Mono- and 1,1′-Disubstituted Aza Ferrocenyl Compounds: Evidence for an Original Electroactive Fluorescent Species

Béatrice Delavaux-Nicot*[a] and Suzanne Fery-Forgues[b]

Keywords: Ferrocenyl ligands / Electrochemistry / Fluorescence / Azaalkyl compounds / Crown compounds

New azaalkyl or azacrown ferrocenyl compounds containing a C_5H_4COCC- linkage are accessible from mono- or diacetylferrocene upon treatment with the appropriate aldehydes ($CHOC_6H_4$-*p*-R, R = NEt_2, N-aza-15-crown-5). Preliminary results concerning the electrochemical behaviour of complexes $[(C_5H_5)Fe(C_5H_4COCH{=}CHC_6H_4NEt_2)]$ (**3a**), $[Fe(C_5H_4COCH{=}CHC_6H_4NEt_2)_2]$ (**5a**), the novel ferrocenophane $[Fe(C_5H_4COCH_2)_2CHC_6H_4NEt_2]$ (**6a**) and its protonated species $[Fe(C_5H_4COCH_2)_2CHC_6H_4NHEt_2][BF_4]$ (**7a**), are reported. The ferrocenyl ligand **5a** is a rare example of a molecule which is both electroactive and fluorescent.

Introduction

The design of ferrocene-based ion sensors constitutes an area of active research,[1] especially for property-directed synthesis.[2] Of special interest are novel functionalised molecules which are able to change an easily measurable physical property by coordination or interaction with a target molecule. Among these new molecules are redox-functionalised receptors which are able to display a shift of the redox potential upon addition of particular substrates, and we have recently been involved in the synthesis of electroactive ferrocenyl receptors for the electrochemical recognition of cations and anions.[3] Studies concerning ion recognition by fluorescent sensors are also well documented and offer a wide range of applications.[4] Despite the development of these two areas, to the best of our knowledge, few examples of fluorescent ferrocenyl ion sensors have been described[5] probably because ferrocene derivatives are known to be efficient fluorescence quenchers.[6] It is noteworthy that Beer et al. have developed two particularly interesting polymetallic [Ru-Fe] systems where anion binding induces a luminescence revival.[5] In the compounds described by Beer et al.[5], luminescence arises from organometallic ruthenium(II) and osmium(II) bipyridyl moieties and the ferrocene residue acts as a quencher. As a complementary part of our research, a *purely organic* fluorescent ion sensor subunit containing an R-aza complexing moiety ($-COCH{=}CHC_6H_4$-*p*-R, R = NEt_2 or aza-15-crown-5)[7] was combined with a redox ferrocenyl fragment to give rise to a new type of ion-sensing device. This choice was mainly made for the following reasons: i) It has recently been shown for a dibenzylideneacetone containing these aza fragments that the photophysical properties of the fluorescent group can be modified upon complexation of the nitrogen atom.[7] ii) Redox active ionophores based on covalently linked crown ether-metallocene systems have received much attention in recent years and give a good selective electrochemical response to the presence of a guest cation.[8] It is worth noting that in our simple ligands, the ferrocenyl moiety is involved in the conjugated π system, and a physical response for ion recognition either by electrochemistry and/or by fluorescence methods can be expected.

In this paper we report the characterization of novel electroactive ferrocenyl ligands presenting a rare C_5H_4COCC linkage[9] (Scheme 1) and preliminary results concerning the physical properties of the original fluorescent electroactive molecule $[Fe(C_5H_4COCH{=}CHC_6H_4NEt_2)_2]$ (**5a**).

