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# Organodiiron(II)-complexes containing a long conjugated hydrazonato spacer. Synthesis, characterization, electrochemical and structural studies

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## Abstract

Organometallic hydrazines of general formula  $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-}p\text{-RC}_6\text{H}_4\text{NHNH}_2)]^+\text{PF}_6^-$  (Cp = C<sub>5</sub>H<sub>5</sub>; R = H, (1)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Me, (2)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; MeO, (3)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Cl, (4)<sup>+</sup>PF<sub>6</sub><sup>-</sup>) react with equimolar quantities of (*E*)-4-(2-ferrocenylvinyl)-benzaldehyde, (*E*)- $[(\eta^5\text{-Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=CH-C}_6\text{H}_4\text{CHO}]$ , to afford stereoselectively, the new homodimetallic hydrazones formulated as (*E*)- $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-}p\text{-RC}_6\text{H}_4)\text{-NHN=CH-C}_6\text{H}_4\text{-CH=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)Fe}(\eta^5\text{-Cp})]^+\text{PF}_6^-$  (R = H, (5)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Me, (6)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; MeO, (7)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Cl, (8)<sup>+</sup>PF<sub>6</sub><sup>-</sup>). These compounds were fully characterized by elemental analysis and spectroscopic techniques (<sup>1</sup>H- and <sup>13</sup>C-NMR, IR and UV-vis) and, in the case of complex (6)<sup>+</sup>PF<sub>6</sub><sup>-</sup>, by single crystal X-ray diffraction methods. The rotations of the ferrocenyl unit by 37.2° out of the -NHN=CH-C<sub>6</sub>H<sub>4</sub>-CH=CH- spacer and coordinated phenyl ring planes, may generate an unfavorable structure to allow π-electron delocalization along the entire hydrazonato backbone between the two metals separated through bonds by more than 1.8 nm, as confirmed by the electrochemical data. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Sandwich complex; Cyclopentadienyl-iron complex; Arenehydrazone-iron complex; X-ray structure; Bimetallic complex; Nanomolecule

## 1. Introduction

The molecular sciences of the transition metals have potential applications in the new fascinating field of molecular electronics, [1,2a,2b] based inter alia on the fact that the oxidation states of transition-metals can be varied to a great extent and thus that many electron transfer processes can result [2a]. By suitable molecular engineering, it should become possible to assemble and tune molecular devices including transition metals and organize their interface with the macroscopic world. In this context, we have focused our attention on simple bimetallic model systems [3], made of the cationic  $[(\eta^5\text{-$

Cp)Fe( $\eta^6\text{-arene})]^+$  (Cp = C<sub>5</sub>H<sub>5</sub>) moiety as an electron withdrawing building block [4] linked to a ferrocenyl unit through the hydrazonic skeleton spacer, NH-N=CH-, in order to investigate the electronic cooperation between both metal centers. Structural, electronic and theoretical (DFT) data have confirmed the ground state electronic interaction between the electron withdrawing mixed sandwich  $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-arene})]^+$  and the donor ferrocene-based termini [5].

As part of our ongoing research interest, in the present work we describe: (i) the preparation of a family of four new Type I [6] organo-iron(II) hydrazone complexes of general formula (*E*)- $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-}p\text{-RC}_6\text{H}_4)\text{-NHN=CH-C}_6\text{H}_4\text{-CH=CH-(}\eta^5\text{-C}_5\text{H}_4\text{)Fe}(\eta^5\text{-Cp})]^+\text{PF}_6^-$  (R = H, (5)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Me, (6)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; MeO, (7)<sup>+</sup>PF<sub>6</sub><sup>-</sup>; Cl, (8)<sup>+</sup>PF<sub>6</sub><sup>-</sup>), where both metal centers are

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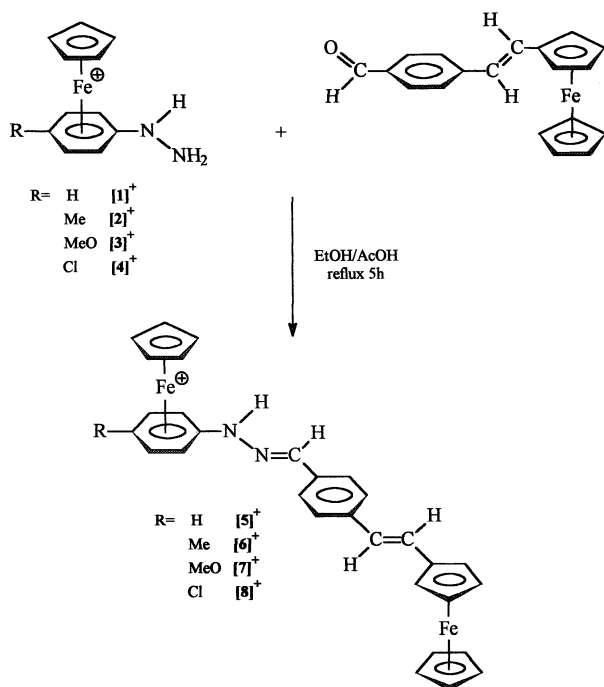
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connected by a long hydrazone spacer with a separation through bonds greater than 1.8 nm, (ii) the analytical and spectroscopic characterization (IR,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, UV-vis, cyclic voltammetry) of these nanosized molecules, and (iii) the X-ray crystal structure of complex  $(6)^+\text{PF}_6^-$ .

