CO)(L)H$ and $CpFe(L)_2H$ [3]. The silyl complex $CpFe(CO)_2SiH_3$ reacted with various donors (L= PMe_3, PPh_3, MeNC, t-BuNC) to give $CpFe(CO)(L)SiH_3$ and $CpFe(L)_2SiH_3$ via stepwise CO substitution [4-6].

The CO-substitution reactions of iron thiocarboxylato complexes have been investigated in our lab. The reaction of the these complexes ($CpFe(CO)_2SCOR$) with ER_3 ligands produced the mono-substituted complexes $CpFe(CO)(ER_3)SCOR'$ (E= P, R= Ph, OEt, E= As, Sb, R= Ph, R'= alkyl, aryl, heterocycle) [11,12]. The reactions of these thiocarboxylato complexes with $Ph_2P(CH_2)_nPPh_2$ (n= 1-6) gave either the mono-substituted complexes $CpFe(CO)(\kappa P\text{-}Ph_2P(CH_2)_nPPh_2)SCOR$ for n= 1-6 or the di-substituted complexes $CpFe(\kappa^2 P,P\text{-}Ph_2P(CH_2)_nPPh_2)SCOR$ only for n= 1 and 2 [13,14]. The ethyldithiocarbonato complexes $Cp'Fe(CO)_2SCSOEt$ (Cp'= C_5H_5, C_5Me_5) reacted with phosphine or phosphite ligands (= L) to form $Cp'Fe(CO(L)SCSOEt$ [15,16].

Thiocarbonato metal complexes have found application in different fields [17-24]. In the medical field, thiocarbonates are used against HIV infections, have antitumor properties [17, 18] and are of great importance for treating Alzheimer's disease [19]. Industrially, they have been used for nanoparticles of metal sulfides production [20,21] and corrosion inhibitors [22]. In agriculture, metal thiocarbonates are used as pesticides [23] and herbicide [24]. This importance prompted us to synthesize thiocarbonate complexes of iron [25-27]. As a continuation to our efforts on the area of thiocarbonate complexes of iron, herein, we report the CO-substitution reactions of iron mono-, di- and tri-thiocarbonato complexes by EPh_3 donors. The molecular structures of two complexes are presented.

Experimental

Materials and Methods

Synthesis and manipulations were performed under an atmosphere of nitrogen using standard Schlenk line techniques. The following solvents: tetrahydrofuran, diethyl ether, hexane were dried over sodium/benzophenone and CH_2Cl_2 was dried over P_2O_5 following standard procedure. The compounds triphenylphosphine, triphenylarsine, triphenylantimony were used as received (Acros) while $CpFe(CO)_2SC(Y)Y'R$ are prepared following reported

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procedures [25-27]. Silica gel of particle size 0.063-0.200 mm (70-230 mesh) was used for column chromatography after drying at 110 °C for several days.

Bruker-Avance 400 MHz spectrometer was used to measure the nuclear magnetic resonance (NMR) spectra of the synthesized complexes. Chemical shifts are reported relative to TMS at 0 ppm for ^{1}H-NMR and relative to H_3PO_4 (as external standard) for ^{31}P-NMR and are reported in ppm. Melting points were reported on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed using a vairo EL III CHNS (Elemental analyse GmbH Hanau) as single determination. The UV-Vis and IR spectra were recorded on a Shimadzu 240-UV–Vis and a JASCO FT-IR spectrophotometer, respectively. The photolytic reactions were carried out using a low pressure mercury lamp (Herauios).

Synthesis of $CpFe(CO)(EPh_3)SC(S)O\text{-}2\text{-}C_6H_4Cl$ ***1***

The compound is prepared following the reported procedure [26]. Orange (88%). m.p.: 105-106 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 2042, 1994 (s); $\nu_{SeC=O}$ 1670 (m). ^{1}H-NMR ($CDCl_3$): 5.05 (s, 5H, C_5H_5), 6.80 (m, 2H, C_6H_4), 7.33 (m, 2H, C_6H_4). Anal. Calc. for $C_{14}H_9ClFeO_4S$: C, 46.12; H, 2.49; S, 8.80%. Found: C, 45.90; H, 2.48; S, 8.32%.

General Procedure for the Preparation of $CpFe(CO)(EPh_3)SC(Y)Y'R$ ***5-8***

A mixture of $CpFe(CO)_2SC(Y)Y'R$ (1.00 mmol) and EPh_3 (1.10 mmol) was dissolved in 50 mL THF and the solution is irradiated by UV-light at 0 ˚C for 60 – 90 min until the disappearance of the spot of the starting dicarbonyl complexes as indicated by TLC. The volatiles were removed under reduced pressure and the resulting solid was re-dissolved in *ca.* 2 mL of CH_2Cl_2 and chromatographed. The column was eluted with hexane to remove any unreacted EPh_3 ligand and then with hexane/diethyl ether solution (1:1 V:V) which gave a dark red band of the products. The products were recrystallized by layering hexane on CH_2Cl_2 solution of them and kept overnight at -4 ˚C. In some experiments, another red band was collected and identified as the chelate complexes CpFe(CO)(κ^2*S*,*S*-SC(S)Y'R).

