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Journal of Organometallic Chemistry 527 (1997) 51–64

Journal of Organometallic Chemistry

# Synthesis, structure and hydrolysis of some [($\eta^5$-cyclopentadienyl)($\eta^6$-arene)iron(II)][$PF_6$] complexes bearing an imine or a nitrone function in $\alpha$-position of the arene ligand

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Received 17 April 1996; revised 28 June 1996

**Abstract**

Condensation between [($\eta^5$-Cp)($\eta^6$-fluorene)Fe]$^+$] **I** and various nitrosoarenes R–Ph–NO (R = H, 2-Me, 3-Me, 4-Me, 3-COMe, 4-COMe and 4-$NMe_2$) were initiated with 5% t-BuOK and led to [($\eta^5$-Cp)($\eta^6$-fluorenone-anil)Fe]$^+$ complexes **Ia–g** (57–88%) as syn–anti mixtures (ca. 30:70 respectively). [($\eta^5$-Cp)($\eta^6$-diphenylmethane)Fe]$^+$ **II** with nitrosobenzene or nitrosotoluenes gave mixtures of [($\eta^5$-Cp)($\eta^6$-benzophenone-*N*-phenylnitrone)Fe]$^+$ **IIa–d** and [($\eta^5$-Cp)($\eta^6$-benzophenone-anil)Fe]$^+$ **IIa–d** complexes (ca. 80:20) with good yields (80–92%). Nitrone complexes **IIa,c,d** were isolated as pure *Z*-isomer by fractional recrystallisation (22–35%). 2D-$^1$H, $^{13}$C NMR correlation and X-ray analysis were used to identify the new compounds. Owing to the high nitrosobenzene oxidative character, condensation with other [($\eta^5$-Cp)($\eta^6$-arene)Fe]$^+$ complexes (arene = toluene, ethylbenzene, indane and tetraline) failed. Acidic hydrolysis of these imine and nitrone complexes has been investigated kinetically using polarography. Macroscale hydrolysis yielded [($\eta^5$-Cp)($\eta^6$-fluorenone)Fe]$^+$ **Ii** (82%) and [($\eta^5$-Cp)($\eta^6$-benzophenone)Fe]$^+$ **IIi** (91%).

*Keywords:* Iron; Cyclopentadienyl; Arene; Imine; Nitrone; Ehrlich–Sachs reaction

## 1. Introduction

One of the most important characteristics of [($\eta^5$-Cp)($\eta^6$-arene)Fe]$^+$ complexes is the considerable increase of reactivity of the arene ligand due to the strong electron-withdrawing effect of the $CpFe^+$ moiety [1].

In particular, the high thermodynamic and kinetic acidities of benzylic protons borne by the arene ligand [2] allow access to species which possess a high reactivity toward electrophilic attack [3].

This has been developed for many electrophiles for synthesis purposes as a way of functionalising activated arenes [4–6] and was recently found to have very interesting applications in the synthesis of organometallic molecular trees [7].

As a part of the study of the reactivity of (Cp Fe arene)$^+$ cations we present a report of the condensation reaction between nitrosoarenes and an activated methylene group bound to the arene ligand. This base-catalysed condensation (Ehrlich–Sachs reaction [8,9]) could lead to an imine or a nitrone function in the $\alpha$-position of the arene ligand (Scheme 1).

Hydrolysis of the imines and nitrones into the corresponding [($\eta^5$-Cp)($\eta^6$-$\alpha$-arylketone)Fe]$^+$ complexes was also considered (Scheme 2).

## 2. Results and discussion

### 2.1. Synthesis and structure of imine and nitrone complexes

Only condensation between (Cp Fe fluorene)$^+$ **I** or (Cp Fe diphenylmethane)$^+$ **II** and nitrosoarenes were successful.

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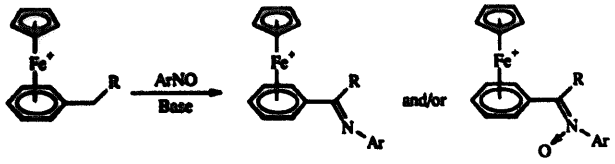
*PII* S0022-328X(96)06632-6




Scheme 1.

### 2.1.1. Condensation with (CpFefluorene)$^+$ I

A small amount of t-BuOK (5% molar) induced a rapid condensation between (CpFe fluorene)$^+$ I and various nitrosoarenes in THF at room temperature, and gave the imine complexes **Ia–g** (Scheme 3) with good yields.

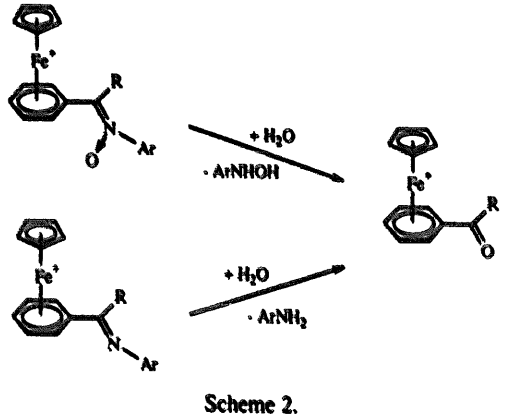
Except for **Ig** which took 3 h to react, a polarographic following of the reactions showed complete disappearance of nitroso derivatives ($E_{1/2} \approx +0.3$ V vs. SCE in 1 N $H_2SO_4$–acetone (1:1)) within 5 min of adding the base.

Nitrosoarenes and fluorene complex I were used in stoichiometric quantities, except for nitrosoacetophenones which needed a 40% excess for completion of the reaction.

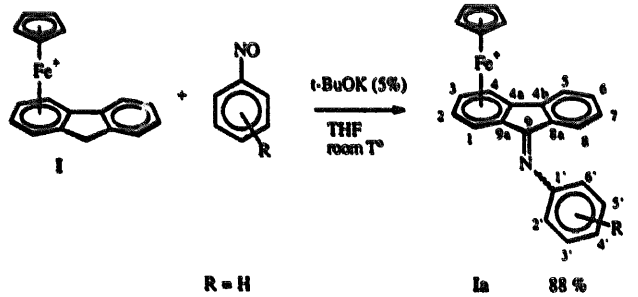
After work-up, satisfactorily pure imines **Ia–g** were isolated and identified by IR spectroscopy (azomethine band at ca. 1650 $cm^{-1}$) and elemental analysis. Polarography in aqueous acidic medium (0.1 N $H_2SO_4$–acetone (1:1)) showed the reduction wave of the imine function at ca. $E_{1/2} = -0.25$ V vs. SCE. This technique allowed detection and measurement of small amounts of nitrone complexes as by-products for **If** (less than 5%, $E_{1/2} = +0.03$ V vs. SCE) and **Ig** (ca. 10%, $E_{1/2} = -0.12$ V vs. SCE). For the latter, this is easily eliminated by recrystallisation.

High resolution $^1H$, $^{13}C$ and 2D ($^1H$, $^{13}C$ correlation) NMR spectroscopy were used to identify the nature of the imines **Ia–g**. $^{13}C$ and $^1H$ NMR data are in agreement with the existence of two isomers (syn and anti, 30:70). Broad band decoupling $^{13}C$ NMR spectrum of **Ic** is shown in Fig. 1. Considering their large upfield shift and their relative intensities, the signals of aromatic complexed carbons of each isomer were attributed. Distinction between the signals of the two non-complexed aromatic rings in each molecule resulted from the chemical shifts and multiplicities of the $^1H$ coupling $^{13}C$ spectrum. Total assignments of proton and carbon signals of both isomers of **Ic** have been made by using $^1H$, $^{13}C$ correlation and gated decoupling experiments.

$^1H$ NMR chemical shifts allowed us to assume that the syn isomer is the minor product. As previously described in literature for other azomethine compounds [10], Fig. 2 illustrates the anisotropic shielding effect of the phenylimino group on fluorene protons. Comparison between chemical shifts of the complexed ring protons of both isomers (protons 1–4) reveals an important effect on the nearest proton $H_1$ of the syn isomer which undergoes an upfield shift of 1.53 ppm. This effect gradually decreases when the distance between fluorene protons and the phenylimino group is increased ($H_2$: −0.37 ppm, $H_3$: −0.08 ppm, $H_4 \approx 0$ ppm). In the downfield area of the spectrum, the same phenomena are observed in non-complexed fluorene ring (protons 5–8). The most shielded protons being $H_8$ (−1.18 ppm) and $H_7$ (−0.37 ppm) of the anti isomer. The crystal structure of the anti isomer of complex **Ia** (Fig. 3 and Table 1) confirmed the tendency of the phenylimino group to be more-or-less perpendicular with respect to the fluorene plane (torsional angles $C_6$–N–$C_{19}$–$C_{24}$ = 79.3° and $C_6$–N–$C_{19}$–$C_{20}$ = −107.4°; bond angle $C_6$–N–$C_{19}$ = 122.5°). In solution this geometry induces a high diamagnetic anisotropic shielding effect on fluorene protons in front of it.




Scheme 2.




| | | |
|---|---|---|
| R = H | Ia | 88 % |
| 2-Me | Ib | 71 % |
| 3-Me | Ic | 82 % |
| 4-Me | Id | 80 % |
| 3-COMe | Ie | 60 % |
| 4-COMe | If | 87 % |
| 4-$NMe_2$ | Ig | 57 % |

Scheme 3.

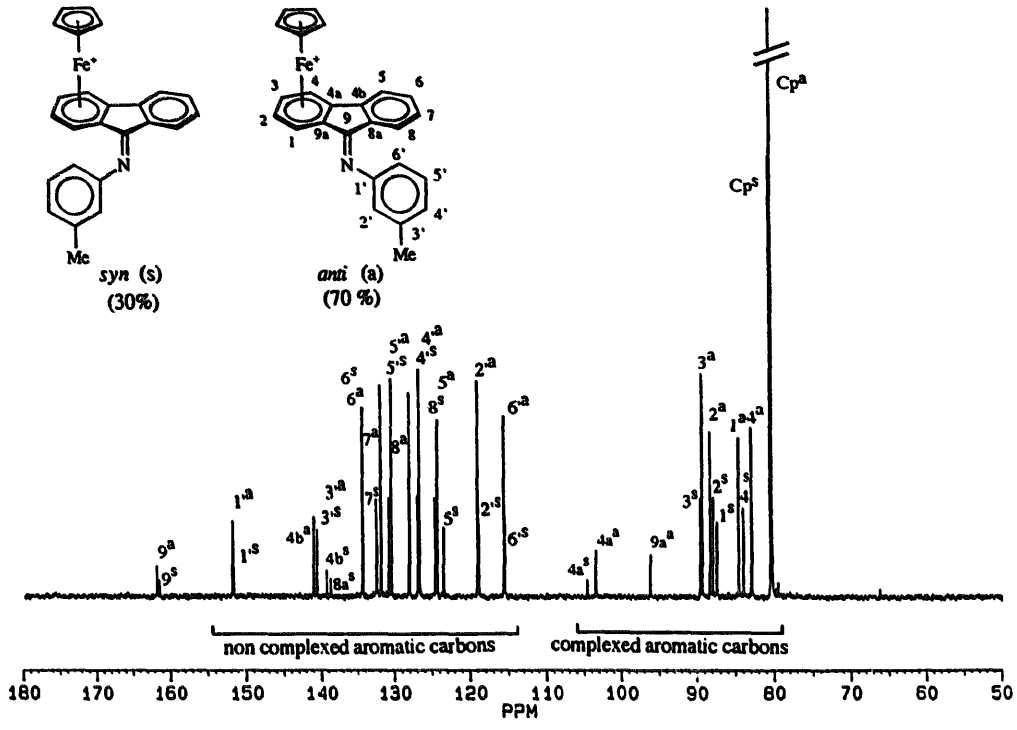



Fig. 1. Aromatic region of the broad band decoupling $^{13}C$ NMR spectrum of **Ic** ($C^a_{8a}$ (132.30 ppm) and $C^s_{9a}$ (88.25 ppm) are not indicated on the figure due to lack of space).

