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Electrochemical reduction of some [(η^5-Cyclopentadienyl) (η^6-arene) iron(II)][PF_6] complexes bearing an imine or a nitrone function in benzylic position of the arene ligand

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Abstract

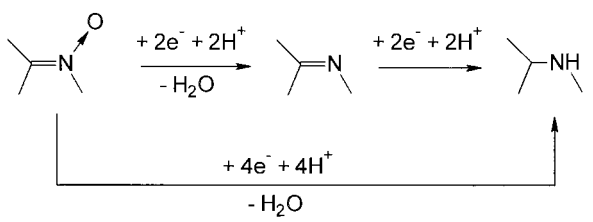
The electrochemical reduction in basic hydro-organic media of mixtures of [(η^5-Cp) (η^6-benzophenone-*N*-(aryl)nitrone) Fe]$^+$ **1a–d** and [(η^5-Cp) (η^6-benzophenone anil) Fe]$^+$ complexes **1′a–d** led to the corresponding [(η^5-Cp) (η^6-α-(arylamino)diphenylmethane) Fe]$^+$ cations **2a–d** with good yields (85–90%). In a similar manner, various [(η^5-Cp) (η^6-9-(arylamino)fluorene) Fe]$^+$ cations **4a–i** were synthesized (70–88% yield) in acidic hydro-organic media from the corresponding [(η^5-Cp) (η^6-fluorenone anil) Fe]$^+$ **3a–i** or the [(η^5-Cp) (η^6-fluorenone-*N*-(2′-methoxycarbonyl phenyl)nitrone) Fe]$^+$ derivative **3′i**. According to ^{1}H NMR chemical shifts, the *exo* isomer is formed in the majority (*exo*:*endo* ca. 75:25) during electrosynthesis of compounds **4a–i**. We could explain these unexpected results by an epimerization in the electrolysis media. The amines **4a,b** were re-oxidized by oxygen into the starting imine **3a,b** under very mild Al_2O_3-catalysis conditions (77–80% yield). © 1998 Elsevier Science S.A.

Keywords: Iron; Cyclopentadienyl; Arene; Electrochemical reduction; Secondary amine; O_2-oxidation

1. Introduction

[(η^5-Cp) (η^6-arene) Fe]$^+$ cations have widely contributed to the transition metal activated aromatic chemistry [1–4]. In the last decade, numerous publications have appeared describing the use of such complexes in the field of macromolecular chemistry [5–15] [16–21] and organic synthesis [22–32] [33–43] [44,45]. However, owing to the reductible character of the organometallic moiety [46–51] and the sensitivity of the arene ligand towards hydride addition [52–55], their use in processes involving a reduction step may be potentially restricted. In this perspective, electrochemistry can be a powerful technique for selective reducing of the functions borne by the ligands [56–61]. Control of the electrode potential has shown to be very efficient to attain a good selectivity in many redox reactions [62].

In a precedent paper [63], we described the condensation reaction of various nitrosoarenes with (Cp Fe diphenylmethane)$^+$ and (Cp Fe fluorene)$^+$ complexes. This reaction afforded a very useful synthesis route to mixtures of (Cp Fe benzophenone-*N*-(aryl)nitrone)$^+$ and (Cp Fe benzophenone anil)$^+$ or to various (Cp Fe fluorenone anil)$^+$ cations. In this work, polarographic investigations revealed the two successive reduction steps of nitrones into amines functions, via the imine compounds [64] (Scheme 1). Following our research on benzylic C–H activation applied to the formation of Carbon–Nitrogen bonds, we report herein a highly effi-



Scheme 1.

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cient electrochemical reduction of these nitrone and imines cations and discuss some particular features of the resulting amines.

2. Results and discussion

2.1. Electrosynthesis of some $[(\eta^5\text{-Cp})\ (\eta^6\text{-}\alpha\text{-(arylamino)diphenylmethane) Fe}]^+$ cations

The controlled potential reduction of nitrone–imine mixtures **1a–d** + **1′a–d** at a mercury cathode, in ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_3, H_2O 0.5 mol l^{-1})-acetone (1:1, v:v) led to the corresponding amine complexes **2a–d** with good yields (Scheme 2). The nitrone functions were reduced by a four-electron process and the imines by a two electron process. We measured coulometric data between two and four Faradays per mole of substrate, depending on the composition of the starting mixtures (Table 1). For each compound, the reduction wave (ca. −1.40 V vs. SCE) which may be attributed to the reduction of the iron unit remained unchanged after the electrochemical process.

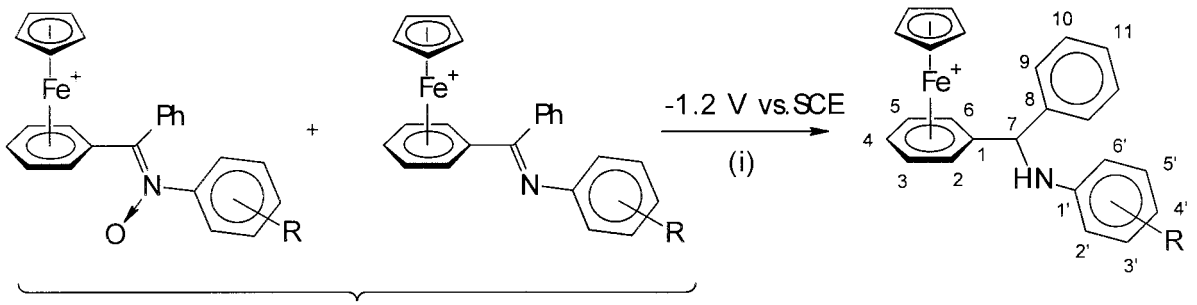
After work-up, the new compounds **2a–d** were fully characterized by high resolution Liquid Secondary Ions Mass Spectrometry (LSIMS), I.R. spectroscopy, elemental analyses, ^1H and ^{13}C NMR spectroscopy. NMR signals assignments were determined on the grounds of shielding effects of the metal complexation, gated decoupling experiments and comparison between the four products of the series (variation of the methyl position). The structural data are reported in Section 4, but some of them have to be highlighted here. All the amines are identified in ^1H NMR by an AB system with a ^3J coupling constant of ca. 9.5 Hz, corresponding to the two protons H-7 and NH. ^{13}C spectra exhibits six metal-bonded carbon signals, showing that C-2, C-3 and C-6, C-5 respectively are diastereotopic. This feature, resulting from the presence of the chiral carbon C-7 and the non equivalence of both sides of the complexed ring, is in agreement with the proposed structures.

The electroreduction is thus highly selective and allows the simultaneous reduction of both nitrone and imine functions with preservation of the organometallic moiety.

Table 1
Electrochemical data of nitrone–imine mixtures **1a–d** + **1′a–d**

Compound	$E_{1/2}$ (V vs. SCE)[a]			Coulometric data[b]
	nitrone	imine	$Fe^{II} \rightarrow Fe^{I}$	±0.1 F mol^{-1}
1a + **1′a** (90:10)	−0.72	−0.95	−1.42	3.8
1b + **1′b** (70:30)	−0.84	−0.97	−1.39	3.4
1c + **1′c** (80:20)	−0.79	−1.07	−1.44	3.5
1d + **1′d** (85:15)	−0.77	−0.97	−1.42	3.6

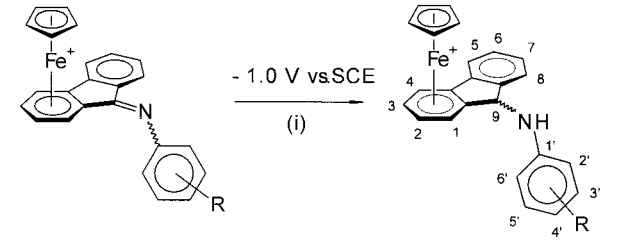
[a]Ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_3,H_2O 0.5 mol l^{-1})-acetone (1:1, v:v).
[b]$E = -1.2$ V vs. SCE.



R =	H	**1 a**	+	**1 'a**	(90:10)	**2 a**	90%
	2'-Me	**1 b**	+	**1 'b**	(70:30)	**2 b**	89%
	3'-Me	**1 c**	+	**1 'c**	(80:20)	**2 c**	85%
	4'-Me	**1 d**	+	**1 'd**	(85:15)	**2 d**	85%

(i) conditions : ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_3,H_2O 0.5 mol l^{-1})-acetone (1:1, v:v), Hg cathode,
nitrone : + $4H^+$ + $4e^-$ - H_2O, imine : + $2H^+$ + $2e^-$

Scheme 2.



R =				
H	**3a**	**4a**	88%
2'-Me	**3b**	**4b**	84%
3'-Me	**3c**	**4c**	81%
4'-Me	**3d**	**4d**	87%
2'-Cl	**3e**	**4e**	88%
4'-Cl	**3f**	**4f**	79%
2'-CH_2CO_2Me	**3g**	**4g**	70%
4'-COMe	**3h**	**4h**	81%

(i) conditions : acetic buffer (CH_3CO_2Na 0.5 or 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v), Hg cathode, + $2H^+$ + $2e^-$

Scheme 3.

2.2. Electrosynthesis of some [(η^5-Cp) (η^6-9-(arylamino)fluorene) Fe]$^+$ cations

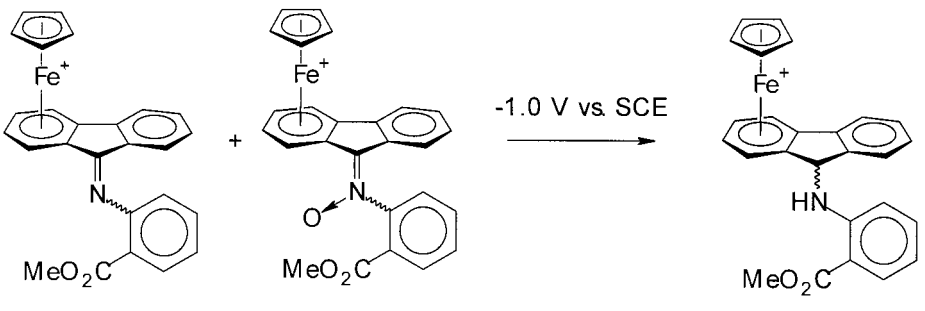
(Cp Fe fluorenone anil)$^+$ derivatives **3a–h** and the imine–nitrone mixture **3i + 3′i** were electrochemically reduced in acidic hydro-organic media, leading to the corresponding amine complexes **4a–i** with good yields (Schemes 3 and 4). The coulometric data reported in Table 2 are in agreement with a two electron process for the reduction of the imines **3a–i** and four electron process for the reduction of the nitrone **3′i**. The reduction waves of the iron units at ca. −1.30 V vs. SCE were not affected by the electroreduction. The air-sensitive complexes **4a–i** were isolated in satisfactory purity under argon atmosphere and fully characterized by I.R. spectroscopy, mass spectrometry (LSIMS), elemental analyses, ^1H and ^{13}C NMR spectroscopy.

Table 2
Electrochemical data of imines complexes **3a–h** and imine–nitrone mixture **3i + 3′i**

Compound	Medium[a]	$E_{1/2}$ (V vs. SCE)		Coulometric data[b]
		imine	$Fe^{II} \rightarrow Fe^{I}$	±0.1 F mol^{-1}
3a	A	−0.47	−1.33	2.0
3b	B	−0.44	−1.31	2.0
3c	A	−0.46	−1.32	2.0
3d	A	−0.42	−1.30	2.0
3e	B	−0.41	−1.29	1.9
3f	C	−0.65	−1.30	2.0
3g	B	−0.45	−1.32	2.1
3h	A	−0.39	−1.33	2.1
3i + 3′i	A	−0.43[c]	−1.30	2.9

[a] **A**: acetic buffer (CH_3CO_2Na 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v); **B**: acetic buffer (CH_3CO_2Na 0.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v); **C**: ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_3,H_2O 0.5 mol l^{-1})-acetone (1:1,v:v).
[b] $E = -1.0$ V vs. SCE.
[c] The imine and the nitrone are reduced at the same potential in this medium.

