Preparation, characterization and structure determination of CpFe(CO)(EPh$_3$)SeCO-het complexes

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ABSTRACT

The mixed CO/ER$_3$ iron complexes bearing heterocyclic selenocarboxylato group CpFe(CO)(ER$_3$)SeCO-het [het = 2-C$_4$H$_3$S (**1**), 2-C$_4$H$_3$O (**2**), −CH$_2$-2-C$_4$H$_3$S (**3**), E = P, R = Ph (**a**), OC$_2$H$_5$ (**b**); E = As (**c**), Sb (**d**), R = Ph)] are synthesized by the reactions of CpFe(CO)$_2$SeCO-het with ER$_3$ under photolytic conditions. The new complexes have been characterized by spectroscopic analysis (UV−Vis, IR, ^{1}H, ^{31}P NMR) and elemental analysis. The structures of CpFe(CO)(PPh$_3$)SeCO-2-C$_4$H$_3$S (**1a**), CpFe(CO)(AsPh$_3$)SeCO-2-C$_4$H$_3$S (**1c**) and CpFe(CO)(SbPh$_3$)SeCO-2-C$_4$H$_3$S (**1d**) have been determined by X-ray crystal structure analysis.

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1. Introduction

Cyclopentadienyl dicarbonyl iron complexes of the general formula Cp'Fe(CO)$_2$X (Cp' = substituted or unsubstituted cyclopentadienyl; X = uni-negative ligand) undergo CO-substitution in the presences of two electron donor ligands under either photolytic or thermal conditions [1−10]. The type of the products depends on the Cp', the ligand X and the reaction conditions [1−10]. The silyl complex CpFe(CO)$_2$SiH$_3$ reacted with various donors (L = PMe$_3$, PPh$_3$, MeNC, t-BuNC) to give CpFe(CO)(L)SiH$_3$ and CpFe(L)$_2$SiH$_3$ via stepwise CO substitution [4,5]. Photolysis of CpFe(CO)$_2$Me in hydrocarbon solvents in the absence of ligand gave the dimer [CpFe(CO)]$_2$, while in the presence of PR$_3$ (R = Me, OMe), the CO-substituted products CpFe(CO)(PR$_3$)Me are formed [6]. Similarly, the photolysis of CpFe(CO)$_2$C(OMe)=CH$_2$ with PMe$_3$ yielded CpFe(CO)(PMe$_3$)C(OMe)=CH$_2$ [7]. The complex CpFe(CO)$_2$SPh reacted with AlX$_3$ (X = halide) to form adducts that reacted with nucleophiles (L = PBu$_3$, PPh$_3$, P(OEt)$_3$, cyclohexene) to form ionic products [CpFe(CO)$_2$L][PhS(AlX$_3$)$_2$] [8].

We [9−14] and others [15−17] studied the photolytic CO-substitution reactions of iron complexes containing sulfur or selenium ligands Cp'Fe(CO)$_2$Q (Q = SCOR, SeCOR, SeSO$_2$R, SCSOEt). The

reaction of the latter complexes with EPh$_3$ ligands were reported to produce the mono-substituted complexes Cp'Fe(CO)(EPh$_3$)Q [9−11,14−17]. The analogous reactions of the thiocarboxylate complexes with Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1−6) gave either the mono-substituted complexes CpFe(CO)(κP-Ph$_2$P(CH$_2$)$_n$PPh$_2$)SCOR for n = 1−6 and the disubstituted complexes CpFe(κ^{2}P,P-Ph$_2$P(CH$_2$)$_n$PPh$_2$)SCOR only for n = 1 and 2 [12,13].

The importance of chalcogenocarboxylato complexes of thiophene and other related heterocycles in thin film industry and hydrodesulfurization process [18−22], prompted scientists to synthesize these complexes. Complexes of Cu, Cd, Zn and Ag containing thiophene thiocarboxylates are reported and their conversion to metal-sulfide thin films are demonstrated [19−22].

In this paper, we report the CO-substitution reactions of iron selenocarboxylates bearing heterocyclic group CpFe(CO)$_2$SeCO-het by ER$_3$ donors. The molecular structures of three representative samples are presented.

2. Experimental

2.1. Materials and methods

The synthesis and separation of the complexes were carried out under an atmosphere of nitrogen using standard Schlenk line techniques. Tetrahydrofuran, diethyl ether, hexane (sodium/

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Table 1
Crystallographic data and refinement parameters of CpFe(CO)(PPh₃)SeCO-2-C₄H₃S (**1a**), CpFe(CO)(AsPh₃)SeCO-2-C₄H₃S (**1c**) and CpFe(CO)(SbPh₃)SeCO-2-C₄H₃S (**1d**).

