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Photosubstitution of the halide ligands (X^-) in (η^5-C_5H_5)Fe(CO)(PPh_3)X

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Abstract

Irradiation of CpFe(CO)(PPh_3)X, (Cp = η^5-cyclopentadienyl, X = Cl, Br or I), **1a**–**c**, with white or red ($\lambda > 600$ nm) light with maleimide or succinimide and di-*iso*-propyl amine (dipa) or ethyldi-*iso*-propyl amine (edipa) in dichloromethane leads to the efficient formation of CpFe(CO)(PPh_3)(η^1-*N*-imidato) complexes **2a**–**b**. Irradiation with white light of CpFe(CO)(PPh_3)Br in dichloromethane in the presence of an excess of Br^- (as tetrabutylammonium bromide) yields CpFe(CO)(PPh_3)Br. These results are discussed in terms of possible photoinduced heterolysis of the iron–halide bond in **1a**–**c**.

Keywords: Halide ligands; Imidato ligands; Photosubstitution

1. Introduction

Photochemistry of cyclopentadienylmetal carbonyl complexes containing halide ligands has been extensively studied, especially for $CpM(CO)_3X$ (Cp = η^5-cyclopentadienyl, M = Mo, W, X = halide) and $CpM(CO)_2X$ (M = Fe, Ru) [1–14]. It has been found that photoexcited states of these compounds undergo a variety of chemical reactions including dissociation of the carbonyl ligand, homolytic or heterolytic cleavage of the metal halide bond, intramolecular isomerization and intraligand rearangements. Photolysis of $CpFe(CO)_2X$ (X = Br or I) in the presence of PPh_3 leads to the formation of covalent complexes CpFe(CO)(PPh_3)X with high quantum efficiency, indicating that CO dissociation is a dominant reaction pathway [1]. This has been confirmed by IR studies in low-temperature matrices, indicating exclusive formation of the 16-electron species CpFe(CO)X [3]. However, other studies have revealed that photoprocesses involving heterolysis of the Fe–X bond are also possible. For example, upon irradiation of $CpFe(CO)_2X$, the dimer $[CpFe(CO)_2]_2$ is formed [4]. Irradiation of $CpFe(CO)_2I$ in the presence of an N–H acid and di-*iso*-propyl amine (dipa) in benzene leads to efficient photosubstitution of iodide by the corresponding N-anions [5–14]. Initially for these reactions, a mechanism involving electron transfer between amine and the organometallic substrate has been suggested [8], but later indirect (via CO-dissociation) halide exchange mechanism was put forward [9]. Finally, in the recent work by Lees et al. [5] a possibility of direct heterolysis of the Fe–I bond was considered, especially when red light ($\lambda = 647$ nm) was used for irradiation.

In contrast to $CpFe(CO)_2X$ complexes their mono carbonyl derivatives CpFe(CO)(L)X, where L is a neutral 2 e donor ligand, have attracted only little attention of photochemists. Only one report has appeared devoted to photochemical transformations of these complexes [15]. It has been found that irradiation CpFe(CO)(PPh_3)Br in pyridine or dmso leads to formation (in low yield)of $[CpFe(CO)_2]_2$ when L = $P(OPh)_3$ and $[CpFe(CO)_2(L)]Br$ when L = PPh_3. Although these reactions proceed with the disruption of the iron–halide bond, their mechanism does not seem to be simple (the isolated products contain two CO ligands) and there is no evidence that this disruption occurs in the first, photochemical step.

In this paper we would like to report the first example of the straightforward photochemical substitution of the halide ligand in CpFe(CO)(PPh_3)X complexes

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1a–**c** (X = Cl (a), Br (b) and I (c)).We have found that irradiation of these complexes with red light in the presence of cyclic imides (maleimide, succinimide) and dipa or ethyldiisopropyl amine (edipa) in dichloromethane brings about substitution of the halide ligands by η^1-*N*-imidato ligands. Furthermore, irradiation of **1c** in dichloromethane in the presence of bromide anions leads to a fast halide exchange.