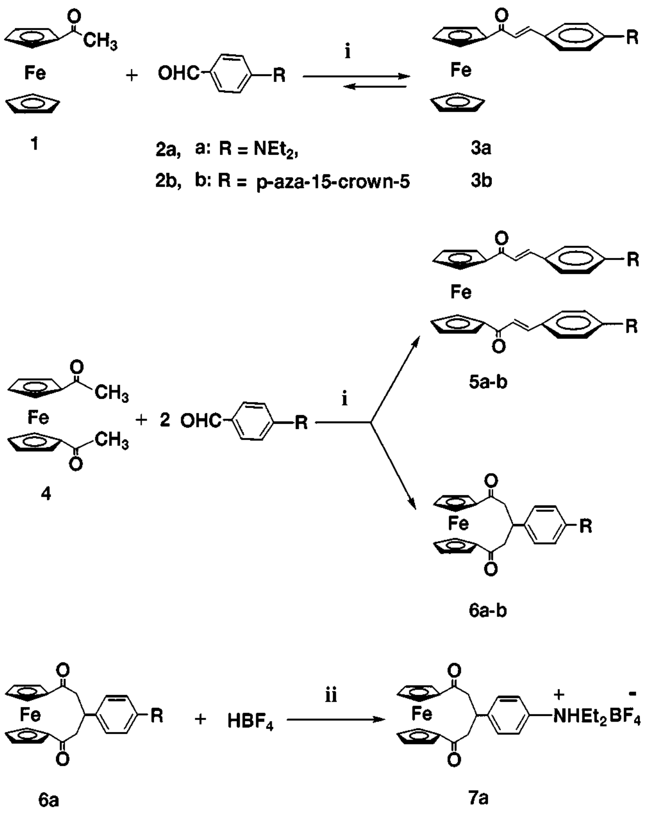
Results and discussion

In order to test the efficiency of the synthesis of easily isolable products presenting the desired properties, a reaction was performed between the monosubstituted ferrocenyl compound $[(C_5H_5)Fe(C_5H_4COCH_3)]$ (**1**) and *p*-diethylaminobenzaldehyde (**2a**) or crown aldehyde [N-(4-formylphenyl)aza-15-crown-5] (**2b**) in basic solution (1:1 ethanol/10% aqueous NaOH). With **2a**, the expected compound $[(C_5H_5)Fe(C_5H_4COCH{=}CHC_6H_4NEt_2)]$ (**3a**) formed in 40% yield (by NMR spectroscopy), after stirring for 6 hours. It was isolated as a red powder after purification and identified by DCI-NH_3 mass spectroscopy ($[M + H]^+ = 388$). The ^1H NMR spectroscopic data were consistent with a *trans* geometry of the ethylenic protons ($^3J_{H-H} = 15.4$ Hz)[10a] and our spectroscopic assignment was in agreement with the literature data for related compounds.[11][12] The isolated yield of **3a** was not improved under different experimental conditions, probably because of a reverse aldol condensation. The compound $[(C_5H_5)Fe(C_5H_4COCH{=}CHC_6H_4$-*p*-aza-15-crown-5$)]$ (**3b**) was obtained, after 31 h of reaction with **2b**, in 50% yield (by NMR spectroscopy) and characterized after isolation as a red oil.

---

[a] Laboratoire de Chimie de Coordination du CNRS,
UPR 8241 lié par conventions à l′Université Paul Sabatier et à l′Institut National Polytechnique de Toulouse,
205, route de Narbonne, F-31077 Toulouse Cedex 04, France
[b] Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique,
UMR 5623 au CNRS, 118 route de Narbonne, F-31062 Toulouse Cedex
E-mail: delavaux@lcc-toulouse.fr

1434−1948/99/1010−1821 $ 17.50+.50/0



Scheme 1. *Reagents and conditions*: i) 1:1 ethanol/10% aqueous NaOH, room temp; ii) CH_3CN, 20°C.

An identical procedure was carried out to obtain the disubstituted ferrocenyl derivative $[Fe(C_5H_4COCH{=}CHC_6H_4NEt_2)_2]$ (**5a**). The analogous compound $[Fe(C_5H_4COCH{=}CHC_6H_4NMe_2)_2]$[13] has been proposed in the literature for photographic use though no characterization or yield have yet been reported. Two equivalents of **2a** were reacted with one equivalent of $[Fe(C_5H_4COCH_3)_2]$ (**4**) to give, after stirring for 4 h at 20°C, a mixture (50%, NMR) of compound **5a** and the ferrocenophane $[Fe(C_5H_4COCH_2)_2CHC_6H_4NEt_2]$ (**6a**) in a 2/3 ratio. A two-step chromatography workup allowed the separation of pure **5a** as a light-sensitive powder and **6a** as an orange powder with 7% and 9% yield, respectively. Attempts to improve the synthesis of **5a**, as reported in the patent in ref.,[12] or in excess of **2a** according to another published procedure,[14a] failed. The yield of ferrocenophane **6a** was increased (40%) by stirring the reagents for 18 hours (4 equivalents of aldehyde) and performing several diffusions in a toluene/pentane mixture of the red fraction obtained after simple chromatography on alumina. According to the literature, **6a** can be formed either by an aldol condensation in a 1/1 stoichiometry followed by an intramolecular Michael addition[14] or by a reverse aldol condensation in basic medium starting from **5a**.[15] This explains why **6a** is the major compound in solution.

