

Oxidative addition of disulfides to the fragment $\text{CpFe}(\text{dppe})^+$: steric and dielectric medium control on the reaction

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Received 24 August 1995; in revised form 17 November 1995

Abstract

Activation of the S–S bond in disulfides by the fragment $\text{CpFe}(\text{dppe})^+$ produces the oxidized thiolate complexes $[\text{CpFe}(\text{dppe})\text{--SR}]\text{PF}_6$, $\text{R} = \text{CH}_3$, C_3H_7 , $\text{CH}_2\text{--C}_6\text{H}_5$, C_6H_5 . With the bulky $(^t\text{Bu})_2\text{S}_2$ the unaltered disulfide complex $[\text{CpFe}(\text{dppe})\text{S}_2(^t\text{Bu})_2]\text{PF}_6$ was obtained. The reaction which yields the $17e^-$ paramagnetic thiolate complexes occurs only in solvents with a high dielectric constant. Formation of diamagnetic $[\text{CpFe}(\text{dppe})\text{S}_2\text{R}_2]\text{PF}_6$ complexes as the first step in the formation of the paramagnetic species $[\text{CpFe}(\text{dppe}\text{--SR})]\text{PF}_6$ is discussed.

Keywords: Iron; Thiolate complexes; Oxidative addition

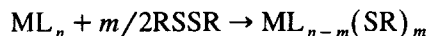
1. Introduction

Organic disulfides are currently the subject of a large number of studies [1,2]. Although transition metal compounds with disulfide as ligands are already known, they are scarce [3–5]. In general, a disulfide can interact with a transition metal fragment in one of the following two ways [6]:

(a) coordination of the unaltered molecule



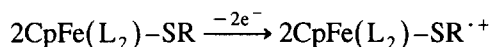
(b) oxidative addition of R--S--S--R to the metal



The product in (a) is usually obtained with an ML_n = coordination fragment which has the metal in a normal (high) oxidation state, while reaction (b) proceeds with organometallic fragments in low oxidation states. Although several coordination compounds with disulfide ligands have been reported, only a limited number of organometallic compounds with these types of sulfur ligand have been reported [7].

Recently we have reported that reactions between $\text{CpFe}(\text{dppe})\text{I}$ and neutral L ligands in the presence of TiPF_6 yield $[\text{CpFe}(\text{dppe})\text{L}]\text{PF}_6$ complexes [8]. With $\text{L} =$

$\text{S}_2(\text{CH}_3)_2$ the respective disulfide complex was obtained, however, when NH_4PF_6 was used as the halogen abstracting agent instead of TiPF_6 and MeOH was used as the solvent, a blue solution was unexpectedly obtained. From this solution the dark-blue solid $[\text{CpFe}(\text{dppe})\text{--SCH}_3]\text{PF}_6$ was isolated and identified. This paper reports on the preparation and characterization of the paramagnetic $17e^-$ $[\text{CpFe}(\text{dppe})\text{--SR}]\text{PF}_6$ complexes. The reverse reaction induced by oxidation of the thiolate complex, which produces a dimeric complex containing a bridging disulfide ligand, has recently been reported [9,10].

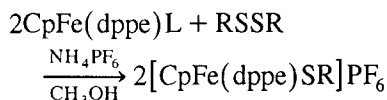


Although organometallic thiolate complexes are well known [11–13], few $17e^-$ thiolate complexes have been reported. To our knowledge the only cyclopentadienyl iron(III) mercaptide complexes are the following: $[\text{CpFe}(\text{dppe})\text{SPh}]\text{PF}_6$ [14] $[\text{CpFe}(\text{PMe}_3)_2\text{SPh}]\text{BF}_4$ [15] and $[\text{CpFe}(\text{P}(\text{O}^i\text{Pr})_3)_2\text{SPh}]\text{BF}_4$ [9]. Each of these complexes was obtained through the oxidation of the neutral thiolate precursor $\text{CpFeL}_2\text{--SPh}$, with AgX ($\text{X} = \text{BF}_4$ or PF_6). Thus, the oxidative addition of RSSR to $\text{CpFe}(\text{dppe})\text{I}$ here reported constitutes the first systematic method of obtaining the cyclopentadienyl–iron–thiolate oxidized complexes in a single step.

