

New bridging ligands from methylation reactions of μ -vinyliminium diiron complexes

Vincenzo G. Albano,⁺⁺ Luigi Busetto,⁺ Fabio Marchetti,⁺ Magda Monari,⁺⁺ Stefano Zacchini⁺ and Valerio Zanutti.^{++*}

⁺*Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy*

⁺⁺*Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*

Abstract

The vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(R')C=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}][\text{SO}_3\text{CF}_3]$ ($\text{R} = \text{Me}$, $\text{R}' = \text{Et}$, **1a**; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$, **1b**; $\text{R} = \text{R}' = \text{Me}$, **1c**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Me}$, **1d**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Et}$, **1e**; $\text{R} = \text{Xyl}$, $\text{R}' = \text{Ph}$, **1f**; $\text{Xyl} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$), react with MeLi affording the corresponding μ -vinylalkylidene complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')C(R')=CHN(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}\}\{\text{C}_5\text{H}_4(\text{Me})\}\}]$ (**2a-f**). The formation of **2a-f** is believed to proceed *via* nucleophilic attack at the Cp ligand, followed by hydrogen migration from the resulting cyclopentadiene to the iminium carbon. Similarly, the complex $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Ph)=C(Ph)C=N(Me)(Xyl)}\}\{\mu\text{-CO(CO)(Cp)}_2\}][\text{SO}_3\text{CF}_3]$ reacts with PhLi to give $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Ph)C(Ph)=CHN(Me)(Xyl)}\}\{\mu\text{-CO(CO)(Cp)}\}\{\text{C}_5\text{H}_4(\text{Ph})\}\}]$ (**4**).

Treatment of **2a** with $\text{CF}_3\text{SO}_3\text{CH}_3$ results in methylation of the nitrogen, yielding the complex $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Et)C(Et)CH(NMe}_3)\}\{\mu\text{-CO(CO)(Cp)}\}\{\text{C}_5\text{H}_4(\text{Me})\}\}][\text{CF}_3\text{SO}_3]$ (**5**).

Analogously, the μ -vinylalkylidene complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')C(R'')=CHN(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}]$, ($\text{R} = \text{Me}$, $\text{R}' = \text{Tol}$, $\text{R}'' = \text{H}$, **3a**; $\text{R} = \text{Me}$, $\text{R}' = \text{SiMe}_3$, $\text{R}'' = \text{H}$, **3b**; $\text{R} = \text{Me}$, $\text{R}' = \text{R}'' = \text{Et}$, **3c**; $\text{R} = \text{Me}$, $\text{R}' = \text{R}'' = \text{Ph}$, **3d**; $\text{R} = \text{Bz}$, $\text{R}' = \text{Tol}$, $\text{R}'' = \text{H}$, **3e**; $\text{R} = \text{Bz}$, $\text{R}' = \text{SiMe}_3$, $\text{R}'' = \text{H}$, **3f**; $\text{R} = \text{Bz}$, $\text{R}' = \text{COOMe}$, $\text{R}'' = \text{H}$, **3g**; $\text{R} = \text{Bz}$, $\text{R}' = \text{R}'' = \text{COOMe}$, **3h**; $\text{R} = \text{Bz}$, $\text{R}' = \text{R}'' = \text{Me}$, **3i**; $\text{Bz} = \text{CH}_2\text{Ph}$), react with $\text{CF}_3\text{SO}_3\text{CH}_3$ to give the corresponding ammonium-functionalized μ -allylidene complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')C(R'')CH(NMe}_2\text{R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}][\text{CF}_3\text{SO}_3]$ (**6a-i**). The molecular structures of **5** and **6c** have been elucidated by X ray diffraction studies.

Finally, protonation of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Et)C(Et)=CH(NMe}_2\text{)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**3c**), with HBF_4 , affords the complex $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Et)C(Et)CH(NHMe}_2\text{)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{BF}_4]$ (**7**).

Keywords: vinyliminium, vinylalkylidene, enaminoalkylidene, aminocarbyne, diiron complexes, crystal structure

Corresponding author e-mail address: valerio.zanotti@unibo.it

1. Introduction

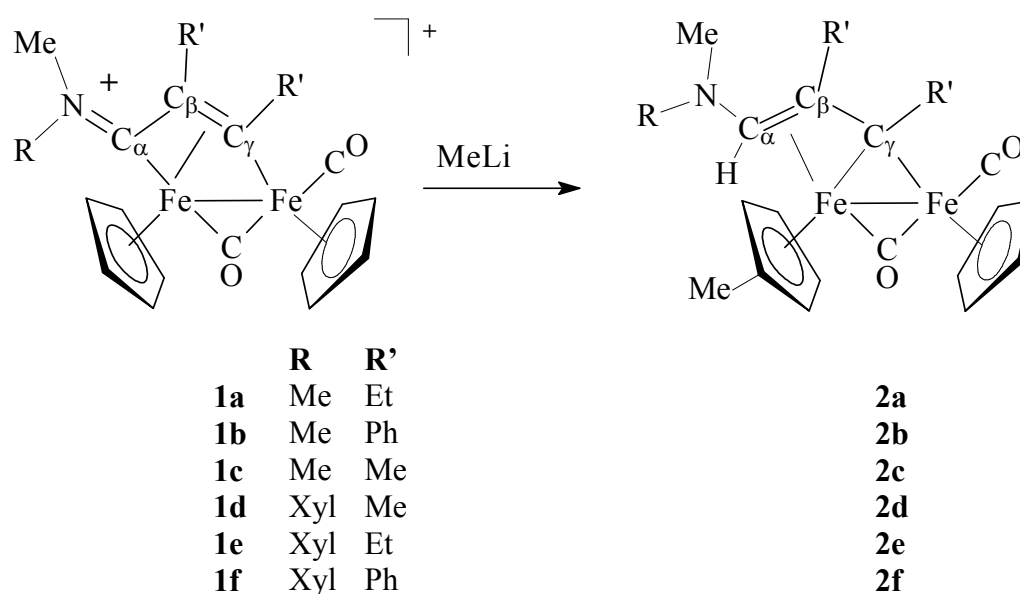
Binuclear complexes are potentially promoters of unique reactivity *via* bridging coordination and activation of organic fragments to two metal centers [1]. We have recently reported [2] on the synthesis and properties of a variety of bridging vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}_\gamma(\text{R}')=\text{C}_\beta(\text{R}'')\text{C}_\alpha=\text{N(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ ($\text{R} = \text{Me, Bz, Xyl}$), obtained by insertion of alkynes ($\text{R}'\text{C}\equiv\text{CR}''$) into the M-C bond of μ -aminocarbyne complexes $[\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$. The μ -vinyliminium ligands in the above complexes display electrophilic character, that can be exploited to generate new and reactive organic fragments stabilized through coordination to the metal centres [3]. In particular it has been shown that hydride addition, by using NaBH_4 , is selectively directed to the iminium carbon (C_α) or the adjacent C_β , depending upon the nature of the substituents at the iminium nitrogen. These reactions generate $\mu\text{-}\eta^1\text{:}\eta^3$ -vinylalkylidene, and $\mu\text{-}\eta^1\text{:}\eta^3$ -bis-alkylidene ligands, respectively [3a-b].

In the present paper, we report on the reactions of the μ -vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R}')=\text{C(R'')C=N(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (**1**) toward some organolithium reagents, and give details on the methylation of the N atom of the bridging ligand.

2. Results and discussion.

2.1. Reactions of vinyliminium complexes with lithium organyls.

The vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=C(R')C=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}][\text{SO}_3\text{CF}_3]$ (**1**), react with MeLi in THF solution at -40°C , affording the μ -vinylalkylidene $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')C(R')=CHN(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}\}\{\eta^5\text{-C}_5\text{H}_4(\text{Me})\}]$ (**2a-f**) (Scheme 1) as a result of a Cp ligand methylation and subsequent hydrogen migration to C_α . The species **2** have been isolated in about 60-70 % yields after chromatography on alumina.



Scheme 1.

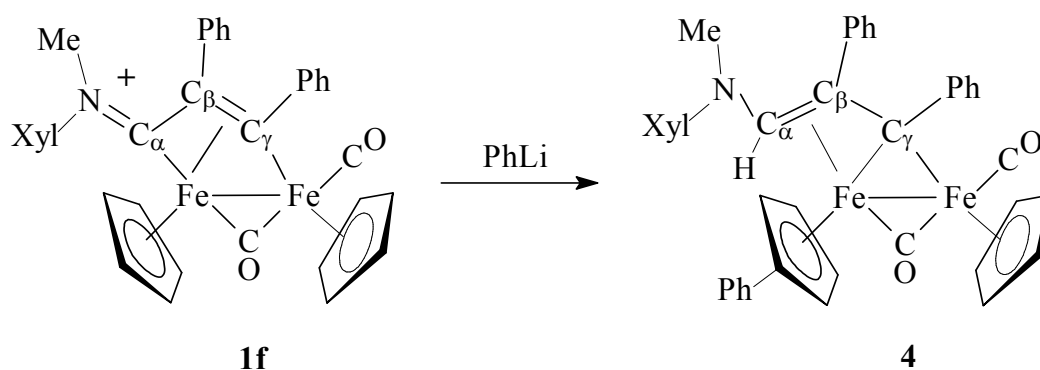
Compounds **2a-f** have been fully characterized by spectroscopy and elemental analysis. Their infrared spectra (in CH_2Cl_2 solution) exhibit absorptions for terminal and bridging carbonyls about 60 cm^{-1} lower than the parent cations **1** [2] (*e.g.* at 1930 and 1751 cm^{-1} for **2a**).

The ^1H NMR spectra of **2a-f** indicate the existence in solution of a single isomeric form. The main feature is the presence of five resonances, attributable to the cyclopentadienyls: one singlet accounts for five equivalent Cp protons (*e.g.* at $\delta\text{ 4.62 ppm}$ for **2a**), whereas four distinct broad resonances are attributable to the non-equivalent protons of

the MeC₅H₄ ring (*e.g.* at δ 4.69, 4.36, 4.13, 3.90 ppm for **2a**). The same pattern is shown by the ¹³C NMR spectra. Compounds **2a-f** closely resemble the μ -vinylalkylidene complexes [Fe₂{ μ - η^1 : η^3 -C(R')C(R')=CHN(Me)(R)}(μ -CO)(CO)(Cp)₂] (**3**), previously reported [3a-b], which have been obtained by direct hydride addition (by NaBH₄) to the iminium carbon (C $_{\alpha}$) of the corresponding parent vinyliminium complexes **1**. Their ¹H and ¹³C NMR resonances are consequently very similar.