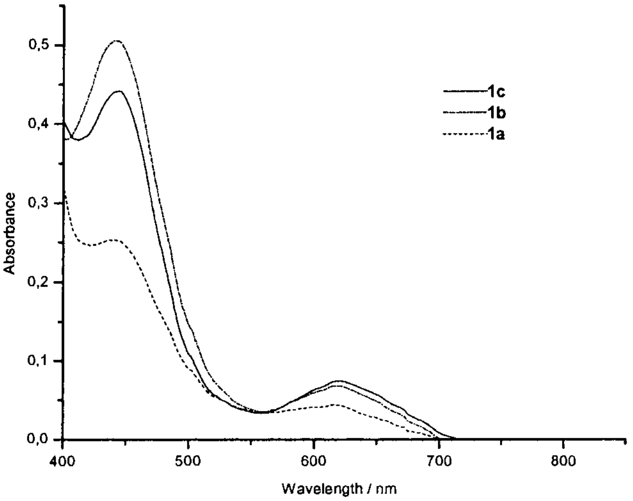
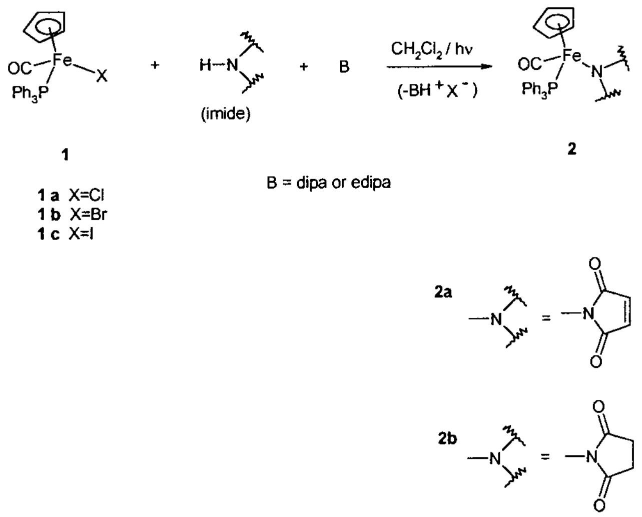


Fig. 1. Electronic absorption spectra of **1a**–**c** in dichloromethane ($c = 5 \times 10^{-4}$ M).

Table 1
Electronic absorption spectra of CpFe(CO)(L)X, **1a**–**c**, in the visible region

Solvent	X	λ_{max} (nm) (ε_{max} (l mol^{-1} cm^{-1}))
CH_2Cl_2	Cl (**1a**)	440 (510); 615 (90)
	Br (**1b**)	443 (1010) 619 (140)
	I (**1c**)	444 (880); 619 (150)
C_6H_6	Cl (**1a**)	443 (860); 618 (270)
	Br (**1b**)	446 (1370);618 (260)
	I (**1c**)	442 (900); 620 (200)



Scheme 1.

Table 2
Photoinduced reaction of CpFe(CO)(PPh_3)X with imides in the presence of an amine

Complex	X	Imide	Base	Product (yield)
1a	Cl	Maleimide	dipa	**2a** (45%)
1b	Br	Maleimide	dipa	**2a** (60%)
1c	I	Maleimide	dipa	**2a** (77%)
1c	I	Succinimide	dipa	**2b** (45%)
1c	I	Maleimide	edipa	**2a** (95%)

2. Results and discussion

The solutions CpFe(CO)(L)X (**1a**–**c**) in benzene and dichloromethane are green and show in the visible region two absorption bands (Fig. 1, Table 1).

Taking into consideration the weak molar absorptivities of these bands and the absence of solvatochromism we assign them to the orbitally forbidden ligand-field (LF) transitions [16].

It has been found that irradiation with visible light of a solution of **1a**–**c** in dichloromethane containing a cyclic imide (maleimide, succinimide) and dipa or edipa leads to the formation of red **2a**–**b**, isolated in 45–95% yield (Scheme 1, Table 2).

Complex **2b**, was earlier obtained by the CO–PPh_3 exchange in CpFe$(CO)_2$(η^1-*N*-succinimidato) [7]. Analogously, for we have prepared **2a** from CpFe$(CO)_2$(η^1-*N*-maleimidato). It has been found that complexes prepared by a photochemical route have the same spectral data and TLC properties as those obtained by the CO–PPh_3 exchange.

Using an appropriate cut-off filter it has been found that reaction occurs at irradiation with the red ($\lambda > 600$ nm) light. We have found that solvent plays a very important role and the photoreaction does not takes place in less polar benzene. This fact may indicate that a polar transition state is involved which is in favor of direct photoinduced heterolysis of the Fe–I bond in the organometallic substrate. An additional argument for that is provided by the fact that the CO ligand in CpFe(CO)(PPh_3)X is more tightly bound to iron than these ligands in CpFe$(CO)_2$X (compare the ν_{CO} frequencies in CpFe$(CO)_2$I, 2039 and 1995 cm^{-1}, with that in CpFe(CO)(PPh_3)I, 1948 cm^{-1} [2]).

