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Organometallic iron (II) hydrazines and hydrazones — syntheses, characterisations and the X-ray crystal structures of $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_5NHNH_2)]^+PF_6^-$ and $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}p\text{-}MeC_6H_4NHN{=}CMe_2)]^+PF_6^-$

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Abstract

The three new organometallic hydrazines $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4NHNH_2)]^+PF_6^-$, Cp=$C_5H_5$, R=H, $[\mathbf{1}]^+PF_6^-$; *m*-Me, $[\mathbf{2}]^+PF_6^-$; *p*-MeO, $[\mathbf{3}]^+PF_6^-$, were synthesised and characterised. They were obtained in CH_2Cl_2 by reaction of the hydrazine monohydrate, $NH_2NH_2{\cdot}H_2O$, with the corresponding precursors $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4Cl)]^+PF_6^-$. Similarly to free conventional organic hydrazines, the organometallic hydrazines $[\mathbf{1}]^+PF_6^-$ and $[\mathbf{3}]^+PF_6^-$ react with acetone affording hydrazones formulated as $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4NHN{=}CMe_2)]^+PF_6^-$, R=H, $[\mathbf{6}]^+PF_6^-$; *p*-MeO, $[\mathbf{7}]^+PF_6^-$. Likewise, the two other organometallic hydrazones containing the substituent groups R=*o*-Cl, $[\mathbf{8}]^+PF_6^-$ and *p*-Me, $[\mathbf{9}]^+PF_6^-$ were also obtained from their parent hydrazine precursors $[\mathbf{4}]^+PF_6^-$ and $[\mathbf{5}]^+PF_6^-$, respectively. All the new compounds were characterised by elemental analysis and IR, UV–vis, ^1H- and ^{13}C-NMR spectroscopy. The crystalline and molecular structures of $[\mathbf{1}]^+PF_6^-$ and $[\mathbf{9}]^+PF_6^-$ were determined by single crystal X-ray crystallographic analysis. Both structures show a cyclohexadienyl-like character at the coordinated C_6 ring of the phenylhydrazine and the *p*-methylphenylhydrazone with a folding angle of 6.0(5) and 7.1(6)°, respectively. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sandwich complex; Cyclopentadienyl–iron complex; Arenehydrazine–iron complex; Arenehydrazone–iron complex; X-ray structure; Aromatic nucleophilic substitution

1. Introduction

In the last few years, hydrazones have revealed to be an important class of organic crystalline materials exhibiting properties for various optical phenomena [1] and high propensity of forming a non-centrosymmetric crystal packing [2]. These compounds contain the asymmetric transmitter backbone –NHN=CH– which allows, for a given electron-donating and -withdrawing group, the formation of two different types of compounds: A–NHN=CH–D (Type I) and D–NHN=CH–A (Type II) (A = acceptor, D = donor) [1a,b]. Particularly, hydrazones Type I containing the *p*-nitrophenyl group as acceptor (A) and *p*-dimethylaminophenyl, *p*-methoxophenyl, *p*-bromophenyl or *p*-methylphenyl groups as donors (D) have shown efficient second-order non-linear activity [1a]. Complexation of aromatic rings with the 12-electron cationic organometallic moiety $[Fe(\eta^5\text{-}Cp)]^+$ (Cp=C_5H_5), leading to the robust $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}arene)]^+$ derivatives, occupies an important position in the development of organometallic chemistry [3]. These ionic electron-acceptor mixed sandwiches [4] have proven to be very useful to study electronic communication between ligand-bridged metals [5], and their

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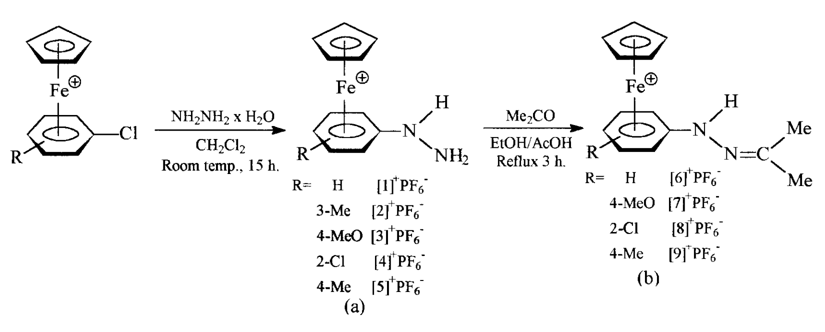
electrochemical and photochemical properties have led to intense investigations [6]. Taking into account that the $[Fe(\eta^5\text{-}Cp)]^+$ fragment is as electron withdrawing as two nitro groups on the arene ring [7], and moreover, that the complexation brings the third dimensionality to the resulting compounds, we thought that hydrazone derivatives of general formula $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4NHN{=}CR'R'')]^+PF_6^-$, R = H, Me, MeO, Cl, R′ = H, Alkyl, Aryl, R″ = H, Alkyl, Aryl, $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}Cp)$, could represent a new Type I class of organometallic materials of interest for non-linear optics. While we were carrying out the present work, the first example of the use of the $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}aryl)]^+$ as organometallic NLO chromophore appeared in the literature [8].