For the disubstituted compound **5a**, DCI-NH_3 mass spectroscopy showed a $[M + H]^+$ molecular peak at the expected value of 589. The IR spectrum exhibited a $\tilde{\nu}(C{=}O)$ vibration at 1644 cm^{-1}, this low value being due to the conjugation of the CO group in the molecule.[10b] The proposed structure was first deduced from NMR spectroscopic data, which revealed high symmetry. The protons of the CH groups, as for the monosubstituted compound **3a**, are in *trans* positions. In the $^{13}C\{^1H\}$-NMR spectrum, a singlet observed at $\delta = 192.4$ in $CDCl_3$ was attributed to the CO groups. 2D NMR experiments were carried out and clearly verified our assignments.

In the case of **6a**, the number and the multiplicity of the signals observed for the cyclopentadienyl protons in the ^1H-NMR spectrum showed the asymmetry of the molecule. In the $^{13}C\{^1H\}$-NMR spectrum a lone singlet was detected for the CO groups ($\delta = 199.5$, $CDCl_3$). Analysis of the ^1H-^{13}C HMBC spectra supported the existence of a bridge linkage between the Cp ring, in which the CO carbon atoms are strongly coupled to the H atom of the CH group and to each proton of the CH_2 groups. The bridge between the Cp rings may force them out of coplanarity and staggers them by less than 36°. It probably also pushes the CO groups out of the Cp ring planes and in the same direction.[16] Selective decoupling ^1H-NMR experiments (400 MHz, 223 K, $CDCl_3$) indicated that the CH_2 protons of the ferrocenophane chain are diastereotopic (at 293 K, a broad singlet at $\delta = 2.50$ and a triplet at $\delta = 2.90$ were detected for both CH_2 groups). X-ray structures of [5]-ferrocenophane are not common but it has been previously reported that the ferrocenophane molecules have conformational mobility in solution: the Cp rings can undergo small torsional vibrations with respect to each other around the axis passing through the center of the rings and the iron atom.[17]

The analogous reaction of **4** with the crown aldehyde **2b** produced, after stirring for 17 h, $[Fe(C_5H_4COCH{=}CHC_6H_4$-*p*-aza-15-crown-5$)_2]$ (**5b**) and $[Fe(C_5H_4COCH_2)_2CHC_6H_4$-*p*-aza-15-crown-5$)]$ (**6b**) in a 3:7 ratio. These compounds were identified by DCI-NH_3 mass spectroscopy ($[M + H]^+ = 881$ and 576, respectively). The NMR spectroscopic data of a pure sample of **6b** were very similar to those obtained for **6a** when considering the same basic cyclic structure for both compounds. 2D NMR experiments allowed a clear assignment of the ^{13}C-NMR chemical shifts, in particular for the carbons of the Cp and crown rings whose signals appeared in the same region of the spectra.

Compound **6a** was protonated to provide useful data concerning the analysis of its electrochemical behaviour. When treated with one equivalent of $HBF_4{\cdot}Et_2O$ in CH_3CN, **6a** afforded $[Fe(C_5H_4COCH_2)_2CHC_6H_4NHEt_2][BF_4]$ (**7a**) (95% NMR, MS (FAB): 430 $[M - BF_4]^+$). The ^1H-^1H COSY NMR spectrum clearly confirmed the nature of the protonation site (nitrogen): a correlation between the NH^+ proton[3e] (broad singlet, $\delta = 8.60$) and the NCH_2 protons (complex multiplet, $\delta = 3.65$) was observed (CD_3CN, 300 MHz).

The electrochemical behaviour of compounds **3a**, **5a** and **6a** ($R = NEt_2$) was investigated. For compounds **3a** and **5a** two redox waves were observed by cyclic voltammetry (CV). The oxidation peak potentials (Epa) of the amine moieties (0.88 V and 0.78 V vs SCE for **3a** and **5a**, respectively) are in the expected range of values.[18] It is to be noted that $CH_3COCH{=}CHC_6H_4NEt_2$ (**8**) was oxidized at Epa = 0.74 V in CH_2Cl_2. For the Fe(II)/Fe(III) couple, the Epa values, 0.65 V and 1.15 V for **3a** and **5a**, respectively, depend on the number of CO substituents, which are strong electron-withdrawing groups.[11b] This was confirmed by the data obtained for **1** and **4** under the same experimental conditions. Stepwise addition of $HBF_4{\cdot}Et_2O$ to a solution of compound **3a** in CH_3CN resulted in a clear evolution of the ferrocene wave from $E_{1/2}$ = 0.61 to 0.67 V, associated with the disappearance of the second wave (Figure 1, top). The solution turned pink and the new species were oxidized (Fe^{III}) and recovered by electrolysis at 0.75 and 0.30 V, respectively, although some decomposition occurred.

