

# C-C bond formation by cyanide addition to diiron and diruthenium vinyliminium complexes

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## Summary

The diiron vinyliminium complexes  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R}')\text{=C(H)C=N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$  (R = Me, R' = SiMe<sub>3</sub>, **1a**; R = Me, R' = CH<sub>2</sub>OH, **1b**; R = CH<sub>2</sub>Ph, R' = Tol, **1c**, Tol = 4-MeC<sub>6</sub>H<sub>4</sub>; R = CH<sub>2</sub>Ph, R' = COOMe, **1d**; R = CH<sub>2</sub>Ph, R' = SiMe<sub>3</sub>, **1e**) undergo regio- and stereo-selective addition by cyanide ion (from NBU<sup>n</sup><sub>4</sub>CN), affording the corresponding bridging cyano-functionalized allylidene compounds  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R}')\text{C(H)C(CN)N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$  (**3a-e**), in good yields. Similarly, the diiron vinyliminium complexes  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R}')\text{=C(R')C=N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$  (R = R' = Me, **2a**; R = Me, R' = Ph, **2b**; R = CH<sub>2</sub>Ph, R' = Me, **2c**; R = CH<sub>2</sub>Ph, R' = COOMe, **2d**) react with cyanide and yield  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R}')\text{C(R')C(CN)N(Me)(R)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$  (**9a-d**). The reactions of the vinyliminium complex  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Tol)\text{=CHC=N(Me)(4-C}_6\text{H}_4\text{CF}_3)\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$  (**4**) with NaBH<sub>4</sub> and NBU<sup>t</sup><sub>4</sub>CN afford the allylidene  $[\text{Fe}_2\{\mu\text{-C(Tol)C(H)\text{=C(H)N(Me)(C}_6\text{H}_4\text{CF}_3)\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$  (**5**) and the cyanoallylidene  $[\text{Fe}_2\{\mu\text{-C(Tol)C(H)\text{=C(CN)N(Me)(C}_6\text{H}_4\text{CF}_3)\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$  (**6**), respectively. Analogously, the diruthenium vinyliminium complex  $[\text{Ru}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(SiMe}_3\text{)\text{=CHC=N(Me)(CH}_2\text{Ph)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$ , (**7**), reacts with NBU<sup>n</sup><sub>4</sub>CN to give  $[\text{Ru}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(SiMe}_3\text{)CHC(CN)N(Me)(CH}_2\text{Ph)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$  (**8**). Finally, cyanide addition to  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(COOMe)\text{=C(COOMe)C=N(Me)(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2][\text{SO}_3\text{CF}_3]$  (**2e**) (Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), yields the cyano-functionalized bis-allylidene complex  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C(COOMe)C(COOMe)(CN)CN(Me)(Xyl)}\}\{\mu\text{-CO}\}\{\text{CO}\}\{\text{Cp}\}_2]$

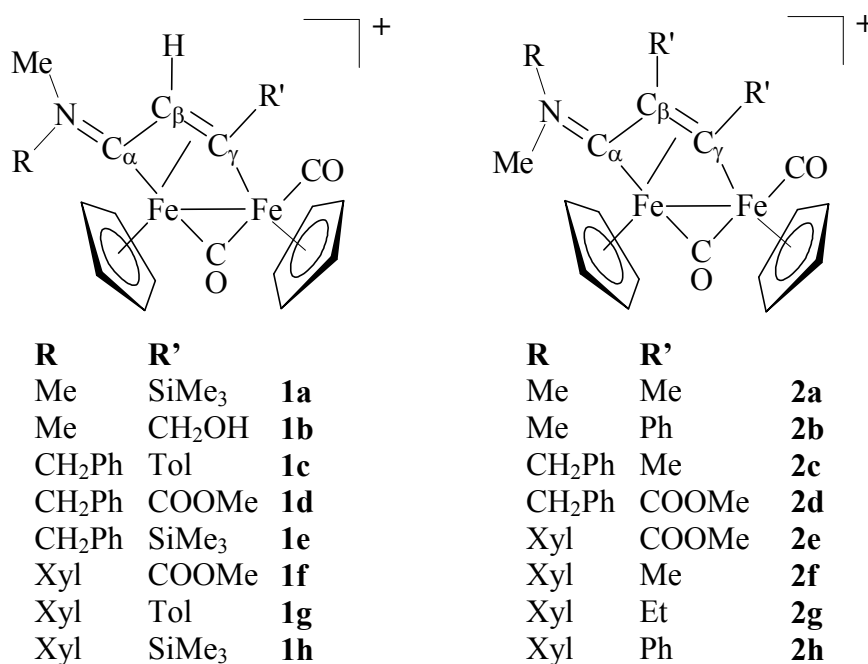
CO)(CO)(Cp)<sub>2</sub>] (**10**). The molecular structures of **3a** and **9a** have been elucidated by X ray diffraction.

*Keywords:* vinyliminium, diiron complexes, allylidene, vinylalkylidene, cyanide addition

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## Introduction

Di- and polynuclear metal complexes are subject of interest since the presence of bridging ligands and cooperation among close metal centres is a potential source of unique reactivity [1]. Our interest in the area has concerned the chemistry of the diiron bridging vinyliminium complexes **1** and **2** (Chart 1). These latter have been obtained by insertion of mono and di-substituted alkynes, respectively, in the metal-carbyne bond of the parent  $\mu$ -aminocarbyne complexes [Fe<sub>2</sub>{ $\mu$ -C=N(Me)(R)}(μ-CO)(CO)(NCMe)(Cp)<sub>2</sub>] [SO<sub>3</sub>CF<sub>3</sub>] [2].



## Chart 1

The bridging vinyliminium ligands in **1** and **2** display a remarkable electrophilic character and have been shown to react with NaBH<sub>4</sub> undergoing hydride addition [3]. The addition occurs selectively at the iminium carbon (C<sub>α</sub>), except for the complexes (**1f-h**) in

which bulky Xyl group (Xyl = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was found to inhibit hydride attack at C<sub>α</sub> and direct the addition to the less hindered C<sub>β</sub>. [3a]. Attempts to extend our studies to the reactions with carbon nucleophiles have evidenced a different reactivity: carbon nucleophiles that are also strong bases (*i.e.* lithium organyls) react with **1** causing deprotonation of the C<sub>β</sub>-H. The deprotonated intermediates have been shown to rearrange affording new mono and polynuclear complexes [4]. On the other hand, type **2** complexes, which do not contain acidic C<sub>β</sub>-H hydrogens, have been found to react with LiR undergoing nucleophilic addition at the C<sub>5</sub>H<sub>5</sub> ligand, rather than at the bridging vinyliminium. Initial attack is followed by an intramolecular rearrangement, which involves hydride migration from the cyclopentadiene ring (C<sub>5</sub>H<sub>5</sub>R) to the vinyliminium ligand affording μ-vinylcarbene complexes [5].

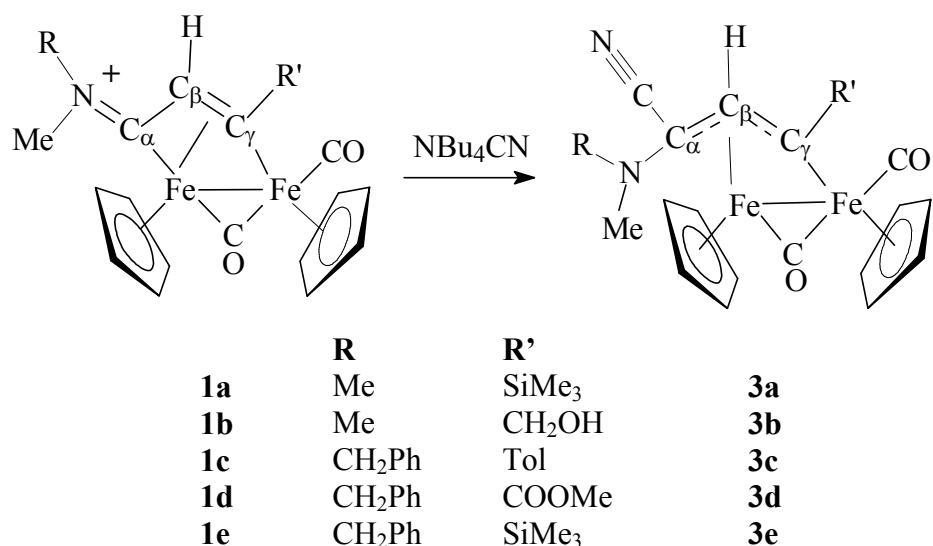
Herein, we report on the reactions of **1-2** and of a similar diruthenium complex [6] with cyanide. Several vinyliminium complexes have been examined in order to determine to which extent the reactivity of the bridging ligand is influenced by steric and electronic features of the substituents (R and R'). The cyanide anion is a 'stabilized carbanion' and, because of its lower basicity compared to other carbanions, is the ideal candidate to give nucleophilic addition at the bridging vinyliminium ligand, in spite of the acidic character of C<sub>β</sub>-H.

A further reason to investigate the functionalization of the bridging ligand by cyanide is the high interest of the cyanocarbon transition metal chemistry, due to various potential applications in the field of new materials and organic synthesis [7].

## 2. Results and discussion

### 2.1 Cyanide addition to vinyliminium complexes containing acidic C<sub>β</sub>-H hydrogen

The vinyliminium complexes [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(R')=CHC=N(Me)(R)}(μ-CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**1a-e**), containing the acidic C<sub>β</sub>-H hydrogen, react with (NBu<sup>n</sup>)<sub>4</sub>(CN), in CH<sub>2</sub>Cl<sub>2</sub> solution, affording the complexes **3a-e**, in about 80-90 % yields (Scheme 1).



