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Sulfur–hydrogen bond activation of thiols by the fragment CpFe(dppe)$^{+}$: cyclopentadienyl iron(III) thiolate complexes

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Abstract—Oxidative addition of thiols RSH, R = CH_3, $CH_2CH_2CH_3$, $CH_2C_6H_5$, $C(CH_3)_3$ and C_6H_4Br, by the complex [CpFe(dppe)I] afforded the oxidized thiolate complexes [CpFe(dppe)-SR]PF_6. The reaction of [CpFe(dppe)I] with $HSC_6H_4NH_2$ produces the diamagnetic [CpFe(dppe)$HSC_6H_4NH_2$]PF_6 instead of the expected thiolate product. The reaction of the dithiol $HS(CH_2)_4SH$ with the same iron fragment, gives the binuclear complex [CpFe(dppe)-$S(CH_2)_2S$-CpFe(dppe)][PF_6]$_2$. The formation of the thiol-containing complexes as intermediates in the activation of the S—H bonds is discussed. Copyright © 1997 Elsevier Science Ltd

Keywords: thiol activation; sulfur–hydrogen bond; thiolate complexes; non-sulfur complexes; non III-thiolate complexes.

The hydrodesulfurization process is an essential step in the effective utilization of crude oil and high sulfur coal [1]. The elimination of organosulfur compounds from these hydrocarbon feedstock mixtures are processes catalysed by a variety of metal and organometallic compounds [2]. A fundamental step in the interaction between a catalyst and sulfur-containing substrates, such as hydrogen sulfide or thiols, is the oxidative addition of S—H bonds to the metal centres [3]. Activation of the S—H bond generally occurs with organometallic fragments in low oxidation states [3, 4]. In the majority of cases the activation is promoted by some drastic conditions, i.e. temperature [5] or UV radiation [6].

Previously we have reported the activation of the S—S bond in dithioethers by the electron-rich fragment CpFe(dppe)$^{-}$, to give the iron–thiolate complexes [CpFe(dppe)-SR]PF_6 [7]. Now we report the mild oxidative addition of thiols to the fragment CpFe(dppe)$^{+}$, to give the paramagnetic complexes [CpFe(dppe)-SR]PF_6.

RESULTS AND DISCUSSION

CpFe(dppe)I reacted with the thiols RSH to give the blue paramagnetic [CpFe(dppe)-SR]PF_6 complexes according to Eq. (1)

$$\mathrm{CpFe(dppe)I + RSH \xrightarrow[CH_3OH]{NH_4PF_6} [CpFe(dppe)\text{-}SR]PF_6} \tag{1}$$

where R = CH_3 (**1**), $CH_2CH_2CH_3$ (**2**), $CH_2C_6H_5$ (**3**), C_6H_5 (**4**), t-$C(CH_3)_3$ (**5**) or C_6H_4Br (**6**). The complexes **1**–**4** have been previously obtained by oxidative addition of the corresponding dithioethers RSSR to the fragment CpFedppe^{+} [7]. The new complexes **5** and **6** were characterized by elemental analysis and IR and UV–vis spectroscroptic methods.

The IR spectra (see Table 1) of **5** and **6** exhibit the typical absorption bands of the CpFe(dppe)$^{+}$ moiety [8]. Absorption bands were observed at 3060, ν(C—H), 1435, ν(C—C) and 1098 cm^{-1} δ (C—H), characteristic of an η^5-bonded cyclopentadienyl group. An intense band around 700 cm^{-1} assigned to the δ (C—H) out-of-plane vibration of the phenyl group of dppe, was also observed. The $\nu(PF_6)$ vibration of complexes **5** and **6** was observed normally at 840 cm^{-1} [8, 9].

The characteristic blue colour exhibited by the complexes is associated with their paramagnetic nature [7]. The lowest absorption bands observed around 450 and 590 nm are assigned to a *d*–*d* transition [7]. The spectrum of **5** is shown in Fig. 1.