As a contribution to the development of new potential non-linear optical materials we report in this article (i) the synthesis and characterisation of new organometallic hydrazines formulated as $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4NHNH_2)]^+PF_6^-$, R = H, $[\mathbf{1}]^+PF_6^-$, *m*-Me, $[\mathbf{2}]^+PF_6^-$ and *p*-MeO, $[3]^+PF_6^-$; (ii) the synthesis and characterisation of the acetone–hydrazones formulated as $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4NHN{=}CMe_2)]^+PF_6^-$, R=H, $[\mathbf{6}]^+PF_6^-$, *p*-MeO, $[\mathbf{7}]^+PF_6^-$, and those derived from known substituted phenylhydrazine complexes, *o*-Cl, $[\mathbf{8}]^+PF_6^-$ and *p*-Me, $[\mathbf{9}]^+PF_6^-$ [9]; and (iii) the X-ray crystal and molecular structure of the organometallic hydrazine $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_5NHNH_2)]^+PF_6^-$, $[\mathbf{1}]^+PF_6^-$, and the organometallic acetone–hydrazone $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}p\text{-}MeC_6H_4NHN{=}CMe_2)]^+PF_6^-$, $[\mathbf{9}]^+PF_6^-$. Some aspects of this work have been communicated [10].

2. Results and discussion

The preparation of the new ionic organometallic hydrazines $[\mathbf{1}]^+PF_6^-$, $[\mathbf{2}]^+PF_6^-$ and $[\mathbf{3}]^+PF_6^-$ (Scheme 1a) was carried out by reacting their respective chloroarene precursor complexes $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4Cl)]^+PF_6^-$, (R=H, *m*-Me and *p*-MeO), with the hydrazine hydrate, $NH_2NH_2{\cdot}H_2O$, according to the procedure reported by Sutherland, Lee et al. [9] for the synthesis of $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}o\text{-}ClC_6H_4NHNH_2)]^+PF_6^-$, $[\mathbf{4}]^+PF_6^-$, and $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}p\text{-}MeC_6H_4NHNH_2)]^+PF_6^-$, $[\mathbf{5}]^+PF_6^-$. However, from an experimental point of view, the best conditions established in order to reach the highest yields were: (i) the use of a hydrazine/precursor molar ratio of 8:1 for R=H, and 12:1 for R=*m*-Me, *p*-MeO; and (ii) a time of reaction of 15 h at room temperature. These complexes have indeed been synthesised under extremely mild conditions owing to the considerably high ability of the $[(\eta^5\text{-}Cp)Fe]^+$ moiety to enhance the reactivity of the chloroarene ligand toward nucleophilic reagents [7].

The organometallic hydrazines $[\mathbf{1}\text{–}\mathbf{3}]^+PF_6^-$ were obtained as yellow–orange, photosensible though air stable microcrystalline solids in yields ranging from 49 to 66%, and were characterised by ^{1}H- and ^{13}C-NMR, IR and UV–vis spectroscopy (see Section 5). The crystalline and molecular structure of $[\mathbf{1}]^+PF_6^-$ was determined by single crystal X-ray diffraction analysis (vide infra). The more salient features of the spectroscopic characterisation of these compounds are (i) the singlet resonance of the C_5-ring protons in the ^{1}H-NMR spectra, indicating that the reactions go to completion, leading to a unique product; and (ii) the signal pattern corresponding to the $-NHNH_2$ group. The ^{1}H-NMR spectra of organometallic hydrazines $[\mathbf{1}]^+PF_6^-$, $[\mathbf{2}]^+PF_6^-$ and $[\mathbf{3}]^+PF_6^-$ exhibit two proton resonances, in a 2:1 ratio, at 3.00 and 8.75, 3.00 and 8.65, and 3.04 and 8.60 ppm, respectively. The high field resonances are attributed to the NH_2 protons, while the low field ones are attributed to the NH protons due to the electron-withdrawing properties of the $Fe(\eta^5\text{-}Cp)^+$ cationic moiety linked to the phenyl ring. The IR spectra of these compounds exhibit two broad weak to medium absorption bands at ca. 3422 and 3382; 3430 and 3383; and 3444 and 3373 cm^{-1}, which have been attributed to the stretching mode of the N–H bond and to the asymmetric and symmetric stretching modes of the terminal NH_2 group. Likewise, at 1550, 1554 and 1506 cm^{-1} a sharp medium to strong band corresponding to the deformation mode of the NH_2 group was also observed.



Scheme 1.

Table 1
Selected bond distances (Å) and angles (°) of cations **[1]**$^+$ and **[9]**$^+$

Bond distances	**[1]**$^+$	**[9]**$^+$	Bond angles	**[1]**$^+$	**[9]**$^+$
Fe–C(1)	2.146(6)	2.201(5)	C(1)–N(1)–N(2)	119.0(8)	118.1(4)
Fe–C(2)	2.072(6)	2.103(5)	C(1)–N(1)–H(1N)	122.0	115(4)
Fe–C(3)	2.068(7)	2.079(5)	N(2)–N(1)–H(1N)	119.0	123(4)
Fe–C(4)	2.092(7)	2.087(5)	N(1)–N(2)–C(13)	–	116.0(4)
Fe–C(5)	2.059(7)	2.062(5)	N(2)–C(13)–C(14)	–	117.0(5)
C(1)–N(1)	1.336(8)	1.370(6)	N(2)–C(13)–C(15)	–	126.4(5)
N(1)–N(2)	1.380(9)	1.379(5)	C(14)–C(13)–C(15)	–	116.5(5)
N(2)–C(13)	–	1.283(6)			
C(13)–C(14)	–	1.504(7)			
C(13)–C(15)	–	1.491(7)			

On the other hand, the synthesis of the new acetone hydrazones **[6–9]**$^+PF_6^-$ (Scheme 1b) was readily accomplished by reaction of the organometallic hydrazines **[1]**$^+PF_6^-$, **[3]**$^+PF_6^-$, **[4]**$^+PF_6^-$, and **[5]**$^+PF_6^-$ with acetone in refluxing ethanol for 3.3 h, in the presence of small quantity of glacial acetic acid. However, all attempts to react **[2]**$^+PF_6^-$ with acetone were unsuccessful. Whatever the conditions of reaction, a small amount of an untractable oily residue was always obtained.