Two diastereomers *exo* and *endo* are formed during the electrolysis, as is evident from the NMR spectra which displays two signal sets of unequal intensity (Table 3). Complete signal attributions were conducted on complexes **4a** and **4i** by using 2D-^1H,^{13}C correlation and ^1H,^1H COSY experiments, and by taking into account the well-known [65] metal-bonding effects on chemical shifts and coupling constants. ^1H and ^{13}C assignments of the other fluorene derivatives **4b–h** were done by reference to **4a** and **4i**, using ^1H coupling ^{13}C spectra and gated decoupling experiments. Some se-



3i + **3'i** (60:40) **4i** 84%

Scheme 4.

Table 3
Diastereomer ratios of amino complexes **4a–i** (based on ^{1}H NMR integrals in CD_3CN)

Compound	R	*exo*:*endo*
4a	H	75:25
4b	2′-Me	85:15
4c	3′-Me	75:25
4d	4′-Me	75:25
4e	2′-Cl	80:20
4f	4′-Cl	80:20
4g	2′-CH_2CO_2Me	80:20
4h	4′-COMe	70:30
4i	2′-CO_2Me	45:55 (60:40) [a]

[a] in DMSO-d_6.

Table 4
Selected ^{13}C and ^{1}H NMR data of amine derivatives **4a–i** (δ (ppm from TMS), *J* (Hz), solvent: CD_3CN)

Complex	$\delta_{C\text{-}9}$		$^1J_{C\text{-}9,H\text{-}9}$		$\delta_{H\text{-}9}$		$^3J_{H\text{-}9,NH}$	
	exo	*endo*	*exo*	*endo*	*exo*	*endo*	*exo*	*endo*
4a	61.07	59.65	142	137	6.12	5.87	9.2	7.9
4b	60.99	59.64	141	136	6.19	5.94	9.3	7.3
4c	61.02	59.64	142	136	6.11	5.86	9.9	8.0
4d	61.49	60.00	142	136	6.07	5.82	8.9	7.9
4e	60.74	58.93	141	135	6.21	6.01	9.5	8.4
4f	61.05	59.63	142	138	6.09	5.84	9.7	7.9
4g	61.06	59.81	142	136	6.18	5.93	9.2	7.8
4h	60.20	58.95	142	138	6.22	5.97	9.2	7.8
4i	60.06	58.12	142	139	6.30	6.09	8.8	8.7

lected data listed in Table 4 emphasize typical differences which permitted the assignments of both isomers signals in each mixture.

According to previous works on electrochemical reduction of (Cp Fe arene)$^+$ complexes in hydro-organic media [58–61], one might attempt that upon electrolysis, the C-9 protonation step takes place in *trans* to the metal, leading preferentially to the *endo* isomer. Surprisingly, it can be taken as evidence that, except for **4i**, the *exo* amino complex is present in the majority. This is based on an analysis of protons chemical shifts of the R-C_6H_4-NH– fragment and H-9. The data resumed in Table 5 point out that H-9 in the major isomer undergoes a downfield shift of 0.25 ppm compared with the minor isomer. In regard to a series of contributions of Moriarty et al. [66], McGlinchey et al. [67] and Top et al. [68], this clearly indicates its localization on the complexed side of the fluorene plane, whereas the opposite effect is being observed for the protons of the arylamino fragment (Fig. 1). McGlinchey et al. analyzed the diamagnetic anisotropy of various organometallic moieties. Their studies suggested that a downfield shift is observed for the protons located on the side of the metal moiety and an upfield shift for protons located on the other side of the plane. Moreover, in (Cp Fe fluorene)$^+$ series these effects has been unambiguously demonstrated in 1977 by Johnson and Treichel [69] (Scheme 5). A transposition of these observations to our phenylamino complexes seems to be reasonably thinkable.

In order to explain these unexpected results, the amine **4b** (*exo*:*endo*-85:15) was submitted to recrystallization in CH_2Cl_2 at −25°C, leading to a mixture enriched with the *endo* isomer (*exo*:*endo*-55:45). By stirring it in acetic buffer-acetone at room temperature for one night, after work-up we could recover in 80% yield the initial mixture ratio (*exo*:*endo*-85:15) (Fig. 2A and B). This result clearly demonstrate that in the acidic electrolysis media, the *endo* isomer is epimerized into the more stable *exo* isomer. According to precedent reports on highly stereoselective electrolyses of (Cp Fe arene)$^+$ cations [58–61], we may assume that our reduction process is also stereoselective. However the experiments described above show that the reaction can be followed by a rearrangement which leads to the thermodynamic equilibrium (Scheme 6). The isomer ratio resulting from the electrosynthesis of **4i** (*exo*:*endo*-45:55) may be explained by a slower epimerization rate. This rate could be enhanced in DMSO, as is evident from an

Table 5
variation of ^{1}H chemical shifts between *exo* and *endo* isomers of **4a–i**. R-C_6H_4-NH– group and H-9 (solvent CD_3CN)

Complex	$\Delta\delta$ (ppm) = $\delta exo - \delta endo$						
	H-9	R-C_6H_4-NH–					
		ortho		*meta*		*para*	*R*
		H-2′	H-6′	H-3′	H-5′	H-4′	
4a	+0.25	−0.37	–	−0.17	–	−0.11	–
4b	+0.25	–	−0.5	−0.2	−0.2	−0.1	−0.22 (2′-Me)
4c	+0.25	−0.32	−0.37	–	−0.17	−0.10	−0.11 (3′-Me)
4d	+0.25	−0.38	–	−0.18	–	–	−0.10 (4′-Me)
4e	+0.20	–	−0.67	−0.17	−0.30	−0.17	–
4f	+0.25	−0.37	–	−0.18	–	–	–
4g	+0.25	–	−0.5	−0.16	−0.2	−0.1	−0.25 (2′-CH_2–)
4h	+0.25	−0.37	–	−0.18	–	–	−0.08 (4′-COMe)
4i	+0.21	–	−0.69	−0.14	−0.30	−0.16	−0.05 (2′-CO_2Me)

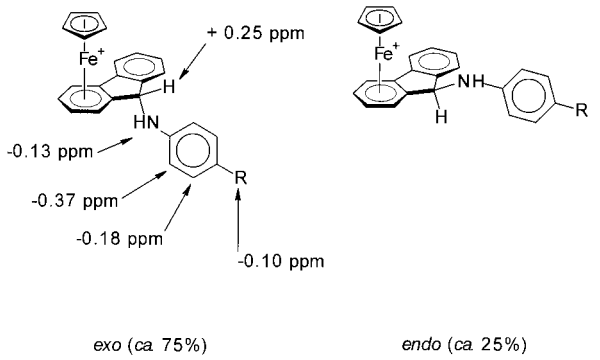


Fig. 1. Variations of ^{1}H NMR chemical shifts between *exo* and *endo* isomers of *para*-substituted amines **4a**, **4d**, **4f** and **4h** (R = H, 4′-Me, 4′-COMe, 4′-Cl).

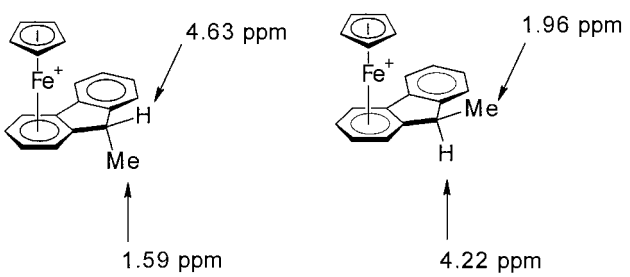
NMR spectrum in this solvent which displayed an *exo*:*endo* isomer ratio of 60:40 respectively.

To support the hypothesis of a stereoselective reaction leading to the *endo* complex, the imine **3b** was reduced into **4b** by sodium borohydride in dichloromethane. Despite a low yield (40%) and an incomplete reduction (20% of **3b** was detected), the *endo* isomer was clearly formed in a large majority (*exo*:*endo*-10:90)(Fig. 2C).

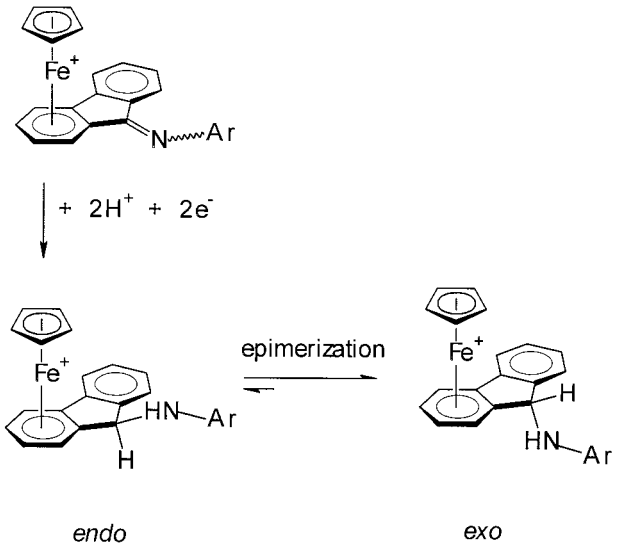
An attempt to characterize the *exo* epimer by X-ray diffraction study failed. From slow crystallization of the isomer mixture **4b** (*exo*:*endo*-85:15) in CH_2Cl_2/pentane, a monocrystal revealed an *endo*-type molecular structure (Fig. 3). This conflicting observation may be easily explained by the lower solubility of the *endo* complex in CH_2Cl_2 as shown above, and by a better ability of this epimer to crystallize.

2.3. O_2-oxidation of [(η^5-Cp) (η^6-9-(arylamino)fluorene) Fe]$^+$ cations

Upon isolation of the amine **4a,b** under air atmosphere, we noticed in the isolated products the presence of appreciable amounts (10–15%) of the starting imine **3a,b**, despite a complete disappearance of their polarographic reduction wave at the end of the electrolysis.



Scheme 5.



Scheme 6.

This observation prompt us to further investigate the reactivity of the amines **4a,b** toward oxygen. When bubbling O_2 in a solution of amines **4a** or **4b** in basic hydro-organic media (ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_3, H_2O 0.5 mol l^{-1})-acetone (1:1,v:v)) the reduction wave of imine functions were rapidly recovered whereas in acidic media, no oxidation was detected. At a preparative scale, O_2-oxidation of amines **4a** and **4b** in the presence of alumina (Al_2O_3) was the more efficient technique and led to the imine complexes **3a** and **3b** with good yields (Scheme 7).

The reaction proceeded selectively under very mild conditions. Oxidation of amines into imines has been thoroughly investigated [70–72] and is generally difficult to control or require harsh oxidant conditions. In a first assumption, the high selectivity observed in our reaction and its base catalysis may be explained by a high stability of the anil cations and by an increased acidity of the proton H-9.

3. Conclusion

This work further demonstrates the efficiency of electrochemical processes. We have shown that highly chemio-selective reduction occurs on (Cp Fe arene)$^+$ complexes, providing various (Cp Fe α-(aryl amino)arene)$^+$ derivatives with good yield. In connection with the nitrosoarene condensation [63], this methodology constitutes an efficient two-step introduction of a secondary arylamino group onto a benzylic chain (Scheme 8).