## 2. Results and discussion

### 2.1. Synthesis and characterization

The synthesis of the new organometallic hydrazones  $(5-8)^+\text{PF}_6^-$  was accomplished by reaction of organometallic hydrazine precursors  $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-}p\text{-RC}_6\text{H}_4\text{NHNH}_2)]^+\text{PF}_6^-$  ( $\text{R} = \text{H}$ ,  $(1)^+\text{PF}_6^-$ ;  $\text{Me}$ ,  $(2)^+\text{PF}_6^-$ ;  $\text{MeO}$ ,  $(3)^+\text{PF}_6^-$ ;  $\text{Cl}$ ,  $(4)^+\text{PF}_6^-$ ) with the ferrocene-based aldehyde  $(E)-[(\eta^5\text{-Cp})\text{Fe}(\eta^5\text{-C}_5\text{H}_4)\text{-CH=CH-C}_6\text{H}_4\text{CHO}]$  in refluxing ethanol containing concentrated acetic acid (Scheme 1). Because these complexes have shown to be fairly light-sensitive in solution, leading to the decomplexation of the  $[\text{Fe}(\eta^5\text{-Cp})]^+$  group, the synthetic procedures were carried out in the absence of light. The four complexes, were obtained as air stable orange microcrystalline solids in yields ranging from 63 to 77%, and they exhibit a good solubility in  $\text{CH}_2\text{Cl}_2$ ,  $\text{MeCN}$ ,  $\text{Me}_2\text{CO}$  and  $\text{DMSO}$ , but are insoluble in diethylether and water. The structure of these four new homodimetallic hydrazones were inferred from satisfactory elemental analyses,  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, IR and UV-vis spectroscopies (see Section 4)



Scheme 1.

and, additionally, in the case of complex  $(6)^+\text{PF}_6^-$ , by X-ray diffraction analysis (vide infra).

The IR spectra of complexes  $(5-8)^+\text{PF}_6^-$  invariably exhibit: (i) a sharp medium absorption band in the  $3310\text{--}3270\text{ cm}^{-1}$  region attributed to the  $\nu(\text{N-H})$  stretching vibration [7]; (ii) a weak band at  $1595\text{--}1598\text{ cm}^{-1}$  region assigned to the  $\nu(\text{C=C})$  stretching mode, (iii) a strong band in the  $1560\text{--}1570\text{ cm}^{-1}$  region which has been attributed to the stretching mode of the  $\text{C=N}$  group; and (iv) a very strong  $\nu(\text{PF}_6)$  band in the  $840\text{--}846\text{ cm}^{-1}$  region and a strong  $\delta(\text{P-F})$  band at  $558\text{ cm}^{-1}$ . There are additional weaker bands in the range  $1550\text{--}1600\text{ cm}^{-1}$ , which occurred for all the complexes and can not be unequivocally assigned. These vibrations could indeed be attributed to either a carbon–nitrogen stretching frequency of the arene  $N$  system (see Section 2.3 below) or carbon–carbon stretching frequencies [8].

Interestingly, the dinuclear organometallic hydrazones  $(5-8)^+\text{PF}_6^-$  are stereoselectively formed as the sterically less hindered *trans*-isomer (about the  $\text{N=C}$  double bond) as indicated by the unique set of signals in their  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra (acetone- $d_6$ , 297 K), and definitively assigned from the structural analysis of  $(6)^+\text{PF}_6^-$  (see below). The *trans* arrangement about the  $\text{HC=CH}$  double bond of the starting organometallic aldehyde is also retained as illustrated by the AB resonance pattern with a characteristic  $^3J_{\text{H-H}}$  coupling constant of ca. 16 Hz (see Section 4). Both Cp resonances appear as singlets at  $\delta$  5.09–5.26 and 4.25–4.58, depending on the nature of the  $p$ -R substituents at the coordinated phenyl ring, for the cationic and the neutral sandwiches, respectively. However, in all the complexes, the  $\text{C}_5\text{H}_4$  proton resonances are poorly resolved and appear as broad singlets. On the other hand, upon complexation, the aromatic protons of the coordinated  $\text{C}_6$ -ring ( $6.22 < \delta < 6.77$ ) are, as expected, up-field shifted relative to those of the phenylene unit ( $7.62 < \delta < 7.85$ ) which shows a well resolved AB system (see Section 4). Likewise, the NH and CH resonances are observed at low-field in agreement with literature data [5,9]. On the other hand, the proton decoupled  $^{13}\text{C}$ -NMR spectra of complexes  $(6)^+\text{PF}_6^-$  ( $\text{R} = \text{Me}$ ) and  $(7)^+\text{PF}_6^-$  ( $\text{R} = \text{MeO}$ ), exhibit the expected characteristic singlet resonances for the  $\text{C}_5$ -ring of two different  $\text{CpFe}$  and  $\text{CpFe}^+$  fragments at ca.  $\delta$  72 and 77, respectively. The two carbon atoms linked to a nitrogen atom appear as broad singlets at lower-field, the imine carbon at  $\delta$  145 and the coordinated  $\text{C}_{\text{ipso}}$  at ca.  $\delta$  119. This latter value agrees well with a partial  $\text{C-N}$  double bond character (see below). The other chemical shifts are unexceptional, and as observed in the  $^1\text{H}$ -NMR spectra, the coordinated carbon atoms are up-field-shifted relative to those of the free arenes.