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2. Results and discussion

The reaction between CpFe(dppe)I and RSSR, in the presence of NH_4PF_6 , using MeOH as the solvent yields the blue solid $[\text{CpFe(dppe)SR}]\text{PF}_6$ complexes



R	Complex
CH_3	1
$\text{CH}_2\text{CH}_2\text{CH}_3$	2
$\text{CH}_2\text{C}_6\text{H}_5$	3
C_6H_5	4

This reaction was investigated using different solvents and several different halide abstraction agents. The formation of the cyclopentadienyl-iron(III)-mercaptide complexes is favored by the presence of high dielectric medium (acetone $\epsilon = 20.7$, methanol $\epsilon = 33.6$); however, the reaction does not occur in a low dielectric medium like dichloromethane ($\epsilon = 9.1$). No effect of halide abstraction agents such as NH_4PF_6 or TIPF_6 on the reaction was observed. Thus we found that the reaction of CpFe(dppe)I with disulfides with bulky substituents, such as $\text{S}_2(\text{tBu})_2$, yields the complex $[\text{CpFe(dppe)S}_2(\text{tBu})_2]\text{PF}_6$ instead of the expected thiolate complex (see Experimental section). UV-visible, ^1H and ^{31}P NMR as well as IR spectral data are similar to those previously reported for the dithioether $[\text{CpFe(dppe)S}_2(\text{CH}_3)_2]\text{PF}_6$ complex [8].

The oxidized thiolate complexes **1–4** are dark-blue solid complexes, moderately stable in the solid state, but decomposing when standing in solution.

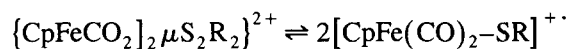
Satisfactory elemental analysis in accord with the proposed formula were obtained. The IR spectra (see Table 1) exhibit the typical absorption bands of the CpFe(dppe)^+ moiety [16]. Absorption bands were observed at 3060 cm^{-1} $\nu(\text{C-H})$ Str., 1430 cm^{-1} $\nu(\text{C-C})$ Str. and 1090 cm^{-1} $\delta(\text{C-H})$ for in-plane bending, characteristic of the η^5 -bonded cyclopentadienyl group. An intense band around 690 cm^{-1} corresponding to the $\delta(\text{C-H})$ bending out-of-plane vibration of the phenyl group of dppe [16] was also observed. The expected $\nu(\text{PF}_6)$

vibration of the complexes appears as an intense band near 840 cm^{-1} . Other characteristic absorption bands were observed as expected.

Magnetic measurements indicate that the solids are paramagnetic with μ values between 1.5 and 2.3 MB. These values are typical of d^5 low-spin iron complexes [9,10]. Thus it is well known that the diamagnetic $\text{CpFe(L}_2\text{)X}$ d^6 complexes are red, while the paramagnetic $[\text{CpFe(L}_2\text{)X}]\text{PF}_6$ are generally dark-blue compounds [9,10]. The characteristic color exhibited by these $17e^-$ complexes appears to be related to the absorption bands around 660 nm observed in the visible-absorption spectra of the thiolate complexes **1–4**. Fig. 1 shows the absorption spectra of **2** in CH_2Cl_2 solution, and the data for the other complexes are displayed in Table 1.

A tentative assignment of the UV-visible spectra for the complexes **1–4** can be made using the approximate MO schemes shown in Fig. 2. These can be established from the orbital interaction between the organometallic CpML_2^+ [17] and the thiolate ligand fragment [13a]. The filled-filled $d\pi$ - $p\pi$ interaction in metal-thiolate complexes [13a] destabilizes the HOMO level, which in turn causes a lower transition energy than that found in the complexes $[\text{CpFe(dppe)L}]^+$ L = sulfur donor ligands [8] (Fig. 2A).