Otherwise, these amino complexes still possess a benzylic carbon liable to be deprotonated and to react

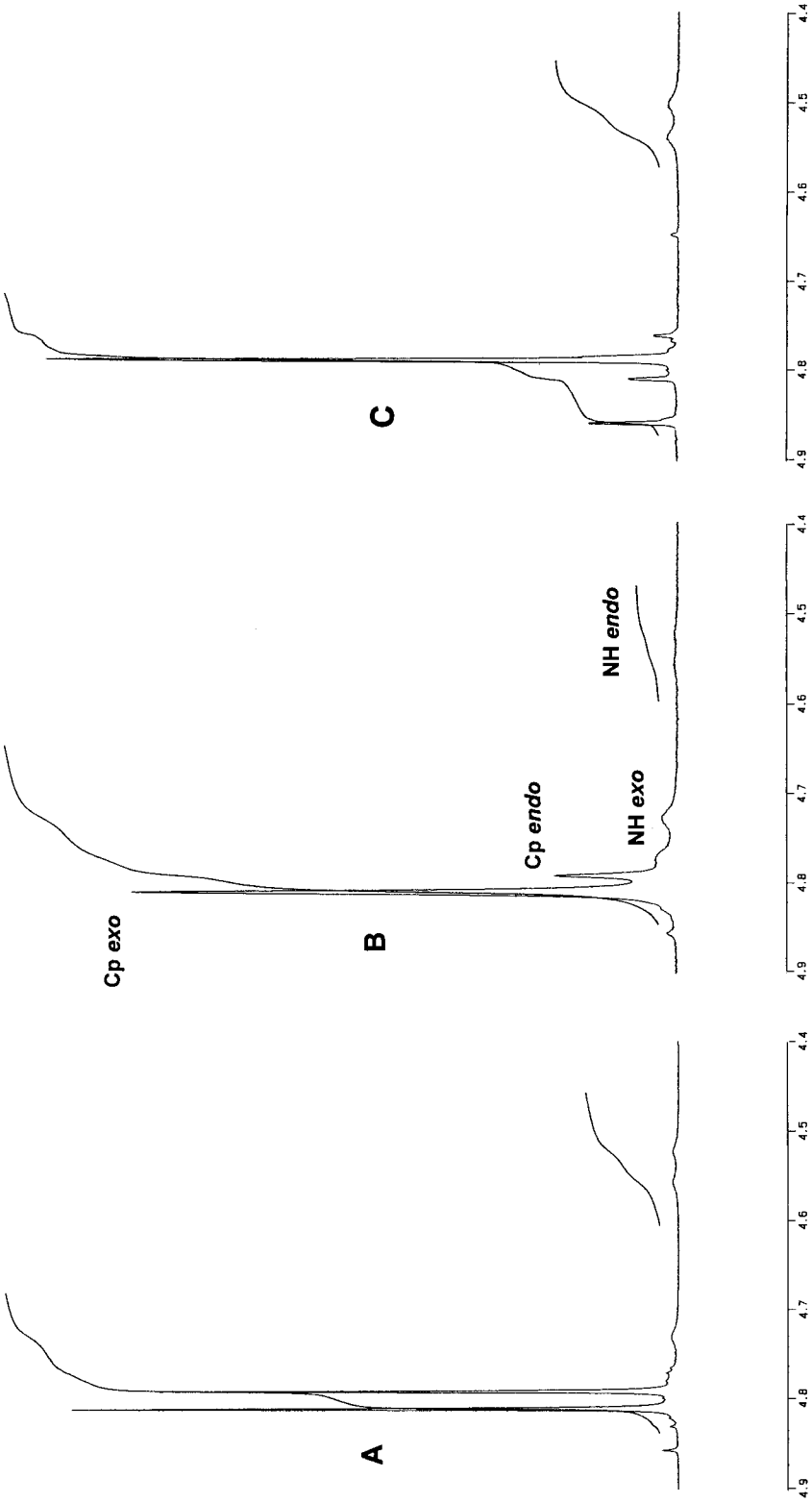


Fig. 2. ^{1}H NMR spectra of varied *exo*–*endo* isomer mixtures of **4b** (ppm from TMS, CD_3CN). (**A**) after recrystallization in CH_2Cl_2 at −25°C, *exo*:*endo*-55:45; (**B**) after epimerization of the precedent mixture in acetic buffer (CH_3CO_2Na 0.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v), *exo*:*endo*-85:15; (**C**) after partial $NaBH_4$ reduction of imine **3b**, *exo*:*endo*-10:90.

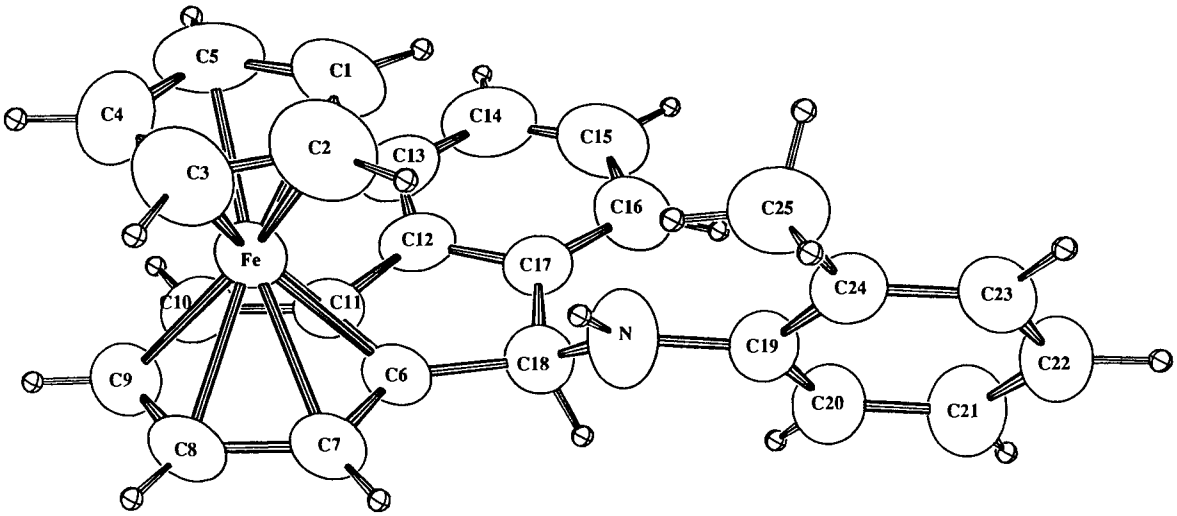


Fig. 3. ORTEP drawing of the *endo* isomer of **4b**. Selected interatomic distances (Å): Fe–C(1) 2.023(9), Fe–C(2) 2.03(1), Fe–C(3) 2.04(1), Fe–C(4) 2.03(1), Fe–C(5) 2.04(1), Fe–C(6) 2.10(1), Fe–C(7) 2.08(1), Fe–C(8) 2.059(9), Fe–C(9) 2.071(8), Fe–C(10) 2.078(8), Fe–C(11) 2.096(9), N–C(18) 1.41(1), N–C(19) 1.38(1), N–H(26) 0.972(8).

with electrophiles. Additional studies are underway to use such complexes in further syntheses.

4. Experimental section

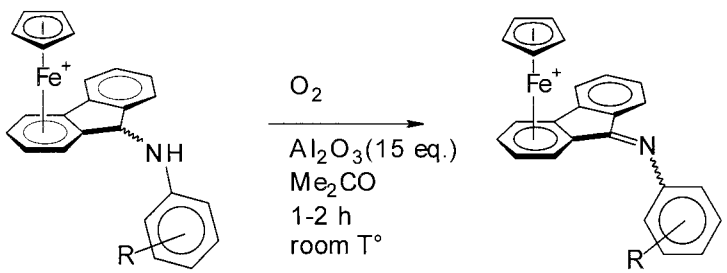
4.1. General methods

Conventional electrochemical equipment was used for polarography and electrolyses (EG&G Princeton Applied Research model 362-scanning potentiostat with an XY recorder). Controlled potential electrolyses were performed at a mercury pool cathode, under nitrogen atmosphere, in a cell previously described by Moinet and Peltier [73,74]. Electrolyses were monitored by polarography (Scan-rate: 5 mV s^{-1}; drop-time τ: 2 s). The coulometric measurements were determined with a current integrator Tacussel model IG 5 N.

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

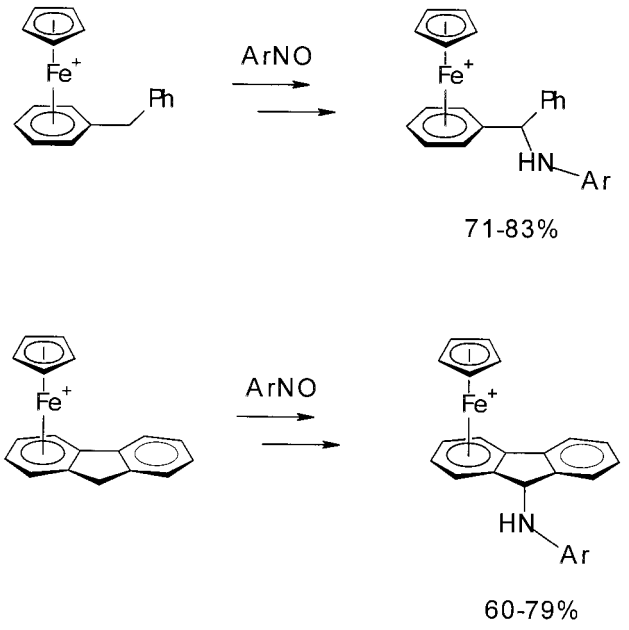
Mass spectra were obtained on a VG Analytical ZAB Spec TOF high resolution mass spectrometer (EBE TOF Geometry) at the Centre Régional de Mesures Physiques de l'Ouest (C.R.M.P.O.). Ionization type was LSIMS (Liquid Secondary Ions Mass Spectrometry) with Cs^+ ions, the matrix was 3-nitro-benzylique alcohol (*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. ^{13}C NMR broad band and gated decoupling spectra were recorded. 2D-^{1}H,^{13}C correlation and ^{1}H,^{1}H-COSY



R = H	**4a**	**3a**	80%
2'-Me	**4b**	**3b**	77%

Scheme 7.



Scheme 8.

spectra were recorded in some particular cases. The solvent was CD_3COCD_3 or CD_3CN. Samples were filtered through a small column of celite 477 (5×10 mm) prior to being poured into the NMR tubes.

4.2. Reagents

All (Cp Fe arene)$^+$ complexes were handled with minimal exposure to visible light. Amine complexes **4a–i** were isolated and manipulated in solution under argon atmosphere by using conventional Schlenck techniques. Solvents (reagent grade) were used without further purification, with the exception of THF which was distilled from sodium benzophenone under nitrogen.

Nitrone–imine mixtures (**1a–d** + **1′a–d**), (**3i** + **3′i**) and imines **3a–h** were synthesized by *t*-BuOK-catalysed condensation of various nitrosoarenes with [(η^5-Cp) (η^6-diphenylmethane) Fe]$^+$ and [(η^5-Cp) (η^6-fluorene) Fe]$^+$ according to our precedent paper [63]. Characterization data of complexes **3e–g** and (**3i** + **3′i**) have not been described in this report.

