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# New bridging ligands from methylation reactions of $\mu$-vinyliminium diiron complexes

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## Abstract

The vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(R')C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ ($R = Me$, $R' = Et$, **1a**; $R = Me$, $R' = Ph$, **1b**; $R = R' = Me$, **1c**; $R = Xyl$, $R' = Me$, **1d**; $R = Xyl$, $R' = Et$, **1e**; $R = Xyl$, $R' = Ph$, **1f**; $Xyl = 2{,}6\text{-}Me_2C_6H_3$), react with MeLi affording the corresponding $\mu$-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')C(R')=CHN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)\{C_5H_4(Me)\}]$ (**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 $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Ph)=C(Ph)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ reacts with PhLi to give $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Ph)C(Ph)=CHN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)\{C_5H_4(Ph)\}]$ (**4**).

Treatment of **2a** with $CF_3SO_3CH_3$ results in methylation of the nitrogen, yielding the complex $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Et)C(Et)CH(NMe_3)\}(\mu\text{-}CO)(CO)(Cp)\{C_5H_4(Me)\}][CF_3SO_3]$ (**5**). Analogously, the $\mu$-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')C(R'')=CHN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$, ($R = Me$, $R' = Tol$, $R'' = H$, **3a**; $R = Me$, $R' = SiMe_3$, $R'' = H$, **3b**; $R = Me$, $R' = R'' = Et$, **3c**; $R = Me$, $R' = R'' = Ph$, **3d**; $R = Bz$, $R' = Tol$, $R'' = H$, **3e**; $R = Bz$, $R' = SiMe_3$, $R'' = H$, **3f**; $R = Bz$, $R' = COOMe$, $R'' = H$, **3g**; $R = Bz$, $R' = R'' = COOMe$, **3h**; $R = Bz$, $R' = R'' = Me$, **3i**; $Bz = CH_2Ph$), react with $CF_3SO_3CH_3$ to give the corresponding ammonium-functionalized $\mu$-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')C(R'')CH(NMe_2R)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (**6a**–**i**). The molecular structures of **5** and **6c** have been elucidated by X-ray diffraction studies.

Finally, protonation of $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Et)C(Et)=CH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**3c**), with $HBF_4$, affords the complex $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Et)C(Et)CH(NHMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]][BF_4]$ (**7**).

*Keywords:* Vinyliminium; Vinylalkylidene; Enaminoalkylidene; Aminocarbyne; Diiron complexes; Crystal structure

## 1. Introduction

Binuclear complexes are potentially promoters of unique reactivity via bridging coordination and activation of organic fragments to two metal centres [1]. We have recently reported [2] on the synthesis and properties of a variety of bridging vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')=C_\beta(R'')C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ ($R = Me$, Bz, Xyl), obtained by insertion of alkynes ($R'C\equiv CR''$) into the M–C bond of $\mu$-aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$. The $\mu$-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

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directed to the iminium carbon ($C_\alpha$) or the adjacent $C_\beta$, depending upon the nature of the substituents at the iminium nitrogen. These reactions generate μ-$\eta^1$:$\eta^3$-vinylalkylidene, and μ-$\eta^1$:$\eta^3$-bis-alkylidene ligands, respectively [3a,3b].

In the present paper, we report on the reactions of the μ-vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R'){=}C(R')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**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 $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R'){=}C(R')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1**), react with MeLi in THF solution at −40 °C, affording the μ-vinylalkylidene $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')C(R'){=}CHN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)\{\eta^5\text{-}C_5H_4(Me)\}]$ (**2a**–**f**) (Scheme 1) as a result of a Cp ligand methylation and subsequent hydrogen migration to $C_\alpha$. The species **2** have been isolated in about 60–70% yields after chromatography on alumina.

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**).

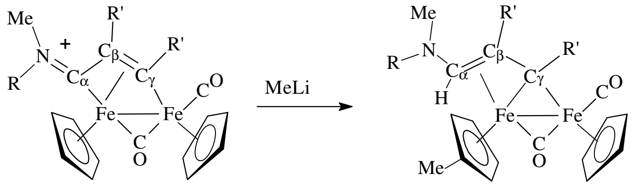
The $^1H$ NMR spectra of **2a**–**f** indicate the existence in solution of a single isomeric form. The main feature is the presence of five resonances, attributable to the cyclopentadienyls: one singlet accounts for five equivalent Cp protons (e.g. at $\delta$ 4.62 ppm for **2a**), whereas four distinct broad resonances are attributable to the non-equivalent protons of the $MeC_5H_4$ ring (e.g. at $\delta$ 4.69, 4.36, 4.13, 3.90 ppm for **2a**). The same pattern is shown by the $^{13}C$ NMR spectra. Compounds **2a**–**f** closely resemble the μ-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')C(R'){=}CHN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**3**), previously reported [3a,3b], which have been obtained by direct hydride addition (by $NaBH_4$) to the iminium carbon ($C_\alpha$) of the corresponding parent vinyliminium complexes **1**. Their $^1H$ and $^{13}C$ 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 $\delta$ 4.23 ppm has resulted in strong enhancements of the resonances associated with the other ring (at $\delta$ 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,3b].