NOE investigations have been carried out on **2f** in order to obtain more information on the nature of the complexes in solution. Irradiation of the Cp resonance at δ 4.23 ppm has resulted in strong enhancements of the resonances associated with the other ring (at δ 5.50, 5.34 and 3.76 ppm), indicating that the Cp ligands adopt *cis* arrangement. Moreover, a significant NOE effect has been found between Cp-*Me* and N-*Me*. This points out that the nucleophilic attack affects the Cp ring adjacent to the iminium group. Finally, it is noteworthy that irradiation of C $_{\alpha}$ -H has no effect on the phenyl resonances. Hence, H(C $_{\alpha}$) is *trans* to the substituent at C $_{\beta}$, coherently with what previously reported for the vinylalkylidene species **3** [3a-b].

The reaction described in Scheme 1 is not of general character: under the same conditions other RLi reagents (BuⁿLi, PhLi) failed to generate addition products. An exception is represented by the reaction of PhLi with **1f**, which afforded [Fe₂{ μ - η^1 : η^3 -C(Ph)C(Ph)=CHN(Me)(Xyl)}(μ -CO)(CO)(Cp){ η^5 -C₅H₄(Ph)}] (**4**), in modest yield (Scheme 2). Complex **4** has been identified *via* IR and NMR spectroscopy, and elemental analysis.

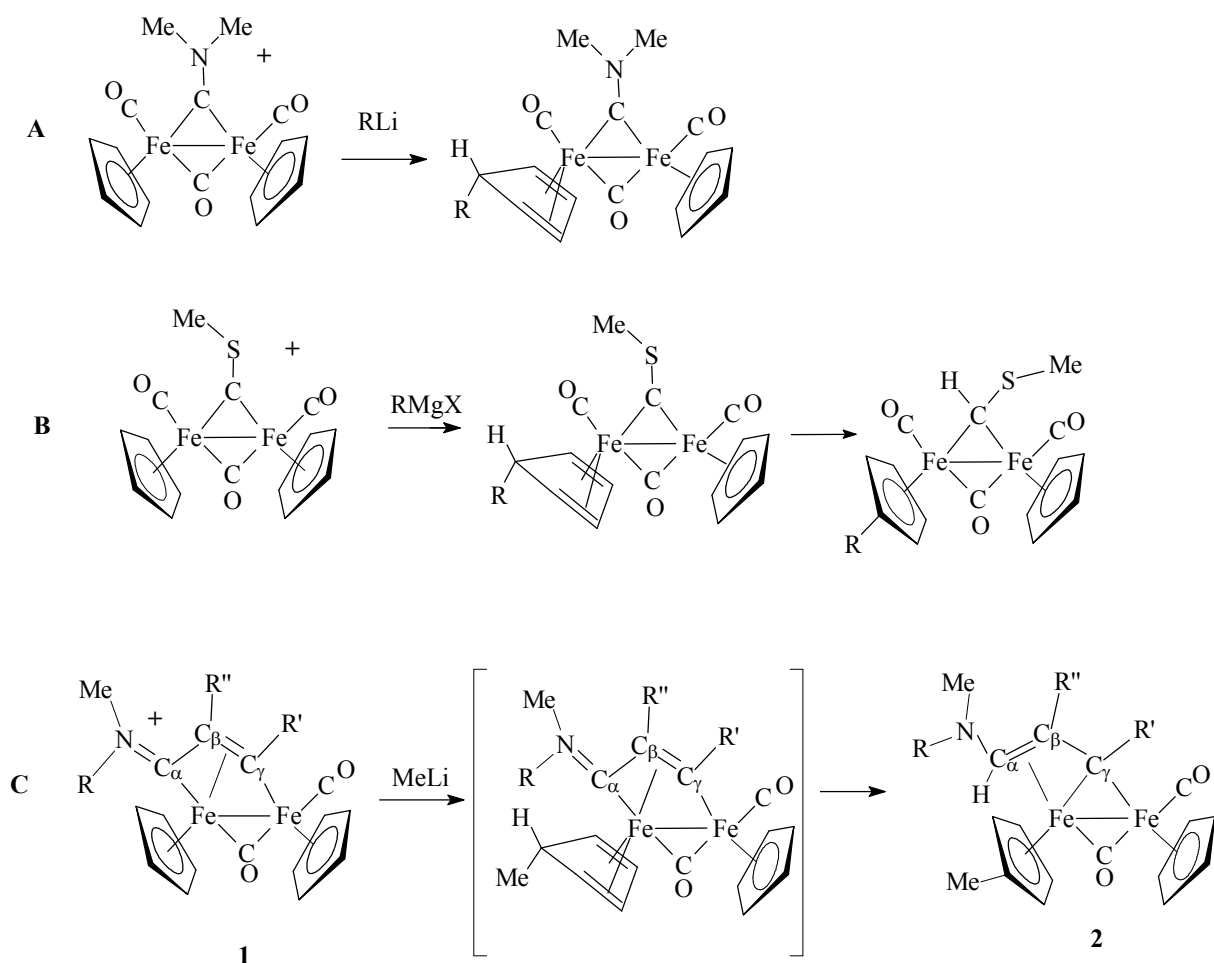


Scheme 2.

There are numerous examples of nucleophilic additions to η^5 -Cp ligands [4]. Powerful nucleophiles, as carbanions or H^- , are generally involved and the reactions usually afford stable η^4 cyclopentadiene complexes. In some cases nucleophilic addition at the Cp ring is followed by hydride abstraction or migration, resulting in Cp ring substitution [5].

The reactions of **1a-f** with MeLi are to be compared to those of the related diiron μ -aminocarbyne [6] and μ -thiocarbyne complexes [7], shown in Scheme 3 (**A** and **B**, respectively). The diiron aminocarbyne complexes $[Fe_2(\mu-CNMe_2)(\mu-CO)(CO)(Cp)_2][SO_3CF_3]$ have been shown to react with lithium alkyls (RLi) or Grignard reagents (RMgCl), affording stable neutral adducts containing the η^4 -C₅H₅R (Scheme 3, **A**). Likewise, Grignard reagents have been reported to attack the Cp of the μ -thiocarbyne complex $[Fe_2(\mu-CSMe)(\mu-CO)(CO)(Cp)_2][SO_3CF_3]$ yielding the cyclopentadiene intermediates $[Fe_2(\mu-CSMe)(\mu-CO)(CO)(Cp)(C_5H_5R)]$, which are stable enough to be isolated. However, these species rearrange by hydrogen migration from the C₅H₅R ring to the μ -C carbyne carbon and generate the alkylidene complexes $[Fe_2\{\mu-C(H)(SMe)\}(\mu-CO)(CO)(Cp)(C_5H_4R)]$ (Scheme 3, **B**). Thus, a possible reaction pathway leading to **2** and **4** from **1** should include a η^4 -C₅H₅Me intermediate (Scheme 3, **C**), which rearranges *via* hydrogen migration from the cyclopentadiene ring to the iminium carbon (C _{α}) of the bridging ligand. Nucleophilic attack on the Cp ligand is likely to occur directly, although we can not exclude alternative reaction pathways, based on nucleophilic attack on the metal.

It is worth noting that in the case **C** the Cp ligands are not equivalent and the nucleophile selectively attacks the ring closer to the electron withdrawing iminium nitrogen.



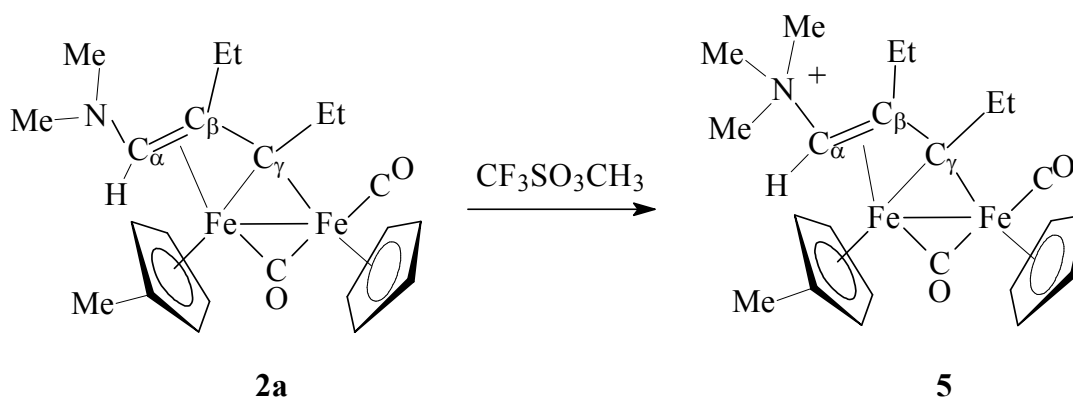
Scheme 3. Nucleophilic additions to the Cp ligand of cationic diiron complexes.

As above mentioned, bridging vinylalkylidene ligands like those found in **2a-f** and **4** can be directly formed by NaBH_4 addition to the C_α of **1a-f**, generating the complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')C(R'')=CHN(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**3**). Exception are the reactions with compounds **1d** and **1e**, which undergo hydride attack at the C_β position. The vinylalkylidene ligands in **2**, **4**, as well as those generated by NaBH_4 addition, adopt a bridging $\eta^1\eta^3$ -coordination mode, quite common among dinuclear complexes [8]. The stability of vinylalkylidene ligands $\mu\text{-}\eta^1\text{:}\eta^3$ coordinated, together with the of penta-atomic ring aromaticity, offer a possible explanation of the supposed hydrogen migration. However it remains unclear the reason why MeLi does not directly attack the vinyliminium ligand at C_α or C_β , rather than giving addition at the Cp ring. Far from providing a satisfactory explanation, it should be remarked that in the related diiron complexes $[\text{Fe}_2(\mu\text{-CX})(\mu\text{-$

$\text{CO}(\text{CO})(\text{Cp})_2]^+$ ($\text{X} = \text{NMe}_2, \text{SMe}$) various carbon nucleophiles preferentially attack the Cp ligand rather than CO or the carbyne ligands [6, 7]. Similar observations concern the regiospecificity of the reactions involving the cationic complexes $[\text{Fe}(\text{CO})_3\text{Cp}]^+$ and $[\text{Co}(\text{CO})_2\text{Cp}]^+$, in which different reaction pathways are possible (*i.e.* nucleophilic attack at the CO, ring addition or CO substitution). In spite of theoretical attempts to explain the regiospecificity of such reactions, it is still difficult to make reliable predictions of either the reaction pathway or final products [4e, 9].