On the other hand the reaction of CpFe(dppe)I with

Table 1. Selected spectroscopic data for the thiolate and thiol complexes

Complex	IR (KBr) (cm^{-1})			Visible λ max (CH_2Cl_2) (nm)	
	C_5H_5[a]	dppe[b]	$\nu(PF_6)$		
5	1098	700	846	457	587
6	1095	698	841	456	590
7[c]	1094	696	842	420	
8	1097	699	847	429	593

[a] (C—H) bending, in-plane vibration.

[b] (C—H) bending, out-of-plane vibration.

[c] ^1H NMR: δ 7.7–7.5 (m, C_6H_5), 4.5 (s, C_5H_5), 2.76 (m, CH_2—CH_2—). ^{31}P NMR: δ 90 (s, dppe), -143 (s, PF_6).

$NH_2C_6H_4SH$ afforded the diamagnetic [CpFe(dppe)($HSC_6H_4NH_2$)]PF_6 (**7**) instead of the expected iron–thiolate oxidized complex. The compound was obtained as a yellow-green oil which

$$\mathrm{CpFe(dppe)I + HS\text{-}C_6H_4\text{-}NH_2} \xrightarrow[CH_3OH]{NH_4PF_6} \mathrm{[CpFe(dppe)(HS\text{-}C_6H_4NH_2)]PF_6} \quad (2)$$

was characterized by IR, ^1H, ^{31}P NMR and UV–vis spectroscopic methods. The IR spectrum showed the typical bands of the CpFe(dppe) moiety [8] (see Table 1).

The ν(S—H) and ν(NH) bands were observed at 2558 and 3461, 3376 cm^{-1}, respectively. Comparing the IR spectra of the free 4-aminothiophenol with the coordinated ligand, the major changes are observed for the ν(S—H) band which suggests an S-coordination to the metal. In the free ligand ν(S—H) appears as a broad band around 2500 (owing to the association) while in the complex a narrow band was observed. More detailed studies in solution are precluded because of the low intensity exhibited by the ν(SH) band in solution [6a].

The ^{31}P NMR spectrum of **7** exhibits the signal for dppe at δ 90, a value typical of cationic [CpFe[dppe)L]$^+$ complexes with L = sulfur donor atom [9,10]. The PF_6 septuplet was observed at δ -143. The ^1H NMR spectrum exhibited the multiplet of C_6H_5 protons of dppe in the range δ 7.0–7.5 and the signal for the CH_2 protons was observed at δ 2.76, also as a multiplet. The C_5H_5 proton signal appeared at δ 4.5. All these values are typical of [CpFe(dppe)L]PF_6 complexes [9,10].

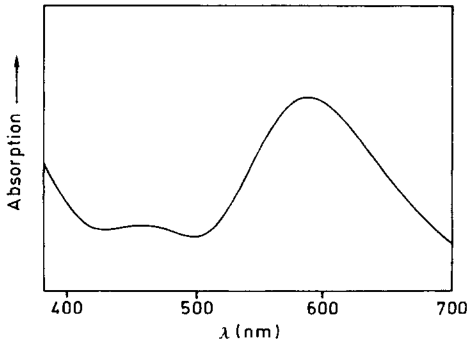

Fig. 1. UV–vis absorption spectrum of [CpFe(dppe)-S-Bu^t]PF_6 in CH_2Cl_2 solution at room temperature.

The UV–vis spectrum showed the absorption maximum around 420 nm, characteristic of [CpFe(dppe)L]$^+$ complexes where L is a neutral donor ligand [9,11]. The position of this maximum suggests S coordination rather than N coordination; amine complexes CpFe(dppe)NR_3^+ absorb around 500 nm [12].

