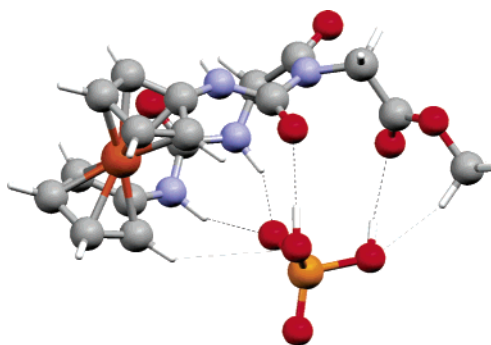# Preparation, Structure, and Anion Sensing Properties of 1,*n*-Diaza[*n*]ferrocenophanes

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*Received March 9, 2005*

The synthesis of structurally new types of azaferrocenophanes is reported in this note: **4**, which comprises a 1,2-fused azaheterocycle to a 1,3-diaza[3]ferrocenophane framework; 1,3-diaza[3]-ferrocenophanes **5** and **7**, which can be considered as a 1,1′-ferrocenylene *N*,*N*′-guanidine or urea, respectively; and 1,3,6,8-tetraza[8]ferrocenophanes **9** and **10**, bearing two ureido moieties in the ansa-bridge. These compounds were prepared directly from 1,1′-bis(isocyanato)ferrocene **1** and thoroughly characterized by spectroscopic means. Tetraza[8]ferrocenophanes **9** and **10** show spectral and electrochemical anion-sensing action: they display a selective downfield shift of the urea protons and a cathodic shift of the ferrocene/ferrocinium redox couple with dihydrogenphosphate and fluoride anions. The crystal structure of compound **4** has been determined by single-crystal X-ray methods.

The most prevalent organometallic analogues of cyclophanes are the ferrocenophanes with a bivalve-like structure, in which the two cyclopentadienyl rings of the ferrocene are joined by an atomic or molecular bridge. In this context, 1,1′-heterodisubstituted ferrocenes by various donor heteroatoms (e.g., P and S) have led to a series of 1,*n*-heteroatomic ferrocenophanes, which have found wide application as chelating ligands in catalytic proccesses.[1] However, the related 1,*n*-diazaferrocenophanes have barely been studied, probably due to difficulties found in the synthesis of the precursor 1,1′-diaminoferrocene.[2] Only recently 1,3-diaza[3]ferrocenophanes in which zirconium,[3] titanium,[3–6] magnesium,[4,5] tin,[7] and palladium[8] fill the gap between the two nitrogen atoms have been reported, and a significant number of such metal complexes have recently been highlighted.[9]

In the course of our ongoing studies involving the synthesis, structural characterization, and properties of new families of azaferrocenophane ligands that incorpo-

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**SCHEME 1.   General Reactions for Synthesizing Ferrocenophanes 4, 5, 7, 9, and 10 from 1,1′-Bis(isocyanato)ferrocene 1**
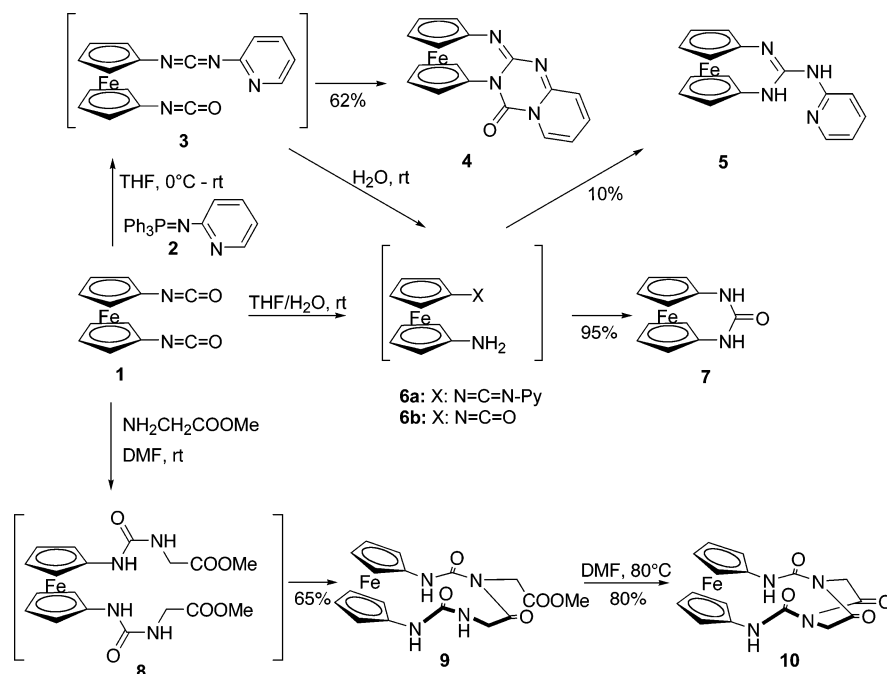


