

**Diiron-aminocarbyne complexes with amine or imine ligands: C-N coupling  
between imine and aminocarbyne ligands promoted by tolylacetylde addition to  
[Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(NH=CPh<sub>2</sub>)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>]**

Luigi Busetto, Fabio Marchetti, Stefano Zacchini, Valerio Zanotti\* and Eleonora Zoli.

*Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy*

### Summary

A terminally coordinated CO ligand in the complexes [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, **1a**; R = Xyl, **1b**; Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), is readily displaced by primary and secondary amines (L), in the presence of Me<sub>3</sub>NO, affording the complexes [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(L)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, L = NH<sub>2</sub>Et, **4a**; R = Xyl, L = NH<sub>2</sub>Et, **4b**; R = Me, L = NH<sub>2</sub>Pr<sup>i</sup>, **5a**; R = Xyl, L = NH<sub>2</sub>Pr<sup>i</sup>, **5b**; R = Xyl, L = NH<sub>2</sub>C<sub>6</sub>H<sub>11</sub>, **6**; R = Xyl, L = NH<sub>2</sub>Ph, **7**; R = Xyl, L = NH<sub>3</sub>, **8**; R = Me, L = NHMe<sub>2</sub>, **9a**; R = Xyl, L = NHMe<sub>2</sub>, **9b**; R = Xyl, L = NH(CH<sub>2</sub>)<sub>5</sub>, **10**). In the absence of Me<sub>3</sub>NO, NH<sub>2</sub>Et gives addition at the CO ligand of **1b**, yielding [Fe<sub>2</sub>{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(O)NH<sub>2</sub>Et}(Cp)<sub>2</sub>] (**11**). Carbonyl replacement is also observed in the reaction of **1a-b** with pyridine and benzophenone imine, affording [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(L)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, L = Py, **12a**; R = Xyl, L = Py, **12b**; R = Me, L = HN=CPh<sub>2</sub>, **13a**; R = Xyl, L = HN=CPh<sub>2</sub>, **13b**). The imino complex **13b** reacts with p-tolylacetylde leading to the formation of the μ-vinylidene-diaminocarbene compound [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>2</sup>-C=C(Tol)C(Ph)<sub>2</sub>N(H)CN(Me)(Xyl)}(μ-CO)(CO)(Cp)<sub>2</sub>] (**15**) which has been studied by X-ray diffraction.

Keywords: amine, imine, diaminocarbene, vinylidene, diiron complexes, crystal structure

Corresponding author e-mail address: [valerio.zanotti@unibo.it](mailto:valerio.zanotti@unibo.it)

### 1. Introduction

Diiron bridging aminocarbyne complexes [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, **1a**; R = Xyl, **1b**; Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) and [Fe<sub>2</sub>(μ-CNMe<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>]<sub>2</sub> (**2**)

exhibit a remarkable electrophilic character. It has been shown that carbon nucleophiles ( $R'$ ) react with **1** to give  $[Fe_2\{\mu-CN(Me)R\}(\mu-CO)(CO)(COR')(Cp)_2]$  or  $[Fe_2\{\mu-CN(Me)R\}(\mu-CO)(CO)_2(\eta^4-C_5H_5R')(Cp)]$  *via* selective addition at the carbonyl (organo-cuprates, acetylides) and cyclopentadienyl ligand (organo-lithium or Grignard reagents), respectively [1]. On the other hand, weaker nucleophiles, including isocyanides,  $CN^-$ , nitriles, halides and phosphines react with **1** and **2**, giving CO replacement, under thermal, photolytic or chemical activation [2]. Reactions involving the bridging aminocarbene ligand of **1** have been limited to the addition of hydride (from  $NaBH_4$ ) and cyanide (from  $NBu_4CN$ ), affording the corresponding aminocarbene complexes [3]. More recently, we have reported on the insertion of alkynes ( $R'CCR''$ ) into the metal-carbonyne carbon bond of the acetonitrile complexes  $[Fe_2\{\mu-CN(Me)R\}(\mu-CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$  ( $R = Me$ , **3a**; Xyl, **3b**;  $CH_2Ph$ , **3c**), which leads to the formation of bridging vinyliminium complexes  $[Fe_2\{\mu-\sigma:\eta^3-C(R')=C(R'')C=N(Me)(R)\}(\mu-CO)(CO)(Cp)_2][SO_3CF_3]$  ( $R' = Me, COOMe, SiMe_3, Ph, Tol$ ;  $R'' = H, Me, Et, Ph$ ) *via* coupling of the alkyne and aminocarbene ligand [4].

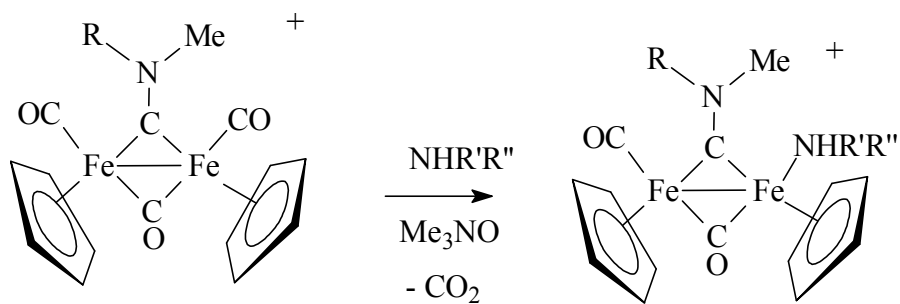
Reactions of the diiron  $\mu$ -aminocarbene complexes with amines have been scarcely investigated. It has been shown that **2** undergoes addition of  $HNR'_2$  at the CO yielding the carbamoyl complexes  $[Fe_2(\mu-CNMe)_2(\mu-CO)\{C(O)NR'\}(Cp)_2][SO_3CF_3]$ . Primary amines generate carbamoyl intermediates which further react, by dehydration, giving isocyanide derivatives [2b].

On the light of a renewed interest towards nitrogen-containing ligands, mainly due to applications in the field of catalysis [5], we have been interested at determining whether nitrogen ligands, including amines and imines, could be coordinated to the Fe atom in the aminocarbene complexes **1a-b** and **3a-b**, and at investigating their chemistry. Our findings are the matter of this paper.

## 2. Results and discussion

### 2.1. Reactions with amines

The reactions of compounds **1a-b**, in tetrahydrofuran solution, at room temperature, with an excess of ethylamine in the presence of  $Me_3NO$ , result in the formation of the amino complexes  $[Fe_2\{\mu-CN(Me)R\}(\mu-CO)(CO)(NH_2Et)(Cp)_2][SO_3CF_3]$  ( $R = Me$ , **4a**;  $R = Xyl$ , **4b**) (scheme 1), which have been isolated in about 65-70% yields after filtration on alumina. Other amines, including secondary amines and ammonia, but not tertiary amines ( $NMe_3, NEt_3$ ), react analogously affording the complexes  $[Fe_2\{\mu-CN(Me)R\}(\mu-CO)(CO)(NHR'R'')(Cp)_2][SO_3CF_3]$  (**5-10**) in comparable yields (Scheme 1).

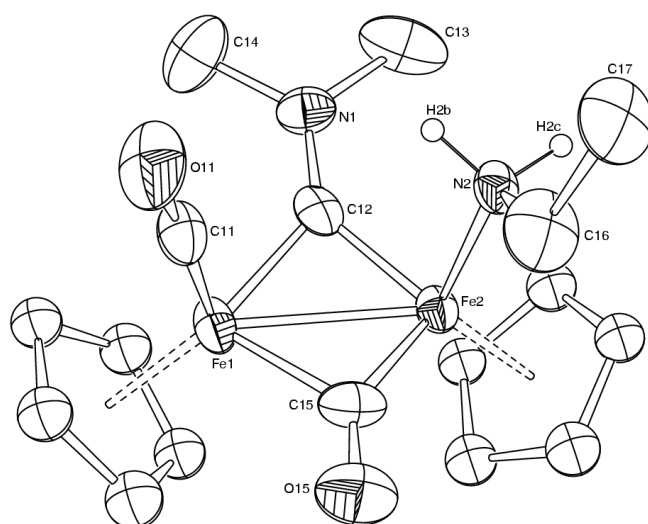


	R
<b>1a</b>	Me
<b>1b</b>	Xyl

	R	NHR'R''
<b>4a</b>	Me	NH <sub>2</sub> Et
<b>4b</b>	Xyl	NH <sub>2</sub> Et
<b>5a</b>	Me	NH <sub>2</sub> Pr <sup>1</sup>
<b>5b</b>	Xyl	NH <sub>2</sub> Pr <sup>1</sup>
<b>6</b>	Xyl	NH <sub>2</sub> C <sub>6</sub> H <sub>11</sub>
<b>7</b>	Xyl	NH <sub>2</sub> Ph
<b>8</b>	Xyl	NH <sub>3</sub>
<b>9a</b>	Me	NHMe <sub>2</sub>
<b>9b</b>	Xyl	NHMe <sub>2</sub>
<b>10</b>	Xyl	NH(CH <sub>2</sub> ) <sub>5</sub>

**Scheme 1**

Complexes **4-10** have been characterized by IR and NMR spectroscopy and elemental analysis. Moreover, the structure of **4a** has been ascertained by an X-ray diffraction experiment; its molecular structure is reported in Figure 1, whereas the main bond lengths and bond angles are reported in Table 1.



**Figure 1**

Molecular structure of **4a**, with key atoms labelled (all H atoms, apart from H2b and H2c, have been omitted). Displacement ellipsoids are at 30% probability level. Only the main images of the disordered Cp ligands are drawn.