**Scheme 1.**

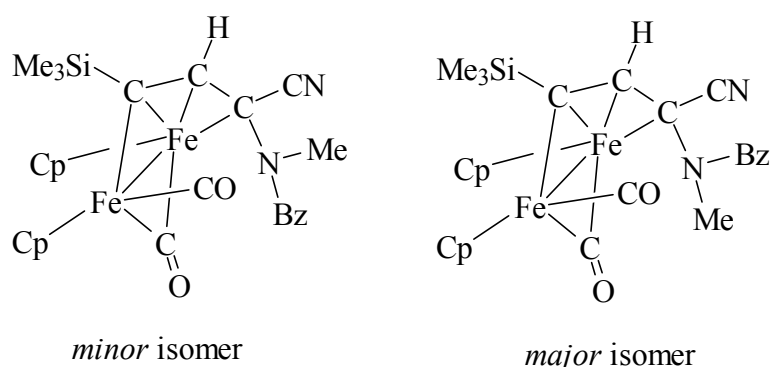
It is worth noting that cyanide exclusively attacks the iminium carbon, rather than following other reaction modes, including C<sub>β</sub>-H proton removal, CO displacement or addition at other sites of the  $\mu$ -ligand. The nature of complexes **3a-e** has been determined by elemental analyses, spectroscopy and X-ray diffraction for **3a**. Two crystallographically independent but chemically equivalent molecules have been found in the crystal (see experimental section). The ORTEP molecular diagram of one of them is shown in Figure 2. Relevant bond lengths and angles are reported in Table 1. It is worth noting that all the corresponding bond distances in the two molecules are equal within experimental errors. Minor differences are observable in the conformation of the ancillary groups. The molecular stereogeometry of **3a** is consistent with that of the parent cation **1a**, in which the C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub> unit of the vinyliminium ligand is bonded to the Fe<sub>2</sub> unit in the non conventional mode shown in Scheme 1. The information conveyed by the X-ray structure is primarily that CN<sup>-</sup> attacks the more electrophilic C<sub>α</sub> carbon [C(5)]. The generation of a C-C bond turns the vinyliminium ligand into an allylidene derivative, as one can infer from the double bond character and the substantial equivalence of the C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub> distances in both molecules [C(5)-C(4) 1.447 and 1.449(3) Å; C(4)-C(3) 1.414 and 1.419(3) Å]. Also the coordination interactions Fe-(C<sub>α</sub>-C<sub>β</sub>-C<sub>γ</sub>) exhibit minor differences [Fe(1)-C(5) 2.068 and 2.077(2) Å; Fe(1)-C(4) 2.012 and 2.007(2) Å; Fe(1)-C(3) 2.045 and 2.037(2) Å].

The spectroscopic data of **3a-e** are in good agreement with the solid state structure. Their infrared spectra, in CH<sub>2</sub>Cl<sub>2</sub> solution, exhibit absorptions for the terminal and bridging

carbonyls (*e.g.* at 1969 and 1787  $\text{cm}^{-1}$  for **3a**) and a  $\nu(\text{CN})$  absorption at about 2190  $\text{cm}^{-1}$ . The NMR spectra of **3a-b**, in  $\text{CDCl}_3$  solution, show the presence of a single isomer. Since the  $\text{CN}^-$  addition at  $\text{C}_\alpha$  could occur either on the same side of  $\text{C}_\beta\text{-H}$  or in the opposite one, generating *syn* and *anti* isomers, respectively, we conclude that the reaction is stereoselective and assume that the geometry adopted in solution is that observed in the solid state with the CN group *syn* to the  $\text{C}_\beta\text{-H}$ . The  $^1\text{H}$  NMR spectra of **3a-b** show two distinct resonances for the  $\text{NMe}_2$  protons (*e.g.* at  $\delta$  2.31 and 1.71 ppm for **3a**). Their inequivalence suggests that free rotation around the  $\text{C}_\alpha\text{-N}$  bond is inhibited for steric reasons, because the  $\text{C}_\alpha\text{-N}$  interaction does not display double bond character [ $\text{C}(5)\text{-N}(1)$  1.445 and 1.431(3) Å]. In fact, the geometry observed for **3a** evidences that the  $\text{CH}_3$  groups in  $\text{NMe}_2$  would bump into the terminal CO ligand [ $\text{C}(2)\text{-O}(2)$ ] upon rotation around the  $\text{C}(5)\text{-N}(1)$  axis [ $\text{N}(1)\text{..C}(2)$  contact Å].

Other NMR features include the typical resonances for  $\text{C}_\alpha$ ,  $\text{C}_\beta$  and  $\text{C}_\gamma$  of the allylidene skeleton (*e.g.* for **3a** at 67.6 ppm, 86.5 ppm, 194.5 ppm respectively) and the resonance of the cyanide carbon, at about 121 ppm.

Complexes **3c-e** exist as a mixtures of two isomers in about 1:5 ratio. These are due to the lack of free orientation of the methyl and benzyl groups around the  $\text{C}_\alpha\text{-N}$  bond, as just discussed for the NMR non equivalence of the  $\text{NMe}_2$  methyl groups in **3a-b**. NOE experiments on the major isomer of **3c** suggest that the most favourable geometry is that with the methyl and benzyl groups pointing toward the bridging and terminal CO, respectively (Chart 2).

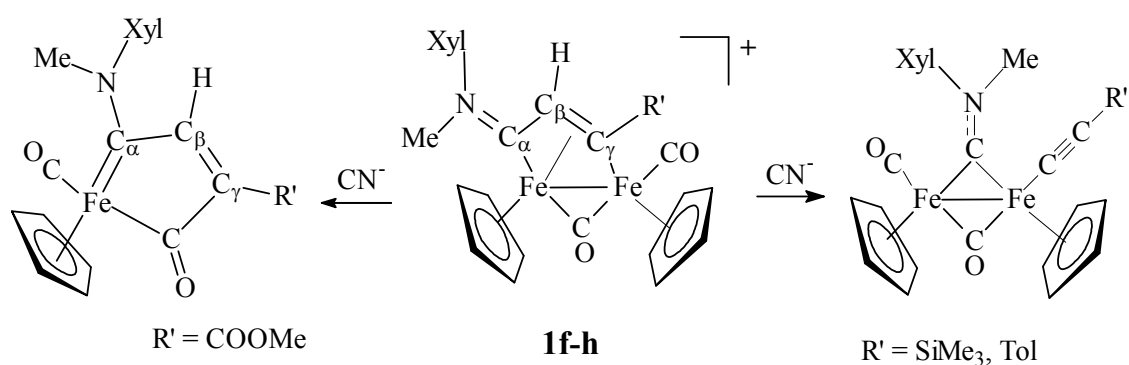


**Chart 2:** isomers due to orientations of the N-substituents for **3c**.

The reactions described in Scheme 1 parallel the corresponding addition of NaBH<sub>4</sub> [3a]. Indeed, complexes **1a-e** undergo hydride attack at the C<sub>α</sub> affording the corresponding μ-allylidene complexes [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(R')CHC(H)N(Me)(R)}(μ-CO)(CO)(Cp)<sub>2</sub>] (R= Me, CH<sub>2</sub>Ph), similar to **3a-e**. In both cases nucleophilic attack occurs exclusively at the iminium carbon and is stereospecific. However, the orientation of the entering groups is different: hydride is found *anti* with respect to the C<sub>β</sub>-H, whereas cyanide is *syn*. The conformational freedom of the NMe(R) substituent is consequently different in the two cases, with hindered rotation observed only in the complexes obtained by CN<sup>-</sup> addition.

It is worth noting that the reaction described above points out the similarities between H<sup>-</sup> (from NaBH<sub>4</sub>) and CN<sup>-</sup> (from NBU<sub>4</sub>CN) as far as nucleophilic additions at bridging ligands in cationic diiron complexes [8] are concerned.

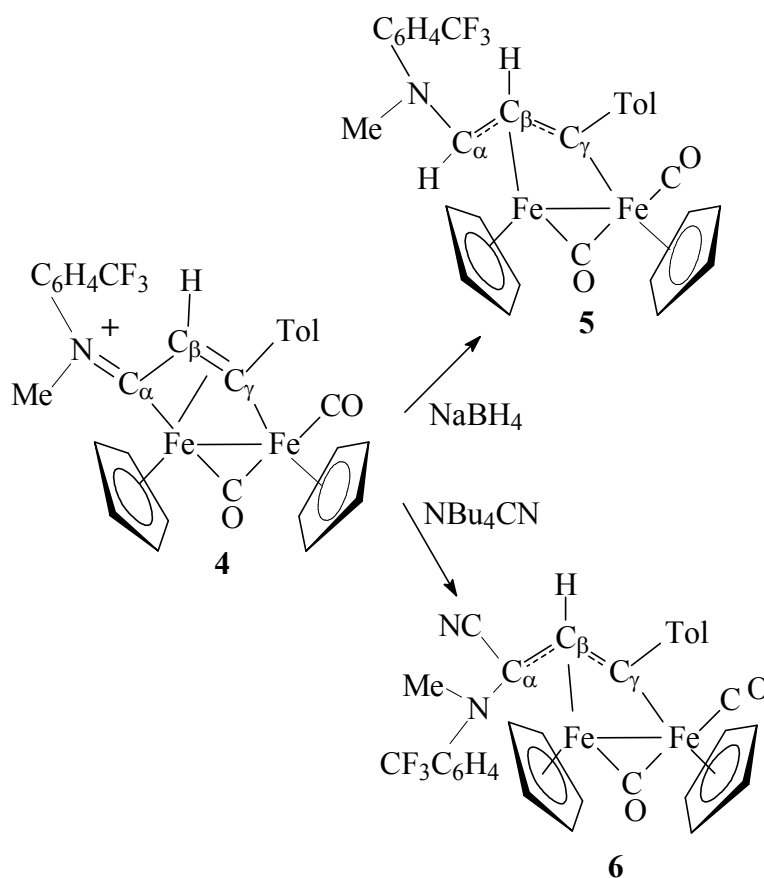
By contrast with the reactions shown in Scheme 1, the complexes [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(R')=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R = CO<sub>2</sub>Me, **1f**; R = Tol, **1g**; R = SiMe<sub>3</sub>, **1h**), characterized by the presence of the bulkier Xyl (2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) group, react with cyanide yielding alkynyl complexes or fragmentation of the dinuclear precursor (Scheme 2). The reaction products are those previously observed by deprotonation of **1f-h** by NaH [4]. Therefore, the presence of the Xyl group in **1f-h** inhibits the attack at the iminium carbon and favours the C<sub>β</sub>-H proton removal.