2.2. Methylation of diiron enamino alkylidene complexes.

The peculiar character of the bridging vinylalkylidene ligands in **2a-f**, **4** and in type **3** complexes, is due to the presence of a $\text{NR}'\text{R}''$ group bound to the vinyl moiety, which can be considered as a coordinated enamino group. The presence of a nitrogen atom is expected to make the ligand susceptible of electrophilic alkylation, although it remains difficult to predict whether the N atom itself, rather than C_β , would be preferentially alkylated. In order to investigate the point, compound **2a** has been treated with the powerful methylating reagent $\text{CF}_3\text{SO}_3\text{CH}_3$. Methylation affords $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{Et})\text{C}(\text{Et})\text{CH}(\text{NMe}_3)\}(\mu\text{-CO})(\text{CO})(\text{Cp})\{\eta^5\text{-C}_5\text{H}_4(\text{Me})\}][\text{CF}_3\text{SO}_3]$ (**5**), (Scheme 4). The nature of **5** has been fully elucidated by X-ray diffraction.



Scheme 4.

The molecular structure of **5**, reported in Figure 1, confirms the structures assigned to the parent compounds **2**. The overall molecular geometry is irregular and no idealized symmetry can be envisaged, in particular C_α [C(5)] is a chiral centre. In order to assess the effects of the nitrogen methylation on the other bond interactions, the relevant bond distances can be

analysed in comparison with those recently reported for the related neutral species $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Tol)CH=CH(NMe}_2\text{)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (Table 1) [3a]. The two molecules exhibit similar stereogeometries, but some bond lengths are worth discussing. The C(3)-C(4) interaction is found equal in the two species [1.44(1) Å] and indicates double bond character. Also the distances of these atoms from the diiron unit are not significantly different [C(3)-Fe(1,2) 2.00(1)_{av}, 1.98(1)_{av}; C(4)-Fe(1) 2.06(1), 2.07(1) Å, respectively]. Therefore the effects of methylation and consequent appearance of a net charge are not measurable for the atoms not contiguous to the reaction centre. On the contrary, a significant lengthening is observed for N-C(5) [1.49(1), 1.38(1) Å, respectively], because this interaction has no longer double bond character. Also the C(5)-C(4) and C(5)-Fe(1) bonds are altered. The former is lengthened [1.49(1) against 1.41(1) Å] and the latter is significantly shortened [2.082(7) against 2.299(6) Å]. The 0.22 Å shortening in the C(5)-Fe(1) interaction indicates that C(5), being no more involved in π interactions in the C(3)-C(4)-C(5)-N unit, acts as a better σ donor to Fe(1) in spite of the contiguous electron withdrawing ammonium nitrogen.

The structural data above discussed indicate that the ammonium μ -vinylalkylidene ligand in **5** can be alternatively described, as bridging ammonium-allylidene [10] (Chart 1, II and III). Apart from any attempt to determine the more appropriate description, the nature of the bridging ligand appears very unusual and interesting. Coordination of vinylammonium ligands has been described only for mononuclear complexes [11], and oxidative addition of vinylammonium salts to Ni complexes has been reported [12]. The latter reaction leads to C-N bond cleavage and generates amine and allyl ligands. In our case, bridging coordination does not promote C-N bond breaking and the bridging ligand appears stable.

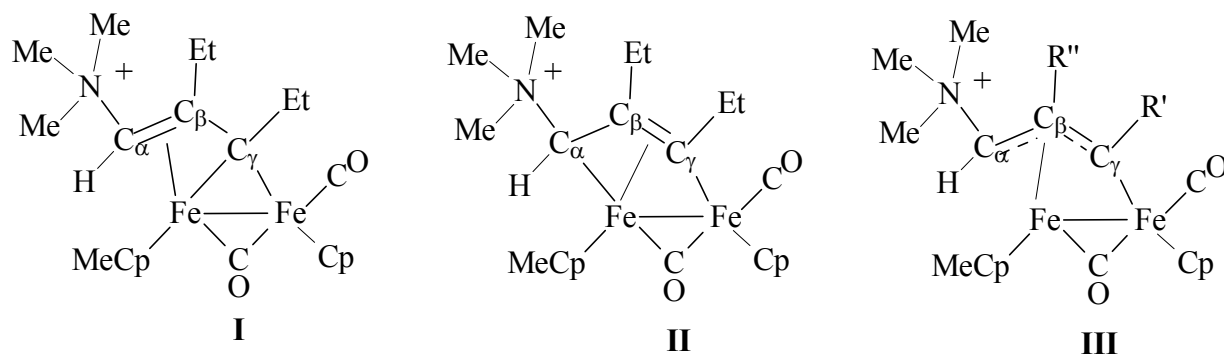
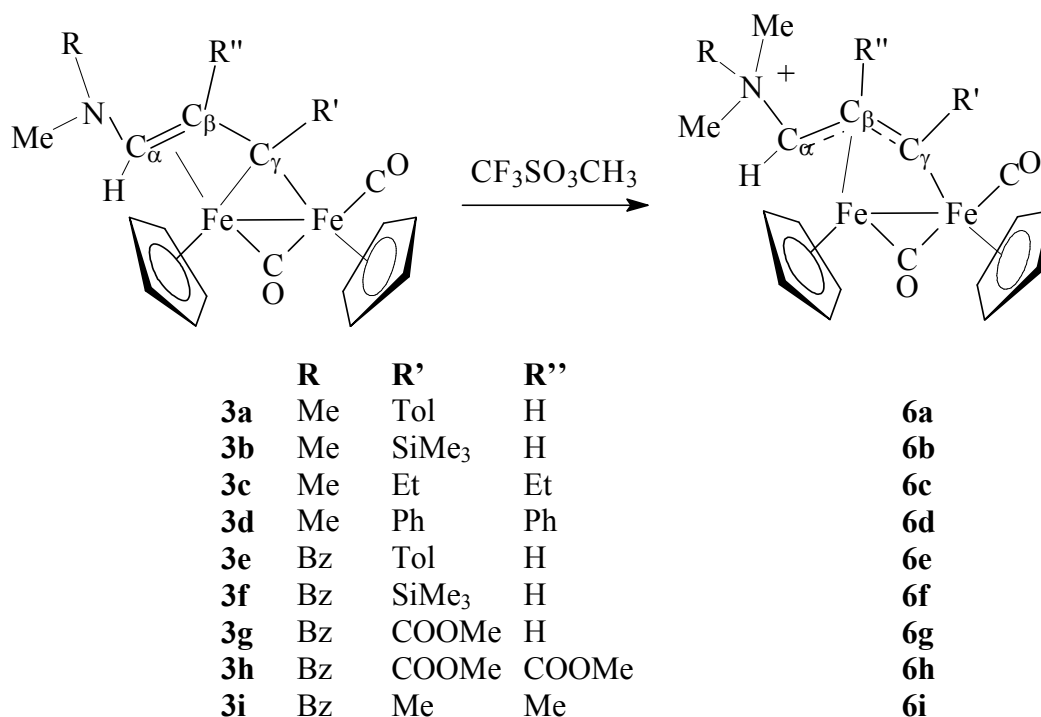


Chart 1: possible descriptions of the bridging ligand in **5**.

The spectroscopic data of complex **5** agree with its structural features. The IR spectra (in CH₂Cl₂ solution) show two absorptions, attributable to a terminal and a bridging carbonyl (at 1953 and 1782 cm⁻¹, respectively), at higher wavenumbers than the parent complex **2a** (1930, 1751 cm⁻¹). The ¹H NMR spectrum exhibits one set of resonances, indicating the presence of a single isomer in solution. Moreover, the three N-methyl groups originate a singlet at δ 3.26 ppm, because of free rotation of the NMe₃ group around the C_α-N axis. Major features of the ¹³C NMR spectrum include the typical low field resonance for the alkylidene C_γ carbon (at δ 198.2 ppm), and the resonances at higher field due to C_α and C_β (at δ 92.3 and 88.3 ppm, respectively).

The selective N-methylation of the bridging vinylalkylidene ligand in **2a** is an interesting result because electrophilic attack to uncoordinated enamines [R₂N-C_α=C_β] usually involves C_β [13] rather than the nitrogen atom [14]. Comparisons with the reactivity of metal-coordinated enamines [15], including binuclear complexes [16], would be more appropriate, but unfortunately this matter is still largely uncovered. The observed selectivity could simply depend upon the nature of the substituents in the bridging ligand (*i.e.* the small Me substituents on the N atom and the more hindered Et groups on the bridging chain). In order to determine to what extent the reaction is of general character and which is the influence of the substituents, we have investigated the methylation reaction with a variety of μ-vinylalkylidene diiron complexes. The compounds examined were [Fe₂{μ-η¹:η³-C(R')C(R'')=CHN(Me)(R)}(μ-CO)(CO)(Cp)₂] (**3**) (R = Me, Bz), instead of **2**, because more conveniently prepared by direct addition of H⁻ to the vinyliminium ligand.

By analogy with **2a**, the compounds **3a-i** react with CF₃SO₃CH₃ affording the complexes [Fe₂{μ-η¹:η³-C(R')C(R'')CH(NMe₂R)}(μ-CO)(CO)(Cp)₂][CF₃SO₃] (**6a-i**), in about 70% yields (Scheme 5).



Scheme 5.

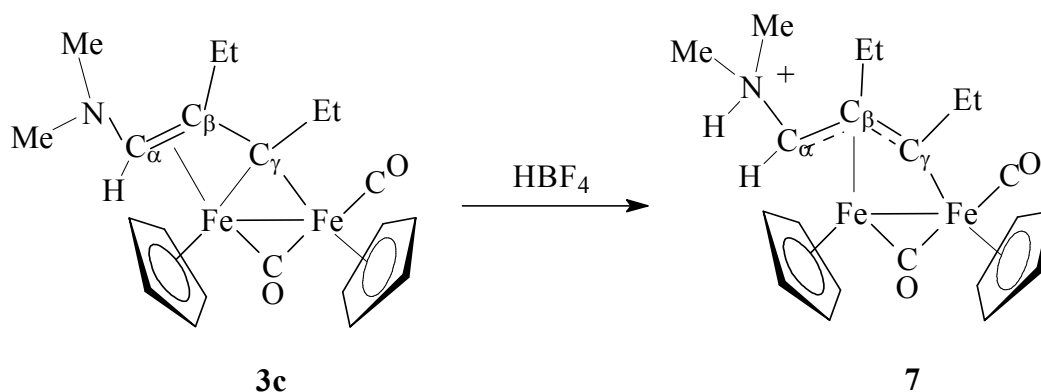
Compounds **6a-i** have been purified by filtration on celite and fully characterized by spectroscopy and elemental analysis. Moreover, the structure of **6c** has been ascertained by X ray diffraction and its molecular structure is shown in Figure 2. The geometry of **6c** is similar to that of **5**, an obvious variation being the absence of the methyl group at the Cp ring. A second and disturbing difference is the presence of disorder for the ethyl group bonded to C(4). As the disorder involves both methyl [C(9)] and methylene [C(8)] atoms it is not a mere conformational effect. Also C(5) is disordered but, unfortunately, not clearly split in separate images, making a rationalisation difficult. We do not discuss further this molecule because the bond distances of interest are scarcely reliable.

