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Photochemical halide exchange in CpFe(CO)(L)X complexes ($Cp = \eta^5\text{-}C_5H_5$; L = CO, PPh_3; X = Br, I). Tandem photosubstitution of X^- and CO

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Abstract

Upon irradiation with visible light in the presence of $Bu_4N^+Y^-$ (Y^- is a halide lighter than X^-) the title complexes undergo halide exchange. In the presence of PPh_3 and $Bu_4N^+Y^-$ tandem photosubstitution of CO by PPh_3 and X^- by Y^- takes place in high yield.

Previous investigations [1–3] have shown that the primary photochemical process for $CpFe(CO)_2X$ complexes **1** ($Cp = \eta^5\text{-}C_5H_5$; X = Cl, Br, I) is the dissociative loss of the carbon monoxide ligand. No evidence was found for either photohomolysis or photoheterolysis of the Fe–X bond. Accordingly, irradiation of the bromo- or iodo-derivatives in the presence of PPh_3 leads to the exclusive formation of $CpFe(CO)(PPh_3)X$ (eq. 1):

$$CpFe(CO)_2X + PPh_3 \xrightarrow[-CO]{h\nu} CpFe(CO)(PPh_3)X \tag{1}$$

In the case of the corresponding chloro-complex the fast "dark" reaction occurs, leading to $[CpFe(CO)_2(PPh_3)]^+Cl^-$ and hampering photochemical study.

It has been suggested that the photostability of the Fe–X bond in **1** is due to the fact that their doubly degenerated HOMO's are the π^* Fe–X orbitals [1,2]. Consequently, photoexcitation leading to partial depopulation of these antibonding orbitals should stabilize the Fe–X bond.

However, it was recently reported [4–6] that irradiation of **1** (X = I) in the presence of a base (diisopropylamine) and a N–H acid (pyrrole, indole, cyclic imides) results in substitution of iodide by the corresponding N-anions (eq. 2):

$$CpFe(CO)_2I + H-N\langle + B \xrightarrow{h\nu} CpFe(CO)_2(N\langle) + BH^+I^- \tag{2}$$

It has been suggested that this reaction involves activation of **1** via a photoinduced electron transfer (presumably from diisopropylamine) and resembles mechanistically well-known $S_{RN}1$ processes [6].

Visible light irradiation of **1** and related $CpFe(CO)(PPh_3)X$ complexes in the presence of $Bu_4N^+Y^-$ (Y^- = halide) in chloroform results in a halide exchange when Y is lighter than X (eq. 3).

$$CpFe(CO)(L)X + Y^- \xrightarrow[-X^-]{h\nu} CpFe(CO)(L)Y \quad (3)$$

$(L = CO, PPh_3)$

Moreover, irradiation of **1** in the presence of PPh_3 and $Bu_4N^+Y^-$ leads to highly efficient tandem photosubstitution of CO by PPh_3 and X^- by Y^- (eq. 4).

$$CpFe(CO)_2X + PPh_3 + Y^- \xrightarrow[-CO,\ -X^-]{h\nu} CpFe(CO)(PPh_3)Y \quad (4)$$

In all experiments a 800 W tungsten lamp was used as a light source. Unfiltered light and light passed through a cut-off ($\lambda > 370$ nm) filter gave practically the same results. The products were isolated by column chromatography ($SiO_2/CHCl_3$) and identified by TLC and spectral (IR, UV–Vis and ^{1}H NMR) comparison with the authentic samples [1,2,7].

When a solution of $CpFe(CO)_2I$ (92 mg, ~ 0.3 mmol) and $Bu_4N^+Br^-$ (770 mg, ~ 3 mmol) in chloroform (20 ml) was photolysed 1 min under argon the color turned from brown to red. The work-up gave ferrocene (26%), $CpFe(CO)_2Br$ (39%) and unreacted $CpFe(CO)_2I$ (24%). When the photolysis time was prolonged to 2 min, the yields of these products were 35, 29 and 15%, respectively. On the other hand, formation of Fe^{2+} has been evidenced (9,10-phenatroline test). This means that, besides halide exchange, decomposition of $CpFe(CO)_2I$ to Cp_2Fe, FeX_2 and CO takes place [7]. Interestingly, this decomposition was totally suppressed when the photolysed solution was saturated with CO (under ambient pressure). Under these conditions 6 min photolysis afforded $CpFe(CO)_2Br$ in 97% yield.