$CpFe(CO)(PPh_3)SCO_2\text{-}2\text{-}C_6H_4Cl$ ***5a*** Brown (61%). m.p.: 115-116 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1955 (s); $\nu_{SC=O}$ 1674 (m). ^{1}H-NMR ($CDCl_3$): 4.51 (s, 5H, C_5H_5), 7.03 (m, 2H, C_6H_4),

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7.18 (m, 2H, C_6H_4), 7.37 (m, 15H, PPh_3). ^{31}P-NMR ($CDCl_3$): δ 68.0. UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, $M^{-1}cm^{-1}$): 402 (3.2 × 10^4). Anal. Calc. for $C_{31}H_{24}ClFeO_3PS$: C, 62.17; H, 4.04; S, 5.35%. Found: C, 62.17; H, 4.19; S, 4.84%.

CpFe(CO)(AsPh$_3$)SCO$_2$-2-C$_6$H$_4$Cl ***5b*** Dark red (56%). m.p.: 131-132 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1951 (s); $\nu_{SC=O}$ 1675 (m). ^{1}H-NMR ($CDCl_3$): 4.63 (s, 5H, C_5H_5), 7.18 (m, 2H, C_6H_4), 7.34 (m, 2H, C_6H_4), 7.48 (m, 15H, $AsPh_3$). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, $M^{-1}cm^{-1}$): 395 (6.6 × 10^4). Anal. Calc. for $C_{31}H_{24}ClFeO_3AsS$: C, 57.32; H, 3.76; S, 4.99%. Found: C, 57.60; H, 3.65; S, 4.54%.

CpFe(CO)(SbPh$_3$)SCO$_2$-2-C$_6$H$_4$Cl ***5c*** Brown (44%). m.p.: 120-122 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1924 (s); $\nu_{SC=O}$ 1666 (m). ^{1}H-NMR ($CDCl_3$): 4.75 (s, 5H, C_5H_5), 6.63 (m, 2H, C_6H_4), 7.16 (m, 2H, C_6H_4), 7.41 (d, 15H, $SbPh_3$). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, $M^{-1}cm^{-1}$): 404 (3.5 × 10^4). Anal. Calc. for $C_{31}H_{24}ClFeO_3SbS$: C, 53.99; H, 3.51; S, 4.65%. Found: C, 53.74; H, 3.67; S, 4.33%.

CpFe(CO)(PPh$_3$)SCO$_2$-4-C$_6$H$_4$Cl ***6a*** Brown (65%). m.p.: 110-111 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1988 (s); $\nu_{SC=O}$ 1674 (m). ^{1}H-NMR ($CDCl_3$): 4.57 (s, 5H, C_5H_5), 7.03 (d, 2H, C_6H_4), 7.29 (d, 2H, C_6H_4), 7.44 (m, 15H, PPh_3). ^{31}P-NMR ($CDCl_3$): δ 71.2. UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, $M^{-1}cm^{-1}$): 398 (5.0 × 10^4). Anal. Calc. for $C_{31}H_{24}ClFeO_3PS$: C, 62.17; H, 4.04; S, 5.35%. Found: C, 61.42; H, 3.78; S, 5.12%.

CpFe(CO)(AsPh$_3$)SCO$_2$-4-C$_6$H$_4$Cl ***6b*** (51%). m.p.: 131-132 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1956 (s); $\nu_{SC=O}$ 1672 (m). ^{1}H-NMR ($CDCl_3$): 4.60 (s, 5H, C_5H_5); 6.93 (d, 2H, C_6H_4), 7.19 (d, 2H, C_6H_4), 7.37 (m, 15H, $AsPh_3$). UV–Vis. in CH_2Cl_2: λ_{max}(nm) (ε_{max}, $M^{-1}cm^{-1}$): 405 (4.8 × 10^4). Anal. Calc. for $C_{31}H_{24}ClFeO_3AsS$: C, 57.32; H, 3.76; S, 4.99%. Found: C, 57.20; H, 3.65; S, 4.67%.

CpFe(CO)(SbPh$_3$)SCO$_2$-4-C$_6$H$_4$Cl ***6c*** Brown (42%). m.p.: 130-132 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1947 (s); $\nu_{SC=O}$ 1647 (m). ^{1}H-NMR ($CDCl_3$): 4.67 (s, 5H, C_5H_5), 7.09 (d, 2H, C_6H_4), 7.34 (d, 2H, C_6H_4), 7.44 (m, 15H, $SbPh_3$). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, $M^{-1}cm^{-1}$): 401 (7.2 × 10^4). Anal. Calc. for $C_{31}H_{24}ClFeO_3SbS$: C, 53.99; H, 3.51; S, 4.65%. Found: C, 53.65; H, 3.70; S, 4.20%.

CpFe(CO)(PPh$_3$)SC(S)O-4-C$_6$H$_4$F ***7a*** (55%). Brown. m.p.: 125-126˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1942 (s); $\nu_{SC=O}$ 1581 (m). ^{1}H-NMR ($CDCl_3$): 4.59 (s, 5H, C_5H_5), 7.09 (d, 2H, C_6H_4), 7.44 (d, 2H, C_6H_4), 7.42 (m, 15H, PPh_3). ^{31}P-NMR ($CDCl_3$): δ 73.0. UV–Vis. in CH_2Cl_2:

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λ_{max} (nm) (ε_{max}, M^{-1}cm^{-1}): 370 (5.3 × 10^4). Anal. Calc. for $C_{31}H_{24}FFeO_2PS_2$: C, 62.21; H, 4.04; S, 10.72%. Found: C, 62.25; H, 4.24; S, 9.96%.