The spectroscopic data of complexes **6a-i** are in good agreement with the structural features of **6c**. The IR spectra (in CH₂Cl₂ solution) show the usual pattern consisting of two carbonyl bands (*e.g.* for **6d** at 1966 and 1794 cm⁻¹, respectively). The ¹H NMR spectra of **6a-i** (in CDCl₃ solution) show a high-field resonance due to C_α-H (*e.g.* at δ -0.10 ppm for **6a**). In addition, when R''= H, the coupling constant value between C_αH and C_βH (³J_{HH} = 6 ÷ 8 Hz) is indicative of a *trans* arrangement.

In the case of complexes **6a-d**, the three methyl groups bound to the ammonium nitrogen give rise to a unique singlet in both ^1H and ^{13}C NMR spectra (*e.g.* at δ 3.21 and 56.3 ppm for **6a**), as a consequence of free rotation of the NMe_3 group around the $\text{C}_\alpha\text{-N}$ bond. In agreement with this, complexes **6e-i**, which contain different substituents on the ammonium group (*i.e.* Me and Bz), exist in solution as a single isomeric form. The main features of the ^{13}C NMR spectra of **6a-i** are given by the C_α , C_β and C_γ resonances (*e.g.* for **6a** at δ 88.9, 70.9, 188.3 ppm, respectively).

The results reported in Scheme 5 suggest that methylation by MeSO_3CF_3 occurs selectively at the N atom and does not depend on the nature of the substituents R, R' and R''.

Finally, the reaction of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Et)C(Et)=CH(NMe}_2\text{)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**3c**) with HBF_4 has also been investigated. Protonation occurs at the N atom, resulting in the formation of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Et)C(Et)CH(NHMe}_2\text{)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{BF}_4]$, (**7**) (Scheme 6).



Scheme 6.

Complex **7** has been purified by filtration on celite and fully spectroscopically characterized. Evidences for the nitrogen bound hydrogen are a sharp IR absorption at 3187 cm^{-1} (in KBr pellets) and a broad ^1H NMR resonance at δ 7.01 ppm. Significant NMR data include the ^1H resonance due to $\text{C}_\alpha\text{-H}$ (at δ -1.11 ppm), and the ^{13}C resonances of C_α (at 80.5 ppm) and N-Me (at 48.7 and 48.6 ppm).

The protonation reaction (Scheme 6) is almost quantitatively reversed to give **3c** by treatment of **7** with sodium hydride in THF solution.

3. Conclusions.

Reactions of the μ -vinyliminium complexes **1** with MeLi show that the ancillary Cp ligand, rather than the bridging vinyliminium, is selectively attacked. However, the

nucleophilic addition is followed by a molecular rearrangement, *i.e.* hydrogen migration to the bridging vinyliminium, confirming that the latter is highly reactive.

The μ -vinylalkylidene complexes **2a** and **3**, generated respectively by hydrogen migration or hydride addition to the iminium carbon, undergo methylation at the enamine nitrogen, affording novel ammonium-functionalized allylidene complexes. In all of the cases examined, methylation occurs selectively at the N atom and is not influenced by the nature of the substituents on the bridging ligand or at the C₅H₅ ring.

4. Experimental details

4.1 General

All reactions were routinely carried out under a nitrogen atmosphere, 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. ESI MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in CH₃CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ¹H and ¹³C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ¹H, ¹³C correlation through gs-HSQC and gs-HMBC experiments [17]. 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 DPGFSE-NOE sequence [18]. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. [Fe₂(CO)₄(Cp)₂] was purchased from Strem and used as received. Compounds **1a-f** [2] and **3a-i** [3a-b] were prepared by published methods.

4.2 Synthesis of [Fe₂{μ-η¹:η³-C_γ(R')C_β(R')=C_αHN(Me)(R)}(μ-CO)(CO)(Cp){η⁵-C₅H₄(Me)}]
(R = Me, R' = Et, **2a**; R = Me, R' = Ph, **2b**; R = R' = Me, **2c**; R = Xyl, R' = Me, **2d**; R = Xyl, R' = Et, **2e**; ; R = Xyl, R' = Ph, **2f**).

Complex **1a** (250 mg, 0.427 mmol), in THF solution (15 mL), was treated with MeLi (0.40 ml, 1.6 M in diethyl ether, 0.64 mmol), at -40 °C. The solution was then warmed to room temperature, stirred for an additional 60 min and filtered on alumina. Removal of the solvent and chromatography on an alumina column, with diethyl ether as eluent, gave a red band, which afforded **2a** upon crystallization at -20 °C. Yield 121 mg (63%). Found: C, 58.55; H, 6.46; N, 3.07%. C₂₂H₂₉Fe₂NO₂ requires: C, 58.57; H, 6.48; N, 3.10%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1930vs and 1751s (CO). ¹H NMR (CD₂Cl₂) δ 4.69, 4.36, 4.13, 3.90 (br, 4 H, C₅H₄Me); 4.62 (s, 5 H, Cp); 4.34, 3.92 (m, 2 H, C_γCH₂CH₃); 2.50, 2.21 (m, 2 H, C_βCH₂); 2.27 (s, 6 H, NMe); 2.00 (s, 3 H, C₅H₄Me); 1.60 (br, 3 H, C_γCH₂CH₃); 1.19 (br, 3H, C_βCH₂CH₃);

−0.98 (s, 1 H, C_αH). ¹³C NMR (CD₂Cl₂) δ 274.4 (μ-CO); 216.0 (CO); 196.5 (C_γ); 96.2, 83.3, 82.8, 80.9, 66.8 (C₅H₄Me); 94.6 (C_α); 93.1 (C_β); 87.3 (Cp); 47.5 (NMe); 42.5 (C_γCH₂CH₃); 23.7 (C_βCH₂CH₃); 21.1 (C_γCH₂CH₃); 16.5 (C_βCH₂CH₃); 12.7 (C₅H₄Me).

Complexes **2b-f** were prepared by the same procedure described for **2a**, by reacting MeLi with **1b-f**.

2b: Yield (61%). Found: C, 65.93; H, 5.25; N, 2.58%. C₃₀H₂₉Fe₂NO₂ requires: C, 65.84; H, 5.34; N, 2.56 %. IR (CH₂Cl₂) ν_{max} (cm^{−1}) 1933vs and 1752s (CO). ¹H NMR (CDCl₃) 8.12-6.63 (m, 10 H, Ph); 4.80, 4.52, 4.43, 4.28 (br, 4H, C₄H₄); 4.30 (s, 5 H, Cp); 2.34 (s, 3 H, C₄H₄CMe); 2.18 (s, 6 H, NMe); 0.91 (s, 1 H, C_αH). ¹³C{¹H} NMR (CDCl₃) δ 278.9 (μ-CO); 216.0 (CO); 185.4 (C_γ); 156.9-123.1 (Ph); 98.9 (C₄H₄CMe); 84.2, 83.2, 81.2, 67.2 (C₄H₄); 98.7 (C_α); 88.2 (Cp); 77.5 (C_β); 42.8 (NMe); 13.7 (C₄H₄CMe).

2c: Yield (64%). Found: C, 56.84; H, 6.02; N, 3.28%. C₂₀H₂₅Fe₂NO₂ requires: C, 56.77; H, 5.96; N, 3.31%. IR (CH₂Cl₂) ν_{max} (cm^{−1}) 1932vs and 1762s (CO). ¹H NMR (CDCl₃) 4.69 (s, 5 H, Cp); 4.53, 4.38, 4.14, 3.74 (br, 4 H, C₄H₄); 3.80 (s, 3 H, C_γMe); 2.31 (s, 6 H, NMe); 2.07 (s, 3 H, C₄H₄CMe); 2.03 (s, 3 H, C_βMe); −0.76 (s, 1 H, C_αH). ¹³C{¹H} NMR (CD₂Cl₂) δ 273.2 (μ-CO); 216.7 (CO); 186.5 (C_γ); 97.5 (C₄H₄CMe); 84.2, 83.3, 81.2, 67.3 (C₄H₄); 92.2 (C_α); 89.4 (C_β); 86.7 (Cp); 46.1 (NMe); 36.3 (C_γMe); 15.6 (C_βMe); 11.6 (C₄H₄CMe).

2d: Yield (58%). Found: C, 63.06; H, 6.00; N, 2.66%. C₂₇H₃₁Fe₂NO₂ requires: C, 63.19; H, 6.09; N, 2.73%. IR (CH₂Cl₂) ν_{max} (cm^{−1}) 1930vs and 1762s (CO). ¹H NMR (CDCl₃) 7.33-6.72 (m, 3 H, Me₂C₆H₃); 4.64 (s, 5 H, Cp); 4.56, 4.31, 4.12, 3.46 (br, 4 H, C₄H₄); 3.82 (s, 3 H, C_γMe); 2.80 (s, 3H, NMe); 2.26 (s, 3 H, C₄H₄CMe); 2.11, 2.05 (s, 6 H, Me₂C₆H₃); 1.75 (s, 3 H, C_βMe); 0.33 (s, 1 H, C_αH). ¹³C{¹H} NMR (CD₂Cl₂) δ 276.4 (μ-CO); 217.9 (CO); 185.2 (C_γ); 147.9 (ipso-Me₂C₆H₃); 136.0, 135.6, 129.2, 128.2, 125.3 (Me₂C₆H₃); 98.5 (C₄H₄CMe); 85.1, 84.2, 83.5, 80.4 (C₄H₄); 95.3 (C_α); 88.8 (C_β); 87.0 (Cp); 41.3 (NMe); 37.5 (C_γMe); 19.7, 18.5 (Me₂C₆H₃); 17.2 (C_βMe); 12.9 (C₄H₄CMe).