The reaction described in Scheme 1 is not of general character: under the same conditions other RLi reagents ($Bu^nLi$, PhLi) failed to generate addition products. An exception is represented by the reaction of PhLi with **1f**, which afforded $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Ph)C(Ph){=}CHN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)\{\eta^5\text{-}C_5H_4(Ph)\}]$ (**4**), in modest yield (Scheme 2). Complex **4** has been identified via IR and NMR spectroscopy, and elemental analysis.

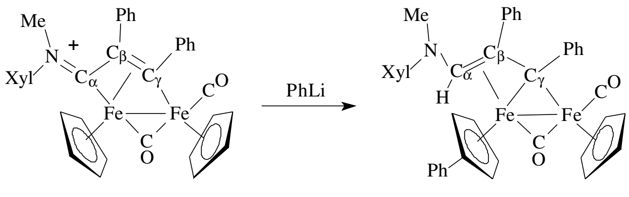
There are numerous examples of nucleophilic additions to $\eta^5$-Cp ligands [4]. Powerful nucleophiles, as carbanions or $H^-$, are generally involved and the reactions usually afford stable $\eta^4$ cyclopentadiene complexes. In some cases nucleophilic addition at the Cp ring is followed by hydride 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 $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ have been shown to react with lithium alkyls (RLi) or Grignard reagents (RMgCl), affording stable neutral adducts containing the $\eta^4$-$C_5H_5R$ (Scheme 3A). Likewise, Grignard reagents have been reported to attack the Cp of the μ-thiocarbyne complex $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2]$-



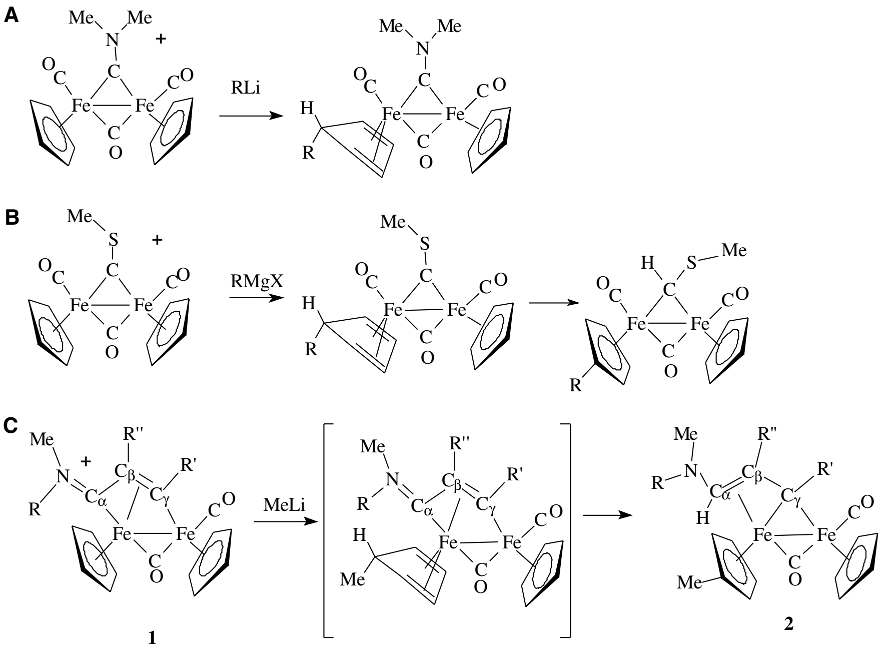
| | R | R' | |
|---|---|---|---|
| **1a** | Me | Et | **2a** |
| **1b** | Me | Ph | **2b** |
| **1c** | Me | Me | **2c** |
| **1d** | Xyl | Me | **2d** |
| **1e** | Xyl | Et | **2e** |
| **1f** | Xyl | Ph | **2f** |

Scheme 1.



**1f** **4**

Scheme 2.



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

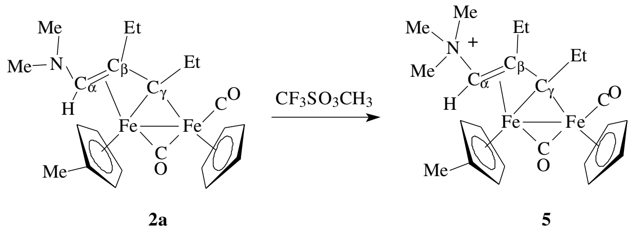
$[SO_3CF_3]$ yielding the cyclopentadiene intermediates $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)(C_5H_5R)]$, which are stable enough to be isolated. However, these species rearrange by hydrogen migration from the $C_5H_5R$ ring to the μ-C carbyne carbon and generate the alkylidene complexes $[Fe_2\{\mu\text{-}C(H)(SMe)\}(\mu\text{-}CO)(CO)_2(Cp)(C_5H_4R)]$ (Scheme 3B). Thus, a possible reaction pathway leading to **2** and **4** from **1** should include a $\eta^4$-$C_5H_5Me$ intermediate (Scheme 3C), which rearranges via hydrogen migration from the cyclopentadiene ring to the iminium carbon ($C_\alpha$) of the bridging ligand. Nucleophilic attack on the Cp ligand is likely to occur directly, although we cannot 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.

