Amination of Bridging Vinyliminium Ligands in Diiron Complexes: C-N Bond Forming Reactions for Amidine-Alkylidene Species

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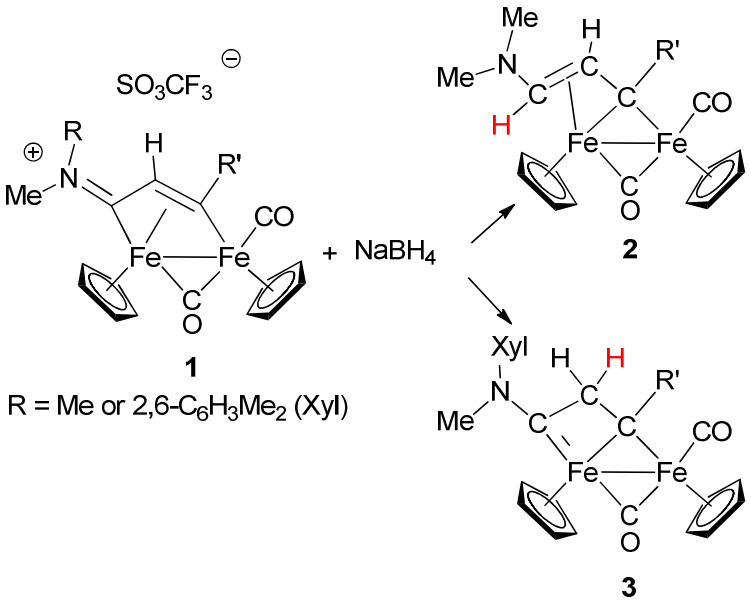
Summary: the vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(CO_2Me)C(H)CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Me, **1a**; R = 4-C_6H_4OMe, **1b**; R = CH_2Ph, **1c**] react with primary amines (NH_2R'; R'= Me, Et, Bu^n, $(CH_2)_2NH_2$, CH_2Ph) and ammonia to give the corresponding bridging amidine-alkylidene complexes $[Fe_2\{\mu\text{-}\kappa^1(N)\text{:}\eta^1(C)\text{:}\eta^1(C)\text{-}C(CO_2Me)CH_2C\{N(Me)(R)\}(NR')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**4a-j**) in 70-90 % yields. Likewise the vinyliminium complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(CO_2Me)C(CO_2Me)CN(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, (**1d)** reacts with NH_2R' (R'= Me, Et) to form the corresponding amidine-alkylidene $[Fe_2\{\mu\text{-}\kappa^1(N)\text{:}\eta^1(C)\text{:}\eta^1(C)\text{-}C(CO_2Me)CH(CO_2Me)C(NMe_2)(NR')\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R'= Me, **8a**; R' = Et, **8b**], generating selectively one of the two diastereoisomers associated with the presence of the methylidene unit -$CH(COO_2Me)$- within the bridging ligand. Amination of the vinyliminium complexes **1a-c** takes place also with hydrazine resulting in the formation of $[Fe_2\{\mu\text{-}\kappa^1(N)\text{:}\eta^1(C)\text{:}\eta^1(C)\text{-}C(CO_2Me)CH_2C\{N(Me)(R)\}(NNH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R = Me, **5a**; R = 4-C_6H_4OMe, **b**; R = CH_2Ph, **5c**]. Complexes **1b** and **1d** react with $NHMe_2$ affording the en-(1,1)di-amino-alkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(CO_2Me)C(R')C(NMe_2)N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R = 4-C_6H_4OMe, R' = H, **9b**; R = Me, R' = CO_2Me, **9d**]. The reaction of **1c** with piperidine results in formation of the amidine-alkylidene $[Fe_2\{\mu\text{-}\kappa^1(N)\text{:}\eta^1(C)\text{:}\eta^1(C)\text{-}C(CO_2Me)CH_2C\{N(Me)(CH_2Ph)\}(CH_2CH_2CH_2\ CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ **(10)**, which implies piperidine ring opening. All the products have been purified by alumina chromatography and characterized by analytical and spectroscopic methods; in addition the molecular structures of **4f**, **5b** and **8a** have been ascertained by X-ray diffraction studies.

[§] Dedicated to Professor Peter Maitlis FRS on occasion of his 85th birthday

INTRODUCTION

Increasing attention to sustainability and the need for new catalysts based on cost-effective and benign transition metal compounds has produced an exponential grown of interest in iron mediated bond formation.[1] Within this field, diiron complexes can play a distinct role for two major reasons. One is the possible cooperative effect of two adjacent Fe atoms resulting in enhanced reactivity and unique catalytic properties. A relevant example is provided by [FeFe]-hydrogenase active site and the corresponding synthetic models based on modification of the dithiolate frame $[Fe_2(\mu\text{-}SR)_2(CO)_6]$, in which the two Fe atoms have a synergic role in the proton reduction to generate H_2.[2] The second interesting aspect is related to the versatility offered by the dinuclear frame, allowing the bridging coordination mode: ligands bridging two adjacent Fe atoms can undergo activation pathways and show reactivity profiles different from those observed when the same fragments are bound to a single Fe atom or are unbound.[3] For example, α,β-unsaturated iminiums (not coordinated), are well known electrophilic compounds, acting as intermediate species in organocatalysis, which undergo conjugated addition by nucleophiles (Michael addition). The same type of fragment, when bridging two Fe units (Scheme 1, compound **1**), exhibits a different site selectivity, as shown in the reactions with hydride: the addition takes place either at α position or at the iminium carbon depending on the steric hindrance of the N-substituents (Scheme 1, compounds **2** and **3**), but not at the β position.[4]

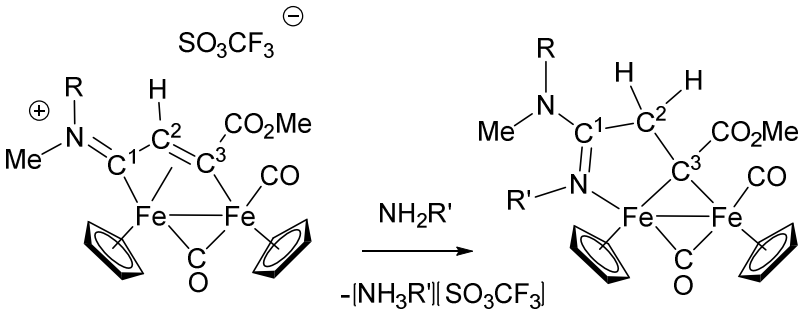


Scheme 1

The same behaviour is also observed in the case of addition of carbon nucleophiles, such as acetylides [5] and cyanide.[6] These and other examples [7] indicate that bridging hydrocarbyl ligands in diiron complexes provide access to the formation of C-H and C-C bonds by means of unique or unusual reaction routes.[8] Based on these considerations, we became interested in expanding the research field to C-N bond formation which is a topic of high current interest. Metal-mediated C−N bond formation takes advantage of different synthetic strategies (e.g. cross-coupling of amines and aryl halides,[9] C-H amination,[10] hydroamination of olefins and alkynes [11]) and include a few examples of iron mediated reactions.[12] Herein, we report on the reactions of a series of vinyliminium complexes of type **1** with amines. Due to the conjugated π-bond character of the bridging frame and its unique coordination mode, reactions with primary amines should possibly result in the formation of hydroamination products, but predictions are difficult in consideration of the peculiar nature of the ligand. Indeed, some unprecedented results are hereafter described.

RESULTS AND DISCUSSION

Reactions of vinyliminium complexes with primary amines and hydrazine. The vinyliminium complexes **1a-c** react with primary amines (NH_2R'), in THF solution at room temperature, affording the diiron bridging alkylidene complexes **4a-m**, in 70-90 % yield (Scheme 2).



1a-c **4a-m**

	R	**R'**	
1a	Me	Me	**4a**
1a	Me	Et	**4b**
1a	Me	Bu^n	**4c**
1a	Me	$(CH_2)_2NH_2$	**4d**
1b	4-C_6H_4OMe	Me	**4e**
1b	4-C_6H_4OMe	Et	**4f**
1b	4-C_6H_4OMe	H	**4g**
1b	4-C_6H_4OMe	$(CH_2)_2NH_2$	**4h**
1b	4-C_6H_4OMe	CH_2Ph	**4i**
1c	CH_2Ph	Me	**4j**
1c	CH_2Ph	Et	**4k**
1c	CH_2Ph	Bu^n	**4l**
1c	CH_2Ph	$(CH_2)_2NH_2$	**4m**

Scheme 2.

In Scheme 2, the carbon atoms of the bridging frame have been numbered in order to make clearer data assignments in the following sections.

The most relevant result shown in Scheme 2 is that addition of the primary amine takes place generating a C-N double bond at the C^1 carbon, which is already bound to a nitrogen atom. The resulting frame can be described as an amidine (carboxyimidamide), which is directly coordinated to one Fe (as N ligand), and connected, through a methylidene unit, to the bridging alkylidene carbon.

The molecular structure of **4f** has been determined by single crystal X-ray diffraction (Figure 1 and Table 1). The molecule is composed by a $Fe_2(\mu\text{-CO})(CO)(Cp)_2$ core, which adopts a *cis*

geometry relatively to the Cp ligands (Cp on the same side with respect to the Fe-Fe bond), and a bridging [μ-κ^1(N):η^1(C):η^1(C)-C(CO_2Me)CH_2C{N(Me)(C_6H_4OMe)}(NEt)] ligand. The latter contains a bridging alkylidene ligand and a terminal amidine ligand, joined by a methylene group. The Fe(2)-N(2) distance [1.980(3) Å] is typical for a σ-interaction between Fe and a sp^2-N.[13] In agreement with this both N(2) and C(1) display an almost perfect sp^2 hybridisation [sum angles 360.0(4) and 360.0(4)°, respectively], and the C(1)-N(1) [1.387(4) Å] and C(1)-N(2) [1.286(4) Å] interactions are very similar to those found in formamide [1.38 Å, single bond] and in different imines [av. 1.28 Å, double bond];[14] these bonding parameters agree, also, with the presence of a terminal N-coordinated amidine. As a result of the different properties, in terms of σ and π interactions, of the latter N-donor ligand coordinated to Fe(2) compared to the terminal CO bonded to Fe(1), there is a substantial electronic difference between the two Fe atoms, which causes a strong asymmetry in both the μ-CO [Fe(1)-C(11) 1.960(3) Å; Fe(2)-C(11) 1.850(4) Å] and the bridging alkylidene [Fe(1)-C(3) 2.024(3) Å; Fe(2)-C(3) 1.951(3) Å]. From a stereochemical point of view, the molecule adopts a *Z* configuration relatively to the C(1)-N(1) bond and an *E* configuration respect C(1)-N(2), allowing the minimisation of the steric repulsions.