## Scheme 2

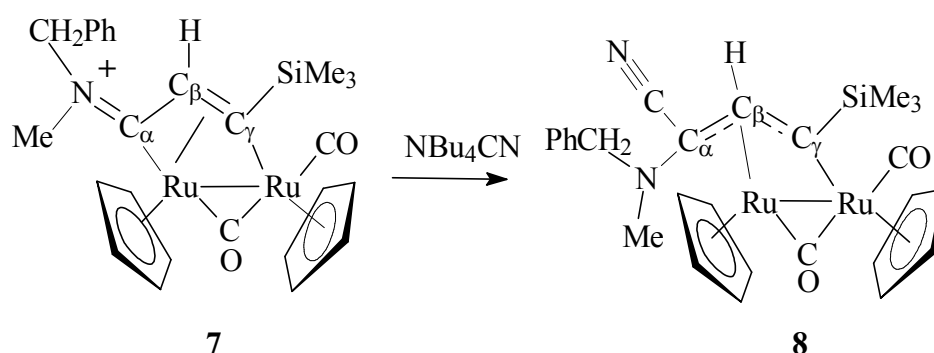
The result is unexpected and markedly different from what observed in the corresponding reactions with NaBH<sub>4</sub>: **1f-h** were found to undergo hydride addition at C<sub>β</sub> affording bis-alkylidene complexes of the type [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>2</sup>-C(R')CH<sub>2</sub>CN(Me)(Xyl)}(μ-CO)(CO)(Cp)<sub>2</sub>]. The reason why CN<sup>-</sup> reacts removing the C<sub>β</sub>-H hydrogen rather than

giving addition at the C $_{\beta}$  carbon remains unclear. The steric influence exerted by the Xyl group is quite evident, but electronic effects due to its electron-withdrawing character should also be taken into account. For a better discrimination between electronic and steric effects, the reactivity of [Fe $_2$ { $\mu$ - $\eta^1$ : $\eta^3$ -C(Tol)=C(H)C=N(Me)(4-C $_6$ H $_4$ -CF $_3$ )}( $\mu$ -CO)(CO)(Cp) $_2$ ][SO $_3$ CF $_3$ ] (**4**), in which a *para*-trifluoro methyl benzene (R = 4-C $_6$ H $_4$ -CF $_3$ ) replaces the Xyl group, has been investigated. The synthesis of **4**, which is a novel compound, is detailed in the experimental part. The p-C $_6$ H $_4$ -CF $_3$  group is less sterically demanding than Xyl, but a better electron-withdrawer. The reactions of **4** with NaBH $_4$  and NBU $_4$ CN have shown that, in both cases, the nucleophilic attack occurs selectively at C $_{\alpha}$  (Scheme 3), suggesting that the steric bulk of the N substituents is dominant. Compounds [Fe $_2$ { $\mu$ -C(Tol)C(H)=C(H)N(Me)(C $_6$ H $_4$ CF $_3$ )}( $\mu$ -CO)(CO)(Cp) $_2$ ] (**5**) and [Fe $_2$ { $\mu$ -C(Tol)C(H)=C(CN)N(Me)(C $_6$ H $_4$ CF $_3$ )}( $\mu$ -CO)(CO)(Cp) $_2$ ] (**6**) have been obtained, respectively, and characterized by IR and  $^1$ H,  $^{13}$ C and  $^{19}$ F NMR spectroscopy. Complex **5** is analogous to previously reported compounds [3a], whereas complex **6** resembles **3a-e**.



**Scheme 3.**

We have recently shown that diruthenium vinyliminium complexes analogous to the diiron species **1** and **2** can also be obtained [6]. Their chemistry parallels that of their diiron counterparts, however some minor differences, regarding the geometry of the complexes and the reactivity of the terminally coordinated ligands have been evidenced. Thus, in order to evidence possible effects due to the presence of ruthenium in the place of iron, the reaction of the diruthenium complex **7** with  $\text{NBu}_4\text{CN}$  has been investigated. The result is the quantitative formation of the cyano-functionalized allylidene complex **8**, analogous to **3e** (Scheme 4).



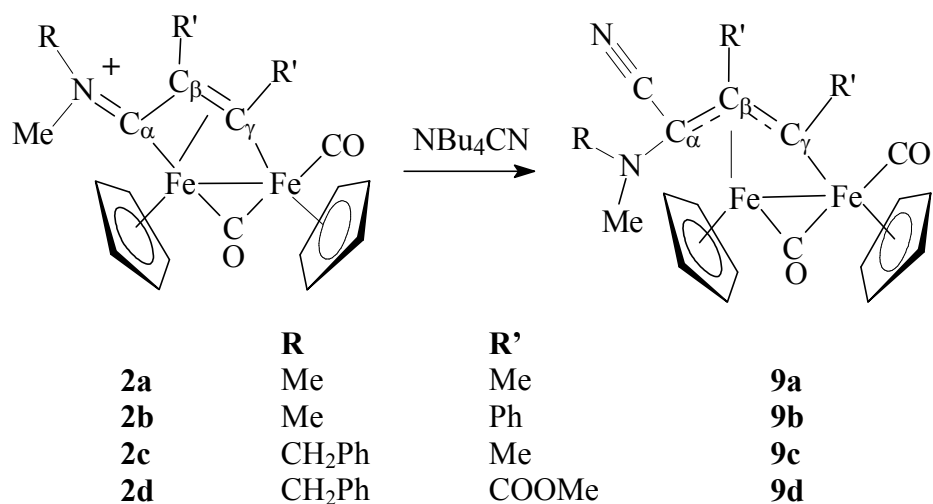
**Scheme 4.**

Therefore ruthenium does not produce any noticeable difference in the reactivity of the bridging ligand. The spectroscopic data of **8** are similar to those of the diiron counterpart **3e**. Moreover, the reaction has also been performed with  $^{13}\text{C}$ -enriched cyanide (by using a 10:1 mixture of  $\text{NBu}_4\text{CN}$  and  $\text{K}^{13}\text{CN}$ , 99%  $^{13}\text{C}$ , from Aldrich). The corresponding reaction product **8** has evidenced, in the  $^{13}\text{C}$  NMR spectrum, an intense resonance at 121.9 ppm ( $\text{C}_\alpha\text{-CN}$ ), and a doublet at  $\delta$  67.9 ppm ( $^1J_{\text{CC}} = 63.3$  Hz,  $\text{C}_\alpha$ ), indicating that addition occurs selectively at the iminium carbon ( $\text{C}_\alpha$ ).

## 2.2 Cyanide addition to disubstituted vinyliminium complexes in the absence of $\text{C}_\beta\text{-H}$

Compounds **2a-d** rapidly react with a slight excess of  $(\text{NBu}_4)(\text{CN})$ , in  $\text{CH}_2\text{Cl}_2$  solution, affording the bridging cyano-functionalized allylidene complexes  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')C(R')C(CN)N(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$  (**9a-d**), in about 80-90% yields (Scheme 5).





**Scheme 5.**

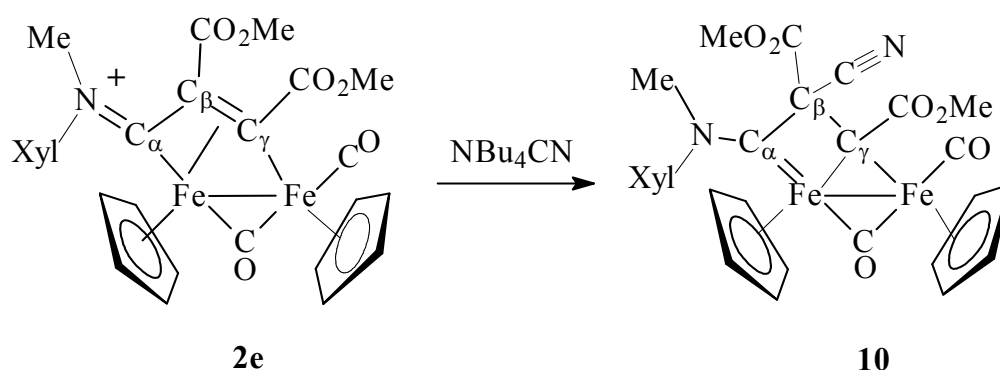
The structure of **9a** has been determined by X-ray diffraction: the ORTEP molecular diagram is shown in Figure 3 and relevant bond lengths and angles are reported in Table 1. The molecular geometry is similar to that of **3a** discussed above. The presence of a methyl substituent at C<sub>β</sub> [C(4)-C(7)] has not influenced the configuration around C<sub>α</sub> [C(5)] and the CN group is oriented *syn* with respect to C<sub>β</sub>-Me. The bond parameters of interest are strictly equivalent to the corresponding ones in **3a**. It is worth noting that also the NMe<sub>2</sub> group is oriented as in **3a**.