Reaction of $HS(CH_2)_2SH$ *with* CpFe(dppe)I

Reaction of $HS(CH_2)_2SH$ with CpFe(dppe)I afforded the binuclear product [CpFe(dppe)-S$(CH_2)_2$-S-CpFe(dppe)]$(PF_6)_2$ according to Eq. (3)

$$\mathrm{2CpFe(dppe)I + HS(CH_2)_2SH} \xrightarrow[CH_3OH]{NH_4PF_6} \underset{\mathbf{8}}{\mathrm{[CpFe(dppe)\text{-}S\text{-}(CH_2)_2\text{-}S\text{-}CpFe(dppe)](PF_6)_2}} \quad (3)$$

Complex **8** was characterized by elemental analysis as well as IR and UV–vis spectroscopic methods.

As observed for the monothiolate complexes, the IR spectrum of **8** exhibits the characteristic bands of the CpFe(dppe)$^+$ moiety [8]. As expected, the ν(S—H) band is absent. The $\nu(PF_6)$ band was observed in the normal range (see Table 1).

Compound **8** which was obtained as a blue solid, exhibited similar absorptions in the UV–vis spectrum to those of the monothiolate complexes **1**–**4**. Data are given in Table 1.

Coordination versus S—H *bond cleavage in thiols*

As suggested for the activation of dithioethers by the fragment CpFe(dppe)$^+$ [7], the activation of the S-H bond in thiols appears to occur through an intermediate involving the sulfur molecule coordinated to the metal fragment (see Fig. 2).

This assumption is supported by molecular orbital calculations [13] which indicate a favourable HOMO [CpFe(dppe)$^+$]-LUMO [RSH] back bonding interaction as shown in Fig. 3. The enhancement of the electron density of the LUMO of the thiol, which has a S—H, S—C antibonding character, produces a weak S—H bond. Thus the isolation of the complex [CpFe(dppe)$HSC_6H_4NH_2$]$^+$, probably coordinated to the metal *via* the sulfur atom, affords additional evidence for the activation mechanism.

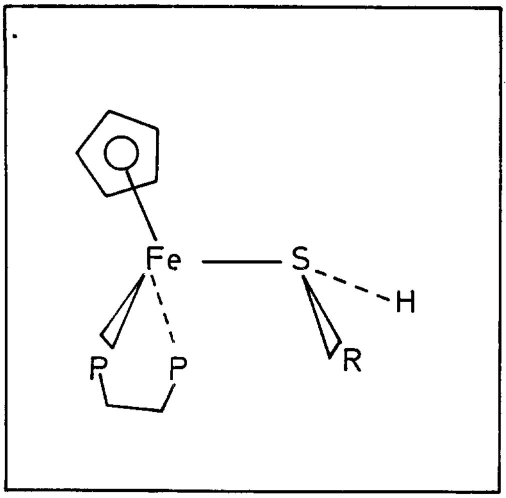

Fig. 2. Possible intermediate involved in the activation of thiols.

EXPERIMENTAL

Infrared spectra were recorded on a Perkin–Elmer FT-IR 2000 spectrophotometer. NMR spectra were recorded on a Bruker AMX 300 instrument. Chemical shifts are given relative to TMS (^1H) or 85% H_3PO_4 (^{31}P proton decoupled) with the shift reference being positive. Visible absorption spectra were measured on a Varian DMS-90 spectrophotometer in 1-cm curvettes. Elemental analyses were performed with a Perkin–Elmer 240 microanalyser.

All reactions were carried out under N_2 using standard Schlenk techniques. Solvents were purified using standard procedures. Thiols (Aldrich) were used without additional purification. CpFe(dppe)I was prepared using previously reported methods [10].

Reaction of thiols with CpFe(dppe)I

The complex CpFe(dppe)I (0.14 g, 0.2 mmol) was placed in a Schlenk vessel with the calculated amount