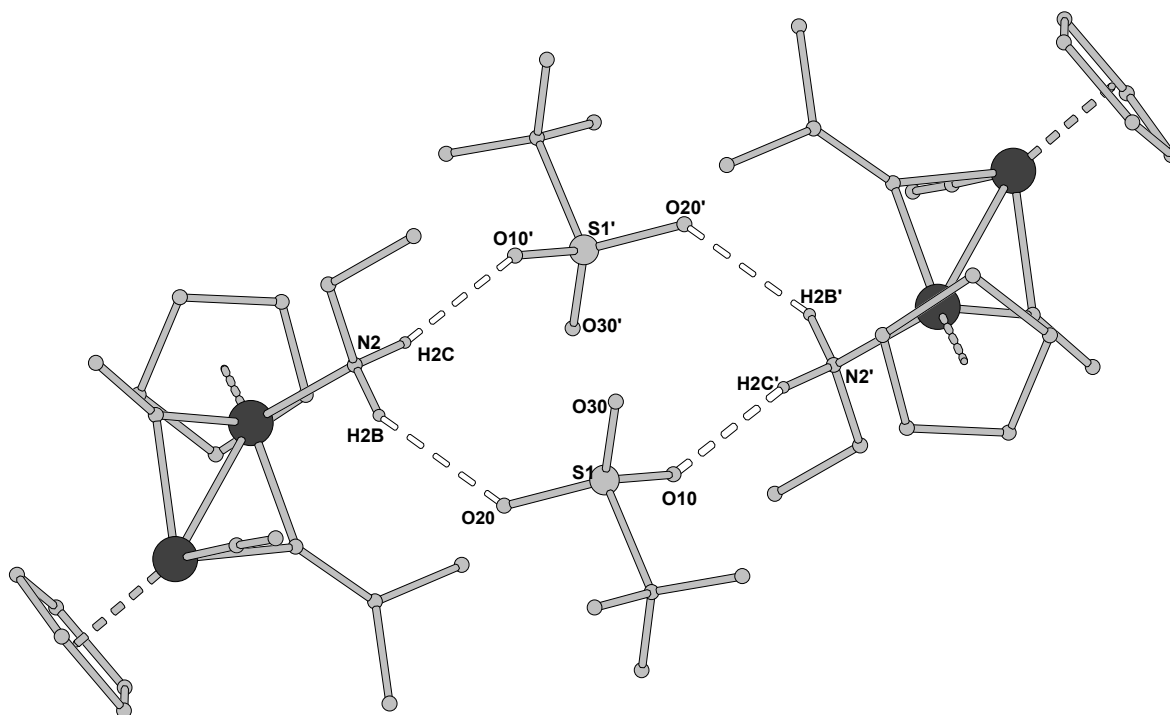
Fe(1)-Fe(2)	2.491(3)	C(11)-O(11)	1.162(14)
Fe(1)-C(11)	1.729(12)	C(15)-O(15)	1.206(15)
Fe(1)-C(12)	1.895(12)	C(12)-N(1)	1.305(15)
Fe(2)-C(12)	1.800(13)	N(1)-C(13)	1.48(2)
Fe(1)-C(15)	1.938(14)	N(1)-C(14)	1.480(18)
Fe(2)-C(15)	1.843(15)	N(2)-C(16)	1.456(17)
Fe(2)-N(2)	2.023(8)	C(16)-C(17)	1.484(19)
Fe(1)-C(12)-Fe(2)	84.7(6)	C(13)-N(1)-C(14)	113.3(12)
Fe(1)-C(15)-Fe(2)	82.4(5)	Fe(2)-N(2)-C(16)	120.1(9)
C(12)-N(1)-C(13)	122.0(13)	Fe(1)-C(12)-N(1)	135.9(10)
C(12)-N(1)-C(14)	124.7(13)	Fe(2)-C(12)-N(1)	139.1(10)

**Table 1**

Selected bond lengths (Å) and angles (°) for complex **4a**.

The Cp ligands in **4a** adopt a *cis* geometry relative to the mean plane determined by the Fe<sub>2</sub>(μ-C)<sub>2</sub> core, as previously reported for analogous diiron complexes containing a bridging

aminocarbyne ligand [1, 2, 6]. The C(12)-N(1) interaction [1.305(15)Å] exhibits a considerably double bond character, suggesting that the  $\mu$ -aminocarbyne ligand can be alternatively described as a  $\mu$ -iminium ligand; in agreement with this, both N(1) and C(12) show an almost perfect  $sp^2$  hybridisation [sum angles 360.0(22) and 359.7(6)°, respectively]. The Fe(2)-N(2) interaction [2.023(8)Å] indicates a pure  $\sigma$ -bond, as expected for a coordinated amine ligand. The compound **4a** exists in the solid state as  $\{[\text{Fe}_2\{\mu\text{-CNMe}_2\}(\mu\text{-CO})(\text{CO})(\text{NH}_2\text{Et})(\text{Cp})_2][\text{SO}_3\text{CF}_3]\}_2$  dimers, because of the presence of hydrogen bonds between the two  $\text{NH}_2$  protons of the cations and two different  $\text{CF}_3\text{SO}_3^-$  anions (Figure 2). Thus, each triflate anion acts as a bridging hydrogen bond acceptor between two distinct  $[\text{Fe}_2\{\mu\text{-CNMe}_2\}(\mu\text{-CO})(\text{CO})(\text{NH}_2\text{Et})(\text{Cp})_2]^+$  cations, *via* two of its three oxygen atoms.

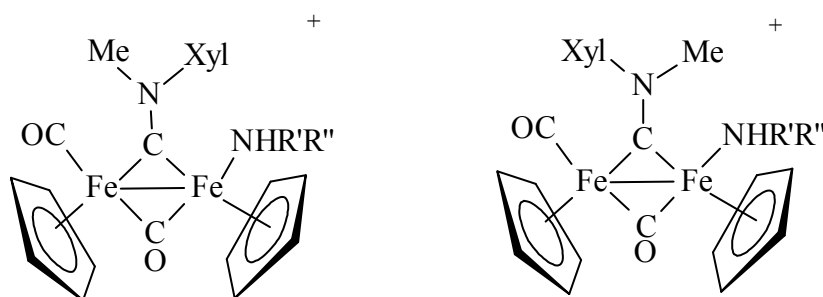


**Figure 2**

Representation of the hydrogen bonded  $\{[\text{Fe}_2\{\mu\text{-CNMe}_2\}(\mu\text{-CO})(\text{CO})(\text{NH}_2\text{Et})(\text{Cp})_2][\text{SO}_3\text{CF}_3]\}_2$  dimers in **4a**[ $\text{CF}_3\text{SO}_3$ ]. N(2)...O(20) 3.098(14) Å, N(2)...O(10') 3.001(12) Å.

The IR spectra of compounds **4-10**, in  $\text{CH}_2\text{Cl}_2$  solution, exhibit the usual  $\nu\text{-CO}$  band pattern, consisting in one terminal and one bridging absorption (e.g. for **4a** at 1969 and 1800  $\text{cm}^{-1}$ ). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complex **4a** show two signals of the same intensity for the non-

equivalent N-bonded methyl groups (at 4.68, 4.25 and 54.0, 52.5 ppm, respectively) and indicate the presence of a single isomer. The two N-bonded hydrogens of the NH<sub>2</sub>Et ligand are also non-equivalent and originate two high field shifted broad multiplets (at 2.45 and -2.76 ppm). The spectra of **4b**, **5b**, **6-8**, **9b** and **10**, which contain the asymmetrically substituted  $\mu$ -CN(Me)(Xyl), show the presence of minor amounts of a second isomeric form, as usually found in complexes of the type  $[\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})(\text{L})(\text{Cp})_2]^+$  (L = CNR, NCR, PR<sub>3</sub>) and  $[\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})(\text{L})(\text{Cp})_2]$  (L = C(O)R, CH<sub>2</sub>CN, CN, Cl) [1, 2]. This is due to the different orientations that Me and Xyl groups can assume with respect to the non-equivalent Fe atoms, and are consequence of the double bond character of the  $\mu\text{-C=N}$  interaction, which do not allow inter-conversion of the isomers *via* rotation around the C–N bond (Figure 3).

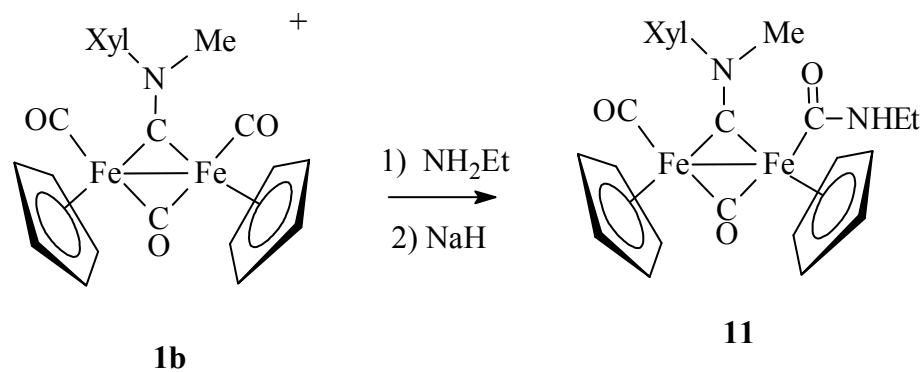


**Figure 3**

Isomers due to the different orientations of the amino carbyne substituents.

Characteristic feature in the <sup>13</sup>C NMR spectra of all the complexes **4-10** is the low field resonance of the bridging carbyne carbon (in the 335-340 ppm range).