The spectroscopic data for **9a-b** are very similar to those of **3a-e**. Again, for **9a-b** the NMR data indicate the presence of a single isomer and the non-equivalence of the two N-bonded methyl groups, whereas two isomers are observed in solution, for the complexes **9c-d**.

The addition of cyanide at the iminium carbon of **2a-d** is in accord with the observation that, in the absence of steric protection offered by the Xyl group, nucleophilic attack occurs selectively at the iminium carbon (C<sub>α</sub>). Conversely, the complexes [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(R')=C(R')C=N(Me)(Xyl)}(μ-CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (R' = Me, **2f**; R' = Et, **2g**; R' = Ph, **2h**), containing the Xyl substituent, do not react with CN<sup>-</sup>. In this case, the iminium carbon is not accessible, neither deprotonation can occur, because of the absence of acidic C<sub>β</sub>-H. An exception among these unreactive vinyliminium complexes is represented by [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(COOMe)=C(COOMe)C=N(Me)(Xyl)}(μ-CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**2e**). Indeed, the latter compound reacts with NBu<sub>4</sub>CN, in CH<sub>2</sub>Cl<sub>2</sub> solution, yielding the cyano-functionalized bis-alkylidene complex **10** (Scheme 6). Compound **10**, fully characterized by spectroscopy and elemental analysis, is the result of selective cyanide addition at the C<sub>β</sub> position and

consequent adjustment of the coordination mode of the bridging ligand, which remains connected to the Fe atoms through the  $C_\alpha$  and  $C_\gamma$  carbons. Both carbons exhibit carbene character: the former is an amino carbene ligand, terminally coordinated, whereas the latter is a bridging alkylidene. This bis-alkylidene coordination mode appears very stable and has been previously found upon hydride addition at  $C_\beta$  [3] or rearrangements promoted by  $C_\beta$ -H proton removal [4] in  $\mu$ -vinyliminium complexes.

An explanation of the higher reactivity of **2e**, compared to **2f-h**, is related to the electron-withdrawing substituents (COOMe) at both  $C_\beta$  and  $C_\gamma$ .



**Scheme 6.**

The infrared spectrum of **10** (in  $\text{CH}_2\text{Cl}_2$  solution) exhibits the usual pattern consisting of two strong absorptions for terminal and bridging carbonyls ( $1947$ ,  $1777\text{ cm}^{-1}$ ), and, in addition, absorptions attributable to  $\text{C}\equiv\text{N}$  (at  $2175\text{ cm}^{-1}$ ) and to the carboxylate (at  $1733$  and  $1683\text{ cm}^{-1}$ ). The NMR spectra show only one isomer, indicating that the addition is stereo- and regio-selective; the  $^{13}\text{C}$  NMR spectrum exhibits the resonances relative to  $C_\alpha$ ,  $C_\beta$  and  $C_\gamma$  in the typical regions for an aminocarbene ( $\delta\ 252.7\text{ ppm}$ ), a quaternary  $\text{sp}^3$  carbon ( $81.5\text{ ppm}$ ) and a bridging alkylidene bound to a carboxylate ( $129.4\text{ ppm}$ ), respectively.

Labelling experiments with  $^{13}\text{C}$ -enriched  $\text{CN}^-$  confirms that cyanide addition occurs selectively at  $C_\beta$ : the  $^{13}\text{C}$  NMR spectrum of the  $^{13}\text{C}$  labelled product **10** displays doublets at  $\delta\ 129.4\text{ ppm}$  ( $^2J_{\text{CC}} = 5.0\text{ Hz}$ ,  $C_\gamma$ ) and  $81.5\text{ ppm}$  ( $^1J_{\text{CC}} = 67.2\text{ Hz}$ ,  $C_\beta$ ), and an intense singlet at  $116.5\text{ ppm}$  ( $C_\beta\text{-CN}$ ).

Since the  $C_\alpha\text{N}(\text{Me})(\text{Xyl})$  moiety in **10** shows aminocarbene character, free rotation around the  $C_\alpha\text{-N}$  bond is not allowed, due to its partial double bond character. Two isomers could consequently arise, according to the orientations of the Me and Xyl substituents. Since

only one isomer is observed, we assume that this is the one with the *NMe* group pointing toward the  $C_\beta$  substituent. This conformation is suggested by NOE experiments, which evidence enhancement only of one methyl group of the Xyl substituent (at 2.12 ppm) upon irradiation of the Cp resonance at 4.19 ppm. A similar geometry has been previously observed in the X-ray structure of the related bis-alkylidene complex  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}(\text{Et})\text{C}(\text{Et})(\text{H})\text{CN}(\text{Me})(\text{Xyl})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$  [3b].

Although no structural investigation has been carried out on complex **10**, it is likely that the addition of  $\text{CN}^-$ , which generates a stereogenic centre at  $C_\beta$ , is completely stereoselective and occurs in the side opposite to the Cp ligands, as previously observed for the addition of hydride to similar complexes [3].

### 3. Conclusions

Diiron vinyliminium complexes undergo regio- and stereo-specific additions by cyanide ion, under mild conditions. In the absence of steric hindrance at the iminium moiety, the addition occurs at the iminium carbon ( $C_\alpha$ ), affording novel bridging cyano-functionalized allylidene complexes. The reaction is not influenced by the nature of the substituent at  $C_\beta$ , neither by the presence of ruthenium in place of iron. Conversely, the xylyl substituent at the iminium nitrogen acts as a protecting group and inhibits  $\text{CN}^-$  addition to  $C_\alpha$ . Different outcomes are consequently observed: in the presence of  $C_\beta\text{-H}$  hydrogen, the cyanide ion promotes deprotonation; otherwise, the vinyliminium is simply unreactive, unless activated by the presence of electron-withdrawing substituents. In the latter case,  $\text{CN}^-$  addition occurs selectively at  $C_\beta$ , affording a cyano-functionalized bis-alkylidene complex.

## 4. Experimental details

### 4.1. 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. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). 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. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for  $^1\text{H}$  and  $^{13}\text{C}$  were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and  $^1\text{H}$ ,  $^{13}\text{C}$  correlation through gs-HSQC and gs-HMBC experiments [9]. All NMR spectra were recorded at 298 K; NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. NOE measurements were recorded using the DPFGE-NOE sequence [10]. All the reagents were commercial products (Aldrich Co.) of the highest purity available and used as received, except for complexes **1a-h**, **2a-e**, and **7**, which were prepared by published methods [2,6].

4.2. Synthesis of  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\gamma(\text{R}')\text{C}_\beta(\text{H})\text{C}_\alpha(\text{CN})\text{N}(\text{Me})(\text{R})\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$  ( $\text{R} = \text{Me}$ ,  $\text{R}' = \text{SiMe}_3$ , **3a**;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{CH}_2\text{OH}$ , **3b**;  $\text{R} = \text{CH}_2\text{Ph}$ ,  $\text{R}' = \text{Tol}$ , **3c**;  $\text{R} = \text{CH}_2\text{Ph}$ ,  $\text{R}' = \text{COOMe}$ , **3d**;  $\text{R} = \text{CH}_2\text{Ph}$ ,  $\text{R}' = \text{SiMe}_3$ , **3e**)

A solution of **1a** (95 mg, 0.158 mmol), in  $\text{CH}_2\text{Cl}_2$  (10 mL), was treated with  $\text{NBu}_4\text{CN}$  (64 mg, 0.239 mmol). After stirring at room temperature for 20 min, the mixture was filtered on alumina. Solvent removal, under reduced pressure, afforded **3a** as a brown microcrystalline powder. Yield: 64 mg, 91%. Crystals suitable for X ray analysis were collected by layering a  $\text{CH}_2\text{Cl}_2$  solution of **3a** with petroleum ether, at  $-20^\circ\text{C}$ . Anal. Calc. for  $\text{C}_{21}\text{H}_{26}\text{Fe}_2\text{N}_2\text{O}_2\text{Si}$ : C, 52.74 %; H, 5.48 %; N, 5.86 %. Found: C, 52.80 %; H, 5.44 %; N, 5.98 %. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{C}\equiv\text{N})$  2188 (m),  $\nu(\text{CO})$  1969 (vs), 1787 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 4.94, 4.49 (s, 10 H, Cp); 4.74 (s, 1 H,  $\text{C}_\beta\text{H}$ ); 2.32, 1.71 (s, 6 H, NMe); 0.63 (s, 9 H,  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  264.9 ( $\mu\text{-CO}$ ); 212.2 (CO); 194.5 ( $\text{C}_\gamma$ ); 121.1 (CN); 87.4, 84.6 (Cp); 86.5 ( $\text{C}_\beta$ ); 67.6 ( $\text{C}_\alpha$ ); 49.8, 42.2 (NMe); 3.6 ( $\text{SiMe}_3$ ).

Compounds **3b-e** were obtained by the same procedure described for **3a**, by reacting  $\text{NBu}_4\text{CN}$  with **1b-e**, respectively.