rate binding sites in the bridge for the purpose of selective recognition and sensing of metal ions,[10] we have now focused our attention on developing convenient synthetic entries to the previously unreported 1,*n*-diaza[*n*]ferrocenophane structural motif, in which the two nitrogen atoms are linked through a carbon chain. An interesting feature of our synthetic methodology is that 1,1′-bis-(isocyanato)ferrocene **1**, prepared from the corresponding 1,1′-ferrocenedicarboxylic acid via its acyl azide derivative,[11] has proved to be an excellent platform on which to build diazaferrocenophane frameworks. Despite its rich functionality, the chemistry of compound **1** remains almost unexplored; only its conversions into 1,1′-diisocyanoferrocene[11b] and a nitrogen-rich tetraza[3.3]-ferrocenophane have been reported.[12] Compound **1** is expected to have synthetic potential because it provides a reaction system in which the two isocyanate groups can react either with a reagent having two functionalities or with two separate reagents bearing the same or different functionality. The utility of compound **1**, however, could be improved if the two isocyanate moieties show different reactivity toward the same functionality. In this case, after the first reaction one isocyanate group survives that could undergo cyclization across the first reaction product or subsequent reaction with another reagent having different functionality.[13]

Here, we describe two different pathways for the construction of *ansa*-azabridges from **1**. The first one is based on the aza-Wittig reaction or hydrolysis of one

isocyanate group and subsequent cyclization across the remaining isocyanate function. The second way involves the reaction with a functionalized nitrogen reagent (α-aminoester) to give the expected bis(urea) derivative that undergoes thermal-promoted cyclization.

1,1′-Bis(isocyanato)ferrocene **1** reacted with 2-(*N*-tri-phenylphosphoranylidene)aminopyridine **2**[14] in THF at 0 °C to give the heteroligand **4** in 62% yield (Scheme 1). This unprecedented structural motif can be considered as an aza-containing heterocycle 1,2-fused to a 1,3-diaza-[3]ferrocenophane. The formation of **4** can be understood by an initial aza-Wittig reaction between one isocyanate moiety of **1** and 1 equiv of the reagent **2** to give **3** as highly reactive intermediate. This difunctionalized compound undergoes an intramolecular hetero-Diels−Alder cycloaddition, whereby the heteroaryl carbodiimide moiety has functioned as a 1,3-diaza-1,3-butadiene, using one cumulative double bond and one carbon−nitrogen double bond of the pyridine ring, and the carbon−nitrogen double bond of the remaining isocyanate group has taken the role of the dienophile.[15] To the best of our knowledge, there have been no reports on this special type of azine fused to a diazaferrocenophane framework.

Exploring parameters that could influence the course of the reaction between the bis(isocyanate) **1** and the iminophosphorane **2**, we found that under similar conditions to those described above, but using shorter reaction times and addition of water to break the reaction, a new [3]ferrocenophane **5** was isolated although in only 10% yield, which was not improved under other different experimental conditions. Formation of **5** could be explained through the same highly reactive intermediate **3**, which by hydrolysis of the remaining isocyanate group

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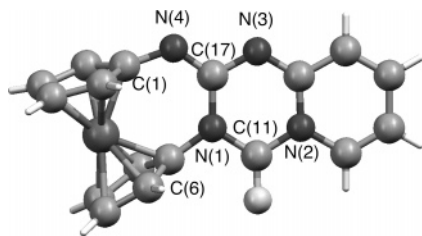
**FIGURE 1.** Crystal structure of **4** (ball-and-stick representation for heavy atoms and capped sticks for H atoms). Selected distances (Å) and angles (°): N(1)−C(6), 1.437(5); N(4)−C(17), 1.291(5); N(4)−C(1), 1.401(5); C(17)−N(4)−C(1), 125.6(3); C(11)−N(1)−C(6), 111.7(3).

leads to **6a**. The subsequent nucleophilic attack of the generated amino function to the carbodiimide moiety would give rise to the formation of the [3]-ferrocenophane framework.

Unexpectedly, when 1,1′-bis(isocyanato)ferrocene **1** was stirred in a mixture of THF/H$_2$O (10/1) at room temperature, the [3]-ferrocenophane **7** was obtained in 95% yield instead of the expected 1,1′-diaminoferrocene (Scheme 1). We believe that formation of **7** involves initial hydrolysis of one of the isocyanate groups present in **1** to give as highly reactive intermediate 1-amino-1′-isocyanato ferrocene **6b**, which subsequently undergoes an intramolecular cyclization affording the urea bridge.