As above mentioned, bridging vinylalkylidene ligands like those found in **2a**–**f** and **4** can be directly formed by $NaBH_4$ addition to the $C_\alpha$ of **1a**–**f**, generating the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')C(R'')\text{=}CHN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**3**). Exception are the reactions with compounds **1d** and **1e**, which undergo hydride attack at the $C_\beta$ 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 μ-$\eta^1$:$\eta^3$ coordinated, together with the pentaatomic 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 $C_\alpha$ or $C_\beta$, rather than giving addition at the Cp ring. Far from providing a satisfactory explanation, it should be remarked that in the related diiron complexes $[Fe_2(\mu\text{-}CX)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ (X = $NMe_2$, 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 $[Fe(CO)_3Cp]^+$ and $[Co(CO)_2Cp]^+$, 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 NR′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 $C_\beta$, would be preferentially alkylated. In order to investigate the point, compound **2a** has been treated with the powerful methylating reagent $CF_3SO_3CH_3$. Methylation affords $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et)C(Et)CH(NMe_3)\}(\mu\text{-}CO)(CO)(Cp)\{\eta^5\text{-}C_5H_4(Me)\}][CF_3SO_3]$ (**5**), (Scheme 4). The nature of **5** has been fully elucidated by X-ray diffraction.



Scheme 4.

The molecular structure of **5**, reported in Fig. 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 $C_\alpha$ [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 $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Tol)CH{=}CH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (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 donor to Fe(1) in spite of the contiguous electron withdrawing ammonium nitrogen.

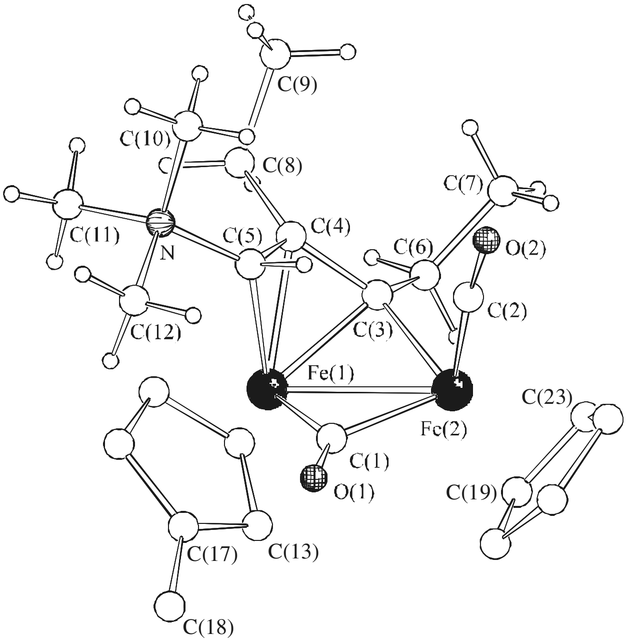


Fig. 1. Molecular structure of the cation $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Et)C(Et)C(H)NMe_3\}(\mu\text{-}CO)(CO)(Cp)\{\eta^5\text{-}C_5H_4(Me)\}]^+$ of **5**. The Cp and $C_5H_4$-Me hydrogens have been omitted for clarity.

Table 1
Comparison of selected bond lengths (Å) and angles (°) between $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Tol)CH{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ **(A)** and $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Et)C(Et)CH(NMe_3)\}(\mu\text{-}CO)(CO)(Cp)\{C_5H_4(Me)\}][CF_3SO_3]$ (**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 |

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.

The spectroscopic data of complex **5** agree with its structural features. The IR spectra (in $CH_2Cl_2$ 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 $\delta$ 3.26 ppm, because of free

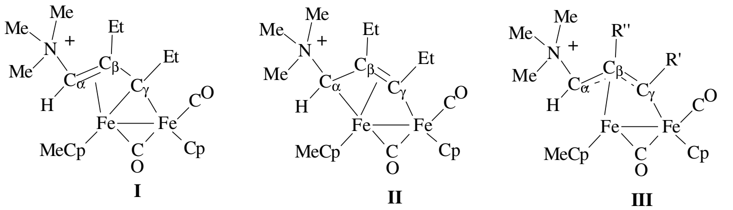
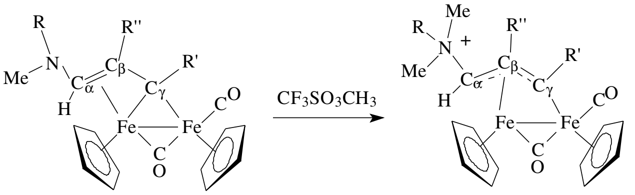