**3b**: Yield: 81%. Anal. Calcd. for  $\text{C}_{19}\text{H}_{20}\text{Fe}_2\text{N}_2\text{O}_3$ : C, 52.33 %; H, 4.62 %; N, 6.42 %. Found: C, 52.27 %; H, 4.71 %; N, 6.33 %. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{C}\equiv\text{N})$  2190 (m),  $\nu(\text{CO})$  1967 (vs), 1790 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 5.94 (m, 2 H,  $\text{CH}_2\text{OH}$ ); 5.05 (s, 1 H,  $\text{C}_\beta\text{H}$ ); 4.89, 4.49 (s, 10 H, Cp); 2.29, 1.73 (s, 6 H, NMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  264.2 ( $\mu\text{-CO}$ ); 212.8 (CO); 200.3 ( $\text{C}_\gamma$ ); 121.0 (CN); 87.4, 85.6 (Cp); 49.3, 44.1 (NMe).

**3c**: Yield: 78%. Anal. Calcd. for  $\text{C}_{31}\text{H}_{28}\text{Fe}_2\text{N}_2\text{O}_2$ : C, 65.06 %; H, 4.93 %; N, 4.90 %. Found: C, 65.05 %; H, 4.97 %; N, 4.81 %. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{C}\equiv\text{N})$  2189 (m),  $\nu(\text{CO})$  1972 (vs), 1784 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.55-7.18 (m, 9 H,  $\text{C}_6\text{H}_4\text{Me}$  and Ph); 4.73, 4.71, 4.65, 4.62 (s, 10 H, Cp); 4.71, 3.29 (d, 2 H,  $^2J_{\text{HH}} = 13$  Hz,  $\text{CH}_2\text{Ph}$ ); 4.47 (s, 1 H,  $\text{C}_\beta\text{H}$ ); 2.47, 2.43 (s, 3 H,  $\text{C}_6\text{H}_4\text{Me}$ ); 2.20, 1.70 (s, 3H, NMe); isomer ratio 7:1.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  264.6 ( $\mu\text{-CO}$ ); 213.3, 212.0 (CO); 200.9 ( $\text{C}_\gamma$ ); 156.1 (ipso- $\text{C}_6\text{H}_4\text{Me}$ ); 135.4-126.8 ( $\text{C}_6\text{H}_4\text{Me}$  and Ph); 121.1, 121.0 (CN); 89.4, 86.3, 86.1 (Cp); 81.6 ( $\text{C}_\beta$ ); 65.7 ( $\text{C}_\alpha$ ); 64.8, 59.8 ( $\text{CH}_2\text{Ph}$ ); 46.4, 39.8 (NMe); 21.1 ( $\text{C}_6\text{H}_4\text{Me}$ ).

**3d**: Yield: 82%. Anal. Calcd. for  $\text{C}_{26}\text{H}_{24}\text{Fe}_2\text{N}_2\text{O}_4$ : C, 57.81 %; H, 4.48 %; N, 5.19 %. Found: C, 57.93 %; H, 4.50 %; N, 5.23 %. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{C}\equiv\text{N})$  2191 (w),  $\nu(\text{CO})$  1982 (vs), 1795 (s), 1704 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.29-7.09 (m, 5 H, Ph); 4.90, 4.84, 4.71, 4.61 (s, 10 H, Cp); 4.86 (s, 1 H,  $\text{C}_\beta\text{H}$ ); 4.51, 3.24, 3.07, 2.95 (d, 2 H,  $^2J_{\text{HH}} = 12$  Hz,  $\text{CH}_2\text{Ph}$ ); 4.09, 4.05 (s, 3 H,  $\text{CO}_2\text{Me}$ ); 2.31, 1.60 (s, 3 H, NMe); isomer ratio 5:1.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  262.4, 260.7 ( $\mu\text{-CO}$ ); 211.2, 210.9 (CO); 180.8, 180.7 ( $\text{C}_\gamma$  and  $\text{CO}_2\text{Me}$ ); 137.2, 129.9, 127.8, 126.9 (Ph); 120.8 (CN); 88.3, 88.3, 87.1, 86.8 (Cp); 80.6 ( $\text{C}_\beta$ ); 64.7 ( $\text{C}_\alpha$ ); 59.7 ( $\text{CH}_2\text{Ph}$ ); 52.4, 52.2 ( $\text{CO}_2\text{Me}$ ); 46.1, 38.6 (NMe).

**3e**: Yield: 93%. Anal. Calcd. for  $\text{C}_{27}\text{H}_{30}\text{Fe}_2\text{N}_2\text{O}_2\text{Si}$ : C, 58.50 %; H, 5.46 %; N, 5.05 %. Found: C, 58.60 %; H, 5.55 %; N, 4.87 %. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{C}\equiv\text{N})$  2188 (m),  $\nu(\text{CO})$  1972 (vs), 1785 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.32-7.08 (m, 5 H, Ph); 5.03, 4.97, 4.57, 4.50 (s, 10 H, Cp); 4.78 (s, 1 H,  $\text{C}_\beta\text{H}$ ); 4.66, 3.26 (d, 2 H,  $^2J_{\text{HH}} = 13$  Hz,  $\text{CH}_2\text{Ph}$ ); 2.43, 1.63 (s, 3 H, NMe); 0.68, 0.58 (s, 9 H,  $\text{SiMe}_3$ ); isomer ratio 5:1.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  264.6 ( $\mu\text{-CO}$ ); 213.1, 211.9 (CO); 195.4, 194.3 ( $\text{C}_\gamma$ ); 138.0, 130.6, 129.3, 127.8, 126.6 (Ph); 121.5 (CN); 87.6, 87.5, 86.2, 84.8 (Cp); 85.0 ( $\text{C}_\beta$ ); 68.1 ( $\text{C}_\alpha$ ); 64.9, 59.9 ( $\text{CH}_2\text{Ph}$ ); 46.5, 40.1 (NMe); 3.6, 3.5 ( $\text{SiMe}_3$ ).

#### 4.3. Synthesis of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(p\text{-C}_6\text{H}_4\text{CF}_3)\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$

CN(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>) (1.00 g, 5.85 mmol) was added to a solution of [Fe<sub>2</sub>(Cp)<sub>2</sub>(CO)<sub>4</sub>] (3.11 g, 8.79 mmol) in MeCN (100 mL), and the mixture was heated at reflux temperature for 24 hours. Then, the solvent was removed under reduced pressure and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). Hence, CH<sub>3</sub>SO<sub>3</sub>CF<sub>3</sub> (0.7 mL, 6.2 mmol) was added, and the mixture was stirred for 5 hours. The resulting solution reduced in volume and treated with and diethyl ether (200 mL). A dark red precipitate, corresponding to [Fe<sub>2</sub>{μ-CN(Me)(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>], was isolated. Yield: 1.74 g, 45%. Anal. Calc. for C<sub>23</sub>H<sub>17</sub>F<sub>6</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 41.78 %; H, 2.59 %; N, 2.12 %. Found: C, 41.69 %; H, 2.44 %; N, 2.16 %. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(CO) 2024 (vs), 1994 (s), 1840 (s), ν(μ-CN) 1539 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.02-7.67 (m, 4 H, C<sub>6</sub>H<sub>4</sub>); 5.45, 4.74 (s, 10 H, Cp); 4.55 (s, 3 H, NMe). <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 326.4 (μ-C); 252.8 (μ-CO); 208.5, 207.2 (CO); 152.5 (ipso-C<sub>6</sub>H<sub>4</sub>); 127.7, 126.1 (C<sub>6</sub>H<sub>4</sub>); 90.4, 90.0 (Cp); 57.2 (NMe). <sup>19</sup>F {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ -63.0 (s, 3 F, *p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); -78.5 (s, 3 F, CF<sub>3</sub>SO<sub>3</sub>).

#### 4.4. Synthesis of [Fe<sub>2</sub>{μ-CN(Me)(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}(μ-CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>]

A solution of [Fe<sub>2</sub>{μ-CN(Me)(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}(μ-CO)(CO)<sub>2</sub>(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (300 mg, 0.453 mmol), in MeCN (20 mL), was treated with Me<sub>3</sub>NO (44 mg, 0.587 mmol), and the resulting mixture was stirred for 30 minutes. Then, the solvent was removed under reduced pressure, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and filtered through a celite pad. Removal of the solvent gave a brown powder. Yield: 275 mg (90 %). Anal. Calc. for C<sub>24</sub>H<sub>20</sub>F<sub>6</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S: C, 42.76 %; H, 2.99 %; N, 4.16 %. Found: C, 42.81 %; H, 3.04 %; N, 4.05 %. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(CO) 1985 (vs), 1819 (s), ν(μ-CN) 1524 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.93-7.66 (m, 4 H, C<sub>6</sub>H<sub>4</sub>); 5.07, 4.75, 4.39, 4.22 (s, 10 H, Cp); 4.87, 4.57 (s, 3 H, NMe); 1.98 (s, 3 H, NCMe). α/β ratio 3:2. <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 337.9, 337.6 (μ-C); 264.6, 264.4 (μ-CO); 211.5, 210.5 (CO); 153.0, 152.5 (ipso-C<sub>6</sub>H<sub>4</sub>); 130.5, 130.1 (NCMe); 127.5, 127.3, 126.4 (C<sub>6</sub>H<sub>4</sub>); 88.8, 88.3, 87.3, 86.7 (Cp); 56.3, 55.6 (NMe); 4.00 (NCMe). <sup>19</sup>F {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) -62.7, -62.8 (s, 3 F, *p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); -78.5 (s, 3 F, CF<sub>3</sub>SO<sub>3</sub>).