It is worth noting that the syntheses above described take place only in the presence of Me<sub>3</sub>NO; otherwise, the amine attack occurs at the terminally coordinated CO, in a way similar to that reported for the reactions of  $[\text{Fe}_2(\mu\text{-CNMe}_2)_2(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]_2$  (**2**) with NH<sub>2</sub>R [2b]. For example, the reaction of  $[\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (**1b**) with a large excess of NH<sub>2</sub>Et, generates the complex  $[\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})\{\text{C(O)NHEt}\}(\text{Cp})_2]$  (**11**). As for the mononuclear complex  $[\text{Fe}(\text{CO})_3\text{Cp}]^+$  [7], the reaction presumably proceeds *via* nucleophilic addition at the coordinated CO, followed by deprotonation due to the excess of amine. The addition is reversible and removal of the volatile materials, including the amine, shifts the equilibrium toward the starting complex. Better yields are obtained upon treatment of the reaction mixture with NaH (Scheme 2).



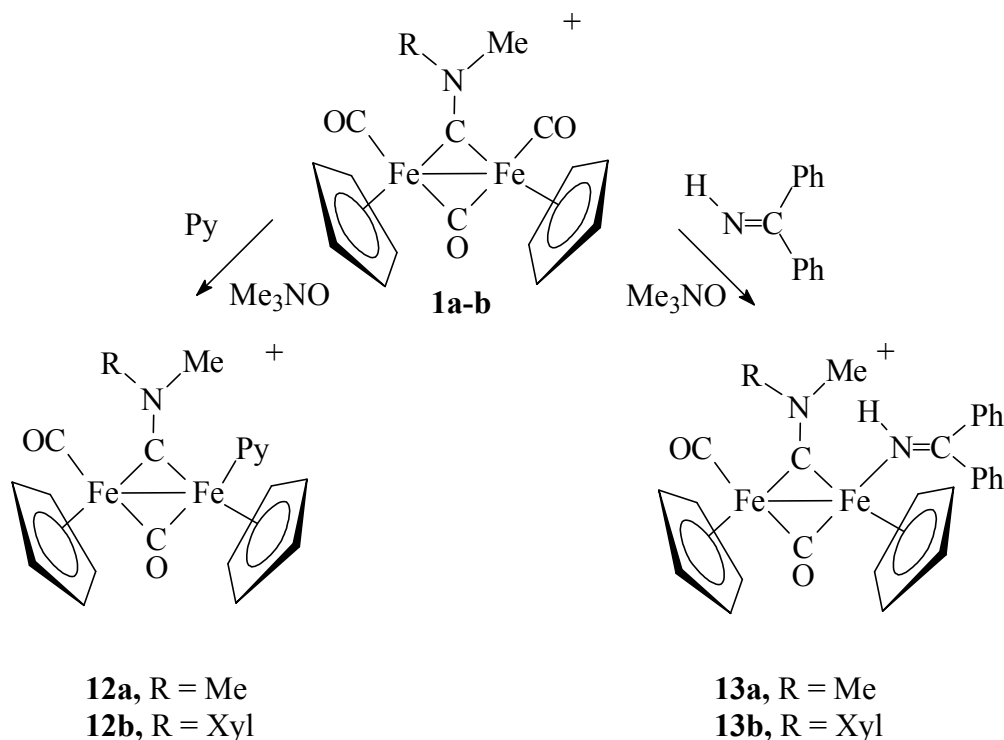
**Scheme 2**

Complex **11** has been characterized by NMR and IR spectroscopy (see experimental part). The presence of the C(O)NHEt ligand is supported by the observed  $^1\text{H}$  NMR broad resonance at 5.74 ppm, attributable to the N-H, and by the  $^{13}\text{C}$  NMR signal at 202.9 ppm due to the carboxamido carbon.

Since complexes **4-10** have been obtained from **1a-b** *via* CO displacement, their syntheses could be alternatively accomplished by removal of the labile MeCN from  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}(\mu\text{-CO})(\text{CO})(\text{NCMe})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (R = Me, **3a**; Xyl, **3b**). However, it should be considered that coordinated nitriles are also susceptible of nucleophilic addition by amines, with formation of metal amidinates [8]. In order to determine which of the two possibilities (addition *vs.* substitution) prevails, **3b** has been treated with amines ( $\text{NH}_2\text{Pr}^i$ ,  $\text{NH}_2\text{Ph}$ ). Our findings show that the reactions proceed with replacement of the nitrile ligand; thus the observed products are the amine complexes **5b** and **7**, respectively, obtained in comparable yields with respect to the synthesis reported in Scheme 1, and no addition at the coordinated MeCN has been revealed to any extent.

## 2.2. Reactions with pyridine and benzophenone imine

Replacement of CO from **1a-b**, in the presence of  $\text{Me}_3\text{NO}$ , has been accomplished also by pyridine (Py =  $\text{NC}_5\text{H}_5$ ), and benzophenone imine ( $\text{HN}=\text{CPh}_2$ ). The reactions lead to the formation of  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}(\mu\text{-CO})(\text{CO})(\text{L})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (R= Me, L= Py, **12a**; R = Xyl, L= Py **12b**; R= Me, L=  $\text{HN}=\text{CPh}_2$ , **13a**; R = Xyl, L=  $\text{HN}=\text{CPh}_2$ , **13b**) (Scheme 3). Compounds **12** and **13** exhibit spectroscopic properties similar to those of **4-10**. Imine coordination in **13a-b** is revealed by the IR absorption  $\nu(\text{N-H})$  at  $3314 \text{ cm}^{-1}$  (in KBr pellets), and the  $^1\text{H}$  NMR resonance at *ca.* 6.1-6.3 ppm. Major features of the  $^{13}\text{C}$  NMR spectrum of **13a-b** include the expected low-field resonance of the  $\mu$ -aminocarbyne carbon, and the resonance attributable to the imine carbon at about 191 ppm.



**Scheme 3**

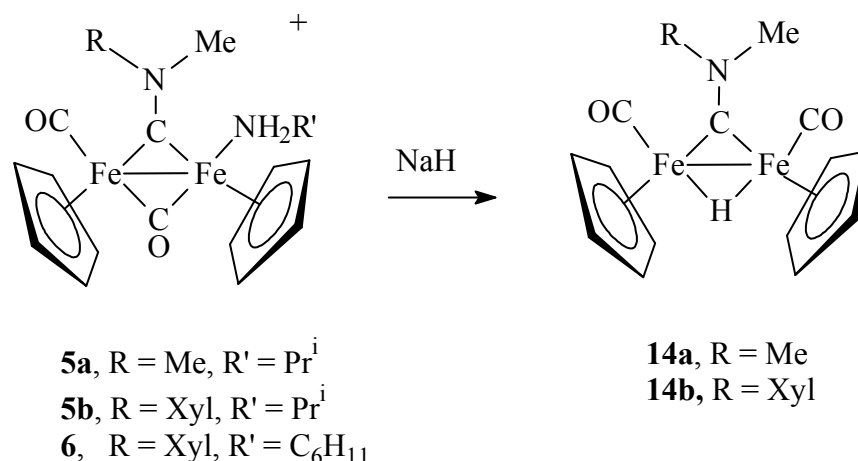
The above described reactions indicate that replacement of the coordinated CO or NCMe by amines are the favourite routes, and that the  $\mu$ -aminocarbyne ligand remains unaffected. This result is not obvious, because other related cationic diiron complexes of the type  $[\text{Fe}_2\{\mu\text{-C}(\text{SMe}_2)\text{CN}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]^+$  [3],  $[\text{Fe}_2(\mu\text{-CAr})(\eta^8\text{-C}_8\text{H}_8)(\text{CO})_4]^+$  [9] and  $[\text{Fe}_2(\mu\text{-CH})(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]^+$  [10] have been shown to react with amines at the bridging carbene or carbyne carbon, rather than involving the terminally coordinated CO.

### 2.3. Reactions of the coordinated amine and imine ligands

Deprotonation of coordinated primary or secondary amines represents a possible route to the synthesis of amide complexes [11], thus the compounds **5a-b** and **6** containing  $\text{NH}_2\text{Pr}^i$  and  $\text{NH}_2\text{C}_6\text{H}_{11}$ , respectively, have been treated with NaH or BuLi with the aim of obtaining the corresponding amide complexes. Unexpectedly, the known bridging hydride complexes  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-H})(\text{CO})_2(\text{Cp})_2]$  (R = Me, **14a**; R = Xyl, **14b**) [2c] have been formed (Scheme 4). The reaction resembles that described for the mononuclear complex  $[\text{CpRu}(\text{HNMe}_2)(\text{PPh}_3)_2]^+$ , in which deprotonation of the coordinated amine was followed by  $\beta$ -hydrogen elimination from the N-Me, leading to the formation of the hydride complex  $[\text{CpRu}(\text{H})(\text{PPh}_3)_2]$ , with release of  $\text{MeN}=\text{CH}_2$  [11b]. A difference consists in the fact that in **14**, the hydride ligand is bridging instead of

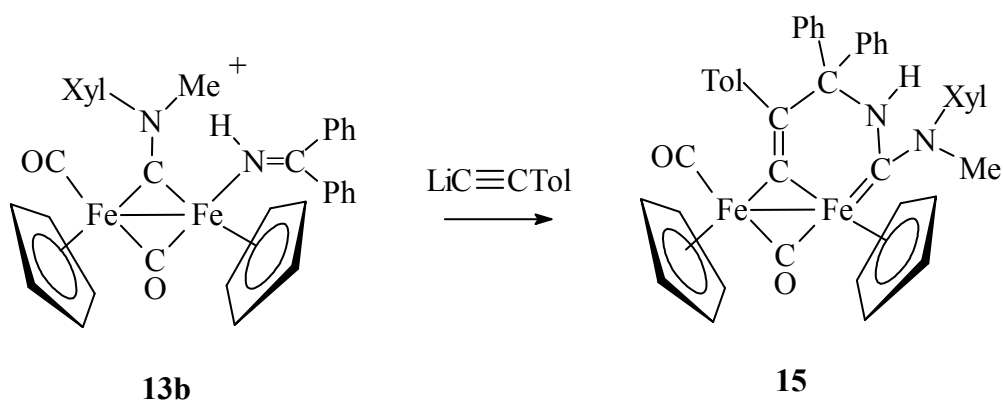


terminally coordinated. This is in accordance with the preference of  $\text{H}^-$  for the bridging coordination and with the exchange that easily occurs between bridging and terminal coordination positions within the  $\text{Fe}_2(\text{CO})_2\text{Cp}_2$  frame. Support to the above assumptions comes by observing that compound **7**, in which the aniline ligand can not undergo  $\beta$ -hydrogen transfer, does not form the hydride complex **14**, under the same reaction conditions.