The IR spectra of **4a-m** (in CH_2Cl_2 solution) exhibit a typical pattern consisting of two ν-CO absorptions due to the terminal and bridging carbonyls, at *ca.* 1925 and 1745 cm^{-1}, respectively. Moreover, another band accounts for the CO_2Me group (*e.g.* at 1663 cm^{-1} for **4a**), whereas the C^1=N(R') interaction gives raise to a weak absorption in the range 1600-1650 cm^{-1}.

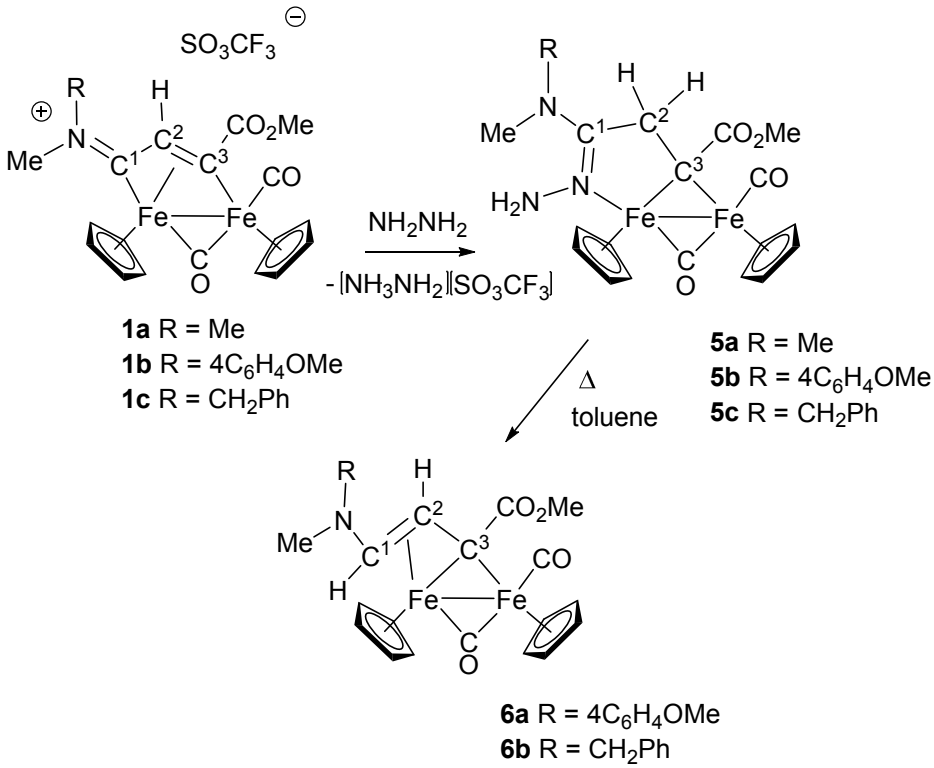
The ^{1}H NMR spectra show the presence of single isomeric forms in solution. The C$^2H_2$ protons resonate as doublets with coupling constant values typical for geminal protons (*e.g.* for **4a**: δ = 3.98, 3.50 ppm; $^2J_{HH}$ = 21.2 Hz). The salient features in the ^{13}C NMR spectra are resonances due to C^1 and C^3, which are consistent for an amidine carbon and a bridging alkylidene carbon, respectively (*e.g.* for **4a** at δ 147.7 and 173.4 ppm, in the order given).

The formation of the complexes **4** upon incorporation of the amine into the bridging frame deserves some further comments. The reaction exhibits a peculiar character not ascribable to classic hydroamination, neither to nucleophilic addition at conjugated iminiums (iminium-mediated aza-Michael addition), which would require nitrogen donor sources different from amines (e.g. nitrogen heterocycles, carbamates).[15] Likewise, the formation of the amidine group only in part resembles the addition of primary amines to activated imines, or to

secondary amide intermediates such as iminium sulfonates, iminium triflates, and imidoyl chlorides, which is one of the possible synthetic methods used to obtain such N,N,N'-trisubstituted amidines.[16] It is worth noting that this latter approach usually requires highly toxic and moisture-sensitive dehydrating agents and much more severe reaction conditions compared to those of the present work (note that NH_2Me, NH_3, $NH_2(CH_2)_2NH_2$ and NH_2NH_2, *vide infra*, have been used as aqueous solutions). Indeed the observed addition of amine (Scheme 2) is assisted and made possible by a rearrangement of the bridging coordination mode: the initial vinyliminium is transformed into a μ-alkylidene that remains anchored to one Fe atom through the amidine group. The observed nitrogen coordination to one of the iron atoms is consistent with the known coordinating properties of amidines,[17] and provides a further example of iron-amidine coordination.[18]

The reactions of **1a-c** with primary amines (Scheme 2) hold a rather general character, and seem to be viable in view of the electron withdrawing effect exerted by the carboxylate group. Indeed the presence of alternative substituents (e.g. ^{n}Bu, *para*-C_6H_4Me) at the C^3 carbon prevented to observe the described amination process. On the other hand, the vinyliminium complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(CO_2Me)C(H)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, differing from **1a** in the presence of a xylyl group instead of methyl at the iminium nitrogen, did not react with NH_2R' (R = Me, Et). This result appears to be the consequence of steric protection exerted by the xylyl towards amine attack at the iminium moiety, and is in agreement with previous findings (see Scheme 1).

Compounds **1a-c** also react with aqueous hydrazine, resulting in formation of **5a-c** in high yields (Scheme 3).



Scheme 3.

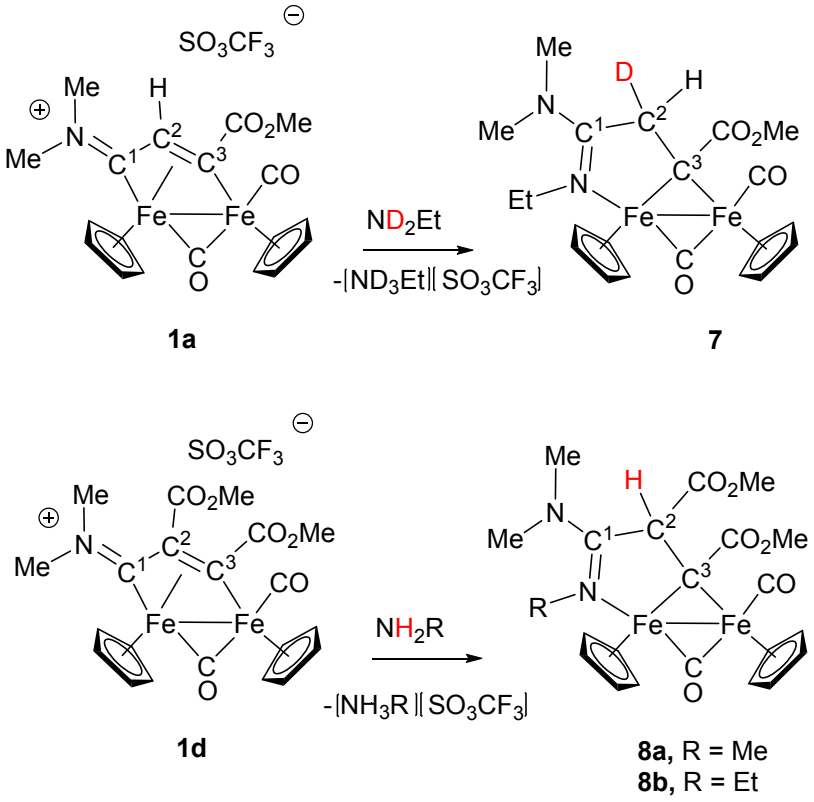
The molecular structure of **5b** (Figure 2 and Table 2) very closely resembles the one of **4f**, the only difference being the presence of a NH_2 group bonded to N(2) instead of an Et. Also all the most relevant bonding parameters and the stereochemistry are very similar and, therefore, they do not deserve any particular comment. An inter-molecular hydrogen bond exists between the $–NH_2$ groups and the terminal CO ligands of two molecules related by an inversion centre, resulting in the formation in the solid state of dimers connected by two of these interactions [N(3)-O(12)#1 3.205(2) Å; N(3)-H(32)-O(12) 140.4(18)°].

The spectroscopic data related to **5a-c** resemble those of the analogous **4a-m**. Moreover, the IR spectra (in KBr pellets) exhibit two weak absorptions which account for the NH_2 moiety (*e.g.* for **5b** at 3364 and 3270 cm^{-1}).

Although complexes **5** are quite stable in organic solvents (CH_2Cl_2, $CDCl_3$, toluene) at room temperature, we found that **5b** and **5c**, upon heating for 4 hours at reflux temperature in toluene (not dry), converted into the vinylalkylidene complexes **6a-b** (50-60% yields, see Scheme 3). Compound **6b** has been previously obtained by a different route: hydride addition ($NaBH_4$) to the vinyliminium **1c**.[4] Compound **6a** has been fully characterized by spectroscopy

and elemental analysis. The formation of **6a-b** formally occurs with the release of a [NH_2NH] fragment; it was not possible to identify the co-products of this degradation.

