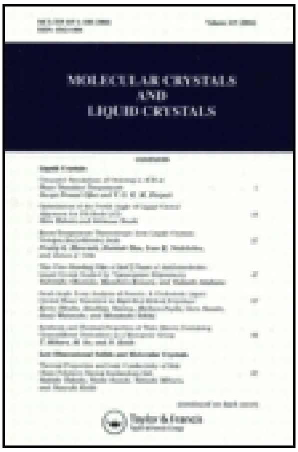

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Photoinduced Electron Transfer Processes in Synthesis and Coordination Chemistry of Azaferrocene

Janusz Zakrzewski [a] [b] & Charles Giannotti [a]

[a] Institut de Chimie des Substances Naturelles du C.N.R.S., Gif-sur-Yvette, 91198, France

[b] Institute of Chemistry, University, 90-136, Lódź, Narutowicza 68, Poland

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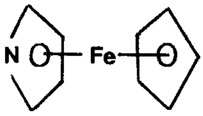
PHOTOINDUCED ELECTRON TRANSFER PROCESSES IN SYNTHESIS AND COORDINATION CHEMISTRY OF AZAFERROCENE

JANUSZ ZAKRZEWSKI* and CHARLES GIANNOTTI
Institut de Chimie des Substances Naturelles du C.N.R.S.,
Gif-sur-Yvette, 91198 France.

Abstract In this work we discuss the role of photoinduced electron transfer processes in synthesis of azaferrocene from (η^5-C_5H_5)Fe(CO)$_2$I, pyrrole and diisopropylamine, as well as in the photochemistry of cobalt chelates containing azaferrocene as an axial ligand.

Keywords: Photoinduced electron transfer reaction, azaferrocene synthesis, photo-ESR, cobalt chelates study

There is considerable interest in the application of photoinduced electron transfer processes (PET) in synthetic organometallic chemistry and in the rationalization of the reactivity pattern of organometallic complexes[1-2]. Following these trends we report here how the PET processes contributed to the development of an efficient synthesis of an interesting organometallic nitrogen ligand, azaferrocene (1) and how such processes influence the photochemistry of some of its binuclear complexes of type 2.



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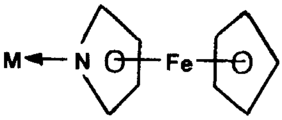

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1 has been known since 1964 but its synthesis is rather low yielding (22%)[3-4]. It consisted in the refluxing in benzene of FpI [Fp = (η^5 - C_5H_5)Fe(CO)$_2$] with pyrrolyl potassium (prepared from pyrrole and potassium metal). Under these conditions, the intermediate 3 underwent decarbonylation to afford 1.

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*Permanent address : Institute of Chemistry, University, 90-136 Łódź, Narutowicza 68, Poland.

$$FpI \xrightarrow{C_4H_4N^-K^+} \underset{\mathbf{3}}{[FpNC_4H_4]} \xrightarrow[-2\ CO]{\Delta} \underline{1} \qquad C_4H_4N = \text{pyrrolyl ligand} \qquad (1)$$

We have recently developed a photochemical approach to 1 in which the thermal reaction of FpI with pyrrolyl potassium is replaced by a photochemical reaction of FpI with pyrrole and diisopropylamine[5].

$$FpI + C_4H_4NH + (\rangle\!\!-)_2\ NH \xrightarrow{h\nu} FpNC_4H_4 \qquad (2)$$

This photoinduced substitution of iodide by the η^1-pyrrolyl ligand gives the thermally labile complex Fp NC_4H_4 in 66% yield (to compare with 19% reported)[4]. Moreover, this procedure avoids the use of dispersed metallic potassium and the highly toxic benzene is replaced by toluene.