Finally, the UV-vis spectra of the four organodir- on(II) hydrazone complexes  $(5-8)^+\text{PF}_6^-$  have been recorded in  $\text{CH}_2\text{Cl}_2$  ( $\epsilon = 8.90$ ) and  $\text{DMSO}$  ( $\epsilon = 47.6$ )

(see Section 4). The spectra are consistent with those observed in other ferrocenyl monosubstituted compounds reported in the literature in that they show two charge-transfer bands in the visible region [5,10]. The complexes exhibit, in  $\text{CH}_2\text{Cl}_2$ , a prominent absorption band at ca. 369 nm assigned to intraligand charge-transfer excitations (ILCT). At longer wavelengths, there are weaker MLCT bands at ca. 450–550 nm, and at shorter wavelengths ( $< 300$  nm) there are LMCT or MLCT bands. The ILCT bands of four compounds are weakly solvatochromic, showing a 6–8 nm red shift upon switching the solvent from  $\text{CH}_2\text{Cl}_2$  to DMSO. The  $\lambda_{\text{max}}$  of the low-energy bands could not be accurately determined, and the broadening is probably the result of the overlap of broad d–d visible bands corresponding to both the  $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-arene})]^+$  [11] and  $(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-Cp})$  [12] fragments.

## 2.2. Electrochemical studies

In order to get a deeper insight into the mutual donor–acceptor electronic influence through a long  $\pi$ -delocalized spacer, we studied the electrochemical behavior of the homodimetallic hydrazone complexes  $(\mathbf{5}\text{--}\mathbf{8})^+\text{PF}_6^-$  by cyclic voltammetry (CV). The CV studies were carried out at room temperature using a Pt wire working electrode in acetonitrile containing 0.1 M  $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$  as supporting electrolyte. Under these conditions, the ferrocene shows a reversible oxidation wave at 0.459 V. All the complexes  $(\mathbf{5}\text{--}\mathbf{8})^+\text{PF}_6^-$  undergo a reversible one-electron oxidation process in the range 441–497 mV versus  $\text{Ag}/\text{AgCl}$ , centered at the ferrocenyl group,  $(\eta^5\text{-C}_5\text{H}_4)\text{FeCp}$  [13] and corresponds to the generation of the dicationic  $\text{Fe(II)–Fe(III)}$  mixed valence species. All mono-/di-cation redox processes were chemically reversible, near-Nernstian processes ( $\Delta E_p = 86\text{--}94$  mV). However, unexpectedly, the electron-withdrawing effect of the  $[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-arene})]^+$  fragment, through the planar  $\text{–NHN=CH–C}_6\text{H}_4\text{–CH=CH–}$  linker (see below), is inexistent or weak [5]. On the other hand, the irreversible cathodic processes ( $-1.290$  to  $-1.310$  V vs.  $\text{Ag}/\text{AgCl}$ ), observed for all the compounds, are centered at the mixed sandwich moiety, and correspond to the single-electron reduction of the  $d^6$ ,  $\text{Fe(II)}$ , 18-electron complexes to the unstable  $d^7$ , 19-electron  $\text{Fe(I)}$  species [2c,14]. Likewise, these cathodic electrode potentials are not affected by the electron-donating effect of the ferrocenyl entity. Probably, either the length and/or the geometric arrangement of the molecules (see below) may generate an unfavorable structure to allow the electronic interaction to extend between electron-donating and electron-accepting termini through the entire hydrazone skeleton.

Finally, as it was established for related binuclear compounds bearing the shorter  $\text{–NHN=CH–}$  spacer [5], no correlation can be found between either the oxida-

tion or reduction potentials of the homodimetallic hydrazone complexes  $(\mathbf{5}\text{--}\mathbf{8})^+\text{PF}_6^-$  and the *para*-substituents (Hammett constants) of the coordinated phenyl groups.