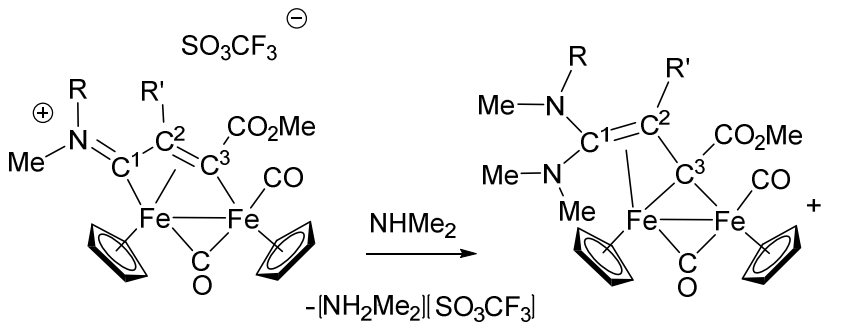
Although there is no clear indication about the nature and the sequence of the steps involved in the formation of **4** and **5** (Schemes 2 and 3), it is reasonable to assume that the reaction occurs *via* amine attack at the iminium carbon (C^1), followed or paralleled by H^+ removal and 1,3 H-migration from N to the C^2 carbon. One further intriguing aspect is the stereochemistry of the transformation: in principle, hydrogen migration may occur at one specific side of the plane associated with the $C^1C^2C^3$ bridging carbons. In fact, a similar feature was previously described for the H^- addition to the μ-vinyliminium, leading to the bis alkylidene complexes of type **3** (Scheme 1). In that case, the addition was found to be steroselective.[4] In order to investigate this point, we studied the reactivity of complex **1a** with ND_2Et (see Experimental). After work-up, compound **7** was isolated and characterized by IR, ^1H NMR spectroscopy and elemental analysis (Scheme 4).



Scheme 4.

Complex **7** displays a stereogenic centre at the C^2 carbon, and its ^1H NMR spectrum shows only one set of resonances. The C^2H resonates at δ 3.61 ppm as a triplet ($^2J_{HD}$ = 4.5 Hz), due to coupling with the adjacent deuterium nucleus. Otherwise, no signal is found at δ ≈ 4.1 ppm (compare with **4b**). Although NOE studies were not conclusive in determining whether deuterium addition occurred at the same side of the Cp rings or at the opposite one, the presence of a single species in solution indicates that C^2-D bond formation occurs at one single side of the bridging ligand plane, which reasonably implies that the 1,3 hydrogen migration involved in the syntheses of complexes **4-5** is also stereoselective. The study of the same reaction with a C^2 substituted complex should further corroborate this hypothesis. Thus, we investigated the reactivity of **1d**, containing an additional carboxylate group bound to C^2, with NH_2R' (R' = Me, Et). The reactions afforded **8a** and **8b**, in 80-85% yield (Scheme 4). The molecular structure of **8a** (Figure 3 and Table 3) is very similar to those discussed for **4f** and **5b**, displaying analogous bonding parameters for the bridging ligand. It is noteworthy the fact that the CO_2Me group bonded to C(2) is placed towards the less hindered side of the plane defined by Fe(2), C(3), C(2), C(1) and N(2), in order to minimise steric repulsions.
The ^1H NMR spectra of **8a-b** display single sets of resonances, suggesting that only one isomeric form is formed in any case, despite the presence of a stereogenic centre at C^2. Reasonably, such isomeric form corresponds to that observed in solid for **8a**, where the C^2-*H* atom is located in opposite position to the Cp ligands, with regard to the Fe-C^3-Fe plane.

Reactions of vinyliminium complexes with secondary and tertiary amines. The studies on the reactivity of vinyliminium complexes **1a-c** with amines were extended to triethylamine and dimethylamine, as prototypes for tertiary and secondary amines, respectively. Complexes **1a-d** revealed to be unreactive towards NEt_3, under reaction conditions similar to those used in the reactions with primary amines. On the contrary, the reactions of **1b** and **1d**, with $NHMe_2$ resulted in formation of the en-(1,1)di-amino-alkylidene complexes **9b**, and **9d**, respectively, in about 75-85% yield (Scheme 5).



1b R =4-C_6H_4OMe, R' = H
1d R = Me, R' = CO_2Me

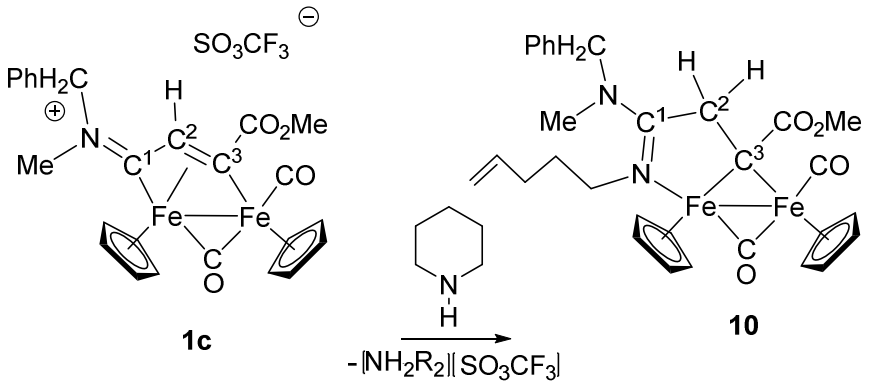
9b R =4-C_6H_4OMe, R' = H
9d R = Me, R' = CO_2Me

Scheme 5.

The IR spectra (in CH_2Cl_2 solution) of the air sensitive compounds **9b-d** exhibit absorptions due to the CO ligands, at *ca.* 1925 and 1750 cm^{-1}. The NMR spectra show the presence in solution of single isomeric forms. Relevant NMR features are given by the ^{13}C resonances due to the bridging carbons C^1, C^2 and C^3. The latter falls at *ca.* 150 ppm, indicating the alkylidene character, whereas the former is found at *ca*. 175 ppm. The nature of the product **9** is somewhat similar to previously reported bridging vinylalkylidene complexes [3a] (e.g. the vinylalkylidene complexes **2** and **6** reported in Scheme 1 and Scheme 3, respectively).

The reactions of complexes of type **1** with the secondary amine ($NHMe_2$) are distinctly different compared to those with primary amines. In both cases amines attack the C^1 position of the iminium carbon, but the secondary amine generates geminal enediamines[19] (otherwise indicated as ketene aminals), as a consequence of a different rearrangement of the bridging frame. A remarkable difference is that the hydrogen migration observed in the reaction with primary amines is no longer accessible because of deprotonation of $NHMe_2$. It is worth underlining the peculiar nature of the organic moiety generated by amine addition: N,N ketene aminals are known but relatively uncommon species, except for heterocyclic ketene aminals (HKAs), which find application as versatile synthetic building blocks in the construction of heterocyclic compounds.[20]

In order to extend the reactivity of vinyliminium complexes to other secondary amines, we considered the use of a cyclic amine (piperidine): the reaction of **1c** with $HN(CH_2)_5$, in THF solution at room temperature for 5 hours, affords complex **10** (Scheme 6), which has been identified on the basis of IR and NMR spectroscopy.



Scheme 6.

The formation of **10** is the result of amine addition to the C^1 (iminium carbon) and implies opening of the piperidine ring, C-H activation and presumable migration to the C^2 position, and N-deprotonation. The resulting ligand matches that generated in the reactions with primary amines (Scheme 2). This result emphasises the great stability of the bridging ligand in type **4-5** complexes, which might be the driving force leading to the activation of the piperidine ring even in the mild conditions employed for the reaction.

CONCLUSIONS

Diiron μ-vinyliminium complexes react with primary amines and hydrazine, undergoing nucleophilic addition at the iminium carbon of the bridging ligand. Generation of a C-N double bond and rearrangement of the bridging frame results in the unprecedented formation of an amidine (carboxyimidamide) moiety, which acts as a nitrogen ligand towards one Fe centre, and is connected, through a methylidene unit, to a bridging alkylidene carbon. The reaction is unique, in that it can not be considered a classic hydroamination of an olefin, neither is consistent with the characteristic reactivity of conjugated iminium functions with nitrogen nucleophiles (iminium-mediated aza-Michael addition). In other words, the reaction provides a further example of peculiar reaction patterns made possible by the bridging coordination of a reactive organic species (vinyliminum) to a diiron framework.

A further interesting point is that the reaction occurs with a relatively large number of primary amines, including aqueous NH_3 and NH_2NH_2, therefore has a quite general character and appears to be water tolerant. Conversely, there are some requirements concerning the

substituents on the bridging ligand that limit the substrate scope, in particular the presence of a strong electron withdrawing group (COOMe).

Amination of the bridging vinyliminium has been observed also with two selected secondary alkyl amines, the C-N bond formation still taking place at the iminium carbon. A geminal enediamine (ketene aminal), i.e. a relatively uncommon function group, may be accessible from this reaction. The overall bridging ligand can be viewed as a vinylalkylidene, not bearing any Fe-N binding.

Although the amination reactions here reported are to be categorized as metal-assisted (stoichiometric) transformations, rather than catalytic processes, they provide a better understanding of the potential associated to organometallic diiron complexes easily available from cheap starting materials, affording the bases for possible synthetic applications.

EXPERIMENTAL SECTION

General Data. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled before use under nitrogen from appropriate drying agents. Chromatographic separations were carried out on columns of deactivated alumina (4% w/w water) under nitrogen. Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. ESI MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in CH3CN. All NMR measurements were performed on a Mercury Plus 400 instrument. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The assignment of spectra was assisted by DEPT experiments and ^{1}H,^{13}C correlation measured using gs-HSQC and gs-HMBC experiments. All NMR spectra were recorded at 298 K. NOE measurements were recorded using the DPFGSE-NOE sequence. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2Cp_2CO)_4]$ was purchased from Strem and used as received. Compounds **1a**,[21] **1b**,[22] **1c**[21] and **1d**[21] were prepared by published methods.

