

# C-N Coupling Between $\mu$ -Aminocarbyne and Nitrile Ligands Promoted by Tolylacetylide Addition to $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ : Formation of a Novel Bridging $\eta^1:\eta^2$ Allene-Diaminocarbene Ligand.

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*This work is dedicated to professor Ernst Otto Fisher on the occasion of his 85<sup>th</sup> birthday*

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## Abstract

The reaction of the  $\mu$ -aminocarbyne complex  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (**2**) (Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) with tolylacetylide, followed by treatment with HSO<sub>3</sub>CF<sub>3</sub> affords the complex  $[\text{Fe}_2\{\mu\text{-}\eta^1:\eta^2\text{C}(\text{Tol})=\text{C}=\text{C}(\text{CMe}_3)\text{N}(\text{H})\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2](\text{SO}_3\text{CF}_3)$  (**3**) (Tol = 4-MeC<sub>6</sub>H<sub>4</sub>). The X-ray molecular structure of **3** reveals the peculiar character of the bridging ligand, which exhibits either  $\eta^1\eta^2$  allene and aminocarbene nature. The formation of **3** proceeds through several intermediate species, which have been detected by IR spectroscopy. Addition of HSO<sub>3</sub>CF<sub>3</sub> at an early stage of the reaction between **2** and LiC $\equiv$ CTol, leads to the formation of the imine complex  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{Xyl}\}(\mu\text{-CO})(\text{CO})\{\text{NHC}(\text{C}\equiv\text{CTol})\text{CMe}_3\}(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (**6**) indicating that the first step of the reaction consists in the acetylide addition at the coordinated NCCMe<sub>3</sub>. The molecular structure of **6** has been elucidated by an X-ray diffraction study.

Keywords: nitrile, carbyne, carbene, allene, diiron complexes, crystal structure,

## Introduction

Since the discovery of the first metal carbene [1] and metal-carbyne complexes [2] these ligands have become increasingly important in the development of organometallic chemistry as well as in the synthesis of organic molecules [3]. Our interest in the field of dinuclear complexes containing bridging carbyne and carbene ligands [4] has been focused on carbon-carbon bond forming reactions *via* addition of carbon nucleophiles to the complexes  $[\text{Fe}_2(\mu\text{-CX})\{\mu\text{-CO}(\text{CO})_2(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  ( $\text{X} = \text{SMe}, \text{N}(\text{R})\text{Me}$ ;  $\text{R} = \text{Me}, \text{CH}_2\text{Ph}$ ) [5] and  $[\text{Fe}_2\{\mu\text{-C}(\text{SMe}_2)\text{CN}\}\{\mu\text{-CO}(\text{CO})_2(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  ( $\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{Xyl}$ ) [6].

More recently we have investigated the diiron complexes  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}\{\mu\text{-CO}(\text{CO})(\text{NCMe})(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  (**1**) ( $\text{R} = \text{Me}, \text{CH}_2\text{Ph}, \text{Xyl}$ ) containing the acetonitrile ligand, and have found that the NCMe displacement promotes C-C bond formation by insertion of acetylenes into the metal-carbyne bond, affording new vinyliminium complexes of the type  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{R}')=\text{CHC}=\text{N}(\text{Me})(\text{R})\}\{\mu\text{-CO}(\text{CO})(\text{Cp})_2\}[\text{SO}_3\text{CF}_3]]$  ( $\text{R}' = \text{SiMe}_3, \text{Me}, \text{Bu}^n, \text{Tol}, \text{Ph}, \text{H}$ ) [7].

By contrast, the reactions of **1** with organo-lithium reagent ( $\text{LiR}'$ ) did not produce any replacement of the coordinated ligands neither nucleophilic attack at  $\mu$ -carbyne carbon; unexpectedly, deprotonation and rearrangement of the acetonitrile was observed, to form the cyanomethyl compounds  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{R}\}\{\mu\text{-CO}(\text{CO})(\text{CH}_2\text{CN})(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  [8].

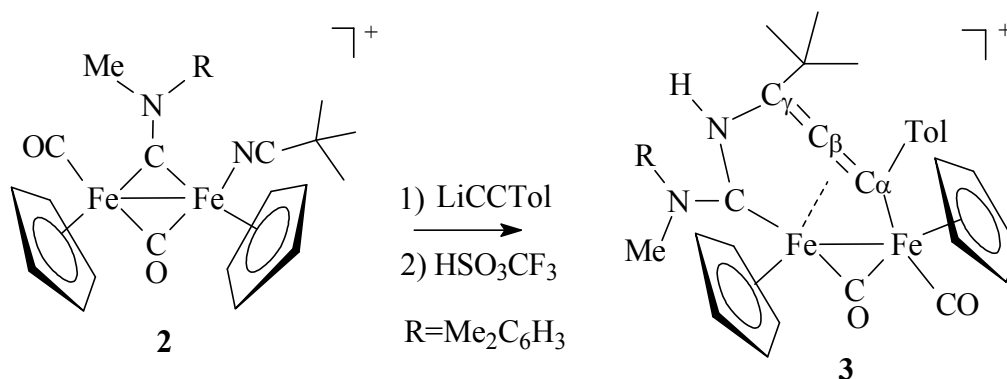
Here we report on the extension of these investigations to nitriles without acidic  $\alpha$ -hydrogens, such as the trimethylacetonitrile ligand in  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2\}[\text{SO}_3\text{CF}_3]]$  (**2**), which allowed us to promote the coupling of the carbyne and nitrile ligands.

## 2 Results and discussion

Treatment of  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}(\text{CO})_2(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  with  $\text{Me}_3\text{NO}$  in the presence of  $\text{NCCMe}_3$  affords the trimethylacetonitrile complex  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  (**2**) in high yields. Its spectroscopic properties are similar to those of the corresponding acetonitrile complex  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}(\text{CO})(\text{NCMe})(\text{Cp})_2\}(\text{SO}_3\text{CF}_3)]$  and indicate the presence of the *cis*-isomer in solution.