## 2.3. X-ray crystallographic studies

X-ray quality crystals of the complex  $(\mathbf{6})^+\text{PF}_6^-$  were grown from a biphasic  $\text{CH}_2\text{Cl}_2\text{:Et}_2\text{O}$  1:1 system at  $20^\circ\text{C}$ , and the crystal structure was determined by single-crystal X-ray diffraction as outlined in the Section 4. The ORTEP plot of the cationic moiety  $(E)\text{–}[(\eta^5\text{-Cp})\text{Fe}(\eta^6\text{-}p\text{-MeC}_6\text{H}_4)\text{–NHN=CH–C}_6\text{H}_4\text{–CH=CH–}(\eta^5\text{-C}_5\text{H}_4)\text{Fe}(\eta^5\text{-Cp})]^+$  with the atom labeling scheme is illustrated in Fig. 1. Selected intramolecular distances and angles are listed in Table 1. The metrical parameters are typical of  $\eta^5\text{-Fe–}\eta^6$  and  $\eta^5\text{-Fe–}\eta^5$  metallocene-type coordination [15–18]. The carbocyclic rings coordinated to the same iron center are essentially parallel with one another, and the ring centroid–iron–ring centroid vectors are almost collinear both in the  $[\text{Cp–Fe–arene}]^+$  and in the ferrocenic fragments (Table 1).

The metal centers are connected by the long anionic  $\pi$ -binucleating hydrazone ligand  $[p\text{-Me–C}_6\text{H}_4\text{–NHN=CH–C}_6\text{H}_4\text{–CH=CH–C}_5\text{H}_4]^-$ , being the  $\text{Fe}\cdots\text{Fe}$  distance through bonds and through space of 18.121 and 13.409 Å, respectively. Likewise, the shortest  $\text{Fe}\cdots\text{Fe}$  intermolecular contact is 6.034 Å and it appears between the  $\text{Fe(1)}$  and  $\text{Fe(2)}$  with the symmetry related position  $1/2 - x, 1/2 + y, 3/2 - z$ . On the other hand, the both sandwich units are attached to the planar  $[\text{19}] \text{–NHN=CH–C}_6\text{H}_4\text{–CH=CH–}$  spacer in quite different forms. While the coordinated phenyl group is nearly coplanar with the spacer, subtending a dihedral angle of  $6.2^\circ$ , the cyclopentadienyl group of the ferrocenyl unit subtends a dihedral angle of  $37.2^\circ$ . A dihedral angle of  $30.4^\circ$ , between the  $\text{C}_6$  and  $\text{C}_5$  rings, has also been found in a related bimetallic compound with the shorter  $\text{–NHN=CH–}$  spacer [9b]. This departure from planarity is accounted for by a sterically-driven process, leading to a more comfortable arrangement of the H atom and the  $\text{C}_5\text{H}_4$  group at the  $\text{sp}^2$ -hybridized C(9)

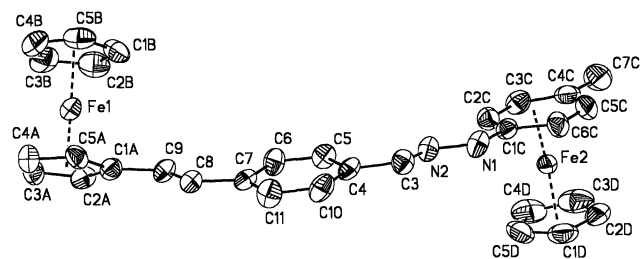


Fig. 1. Molecular structure of complex  $(\mathbf{6})^+$  showing the atom numbering scheme. Hydrogen atoms and counter anion  $\text{PF}_6^-$  have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Table 1  
Selected bond distances (Å) and angles (°) of complex (6)<sup>+</sup> <sup>a</sup>

Distances			
Fe(2)–C(1c)	2.183(4)	Fe(1)–C(1a)	2.045(4)
Fe(2)–C(2c–6c)	2.079 <sup>b</sup>	C(1c)–N(1)	1.362(5)
N(1)–N(2)	1.369(5)	N(2)–C(3)	1.272(5)
C(3)–C(4)	1.453(6)	C(4)–C(5)	1.384(6)
C(5)–C(6)	1.375(6)	C(6)–C(7)	1.392(6)
C(4)–C(10)	1.381(6)	C(10)–C(11)	1.389(6)
C(7)–C(8)	1.468(6)	C(8)–C(9)	1.327(6)
C(9)–C(1a)	1.457(6)	C–C(Cp')	1.416 <sup>b</sup>
Fe(1)–Fe(2)	18.087 <sup>c</sup>	Fe(1)–Fe(2)	13.409 <sup>d</sup>
Fe(1)–Cp <sub>CNT</sub>	1.654	Fe(1)–Cp <sub>CNT</sub>	1.652
Fe(2)–Cp <sub>CNT</sub>	1.662	Fe(2)–Ph <sub>CNT</sub>	1.556
Angles			
C(1c)–N(1)–N(2)	120.5(4)	N(1)–N(2)–C(3)	117.1(4)
N(2)–C(3)–C(4)	121.9(4)	C(7)–C(8)–C(9)	127.3(4)
C(8)–C(9)–C(1a)	125.2(4)	Cp <sub>CNT</sub> –Fe(1)–Cp <sub>CNT</sub>	178.93
Cp–Fe(2)–Ph <sub>CNT</sub>	178.96		