CpFe(CO)(AsPh$_3$)SC(S)O-4-C$_6$H$_4$F ***7b*** (68%). Red. m.p.: 135-136 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1990 (s); $\nu_{SC=O}$ 1504 (m). ^{1}H-NMR ($CDCl_3$): 4.60 (s, 5H, C_5H_5), 6.69 (d, 2H, C_6H_4), 7.03 (d, 2H, C_6H_4), 7.14 (m, 15H, $AsPh_3$). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, M^{-1}cm^{-1}): 378 (5.5 × 10^4). Anal. Calc. for $C_{31}H_{24}FFeO_2AsS_2$: C, 57.96; H, 3.77; S, 9.98%. Found: C, 58.63; H, 3.54; S, 9.93%.

CpFe(CO)(PPh$_3$)SC(S)O-4-C$_6$H$_4$F ***7c*** Brown. (64%). m.p.: 149-150 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1942 (s); $\nu_{SC=O}$ 1449 (m). ^{1}H-NMR ($CDCl_3$): 4.66 (s, 5H, C_5H_5), 6.85 (d, 1H, C_6H_4), 7.09 (d, 1H, C_6H_4), 7.10 (m, 15H, $SbPh_3$). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, M^{-1}cm^{-1}): 386 (1.2 × 10^4). Anal. Calc. for $C_{31}H_{24}FFeO_2S_2Sb$: C, 54.02; H, 3.51; S, 9.30%. Found: C, 53.98; H, 3.41; S, 8.44%.

CpFe(CO)(PPh$_3$)SCS$_2$C$_6$H$_5$ ***8a*** Brwon (48%). m.p.: 142-143 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1941 (s); $\nu_{SC=O}$ 1589 (m). ^{1}H-NMR ($CDCl_3$): 4.61 (s, 5H, C_5H_5), 7.11 (m, 3H, C_6H_5), 7.46 (d, 2H, C_6H_5), 7.48 (m, 15H, PPh_3). ^{31}P-NMR ($CDCl_3$): δ 77.5. UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, M^{-1}cm^{-1}): 364 (3.3 × 10^4). Anal. Calc. for $C_{31}H_{26}FeOPS_3$: C, 62.41; H, 4.22; S, 16.13%. Found: C, 63.22; H, 4.47; S, 16.23%.

CpFe(CO)(AsPh$_3$)SCS$_2$C$_6$H$_5$ ***8b*** Red (58%). m.p.: 158-160˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1932 (s); $\nu_{SC=O}$ 1573 (m). ^{1}H-NMR ($CDCl_3$): 4.49 (s, 5H, C_5H_5), 6.94 (m, 3H, C_6H_5), 7.38 (d, 1H, C_6H_5), 7.39 (m, 15H, $AsPh_3$). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, M^{-1}cm^{-1}): 374 (4.6 × 10^4). Anal. Calc. for $C_{31}H_{25}FeOAsS_3$: C, 58.13; H, 3.39; S, 15.02%. Found: C, 58.54; H, 3.51; S, 15.20%.

CpFe(CO)(SbPh$_3$)SCS$_2$C$_6$H$_5$ ***8c*** Brown (62%). m.p.: 158-159 ˚C. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 1923 (s); $\nu_{SC=O}$ 1648 (m). ^{1}H-NMR ($CDCl_3$): 4.75 (s, 5H, C_5H_5), 6.95 (m, 3H, C_6H_5), 7.36 (m, 15H, $SbPh_3$); 7.42 (d, 2H, C_6H_5). UV–Vis. in CH_2Cl_2: λ_{max} (nm) (ε_{max}, M^{-1}cm^{-1}): 365 (1.9 × 10^4). Anal. Calc. for $C_{31}H_{25}FeOS_3Sb$: C, 54.17; H, 3.67; S, 14.00%. Found: C, 54.37; H, 3.57; S, 13.64%.

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Crystal Structure Determination

Crystallographic data, data collection and refinement parameters for **5a** (120 K, Mo Kα radiation) and **1** (120 K, Cu Kα radiation) are summarized in Table 1. The structures were solved by direct methods (SHELXS-2013 [28]) and refined by full-matrix least squares techniques against F^2 (SHELXL-2013 [28]). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included at calculated positions with default SHELXL-2013 constraints. In case of **1** the C_6H_4ClO group composed of the atoms C9–C14, Cl1 and O4 was refined disordered with split occupancies of 0.55/0.45.

Table 1: Crystallographic data and refinement details for $CpFe(CO)_2SCO_2$-2-C_6H_4Cl, **1** and $CpFe(CO)(PPh_3)SCO_2$-2-C_6H_4Cl, **5a**

	5a	**1**
Empirical formula	$C_{31}H_{24}ClFeO_3PS$	$C_{14}H_9ClFeO_4S$
Formula weight (g/mol)	598.83	364.57
Temperature (K)	120	120
Wavelength (Å)	0.71073	1.54184
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$
Unit cell dimension		
a (Å)	9.7885(2)	22.4764(5)
b (Å)	13.5466(3)	9.0964(2)
c (Å)	20.6635(5)	14.0733(3)
α (°)	90	90
β (°)	96.571(2)	92.048(2)
γ (°)	90	90
Volume (Å)	2722.00(11)	2875.51(11)
Z	4	8
Density(calculate) Mg/m^3	1.461	1.684
Absorption coefficient mm^{-1}	0.820	11.599
F(000)	1232	1472
Theta range for data collection (°)	3.007 to 24.999	5.246 to 66.453
Indices ranges	$-11 \le h \le 11$ $-16 \le k \le 15$ $-24 \le l \le 24$	$-21 \le h \le 26$ $-9 \le k \le 10$ $-16 \le l \le 16$
Reflections collected	11922	4294
Independent reflections	4764 $R_{int}{}^a = 0.0294$	2501 $R_{int}{}^a = 0.0233$
Completeness (%),	99.3,	98.5,