#### 4.5. Synthesis of [Fe<sub>2</sub>{μ-η<sup>1</sup>: η<sup>3</sup>-C<sub>7</sub>(Tol)=C<sub>β</sub>HC<sub>α</sub>=N(Me)(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}(μ-CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (4)

Compound [Fe<sub>2</sub>{μ-CN(Me)(*p*-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}(μ-CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (200 mg, 0.297 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (25 mL), treated with HC≡CTol (0.33 mmol) and heated at boiling temperature for 4 hours. Solvent removal and chromatography of the residue

on an alumina column, with MeOH as eluent, gave a brown band corresponding to **4**. Yield: 156 mg (70 %). Anal. Calc. for C<sub>31</sub>H<sub>25</sub>F<sub>6</sub>Fe<sub>2</sub>NO<sub>5</sub>S: C, 49.69 %; H, 3.36 %; N, 1.87 %. Found: C, 49.78 %; H, 3.45 %; N, 1.79 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO) 1992 (vs), 1813 (s),  $\nu$ (C <sub>$\alpha$</sub> N) 1607 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.84-7.26 (m, 8 H, C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>Me); 5.26, 5.02, 4.94, 4.85 (s, 10 H, Cp); 4.38 (s, 1 H, C <sub>$\beta$</sub> H); 4.30, 3.69 (s, 3 H, NMe); 2.37 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me). Z/E ratio 4:3. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  255.5, 254.2 ( $\mu$ -CO); 231.6, 229.9 (C <sub>$\alpha$</sub> ); 209.5, 209.4 (CO); 207.5, 205.8 (C <sub>$\gamma$</sub> ); 153.3, 153.0 (ipso-C<sub>6</sub>H<sub>4</sub>Me); 148.1-122.5 (C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> + C<sub>6</sub>H<sub>4</sub>Me); 91.9, 91.5, 89.0, 88.5 (Cp); 56.1, 55.8 (C <sub>$\beta$</sub> ); 55.0, 52.3 (NMe); 20.9 (C<sub>6</sub>H<sub>4</sub>Me).

4.6. Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C <sub>$\gamma$</sub> (Tol)C <sub>$\beta$</sub> (H)=C <sub>$\alpha$</sub> (H)N(Me)(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>] (**5**)

Complex **4** (100 mg, 0.134 mmol) was dissolved in THF (10 mL) and treated with NaBH<sub>4</sub> (27 mg, 0.711 mmol). The mixture was stirred for 15 minutes. Then, the solvent was removed, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and filtered on alumina. salts. Complex **5** was obtained as an orange powder upon removal of the solvent. Yield: 64 mg (80 %). Anal. Calc. for C<sub>30</sub>H<sub>26</sub>F<sub>3</sub>Fe<sub>2</sub>NO<sub>2</sub>: C, 59.93 %; H, 4.36 %; N, 2.33 %. Found: C, 60.03 %; H, 4.41 %; N, 2.27 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (CO) 1958 (vs), 1777 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.76-7.32 (m, 8 H, C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>Me); 4.67 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 8.42 Hz, C <sub>$\beta$</sub> H); 4.51, 4.49 (s, 10 H, Cp); 2.80 (s, 3 H, NMe); 2.49 (s, 3 H, C<sub>6</sub>H<sub>4</sub>Me); 1.54 (d, 1 H, <sup>3</sup>J<sub>HH</sub> = 8.42 Hz, C <sub>$\alpha$</sub> H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  263.0 ( $\mu$ -CO); 214.9 (CO); 202.1 (C <sub>$\gamma$</sub> ); 157.7 (ipso-C<sub>6</sub>H<sub>4</sub>Me); 153.0 (ipso-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); 134.6-124.2 (C<sub>6</sub>H<sub>4</sub>Me); 88.9, 85.0 (Cp); 84.5 (C <sub>$\alpha$</sub> ); 74.5 (C <sub>$\beta$</sub> ); 49.5 (NMe); 21.1 (C<sub>6</sub>H<sub>4</sub>Me). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) -141.4 (s, 3 F, p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>).

4.7. Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C <sub>$\gamma$</sub> (Tol)C <sub>$\beta$</sub> (H)C <sub>$\alpha$</sub> (CN)N(Me)(p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>)}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>] (**6**)

A solution of **4** (90 mg, 0.120 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), was treated with NBu<sup>t</sup><sub>4</sub>CN (42 mg, 0.157 mmol), and the resulting mixture was stirred for 20 minutes. Then, the solution was filtered through an alumina pad. Complex **6** was obtained as an orange powder upon removal of the solvent. Yield: 275 mg (90 %). Anal. Calc. for C<sub>31</sub>H<sub>25</sub>F<sub>3</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 59.46 %; H, 4.02 %; N, 4.47 %. Found: C, 59.56 %; H, 4.08 %; N, 4.39 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu$ (C $\equiv$ N) 2195 (w),  $\nu$ (CO) 1972 (vs), 1788 (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.79-6.93 (m, 8 H, C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> and C<sub>6</sub>H<sub>4</sub>Me); 4.80, 4.79, 4.62, 4.61 (s, 10 H, Cp); 3.38 (s, 1 H, C <sub>$\beta$</sub> H); 3.19, 2.60 (s, 3 H, NMe); 2.49, 2.48

(s, 3 H, C<sub>6</sub>H<sub>4</sub>Me). Isomer ratio 1:1. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 260.1 (μ-CO); 212.8, 211.0 (CO); 202.1, 200.3 (C<sub>γ</sub>); 156.2 (ipso-C<sub>6</sub>H<sub>4</sub>Me); 153.6 (ipso-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>); 149.9-124.3 (C<sub>6</sub>H<sub>4</sub>Me and Ph); 123.0, 122.8 (CN); 117.9, 115.8 (C<sub>β</sub>); 90.0, 86.5, 86.4 (Cp); 86.6, 85.8 (C<sub>α</sub>); 48.1, 42.5 (NMe); 21.1 (C<sub>6</sub>H<sub>4</sub>Me). <sup>19</sup>F{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) -61.6, -61.8 (s, 3 F, p-C<sub>6</sub>H<sub>4</sub>CF<sub>3</sub>).

#### 4.8. Synthesis of [Ru<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C<sub>γ</sub>(SiMe<sub>3</sub>)C<sub>β</sub>(H)C<sub>α</sub>(CN)N(Me)(CH<sub>2</sub>Ph)}(μ-CO)(CO)(Cp)<sub>2</sub>] (**8**)

NBu<sup>n</sup><sub>4</sub>CN (40.0 mg, 0.149 mmol) was added to a solution of **7** (64 mg, 0.083 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and the solution stirred for 20 min. Solvent removal and chromatography on an alumina column, with CH<sub>2</sub>Cl<sub>2</sub> as eluent, gave **8** as an orange fraction. Yield: 47 mg (88%). Anal. Calc. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>2</sub>Ru<sub>2</sub>Si: C, 50.30 %; H, 4.69 %; N, 4.34 %. Found: C, 50.59 %; H, 4.87 %; N, 4.21 %. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(C≡N) 2189 (m), ν(CO) 1971 (vs), 1786 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.01-7.30 (m, 5 H, Ph); 5.34, 4.90 (s, 10 H, Cp); 4.83 (s, 1 H, C<sub>β</sub>H); 4.39, 3.21 (d, 2 H, <sup>2</sup>J<sub>HH</sub> = 12.6 Hz, CH<sub>2</sub>Ph); 1.88 (s, 3 H, NMe); 0.30 (s, 9 H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 237.3 (μ-CO); 200.5 (CO); 176.6 (C<sub>γ</sub>); 137.9 (ipso-Ph); 129.9, 127.8, 126.8 (Ph); 122.0 (CN); 89.2, 86.8 (Cp); 84.4 (C<sub>β</sub>); 67.9 (C<sub>α</sub>); 60.5 (CH<sub>2</sub>Ph); 45.9 (NMe); 3.1 (SiMe<sub>3</sub>). A <sup>13</sup>C-enriched sample on the CN position was obtained using the same procedure as above, where a solution of K<sup>13</sup>CN (10.0 mg, 0.150 mmol) and NBu<sup>n</sup><sub>4</sub>CN (20.0 mg, 0.075 mmol) in CH<sub>3</sub>CN/MeOH (3 + 3 mL) was used instead of solid NBu<sup>n</sup><sub>4</sub>CN. Purification was the same as above. Spectroscopic data are given only for the enriched part of the sample. IR (CH<sub>2</sub>Cl<sub>2</sub>) ν(<sup>13</sup>CN) 2139 (m), ν(CO) 1972 (vs), 1786 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.01-7.30 (m, 5 H, Ph); 5.34, 4.90 (s, 10 H, Cp); 4.83 (d, 1 H, <sup>3</sup>J<sub>CH</sub> = 4.6 Hz, C<sub>β</sub>H); 4.39, 3.21 (d, 2 H, <sup>2</sup>J<sub>HH</sub> = 12.6 Hz, CH<sub>2</sub>Ph); 1.88 (s, 3 H, NMe); 0.30 (s, 9 H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 237.29 (μ-CO); 200.5 (CO); 176.6 (d, <sup>3</sup>J<sub>CC</sub> = 5.1 Hz, C<sub>γ</sub>); 137.9 (ipso-Ph); 129.9, 127.8, 126.8 (Ph); 121.9 (CN); 89.2, 86.8 (Cp); 84.4 (d, <sup>2</sup>J<sub>CC</sub> = 5.1 Hz, C<sub>β</sub>); 67.9 (d, <sup>1</sup>J<sub>CC</sub> = 63.3 Hz, C<sub>α</sub>); 60.4 (CH<sub>2</sub>Ph); 45.9 (NMe); 3.0 (SiMe<sub>3</sub>).