4.2.1. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-fluorenone-(2′-chloro)-anil]iron(II) hexafluorophosphate (syn–anti mixture (25:75)) (**3e**$(PF_6)^-$)

Obtained by reacting (Cp Fe fluorene)$^+(PF_6)^-$ (1.08 g, 2.5 mmol), 2-chloronitrosobenzene (0.55 g, 3.5 mmol) and *t*-BuOK (15 mg, 0.13 mmol) for 5 min (90% yield). $[C_{24}H_{17}NFeCl][PF_6]$ found (calc.): C, 51.95 (51.87); H, 3.11 (3.09); N, 2.47 (2.52); Cl, 6.50 (6.38%). HRMS (LSIMS): calc. for $[C_{24}H_{17}NFeCl]^+$ 410.0399, found 410.0400. IR ν (cm^{-1}): C=N (1658). $E_{1/2}$ (0.1 N H_2SO_4-acetone (1:1,v:v)): -0.23 V vs. SCE. ^{1}H NMR (CD_3CN): **anti** (75%): $\delta = 4.89$ (s, Cp), 7.02 (d, ^3J = 6.3, H-1), 6.50 (t, $^3J = 6.2$, H-2), 6.55 (t, $^3J = 6.1$, H-3), 7.09 (d, $^3J = 6.4$, H-4), 7.99 (d, $^3J = 7.7$, H-5), 7.64 (t, $^3J = 7.7$, H-6), 7.31 (t, $^3J = 7.7$, H-7), 6.74 (d, $^3J = 7.9$, H-8), 7.63 (d, $^3J = 7.8$, H-3′), 7.33 (t, $^3J = 7.8$, H-4′*), 7.47 (t, $^3J = 7.7$, H-5′*), 7.12 (d, $^3J = 7.9$, H-6′), for attribution of H-5, H-6, H-7 and H-8 irradiation at 6.74 and 7.99 ppm; **syn** (25%): $\delta = 4.79$ (s, Cp), 5.56 (d, $^3J = 6.5$, H-1), 6.10 (t, $^3J = 6.4$, H-2), 6.46 (t, $^3J = 6.3$, H-3), 7.03 (d, $^3J = 6.4$, H-4), 8.06 (d, $^3J = 7.5$, H-5), 7.76 (t, $^3J = 7.5$, H-6), 7.68 (t, $^3J = 7.5$, H-7), 7.99 (d, $^3J = 7.7$, H-8), 7.68 (d, $^3J = 8.0$, H-3′), 7.37 (t, $^3J = 7.8$, H-4′*), 7.49 (t, $^3J \approx 8$, H-5′*), 7.13 (d broad, $^3J \approx 8$, H-6′), for attribution of H-1, H-2, H-3 and H-4 irrad. at 6.46 ppm. ^{13}C NMR (CD_3CN): **anti** : $\delta = 80.41$ (Cp), 84.70 (C-1), 88.11 (C-2), 89.20 (C-3), 83.01 (C-4), 103.57 (C-4a), 95.51 (C-9a), 140.81 (C-4b), 124.48 (C-5), 135.09 (C-6), 132.50 (C-7), 127.57 (C-8), 132.62 (C-8a), 164.07 (C-9), 148.25 (C-1′), 122.29 (C-2′), 131.39 (C-3′), 127.48* (C-4′), 129.59* (C-5′), 120.31 (C-6′), for attribution of C-3′, irradiation at 7.62 ppm; **syn**: $\delta = 80.65$ (Cp), 86.89 (C-1), 87.87 (C-2), 89.63 (C-3), 84.06 (C-4), 104.31 (C-4a), 88.29 (C-9a), 139.44 (C-4b), 123.70 (C-5), 135.00 (C-6), 132.74 (C-7), 124.91 (C-8), 138.19 (C-8a), 163.69 (C-9), 148.09 (C-1′), C-2′ non detected, 131.74 (C-3′), 127.76* (C-4′), 129.79* (C-5′), 120.16 (C-6′).

4.2.2. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-fluorenone-(4′-chloro)-anil]iron(II) hexafluorophosphate (syn–anti mixture (30:70)) (**3f**$(PF_6)^-$)

Obtained by reacting (Cp Fe fluorene)$^+(PF_6)^-$ (1.08 g, 2.5 mmol), 4-chloronitrosobenzene (0.55 g, 3.5 mmol) and *t*-BuOK (15 mg, 0.13 mmol) for 10 min. Recrystallized in CH_2Cl_2/Ether for eliminating of ca. 5% of (Cp Fe fluorenone)$^+(PF_6)^-$ detected as by-product (61% yield) $[C_{24}H_{17}NFeCl][PF_6]$ found (calc.): C, 51.67 (51.87); H, 3.10 (3.09); N, 2.47 (2.52); Cl, 6.14 (6.38%). HRMS (LSIMS): calc. for $[C_{24}H_{17}NFeCl]^+$ 410.0399, found 410.0403. IR ν (cm^{-1}): C = N (1655). $E_{1/2}$ (0.1 N H_2SO_4-acetone (1:1,v:v)): -0.23 V vs. SCE. ^{1}H NMR (CD_3CN): **anti** (70%): $\delta = 4.86$ (s, Cp), 7.00 (d, $^3J \approx 6$, H-1*), 6.47 (t, $^3J = 6.3$, H-2), 6.52 (t, $^3J = 6.2$, H-3), 7.02 (d, $^3J \approx 6$, H-4*), 7.98 (d, $^3J = 7.5$, H-5), 7.62 (t, $^3J = 7.6$, H-6), 7.31 (t, $^3J = 7.7$, H-7), 6.88 (d, $^3J = 7.8$, H-8), 7.09 (d, $^3J = 8.8$, H-2′), 7.53 (d, $^3J = 8.8$, H-3′); **syn** (30%): $\delta = 4.77$ (s, Cp), 5.61 (d, $^3J = 6.5$, H-1), 6.09 (t, $^3J = 6.3$, H-2), 6.44 (t, $^3J = 6.3$, H-3), H-4 overlapped with H-1 and H-4 anti (7.0 ppm), 8.00 (d, $^3J = 7.3$, H-5), 7.66 (t, $^3J = 7.5$, H-6), 7.74 (t, $^3J = 7.4$, H-7), 7.97 (d, $^3J = 7.4$, H-8), 7.11 (d, $^3J = 8.6$, H-2′), 7.57 (d, $^3J = 8.8$, H-3′). ^{13}C NMR (CD_3CN): **anti** : $\delta = 80.35$ (Cp), 84.45 (C-1), 88.06 (C-2), 89.14 (C-3), 82.80 (C-4), 103.30 (C-4a), 95.75 (C-9a), 140.97 (C-4b), 124.41 (C-5), 134.73 (C-6), 132.06 (C-7), 128.18

(C-8), 132.19 (C-8a), 162.69 (C-9), 150.20 (C-1′), 120.60 (C-2′), 130.79 (C-3′), 131.14 (C-4′); **syn**: δ = 80.50 (Cp), 87.35 (C-1), 87.71 (C-2), 89.42 (C-3), 83.84 (C-4), 104.45 (C-4a), 88.11 (C-9a), 139.19 (C-4b), 123.57 (C-5), 134.73 (C-6), 132.65 (C-7), 124.77 (C-8), 138.47 (C-8a), 162.43 (C-9), 149.99 (C-1′), 120.38 (C-2′), 131.18 (C-3′), 131.34 (C-4′).

*4.2.3. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-fluorenone-(2′-methoxycarbonylmethylene)-anil]iron(II) hexafluorophosphate (syn–anti mixture (20:80)) (**3g**$(PF_6)^-$)*

Obtained by reacting (Cp Fe fluorene)$^+(PF_6)^-$ (1.08 g, 2.5 mmol), methyl-(2-nitroso)phenylacetate (0.63 g, 3.5 mmol) and *t*-BuOK (15 mg, 0.13 mmol) for 10 min (95% yield). $[C_{27}H_{22}NO_2Fe][PF_6]$ found (calc.): C, 54.59 (54.66); H, 3.74 (3.75); N, 2.66 (2.36%). HRMS (LSIMS): calc. for $[C_{27}H_{22}NO_2Fe]^+$ 448.1000, found 448.0991. IR ν (cm^{-1}): C=N (1660), C=O (1737). $E_{1/2}$ (0.1 N H_2SO_4-acetone (1:1,v:v)): −0.28 V vs. SCE. ^{1}H NMR (CD_3COCD_3): Owing to very broad signals, aromatic protons were not attributed. This is probably due to slow rotation around the C1′–N bond. Attempts to simplify the spectrum at lower or higher temperature failed; δ = 6.0–8.2 (m, 12H, aromatic), 5.13 (anti, 80%) and 5.08 (syn, 20%) (two singlets, 5H, Cp), 3.79 (AB, δ_A = 3.83, δ_B = 3.75, J_{AB} = 15.3, 2H, CH_2), 3.42 (s, 3H, Me). ^{13}C NMR (CD_3COCD_3): **anti** : δ = 80.25 (Cp), 84.50 (C-1), 87.99 (C-2), 89.19 (C-3), 83.00 (C-4), 103.34 (C-4a), 95.72 (C-9a), 140.94 (C-4b), 124.16 (C-5), 134.49 (C-6), 131.77 (C-7), 127.97 (C-8), 132.41 (C-8a), 162.45 (C-9), 150.03 (C-1′), 125.42 (C-2′), 132.47 (C-3′), 126.57 (C-4′), 129.24 (C-5′), 118.54 (C-6′), 38.27 (CH_2), 172.12 (CO), 52.16 (CH_3); **syn**: δ = 80.60 (Cp), 87.21* (C-1), 87.39* (C-2), 89.64 (C-3), 83.92 (C-4), 103.92 (C-4a), 88.83 (C-9a), 139.25 (C-4b), 123.41 (C-5), 134.42 (C-6), 132.28 (C-7), 124.53 (C-8), 138.76 (C-8a), 161.91 (C-9), 149.50 (C-1′), C-2′ non detected, 132.70 (C-3′), 126.91 (C-4′), 129.41 (C-5′), 118.73 (C-6′), 37.85 (CH_2), 172.42 (CO), 52.16 (CH_3).

*4.2.4. Mixture of (η^5-cyclopentadienyl) [1-9$_a$-η^6-fluorenone-(2′-methoxycarbonyl)-anil]iron(II) hexafluorophosphate and (η^5-Cyclopentadienyl) [1-9$_a$-η^6-fluorenone-n-(2′-methoxycarbonyl phenyl)nitrone]iron(II) hexafluorophosphate ((**3i**$_{0.6}$ + **3′i**$_{0.4}$)$(PF_6)^-$)*

Obtained by reacting (Cp Fe fluorene)$^+(PF_6)^-$ (1.08 g, 2.5 mmol), methyl-(2-nitroso)benzoate (1.24 g, 7.5 mmol) and *t*-BuOK (15 mg, 0.13 mmol) for 1 h (77% yield). $[C_{26}H_{20}NO_{2.4}Fe][PF_6]$ found (calc.): C, 53.17 (53.33); H, 3.36 (3.44); N, 2.36 (2.39%). HRMS (LSIMS): calc. for $[C_{26}H_{20}NO_3Fe]^+$ 450.0793, found 450.0807, calc. for $[C_{26}H_{20}NO_2Fe]^+$ 434.0843, found 434.0844. The ratio of each compound could be estimated by polarography according to our precedent work [63], $E_{1/2}$ (1 N H_2SO_4-acetone (1:1,v:v)): nitrone −0.09 V vs. SCE, imine −0.18 V vs. SCE. IR ν (cm^{-1}): C=N (1657), C=O (1722), N→O (1288). ^{1}H NMR (CD_3COCD_3): The spectrum indicate the presence of several isomers for the imine **3i** and the nitrone **3′i**. Owing to broad signals (slow rotation around the C1′–N bond) and complexity of the spectrum, we could not achieve the complete interpretation of the data.; δ = 5.7–8.9 (m, 12H, aromatic), 5.17, 5.10, 5.03, 5.00 (broad), 4.91 (five singlets, 5H, Cp), 3.99, 3.91, 3.81, 3.70, 3.62 (five singlets, 3H, CO_2Me). The reduction of the mixture into the amine **4i** (84% yield) and the coulometric data (2.9 F mol^{-1}) are in agreement with the composition of the mixture.

*4.3. General synthesis procedure of amine complexes **2a–d***

The nitrone–imine mixture (**1a**$_{0.9}$ + **1′a**$_{0.1}$)$(PF_6)^-$ (0.50 g, 0.93 mmol) was dissolved in a mixture (150 ml) of ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_3,H_2O 0.5 mol l^{-1}) and acetone (1:1,v:v). The solution was electrolyzed at a mercury pool cathode at −1.20 V vs. SCE until consumption of 3.8 Faradays per mole of substrate. The electrolysis was stopped and the hydro-organic mixture was separated from mercury. After elimination of acetone by rotary evaporation and addition of 1 g of NH_4PF_6, the amine complex **2a** was extracted with CH_2Cl_2 (2 × 75 ml). The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation. Addition into 300 ml of cold ether induced formation of a precipitate which was filtered and washed with ether. After drying under vacuum, **2a**$(PF_6)^-$ (0.44 g, 0.84 mmol) was isolated as a fine pale yellow powder (90% yield).