$^1H$, $^{13}C$ correlation data of **Ic** are listed in Section 4. $^1H$ and $^{13}C$ NMR assignments of the other complexes **Ia–b, Id–g** were made by reference to **Ic**, using $^1H$ coupling $^{13}C$ spectrum, gated decoupling experiments, and by considering different coupling constants. Typically, aromatic $^1J_{C-H}$ and $^3J_{H-H}$ were ranged between 179–184 Hz and 6.0–6.5 Hz respectively for the complexed rings, and between 158–166 Hz and 7.5–7.9 Hz respectively for the non-complexed rings.

The isomer ratio of **Ib** (20:80), which is appreciably different, probably results from a steric effect during the condensation due to the methyl group in the ortho position to the nitroso function.

### 2.1.2. Condensation with (Cp Fe diphenylmethane)$^+$ II

One equivalent of (Cp Fe diphenylmethane)$^+$ **II** and three equivalents of nitrosobenzene or nitrosotoluenes reacted rapidly in THF at room temperature, in the

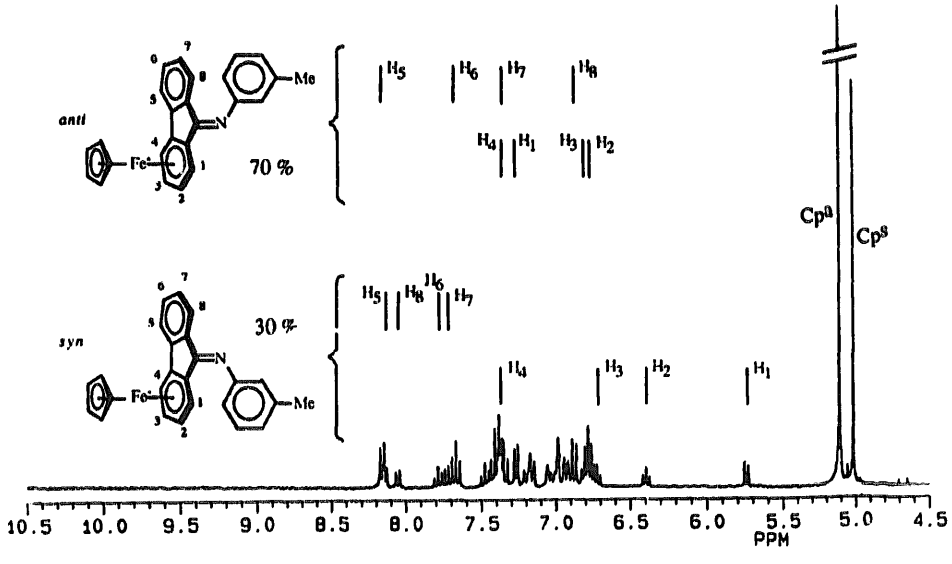



Fig. 2. Aromatic region of the $^1H$ NMR spectrum of **Ic**.

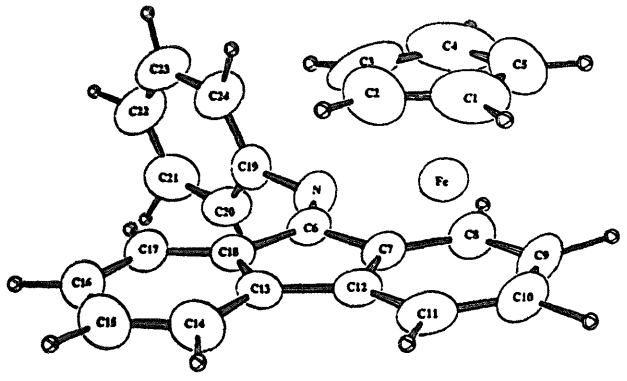


Fig. 3. X-ray structure of the anti isomer of **Ia**.

Table 1
Selected bond distances in the anti isomer of **Ia**

| Atom 1 | Atom 2 | Distance (Å) |
|---|---|---|
| N | C6 | 1.285(9) |
| N | C19 | 1.424(9) |
| Fe | C1 | 2.03(2) |
| Fe | C2 | 2.03(4) |
| Fe | C3 | 2.03(1) |
| Fe | C4 | 2.04(3) |
| Fe | C5 | 2.03(3) |
| Fe | C7 | 2.08(8) |
| Fe | C8 | 2.08(6) |
| Fe | C9 | 2.10(4) |
| Fe | C10 | 2.09(6) |
| Fe | C11 | 2.09(1) |
| Fe | C12 | 2.08(8) |

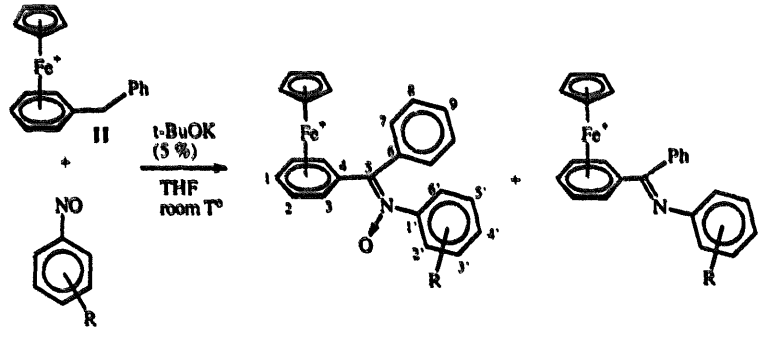
presence of 0.05 equivalents of t-BuOK and gave mixtures of nitrones **IIa–d** as the major products and imines **II'a–d** (Scheme 4).

Attempts to condense nitrosoacetophenones under the same conditions were unsuccessful and caused the complete reduction of the nitroso function. When using *p*-nitrosodimethylaniline, 70% of the starting complex was recovered at the end of the manipulation.

The reaction was monitored by polarography and showed a rapid decrease of the nitrosoarene in less than 5 min and the appearance of azoxybenzene identified by its reduction wave (−0.25 V vs. SCE in 1 N $H_2SO_4$–acetone (1:1)) and by cyclic voltammetry (Fig. 4). After irreversible electrode reduction of azoxybenzene into hydrazobenzene, the reversible azo–hydrazobenzene system appeared (confirmed with an authentic sample of azobenzene).

Mixtures have been isolated by filtration from the THF solution either directly, when precipitation occurred, or after concentration and precipitation with ether. They were characterised by $^1H$ NMR spectroscopy and polarography [11].

As shown in Fig. 5, polarographic monitoring of the reaction in an acidic aqueous medium (0.1 N $H_2SO_4$–acetone (1:1)), the isolated mixture **IIb** + **II'b** (70:30) at first showed two reduction waves (1 and 2) respectively assigned to nitrone **IIb** ($E_{1/2}$ = −0.31 V vs. SCE) and to imine **II'b** ($E_{1/2}$ = −0.41 V vs. SCE). In these pH conditions, only imine **II'b** is hydrolysed into the (CpFe benzophenone)$^+$ complex **III**. After complete hydrolysis of **II'b** three waves appear, the first corresponding to the 2 F mol$^{-1}$ reduction of the nitrone into the imine, the second to the 2 F mol$^{-1}$ reduction of electrode-formed imine into amine, and the third (3) to the 2 F mol$^{-1}$ reduction of ketone **III** ($E_{1/2}$ = −0.6 V vs. SCE) into the alcohol.




| | | | | |
|---|---|---|---|---|
| R = H | **IIa** | + | **II'a** (90:10) | 92 % |
| 2-Me | **IIb** | + | **II'b** (70:30) | 80 % |
| 3-Me | **IIc** | + | **II'c** (80:20) | 91 % |
| 4-Me | **IId** | + | **II'd** (85:15) | 92 % |

Scheme 4.

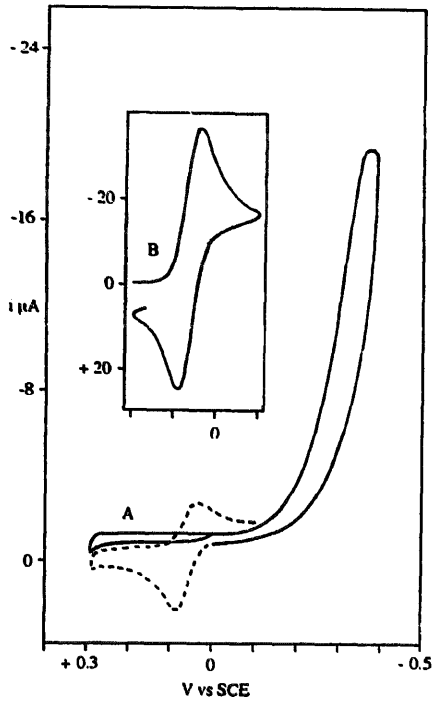



Fig. 4. (A) Cyclic voltammogram of a sample from the reaction between (CpFe diphenylmethane)$^+$ **II** and PhNO (200 μl of reaction mixture diluted in 20 ml of 1 N $H_2SO_4$–acetone (1:1)), Hg drop, scan rate 200 mV $s^{-1}$; (————) first scan (+0.3 to −0.4 V), (— — —) second scan (+0.3 to −0.1 V). (B) Cyclic voltammogram of azobenzene in the same medium.

Considering the ratio of the first and third waves, we could evaluate the percentages of imine **II'b** and nitrone **IIb** in the initial mixture. We verified, on pure samples of nitrone complexes, that they have similar diffusion coefficients compared with the (Cp Fe benzophenone)$^+$ complex **III**.

Nitrone **IIb** can be hydrolysed in a stronger acidic medium (2 N $H_2SO_4$–acetone (1:1)). In these conditions a new reduction wave appeared ($E_{1/2} = -1.04$ V vs. SCE) corresponding to the *o*-methylphenylhydroxylamine resulting from hydrolysis of the nitrone **IIb** (see Scheme 2 and Section 2.2).