Reactions of 1 with primary amines. Syntheses of $[Fe_2\{\mu\text{-}\eta^1(C):\eta^1(N):\eta^1(C)\text{-}C^3(CO_2Me)C^2H_2C^1\{N(Me)(R)\}(NR')\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R = Me, R' = Me, 4a R = Me, R' = Et, 4b R = Me, R' = Bu^n, 2c; R = Me, R' = $(CH_2)_2NH_2$, 4d R = 4-C_6H_4OMe, R' = Me, 4e; = 4-C_6H_4OMe, R' = Et, 4f R = 4-C_6H_4OMe, R' = H, 4g R = 4-C_6H_4OMe, R' =

$(CH_2)_2NH_2$, 4h R = 4-C_6H_4OMe, R' = CH_2Ph, 4i R = CH_2Ph, R' = Me, 4j R = CH_2Ph, R' = Et, 4k R = CH_2Ph, R' = Bu^n, 2l; R = CH_2Ph, R' = $(CH_2)_2NH_2$, 4m. An aqueous solution of NH_2Me (40 % W/W, 0.6 mL, d= 0.901 g/mL) was added to a solution of complex **1a** (98 mg, 0.168 mmol) in THF (10 mL). The mixture was stirred for 1 hour, then it was filtered on alumina. Hence, the volatiles were removed under reduced pressure, and the residue dissolved in diethyl ether and charged on alumina column. Elution with a 1:1 mixture of Et_2O and CH_2Cl_2 gave a yellow band corresponding to **4a**. The product was obtained as an ochre yellow powder upon removal of the solvent. Yield: 64 mg, 81%. Anal. Calcd. for $C_{20}H_{24}Fe_2N_2O_4$: C, 51.32; H, 5.17; N, 5.98. Found: C, 51.35; H, 5.10; N, 6.08. IR (CH_2Cl_2): ν (CO) 1926 (vs), 1747 (s), 1663 (w), ν(C^1=N) 1651 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.47, 4.35 (s, 10 H, Cp); 3.98, 3.50 (d, 2H, $^2J_{HH}$ = 21.2 Hz, C^2H_2); 3.89 (s, 3 H, CO_2Me); 2.39 (s, 9 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.6 (μ-CO); 217.8 (CO); 186.5 (*C*O_2Me); 173.4 (C^1); 147.7 (C^3); 87.6, 84.4 (Cp); 59.9 (C^2); 50.6 (CO_2*Me*); 42.3 (NMe); 41.4 (NMe_2). Compounds **4b-m** were prepared by the same procedure described for **2a**, by reacting **1a-c** with the appropriate amine (NH_2R'). NH_2Et, NH_2Bu^n, NH_2CH_2Ph were used anhydrous, whereas NH_2Me, NH_3 and $NH_2(CH_2)_2NH_2$ were used in aqueous solution. Crystals of **2f** suitable for X-ray analysis were collected from a $CDCl_3$ solution layered with n-pentane and stored at –20 °C.

4b (yield: 92 %; colour: orange). Anal. Calcd. for $C_{21}H_{26}Fe_2N_2O_4$: C, 52.28; H, 5.44; N, 5.81. Found: C, 52.21; H, 5.39; N, 5.86. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1745 (s), 1663 (m), ν (C^1=N) 1637 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.51, 4.40 (s, 10 H, Cp); 4.12, 3.60 (d, 2 H, $^2J_{HH}$ = 20.5 Hz, C^2H_2); 3.93 (s, 3 H, CO_2Me); 2.99, 2.69 (m, 2 H, N*C*H_2CH_3); 2.47 (s, 6 H, NMe); 1.04 (t, 3 H, $^3J_{HH}$ = 7 Hz, NCH_2C*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 287.0 (μ-CO); 216.0 (CO); 186.7 (*C*O_2Me); 171.7 (C^1); 147.8 (C^3); 87.8, 84.3 (Cp); 61.6 (C^2); 50.6 (CO_2*Me*); 49.5 (N*C*H_2CH_3); 41.8 (NMe); 13.9 (NCH_2*C*H_3).

4c (yield: 81 %; colour: ochre yellow). Anal. Calcd. for $C_{23}H_{30}Fe_2N_2O_4$: C, 54.15; H, 5.93; N, 5.49. Found: C, 54.21; H, 6.00; N, 5.49. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1749 (s), 1662 (w), ν (C^1=N) 1637 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.48, 4.37 (s, 10 H, Cp); 4.09, 3.58 (d, 2 H, $^2J_{HH}$ = 20.1 Hz, C^2H_2); 3.91 (s, 3 H, CO_2Me); 2.84, 2.56, 1.95, 1.56, 1.36, 1.20 (m, 6 H, N*C*H_2*C*H_2*C*H_2); 2.42 (s, 6 H, NMe); 0.91 (m, 3 H, $NCH_2CH_2CH_2C$*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 287.0 (μ-CO); 217.9 (CO); 186.6 (*C*O_2Me); 171.7 (C^1); 147.8 (C^3); 87.8, 84.3

(Cp); 61.6 (C^2); 55.6, 30.4, 20.7 ($NCH_2CH_2CH_2$); 50.6 (CO_2Me); 41.7 (NMe); 13.9 ($NCH_2CH_2CH_2CH_3$).

4d (yield: 71 %; colour: orange). Anal. Calcd. for $C_{21}H_{27}Fe_2N_3O_4$: C, 50.73; H, 5.47; N, 8.45. Found: C, 50.76; H, 5.50; N, 8.41. IR (CH_2Cl_2): ν(CO) 1924 (vs), 1748 (s), 1654 (w), ν(C^1=N) 1636 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.02, 6.60, 6.53 (br, 4 H, NCH_2); 4.52, 4.43 (s, 10 H, Cp); 3.92 (s, 3 H, CO_2Me); 3.96, 3.64 (d, 2 H, $^2J_{HH}$ = 20 Hz, C^2H_2); 2.48 (s, 6 H, NMe); *NH not observed*. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 288.5 (μ-CO); 216.9 (CO); 186.4 (CO_2Me); 173.9 (C^1); 148.4 (C^3); 87.6, 84.1 (Cp); 67.9, 57.7 (NCH_2); 63.2 (C^2); 51.4 (CO_2Me); 41.5 (NMe). ESI-MS(ES^+): 497 [31 %, M^+], 453 [100 %, $M^+ - CH_2CH_2NH_2$] m/z.

4e (yield: 78 %; colour: ochre yellow). Anal. Calcd. for $C_{26}H_{28}Fe_2N_2O_5$: C, 55.74; H, 5.04; N, 5.00. Found: C, 55.77; H, 5.12; N, 4.96. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1741 (s), 1665 (w), ν(C^1=N) 1615 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.27-6.53 (4 H, C_6H_4); 4.54, 4.39 (s, 10 H, Cp); 3.91, 3.62 (d, 2 H, $^2J_{HH}$ = 20.1 Hz, C^2H_2); 3.94 (s, 3 H, CO_2Me); 3.78 (s, 3 H, OMe); 2.93, 2.02 (s, 6 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.4 (μ-CO); 217.6 (CO); 186.6 (CO_2Me); 172.7 (C^1); 148.5 (C^3); 155.4 (ipso-C_6H_4OMe); 140.2, 124.0, 114.4 (C_6H_4OMe); 87.7, 84.0 (Cp); 60.8 (C^2); 55.4 (OMe); 50.6 (CO_2Me); 43.1, 40.6 (NMe).

4f (yield: 80 %; colour: ochre yellow). Anal. Calcd. for $C_{27}H_{30}Fe_2N_2O_5$: C, 56.47; H, 5.27; N, 4.88. Found: C, 56.51; H, 5.29; N, 4.79. IR (CH_2Cl_2): ν(CO) 1928 (vs), 1755 (s), 1666 (m), ν(C^1=N) 1642 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.28-6.60 (4 H, C_6H_4); 4.54, 4.41 (s, 10 H, Cp); 4.25, 3.62 (d, 2 H, $^2J_{HH}$ = 21.0 Hz, C^2H_2); 3.94 (s, 3 H, CO_2Me); 3.76 (s, 3 H, OMe); 3.05, 2.69 (m, 2 H, NCH_2CH_3); 2.86 (s, 3 H, NMe); 1.16 (t, 3 H, $^3J_{HH}$ = 7 Hz, NCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.3 (μ-CO); 218.1 (CO); 186.6 (CO_2Me); 169.8 (C^1); 156.3 (*ipso*-C_6H_4OMe); 148.6 (C^3); 139.4, 123.7, 114.5 (C_6H_4OMe); 87.9, 84.1 (Cp); 61.8 (C^2); 55.4 (OMe); 50.6 (CO_2Me); 50.4 (NCH_2CH_3); 42.3 (NMe); 12.7 (NCH_2CH_3).

4g (yield: 75 %; colour: orange). Anal. Calcd. for $C_{25}H_{26}Fe_2N_2O_5$: C, 54.98; H, 4.80; N, 5.13. Found: C, 55.02; H, 4.76; N, 5.14. IR (CH_2Cl_2): ν(CO) 1923 (vs), 1740 (s), 1660 (w), ν(C^1=N) 1613 (m) cm^{-1}. IR (KBr): ν(NH) 3108 (w-m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 11.78 (br, 1 H, NH); 7.01-6.51 (4 H, C_6H_4); 4.52, 4.37 (s, 10 H, Cp); 4.20, 3.61 (d, 2 H, $^2J_{HH}$ = 20 Hz, C^2H_2); 3.89 (s, 3 H, CO_2Me); 3.76 (s, 3 H, OMe); 2.86 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 289.7 (μ-CO); 218.6 (CO); 187.4 (CO_2Me); 170.3 (C^1); 158.3 (*ipso*-C_6H_4OMe); 148.0 (C^3);

137.3, 127.8, 114.8 (C_6H_4OMe); 87.4, 84.2 (Cp); 67.9 (C^2); 55.4 (OMe); 50.5 (CO_2Me); 39.3 (NMe).

