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Communications

A New Iron(II) Mixed Sandwich Featuring a Hybrid η^6-Zwitterionic/η^5-Iminocyclohexadienyl Structure

Walter Figueroa,[1a] Mauricio Fuentealba,[1a] Carolina Manzur,[1a] David Carrillo,*,[1a]
Andrés I. Vega,†,[1b] Jean-Yves Saillard,*,[1b] and Jean-René Hamon*,[1c]

Laboratorio de Química Inorgánica, Instituto de Química, Pontificia Universidad Católica de Valparaíso, Avenida Brasil 2950, Valparaíso, Chile, UMR 6511 CNRS-Université de Rennes 1, LCSIM, Institut de Chimie, Campus de Beaulieu, 35042 Rennes-Cedex, France, and UMR 6509 CNRS-Université de Rennes 1, Institut de Chimie, Campus de Beaulieu, 35042 Rennes-Cedex, France

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*Summary: The neutral air-sensitive Fe(II) hydrazonyl complex CpFe{(η-C_6H_5)NN=CHC_6H_4-p-NMe_2} (**2**) is obtained by deprotonation of its cationic hydrazone precursor [CpFe{(η^6-C_6H_5)NHN=CHC_6H_4-p-NMe_2}]$^+PF_6^-$ (**1**) with t-BuOK in tetrahydrofuran. The spectroscopic data, the X-ray molecular structure, and a DFT MO analysis revealed that **2** is best described as a hybrid of η^5-iminocyclohexadienyl and η^6-zwitterionic complexes.*

The ability of transition-metal moieties to activate π-coordinated aromatics has been a dynamic research area, where nucleophilic addition or substitution reactions represent the most studied modes of activation.[2] In particular, η^6coordination of aromatic molecules to the electron-withdrawing $CpFe^+$ moiety (Cp = η^5-C_5H_5) dramatically enhances the acidity of the benzylic protons in the robust 18-electron cationic complexes [CpFe{η^6-$C_6H_{6-n}(CH_3)_n$}]$^+$ ($n = 1-6$).[3] In such complexes, the benzylic C−H bonds can be easily activated by bases, and this C−H activation reaction is of great synthetic interest because it allows the formation of many C−element bonds by smooth reactions of a variety of electrophiles with the neutral deprotonated species.[4] The nature of the C−H-activated product has been unambiguously established by an X-ray crystal structure of the pentamethylbenzyl complex CpFe(η^5-C_6Me_5=CH_2), showing a η^5-cyclohexadienylidene structure (Chart 1; **A**, X = CH_2) for the six-membered ring with a folding

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* To whom correspondence should be addressed. Fax: +33 2 23 23 56 37. E-mail: jean-rene.hamon@univ-rennes1.fr.

† Present address: Universidad de Tarapacá, Av. General Velasquez 1775, Arica, Chile.

[1] (a) Pontificia Universidad Católica de Valparaíso. (b) UMR 6511 CNRS-Université de Rennes 1. (c) UMR 6509 CNRS-Université de Rennes 1.

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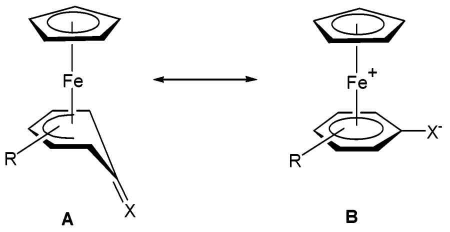
Chart 1