The MO schemes also provide some information about the formation of the thiolate complexes from the disulfide complex $[\text{CpFe(dppe)S}_2\text{R}_2]^+$, assuming this latter to be an intermediate in the overall reaction. In fact, the complex $[\text{CpFe(dppe)S}_2(\text{CH}_3)_2]\text{PF}_6$ has recently been isolated [8]. Thus, in $[\text{CpFe(dppe)S}_2\text{R}_2]^+$ complexes the electron-rich fragment CpFe(dppe)^+ promotes an easy electron shift $\text{HOMO}[\text{CpFe(dppe)}] \rightarrow \text{LUMO}(\text{S}_2\text{R}_2)$ which weakens the S-S bond owing to the $(\text{S-S})^*$ character of the LUMO of disulfide ligands [18,19]. These arguments are consistent with the fact that in the related less electron-rich fragment CpFe(CO)_2^+ , the reaction equilibrium is shifted to the formation of a disulfide complex [10]



owing to a reduction of energy of the π (HOMO) orbital. This energy decrease on the HOMO level,

Table 1
Spectroscopic and magnetic data for the $[\text{CpFe(dppe)-SR}]\text{PF}_6$ complexes

Complex	IR			Visible		
	C_5H_5 ^a	dppe ^b	$\nu(\text{PF}_6)$	λ_{max}		μ_{eff} (MB)
1	1089	689	835	422	578	1.55
2	1092	690	835	430	580	2.12
3	1091	692	836	440	585	2.3
4	1098	696	828	432	581	1.6

^a $\delta(\text{C-H})$ bending in-plane vibration.

^b $\delta(\text{C-H})$ bending out-of-plane vibration.

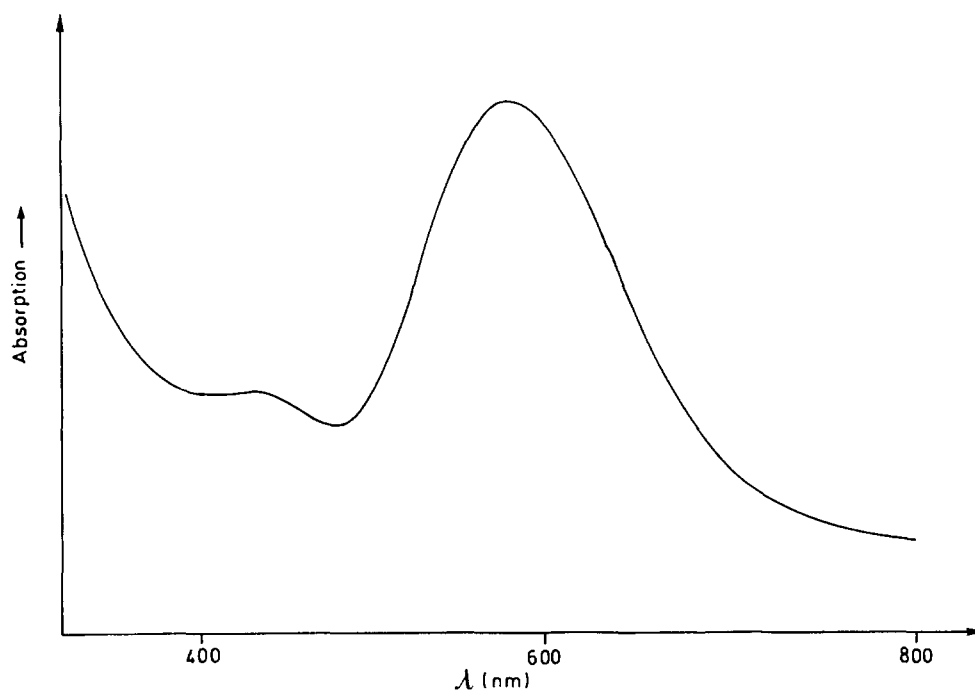


Fig. 1. UV-visible absorption spectrum of $[\text{CpFe}(\text{dppe})\text{-SC}_3\text{H}_7]\text{PF}_6$ in CH_2Cl_2 solution at room temperature.

detected when diphosphine or phosphine are converted into carbonyl ligands, has been found in several MO studies [13a,b] (Fig. 3).