*4.3.1. (η^5-Cyclopentadienyl) [1-6-η^6-α-(phenylamino)diphenylmethane]iron(II) hexafluorophosphate (**2a**$(PF_6)^-$)*

$[C_{24}H_{22}NFe][PF_6]$ found (calc.): C, 54.81 (54.88); H, 4.28 (4.22); N, 2.71 (2.67%). HRMS (LSIMS): calc. for $[C_{24}H_{22}NFe]^+$ 380.1102, found 380.1108. IR ν (cm^{-1}): N-H (3416). ^{1}H NMR (CD_3COCD_3): δ = 5.10 (s, 5H, Cp), 6.46–6.52 (m, 3H) 6.57 (t, ^3J = 6.0, 1H) 6.87 (d, ^3J = 6.5, 1H) (H-2, H-3, H-4, H-5 and H-6), 7.65 (d, ^3J = 7.1, 2H, H-9), 7.42 (t, $^3J \approx 7$, 2H, H-10), 7.32 (t, ^3J = 7.3, 1H, H-11), 6.13 (AB, δ_A = 6.09 (H-7), δ_B = 6.18 (broad,NH), $^3J_{AB}$ = 9.5, 2H), 6.95 (d, ^3J = 7.7, 2H, H-2′), 7.15 (t, $^3J \approx 7$, 2H, H-3′), 6.68 (t, ^3J = 7.3, 1H, H-4′). ^{13}C NMR (CD_3COCD_3): δ = 78.04 (Cp),.86.97, 88.19, 88.27, 88.33 and 88.52 (C-2, C-3, C-4, C-5 and C-6), 111.21 (C-1), 60.48 (C-7), 142.49 (C-8), 128.21 (C-9), 129.92* (C-10), 129.08 (C-11), 147.91 (C-1′), 114.97 (C-2′), 130.07* (C-3′), 119.05 (C-4′).

*4.3.2. (η^5-Cyclopentadienyl) [1-6-η^6-α-(2′-methyl phenylamino)diphenylmethane]iron(II) hexafluorophosphate (**2b**$(PF_6)^-$)*

Electrolysis of the nitrone–imine mixture (**1b**$_{0.7}$ + **1′b**$_{0.3}$)$(PF_6)^-$ (0.55 g, 1.00 mmol) consumed 3.4 Faradays per mole of substrate and lead to 0.48 g of **2b**$(PF_6)^-$ (89% yield). $[C_{25}H_{24}NFe][PF_6]$ found (calc.): C, 55.01 (55.68); H, 4.53 (4.49); N, 2.48 (2.60%). HRMS (LSIMS): calc. for $[C_{25}H_{24}NFe]^+$ 394.1258, found 394.1252. IR ν (cm^{-1}): N-H (3413). ^{1}H NMR (CD_3COCD_3): $\delta = 5.10$ (s, 5H, Cp), 6.40–6.52 (m, 3H) 6.58 (t, $^3J \approx 6$, 1H) 6.96 (d, $^3J = 6.5$, 1H) (H-2, H-3, H-4, H-5 and H-6), 7.72 (d, $^3J = 7.1$, 2H, H-9), 7.45 (t, $^3J \approx 7$, 2H, H-10), 7.35 (t, $^3J \approx 7$, 1H, H-11), 6.16 (d, $^3J = 8.9$, 1H, H-7), 5.30 (d broad, $^3J = 9.0$, 1H, NH), 7.07 (d, $^3J = 7.6$, 1H, H-3′), 6.64 (t, $^3J = 7.3$, 1H, H-4′), 7.02 (t, $^3J = 7.5$, 1H, H-5′), 6.91 (d, $^3J \approx 8$, 1H, H-6′), 2.29 (s, 3H, Me). ^{13}C NMR (CD_3COCD_3): $\delta =$ 78.00 (Cp), 87.68, 88.15, 88.24, 88.40 and 88.58 (C-2, C-3, C-4, C-5 and C-6), 111.03 (C-1), 60.55 (C-7), 142.22 (C-8), 128.34 (C-9), 129.97 (C-10), 129.18 (C-11), 145.43 (C-1′), 124.45 (C-2′), 131.30 (C-3′), 119.17 (C-4′), 127.63 (C-5′), 112.89 (C-6′), 18.08 (Me).

*4.3.3. (η^5-Cyclopentadienyl) [1-6-η^6-α-(3′-methyl phenylamino)diphenylmethane]iron(II) hexafluorophosphate (**2c**$(PF_6)^-$)*

Electrolysis of the nitrone–imine mixture (**1c**$_{0.8}$ + **1′c**$_{0.2}$)$(PF_6)^-$ (1.10 g, 2.00 mmol) consumed 3.5 Faradays per mole of substrate and lead to 0.92 g of **2c**$(PF_6)^-$ (85% yield). $[C_{25}H_{24}NFe][PF_6]$ found (calc.): C, 55.80 (55.68); H, 4.71 (4.49); N, 2.59 (2.60%). HRMS (LSIMS): calc. for $[C_{25}H_{24}NFe]^+$ 394.1258, found 394.1259. IR ν (cm^{-1}): N-H (3406). ^{1}H NMR (CD_3COCD_3): $\delta = 5.10$ (s, 5H, Cp), 6.41–6.61 (m, 4H) 6.87 (d, $^3J = 6.5$, 1H) (H-2, H-3, H-4, H-5 and H-6), 7.63 (d, $^3J = 7.1$, 2H, H-9), 7.41 (t, $^3J \approx 7$, 2H, H-10), 7.32 (t, $^3J = 7.3$, 1H, H-11), 6.09 (AB, $\delta_A = 6.06$ (broad,NH), $\delta_B = 6.12$ (H-7), $^3J_{AB} = 9.6$, 2H), 6.82 (s broad, 1H, H-2′), 6.76 (d, $^3J = 8.0$, 1H, H-4′), 7.03 (t, $^3J = 7.8$, 1H, H-5′), 6.52 (d, $^3J \approx 8$, 1H, H-6′), 2.22 (s, 3H, Me), for attribution of H-4′ and H-6′ irradiation at 7.03 ppm. ^{13}C NMR (CD_3COCD_3): $\delta = 78.04$ (Cp), 86.79, 88.21, 88.25, 88.29 and 88.48 (C-2, C-3, C-4, C-5 and C-6), 111.37 (C-1), 60.43 (C-7), 142.65 (C-8), 128.17 (C-9), 129.89 (C-10), 129.02 (C-11), 147.91 (C-1′), 115.75 (C-2′), 139.59 (C-3′), 120.00 (C-4′), 129.99 (C-5′), 112.14 (C-6′), 21.67 (Me), for attribution of C-8 and C-9 irrad. at 6.12 ppm, for C-1′, C-2′, C-3′ and C-4′ irrad. at 2.22 ppm.

*4.3.4. (η^5-Cyclopentadienyl) [1-6-η^6-α-(4′-methyl phenylamino)diphenylmethane]iron(II) hexafluorophosphate (**2d**$(PF_6)^-$)*

Electrolysis of the nitrone–imine mixture (**1d**$_{0.85}$ + **1′d**$_{0.15}$)$(PF_6)^-$ (0.90 g, 1.63 mmol) consumed 3.6 Faradays per mole of substrate and lead to 0.75 g of **2d**$(PF_6)^-$ (85% yield). $[C_{25}H_{24}NFe][PF_6]$ found (calc.): C, 55.67 (55.68); H, 4.63 (4.49); N, 2.54 (2.60%). HRMS (LSIMS): calc. for $[C_{25}H_{24}NFe]^+$ 394.1258, found 394.1253. IR ν (cm^{-1}): N-H (3405). ^{1}H NMR (CD_3COCD_3): $\delta = 5.12$ (s, 5H, Cp), 6.43–6.55 (m, 3H) 6.59 (t, $^3J \approx 6$, 1H) 6.87 (d, $^3J \approx 6$, 1H) (H-2, H-3, H-4, H-5 and H-6), 7.63 (d, $^3J = 7.8$, 2H, H-9), 7.41 (t, $^3J \approx 7$, 2H, H-10), 7.32 (t, $^3J = 7.3$, 1H, H-11), 6.02 (AB, $\delta_A = 5.98$ (broad, NH), $\delta_B = 6.07$ (H-7), $^3J_{AB} =$ 9.7, 2H), 6.91 (AB, $\delta_A = 6.86$, $\delta_B = 6.97$, $^3J_{AB} = 8.4$, 4H, H-2′ and H-3′), 2.17 (s, 3H, Me). ^{13}C NMR (CD_3COCD_3): $\delta = 78.03$ (Cp), 86.86, 88.19, 88.24, 88.27 and 88.47 (C-2, C-3, C-4, C-5 and C-6), 111.36 (C-1), 60.84 (C-7), 142.68 (C-8), 128.18 (C-9), 129.87 (C-10), 129.00 (C-11), 145.60 (C-1′), 115.28 (C-2′), 130.54 (C-3′), 128.04 (C-4′), 20.43 (Me).

*4.4. General synthesis procedure of amine complexes **4a–i***

The imine complex **3a**$(PF_6)^-$ (0.98 g, 1.88 mmol) was dissolved in a mixture (150 ml) of acetic buffer (CH_3CO_2Na 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1}) and acetone (1:1,v:v). The solution was electrolyzed at a mercury pool cathode at −1.00 V vs. SCE until consumption of 2.0 Faradays per mole of substrate. The electrolysis was stopped and the hydro-organic mixture was poured into a schlenk tube under argon atmosphere. After elimination of acetone by evaporation under vacuum and addition of 1 g of NH_4PF_6, the amine complex **4a** was extracted with CH_2Cl_2 (2 × 25 ml). The organic layer was dried over $MgSO_4$ and concentrated. Addition into 200 ml of cold ether induced formation of a precipitate which was filtered and washed with ether. After drying under vacuum, **4a**$(PF_6)^-$ (0.87 g, 1.66 mmol) was isolated as a fine pale yellow powder (88% yield).