These compounds have been characterized by means of standard spectroscopic techniques (IR, $^1$H NMR, and $^{13}$C NMR), mass spectrometry, and elemental analyses, all data being in agreement with the proposed structures, and the structure of the new heteroligand 1,3-diaza[3]-ferrocenophane **4** was unambiguously determined through a single-crystal X-ray diffraction analyses carried out on a sample of **4** (Figure 1). Moreover, for the sake of comparison and to explain some of the observed geometrical features, an ab initio DFT calculation was performed on this structure. An inspection of the X-ray structure of **4** reveals that the three-atom bridge locates the heterocyclic ring in a plane almost aligned with the Cp$_1$*−Fe−Cp$_2$* plane (Cp* standing for the Cp ring centroid) and promotes the expected distortion of the ferrocene sandwich structure with a tilt angle between both Cp mean planes of 16.7° (calcd 17.0°). This kind of geometrical distortion is often referred to by the deviation from linearity of the deformation angle at Fe between Cp midpoints, in this case being 12.0° (calcd 10.9°).

More striking is the fact that lengths for the latter exocyclic bonds are substantially different (1.437 and 1.401 Å, respectively; calcd: 1.438 and 1.390 Å), which is rather unusual, taking into account that both are expected to behave as unconjugated (single-bonded) sp$^2$-hybridized amino ferrocene systems. Thorough inspection of the electronic structure of this compound reveals the existence of an Fe(1)(d$_{x^2-z^2}$2)−C(1)(p$_z$)−N(4)(sp$^2$) bonding interaction in HOMO-10 of π-symmetry for the C−N bond, resulting in bond orders between N(4) and both C(1) and Fe(1) (Wiber bond index:[16] WBI$_{N4−C1}$ = 1.082; WBI$_{N4−Fe1}$ = 0.045) higher than those corresponding for N(1) (WBI$_{N1−C6}$ = 0.941; WBI$_{N1−Fe1}$ = 0.011).

The structural assignment of **7** was made on the basis of its spectral data, and its calculated structure at the

B3LYP/6-31+G* level confirms its $C_s$ symmetry with the carbonyl moiety nearly orthogonal to the plane of the ferrocenyl exocyclic bonds (dihedral C(1)NCO = 90.5°). This approaches the carbonyl carbon atom to the iron center (3.080 Å) and seems to be more a consequence of the plane strain than due to a d-π* electronic interaction, as pointed out by the low calculated bond order (WBI$_{Fe−CO}$ = 0.014) for this interaction.

Recently, it has been reported[17] that a ferrocenophane bearing two urea bridges shows a reversible redox process for the ferrocene moiety, which is cathodically shifted versus the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. In contrast, the cyclic voltammetric (CV) response of **7** under the same conditions (DMSO containing 0.1 M [$n$Bu$_4$N]PF$_6$ as supporting electrolyte) shows not only an irreversible redox process but also an oxidation potentital anodically shifted versus the Fc/Fc$^+$ redox couple ($E_{pa}$ = +0.150 V). This unexpected behavior could be explained on the basis of the above-mentioned low but significant Fe−CO interaction. On the other hand, the observed irreversible process probably indicates that a reaction should take place after the oxidation step (EC mechanism), giving rise to a new active redox species ($E_{1/2}$ = −0.360 V; $\Delta E_p$ = 70 mV) whose structure is now under investigation.

Next, we turned our attention to the use of α-aminoesters to prepare derivatives bearing the ester and the urea functionalities, both at 1 and 1′ positions, which could also be appropriate candidates for intramolecular cyclization processes to yield the azaferrocenophane framework. In fact, when the reaction of **1** with 3 molar equivalents of glycine methyl ester hydrochloride was carried out in the presence of triethylamine in DMF at room temperature, the 3,4-difunctionalized 1,3,6,8-tetraza[8]-ferrocenophane **9** was isolated in 65% yield. However, on performing the reaction at 80 °C a new type of ferrocenophane **10**, in which additionally the N(1) and N(6) atoms are bridged by a methylenecarbonyl moiety, was obtained in 80% yield. Remarkably, **9** was transformed directly into **10** in almost quantitative yield, on heating at 80 °C in DMF. With regard to the mechanism for the formation of **9**, we believe that the first step of this reaction should involve the in situ formation of the corresponding bis-ureidoacetate intermediate **8**. Formation of the 1,2,4,5-tetrahydropyrazine-3,6-dione ring takes place by two consecutive thermal-promoted intramolecular acylation reactions (Scheme 1). It should be noted that the most interesting feature of this unprecedented structural motif is that the two Cp rings are joined by a nitrogen-rich bridge in which two nitrogen atoms are doubly linked, giving rise to a 1,2,4,5-tetrahydropyrazine-3,6-dione ring. These two new [8]ferrocenophanes were characterized on the basis of spectroscopic and analytical methods, as is shown in the Experimental Section, and which were further supported by ab initio DFT calculations (see SI).