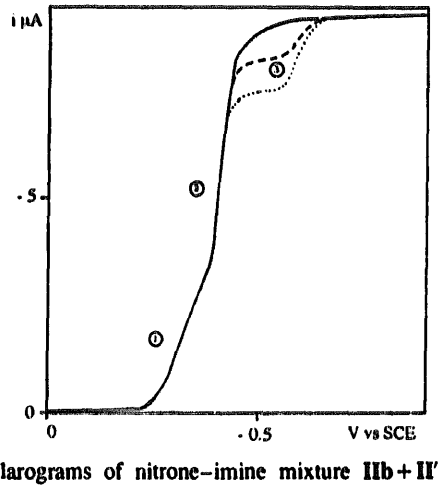



Fig. 5. Polarograms of nitrone–imine mixture **IIb** + **II'b** (70:30). 20 mg of the mixture in 20 ml of 0.1 N $H_2SO_4$–acetone (1:1), $\tau = 2$ s; (————) $t = 0$, (— — —) $t = 20$ min, (· · ·) $t = 60$ min.

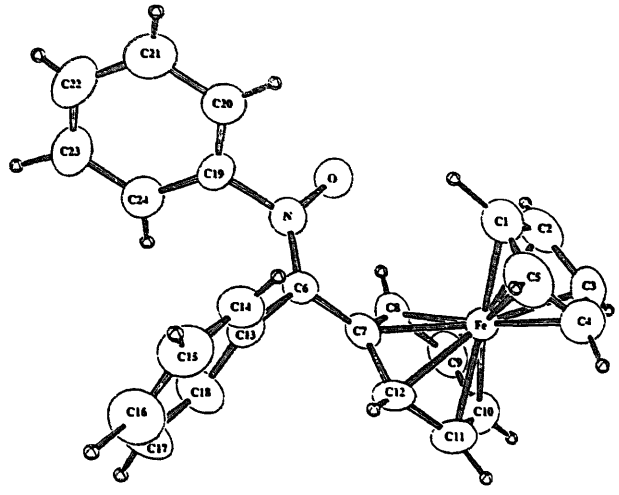


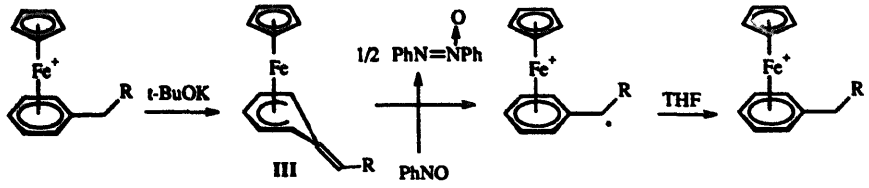
Fig. 6. X-ray structure of nitrone **IIa**.

In the $^1$H NMR spectrum of the mixtures, ratios of each compound could be estimated with integrals of Cp and methyl signals and are in agreement with electrochemical estimations. Composition of the mixtures is confirmed in **IIb** + **II'b** by elemental analysis, $^{13}$C NMR spectroscopy (azomethine carbon signal at 166.13 ppm, nitrone at 148.47 ppm). High resolution mass spectroscopy (LSIMS ionisation type) indicates the presence of two molecular ions with a mass-difference of one oxygen. Only one isomer is detected for each compound, even in high resolution $^1$H NMR, for **IIb** + **II'b**.

Except for **IIb** + **II'b**, fractional .ecrystallisation in dichloromethane of the other mixtures gave nitrones **IIa,c,d** with a satisfactory purity (greater than 95%) but resulted in a considerable decrease of yields (22–35%

Table 2
Selected bond distances in **IIa**

| Atom 1 | Atom 2 | Distance (Å) |
|---|---|---|
| N | O | 1.298(8) |
| N | C6 | 1.295(9) |
| N | C19 | 1.47(1) |
| Fe | C1 | 2.05(1) |
| Fe | C2 | 2.02(2) |
| Fe | C3 | 2.02(6) |
| Fe | C4 | 2.03(2) |
| Fe | C5 | 2.02(2) |
| Fe | C7 | 2.09(9) |
| Fe | C8 | 2.08(8) |
| Fe | C9 | 2.05(8) |
| Fe | C10 | 2.06(1) |
| Fe | C11 | 2.06(1) |
| Fe | C12 | 2.07(1) |




Scheme 5.

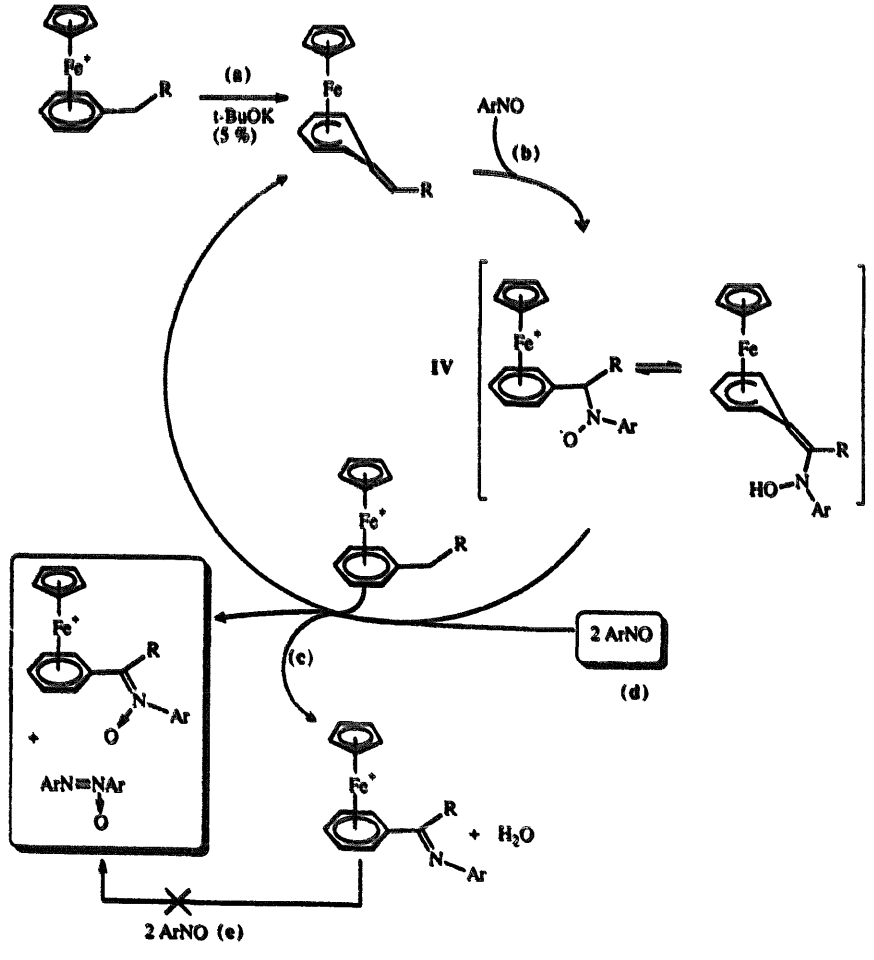
calculated from II). These compounds have been characterised by elemental analysis, IR spectroscopy, by two reduction steps in polarography and by $^{1}H$ and $^{13}C$ NMR spectroscopy. $^{13}C$ assignments resulted from shielding effects due to the complexation with the metal, $^{1}H$ coupling $^{13}C$ spectrum and a comparison between the three products (variation of the methyl position).

The Z-isomerism of IIa determined by X-ray analysis (Fig. 6 and Table 2) could reasonably be generalised for the other nitrone complexes if we consider the small differences of chemical shifts between their NMR spectra.

### 2.1.3. *Attempted condensations with other (Cp Fe arene)$^{+}$ complexes*

For other (Cp Fe arene)$^{+}$ complexes (arene = toluene, ethylbenzene, tetraline and indane) in solution with nitrosobenzene, no evolution or a partial reduction of the nitrosoarene could be detected after adding a slight amount of t-BuOK (5%).

However, addition of nitrosobenzene to the deprotonated species of these compounds (obtained by reaction with a stoichiometric amount of base) resulted in a rapid conversion of nitrosobenzene into azoxybenzene (with a yield of about 90%) and the recovery of the initial




Scheme 6.

cation characterised by $^1H$ NMR. Azoxybenzene has been detected by polarography and cyclic voltammetry of reaction mixture extracts by TLC ($R_f = 0.5$, ether–petroleum ether 20:80) after precipitation of the complex.

This failure could be interpreted as a rapid nitrosobenzene oxidation of the deprotonated species **III** followed by an H-atom abstraction from the solvent which restored the initial complex (Scheme 5).

In contrast, the same experiments using a stoichiometric amount of t-BuOK with (Cp Fe fluorene)$^+$ **I** and (Cp Fe diphenylmethane)$^+$ **II** yielded mixtures of nitrones and imines being in a ratio of 20:80 for **I** (85% yield) and 55:35 for **II** (74% yield, including 10% of starting complex **II**).

### 2.1.4. Mechanism

Formation of imine and/or nitrone and the use of a small amount of base are justified by a mechanism derived from other work [9,12,13] (Scheme 6).

Deprotonation of a small quantity of starting complex (a) is followed by an addition (b) of nitrosoarene to form an intermediate-type aminohydroxymate **IV** which can exist as two tautomeric forms. The intermediate **IV** may undergo either a dehydration (c) and yield imine, or a nitrosoarene oxidation (d) to form nitrone and azoxybenzene. We verified that the imine could not be directly oxidised into nitrone (e) in these experimental conditions.

The chain reaction is continued by subsequent deprotonations of the starting complex with the base which could be the intermediate **IV** proposed by Mugnier et al. [12] in their work on electrochemically initiated condensation between nitrosobenzene and fluorene. In this case, dehydration (c) o. .xidation (d) of **IV** could take place after its reprotonation. If reactions (c) and (d) occur before its reprotonation, the base could be the hydroxide ions originating from dehydration of **IV** or from formation of azoxybenzene. Other intermediates from reduction of nitrosobenzene such as $PhNO^{\cdot-}$ or $ArNHO^-$ could also be basic enough to deprotonate the cation.

This mechanism explains the need of three equivalents of nitroso in reaction with (Cp Fe diphenylmethane)$^+$ **II** for which nitrones are the major products. Polarographic analysis showed that these three equivalents did not react completely due to partial formation of imine.

When the nitrosoarene possesses an electron-withdrawing group, its oxidative character is enhanced and direct oxidation of deprotonated species can be observed (see Scheme 5). This could explain the need of an excess of nitrosoacetophenone to achieve the reaction with fluorene complex **I** and the failure of condensation between nitrosoacetophenones and diphenylmethane complex **II**.

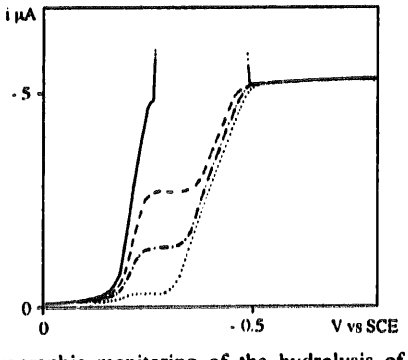



Fig. 7. Polarographic monitoring of the hydrolysis of imine **Ie** in 0.1 N $H_2SO_4$–acetone (1:1); $C_0 = 2 \times 10^{-3}$ mol l$^{-1}$; $\tau = 2$ s; (———) $t = 0$, (– – –) $t = 30$ min, (– · –) $t = 60$ min, (· · ·) $t = 160$ min.