*4.4.1. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (75:25)) (**4a**$(PF_6)^-$)*

$[C_{24}H_{20}NFe][PF_6]$ found (calc.): C, 54.79 (55.09); H, 3.97 (3.86); N, 2.66 (2.68%). HRMS (LSIMS): calc. for $[C_{24}H_{20}NFe]^+$ 378.0945, found 378.0946. IR ν (cm^{-1}): N-H (3416 broad). NMR: ^{1}H, ^{13}C-correlation experiment. ^{1}H NMR (CD_3CN): **exo** (75%): $\delta = 4.80$ (s, Cp), 6.71 (d, $^3J = 6.2$, H-1), 6.17 (t, $^3J = 6.2$, H-2), 6.31 (t, $^3J = 6.2$, H-3), 6.91 (d, $^3J = 6.2$, H-4), 7.98 (d, $^3J \approx 7$, H-5), 7.58 (t, $^3J \approx 7$, H-6), 7.56 (t, $^3J \approx 7$, H-7), 7.66 (d, $^3J \approx 7$, H-8), 6.12 (d, $^3J = 9.2$, H-9), 5.10 (d broad, $^3J = 9.4$, NH),6.75 (d, $^3J \approx 8$, H-2′), 7.16 (t, $^3J \approx 8$, H-3′), 6.74 (t, $^3J \approx 8$, H-4′), for attribution of H-9 irrad. at 5.10 ppm, for H-1, H-2, H-3 and H-4 irrad. at 6.17 and 6.31 ppm and gated decoupling ^{13}C experiment (6.12 ppm) showing by off-resonance the long range coupling of H-2 with C-9a, for attribution of H-5, H-6, H-7 and H-8 gated dec. ^{13}C at 7.99 ppm showing long

range coupling of H-5 with C-4a, C-7 and C-8a; **endo** (25%): $\delta = 4.75$ (s, Cp), 6.55 (d, $^3J = 6.4$, H-1), 6.13 (t, $^3J = 6.2$, H-2), 6.32 (t, $^3J = 6.1$, H-3), 6.94 (d, $^3J \approx 6$, H-4), 7.98 (d, $^3J \approx 7$, H-5), 7.68 (t, $^3J \approx 7$, H-6 and H-7), 7.68 (d, $^3J \approx 7$, H-8), 5.87 (d, $^3J = 7.9$, H-9), 5.23 (d broad, $^3J = 7.7$, NH), 7.12 (d, $^3J \approx 8$, H-2′), 7.33 (t, $^3J \approx 8$, H-3′), 6.85 (t, $^3J = 7.3$, H-4′), for attribution of H-2′, H-3′ and H-4′ irrad. at 7.13 and 7.33 ppm. ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.11$ (Cp), 86.61 (C-1), 86.74 (C-2), 87.57 (C-3), 80.99 (C-4), 104.96 (C-4a), 110.07 (C-9a), 136.86 (C-4b), 123.35 (C-5), 130.75 (C-6), 132.06 (C-7), 126.80 (C-8), 145.71 (C-8a), 61.07 (C-9), 147.79 (C-1′), 115.20 (C-2′), 130.51 (C-3′), 119.67 (C-4′), for attribution of C-7, quaternary carbons C-9a, C-4a, C-4b, C-8a and C-1′ irrad. at 6.12 and 7.99 ppm; **endo**: $\delta = 78.43$ (Cp), 85.12 (C-1), 85.76 (C-2), 87.57 (C-3), 81.30 (C-4), 103.50 (C-4a), 112.85 (C-9a), 137.29 (C-4b), 123.57 (C-5), 130.63 (C-6), 131.61 (C-7), 126.63 (C-8), 147.07 (C-8a), 59.65 (C-9), 148.89 (C-1′), 114.15 (C-2′), 130.85 (C-3′), 119.54 (C-4′) for attribution of C-7, C-9a, C-4a, C-4b and C-8a irrad. at 7.99 ppm.

*4.4.2. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(2′-methyl phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (85:15)) (**4b**(PF_6)$^-$)*

Electrolysis of the imine **3b**(PF_6)$^-$ (0.70 g, 1.31 mmol) in acetic buffer (CH_3CO_2Na 0.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.0 Faradays per mole of substrate and lead to 0.59 g of **4b**(PF_6)$^-$ (84% yield). [$C_{25}H_{22}NFe$][PF_6] found (calc.): C, 55.64 (55.89); H, 4.15 (4.14); N, 2.67 (2.61%). HRMS (LSIMS): calc. for [$C_{25}H_{22}NFe$]$^+$ 392.1102, found 392.1104. IR ν (cm^{-1}): N-H (3411). ^{1}H NMR (CD_3CN): **exo** (85%): $\delta = 4.81$ (s, Cp), 6.73 (d, $^3J = 6.5$, H-1), 6.18 (t, $^3J = 6.2$, H-2), 6.32 (t, $^3J = 6.2$, H-3), 6.92 (d, $^3J = 6.3$, H-4), 7.97–8.04 (m, H-5), 7.53–7.64 (m, H-6 and H-7), 7.64–7.80 (m, H-8), 6.19 (d, $^3J = 9.3$, H-9), 4.74 (d broad, $^3J = 9.5$, NH), 7.07 (d broad, $^3J \approx 8$, H-3′), 6.68 (t, $^3J = 7.4$, H-4′), 7.02 (t broad, $^3J = 7.4$, H-5′), 6.76 (d, $^3J = 7.5$, H-6′), 2.08 (s, Me),for attribution of H-9 irrad. at 4.74 ppm and gated dec. ^{13}C at 6.19 ppm, for H-3′, H-4′, H-5′ and H-6′gated dec. ^{13}C at 7.02, 7.07, 6.68 and 6.76 ppm; **endo** (15%): $\delta = 4.79$ (s, Cp), 6.61 (d, $^3J = 6.2$, H-1), 6.17 (t, $^3J = 6.2$, H-2), 6.34 (t, $^3J = 6.2$, H-3), 6.96 (d, $^3J = 6.2$, H-4), 7.97–8.04 (m, H-5), 7.53–7.64 (m, H-6 and H-7), 7.64–7.80 (m, H-8), 5.94 (d, $^3J = 7.4$, H-9), 4.52 (d broad, $^3J = 7.3$, NH), 7.21–7.29 (m, H-3′, H-5′ and H-6′), 6.80–6.85 (m, H-4′), 2.30 (s, Me). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.09$ (Cp), 86.74 (C-1), 86.74 (C-2), 87.53 (C-3), 80.85 (C-4), 105.14 (C-4a), 110.39 (C-9a), 136.85 (C-4b), 123.36 (C-5), 130.69 (C-6), 132.11 (C-7), 126.69 (C-8), 146.09 (C-8a), 60.99 (C-9), 145.47 (C-1′), 124.62 (C-2′), 131.73 (C-3′), 119.39 (C-4′), 128.00 (C-5′), 112.54 (C-6′), 18.01 (Me), for attribution of C-7 and quaternary carbons C-9a, C-4a, C-4b, C-8a irrad. at 8.01, 7.57 and 7.60 ppm; **endo**: $\delta = 78.37$ (Cp), 85.02 (C-1), 85.85 (C-2), 87.71 (C-3), 81.40 (C-4), 103.57 (C-4a), 112.28 (C-9a), 137.26 (C-4b), 123.57 (C-5), 130.60 (C-6), 131.64* (C-7), 126.78 (C-8), 147.50 (C-8a), 59.64 (C-9), 146.39 (C-1′), 124.18 (C-2′), 131.92* (C-3′), 119.65 (C-4′), 128.52 (C-5′), 111.64 (C-6′), 18.48 (Me).

*4.4.3. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(3′-methyl phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (75:25)) (**4c**(PF_6)$^-$)*

Electrolysis of the imine **3c**(PF_6)$^-$ (0.92 g, 1.71 mmol) in acetic buffer (CH_3CO_2Na 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.0 Faradays per mole of substrate and lead to 0.75 g of **4c**(PF_6)$^-$ (81% yield). [$C_{25}H_{22}NFe$][PF_6] found (calc.): C, 55.80 (55.89); H, 4.11 (4.14); N, 2.62 (2.61%). HRMS (LSIMS): calc. for [$C_{25}H_{22}NFe$]$^+$ 392.1102, found 392.1124. IR ν (cm^{-1}): N-H (3419 broad). ^{1}H NMR (CD_3CN): **exo** (75%): $\delta = 4.80$ (s, Cp), 6.71 (d, $^3J = 6.1$, H-1), 6.17 (t, $^3J = 6.2$, H-2), 6.31 (t, $^3J = 6.2$, H-3), 6.91 (d, $^3J = 6.6$, H-4), 7.95–8.03 (m, H-5), 7.52-7.64 (m, H-6 and H-7), 7.64–7.75 (m, H-8), 6.11 (d, $^3J = 9.9$, H-9), 4.74 (d broad, $^3J = 9.7$, NH), 6.64 (s broad, H-2′), 6.59 (d, $^3J \approx 8$, H-4′), 7.04 (t, $^3J = 7.7$, H-5′), 6.55 (d, $^3J \approx 8$, H-6′), 2.24 (s, Me), for attribution of H-4′, H-5′ and H-6′ irrad. at 7.04 ppm; **endo** (25%): $\delta = 4.75$ (s, Cp), H-1 overlapped with H-4′ and H-6′ exo (6.55–6.59 ppm), 6.13 (t, $^3J = 6.2$, H-2), 6.32 (t, $^3J = 6.1$, H-3), 6.93 (d, $^3J = 6.5$, H-4), 7.95-8.03 (m, H-5), 7.52-7.64 (m, H-6 and H-7), 7.64–7.75 (m, H-8), 5.86 (d, $^3J = 8.0$, H-9), 5.13 (d broad, $^3J = 8.2$, NH), 6.96 (s broad, H-2′), 6.69 (d, $^3J \approx 8$, H-4′), 7.21 (t, $^3J = 7.7$, H-5′), 6.92 (d, $^3J \approx 8$, H-6′), 2.35 (s, Me). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.11$ (Cp), 86.59 (C-1), 86.71 (C-2), 87.57 (C-3), 80.99 (C-4), 104.91 (C-4a), 110.09 (C-9a), 136.86 (C-4b), 123.32 (C-5), 130.75 (C-6), 132.04 (C-7), 126.80 (C-8), 145.81 (C-8a), 61.02 (C-9), 147.83 (C-1′), 116.06 (C-2′), 140.38 (C-3′), 120.59 (C-4′), 130.41 (C-5′), 112.21 (C-6′), 21.76 (Me); **endo**: $\delta = 78.41$ (Cp), 85.16 (C-1), 85.74 (C-2), 87.57 (C-3), 81.28 (C-4), 103.48 (C-4a), 112.91 (C-9a), 137.28 (C-4b), 123.57 (C-5), 130.62 (C-6), 131.61 (C-7), 126.63 (C-8), 147.11 (C-8a), 59.64 (C-9), 148.90 (C-1′), 114.85 (C-2′), 140.71 (C-3′), 120.43 (C-4′), 130.75 (C-5′), 111.32 (C-6′), 21.91 (Me).

*4.4.4. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(4′-methyl phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (75:25)) (**4d**(PF_6)$^-$)*

Electrolysis of the imine **3d**(PF_6)$^-$ (0.56 g, 1.04 mmol) in acetic buffer (CH_3CO_2Na 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.0 Faradays per mole of substrate and lead to 0.49 g of **4d**(PF_6)$^-$ (87% yield). [$C_{25}H_{22}NFe$][PF_6] found (calc.): C, 55.54 (55.89); H, 4.04 (4.14); N, 2.68 (2.61%).

HRMS (LSIMS): calc. for $[C_{25}H_{22}NFe]^+$ 392.1102, found 392.1091. IR ν (cm^{-1}): N-H (3419 broad). ^1H NMR (CD_3CN): **exo** (75%): $\delta = 4.79$ (s, Cp), 6.68 (d, $^3J = 6.2$, H-1), 6.16 (t, $^3J = 6.2$, H-2), 6.30 (t, $^3J = 6.2$, H-3), 6.90 (d, $^3J = 6.4$, H-4), 7.90–8.05 (m, H-5), 7.50–7.63 (m, H-6 and H-7), 7.63–7.75 (m, H-8), 6.07 (d, $^3J = 8.9$, H-9), 4.90 (d broad, $^3J = 9.0$, NH), 6.65 (d, $^3J = 8.3$, H-2′), 6.97 (d broad, $^3J = 8.1$, H-3′), 2.20 (s, Me), for attribution of H-2′ gated dec. ^{13}C at 6.65 ppm; **endo** (25%): $\delta = 4.75$ (s, Cp), 6.54 (d, $^3J = 6.2$, H-1), 6.13 (t, $^3J = 6.2$, H-2), 6.32 (t, $^3J \approx 6$, H-3), 6.92 (d, $^3J \approx 6$, H-4), 7.90–8.05 (m, H-5), 7.50–7.63 (m, H-6 and H-7), 7.63–7.75 (m, H-8), 5.82 (d, $^3J = 7.9$, H-9), 5.01 (d broad, $^3J = 8.0$, NH), 7.09 (AB, $\delta_A = 7.03$, $\delta_B = 7.15$, $^3J_{AB} = 8.4$, H-2′ and H-3′), 2.30 (s, Me). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.08$ (Cp), 86.57 (C-1), 86.70 (C-2), 87.53 (C-3), 80.96 (C-4), 104.95 (C-4a), 110.19 (C-9a), 136.84 (C-4b), 123.31 (C-5), 130.69 (C-6), 132.01 (C-7), 126.80 (C-8), 145.86 (C-8a), 61.49 (C-9), 145.39 (C-1′), 115.55 (C-2′), 130.92 (C-3′), 128.98 (C-4′), 20.53 (Me); **endo**: $\delta = 78.40$ (Cp), 85.11 (C-1), 85.73 (C-2), 87.53 (C-3), 81.28 (C-4), 103.47 (C-4a), 113.00 (C-9a), 137.25 (C-4b), 123.55 (C-5), 130.58 (C-6), 131.59 (C-7), 126.58 (C-8), 147.31 (C-8a), 60.00 (C-9), 146.55 (C-1′), 114.36 (C-2′), 131.25 (C-3′), 128.72 (C-4′), 20.59 (Me).