4h (yield: 70 %; colour: pale green). Anal. Calcd. for $C_{27}H_{31}Fe_2N_3O_5$: C, 55.04; H, 5.30; N, 7.13. Found: C, 55.10; H, 5.41; N, 7.00. IR (CH_2Cl_2): ν(CO) 1928 (vs), 1745 (s), 1659 (w), ν (C^1=N) 1625 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.29-5.94 (8 H, C_6H_4OMe and NCH_2); 4.51, 4.39 (s, 10 H, Cp); 3.94 (s, 3 H, CO_2Me); 3.90, 3.70 (d, 2 H, $^2J_{HH}$ = 20 Hz, C^2H_2); 2.88 (s, 3 H, NMe); *NH not observed.* $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 291.1 (μ-CO); 217.2 (CO); 186.5 (CO_2Me); 175.1 (C^1); 157.3 (*ipso*-C_6H_4OMe); 149.4 (C^3); 139.1, 126.2, 113.7 (C_6H_4OMe); 87.9, 84.1 (Cp); 67.5, 58.7 (NCH_2); 63.6 (C^2); 50.7 (CO_2Me); 41.9 (NMe).

4i (yield: 68 %; colour: ochre yellow). Anal. Calcd. for $C_{32}H_{32}Fe_2N_2O_5$: C, 60.40; H, 5.07; N, 4.40. Found: C, 60.30; H, 5.16; N, 4.39. IR (CH_2Cl_2): ν(CO) 1929 (vs), 1754 (s), 1669 (w), ν (C^1=N) 1645 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.16-6.32 (9 H, Ph and C_6H_4); 5.65, 5.30 (br, 2 H, NCH_2); 4.58, 4.35 (s, 10 H, Cp); 4.22, 3.60 (d, 2 H, $^2J_{HH}$ = 18.7 Hz, C^2H_2); 3.94 (s, 3 H, CO_2Me); 3.76 (s, 3 H, OMe); 2.80 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 287.3 (μ-CO); 218.0 (CO); 186.9 (CO_2Me); 170.0 (C^1); 155.3 (*ipso*-C_6H_4OMe); 148.8 (C^3); 139.0, 123.9, 114.0 (C_6H_4OMe and Ph); 87.8, 83.8 (Cp); 63.0 (NCH_2); 61.2 (C^2); 55.0 (OMe); 50.9 (CO_2Me); 41.1 (NMe).

4j (yield: 75 %; colour: ochre yellow). Anal. Calcd. for $C_{26}H_{28}Fe_2N_2O_5$: C, 57.38; H, 5.19; N, 5.15. Found: C, 57.42; H, 5.12; N, 5.20. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1747 (s), 1664 (w), ν (C^1=N) 1614 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.29-7.00 (5 H, Ph); 4.54, 4.40 (s, 10 H, Cp); 4.12, 3.71 (d, 2 H, $^2J_{HH}$ = 20.49 Hz, C^2H_2); 3.90, 3.80 (d, 2 H, $^2J_{HH}$ = 15.37 Hz, CH_2Ph); 3.94 (s, 3 H, CO_2Me); 2.47 (s, 3 H, NMe), 2.38 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.3 (μ-CO); 217.9 (CO); 186.5 (CO_2Me); 173.5 (C^1); 147.9 (C^3); 137.0 (*ipso*-Ph); 128.6, 127.3, 127.0 (Ph); 87.7, 84.4 (Cp); 60.6 (C^2); 57.0 (CH_2Ph); 50.6 (CO_2Me); 42.3 (NMe); 39.4 (NMe).

4k (yield: 81 %; colour: ochre yellow). Anal. Calcd. for $C_{27}H_{30}Fe_2N_2O_4$: C, 58.09; H, 5.42; N, 5.02. Found: C, 58.04; H, 5.47; N, 4.96. IR (CH_2Cl_2): ν(CO) 1924 (vs), 1747 (s), 1664 (w), ν (C^1=N) 1625 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.32-7.00 (5 H, Ph); 4.51, 4.37 (s, 10 H, Cp); 4.23, 3.64 (d, 2 H, $^2J_{HH}$ = 21 Hz, C^2H_2); 3.91 (s, 3 H, CO_2Me); 3.90, 3.80 (d, 2 H, $^2J_{HH}$ = 15 Hz, CH_2Ph); 2.93, 2.66 (m, 2 H, NCH_2CH_3); 2.37 (s, 3 H, NMe); 1.00 (t, 3 H, $^3J_{HH}$ = 7 Hz, NCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.9 (μ-CO); 218.0 (CO); 186.6 (CO_2Me); 172.3 (C^1);

148.0 (C^3); 137.2 (*ipso*-Ph); 128.5, 127.3, 127.0 (Ph); 87.9, 84.3 (Cp); 61.8 (C^2); 57.8 (CH_2Ph); 50.6 (CO_2Me); 49.6 (NCH_2CH_3); 39.7 (NMe); 14.2 (NCH_2CH_3).

4l (yield: 81 %; colour: ochre yellow). Anal. Calcd. for $C_{29}H_{34}Fe_2N_2O_4$: C, 59.41; H, 5.85; N, 4.78. Found: C, 59.41; H, 5.75; N, 4.89. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1752 (s), 1664 (w), ν(C^1=N) 1643 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.32-6.94 (5 H, Ph); 4.46, 4.31 (s, 10 H, Cp); 4.23, 3.78 (d, 2 H, $^2J_{HH}$ = 20.5 Hz, C^2H_2); 3.86 (s, 3 H, CO_2Me); 3.73, 3.65 (d, 2 H, $^2J_{HH}$ = 15.4 Hz, CH_2Ph); 2.76, 2.48, 1.92, 1.47, 1.32, 1.20 (m, 6 H, $NCH_2CH_2CH_2$); 2.31 (s, 3 H, NMe); 0.85 (m, 3 H, $NCH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.9 (μ-CO); 218.0 (CO); 186.6 (CO_2Me); 172.4 (C^1); 147.9 (C^3); 137.1 (*ipso*-Ph); 135.6, 128.5, 126.9 (Ph); 87.9, 84.3 (Cp); 61.8 (C^2); 57.8 (CH_2Ph); 55.6, 30.8, 20.6 ($NCH_2CH_2CH_2$); 50.6 (CO_2Me); 39.6 (NMe); 13.8 ($NCH_2CH_2CH_2CH_3$).

4m (yield: 77 %; colour: pale green). Anal. Calcd. for $C_{27}H_{31}Fe_2N_3O_4$: C, 56.57; H, 5.45; N, 7.33. Found: C, 56.68; H, 5.30; N, 7.20. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1744 (s), 1665 (w), ν(C^1=N) 1596 (w) cm^{-1}. IR (KBr): ν(NH) 3255 (w-m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.51-7.04 (5 H, Ph); 6.96, 6.76, 6.40, 6.03 (br, 4 H, NCH_2); 4.53, 4.39 (s, 10 H, Cp); 3.95, 3.75 (d, 2 H, $^2J_{HH}$ = 20 Hz, C^2H_2); 3.93 (s, 3 H, CO_2Me); 2.26 (s, 3 H, NMe); *NH not observed*. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 288.6 (μ-CO); 218.0 (CO); 186.7 (CO_2Me); 173.6 (C^1); 147.8 (C^3); 136.2 (*ipso*-Ph); 128.4, 127.1, 126.6 (Ph); 87.8, 84.3 (Cp); 67.6, 57.7 (NCH_2); 61.1 (C^2); 57.7 (CH_2Ph); 50.4 (CO_2Me); 40.9 (NMe).

Reactions of 1a-c with hydrazine. Syntheses of [Fe_2{μ-η^1(C):η^1(N):η^1(C)-$C^3(CO_2Me)C^2H_2C^1${N(Me)(R)}(NNH$_2$)}(μ-CO)(CO)(Cp)$_2$] [R = Me, 5a; R = 4-C_6H_4OMe, 5b; R = CH_2Ph, 5c]. A solution of **1a** (94 mg, 0.161 mmol), in THF (10 mL), was treated with a large excess of $NH_2NH_2 \cdot 2H_2O$ (80 % W/W, 1.0 mL, d= 1.03 g/mL). The mixture was stirred for 15 minutes, and then filtered on alumina. Hence, the volatiles were removed, and the residue was dissolved in CH_2Cl_2 and chromatographed on alumina. Elution with a 1:1 mixture of THF and CH_2Cl_2 gave an orange band corresponding to **5a**. The product was obtained as a microcrystalline powder upon removal of the solvent. Yield: 58 mg, 77 %. Anal. Calcd. for $C_{19}H_{23}Fe_2N_3O_4$: C, 48.65; H, 4.94; N, 8.96. Found: C, 48.50; H, 5.12; N, 9.02. IR (CH_2Cl_2): ν(CO) 1927 (vs), 1742 (s), 1665 (w), ν(C=N) 1631 (w) cm^{-1}. IR (KBr): ν(NH) 3242 (w-m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.51, 4.46 (s, 10 H, Cp); 4.05 (s, 2 H, NH_2); 3.94, 3.46 (d, 2 H, $^2J_{HH}$ = 21 Hz, C^2H_2); 3.93 (s, 3 H, CO_2Me); 2.36 (s, 6 H, NMe). $^{13}C\{^1H\}$ NMR

($CDCl_3$) δ 287.9 (μ-CO); 217.4 (CO); 186.6 (*C*O_2Me); 161.6 (C^1); 150.7 (C^3); 87.7, 84.1 (Cp); 56.4 (C^2); 50.7 (CO_2*Me*); 37.8 (NMe). Compounds **5b-c** were prepared by the same procedure described for **5a**, by reacting $NH_2NH_2 \cdot 2H_2O$ with **1b** and **1c**, respectively. Crystals of **5b** suitable for X-ray analysis were collected by a CH_2Cl_2 solution layered with n-pentane and stored at –20 °C.