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$\theta_{\max}$ (°)	24.999	66.453
Data / restraints / parameters	4764 / 0 / 343	2501 / 4 / 239
Goodness-of-fit on F^{2}[b]	1.004	1.025
Final R indices $[I > 2\sigma(I)]$ [c]	$R_1 = 0.0475$, $wR_2 = 0.1170$	$R_1 = 0.0334$, $wR_2 = 0.0864$
R indices (all data) [c]	$R_1 = 0.0593$, $wR_2 = 0.1233$	$R_1 = 0.0362$, $wR_2 = 0.0884$
Largest diff. peak and hole ($e \cdot A^{-3}$)	1.104 and –0.677	0.402 and –0.313

[a] $R_{int} = \Sigma | F_o^2 - F_o^2(\text{mean}) | / \Sigma F_o^2$, where F_o^2(mean) is the average intensity of symmetry equivalent diffractions. [b] $S = [\Sigma w(F_o^2 - Fc^2)^2]/(n - p)^{1/2}$, where n = number of reflections, p = number of parameters. [c] $R = [\Sigma(||F_o| - |F_c|)/\Sigma|F_o|)$; $wR = [\Sigma(w(F_o^2 - F_c^2)2)/\Sigma(wF_o^4)]^{1/2}$.

Results and Discussion

Synthesis

Treatment of the thiocarbonato complexes of iron (**1-4**) with EPh_3 under photolytic conditions produced the mono-substituted complexes in moderate yields (Scheme 1). For the di- (**3**: Y= S) and tri-thiocarbonato complexes (**4**: Y= Y'= S) small amounts of the chelated complexes (**9**, **10**) were obtained from these reactions (Scheme 1). They have been identified by their spectroscopic techniques and compared to the reported values [26,27]. Treatment of the chelated complexes with EPh_3, either photolytically or thermally, did not lead to the substituted products **5-8**, only decomposition of the reactants are observed.

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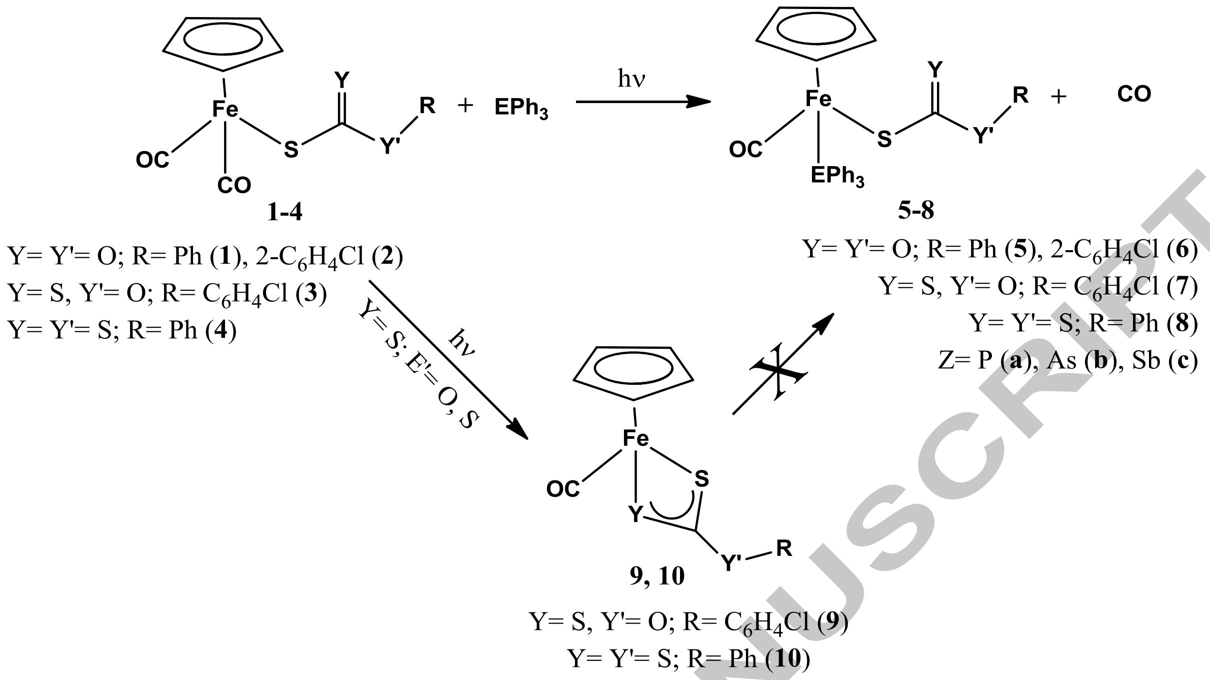

1-4

Y= Y'= O; R= Ph (**1**), 2-C_6H_4Cl (**2**)
Y= S, Y'= O; R= C_6H_4Cl (**3**)
Y= Y'= S; R= Ph (**4**)

5-8

Y= Y'= O; R= Ph (**5**), 2-C_6H_4Cl (**6**)
Y= S, Y'= O; R= C_6H_4Cl (**7**)
Y= Y'= S; R= Ph (**8**)
Z= P (**a**), As (**b**), Sb (**c**)

9, 10

Y= S, Y'= O; R= C_6H_4Cl (**9**)
Y= Y'= S; R= Ph (**10**)