The electrochemical oxidation of compound **6a** resulted in the observation of quasi-reversible redox waves of equal intensity at 0.77 and 0.99 V (Epa vs SCE), assigned to the amine and ferrocene parts, respectively (Figure 1, bottom). This was verified by a two-step electrolysis at controlled potential (0.90 and 1.10 V, respectively), coupled with cyclic and linear voltammetry measurements. The stepwise addition of 1 equivalent of $HBF_4{\cdot}Et_2O$ in CH_3CN to compound **6a** induced the disappearance of the first wave, whereas there was no effect on the second. Moreover, the new species formed had the same electrochemical characteristics and behaviour towards electrochemical oxidation (at 1V) as compound **7a** under the same conditions.

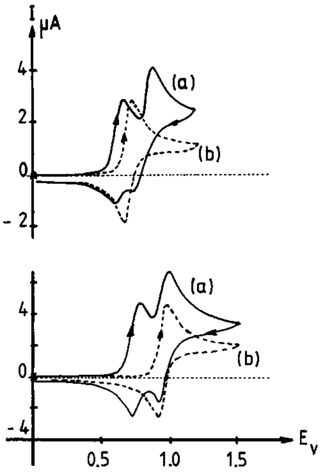


Figure 1. Cyclic voltammograms of (a) **3a**, (b) **3a** + 1 equiv. of $HBF_4{\cdot}Et_2O$ (top); cyclic voltammograms of (a) **6a**, (b) **6a** + 1 equiv. of $HBF_4{\cdot}Et_2O$, at 0.1 V s^{-1} in CH_3CN (bottom); experimental conditions: Pt electrode (1 mm) in 0.1 mol L^{-1} solution of Bu_4NPF_6 in CH_3CN, complex concentration 10^{-3} M

It has been shown that in a molecule with a saturated spacer such as **6a**, the protonation of the nitrogen atom may induce an anodic shift of the oxidation potential of the Fe^{II}/Fe^{III} couple.[3e,19] However, the nitrogen-iron distance is too long in **6a** for such an effect to be detected.[19] Interposition of a conjugated spacer between the ionophore and the ferrocene unit produces a noticeably different electrochemical response towards H^+ addition for **3a**. Electronic communication becomes possible through the spacer between the redox center and the protonated site, inducing an anodic shift of $\Delta E_{1/2}$ = 60 mV for this couple. This property is of real importance and suggests that molecules such as **3a**,**b** and **5a**,**b** could be electrochemical cation sensors.

The spectroscopic properties of compounds **3a** and **5a** were investigated in CH_3CN. The absorption spectra of these compounds (Figure 2) can be interpreted in accordance with the literature data.[6b,20] The broad low-intensity band located above 460 nm and well visible in the case of **3a** can be assigned to the d-d transition of iron in ferrocene. The intense band at 408 nm for **3a** and 416 nm for **5a** can similarly be attributed to charge transfer (CT) between the donor amino group and the acceptor carbonyl group. This band was strongly red-shifted with respect to the CT band of chalcone **8** (λ_{abs} = 382 nm in CH_3CN), which is in agreement with the extension of the conjugated system. The absorption spectrum of crown compounds **3b** and **5b** is similar in shape to that of **3a** and **5a**, respectively. Molar absorption coefficients were also found to be very close (for example ε_{404} = 28 600 and 30 000 L mol^{-1} cm^{-1} for **3a** and **3b**, respectively). The absorption spectrum of **6a** in CH_2Cl_2 displays a strong absorption band peaking around 264 nm and two weak bands between 300 and 360 nm, the latter two being assigned to the ferrocenyl moiety. It was checked that the protonated compound **7a** did not exhibit the long wavelength absorption band characteristic of the ferrocenium ion.