We suggest that this reaction may proceed by Electron Transfer Catalysis (ETC) chain mechanism shown below (it is reminiscent of the well known $S_{RN}1$ reactions of organic halides).

$$\begin{aligned}
&FpI \xrightarrow{h\nu(e-)} FpI^{\overset{\cdot}{-}}\\
&FpI^{\overset{\cdot}{-}} \longrightarrow Fp\cdot + I^-\\
&Fp\cdot + C_4H_4N^- \longrightarrow \underline{3}^{\overset{\cdot}{-}}\\
&\underline{3}^{\overset{\cdot}{-}} + FpI \longrightarrow \underline{3} + FpI^{\overset{\cdot}{-}} \quad \ldots
\end{aligned}$$

We have some evidence in favor of this mechanism : (i) spin trapping with nitrosodurene (ND) gives evidence of a spin adduct with Fp$^\cdot$; (ii) Fp_2 has been characterised ; (iii) if the reaction is conducted with an excess of ND the formation of 3 is completely inhibited.

Azaferrocene acts as 2 e$^-$donor ligand to cobalt chelates related to vitamine B_{12} (alkylcobaloximes, cobalt porphyrins)[6]. Its ligating properties are close to those of pyridine (Py). However, we have observed[7] that $CoP(O_2)$ (1) and $CoP(O_2)$ (Py) (CoP = cobalt II porphyrin) have different photochemical properties. The former complex ejects $^3O_2$ on irradiation with visible light and forms CoP (1), whereas the latter is photostable.

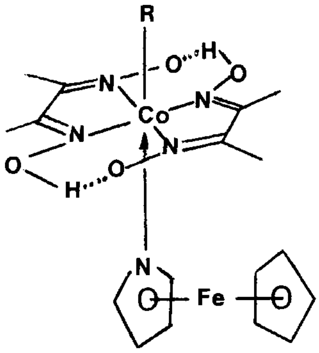
$$CoP\ (1)\ (O_2) \xrightarrow{h\nu\ (\lambda > 360\ nm)} Co\ P\ (1) + {}^3O_2$$

We have attributed this behaviour to a possible PET between cobalt and iron centers in $CoP(O_2)$ (1). Indeed, one can expect that if such transfer reduces the electron density of the cobalt center (Co --> Fe) it may result in the marked destabilisation of the (η^1-O_2) complex (the complexation of dioxygen is mainly due to the donation of electronic density from metal to antibonding π^* orbitals of O_2)[8].

Consequently, the decomplexation of O_2 might occur, followed by the back ET (i.e. Co --> Fe) giving CoP (1). However, the possibility of the photoexpulsion of(1) followed by ejection of dioxygen and recombination of(1) is not excluded.

More recently, we have turned our attention on the photochemistry of alkylcobaloximes R-$Co(dmgH)_2$ (1) (dmgH = dimethylglioxymato) (Structure 4). The cobaloxime system attracts continuing attention as a simple model of Co-C bond in the environment related to that of B_{12}. One of us (C. Giannotti)[9] has performed extensive ESR study on the photochemistry of R-$Co(dmgH)_2$ (py) complexes that pointed out the importance of electron transfer processes from the equatorial macrocyclic system to the cobalt atom on the homolytic rupture of the Co-C bond. In the case of R-$Co(dmgH)_2$ (1) similar ET transfer processes are envisageable between Co^{III} and Fe^{II} centers.

In fact, we have found that irradiation with the visible light of $C_6H_5CH_2Co(dmgH)_2$ (1) in toluene at 180-200 K gives rise to the appearance of ESR features that we have earlier attributed to the complex resulting from the ET from equatorial ligands to the cobalt atom. In the case of $C_6H_5CH_2Co(dmgH)_2$ (1) such a complex may result, however, from the electron transfer from the Fe^{II} atom in coordinated 1 to the cobalt (III) center. Indeed, when the sample is frozen to 100 K characteristic features of Fe^{III} (high spin) species appear (Fig. 1).



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The low temperature (100 K) photolysis of $Me_2CHCo(dmgH)_2$ (1) gives different results, resulting in the formation of features at g≃ 2, which have disappeared between 100-130 K. We attribute this species to the isopropyl free radical.

Accordingly, the formation of a weak large signal at g ≃ 2.3, assignable to $Co^{II}(dmgH)_2$ (1)is observed.

