Organometallic color chemistry: studies on [FcCH=CHC$_5$H$_4$NCH$_2$C$_6$H$_4$(^{t}Bu)]X (X = BPh$_4^-$, ClO$_4^-$)

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Abstract

The title dyes, [FcCH=CHC$_5$H$_4$NCH$_2$C$_6$H$_4$(^{t}Bu)]X (X = BPh$_4^-$, ClO$_4^-$), developed for rapid screening of catalysts, are intensely colored, but bleach on exposure to visible light in solution. Detailed study shows that on irradiation these alkene dyes first undergo a *trans–cis* isomerization, then give an irreversible bleaching via decomposition. Both dyes show color dependence on the nature of the anion as a result of ion-pairing, which affects the intensity and position of the visible absorption. NMR, MS and EPR data are also reported. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Organometallic dyes; *Trans–cis* isomerization; Ion-pair

1. Introduction

A dye molecule normally consists of an electron donor (*D*) connected by an unsaturated link to an electron acceptor (*A*), as in the diazo dyes of general type *D*–N=N–*A*. Many organometallic functional groups are good donors and many others are good acceptors, so in principle numerous organometallic dyes should be readily accessible. Organometallic functional groups were essentially unknown during the classic period of the development of color chemistry [1], and so it is not surprising that few, if any, of the standard commercially available organic dyes are organometallic species. Recent developments in non linear optical (NLO) materials have led to the very recent synthesis of a number of interesting organometallic dyes [2].

2. Results and discussion

2.1. Design of the dyes

We wanted to develop a color assay for homogeneous catalytic activity for use in rapid screening of catalysts [3]. Bleaching of a dye on reduction of the unsaturated link seemed appropriate, so we were led to consider dyes of the type *D*–CH=CH–*A* and *D*–N=CH–*A*, because catalytic reactions involving alkenes, and to a lesser extent, imines, are common. If the C=C group acting as the unsaturated link were reduced, the electronic connection between *D* and *A* would be severed and the color would be lost. It was also important to ensure that there were no functional groups present that could bind to the catalyst and inhibit catalytic activity. Almost all the organic *D* and *A* groups have such functionalities, such as Me$_2$N or MeO for donors and –NO$_2$ for acceptors. The organometallic donor ferrocenyl (Fc) (**1**) (Fig. 1) has no functionality that would be expected to interfere with the catalysts and so we have adopted this group as our donor. For the acceptor, we considered a quaternized pyridinium because there would again be no interfering functional group and this choice would allow the dye precursor pyridine derivatives to be covalently attached to

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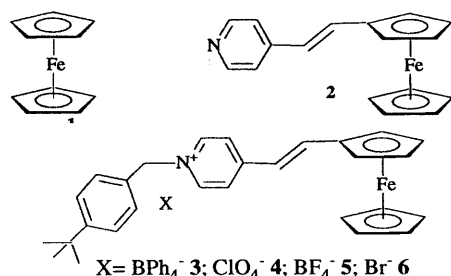[2] *Corresponding author. Tel.: +1-203-4323925; fax: +1-203-4326144; e-mail: robert.crabtree@yale.edu

Fig. 1.

chloromethyl groups of a solid support if required. The counter-ion would also have to be non-coordinating, such as BPh_4^-. This line of reasoning led us to synthesize the organometallic dye, [Fc–CH=CH–$C_5H_4NR]BPh_4$. Initial experiments [3] suggested that using 4-$CH_2C_6H_4$('Bu) as the R group gave good solubility for the resulting salt and so this became our first dye, **3** (Fig. 1). In this paper we describe some of its key properties. The major significant practical limitation proves to be instability of the dye to light, in solution. This study was carried out in the hope of suggesting improvements for future dyes.