The reaction of **2** with lithium-tolyl acetylide (1 equiv) in THF solution at  $-30\text{ }^\circ\text{C}$  results in immediate colour change, from brown to green, of the reaction mixture. The reaction proceeds at room temperature with a further colour change to reddish-brown and is monitored by IR spectroscopy until the appearance of CO bands at  $1941, 1775\text{ cm}^{-1}$  (in THF solution). Then

HSO<sub>3</sub>CF<sub>3</sub> is added (1 equiv) affording [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>C(Tol)=C=C(CMe<sub>3</sub>)N(H)CN(Me)(Xyl)}(μ-CO)(CO)(Cp<sub>2</sub>)][SO<sub>3</sub>CF<sub>3</sub>] (**3**) (Scheme 1).



Scheme 1

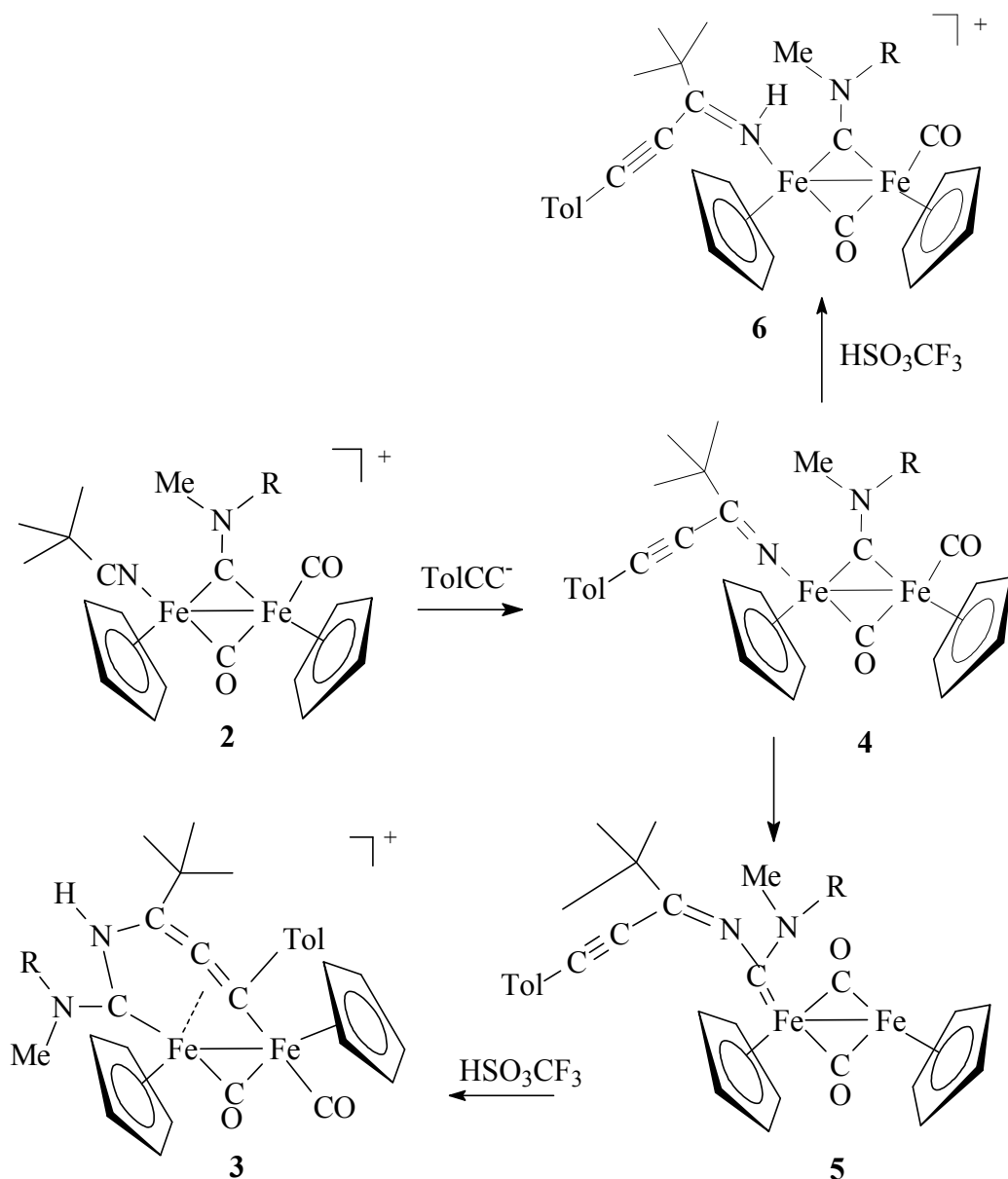
The cation **3** is obtained, in about 60% yield, as dark brown crystals after filtration on alumina and crystallization from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O mixture. It has been identified by X-ray diffraction and its structure is illustrated in Figure 1a. The new asymmetric stereogeometry is better illustrated in Figure 1b, whereas relevant bond lengths and angles are reported in Table 1. The fragment Fe<sub>2</sub>(μ-CO)(CO)(Cp)<sub>2</sub> is readily recognised. It differs from the corresponding fragment in the starting cation **2** because the Cp ligands adopt a *trans* configuration with respect to the Fe-Fe axis [Fe(1)-Fe(2) distance 2.579(1) Å]. It should be noted that, in spite of the non equivalence of the iron atoms, the bridging CO ligand exhibits a symmetric bonding mode [Fe(1)-C(1) 1.945(7), Fe(2)-C(1) 1.943(6) Å], indicating a well balanced electron saturation of the metal atoms. The new ligand (Tol)C(20)C(21)C(22)(Bu<sup>t</sup>)N(2)(H)C(27)N(1)(Xyl)(Me) is anchored to the Fe<sub>2</sub> nuclei via η<sup>1</sup>-C(20), η<sup>2</sup>-C(20)-C(21), η<sup>1</sup>-C(27) bonds. A seven-membered ring including the metal atoms results, stabilized by the η<sup>2</sup> interaction. The entering acetylide, the nitrile and aminocarbene ligands can be recognized in the fragments (Tol)-C(20)-C(21), Bu<sup>t</sup>-C(22)-N(2), and C(27)-N(1)-C(28)-(Xyl). No atom has gone lost, while extensive bond rearrangements have taken place. C(20) acts as a carbene bonded to Fe(2) [bond length 1.981(6) Å]. The sequence C(20)-C(21)-C(22) makes an allene unit [C(20)-C(21) 1.359(7), C(21)-C(22) 1.348(7) Å, C(20)-C(21)-C(22) 161.8(6)°] which is asymmetrically coordinated in αβ mode to Fe(1) [Fe(1)-C(20) 2.168(5), Fe(1)-C(21) 1.997(7) Å]. The allenic nature of this grouping is confirmed by the dihedral angle between the flat fragments C(21)C(22)C(23)N(2) and C(21)C(20)C(13)Fe(2) [58.2(3)°]. The third iron-ligand bond is with the aminocarbene group centred at C(27) [Fe(1)-C(27) 2.005(5) Å].