Despite the fact that photolysis of CpFe$(CO)_2$X in low temperature matrices produces only the 16 e CpFe(CO)X as a result of the CO dissociation, Lees and co-workers suggest that photoreaction CpFe$(CO)_2$I with NH acids in the presence of an amine involves heterolysis if the Fe–I bond [5]. They emphasize a different nature of the lowest excited state of the iodo complex, in comparison with its bromo- and chloro counterparts, and the possibility of the assistance of dipa in the cleavage of the Fe–I bond. However, we have found that $CpFe(CO)_2Br$ displays similar photoreactivity toward cyclic imides–amine as $CpFe(CO)_2I$ [17]. On the other hand, the replacement of dipa by edipa improves significantly the yield of $CpFe(CO)(PPh_3)X$ (Table 2). The latter amine does not form hydrogen bond with iodide and cannot, therefore, facilitate the leave of I^- as it was suggested [5].

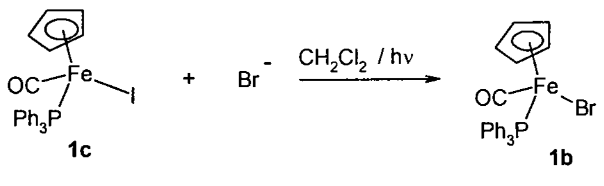
The results obtained in this work suggest that irradiation of $CpFe(CO)(PPh_3)X$ brings about a heterolysis of the iron–halide bond, forming $CpFe(CO)(PPh_3)^+$ and X^-. To confirm this we irradiated $CpFe(CO)(PPh_3I$ in the presence of excess Br^- (as tetrabutylammonium bromide). We have observed efficient halide exchange yielding $CpFe(CO)(PPh_3)Br$. The reaction occurs *in the absence of amine*, indicating that its role is presumably limited to deprotonation of imide (free or bound to Fe) Scheme 2.

In conclusion, it has been found that the halide ligands in $CpFe(CO)(PPh_3)X$ complexes (**1a**–**c**) undergo substitution by η^1-*N*-imidato ligands a upon irradiation with red light with cyclic imides and an amine in dichloromethane solvent. The reaction did not take place in less polar benzene. This fact, together with the observed halide exchange suggest that these reactions may proceed via photoinitiated heterolysis of the iron–halide bond, forming $CpFe(CO)(PPh_3)^+$ and X^-. Obviously, photophysical studies (e.g. photolysis in low-temperature matrices) are now required to confirm this hypothesis.

3. Experimental

Compounds **1a**–**c** and **2b** were prepared according to earlier published procedures [7,18].

The photolyses were carried out under argon using 4 × 150 W domestic tungsten lamps, The photolytes were magnetically stirred and externally cooled with water–ice. Dichloromethane was distilled over CaH_2 and benzene from sodium-benzophenone. Other solvents were reagent-grade and were used without prior purification. Silica gel 60 (230–400 mesh ASTM), purchased by Merck was used for chromatography. Chloroform was used as eluent.



Scheme 2.

3.1. Synthesis of $CpFe(CO)(PPh_3)(\eta^1$-*N*-maleimidato) (**2a**)

A solution of $CpFe(CO)_2(\eta^1$-*N*-maleimidato) [9] (300mg, 1.1 mmol) and triphenylphosphine (343 mg, 1.3 mmol) in benzene (10 ml) was refluxed for 3 h. Evaporation to dryness and column chromatography gave red–brown **2a** (515 mg, 92%). An analytical sample was prepared by recrystallization from Et_2O–*n*-heptane. ^{1}H-NMR (200 MHz, $CDCl_3$, δ) 7.35–7.3 (m 15H, aromatic H's), 6.18 (s, 2H, olefinic), 4, 62 (s, 5H, Cp). IR ($CHCl_3$, cm^{-1}): 1968, 1641. Elemental analysis: Anal. Calc. for $C_{28}H_{22}FeNO_3P$: C, 66.28; H, 4.38; N, 2.73; P, 6.10. Found: C, 66.56; H, 4.44; N, 2.43; P, 5.94%.

3.2. Photoinduced reaction of $CpFe(CO)(PPh_3)X$ with imides in the presence of an amine

A solution of $CpFe(CO)(PPh_3)X$ (0.56 mmol), imide (0.56 mmol) in dichloromethane (17 ml) and amine (1 ml) was photolyzed for 3 h. The green color of the photolyte gradually turned to brown. After filtration and evaporation to dryness the residue was chromatographed. The deep red band of the product, which followed a small green band of unreacted $CpFe(CO)(PPh_3)X$ was collected. The products were recrystallized from chloroform–hexane·and identified by comparison of their spectral and TLC properties with those of authentic samples. The yields are given in Table 1.

3.3. Photoinduced halide exchange in $CpFe(CO)(PPh_3)I$

An argon-saturated solution of **1c** (54 mg, ~0.1 mmol) and $Bu_4N^+Br^-$ (322 mg, 1 mmol) in dichloromethane (10 ml) was photolyzed for 1 h. Evaporation to dryness and chromatography (SiO_2–chloroform) gave 32 mg (65%) of **1b**, identified by comparison with an authentic sample.

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