2.2. Properties of the dyes

The new dyes **3** and **4** (Fig. 1) proved suitable for rapid screening for catalyst activity [3] but qualitative studies showed that in tetrahydrofuran solution they were not very stable to light, bleaching in tens of hours under conventional laboratory fluorescent illumination. Another problem was that the intensity of color seemed to depend on the nature of the solvent. In the work described below we show that *trans–cis* photoisomerization occurs readily, followed by decomposition. Experiments using dyes with different anions (Fig. 1) show that ion pairing also influences the color. In pursuit of

a better understanding of these molecules, we also study the NMR, MS and EPR data. Although there are a number of reports of stability studies for all-organic NLO dyes, as far as we know, this paper represents the first detailed study of the stabilities of organometallics dyes.

2.3. Synthesis

The structures of key compounds referred to in this study along with the labelling scheme are shown in Fig. 1. We previously showed [3] how the known Fc–CH=CH–C_5H_4N (**2**) [4] can be readily quaternized (dimethylformamide, 25–80°C) with the commercially available 4-$BrCH_2C_6H_5$('Bu), to give the new dye as the bromide salt **6**. This particular benzyl group was chosen to impart solubility. Anion exchange with AgX in acetone (X = BPh_4^-, ClO_4^-, BF_4^-) gives the other salts studied; we described the BPh_4 (**3**) salt previously [3] but the ClO_4^- and BF_4^- salts, **4** and **5**, respectively, are new.

2.4. Detailed studies of the dyes

2.4.1. Electronic spectroscopy

Unsubstituted ferrocene **1** is weakly colored and exhibits two strong low energy bands at 326 and 440 nm (Table 1) in the visible range of the electronic spectrum which have been assigned [4,5] to $^1A_{2g} \rightarrow {}^1E_{2g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ ligand-field (d–d) transitions.

The spectrum and visible color change dramatically upon substitution of the cyclopentadienyl ring with conjugated and/or acceptor groups. In such a case, a strong increase of color intensity is observed as a result of intramolecular charge transfer transitions between the donor (ferrocene) and the acceptor [3,4,6]. Previous studies on ferrocene derivatives containing a terminal 4-pyridyl (= 4-py) group linked to the ferrocene by a

Table 1
Selected visible spectral data for compounds ferrocene (**1**), Fc–CH=CH(4-py) (**2**), [Fc–CH=CH(4-pyBz)]BPh$_4$ (**3**), [Fc–CH=CH(4-pyBz)]ClO$_4$ (**4**), [Fc–CH=CH(4-pyBz)]BF$_4$ (**5**), [Fc–CH=CH(4-pyBz)]Br (**6**) recorded in THF and CH$_3$CN

| Compound	Solvent	Concentration (mM)	Color	λ_{max} (nm) (ε dm^3 mol^{-1} cm^{-1})	
1	THF	1	Light yellow	326 (420)	440 (100)
	CH$_3$CN	1	Light yellow	325 (415)	440 (90)
2	THF	0.073	Light yellow	374 (1640)	466 (1360)
	CH$_3$CN	0.073	Light yellow	373 (1640)	466 (1360)
3	THF	0.049	Purple	370 (22 450)	565 (6130)
	CH$_3$CN	0.037	Purple	366 (24 050)	558 (6760)
4	THF	0.035	Purple	365 (18 290)	554 (4860)
	CH$_3$CN	0.037	Purple	366 (17 570)	557 (6760)
5	THF [a]	0.037	Pink	361	549
	CH$_3$CN	0.037	Light purple	362 (24 050)	555 (6490)
6	THF [a]	0.0445	Light purple	361	511
	CH$_3$CN	0.0445	Purple	361 (23 860)	558 (5955)