The four organometallic hydrazones were obtained as orange air stable microcrystalline solids in yields ranging from 54 to 77%, and were characterised by ^{1}H- and ^{13}C-NMR, IR and UV–vis spectroscopy (see Section 5). The crystalline and molecular structure of **[9]**$^+PF_6^-$ was determined by single crystal X-ray diffraction analysis (vide infra). The more important changes registered in the ^{1}H-NMR and IR spectra of these compounds, associated with the formation of the hydrazone backbone, $-NHN{=}CMe_2$, are: (i) appearance of a new singlet for the Cp signal in the ^{1}H-NMR spectra, this signal being upfield shifted relative to the starting materials due to the increase electron density on the arene ring; (ii) disappearance of the signal corresponding to the NH_2 proton resonances; (iii) appearance in the 1.94–2.14 ppm region of two different methyl proton resonances of the $-N{=}CMe_2$ fragment; (iv) disappearance of the asymmetric and symmetric ν(N–H) stretching vibrations corresponding to the NH_2 group, only the medium stretching band corresponding to the N–H group, in the 3355–3365 cm^{-1} region, remains; and (v) appearance of a new stretching band at ca. 1560 cm^{-1} corresponding to the C=N group.

A peculiar feature observed in the ^{1}H-NMR spectra of both compounds **[3]**$^+PF_6^-$ and **[7]**$^+PF_6^-$ is that the four aromatic protons appear, for both complexes, as a single resonance at δ 6.28 ppm, integrating for 4 H with respect to the Cp signal. This simplification of the expected AA′BB′ system into a single resonance, is probably due to accidental degeneracy. Such a phenomenon has already been noted in the [Fe(η^5-Cp)(η^6-p-MeC_6H_4X)]$^+$ complex (X = OMe, Et) [11]. Nevertheless, the proton-decoupled ^{13}C-NMR spectra of these complexes exhibit the two expected signals for the magnetically non-equivalent aromatic C–H atoms in position 2.6 and 3.5, respectively (see Section 5), thus confirming the structure of **[3]**$^+PF_6^-$ and **[7]**$^+PF_6^-$. Recent DFT calculations on [Fe(η^5-Cp)(η^6-$C_6H_5NH_2$)]$^+$ derivative [12], have indicated a significant decoordination of the *ipso* carbon, emphasizing the weight of an iminocyclohexadienyl mesomeric form in the description of such cationic complexes. However, based on our ^{13}C-NMR chemical shifts for the *ipso* carbon, such a cyclohexadienyl-like structure, ascertained in the solid state for **[1]**$^+$ and **[9]**$^+$ (vide infra), could not be confidently ascribed to the above described hydrazine and hydrazone compounds. Specific down field shifts (145–156 ppm) have been reported for *ipso* carbon of genuine cyclohexadienyl–iron complexes [13].

The UV–vis spectra of the four organometallic hydrazones **[6–9]**$^+PF_6^-$ have been recorded in solvents of various dielectric constants (THF, CH_2Cl_2, DMSO and MeOH; see Sections 5 and 6). All compounds present similar spectra with the expected intraligand CT excitation (338–350 nm), MLCT band at ca. 410 nm, and LMCT band at shorter wavelengths (< 300 nm) [14]. No solvatochromism is observed, the variation of λ_{max} values being in the experimental error limits.

3. Structural results

Selected bond distances and angles for compounds **[1]**$^+PF_6^-$ and **[9]**$^+PF_6^-$ are listed in Table 1. ORTEP drawings of the two cationic organometallic moieties, **[1]**$^+$ and **[9]**$^+$, with the atom labelling schemes, in similar perspectives for the sake of comparison, are presented in Figs. 1 and 2. High anisotropic thermal motion was noted for the carbon atoms of the Cp ligand in **[1]**$^+$ (Fig. 1). The observed orientations are presumably due to partial rotation of the C_5 ring about the Fe–Cp (centroid) axis [15]. However, both compounds display the classical sandwich structure of the type [(cyclopentadienyl)iron(arene)]$^+$ cations with the Fe–Cp and Fe–(Arene) centroid distances of 1.668 and 1.552 Å, respectively, for [**1**]$^+$, and 1.655 and 1.563 Å, respectively, for [**9**]$^+$. The ring centroid–iron–ring centroid vectors are essentially collinear (Cp–Fe–Arene = 179.4 for [**1**]$^+$ and 178.6° for [**9**]$^+$). These values are typical of a η^5-Fe-η^6 coordination [16].

On the other hand, one of the most remarkable deviations observed in the molecular parameters of [**1**]$^+$ and [**9**]$^+$ correspond to the Fe–C(1) bond length, 2.146(6) and 2.201(5) Å, respectively, which are ca. 0.071 and 0.12 Å longer than the mean of the other Fe–C (C_6 ring) bond lengths. It is noteworthy that these experimentaly determined Fe–C_{ipso} bond distances are in full agreement with the value of 2.236 Å, calculated for the $[FeCp(C_6H_5NH_2)]^+$ derivative [12]. Such a Fe–C_{ipso} bond elongation (0.18 Å) has also been reported for the μ-aryldiazenido complex [WF{N=N[η^6-*p*-C_6H_4Me)Fe(η^5-Cp]}(dppe)$_2$]$PF_6 \cdot Me_2CO$ [15c]. Moreover, the C(1)–N(1) bond lengths, 1.333(9) and 1.370(6) Å, respectively, are ca. 0.104 and 0.067 Å shorter than the mean reported for a C–N single bond and ca. 0.044 and 0.076 Å longer than the mean reported for a C=N double bond [17]. These data indicate a partial delocalization of the electron lone-pair of the N(1) atom toward the organometallic fragment which involves its partial depyramidalization. This hypothesis is supported taking into account the bond angles around the N(1) atom for [**9**]$^+$ (see Table 1). The sum of these bond angles is 356(4)°, which indicates the near planar character of the C(1)–N(1)H(1N)–N(2) fragment. A similar description could be made for [**1**]$^+$. These observations lead us to attribute (i) a partial positive charge on the N(1) atom of both organometallic cations and, consequently; (ii) a cyclohexadienyl-like character of the arene ring with a partial negative charge. The dihedral angle between the plane containing the five phenyl carbon atoms C(2)···C(6) and the C(2)–C(1)–C(6) plane, of 6.0(5) and 7.1(6)°, respectively, supports unequivocally this description, corroborating the theoretical work performed by Saillard et al. [12].