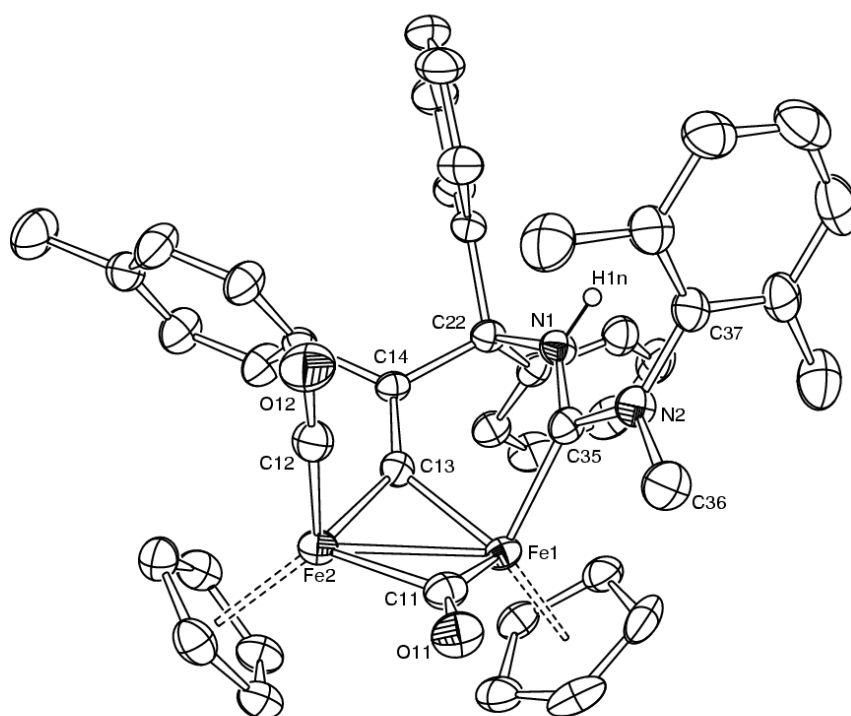


**Scheme 4**

Stable azavynilidene complexes can be generated by deprotonation of coordinated imines [12]. However, we have recently reported that the azavynilidene complex  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{NC}(\text{C}\equiv\text{CTol})\text{Bu}^t\}(\text{Cp})_2]$  is unstable and undergoes an intramolecular rearrangement, with coupling of the azavynilidene with the aminocarbene ligands [13]. The reaction ultimately led to the formation of the  $\mu$ -allenyl-diaminocarbene complex  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{Tol})=\text{C}=\text{C}(\text{CMe}_3)\text{N}(\text{H})\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp}_2)][\text{SO}_3\text{CF}_3]$ . In the light of these observations, we have investigated the reactions of **13a-b** with NaH, in order to obtain the deprotonation of the imine ligand and possibly promote further rearrangements and C-N bond formation. Unfortunately, these attempts failed to produce any stable product. However, we have found that the coordinated imine can be attacked by acetylides. In fact, addition of  $\text{TolC}\equiv\text{CLi}$  (2.5-3 equivalents) to a THF solution of **13b**, at low temperature, results, after work up, in the new neutral complex  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}=\text{C}(\text{Tol})\text{C}(\text{Ph})_2\text{N}(\text{H})\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp}_2)]$  (**15**), obtained in moderate yields (52 %) (Scheme 5). The nature of **15** has been fully elucidated by X-ray and the molecular structure is reported in Figure 4, whereas relevant bond lengths and angles are reported in Table 2.



**Scheme 5**



**Figure 4**

Molecular structure of **15**, with key atoms labelled (all H atoms, apart from H1n, have been omitted). Displacement ellipsoids are at 30% probability level.

Fe(1)-Fe(2)	2.5353(9)	C(12)-O(12)	1.144(4)
Fe(1)-C(12)	1.741(4)	C(13)-C(14)	1.341(4)
Fe(1)-C(11)	1.842(4)	C(14)-C(22)	1.537(4)
Fe(2)-C(11)	2.002(4)	C(22)-N(1)	1.503(4)
Fe(1)-C(13)	1.898(3)	N(1)-C(35)	1.353(4)

Fe(2)-C(13)	1.906(3)	C(35)-N(2)	1.355(4)
Fe(1)-C(35)	1.951(4)	N(2)-C(36)	1.476(5)
C(11)-O(11)	1.199(4)	N(2)-C(37)	1.439(4)
Fe(1)-C(11)-Fe(2)	82.41(15)	N(1)-C(35)-N(2)	111.8(3)
Fe(1)-C(13)-Fe(2)	83.60(14)	N(1)-C(35)-Fe(1)	121.6(2)
C(13)-C(14)-C(22)	116.8(3)	N(2)-C(35)-Fe(1)	126.1(2)
C(22)-N(1)-C(35)	128.8(3)	C(35)-N(2)-C(36)	122.9(3)
C(22)-N(1)-H(1n)	115(2)	C(35)-N(2)-C(37)	124.5(3)
C(35)-N(1)-H(1n)	116(2)	C(36)-N(2)-C(37)	112.6(3)

**Table 2**

Selected bond lengths (Å) and angles (°) for complex **15**.

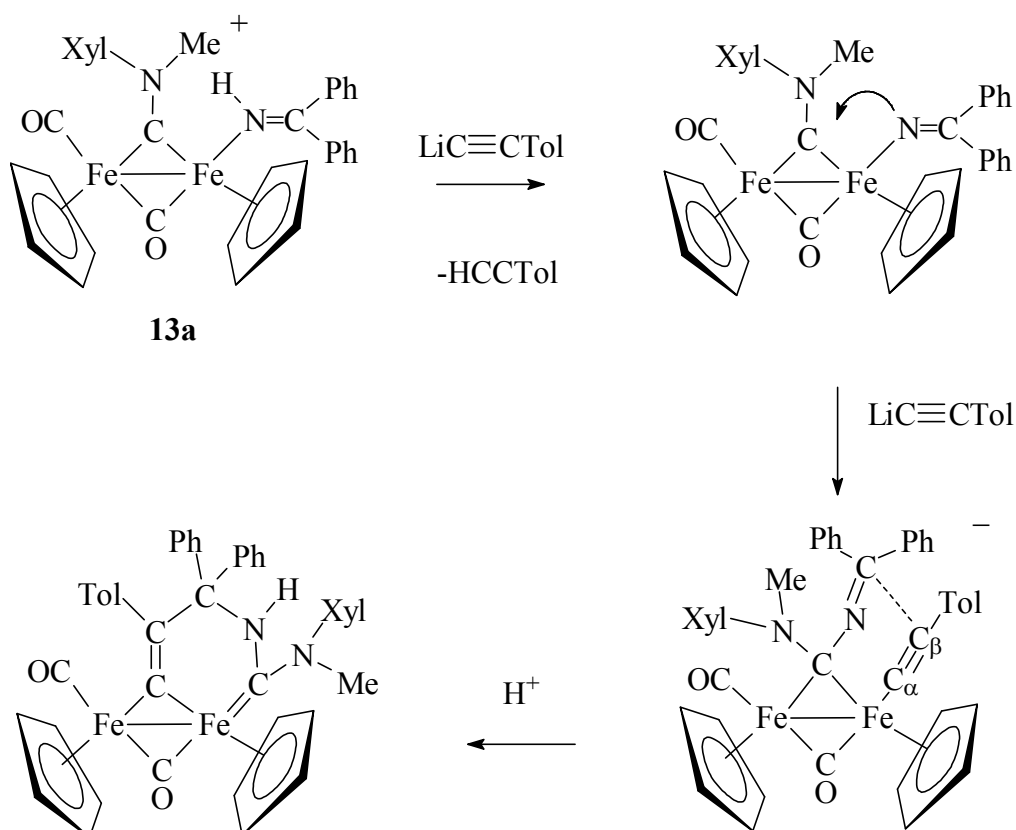
The molecule contains a novel  $\eta^1:\eta^2$  vinylidene-diaminocarbene ligand [*i.e.*  $\mu\text{-}\eta^1:\eta^2\text{-C=C(Tol)C(Ph)}_2\text{N(H)CN(Me)(Xyl)}$ ] coordinated to a  $\text{Fe}_2(\mu\text{-CO})(\text{CO})(\text{Cp}_2)$  core. The latter shows the usual *cis* arrangement of the Cp ligands, and the Fe-Fe distance [2.5353(9) Å] is typical for a single bond. The bridging CO ligand presents a significant asymmetry [Fe(1)-C(11), 1.842(4) Å; Fe(2)-C(11), 2.002(4) Å], which is probably due to the different electronic environment of the two iron atoms. In particular, Fe(1) results to be electron richer than Fe(2), because the former is bound to a  $\sigma$ -donating diaminocarbene ligand, whereas the latter is attached to a  $\pi$ -acidic CO ligand. The bridging  $\mu\text{-}\eta^1:\eta^2\text{-C=C(Tol)C(Ph)}_2\text{N(H)CN(Me)(Xyl)}$  ligand contains two distinct groups; *i.e.* the bridging vinylidene and a terminal diaminocarbene, linked by a saturated  $\text{CPh}_2$  group. The bridging vinylidene  $\mu\text{-C=C}$  is bound almost symmetrically to the iron atoms and the C(13)-C(14) distance [1.341(4) Å] is typical for bridging vinylidenes [14]. Despite the remarkable differences between N(1) and N(2) (*i.e.* different substituents, one is endo-cyclic the other exo-cyclic), the distances C(35)-N(1) [1.353(4) Å] and C(35)-N(2) [1.355(4) Å] are almost identical and show partial double bond character, suggesting electron donation from the two nitrogen atoms to the central carbon. As a consequence, all three atoms show a nearly perfect  $\text{sp}^2$  hybridisation [sum angles 359.5(4), 360(3) and 360.0(5)° at C(35), N(1) and N(2), respectively] and the diaminocarbene unit is almost planar [N(1)-C(35)-N(2)-Fe(1) torsion angle  $-171.84(47)^\circ$ ]. Fe(1) can also be viewed as part of a six membered ring constituted by Fe(1), C(35), N(1), C(22), C(14) and C(13) which can be described as a 1-metalla-3-aza-1,5-hexadiene with a boat conformation.