[a] Poorly soluble in THF; some decomposition observed.
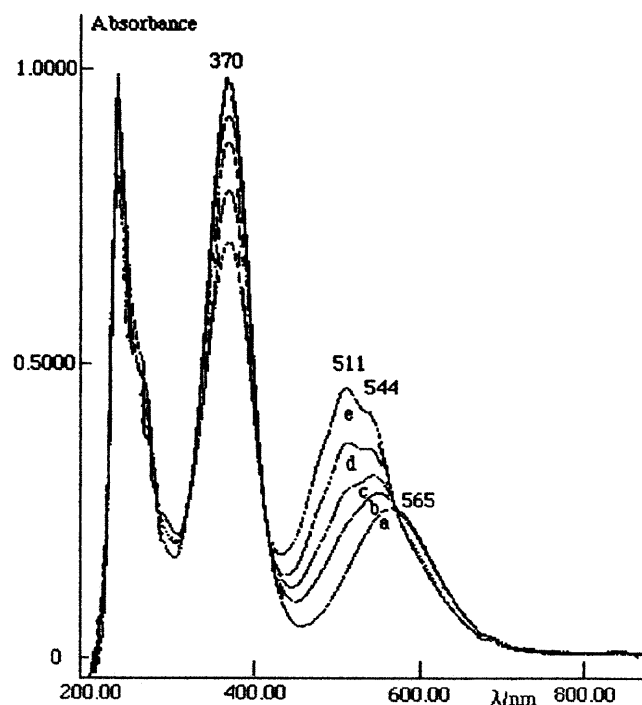
Fig. 2. UV–vis spectral changes during irradiation of a 3.7×10^{-5} M solution of compound **3** in tetrahydrofuran. (a) $t = 0$ s, (b) $t = 30$ min, (c) $t = 2$ h, (d) $t = 3$ h, (e) $t = 5$ h.

C=C and/or a phenyl group show that the two lowest-energy transitions of the visible region for these types of substituted ferrocenes are substantially red-shifted with respect to unsubstituted ferrocene with enhanced intensities ($1000 < \varepsilon < 4600$ l mol^{-1} cm^{-1} compared to $\varepsilon <$ 420 for ferrocene). Increased mixing of metal and ligand orbitals give the d–d transistion a significant ligand character and make them more 'allowed' [3,4,6]. Thus, for Fc–CH=CH(4-py) (**2**), these bands appear at 374 and 466 nm (Table 1).

If the acceptor is a pyridinium group (compounds [Fc–CH=CH(4-pyBz)]X (**3–6**), X = BPh$_4^-$, ClO$_4^-$, BF$_4^-$ and Br$^-$, 4-pyBz = 4-(N-{4-*t*-butylbenzyl}pyridinium), we find that these effects are even more enhanced (Table 1). Thus, for example, for complex [Fc–CH=CH(4-pyBz)]BPh$_4$ (**3**), the visible spectrum shows the two lowest-energy transitions at 370 and 565 nm ($\varepsilon = 22450$ and 6130 l mol^{-1} cm^{-1}, respectively). The strong enhancement of color intensity and the red shift seen in the pyridinium salts compared to the parent pyridyl compound are ascribed to the stronger acceptor character of the cationic pyridinium ring. In moving from neutral compounds **1** and **2** to the ionic compounds **3–6** the low energy band is more strongly red-shifted than the high energy one. While the situation is very different, moving from **1** to **2**, both neutral compounds, the high energy band is red-shifted to a greater extent [6]. The slight shifts of the two lowest energy bands (< 10 nm) observed on changing the

anion was the first indication that the formation of ion pairs between the pyridinium cation and the anions could affect the color both in tetrahydrofuran and acetonitrile solvents.

As a test of this ion pairing idea, we added an excess of ClO$_4^-$ (as Bu$_4$N$^+$ salt) to tetrahydrofuran or acetonitrile solutions containing the BPh$_4^-$, BF$_4^-$ or Br$^-$ pyridinium compound. In all cases the resulting solutions exhibited the same UV–vis spectra as that of a solution of [Fc–CH=CH(4-pyBz)]ClO$_4$. This indicates that the initial ions pairs formed with BPh$_4^-$, BF$_4^-$ and Br$^-$ are displaced in favour of ClO$_4^-$ when an excess of this ion is present in either solvent. This proposal is consistent with literature data: the formation of ion pairs between 1,1′-dimethyl-4,4′-bipyridinium (methyl viologen or paraquat) PQ^{2+} with anions like BPh$_4^-$, Br$^-$, Cl$^-$, I$^-$, Ph$_2$C(OH)COO$^-$ has been demonstrated from the observation of charge transfer bands in the UV–vis spectrum [7–11].