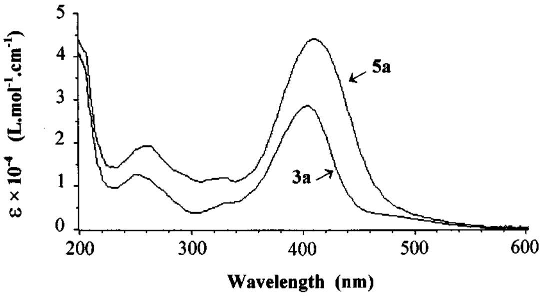


Figure 2. Absorption spectra of **3a** and **5a** in CH_3CN, ε = molar absorption coefficient

Very weak emission could be expected for compounds **3a** and **5a**, since ferrocenyl residues are known to quench luminescence. Indeed, when excited at the absorption band maximum, **3a** displays a very weak ($\Phi = 1 \times 10^{-4}$) fluorescence signal around 560 nm at room temperature. In contrast, an intense unresolved emission band was observed for compound **5a** (Figure 3). Absorption or excitation spectra of compound **5a** were similar. The quantum yield reached 7.7×10^{-2}, i.e. around ten times higher than that of **8** and only two times lower than that of diaminodibenzylidenacetone (**9**) in the same solvent.[7] This shows that in **5a** the ferrocenyl moiety, far from acting as a simple fluorescence quencher, behaves essentially as an auxochrome. Compound **5a** was studied in different solvents (Table 1). A strong positive solvatochromic effect was observed both in the absorption and emission spectra, which is also reminiscent of the behaviour of **9**.[21] This trend was accompanied by a drastic increase of the fluorescence quantum yield in polar media, which generally indicates the involvement of an emissive intramolecular CT in the excited state.

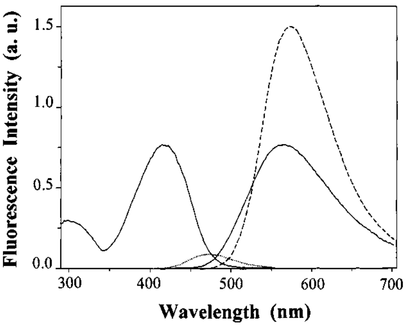


Figure 3. Excitation (λ_{em} = 560 nm) and emission (λ_{ex} = 416 nm) spectra of **5a** in CH_3CN (full line); emission spectra of **8** (λ_{ex} = 382 nm, dotted line) and **9** (λ_{ex} = 444 nm, broken line); the emission spectra are normalized according to the fluorescence quantum yield

Table 1. Spectroscopic data for **5a** in different solvents: absorption wavelength (λ_{abs}), emission wavelength (λ_{em}), fluorescence quantum yield (Φ_F) and Lippert polarity parameter (Δ_f)

Solvent	λ_{abs} (nm)	λ_{em} (nm)	Φ_F[a]	Δ_f
Cyclohexane	386	–	$<10^{-4}$	−0.001
Toluene	404	487	1.3×10^{-3}	0.013
Dioxane	404	495	4.3×10^{-3}	0.021
Ethyl acetate	404	516	1.4×10^{-2}	0.202
Tetrahydrofuran	412	523	2.1×10^{-2}	0.210
Acetone	410	541	2.4×10^{-2}	0.287
Acetonitrile	416	560	7.7×10^{-2}	0.306

[a] $\lambda_{ex} = \lambda_{abs}$.

Preliminary studies showed that crown compound **5b** was also fluorescent and could therefore find interesting applications as a fluoroionophore.

Conclusion

These results clearly indicate that new electroactive and fluorescent species containing only ferrocene as a metallic moiety can be obtained. Work is in progress to understand the electrochemical and unusual photophysical properties of **5a−b** better, and to test their potential ability for cation recognition by both techniques.

Experimental Section

Physical Methods: NMR, electrochemical and photophysical measurements were made as previously reported.[3e,7] The fluorescence spectra were corrected. The fluorescence quantum yield was determined relative to coumarin 6 in ethanol as the standard (Φ_F = 0.78).[22] Fast atom bombardment (FAB^+) or desorption chemical ionization (DCI) mass spectrometry were performed on a Nermag R 10 at the Service Commun de Spectrométrie de Masse de l'Université Paul Sabatier et du CNRS, Toulouse.