The IR spectrum of **3** shows two ν-CO absorption bands at 1979 and 1804 cm<sup>-1</sup> (in CH<sub>2</sub>Cl<sub>2</sub> solution), due to the terminal and bridging carbonyls, respectively. The <sup>1</sup>H NMR spectrum exhibits

two signals for the two non-equivalent Cp ligands, a broad resonance for the NH (at 6.92 ppm), and four singlet signals which account for the seven methyl groups present in the molecule.

Concerning the multidentate ligand, the diaminocarbene nature of the Fe(2)-C(27)(N)N interaction is evidenced in the  $^{13}\text{C}$  NMR spectrum by the downfield resonance at 220 ppm, in the expected range for terminal amino carbene carbons [6d]. The three carbons of the 'allenic' unit coordinated in the  $\mu\text{-}\eta^1\text{:}\eta^2_{\alpha\beta}$  mode, a typical mode of ligation of  $\mu$ -allenyls [9], originate  $^{13}\text{C}$  NMR resonances in the range 180-140 ppm. A signal at 178.6 ppm is assigned to  $\text{C}_\beta$  on the basis of previously reported attributions for  $\sigma$ ,  $\eta$  allenyl complexes coordinated through the  $\text{C}_\alpha\text{C}_\beta$  double bond [10]. Resonances due to  $\text{C}_\alpha$  and  $\text{C}_\gamma$  fall in the same region of the quaternary carbons of the aromatic rings and could not be assigned unambiguously.

Formation of **3** is presumably the result of a multi-step process in which the trimethylacetonitrile undergoes nucleophilic attack and is involved in the formation of one C-C and one C-N bond. A plausible hypothesis about the steps leading to the formation of **3** can be traced out (Scheme 2). The process presumably starts from the nucleophilic attack of the tolylacetylde at the coordinated trimethylacetonitrile, resulting in the formation the azavynilidene (methyleneamide) intermediate **4**. Additions of carbon nucleophiles to coordinated nitriles are known, [11] although less common than attacks of amines, alcohols, or water.



Scheme 2

In spite of the fact that quite a number of stable azavinylidene complexes are known [12], the intermediate **4** could not be isolated. A possible explanation is that the  $\text{N}=\text{C}(\text{CCTol})\text{CMe}_3$  ligand can not bind to iron and provide stabilization by further donation to the saturated metal centers. Therefore the ligand migrates to the bridging aminocarbene carbon generating a bridging diaminocarbene ligand. The intramolecular coupling is presumably followed by site exchange between diaminocarbene and terminal carbonyl, to yield the intermediate **5** (Scheme 2). The above assumption is supported by the observation of a green intermediate with a unique IR  $\nu(\text{CO})$  absorption at  $1728\text{ cm}^{-1}$  (in THF solution) in accord with a type **5** formulation.

Bridging - terminal rearrangement of diaminocarbene ligands has already been reported for the analogous diiron complexes  $[\text{Fe}_2\{\mu\text{-C(H)N(Me)R}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]$  and  $[\text{Fe}_2\{\mu\text{-}\overline{\text{CN(CH}_2)_2\text{N}}\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]$  in which the  $\mu$ -aminocarbene ligands migrate to less hindered terminal positions affording  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})\{\text{C(H)N(Me)R}\}(\text{Cp})_2]$  and  $[\text{Fe}_2(\mu\text{-CO})_2(\text{CO})\{\overline{\text{CN(CH}_2)_2\text{N}}\}(\text{Cp})_2]$ , respectively [6d]. In the end, coordination of the alkynyl group to the unsaturated Fe atom and protonation of the iminic nitrogen lead to the metallacycle observed in **3**. To complete the picture one should note the *trans* configuration of the Cp ligands in **3**, whereas they are *cis* in the parent compound **2**. This implies a rearrangement along the reaction path, presumably during the formation of the intermediate **5**.

The most convincing evidence that the first step of the process, described in Scheme 2, is the tolylacetylide addition at the coordinated nitrile is represented by the isolation of the imine complex **6**. It has been obtained upon addition of  $\text{HSO}_3\text{CF}_3$  at an early stage of the reaction, soon after the treatment of **2** with LiCCTol. Protonation converts the azavinylidene intermediate **4** into the more stable imine complex  $[\text{Fe}_2\{\mu\text{-CN(Me)Xyl}\}(\mu\text{-CO})(\text{CO})\{\text{N(H)C(C}\equiv\text{CTol)CMe}_3\}(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (**6**), that has been characterized by X-ray diffraction and spectroscopy.