2.4.2. Photolysis of compounds 3 and 4

Compounds **3** and **4** are stable in tetrahydrofuran solution in the dark even over several months. Irradiation of **3** (X = BPh$_4^-$) (3.7×10^{-5} M) in tetrahydrofuran under argon (high pressure Hg lamp, 200 W) produces a slow change of color. The solution turns from deep purple to lighter purple after 30 min, then red after 2 h, and finally light brown after 24 h of continuous illumination.

The UV–vis absorption spectra shown in Fig. 2 indicate that in the time between 30 min and 2 h of illumination, the initial absorption at 565 nm slowly shifted to the blue (544 nm) and the band at 370 nm progressively decreased in intensity. A new band at 511 nm appeared after 2 h. The new absorption peak at 511 nm as well as that at 544 nm then increaseed in intensity with time while that at 370 nm decreased. After 5 h of illumination no further changes in the UV–vis spectrum were observed. Prolonged irradiation (24 h) gave only decomposition of the sample (see Sections 2.4.4 and 2.4.6).

The same behaviour has been observed in the case of irradiation of compound **4**, where the anion is ClO$_4^-$ (Fig. 3). Thus, after 2 h of irradiation, the initial absorption at 554 nm shifted to the blue (535 nm), a new band at 514 nm appeared and the signal at 365 nm decreased in intensity. In this case, too, prolonged irradiation (48 h) gave decomposition.

Spectral changes of the type observed in the first 5 h are analogous to those previously reported for *trans–cis* isomerization of styrylpyridines and stilbenes [12] suggesting that *trans–cis* isomerization may be responsible for the initial photochemical changes for our dyes. The slight anion-dependent shifts in the absorption maxima found for compounds **3** versus **4** after 5 h of irradiation could indicate that the ion-pairs are still present in the *cis*-isomer.
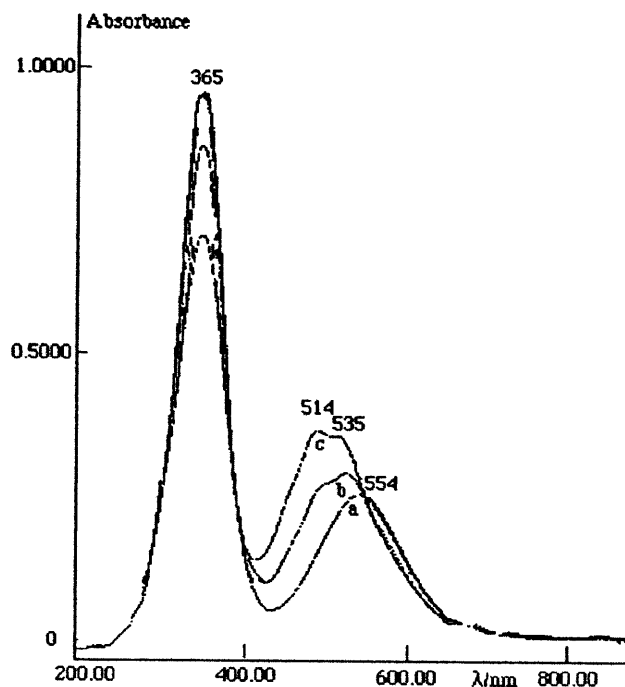
Fig. 3. UV–vis spectral changes during irradiation of a 3.7×10^{-5} M solution of compound **4** in tetrahydrofuran. (a) $t = 0$ s, (b) $t = 2$ h, (c) $t = 5$ h.

The use of optical filters shows that irradiation at 370 nm is chiefly responsible for the photochemical changes observed.

In order to confirm the proposal of *trans–cis* isomerization, GCMS and NMR studies for compounds **3** and **4** and photolysis of compound **2** have also been carried out.