Chart 1. Possible descriptions of the bridging ligand in **5**.

rotation of the $NMe_3$ group around the $C_\alpha$–N axis. Major features of the $^{13}C$ NMR spectrum include the typical low field resonance for the alkylidene $C_\gamma$ carbon (at $\delta$ 198.2 ppm), and the resonances at higher field due to $C_\alpha$ and $C_\beta$ (at $\delta$ 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 [$R_2N–C_\alpha{=}C_\beta$] usually involves $C_\beta$ [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 $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')C(R''){=}CHN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**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 $CF_3SO_3CH_3$ affording the complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')C(R'')CH(NMe_2R)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (**6a**–**i**), in about 70% yields (Scheme 5).



| | R | R' | R'' | |
|---|---|---|---|---|
| **3a** | Me | Tol | H | **6a** |
| **3b** | Me | SiMe₃ | H | **6b** |
| **3c** | Me | Et | Et | **6c** |
| **3d** | Me | Ph | Ph | **6d** |
| **3e** | Bz | Tol | H | **6e** |
| **3f** | Bz | SiMe₃ | H | **6f** |
| **3g** | Bz | COOMe | H | **6g** |
| **3h** | Bz | COOMe | COOMe | **6h** |
| **3i** | Bz | Me | Me | **6i** |

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 Fig. 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 $CH_2Cl_2$ 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 $CDCl_3$ solution) show a high-field resonance due to $C_\alpha–H$ (e.g. at $\delta$ −0.10 ppm for **6a**). In addition, when R''=H, the coupling constant value between $C_\alpha H$

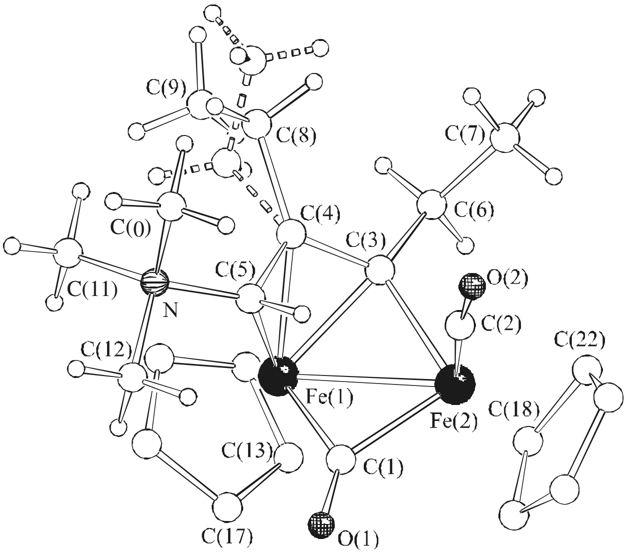
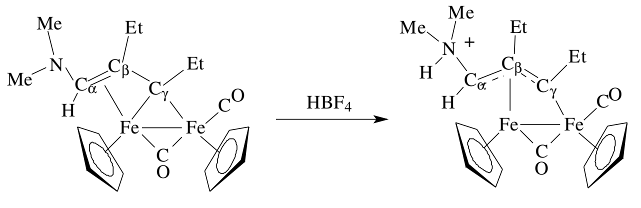


Fig. 2. Molecular structure of the cation $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Et)C(Et)C(H)N(Me)_3\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ of **6c**. The Cp hydrogens have been omitted for clarity.



**3c** **7**

Scheme 6.

and $C_\beta H$ ($^3J_{HH} = 6$–$8$ 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 $\delta$ 3.21 and 56.3 ppm for **6a**), as a consequence of free rotation of the $NMe_3$ group around the $C_\alpha$–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 $C_\alpha$, $C_\beta$ and $C_\gamma$ resonances (e.g. for **6a** at $\delta$ 88.9, 70.9, 188.3 ppm, respectively).

The results reported in Scheme 1 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 $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et)C(Et){=}CH(NMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**3c**) with $HBF_4$ has also been investigated. Protonation occurs at the N atom, resulting in the formation of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et)C(Et)CH(NHMe_2)\}(\mu\text{-}CO)(CO)(Cp)_2][BF_4]$, (**7**) (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 $\delta$ 7.01 ppm. Significant NMR data include the $^1H$ resonance due to $C_\alpha$–*H* (at $\delta$ −1.11 ppm), and the $^{13}C$ resonances of $C_\alpha$ (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 $C_5H_5$ 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 $CH_3CN$. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for $^1H$ and $^{13}C$ were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and $^1H$,$^{13}C$ 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 DPFGSE-NOE sequence [18]. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds **1a**–**f** [2] and **3a**–**i** [3a,3b] were prepared by published methods.