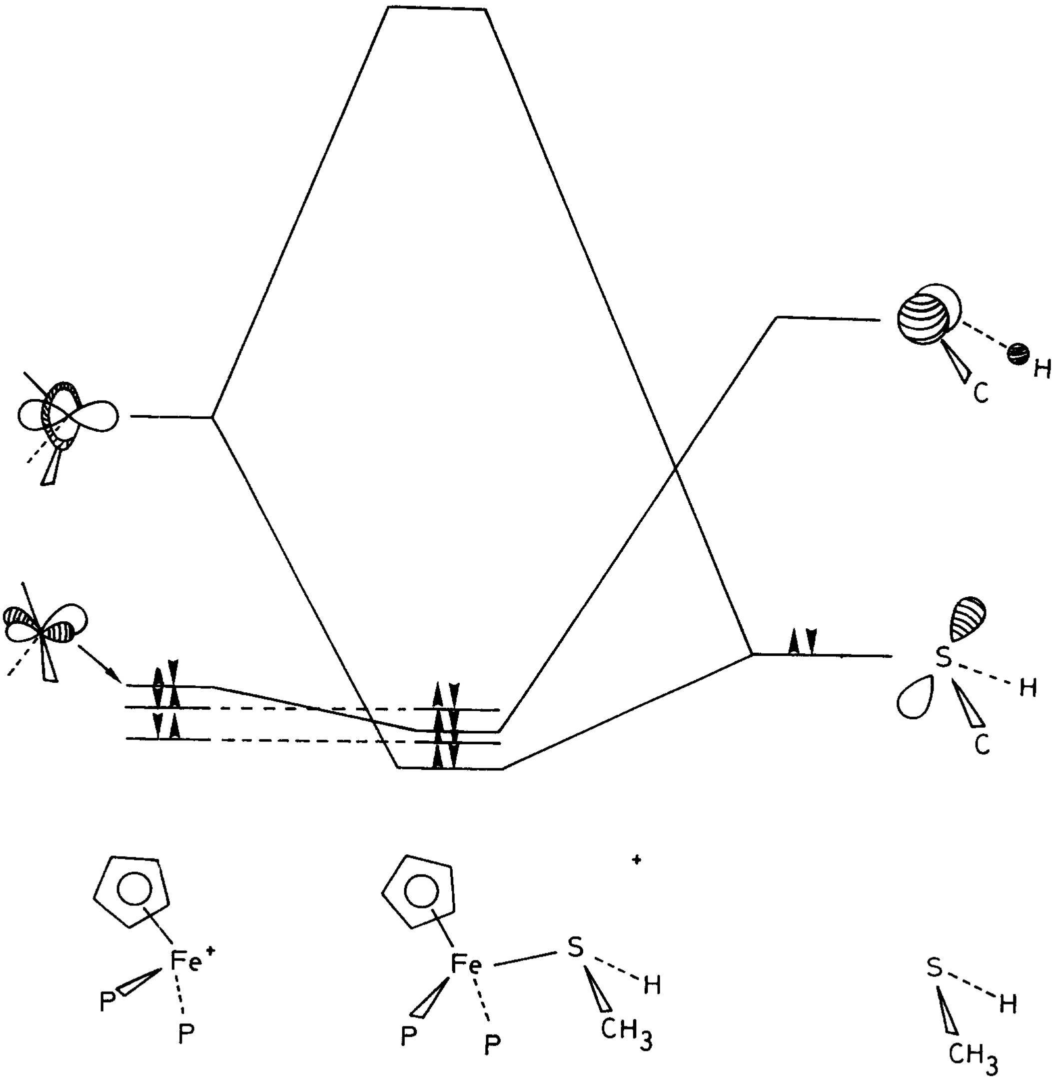

Fig. 3. Simplified molecular orbital diagram for $[CpFe(dppe)HSR]^+$. Possible geometries of the complexes adapted from refs [6a] and [14].

of thiol, RSH (R = CH_3, $CH_2CH_2CH_3$, $CH_2C_6H_5$ and C_6H_5) in the molar ratio 1 : 1 and in the presence of NH_4PF_6. A total of 20 cm^3 of CH_3OH was added and the reaction mixture was stirred for 12 h. After this, the solution, initially black, changed to blue. The solvent was removed *in vacuo* and the solid residue was extracted with CH_2Cl_2. The solutions were filtered through Celite and the solvent was partially evaporated *in vacuo*. Upon addition of a 1 : 10 mixture of n-hexane/diethyl ether the product, a dark blue powder, precipitated and was washed twice with the same solvent mixture. Identification of the products was by comparison of their IR and UV–vis spectra with those of an authentic sample [7].