2.4.3. GCMS studies

A series of GCMS spectra obtained for **3** and **4** (3.7×10^{-5}M) during the course of the irradiation in tetrahydrofuran did not show any mass change, consistent with *trans–cis* isomerization. Thus, the mass spectra for **3** and **4** show the highest mass ions at m/z values of 218 corresponding to loss of BPh_4^- and ClO_4^- from the half molecule, respectively. Different GCMS spectra are obtained when the sample was irradiated for 24 h

for **3** and 48 h for **4**. The peaks located at m/z 218 disappear and the mass spectra show new peaks at lower m/z values that could be attributed to the degradation of the compounds (see Sections 2.4.4 and 2.4.6).

2.4.4. NMR spectroscopy

The ^{1}H-NMR spectra (Table 2) of compounds **3** and **4** were assigned using COSY and irradiation experiments. The protons of the substituted cyclopentadienyl groups resonate as two triplets at δ 4.52 and 4.61 ppm for compound **3** and at δ 4.53 and 4.74 ppm for **4**. The five protons of the unsubstituted Cp ring appear as a broad singlet at δ 4.18 and 4.19 ppm for compounds **3** and **4**, respectively. The two methylenic protons of CH_2 group appear as a singlet at δ 4.81 ppm for **3** while this signal appears at much lower field in compound **4**: δ 5.69 ppm. The shift in the CH_2 signal depends on the anion involved and may be associated with the formation of ion pairs with contact between the pyridinium groups and the anions.

The ^{1}H-NMR spectra of the starting materials show the olefinic protons of the double bond as two doublets (Table 2) with a ^3J(H–H) coupling constant around 15.6 Hz, consistent with a *trans* geometry for both compounds **3** and **4** [3,4]. In the case of compound **3** the protons of the 4-pyBz and BPh_4^- groups are very close together (between δ 6.80 and 7.60 ppm) and are not sufficiently resolved to be assigned reliably.

2.4.5. NMR behaviour: photolysis of compounds 3 and 4

During the irradiation process the ^{1}H-NMR shows clear changes in the cyclopentadienyl and olefinic region as expected for the formation of the *cis*-isomer. This is in good agreement with the different environment expected for these groups in the *cis*-isomer. Examination of models suggests that steric hindrance should cause a strong deviation from planarity of the 4-pyridyl or ferrocenyl groups in order to avoid strong repulsive interactions in the *cis*-isomer [13].

Thus, in the case of complex **4**, (Fig. 4) a new singlet signal appears at δ 4.18 ppm that increases in intensity with time; this is attributed to the protons of the

Table 2
NMR spectroscopic data for complexes **3** and **4** [a]

Compound	–Cp$_{Substituted}$	–Cp$_{Unsubstituted}$	–CH=CH–	CH_2	Py	–Ph	CH_3
3	4.52 (t)	4.18 (bs)	6.72 (d)	4.81 (s)	6.80–7.60 (m)	6.80–7.60 (m)	1.30(s)
	4.61 (t)		7.51 (d)				
	$J_{H-H} = 1.8$		$J_{H-H} = 15.7$				
4	4.53 (t)	4.19 (bs)	6.90 (d)	5.69 (s)	8.11 (d)	7.51 (m)	1.30 (s)
	4.74 (t)		7.90 (d)		8.87 (d)		
	$J_{H-H} = 1.5$		$J_{H-H} = 15.6$		$J_{H-H} = 6.7$		