Complex 3b: To 20 mL of a basic solution (1:1 ethanol/10% aqueous NaOH) was added dropwise a mixture of 1 equiv. of **1** (315 mg, 1.38 mmol) and 1.1 equiv. of **2b** (490 mg, 1.52 mmol) dissolved in 10 mL ethanol. The light-protected mixture was stirred for 31 h at room temperature and the solvent evaporated to dryness. The organic phase was extracted with dichloromethane. The solution was filtered with a cannula under nitrogen, the solvent was evaporated off and the residue washed with pentane. The product was purified by column chromatography on alumina (eluent: pentane/CH_2Cl_2) and collected as a red fraction. After evaporation of the solvent, the product was washed with pentane and dried under vacuum for several hours to afford a red oil (240 mg, 33% yield). − ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ = 3.67 (m, 16 H), 3.80 (m, 4 H) (CH_2 Crown), 4.22 (s, 5 H, C_5H_5), 4.56, 4.92 (each t, J_{HH} = 1.9 Hz, 4 H, C_5H_4), 6.70 (*CH*−CN), 7.55 (*CH*−CH−CN) (each d, J_{HH} = 8.9 Hz, 4 H, C_6H_4), 6.96 (CH=*CH*−CO), 7.76 (*CH*=CH−CO) (each d, J_{HH} = 15.5 Hz, 2 H). − $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 293 K): δ = 53.13, 68.69, 70.49, 70.66, 71.75 (s, CH_2 Crown), 69.99, 72.65, 81.69 (C_5H_4), 70.41 (C_5H_5), 111.93 (*CH*−CN), 123.08 (C_{ipso}−C=C), 130.65 (*CH*−CH−CN), 149.69 (C_{ipso}−N) (C_6H_4), 118.30 (CH=*CH*−CO), 141.92 (*CH*=CH−CO), 193.46 (CO), each s. MS (FAB); *m*/*z*: 533 $[M]^+$. − $C_{29}H_{35}FeNO_5$: calcd. C 65.27, H 6.62, N 2.63; found C 64.95, H 6.41, N 2.64.

Complex 5a and 6a: A mixture of 1 equiv. of **4** (400 mg, 1.48 mmol) and 2 equiv. of **2a** (524 mg, 2.96 mmol) in 20 mL ethanol was added dropwise to 20 mL of a basic solution (1:1 ethanol/10% aqueous NaOH). After stirring for 4 h at 20°C, the organic phase was extracted with dichloromethane, the solution filtered and the solvent evaporated to dryness. After column chromatography on alumina (eluent: CH_2Cl_2 then THF) a red fraction was collected and protected from light. Compounds **5a** and **6a** were separated by thin layer chromatography on silica gel (eluent: ethyl acetate/toluene: 1:2.5) in the dark. The products were rapidly extracted with acetone. Compound **5a** (red band) was purified by diethyl ether extraction and washing with pentane, and dried under vacuum to afford a red powder (61 mg, 7% yield). Compound **6a** (orange band) was washed with pentane, dried under vacuum and obtained as an orange powder (57 mg, 9% yield). Complex **5a**. − ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ = 1.20 (t, J_{HH} = 7.1 Hz, 12 H, CH_3), 3.41 (q, J_{HH} = 7.1 Hz, 8 H, CH_2N), 4.53, 4.91 (each t, J_{HH} = 1.9 Hz, 8 H, C_5H_4), 6.62 (*CH*−CN), 7.51 (*CH*−CH−CN) (each d, J_{HH} = 8.9 Hz, 8 H, C_6H_4), 6.90 (CH=*CH*−CO), 7.75 (*CH*=CH−CO) (each d, J_{HH} = 15.4 Hz, 4 H). − $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$, 293 K): δ = 12.59 (CH_3), 44.47 (CH_2N), 70.99, 74.03, 82.47 (C_5H_4), 111.16 (*CH*−CN), 121.69 (C_{ipso}−C=C), 130.65 (*CH*−CH−CN), 149.37 (C_{ipso}−N) (C_6H_4), 116.87 (CH=*CH*−CO), 142.70 (*CH*=CH−CO), 192.38 (CO), each s. − MS (DCI): 589 $[M + H]^+$. − $C_{36}H_{40}N_2O_2Fe$: calcd. C 73.45, H 6.85, N 4.76; found C 73.07, H 6.97, N 4.64. Complex **6a.** − NMR: See text, close to **6b** (vide infra). MS (DCI): 430 $[M + H]^+$. − $C_{25}H_{27}FeNO_2$: calcd. C 69.91, H 6.34, N 3.26; found C 69.72, H 6.20, N 3.11.

