

## The Role of the Excited States in the Photochemical Behavior of Ruthenocene in Halocarbon Solvents

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*Halocarbon solvents appears to form charge-transfer complexes with ruthenocene. Ruthenocene in halocarbon solvents exhibits a new band of electron transfer to solvent type at 285 nm. Irradiation by light, which excites the complexes and not the components, caused the oxidation of ruthenocene to ruthenocenium cation. A possible mechanism of the thermal decomposition of the ruthenocenium cation is discussed.*

### Introduction

Mixtures in solutions of electron-donors and electron-acceptors rapidly form charge-transfer complexes which can be detected by the appearance of a new band in the visible or ultraviolet absorption spectrum at wavelengths different than those for bands due to separate components. The properties and valence theory of charge-transfer complexes have been described in a number of reviews.<sup>2,3</sup>

Several photochemical reactions are known in which the first step is the excitation of a charge-transfer complex. Those resulting from irradiation of inorganic charge-transfer complexes have been reviewed by Orgel.<sup>3</sup> More recently, two reactions resulting from irradiation of ferrocene-to-halocarbon solvent charge-transfer complex have been reported.<sup>4,5</sup> Excitation of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  CTTS absorption gives the electron transfer product, ferricenium cation. No photoreaction was detected when the irradiation was carried out in the intramolecular ferrocene band. It seemed likely that selective irradiation of the new absorption bands which appears in donor-acceptor systems might give information in order to establish that these bands were due to CTTS transitions and not due to intramolecular charge-transfer bands shifted in energy by solvent effects. This paper records the result of an examination of this possibility. Ruthenocene was selected as the donor molecule and the acceptors chosen were halocarbon solvents with which  $\text{Ru}(\text{C}_5\text{H}_5)_2$  form charge-transfer complex.

### Experimental

#### *Preparation and Purification of Compounds*

$\text{Ru}(\text{C}_5\text{H}_5)_2$  was prepared with yields of 40–50% by the reaction of the appropriate metal chloride with cyclopentadienylsodium in tetrahydrofuran. The reaction mixture was refluxed, the solvent was distilled under reduced pressure, and the residue was sublimed under vacuum. Light yellow single crystals with well-developed faces were obtained, m.p. 199–200°C (reported m.p. 195.5).

Reagent grade  $\text{RuCl}_3$  (ROC/RIC) was used without further purification. All of the solvents used were of spectroscopic grade.

#### $[\text{Ru}(\text{C}_5\text{H}_5)_2]\text{RuCl}_4$

$10^{-2}M$   $\text{Ru}(\text{C}_5\text{H}_5)_2$  1,2-dichloroethane solutions were saturated with  $\text{N}_2$  and irradiated with 280 nm light. When decomposition sets in and a clouding of the yellow solution is observed (after *ca.* 1 hr), the mixture is filtered through a G 4 sinter in a nitrogen atmosphere. The yellow crystals thus obtained were washed with ethanol and dried under vacuum.

*Anal.* Calcd for  $[\text{Ru}(\text{C}_5\text{H}_5)_2]\text{RuCl}_4$ : Ru, 42.46; C, 25.22; H, 2.54; Cl, 29.78; found: Ru, 42.51; C, 25.20; H, 2.50; Cl, 29.70.

#### $\text{Ru}(\text{C}_5\text{H}_5)_2\text{Cl}$

Ruthenocenium chloride was prepared by photochemical reaction using the following procedure. Before irradiating, a small volume of 0.1M HCl was added to the  $10^{-2}M$   $\text{Ru}(\text{C}_5\text{H}_5)_2$  solution (solvent:carbon tetrachloride) contained in the reaction cell. The irradiation conditions were such that the aqueous layer, floating on the organic phase, was not irradiated. After a suitable irradiation period, the reaction cell was removed and then shaken, in order to obtain a complete extraction of the  $\text{Ru}(\text{C}_5\text{H}_5)_2\text{Cl}$  in the aqueous acid solution. That the extraction only involved the  $\text{Ru}(\text{C}_5\text{H}_5)_2\text{Cl}$  was proved by the constancy of the characteristic ruthenocenium absorption (see Results).