[a] In THF-d_8. Chemical shifts in ppm, coupling constants in Hz; room temperature. Abbreviations: s, singlet; bs, broad singlet; m, multiplet; d, doublet; t, triplet.
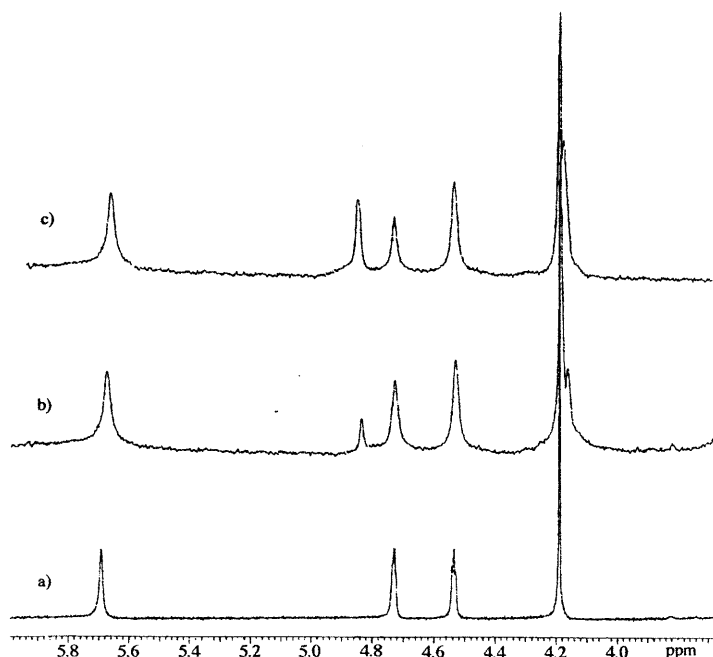
Fig. 4. ^{1}H-NMR spectral changes in the Cp region during irradiation of compound **4** in THF-d_8 solution. (a) $t = 0$ s, (b) $t = 2$ h, (c) $t = 3$ h.
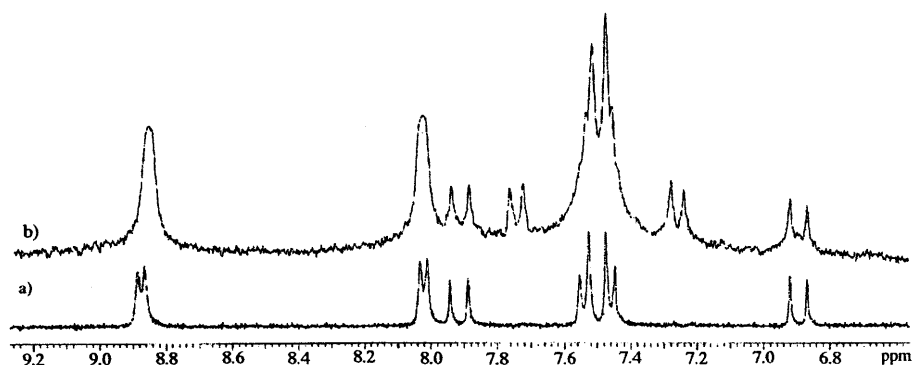

Fig. 5. ^{1}H-NMR spectral changes in the aromatic region during irradiation of compound **4** in THF-d_8 solution. (a) $t = 0$ s, (b) $t = 3$ h.

unsubstituted Cp for the *cis*-isomer. A new signal appears at δ 4.83 ppm in the substituted Cp region, that also increases in intensity in the same way with time, while the signal at δ 4.53 ppm remains constant, due to an overlap of one of the signals from the substituted Cp of the remaining *trans*-isomer.

In the olefinic region two new doublets at δ 7.28 and δ 7.72 ppm appear which correspond to the CH=CH protons of the *cis*-isomer. In a key result, the ^3J(H–H) value of 11.8 Hz (Fig. 5) [13] is consistent with a *cis* geometry.

A similar splitting has been observed in the Cp region on irradiation of compound **3**. Thus, the new signals at δ 4.70 and 4.12 ppm are attributed to substituted and unsubstituted Cp protons, respectively. For the *cis*-complex the new signals from the olefinic protons overlap with the signals from the pyridium and BPh$_4^-$ groups.

Under prolonged irradiation for 24 (**3**) or 48 h (**4**), a brown solution is formed as a result of decomposition and the NMR signals are broadened due to the presence of paramagnetic Fe^{3+} (see Section 2.4.6).[3]

2.4.6. EPR properties

The EPR spectra obtained for the initial tetrahydrofuran solution of **3** (3.7×10^{-5} M), after 4 h of irradiation (red solution) and after 24 h of irradiation are shown in Fig. 6 (a) (b) and (c), respectively. The EPR spectrum of the initial solution (Fig. 6 (a)) shows very small signals at $g = 4.27$ and 1.98 attributed to a highly