The IR spectrum of **15**, in CH<sub>2</sub>Cl<sub>2</sub>, shows two bands at 1934vs and 1734s cm<sup>-1</sup>, attributable to the terminal and bridging CO ligands, respectively. These bands are strongly shifted toward lower frequencies compared to the starting complex **13b** (1978vs and 1813s cm<sup>-1</sup>), as a direct consequence of the different charge of the two complexes. The main features of the <sup>1</sup>H NMR spectrum of **15** in CD<sub>2</sub>Cl<sub>2</sub> are the presence of two distinct resonances for the inequivalent Cp ligands and a broad resonance at 8.87 ppm due to the NH group. The bridging vinylidene ligand μ-C<sub>α</sub>=C<sub>β</sub> shows two resonances in the <sup>13</sup>C NMR spectrum at 286-280 ppm (C<sub>α</sub>) and 149-141 ppm (C<sub>β</sub>), which are typical regions for this class of ligands [14]. The resonance due to C<sub>α</sub> falls in the high frequencies region of the spectrum, very close to the one due to μ-CO, whereas C<sub>β</sub> resonates in the same region of the quaternary carbons of the aromatic rings (see experimental for further details). Two other resonances are present at relatively high frequencies, *i.e.* 220.5 and 216.3 ppm attributable to the diaminocarbene carbon and the terminal CO, respectively. Finally, the ESI MS spectrum of **15** in CH<sub>3</sub>CN shows the presence of a positive ion at *m/z* = 740, due to ionisation of **15**.

Unfortunately, the reaction reported in Scheme 5 is not of general character. Thus, addition of TolC≡CLi to a THF solution of [Fe<sub>2</sub>{μ-CN(Me)<sub>2</sub>}(μ-CO)(CO)(Ph<sub>2</sub>C=NH)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**13a**) failed to produce any identifiable product. Also changing the acetylide reagent has a dramatic effect on the reaction. Therefore, the reaction of PhC≡CLi with **13b** led to the formation of the η<sup>1</sup>:η<sup>2</sup> vinylidene-diaminocarbene [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>2</sup>-C=C(Ph)C(Ph)<sub>2</sub>N(H)CN(Me)(Xyl)}(μ-CO)(CO)(Cp)<sub>2</sub>] (**16**), in lower yields (31%), whereas the corresponding reaction with CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>C≡CLi resulted in a mixture of decomposition products.

The formation of **15** is worth some more comments. The bridging vinylidene-diaminocarbene ligand μ-η<sup>1</sup>:η<sup>2</sup>-C=C(Tol)C(Ph)<sub>2</sub>N(H)CN(Me)(Xyl) is clearly the result of the coupling between the μ-aminocarbyne, the benzophenone imine ligand and the tolylacetylide, however, the mechanism of formation is not obvious and presumably requires several steps. New C-N and C-C bonds [C(35)-N(1) and C(14)-C(22) in Figure 4] are formed as a consequence of these couplings. Interestingly, the new C-C bond is generated between the imine carbon and the C<sub>β</sub> carbon of TolC<sub>β</sub>≡C<sub>α</sub>Li, and not with C<sub>α</sub>, as it would be expected if the reaction was simply the nucleophilic addition of the tolylacetylide to the coordinated imine ligand. Therefore, we assume that the first step of the reaction consists in the deprotonation of the coordinated imine by the acetylide to give the η<sup>1</sup>-azavinylidene intermediate [Fe<sub>2</sub>{μ-CN(Me)(Xyl)}(μ-CO)(CO)(Ph<sub>2</sub>C=N)(Cp)<sub>2</sub>] (Scheme 6). Migration of the azavinylidene to the bridging carbyne accounts for the observed C-N bond formation and is in agreement with a similar rearrangement observed in [Fe<sub>2</sub>{μ-CN(Me)(Xyl)}(μ-CO)(CO){NC(C≡CTol)Bu<sup>†</sup>}(Cp)<sub>2</sub>] [13] and with the existence of species like [Fe<sub>2</sub>{μ-

$\text{CH}(\text{NCPH}_2)\{\mu\text{-CO}(\text{CO})(\text{Cp})_2\}$  [10]. As a consequence of the migration, an unsaturation is formed on one iron and this can be occupied by an acetylide ligand. This hypothesis would explain why the stoichiometry of the reaction requires, at least, 2 moles of acetylide per mole of compound **13a**, in order to obtain good yields. The acetylide ligand,  $\sigma$ -coordinated, could be directly available for coupling with the imine carbon group or, alternatively, could be transformed, after protonation, into a bridging vinylidene ligand. Several examples describe the transformation of alkynes into  $\mu$ -vinylidenes in dinuclear complexes [15]. In both cases, coupling with  $\{\mu\text{-C}[\text{N}(\text{Me})(\text{Xyl})][\text{NC}(\text{Ph})_2]\}$  necessarily involves the  $\text{C}_\beta$  carbon of the acetylide in order to explain the observed C-C bond formation (Scheme 6).



This hypothesis, far from providing any exhaustive interpretation of the mechanism leading to the novel vinylidene-diaminocarbene **15**, simply underlines the complexity of the reaction, which further emphasizes the attitude of dinuclear aminocarbene complexes in promoting C-C and C-N bond formation [1, 4, 13, 16].

### 3. Experimental details

### 3.1. General

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. Infrared spectra were recorded 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 a Waters Micromass ZQ 4000 with samples dissolved in CH<sub>3</sub>CN. All NMR measurements were performed on Varian Gemini 300 and Varian Mercury 400 instruments. The chemical shifts for <sup>1</sup>H and <sup>13</sup>C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and <sup>1</sup>H,<sup>13</sup>C correlation through gs-HSQC and gs-HMBC experiments [17]. Unless otherwise stated, NMR signals due to trace amounts of second isomeric form are italicised. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. [Fe<sub>2</sub>(CO)<sub>4</sub>(Cp)<sub>2</sub>] was from Strem and used as received. Compounds [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, **1a**; Xyl, **1b**) and [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, **3a**; Xyl, **3b**) were prepared as described in the literature. [2a, 2c, 18]

### 3.2. Synthesis of [Fe<sub>2</sub>(μ-CNMe<sub>2</sub>)(μ-CO)(CO)(NH<sub>2</sub>Et)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**4a**) and [Fe<sub>2</sub>{μ-CN(Me)(Xyl)}(μ-CO)(CO)(NH<sub>2</sub>Et)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**4b**)

Gaseous NH<sub>2</sub>Et was bubbled into a stirred solution of [Fe<sub>2</sub>(μ-CN(Me<sub>2</sub>))(μ-CO)(CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**1a**) (160 mg, 0.30 mmol) in THF (15 ml) containing Me<sub>3</sub>NO (39 mg, 0.51 mmol). The mixture was stirred for 40 min and, then, the volatile material was removed *in vacuo*. Chromatography of the residue on an alumina column, with MeCN as eluent, gave **4a**, which was crystallized from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O mixture (v/v ratio 1/1). Yield 104 mg (63%). Found: C, 39.66; H, 4.26, N 5.28%. C<sub>18</sub>H<sub>23</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 39.44; H, 4.23, N, 5.11%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1969vs and 1800s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.88, 4.83 (s, 10H, Cp); 4.68, 4.25 (s, 6H, NMe<sub>2</sub>); 2.45 (br, 1H, NH<sub>2</sub>); 2.08 (q, 2H, <sup>3</sup>J<sub>HH</sub>=7Hz, N-CH<sub>2</sub>-CH<sub>3</sub>); 0.75 (t, 3H, <sup>3</sup>J<sub>HH</sub>=7Hz, N-CH<sub>2</sub>-CH<sub>3</sub>); -2.76 (br, 1H, NH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 331.3 (μ-C); 268.8 (μ-CO); 212.9 (CO); 88.1, 86.5 (Cp); 54.0, 52.5 (NMe<sub>2</sub>); 43.6 (N-CH<sub>2</sub>-CH<sub>3</sub>); 17.2 (N-CH<sub>2</sub>-CH<sub>3</sub>).