*Anal.* Calcd for  $\text{Ru}(\text{C}_5\text{H}_5)_2\text{Cl}$ : Ru, 37.9; C, 45.02; H, 3.78; Cl, 13.30; found: Ru, 37.5; C, 44.08; H, 3.80; Cl, 13.0%.

#### Absorption Spectral Measurements

Visible and near-ultraviolet absorption spectra were recorded on a Perkin-Elmer spectrophotometer. Exact solution absorption band intensity measurements at room temperature were completed using the following solvents: ethanol, chloroform, 1,2-dibromoethane, 1,2-dichloroethane, methylene chloride, benzotrithloride and carbon tetrachloride.

Infrared spectra were obtained with a Bekam IR 10 and Perkin-Elmer model 257 spectrophotometers. Nujol mulls were used for the  $300\text{--}450\text{ cm}^{-1}$  region and both KBr pellets and nujol mulls were used for the  $450\text{--}4000\text{ cm}^{-1}$  region.

#### Irradiation Procedures

The light source used for irradiating purposes was a Hanau Q400 medium-pressure mercury lamp with quartz optics. 280, 313, 334 nm radiations were isolated by means of Ealing-TFP interference filters. The general irradiation train was similar to that previously described.<sup>6</sup> The incident light was measured by means of the ferric oxalate actinometer. The incident light intensity was of the order of  $10^{-7}$  to  $10^{-6}$  Nh $\nu$ /min.

The complex was dissolved in the selected medium as quickly as possible in red light. All of the experiments were carried out at  $25^\circ\text{C}$ .

The changes in absorbance for the photochemical experiments were measured by the differential spectrophotometric method in order to take into account only the photochemical effects. The photoreaction was followed (see Results) measuring the increase in absorbance at 320 nm. When necessary, appropriate corrections were made for light absorbed by the complex. Deaerated solutions were obtained by successive freeze-thaw pumping cycles.

For the experiments in the presence of acrylamide, which were also carried out on deaerated solutions, the formation of the acrylamide polymer was looked for by diluting the irradiated solutions with an excess (10:1 in vol.) of methanol.

## Results

#### Spectral Properties of $\text{Ru}(\text{C}_5\text{H}_5)_2$ in Acceptor Solvents

The most evident feature of a CTTS complex is a new absorption band which cannot be attributed to either of the separate components of the complex.

The ultraviolet spectra of  $\text{Ru}(\text{C}_5\text{H}_5)_2$  in ethanol and in carbon tetrachloride are very different (Figure 1). The absorption band at 285 nm of  $\text{Ru}(\text{C}_5\text{H}_5)_2$  in carbon tetrachloride is attributed to a CTTS transition. Several alternative rationalizations of the origin

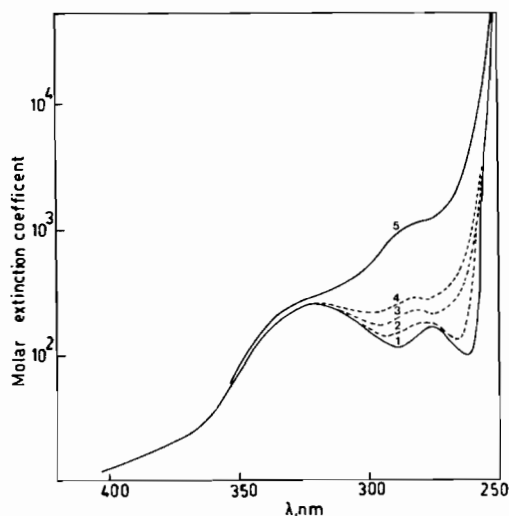


Figure 1. Spectra of ruthenocene in: 1, ethanol; 5, carbon tetrachloride; 2, 3, 4 spectra of ruthenocene in  $\text{CCl}_4$ -ethanol solvent mixtures (5%, 10%, 15%,  $\text{CCl}_4$  respectively).

of the new absorption in  $\text{CCl}_4$  and in a series of halogen-containing solvents were considered:

*i*) formation of a light-absorbing decomposition product; a stock solution of  $\text{Ru}(\text{C}_5\text{H}_5)_2$  in  $\text{CCl}_4$  (Figure 1, curve 5) was diluted with increasing percentages of ethanol. The absorption spectrum progressively changed until the "ethanol spectrum" (Figure 1, curve 1) was reached. Successively, a progressive dilution of an ethanol stock solution with  $\text{CCl}_4$  gave an opposite result. The spectral changes as a function solvent are, therefore, reversible and cannot be attributed to the formation of a decomposition product; *ii*) in the ultraviolet region of the ruthenocene solution absorption spectrum, a strong band at 200 nm and two shoulders at 215 and 238 nm have been observed as reported.<sup>7</sup> The band at 200 nm has an oscillator strength similar to that of a ferrocene band at  $50,000\text{ cm}^{-1}$  and most probably is due to the same type of allowed charge-transfer  $\text{L}\rightarrow\text{M}$  transition. The characterization of the two shoulders is not as definitive since the band positions and intensities are both difficult to determine accurately. However, as already reported for ferrocene<sup>8</sup> the system of ruthenocene bands at 215 and 238 nm is probably the result of transitions with an intramolecular transfer of charge from the ruthenium atom to the cyclopentadienyl rings. Therefore, one might consider the possibility of spectral perturbations on these CT transitions due to the nature of the solvent even though such phenomena are not observed in complexes with neutral ground states.<sup>9</sup> In any case, we have tried to extend the Kosower treatment<sup>9</sup> to cover the observed spectral changes. However, we did not find a good correlation between Kosower's  $Z$  parameter of the solvents used and the observed spectral variations.

Thus, it appears that solvent polarity is not the main factor determining the new spectral feature observed in going from ethanol to halogen-containing solvents. The preceding arguments contradict several possible explanations of the ruthenocene absorption spectrum in halogen-containing solvents. Thus, the formation of a CTTS complex remains a reasonable postulate, especially when we consider the fact that the  $\text{Ru}(\text{C}_5\text{H}_5)_2$  spectrum in halocarbon solvents (Figure 2) changes in a manner which can be correlated with the number of halogen substituents in the solvent molecule and with the mass of the halogen. The spectrum observed in methylene chloride is only slightly different from that in ethanol; in 1,2-dibromoethane and ethyl iodide it is very similar to that seen in chloroform. Finally, in benzotrichloride and in 1,2-dichloroethane it closely resembles that in carbon tetrachloride.

An examination of these results indicates that 1,2-dichloroethane is more effective than methylene chloride, and benzotrichloride is more effective than chloroform in determining the spectral variations. Thus, the halogen mass appears to be a secondary factor in causing the extent of the spectral changes as it would be if we were observing the intensification of the spectral band. In addition, a more interesting correlation was found with the half-wave potentials of the solvents used as reported by Brand and Snedden for  $\text{Fe}(\text{C}_5\text{H}_5)_2$ -halocarbon solvent system.<sup>4</sup> In fact, the half-wave potentials decrease is roughly parallel to the increasing influence on the  $\text{Ru}(\text{C}_5\text{H}_5)_2$  spectrum (Figure 3). Thus, it should be emphasized that the  $E_{1/2}$  value can be plausibly related to the capacity of a molecule to act as an acceptor in an electron transfer reaction.

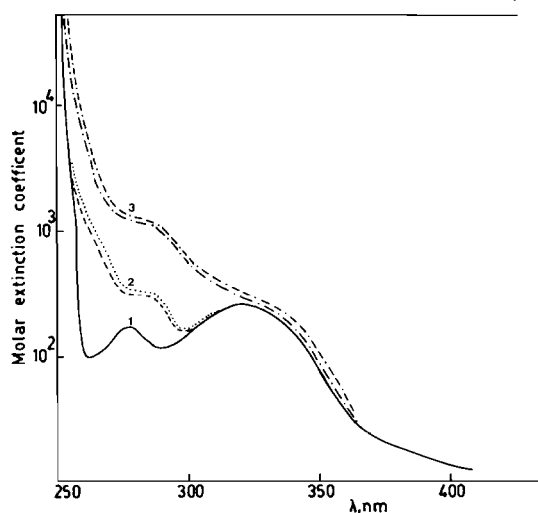


Figure 2. Spectrum of ruthenocene in ethanol and in acceptor solvents. Curve 1, ethanol or dichloromethane; 2(—) chloroform; 2(· · ·) 1,2-dibromoethane; 3(- · -) carbon tetrachloride; 3(---) 1,2-dichloroethane.