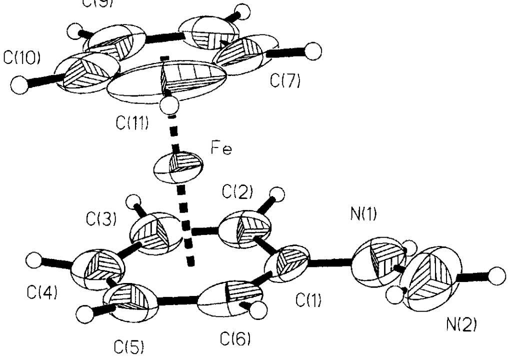


Fig. 1. ORTEP view of $[Fe(\eta^5\text{–}C_5H_5)(\eta^6\text{–}C_6H_5NHNH_2)]^+$, [**1**]$^+$, with the atom-labelling scheme.

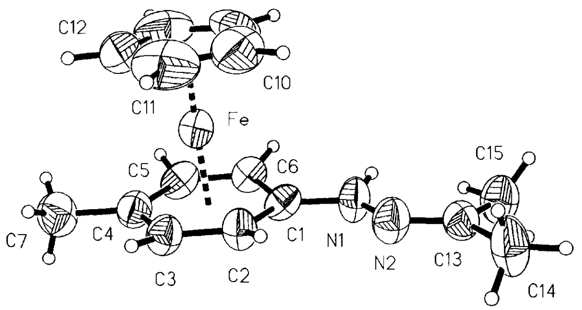


Fig. 2. ORTEP view of $[Fe(\eta^5\text{–}C_5H_5)(\eta^6\text{-}p\text{-}MeC_6H_4NHN{=}CMe_2)]^+$, [**9**]$^+$, with the atom-labelling scheme.

This depyramidalization of the N(1) atom promoted by the delocalization of its electron lone-pair toward the [CpFe(arene)]$^+$ fragment is also observable in the dicationic bimetallic complex μ-(η^6:η^6-phenoxaxine)-bis[η^5-cyclopentadienyl)iron(II)]$^{2+}$ [18]. In this case the C–N bond distances, 1.375(4) and 1.378(4) Å, are also intermediates between a single and double bond [17]. Likewise, the heterocycle ring containing the NH fragment is nearly planar having a dihedral angle between planes through the phenyl rings of 3.1(1)°. Nevertheless, no cyclohexadienyl-like deformation was reported for this complex.

On the other hand, in the $[Cr(CO)_3(\eta^6\text{-}C_6H_5NEt_2)]$ complex [19], the $Cr(CO)_3$ fragment promotes a similar effect on the $C_6H_5NEt_2$ ligand, the C–N bond distance being 1.357(3) Å and the sum of the bond angles around the nitrogen atom being 359.19°. These parameters indicate, for the N atom, a planar sp^2 hybridization. Likewise, the plane containing the carbon atom bonded to the NEt_2 group is tilted by 7.4°.

4. Concluding remarks

As a result of our studies we have succeded in the preparation of three new organometallic hydrazines of general formula $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}RC_6H_4NHNH_2)]^+PF_6^-$. The presence of classical organohydrazines linked to the iron atom of the $Fe(\eta^5\text{-}Cp)^+$ fragment through the phenyl group in an hexahapto fashion, as demonstrated by X-ray structure of [**1**]$^+PF_6^-$, is an exceptional opportunity to re-create the chemistry of this important class of organic compounds. Considering the recent applications of classical hydrazones as new materials for the non-linear optics we have synthesised four unprecedented organometallic acetone–hydrazones, one of them, **[9]**$^+$PF$_6^-$, being crystallographically characterised, as a first step toward the designing of new Type I non-rod-shaped dipolar chromophores. In this type of compound the [Fe(η^5-Cp)]$^+$ cationic fragment would act as an acceptor unit which can be used in push-pull substituted-electron system. We are currently exploring the synthesis of other organometallic hydrazines and hydrazones in order to evaluate their non-linear optical properties. These results will be the subject of forthcoming publications.