Scheme 1: Synthesis of Complexes

The brown-red complexes (**5-8**) are stable solids and are soluble in common organic solvents. They have been characterized by UV-Vis, IR, ^{1}H-, ^{31}P-NMR spectral data and by elemental analysis. The IR spectra of **5** and **6** showed only one strong band for the terminal carbonyl ligand in the ranges of 1924-1963 cm^{-1}, while that of **7** and **8** are in the ranges1946-1942 cm^{-1}, 1941-1923 cm^{-1}, respectively. These ranges are lower than those reported for the parent thiocarbonates [25-27] which might be due to weaker π–acceptor properties of the ER_3 compared to that of CO ligand. The stretching frequency of the terminal carbonyl group of these three families of complexes decreased on going from the PPh_3 to $AsPh_3$ to $SbPh_3$ substituted complexes. This may be due to increase of the electron density on the metal center in accordance to the σ–donating and π-accepting ability of the EPh_3 ligands. In terms of changing the thiocarbonato ligands, the CO frequency decreases from the mono- to di- to trithiocarbonato ligands for the same EPh_3 ligand. This might be due to the weaker electron withdrawing ability of the S atom compared to that of O atom, which resulted in a higher electron density on the iron atom in case of increasing the number of S atoms. The spectra of **5** and **6** show the ketonic CO-group of the thiocarbonato ligand in the range of 1666–1674 cm^{-1} which decreases on going from PPh_3 to $SbPh_3$. This peak is absent from the spectra of **7** and **8** which is replaced by the C=S frequency in the range of 1589-1494 cm^{-1} which also depends on the EPh_3 ligand as shown for complexes **5** and **6**.

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The cyclopentadienyl ligand protons of complexes **5** – **8** appeared in the ^{1}H-NMR spectra of these complexes as one singlet in the ranges of 4.51-4.75 ppm. This range is lower than that of dicarbonyl parents [26], which might be due to higher electron density around iron resulting from the stronger σ–donor ability of the ER_3 ligands. The Cp-chemical shifts of these complexes change with substitution in the order PPh_3 < $AsPh_3$ < $SbPh_3$ derivatives for the same thiocarbonato ligand. The aromatic protons of the EPh_3 ligands and the thiocarbonato phenyl ring are observed at the aromatic ranges. These chemical shifts are similar to those observed for the analogous thiocarboxylato complexes [12]. The ^{31}P-NMR spectra of **5a**-**8a** showed a singlet for the P-atom of the PPh_3 ligand in the range of 77.5-68.0 ppm which are lower than those observed for the corresponding thiocarboxylate complexes [12].

The UV-Vis. spectra of complexes **5** - **8** were measured in dichloromethane solution and Figure 1 showed the UV-Vis spectrum of complexes **6b** as a representative example. A broad band in the range of 381-445 nm is observed in the spectra of **5** - **8** which may be assigned to the Fe → Cp metal-ligand charge transfer (MLCT) transition [29]. The λ_{max} for these complexes is not very sensitive to the type of ER_3 ligand [12,29].

Crystal structures of 1 and 5a

The molecular structures of **1** and **5a** are shown in Figures 2 and 3 while selected bond lengths and angles are summarized in Table 2. Three legged piano stool structures are representation of these complexes with the Cp ring as their base. The average Fe-C(Cp) bond distance of **1** is with 2.091(6) Å comparable to that reported for related systems [25-27] as well as to that of **5a** (2.094(7) Å). The Fe–CO bond distances of **1** (1.782(3), 1.787(3) Å) are longer than that of **5a** (1.747(4) Å) in consistence with the IR-data. The Fe–S bond distance of **5a** (2.2666(9) Å) is shorter than the corresponding distance of **1** (2.2763(6) Å). The Fe–P bond distance of **5a** (2.2066(9) Å) is shorter than that of $CpFe(CO(PPh_3)SCO(2\text{-}C_4H_3S)$ of 2.2284(9) Å [31]. The ketonic CO bond lengths of the thiocarbonato ligand of **1** (1.192(3) Å) and of **5a** (1.190(4) Å) are comparable to each other and to those found in analogous complexes [25-27]. The angles around the iron center of **1** and **5a** are around 90º showing disordered octahedral geometry. The Fe–S–CO angles (**1**: 106.80(2)º, **5a**: 104.67(12)º) are consistent with an sp^3 hybridized S atom. The S-C=O, O-C=O and S-C-O angles of the

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thiocarbonato ligand in both **1** and **5a** (Table 2) are close to 120° indicating the planarity of this moiety.

Table 2: Selected bond lengths (Å) and angles (°) of $CpFe(CO)_2SCO_2$-2-C_6H_4Cl, **1** and $CpFe(CO)(PPh_3)SCO_2$-2-C_6H_4Cl, **5a**

5a		**1**b)	
Fe1–C1	2.081(3)	Fe1–C1	2.111(2)
Fe1–C2	2.074(3)	Fe1–C2	2.085(3)
Fe1–C3	2.107(3)	Fe1–C3	2.071(3)
Fe1–C4	2.113(3)	Fe1–C4	2.081(3)
Fe1–C5	2.095(3)	Fe1–C5	2.106(2)
Fe1–C6	1.747(4)	Fe1–C6	1.782(3)
Fe1–P1	2.2066(9)	Fe1–C7	1.787(3)
Fe1–S3	2.2666(9)	Fe1–S1	2.2763(6)
C7–O2	1.190(4)	C8–O3	1.192(3)
Fe1–D1a)	1.721(2)	Fe1–D1	1.715(1)
C6–Fe1–P1	94.86(11)	C6–Fe1–C7	94.03(12)
C6–Fe1–S3	92.46(11)	C6–Fe1–S1	92.57(8)
P1–Fe1–S3	91.31(3)	C7–Fe1–S1	93.96(7)
C7–S3–Fe1	104.67(12)	C8–S1–Fe1	106.82(8)
O2–C7–O3	120.7(3)	O3–C8–O4	120.3(3)
O2–C7–S3	130.3(3)	O3–C8–S1	129.69(19)
O3–C7–S3	109.0(2)	O4–C8–S1	108.7(3)

a) D1 denotes the geometrical centroids of C_5H_5 groups. b) For the disordered fragments of **1** only bond angles of fragment are given.