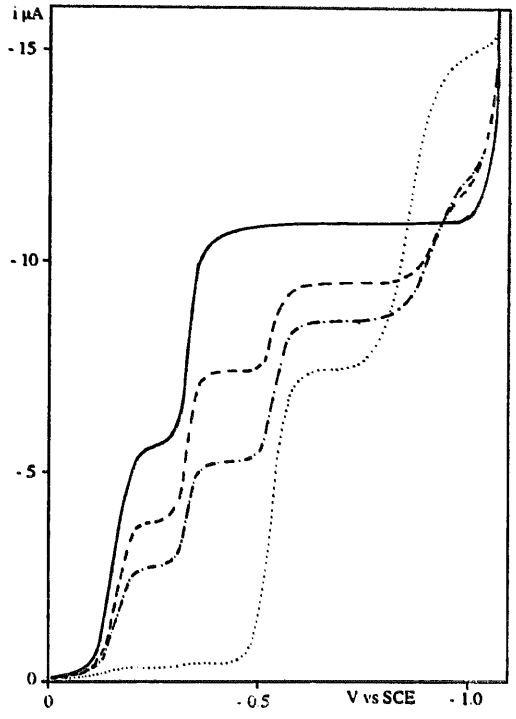



Fig. 8. Polarographic monitoring of the hydrolysis of nitrone **IIa** in 2 N $H_2SO_4$–acetone (1:1); $C_0 = 2 \times 10^{-3}$ mol l$^{-1}$; $\tau = 2$ s; (———) $t = 0$, (– – –) $t = 18$ min, (– · –) $t = 40$ min, (· · ·) $t = 4$ h.

## 2.2. Hydrolysis of nitrone and imine complexes

The hydrolysis rate of imines **Ia–g** and nitrones **IIa–d** resulted from polarographic measurements made in a light-sheltered cell, at room temperature, in 0.1 N $H_2SO_4$–acetone (1:1) for imines **Ia–g** and in 2 N $H_2SO_4$–acetone (1:1) for nitrones **IIa–d**.

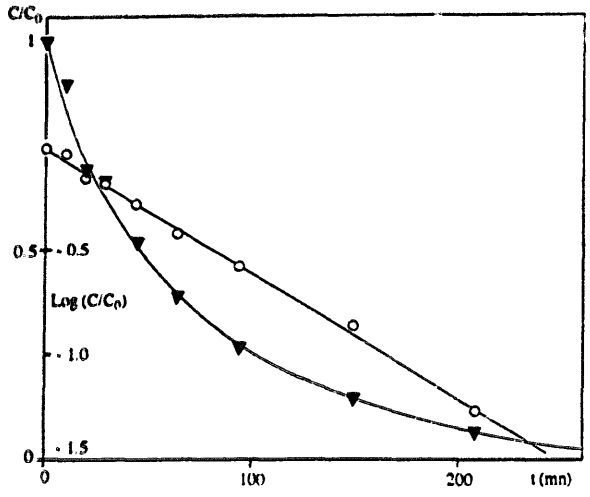



Fig. 9. Rate of change of the concentration of nitrone **IId** in 2N $H_2SO_4$–acetone (1:1); initial concentration $C_0 = 2 \times 10^{-3}$ mol $l^{-1}$; (▼) $C/C_0 = f(t)$; (○) $\log(C/C_0) = f(t)$.

The acidic solutions and the acetone containing $4 \times 10^{-3}$ mol $l^{-1}$ of imines or nitrones were separately deoxygenated by bubbling nitrogen through them and then the two solutions mixed together.

Polarogram plotting at different times indicated a decrease of imine **Ia–g** reduction waves ($E_{1/2} \approx -0.25$ V vs. SCE) in favour of the fluorenone complex **Ii** wave at more cathodic potentials ($E_{1/2} = -0.44$ V vs. SCE) (Fig. 7).

A simultaneous decrease of the two reduction waves of nitrones **IIa–d** ($E_{1/2} \approx -0.20$ and $-0.35$ V vs. SCE) in favour of the benzophenone complex **III** ($E_{1/2} = -0.55$ V vs. SCE) and phenylhydroxylamines ($E_{1/2} \approx -0.9$ V vs. SCE) waves was observed (Fig. 8).

We determined all the hydrolysis to follow kinetics of the first order (Fig. 9). Listed in Table 3 are hydrolysis half-reaction times of compounds **Ia–g** and **IIa–d**. These results indicate a high steric effect on the hydrolysis rate when a methyl group is in the ortho position to either an imine (**Ib**) or a nitrone (**IIb**) function.

Table 3
Hydrolysis half-reaction times of imines **Ia–g** and nitrones **IIa–d**

| Complex | R | $t_{1/2}$ (min) |
|---|---|---|
| **Ia** [a] | H | 35 |
| **Ib** | 2′-Me | 240 |
| **Ic** | 3′-Me | 35 |
| **Id** | 4′-Me | 30 |
| **Ie** | 3′-COMe | 25 |
| **If** | 4′-COMe | 50 |
| **Ig** | 4′-$NMe_2$ | 30 |
| **IIa** [b] | H | 30 |
| **IIb** [c] | 2′-Me | 140 |
| **IIc** | 3′-Me | 35 |
| **IId** | 4′-Me | 45 |

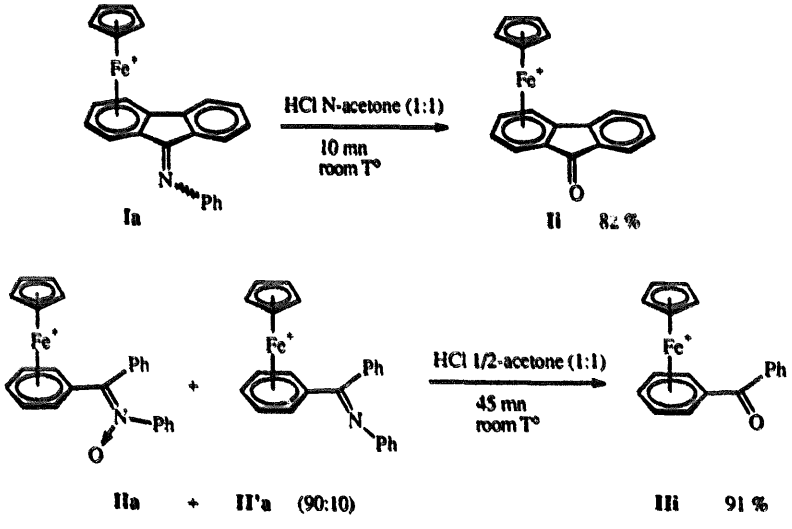
[a] In 0.1 N $H_2SO_4$–acetone (1:1) for **Ia–g**. [b] In 2N $H_2SO_4$–acetone (1:1) for **IIa–d**. [c] Measured on imine–nitrone mixture **IIb** + **II′b** (70:30); on the first polarogram imine was totally hydrolysed.

Macroscale hydrolyses of imine **Ia** were completed after a 10 min reaction in a mixture of diluted hydrochloric acid and acetone (1:1) and led to (Cp Fe fluorenone)$^+$ **Ii** with a good yield. Hydrolysis of the imine–nitrone mixture **IIa** + **II′a** (90:10) into (Cp Fe benzophenone)$^+$ **III** needed a stronger acidic medium and a longer reaction time (Scheme 7).

$^1$H, $^{13}$C NMR, IR and polarographic characteristics of complexes **Ii** and **III** are in agreement with the literature data [6,14].

## 3. Conclusion

Our study indicates a high reactivity of (Cp Fe arene)$^+$ complexes with a number of nitrosoarenes and provides a very useful synthesis route to new complexes of fluorenone–anils or benzophenone–phenylnitrones as well as a new method to synthesise




Scheme 7.

their corresponding ketones already obtainable by other methods [6,14,15].

Unfortunately, the condensation reaction seems to be of limited use for other arene complexes owing to the high oxidative character of nitrosoarenes which is sometimes in competition with its electrophilic properties.

Further investigations on electrochemical activation of imine and nitrone functions are now in progress.

## 4. Experimental section

### 4.1. Reagents

All (Cp Fe arene)$^+$ complexes were handled with minimal exposure to visible light. New complexes were not air- or water-sensitive. Some of them were found to be stable for over a year at room temperature.

All solvents (reagent grade) were used without further purification, with the exception of THF which was distilled from sodium benzophenone under nitrogen.

The starting complexes were prepared using the general ligand exchange reaction [16]. **I** and **II** were also synthesised according to the recently reported [17] microwave dielectric heating method in an unmodified commercial oven (Whirlpool Jet M430 at a power of 500 W).

Nitrosobenzene, 2-nitrosotoluene and *N,N*-nitroso-4-dimethylaniline are commercially available and were used without further purification. 3- and 4-nitrosotoluenes were prepared from the corresponding nitro derivatives according to literature methods [18]. 3- and 4-nitrosoacetophenones were obtained electrochemically from the corresponding nitro compound using a 'redox' flow cell [19] fitted with two consecutive graphite felt electrodes of opposite polarities

### 4.2. General methods

Conventional electrochemical equipment was used for polarography and cyclic voltammetry (EG&G Princeton Applied Research model 362-scanning potentiostat with an *XY* recorder). The polarography scan-rate was 5 mv s$^{-1}$ and the drop-time $\tau$ 2 s. Half-wave potentials of the complexes were determined in 0.1 N $H_2SO_4$–acetone (1:1, v:v) at room temperature.

IR spectra were recorded on a Nicolet 205 FT-IR instrument (in KBr powder). Elemental analysis were done at the 'Service Central d'Analyse, Département Analyse Elémentaire' (Vernaison).

Mass spectra were obtained on a VG Analytical ZAB Spec TOF high resolution mass spectrometer (EBE TOF Geometry) at the 'Centre Regional de Mesures Physiques de l'Ouest' (C.R.M.P.O.). Ionisation type was LSIMS with $Cs^+$ ions, the matrix was 3-nitrobenzylique alcohol (*m*-NBA) and the acceleration potential was 8 kV.

NMR spectra were recorded on a Brucker AM 300 FT spectrometer at the C.R.M.P.O. at 300 MHz ($^1$H) and 75.5 MHz ($^{13}$C). Chemical shifts were expressed in ppm downfield from TMS and coupling constants *J* in hertz. Values with an asterisk could be inverted. The solvent was $CD_3COCD_3$. $^{13}$C NMR broad band and gated decoupling spectra were recorded. Imine **Ic** was analysed using a 2D-$^1$H,$^{13}$C correlation experiment. Nitrone–imine mixtures **IIa,c,d + II'a,c,d** were just analysed by $^1$H NMR at 60 MHz on a Varian EM 360A apparatus ($CD_3COCD_3$).