5. Experimental

5.1. General

All operations were performed under inert atmosphere using standard vacuum/nitrogen line (Schlenk) techniques. Solvents were dried and distilled under nitrogen by standard methods prior to use. Microanalytical data were obtained on a Perkin–Elmer Model 2400 elemental analyser. IR spectra were obtained as KBr disks on a Perkin–Elmer Model 1600 FT-IR spectrophotometer. All the NMR spectra were recorded on a multinuclear Brucker DPX 200 spectrometer at 297 K. ^{1}H-NMR spectra were recorded at 200 MHz, and all chemical shifts are reported in ppm relative to internal tetramethylsilane or the proton resonance resulting from incomplete deuteration of the NMR solvent. ^{13}C-NMR spectra were recorded at 50 MHz, and all chemical shifts are reported in ppm relative to the carbon on the deuterated NMR solvent. Melting points were determined in evacuated capillaries and were not corrected. Reagents were obtained as follows: Ferrocene, aluminium chloride, hydrazine hydrate, ammonium hexafluorophosphate, and the five chloroarenes used in this work were purchased from commercial sources and used as received. The CpFe(chloroarene) hexafluorophosphate complexes: [Fe(η^5-Cp)(η^6-C$_6$H$_5$Cl)]$^+$PF$_6^-$, [Fe(η^5-Cp)(η^6-*m*-MeC$_6$H$_4$Cl)]$^+$PF$_6^-$, [Fe(η^5-Cp)(η^6-*p*-MeOC$_6$H$_4$Cl)]$^+$PF$_6^-$, [Fe(η^5-Cp)(η^6-*o*-ClC$_6$H$_4$Cl)]$^+$PF$_6^-$ and [Fe(η^5-Cp)(η^6-*p*-MeC$_6$H$_4$Cl)]$^+$PF$_6^-$ were synthesised by ligand exchange between ferrocene and R–C$_6$H$_4$Cl in the presence of AlCl$_3$ according to ref. [20]; the arene is used as solvent at reflux overnight. Al powder was not used to avoid dehalogenation of chloroarenes, therefore, care must be taken to keep the reaction medium under inert atmosphere to avoid oxidation of the ferrocene. The hydrazine complexes **[4]**$^+$PF$_6^-$ and **[5]**$^+$PF$_6^-$ were prepared according to published procedures [9], that we have slightly modified by using a hydrazine/precursor molar ratio of 8:1 and 6:1, respectively, and stirring at room temperature for 15 h.

5.2. Preparation of [Fe(η^5-Cp)(η^6-C$_6$H$_5$NHNH$_2$)]$^+$PF$_6^-$, [1]$^+$PF$_6^-$

A mixture of 187 mg (0.50 mmol) of [Fe(η^5-Cp)(η^6-C$_6$H$_5$Cl)]$^+$PF$_6^-$ and 0.2 ml (4.0 mmol) of NH$_2$NH$_2$·H$_2$O in 3.0 ml of CH$_2$Cl$_2$ was stirred at room temperature for 15 h. Standard work up provided 92 mg (Yield 49%), m.p. 165°C dec. C$_{11}$H$_{13}$F$_6$FeN$_2$P (374.05): calc. C, 35.3, H, 3.50; Found C, 36.0, H, 3.76. UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 248 nm (4.15), 410 (2.72). IR (KBr): ν3422 cm^{-1} (w), ν(NH); 3382 (m), ν(NH); 3117 (vw), ν(CH) arom; 1550 (m), δ(NH); 830 (br, vs), ν(PF$_6$) and 557 (vs), δ(P–F). ^{1}H-NMR (CD$_3$COCD$_3$): δ = 3.00 (s, 2H, N*H*$_2$), 5.07 (s, 5H, C$_5$*H*$_5$), 6.16–6.41 (m, 5H, C$_6$*H*$_5$), 8.75 (s, 1H, N*H*). ^{13}C{^{1}H}-NMR (CD$_3$COCD$_3$): δ = 112.0 (C–NH), 86.4, 82.2, 76.2 (C–H arom), 70.1 (C–Cp). Suitable single crystals for X-ray diffraction studies were obtained during the recrystallisation step.

5.3. Preparation of [Fe(η^5-Cp)(η^6-m-MeC$_6$H$_4$NHNH$_2$)]$^+$PF$_6^-$, [2]$^+$PF$_6^-$

A mixture of 197 mg (0.50 mmol) of [Fe(η^5-Cp)(η^6-*m*-MeC$_6$H$_4$Cl)]$^+$PF$_6^-$ and 0.3 ml (6.0 mmol) of NH$_2$NH$_2$·H$_2$O in 5.0 ml of CH$_2$Cl$_2$ was stirred at room temperature for 15 h. Standard work up provided 123 mg (Yield 63%), m.p. 152–153°C dec. C$_{12}$H$_{15}$F$_6$FeN$_2$P (388.08): Calc. C, 37.1, H, 3.90; Found C, 38.2, H, 3.83. UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 248 nm (3.09), 413 (1.50). IR (KBr): ν3430 cm^{-1} (m), ν(NH); 3383 (w), ν(NH); 3120 (vw), ν(CH) arom; 2921 (vw), ν(CH) aliph; 1554 (m), δ(NH); 831 (br, vs), ν(PF$_6$) and 558 (s), δ(P–F). ^{1}H-NMR (CD$_3$COCD$_3$): δ = 2.59 (s, 3H, C*H*$_3$), 3.00 (s, 2H, N*H*$_2$), 5.02 (s, 5H, C$_5$*H*$_5$), 6.10–6.37 (m, 4H, C$_6$*H*$_4$), 8.65 (s, 1H, N*H*).