The molecular structure is shown in Figure 2 and relevant bond parameters are listed in Table 2. The  $\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2$  moiety exhibits stereogeometry and bond distances in agreement with what found in the numerous species of similar constitution. Some comments are worth for the unprecedented imine ligand  $\text{N(H)C(CCTol)CMe}_3$ . The N(2)(imine)-C(22) interaction [1.290(5) Å] is a typical double bond. The tolylacetylene group bonded to C(22) keeps its individuality and shows the linear arrangement C(22)-C(21) $\equiv$ C(20)-C(13) [angles at C(21) and C(20) 176.8(5)° and 178.3(5)°, respectively] and bond lengths in accord with the hybridisation states and bond order [13] [C(22)-C(21) 1.421(6), C(21) $\equiv$ C(20) 1.206(6), C(20)-C(13) 1.435(7) Å]. The Fe(1)-N(2) bond [1.964(3) Å] is essentially a  $\sigma$  donation that makes Fe(1) electron richer than Fe(2). That explains the significant asymmetry of the bridging carbonyl [Fe(1)-C(1) 1.888(5), Fe(2)-C(1) 1.977(4) Å] that, being a good  $\pi$  acceptor makes a stronger bond to Fe(1). The same can not be said for the bridging aminocarbyne carbon whose asymmetry is only just observable [Fe(1)-C(27) 1.854(4), Fe(2)-C(27) 1.868(4) Å].

The IR spectrum of **6** shows  $\nu(\text{CO})$  absorptions at 1977 and 1817  $\text{cm}^{-1}$  and a band at 2200  $\text{cm}^{-1}$  attributable to the  $\nu(\text{C}\equiv\text{C})$ . Evidences of the imine proton are given by the IR absorption,  $\nu(\text{N-H})$  at 3314  $\text{cm}^{-1}$  (in KBr pellets), and the  $^1\text{H}$  NMR resonance at 6.09 ppm. Major features of the  $^{13}\text{C}$  NMR spectrum of **6** include the expected low-field resonance of the  $\mu$ -aminocarbyne carbon (at

340.1 ppm), indicating that the carbyne ligand has not been involved in the reaction and the signal attributable to the imine carbon at 186.6 ppm.

Transition metal  $\sigma$ -imine complexes are cornerstones of the classical coordination chemistry [14]. Routes to imino complexes include use of free imines [15] and modification of ligands such as nitriles, oximes and amines [16]. Only in a limited number of cases the imine ligands have been obtained by addition of a carbon nucleophile at the coordinated nitrile, followed by protonation of the nitrogen [17], in a sequence similar to that we have found. Moreover, since it has been shown that imine can be converted to azavinylidene by deprotonation [16e, 18], we have investigated the reaction of **6** with NaH in a further attempt to isolate the azavinylidene species **4**. Treatment with a strong base, effectively removes the N-H proton, however, once formed, **4** undergoes migration of the nitrogen ligand to the carbyne carbon, as described in Scheme 2. This step is invariably followed by decomposition unless a protic acid is added, to form **3**.

A final consideration concerns the role played, in the above described reactions, by the trimethylacetone nitrile ligand which, far from behaving as a labile ligand, is not removed but undergoes nucleophilic attack to form a C-C bond. This opens the way to C-N bond formation by the unprecedented coupling with aminocarbyne.

### 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 983-G spectrophotometer,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra on a Varian Gemini 300. All the reagents were commercial products (Aldrich) of the highest purity available and used as received.  $[\text{Fe}_2(\text{CO})_4(\text{Cp})_2]$  was from Strem and used as received. Compound  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (**1**) was prepared as described in the literature [19].

#### 3.2 Synthesis of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2](\text{SO}_3\text{CF}_3)$ (**2**)

A mixture of **1** (591 mg, 0.952 mmol) and  $\text{NCC}(\text{CH}_3)_3$  (0.35 mL, 3.2 mmol) in THF (20 ml), was treated with anhydrous  $\text{Me}_3\text{NO}$  (105 mg, 1.40 mmol). The solution was stirred for 30 min, then filtered on a Celite pad. Removal of the solvent gave a residue that was crystallized from  $\text{CH}_2\text{Cl}_2$  and  $\text{Et}_2\text{O}$  affording **2** as a brown microcrystalline solid (450 mg, 70%).

Anal. Found: C, 49.81; H, 4.61%. C<sub>28</sub>H<sub>31</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S: C, 49.73; H, 4.62%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}$ (cm<sup>-1</sup>): 1988 vs and 1820 s (CO), 1520 m ( $\mu$ -CN). NMR  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 7.41-6.95 (3 H, m, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.01, 4.48 (10 H, s, Cp); 4.81 (3 H, s, NMe); 2.69, 2.15 (6 H, s, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 1.11 (9 H, CMe<sub>3</sub>).  $\delta_{\text{C}}$  (CDCl<sub>3</sub>): 338.1 ( $\mu$ -C); 264.3 ( $\mu$ -CO); 211.7 (CO); 148.1 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 139.4 (NCCMe<sub>3</sub>); 133.3, 132.4, 131.9, 130.0, 129.0 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 88.4, 88.0 (Cp); 56.1 (NMe); 30.7 (CMe<sub>3</sub>); 28.3 (CMe<sub>3</sub>); 18.8, 17.5 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

### 3.2 Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\sigma$ : $\eta^3$ C <sub>$\alpha$</sub> (C<sub>6</sub>H<sub>4</sub>Me-4)=C <sub>$\beta$</sub> =C <sub>$\gamma$</sub> (CMe<sub>3</sub>)NHCN(Me)(Xyl)}( $\mu$ -CO)(CO)(Cp<sub>2</sub>)](SO<sub>3</sub>CF<sub>3</sub>) (**3**)

A solution of **2** (644 mg, 0.952 mmol) in THF (12 mL) was treated with LiC $\equiv$ CTol (1.74 ml in THF solution, 1.25 mmol), freshly prepared from n-butyl-lithium and 4-ethynyltoluene, at -30 °C. The mixture was stirred for 30 min, then allowed to warm to room temperature. Additional stirring for further 60 min, until  $\nu$ (CO) bands appeared at 1941 and 1775 cm<sup>-1</sup> (in THF solution), was followed by dropwise addition of HSO<sub>3</sub>CF<sub>3</sub> (0.085 ml, 0.96 mmol). The mixture, which immediately turned brown, was filtered through a Celite pad. A subsequent chromatography on alumina, with a THF/CH<sub>3</sub>CN (2:1) mixture as eluent, afforded a dark brown fraction: crystallization from CH<sub>2</sub>Cl<sub>2</sub> layered with diethyl-ether gave brown crystals of **3** (450 mg, 60%).