Compound **4b** was obtained reacting NH<sub>2</sub>Et with **1b** (200 mg, 0.322 mmol), with the same procedure described for the synthesis of **4a**

**4b**: Yield 146 mg (72%). Found: C, 47.28; H, 4.35, N 4.11%. C<sub>25</sub>H<sub>29</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 47.05; H, 4.58; N, 4.39%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1966vs and 1802s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ

7.54-7.01 (m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.01, 4.96, 4.48, 4.40 (s, 10 H, Cp); 4.84 (s, 3H, NMe); 3.01 (br, 1H, NH<sub>2</sub>); 2.65, 2.16 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 2.25 (q, 2H, <sup>3</sup>J<sub>HH</sub>=7Hz, N-CH<sub>2</sub>-CH<sub>3</sub>); 0.84, 0.76 (t, 3H, <sup>3</sup>J<sub>HH</sub>=7Hz, N-CH<sub>2</sub>-CH<sub>3</sub>); -2.70 (br, 1H, NH<sub>2</sub>); (Isomer ratio = 10). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 338.6 (μ-C); 266.8 (μ-CO); 213.5 (CO); 148.6 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 132.6, 132.5, 130.3, 129.0, 128.9 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 88.0, 87.1 (Cp); 54.0 (NMe); 44.1 (N-CH<sub>2</sub>-CH<sub>3</sub>); 18.5, 17.8, 17.4 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> + NCH<sub>2</sub>-CH<sub>3</sub>).

### 3.3. Synthesis of [Fe{μ-CN(Me)R}(μ-CO)(CO)(NH<sub>2</sub>Pr<sup>i</sup>)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, **5a**; R = Xyl **5b**)

A solution of **1a** (180 mg; 0.340 mmol) in THF (15.0 mL) was treated with Me<sub>3</sub>NO (50 mg; 0.66 mmol) and NH<sub>2</sub>Pr<sup>i</sup> (0.300 mL; 3.52 mmol). The mixture was stirred for 2 h, then the solvent was removed under reduced pressure. Chromatography of the residue on alumina with CH<sub>3</sub>CN as eluent, afforded **5a**. Yield 141 mg (74%). Found: C, 40.87; H, 4.23; N, 5.10%. C<sub>19</sub>H<sub>25</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 40.66; H, 4.49; N, 4.99%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1970vs and 1802s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.84, 4.78 (s, 10H, Cp); 4.70, 4.24 (s, 6H, NMe<sub>2</sub>); 2.10 (d, 1H, <sup>2</sup>J<sub>HH</sub>= 13 Hz, NH<sub>2</sub>); 1.74 (m, 1H, CHMe<sub>2</sub>); 1.30, 0.61 (d, 6H, <sup>3</sup>J<sub>HH</sub>= 6.1 Hz, CH(CH<sub>3</sub>)<sub>2</sub>); -2.36, (d, 1H, <sup>2</sup>J<sub>HH</sub>=13 Hz, NH<sub>2</sub>).

Compound **5b** was obtained reacting NH<sub>2</sub>Pr<sup>i</sup> with **1b** (106 mg, 0.170 mmol), with the same procedure described for the synthesis of **5a**.

**5b**: Yield 80.1 mg (72%). Found: C, 48.01; H, 4.65; N, 4.30%. C<sub>26</sub>H<sub>31</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 47.74; H, 4.78; N, 4.28%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1968vs and 1805s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.35-7.20 (m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 4.99, 4.95, 4.36, 4.41 (s, 10H, Cp); 4.85, 4.83 (s, 3H, NMe); 2.68 (d, 1H, <sup>2</sup>J<sub>HH</sub>= 12.9 Hz, NH<sub>2</sub>); 2.73, 2.67, 2.17, 2.13 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 1.91 (m, 1H, (CH<sub>3</sub>)<sub>2</sub>CH); 1.21, 1.13, 0.74, 0.69 (d, 6H, <sup>3</sup>J<sub>HH</sub>= 6.3 Hz, (CH<sub>3</sub>)<sub>2</sub>CH); -2.22 (d, 1H, <sup>2</sup>J<sub>HH</sub>=12.9 Hz, NH<sub>2</sub>); (Isomers ratio = 10). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 339.8 (μ-C); 266.1 (μ-CO); 213.7 (CO); 148.7 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 132.5, 130.4, 129.0 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 88.6, 88.0, 87.4, 87.0, (Cp); 53.9 (NMe); 48.7 (Me<sub>2</sub>CH); 25.1, 20.9 (Me<sub>2</sub>CH); 18.8, 17.7 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>). ESI MS: ES+ m/z 503; ES- m/z 149.

### 3.4. Synthesis of [Fe{μ-CN(Me)(Xyl)}(μ-CO)(CO)(NH<sub>2</sub>R)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = C<sub>6</sub>H<sub>11</sub>, **6**; R = Ph, **7**; R = H, **8**)

Complexes **6-8** have been obtained by reacting **1b** (100 mg, 0.161 mmol) with the appropriate amine, with the same procedure described for the synthesis of **5b**. Compound **7** was filtered on Celite instead of alumina. Ammonia used for the synthesis of **8** was a 0.5 M solution in 1,4-dioxane.

**6**: Yield 79 mg (67%). Found: C, 49.97; H, 5.14; N, 4.10%. C<sub>29</sub>H<sub>35</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 50.16; H, 5.08; N, 4.03%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1968vs and 1802s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.40-7.28 (m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.05, 4.95, 4.41, 4.33 (s, 10H, Cp); 4.91, 4.81 (s, 3H, NMe); 2.76,

2.66, 2.27, 2.15 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); 2.40 (d, 1H, <sup>2</sup>J<sub>HH</sub>=12.1 Hz, NH<sub>2</sub>); 2.20-0.82 (m, 11H, C<sub>6</sub>H<sub>11</sub>); -2.18, -2.22 (d, 1H, <sup>2</sup>J<sub>HH</sub>=12.1 Hz, NH<sub>2</sub>); (Isomers ratio = 10). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 340.2 (μ-C); 267.4, 266.3 (μ-CO); 213.8, 212.5 (CO); 148.5 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 132.7, 132.2, 130.2, 128.9 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 88.6, 88.0, 86.9, 86.4 (Cp); 55.6, 54.8, 35.6, 31.1, 25.0, 24.7 (C<sub>6</sub>H<sub>11</sub>); 53.5, 52.2 (NMe); 18.5, 17.6 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>).

**7:** Yield 79 mg (71 %). Found: C, 50.62; H, 4.41; N, 3.98%. C<sub>29</sub>H<sub>29</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 50.64; H, 4.25; N, 4.07%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1965vs and 1808s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.27-6.60 (m, 9H, arom); 4.97, 4.73, 4.35, 4.32 (s, 10H, Cp); 4.84 (s, 3H, NMe); 4.45 (d, 1H, <sup>2</sup>J<sub>HH</sub>=11.4 Hz, NH<sub>2</sub>); 2.33, 2.10, 1.97 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); -0.16 (d, 1H, <sup>2</sup>J<sub>HH</sub>=11.4 Hz, NH<sub>2</sub>); (Isomers ratio = 10). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 338.0 (μ-C); 265.9 (μ-CO); 214.4 (CO); 148.4, 142.8, 132.6, 130.2, 128.9, 125.3, 120.6 (arom); 88.4, 87.3 (Cp); 54.4 (NMe); 18.5, 17.8 (C<sub>6</sub>H<sub>3</sub>Me)

**8:** Yield 42 mg (42 %). Found: C, 45.01; H, 4.32; N, 4.25%. C<sub>23</sub>H<sub>25</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 45.27; H, 4.13; N, 4.59%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1973vs and 1810s (CO). <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 7.47-7.33 (m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.16, 5.12, 4.47, 4.35 (s, 10H, Cp); 4.76, 4.44 (s, 3H, NMe); 2.74, 1.91 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); -0.41, -0.76 (s, 3H, NH<sub>3</sub>); (Isomers ratio = 3). <sup>13</sup>C NMR (CD<sub>3</sub>CN) δ 339.0 (μ-C); 268.9 (μ-CO); 214.1 (CO); 149.2 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 135.1, 133.2, 131.1, 130.0, 129.6 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 89.7, 87.1 (Cp); 55.7 (NMe); 19.1, 17.8 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)

3.5. Synthesis of [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(NHR'<sub>2</sub>)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = R' = Me, **9a**; R = Xyl, R' = Me, **9b**; R = Xyl, NHR'<sub>2</sub> = NHC<sub>5</sub>H<sub>10</sub>, **10**)

Complexes **9-10** have been obtained by reacting [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>]<sup>+</sup>[CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> (0.200 mmol) with the appropriate secondary amine, in the presence of Me<sub>3</sub>NO, using the same procedure described for the synthesis of **4a**.

**9a:** Yield 77 mg (70%) Found: C, 39.63; H, 4.24; N, 5.16%. C<sub>18</sub>H<sub>23</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 39.50; H, 4.24; N, 5.12%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1974vs and 1801s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 4.84, 4.69 (s, 10H, Cp); 4.63, 4.20 (s, 6H, μ-CNMe<sub>2</sub>); 1.90, 0.94 (d, 6H, <sup>3</sup>J<sub>HH</sub>=5.6 Hz, NMe<sub>2</sub>); 1.22 (br, 1H, NH). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 331.4 (μ-C); 269.1 (μ-CO); 214.4 (CO); 88.3, 86.6 (Cp); 53.9, 52.30 (μ-CNMe<sub>2</sub>); 47.0, 43.0 (NMe<sub>2</sub>).