*4.4.5. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(2′-chloro phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (80:20)) (**4e**$(PF_6)^-$)*

Electrolysis of the imine **3e**$(PF_6)^-$ (0.70 g, 1.26 mmol) in acetic buffer (CH_3CO_2Na 0.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 1.9 Faradays per mole of substrate and lead to 0.62 g of **4e**$(PF_6)^-$ (88% yield). $[C_{24}H_{19}NClFe][PF_6]$ found (calc.): C, 52.10 (51.68); H, 3.56 (3.44); N, 2.44 (2.51); Cl, 6.43 (6.36%). HRMS (LSIMS): calc. for $[C_{24}H_{19}NClFe]^+$ 412.0556, found 412.0575. IR ν (cm^{-1}): N-H (3402). ^1H NMR (CD_3CN): **exo** (80%): $\delta = 4.82$ (s, Cp), 6.75 (d, $^3J \approx 6$, H-1), 6.21 (t, $^3J = 6.2$, H-2), 6.33 (t, $^3J = 6.2$, H-3), 6.93 (d, $^3J = 6.4$, H-4), 8.00–8.03 (m, H-5), 7.54–7.72 (m, H-6, H-7 and H-8), 6.21 (d, $^3J = 9.5$, H-9), 5.42 (d broad, $^3J = 9.5$, NH), 7.30 (d, $^3J = 7.9$, H-3′), 6.72 (t, $^3J = 7.6$, H-4′), 7.08 (t, $^3J = 7.8$, H-5′), 6.76 (d, $^3J \approx 8$, H-6′), for attribution of H-3′, H-4′, H-5′ and H-6′ irrad. at 7.30 ppm and gated dec. ^{13}C at 6.72, 7.08 and 7.30 ppm; **endo** (20%): $\delta = 4.82$ (s, Cp), 6.55 (d, $^3J = 6.2$, H-1), 6.17 (t, $^3J = 6.2$, H-2), 6.36 (t, $^3J = 6.3$, H-3), 6.97 (d, $^3J = 6.4$, H-4), 8.00–8.03 (m, H-5), 7.54–7.72 (m, H-6, H-7 and H-8), 6.01 (d, $^3J = 8.4$, H-9), 5.04 (d broad, $^3J = 8.6$, NH), 7.47 (d, $^3J = 8.1$, H-3′), 6.89 (t, $^3J = 7.5$, H-4′), 7.38 (t, $^3J \approx 8$, H-5′), 7.43 (d, $^3J \approx 8$, H-6′). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.20$ (Cp), 86.85 (C-1), 86.85 (C-2), 87.67 (C-3), 80.98 (C-4), 105.07 (C-4a), 109.53 (C-9a), 136.93 (C-4b), 123.53 (C-5), 130.90 (C-6), 132.22 (C-7), 126.57 (C-8), 145.22 (C-8a), 60.74 (C-9), 143.31 (C-1′), 120.74 (C-2′), 130.74 (C-3′), 120.10 (C-4′), 129.12 (C-5′), 114.22 (C-6′) for attribution of C-1′ irrad. at 7.08 ppm; **endo**: $\delta = 78.43$ (Cp), 85.00 (C-1), 85.91 (C-2), 87.84 (C-3), 81.56 (C-4), 103.82 (C-4a), 111.15 (C-9a), 137.23 (C-4b), 123.72 (C-5), C-6 non detected, 131.87 (C-7), 126.64 (C-8), 146.98 (C-8a), 58.93 (C-9), 144.05 (C-1′), 120.46 (C-2′), 130.86 (C-3′), 120.46 (C-4′), 129.75 (C-5′), 113.60 (C-6′).

*4.4.6. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(4′-chloro phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (80:20)) (**4f**$(PF_6)^-$)*

Electrolysis of the imine **3f**$(PF_6)^-$ (0.70 g, 1.26 mmol) in ammonium buffer ($(NH_4)_2SO_4$ 0.25 mol l^{-1} + NH_4,H_2O 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.0 Faradays per mole of substrate and lead to 0.55 g of **4f**$(PF_6)^-$ (79% yield). $[C_{24}H_{19}NClFe][PF_6]$ found (calc.): C, 51.84 (51.68); H, 3.54 (3.44); N, 2.32 (2.51); Cl, 6.26 (6.36%). HRMS (LSIMS): calc. for $[C_{24}H_{19}NClFe]^+$ 412.0556, found 412.0575. IR ν (cm^{-1}): N-H (3444). ^1H NMR (CD_3CN): **exo** (80%): $\delta = 4.80$ (s, Cp), 6.70 (d, $^3J = 6.5$, H-1), 6.18 (t, $^3J = 6.2$, H-2), 6.32 (t, $^3J = 6.1$, H-3), 6.91 (d, $^3J = 6.2$, H-4), 7.96-8.01 (m, H-5), 7.51–7.63 (m, H-6 and H-7), 7.64–7.70 (m, H-8), 6.09 (d, $^3J = 9.7$, H-9), 5.19 (d broad, $^3J = 9.7$, NH), 6.73 (d, $^3J = 8.9$, H-2′), 7.14 (d, $^3J = 8.9$, H-3′); **endo** (20%): $\delta = 4.75$ (s, Cp), 6.54 (d, $^3J = 6.3$, H-1), 6.13 (t, $^3J = 6.5$, H-2), 6.33 (t, $^3J = 6.2$, H-3), 6.93 (d, $^3J \approx 6$, H-4), 7.96–8.01 (m, H-5), 7.51–7.63 (m, H-6 and H-7), 7.64–7.70 (m, H-8), 5.84 (d, $^3J = 7.9$, H-9), 5.33 (d broad, $^3J = 8.0$, NH), 7.10 (d, $^3J = 9.0$, H-2′), 7.32 (d, $^3J = 8.8$, H-3′). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.14$ (Cp), 86.67 (C-1), 86.78 (C-2), 87.62 (C-3), 81.03 (C-4), 104.93 (C-4a), 109.67 (C-9a), 136.85 (C-4b), 123.39 (C-5), 130.84 (C-6), 132.11 (C-7), 126.80 (C-8), 145.34 (C-8a), 61.05 (C-9), 146.70 (C-1′), 116.54 (C-2′), 130.19 (C-3′), 123.60 (C-4′); **endo**: $\delta = 78.46$ (Cp), 85.13 (C-1), 85.76 (C-2), 87.62 (C-3), 81.33 (C-4), 103.60 (C-4a), 112.48 (C-9a), 137.29 (C-4b), 123.60 (C-5), 130.71 (C-6), 131.63 (C-7), 126.65 (C-8), 146.70* (C-8a), 59.63 (C-9), 147.79* (C-1′), 115.47 (C-2′), 130.50 (C-3′), 123.39 (C-4′).

*4.4.7. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(2′-methoxy-carbonylmethylene phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (80:20)) (**4g**$(PF_6)^-$)*

Electrolysis of the imine **3g**$(PF_6)^-$ (0.50 g, 0.84 mmol) in acetic buffer (CH_3CO_2Na 0.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.1 Faradays per mole of substrate and lead to 0.35 g of **4g**$(PF_6)^-$ (70% yield). $[C_{27}H_{24}NO_2Fe][PF_6]$ found (calc.): C, 54.59 (54.47); H, 4.20 (4.07); N, 2.23 (2.35); P, 5.19 (5.20%). HRMS (LSIMS): calc. for $[C_{27}H_{24}NO_2Fe]^+$ 450.1157, found 450.1138. IR ν (cm^{-1}): N-H (3423 broad), C=O (1733). ^1H NMR

(CD_3CN): **exo** (80%): $\delta = 4.81$ (s, Cp), 6.71 (d, $^3J =$ 6.2, H-1), 6.19 (t, $^3J = 6.2$, H-2), 6.32 (t, $^3J = 6.2$, H-3), 6.92 (d, $^3J = 6.3$, H-4), 7.99–8.03 (m, H-5), 7.54–7.64 (m, H-6 and H-7), 7.65–7.72 (m, H-8), 6.18 (d, $^3J = 9.3$, H-9), 5.01 (d broad, $^3J = 9.2$, NH), 7.10 (d, $^3J = 7.5$, H-3′), 6.76 (t, $^3J = 7.4$, H-4′), 7.13 (t, $^3J = 7.8$, H-5′), 6.86 (d, $^3J = 7.5$, H-6′), 3.52 (s, CH_2), 3.53 (s, CH_3), for attribution of H-3′, H-4′ and H-5′ irrad. at 6.86 ppm; **endo** (20%): $\delta = 4.82$ (s, Cp), 6.63 (d, $^3J = 6.3$, H-1), 6.21 (t, $^3J = 6.2$, H-2), 6.36 (t, $^3J = 6.2$, H-3), 6.98 (d, $^3J = 6.3$, H-4), 7.99–8.03 (m, H-5), 7.54–7.64 (m, H-6 and H-7), 7.65–7.72 (m, H-8), 5.93 (d, $^3J = 7.8$, H-9), 5.26 (d broad, $^3J = 7.8$, NH), 7.26 (d, $^3J = 7.0$, H-3′), H-4′ overlapped with H-6′ and H-4 exo (≈ 6.9 ppm), 7.32–7.39 (m, H-5′ and H-6′), 3.77 (s, CH_2), 3.62 (s, CH_3). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.12$ (Cp), 86.74* (C-1), 86.81* (C-2), 87.57 (C-3), 80.95 (C-4), 105.01 (C-4a), 110.14 (C-9a), 136.83 (C-4b), 123.41 (C-5), 130.76 (C-6), 132.12 (C-7), 126.76 (C-8), 145.91 (C-8a), 61.06 (C-9), 145.82 (C-1′), 122.04 (C-2′), 132.71 (C-3′), 119.86 (C-4′), 129.59 (C-5′), 113.99 (C-6′), 38.20 (CH_2), 172.80 (CO), 52.63 (CH_3), for attribution of C-1′ irrad. at 6.18 and 3.52 ppm; **endo**: $\delta = 78.53$ (Cp), 84.75 (C-1), 85.78 (C-2), 87.80 (C-3), 81.66 (C-4), 103.22 (C-4a), 111.60 (C-9a), 137.28 (C-4b), 123.63 (C-5), 130.60 (C-6), 131.63 (C-7), 126.44 (C-8), 148.00 (C-8a), 59.81 (C-9), 147.17 (C-1′), 121.71 (C-2′), 132.91 (C-3′), 120.18 (C-4′), 130.18 (C-5′), 113.21 (C-6′), 39.15 (CH_2), 173.80 (CO), 53.05 (CH_3).