Owing to the relatively strong hydrogen-bonding ability of the urea group, a number of molecules possessing the urea motif have been designed as neutral receptors for various anions.[18] For strong and selective binding, this

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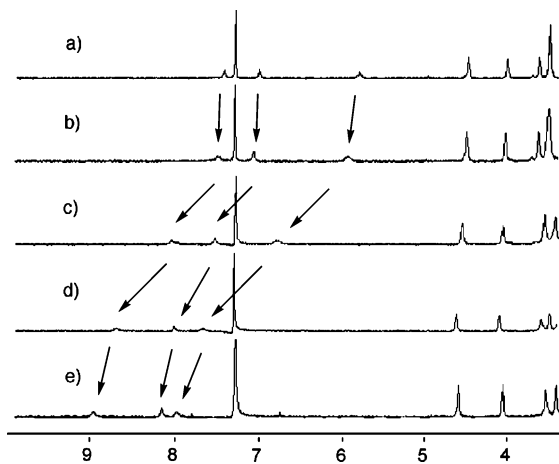(18) Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191.

**FIGURE 2.** Evolution of the $^1$H NMR spectra of **9** in CDCl$_3$ ($c = 5 \times 10^{-3}$ M) upon addition of increasing amounts of F$^-$ anions: (a) **9**, (b) **9** + 0.8 equiv, (c) **9** + 1.2 equiv, (d) **9** + 2 equiv, (e) **9** + 2.8 equiv.

group should be preorganized to complement the target anion and minimize intermolecular hydrogen bonding.[19] There are, however, few examples of urea/ferrocene redox active anionophores.[17,20]

The binding and recognition abilities of these new ligands, **9** and **10**, bearing a ferrocene unit substituted at 1 and 1′ positions by two urea groups, toward various anions were evaluated by electrochemical and spectral analysis. The CV response of **9** in dichloromethane, also containing 0.1 M [$n$Bu$_4$N]PF$_6$ as supporting electrolyte, showed an electrochemically reversible one-electron oxidation process at $E_{1/2} = -0.130$ V versus the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. However, as was observed in compound **7**, the CV of ligand **10** in DMSO, under the same conditions, showed an oxidation wave at $E_{1/2} = +0.034$ V ($\Delta E_p = 97$ mV) versus the ferrocenium/ferrocene (Fc$^+$/Fc) redox couple, inspection of which reveals features diagnostic of a EC mechanism, giving rise to a new active redox species ($E_{1/2} = -0.313$ V; $\Delta E_p = 96$ mV). Electrochemical anion sensing experiments were carried out by differential pulse voltammetry (DPV). On stepwise addition of H$_2$PO$_4^-$ and F$^-$ anions (as their TBA$^+$ salt) to an electrochemical solution of **9** in dichloromethane, a cathodic shift of the ferrocene/ferrocenium (Fc/Fc$^+$) redox peak was observed. The maximun shift was obtained when 2.5 equiv of H$_2$PO$_4^-$ ($\Delta E_{1/2} = -136$ mV) (Figure 2) or 3.5 equiv of F$^-$ anions ($\Delta E_{1/2} = -63$ mV) (see SI) was added, being 199 and 92 the value of the binding enhancement factor[21] in each case. This means that the complexation in the reduced form of the ligand **9** with H$_2$PO$_4^-$ and F$^-$ anions is 199 and 92 times more difficult, respectively, than that in the oxidized one. Remarkably, the presence of Cl$^-$, Br$^-$, and HSO$_4^-$ anions had no effect on the DPV, even when present in a large

excess. These findings underscore the selectivity of the new ferrocene/urea derivative **9** for the H$_2$PO$_4^-$ and F$^-$ anions.

The binding constants of **9** and **10** with several guest anions, as their TBA$^+$ salts, were determined by the titration methods using $^1$H NMR spectroscopy following the chemical shift change of the NH protons. Thus, addition of 2 equiv of H$_2$PO$_4^-$ to a solution of compound **9** in CDCl$_3$ ($c = 5 \times 10^{-3}$ M) promotes the total disappearance of the signal at $\delta = 7.36$ ppm, corresponding to one of the NH protons of the receptor, while the signals corresponding to the other two NH protons ($\delta = 7.05$ and $\delta = 5.88$ ppm) are significantly downfield-shifted ($\Delta\delta = +0.40$ and $+0.74$ ppm, respectively), indicating that all these protons participate in an authentic hydrogen-bonded formation.[22] It is worth noting that, simultaneously, a shielding of the signals corresponding to the ferrocene unit as well as to the methylene and methyl groups was also observed (see SI).