The MO arguments above explaining the equilibrium which leads to thiolate complexes are also supported by the higher oxidation potential values found in

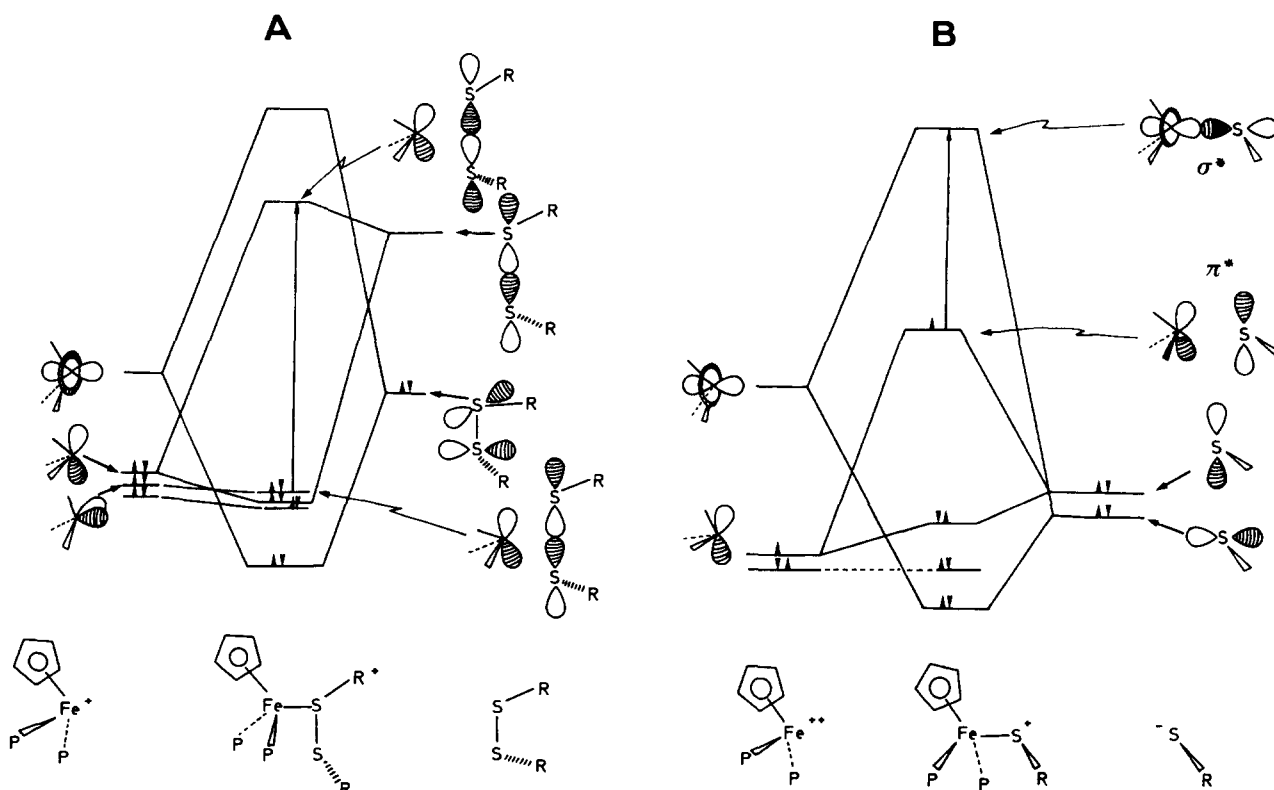


Fig. 2. Simplified molecular orbital diagrams for $[\text{CpFe}(\text{phosphine})_2\text{S}_2\text{R}_2]^+$ (A) and $[\text{CpFe}(\text{phosphine})_2\text{-SR}]^+$ (B) complexes. Possible geometries of the complexes, adapted from Refs. [3–5] and [13a]. Arrows represent possible transitions. MO levels are scaled according to energy values of the respective fragments.