### 4.2. Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')C_\beta(R'){=}C_\alpha HN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)\{\eta^5\text{-}C_5H_4(Me)\}]$ (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%. $C_{22}H_{29}Fe_2NO_2$ requires: C, 58.57; H, 6.48; N, 3.10. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1930vs and 1751s (CO). $^1H$ NMR ($CD_2Cl_2$) δ 4.69, 4.36, 4.13, 3.90 (br, 4H, $C_5H_4$ Me); 4.62 (s, 5H, Cp); 4.34, 3.92 (m, 2H, $C_\gamma CH_2CH_3$); 2.50, 2.21 (m, 2H, $C_\beta CH_2$); 2.27 (s, 6H, NMe); 2.00 (s, 3H, $C_5H_4$ *Me*); 1.60 (br, 3H, $C_\gamma CH_2CH_3$); 1.19 (br, 3H, $C_\beta CH_2CH_3$); −0.98 (s, 1H, $C_\alpha H$). $^{13}C$ NMR ($CD_2Cl_2$) δ 274.4 (μ-CO); 216.0 (CO); 196.5 ($C_\gamma$); 96.2, 83.3, 82.8, 80.9, 66.8 ($C_5H_4Me$); 94.6 ($C_\alpha$); 93.1 ($C_\beta$); 87.3 (Cp); 47.5 (NMe); 42.5 ($C_\gamma CH_2CH_3$); 23.7 ($C_\beta CH_2CH_3$); 21.1 ($C_\gamma CH_2CH_3$); 16.5 ($C_\beta CH_2CH_3$); 12.7 ($C_5H_4$ *Me*).

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%. $C_{30}H_{29}Fe_2NO_2$ requires: C, 65.84; H, 5.34; N, 2.56. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1933vs and 1752s (CO). $^1H$ NMR ($CDCl_3$) 8.12–6.63 (m, 10H, Ph); 4.80, 4.52, 4.43, 4.28 (br, 4H, $C_4H_4$); 4.30 (s, 5H, Cp); 2.34 (s, 3H, $C_4H_4CMe$); 2.18 (s, 6H, NMe); 0.91 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 278.9 (μ-CO); 216.0 (CO); 185.4 ($C_\gamma$); 156.9–123.1 (Ph); 98.9 ($C_4H_4CMe$); 84.2, 83.2, 81.2, 67.2 ($C_4H_4$); 98.7 ($C_\alpha$); 88.2 (Cp); 77.5 ($C_\beta$); 42.8 (NMe); 13.7 ($C_4H_4CMe$).

**2c**: Yield (64%). Found: C, 56.84; H, 6.02; N, 3.28%. $C_{20}H_{25}Fe_2NO_2$ requires: C, 56.77; H, 5.96; N, 3.31. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1932vs and 1762s (CO). $^1H$ NMR ($CDCl_3$) 4.69 (s, 5H, Cp); 4.53, 4.38, 4.14, 3.74 (br, 4H, $C_4H_4$); 3.80 (s, 3H, $C_\gamma Me$); 2.31 (s, 6H, NMe); 2.07 (s, 3H, $C_4H_4CMe$); 2.03 (s, 3H, $C_\beta Me$); −0.76 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) δ 273.2 (μ-CO); 216.7 (CO); 186.5 ($C_\gamma$); 97.5 ($C_4H_4CMe$); 84.2, 83.3, 81.2, 67.3 ($C_4H_4$); 92.2 ($C_\alpha$); 89.4 ($C_\beta$); 86.7 (Cp); 46.1 (NMe); 36.3 ($C_\gamma Me$); 15.6 ($C_\beta Me$); 11.6 ($C_4H_4CMe$).

**2d**: Yield (58%). Found: C, 63.06; H, 6.00; N, 2.66%. $C_{27}H_{31}Fe_2NO_2$ requires: C, 63.19; H, 6.09; N, 2.73. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1930vs and 1762s (CO). $^1H$ NMR ($CDCl_3$) 7.33–6.72 (m, 3H, $Me_2C_6H_3$); 4.64 (s, 5H, Cp); 4.56, 4.31, 4.12, 3.46 (br, 4H, $C_4H_4$); 3.82 (s, 3H, $C_\gamma Me$); 2.80 (s, 3H, NMe); 2.26 (s, 3H, $C_4H_4CMe$); 2.11, 2.05 (s, 6H, $Me_2C_6H_3$); 1.75 (s, 3H, $C_\beta Me$); 0.33 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) δ 276.4 (μ-CO); 217.9 (CO); 185.2 ($C_\gamma$); 147.9 (*ipso*-$Me_2C_6H_3$); 136.0, 135.6, 129.2, 128.2, 125.3 ($Me_2C_6H_3$); 98.5 ($C_4H_4CMe$); 85.1, 84.2, 83.5, 80.4 ($C_4H_4$); 95.3 ($C_\alpha$); 88.8 ($C_\beta$); 87.0 (Cp); 41.3 (NMe); 37.5 ($C_\gamma Me$); 19.7, 18.5 ($Me_2C_6H_3$); 17.2 ($C_\beta Me$); 12.9 ($C_4H_4CMe$).