5b (yield: 78 %; colour: orange). Anal. Calcd. for $C_{25}H_{27}Fe_2N_3O_5$: C, 53.51; H, 4.85; N, 7.49. Found: C, 53.57; H, 4.96; N, 7.55. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1748 (s), 1666 (w), ν(C=N) 1630 (w) cm^{-1}. IR (KBr): ν(NH) 3364, 3270 (w-m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.76, 6.49 (d, 4 H, $^3J_{HH}$ = 8.79 Hz, C_6H_4); 4.56, 4.51 (s, 10 H, Cp); 4.09, 3.67 (d, 2 H, $^2J_{HH}$ = 20.9 Hz, C^2H_2); 4.07 (s, 2 H, NH_2); 3.94 (s, 3 H, CO_2Me); 3.75 (s, 3 H, OMe); 2.84 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 287.5 (μ-CO); 217.5 (CO); 186.1 (*C*O_2Me); 156.8 (*ipso*-*C*$_6H_4$OMe); 155.6 (C^1); 150.1 (C^3); 138.4, 121.4, 114.3 (*C*$_6H_4$OMe); 87.8, 84.1 (Cp); 56.6 (C^2); 55.4 (OMe); 50.7 (CO_2*Me*); 40.3 (NMe).

5c (yield: 72 %; colour: orange). Anal. Calcd. for $C_{25}H_{27}Fe_2N_3O_4$: C, 55.08; H, 4.99; N, 7.71. Found: C, 54.96; H, 5.04; N, 7.80. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1743 (s), 1666 (w), ν(C=N) 1630 (w) cm^{-1}. IR (KBr): ν(NH) 3361, 3248 (w-m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.30-7.01 (5 H, Ph); 4.54, 4.48 (s, 10 H, Cp); 4.14 (s, 2 H, NH_2); 4.01, 3.71 (d, 2 H, $^2J_{HH}$ = 14.6 Hz, C*H*$_2$Ph); 3.9 , 3.6 (d, 2 H, $^2J_{HH}$ = 21.96 Hz, C^2H_2); 3.93 (s, 3 H, CO_2Me); 2.33 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 287.5 (μ-CO); 217.3 (CO); 186.1 (*C*O_2Me); 161.6 (C^1); 150.1 (C^3); 137.1, 128.5, 127.7, 127.4 (Ph); 87.7, 84.1 (Cp); 56.3 (C^2); 54.9 (*C*H_2Ph); 50.7 (CO_2*Me*); 37.8 (NMe).

Conversion of 5 to 6. Syntheses of [Fe_2{μ-η^1:η^3-C^3(CO_2Me)C^2H=C^1HN(Me)(4-C_6H_4OMe)}(CO)(μ-CO)($Cp)_2$] [R = C_6H_4OMe, 6a; R = CH_2Ph, 6b]. Complex **5b** (90 mg, 0.160 mmol) was dissolved in toluene (15 mL), and the solution was stirred at boiling temperature for 4 hours. Hence, the solution was allowed to cool to room temperature and, then, chromatographed on an alumina column. Elution with CH_2Cl_2 gave a green band, corresponding to **6a** which was obtained as solid upon removal of the solvent. Yield: 48 mg, 56 %. Anal. Calcd. for $C_{25}H_{25}Fe_2NO_5$: C, 56.53; H, 4.74; N, 2.64. Found: C, 56.60; H, 4.69; N, 2.58. IR (CH_2Cl_2): ν(CO) 1942 (vs), 1765 (s), 1693 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.29, 6.94, *6.78*, *6.57* (d, 4 H, $^3J_{HH}$ = 8.42 Hz, C_6H_4); 4.70, 4.46 (s, 10 H, Cp); 4.81 (d, 2 H, $^3J_{HH}$ =

9.6 Hz, C^2H); 4.09 (s, 3 H, CO_2Me); 3.80 (s, 3 H, OMe); 2.77 (s, 3 H, NMe); 1.82 (d, 2 H, $^3J_{HH}$ = 9.6 Hz, C^1H).

Complex **6b** was obtained by an analogous procedure described for **6a** starting from **5c** (yield: 58 %). Complex **6b** was identified upon comparison of its spectroscopic properties with those reported in the literature.[4]

Synthesis of $[Fe_2\{\mu\text{-}\eta^1(C):\eta^1(N):\eta^1(C)\text{-}C^3(CO_2Me)C^2(H)(D)C^1(NMe_2)(NEt)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (7). A large excess of NH_2Et was bubbled into 5.0 mL of D_2O, for 20 s. The solution was stirred for 2 hours, and then it was added to a THF solution (20 mL) of **1a** (80 mg, 0.137 mmol). The resulting mixture was stirred for 30 minutes and then filtered on an alumina pad. Solvent removal and chromatography of the residue on alumina with CH_2Cl_2 gave **7,** which was obtained as an orange powder upon removal of the solvent. Yield: 40 mg, 61 %. Anal. Calcd. for $C_{21}H_{25}DFe_2N_2O_4$: C, 52.21; H, 5.63; N, 5.80. Found: C, 52.31; H, 5.53; N, 5.84. IR (CH_2Cl_2): ν(CO) 1925 (vs), 1746 (s), 1665 (m), ν(C=N) 1640 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.51, 4.40 (s, 10 H, Cp); 3.61 (m, 1 H, C^2H); 3.93 (s, 3 H, CO_2Me); 2.91, 2.69 (m, 2 H, NCH_2CH_3); 2.46 (s, 6 H, NMe); 1.04 (t, 3 H, $^3J_{HH}$ = 7 Hz, NCH_2CH_3).

Reactions of 1d with primary amines. Syntheses of $[Fe_2\{\mu\text{-}\eta^1(C):\eta^1(N):\eta^1(C)\text{-}C^3(CO_2Me)C^2(CO_2Me)(H)C^1(NMe_2)(NR')\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R' = Me, 8a; R' = Et, 8b]. Complexes **8a** and **8b** were obtained by the same procedures described for **4a**, upon treatment of **1d** with NH_2Me in aqueous solution, and anhydrous NH_2Et, respectively. A single crystal of **8a** suitable for X-ray analysis was obtained by a $CDCl_3$ solution layered with n-pentane, at –20 °C.

8a (yield: 81 %; colour: orange). Anal. Calcd. for $C_{22}H_{26}Fe_2N_2O_6$: C, 50.22; H, 4.98; N, 5.32. Found: C, 50.27; H, 5.02; N, 5.21. IR (CH_2Cl_2): ν(CO) 1928 (vs), 1753 (s), 1727 (vs), ν (C=N) 1651 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.79 (s, 1 H, C^2H); 4.53, 4.50 (s, 10 H, Cp); 3.85 (s, 6 H, CO_2Me); 2.48 (s, 9 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 285.2 (μ-CO); 217.5 (CO); 184.6, 171.0 (CO_2Me); 172.1 (C^1); 147.3 (C^3); 87.9, 85.4 (Cp); 73.4 (C^2); 51.8, 50.3 (CO_2Me); 43.0 (NMe); 41.2 (NMe_2).

8b (yield: 85 %; colour: orange). Anal. Calcd. for $C_{23}H_{28}Fe_2N_2O_6$: C, 51.14; H, 5.22; N, 5.19. Found: C, 51.24; H, 5.15; N, 5.19. IR (CH_2Cl_2): ν(CO) 1927 (vs), 1754 (s), 1708 (m), 1651 (m) ν(C=N) 1640 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.82 (s, 1 H, C^2H); 4.54, 4.49 (s, 10 H, Cp);

3.86, 3.85 (s, 6 H, CO_2Me); 3.12, 2.97 (m, 2 H, NCH_2CH_3); 2.50 (s, 6 H, NMe); 0.80 (t, 3 H, $^3J_{HH}$ = 7 Hz, NCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 291.0 (μ-CO); 218.2 (CO); 187.9, 169.2 (CO_2Me); 172.3 (C^1); 147.1 (C^3); 88.2, 85.3 (Cp); 74.6 (C^2); 51.8, 50.4 (CO_2Me); 50.7 (NCH_2CH_3); 41.5 (NMe); 13.2 (NCH_2CH_3).

Reaction of 1b with $NHMe_2$. Syntheses of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C^3(CO_2Me)C^2(R')C^1(NMe_2)N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$, [R = 4-$C_6H_4OMe$, R' = H, 9b; R = Me, R' = CO_2Me, 9d]. Complex **1b** (150 mg, 0.221 mmol), was dissolved in THF (10 mL) and treated with a large excess of $NHMe_2$ in anhydrous THF solution. The mixture was stirred at room temperature for 3 hours, then it was filtered through alumina by using THF as eluent. Subsequently, the solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 and chromatographed on an alumina column. Elution with CH_2Cl_2 gave a green band, which afforded **9b** as solid upon removal of the solvent. Yield: 95 mg, 75 %. Anal. Calcd. for $C_{27}H_{30}Fe_2N_2O_5$: C, 56.47; H, 5.27; N, 4.88. Found: C, 56.57; H, 5.17; N, 4.77. IR (CH_2Cl_2): ν (CO) 1925 (vs), 1750 (s), 1660 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.53-6.82 (4 H, C_6H_4OMe); 4.85, 4.72 (s, 10 H, Cp); 4.60 (s, 1 H, C^2H); 4.02 (s, 3 H, CO_2Me); 3.74 (s, 3 H, OMe); 2.93 (s, 6 H, NMe); 2.33 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 289.6 (μ-CO); 217.8 (CO); 188.3 (CO_2Me); 177.6 (C^1); 151.8 (C^3); 142.6-112.7 (C_6H_4OMe); 85.5, 81.0 (Cp); 57.2 (C^2); 54.6 (OMe); 50.5 (CO_2Me); 49.6, 43.9, 41.4 (NMe).

Complex **9d** was obtained by the same procedure described for **9b**, by reacting **1d** with $NHMe_2$.

9d (yield: 82 %; colour: reddish brown). Anal. Calcd. for $C_{23}H_{28}Fe_2N_2O_6$: C, 51.14; H, 5.22; N, 5.19. Found: C, 51.10; H, 5.10; N, 5.29. IR (CH_2Cl_2): ν(CO) 1926 (vs), 1745 (s), 1662 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 4.70, 4.17 (s, 10 H, Cp); 3.86 (s, 6 H, CO_2Me); 3.31, 3.05, 2.83, 2.71 (s, 12 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 290.0 (μ-CO); 216.4 (CO); 187.8, 165.7 (CO_2Me); 175.4 (C^1); 152.4 (C^3); 87.2, 83.1 (Cp); 75.1 (C^2); 52.0, 50.9 (CO_2Me); 41.5, 41.1, 40.5, 40.2 (NMe).