#### 4.9. Synthesis of [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C<sub>γ</sub>(R')C<sub>β</sub>(R')C<sub>α</sub>(CN)N(Me)(R)}(μ-CO)(CO)(Cp)<sub>2</sub>] (R = Me, R' = Me, **9a**; R = Me, R' = Ph, **9b**; R = CH<sub>2</sub>Ph, R' = Me, **9c**; R = CH<sub>2</sub>Ph, R' = COOMe, **9d**)

A solution of **2a** (90 mg, 0.162 mmol), in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), was treated at room temperature with NBu<sup>n</sup><sub>4</sub>CN (68 mg, 0.254 mmol). The mixture was stirred for 20 min, then it was filtered on alumina. Solvent removal, under reduced pressure, gave **2a** as microcrystalline powder. Yield: 64 mg (91%). Crystals suitable for X ray analysis were collected by layering



a diethyl ether solution of **9a** with petroleum ether (b.p. 40-60 °C), at -20°C. Anal. Calcd. for C<sub>20</sub>H<sub>22</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 55.34 %; H, 5.11 %; N, 6.45 %. Found: C, 55.39; H, 5.08 %; N, 6.49 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu(\text{C}\equiv\text{N})$  2184 (m),  $\nu(\text{CO})$  1956 (vs), 1781 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.85, 4.38 (s, 10 H, Cp); 3.80 (s, 3 H, C<sub>γ</sub>Me); 2.22 (s, 3 H, C<sub>β</sub>Me); 2.12, 1.60 (s, 6 H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  268.3 ( $\mu$ -CO); 213.3 (CO); 195.1 (C<sub>γ</sub>); 120.0 (CN); 88.9, 86.7 (Cp); 89.1 (C<sub>β</sub>); 64.0 (C<sub>α</sub>); 48.1, 41.2 (NMe); 39.3 (C<sub>γ</sub>Me); 22.3 (C<sub>β</sub>Me).

Complexes **9b-9d** were prepared by the same procedure described for **9a**, by reacting NBu<sup>n</sup><sub>4</sub>CN with **2b-d**, respectively.

**9b**: Yield: (85%). Anal. Calc. for C<sub>30</sub>H<sub>26</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 64.55 %; H, 4.69 %; N, 5.02 %. Found: C, 64.63 %; H, 4.74 %; N, 5.10 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu(\text{C}\equiv\text{N})$  2187 (m),  $\nu(\text{CO})$  1968 (vs), 1788 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) 7.96-6.63 (m, 10 H, Ph); 4.76, 4.53 (s, 10 H, Cp); 2.38, 2.03 (s, 6 H, NMe). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  265.3 ( $\mu$ -CO); 214.1 (CO); 197.9 (C<sub>γ</sub>); 158.3, 140.7, 133.2, 129.0, 128.3, 128.1, 127.6, 127.2, 124.7 (Ph); 120.1 (CN); 96.5 (C<sub>β</sub>); 91.3, 87.9 (Cp); 63.3 (C<sub>α</sub>); 50.3, 43.1 (NMe).

**9c** Yield: (77%). Anal. Calc. for C<sub>26</sub>H<sub>26</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: C, 61.21 %; H, 5.14 %; N, 5.49 %. Found: C, 61.15 %; H, 5.16 %; N, 5.50 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu(\text{C}\equiv\text{N})$  2183 (m),  $\nu(\text{CO})$  1965 (vs), 1779 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.27-7.04 (m, 5 H, Ph); 4.93, 4.89, 4.44, 4.35 (s, 10 H, Cp); 3.87, 3.76 (s, 3 H, C<sub>γ</sub>Me); 4.43, 3.10, 3.04, 2.94 (d, 2 H, <sup>2</sup>J<sub>HH</sub> = 12 Hz, CH<sub>2</sub>Ph); 2.26, 2.21 (s, 3 H, C<sub>β</sub>Me); 2.08, 1.51 (s, 3 H, NMe); Isomer ratio 6:5. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  269.1, 267.4 ( $\mu$ -CO); 214.2, 212.7 (CO); 196.5, 195.5 (C<sub>γ</sub>); 137.7-126.7 (Ph); 120.3 (CN); 89.2, 89.0, 87.2, 87.0 (Cp); 90.4, 88.4 (C<sub>β</sub>); 65.2, 64.6 (C<sub>α</sub>); 59.5 (CH<sub>2</sub>Ph); 45.1, 39.4 (NMe); 38.7 (C<sub>γ</sub>Me); 23.3, 22.5 (C<sub>β</sub>Me).

**9d** Yield: (80%). Anal. Calc. for C<sub>28</sub>H<sub>26</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub>: C, 56.22 %; H, 4.38 %; N, 4.68 %. Found: C, 56.30 %; H, 4.27 %; N, 4.72 %. IR (CH<sub>2</sub>Cl<sub>2</sub>)  $\nu(\text{C}\equiv\text{N})$  2191 (w),  $\nu(\text{CO})$  1987 (vs), 1801 (s), 1720 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 7.36-7.19 (m, 5 H, Ph); 4.93, 4.89, 4.79, 4.70 (s, 10 H, Cp); 4.35, 3.74, 3.64, 3.21 (d, 2 H, <sup>2</sup>J<sub>HH</sub> = 12Hz, CH<sub>2</sub>Ph); 4.04, 4.01, 3.91, 3.87 (s, 6 H, CO<sub>2</sub>Me); 2.07, 1.67 (s, 3 H, NMe); Isomer ratio 3:1. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  260.2 ( $\mu$ -CO); 211.8, 210.2 (CO); 186.0, 184.7, 179.1, 170.8 (C<sub>γ</sub> and CO<sub>2</sub>Me); 136.9-127.0 (Ph); 119.4, 119.2 (CN); 89.5, 89.2, 89.0, 88.6 (Cp); 88.1 (C<sub>β</sub>); 65.3, 59.2 (CH<sub>2</sub>Ph); 62.9 (C<sub>α</sub>); 53.2, 52.9, 52.4, 52.2 (CO<sub>2</sub>Me); 45.4, 36.9 (NMe).

#### 4.10. Synthesis of $[Fe_2\{\mu-\eta^1:\eta^2-C_\gamma(CO_2Me)C_\beta(CO_2Me)(CN)C_\alpha N(Me)(Xyl)\}(\mu-CO)(CO)(Cp)_2]$ (**10**)

A solution of  $[Fe_2\{\mu-\eta^1:\eta^3-C(COOMe)=C(COOMe)C=N(Me)(Xyl)\}(\mu-CO)(CO)(Cp)_2]$   $[SO_3CF_3]$ , **2e** (98 mg, 0.133 mmol), in  $CH_2Cl_2$  (10 mL), was treated at room temperature with  $NBu^n_4CN$  (43 mg, 0.160 mmol). The mixture was stirred for 30 min, then the solvent was removed under reduced pressure. A subsequent chromatography on alumina afforded a brown band corresponding to **10**. The product was stored at  $-20^\circ C$ . Yield: 59 mg (71%). Anal. Calc. for  $C_{29}H_{28}Fe_2N_2O_6$ : C, 56.89 %; H, 4.61 %; N, 4.58 %. Found: C, 56.77 %; H, 4.62 %; N, 4.53 %. IR ( $CH_2Cl_2$ )  $\nu(C\equiv N)$  2175 (w),  $\nu(CO)$  1947 (vs), 1777 (s), 1733 (m), 1683 (m)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ) 7.33-7.14 (m, 3 H,  $Me_2C_6H_3$ ); 4.69, 4.19 (s, 10 H, Cp); 3.95, 3.91 (s, 6 H,  $CO_2Me$ ); 3.36 (s, 3 H, NMe); 2.15, 2.12 (s, 6 H,  $Me_2C_6H_3$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ )  $\delta$  272.3 ( $\mu-CO$ ); 252.7 ( $C_\alpha$ ); 214.6 (CO); 182.3 ( $C_\gamma-CO_2Me$ ); 168.5 ( $C_\beta-CO_2Me$ ); 145.2 (ipso- $Me_2C_6H_3$ ); 134.1, 132.8, 129.7, 128.6, 128.3 ( $Me_2C_6H_3$ ); 129.4 ( $C_\gamma$ ); 116.5 ( $C_\beta CN$ ); 88.3, 87.6 (Cp); 81.5 ( $C_\beta$ ); 53.5, 50.9 ( $CO_2Me$ ); 44.9 (NMe); 18.1, 17.5 ( $Me_2C_6H_3$ ). A  $^{13}C$ -enriched sample on the CN position was obtained using the same procedure as above, where a solution of  $K^{13}CN$  (6.0 mg, 0.091 mmol) and  $NBu^n_4CN$  (23 mg, 0.086 mmol) in  $CH_3CN$  (4 mL) was used instead of solid  $NBu^n_4CN$ . Purification was the same as above. Spectroscopic data are given only for the enriched part of the sample. IR ( $CH_2Cl_2$ )  $\nu(^{13}C\equiv N)$  2090 (m),  $\nu(CO)$  1947 (vs), 1777 (s), 1733 (m), 1683 (m)  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ ) 7.33-7.14 (m, 3 H,  $Me_2C_6H_3$ ); 4.69, 4.19 (s, 10 H, Cp); 3.95, 3.91 (s, 6 H,  $CO_2Me$ ); 3.36 (s, 3 H, NMe); 2.15, 2.12 (s, 6 H,  $Me_2C_6H_3$ ).  $^{13}C\{^1H\}$  NMR ( $CDCl_3$ )  $\delta$  272.7 ( $\mu-CO$ ); 253.0 ( $C_\alpha$ ); 214.8 (CO); 182.5 ( $C_\gamma-CO_2Me$ ); 168.7 ( $C_\beta-CO_2Me$ ); 145.3 (ipso- $Me_2C_6H_3$ ); 134.2, 133.0, 129.8, 128.7, 128.4 ( $Me_2C_6H_3$ ); 129.4 (d,  $^2J_{CC} = 5.0$  Hz,  $C_\gamma$ ); 116.6 ( $C_\beta CN$ ); 88.3, 87.6 (Cp); 81.5 (d,  $^1J_{CC} = 67.2$  Hz,  $C_\beta$ ); 53.5, 50.9 ( $CO_2Me$ ); 44.8 (NMe); 18.0, 17.4 ( $Me_2C_6H_3$ ).