Anal. Found: C, 56.11; H, 5.02%. C<sub>37</sub>H<sub>39</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S: C, 56.08; H, 4.96%. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\max}$ (cm<sup>-1</sup>): 1979 vs and 1804 s (CO). IR(KBr)  $\nu_{\max}$ (cm<sup>-1</sup>): 3351 m (N-H). NMR  $\delta_{\text{H}}$  (CDCl<sub>3</sub>): 8.08-7.22 (7 H, m, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and MeC<sub>6</sub>H<sub>4</sub>); 6.92 (1 H, s, N-H); 4.71, 4.63 (10 H, s, Cp); 4.38 (3 H, s, NMe); 2.47, 2.00 (6 H, s, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 2.47 (3 H, s, MeC<sub>6</sub>H<sub>4</sub>); 1.00 (s, 9 H, CMe<sub>3</sub>).  $\delta_{\text{C}}$  (CDCl<sub>3</sub>): 256.8 ( $\mu$ -CO); 221.7 (N-C-N); 209.7 (CO); 178.0 (C <sub>$\beta$</sub> ); 143.7, 141.8, 141.3, 138.3 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, ipso-MeC<sub>6</sub>H<sub>4</sub>, C <sub>$\alpha$</sub>  and C <sub>$\gamma$</sub> ); 134.1-129.1 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> and MeC<sub>6</sub>H<sub>4</sub>); 92.5, 90.1 (Cp); 42.8 (NMe); 35.0 (CMe<sub>3</sub>); 29.3 (CMe<sub>3</sub>); 20.8 (Me-C<sub>6</sub>H<sub>4</sub>); 17.2, 16.1 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

### 3.3 Synthesis of [Fe<sub>2</sub>{ $\mu$ -CN(Me)Xyl}( $\mu$ -CO)(CO){NHC(C $\equiv$ CTol)CMe<sub>3</sub>}(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**6**).

A THF solution of LiC $\equiv$ CTol (0.82 ml, 0.59 mmol), was added to a stirred solution of **2** (320 mg, 0.473 mmol), in THF (7 ml), at -30 °C. The stirring was maintained for 15 min: the colour changed to green and lowering of the  $\nu$ (CO) absorptions was observed at 1969 and 1812 cm<sup>-1</sup> (in THF). Then, HSO<sub>3</sub>CF<sub>3</sub> (0.045 ml, 0.51 mmol) was added dropwise and the mixture, which immediately turned dark yellow, was allowed to warm to room temperature and filtered on a Celite pad. Solvent removal and chromatography on an alumina column, using a mixture of THF and CH<sub>3</sub>CN (1:1/v:v) as eluent, afforded a brown band that was collected. Crystallization from CH<sub>2</sub>Cl<sub>2</sub> layered with diethyl ether gave brown crystals of **6** (244 mg, 65%).



Anal. Found: C, 56.21; H, 5.01%.  $C_{37}H_{39}F_3Fe_2N_2O_5S$ : C, 56.08; H, 4.96%. IR ( $CH_2Cl_2$ )  $\nu_{max}(cm^{-1})$ : 2200 m ( $C\equiv C$ ), 1977 vs and 1817 s (CO). IR(KBr)  $\nu_{max}(cm^{-1})$ : 3314 m (N-H). NMR  $\delta_H$  ( $CDCl_3$ ): 7.80-7.20 (7 H, m,  $Me_2C_6H_3$  and  $MeC_6H_4$ ), 6.12 (1 H, s, N-H), 5.08, 4.44 (10 H, s, Cp), 4.97 (3 H, s, NMe), 2.71, 2.19 (6 H, s,  $Me_2C_6H_3$ ), 2.48 (3 H, s,  $MeC_6H_4$ ), 0.98 (s, 9 H,  $CMe_3$ ).  $\delta_C$  ( $CDCl_3$ ): 339.8 ( $\mu-C$ ); 263.8 ( $\mu-CO$ ); 212.6 (CO); 186.6 (N=C); 148.4, 141.7 (*ipso*- $Me_2C_6H_3$  and *ipso*- $MeC_6H_4$ ); 133.2-128.9 ( $Me_2C_6H_3$  and  $MeC_6H_4$ ); 117.4, 107.1 ( $C\equiv C$ ); 88.2, 88.0 (Cp); 53.8 (N-Me); 44.2 ( $CMe_3$ ); 26.6 ( $CMe_3$ ); 21.8 ( $MeC_6H_4$ ); 18.6, 17.6 ( $Me_2C_6H_3$ ).

### 3.4. X-ray data collection and structure determination of **3** and **6**.

The diffraction experiments for the title compounds were carried out at room temperature on a Bruker AXS SMART 2000 CCD diffractometer using Mo-K $\alpha$  radiation. Intensity data were measured over full diffraction spheres using 0.3° wide  $\omega$  scans, crystal-to-detector distance 5.0 cm. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in three different  $\omega$  regions and eventually refined against all reflections. The software SMART [1a] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the software SAINT [1a] and an empirical absorption correction was applied with SADABS [1b] for **7**. Both structures were solved by direct methods (SIR 97) [1c] and subsequent Fourier syntheses and refined by full matrix least-squares on  $F^2$  (SHELXTL)[1d] using anisotropic thermal parameters for all non hydrogens atoms. Complex **7** crystallised in the acentric space group  $P2_12_12_1$  of the orthorhombic system and appeared to be racemically twinned within the crystal with a refined Flack parameter of 0.49(2) [2]. It was therefore refined using the TWIN refinement routine of the SHELXTL program. The hydrogen atoms bonded to carbons were included in calculated positions and allowed to ride the carrier atoms with thermal parameters tied to those of the pertinent atoms. The hydrogen attached to N(2) in both **3** and **7** was refined and its isotropic thermal parameter defined as  $U(H) = 1.2U_{eq}(N)$ .