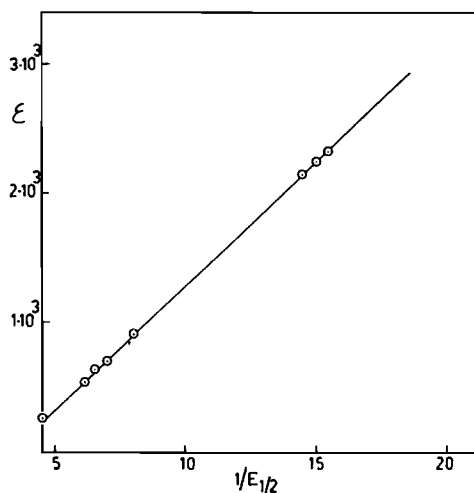
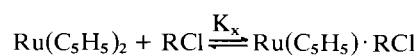


Figure 3. Change of ruthenocene molar extinction coefficient (285 nm) with  $E_{1/2}$  values of the acceptor solvents used (Ref. 4).

In summary, the preceding data establish a CT ruthenocene complex in halocarbon solvents. Trivial explanations are ruled out and the study of the spectral changes in several halogen-containing solvents suggests that in carbon tetrachloride the band at 285 nm is a new one of CTTS type. This CTTS absorption is not connected with the 278 nm ruthenocene band which is eclipsed in halocarbon solvents.

#### Complex Association Constant and Molar Extinction Coefficient

The ruthenocene spectra in several  $\text{CCl}_4$ -ethanol solvent mixtures is shown in Figure 1. The presence of the complex is evidenced by the increase in the charge transfer-to-solvent absorption with a maximum at 285 nm. The association constant for complex formation has been determined in these solutions by application of the Benesi-Hildebrand equation.<sup>10</sup> For a 1:1 complex:



the association constant  $K_x$  may be defined by the expression

TABLE I. Near-ultraviolet Spectrum of  $\text{Ru}(\text{C}_5\text{H}_5)_2$ .

$\lambda_{\text{max}}$ , nm <sup>a</sup>	Molar Absorptivity
200	>50000
215	4180
238	2000
278	145
325	200

<sup>a</sup> Ref. 7.

$$\frac{1}{\epsilon - \epsilon_{Ru}} = \frac{1}{\epsilon_C - \epsilon_{Ru}} + \frac{1}{\epsilon_C - \epsilon_{Ru} K} \cdot \frac{1}{[RCl]} \quad (1)$$

where  $[RCl]$  is the mol fraction concentration of the solvent acceptor,  $\epsilon$  is the molar extinction coefficient in the binary solvent based on total  $Ru(C_5H_5)_2$  concentration, and  $\epsilon_{Ru}$  and  $\epsilon_C$  are extinction coefficients of  $Ru(C_5H_5)_2$  and of the complex. In the case of  $CCl_4$  and 1,2-dichloroethane the experimental points, evaluated from the charge-transfer absorption intensity fall on linear straight lines. The values of  $K_x$  and  $\epsilon$  for the carbon tetrachloride and 1,2-dichloroethane complexes of ruthenocene are summarized in Table II.

According to the classical work of Mulliken and Orgel on the molecular complex formation, it must be noted that Eq. 1 may be obtained either assuming that the absorption band results from a charge transfer within a thermodynamically stable donor-acceptor complex or by considering that there is a "contact C-T" between  $Ru(C_5H_5)_2$  and the solvent. In the latter case, the apparent association constant  $K_x$  should have the meaning of a probability factor, the contact charge transfer spectrum being due to absorption of light when the  $Ru(C_5H_5)_2$  molecules come together with those of the solvent during a charge encounter.