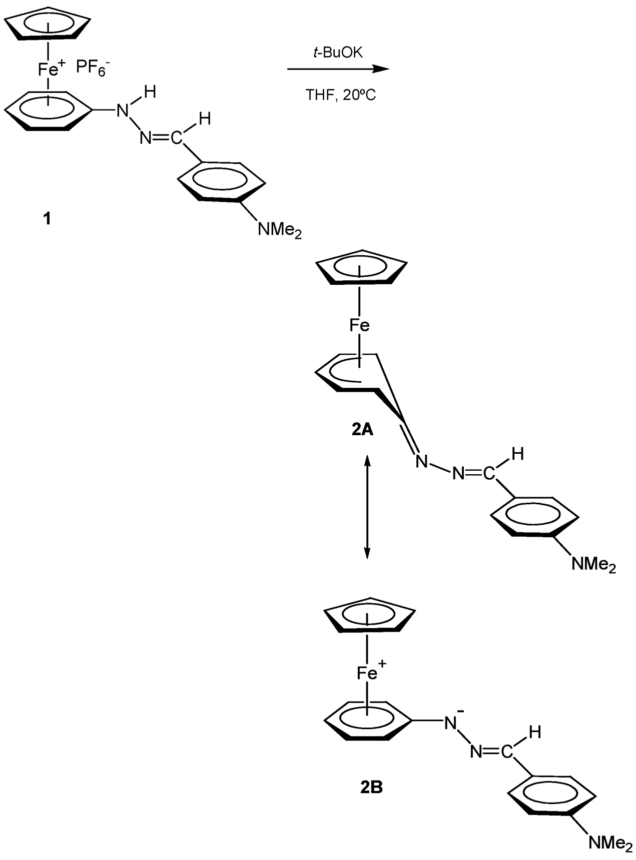


dihedral angle of 32.6°.[5] However, this bending angle can dramatically decrease to 11°, as observed in the CpFe(η-fluorenyl) complex, affording a structural intermediate between η^5-cyclohexadienyl and η^6-zwitterionic forms.[6] The polycyclic nature of the fluorenyl ligand probably prohibits a high degree of bending around the axis of the two outer dienyl carbons. A pure zwitterionic structure (Chart 1; **B**, X = O) has been reported for the phenate complex $Cp^*Fe^+(\eta^6\text{-}C_6H_5O^-)$ ($Cp^* = \eta^5\text{-}C_5Me_5$); the angle between the C_{ipso}−O vector and the C_6 plane is 1.55°.[7]

Benzylic N−H activation also occurs at the aminoarene ligand coordinated to the $CpFe^+$ fragment to yield the corresponding imine complex.[8] From spectroscopic and Mössbauer data,[8b] the structure of the imino derivative $CpFe(C_6R_5NH)$ (R = H, Me) is expected to have more zwitterionic character than their $CpFe(C_6R_5CH_2)$ counterparts. Unfortunately, this cannot be quantified, owing to the lack of X-ray crystal structure data of imino-substituted arene transition-metal complexes.

Within our ongoing research project to build non-rod-shaped organoiron hydrazone chromophores of the type $[CpFe(\eta^6\text{-arylhydrazone})]^+PF_6^-$,[9] we have shown that, in the solid state, the acidic benzylic N−H group underwent hydrogen bonding either with a fluorine of the PF_6^- counteranion[9b] or with the oxygen atom of an *o*-methoxy substituent[9c] and that no cyclic voltammograms of the cationic hydrazone compounds could be recorded in DMF,[9d] due to in situ deprotonation to generate their conjugated bases $CpFe\{(\eta\text{-aryl})NN{=}CHC_6H_4\text{-}p\text{-}R)$. These observations prompted us to isolate and to rationalize the structure and bonding of such a species. We now report for the first time the X-ray crystal structure analysis of a neutral d^6 Fe(II) iminoaryl complex, $CpFe\{(\eta\text{-}C_6H_5)NN{=}CHC_6H_4\text{-}p\text{-}NMe_2\}$ (**2**), its spectroscopic characterization, and a preliminary theoretical investigation.

Scheme 1



Dark red, air-sensitive $CpFe\{(\eta\text{-}C_6H_5)NN{=}CHC_6H_4\text{-}p\text{-}NMe_2\}$ (**2**) was obtained by the deprotonation of its orange hydrazone precursor $[CpFe\{(\eta^6\text{-}C_6H_5)NHN{=}CHC_6H_4\text{-}p\text{-}NMe_2\}]^+PF_6^-$ (**1**)[9d] with potassium *tert*-butoxide in tetrahydrofuran (THF) (Scheme 1). The neutral complex **2** is readily isolated in 70% yield as a crystalline solid from CH_2Cl_2/hexane solution.[10] The crystal chosen for the X-ray structure was a CH_2Cl_2 solvate, but the sample used for microanalysis had partially lost solvent.

As expected by the increased electron density on the benzylic nitrogen atom of the deprotonated species, the ^1H NMR spectrum clearly shows that both the cyclopentadienyl and the complexed C_6 ring protons are shifted upfield: δ(Cp) 4.62 in **2** vs 5.11 in **1** and $\delta(C_6H_5)$

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[7] Spectroscopic data (IR, ^1H and ^{13}C NMR) indicate that the solution structure of $Cp^*Fe(C_6H_5O)$ is intermediate between that of a η^5-oxocyclohexadienyl species and that of a η^6-phenate complex. However, $Cp^*Fe(C_6H_5O)$ crystallizes as a monohydrate, with dimeric H-bonding interactions of the water molecules with the phenate oxygen atom inducing the fully η^6 form in the solid state. (a) Moulines, F.; Djakovitch, L.; Delville-Desbois, M.-H.; Robert, F.; Gouzerh, P.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1995**, 463. (b) Djakovitch, L.; Moulines, F.; Astruc, D. *New J. Chem.* **1996**, *20*, 1071.