2e: Yield (74%). Found: C, 64.48; H, 6.37; N, 2.61%. C₂₉H₃₅Fe₂NO₂ requires: C, 64.35 ; H, 6.52; N, 2.59%. IR (CH₂Cl₂) ν_{max} (cm^{−1}) 1932vs and 1773s (CO). ¹H NMR (CD₂Cl₂) 7.25-6.82 (m, 3 H, Me₂C₆H₃); 4.66 (s, 5 H, Cp); 4.43, 4.37, 3.91, 3.46 (br, 4H, C₄H₄); 4.36, 3.98 (m, 2 H, C_γCH₂); 2.88 (s, 3 H, NMe); 2.73, 2.30 (m, 2 H, C_βCH₂); 2.21 (s, 3 H, C₄H₄CMe); 2.14, 2.08 (s, 6 H, Me₂C₆H₃); 1.62 (t, 3 H, ³J_{HH} = 7.3 Hz, C_γCH₂CH₃); 0.57 (t, 3H, ³J_{HH} = 7.3 Hz, C_βCH₂CH₃); 0.10 (s, 1 H, C_αH). ¹³C{¹H} NMR (CD₂Cl₂) δ 276.7 (μ-CO);

218.6 (CO); 196.2 (C_γ); 149.5 (ipso-Me₂C₆H₃); 136.3, 136.0, 129.7, 128.5, 125.5 (Me₂C₆H₃); 99.1 (C₄H₄CMe); 85.7, 84.0, 82.2, 80.8 (C₄H₄); 96.4 (C_α); 91.7 (C_β); 87.3 (Cp); 42.4 (C_γCH₂CH₃); 42.0 (NMe); 24.7 (C_βCH₂CH₃); 21.0 (C_γCH₂CH₃); 20.2, 19.1 (Me₂C₆H₃); 14.2 (C_βCH₂CH₃); 12.9 (C₄H₄CMe). ESI-MS (ES⁺): 541 [M⁺, 10 %], 420 [M⁺ – Xyl – Me – H, 57 %], 406 [M⁺ – N(Me)(Xyl) – H, 100 %] m/z.

2f: Yield (58%). Found: C, 69.59; H, 5.44; N, 2.12%. C₃₇H₃₅Fe₂NO₂ requires: C, 69.72; H, 5.53; N, 2.20%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1927vs and 1762s (CO). ¹H NMR (CDCl₃) 8.17-6.77 (m, 13 H, Ph and Me₂C₆H₃); 5.50, 5.34, 4.55, 3.76 (br, 4H, C₄H₄); 4.23 (s, 5 H, Cp); 2.92, 2.25 (s, 6 H, Me₂C₆H₃); 2.17 (s, 3 H, C₄H₄CMe); 2.01 (s, 3 H, NMe); 1.26 (s, 1 H, C_αH). ¹³C{¹H} NMR (CDCl₃) δ 278.7 (μ-CO); 218.2 (CO); 186.0 (C_γ); 157.1-123.0 (Ph and Me₂C₆H₃); 103.5 (C_α); 89.2, 82.4, 82.2, 77.8 (C₄H₄); 88.0 (Cp); 77.5 (C_β); 38.2 (NMe); 20.1, 20.0 (Me₂C₆H₃); 13.5 (C₄H₄CMe).

4.3 Synthesis of [Fe₂{μ-η¹:η³-C(Ph)C(Ph)=CHN(Me)(Xyl)}(μ-CO)(CO)(Cp){η⁵-C₅H₄(Ph)}] (4)

Complexes **4** was prepared by the same procedure described for the synthesis of **2a**, by reacting **1f** (125 mg, 0.162 mmol) with PhLi (0.13 mL, 1.8 M in hexane, 0.24 mmol). Yield 39 mg (34%). Found: C, 72.23; H, 5.30; N, 2.06%. C₄₂H₃₇Fe₂NO₂ requires: C, 72.12; H, 5.33; N, 2.00%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1932vs and 1772s (CO). ¹H NMR (CD₂Cl₂) 7.84-6.82 (m, 18 H, Ph and Me₂C₆H₃); 4.99, 4.81, 4.57, 3.52 (br, 4H, C₄H₄); 4.25 (s, 5 H, Cp); 3.06, 1.78 (s, 6 H, Me₂C₆H₃); 2.79 (s, 3 H, NMe); 1.31 (s, 1 H, C_αH). ¹³C{¹H} NMR (CD₂Cl₂) δ 141.3-125.6 (Ph and Me₂C₆H₃); 89.4 (C_α); 81.8 (Cp); 40.0 (NMe); 18.2, 18.1 (Me₂C₆H₃).

4.4 Synthesis of [Fe₂{μ-η¹:η³-C(Et)C(Et)CH(NMe₃)}(μ-CO)(CO)(Cp){η⁵-C₅H₄(Me)}][CF₃SO₃] (5)

A solution of **2a** (102 mg, 0.226 mmol), in CH₂Cl₂ (10 ml), was treated with CF₃SO₃CH₃ (0.030 ml, 0.27 mmol) and stirred for about 60 min. Removal of the volatile material, under reduced pressure, gave a residue which was washed with diethyl ether (2 x 20 mL), dissolved in CH₂Cl₂ and filtered on a celite pad. Crystallization at -20°C from dichloromethane solution layered with diethyl ether gave dark brown crystals of **5**. Yield 80 mg, (58 %). Found: C, 46.96; H, 5.29; N, 2.24%. C₂₄H₃₂F₃Fe₂NO₅S requires: C, 46.85; H, 5.24; N, 2.28 %. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1953vs and 1782s (CO). ¹H NMR (CDCl₃) 5.01 (s,

1 H, C₄H₄); 4.86 (s, 5 H, Cp); 4.83, 4.51, 4.13 (br, 3 H, C₄H₄); 4.29, 3.86 (m, 2 H, C_γCH₂); 3.26 (s, 9 H, NMe); 3.20, 2.10 (m, 2 H, C_βCH₂); 2.16 (s, 3 H, C₄H₄CMe); 1.68 (t, 3 H, ³J_{HH} = 7.3 Hz, C_γCH₂CH₃); 1.38 (t, 3H, ³J_{HH} = 7.5 Hz, C_βCH₂CH₃); -1.38 (s, 1 H, C_αH). ¹³C{¹H} NMR (CDCl₃) δ 270.9 (μ-CO); 215.6 (CO); 198.2 (C_γ); 101.5 (C₄H₄CMe); 92.9 (C_α); 88.7 (Cp); 88.3 (C_β); 84.8, 83.3, 82.9, 81.6 (C₄H₄); 57.5 (NMe); 42.4 (C_γCH₂); 21.8 (C_βCH₂); 20.4 (C_γCH₂CH₃); 16.6 (C_βCH₂CH₃); 12.6 (C₄H₄CMe).

4.5 Synthesis of $[Fe_2(\mu-\eta^1: \eta^3-C(R')C(R'')CH(NMe_2R))(\mu-CO)(CO)(Cp)_2][CF_3SO_3]$ (*R* = Me, *R'* = Tol, *R''* = H, **6a**; *R* = Me, *R'* = SiMe₃, *R''* = H, **6b**; *R* = Me, *R'* = *R''* = Et, **6c**; *R* = Me, *R'* = *R''* = Ph, **6d**; *R* = Bz, *R'* = Tol, *R''* = H, **6e**; *R* = Bz, *R'* = SiMe₃, *R''* = H, **6f**; *R* = Bz, *R'* = COOMe, *R''* = H, **6g**; *R* = Bz, *R'* = *R''* = COOMe, **6h**; *R* = Bz, *R'* = *R''* = Me, **6i**).

Complex **3a** (118 mg, 0.251 mmol), in CH₂Cl₂ solution (10 mL), was treated with CF₃SO₃CH₃ (0.03 ml, 0.27 mmol) and stirred for about 120 min. Removal of the volatile material, under reduced pressure, gave a residue which was washed with diethyl ether (2 x 20 mL), dissolved in CH₂Cl₂ and filtered on a celite pad. Crystallization at -20°C from dichloromethane solution layered with diethyl ether gave dark brown crystals of **6a**. Yield 112 mg (70%). Found: C, 49.02; H, 4.38; N, 2.23%. C₂₆H₂₈F₃Fe₂NO₅S requires: C, 49.16; H, 4.44; N, 2.20%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1964vs and 1794s (CO). ¹H NMR (CDCl₃) 7.60, 7.32 (d, ³J_{HH} = 8.1 Hz, 4H, C₆H₄Me); 4.83, 4.69 (s, 10 H, Cp); 4.80 (d, 1 H, ³J_{HH} = 6.6 Hz, C_βH); 3.21 (s, 9 H, NMe); 2.47 (s, 3 H, C₆H₄Me); -0.10 (d, 1 H, ³J_{HH} = 6.6 Hz, C_αH). ¹³C{¹H} NMR (CDCl₃) δ 266.7 (μ-CO); 213.8 (CO); 188.3 (C_γ); 154.1 (ipso-C₆H₄Me); 136.7, 129.6, 129.0, 128.4 (C₆H₄Me); 89.8, 83.9 (Cp); 88.9 (C_α); 70.9 (C_β); 56.3 (NMe); 21.1 (C₆H₄Me).

Complexes **6b-i** were prepared by the same procedure described for **6a**, by reacting CF₃SO₃CH₃ with **3b-i**, respectively. Crystals of **6c** suitable for X ray analysis were obtained from a dichloromethane solution layered with diethyl ether, at -20 °C.

6b: Yield (75%). Found: C, 42.95; H, 4.85; N, 2.33%. C₂₂H₃₀F₃Fe₂NO₅SSi requires: C, 42.80; H, 4.90; N, 2.27%. IR (CH₂Cl₂) ν_{max} (cm⁻¹) 1962vs and 1790s (CO). ¹H NMR (CDCl₃) 4.94, 4.69 (s, 10 H, Cp); 5.04 (d, 1 H, ³J_{HH} = 6.0 Hz, C_βH); 3.10 (s, 9 H, NMe); 0.65 (s, 9H, SiMe₃); -0.28 (d, 1 H, ³J_{HH} = 6.0 Hz, C_αH). ¹³C{¹H} NMR (CDCl₃) δ 266.7 (μ-CO); 213.5 (CO); 181.9 (C_γ); 90.3 (C_α); 87.5, 82.1 (Cp); 75.8 (C_β); 55.7 (NMe); 3.1 (SiMe₃).

6c: Yield (81%). Found: C, 46.07; H, 5.09; N, 2.41%. $C_{23}H_{30}F_3Fe_2NO_5S$ requires: C, 45.95; H, 5.03; N, 2.33%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1956vs and 1786s (CO). 1H NMR ($CDCl_3$) 4.90, 4.63 (s, 10 H, Cp); 4.33, 3.91 (m, 2 H, $C_\gamma CH_2$); 3.32 (s, 9 H, NMe); 3.17, 2.18 (m, 2 H, $C_\beta CH_2$); 1.69 (m, 3 H, $C_\gamma CH_2 CH_3$); 1.40 (t, 3 H, $C_\gamma CH_2 CH_3$); -1.38 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 269.7 (μ -CO); 215.1 (CO); 198.7 (C_γ); 93.0 (C_α); 89.0, 84.2 (Cp); 88.0 (C_β); 57.4 (NMe); 42.3 ($C_\gamma CH_2$); 21.9 ($C_\beta CH_2$); 20.4 ($C_\gamma CH_2 CH_3$); 16.5 ($C_\beta CH_2 CH_3$).