#### Photochemical behavior of $Ru(C_5H_5)_2$

$Ru(C_5H_5)_2$  halocarbon solutions were stable in the dark for long periods. When these solutions were irradiated with 280 nm light, an increase in absorbance with a maximum at 320 nm could be observed after a short irradiation time. This spectral behaviour is indicative of the ruthenocenium cation formation (Figure 4). Quantitative experiments were carried out on solutions of ruthenocene in carbon tetrachloride and in 1,2-dichloroethane. For short irradiation time good zero order plots of ruthenocenium concentration vs irradiation time were observed. Under these conditions, chloride ions are also formed. The quantum yields of the  $Ru(C_5H_5)_2^+$  photoproduction were calculated from the slope of the initial zero order plots. For longer irradiation periods, the photolysis rate deviates markedly from zero-order behaviour. Continuous irradiation, in fact, results in the clouding of the irradiated solutions and the formation of a yellow solid. The yellow crystalline product from the  $Ru(C_5H_5)_2$  photoreaction gave analytical data in excellent agreement with the formula  $[Ru(C_5H_5)_2]RuCl_4$ .

TABLE II. Association Constants ( $K_x$ ) and Molar Extinction Coefficients ( $\epsilon_{max}$ ) for  $Ru(C_5H_5)_2$  CTTS Complexes.

Acceptor Solvents	$K_x, (\text{mol fr.})^{-1}$	$\lambda_{max}, \text{nm}$	$\epsilon_{max}$
$CCl_4$	0.32	285	2100
$CH_2ClCH_2Cl$	0.35	285	2350

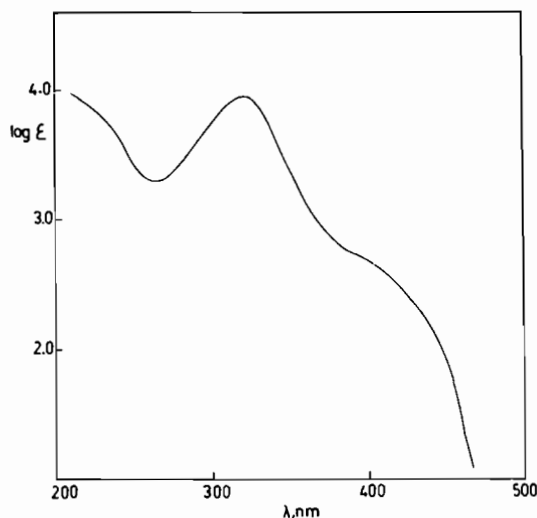


Figure 4. Absorption spectrum of ruthenocenium chloride in 0.1N HCl.

The infrared  $Ru(C_5H_5)_2$  and  $[Ru(C_5H_5)_2]RuCl_4$  spectra are compared in Table III.

The most striking spectral feature of  $Ru(C_5H_5)_2^+$  is the presence of two absorptions at 410 and 1010  $cm^{-1}$ , which are absent in the i.r. spectra of the  $Ru(C_5H_5)_2$  complex. It may be noted that these new infrared bands correspond to two Raman-active vibrations in ruthenocene (402 and 996  $cm^{-1}$ )<sup>8</sup> that have become i.r. active, presumably due to the lower molecular symmetry. In this regard, it is interesting to note that analogous i.r. features are observed in the change of ferrocene to the corresponding ferricenium chloroferrate.<sup>4,11</sup>

As known,<sup>8</sup>  $Ru(C_5H_5)_2^+$  was too unstable at room temperature in organic solvents to be isolated in a pure form. However, it was possible to treat a  $Ru(C_5H_5)_2^+$  1,2-dichloroethane solution following short irradiation periods, with dilute HCl (a treatment which stabilizes the ruthenocenium salt<sup>8</sup>). From follow-up work and extraction, it was possible to isolate aqueous  $Ru(C_5H_5)_2^+$  acid solutions. By refluxing these solutions with  $RuCl_2$ ,  $Ru(C_5H_5)_2$  was produced, which was identified by m.p., u.v. and i.r. spectrometry. Further aqueous  $Ru(C_5H_5)_2Cl$  acid solutions are observed to react with  $RuCl_3$ , to form  $[Ru(C_5H_5)_2]RuCl_4$ .

TABLE III. Infrared Spectra for  $Ru(C_5H_5)_2$  and  $[Ru(C_5H_5)_2]RuCl_4$  ( $cm^{-1}$ ).

