

An improved photochemical synthesis of azaferrocene

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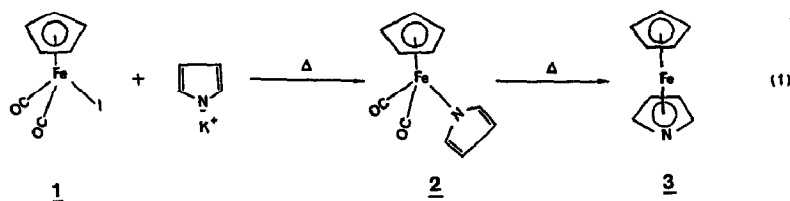
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Abstract

A new synthesis of azaferrocene, $(\eta^5\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$, involving photo-substitution of iodide in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ by the η^1 -pyrrolyl ligand, followed by decarbonylation of the resulting dicarbonyl η^1 -pyrrolyl complex, is described. The mechanism of the former reaction is discussed in terms of the photo-induced $S_{\text{RN}}1$ -type chain process.

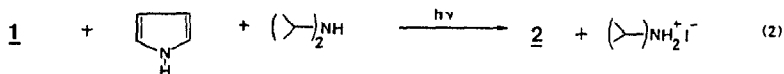
Introduction

η^5 -Pyrrolyl transition metal complexes have attracted considerable attention in the last few years since they: (a) display greater reactivity at the metal center compared with their η^5 -cyclopentadienyl counterparts [1]; (b) undergo interesting reactions at the coordinated pyrrole ring [2]; and (c) may be used as 2e donor ligands for synthesis of bi- and poly-nuclear complexes [3]. Unfortunately, available preparative routes to these complexes are often inefficient and low yielding. For example, azaferrocene, $(\eta^5\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ (**3**), was synthesized by Pauson et al. in 1964 [4] in only 22% yield by refluxing of the iodo complex **1** with pyrrolylpotassium in benzene (see eq. 1). When the reaction was carried out at lower temperature (60 °C) the intermediate η^1 -pyrrolyl complex **2** was isolated in 19% yield [5]. We have repeated this procedure a number of times and obtained **3** in only 8–12% yield. Another serious disadvantage is that the preparation of pyrrolylpotassium involves use of potassium metal.



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Recently we have reported [6] that **2** is formed in good yield on sunlight irradiation of **1** with pyrrole and diisopropylamine in heptane (eq. 2).



We describe below a more reliable version of this procedure involving use of a tungsten lamp as a source of the visible light. The decarbonylation of **2** to **3** has also been optimized. In consequence, we have transformed **1** into **3** via a two-step procedure in 61% overall yield. Furthermore, it has emerged that the mechanism of the photo-substitution of iodide in **1** appears to involve an electron transfer catalysed chain process, similar to the well known $S_{RN}1$ reactions [7].

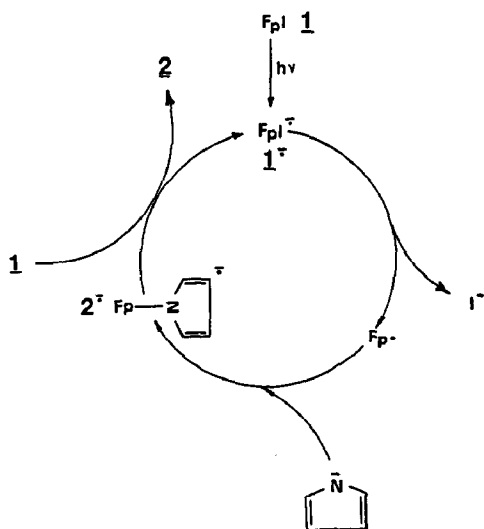
Results and discussion

Irradiation (W light) of argon-saturated solutions of **1** in toluene containing pyrrole and diisopropylamine resulted in the rapid precipitation of diisopropylamine hydroiodide. The orange-red supernatant liquid contained **2** as a major product, contaminated with small amounts of unchanged **1**, ferrocene, the dimer $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$, (Fp_2), and azaferrocene **3**. The components were separated by column chromatography ($\text{SiO}_2/\text{CHCl}_3$), and they were identified by comparison of the IR, ^1H NMR and mass spectra with those of authentic samples. The best yields of **2** (66%) were obtained when an excess of both pyrrole and diisopropylamine was used. Otherwise, the reaction is slow and the amount of recovered **1** and Fp_2 is markedly larger. The η^1 -pyrrolyl complex **2** forms orange crystals, which melt with decomposition at 102–103°C (Lit. [5] m.p. 91°C (decomp)).