<sup>a</sup> Abbreviations: Cp, C<sub>5</sub>H<sub>5</sub>; Cp', C<sub>5</sub>H<sub>4</sub>; Ph, C<sub>6</sub>H<sub>4</sub>Me; CNT, centroid.

<sup>b</sup> Average bond distances.

<sup>c</sup> Sum of the bond distances.

<sup>d</sup> Measured through-space distance.

carbon atom. However, structural data indicate  $\pi$ -electron delocalization between the cationic sandwich and the bent hydrazonato skeleton backbone, through (i) the slight cyclohexadienyl-like character at the coordinated C<sub>6</sub> phenyl ring [20,21] with a folding angle of 5.03°; (ii) some C<sub>ipso</sub>–N multiple bond character as indicated by the C(1c)–N(1) distance of 1.362(5) Å [18]; and (iii) the depyramidalization of the N(1) benzylic-type nitrogen atom, which is reflected by a typical bond angle at the sp<sup>2</sup>-hybridized N(1) atom (C(1c)–N(1)–N(2) = 120.5(4)°). Finally, the structure is stabilized by a PF<sub>6</sub><sup>−</sup> counteranion through a short contact between the hydrogen atom attached to the N(1) atom and one of the fluorine. The estimated bond distance and angle for N(1)–H(1)···F(2) are 2.20(1) Å and 167(3)°, respectively.

### 3. Concluding remarks

We have presented a facile synthetic methodology leading to a homogeneous series of four new organo-iron(II) complexes containing a long  $\pi$ -conjugated hydrazonato spacer, in which the two metal centers are separated by more than 1.8 nm. Structural and electrochemical data indicate the lack of electronic interaction between the mixed sandwich [CpFe(arene)]<sup>+</sup> and ferrocene based termini, through the long delocalized hydrazonato  $\pi$ -system. The decay of the metal–metal interaction with distance has already been observed and quantified [22].

## 4. Experimental

### 4.1. General remarks

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 analyzer. IR spectra were obtained as KBr disks on a Perkin–Elmer Model 1600 FTIR spectrophotometer. Electronic spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> and DMSO solutions with a Spectronic, Genesys 2, spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were acquired at 297 K on a multinuclear Bruker DPX 200 spectrometer 200 and 50.3 MHz, respectively. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS). CV studies were carried out at room temperature with Radiometer PGZ100 potentiostat, using a standard three-electrode setup with a platinum working and auxiliary electrodes and a Ag/AgCl electrode as the reference. Acetonitrile solutions were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte *n*-Bu<sub>4</sub>N<sup>+</sup>PF<sub>6</sub><sup>−</sup> with a voltage scan rate = 0.1 V s<sup>−1</sup>. Under these experimental conditions the Cp<sub>2</sub>Fe–Cp<sub>2</sub>Fe<sup>+</sup> couple was located at 0.459 V. *E*<sub>1/2</sub> is defined as equal to (E<sub>pa</sub>+E<sub>pc</sub>)/2. Melting points (m.p.) were determined in evacuated capillaries and were not corrected. The hydrazine complexes [( $\eta^5$ -Cp)Fe( $\eta^6$ -*p*-RC<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub>)]<sup>+</sup>PF<sub>6</sub><sup>−</sup>, (R = H (1)<sup>+</sup>PF<sub>6</sub><sup>−</sup>, Me (2)<sup>+</sup>PF<sub>6</sub><sup>−</sup>, MeO (3)<sup>+</sup>PF<sub>6</sub><sup>−</sup> [9a], Cl (4)<sup>+</sup>PF<sub>6</sub><sup>−</sup> [5]) were synthesized as previously described. Ferrocene-based aldehyde (*E*)-[( $\eta^5$ -Cp)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)-CH=CH-C<sub>6</sub>H<sub>4</sub>-CHO] was prepared according to published procedures [23].