Selected data for **6b:** ^1H NMR (400 MHz, $CDCl_3$, 223 K): δ = 2.41 (br d, J_{HH} = 12.0 Hz, 2 H, CH_2CO), 2.87 (br t, J_{HH} = 12.5 Hz, 2 H, CH_2CO), 3.66 (m, 20 H, CH_2 Crown), 4.25 (br t, J_{HH} = 11.5 Hz, 1 H, CH), 4.63, 4.66, 4.87, 4.91 (each br s, 8 H, C_5H_4), 6.61 (*CH*−CN), 7.21 (*CH*−CH−CN) (each d, J_{HH} = 8.5 Hz, 4 H, C_6H_4). − $^{13}C\{^1H\}$ NMR, (100.62 MHz, $CDCl_3$, 223 K): δ = 45.39 (CH), 46.61 (CH_2), 52.75, 67.84, 69.88, 71.57 (CH_2, crown), 68.84, 72.47, 74.25, 75.05, 81.81 (C_5H_4), 110.70 (*CH*−CN), 127.74 (*CH*−CH−CN), 131.64 (C_{ipso}−CH), 145.58 (C_{ipso}−N) (C_6H_4), 199.44 (CO), each s.

Selected data for **7a:** ^1H NMR (300 MHz, CD_3CN, 293 K): δ = 1.08 (t, J_{HH} = 7.1 Hz, 6 H, CH_3), 2.29 (m, 2 H, CH_2CO), 3.09 (br t, J_{HH} = 12.4 Hz, 2 H, $\mathrm{CH_2CO}$), 3.65 (m, 4 H, $\mathrm{CH_2N}$), 4.15 (br t, J_{HH} = 11.4 Hz, 1 H, CH), 4.65, 5.07 (m, 8 H, $\mathrm{C_5H_4}$), 7.46 (CH−CN), 7.65 (*CH*−CH−CN) (each d, J_{HH} = 8.6 Hz, 4 H, $\mathrm{C_6H_4}$), 8.60 (br s, 1 H, NH). − $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR (75.47 MHz, $\mathrm{CDCl_3}$, 223 K): δ = 10.03 ($\mathrm{CH_3}$), 46.14 (CH_2,CO, CH), 54.62 ($\mathrm{CH_2N}$), 68.79, 72.83, 74.44, 74.94, 82.61 ($\mathrm{C_5H_4}$), 122.87 (*CH*−CN), 129.60 (*CH*−CH−CN), 135.47 (C_{ipso}−N) 148.89 (C_{ipso}−CH) ($\mathrm{C_6H_4}$), 179.78 (CO), each s.

Acknowledgments

We gratefully acknowledge Dominique de Montauzon (Service d′Electrochimie du LCC, Toulouse, CNRS) for expert technical assistance and fruitful discussions.

---

[1] For example: [1a] M. C. Grossel, M. R. Goldspink, J. A. Hriljac and S. C. Weston, *Organometallics* **1991**, *10*, 851−860 and references therein. − [1b] E. C. Constable, *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 407−408 and references therein. − [1c] P. D. Beer, *Chem. Soc. Rev.* **1989**, *18*, 409−450. − [1d] P. D. Beer, *Adv. Inorg. Chem.* **1992**, *39*, 79−157. − [1e] J. C. Medina, T. T. Goodnow, M. T. Rojas, J. L. Atwood, B. C. Lynn, A. E. Kaifer and G. W. Gokel, *J. Am. Chem. Soc.* **1992**, *114*, 10583−10595.

[2] H. Plenio and C. Aberle, *Organometallics* **1997**, *16*, 5950−5957 and references therein.

[3] [3a] B. Delavaux-Nicot, N. Lugan, R. Mathieu and J.-P. Majoral, *Inorg. Chem.* **1992**, *31*, 334−336. − [3b] B. Delavaux-Nicot, R. Mathieu, D. de Montauzon, G. Lavigne and J.-P. Majoral, *Inorg. Chem.* **1994**, *33*, 434−443. − [3c] B. Delavaux-Nicot, B. Douziech, R. Mathieu and G. Lavigne, *Inorg. Chem.* **1995**, *34*, 4256−4261. − [3d] B. Delavaux-Nicot, Y. Guari, B. Douziech and R. Mathieu, *J. Chem. Soc., Chem. Commun.* **1995**, 585−587. − [3e] B. Delavaux-Nicot, A. Bigeard, A. Bousseksou, B. Donnadieu and G. Commenges, *Inorg. Chem.* **1997**, *36*, 4789−4797.