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[10] Synthesis of **2**: to a slurry of **1** (162.2 mg, 0.323 mmol) in 20 mL of THF was added 38.5 mg (0.343 mmol) of *t*-BuOK. The reaction mixture immediately turned deep red and was stirred for 1 h. Volatile components were removed in vacuo, and the solid residue was extracted with toluene (5 × 10 mL). The combined extracts were filtered through Celite, and the solvent was evaporated under vacuum. The resulting material was dissolved in 10 mL of methylene chloride, and the solution was layered with 40 mL of hexane. After 1 day dark red crystals deposited. They were collected by filtration and dried under a stream of nitrogen. Yield: 105 mg (70%). Mp: 186−188 °C dec. IR (KBr, cm^{-1}): 1607, 1520 (ν(C=N)). ^1H NMR (400.13 MHz, CD_3COCD_3): δ_H 2.99 (s, 6H, $N(CH_3)_2$), 4.62 (s, 5H, C_5H_5), 5.19−5.43 (br s, 1H, coord Ph), 5.49 (br s, 2H, coord Ph), 5.64 (s, 1.65H, CH_2Cl_2), 5.79 (br s, 1H, *p*-H coord Ph), 6.75 (d, *J* = 7.9 Hz, 2H, Ph), 7.58 (d, *J* = 7.9 Hz, 2H, Ph), 8.09 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_3COCD_3): δ_C 39.6 ($N(CH_3)_2$), 54.1 (CH_2Cl_2), 61.7 (*o*-C coord Ph), 73.1 (C_5H_5), 75.1 (*p*-C coord Ph), 83.6 (*m*-C coord Ph), 112.1 (Ph, C ortho to $CNMe_2$), 125.8 (Ph, C para to $CNMe_2$), 127.7 (Ph, C meta to $CNMe_2$), 128.9 (C_{ipso}, coord Ph), 146.7 (N=CH), 150.1 (Ph, $CNMe_2$). Anal. Calcd for $C_{20}H_{21}FeN_3\cdot 0.4CH_2Cl_2$: C, 62.31; H, 5.59; N, 10.68. Found: C, 62.44; H, 5.94; N, 10.49.

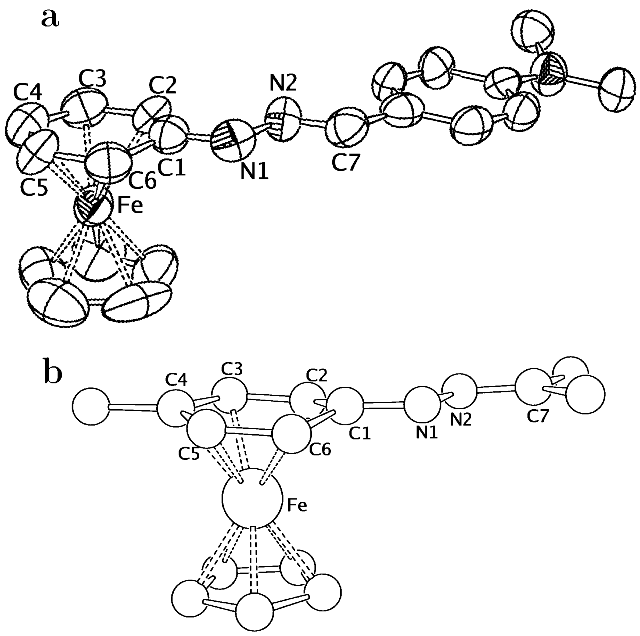

Figure 1. (a) ORTEP diagram for CpFe{(η-C_6H_5)NN=CHC_6H_4-*p*-NMe_2} (**2**) showing a partial numbering scheme and 33% displacement ellipsoids. Hydrogen atoms and solvating CH_2Cl_2 were omitted for clarity. (b) DFT-optimized molecular structure of CpFe{(η-*p*-MeC_6H_4)NN=CMe_2}. Selected bond distances (Å) and angles (deg) were computed from the X-ray structure [DFT results]: Fe−C1 = 2.303(13) [2.336], Fe−C2−6(av) = 2.063 [2.060], Fe−CCp(av) = 2.034 [2.050], C1−N1 = 1.309(13) [1.315], N1−N2 = 1.416(12) [1.358], N2−C7 = 1.265(13) [1.290]; C1−N1−N2 = 111.1(9) [112.7], N1−N2−C7 = 115.0(10) [115.9].