### 4.2. Preparation of hydrazone complexes

4.2.1. Preparation of (*E*)-[( $\eta^5$ -Cp)Fe( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>)-NH-N=CH-C<sub>6</sub>H<sub>4</sub>-CH=CH-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Fe( $\eta^5$ -Cp)]<sup>+</sup>PF<sub>6</sub><sup>−</sup>, (5)<sup>+</sup>PF<sub>6</sub><sup>−</sup>

A mixture of 57.8 mg (0.16 mmol) of (1)<sup>+</sup>PF<sub>6</sub><sup>−</sup> and 53.8 mg (0.17 mmol) of (*E*)-[( $\eta^5$ -Cp)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)-CH=CHC<sub>6</sub>H<sub>4</sub>CHO], was dissolved in 5.0 ml of EtOH, and several drops of concentrated acetic acid were added. The solution was refluxed for 5 h. The reaction mixture was allowed first to stand at r.t. and then at −30 °C overnight. The red crystalline solid formed was filtered off and washed with cold EtOH and then with Et<sub>2</sub>O. Finally, the complex was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O 1:1. Yield: 77% (80 mg). M.p. (dec.): 215 °C. Anal. Calc. for C<sub>30</sub>H<sub>27</sub>F<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>P (Mr = 672.05 g mol<sup>−1</sup>): C, 53.60; H, 4.05. Found: C, 53.42; H, 3.98%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm, TMS): 4.33 (s, 5H, CpFe), 4.54 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.80 (br s, 2H, C<sub>5</sub>H<sub>4</sub>),

5.16 (s, 5H, CpFe<sup>+</sup>), 6.22–6.56 (m, 5H, coord-Ph), 6.82 (d,  $J_{\text{H-H}} = 16.4$  Hz, 1H, CH=CH), 7.16 (d,  $J_{\text{H-H}} = 16.4$  Hz, 1H, CH=CH), 7.62 (d,  $J_{\text{H-H}} = 8.3$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.84 (d,  $J_{\text{H-H}} = 8.3$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 8.48 (s, 1H, CH), 9.80 (s, 1H, NH). IR (KBr, cm<sup>-1</sup>): 3310(m),  $\nu(\text{NH})$ ; 3098(w),  $\nu(\text{CH})$ ; 2982, 2925(vw),  $\nu(\text{CH})$ ; 1598(w),  $\nu(\text{C}=\text{C})$ ; 1560(s),  $\nu(\text{C}=\text{N})$ ; 846(vs),  $\nu(\text{PF}_6)$ ; 558(m),  $\delta(\text{PF}_6)$ . UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 242 (4.35), 368 (4.40), 475 (3.76). (DMSO,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 374 (4.20), 470 (3.80). CV:  $E_{1/2}(\text{Fc}) = +0.497$  V; Epc ([CpFe(arene)]<sup>+</sup>) = -1.31 V.

4.2.2. Preparation of (E)-[( $\eta^5$ -Cp)Fe( $\eta^6$ -p-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)-NH-N=CH-C<sub>6</sub>H<sub>4</sub>-CH=CH-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Fe( $\eta^5$ -Cp)]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, (6)<sup>+</sup>PF<sub>6</sub><sup>-</sup>

The synthesis of this orange complex was carried out using a procedure similar to that described for complex (5)<sup>+</sup>PF<sub>6</sub><sup>-</sup>, using in this case 94.4 mg (0.26 mmol) of (2)<sup>+</sup>PF<sub>6</sub><sup>-</sup> and 79.4 mg (0.25 mmol) of (E)-[( $\eta^5$ -Cp)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)-CH=CHC<sub>6</sub>H<sub>4</sub>CHO]. Yield: 77% (133 mg). M.p. (dec.): 158 °C. Anal. Calc. for C<sub>31</sub>H<sub>29</sub>F<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>P (Mr = 686.07 g mol<sup>-1</sup>): C, 54.26; H, 4.26. Found: C, 54.32; H, 4.24%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm, TMS): 2.56 (s, 3H, CH<sub>3</sub>), 4.28 (s, 5H, CpFe), 4.47 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.72 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.10 (s, 5H, CpFe<sup>+</sup>), 6.34 (d,  $J_{\text{H-H}} = 6.6$  Hz, 2H, coord-Ph), 6.46 (d,  $J_{\text{H-H}} = 6.6$  Hz, 2H, coord-Ph), 6.88 (d,  $J_{\text{H-H}} = 15.5$  Hz, 1H, CH=CH), 7.19 (d,  $J_{\text{H-H}} = 16.0$  Hz, 1H, CH=CH), 7.64 (d,  $J_{\text{H-H}} = 8.1$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.84 (d,  $J_{\text{H-H}} = 8.1$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 8.15 (s, 1H, CH), 9.81 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H}-NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm, TMS): 20.3 (CH<sub>3</sub>), 68.6 (C, C<sub>5</sub>H<sub>4</sub>), 68.7 (C, coord-Ph), 70.2 (C, C<sub>5</sub>H<sub>4</sub>), 70.3 (CpFe), 71.2 (C, quaternary C<sub>5</sub>H<sub>4</sub>), 77.7 (CpFe<sup>+</sup>), 87.6 (C, coord-Ph), 98.8 (C-Me, coord-Ph), 120.6 (C<sub>ipso</sub>, coord-Ph), 126.8 (CH=CH), 127.4 (C, Ph), 128.5 (C, Ph), 129.8 (CH=CH), 134.2 (C, quaternary Ph), 140.7 (C, quaternary Ph), 145.3 (C=N). IR (KBr, cm<sup>-1</sup>): 3323(m),  $\nu(\text{NH})$ ; 3090(w),  $\nu(\text{CH})$ ; 2988, 2925(vw),  $\nu(\text{CH})$ ; 1596(w),  $\nu(\text{C}=\text{C})$ ; 1570(s),  $\nu(\text{C}=\text{N})$ ; 844(vs),  $\nu(\text{PF}_6)$ ; 558(m),  $\delta(\text{PF}_6)$ . UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 240 (4.37), 368 (4.39), 474 (3.83). (DMSO,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 375 (4.15), 472 (3.75). CV:  $E_{1/2}(\text{Fc}) = +0.459$  V; Epc ([CpFe(arene)]<sup>+</sup>) = -1.29 V.