For the reaction with methanethiol, the mercaptan was bubbled through the solution of [CpFe(dppe)I] in the presence of NH_4PF_6.

[CpFe(dppe)-S-Bu^t]PF_6 (**5**). The complex CpFe (dppe)I (0.14 g, 0.2 mmol) and $(CH_3)_3C$—SH (0.13 cm^3, 1.15 mmol) in the presence of NH_4PF_6 (0.21 g, 1.28 mmol) were stirred for 16 h in CH_3OH (20 cm^3). The solution changed from black to blue after 1 h. The solvent was removed *in vacuo* and the solid extracted with CH_2Cl_2, and then filtered through Celite. The solvent was partially evaporated at reduced pressure and a 1 : 10 mixture of n-hexane/diethyl ether was added. The blue–green powder precipitated was washed twice with the same solvent mixture and dried *in vacuo*. Yield 0.1 g (61%). Found : C, 55.6; H, 5.5. Calc. for $C_{35}H_{38}F_6SP_3Fe$: C, 55.8; H, 5.0%.

[CpFe(dppe)-S-C_6H_4Br]PF (**6**). CpFe(dppe)I (0.14 g, 0.2 mmol) and HSC_6H_4Br (0.061 g, 0.32 mmol) were stirred in the presence of NH_4PF_6 (0.24 g, 0.15 mmol) for 18 h at room temperature in CH_3OH. Separation and purification procedures similar to that for (**5**) afforded a black–blue powder. Yield 0.12 g, (65%). Found : C, 53.2; H, 3.4. Calc. for $C_{37}H_{33}F_6SP_3BrFe$: C, 52.1; H, 3.9%.

[CpFe(dppe)$HSC_6H_4NH_2$]PF_6 (**7**). CpFe(dppe)I (0.14 g, 0.2 mmol) and HS-C_6H_4-NH_2 (0.054 g, 0.43 mmol) in the presence of NH_4PF_6 (0.2 g, 0.6 mmol) and using CH_3OH as solvent were stirred for 20 h at room temperature. After this the solution changed from black to yellow–green. The solvent was removed *in vacuo* and the solid residue extracted with CH_2Cl_2 and filtered through Celite. Elimination of the solvent to dryness affords an oil which could not be converted to a solid in spite of various attempts with several solvents. The dark yellow product was identified spectroscopically: ^1H and ^{31}P NMR data are shown in Table 1. IR(film): 3461s, 3376vs, 3215m, 3055m, 3030m, 2924m, 2558w, 1889w, 1623vs, 1623vs, 1493vs, 1431m, 1289vs, 1177m, 1094s, 1007w, 842vs, 745m, 696s.

[CpFe(dppe)-S$(CH_2)_2$S-CpFe(dppe)]$PF_6)_2$ (**8**). CpFe(dppe)I (0.2 g, 0.31 mmol) and $HS(CH_2)_2SH$ (0.02 cm^3, 0.208 g, 1.7 mmol) were stirred in the presence of NH_4PF_6 (0.29 g, 1.7 mmol) using CH_3OH as solvent (30 cm^3) at room temperature. After 5 min the solution changed from black to blue. The solution was stirred additionally for a further 5 h, and the solvent removed *in vacuo*. The solid residue was extracted with CH_2Cl_2 and filtered through Celite. The solution was concentrated to *ca* 10 cm^3 and then a mixture of 1 : 10 ether/n-hexane was added. The black-blue solid precipitated was washed twice with the same mixture and dried *in vacuo*. Yield 0.18 g (81%). Found: C, 53.8; H, 4.6. Calc. for $C_{66}H_{66}F_{12}P_6S_2Fe_2$: C, 54.7; H, 4.5%.

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