### 4.3. General synthesis procedure of imine complexes *Ia–g*

In a conical flask equipped with a nitrogen inlet (Cp Fe fluorene)$^+$($PF_6$)$^-$ (**I**($PF_6$)$^-$) (1.08 g, 2.5 mmol) and nitrosobenzene (0.27 g, 2.5 mmol) were dissolved in 50 ml of THF. After adding t-BuOK (15 mg, 0.13 mmol) the solution became instantaneously dark brown and the complex (**Ia**($PF_6^-$)) started to precipitate. After stirring for 10 min the solid was removed by filtration and washed with 20 ml of ether. The compound was dissolved in 20 ml of acetone and passed through a small alumina column (5 cm of activated neutral $Al_2O_3$ 150 mesh (Aldrich)) and added dropwise into cold ether under stirring. Filtration and drying under vacuum of the resulting precipitate gave 1.14 g (88% yield) of (**Ia**($PF_6$)$^-$) as a fine yellow powder.

#### 4.3.1. ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluorenone-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (*Ia*($PF_6$)$^-$)

[$C_{24}H_{18}$FeN][$PF_6$] found (calc.): C, 55.44 (55.31); H, 3.57 (3.48); Fe, 10.48 (10.71); N, 2.91 (2.69); P, 6.00 (5.94%). IR $\nu$ (cm$^{-1}$): C=N (1651). $E_{1/2}$ (V vs. SCE): −0.26. $^1$H NMR: non-assigned signals $H_4$ and $H_{4'}$ *anti*, $H_4$ and $H_{4'}$ *syn* 7.30–7.42 ($2H_{anti} + 2H_{syn}$, m); ***anti*** (70%): Cp 5.13 (s), $H_1$ 7.29 (d, $^3J$ = 6.1), $H_2$ 6.79 (t, $^3J$ = 6.1), $H_3$ 6.83 (t, $^3J$ = 6.0), $H_5$ 8.18 (d, $^3J$ = 7.5), $H_6$ 7.68 (t, $^3J$ = 7.6), $H_7$ 7.36 (t, $^3J$ = 7.6), $H_8$ 6.83 (d, $^3J$ = 7.9), $H_{2'}$ 7.16 (d, $^3J$ = 8), $H_{3'}$ 7.55 (t, $^3J$ = 8); for attribution of $H_6$, $H_7$ and $H_8$ irradiation at 6.84 ppm, for $H_{2'}$ and $H_{3'}$ irrad. at 7.16 ppm; ***syn*** (30%): Cp 5.04 (s), $H_1$ 5.69 (d, $^3J$ = 6.5), $H_2$ 6.42 (t, $^3J$ = 6.3), $H_3$ 6.75 (t, $^3J$ = 6.3), $H_5$ 8.16 (d, $^3J$ = 7.2), $H_6$ 7.80 (t, $^3J$ = 7.5), $H_7$ 7.73 (t, $^3J$ = 7.4), $H_8$ 8.07 (d, $^3J$ = 7.4), $H_{2'}$ 7.25 (d, $^3J$ = 8), $H_{3'}$ 7.61 (t, $^3J$ = 8); for attribution of $H_1$, $H_2$ and $H_3$ irrad. at 5.69 ppm. $^{13}$C NMR: ***anti***: Cp 80.28, $C_1$ 84.53, $C_2$ 88.16, $C_3$ 89.25, $C_4$ 82.86, $C_{4a}$ 103.33, $C_{9a}$ 96.01, $C_{4b}$ 140.98, $C_5$ 124.26, $C_6$ 134.37, $C_7$ 131.78, $C_8$ 127.89, $C_{8a}$ 132.27, $C_9$ 161.89, $C_{1'}$ 151.71, $C_{2'}$ 118.57, $C_{3'}$ 130.54, $C_{4'}$ 125.99; ***syn***: Cp 80.48, $C_1$ 87.23, $C_2$ 87.77, $C_3$ 89.47, $C_4$ 83.92, $C_{4a}$ 104.46, $C_{9a}$

88.25, $C_{4b}$ 139.20, $C_5$ 123.43, $C_6$ 134.37, $C_7$ 132.41, $C_8$ 124.55, $C_9$ 161.52, $C_{1'}$ 151.56, $C_{2'}$ 118.45, $C_{3'}$ 130.90, $C_{4'}$ 126.16.

#### 4.3.2. ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluorenone-(2'-methyl)-anil]iron(II) hexafluorophosphate (syn–anti mixture (20:80)) (Ib(PF$_6$)$^-$)

The synthesis procedure used for **Ia** led to (**Ib**(PF$_6$)$^-$) as a fine yellow powder (71% yield). [$C_{25}H_{20}FeN$][$PF_6$] found (calc.): C, 55.92 (56.10); H, 3.88 (3.77); Fe, 10.06 (10.43); N, 2.63 (2.62); P, 5.82 (5.79%). IR $\nu$ (cm$^{-1}$): C=N (1653). $E_{1/2}$ (V vs. SCE): −0.30. $^1$H NMR: non-assigned signals $H_1$, $H_4$, $H_{3'}$, $H_{4'}$ and $H_{5'}$ *anti*, $H_4$, $H_{3'}$, $H_{4'}$ and $H_{5'}$ *syn*: 7.20–7.50 ($5H_{anti}$ + $4H_{syn}$, m); ***anti*** (80%): Cp 5.12 (s), $H_2$ 6.79 (t, $^3J$ = 6.1), $H_3$ 6.83 (t, $^3J$ = 6.1), $H_5$ 8.18 (d, $^3J$ = 7.6), $H_6$ 7.69 (t, $^3J$ = 7.6), $H_7$ 7.36 (t, $^3J$ = 7.6), $H_8$ 6.81 (d, $^3J$ = 7.9), Me 2.24 (s), $H_{6'}$ 7.01 (d, $^3J$ = 7.6); ***syn*** (20%): Cp 5.04 (s), $H_1$ 5.75 (d, $^3J$ = 6.5), $H_2$ 6.43 (t, $^3J$ = 6.4), $H_3$ 6.75 (t, $^3J$ = 6.3), $H_5$ 8.17 (d, $^3J$ = 7.5), $H_6$ 7.80 (t, $^3J$ = 7.5), $H_7$ 7.74 (t, $^3J$ = 7.5), $H_8$ 8.12 (d, $^3J$ = 7.5), Me 2.24 (s), $H_{6'}$ 7.14 (d, $^3J$ = 7.5). $^{13}$C NMR: ***anti***: Cp 80.16, $C_1$ 84.56, $C_2$ 88.09, $C_3$ 89.19, $C_4$ 82.89, $C_{4a}$ 103.46, $C_{9a}$ 96.03, $C_{4b}$ 140.78, $C_5$ 124.25, $C_6$ 134.45, $C_7$ 132.08, $C_8$ 127.91, $C_{8a}$ 132.62, $C_9$ 161.75, $C_{1'}$ 150.22, $C_{2'}$ 126.68, Me 18.04, $C_{3'}$ 131.87, $C_{4'}$ 126.15*, $C_{5'}$ 127.39*, $C_{6'}$ 117.80; ***syn***: Cp 80.40, $C_1$ 86.81, $C_2$ 87.84, $C_3$ 89.55, $C_4$ 83.93, $C_{4a}$ 104.39, $C_{9a}$ 88.48, $C_{4b}$ 139.22, $C_5$ 123.44, $C_6$ 134.33, $C_7$ 132.41, $C_8$ 124.53, $C_{8a}$ 138.56, $C_9$ 161.43, $C_{1'}$ 149.93, $C_{2'}$ 127.17, Me 17.99, $C_{3'}$ 132.21, $C_{4'}$ 126.44*, $C_{5'}$ 128.10*, $C_{6'}$ 117.92.

#### 4.3.3. ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluorenone-(3'-methyl)-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (Ic(PF$_6$)$^-$)

15 min after adding t-BuOK, the complex (**Ic**(PF$_6$)$^-$) was removed after concentration by rotary evaporation of the THF solution and precipitated by ether. Purification by filtration on alumina as before gave (**Ic**(PF$_6$)$^-$) as a fine yellow powder (82% yield). [$C_{25}H_{20}FeN$][$PF_6$] found (calc.): C, 55.92 (56.10); H, 4.01 (3.77); Fe, 10.19 (10.43); N, 2.73 (2.62); P, 5.89 (5.79%). IR $\nu$ (cm$^{-1}$): C=N (1650). $E_{1/2}$ (V vs. SCE): −0.26. NMR: $^1$H and $^{13}$C signals were correlated using a 2D experiment; $^1$H NMR: ***anti*** (70%): Cp 5.11 (s), $H_1$ 7.27 (d, $^3J$ = 6.1), $H_2$ 6.76 (t, $^3J$ = 6.0), $H_3$ 6.81 (t, $^3J$ = 6.2), $H_4$ 7.37 (d, $^3J$ = 6), $H_5$ 8.16 (d, $^3J$ = 7.5), $H_6$ 7.67 (t, $^3J$ = 7.6), $H_7$ 7.35 (t, $^3J$ = 7.7), $H_8$ 6.88 (d, $^3J$ = 7.8), $H_{2'}$ 6.99 (s broad), Me 2.41 (s), $H_{4'}$ 7.16 (d broad, $^3J$ = 7.6), $H_{5'}$ 7.41 (t, $^3J$ = 7.7), $H_{6'}$ 6.93 (d broad, $^3J$ = 7.8), for attribution of $H_1$, $H_2$, $H_3$ and $H_4$ irradiation at 7.26 ppm, for $H_5$, $H_6$, $H_7$ and $H_8$ irrad. at 7.67 ppm, gated decoupling $^{13}$C experiments (vide infra) were also considered; ***syn*** (30%): Cp 5.01 (s), $H_1$ 5.74 (d, $^3J$ = 6.5), $H_2$ 6.39 (t, $^3J$ = 6.3), $H_3$ 6.73 (t, $^3J$ = 6.2), $H_4$ 7.38 (d, $^3J$ = 6.4), $H_5$ 8.15 (d, $^3J$ = 7.3), $H_6$ 7.79 (t, $^3J$ = 7.5), $H_7$ 7.72 (t, $^3J$ = 7.4), $H_8$ 8.06 (d, $^3J$ = 7.4), $H_{2'}$ 7.06 (s broad), Me 2.45 (s), $H_{4'}$ 7.20 (d broad, $^3J$ = 7.6), $H_{5'}$ 7.48 (t, $^3J$ = 7.7), $H_{6'}$ 7.02 (d broad, $^3J$ = 7.9), for attribution of $H_5$, $H_6$, $H_7$ and $H_8$ irradiation at 8.06 and 7.79 ppm and gated decoupling $^{13}$C experiments. $^{13}$C NMR: ***anti***: Cp 80.25, $C_1$ 84.49, $C_2$ 88.14, $C_3$ 89.22, $C_4$ 82.84, $C_{4a}$ 103.35, $C_{9a}$ 96.06, $C_{4b}$ 140.92, $C_5$ 124.21, $C_6$ 134.30, $C_7$ 131.79, $C_8$ 127.98, $C_{8a}$ 132.30, $C_9$ 161.68, $C_{1'}$ 151.72, $C_{2'}$ 118.97, $C_{3'}$ 140.51, Me 21.46, $C_{4'}$ 126.64, $C_{5'}$ 130.38, $C_{6'}$ 115.51, for attribution of quaternary carbons $C_{9a}$, $C_{4a}$, $C_{4b}$ and $C_{8a}$ irradiations at 8.15, 7.26 and 7.34 ppm; ***syn***: Cp 80.44, $C_1$ 87.33, $C_2$ 87.79, $C_3$ 89.45, $C_4$ 83.89, $C_{4a}$ 104.47, $C_{9a}$ 88.25, $C_{4b}$ 139.17, $C_5$ 123.41, $C_6$ 134.30, $C_7$ 132.40, $C_8$ 124.50, $C_{8a}$ 138.63, $C_9$ 161.34, $C_{1'}$ 151.59, $C_{2'}$ 118.83, $C_{3'}$ 140.51, Me 21.56, $C_{4'}$ 126.82, $C_{5'}$ 130.72, $C_{6'}$ 115.43, for attribution of quaternary carbons $C_{4a}$, $C_{4b}$, $C_{9a}$ and $C_{8a}$ irradiations at 7.67 and 8.15 ppm.