5.4. Preparation of [Fe(η^5-Cp)(η^6-p-MeOC$_6$H$_4$NHNH$_2$)]$^+$PF$_6^-$, [3]$^+$PF$_6^-$

A mixture of 0.203 mg (0.50 mmol) of [Fe(η^5-Cp)(η^6-*p*-MeOC$_6$H$_4$Cl)]$^+$PF$_6^-$ and 0.30 ml (6.0 mmol) of NH$_2$NH$_2$·H$_2$O in 5.0 ml of CH$_2$Cl$_2$ was stirred at room temperature for 15 h. Standard work up provided 133 mg (Yield 66%), m.p. 116–117°C. C$_{12}$H$_{15}$F$_6$FeN$_2$OP (404.12): calc. C, 35.7, H, 3.74; Found C, 36.2, H, 3.78. UV–vis (CH$_2$Cl$_2$): $\lambda_{\max}$ ($\log \varepsilon$) = 245 nm (3.15), 329 (2.35), 407 (1.38). IR (KBr): ν3444 cm^{-1} (w), ν(NH); 3373 cm^{-1} (m), ν(NH); 3114 (w), ν(CH) arom; 2976 (vw), ν(CH) aliph; 1560 (s), δ(NH); 1256 (m), ν(C–O); 843 (br, vs), ν(PF$_6$) and 558 (vs), δ(P–F). ^{1}H-NMR (CD$_3$COCD$_3$): δ = 3.04 (s, 2H, N*H*$_2$), 4.06 (s, 3H, C*H*$_3$); 5.07 (s, 5H, C$_5$*H*$_5$); 6.28 (s, 4H, C$_6$*H*$_4$), 8.60 (s, 1H, N*H*). ^{13}C{^{1}H}-NMR (CD$_3$COCD$_3$): δ = 57.70 (*C*H$_3$–O), 68.34 and 72.88 (*C*–H arom), 77.34 (*C*–Cp), 119.87 (*C*–NH) and 132.06 (*C*–OMe).

5.5. Preparation of $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}C_6H_5NHN{=}CMe_2)]^+PF_6^-$, $[\mathbf{6}]^+PF_6^-$

To a suspension of 40.0 mg (0.11 mmol) of $[\mathbf{1}]^+PF_6^-$ in 5.0 ml of EtOH are added 1.0 ml of Me_2CO and two drops of glacial acetic acid. The solution was refluxed for 3 h, allowed to stand at room temperature and concentrated in vacuo until a solid was formed. Then, 6.0 ml of Et_2O were added and allowed to stand at − 30°C overnight. The yellow–orange crystalline solid was filtered and washed with Et_2O and dried in vacuo. Finally, the complex was recrystallised from a Me_2CO–Et_2O mixture. Yield 24 mg (54%), m.p. 152–153°C. $C_{14}H_{17}F_6FeN_2P$ (414.12): Calc. C, 40.6, H, 4.14; Found C, 40.9, H, 4.34. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.15), 266 (4.23), 338 (3.40), 413 (2.81). IR (KBr): ν3359 cm^{-1} (s), ν(NH); 3105 (w), ν(CH) arom; 2959 (vw), 2919 (w), ν(CH) aliph; 1566 (vs), ν(C=N); 840 (br, vs), $\nu(PF_6)$ and 558 (vs), δ(P–F). ^{1}H-NMR [$CDCl_3$]: δ = 1.96 (s, 3H, CH_3), 2.01(s, 3H, CH_3), 4.84 (s, 5H, C_5H_5), 5.76–6.60 (m, 5H, C_6H_5), 7.74 (s, 1H, N*H*).

5.6. Preparation of $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}p\text{-}MeOC_6H_4NHN{=}CMe_2)]^+PF_6^-$, $[\mathbf{7}]^+PF_6^-$

To a suspension of 40.0 mg (0.099 mmol) of $[\mathbf{3}]^+PF_6^-$ in 5.0 ml of EtOH are added 1.0 ml of Me_2CO and two drops of glacial acetic acid. The solution was refluxed for 3 h, allowed to stand at room temperature and concentrated to dryness in vacuo. The oily residue was dissolved in CH_2Cl_2 and precipitated with Et_2O. The yellow–orange crystalline solid was finally recrystallised from a Me_2CO–Et_2O mixture. Yield 26 mg (59%), m.p. 159°C dec. $C_{15}H_{19}F_6FeN_2OP$ (444.14): Calc. C, 40.6, H, 4.31; Found C, 40.0, H, 4.50. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 233 (4.28), 266 (4.27), 350 (3.45), 410 (2.04). IR (KBr): ν3355 cm^{-1} (m), ν(NH); 3114 (w), ν(CH) arom; 3015, 2952, 2881 (vw), ν(CH) aliph; 1570 (m), ν(C=N); 841 (br, vs), $\nu(PF_6)$ and 559 (m), δ(P–F). ^{1}H-NMR [CD_3COCD_3]: δ = 2.04(s, 3H, CH_3), 2.14 (s, 3H, CH_3), 4.06 (s, 3H, *p*-OCH_3), 5.07 (s, 5H, C_5H_5), 6.28 (s, 4H, C_6H_4), 8.59 (s, 1H, N*H*). $^{13}C\{^1H\}$-NMR (CD_3COCD_3): δ = 17.21 and 25.75 (*C*H_3–C), 57.70 (*C*H_3–O), 68.38 and 72.89 (*C*–H arom), 77.34 (*C*–Cp), 119.76 (*C*–NH), 132.08 (*C*–OMe), 153.32 (C=N).

5.7. Preparation of $Fe(\eta^5\text{-}Cp)(\eta^6\text{-}o\text{-}ClC_6H_4NHN{=}CMe_2)]^+PF_6^-$, $[\mathbf{8}]^+PF_6^-$

The synthesis of this yellow–orange complex was carried out using a procedure similar to that described for complex $[\mathbf{6}]^+PF_6^-$, using in this case 40.0 mg (0.098 mmol) of $[\mathbf{1}]^+PF_6^-$. Yield 34 mg (77%), m.p. 143–145°C. $C_{14}H_{16}ClF_6FeN_2P$ (450.56): calc. C, 37.5, H, 3.60; Found C, 36.9, H, 3.65. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 239 (4.21), 263 (4.22), 338 (3.44), 413 (2.47). IR (KBr): ν3365 cm^{-1} (m), ν(NH); 3134 (w), ν(CH) arom; 3100 (w), ν(CH) arom; 3000, 2940, 2906 (w), ν(CH) aliph; 1553 (vs), ν(C=N); 842 (br, vs), $\nu(PF_6)$ and 558 (s), δ(P–F). ^{1}H-NMR [$CDCl_3$]: δ = 1.98 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 4.91(s, 5H, C_5H_5), 6.06–6.54 (m, 4H, C_6H_4), 8.14 (s, 1H, N*H*).