6d: Yield (72%). Found: C, 53.42; H, 4.41; N, 2.01%. $C_{31}H_{30}Fe_2F_3NO_5S$ requires: C, 53.39; H, 4.34; N, 2.01%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1966vs and 1794s (CO). 1H NMR ($CDCl_3$) 7.77-6.77 (m, 10 H, Ph); 5.18, 4.58 (s, 10 H, Cp); 3.07 (s, 9 H, NMe); -0.72 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 266.6 (μ -CO); 214.3 (CO); 189.8 (C_γ); 153.7, 134.4 (ipso-Ph); 132.0, 130.6, 129.1, 129.0, 127.8, 127.7, 127.3, 127.0, 126.8, 124.7 (Ph); 90.7, 84.0 (Cp); 87.7 (C_β); 86.3 (C_α); 56.6 (NMe).

6e: Yield (70%). Found: C, 54.07; H, 4.40; N, 1.92%. $C_{32}H_{32}F_3Fe_2NO_5S$ requires: C, 54.03; H, 4.53; N, 1.97%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1958vs and 1792s (CO). 1H NMR ($CDCl_3$) 7.60-7.20 (m, 9 H, Ph and C_6H_4Me); 4.80, 4.06 (d, 2 H, $^2J_{HH} = 13.2$ Hz, CH_2Ph); 4.74, 4.71 (s, 10 H, Cp); 4.11 (d, 1 H, $^3J_{HH} = 7.1$ Hz, $C_\beta H$); 3.59, 2.76 (s, 6 H, NMe); 2.42 (s, 3 H, C_6H_4Me); -0.26 (d, 1 H, $^3J_{HH} = 7.1$ Hz, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 267.3 (μ -CO); 215.0 (CO); 186.5 (C_γ); 154.3 (ipso- C_6H_4Me); 136.7-127.2 (Ph and C_6H_4Me); 89.9, 83.9 (Cp); 88.7 (C_α); 74.6 (CH_2Ph); 72.6 (C_β); 57.0, 46.1 (NMe); 20.9 (C_6H_4Me).

6f: Yield (77%). Found: C, 48.57; H, 5.01; N, 2.06%. $C_{28}H_{34}F_3Fe_2NO_5SSi$ requires: C, 48.50; H, 4.94; N, 2.02%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1957vs and 1793s (CO). 1H NMR ($CDCl_3$) 7.60-7.19 (m, 5 H, Ph); 4.95, 4.60 (s, 10 H, Cp); 4.75, 3.88 (d, 2 H, $^2J_{HH} = 13.0$ Hz, CH_2Ph); 4.16 (d, 1 H, $^3J_{HH} = 6.9$ Hz, $C_\beta H$); 3.52, 2.68 (s, 6 H, NMe); 0.42 (s, 9 H, $SiMe_3$); -0.45 (d, 1 H, $^3J_{HH} = 6.9$ Hz, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 266.7 (μ -CO); 214.6 (CO); 179.8 (C_γ); 133.2, 130.7, 128.7, 127.0 (Ph); 87.7, 82.1 (Cp); 85.7 (C_α); 78.1 (C_β); 74.0 (CH_2Ph); 56.9, 45.6 (NMe); 2.8 ($SiMe_3$).

6g: Yield (68%). Found: C, 47.82 %; H, 4.11 %; N, 2.08 %. $C_{27}H_{28}F_3Fe_2NO_7S$ requires: C, 47.74; H, 4.15; N, 2.06%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1970vs, 1805s and 1701m (CO). 1H NMR ($CDCl_3$) 7.56-7.31 (m, 5 H, Ph); 4.90, 4.78 (s, 10 H, Cp); 4.63, 4.18 (d, 2 H, $^2J_{HH} = 12.1$ Hz, CH_2Ph); 4.48 (d, 1 H, $^3J_{HH} = 8.2$ Hz, $C_\beta H$); 4.03 (s, 3 H, CO_2Me); 3.39, 2.82 (s, 6 H, NMe); -0.43 (d, 1 H, $^3J_{HH} = 8.2$ Hz, $C_\alpha H$).

6h: Yield (69%). Found: C, 47.40; H, 4.02; N, 1.94%. $C_{29}H_{30}F_3Fe_2NO_9S$ requires: C, 47.24; H, 4.10; N, 1.90%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1981vs, 1811s and 1714m (CO). 1H NMR ($CDCl_3$) 7.57-7.34 (m, 5 H, Ph); 5.02, 4.89 (s, 10 H, Cp); 4.84, 4.70 (d, 2 H, $^2J_{HH} = 12.3$ Hz, CH_2Ph); 4.05, 4.04 (s, 6 H, CO_2Me); 3.36, 2.94 (s, 6 H, NMe); -1.43 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 259.9 (μ -CO); 211.9 (CO); 177.7, 174.3, 169.5 (C_γ and C_γ - CO_2Me and C_β - CO_2Me); 133.1, 130.9, 129.5, 126.9 (Ph); 89.8, 87.1 (Cp); 79.7 (C_α); 79.2 (C_β); 73.8 (CH_2Ph); 56.4, 54.9 (NMe); 52.7 (CO_2Me).

6i: Yield (72%). Found: C, 50.03; H, 4.71; N, 2.19%. $C_{27}H_{30}F_3Fe_2NO_5S$ requires: C, 49.95; H, 4.66; N, 2.16%. IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1954vs and 1788s (CO). 1H NMR ($CDCl_3$) 7.60-7.25 (m, 5 H, Ph); 4.92, 4.26 (d, 2 H, $^2J_{HH} = 13$ Hz, CH_2Ph); 4.87, 4.57 (s, 10 H, Cp); 3.73 (s, 3 H, $C_\gamma Me$); 3.41, 3.08 (s, 6 H, NMe); 1.99 (s, 3 H, $C_\beta Me$); -1.39 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 269.1 (μ -CO); 215.4 (CO); 189.0 (C_γ); 132.9, 130.8, 129.3, 126.9 (Ph); 89.4, 85.2 (Cp); 89.0 (C_α); 85.9 (C_β); 72.7 (CH_2Ph); 57.3, 49.6 (NMe); 37.9 ($C_\gamma Me$); 16.8 ($C_\beta Me$).

4.6 Syntheses of $[Fe_2\{\mu-\eta^1: \eta^3-C(Et)C(Et)CH(NHMe_2)\}(\mu-CO)(CO)(Cp)_2][BF_4]$ (7)

Compound **3c** (91 mg, 0.208 mmol), in CH_2Cl_2 (10 mL), was treated with tetrafluoroboric acid in diethyl ether solution (0.25 mmol; 7.2 M), and the mixture was stirred for 30 min. Removal of the volatile material, under reduced pressure, gave a residue which was washed with diethyl ether (2 x 20 ml). Yield: 81 mg, (73%). Found: C, 49.12; H, 5.37; N, 2.74%. $C_{22}H_{28}BF_4Fe_2NO_2$: requires: C, 49.21; H, 5.26; N, 2.61%. IR (KBr pellets) IR (CH_2Cl_2) ν_{max} (cm^{-1}) 1958vs and 1785s (CO); 3187m (NH) in KBr. 1H NMR ($CDCl_3$) 7.01 (s, 1 H, NH); 4.87, 4.54 (s, 10 H, Cp); 4.28, 3.87 (m, 2 H, $C_\gamma CH_2$); 3.39, 2.87 (s, 6 H, NMe); 3.03, 2.35 (m, 2 H, $C_\beta CH_2$); 1.66 (m, 3 H, $C_\gamma CH_2CH_3$); 1.36 (t, 3 H, $C_\gamma CH_2CH_3$); -1.11 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 269.4 (μ -CO); 214.5 (CO); 197.8 (C_γ); 88.7, 85.0 (Cp); 87.6 (C_β); 80.5 (C_α); 48.7, 48.6 (NMe); 42.4 ($C_\gamma CH_2$); 23.4 ($C_\beta CH_2$); 21.3 ($C_\gamma CH_2CH_3$); 17.0 ($C_\beta CH_2CH_3$).

4.7. X-ray data collection and structure determination of $(5) \cdot CH_2Cl_2$ and $(6c) \cdot CH_2Cl_2$.

X-ray intensity data for $(5) \cdot CH_2Cl_2$ and $(6c) \cdot CH_2Cl_2$ were measured on a Bruker AXS SMART 2000 diffractometer, equipped with a CCD detector. Cell dimensions and the

orientation matrix were initially determined from a least-squares refinement on reflections measured in three sets of 20 exposures, collected in three different ω regions, and eventually refined against all data. For both crystals, a full sphere of reciprocal space was scanned by 0.3° ω steps, with the detector kept at 5.0 cm from the sample. Intensity control was monitored by recollecting the initial 50 frames at the end of the data collection and analyzing the duplicate reflections. The software SMART [19a] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by the SAINT program [19a], and an empirical absorption correction was applied using SADABS [19b]. The structures were solved by direct methods (SIR 97) [19c] and subsequent Fourier syntheses and refined by full-matrix least-squares on F^2 (SHELXTL) [19d], using anisotropic thermal parameters for all non-hydrogen atoms except C(4) and C(5) in **6c** (see further on). The highest residual electron density peak in **5** is located in the vicinity of the triflate indicating some disorder usual for this anion. In **6c** one ethyl chain [bound to C(4)] was found disordered over two well separated positions and the site occupation factors were refined to 0.60 and 0.40, respectively. Some disorder was also detected at C(4) and C(5) showing high and unreliable thermal ellipsoids, in particular the thermal ellipsoid of C(5) resulted 'not definite positive' in spite of the low temperature experiment (100 K). All hydrogen atoms, except the hydrogen bound to the C_α carbon [C(5)] in complex **5** and **6c** which was located in the Fourier map and refined isotropically, were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, $U(H) = 1.2 U_{eq}(C)$ [$U(H) = 1.5 U_{eq}(C-Me)$], and allowed to ride on their carrier carbons. Crystal data and details of the data collection for all structures are reported in Table 2.