On the other hand, Figure 2 displays the spectra for titration of a $5 \times 10^{-3}$ M solution of **9** with F$^-$ and shows that upon addition of this anion the urea protons at $\delta = 5.88$, 7.05, and 7.36 ppm are also distinctly shifted downfield: $\Delta\delta = 2.23$, 1.19, and 1.60 ppm, respectively. Notably, this significant shift is mainly observed when more than 1 equiv of F$^-$ is added. Titration isotherms, generated from the change in chemical shift of the above-mentioned host NH signals upon addition of the H$_2$PO$_4^-$ and F$^-$ anions, were nicely fitted to a 1:1 binding model, using the computer program EQNMR[23] (see SI). The derived association constants were 720 and 440 M$^{-1}$ (error < 10%), respectively. In contrast, with Cl$^-$, NO$_3^-$, and HSO$_4^-$ anions, there were no chemical shift changes for the NH peaks, even when up to 2 equiv of these anions was added.

Theoretical calculations show that **9** mainly exists as a major conformer in which the carbonyl oxygen atom of the pendant N-linked sidearm is bound to two N−H groups of the other urea moiety yielding a six-membered chelate ring. At least six other intramolecular X−H⋯O=C hydrogen bonds (X: C, N) contribute to render a relatively rigid structure behaving as a highly preorganized cavity with a mobile pendant sidearm. Such arrangement seems to be well fitted for binding H$_2$PO$_4^-$ anions (complexation electronic energy in acetonitrile: −11.28 kcal/mol) upon little deformation of the free-ligand structure (calculated induced strain in the gas phase: 1.79 kcal/mol) mainly consisting on a simple rotation of the sidearm (Figure 3). The H$_2$PO$_4^-$ anion is anchored to the host by a six-point interaction (total WBI$_{ligand-anion}$ = 0.158). Contrary to that very recently reported by Hay,[24] the strongest interaction with the urea moiety results in a six-membered chelate fashion involving one oxygen atom instead of two (NH⋯OP distances: 1.779 and 1.836 Å; WBI = 0.064 and 0.046, respectively) and mainly supplemented by two C=O⋯HO−P highly linear hydrogen bonds (O⋯H−O angles: 175.6 and 153.5°; WBI = 0.020 and 0.016, respectively). The alternative eight-membered chelate binding mode resulted in

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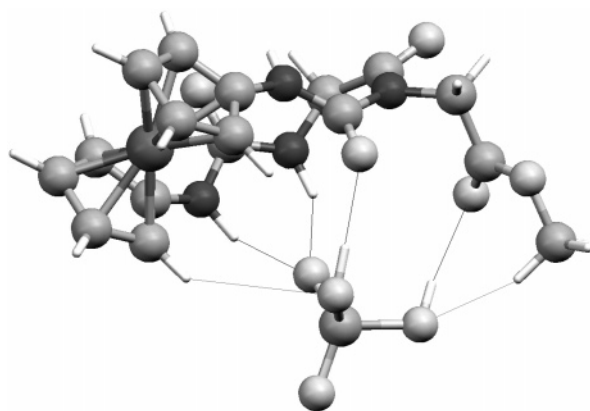
**FIGURE 3.** Calculated structure for the **9**·$H_2PO_4^-$ complex.

another local minimum 1.24 kcal/mol less stable on the gas-phase potential energy surface (2.01 kcal/mol, in acetonitrile). For the related interaction with $F^-$ anion (see SI), a weaker binding energy was obtained (−9.72 kcal/mol, in acetonitrile), probably due to both an increased distortion of the host **9** (calculated induced strain in the gas phase: 11.21 kcal/mol) and a higher heat of solvation for the anion (−73.98 and −89.52 kcal/mol for $H_2PO_4^-$ and $F^-$, respectively).

On the other hand, addition of 4 equiv of $F^-$ anion to a solution of the ligand **10** in DMSO-$d_6$ ($c = 5 \times 10^{-3}$ M) promotes a deshielding ($\Delta\delta = +1.91$) of the signal corresponding to the NH protons ($\delta = 8.23$ ppm), this downfield shift being much lower ($\Delta\delta = +0.30$) when 2.5 equiv of $H_2PO_4^-$ was added. Titration isotherms, generated from the change in chemical shift of the host NH signal upon addition of both anions, were fitted to a 1:2 and 1:1 (anion−ligand) binding model, for the case of $F^-$ and $H_2PO_4^-$, respectively, using the EQNMR program. The derived association constants were 790 and 500 $M^{-1}$ for $F^-$ (error < 10%) and 465 for $H_2PO_4^-$ $M^{-1}$ (error < 10%). With $Br^-$, $Cl^-$, $NO_3^-$, and $HSO_4^-$ anions, there were no chemical shift changes in the $^1H$ NMR spectra.