[4] For example: [4a] A. Prasanna de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515−1566. − [4b] *Fluorescent Chemosensors for Ion and Molecule Recognition*; A.W. Czarnik, ACS Symposium Ser. 538: Washington DC, **1993**.

[5] [5a] P. D. Beer, A. R. Graydon and L. R. Sutton, *Polyhedron* **1996**, *15*, 2457−2461. − [5b] P. D. Beer, F. Szemes, V. Balzani, C. M. Salà, M. G. B. Drew, S. W. Dent and M. Maestri, *J. Am. Chem. Soc.* **1997**, *119*, 11864−11875.

[6] [6a] G. L. Geoffroy and M. S. Wrighton, *Organometallic photochemistry*, Academic Press, New York, **1979**, chapter 5, 230−257. − [6b] P. D. Harvey, L. Gan and C. Aubry, *Can. J. Chem.* **1990**, *68*, 2278−2288. − [6c] P. D. Harvey and L. Gan, *Inorg. Chem.* **1991**, *30*, 3239−3241.

[7] N. Marcotte, S. Fery-Forgues, D. Lavabre, S. Marguet and V. G. Pivovarenko, *J. Phys., Chem.* **1999**, *103*, 3163−3170.

[8] M. C. Grossel, D. G. Hamilton, J. I. Fuller and E. Millan-Barios, *J. Chem. Soc., Dalton. Trans.* **1997**, 3471−3477.

[9] For example: *Ferrocenes* A. Togni and T. Hayashi ed., VCH, New York, **1995**.

[10] [10a] R. M. Silverstein, G. C. Bassler and T. C. Morril, in *Spectrometric Identification of Organic Compounds*, Fourth Edition, J. Wiley and Sons, New York, **1981**, Chapter 4, 205. − [10b] R. M. Silverstein, G. C. Bassler and T. C. Morril, in *Spectrometric Identification of Organic Compounds*, Fourth Edition, J. Wiley and Sons, New York, **1981**, Chapter 3, 117−118.

[11] [11a] A. N. Nesmeyanov, G. B. Shulp′in, L. V. Rybin, N. T. Gubenko, M. I., Rybinskaya, P. V. Petrovskii and V. I. Robas, *J. Gener. Chem. USSR*, **1974**, *44*, 1994−2001. − [11b] A. G. Nagy and S. Tomas, *J. Org. Chem.* **1984**, *266*, 257−268.

[12] A. G. Nagy, *J. Org. Chem.* **1985**, *291*, 335−340.

[13] J. P. C. G. Dubosc, U.S. Patent 1967, 3,335,008.

[14] [14a] T. A. Mashburn Jr., C. E. Cain and C. R. Hauser, *J. Org. Chem.* **1960**, *25*, 1982−1986. − [14b] T. H. Barr and W. E. Watts, *Tetrahedron* **1968**, *24*, 3219−3235.

[15] J. A. Winstead, *J. Org. Chem.* **1972**, *37*, 1271−1272.

[16] E. Gyepes, T. Glowiack and S. Toma, *J. Organomet. Chem.* **1986**, *316*, 163−168.

[17] T. N. Sal′nikova, V. G. Andrianov, M. Y. Antipin and Y. T. Struchkov, *Sov. J. Coord. Chem.* **1977**, *3*, 732−737.

[18] P. D. Beer, C. Blackburn, J. F. McAleer and H. Sikanyika, *Inorg. Chem.* **1990**, *29*, 378−381.

[19] H. Plenio, J. Yang, R. Diodone and J. Heinze, *Inorg. Chem.* **1994**, *33*, 4098−4104.

[20] [20a] S. Toma, A. Gaplovsky and I. Pavlik, *Monatsh. Chem.* **1985**, *116*, 479−486. − [20b] P. D. Harvey and J. G. Sharma, *Can. J. Chem.* **1990**, *68*, 223−227.

[21] [21a] A. A. Khalaf, S. H. Etaiw, R. M. Issa and A. K. El-Shafei, *Rev. Roum. Chim.* **1977**, *22*, 1251−1259. − [21b] J. M. Eisenhart and A. B. Ellis, *J. Org. Chem.* **1985**, *50*, 4108−4113. − [21c] R. J. De Voe, M. R. V. Sahyun, E. Schmidt, M. Sadrai, N. Serpone and D. K. Sharma, *Can. J. Chem.* **1989**, *67*, 1565−1575.

[22] G. A. Reynolds and K. H. Drexhage, *Opt. Commun.* **1975**, *13*, 222−225.

Received January 18, 1999
[I99013]