	1a	1c	1d
CCDC No.	1417778	1417777	1417779
Empirical formula	$C_{29}H_{23}FeO_2PSSe$	$C_{29}H_{23}FeO_2AsSSe$	$C_{29}H_{23}FeO_2SbSSe$
Formula weight (g/mol)	601.35	645.26	692.09
Temperature (K)	150.0	100.01	149.99
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2₁/n	P2₁/n	P2₁/n
Unit cell dimensions			
a (Å)	10.3778(10)	10.3775(13)	10.4793(6)
b (Å)	14.5658(14)	14.5337(18)	14.5838(9)
c (Å)	17.3019(17)	17.581(2)	18.0826(11)
α (°)	90	90	90
β (°)	101.5852(19)	102.021(3)	102.6714(11)
γ (°)	90	90	90
Volume (Å³)	2562.1(4)	2593.5(6)	2696.2(3)
Z	4	4	4
Density (calculate) Mg/m³	1.5589	1.653	1.705
Absorption coefficient mm⁻¹	2.179	3.357	2.992
F(000)	1218.4	1288.0	1360.0
Crystal size mm³	0.15 × 0.1 × 0.1	0.15 × 0.12 × 0.1	0.15 × 0.1 × 0.1
Theta range for data collection (°)	3.68–56.72	3.67–57.078	3.624–56.67
Index ranges	−13 ≤ h ≤ 13	−13 ≤ h ≤ 13	−13 ≤ h ≤ 13
	−19 ≤ k ≤ 19	−19 ≤ k ≤ 19	−19 ≤ k ≤ 19
	−23 ≤ l ≤ 23	−23 ≤ l ≤ 23	−24 ≤ l ≤ 24
Reflections collected	49877	41027	49148
Independent reflections	6390 [R_int = 0.0296, R_sigma = 0.0193]	6542 [R_int = 0.1188, R_sigma = 0.0857]	6698 [R_int = 0.0518, R_sigma = 0.0334]
Data/restraints/parameters	6390/0/316	6542/0/317	6698/0/317
Goodness-of-fit on F2	1.042	0.989	1.002
Final R indices [I > 2σ(I)]	R₁ = 0.0228, wR₂ = 0.0521	R₁ = 0.0441, wR₂ = 0.0590	R₁ = 0.0266, wR₂ = 0.0456
R indices (all data)[a, b]	R₁ = 0.0311, wR₂ = 0.0554	R₁ = 0.0903, wR₂ = 0.0683	R₁ = 0.0424, wR₂ = 0.0495
Largest diff. peak and hole (e.Å⁻³)	0.44/−0.34	0.66/−0.64	0.44/−0.35
Absorption method	NONE	NONE	NONE

[a] Definition of the R indices: $R_1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2)]/3$.
[b] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

benzophenone) and CH_2Cl_2 (P_2O_5) were dried following standard procedure. The compounds CpFe(CO)₂SeCO-het were prepared by reported procedures [23]. The ligands triphenylphosphine, triethylphosphite, triphenylarsine, triphenylantimony were used as received (Acros). For column chromatography, silica gel of particle size 0.063–0.200 mm (70–230 mesh) was employed and the reaction steps were monitored by thin layer chromatography (TLC).
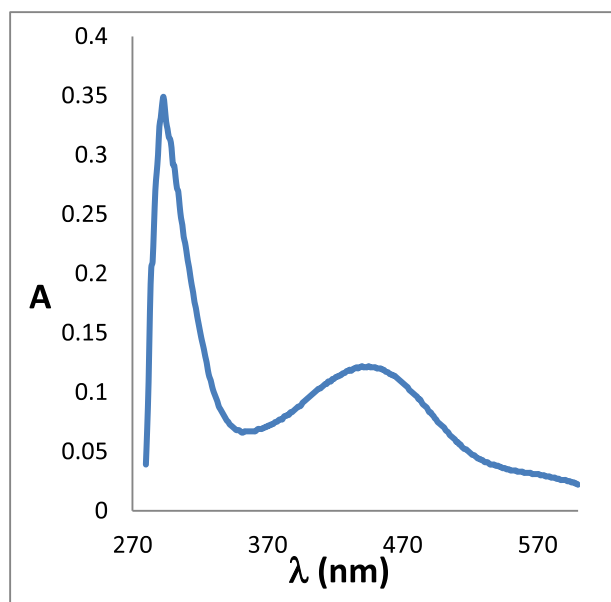

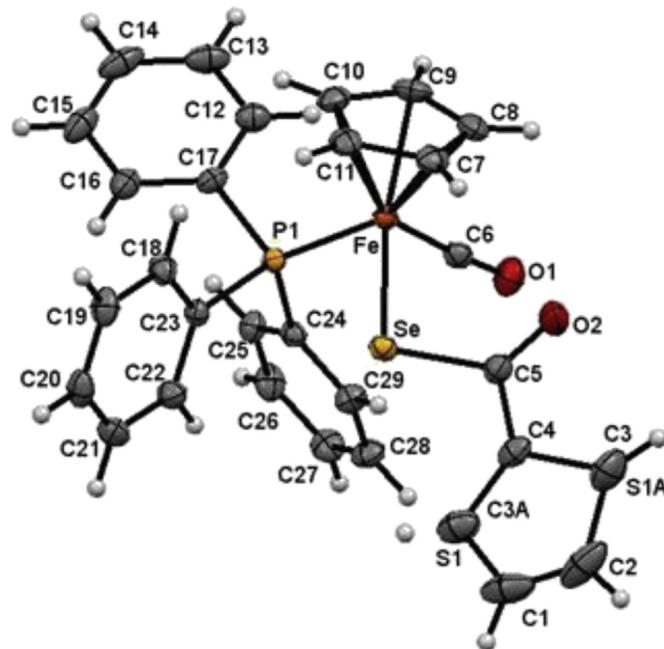**Fig. 1.** UV–Vis spectrum of CpFe(CO)(P(OEt)₃)SeCO-2-C₄H₃S (**1b**) 4.4 × 10⁻⁶ M in acetonitrile.

Fig. 2. Molecular structure of CpFe(CO)(PPh₃)SeCO-2-C₄H₃S, (**1a**).