This signal becomes strong when the irradiation is carried out at 160 K. Both hyperfine (^{59}Co) and super-hyperfine (^{14}N of azaferrocene) splitting are observed, making the identification unambiguous. The spectral parameters at 100 K are :

$g_{\perp} = 2.308$ $g_{\parallel} = 1.942$ $a^{\parallel}_{N} = 13$ G $a^{\perp}_{Co} = 55$ G $a^{\parallel}_{Co} = 83$ G

When the irradiation has been carried out in isopropanol at 100 K the characteristic 7 line spectrum $g_{iso} = 2.015$ $a_H = 20$ G of $(CH_3)_2\dot{C}$-OH is observed, but no formation of Co^{II}. However, after annealing to 170 K in the dark, the characteristic features of $Co^{II}(dmgH)_2$ (1) appear. The radical $(CH_3)_2\dot{C}$ -OH is formed by H transfer from the solvent to $(CH_3)_2\dot{C}H$ initially formed. Consequently, homolysis of the carbon-cobalt bond does not apparently involve the formation of Co(II). This can be explained if one assumes that such a homolysis proceeds with an electron transfer from Fe to Co forming the ESR-silent Co^{I} and Fe^{III}.

Obviously, the results presented above, concerning alkylcobaloximes, containing axially coordinated (1) are still only

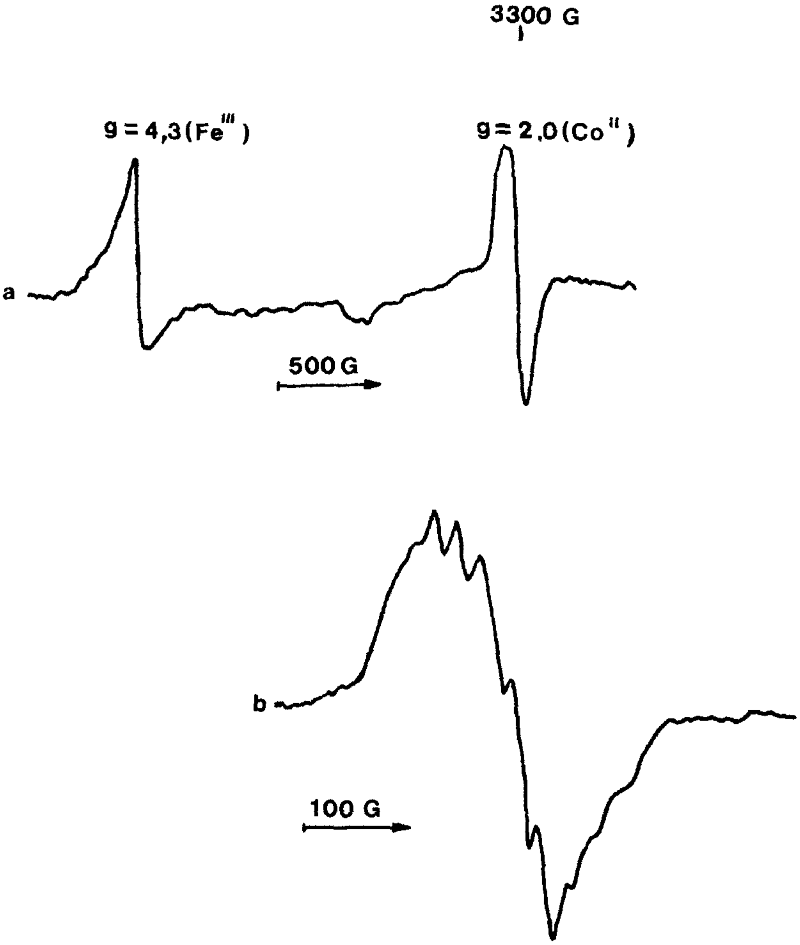

FIGURE 1 ESR spectrum (9.3 GHz) : (a) $PhCH_2Co(dmgH)_2$ 1 in toluene irradiated at 170 K and refreezed to 100 K ; (b) signal of Co(II) enregistered at 170 K.

preliminary. Nevertheless, they indicate that 1 markedly influences the photochemical behaviour of this system.

In conclusion, we have found that azaferrocene is a ligand of choice for constructing cobalt macrocyclic complexes of unusual properties.

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