5.8. Preparation of $[Fe(\eta^5\text{-}Cp)(\eta^6\text{-}p\text{-}MeC_6H_4NHN{=}CMe_2)]^+PF_6^-$, $[\mathbf{9}]^+PF_6^-$

This yellow–orange complex was synthesised according to the procedure described above for $[\mathbf{6}]^+PF_6^-$, using in this case 41.0 mg (0.11 mmol) of $[\mathbf{5}]^+PF_6^-$. Yield 28 mg (62%), m.p. 197–198°C dec. $C_{15}H_{19}F_6FeN_2P$ (428.14): calc. C, 42.1; H, 4.47; Found C, 41.4; H, 4.30. UV–vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.18), 266 (4.21), 338 (3.38), 410 (2.37). IR (KBr): ν3356 cm^{-1} (m), ν(NH); 3095 (vw), ν(CH) arom; 2918 (vw), ν(CH) aliph; 1566 (s), ν(C=N); 840 and 828 (vs), $\nu(PF_6)$ and 558 (vs), δ(P–F). ^{1}H-NMR [CD_2Cl_2]: δ = 2.03. (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.41 (s, 3H, *p*-CH_3), 4.85 (s, 5H, C_5H_5), 5.90 (d, 2H, C_6H_4, J_{H-H} 6.82), 6.20 (d, 2H, C_6H_4, J_{H-H} 6.84 Hz), 7.58 (br s, 1H, N*H*). $^{13}C\{^1H\}$-NMR [CD_2Cl_2]: δ = 16.57 and 20.32 (CH_3), 25.61 (4-*C*H_3), 69.34 and 86.09 (*C*–H arom), 76.52 (*C*–Cp), 96.84 (*C*-4 arom), 120.78 (*C*–NH), 153.85 (N=*C*Me_2). Suitable single crystals for X-ray diffraction studies were obtained during the recrystallisation step.

5.9. X-ray structure determination of $[\mathbf{1}]^+PF_6^-$ and $[\mathbf{9}]^+PF_6^-$

Crystallographic data for $[\mathbf{1}]^+PF_6^-$: $C_{11}H_{13}F_6FeN_2P$, Mr = 374.05, unit cell dimensions: a = 7.524(2), b = 16.575(4), c = 11.515(3) Å, β = 90.51(3)°, V = 1436.0(6) Å^3, monoclinic, $P2_1/n$, Z = 4, crystal size (mm): 0.30 × 0.28 × 0.20, range 2.15–29.09° at 298(2) K, reflections collected 5368, independent reflections 2540 (R_{int} = 0.0548), 1383 reflections with $I > 2\sigma(i)$. Convergence at conventional $R_1 = 0.0644$, $wR_2 = 0.1657$. Cell parameters were determined from least-squares fit of 50 reflections with $8 \leq 2\theta \leq 30°$. High thermal motion was noted for the C atoms of the Cp ligand; however, a disorder model could not be resolved.

Crystallographic data for $[\mathbf{9}]^+PF_6^-$: $C_{15}H_{19}F_6FeN_2P$, Mr = 428.14 g mol^{-1}, unit cell dimensions: a = 10.975(2), b = 11.109(1), c = 15.304(3) Å, β = 109.58(1)°, V = 1758.0(5) Å^3, monoclinic, $P2_1/n$, Z = 4, crystal size (mm): 0.20 × 0.16 × 0.09, range 2.00–25.05° at 297(2) K, reflections collected 3410, independent reflections 3124 (R_{int} = 0.0178), 1407 reflections with $i > 2\sigma(i)$. Convergence at $R_1 = 0.0487$, $wR_2 = 0.0946$. Cell parameters were determined from least-squares fit of 50 reflections with $8 \leq 2\theta \leq 30°$.

Intensity data were collected on a Siemens R_3m/V four circle diffractometer, Mo–K$_\alpha$ radiation (λ = 0.71073 Å, scan type θ–2θ. Semi-empirical corrections, via ψ-scans, were applied for absorption. The structures were solved by direct methods and refined on F^2 with SHELXL-97 [21], with all non-H atoms anisotropic. A riding model was applied to H-atoms which were placed at calculated positions with C–H = 0.96 and N–H = 0.90 Å with equivalent isotropic thermal parameter equal to 1.2 times the equivalent isotropic thermal parameter of their attached parent atoms. Exception was made with atom H(1) of $[\mathbf{9}]^+\mathrm{PF}_6^-$, bonded to atom N(1), which was determined from a difference Fourier synthesis in order to study the depyramidalization of the N(1) atom in the C(1)–N(1)H(1N)–N(2) group.