As shown by theoretical calculations, both the **10**·$H_2PO_4^-$ and either the **10**·$F^-$ or the **10**$_2$·$F^-$ complexes are expected to be formed from the host in a atropoisomeric form, **10**$^{atr}$, with both N−H units directed to the same half of the molecule. In the potential energy surface, computed in DMSO as solvent, **10**$^{atr}$ is only 3.54 kcal/mol (8.70 kcal/mol in the gas phase) less stable than that with $C_2$ symmetry and can be obtained from the latter through a low energy transition state **10**$^{TS}$ (activation barrier of 7.79 or 12.29 kcal/mol in DMSO or in the gas phase, respectively) generated by rotation of one of the −NHCO− moieties (amide proton inward). The (**10**$^{atr}$)$_2$·$F^-$ complex, with overall $C_2$ symmetry, is formed in two consecutive steps with computed changes in Gibbs free energy of −4.06 and −2.50 kcal/mol (in DMSO) and consists on a $F^-$ strongly linked to one N−H (1.617 Å) and weakly to one C−H (1.940 Å) proton atoms of every heteroligand (Figure 4). In the weaker **10**$^{atr}$·$H_2PO_4^-$ complex (calculated $\Delta\Delta G° = -1.13$ kcal/mol, in DMSO), there is a five-point interaction (see SI) as every terminal O atom in the anion is doubly linked to one NH (1.774, 1.973 Å) and one C−H (2.078 Å) or $C_{Cp}$−H (2.264 Å) hydrogen atoms, respectively, and one P−OH group is linked to a carbonyl O atom (2.011 Å).
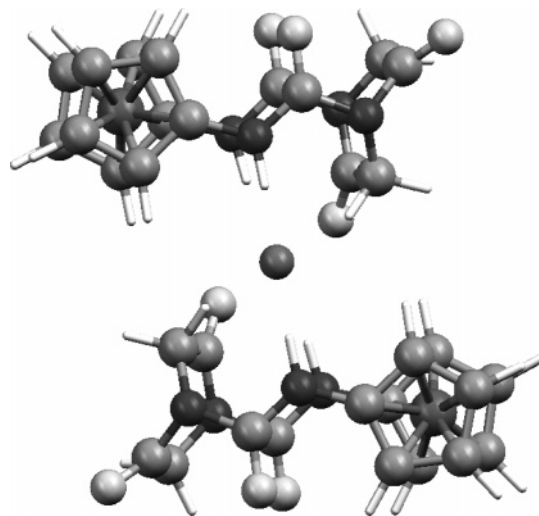


**FIGURE 4.** Calculated structure for the (**10**$^{atr}$)$_2$·$F^-$ complex.

In conclusion, we describe the preparation and structural characterization of the first members of a new family of azaferrocenophanes, 1,3-diaza[3]ferrocenophanes, by using 1,1′-bis(isocyanato)ferrocene **1**, in which the two isocyanate moieties surprisingly show different reactivity. Taking into account that the formation of the ferrocene framework involves the initial reaction of one isocyanate group in **1** with the adequate reagent, followed by trapping the product either by the remaining isocyanate group (compounds **4** and **5**) or by hydrolysis with concomitant cyclization (compound **7**), the preparation reported here represents an unprecedent way for the construction of the diazaferrocenophane skeletons. In addition, the use of appropriated nitrogen reagents (α-aminoesters) opens the way for the preparation of highly functionalizad nitrogen-rich [8]ferrocenophanes which have found applications as spectral and electrochemical selective sensors for $F^-$ and $H_2PO_4^-$ anions.

## Experimental Section

General experimental data and calculation details are given in the Supporting Information. 1,1′-Bis(isocyanato)ferrocene **1** was synthesized according to a previously published method.[11]