*4.4.8. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(4′-acetyl phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (70:30)) (**4h**$(PF_6)^-$)*

Electrolysis of the imine **3h**$(PF_6)^-$ (0.63 g, 1.12 mmol) in acetic buffer (CH_3CO_2Na 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.1 Faradays per mole of substrate and lead to 0.51 g of **4h**$(PF_6)^-$ (81% yield). $[C_{26}H_{22}NOFe][PF_6]$ found (calc.): C, 54.75 (55.24); H, 3.85 (3.93); N, 2.51 (2.48%). HRMS (LSIMS): calc. for $[C_{26}H_{22}NOFe]^+$ 420.1051, found 420.1058. IR ν (cm^{-1}): N-H (3412 broad, 3360 broad), C = O (1661). ^{1}H NMR (CD_3CN): **exo** (70%): $\delta = 4.82$ (s, Cp), 6.75 (d, $^3J = 6.5$, H-1), 6.20 (t, $^3J = 6.2$, H-2), 6.34 (t, $^3J = 6.2$, H-3), 6.94 (d, $^3J = 6.2$, H-4), 8.00 (d, $^3J = 7.1$, H-5), 7.50–7.75 (m, H-6, H-7 and H-8), 6.22 (d, $^3J = 9.2$, H-9), 5.76 (d broad, $^3J = 9.2$, NH), 6.78 (d, $^3J = 8.8$, H-2′), 7.79 (d, $^3J = 8.8$, H-3′), 2.44 (s, Me), for attribution of H-9 irrad. at 5.76 ppm, for H-1, H-2′ and H-3′ irrad. at 7.79 ppm; **endo** (30%): $\delta = 4.79$ (s, Cp), 6.55 (d, $^3J = 6.3$, H-1), 6.15 (t, $^3J = 6.2$, H-2), 6.34 (t, $^3J \approx 6$, H-3), 6.95 (d, $^3J = 6.1$, H-4), 8.00 (d, $^3J = 7.1$, H-5), 7.50–7.75 (m, H-6, H-7 and H-8), 5.94 (AB, $\delta_A = 5.91$ (broad, NH), $\delta_B = 5.97$ (H-9), $^3J_{AB} = 7.8$), 7.15 (d, $^3J = 8.8$, H-2′), 7.97 (d, $^3J = 8.8$, H-3′), 2.52 (s, Me), for attribution of H-2′ and H-3′ irrad. at 7.14 ppm. ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.25$ (Cp), 86.79* (C-1), 86.86* (C-2), 87.72 (C-3), 81.13 (C-4), 104.89 (C-4a), 109.30 (C-9a), 136.90 (C-4b), 123.50 (C-5), 130.98 (C-6), 132.20 (C-7), 126.79 (C-8), 144.96 (C-8a), 60.20 (C-9), 151.97 (C-1′), 113.72 (C-2′), 131.66 (C-3′), 128.83 (C-4′), 197.08 (CO), 26.52 (Me); **endo**: $\delta = 78.53$ (Cp), 85.07 (C-1), 85.85 (C-2), 87.72 (C-3), 81.39 (C-4), 103.55 (C-4a), 111.97 (C-9a), 137.39 (C-4b), 123.68 (C-5), 130.87 (C-6), 131.66 (C-7), 126.79 (C-8), 146.00 (C-8a), 58.95 (C-9), 153.06 (C-1′), 113.01 (C-2′), 132.05 (C-3′), 128.97 (C-4′), 197.15 (CO), 26.61 (Me) for attribution of C-3′ and C-7 (overlapped with C-3′ exo) irrad. at 7.97 ppm.

*4.4.9. (η^5-Cyclopentadienyl) [1-9$_a$-η^6-9-(2′-methoxycarbonyl phenylamino)fluorene]iron(II) hexafluorophosphate (exo–endo mixture (45:55)) (**4i**$(PF_6)^-$)*

Electrolysis of the imine–nitrone mixture (**3i**$_{0.6}$ + **3′i**$_{0.4}$)$(PF_6)^-$ (0.86 g, 1.47 mmol) in acetic buffer (CH_3CO_2Na 1.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1})-acetone (1:1,v:v) consumed 2.9 Faradays per mole of substrate and lead to 0.72 g of **4i**$(PF_6)^-$ (84% yield). $[C_{26}H_{22}NO_2Fe][PF_6]$ found (calc.): C, 52.55 (53.72); H, 3.64 (3.82); N, 2.44 (2.41); P, 5.28 (5.33%). HRMS (LSIMS): calc. for $[C_{26}H_{22}NO_2Fe]^+$ 436.1000, found 436.0995. IR ν (cm^{-1}): N-H (3420 broad, 3328 broad), C=O (1682). NMR: ^{1}H,^{13}C-correlation and ^{1}H,^{1}H-COSY experiments. ^{1}H NMR (CD_3CN): **exo** (45%): $\delta = 4.83$ (s, Cp), 6.78 (d, $^3J = 6.1$, H-1), 6.21 (t, $^3J =$ 6.2, H-2), 6.33 (t, $^3J = 6.2$, H-3), 6.95 (d, $^3J = 6.3$, H-4), 8.03 (d, $^3J = 7.4$, H-5), 7.54–7.70 (m, H-6, H-7 and H-8), 6.30 (d, $^3J = 8.8$, H-9), 8.42 (d broad, $^3J =$ 8.5, NH), 7.92 (d, $^3J = 8.1$, H-3′), 6.72 (t, $^3J = 8.1$, H-4′), 7.32 (t, $^3J = 8.4$, H-5′), 6.77 (d, $^3J = 8.5$, H-6′), 3.79 (s, CH_3),; **endo** (55%): $\delta = 4.81$ (s, Cp), 6.58 (d, $^3J = 6.3$, H-1), 6.19 (t, $^3J = 6.2$, H-2), 6.38 (t, $^3J = 6.2$, H-3), 6.99 (d, $^3J = 6.3$, H-4), 8.03 (d, $^3J = 7.4$, H-5), 7.54–7.70 (m, H-6, H-7 and H-8), 6.09 (d, $^3J = 8.7$, H-9), 8.42 (d broad, $^3J = 8.5$, NH), 8.06 (d, $^3J = 8.1$, H-3′), 6.88 (t, $^3J = 8.1$, H-4′), 7.62 (t, $^3J = 8.5$, H-5′), 7.46 (d, $^3J = 8.5$, H-6′), 3.84 (s, CH_3). ^{13}C NMR (CD_3CN): **exo** : $\delta = 79.24$ (Cp), 86.78 (C-1), 86.86 (C-2), 87.66 (C-3), 81.14 (C-4), 104.88 (C-4a), 109.75 (C-9a), 136.83 (C-4b), 123.66 (C-5), 130.98 (C-6), 132.28 (C-7), 126.53 (C-8), 145.20 (C-8a), 60.06 (C-9), 150.26 (C-1′), 112.82 (C-2′), 132.90 (C-3′), 117.78 (C-4′), 135.81 (C-5′), 113.85 (C-6′), 169.70 (CO), 52.52 (CH_3); **endo**: $\delta = 78.64$ (Cp), 84.69 (C-1), 85.84 (C-2), 87.91 (C-3), 81.87 (C-4), 103.64 (C-4a), 110.63 (C-9a), 137.29 (C-4b), 123.80 (C-5), 130.83 (C-6), 131.93 (C-7), 126.08 (C-8), 147.88 (C-8a), 58.12 (C-9), 151.41 (C-1′), 112.31 (C-2′), 133.05 (C-3′), 117.92 (C-4′), 136.53 (C-5′), 113.06 (C-6′), 170.39 (CO), 52.73 (CH_3). For attribution of quaternary carbons of both isomers, irrad. at 3.84 and 3.79 ppm (CO), irrad. at 6.98 and 6.94 ppm (C-9a), irrad. at 6.08 ppm (C-1′, C-8a, C-9a and C-4a),

irrad. at 7.45 ppm (C-2′). ^{1}H NMR (DMSO-d_6): **exo** (60%): $\delta = 4.98$ (s, 5H, Cp), 3.76 (s, 3H, Me), 6.58 (d, $^3J \approx 9$, H-9); **endo** (40%): $\delta = 4.88$ (s, 5H, Cp), 3.83 (s, 3H, Me), 6.40 (d, $^3J = 9.8$, H-9), the other signals were not attributed: 6.3-8.6 (m, 13H).

4.5. Epimerization of the endo isomer of *4b*

50 mg of the amine **4b** enriched with the *endo* isomer (*exo*:*endo*-55:45) was dissolved in a mixture (10 ml) of acetic buffer (CH_3CO_2Na 0.5 mol l^{-1} + CH_3CO_2H 0.5 mol l^{-1}) and acetone (1:1,v:v). After stirring at room temperature overnight and work-up as described in Section 4.4, 40 mg (80% yield) of the amine **4b** was isolated (*exo*:*endo*-85:15).

4.6. $NaBH_4$ reduction of the imine complex *3b*

In a Schlenck tube the imine **3b** (0.50 g, 0.93 mmol) was dissolved in 30 ml of CH_2Cl_2 and 1 ml of water. $NaBH_4$ (70 mg, 1.86 mmol) was added and the solution was stirred at room temperature for 3 h. After hydrolysis with 20 ml of 1N HCl, the organic layer was decanted and washed with 20 ml of a saturated aqueous solution of NH_4PF_6. The solution was dried over $MgSO_4$ and the solvent evaporated under vacuum. Precipitation of the resulting dark brown residue in acetone/ether, filtration and washing with ether gave 0.2 g (40% yield) of a mixture containing 80% of the amine **4b** (*exo*:*endo*-10:90) and 20% of the starting imine **3b**.

4.7. O_2-oxidation of amines *4a* and *4b*

In a conical flask equipped with an oxygen inlet the amine **4a** (0.35 g, 0.67 mmol) was dissolved in 15 ml of acetone. 1 g (10 mmol) of Alumina (activated neutral, aldrich type 507 C, brockman 1 standard, 150 mesh) was added and the solution was stirred under bubbling of O_2 for two hours. The solution was filtered to remove Al_2O_3 and added dropwise in 100 ml of ether. Filtration and drying under vacuum of the resulting precipitate led to 0.28 g of pure imine **3a** (*syn*:*anti*-30:70) as a fine yellow powder (80% yield).

Under the same experimental conditions, the amine **4b** was oxidized within one hour into imine **3b** (*syn*:*anti*-20:80) in 77% yield.

4.8. X-ray analysis of the endo isomer of the amine *4b*

A monocrystal of this isomer was obtained from crystallization in CH_2Cl_2/pentane of the *exo–endo* mixture of **4b**.

$FeNC_{25}H_{22}$, PF_6: Mr = 536.26, triclinic, P-1, a = 10.874(3), b = 10.903(4), c = 11.226(2) Å, α = 117.76(2), β = 101.10(1), γ = 91.47(3), V = 1145.4(6) Å^{-3}, $Z = 2$, $D_x = 1.555$ Mg m^{-3}, λ(MoKα) = 0.70926 Å, $\mu = 7.862$ cm^{-1}, $F(000) = 546$, $T = 294$ K, final $R = 0.074$ for 2222 observations.

The sample (0.20 * 0.30 * 0.35 mm) was studied on an automatic diffractometer CAD4 ENRAF-NONIUS with graphite monochromatized MoKα radiation. The cell parameters were obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max} = 50°$, scan $\omega/2\theta = 1$, $\mathbf{t}_{max} = 60$ s, range *HKL*: *H* 0,12 *K* −12,12 *L* −13,13, intensity controls without appreciable decay (0.4%) gave 4263 reflections from which 2222 independent ($R = 0.011$) with $I > 3\sigma(I)$.

After Lorenz and polarization corrections the structure was solved by direct method with the program SHELX-86 (Sheldrick, 1985) which revealed all the non hydrogen atoms of the compound (in particular disordered anion). After isotropic ($R = 0.11$), then anisotropic refinement ($R = 0.086$), some hydrogen atoms were found with a Fourier Difference. The whole structure was refined by the full-matrix least square techniques (use of F magnitude; x, y, z, β_{ij} for Fe, P, N and C atoms, x, y, z, B for F atoms and x, y, z fixed for H atoms; 294 variables and 2222 observations: $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04\ F_o^2)^2]^{-1/2}$) with the resulting $R = 0.077$, $R_w = 0.074$ and $S_w = 1.88$ (residual $\Delta\rho \leq 1.26$ 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 [75–78].

5. Supplementary material

Complete crystallographic data of complex **4b** are available from the authors.

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