Reaction of 1c with piperidine. Synthesis of $[Fe_2\{\mu\text{-}\eta^1(C)\text{:}\eta^1(N)\text{:}\eta^1(C)\text{-}C^3(CO_2Me)C^2H_2C^1\{N(Me)(CH_2Ph)\}(CH_2CH_2CH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$, (10).

A solution of complex **1c** (120 mg, 0.181 mmol), in THF (10 mL), was treated with piperidine (0.40 mL, 4.04 mmol). The mixture was stirred for 5 hours, then it was filtered on an alumina

column. An ochre yellow band was collected. Compound **10** was obtained as a powder upon removal of the solvent under reduced pressure. Yield: 79 mg, 75 %. Anal. Calcd. for $C_{30}H_{34}Fe_2NO_4$: C, 61.63; H, 5.87; N, 2.40. Found: C, 61.66; H, 5.70; N, 2.36. IR (CH_2Cl_2): ν (CO) 1928 (vs), 1733 (s), 1667 (w), ν(C=N) 1633 (w) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.34-7.01 (5 H, Ph); 5.91 (s, 1 H, CH_2CH); 4.56, 4.44 (s, 10 H, Cp); 4.36, 3.75 (d, $^2J_{HH}$ = 20.13 Hz, C^2H_2); 4.40, 4.12, 3.88, 3.74, 3.54, 3.19, 2.97, 2.36 (br, 4 H, CH_2); 4.02, 3.85 (d, $^2J_{HH}$ = 15.7 Hz, CH_2Ph); 3.95 (s, 3 H, CO_2Me); 2.45 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 286.2 (μ-CO); 217.6 (CO); 186.3 (CO_2Me); 174.8 (C^1); 149.8 (C^3); 137.2, 128.6, 127.2, 126.7 (Ph); 125.4 ($CH_2=CH$); 116.0 ($CH_2=CH$); 88.2, 84.7 (Cp); 61.9 (C^2); 61.4, 59.1, 57.9 (CH_2); 56.9 (CH_2Ph); 50.7 (CO_2Me); 40.3 (NMe).

X-ray Crystallography.

Crystal data and collection details for **4f**, **5b** and **8a·CHCl$_3$** are reported in Table S1 (Supporting Information). The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[23] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[24] All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. H-atoms were placed in calculated positions, except positions of H(31) and H(32) in **5b** and H(14) in **8a·0.5CHCl$_3$** which were located in the Fourier map. H-atom were treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atoms. The two Cp ligands in **4f** and the Cp ligand bonded to Fe(1) in **5b** are disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format, and crystallographic parameters for **4f**, **5b** and **8a**.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Bauer, I.; Knölker, H.-J. *Chem. Rev*. **2015**, *115*, 3170–3387. (b) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev*. **2011**, *111*, 1293-1314. (c) Bolm, C.; Legros, J.; Le Paih, J.; Zani, L. *Chem. Rev*. **2004**, *104*, 621-6254. (d) Martin, R.; Fürstner, A. *Angew. Chem., Int. Ed*. **2004**, *43*, 3955-3957.

(2) (a) Schilter, D.; Camara, J. M.; Huynh, M. T.; Hammes-Schiffer, S.; Rauchfuss, T. B. *Chem. Rev.* **2016**, *116*, 8693-8749. (b) Rauchfuss, T. B. *Acc. Chem. Res*. **2015**, *48*, 2107-2116. (c) Capon, J. F.; Gloaguen, F.; Pétillon, F.Y.; Schollhammer, Talarmin, P. J. *Coord. Chem. Rev.* **2009**, *253*, 1476-1494. (d) Mejia-Rodriguez, R.; Chong, D. S.; Reibenspies, J. H.; Soriaga, M. P.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2004**, *126*, 12004-12014. (e) Cheah, M. H.; Tard, C.; Borg, S. J.; Liu, X.; Ibrahim, S. K.; Pickett, C. J.; Best, S. P. *J. Am. Chem. Soc.* **2007**, *129*, 11085-11092.

(3) (a) Busetto, L.; Maitlis, P. M.; Zanotti, V. *Coord. Chem. Rev.* **2010**, *254*, 470-486. (b) Busetto, L.; Zanotti, V. *J. Organomet. Chem.* **2005**, *690*, 5430-5440.

(4) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *Organometallics*, **2004**, *23*, 3348-3354.

(5) Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *Eur. J. Inorg. Chem.,* **2007**, 1799-1807.

(6) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2006**, *691*, 4234-4243.

(7) Zanotti, V. *Pure Appl. Chem*. **2010**, *82*, 1555-1568.

(8) Mazzoni, R.; Salmi, M.; Zanotti, V. *Chem. Eur. J.* **2012**, *18*, 10174-10194.

(9) Ruiz-Castillo, P.; Buchwald, S. L. *Chem. Rev*. **2016**, *116*, 12564-12649.

(10) (a) Ramirez, T. A.; Zhao. B.; Shi, Y. *Chem. Soc. Rev*., **2012**, *41*, 931-942. (b) Muller, P.; Fruit, C.; *Chem. Rev.,* **2003**, *103*, 2905-2919. (c) Davies H. M. L.; Manning, J. R., *Nature*, **2008**, 451, 417-424. (d) Fantauzzi, S.; Caselli, A.; Gallo, E.; *Dalton Trans.*, **2009**, 5434-5443. (e) Collet, F.; Lescot, C.; Dauban, P. *Chem. Soc. Rev*. **2011**, *40*, 1926-1936.

(11) (a) Huang, L.; Arndt, M.; Goossen, K.; Heydt, H.;. Goossen, L. J. *Chem. Rev.* **2015**, *115*, 2596-2697. (b) Pirnot, Michael T.; Wang, Yi-Ming; Buchwald, Stephen L. *Angew. Chem. Int. Ed.* **2016**, *55*, 48-57.

(12) (a) Correa, A.; Olga Garcıa Mancheno, O. G.; Bolm, C. *Chem. Soc. Rev.*, **2008**, *37*, 1108-1117. (b) Greenhalgh, M. D.; Jones, A. S.; Thomas, S. P. *Chem. Cat. Chem.*, **2015**, *7*, 190- 222.

(13) Albano, V. G; Bordoni, S.; Busetto, L.; Marchetti, F.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2003**, *684*, 37-43.

(14) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th Edition, Wiley Inter-Science, **2001.**

(15) Enders, D.; Wang, C.; Liebich, J. X. *Chem. Eur. J.* **2009**, *15*, 11058-11076.

(16) (a) Silva dos Santos, M.; Rolim Bernardino, A. M.; Costa de Souza, M. *Quim. Nova*, **2006**, *29*, 1301-1306. (b) Phakhodee, W.; Wangngae, S.; Wiriya, N.; Pattarawarapan, M. *Tetrahedron Lett*. **2016**, *57*, 5351-5354.

(17) Barker, J.; Kilner, M. *Coord. Chem. Rev*., **1994**, *133*, 219-300.

(18) (a) Hagadorn, J. R.; Arnold, J. *J. Organomet. Chem.* **2001**, *637–639*, 521–530. (b) Rau, S.; Böttcher, L.; Schebesta, S.; Stollenz, M.; Görls, H.; Walther, D. *Eur. J. Inorg. Chem.* **2002**, *11*, 2800-2809.

(19) (a) Bakulina, O. Y.; Ivanov, A. Y,; Lobanov, P. S.; Dar'in, D. V. *Tetrahedron* **2014**, *70*,7900-7905. (b) Mishina, M. S.; Ivanov, A. Y,; Lobanov, P. S.; Dar'in, D. V. *Synthesis* **2016**, *48*, 2851-2862.

(20) (a) Wang, K.-M.; Yan, S.-J.; Lin, J. *Eur. J. Org. Chem*. **2014**, 1129–1145. (b) Yang, P. H. *Res. Chem. Intermed.* **2016**, *42*, 5617-5637. (c) Liu, J.; Yan, S.-J.; Cao, Z.-M.; Cui, S.-S.; Lin, J. *RSC Adv.,* **2016**, *6*, 103057-103064.

(21) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem*. **2004**, *689*, 528-538.

(22) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Organometallics* **2008**, *27*, 5058-5066.

(23) Sheldrick, G. M. SADABS, Program for empirical absorption correction, University of Göttingen, Germany, **1996**.

(24) Sheldrick, G. M. SHELX97, Program for crystal structure determination, University of Göttingen, Germany, **1997**.

Figures

Figure 1. Molecular structure of **4f**. Only the main images of the disordered Cp ligands are drawn. Displacement ellipsoids are at the 30% probability level.

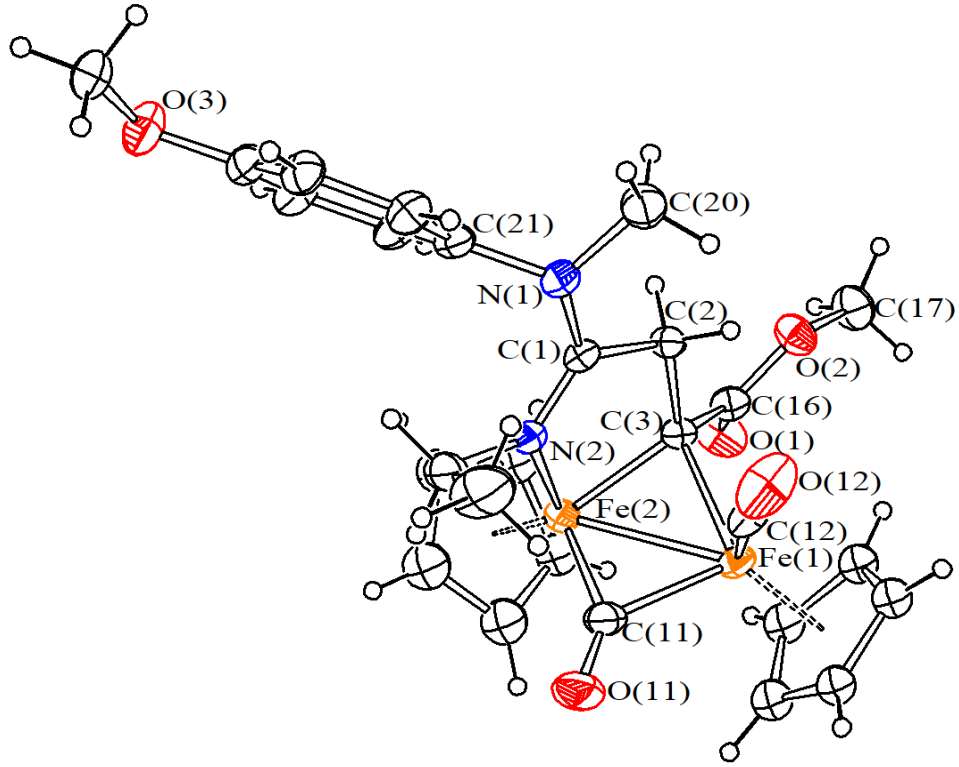

Figure 2. Molecular structure of **5b**. Only the main image of the disordered Cp ligand bonded to Fe(1) is drawn. Displacement ellipsoids are at the 30% probability level.