5.19−5.79 in **2** vs 6.22−6.44 in **1**. Similarly, in the ^{13}C NMR spectrum the Cp signal appeared at 72.8 ppm and the five C(2)−C(6) dienyl carbons (see Figure 1 for atom labeling) at 61.7, 75.1, and 83.6 ppm, as a 2:1:2 pattern, were shifted upfield by 3 and 3−7 ppm, respectively, from the corresponding carbon resonances in **1**. More interesting is the slightly downfield shifted position of the C(1) carbon at 128.9 ppm. The corresponding carbon resonance in the cationic η^6-hydrazone precursor **1** appeared at 121.3 ppm, whereas the decoordinated carbon appeared at 145.0 ppm in the η^5-pentamethylbenzyl complex CpFe(η^5-C_6Me_5=CH_2).[11] These changes are associated with the hapticity change of the structure of **2**, where the hydrazonyl ligand adopts a hybrid η^5-iminocyclohexadienyl/η^6-zwitterionic structure (vide infra). On the other hand, the singlets appearing at 5.64 ppm (integrated for 1.65 H) and at 54.1 ppm in the ^1H and ^{13}C NMR spectra, respectively, were assigned to the CH_2Cl_2 solvate found in the crystal lattice (see below).

Despite the low quality of the crystals affording a poor resolution of the structure, the structure of **2** was unequivocally determined by the X-ray diffraction study.[12] An ORTEP drawing is depicted in Figure 1a, with selected metric data given in its caption. Complex **2** crystallizes with 0.8 CH_2Cl_2 solvate per organometallic entity. The molecule adopts a typical mixed-sandwich-type structure, and the coordinated six-membered ring of the hydrazonyl ligand is not planar, with C(1) out of the plane. The folding dihedral angle is 12.5°, almost 4 times less than in genuine η^5-cyclohexadienyl−iron complexes (>40°).[14] However, this degree of bending is indicative of some cyclohexadienyl character (Scheme 1; **2A**) in the bonding of complex **2**. This involves coordination of the hydrazonyl ligand to the metal through only five carbons (C(2)−C(6)) and C(1) doubly bonded to N(1). On the other hand, the Fe−C(1) bond length, 2.303(13) Å, suggests a weak bonding interaction, thus arguing for some contribution of the zwitterionic representation (Scheme 1; **2B**), with the negative charge localized at N(1) and the positive charge on the metal. Of course, a metal−arene structure, as represented by such a zwitterionic formulation, should show no significant deviation from planarity in the complexed six-membered ring. This bonding situation is in fact reminiscent of that observed in CpFe(η-fluorenyl).[6] Greater dihedral folding angles have been reported by Astruc and co-workers for two unconstrained cyclohexadienylidene−iron compounds: 32.6° as mentioned above in the η^5-benzyl complex CpFe(η^5-C_6Me_5=CH_2)[5] and 25.0° in the bis(cyclohexadienylidene) compound [(Cp*Fe)$_2$(μ-η^5:η^5-C_6H_5=C_6H_5)].[15]

The juxtacyclic C(1)−N(1) bond, 1.309(13) Å, exhibits a strong double-bond character, being slightly longer than the imine N(2)=C(7) length (1.265(13) Å) and much shorter than that measured in the η^6 cationic methylated counterpart [CpFe(η^6-C_6H_5)N(Me)N=CHC_6H_4-*p*-NMe_2]$^+$$PF_6^-$ (**3**; 1.369(9) Å).[16] As a consequence, the N(1)−N(2) bond distance is larger in **2**, 1.416(12) Å, vs 1.374(8) Å in **3**. The other bond distances and angles remain identical, within the experimental error, in the two compounds. Moreover, the exocyclic C(1)−N(1) bond is not exactly in the C(2)C(1)C(6) plane but is slightly bent upward by 8.2°. Angles of 11 and 5° have also been measured in the two aforementioned mono- and bi-