#### 4.3.4. ($\eta^5$-Cyclopentadienyl) [(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluorenone-(4'-methyl)-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (Id(PF$_6$)$^-$)

The synthesis procedure used for **Ic** led to (**Id**(PF$_6$)$^-$) as a fine yellow powder (80% yield). [$C_{25}H_{20}FeN$][$PF_6$] found (calc.): C, 55.93 (56.10); H, 3.91 (3.77); Fe, 10.03 (10.43); N, 2.63 (2.62); P, 5.77 (5.79%). IR $\nu$ (cm$^{-1}$): C=N (1650). $E_{1/2}$ (V vs. SCE): −0.26. $^1$H NMR: non-assigned signals $H_{4,syn}$ and $H_{4anti}$, integrals indicated that their signals and those of $H_{7anti}$ and $H_{3'anti}$ are overlapped; ***anti*** (70%): Cp 5.09 (s), $H_1$ 7.26 (d, $^3J$ = 6.0), $H_2$ 6.75 (t, $^3J$ = 6.0), $H_3$ 6.79 (t, $^3J$ = 6.1), $H_5$ 8.16 (d, $^3J$ = 7.6), $H_6$ 7.67 (t, $^3J$ = 7.6), $H_7$ 7.35 (t, $^3J$ = 7.5), $H_8$ 6.95 (d, $^3J$ = 7.8), $H_{2'}$ 7.05 (d, $^3J$ = 8.2), $H_{3'}$ 7.35 (d, $^3J$ = 8.5), Me 2.43 (s), for attribution of $H_1$, $H_2$ and $H_3$ irrad. at 7.26 ppm, for $H_6$, $H_7$ and $H_8$ irrad. at 6.95 ppm; ***syn*** (30%): Cp 5.00 (s), $H_1$ 5.79 (d, $^3J$ = 6.5), $H_2$ 6.38 (t, $^3J$ = 6.5), $H_3$ 6.71 (t, $^3J$ = 6.3), $H_5$ 8.14 (d, $^3J$ = 7.5), $H_6$ 7.78 (t, $^3J$ = 7.4), $H_7$ 7.71 (t, $^3J$ = 7.4), $H_8$ 8.05 (d, $^3J$ = 7.1), $H_{2'}$ 7.13 (d, $^3J$ = 8.2), $H_{3'}$ 7.41 (d, $^3J$ = 8.0), Me 2.44 (3H, s), for attribution of $H_1$, $H_2$ and $H_3$ irrad. at 6.38 ppm; $^{13}$C NMR: ***anti***: Cp 80.22, $C_1$ 84.45, $C_2$ 88.12, $C_3$ 89.17, $C_4$ 82.79, $C_{4a}$ 103.27, $C_{9a}$ 96.18, $C_{4b}$ 140.92, $C_5$ 124.21, $C_6$ 134.27, $C_7$ 131.74, $C_8$ 127.82, $C_{8a}$ 132.31, $C_9$ 161.70, $C_{1'}$ 149.11, $C_{2'}$ 118.69, $C_{3'}$ 131.00, $C_{4'}$ 135.66, Me 21.04; ***syn***: Cp 80.45, $C_1$ 87.28, $C_2$ 87.69, $C_3$ 89.42, $C_4$ 83.85, $C_{4a}$ 104.40, $C_{9a}$ 88.35, $C_{4b}$ 139.16, $C_5$ 123.37, $C_6$ 134.22, $C_7$ 132.36, $C_8$ 124.47, $C_{8a}$ 138.72, $C_9$ 161.41, $C_{1'}$ 149.02, $C_{2'}$ 118.51, $C_{3'}$ 131.37, $C_{4'}$ 135.79, Me 21.09.

#### 4.3.5. ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluorenone-(3'-methylcarbonyl)-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (Ie(PF$_6$)$^-$)

The synthesis procedure used for **Ia** using 1.08 g (2.5 mmol) of (**I**(PF$_6$)$^-$), 0.52 g (3.5 mmol) of 3-

nitrosoacetophenone and 15 mg (0.13 mmol) of t-BuOK gave 0.84 g of (Ie $(PF_6)^-$) as a fine yellow powder (60% yield). $[C_{26}H_{20}FeNO][PF_6]$ found (calc.): C, 55.47 (55.44); H, 3.72 (3.58); Fe, 9.63 (9.91); N, 2.36 (2.49); P, 5.48 (5.50%). IR $\nu$ ($cm^{-1}$): C=N (1650), C=O (1676). $E_{1/2}$ (V vs. SCE): −0.22. $^1H$ NMR: non-assigned signals $H_{2'}$ and $H_{5'}$ *anti*, $H_6$, $H_7$, $H_{2'}$ and $H_{5'}$ *syn*: 7.65–7.85 ($2H_{anti} + 4H_{syn}$, m); ***anti*** (70%): Cp 5.14 (s), $H_1$ 7.30 (d, $^3J = 6.1$), $H_2$ 6.79 (t, $^3J = 6.2$), $H_3$ 6.84 (t, $^3J = 6.1$), $H_4$ 7.40 (d, $^3J = 6.3$), $H_5$ 8.18 (d, $^3J = 7.6$), $H_6$ 7.69 (t, $^3J = 7.6$), $H_7$ 7.35 (t, $^3J = 7.8$), $H_8$ 6.83 (d, $^3J \approx 8$), MeCO 2.64 (s), $H_{4'}$ 7.97 (d, $^3J = 7.8$), $H_{6'}$ 7.43 (d, $^3J = 7.8$); ***syn*** (30%): Cp 5.07 (s), $H_1$ 5.76 (d, $^3J = 6.5$), $H_2$ 6.37 (t, $^3J = 6.4$), $H_3$ 6.74 (t, $^3J = 6.3$), $H_4$ 7.40 (d, $^3J = 6.3$), $H_5$ 8.16 (d, $^3J = 7.2$), $H_8$ 8.09 (d, $^3J = 7.3$), MeCO 2.66 (s), $H_{4'}$ 8.00 (d, $^3J = 7.8$), $H_{6'}$ 7.51 (d, $^3J = 7.8$), for attribution of $H_1$, $H_2$, $H_3$ and $H_4$ of both isomers, irrad. at 7.40 ppm; $^{13}C$ NMR: ***anti***: Cp 80.36, $C_1$ 84.60, $C_2$ 88.23, $C_3$ 89.34, $C_4$ 82.95, $C_{4a}$ 103.36, $C_{9a}$ 95.76, $C_{4b}$ 141.11, $C_5$ 124.36, $C_6$ 134.57, $C_7$ 131.91, $C_8$ 127.05, $C_{8a}$ 132.18, $C_9$ 162.58, $C_{1'}$ 151.82, $C_{2'}$ 118.13, $C_{3'}$ 139.65, Me 26.92, CO 197.67, $C_{4'}$ 125.86*, $C_{5'}$ 130.96, $C_{6'}$ 123.21*; ***syn***: Cp 80.54, $C_1$ 87.21, $C_2$ 87.88, $C_3$ 89.55, $C_4$ 83.99, $C_{4a}$ 104.54, $C_{9a}$ 88.09, $C_{4b}$ 139.26, $C_5$ 123.49, $C_6$ 134.54, $C_7$ 132.47, $C_8$ 124.68, $C_{8a}$ 138.49, $C_9$ 162.23, $C_{1'}$ 151.67, $C_{2'}$ 117.82, $C_{3'}$ 139.77, Me 26.92, CO 197.87, $C_{4'}$ 126.02*, $C_{5'}$ 131.39, $C_{6'}$ 123.21*.

#### *4.3.6. ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluoren-one-(4'-methylcarbonyl)-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (If$(PF_6)^-$)*

The synthesis procedure used for Ic using 1.08 g (2.5 mmol) of (I$(PF_6)^-$), 0.52 g (3.5 mmol) of 4-nitrosoacetophenone and 15 mg (0.13 mmol) of t-BuOK gave 1.22 g of (If$(PF_6)^-$) as a fine yellow powder (87% yield). $[C_{26}H_{20}FeNO][PF_6]$ found (calc.): C, 55.76 (55.44); H, 3.81 (3.58); Fe, 9.70 (9.91); N, 2.52 (2.49); P, 5.45 (5.50%). IR $\nu$ ($cm^{-1}$): C=N (1652), C=O (1682). $E_{1/2}$ (V vs. SCE): −0.19. $^1H$ NMR: non-assigned signals $H_{5syn}$ and $H_{5anti}$, integrals indicated that their signals and the signal of $H_{3'anti}$ are overlapped; $H_{1anti}$ overlapped with $H_{2'anti}$; ***anti*** (70%): Cp 5.14 (s), $H_2$ and $H_3$ 6.77–6.85 (m), $H_4$ 7.39 (d, $^3J \approx 6$), $H_6$ 7.69 (t, $^3J = 7.6$), $H_7$ 7.35 (t, $^3J = 7.8$), $H_8$ 6.86 (d, $^3J = 7.8$), $H_{2'}$ 7.29 (d, $^3J = 8.4$), $H_{3'}$ 8.17 (d, $^3J = 8.6$), MeCO 2.65 (s), for attribution of $H_{2'}$ and $H_{3'}$ irrad. at 7.29 ppm; ***syn*** (30%): Cp 5.06 (s), $H_1$ 5.81 (d, $^3J = 6.5$), $H_2$ 6.39 (t, $^3J = 6.4$), $H_3$ 6.74 (t, $^3J = 6.4$), $H_4$ 7.39 (d, $^3J = 6$), $H_6$ 7.81 (t, $^3J = 7.4$), $H_7$ 7.73 (t, $^3J = 7.4$), $H_8$ 8.07 (d, $^3J = 7.4$), $H_{2'}$ 7.37 (d, $^3J = 8.9$), $H_{3'}$ 8.22 (d, $^3J = 8.5$), MeCO 2.66 (s), for attribution of $H_{2'}$ and $H_{3'}$ irrad. at 7.38 ppm. $^{13}C$ NMR: ***anti***: Cp 80.43, $C_1$ 84.70, $C_2$ 88.28, $C_3$ 89.41, $C_4$ 83.05, $C_{4a}$ 103.36, $C_{9a}$ 95.52, $C_{4b}$ 141.13, $C_5$ 124.42, $C_6$ 134.71, $C_7$ 131.93, $C_8$ 128.08, $C_{8a}$ 132.18, $C_9$ 162.08, $C_{1'}$ 155.61, $C_{2'}$ 118.62, $C_{3'}$ 131.04, $C_{4'}$ 135.11, Me 26.64, CO 196.90; ***syn***: Cp 80.63, $C_1$ 87.34, $C_2$ 87.90, $C_3$ 89.63, $C_4$ 84.07, $C_{4a}$ 104.48, $C_{9a}$ 88.15, $C_{4b}$ 139.35, $C_5$ 123.54, $C_6$ 134.67, $C_7$ 132.49, $C_8$ 124.76, $C_{8a}$ 138.28, $C_9$ 161.69, $C_{1'}$ 155.36, $C_{2'}$ 118.51, $C_{3'}$ 131.42, $C_{4'}$ 135.17, Me 26.64, CO 196.94.