**Preparation of $N$,3-(2-Imino-4-oxopyrido[1,2-a]-1,3,5-triazino)-1,1′-ferrocenophane 4.** To a solution of 1,1′-bis-(isocyanato)ferrocene **1** (0.080 g, 0.30 mmol) in freshly distilled dry THF (10 mL) a solution of 2-($N$-triphenylphosphoranyliden)aminopyridine **2** (0.10 g, 0.30 mmol) in the same solvent (5 mL) was added dropwise and under nitrogen. The solution was stirred for 5 h and at room temperature, and then the solvent was removed under reduced pressure to give a residue that was triturated with $n$-hexane/Et$_2$O (1:1) to give **4**, which was crystallized from CH$_2$Cl$_2$/Et$_2$O (1:1). Yield: 50 mg (62%); mp 195−198 °C. IR (Nujol; cm$^{-1}$) 1659 (C=O), 1619, 1584, 1549. $^1H$ NMR (400 MHz, CDCl$_3$): δ 3.93 (st, 2H), 4.14 (st, 2H), 4.21 (st, 2H), 4.33 (st, 2H), 6.50 (ddd, 1H, $J = 6.9$ Hz, $J = 6.9$ Hz, $J = 1.2$ Hz), 6.96 (d, 1H, $J = 9.3$ Hz), 7.37 (ddd, 1H, $J = 9.3$ Hz, $J = 6.9$ Hz, $J = 1.2$ Hz), 8.12 (d, 1H, $J = 6.9$ Hz). $^{13}C$ NMR (75.3 MHz, CDCl$_3$): δ 63.9 (CH), 66.8 (CH), 70.0 (CH), 70.8 (CH), 88.3 (q), 100.8 (q), 111.0 (CH), 124.2 (CH), 128.1 (CH), 138.8 (CH), 148.5 (q), 149.5 (q), 150.8 (q). EIMS, $m/z$ (relative intensity): 344 (M$^+$, 100), 238 (43), 134 (26), 78 (24). Anal. Calcd for C$_{17}$H$_{12}$FeN$_4$O: C, 59.33; H, 3.51; N, 16.28. Found: C, 59.10; H, 3.38; N, 16.49.

**Preparation of $N'$-(2-Pyridyl)-$N$,$N''$-guanidino-1,1′-ferrocenophane 5.** To a solution of 1,1′-bis(isocyanato)ferrocene

**1** (0.54 g, 2 mmol) in THF (40 mL) a solution of 2-(*N*-triphenylphosphoranyliden)aminopyridine **2** (0.72 g, 2 mmol) in the same solvent (20 mL) was added dropwise, and the solution was stirred for 30 min at room temperature. Then, water (5 mL) was added, and the reaction mixture was stirred for 10 min. The solvent was removed under vacuum, and the resulting residue was chromatographed on a silica gel column using ethyl acetate as eluent to give **5** ($R_f$ = 0.1), which was crystallized from $CH_2Cl_2$/$Et_2O$ (1:2). Yield: 64 mg (10%); mp 185–190 °C (d). IR (Nujol; cm$^{-1}$) 3390 (NH). $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 4.36 (m, 8H), 7.08 (t, 1H, $J$ = 8.2 Hz), 7.38 (d, 1H, $J$ = 8.2 Hz), 7.76 (t, 1H, $J$ = 8.2 Hz), 8.18 (d, 1H, $J$ = 8.2 Hz). $^{13}$C NMR (75.3 MHz, CDCl$_3$): $\delta$ 68.7 (CH), 68.6 (CH), 89.3 (q), 108,9 (CH), 113.0 (CH), 138.1 (CH), 141.5 (q), 149.0 (CH), 161.1 (q). EIMS, *m/z* (relative intensity): 318 (M$^+$, 100), 238 (36), 225 (24) Anal. Calcd for C$_{16}$H$_{14}$FeN$_4$: C, 60.79; H, 3.83; N, 17.72. Found: C, 60.51; H, 3.56; N, 17.50.

**Preparation of Ureido-1,1′-ferrocenophane 7.** To a solution of 1,1′-bis(isocyanato)ferrocene **1** (0.1 g, 0.37 mmol) in THF (10 mL) distilled water (1 mL) was added, and the reaction mixture was stirred at room temperature for 3 h. The resulting yellow solid was filtered, washed with diethyl ether, and crystallized from MeOH/Et$_2$O (10:1) to give **7**. Yield: 85 mg (95%); mp 208–210 °C. IR (Nujol; cm$^{-1}$) 3174 (NH), 1668 (C=O). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.15 (st, 4H), 4.19 (st, 4H), 7.51 (bs, 2H). $^{13}$C NMR (75.3 MHz, CDCl$_3$): $\delta$ 69.6 (CH), 69.6 (CH), 89.3 (q), 163.0 (q). EIMS, *m/z* (relative intensity): 242 (M$^+$, 100), 197 (10), 162 (12), 135 (24), 131 (20). Anal. Calcd for C$_{11}$H$_{10}$FeN$_2$O: C, 54.58; H, 4.16; N, 11.57. Found: C, 54.34; H, 4.25; N, 11.29.