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(12) Single crystals of **2** were obtained as described in ref 10. Data were collected at 293 K on a Bruker SMART APEX diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystal data: $C_{20}H_{21}FeN_3\cdot0.8CH_2Cl_2$: M_r = 427.19, monoclinic, space group $P2_1/c$, red plate (0.90 × 0.80 × 0.05 mm), *a* = 18.19(3) Å, *b* = 8.056(15) Å, *c* = 14.43(3) Å, β = 102.40(3)°, *V* = 2065(7) Å^3, *Z* = 4, D_c = 1.374 g cm^{-3}, μ = 0.947 mm^{-1}, *F*(000) = 886, 3768 independent reflections measured, ϕ/ω scans. The data set was collected with the crystal inside a sealed capillary glass, taking 10 s per frame and 0.3° between frames. Data reduction and absorption correction was achieved with Bruker SAINT[13a] and structure solution by direct methods and least-squares refinement with Bruker SHELXTL.[13b] Structure solution in the triclinic *P*1 space group showed four independent CpFe{(η-C_6H_5)-NN=CH−C_6H_4-*p*-NMe_2} units clearly related by symmetry, prompting us to use a higher symmetry group. Refinement in the monoclinic space group $P2_1/c$ shows a unique organometallic unit as expected, but the *R* factor was reduced only to 10.5%. This fact can be attributed to a rather poor crystal quality: initial reciprocal space exploration showed slightly misaligned series of reflections, which could not be treated as twin components. The solved structure shows a packing pattern which is consistent with this and with the crystal habit (very thin plate), since it is composed of layers of organometallic iron molecules noncovalently sandwiched by solvent. CCDC number 225315 (see http://www. ccdc.cam.ac.uk).

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nuclear cyclohexadienylidene iron complexes, respectively.[5,15] Of further interest is the good coplanarity of both free and coordinated phenyl rings (dihedral angles 4.5°), which is important for an efficient π-electron delocalization between the donating and accepting termini along the entire hydrazonyl backbone.

To provide a rationalization of the structure and bonding of the title compound, preliminary DFT calculations[17−20] have been carried out on the real compound $[CpFe(\eta^6\text{-}p\text{-}MeC_6H_4)NHN{=}CMe_2]^+$ (**4**)[21] and its hypothetical deprotonated counterpart $CpFe\{(\eta\text{-}p\text{-}MeC_6H_4)NN{=}CMe_2\}$ (**5**). The DFT-optimized geometries of **4** and **5** (Figure 1b) are in very good agreement with the X-ray structures of **4**[21] and **2**, respectively. Interesting structural comparison between the DFT geometries of **5** and **4** can be made. In the latter, the Fe−C(1) distance is 2.187 Å, whereas the C(1)−N(1) distance is 1.351 Å. The C_6 bending angle is only 4.3°, as compared to 11.0° for **5** and 12.5° in the X-ray structure of **2**. Clearly, unlike **4**, **5** exhibits a coordination mode which is intermediate between η^5 and η^6. Interestingly, the computed Fe−C(1) Mulliken overlap population (+0.007 vs +0.107 for the average Fe−C(2−6) value) suggests an almost nonbonding interaction. A detailed analysis of the electronic structure of a series of related species is in progress to evaluate more quantitatively the strength of such bonds.

In conclusion, the unexpected structure of the new neutral iron(II) derivative $CpFe\{(\eta\text{-}C_6H_5)NN{=}CHC_6H_4\text{-}p\text{-}NMe_2\}$ (**2**) formed through the deprotonation of its cationic *N*−H precursor has been characterized by an X-ray diffraction study for the first time. The spectroscopic data, the X-ray analysis, and the DFT calculations revealed that this 18-electron mixed sandwich is best described as a hybrid of η^5-iminocyclohexadienyl and η^6-zwitterionic complexes. We are presently examining the chemistry and redox reactivity of this and related complexes in search of new chemical transformations and physical properties.

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Supporting Information Available: Tables of atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for $CpFe\{(\eta\text{-}C_6H_5)NN{=}CHC_6H_4\text{-}p\text{-}NMe_2\}$ (**2**); these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Computational details: DFT calculations were carried out using the Amsterdam Density Functional (ADF) program.[18] The Vosko−Wilk−Nusair parametrization[19] was used to treat electron correlation within the local density approximation. The standard ADF TZP basis set was used for all the atoms: a triple-ξ Slater-type orbital (STO) basis set for valence orbital plus a polarization single-ξ STO. The frozen-core approximation was used to treat core electrons. Full geometry optimizations were carried out on each complex using the analytical gradient method implemented by Verluis and Ziegler.[20] No symmetry constraint was used in all the geometry optimizations.

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