**9b:** Yield 92 mg (72%). Found: C, 47.19; H, 4.29; N, 4.54%. C<sub>25</sub>H<sub>29</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 47.07; H, 4.58; N, 4.39%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1971vs and 1803s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.47-6.97



(m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.04, 4.93, 4.39, 4.31 (s, 10H, Cp); 4.91, 4.87 (s, 3H, NMe); 2.66, 2.21 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); 2.18 (d, 3H, <sup>3</sup>J<sub>HH</sub>=6.9 Hz, NMe<sub>2</sub>); 1.24 (br, 1H, NH); 1.09 (d, 3H, <sup>3</sup>J<sub>HH</sub>=6.2 Hz, NMe<sub>2</sub>); (Isomers ratio = 10). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 339.3 (μ-C); 266.3 (μ-CO); 215.4. (CO); 148.3 (ipso-Xy); 132.9, 132.8, 130.5, 129.2, 129.0 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 89.4, 88.3, 87.8 86.7, (Cp); 54.2, 53.4 (NMe); 49.1, 47.3, 46.9, 44.8 (NMe<sub>2</sub>), 18.7, 18.0 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)

**10**: Yield 94 mg (69%). Found: C, 49.21; H, 5.02; N, 3.99%. C<sub>28</sub>H<sub>33</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 49.44; H, 4.89; N, 4.12%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1969vs and 1801s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.40-7.20 (m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 4.99, 4.94, 4.47, 4.42 (s, 10H, Cp); 4.91 (s, 3H, NMe); 2.63, 2.42, 2.17, 2.08 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); 2.8-2.6, 1.4-1.0 (m, 11H, C<sub>5</sub>H<sub>10</sub> + NH); (Isomers ratio = 10). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 338.5 (μ-C); 267.4 (μ-CO); 215.3. (CO); 148.3 (ipso-Xy); 132.7, 132.3, 130.2, 129.1, 128.9 (Xy); 88.5, 87.9, 87.5, 86.4 (Cp); 54.3 (NMe); 57.4, 54.8, 27.4, 27.1, 22.7 (NH(CH<sub>2</sub>)<sub>5</sub>); 18.6, 17.7 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>).

### 3.6. Synthesis of [Fe<sub>2</sub>{μ-CN(Me)Xyl}(μ-CO)(CO){C(O)NHEt}(Cp)<sub>2</sub>] (**11**)

Gaseous NH<sub>2</sub>Et was bubbled into a stirred solution of [Fe<sub>2</sub>{μ-CN(Me)(Xyl)}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>]<sup>+</sup>[CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> (**1a**) (98 mg, 0.158 mmol) in THF (15 ml). Then, NaH (18 mg, 0.750 mol) was added and the mixture stirred for further 10 min. Filtration on a celite pad and removal of the volatile materials gave a green solid residue of **11**. Yield 75 mg (92%). Found: C, 58.31; H, 5.19; N, 5.51%. C<sub>25</sub>H<sub>28</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>3</sub> requires: C, 58.14; H, 5.43; N, 5.42%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1962vs, 1756s and 1556s (CO); 3276m (NH) in KBr. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 7.46-7.17 (m, 3H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.74 (s, br, 1H, NH); 4.74, 4.23 (s, 10H, Cp); 4.45 (s, 3H, NMe); 2.83, 2.74 (m, 2H, N-CH<sub>2</sub>-CH<sub>3</sub>); 2.59, 2.15 (s, 6H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 0.77 (t, 3H, <sup>3</sup>J<sub>HH</sub>=7.3 Hz, N-CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 334.3 (μ-C); 274.1 (μ-CO); 214.7 (CO); 202.9 (C(O)NHET); 149.8 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 135.2, 133.8, 130.4, 128.6, 128.4 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 89.0, 86.8 (Cp); 51.3 (NMe); 35.7 (N-CH<sub>2</sub>-CH<sub>3</sub>); 19.1, 18.0 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 15.9 (N-CH<sub>2</sub>-CH<sub>3</sub>).

### 3.7. Synthesis of [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(Py)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (Py = NC<sub>5</sub>H<sub>5</sub>; R = Me, **12a**; R = Xyl, **12b**)

Complexes **12a-b** have been obtained by reacting pyridine with [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>]<sup>+</sup>[CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> (0.200 mmol) following the same procedure described for the synthesis of **5a-b**.

**12a**: Yield 72 mg (68%). Found: C, 47.40; H, 4.11; N, 5.33%. C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 47.56; H, 3.99; N, 5.28%. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν<sub>max</sub>(cm<sup>-1</sup>) 1971vs and 1795s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.15

(d, 2H,  $^3J_{\text{HH}} = 5.5$  Hz, o-Py); 7.37 (t, 1H,  $^3J_{\text{HH}} = 7.7$  Hz, p-Py); 6.94 (t, 2H,  $^3J_{\text{HH}} = 7.0$  Hz, m-Py); 4.96, 4.36 (s, 6H, NMe<sub>2</sub>); 4.94, 4.70 (s, 10H, Cp). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 332.3 (μ-C); 272.7 (μ-CO); 210.2 (CO); 155.1 (o-Py); 137.3 (p-Py); 124.8 (m-Py); 88.5, 86.7 (Cp); 54.9, 52.8 (N-Me<sub>2</sub>).

**12b** Yield 97 mg (78 %): Found: C, 50.18; H, 3.89; N, 4.25%. C<sub>28</sub>H<sub>27</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 50.04; H, 4.05; N, 4.17%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{max}}$ (cm<sup>-1</sup>) 1975vs and 1795s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.68-6.85 (m, 18H, arom); 5.18, 4.91, 4.51, 4.36, (s, 10H, Cp); 5.21, 4.44 (s, 3H, NMe); 2.91, 2.66, 2.17, 1.06 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); (Isomers ratio = 2). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 339.1, 334.8 (μ-C); 271.7, 270.8 (μ-CO); 211.4, 210.5. (CO); 155.8-122.8 (arom); 89.4, 88.7, 87.8, 87.5 (Cp); 56.1, 54.4 (NMe); 29.4 25.4 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>)

3.7. Synthesis of [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)(HNC=CPh<sub>2</sub>)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = Me, **13a**; R = Xyl, **13b**).

Complexes **13a-b** have been obtained by reacting benzophenone imine (Ph<sub>2</sub>C=NH) with [Fe<sub>2</sub>{μ-CN(Me)R}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>]<sup>+</sup>[CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> (0.300 mmol) following the same procedure described for the synthesis of **5a-b**.

**13a**: Yield 161 (76%). Found: C, 50.91; H, 4.05; N, 4.21%. C<sub>29</sub>H<sub>27</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 50.76; H, 3.97; N, 4.08%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{max}}$ (cm<sup>-1</sup>) 1974vs and 1803s (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.68-7.20 (m, 10H, arom); 6.09 (s, 1H, NH); 5.00, 4.52 (s, 10H, Cp); 4.80, 4.43 (s, 6H, NMe<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 332.0 (μ-C); 267.6 (μ-CO); 211.8 (CO); 191.5 (N=C); 137.8-126.4(arom); 88.6, 87.6 (Cp); 54.1, 52.7 (N-Me<sub>2</sub>).

**13b**: 182 mg (78 %). Found: C, 55.89; H, 4.28; N, 3.85%. C<sub>36</sub>H<sub>33</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S requires: C, 55.71; H, 4.29; N, 3.61%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{max}}$ (cm<sup>-1</sup>) 1978vs and 1813s (CO); 3276m (NH) in KBr. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.73-6.88 (m, 13H, arom); 6.29 (s, 1H, NH); 4.88, 4.54, 4.36, 4.34 (s, 10H, Cp); 4.94, 4.92 (s, 3H, NMe); 2.58, 2.14 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>); (Isomers ratio = 4). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 340.3 (μ-C); 264.7 (μ-CO); 212.3. (CO); 192.0 (N=C); 147.9 (ipso-Xyl); 140.0-125.0 (arom); 88.3, 87.8, 87.3, 87.1 (Cp); 54.2, 53.8 (N-Me); 18.4, 17.5 (C<sub>6</sub>H<sub>3</sub>Me). ESI MS: ES+ *m/z* 625; ES- *m/z* 149.

3.8. Synthesis of [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>2</sup>-C=C(Tol)C(Ph)<sub>2</sub>N(H)CN(Me)(Xy)}(μ-CO)(CO)(Cp)<sub>2</sub>] (**15**).

TolC≡CLi (0.58 mmol in THF) was added dropwise to a solution of **1b** (148 mg, 0.19 mmol) in THF (10 mL) at -50 °C and the resulting solution was stirred at room temperature for 30 min. The solvent, then, was removed *in vacuo* and the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and filtered through an Al<sub>2</sub>O<sub>3</sub> pad. Subsequently, the filtrate was evaporated and washed with petroleum

ether (3x5 mL). The final product was further purified by chromatography on an Al<sub>2</sub>O<sub>3</sub> column using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Yield 73.4 mg (52 %). Found: C, 71.33; H, 5.15; N, 4.10%. C<sub>44</sub>H<sub>40</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 71.15; H, 5.43; N, 3.79%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}(\text{cm}^{-1})$  1934vs and 1734s (CO); 3321m (NH) in KBr. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.87 (br, 1H, NH), 7.78-6.55 (m, 17H, 2Ph + Xyl + Tol), 4.51, 4.08 (s, 10H, Cp), 3.94 (s, 3H, NMe), 2.20 (s, 3H, p-MeC<sub>6</sub>H<sub>4</sub>), 2.18, 1.82 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  285.8, 280.6 ( $\mu$ -C=C +  $\mu$ -CO), 220.5 (C=Fe), 216.3 (CO), 149.4, 147.6, 146.7, 141.6, 141.0 (ipso Xyl + ipso Tol + ipso 2Ph +  $\mu$ -C=C), 136.0, 134.9, 133.2 (C-Me Tol + Xyl), 131.7-126.5 (C-H arom), 87.2, 86.5 (Cp), 78.2 (CPh<sub>2</sub>), 43.4 (NMe), 21.0 (p-MeC<sub>6</sub>H<sub>4</sub>), 18.1, 17.6 (C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>). ESI MS: ES+ *m/z* 740.