**2e**: Yield (74%). Found: C, 64.48; H, 6.37; N, 2.61%. $C_{29}H_{35}Fe_2NO_2$ requires: C, 64.35; H, 6.52; N, 2.59%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1932vs and 1773s (CO). $^1H$ NMR ($CD_2Cl_2$) 7.25–6.82 (m, 3H, $Me_2C_6H_3$); 4.66 (s, 5H, Cp); 4.43, 4.37, 3.91, 3.46 (br, 4H, $C_4H_4$); 4.36, 3.98 (m, 2H, $C_\gamma CH_2$); 2.88 (s, 3H, NMe); 2.73, 2.30 (m, 2H, $C_\beta CH_2$); 2.21 (s, 3H, $C_4H_4CMe$); 2.14, 2.08 (s, 6H, $Me_2C_6H_3$); 1.62 (t, 3H, $^3J_{HH} = 7.3$ Hz, $C_\gamma CH_2CH_3$); 0.57 (t, 3H, $^3J_{HH} = 7.3$ Hz, $C_\beta CH_2CH_3$); 0.10 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) δ 276.7 (μ-CO); 218.6 (CO); 196.2 ($C_\gamma$); 149.5 (*ipso*-$Me_2C_6H_3$); 136.3, 136.0, 129.7, 128.5, 125.5 ($Me_2C_6H_3$); 99.1 ($C_4H_4CMe$); 85.7, 84.0, 82.2, 80.8 ($C_4H_4$); 96.4 ($C_\alpha$); 91.7 ($C_\beta$); 87.3 (Cp); 42.4 ($C_\gamma CH_2CH_3$); 42.0 (NMe); 24.7 ($C_\beta CH_2CH_3$); 21.0 ($C_\gamma CH_2CH_3$); 20.2, 19.1 ($Me_2C_6H_3$); 14.2 ($C_\beta CH_2CH_3$); 12.9 ($C_4H_4CMe$). 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%. $C_{37}H_{35}Fe_2NO_2$ requires: C, 69.72; H, 5.53; N, 2.20. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1927vs and 1762s (CO). $^1H$ NMR ($CDCl_3$) 8.17–6.77 (m, 13H, Ph and $Me_2C_6H_3$); 5.50, 5.34, 4.55, 3.76 (br, 4H, $C_4H_4$); 4.23 (s, 5H, Cp); 2.92, 2.25 (s, 6H, $Me_2C_6H_3$); 2.17 (s, 3H, $C_4H_4CMe$); 2.01 (s, 3H, NMe); 1.26 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 278.7 (μ-CO); 218.2 (CO); 186.0 ($C_\gamma$); 157.1–123.0 (Ph and $Me_2C_6H_3$); 103.5 ($C_\alpha$); 89.2, 82.4, 82.2, 77.8 ($C_4H_4$); 88.0 (Cp); 77.5 ($C_\beta$); 38.2 (NMe); 20.1, 20.0 ($Me_2C_6H_3$); 13.5 ($C_4H_4CMe$).

### *4.3. Synthesis of [$Fe_2\{\mu$-$\eta^1$:$\eta^3$-C(Ph)C(Ph)=CHN(Me)(Xyl)$\}$(μ-CO)(CO)(Cp)$\{\eta^5$-$C_5H_4$(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%. $C_{42}H_{37}Fe_2NO_2$ requires: C, 72.12; H, 5.33; N, 2.00. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1932vs and 1772s (CO). $^1H$ NMR ($CD_2Cl_2$) 7.84–6.82 (m, 18H, Ph and $Me_2C_6H_3$); 4.99, 4.81, 4.57, 3.52 (br, 4H, $C_4H_4$); 4.25 (s, 5H, Cp); 3.06, 1.78 (s, 6H, $Me_2C_6H_3$); 2.79 (s, 3H, NMe); 1.31 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) δ 141.3–125.6 (Ph and $Me_2C_6H_3$); 89.4 ($C_\alpha$); 81.8 (Cp); 40.0 (NMe); 18.2, 18.1 ($Me_2C_6H_3$).

### *4.4. Synthesis of [$Fe_2\{\mu$-$\eta^1$:$\eta^3$-C(Et)C(Et)CH($NMe_3$)$\}$(μ-CO)(CO)(Cp)$\{\eta^5$-$C_5H_4$(Me)$\}$][$CF_3SO_3$] (5)*