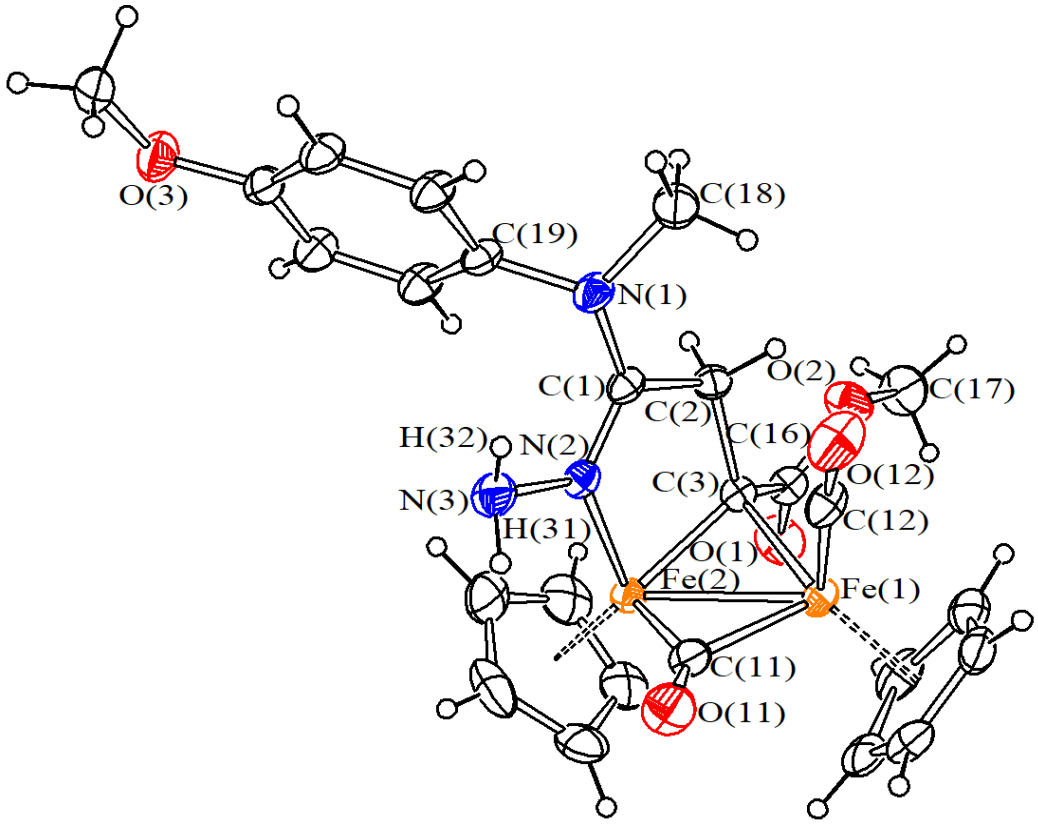

Figure 3. Molecular structure of **8a**. Displacement ellipsoids are at the 30% probability level.

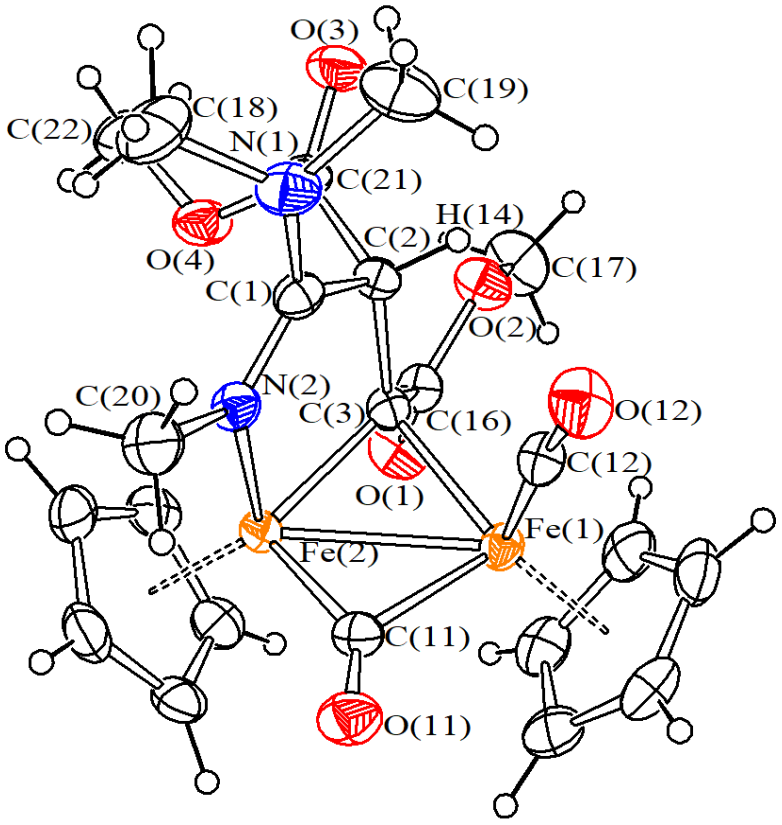

Table 1. Selected bond lengths (Å) and angles (°) for **4f**.

Fe(1)-Fe(2)	2.5104(6)	C(12)-O(12)	1.148(4)
Fe(1)-C(11)	1.960(3)	C(2)-C(3)	1.534(4)
Fe(2)-C(11)	1.850(4)	C(1)-C(2)	1.496(4)
Fe(1)-C(12)	1.727(3)	C(1)-N(1)	1.387(4)
Fe(1)-C(3)	2.024(3)	C(1)-N(2)	1.286(4)
Fe(2)-C(3)	1.951(3)	C(3)-C(16)	1.494(4)
Fe(2)-N(2)	1.980(3)	C(16)-O(1)	1.208(4)
C(11)-O(11)	1.181(4)	C(16)-O(2)	1.347(4)
C(1)-C(2)-C(3)	110.6(2)	Fe(1)-C(3)-C(2)	120.05(19)
C(2)-C(1)-N(2)	115.2(2)	Fe(1)-C(3)-Fe(2)	78.30(10)
C(2)-C(1)-N(1)	119.2(2)	C(1)-N(2)-Fe(2)	117.4(2)
N(1)-C(1)-N(2)	125.3(3)	Fe(1)-C(11)-Fe(2)	82.38(13)

Table 2. Selected bond lengths (Å) and angles (°) for **5b**.

Fe(1)-Fe(2)	2.5051(4)	C(12)-O(12)	1.151(2)
Fe(1)-C(11)	1.9451(17)	C(2)-C(3)	1.536(2)
Fe(2)-C(11)	1.8610(16)	C(1)-C(2)	1.492(2)
Fe(1)-C(12)	1.7321(16)	C(1)-N(1)	1.3914(19)
Fe(1)-C(3)	2.0311(14)	C(1)-N(2)	1.283(2)
Fe(2)-C(3)	1.9575(15)	C(3)-C(16)	1.494(2)
Fe(2)-N(2)	1.9539(13)	C(16)-O(1)	1.203(2)
C(11)-O(11)	1.179(2)	C(16)-O(2)	1.353(2)
C(1)-C(2)-C(3)	109.83(12)	Fe(1)-C(3)-C(2)	119.66(10)
C(2)-C(1)-N(2)	114.38(13)	Fe(1)-C(3)-Fe(2)	77.79(5)
C(2)-C(1)-N(1)	122.25(14)	C(1)-N(2)-Fe(2)	119.99(10)
N(1)-C(1)-N(2)	123.36(14)	Fe(1)-C(11)-Fe(2)	82.28(6)

Table 3. Selected bond lengths (Å) and angles (°) for **8a**.

Fe(1)-Fe(2)	2.5200(5)	C(12)-O(12)	1.150(3)
Fe(1)-C(11)	1.968(3)	C(2)-C(3)	1.545(3)
Fe(2)-C(11)	1.851(3)	C(1)-C(2)	1.509(3)
Fe(1)-C(12)	1.743(3)	C(1)-N(1)	1.378(3)
Fe(1)-C(3)	2.027(2)	C(1)-N(2)	1.282(3)
Fe(2)-C(3)	1.953(2)	C(3)-C(16)	1.487(3)
Fe(2)-N(2)	1.971(2)	C(16)-O(1)	1.206(3)
C(11)-O(11)	1.181(3)	C(16)-O(2)	1.366(3)
C(1)-C(2)-C(3)	108.92(19)	Fe(1)-C(3)-C(2)	117.53(16)
C(2)-C(1)-N(2)	115.4(2)	Fe(1)-C(3)-Fe(2)	78.54(8)
C(2)-C(1)-N(1)	120.32)	C(1)-N(2)-Fe(2)	118.58(17)
N(1)-C(1)-N(2)	124.2(2)	Fe(1)-C(11)-Fe(2)	82.51(10)

TOC graphic

Amination of Bridging Vinyliminium Ligands in Diiron Complexes: C-N Bond Forming Reactions for Amidine-Alkylidene Species

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