**Preparation of 3-Methoxycarbonylmethyl-1,3,6,8-tetraza-2,4,7-trioxo-[8]ferrocenophane 9.** To a solution of 1,1′-bis(isocyanato)ferrocene **1** (0.1 g, 0.37 mmol) in anhydrous DMF (2 mL) a solution of glycine methyl ester hydrochloride (140 mg, 1.11 mmol) and triethylamine (112 mg, 1.11 mmol) in the same solvent (10 mL) was added dropwise at room temperature and under nitrogen. The solution was stirred for 3 h, and the solvent was removed under vacuum to give a residue that was chromatographed on a silica gel column, using 9:1 $CH_2Cl_2$/$CH_3OH$ as eluent to give **9** ($R_f$ = 0.65) in 65% yield, which was crystallized from $CH_2Cl_2$/$Et_2O$ (2:1); 65%; mp 172–175 °C. IR (Nujol; cm$^{-1}$) 3360 (NH), 3294 (NH), 1755 (COOMe), 1717 (C=O). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.38 (s, 3H), 3.55 (s, 2H), 3.75–3.78 (m, 4H), 3.90 (bs, 2H), 4.25 (bs, 2H), 4.74 (bs, 2H), 5.88 (s, 1H), 7.05 (s, 1H), 7.36 (s, 1H). $^{13}$C NMR (75.3 MHz, DMSO-*d*$_6$): $\delta$ 41.3 (CH$_2$), 45.6 (CH$_2$) 51.5

(CH$_3$), 60.6 (CH), 62.5 (CH), 64.5 (CH), 65.4 (CH), 89.7 (q), 98.5 (q), 155.4 (q), 156.1 (q), 170.5 (q), 171.4 (q). FAB$^+$ MS (*m/z* (relative intensity): 415 (M$^+$ + 1, 100). Anal. Calcd for C$_{17}$H$_{18}$FeN$_4$O$_5$: C, 49.30; H, 4.38; N, 13.53. Found: C, 49.10; H, 4.19; N, 13.72.

**Preparation of 3,6-Methylenecarbonyl-1,3,6,8-tetraza-2,4,7-trioxo-[8]ferrocenophane 10. Method A.** To a solution of 1,1′-bis(isocyanato)ferrocene **1** (0.1 g, 0.37 mmol) in anhydrous DMF (2 mL) a solution of glycine methyl ester hydrochloride (140 mg, 1.11 mmol) and triethylamine (112 mg, 1.11 mmol) in the same solvent (10 mL) was added dropwise under nitrogen. The solution was stirred at 80 °C for 1.5 h and then poured into water. The resulting solid was filtered, washed with diethyl ether (4 × 20 mL), and crystallized to give **10** in 80% yield; mp 248–250 °C. IR (Nujol; cm$^{-1}$) 3323 (NH), 3245 (NH), 1713 (C=O). $^1$H NMR (300 MHz, DMSO-*d*$_6$): $\delta$ 3.79 (s, 4H), 4.15 (bs, 4H), 4.87 (bs, 4H), 8.23 (s, 2H). $^{13}$C NMR (75.3 MHz, DMSO-*d*$_6$): $\delta$ 45.5 (CH$_2$), 63.0 (CH), 65.7 (CH), 90.4 (q), 156.0 (q), 170.50 (q). EIMS (*m/z* (relative intensity): 382 (M$^+$, 2), 340 (5), 337 (100), 298 (18). Anal. Calcd for C$_{16}$H$_{14}$FeN$_4$O$_4$: C, 50.29; H, 3.69; N, 14.66. Found: C, 50.42; H, 3.48; N, 14.41.

**Method B.** A solution of **9** (100 mg) in DMF (10 mL) was heated at 80 °C for 1.5 h. Then, the solution was poured into water, and the solid formed was isolated and purified as above to give **9** in 96% yield.

**Supporting Information Available:** General experimental comments. X-ray crystallographic data of **4**. Calculated structures for **4**, **7**, **9**, **10**, **9·H$_2$PO$_4$$^-$**, **9·F$^-$**, **10·H$_2$PO$_4$$^-$**, **10·F$^-$**, and **10$_2$·F$^-$**. Calculated energy diagrams for the complexation of **9** and **10** with H$_2$PO$_4$$^-$ and F$^-$. DPV response of **9** after addition of H$_2$PO$_4$$^-$ and F$^-$. CV of **7**, **9**, and **10**. Evolution of the $^1$H NMR of **9** upon addition of H$_2$PO$_4$$^-$ and of **10** upon addition of F$^-$ and H$_2$PO$_4$$^-$. Changes in the chemical shift of the NH of **9** and **10** upon addition of F$^-$ and H$_2$PO$_4$$^-$. Crystal structure coordinates of **4**, tables of bonds lengths, bond angles and torsion angles are also available from the Cambridge Structure Data File (CCDC No. 275697). This material is available free of charge via the Internet at http://pubs.acs.org.

JO050458P