Having established a good synthetic route to **2** we concentrated on the optimization of the decarbonylation step (**2** → **3**). According to Pauson [5] refluxing of a solution of **2** in benzene for 3 h gives **3** in 65% yield. We found that use of a mixture of toluene and cyclohexane (~ 1/12) as solvent gives a better yield of **3** (92%), and this also avoids the use of the highly toxic benzene. However, the reaction must be carried out in relatively dilute solutions (~ 8 mM), otherwise the yield of **3** is markedly lower.

We suggest that the transformation **1** → **2** may proceed by the ETC (Electron Transfer Catalysis) chain mechanism shown in Scheme 1. This mechanism, reminiscent of the well known $S_{RN}1$ reactions of organic halides, agrees with the following facts:

- It is known that **1** is an electron acceptor (e.g., it forms $\mathbf{1}^\ominus$ on exposure to γ -rays [8]. On the other hand amines (diisopropylamine) are strong electron donors [9]. Initiation of the reaction by electron transfer is therefore possible.
- Although we could not detect $\mathbf{1}^\ominus$ in our system (the ESR spectrum of this $19e$ complex is described in ref. 8), we did detect Fp^\ominus (nitrosodurene as a spin trap, 243 K, $g = 2.005$, $a^N = 17.8$ G; Lit. [10] $g = 2.005$, $a^N = 17.5$ G).
- The high reactivity of Fp^\ominus towards nucleophilic ligands is well documented [11]. However, it should be noted that in our system the nature of the nucleophile attacking Fp^\ominus is not certain; it could be pyrrole itself or pyrrolyl anion.
- A small amount of the dimer Fp_2 is always formed (by dimerization of Fp^\ominus). The amount increases as the concentration of pyrrole or amine is decreased.



Scheme 1. Photoinduced formation of **2** from **1** and pyrrolediisopropylamine. Fp = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$.

(e) Nitrosodurene, which is efficient spin trap for Fp' [10], markedly inhibits the formation of **2**.

(f) For the chain transfer ($2^- + 1 \rightarrow 2 + 1^-$) to be efficient **1** must be better electron acceptor than **2**. Although comparative electrochemical data are not available, the IR spectra (CHCl_3) suggest that the electron density at iron is lower in **1** than in **2** (CO stretching vibrations appear at 2020 and 2005 cm^{-1} for **1**, and at 1995 and 1960 cm^{-1} for **2**)

Even in light of the above facts the proposed photo-catalytic mechanism must remain to some extent speculative, (For example, the initial step could involve the homolysis $\text{FpI} \rightarrow \text{Fp}' + \text{I}'$). However, if our mechanistic proposal is correct the reaction of **1** with pyrrole and diisopropylamine represents a new example of an organometallic $S_{\text{RN}}1$ substitution of halide by a nitrogen nucleophile, analogous to well known $S_{\text{RN}}1$ reactions of organic halides, and confirms the view that this mechanism can operate in organic as well as in inorganic and organometallics chemistry [2]. The synthetic potential of such a photosubstitution has not yet been explored [3].

It can be seen that we have developed an efficient (61% overall yield) synthetic route to azaferrocene involving mild conditions and starting from the commercially available complex $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$. We note that during preparation of this manuscript an efficient synthesis of 2,3,4,5-tetramethylazaferrocene from $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{SMe}_2)_3^+$ was described [4].