#### *4.3.7. ($\eta^5$-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-$\eta^6$)-fluoren-one-(4'-N',N'-dimethylamino)-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (Ig$(PF_6)^-$)*

The procedure used for Ic that needed 3 h to react gave (Ig$(PF_6)^-$) mixed with 10% of its corresponding nitrone (80% yield). The mixture was dissolved in a minimum amount of boiling THF and cooled to −25 °C. Most of the nitrone was eliminated by filtration. Precipitation of the filtrate into ether led to (Ig$(PF_6)^-$) in a reasonable purity (greater than 95%) as a fine dark purple powder (57% yield). $[C_{26}H_{23}FeN_2][PF_6]$ found (calc.): C, 55.13 (55.34); H, 4.26 (4.11); Fe, 9.58 (9.90); N, 4.66 (4.96); P, 5.65 (5.49%). IR $\nu$ ($cm^{-1}$): C=N (1635). $E_{1/2}$ (V vs. SCE): −0.25. $^1H$ NMR: non-assigned signals $H_4$, $H_7$ and $H_8$ *anti*, $H_4$ *syn*: 7.30–7.51 ($3H_{anti} + 1H_{syn}$, m); ***anti*** (70%): Cp 5.05 (s), $H_1$ 7.25 (d, $^3J = 6$), $H_2$ and $H_3$ 6.70–6.79 (m), $H_5$ 8.17 (d, $^3J = 7.6$), $H_6$ 7.67 (t, $^3J = 7.6$), $H_{2'}$ 7.16 (d, $^3J = 8.9$), $H_{3'}$ 6.90 (d, $^3J = 8.9$), $Me_2N$ 3.05 (s); ***syn*** (30%): Cp 4.94 (s), $H_1$ 6.27 (d, $^3J = 6.5$), $H_2$ 6.42 (t, $^3J = 6.2$), $H_3$ 6.71 (t, $^3J = 6.4$), $H_5$ 8.14 (d, $^3J = 7.6$), $H_6$ 7.75 (t, $^3J = 7.4$), $H_7$ 7.69 (t, $^3J = 7.4$), $H_8$ 8.04 (d, $^3J = 7.3$), $H_{2'}$ 7.18 (d, $^3J = 8.9$), $H_{3'}$ 6.96 (d, $^3J = 8.9$), $Me_2N$ 3.07 (s). $^{13}C$ NMR: ***anti***. Cp 79.90, $C_1$ 84.09, $C_2$ 87.83, $C_3$ 88.65, $C_4$ 82.41, $C_{4a}$ 102.92, $C_{9a}$ 97.44, $C_{4b}$ 140.57*, $C_5$ 124.01, $C_6$ 133.64, $C_7$ 131.70, $C_8$ 126.97, $C_{8a}$ 132.66, $C_9$ 159.03, $C_{1'}$ 140.20*, $C_{2'}$ 122.00, $C_{3'}$ 113.53, $C_{4'}$ 150.37, $Me_2N$ 40.69; ***syn***: Cp 80.23, $C_1$ 87.18*, $C_2$ 87.45*, $C_3$ 89.07, $C_4$ 83.51, $C_{4a}$ 104.10, $C_{9a}$ 89.41, $C_{4b}$ *139.62**, $C_5$ 123.11, $C_6$ 133.48, $C_7$ 132.16, $C_8$ 124.13, $C_{8a}$ *138.83**, $C_9$ 159.28, $C_{1'}$ 140.38, $C_{2'}$ 121.45, $C_{3'}$ 113.89, $C_{4'}$ 150.23, $Me_2N$ 40.69.

### *4.4. General synthesis procedure of nitrone–imine mixtures IIa–d + II'a–d and pure nitrones IIa,c,d*

In a conical flask equipped with a nitrogen inlet (Cp Fe diphenylmethane)$^+(PF_6)^-$ (II$(PF_6)^-$) (1.08 g, 2.5 mmol) and nitrosobenzene (0.80 g, 7.5 mmol) were dissolved in 25 ml of THF. After adding t-BuOK (15 mg, 0.13 mmol) the solution became instantaneously dark brown and the mixture ($IIa_{0.9}$ + $II'a_{0.1}$)$(PF_6)^-$ started to precipitate. The solution was stirred for 10 min and the mixture removed by filtration. Washing with 5 ml of cold THF, 40 ml of ether and drying under vacuum led to the mixture ($IIa_{0.9}$ + $II'a_{0.1}$)$(PF_6)^-$ as a fine yellow powder (92% yield). A satisfactory purity (97%) of nitrone IIa$(PF_6)^-$ was obtained after three recrystallisa-

tions of the mixture in $CH_2Cl_2$ at −25 °C (35% yield calc. from **II**).

*4.4.1. Nitrone–imine mixture ($IIa_{0.9} + II'a_{0.1}$)$(PF_6)^-$*

$^1$H NMR (60 MHz): **IIa** (90%): Cp 5.40 (5H, s); **II'a** (10%): Cp 5.33 (5H, s); aromatics 6.50–7.70 (15H, m).

*4.4.2. Z-(η⁵-Cyclopentadienyl)[(1,2,2,3,3,4-η⁶)-benzophenone-N-phenyl)nitrone]iron(II) hexafluorophosphate ($IIa(PF_6)^-$)*

$[C_{24}H_{20}FeNO][PF_6]$ found (calc.): C, 53.38 (53.46); H, 3.61 (3.74); Fe, 10.08 (10.36); N, 3.09 (2.60); P, 5.54 (5.74%). IR $\nu$ (cm$^{-1}$): N → O (1248). $E_{1/2}$ (V vs. SCE): −0.22, −0.41. $^1$H NMR: Cp 5.40 (5H, s), complexed ring 6.61–6.45 (3H, m), 7.03–7.08 (2H, m), non-complexed rings 7.31–7.41 (6H, m), 7.44–7.86 (4H, m). $^{13}$C NMR: Cp 78.46, $C_1$ 88.80, $C_2$ and $C_3$ 88.98, $C_4$ 97.93, $C_5$ 149.87, $C_6$ 134.80, $C_7$ 132.24, $C_8$ 129.83, $C_9$ 130.51, $C_{1'}$ 143.29, $C_{2'}$ 125.46, $C_{3'}$ 129.64, $C_{4'}$ 130.05.

*4.4.3. Nitrone–imine mixture ($IIb_{0.7} + II'b_{0.3}$)$(PF_6)^-$*

15 min after adding t-BuOK the mixture was isolated by concentration of the THF solution and precipitation with ether (80% yield). Attempts to isolate pure nitrone by recrystallisation were unsuccessful. $[C_{25}H_{22}FeNO_{0.7}][PF_6]$ found (calc.): C, 54.94 (54.74); H, 3.85 (4.01); Fe, 9.85 (10.19); N, 2.40 (2.55); P, 5.46 (5.66%). IR $\nu$ (cm$^{-1}$): N → O (1258). $E_{1/2}$ (V vs. SCE): −0.31, −0.41. $^1$H NMR: **IIb** (70%): Cp 5.41 (5H, s), Me 2.46 (3H, s); **II'b** (30%): Cp 5.32 (5H, s) Me 2.36 (3H, s); aromatics 6.50–7.50 (14H, m). $^{13}$C NMR: **IIb**: Cp 78.45, Me 17.40, $C_5$ 148.47 (4°); **II'b**: Cp 78.91, Me 18.73, $C_5$ 166.13 (4°); other signals (not attributed): complexed arenes 88.88, 88.97, 89.30, 89.34, 89.43, 89.86, 97.84 (4°), 100.60 (4°), non-complexed arenes (one carbon was not detected) 119.95, 125.35, 125.85, 126.88, 127.17, 129.21 (4°), 129.51, 129.61, 129.74, 129.99, 130.71, 131.01, 131.43, 131.81 (4°), 132.01, 134.13 (4°), 135.01 (4°), 144.12 (4°), 149.77 (4°). HRMS (LSIMS): **IIb** calc. for $[C_{25}H_{22}FeNO]^+$ 408.1051, found 408.1061, **II'b** calc. for $[C_{25}H_{22}FeN]^+$ 392.1102, found 392.1119.

*4.4.4. Nitrone–imine mixture ($IIc_{0.8} + II'c_{0.2}$)$(PF_6)^-$*

The procedure used for **IIa** + **II'a** gave the mixture ($IIc_{0.8} + II'c_{0.2}$)$(PF_6)^-$ as a yellow powder (91% yield). $^1$H NMR (60 MHz): **IIc** (80%): Cp 5.38 (5H, s), Me 2.27 (3H, s); **II'c** (20%): Cp 5.35 (5H, s) Me 2.25 (3H, s); aromatics 6.40–7.60 (14H, m).

*4.4.5. Z-(η⁵-Cyclopentadienyl)[(1,2,2,3,3,4-η⁶)-benzophenone-N-(3'-methyl phenyl)nitrone]iron(II) hexafluorophosphate ($IIc(PF_6)^-$)*

Four recrystallisations of the nitrone–imine mixture gave pure ($IIc(PF_6)^-$) as an orange microcrystalline solid (22% yield calc. from **II**). $[C_{25}H_{22}FeNO][PF_6]$ found (calc.): C, 53.94 (54.27); H, 3.97 (4.01); Fe, 9.75 (10.09); N, 2.34 (2.53); P, 5.56 (5.60%). IR $\nu$ (cm$^{-1}$): N → O (1252). $E_{1/2}$ (V vs. SCE): −0.23, −0.40. $^1$H NMR: Cp 5.38 (5H, s), Me 2.27 (3H, s), complexed ring 6.60–6.63 (3H, m), 7.02–7.07 (2H, m), non-complexed rings 7.12–7.27 (3H, m), 7.36–7.40 (4H, m), 7.44–7.50 (2H, m). $^{13}$C NMR: Cp 78.43, $C_1$ 88.77, $C_2$ 88.97*, $C_3$ 88.95*, $C_4$ 98.02, $C_5$ 149.83, $C_6$ 134.84, $C_7$ 132.20, $C_8$ 129.77, $C_9$ 130.46, $C_{1'}$ 143.06, $C_{2'}$ 125.96, $C_{3'}$ 139.83, Me 21.02, $C_{4'}$ 130.63, $C_{5'}$ 129.35, $C_{6'}$ 122.48.