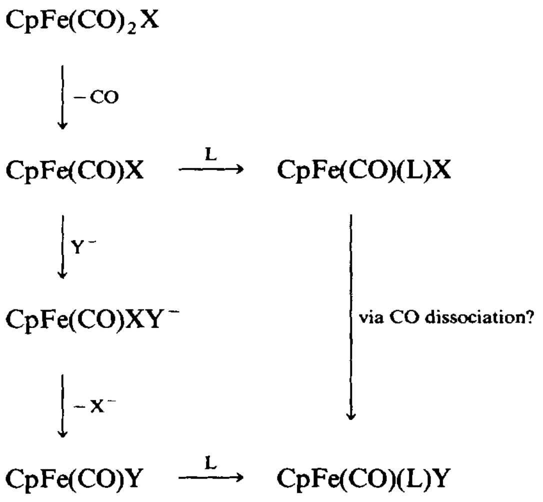
Irradiation of $CpFe(CO)_2Br$ in the presence of $Bu_4N^+I^-$ does not afford any traces of $CpFe(CO)_2I$. The results obtained for photolysis of $CpFe(CO)_2X$ in the presence of PPh_3 and $Bu_4N^+Y^-$ (eq. 4) are summarized in Table 1. In general, irradiation was carried out until complete disappearance of the starting complex monitored by TLC and IR (~ 4–6 min).

Irradiation of **1** in the presence of equimolar amounts of PPh_3 and $Bu_4N^+Y^-$

Table 1

Yields of $CpFe(CO)(PPh_3)Y$ and $CpFe(CO)(PPh_3)X$ formed by irradiation of $CpFe(CO)_2X$ (**1**) in the presence of PPh_3 and $Bu_4N^+Y^-$

Entry	X	Y	$1:PPh_3:Y^-$	Yield (%)	
				$CpFe(CO)(PPh_3)Y$	$CpFe(CO)(PPh_3)X$
1	I	Cl	1:1:1	91	5
2	I	Cl	1:1:10	92	3
3	I	Br	1:1:1	87	8
4	I	Br	1:1:10	90	5
5	I	Br	1:5:1	58	34
6	I	Br + Cl	1:1:(1+1)	72 (Y = Cl) 19 (Y = Br)	4
7	Br	Cl	1:1:1	86	10
8	Br	I	1:1:1	3	91



Scheme 1 ($L = CO, PPh_3$).

gives rise to efficient tandem substitution of CO by PPh_3 and X^- by Y^- when Y is a lighter homolog of X (entries 1, 3 and 7). Otherwise, practically only CO substitution takes place (entry 8). Cl^- is more reactive than Br^- (entry 6). When the concentration of Y^- increases, the yield of the product of the tandem photosubstitution slightly increases (entries 2 and 4), whereas increase of the PPh_3 concentration causes the opposite effect (entry 5).

On the other hand, complexes $CpFe(CO)(PPh_3)X$ also undergo photochemical halide exchange, although less efficiently. Thus, $CpFe(CO)(PPh_3)I$ (0.3 mmol) irradiated in the presence of $Bu_4N^+Br^-$ (3 mmol) in chloroform (20 ml) for 5 min gave $CpFe(CO)(PPh_3)Br$ in 56% yield (40% of the unreacted starting complex was recovered).

The halide exchange and tandem photosubstitution of halide and CO represented in eqs. 3 and 4 do not seem to involve a photoinduced electron transfer process. Indeed, for obvious reasons such a process between $CpFe(CO)_2Br$ and I^- should be more probable than that between $CpFe(CO)_2I$ and Br^-. Nevertheless, the halide exchange takes place only in the latter case.

A tentative mechanistic interpretation of the above results is given in Scheme 1. The primary photochemical process is the CO loss [1–3]. The high reactivity of coordinatively unsaturated metal species towards halides is now well documented [8]. The halide exchange in the 16-electron fragment CpFe(CO)X via an associative mechanism could be, therefore, a likely process. Its driving force could be the increase of the bond energy Fe–I < Fe–Br < Fe–Cl (in complexes FeX_2 279, 340 and 400 kJ/mol, respectively [9]).

Obviously, at this stage the problem of reversibility of some steps involved in Scheme 1 as well as the mechanism of the halide exchange in $CpFe(CO)(PPh_3)X$ must remain unanswered.

In my opinion photoinduced "CO-dissociation-driven" halide exchange can be a general process for other transition metal carbonyl halides. Research in this field is currently underway.

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