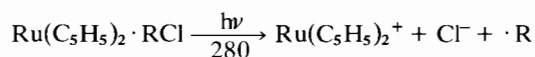
$Ru(C_5H_5)_2$	380 w, 445 s, 810 s, 860 m, 1000 s, 1050 w, 1100 s, 1400 s, 1600 w, 1800 w, 3090 m
$[Ru(C_5H_5)_2]RuCl_4$	410 m, 430 m, 850 s, 1010 s, 1050 m, 1410 s, 3100 s

Experiments were also performed in the presence of acrylamide monomer. It was found that the  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  photoproduction was accompanied with the acrylamide polymerization. No effects on the rate or course of photoreaction were apparent when the acrylamide was added to the  $\text{Ru}(\text{C}_5\text{H}_5)_2$  solution.

## Discussion

The systematic pattern of u.v. and i.r. changes following irradiation of ruthenocene in a series of halogen-containing solvents such as carbon tetrachloride, chloroform, 1,2-dichloroethane and benzotrithloride indicates that a single general type of photochemical process is operative.

The experimental results in the first photoreaction stages show that  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  is formed by zero order kinetics. Moreover,  $\text{Cl}^-$  appearance was observed in the irradiated solutions. On the basis of these results and using short irradiation periods, the primary reaction is virtually the following:



The nature of this primary photoreaction is also confirmed by the observed acrylamide polymerization due to  $\cdot\text{R}$  radical capture. However, other experimental results suggest that the photolysis rate deviates markedly from zero order kinetics when relatively long irradiation periods were used. Furthermore, as indicated in the Results section,  $[\text{Ru}(\text{C}_5\text{H}_5)_2] \text{RuCl}_4$  formation was observed, indicating that some secondary thermal process must have taken place. The role in these thermal reactions of the ruthenocenium, which is produced in the primary photoreaction, can be deduced from its known instability in organic solvents<sup>8</sup> and from the experiments performed on the  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  species with  $\text{RuCl}_2$  and  $\text{RuCl}_3$ .

### Excited State Responsible for Photoreaction

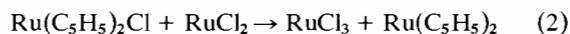
The observed experimental results establish a role for an excited charge transfer complex in the ruthenocene photolysis in halogen containing solvents. The chief characteristic of charge transfer light absorption is that it causes an electron principally localized on the donor to be transferred to the acceptor. Therefore, it is reasonable that irradiation within the narrow charge-transfer region of the  $\text{Ru}(\text{C}_5\text{H}_5)_2 \cdot \text{RCl}$  complex gives electron transfer reactions, leading to  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$ . On the other hand, since light absorption in the unperturbed  $\text{Ru}(\text{C}_5\text{H}_5)_2$  bands with maxima at 238 and 278 nm is completely inefficient, a photoelectron process followed by dissociative capture of the ejected electron by the solvent can be ruled out.

The value of the primary quantum yield ( $\Phi = 1$ ) indicates that the selective irradiation of the CT transi-

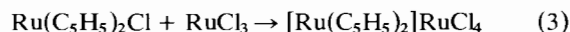
tion gives efficient  $\text{Ru}(\text{C}_5\text{H}_5)_2$  photooxidation. This means that the CTTS excited states collapse to the dissociation product by means of a diffusive pathway, the cage recombination being unimportant  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  formed in a solvent cage).

### Mechanism of the Production of $[\text{Ru}(\text{C}_5\text{H}_5)_2]\text{RuCl}_4$

The overall reaction scheme leading to  $[\text{Ru}(\text{C}_5\text{H}_5)_2]\text{RuCl}_4$  appears from the observed reaction of  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  with  $\text{RuCl}_2$  and  $\text{RuCl}_3$ . One possible sequence (Eq. 2, 3) involves an intermediate species such as that found in the reaction of  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  with  $\text{RuCl}_2$ :



Therefore, a further reaction of the intermediate  $\text{RuCl}_3$  with  $\text{Ru}(\text{C}_5\text{H}_5)_2^+$  can be according to Eq. 3:



which causes the precipitation of the stable  $[\text{Ru}(\text{C}_5\text{H}_5)_2]\text{RuCl}_4$  complex. This reaction scheme can be correlated to that proposed by Koerner von Gustorf for the photolytic  $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeCl}_4$  formation.<sup>12</sup> Even though our experimental results indicate that the reported overall reaction scheme is operative, the secondary photolysis of all the intermediates outlined in Eq. 2, 3 cannot be completely ruled out.

## Acknowledgements

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