Experimental

All reactions described were carried out under argon. Toluene and cyclohexane were distilled from CaH_2 . Diisopropylamine (Aldrich) was distilled and stored over KOH. Pyrrole (Aldrich) was distilled and passed through a short alumina (I) column immediately before use. Spectroscopic instrumentation: ^1H NMR: Bruker AC 200 (200 MHz); ESR: Bruker ER 420; IR: Perkin Elmer 297; MS: MS 50 AEI.

Complexes **2**, **3** as well as ferrocene and Fp_2 were identified by comparison with the authentic samples.

$(\eta^1\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ (**2**)

A solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{I}$ (**1**) (608 mg, 2 mmol) in the mixture of toluene (90 ml), diisopropylamine (10 ml) and pyrrole (4 ml, ~ 60 mmol) was irradiated with a 800 W tungsten lamp, the solution being cooled during the irradiation by immersion in an ice-water bath. Precipitation of diisopropylamine hydroiodide was observed, and the solution gradually turned orange-red. Monitoring by TLC showed that the reaction was practically complete within 1 h. The amine salt was filtered off (408 mg, 89%) and the filtrate evaporated below 40 °C (oil pump vacuum). The orange red residue was chromatographed on silica gel with CHCl_3 as eluent. The following well separated fractions were collected: (i) yellow, identified as ferrocene (5 mg); (2) dark brown, identified as a mixture of Fp_2 and **1** (35 mg, Fp_2 : **1** ratio 1.5/1), which were subsequently separated on preparative TLC plates ($\text{SiO}_2/\text{CHCl}_3$); (3) orange-red; crystallized from CH_2Cl_2 /pentane and identified as **2**. Yield 323 mg (66%). M.p. 102–103 °C (decomp.) (Lit. [5] m.p. 91–93 °C (decomp)). ^1H NMR (CDCl_3): δ 6.36 (s, 2H, α -pyrrolyl); 6.27 (s, 2H, β -pyrrolyl); 5.03 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$). IR (CHCl_3): 1995, 1960 cm^{-1} ($\nu(\text{C}\equiv\text{O})$). MS: m/e 2.43 (M^+), 215 ($M - \text{CO}$), 187 ($M - 2\text{CO}$); (4) orange, identified as azaferrocene (**3**) (5 mg).

When only 1 ml of pyrrole was used the yield of fraction 2 increased to 155 mg (ratio $\text{Fp}_2/\mathbf{1} \approx 1/1$) and the yield of **2** fell to 23%. Approximately the same effect was caused by reduction of the amount of diisopropylamine from 10 to 3 ml.

When the same reaction was carried out in the presence of 0.5 mmol of nitrosodurene only 5% of **2** was isolated, whereas the amount of fraction 2 increased to 280 mg (ratio $\text{Fp}_2/\mathbf{1} \approx 0.5$). Other (unidentified) products were also formed.

ESR experiment on spin-trapping of Fp^\cdot

A solution of **1** (10^{-3} M) pyrrole (10^{-3} M), nitrosodurene (10^{-3} M) and diisopropylamine (10^{-1} M) in toluene was irradiated (1000 W Xe lamp) at 243 K directly in the cavity of the ESR spectrometer. The appearance of a triplet ($g = 2.005$, $a^N 17.8$ G) was observed.

Azaferrocene

A solution of $(\eta^1\text{-C}_4\text{H}_4\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2$ (**2**), (400 mg, 1.65 mmol) in 15 ml of toluene was diluted with 185 ml of cyclohexane and the mixture was refluxed for 3 h then cooled to room temperature. The solvent was evaporated under reduced pressure and the residue chromatographed on silica gel with chloroform as eluent. The following well separated fraction were collected: (1) yellow, identified as ferrocene (5 mg); (2) dark red, identified as Fp_2 (12 mg); (3) orange-red, identified as azaferrocene (**3**). Yield 283 mg (92%). ^1H NMR (CDCl_3): δ 5.48 (s, 2H, α -pyrrolyl), 4.67 (s, 2H, β -pyrrolyl), 4.33 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$). IR: no $\text{C}\equiv\text{O}$ absorption. MS: 187(M^+), 121 (FeCp).

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