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 205521 for **3** and no. 205522 for **6**. 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; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www.ccdc.cam.ac.uk>).

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Table 1

Selected bond lengths (Å) and angles (°) for complex **3**.

Fe(1)-Fe(2)	2.579(1)	N(2)-C(22)	1.411(7)
Fe(1)-C(1)	1.945(7)	C(1)-O(1)	1.165(7)
Fe(2)-C(1)	1.943(6)	C(2)-O(2)	1.155(7)
Fe(1)-C(21)	1.997(6)	C(20)-C(21)	1.359(7)
Fe(1)-C(20)	2.168(5)	C(21)-C(22)	1.348(7)
Fe(1)-C(27)	2.005(5)	C(22)-C(23)	1.512(7)
Fe(2)-C(2)	1.753(6)	C(23)-C(26)	1.526(8)
Fe(2)-C(20)	1.981(6)	C(23)-C(25)	1.545(9)
N(1)-C(27)	1.325(7)	C(23)-C(24)	1.550(7)
N(1)-C(28)	1.478(7)	Fe(1)-C(Cp)	2.143
N(1)-C(29)	1.467(6)	Fe(2)-C(Cp)	2.126
N(2)-C(27)	1.357(7)		
Fe(1)-C(1)-O(1)	139.4(5)	Fe(2)-C(20)-C(13)	127.3(4)
Fe(2)-C(1)-O(1)	137.3(5)	C(20)-C(21)-C(22)	161.8(6)
C(27)-N(1)-C(29)	120.1(4)	C(21)-C(22)-N(2)	110.8(5)
C(27)-N(1)-C(28)	127.2(4)	C(21)-C(22)-C(23)	131.1(5)
C(28)-N(1)-C(29)	112.7(4)	N(2)-C(22)-C(23)	118.1(4)
C(22)-N(2)-C(27)	117.4(4)	N(1)-C(27)-N(2)	114.6(4)
C(13)-C(20)-C(21)	125.4(6)	N(1)-C(27)-Fe(1)	132.6(4)
Fe(2)-C(20)-C(21)	106.5(4)	N(2)-C(27)-Fe(1)	112.7(4)

Table 2

Selected bond lengths (Å) and angles (°) for complex **6**.

Fe(1)-Fe(2)	2.5171(7)	N(1)-C(29)	1.460(5)
Fe(1)-C(1)	1.888(5)	N(1)-C(28)	1.472(5)
Fe(1)-C(27)	1.854(4)	N(2)-C(22)	1.290(5)
Fe(2)-C(27)	1.868(4)	C(21)-C(22)	1.421(6)
Fe(1)-N(2)	1.964(3)	C(20)-C(21)	1.200(6)
Fe(2)-C(2)	1.744(5)	C(20)-C(13)	1.435(7)
Fe(2)-C(1)	1.977(4)	C(22)-C(23)	1.520(6)
N(1)-C(27)	1.321(5)	C(23)-C(24)	1.523(7)
Fe(1)-C(Cp)(av)	2.119	C(23)-C(25)	1.523(7)
Fe(2)-C(Cp)(av)	2.118	C(23)-C(26)	1.545(7)
C(28)-N(1)-C(29)	114.1(3)	C(20)-C(21)-C(22)	176.8(5)
C(27)-N(1)-C(29)	122.2(3)	N(2)-C(22)-C(23)	124.3(4)
C(27)-N(1)-C(28)	123.7(3)	N(2)-C(22)-C(21)	119.5(4)
Fe(1)-N(2)-C(22)	135.0(3)	Fe(2)-C(1)-O(1)	134.2(3)
Fe(1)-C(1)-O(1)	144.5(4)	C(21)-C(20)-C(13)	178.3(5)
Fe(2)-C(2)-O(2)	177.1(5)		

Table 3.

Crystal data and experimental details for **3** and **6**.

Compound	<b>3</b>	<b>6</b>
Formula	C <sub>37</sub> H <sub>39</sub> F <sub>3</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S	C <sub>37</sub> H <sub>39</sub> F <sub>3</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>5</sub> S
<i>F</i> <sub>w</sub>	792.46	792.46
T, K	233(2)	298(2)
λ, Å	0.71073	0.71073
Crystal symmetry	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> , Å	10.203(1)	11.9967(2)
<i>b</i> , Å	13.800(2)	14.1311(2)
<i>c</i> , Å	14.928(2)	22.0341(4)
α, °	64.779(4)	90
β, °	71.994(2)	90
γ, °	71.733(4)	90
Cell volume, Å <sup>3</sup>	1767.6(4)	3735.4(1)
<i>Z</i>	2	4
D <sub>c</sub> , Mg m <sup>-3</sup>	1.489	1.409
μ(Mo-Kα), mm <sup>-1</sup>	0.941	0.891
F(000)	820	1640
Crystal size/ mm	0.25 x 0.15 x 0.10	0.36 x 0.30 x 0.25
θ limits, °	2.65-26.99	1.85-25.19
Reflections collected	17967(±h, ±k, ±l)	36324(±h, ±k, ±l)
Unique observed reflections [F <sub>o</sub> > 4σ(F <sub>o</sub> )]	7681[R(int) = 0.0976]	6721[R(int) = 0.0944]
Goodness-of-fit-on F <sup>2</sup>	0.889	0.965
R <sub>1</sub> (F) <sup>a</sup> , wR <sub>2</sub> (F <sup>2</sup> ) <sup>b</sup>	0.0690, 0.1608	0.0458, 0.1104
Largest diff. peak and hole, e. Å <sup>-3</sup>	1.401/−0.854	0.539/−0.497

<sup>a</sup> R<sub>1</sub> = Σ||F<sub>o</sub>−|F<sub>c</sub>|/Σ|F<sub>o</sub>|.