6. Supplementary material

UV–vis data of compounds $[\mathbf{6}\text{–}\mathbf{9}]^+\mathrm{PF}_6^-$ in THF, $\mathrm{CH_2Cl_2}$, DMSO and MeOH are available from the authors. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 143536 for compound $[\mathbf{1}]^+\mathrm{PF}_6^-$ and CCDC no. 132378 for compound $[\mathbf{9}]^+\mathrm{PF}_6^-$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033; e-mail:deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) C. Serbutoviez, C. Bosshard, G. Knöpfle, P. Wyss, P. Prêtre, P. Günter, K. Schenk, E. Solari, G. Chapuis, Chem. Mater. 7 (1995) 1198. (b) M.S. Wong, U. Meier, F. Pan, V. Gramlich, C. Bosshard, P. Günter, Adv. Mater. 8 (1996) 416. (c) M.S. Wong, C. Bosshard, F. Pan, P. Günter, Adv. Mater. 8 (1996) 677. (d) F. Pan, C. Bosshard, M. S. Wong, C. Serbutoviez, S. Follonier, P. Günter, K. Schenk, J. Cryst. Growth 165 (1996) 273. (e) S. Follonier, C. Bosshard, U. Meier, G. Knöpfle, C. Serbutoviez, F. Pan, P. Günter, J. Opt. Soc. Am. Sect B 14 (1997) 593. (f) F. Pan, M.S. Wong, M. Bösch, C. Bosshard, U. Meier, Appl. Phys. Lett. 71 (1997) 2064. (g) M.S. Wong, V. Gramlich, C. Bosshard, P. Günter, J. Mater. Chem. 7 (1997) 2021. (h) I. Liakatas, M.S. Wong, V. Gramlich, C. Bosshard, P. Günter, Adv. Mater. 10 (1998) 777.

[2] (a) D. Lupo, W. Prass, U. Scheunemann, A. Laschewasky, H. Ringsdorf, I. Ledoux, J. Opt. Soc. Am., B5 (1988) 300. (b) C. Bubeck, A. Laschewsky, D. Lupo, D. Neher, P. Ottenbreit, W. Paulus, H. Ringsdorf, G. Wegner, Adv. Mater, 3 (1991) 54.

[3] (a) D. Astruc, The Chemistry of the Metal–Carbon Bond, vol. 4, in: F.R. Hartley, S. Patai (Eds.), Wiley, New York, 1987, pp. 625. (b) R.G. Sutherland, M. Igbal, A. Piorkó, J. Organomet. Chem. 302 (1986) 307. (c) R. G. Sutherland, J. Organomet. Chem. Library 3 (1977) 311.

[4] H.A. Trujillo, C.M. Casado, J. Ruiz, D. Astruc, J. Am. Chem. Soc. 121 (1999) 5674.

[5] D. Astruc, Acc. Chem. Res. 30 (1997) 383.

[6] (a) D. Astruc, Chem. Rev. 88 (1988) 1189. (b) W.A. Hendrickson, M.C. Palazzotto, Photosensitive Metal–Organic Systems, in: C. Kutal, N. Serpone (Eds.), Advanced Chemistry Series, Washington, DC, 1993, pp. 411.

[7] (a) D. Astruc, Tetrahedron Report No. 157, Tetrahedron 39 (1983) 4027 (and references therein). (b) D. Astruc, Top. Curr. Chem. 160 (1991) 47 (and references therein).

[8] C. Lambert, W. Gaschler, M. Zabel, R. Matschiner, R. Wortmann, J. Organomet. Chem. 592 (1999) 109.

[9] (a) C.C. Lee, A.S. Abb-El-Aziz, R.L. Chowdhury, U.S. Gill, A. Piórko, R.G. Sutherland, J. Organomet. Chem. 315 (1986) 79. (b) A. Piórko, R.G. Sutherland, A.Vessières-Jaouen, G. Jaouen, J. Organomet. Chem. 512 (1996) 79.

[10] C. Manzur, L. Millán, M. Fuentealba, J.R. Hamon, D. Carrillo, Tetrahedron Lett. 41 (2000) 3615.

[11] A.N. Nesmeyanov, I.F. Leshchova, Y.A. Ustynyuk, Y.I. Sirotkina, I.N. Bolesova, L.S. Isayeva, N.A. Vol'kenau, J. Organomet. Chem. 22 (1970) 689.

[12] J. Ruiz, F. Ogliaro, J.Y. Saillard, J.F. Halet, F. Varret, D. Astruc, J. Am. Chem. Soc. 120 (1998) 11693.

[13] (a) P. Michaud, D. Astruc, J. Chem. Commun. (1982) 416. (b) D. Astruc, J.R. Hamon, E. Roman, P. Michaud, J. Am. Chem. Soc. 103 (1981) 7502.

[14] (a) A.L. Beuze, R. Lissilour, J. Weber, Organomet., 12 (1993) 47; (b) See also references 5(a) and 8. (c) J.R. Hamon, D. Astruc, P. Michaud, J. Am. Chem. Soc. 103 (1981) 758.

[15] (a) J.L. Fillaut, R. Boese, D. Astruc, Synlett (1992) 55. (b) S. Subramanian, L. Wang, M. Zaworotko, Organomet. 12 (1993) 310. (c) Y. Ishii, M. Kawaguchi, Y. Ishino, T. Aoki, M. Hidai, Organomet. 13 (1994) 5062.

[16] (a) By comparison to a collection of structural data obtained through a Cambridge Data Base search covering 50 $[\mathrm{Fe}(\eta^5\text{–}\mathrm{C}_5\mathrm{H}_5)(\eta^6\text{–arene})]^+$ compounds. Cambridge Data Base System, Cambridge Crystallographic Data Center, Version 5.12; (b) see also reference 17.

[17] A.G. Orpen, L. Brammer, F.H. Allen, D. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc. Dalton Trans. S1 (1989).

[18] V.M. Lynch, S.N. Thomas, S.H. Simonses, A. Piórko, R.G. Sutherland, Acta Crystallogr. Sect. C 42 (1986) 1144.

[19] J.Y. Saillard, D. Grandjean, P.L. Maux, G. Jaouen, Nouv. J. Chim. 5 (1981) 153.

[20] (a) D. Astruc, personal communication to D.C. (b) J.F. Helling, W.A. Hendrickson, J. Organomet. Chem. 168 (1979) 87.

[21] G.M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.