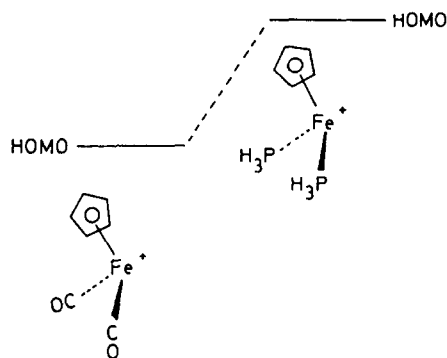


Fig. 3. Substitution effect on the HOMO's energy in going from carbonyl to phosphine ligands.

$\text{CpFe(CO)}_2\text{X}$ compared with those for CpFe(dppe)X complexes [14,15].

2.1. Reduction of the $[\text{CpFe(dppe)}-\text{SR}]\text{PF}_6$ complexes

Attempts to reduce the $[\text{CpFe(dppe)}-\text{SR}]\text{PF}_6$ complexes with CaH_2 and Na produce impure red-brown solids whose ^{31}P NMR spectra exhibit signals above 100 ppm indicating the formation of neutral CpFe(dppe)X complexes [20]. The signal corresponding to PF_6^- is absent in these spectra. The solution containing the reduced compounds is red-orange (absorption near 450 nm), which is typical of CpFe(dppe)X complexes [20].

3. Comments and conclusions

The reactions between CpFe(dppe)I and dialkyl disulfides R-S-S-R in the presence of NH_4PF_6 (or TiPF_6) used to abstract halide depend on two factors: (i) the polarity of the medium and (ii) the steric effect on the R substituents.

The solvent effects arise from the stabilization in solvents of the high dielectric constant of the Fe^{III} cation, $[\text{CpFe(dppe)}-\text{SR}]^+$, which has a higher charge density than the more bulky Fe^{II} cation, $[\text{CpFe(dppe)}-\text{S}_2\text{R}_2]^+$. Polar solvents are well known to facilitate oxidation processes as well as the formation of charged species. In fact, we have found recently that ionization of the CpFe(dppe)X $\text{X} = \text{Cl}, \text{I}$ complexes occurs in solvents with a high dielectric constant [21]. The steric effect probably arises from the stabilization of the disulfide complex with the bulky tert-butyl substituents which block access to the cation CpFe(dppe)^+ , producing the thiolate product (Fig. 4).

Stabilization of the t -butyl-sulfur ligand with several organometallic fragments has been reported [22,23].

Finally, both dielectric medium and steric factors appear to be necessary elements in the production of the

iron(III)-thiolate products reported here. Some of these mechanistic considerations are, however, speculative and need further experimental confirmation.

4. Experimental

Infrared spectra were run on an FT-IR Perkin-Elmer 2000 spectrophotometer. NMR spectra were recorded on a Bruker AMX 300 instrument. Chemical shifts are given in δ relative to TMS (^1H) or 85% H_3PO_4 (^{31}P proton decoupled) with shift reference being positive. Visible absorption spectra were measured on a Varian DMS-90 spectrophotometer in 1 cm length cuvettes. Magnetic susceptibility data were obtained using a Faraday balance. 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. Disulfides (Aldrich) were used without additional purification. CpFe(dppe)I was prepared using previously reported methods [24,25].

$[\text{CpFe(dppe)S-CH}_3]\text{PF}_6$ (1). To 0.15 g (0.23 mmol) of CpFe(dppe)I in CH_3OH (20 ml), 0.5 ml (0.52 g 5.5 mmol) of $\text{S}_2(\text{CH}_3)_2$ and 0.16 g (0.98 mmol) of NH_4PF_6 was added and the mixture was stirred for 20 h at room temperature. After 2 h, at the end of the reaction, the solution turned black-violet and dark-blue. The solvent was removed in a vacuum and the solid residue was extracted with CH_2Cl_2 . The solution was filtered through Kieselguhr 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. Yield 0.17 g (64%).