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[3] The irradiation process has been carried out under argon and at 0°C in order to avoid the formation of paramagnetic Fe^{3+} during the maximum time. All attempts to obtain the NMR of the pure *cis*-product have been unsuccessful. Prolonged irradiation for more than 3 h gave an NMR with broad signals due to the formation of paramagnetic Fe^{3+} (see Section 2.4.6).

rhombic high-spin Fe^{3+} ion and an organic radical species, respectively, that we initially ascribed to impurities or slight decomposition during sample handling [14]. There is a slight increase in these peaks after photolysis of the initial compound at 366 nm upon irradiation for 4 h (Fig. 6 (b)). Irradiation of the sample for 24 h yields a brown solution that shows much enhanced Fe^{3+} and radical EPR signals (Fig. 6 (c)). The yield of free Fe^{3+} generated upon photolysis is about 15%, determined using a $Fe(NO_3)_3$ standard. After 48 h of illumination, the yield of Fe^{3+} is as high as 50%. The presence of a radical species may possibly be attributed to the photolytic electron transfer within the ion pair [7], but the absence of charge transfer band in the ion pair between the anions and pyridium group suggests another possible origin for these radicals. A second, more plausible possibility is that the prolonged irradiation could induce the transfer of one electron from the donor to the acceptor group, generating Fe^{3+}
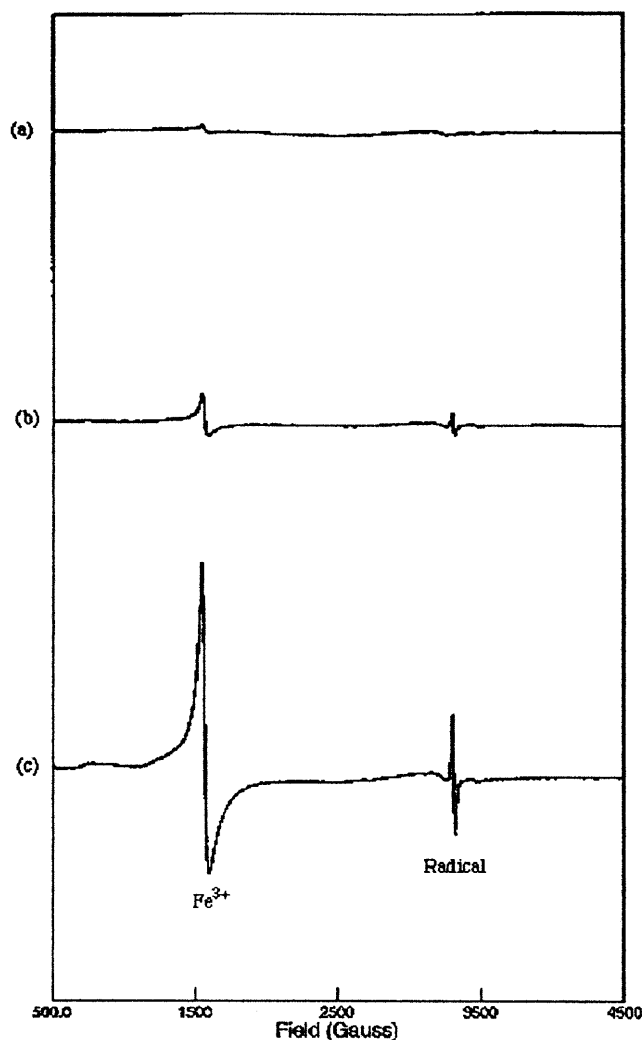

Fig. 6. EPR spectral changes during irradiation of a solution of compound **3** in tetrahydrofuran. (a) $t = 0$ s, (b) $t = 4$ h, (c) $t = 24$ h.

and an organic radical species. It is well known that the ferricinium [15] forms of this type of compounds are not stable and tend to decompose rapidly, a similar pathway could operate in the photochemical work.