Conclusion

The substitution reactions of the thiocarbonato complexes of iron resulted in the formation of the mono-substituted complexes. The substitution of CO ligand by EPh_3 group in these complexes resulted in increasing the electron density around the iron atom in the order PPh_3 < $AsPh_3$ < $SbPh_3$. This is observed in the stretching frequency of the terminal carbonyl group in the IR spectra, the position of the Cp-protons in the ^{1}H-NMR spectra and by shortening of the Fe-CO bond length as observed in the X-ray crystal structure determination.

Supporting Information available: Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, CCDC-1545317 for **5a**, and CCDC-1545318 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

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Acknowledgements

M.E. thanks the Deanship of Research, Jordan University of Science and Technology for financial support Grant No. 105/2016.

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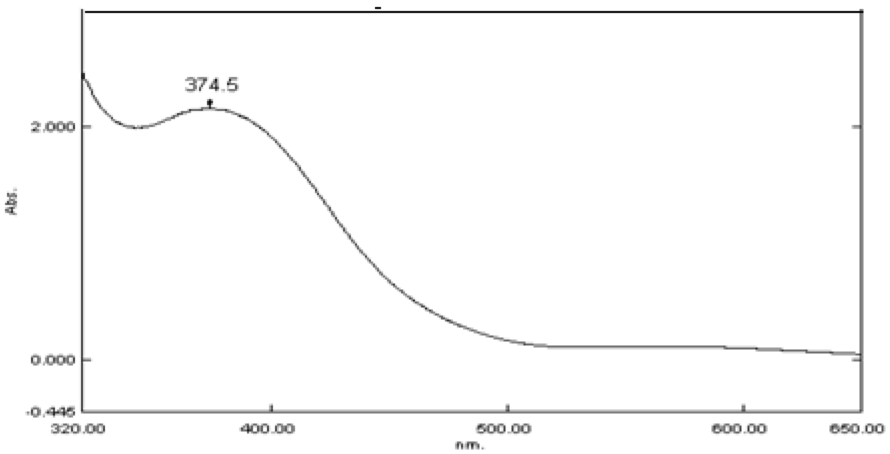

Figure 1: UV-Vis spectrum of $CpFe(CO)(AsPh_3)SCO_2$-4-C_6H_4Cl, **6b** in CH_2Cl_2

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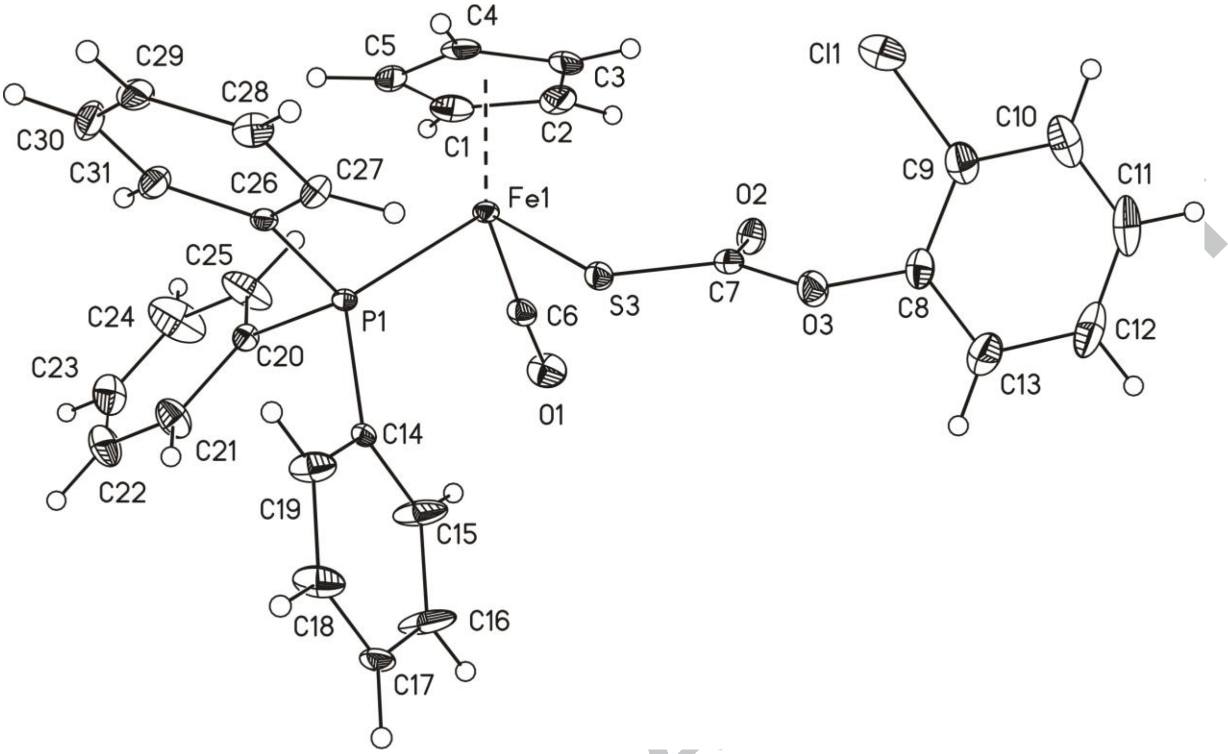