% Anal. Found: C, 53.88; H, 4.44. $\text{C}_{32}\text{H}_{32}\text{P}_3\text{F}_6\text{SFe} \cdot \text{CH}_3\text{OH}$ Calc.: C, 53.30; H, 4.84 IR (KBr): 2970(s), 2910(s), 1550(m), 1475(w), 1430(s), 1389(m), 1380(m), 1310(w), 1290(m), 1248(m), 1200(m), 1089(m), 835(vs), 730(m), 689(s), 555(s), 535(s).

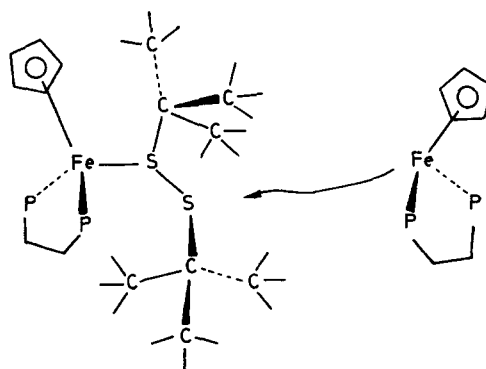


Fig. 4. Proposed steric hindrance from the complex $[\text{CpFe(dppe)}]^+ \text{Bu}_2\text{S}_2\text{PF}_6^-$ towards attack of the fragment CpFe(dppe)^+ .

[CpFe(dppe)–S–CH₂CH₂CH₃]₂PF₆ (**2**). A solution containing 0.15 g (0.23 mmol) of CpFe(dppe)I in ca. 20 ml of solvent CH₃OH and 0.7 ml (0.67 g, 4.4 mmol) of S₂(C₃H₇)₂ in the presence of NH₄PF₆ (0.12 g, 0.74 mmol) was stirred at room temperature for 20 h. Separation and purification procedures similar to those used for **1** produced a blue powder; yield 0.15 g (80%).

Anal. Found: C, 54.42; H, 4.82. C₃₄H₃₆F₆P₃SFe · CH₃OH Calc.: C, 54.48; H, 4.67%. IR (Nujol): 1430(m), 1389(m), 1300(w), 1220(m), 1092(s), 835(vs), 740(s), 690(s).

[CpFe(dppe)–S–CH₂C₆H₅]₂PF₆ (**3**). A mixture of 0.15 g (0.23 mmol) of CpFe(dppe)I and 0.5 g (2.0 mmol) of S₂(CH₂–C₆H₅)₂ in the presence of NH₄PF₆ (0.1 g, 0.61 mmol) in CH₃OH (20 ml) was stirred at room temperature for 20 h. After separation and purification, similar to that described for **1**, a dark-blue solid was obtained, yield 0.13 g (61%).

Anal. Found: C, 58.89; H, 5.66. C₃₈H₃₆F₆P₃SFe · (C₂H₅)₂O Calc.: C, 58.54; H, 5.34%. IR (Nujol): 1470(s), 1435(s), 1365(m), 1305(w), 1185(m), 1215(w), 1091(s), 836(vs), 760(m), 740(s), 692(s), 560(s), 529(s).

[CpFe(dppe)–S–C₆H₅]₂PF₆ (**4**). 0.4 g (1.83 mmol) of S₂(C₆H₅)₂ was added to 0.15 g (0.23 mmol) of CpFe(dppe)I and 0.10 g (0.61 mmol) of NH₄PF₆ in CH₃OH (20 ml) and the solution was stirred for 20 h at room temperature. Treatment of the solution similar to **1** produced a blue solid; yield 0.13 g (72%).

Anal. Found: C, 58.27; H, 5.27. C₃₇H₃₄F₆P₃SFe · (C₂H₅)₂O Calc.: C, 58.09; H, 5.19%. IR: 1470(s), 1435(s), 1290(m), 1200(s), 1098(m), 1040(m), 1060(m), 828(vs), 770(vs), 710(vs), 696(vs), 570(s).