A solution of **2a** (102 mg, 0.226 mmol), in $CH_2Cl_2$ (10 ml), was treated with $CF_3SO_3CH_3$ (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 × 20 mL), dissolved in $CH_2Cl_2$ 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%. $C_{24}H_{32}F_3Fe_2NO_5S$ requires: C, 46.85; H, 5.24; N, 2.28. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1953vs and 1782s (CO). $^1H$ NMR ($CDCl_3$) 5.01 (s, 1H, $C_4H_4$); 4.86 (s, 5H, Cp); 4.83, 4.51, 4.13 (br, 3H, $C_4H_4$); 4.29, 3.86 (m, 2H, $C_\gamma CH_2$); 3.26 (s, 9H, NMe); 3.20, 2.10 (m, 2H, $C_\beta CH_2$); 2.16 (s, 3H, $C_4H_4CMe$); 1.68 (t, 3H, $^3J_{HH} = 7.3$ Hz, $C_\gamma CH_2CH_3$); 1.38 (t, 3H, $^3J_{HH} = 7.5$ Hz, $C_\beta CH_2CH_3$); −1.38 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 270.9 (μ-CO); 215.6 (CO); 198.2 ($C_\gamma$); 101.5 ($C_4H_4CMe$); 92.9 ($C_\alpha$); 88.7 (Cp); 88.3 ($C_\beta$); 84.8, 83.3, 82.9, 81.6 ($C_4H_4$); 57.5 (NMe); 42.4 ($C_\gamma CH_2$); 21.8 ($C_\beta CH_2$); 20.4 ($C_\gamma CH_2CH_3$); 16.6 ($C_\beta CH_2CH_3$); 12.6 ($C_4H_4CMe$).

### *4.5. Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')C(R'')CH(NMe_2R)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (R = Me, R′ = Tol, R″ = H (**6a**); R = Me, R′ = $SiMe_3$, 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′ $SiMe_3$, 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 $CH_2Cl_2$ solution (10 mL), was treated with $CF_3SO_3CH_3$ (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 × 20 mL), dissolved in $CH_2Cl_2$ 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%. $C_{26}H_{28}F_3Fe_2NO_5S$ requires: C, 49.16; H, 4.44; N, 2.20. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1964vs and 1794s (CO). $^1H$ NMR ($CDCl_3$) 7.60, 7.32 (d, $^3J_{HH} = 8.1$ Hz, 4H, $C_6H_4Me$); 4.83, 4.69 (s, 10H, Cp); 4.80 (d, 1H, $^3J_{HH} = 6.6$ Hz, $C_\beta H$); 3.21 (s, 9H, NMe); 2.47 (s, 3H, $C_6H_4Me$); −0.10 (d, 1H, $^3J_{HH} = 6.6$ Hz, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 266.7 (μ-CO); 213.8 (CO); 188.3 ($C_\gamma$); 154.1 (*ipso*-$C_6H_4Me$); 136.7, 129.6, 129.0, 128.4 ($C_6H_4Me$); 89.8, 83.9 (Cp); 88.9 ($C_\alpha$); 70.9 ($C_\beta$); 56.3 (NMe); 21.1 ($C_6H_4Me$).

Complexes **6b–i** were prepared by the same procedure described for **6a**, by reacting $CF_3SO_3CH_3$ 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%. $C_{22}H_{30}F_3Fe_2NO_5SSi$ requires: C, 42.80; H, 4.90; N, 2.27. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1962vs and 1790s (CO). $^1H$ NMR ($CDCl_3$) 4.94, 4.69 (s, 10H, Cp); 5.04 (d, 1H, $^3J_{HH} = 6.0$ Hz, $C_\beta H$); 3.10 (s, 9H, NMe); 0.65 (s, 9H, $SiMe_3$); −0.28 (d, 1H, $^3J_{HH} = 6.0$ Hz, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 266.7 (μ-CO); 213.5 (CO); 181.9 ($C_\gamma$); 90.3 ($C_\alpha$); 87.5, 82.1 (Cp); 75.8 ($C_\beta$); 55.7 (NMe); 3.1 ($SiMe_3$).

**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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1956vs and 1786s (CO). $^1H$ NMR ($CDCl_3$) 4.90, 4.63 (s, 10H, Cp); 4.33, 3.91 (m, 2H, $C_\gamma CH_2$); 3.32 (s, 9H, NMe); 3.17, 2.18 (m, 2H, $C_\beta CH_2$); 1.69 (m, 3H, $C_\gamma CH_2CH_3$); 1.40 (t, 3H, $C_\gamma CH_2CH_3$); −1.38 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 269.7 (μ-CO); 215.1 (CO); 198.7 ($C_\gamma$); 93.0 ($C_\alpha$); 89.0, 84.2 (Cp); 88.0 ($C_\beta$); 57.4 (NMe); 42.3 ($C_\gamma CH_2$); 21.9 ($C_\beta CH_2$); 20.4 ($C_\gamma CH_2CH_3$); 16.5 ($C_\beta CH_2CH_3$).

**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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1966vs and 1794s (CO). $^1H$ NMR ($CDCl_3$) 7.77–6.77 (m, 10H, Ph); 5.18, 4.58 (s, 10H, Cp); 3.07 (s, 9H, NMe);−0.72 (s, 1H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 266.6 (μ-CO); 214.3 (CO); 189.8 ($C_\gamma$); 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 ($C_\beta$); 86.3 ($C_\alpha$); 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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1958vs and 1792s (CO). $^1H$ NMR ($CDCl_3$) 7.60–7.20 (m, 9H, Ph and $C_6H_4Me$); 4.80, 4.06 (d, 2H, $^2J_{HH} = 13.2$ Hz, $CH_2Ph$); 4.74, 4.71 (s, 10H, Cp); 4.11 (d, 1H, $^3J_{HH} = 7.1$ Hz, $C_\beta H$); 3.59, 2.76 (s, 6H, NMe); 2.42 (s, 3H, $C_6H_4Me$); −0.26 (d, 1H, $^3J_{HH} = 7.1$ Hz, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 267.3 (μ-CO); 215.0 (CO); 186.5 ($C_\gamma$); 154.3 (*ipso*-$C_6H_4Me$); 136.7–127.2 (Ph and $C_6H_4Me$); 89.9, 83.9 (Cp); 88.7 ($C_\alpha$); 74.6 ($CH_2Ph$); 72.6 ($C_\beta$); 57.0, 46.1 (NMe); 20.9 ($C_6H_4Me$).