4.2.3. Preparation of (E)-[( $\eta^5$ -Cp)Fe( $\eta^6$ -p-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>)-NH-N=CH-C<sub>6</sub>H<sub>4</sub>-CH=CH-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Fe( $\eta^5$ -Cp)]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, (7)<sup>+</sup>PF<sub>6</sub><sup>-</sup>

The synthesis of this orange complex was carried out using a procedure similar to that described for complex (5)<sup>+</sup>PF<sub>6</sub><sup>-</sup>, using in this case 102.3 mg (0.25 mmol) of (3)<sup>+</sup>PF<sub>6</sub><sup>-</sup> and 77.8 mg (0.25 mmol) of (E)-[( $\eta^5$ -Cp)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)-CH=CHC<sub>6</sub>H<sub>4</sub>CHO]. Yield: 69% (125 mg). M.p. (dec.): 210 °C. Anal. Calc. for C<sub>31</sub>H<sub>29</sub>F<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>OP (Mr = 702.23 g mol<sup>-1</sup>): C, 53.02; H, 4.16. Found: C, 53.10; H, 4.33%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm, TMS): 4.10 (s, 3H, CH<sub>3</sub>O), 4.27 (s, 5H, CpFe), 4.47

(br s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.72 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.14 (s, 5H, CpFe<sup>+</sup>), 6.35 (d,  $J_{\text{H-H}} = 7.3$  Hz, 2H, coord-Ph), 6.42 (d,  $J_{\text{H-H}} = 7.3$  Hz, 2H, coord-Ph), 6.88 (d,  $J_{\text{H-H}} = 16.2$  Hz, 1H, CH=CH), 7.40 (d,  $J_{\text{H-H}} = 16.2$  Hz, 1H, CH=CH), 7.64 (d,  $J_{\text{H-H}} = 8.2$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.83 (d,  $J_{\text{H-H}} = 8.2$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 8.15 (s, 1H, CH), 9.75 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H}-NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm, TMS): 57.7 (OMe), 62.7 (C, coord-Ph), 68.3 (C, coord-Ph), 68.8 (C, C<sub>5</sub>H<sub>4</sub>), 71.6 (C, quaternary C<sub>5</sub>H<sub>4</sub>), 72.9 (C, C<sub>5</sub>H<sub>4</sub>), 72.9 (CpFe), 77.5 (CpFe<sup>+</sup>), 118.6 (C<sub>ipso</sub>, coord-Ph), 127.0 (CH=CH), 127.4 (C, Ph), 128.4 (C, Ph), 129.7 (CH=CH), 132.3 (C-OMe, coord-Ph), 134.3 (C, quaternary Ph), 140.6 (C, quaternary Ph), 145.1 (C=N). IR (KBr, cm<sup>-1</sup>): 3274(m),  $\nu(\text{NH})$ ; 3106(w),  $\nu(\text{CH})$ ; 3019(vw),  $\nu(\text{CH})$ ; 1595(w),  $\nu(\text{C}=\text{C})$ ; 1570(s),  $\nu(\text{C}=\text{N})$ ; 1270(s),  $\nu(\text{C}-\text{O})$ ; 844(vs),  $\nu(\text{PF}_6)$ ; 558(m),  $\delta(\text{PF}_6)$ . UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 242 (4.37), 369 (4.41), 468 (3.78). (DMSO,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 377 (4.18), 472 (3.85). CV:  $E_{1/2}(\text{Fc}) = +0.471$  V; Epc ([CpFe(arene)]<sup>+</sup>) = -1.31 V.