### 3.9. Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^2$ -C=C(Ph)C(Ph)<sub>2</sub>N(H)CN(Me)(Xy)}( $\mu$ -CO)(CO)(Cp<sub>2</sub>)] (**16**).

Compound **16** was obtained following a procedure similar to that reported for **15**, using PhC≡CLi instead of TolC≡CLi. Yield 42.9 mg (31 %). Found: C, 71.22; H, 4.95; N, 3.68%. C<sub>43</sub>H<sub>37</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub> requires: C, 70.94; H, 5.12; N, 3.85%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}(\text{cm}^{-1})$  1936vs and 1735s (CO); 3321m (NH) in KBr. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.80 (br, 1H, NH), 7.60-6.53 (m, 18H, 3Ph + Xyl), 4.49, 4.08 (s, 10H, Cp), 3.93 (s, 3H, NMe), 2.16, 1.84 (s, 6H, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>).

### 3.10 Crystallography.

Crystal data for **4a**[CF<sub>3</sub>SO<sub>3</sub>] and **15·0.5CH<sub>2</sub>Cl<sub>2</sub>** were collected at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation. Structures were solved by direct methods and structures refined by full-matrix least-squares based on all data using *F*<sup>2</sup> [19]. Crystal data are listed in Table 3. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except position of the N-bonded H atom in **15·0.5CH<sub>2</sub>Cl<sub>2</sub>** which was located in the Fourier map. H-atoms were treated isotropically using the 1.2 fold *U*<sub>iso</sub> value of the parent atom except methyl protons, which were assigned the 1.5 fold *U*<sub>iso</sub> value of the parent C-atom.

Crystals of **4a** are pseudo-merohedrally twinned. The TWIN routine of SHELX97 was used during the refinement with the appropriate twin matrix (1 0 0 0 -1 0 0 0 -1), giving a final BASF factor of 0.41156.

The two Cp rings in **4a**[CF<sub>3</sub>SO<sub>3</sub>] and the molecule of CH<sub>2</sub>Cl<sub>2</sub> in **15·0.5CH<sub>2</sub>Cl<sub>2</sub>** are disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group.

**Table 3**Crystal data and experimental details for **4a**[CF<sub>3</sub>SO<sub>3</sub>] and **15·0.5CH<sub>2</sub>Cl<sub>2</sub>**.

<b>Complex</b>	<b>4a</b> [CF <sub>3</sub> SO <sub>3</sub> ]	<b>15·0.5CH<sub>2</sub>Cl<sub>2</sub></b>
Empirical formula	C <sub>18</sub> H <sub>23</sub> F <sub>3</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S	C <sub>44.5</sub> H <sub>41</sub> ClFe <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
<i>F<sub>w</sub></i>	548.14	782.94
T, K	293(2)	293(2)
$\lambda$ , Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	9.2094(18)	10.350(2)
<i>b</i> , Å	13.888(3)	10.746(2)
<i>c</i> , Å	17.363(4)	17.380(4)
$\alpha$ , °	90	86.55(3)
$\beta$ , °	90.07(3)	80.57(3)
$\gamma$ , °	90	87.91(3)
Cell volume, Å <sup>3</sup>	2220.8(8)	1902.8(7)
<i>Z</i>	4	2
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.639	1.367
$\mu$ , mm <sup>-1</sup>	1.457	0.872
F(000)	1120	814
Crystal size, mm	0.22x0.19x0.13	0.30x0.24x0.13
$\theta$ limits, °	1.17-25.02	1.19-25.03
Reflections collected	19659	16614
Independent reflections	3917 [ <i>R</i> <sub>int</sub> = 0.0819]	6729 [ <i>R</i> <sub>int</sub> = 0.0526]
Data/restraints/parameters	3917/ 182 / 275	6729 / 16 / 483
Goodness on fit on F <sup>2</sup>	1.088	0.979
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0808	0.0469
w <i>R</i> <sub>2</sub> (all data)	0.2199	0.1252
Largest diff. peak and hole, e.Å <sup>-3</sup>	0.953 / -0.722	0.416 / -0.403

#### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 245010 for **4a**[CF<sub>3</sub>SO<sub>3</sub>] and 245011 for **15·0.5CH<sub>2</sub>Cl<sub>2</sub>**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336033; [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

#### Acknowledgements.

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MIUR) (project: "New strategies for the control of reactions: interactions of molecular fragments with metallic sites in unconventional species") and the University of Bologna ("Funds for Selected Research Topics") for financial support.

#### References

- [1] (a) V.G. Albano, L. Busetto, C. Camiletti, C. Castellari, M. Monari and V. Zanotti, *J. Chem. Soc., Dalton Trans.* (1997) 4671; (b) V.G. Albano, S. Bordoni, L. Busetto, C. Camiletti, M. Monari, A. Palazzi, F. Prestopino, V. Zanotti, *J. Chem. Soc., Dalton Trans.* (1997) 4665.
- [2] (a) K. Boss, C. Dowling, A.R. Manning, *J. Organomet. Chem.* 509 (1996) 197; (b) K. Boss, M.G. Cox, C. Dowling, A.R. Manning, *J. Organomet. Chem.* 612 (2000) 18; (c) V.G. Albano, L. Busetto, M. Monari, V. Zanotti, *J. Organomet. Chem.* 606 (2000) 163.
- [3] V. Zanotti, S. Bordoni, L. Busetto, L. Carlucci, A. Palazzi, R. Serra, V.G. Albano, M. Monari, F. Prestopino, F. Laschi, P. Zanello, *Organometallics* 14 (1995) 5232.
- [4] (a) V.G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti, *Organometallics* 22 (2003) 1326; (b) V.G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanotti *J. Organomet. Chem.* 689 (2004) 528.
- [5] (a) C.J. Elsevier, *Coord. Chem. Rev.* 809 (1999) 185; (b) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283; (c) F. Fache, E. Schulz, M.L. Tommasino, M. Lemaire, *Chem. Rev.* 100 (2000) 2159; (d) S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (2000) 1169; (e) R. Kempe, *Angew. Chem. Int. Ed.* 39 (2000) 468.

- [6] V.G. Albano, L. Busetto, F. Marchetti, M. Monari, V. Zanotti, *J. Organomet. Chem.* 649 (2002) 64.
- [7] L. Busetto, R.J. Angelici, *Inorg. Chim. Acta* 2 (1968) 391
- [8] (a) R.A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* 147 (1996) 299; (b) V.Y. Kukuskin, A.J.L. Pombeiro, *Chem. Rev.* 102 (2002) 1771; (c) C.S. Chin, D. Chong, S. Lee, Y.J. Park, *Organometallics* 19 (2000), 4043.
- [9] S. Zhang, Q. Xu, J. Sun, J. Chen, *Organometallics* 22 (2003) 1816.
- [10] C.P. Casey, M. Crocker, P.C. Vosejka, P.J. Fagan, S.R. Marder, M.A. Gohdes, *Organometallics* 7 (1988) 670.
- [11] (a) E.H.J. Pérez, V. Riera *Organometallics* 21 (2002) 1966. (b) F.L. Joslin, M.P. Johnson, J.T. Mague, D.M. Roundhill *Organometallics* 10 (1991) 2781. (c) M.A. Dewey, J.M. Bakke, J.A. Gladysz *Organometallics* 9 (1990) 1349. (d) C.G. Martin, J.M. Boncella, *Inorg. Chem* 29 (1990) 2027.
- [12] (a) R. Castarlenas, M.A. Esteruelas, Y. Jean, A. Lledos, E. Oñate, J. Tomas, *Eur. J. Inorg Chem.* (2001) 2871 and references therein; (b) G.A. Stark, J.A. Gladysz, *Inorg. Chem.* 35 (1996) 5509.
- [13] V.G. Albano, S. Bordoni, L. Busetto, F. Marchetti, M. Monari, V. Zanotti, *J. Organomet. Chem.* 684 (2003) 37.
- [14] M.I. Bruce, *Chem. Rev.* 91 (1991) 197.
- [15] (a) C. Kluwe, J.A. Davies, *Organometallics* 14 (1995) 4257; (b) J.R. Torkelson, R. McDonald, M. Cowie, *Organometallics* 18 (1999) 4146; (c) M.V. Jiménez, E. Sola, P. Martinez, F.J. Lahoz, L.A. Oro, *Organometallics* 18 (1999) 1125.
- [16] L. Busetto, F. Marchetti, S. Zacchini, V. Zanotti, *Eur. J. Inorg. Chem.* (2004) 1494.
- [17] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem.* 31 (1993) 287.
- [18] G. Cox, C. Dowling, A.R. Manning, P. McArdle, D. Cunningham, *J. Organomet. Chem.* 438 (1992) 143.
- [19] G.M. Sheldrick, SHELX97, Program for crystal structure determination, Universität Göttingen, 1997.

**Diiron-aminocarbyne complexes with amine or imine ligands: C-N coupling between imine and aminocarbyne ligands promoted by tolylacetylide addition to**



Luigi Busetto, Fabio Marchetti, Stefano Zacchini, Valerio Zanotti\* and Eleonora Zoli.

*Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy*

Primary and secondary amines, pyridine and benzophenone imine can be coordinated in the dinuclear complexes  $[\text{Fe}_2\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  ( $\text{R} = \text{Me}, \text{Xyl}$ ) via CO displacement, promoted by  $\text{Me}_3\text{NO}$ . The imino complex **13b** reacts with p-tolylacetylide, generating C-C and C-N bonds with formation of a new bridging vinylidene-diaminocarbene complexes **15**.