#### 4.11. X-ray Crystallography for **3a** and **9a**

The diffraction experiments were carried out at room temperature on a Bruker AXS SMART 2000 CCD based diffractometer using graphite monochromatic (??) Mo- $K\alpha$  radiation ( $\lambda=0.71073$  Å). Intensity data were measured over full diffraction sphere using  $0.3^\circ$  wide  $\omega$  scans. The software SMART [11] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by software SAINT [11] and an empirical absorption correction was applied

with SADABS [12]. The structures were solved by direct methods (SIR97) [13] and subsequent Fourier syntheses, and refined by full-matrix least-squares calculations on  $F^2$  (SHELXTL) [14] attributing anisotropic thermal parameters to all the non-hydrogen atoms. In complex **3a** the Cp ligand bound to Fe(1) was disordered over two positions and the site occupation factors were refined yielding the values 0.60 and 0.40, respectively whereas in complex **9a** both Cp ligands were disordered over two positions and their site occupation factors were refined yielding the values 0.73 and 0.27 for the Cp bound to Fe(1) [0.64 and 0.36 respectively for the Cp bound to Fe(2)]. The methyl and aromatic hydrogen atoms were placed in calculated positions and refined with idealized geometry, whereas the H atom bound to C(4) in **3a** was located in the Fourier map and refined isotropically. In order to be sure about the mode of bonding of **3a** and **9a**, structure models of alternative assignments of the carbon and nitrogen positions were refined (cyanide, isocyanide). The isocyanide models for the independent molecules in **3a** and **9a** showed worsening of the agreement indices and physically unreasonable thermal motion ellipsoids.

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#### **Appendix A. Supplementary Material**

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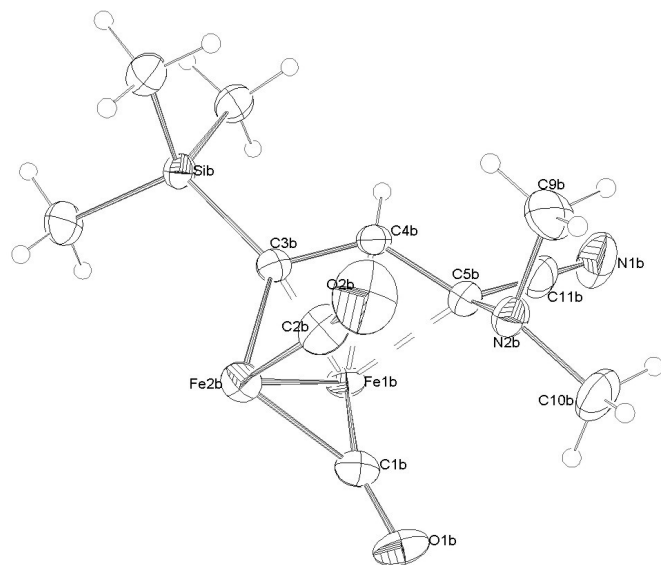
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## Figures

**Figure 1.** ORTEP drawing of  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{SiMe}_3)\text{C}(\text{H})\text{C}(\text{CN})\text{N}(\text{Me})_2\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ ,

**Figure 2.** ORTEP drawing of  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{Me})\text{C}(\text{Me})\text{C}(\text{CN})\text{N}(\text{Me})_2\}\{\mu\text{-CO}\}(\text{CO})(\text{Cp})_2]$ ,

3a



3b

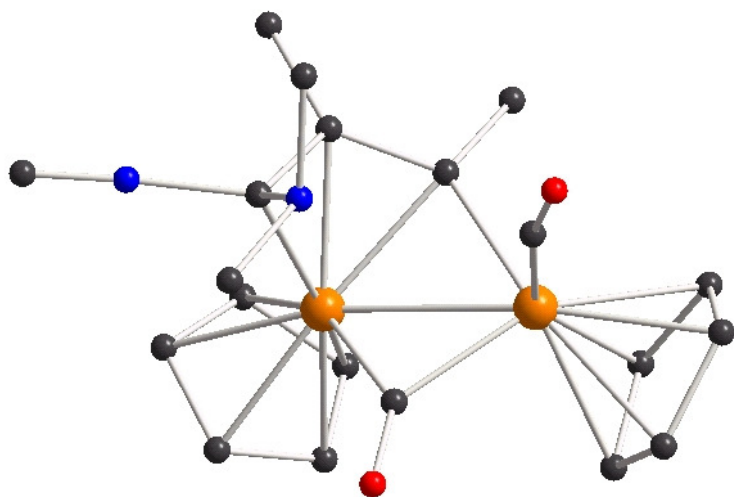


Table 1.

Selected bond lengths (Å) and angles (deg) for **3a** and **9a**.

	<b>3a</b> <sup>a</sup>	<b>9a</b>
Fe(1)-C(1)	1.910(2) [1.909(2)]	1.914(2)
Fe(1)-C(3)	2.045(2) [2.037(2)]	2.027(1)
Fe(1)-C(4)	2.012(2) [2.007(2)]	2.037(1)
Fe(1)-C(5)	2.068(2) [2.077(3)]	2.059(1)
Fe(2)-C(1)	1.935(2) [1.932(3)]	1.927(1)
Fe(2)-C(2)	1.742(2) [1.753(3)]	1.765(2)
Fe(2)-C(3)	1.969(2) [1.973(2)]	1.975(2)
Fe(1)-Fe(2)	2.5408(5) [2.5488(5)]	2.5327(3)
C(1)-O(1)	1.168(3) [1.176(3)]	1.173(2)
C(2)-O(2)	1.154(3) [1.150(3)]	1.143(2)
C(5)-N(1)	1.445(3) [1.431(3)]	1.437(2)
C(9)-N(1)	1.470(3) [1.461(3)]	1.469(2)
C(10)-N(1)	1.459(3) [1.463(3)]	1.462(2)
C(3)-C(4)	1.414(3) [1.419(3)]	1.418(2)
C(4)-C(5)	1.447(3) [1.449(3)]	1.469(2)
C(5)-C(11)/C(5)-C(8)	1.465(4) [1.470(4)]	1.467(2)
C(11)-N(2)/C(8)-N(2)	1.137(3) [1.133(4)]	1.143(2)
C(3)-Si	1.883(2) [1.886(2)]	-
N(2)-C(11)/N(2)-C(8)	1.137(3) [1.133(4)]	1.143(2)
Fe(1)-C(Cp)(av) <sup>b</sup>	2.082 [2.106]	2.102
Fe(2)-C(Cp)(av) <sup>b</sup>	2.138 [2.130]	2.114
Fe(1)-C(1)-O(1)	141.3(2) [140.0(2)]	140.9(1)
Fe(2)-C(1)-O(1)	135.4(2) [136.2(2)]	136.1(1)
C(3)-C(4)-C(5)	125.5(2) [125.5(2)]	119.2(1)
N(1)-C(5)-C(4)	122.1(2) [122.5(2)]	120.0(1)
C(5)-C(8)-N(2)	-	175.2(2)

C(5)-C(11)-N(2)	177.2(3) [178.0(4)]	-
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<sup>a</sup> Values in parentheses refer to the second conformer in the asymmetric unit.

<sup>b</sup> Main image of the Cp ligand.



**Table 2** Crystal data and experimental details for **3a** and **9a**.

Compound	<b>3a</b>	<b>9a</b>
Formula	C <sub>21</sub> H <sub>26</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>2</sub> Si	C <sub>20</sub> H <sub>22</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>2</sub>
<i>F</i> <sub>w</sub>	478.23	434.10
T, K	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal symmetry	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> , Å	10.5739(3)	7.9451(3)
<i>b</i> , Å	28.4979(8)	16.3339(7)
<i>c</i> , Å	15.2823(4)	14.3416(6)
α, °	90	90
β, °	109.319(1)	99.369(1)
γ, °	90	90
Cell volume, Å <sup>3</sup>	4345.8(2)	1836.4(1)
<i>Z</i>	8	4
D <sub>c</sub> , Mg m <sup>-3</sup>	1.462	1.596
μ(Mo-Kα), mm <sup>-1</sup>	1.409	1.596
F(000)	1984	896
Crystal size, mm	0.35x 0.30 x 0.28	0.30 x 0.28 x 0.25
θ limits, °	1.43-30.02	1.90-30.03
Reflections collected	56753(±h, ±k, ±l)	23289(±h, ±k, ±l)
Unique observed reflections [F <sub>o</sub> > 4σ(F <sub>o</sub> )]	12692[R(int) = 0.0652]	5364[R(int) = 0.0264]
Goodness-of-fit-on F <sup>2</sup>	0.934	1.034
R <sub>1</sub> (F) <sup>a</sup> , wR <sub>2</sub> (F <sup>2</sup> ) <sup>b</sup>	0.0419, 0.0964	0.0286, 0.0772
Largest diff. peak and hole, e. Å <sup>-3</sup>	0.504/ -0.471	0.270/ -0.485

<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