5. Supplementary Material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 271171 for **5** and 271172 for **6c**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (M.I.U.R.) (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) P. Braunstain, J. Rosè in *Metal Cluster in Chemistry*, P. Braunstain, L. A. Oro, P. R. Raithby Eds.; Wiley –VCH: Weinheim 1999 p 616;
(b) R. D. Adams, B. Captain, *J. Organomet.Chem.* 689 (2004) 4521;
(c) B. Bosnich, *Inorg. Chem.* 38 (1999) 2554;
(d) A. E. Martell, J. Perutka, D. Kong, *Coord. Chem. Rev.* 216-217 (2001) 55;
(e) M. P. Doyle, T. Ren, *Progress in Inorg.Chem.* 49 (2001) 113;
(f) J. C. Qin, A. Gavrilova, B. Bosnich, *Pure Appl. Chem.* 73 (2001) 221;
(g) K. Severin, *Chem. Eur. J.* 8 (2002) 1514;
(h) E. K. Van Den Beuken, B. L. Feringa *Tetrahedron* 54 (1998) 12985.
- [2] (a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanolli, *Organometallics* 22 (2003) 1326;
(b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanolli, *J. Organomet. Chem.* 689 (2004) 528.
- [3] (a) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanolli, *Organometallics* 23 (2004) 3348;
(b) V. G. Albano, L. Busetto, F. Marchetti, M. Monari, S. Zacchini, V. Zanolli, *J. Organomet. Chem.* 690 (2005) 837.
(c) L. Busetto, F. Marchetti, S. Zacchini, V. Zanolli, *Organometallics* 24 (2005) 2297.
- [4] (a) M. L. H. Green, L. Pratt, G. Wilkinson, *J. Chem. Soc.* (1959) 3753;
(b) A. Davison, M. L. H. Green, G. Wilkinson, *J. Chem. Soc.* (1961) 3172;
(c) P. M. Treichel, R. L. Shubkin, *Inorg. Chem.* 6 (1967) 1328;
(d) I. U. Khand, P. L.; Pauson, W. E. Watts, *J. Chem. Soc. (C)*, (1969) 2024;
(e) S. G. Davies, M. L. H. Green, D. M. P. Mingos, *Tetrahedron* 34 (1978) 3047;
(f) J. W. Faller, *Inorg. Chem.* 19 (1980) 2857;
(g) S. G. Davies, S. J. Simpson, H. Felkin, T. Fillebeen-Khan, *Organometallics* 2 (1983) 539;
(h) L. K. Liu, L. S. Luh, *Organometallics* 13 (1994) 2816;
(i) L. S. Luh, L. K. Liu, *Organometallics* 14 (1995) 1514.
- [5] (a) R. M. Bullock, C. E. L. Headford, S. E. Kegley, J. R. Norton, *J. Am. Chem. Soc.* 107 (1985) 727;
(b) C. Zou, M. S. Wrighton, J. P. Blaha, *Organometallics* 6 (1987) 1452;

- (c) K. Kirchner, H. Taube, *J. Am. Chem. Soc.* 113 (1991) 7039;
- (d) L. K. Liu, L. S. Luh, *Organometallics* 15 (1996) 5263;
- (e) M. Basato, A. Biffis, C. Tubaro, C. Graiff, A. Tiripicchio, *J. Chem. Soc., Dalton Trans.* (2004) 4092.
- [6] V. G. Albano, L. Busetto, C. Camiletti, C. Castellari, M. Monari, V. Zanotti, *J. Chem. Soc., Dalton Trans.* (1997) 4671.
- [7] (a) V. G. Albano, S. Bordoni, L. Busetto, M. Monari, V. Zanotti, *Organometallics* 14 (1995) 5456;
- (b) S. Bordoni, L. Busetto, C. Camiletti, V. Zanotti, V. G. Albano, M. Monari, F. Prestopino, *Organometallics* 16 (1997) 1224.
- [8] (a) A. F. Dyke, S. A. R. Knox, P. J. Naish, G. E. Taylor, *J. Chem. Soc., Chem. Commun.* (1980) 803;
- (b) C. E. Sumner Jr, J. A. Collier, R. Pettit, *Organometallics* 1 (1982) 1350;
- (c) A. Eisenstadt, A. Efraty, *Organometallics* 1 (1982) 1100;
- (d) R. E. Colborn; A. F. Dyke, S. A. R. Knox, K. A. Mcpherson, A. G. Orpen, *J. Organomet. Chem.* 239 (1982) C15;
- (e) P. Q. Adams, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, P. Woodward, *J. Chem. Soc. Chem. Commun.* (1983) 222;
- (f) R. E. Colborn, D. L. Davies, A. F. Dyke, S. A. R. Knox, K. A. Mead, A. G. Orpen, J. E. Guerchais, J. Roué, *J. Chem. Soc., Dalton Trans.* (1989) 1799;
- (g) C. P. Casey, G. P. Niccolai, *Organometallics* 13 (1994), 2527;
- (h) M. Akita, R. Hua, S. Nakanishi, M. Tanaka, Y. Moro-oka, *Organometallics* 16 (1997) 5572;
- (i) B. D. Rowsell, R. McDonald, M. J. Ferguson, M. Cowie, *Organometallics* 22 (2003) 2944;
- (j) J. Kaneko, T. Suzuki, K. Isobe, P. M. Maitlis, *J. Organomet. Chem.* 554 (1998) 155.
- [9] (a) D. A. Brown, N. J. Fitzpatrick, P. J. Groarke N. Koga, K. Morokuma *Organometallics* 12 (1993) 2521;
- (b) K. J. van den Berg, S. Ingemann N. M. M. Nibbering, *Organometallics* 11 (1992) 2389.
- [10] (a) M. Green, A. G. Orpen, C. J. Schaverien, I. D. Williams, *J. Chem. Soc. Dalton Trans.* (1987) 1313;

- (b) J.-J. Peng, K.-M. Horng, P.-S. Cheng, Y. Chi, S.-M. Peng, G.-H. Lee, *Organometallics* 13 (1994) 2365.
- [11] (a) O. P. Melnyk, D. Schollmeyer, V. V. Olijnyk, Y. E. Filinchuk, *Acta Crystallogr., Sect. C* 57 (2001) 151;
 (b) P. Mura, R. Spagna, L. Zambonelli, *J. Organomet. Chem.* 142 (1977) 403;
 (c) F. R.; Hartley, J. L. Wagner, *J. Chem. Soc., Dalton Trans.* (1972) 2282.
- [12] (a) M. Aresta, A. Dibenedetto, E. Quaranta, M. Lanfranchi, A. Tiripicchio, *Organometallics* 19 (2000) 4199;
 (b) M. Aresta, E. Quaranta, A. Dibenedetto, P. Giannoccaro, I. Tommasi, M. Lanfranchi, A. Tiripicchio, *Organometallics* 16 (1997) 834.
- [13] (a) Che-P. Chuang, Yi-L. Wu, *Tetrahedron* 60 (2004) 1841 ;
 (b) J. A. Hrabie, E. V. Arnold, M. L. Citro, G. Clifford, L. K. Keefer, *J. Org. Chem.* 65 (2000) 5745 ;
 (c) F. Aznar, C. Valdes, M.-P. Cabal, *Tetrahedron Letters* 41 (2000) 5683 ;
 (d) Mei-X. Wang, Wei-S. Miao, Y. Cheng, Zhi-T. Huang, *Tetrahedron* 55 (1999) 14611 ;
 (e) B. De Jeso, J. C. Pommier, *J. Organomet. Chem.* 186 (1980) C9;
 (f) S. Fatutta, G. Pitacco, C. Russo, E. Valentin, *J. Chem. Soc., Perkin Trans.* 9 (1982) 2045.
 (g) J. Wagler, U. Bohme, G. Roewer, *Angew. Chem., Int. Ed.* 41 (2002) 1732.
- [14] M. E. Kuehne, T. Garbacik, *J. Org. Chem.* 35 (1970) 1555.
- [15] (a) G. Balacco, G. Natile, *J. Chem. Soc., Dalton Trans.* (1990) 3021;
 (b) S. L. Doran, D. B.; Brown, C. W. Allen, *J. Organomet. Chem.* 340 (1988) 111;
 (c) H. C. Clark, C. R. C. Milne, N. C. Payne, *J. Am. Chem. Soc.* 100 (1978) 1164;
 (d) M. del Rosario Benites, F. R. Fronczek, R. P.; Hammer, A. W. Maverick, *Inorg. Chem.* 36 (1997) 5826.
- [16] (a) R. D. Adams, G. Chen, J. Yin, *Organometallics* 10 (1991) 2087;
 (b) S. Doherty, G. Hogarth, M. R. J. Elsegood, W. Clegg, N. H. Rees, M. Waugh, *Organometallics* 17 (1998) 3331.
- [17] W. Wilker, D. Leibfritz, R. Kerssebaum, W. Beimel, *Magn. Reson. Chem.* 31 (1993) 287.
- [18] Stott, J. Stonehouse, J. Keeler, T. L. Hwang, A. J. Shaka, *J. Am. Chem. Soc.* 117 (1995) 4199.

- [19] (a) SMART and SAINT Software Reference Manuals, Version 5.051 (Windows NT Version), Bruker Analytical X-ray Instruments, Inc., Madison, WI, 1998;
- (b) G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction, University of Göttingen, Germany, 1996;
- (c) A. Altomare, M. C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J Appl. Crystallogr. 32 (1999) 115;
- (d) G. M. Sheldrick, SHELXTLplus Version 5.1 (Windows NT Version) -Structure Determination Package, Bruker Analytical X-ray Instruments Inc, Madison, WI, USA, 1998.