4.2.4. Preparation of (E)-[( $\eta^5$ -Cp)Fe( $\eta^6$ -p-Cl-C<sub>6</sub>H<sub>4</sub>)-NH-N=CH-C<sub>6</sub>H<sub>4</sub>-CH=CH-( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Fe( $\eta^5$ -Cp)]<sup>+</sup>PF<sub>6</sub><sup>-</sup>, (8)<sup>+</sup>PF<sub>6</sub><sup>-</sup>

The synthesis of this orange complex was carried out using a procedure similar to that described for complex (5)<sup>+</sup>PF<sub>6</sub><sup>-</sup>, using in this case 85.0 mg (0.21 mmol) of (4)<sup>+</sup>PF<sub>6</sub><sup>-</sup> and 66.0 mg (0.21 mmol) of (E)-[( $\eta^5$ -Cp)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)-CH=CHC<sub>6</sub>H<sub>4</sub>CHO]. Yield: 63% (92 mg). M.p. (dec.): 198 °C. Anal. Calc. for C<sub>30</sub>H<sub>26</sub>ClF<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>P (Mr = 706.01 g mol<sup>-1</sup>): C, 50.99; H, 3.71. Found: C, 50.53; H, 3.74%. <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm, TMS): 4.25 (s, 5H, CpFe), 4.44 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 4.68 (br s, 2H, C<sub>5</sub>H<sub>4</sub>), 5.26 (s, 5H, CpFe<sup>+</sup>), 6.63 (br s, 2H, coord-Ph); 6.77 (br s, 2H, coord-Ph); 6.92 (d,  $J_{\text{H-H}} = 15.8$  Hz, 1H, CH=CH), 7.22 (d,  $J_{\text{H-H}} = 15.8$  Hz, 2H, CH=CH), 7.66 (d,  $J_{\text{H-H}} = 7.6$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 7.85 (d,  $J_{\text{H-H}} = 7.6$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>), 8.19 (s, 1H, CH), 10.60 (s, 1H, NH). IR (KBr, cm<sup>-1</sup>): 3296(m),  $\nu(\text{NH})$ ; 3088(w),  $\nu(\text{CH})$ ; 2974, 2926(vw),  $\nu(\text{CH})$ ; 1596(w),  $\nu(\text{C}=\text{C})$ ; 1560(s),  $\nu(\text{C}=\text{N})$ ; 1099(w),  $\nu(\text{C}-\text{Cl})$ ; 840(vs),  $\nu(\text{PF}_6)$ ; 556(s),  $\delta(\text{PF}_6)$ . UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 242 (4.40), 369 (4.39), 467 (3.80). (DMSO,  $\lambda_{\text{max}}$ , nm (log  $\epsilon$ )): 375 (4.20), 470 (3.82). CV:  $E_{1/2}(\text{Fc}) = +0.441$  V; Epc ([CpFe(arene)]<sup>+</sup>) = -1.29 V.

4.3. X-ray crystallographic study of (6)<sup>+</sup>PF<sub>6</sub><sup>-</sup>

C<sub>31</sub>H<sub>29</sub>F<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>P, Mr = 686.23 g mol<sup>-1</sup>, unit cell dimensions:  $a = 10.841(7)$ ,  $b = 16.222(8)$ ,  $c = 16.552(11)$  Å,  $\beta = 96.59(5)^\circ$ ,  $V = 2892(3)$  Å<sup>3</sup>, monoclinic,  $P2_1/n$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.58$  g cm<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 1.12$  mm<sup>-1</sup>,  $F(000) = 1456$ , crystal size (mm): 0.20 × 0.18 × 0.06. Siemens R<sub>3</sub>m/V four-circle diffractometer equipped with graphite-monochromated Mo-K $\alpha$  ( $\lambda = 0.7107$  Å) radiation,  $2\theta$  range 3.0–50° at 298 K, reflections collected 5101 ( $R_{\text{int}} = 0.051$ ). Convergence at  $wR_2 =$

0.099. The unit cell parameters were determined by least-squares refinement of 30 reflexions in the range  $15 < 2\theta < 30^\circ$ . Intensity data were collected in the range  $3 < 2\theta < 50^\circ$  by the  $\omega-2\theta$  scan technique, and corrected by Lorentz Polarization and absorption effects ( $\Psi$ -scan). Two standard reflections were monitored every 98, and showed no significant changes ( $< 2\%$ ). The structure was solved by a combination of direct methods and difference Fourier syntheses. Refinement was performed by full-matrix least-squares in  $F^2$ , with anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms were positioned at their expected values and allowed to ride both in coordinates ( $C-H = 0.96 \text{ \AA}$ ) as well as in displacement factors (1.2 times their hosts'). Computer programs used in this study were SHELXL-97 [24], SHELXTL-PC [25] software packages and PARST [26].

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-167428. Copies of the data can be obtained free of charge on application to 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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