*4.4.6. Nitrone–imine mixture ($IId_{0.85} + II'd_{0.15}$)$(PF_6)^-$*

The procedure used for **IIb** + **II'b** gave the mixture ($IId_{0.85}$ + $II'd_{0.15}$)$(PF_6)^-$ as a yellow powder (92% yield). $^1$H NMR (60 MHz): **IId** (85%): Cp 5.39 (5H, s), Me 2.28 (3H, s); **II'd** (15%): Cp 5.30 (5H, s) Me 2.23 (3H, s); aromatics 6.40–7.60 (14H, m).

*4.4.7. Z-(η⁵-Cyclopentadienyl)[(1,2,2,3,3,4-η⁶)-benzophenone-N-(4'-methyl phenyl)nitrone]iron(II) hexafluorophosphate ($IId(PF_6)^-$)*

Five recrystallisations of the nitrone–imine mixture gave pure ($IId(PF_6)^-$) as an orange microcrystalline solid (25% yield calc. from **II**). $[C_{25}H_{22}FeNO][PF_6]$ found (calc.): C, 54.55 (54.27); H, 3.93 (4.01); Fe, 9.84 (10.09); N, 2.51 (2.53); P, 5.35 (5.60%). IR $\nu$ (cm$^{-1}$): N → O (1244). $E_{1/2}$ (V vs. SCE): −0.27, −0.42. $^1$H NMR: Cp 5.39 (5H, s), Me 2.28 (3H, s), complexed ring 6.60–6.64 (3H, m), 7.02–7.05 (2H, m), non-complexed rings 7.14 (2H, d, $^3J$ = 8), 7.36–7.41 (5H, m), 7.44–7.48 (2H, m). $^{13}$C NMR: Cp 78.43, $C_1$ 88.74, $C_2$ 88.96*, $C_3$ 88.92*, $C_4$ 98.13, $C_5$ 147.71, $C_6$ 134.99, $C_7$ 132.21, $C_8$ 129.84, $C_9$ 130.45, $C_{1'}$ 142.98, $C_{2'}$ 125.32, $C_{3'}$ 130.03, $C_{4'}$ 140.21, Me 21.03.

*4.5. General synthesis procedure of [(η⁵-Cp)(η⁶-α-arylketone)Fe]⁺ complexes*

Imine complex **Ia**$(PF_6)^-$ (0.80 g, 1.54 mmol) was dissolved and stirred for 10 min in 60 ml of a mixture of acetone and aqueous 1 N HCl (1:1, v:v) at room temperature. After elimination of acetone by rotary evaporation, dilution with water and addition of 1 g of $NH_4PF_6$, the ketone complex **Ii**$(PF_6)^-$ was extracted with $CH_2Cl_2$. The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation. Addition of cold ether induced formation of a precipitate which was filtered and washed with ether. After drying under vacuum, 0.56 g of **Ii**$(PF_6)^-$ was isolated as a fine yellow-orange powder (82% yield).

*4.5.1. (η⁵-Cyclopentadienyl)[(1,2,3,4,4$_a$,9$_a$-η⁶)-fluorenone]iron(II) hexafluorophosphate ($Ii(PF_6)^-$)*

IR $\nu$ (cm$^{-1}$): C=O (1719). $E_{1/2}$ (V vs. SCE): −0.44. $^1$H NMR: Cp 5.16 (5H, s), complexed ring 6.83

(1H, t, $^3J = 6$), 6.92 (1H, t, $^3J = 6$), 7.07 (1H, d, $^3J = 6$), 7.38 (1H, d, $^3J = 6$), non-complexed ring 7.71 (1H, t, $^3J = 7$), 7.85–7.91 (2H, m), 8.14 (1H, d, $^3J = 7$). $^{13}$C NMR: Cp 80.97, CO 192.15, complexed ring 84.46, 85.59, 88.97, 90.57, 88.82 (4°), 103.97 (4°), non-complexed ring 124.39, 125.71, 132.94, 137.41, 134.87 (4°), 142.05 (4°).

#### 4.5.2. *($\eta^5$-Cyclopentadienyl)[(1,2,2,3,3,4-$\eta^6$)-benzophenone]iron(II) hexafluorophosphate (IIi($PF_6$)$^-$)*

Hydrolysis of the nitrone–imine mixture (**IIa**$_{0.9}$ + **II'a**$_{0.1}$)($PF_6$)$^-$ in 6N HCl–acetone (1:1, v:v) for 45 min at room temperature led to the ketone complex (**IIi**($PF_6$)$^-$) as a yellow powder (91% yield). IR $\nu$ (cm$^{-1}$): C=O (1672). $E_{1/2}$ (V vs. SCE): −0.60. $^1$H NMR: Cp 5.30 (5H, s), complexed ring 6.70–6.78 (3H, m), 6.93 (2H, d, $^3J = 6$), non-complexed ring 7.63 (2H, t, $^3J = 7$), 7.78 (1H, t, $^3J = 7$), 7.97 (2H, d, $^3J = 7$). $^{13}$C NMR: Cp 79.54, CO 194.30, complexed ring 88.90, 90.17, 90.61, 100.21 (4°), non-complexed ring 129.84, 130.89, 135.20, 136.41 (4°).

#### 4.5.3. *X-ray analysis of the anti isomer of the compound Ia*

A monocrystal of this isomer was obtained from slow evaporation of a THF solution of the syn–anti mixture of **Ia**.

$FeNC_{24}H_{18}$, $PF_6$: $M_r = 521.23$; monoclinic, $P2_1/n$, $a = 9.072(3)$, $b = 12.729(6)$, $c = 19.345(6)$ Å, $\beta = 102.88(2)°$, $V = 2178(1)$ Å$^{-3}$, $Z = 4$, $D_x = 1.590$ Mg m$^{-3}$, $\lambda$(Mo K$\alpha$) = 0.70926 Å, $\mu = 8.25$ cm$^{-1}$, $F(000) = 1056$, $T = 294$ K, final $R = 0.059$ for 1912 observations. The sample (0.25 × 0.25 × 0.40 mm$^3$) was studied on an automatic diffractometer CAD4 Enraf–Nonius with graphite monochromatised Mo K$\alpha$ radiation. The cell parameters were obtained by fitting a set of 25 high-$\Theta$ reflections. The data collection ($2\Theta_{max} = 50°$, scan $\omega/2\Theta = 1$, $t_{max} = 60$ s, range *hkl*: *h* 0,10 *k* 0,15 *l* −22,22, intensity controls without appreciable decay (0.2%) gave 4283 reflections from which 1912 independent ($R = 0.028$) with $I > 3\sigma(I)$. After Lorentz and polarisation corrections the structure was solved by direct methods which revealed all the non-hydrogen atoms of the compound. After isotropic ($R = 0.13$), then anisotropic refinement ($R = 0.09$), many hydrogen atoms were found with a Fourier difference (between 0.51 and 0.30 e Å$^{-3}$). The whole structure was refined by the full-matrix least squares techniques (use of $F$ magnitude; $x$, $y$, $z$, $\beta_{ij}$ for Fe, P, N and C atoms, $x$, $y$, $z$, $B$ for F atoms and $x$, $y$, $z$ for H atoms; 299 variables and 1912 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting $R = 0.064$, $R_w = 0.059$ and $S_w = 1.90$ (residual $\Delta\rho \leq 0.39$ e Å$^{-3}$). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The calculations were performed on a Digital Micro VAX 3100 computer with the MOLEN package (Enraf–Nonius, 1990) [20].

#### 4.5.4. *X-ray analysis of the compound IIa*

A monocrystal was obtained from slow evaporation of a THF–acetone solution of **Ia**. The compound crystallised with one molecule of acetone.

$FePF_6O_2NC_{28}H_{26}$: $M_r = 609.34$; triclinic, $P\bar{1}$, $a = 8.294(9)$, $b = 11.71(2)$, $c = 14.798(9)$ Å, $\alpha = 86.60(9)$, $\beta = 87.84(7)°$, $V = 1433(3)$ Å$^{-3}$, $Z = 2$, $D_x = 1.412$ Mg m$^{-3}$, $\lambda$(Mo K$\alpha$) = 0.70926 Å, $\mu = 6.418$ cm$^{-1}$, $F(000) = 624$, $T = 294$ K, final $R = 0.082$ for 3047 observations. The sample (0.25 × 0.35 × 0.35 mm$^3$) was studied on an automatic diffractometer CAD4 Enraf–Nonius with graphite monochromatised Mo K$\alpha$ radiation. The cell parameters were obtained by fitting a set of 25 high-$\Theta$ reflections. The data collection ($2\Theta_{max} = 50°$, scan $\omega/2\Theta = 1$, $t_{max} = 60$ s, range *hkl*: *h* 0,9 *k* −13,13 *l* −17,17, intensity controls without appreciable decay (0.3%) gave 5413 reflections from which 3047 independent ($R = 0.023$) with $I > 3\sigma(I)$. After Lorentz and polarisation corrections the structure was solved by direct methods with the program SHELX-86 (Sheldrick, 1985) which revealed all the non hydrogen atoms of the compound. After isotropic ($R = 0.12$), then anisotropic refinement ($R = 0.09$), many hydrogen atoms were found with a Fourier difference (between 0.62 and 0.27 e Å$^{-3}$). The whole structure was refined by full-matrix least squares techniques (use of $F$ magnitude; $x$, $y$, $z$, $\beta_{ij}$ for Fe, P, N, C and O atoms, $x$, $y$, $z$, $B$ for F atoms and $x$, $y$, $z$ for H atoms; 410 variables and 3047 observations; $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{-1/2}$) with the resulting $R = 0.086$, $R_w = 0.082$ and $S_w = 1.98$ (residual $\Delta\rho \leq 0.86$ e Å$^{-3}$). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The calculations were performed on a Hewlett Packard 9000-710 for structure determination and on a Digital Micro VAX 3100 computer with the MOLEN package (Enraf–Nonius, 1990) for refinement and ORTEP calculations [20,21].

## 5. Supplementary material

Complete crystallographic data of complexes **Ia** and **IIa** are available from the authors.

## Acknowledgements

The authors gratefully thank Dr. S. Sinbandhit, Dr. P. Guenot, D. Rondeau (C.R.M.P.O.) for NMR and HRMS, and Dr. R.M.G. Roberts (University of Essex) for his generous communication of preliminary results on microwave synthesis of (Cp Fe arene)$^+$ complexes.

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