Figures

Figure 1. Molecular structure of the cation $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{H})\text{NMe}_3\}(\mu\text{-CO})(\text{CO})(\text{Cp})\{\eta^5\text{-C}_5\text{H}_4(\text{Me})\}]^+$ of **5**. The Cp and $\text{C}_5\text{H}_4\text{Me}$ hydrogens have been omitted for clarity

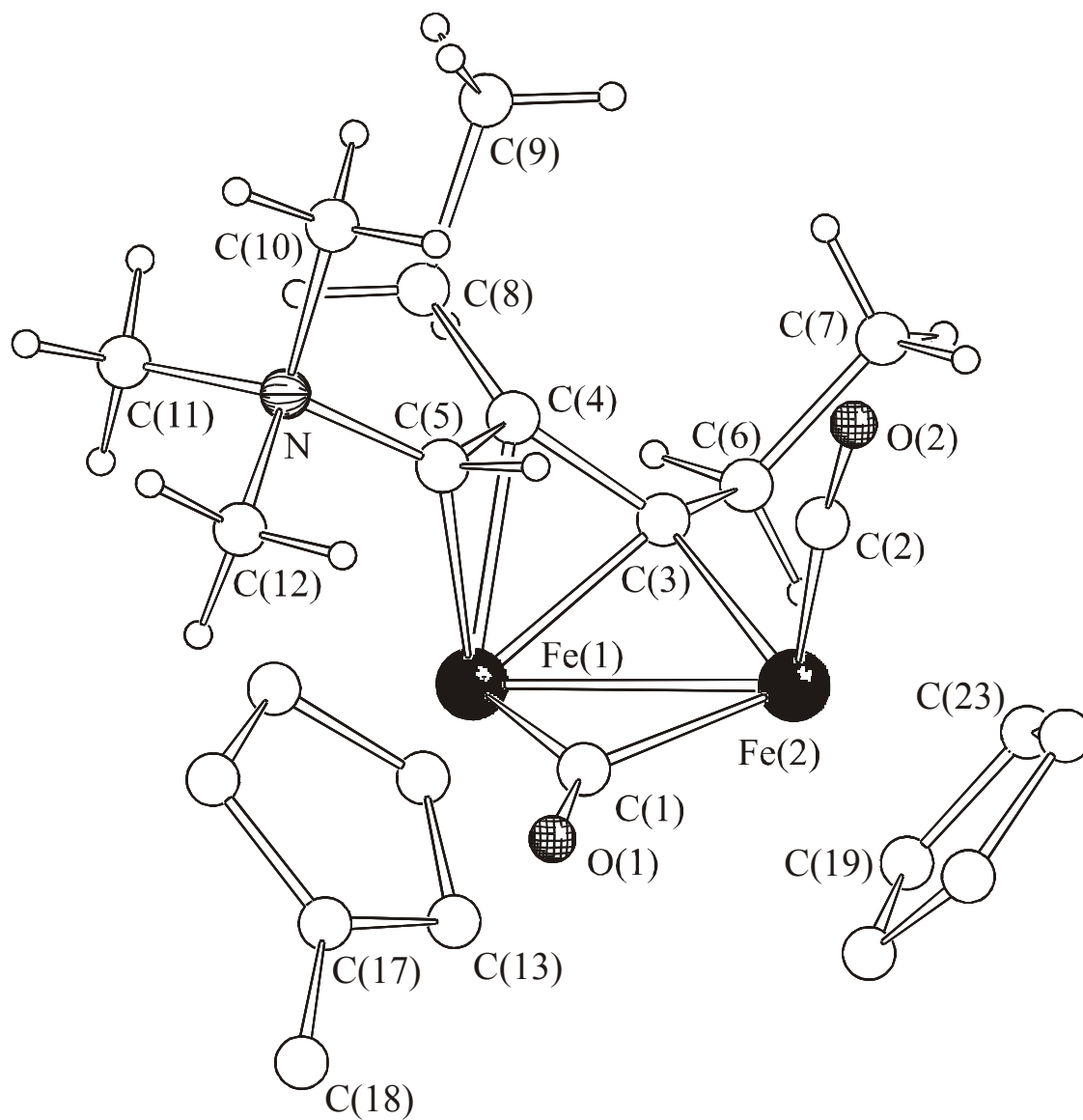


Figure 2. Molecular structure of the cation $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{H})\text{N}(\text{Me})_3\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]^+$ of **6c**. The Cp hydrogens have been omitted for clarity.

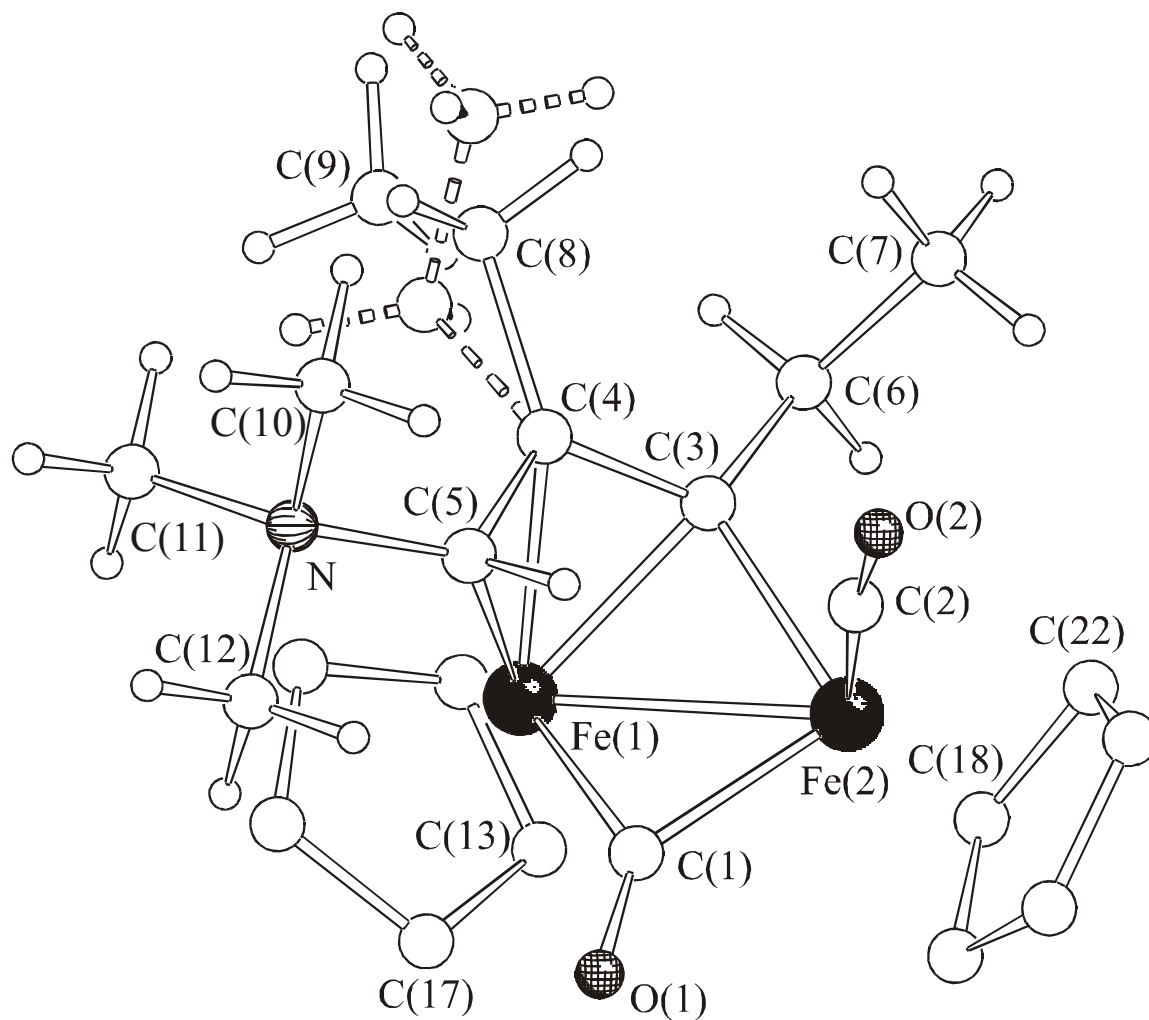


Table 1.

Comparison of selected bond lengths (Å) and angles (°) between $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Tol)CH=CHNMe}_2\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (**A**) and $[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Et)C(Et)CH(NMe}_3\})\}(\mu\text{-CO})(\text{CO})(\text{Cp})\{\text{C}_5\text{H}_4(\text{Me})\}][\text{CF}_3\text{SO}_3]$ (**5**).

	(A)	5
Fe(1)-Fe(2)	2.545(1)	2.543(1)
Fe(1)-C(1)	1.849(7)	1.907(5)
Fe(2)-C(1)	2.012(6)	1.941(5)
Fe(1)-C(3)	1.979(6)	1.995(5)
Fe(2)-C(3)	1.977(6)	2.004(5)
Fe(1)-C(4)	2.070(6)	2.055(5)
Fe(1)-C(5)	1.844(6)	2.072(5)
C(3)-C(4)	1.441(8)	1.445(7)
C(4)-C(5)	1.408(9)	1.492(8)
C(5)-N	1.375(8)	1.486(7)
N-C(10)		1.517(8)
N-C11/C14	1.445(9)	1.489(7)
N-C12/C13	1.444(8)	1.524(7)
C(4)-C(8)		1.527(7)
C(8)-C(9)		1.530(8)
Fe(1)-C(Cp')(av)	2.110	2.112
Fe(2)-C(cp)(av)	2.132	2.136

Table 2

Crystal data and experimental details for [5].CH₂Cl₂ and [6c].CH₂Cl₂.

Compound	[5].CH ₂ Cl ₂	[6c].CH ₂ Cl ₂
Formula	C ₂₄ H ₃₂ F ₃ Fe ₂ NO ₅ S.CH ₂ Cl ₂	C ₂₃ H ₃₀ F ₃ Fe ₂ NO ₅ S. CH ₂ Cl ₂
<i>F_w</i>	700.19	686.17
T (K)	100	100
λ (Å)	0.71073	0.71073
Crystal symmetry	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.6268(6)	11.151(2)
<i>b</i> (Å)	21.399(2)	9.447(2)
<i>c</i> (Å)	17.340(1)	26.075(4)
α (°)	90	90
β (°)	92.135(2)	94.469(3)
γ (°)	90	90
Cell volume (Å ³)	2828.0(4)	2738.5(8)
<i>Z</i>	4	4
<i>D_c</i> (Mg m ⁻³)	1.645	1.664
μ (Mo-K α) (mm ⁻¹)	1.346	1.388
<i>F</i> (000)	1440	1408
Crystal size (mm ³)	0.30 x 0.25 x 0.23	0.25 x 0.20 x 0.15
θ limits (°)	2.54-26.99	1.57-29.86
Reflections collected	29267[R(int)= 0.0593]	33297[R(int)= 0.0721]
Unique observed reflections [<i>F_o</i> > 4 σ (<i>F_o</i>)]	6132	7844
Goodness-of-fit-on <i>F</i> ²	1.077	1.076
<i>R</i> ₁ (<i>F</i>) ^a , <i>wR</i> ₂ (<i>F</i> ²) ^b	0.0708, 0.1848	0.0605, 0.1488
Largest diff. peak and hole (e. Å ⁻³)	1.983 and -1.133	1.558 and -1.520

^a $R_1 = \Sigma ||F_o| - |F_c| / \Sigma |F_o|$.^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ where $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2) / 3$

New bridging ligands from methylation reactions of μ -vinyliminium diiron complexes

Vincenzo G. Albano,⁺⁺ Luigi Busetto,⁺ Fabio Marchetti,⁺ Magda Monari,⁺⁺ Stefano Zacchini⁺ and Valerio Zanotti.^{++*}

⁺Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

⁺⁺Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy

Methylolithium addition at the Cp ligand of the diiron vinyliminium complexes **1** is followed by hydrogen migration from the C₅H₅Me ring to the iminium carbon. Bridging vinylcarbene complexes of type **2** are consequently formed. Treatment of **2** with MeSO₃CF₃ selectively produces the methylation of the nitrogen atom, affording the ammonium μ -allylidene **5**.