Figure 2: ORTEP (30 % ellipsoid probability) of the molecular structure of

CpFe(CO)(PPh$_3$)SCO$_2$-2-C$_6$H$_4$Cl (**5a).**

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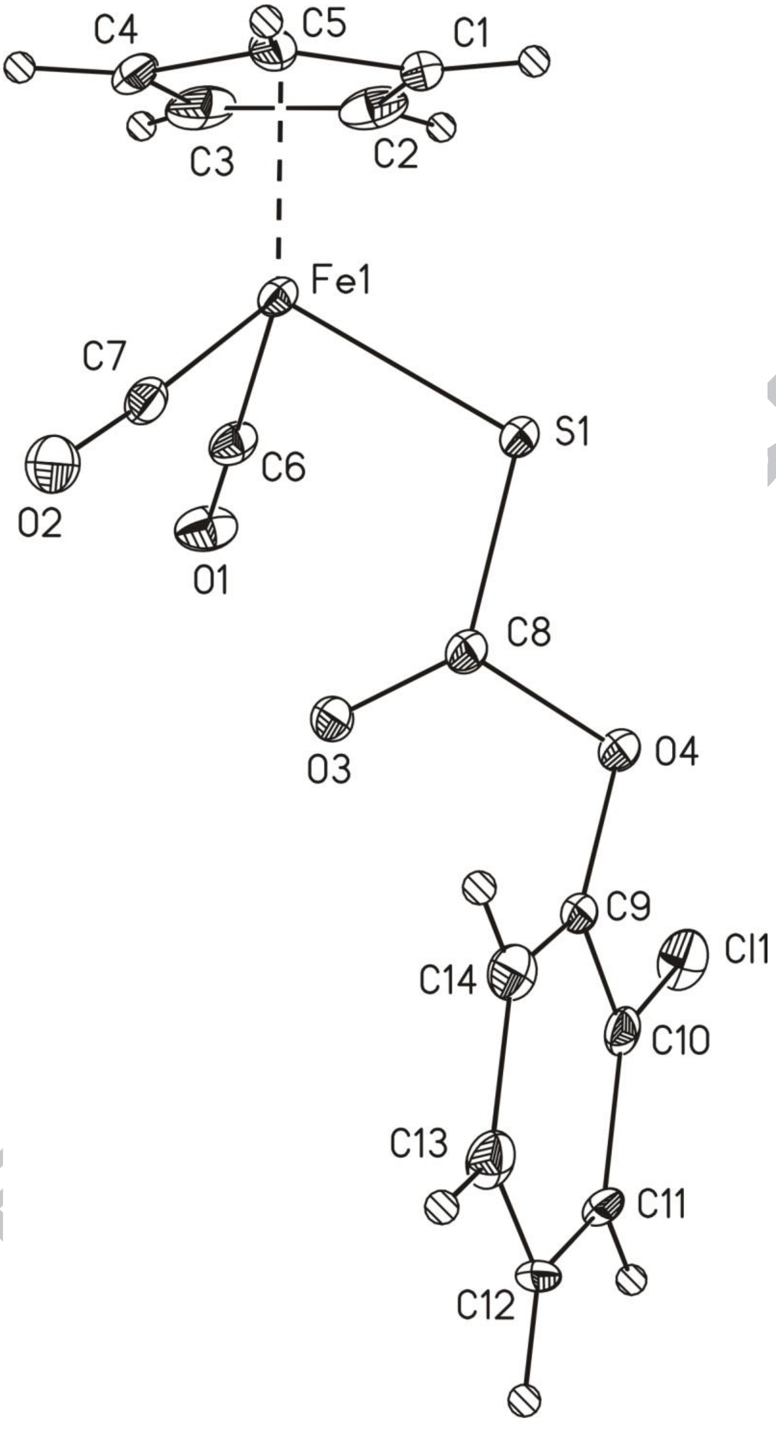

Figure 3: ORTEP (30 % ellipsoid probability) of the molecular structure of $CpFe(CO)_2SCO_2$-2-C_6H_4Cl (**1**). Of disordered atoms only one atomic position is shown.

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checkCIF/PLATON report

Structure factors have been supplied for datablock(s) shelx

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No syntax errors found.   CIF dictionary   Interpreting this report