2.4.7. Isomerization of Fc–CH=CH(4-py) (2)

In order to confirm that compound **3** and **4** can undergo to *trans–cis* isomerization process by photolysis, the related neutral compound **2** was also studied. Photolysis at 366 nm of **2** (3.7×10^{-5} M) in tetrahydrofuran induces a slow change of the UV–vis absorption spectrum with a shift of the absorption to the blue. Thus, the absorption maxima at 466 and 374 nm are shifted to 460 and 335 nm, respectively. These spectral changes are in good agreement with literature data for *trans–cis* isomerization of 4-stilbazone [16] and with related non-ionic substituted ferrocenes compounds as *trans–cis*-[1-ferrocenyl-2-(4-nitrophenyl)ethylene] [6]. Slow decomposition did occur on long photolysis, but only over ca. 3 weeks.

Work is in progress to synthesize new dyes that avoid these problems. For example, the incorporation of the double bond into a ring should lock the conformation and prevent *cis–trans* isomerization process. This strategy has previously been used with success for organic NLO dyes [17].

2.4.8. Conclusion

Compounds **3** and **4**, developed for rapid screening of catalysts, are intensely colored but bleach in solution on exposure to visible light. Detailed study shows that the dyes first undergo a *trans–cis* isomerization, then give an irreversible bleaching process via decomposition. The dyes show a color dependence as a result of ion-pairing [18], which affects the intensity and position of the visible absorption. NMR, MS and EPR data are also reported.

3. Experimental

3.1. General methods

All operations were performed under an atmosphere of nitrogen or argon. Solvents were dried and distilled prior to use. ^{1}H-NMR spectra were recorded on a Variant Gemini 400 MHz spectrometer. The GCMS experiments were recorded on a Hewlett-Packard 5890II gas chromatograph equipped with a Hewlett-Packard 5971 mass spectrometer. Absorption spectra were recorded on a Shimadsu UV-1203 spectrophotometer. [Fc–CH=CH(4-pyBz)]BPh$_4$, [Fc–CH=CH(4-pyBz)]Br, [Fc–CH=CH(4-pyBz)]Cl and Fc–CH=CH-(4-pyBz) were prepared by previously reported methods [3,4].

3.2. Synthesis of [Fc–CH=CH(4-pyBz)]ClO$_4$ (4)

To an acetone solution (25 ml) of [Fc–CH=CH(4-pyBz)]Br (1 g, 1.9 mmol), AgClO$_4$ (414 mg, 2 mmol) was added. After 20 min, the AgBr precipitate was filtered off. The addition of ether (50 ml) to the filtrate afforded microcrystals of complex **4**, which were filtered off, washed with cold ether (3 × 10 ml) and vacuum dried. (0.81 g, 80%). Anal. Found: C, 62.79; H, 5.70; N, 2.63. Calc. for C$_{28}$H$_{30}$ClFeNO$_4$: C, 62.76; H, 5.64; N, 2.61%.

3.3. Synthesis of [Fc–CH=CH(4-pyBz)]BF$_4$ (5)

Treatment of [Fc–CH=CH(4-pyBz)]Br (1 g, 1.9 mmol) with AgBF$_4$ (389 mg, 2 mmol) as described for **4** afforded complex **5**. (0.92 g, 90%) Anal. Found: C, 63.95; H, 5.73; N, 2.79. Calc. for C$_{28}$H$_{30}$BF$_4$FeN: C, 64.28; H, 5.78; N, 2.68%.

3.4. Photolysis

Photolysis was carried out with an Oriel Corporation high pressure mercury lamp, (200W). The photolysis cell was an optical cuvette of 1 cm pathlength. The solution and cell was purged with argon. Irradiation was run in tetrahydrofuran. Photoisomerization was investigated for compounds **2**, **3** and **4** at a temperature (< 30°C) sufficiently low to stop thermal *trans* to *cis* isomerization.

3.5. EPR

EPR data were measured on a Varian E-9 spectrometer with a TE102 cavity and helium flow transfer (Oxford Instruments), with the following experimental parameters: microwave frequency = 9.28 GHz; modulation frequency = 100 kHz.; modulation amplitude = 20 G; microwave power = 2 mW; temperature = 10 K.

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