4.1. Reaction of CpFe(dppe)I with S₂(^tBu)₂

A mixture of 0.3 g (0.46 mmol) of CpFe(dppe)I and 0.5 ml (0.46 g, 2.6 mmol) of S₂(^tBu)₂ in the presence of NH₄PF₆ (0.32 g, 1.9 mmol) was stirred into 30 ml of CH₃OH at room temperature. After 18 h the solution changed from black to dark-red. The solvent was evaporated and the red-brown solid residue was extracted with CH₂Cl₂ and then filtered through Kieselguhr. The solution was concentrated to ca. 10 ml, to which a mixture of 5 ml 1:10 *n*-hexane-ether was then added. The precipitated red solid was washed twice with a mixture of *n*-hexane and ether and dried in vacuo.

Anal. Found: C, 55.71; H, 5.61. C₃₉H₄₉F₆P₃S₂Fe Calc.: C, 55.59; H, 5.58%.

¹H NMR: (δ, acetone-*d*₆), 1.38 s, (C(CH₃)₃); 2.14 s, (C(CH₃)₃); 2.56 m, (CH₂)₂–P; 4.55 s, (C₅H₅); 7.27–7.76 m br, [C₆H₅–P].

³¹P NMR: (δ, acetone-*d*₆), 92.54 d, (P–CH₂); –138.8 m, (PF₆).

IR (Nujol): 1170(m), 1117(w), 1093(m), 1076(m), 1024(w), 995(w), 836(vs), 739(s), 720(m), 692(s), 558(s), 536(s).

4.2. Attempted reduction of thiolates

(a) With CaH₂. To a solution of 0.08 g (0.11 mmol) of [CpFe(dppe)S–C₃H₇]₂PF₆ in ca. 4 ml of THF, 0.009 g (0.21 mmol) of CaH₂ was added. The resulting mixture was stirred at room temperature for 18 h. The initially dark-blue solution changed to red-brown. The solvent was removed at reduced pressure and the solid residue was extracted with CH₂Cl₂ and filtered through Kieselguhr. Evaporation of the solvent from the orange solution produced an oily residue.

(b) With Na. 0.04 g (0.05 mmol) of [CpFe(dppe)–S–C₃H₇]₂PF₆ was stirred at –80°C together with metallic Na in 5 ml of THF and with 0.1 g (0.6 mmol) of NaPF₆. After 30 min the solution turned violet and then red. The solution was then stirred for an additional 12 h, after which time it turned red-brown. The unreacted Na was deactivated with methanol and the solvent was evaporated under vacuum. The solid residue was extracted with CH₂Cl₂ and filtered through Kieselguhr. The orange solution was evaporated to dryness. The yellow residue was washed twice with an *n*-hexane-diethyl ether mixture and dried under vacuum.

³¹P NMR: δ 102 ppm(dppe).

4.2.1. Reduction of **3**

To a THF solution containing 0.04 g (0.05 mmol) of [CpFe(dppe)–S–CH₂–C₆H₅]₂PF₆ and 0.1 g (0.06 mmol) of NaPF₆ cooled to –80°C was added metallic Na (0.05 g, 2 mmol). Separation and purification procedures were similar to those used in the reduction of [CpFe(dppe)–S–C₃H₇]₂PF₆. An orange solid product was obtained.

³¹P NMR: δ 102.5 ppm(dppe).

4.2.2. Reduction of **1**

0.08 g (0.11 mmol) of [CpFe(dppe)–SCH₃]₂PF₆ and metallic Na in the presence of NaPF₆ were stirred into 20 ml of THF at –80°C. After 20 h the solution turned red. Separation procedures similar to those in the other reductions produced a dark-red solid.

³¹P NMR: δ 102.7 ppm(dppe).

Acknowledgements

We thank the FONDECYT (Projects 1950305, 1940588) and DTI, Universidad de Chile (Q-3280) for financial support.

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