<sup>b</sup> wR<sub>2</sub> = [Σw(F<sub>o</sub><sup>2</sup>−F<sub>c</sub><sup>2</sup>)<sup>2</sup>/Σw(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]<sup>1/2</sup> where w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (aP)<sup>2</sup> + bP] where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

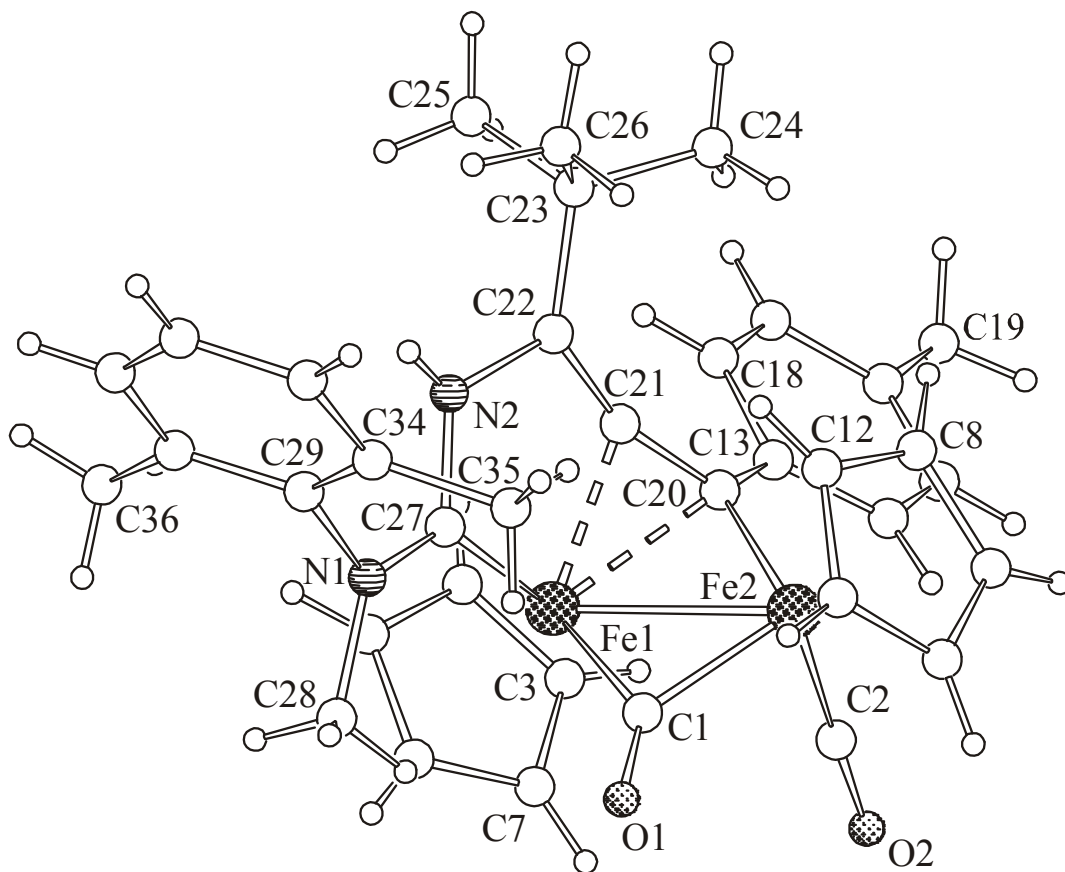


Figure 1a



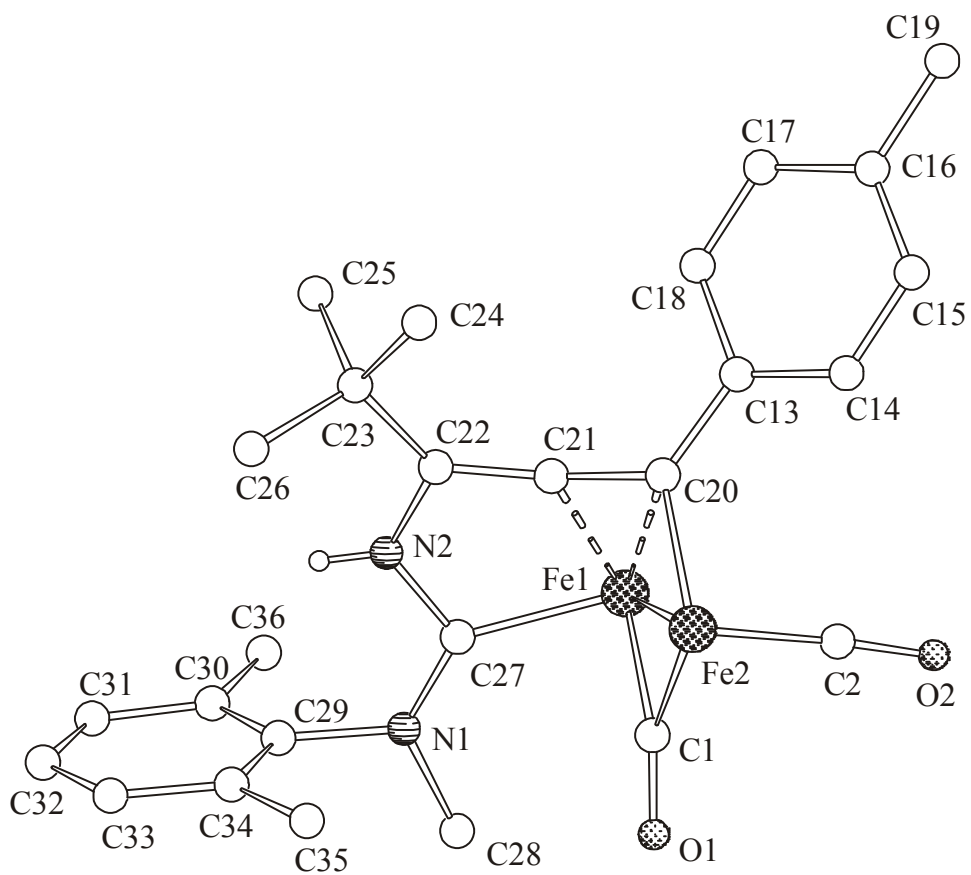


Figure 1b

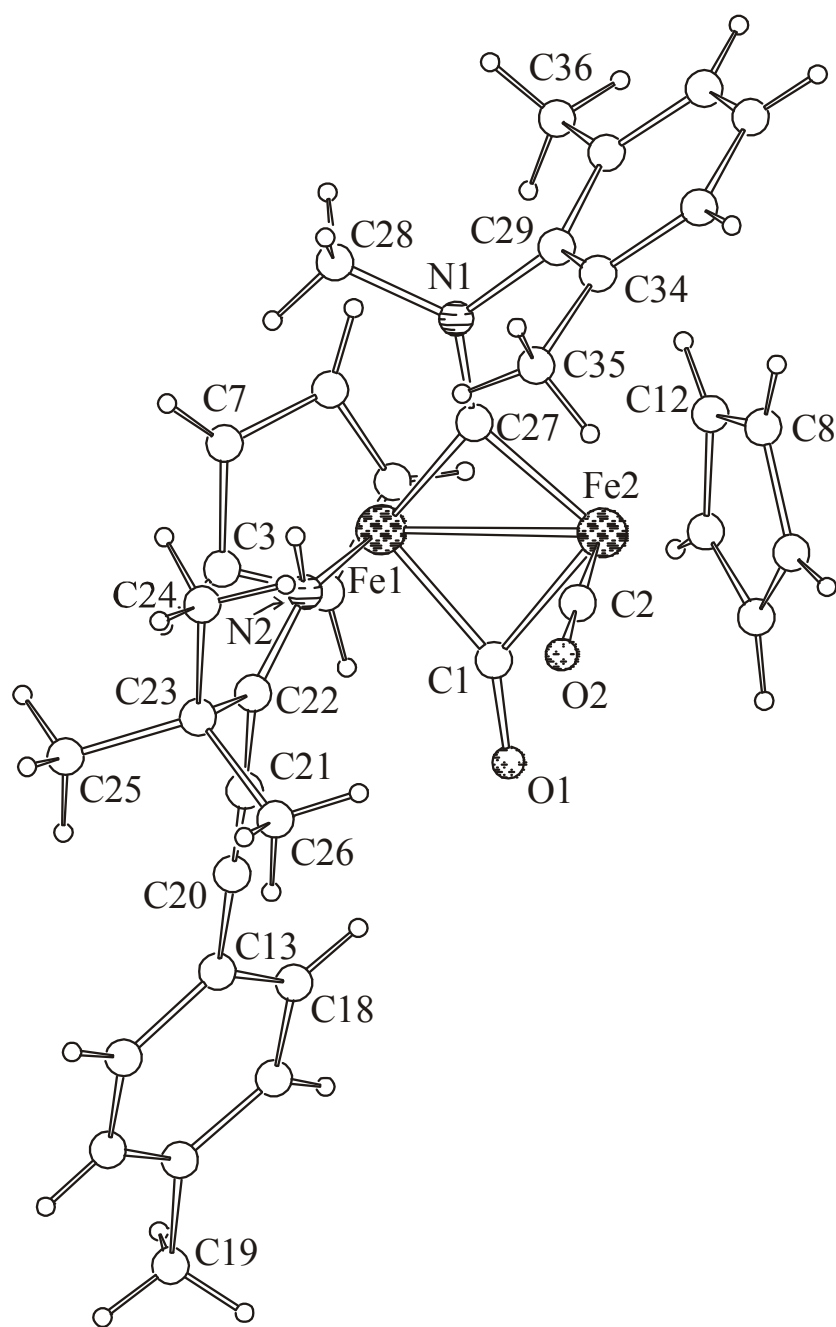


Figure 2

## Figure Captions

Figure 1. (a) Molecular structure of the cation  $[\text{Fe}_2\{\mu\text{-}\sigma\text{:}\eta^3\text{C}(\text{C}_6\text{H}_4\text{Me-4})=\text{C}=\text{C}(\text{CMe}_3)\text{NHCN}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp}_2)]^+$ ; (b) view of the cation illustrating the structure of the seven-membered cyclometallated ligand (Cp ligands and hydrogens omitted).

Figure 2. Molecular structure of the cation  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})\text{Xyl}\}\{\mu\text{-CO}\}(\text{CO})\{\text{N}(\text{H})\text{C}(\text{C}\equiv\text{CTol})\text{CMe}_3\}(\text{Cp})_2]^+$

*For Table of Contents Use Only*

**C-N Coupling Between  $\mu$ -Aminocarbonyl and Nitrile Ligands Promoted by Tolylacetylide Addition to  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{NCCMe}_3)(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ : Formation of a Novel Bridging  $\eta^1:\eta^2$  Allene-Diaminocarbene Ligand.**

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The reaction of  $\mu$ -aminocarbonyl complex **2** with tolylacetylide, followed by treatment with  $\text{HSO}_3\text{CF}_3$  yields the complex **3** in which the novel bridging  $\eta^1:\eta^2$  allene-aminocarbene ligand comes from acetylide addition at the nitrile and C-N coupling with the  $\mu$ -carbonyl. The addition intermediate is trapped as imine complex  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{NHC}(\text{C}\equiv\text{CTol})\text{CMe}_3\}(\text{Cp})_2][\text{SO}_3\text{CF}_3]$  (**6**), by treatment with  $\text{HSO}_3\text{CF}_3$  at an early stage of the reaction. The molecular structures of **3** and **6** have been elucidated by X-ray diffraction studies.