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                Calculated                  Reported
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Space group     P 21/n                      P 21/n
Hall group      -P 2yn                      -P 2yn
Moiety formula  C31 H24 Cl Fe O3 P S        C31 H24 Cl Fe O3 P S
Sum formula     C31 H24 Cl Fe O3 P S        C31 H24 Cl Fe O3 P S
Mr              598.83                      598.83
Dx,g cm-3       1.461                       1.461
Z               4                           4
Mu (mm-1)       0.820                       0.820
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F000'           1235.28
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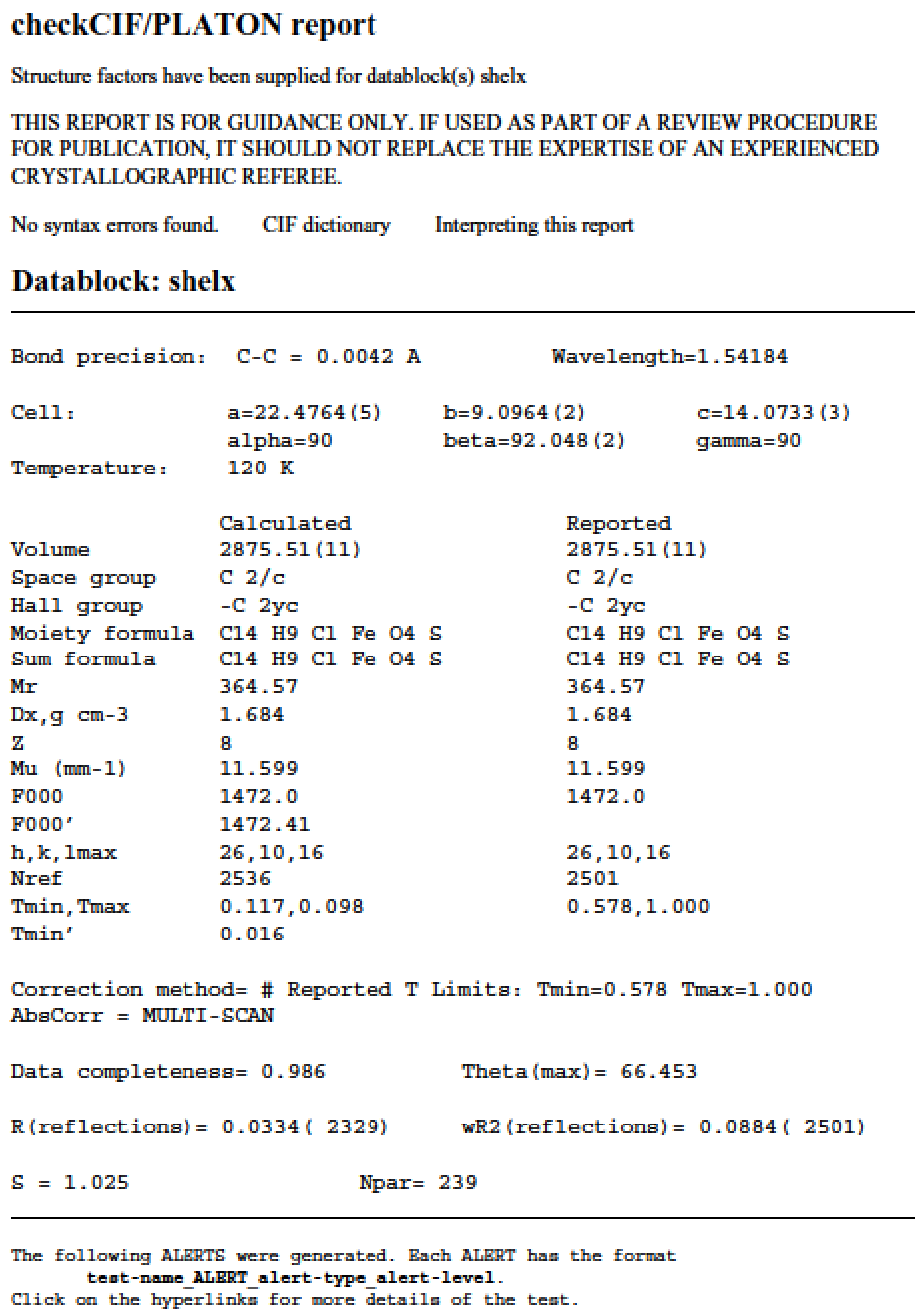

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Structure factors have been supplied for datablock(s) shelx

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

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Temperature:     120 K

                Calculated                Reported
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Space group     C 2/c                     C 2/c
Hall group      -C 2yc                    -C 2yc
Moiety formula  C14 H9 Cl Fe O4 S         C14 H9 Cl Fe O4 S
Sum formula     C14 H9 Cl Fe O4 S         C14 H9 Cl Fe O4 S
Mr              364.57                    364.57
Dx,g cm-3       1.684                     1.684
Z               8                         8
Mu (mm-1)       11.599                    11.599
F000            1472.0                    1472.0
F000'           1472.41
h,k,lmax        26,10,16                  26,10,16
Nref            2536                      2501
Tmin,Tmax       0.117,0.098               0.578,1.000
Tmin'           0.016

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S = 1.025                  Npar= 239
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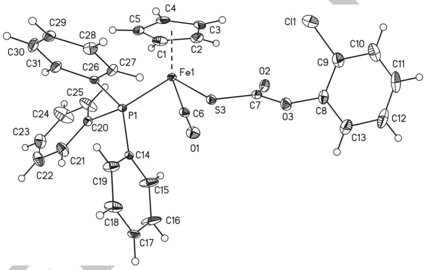
Substitution Reactions of Mono-, Di- and Tri-thiocarbonato Complexes of Iron

M. El-khateeb, A. Mansor, I. Jibril, T. Rüffer, H. Lang

Monosubstituted complexes of the general formula CpFe(CO)(EPh$_3$)SC(Y)Y'R [Y= Y'= O; R= 2-C$_6$H$_4$Cl (**5**), 4-C$_6$H$_4$Cl (**6**). Y= S, Y'= O; R= C$_6$H$_4$F (**7**), Y= Y' = S; R= Ph (**8**). E= P (**a**), As (**b**), Sb (**c**)] have been isolated and characterized by spectroscopic analysis (UV-Vis, IR, ^{1}H-, ^{31}P-NMR) and elemental analysis. The molecular structures of CpFe(CO)(PPh$_3$)SCO$_2$-2-C$_6$H$_4$Cl (**5a**) and its dicarbonyl parent CpFe(CO)$_2$SCO$_2$-2-C$_6$H$_4$Cl (**1**) have been determined by X-ray crystallography.



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