**6f**: Yield (77%). Found: C, 48.57; H, 5.01; 2.06%. $C_{28}H_{34}F_3Fe_2NO_5SSi$ requires: C, 48.50; H, 4.94; N, 2.02%. IR ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1957vs and 1793s (CO). $^1H$ NMR ($CDCl_3$) 7.60–7.19 (m, 5H, Ph); 4.95, 4.60 (s, 10H, Cp); 4.75, 3.88 (d, 2H, $^2J_{HH} = 13.0$ Hz, $CH_2Ph$); 4.16 (d, 1H, $^3J_{HH} = 6.9$ Hz, $C_\beta H$); 3.52, 2.68 (s, 6H, NMe); 0.42 (s, 9H, $SiMe_3$); −0.45 (d, 1H, $^3J_{HH} = 6.9$ Hz, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 266.7 (μ-CO); 214.6 (CO); 179.8 ($C_\gamma$); 133.2, 130.7, 128.7, 127.0 (Ph); 87.7, 82.1 (Cp); 85.7 ($C_\alpha$); 78.1 ($C_\beta$); 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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1970vs, 1805s and 1701m (CO). $^1H$ NMR ($CDCl_3$) 7.56–7.31 (m, 5H, Ph); 4.90, 4.78 (s, 10H, Cp); 4.63, 4.18 (d, 2H, $^2J_{HH} = 12.1$ Hz, $CH_2Ph$); 4.48 (d, 1H, $^3J_{HH} = 8.2$ Hz, $C_\beta H$); 4.03 (s, 3 H, $CO_2Me$); 3.39, 2.82 (s, 6H, NMe); −0.43 (d, 1H, $^3J_{HH} = 8.2$ 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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1981vs, 1811s and 1714m (CO). $^1H$ NMR ($CDCl_3$) 7.57–7.34 (m, 5H, Ph); 5.02, 4.89 (s, 10H, Cp); 4.84, 4.70 (d, 2H, $^2J_{HH} = 12.3$ Hz, C$H_2$Ph); 4.05, 4.04 (s, 6H, $CO_2Me$); 3.36, 2.94 (s, 6H, NMe); −1.43 (s, 1H, $C_\alpha$H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 259.9 (μ-CO); 211.9 (CO); 177.7, 174.3, 169.5 ($C_\gamma$ and $C_\gamma$–$CO_2$Me and $C_\beta$–$CO_2$Me); 133.1, 130.9, 129.5, 126.9 (Ph); 89.8, 87.1 (Cp); 79.7 ($C_\alpha$); 79.2 ($C_\beta$); 73.8 ($C$H$_2$Ph); 56.4, 54.9 (NMe); 52.7 ($CO_2$*Me*).

**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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1954vs and 1788s (CO). $^1$H NMR ($CDCl_3$) 7.60–7.25 (m, 5H, Ph); 4.92, 4.26 (d, 2H, $^2J_{HH} = 13$ Hz, C$H_2$Ph); 4.87, 4.57 (s, 10H, Cp); 3.73 (s, 3H, $C_\gamma$Me); 3.41, 3.08 (s, 6H, NMe); 1.99 (s, 3H, $C_\beta$Me); −1.39 (s, 1H, $C_\alpha$H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 269.1 (μ-CO); 215.4 (CO); 189.0 ($C_\gamma$); 132.9, 130.8, 129.3, 126.9 (Ph); 89.4, 85.2 (Cp); 89.0 ($C_\alpha$); 85.9 ($C_\beta$); 72.7 ($C$H$_2$Ph); 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-($NHMe_2$)$\}$(μ-CO)(CO)$(Cp)_2$][$BF_4$] (7)*

Compound **3c** (91 mg, 0.208 mmol), in $CH_2Cl_2$ (10 mL), was treated with tetrafluroboric 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 × 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 ($CH_2Cl_2$) $\nu_{max}$ ($cm^{-1}$) 1958vs and 1785s (CO); 3187m (NH) in KBr. $^1$H NMR ($CDCl_3$) 7.01 (s, 1H, NH); 4.87, 4.54 (s, 10H, Cp); 4.28, 3.87 (m, 2H, $C_\gamma CH_2$); 3.39, 2.87 (s, 6H, NMe); 3.03, 2.35 (m, 2H, $C_\beta CH_2$); 1.66 (m, 3H, $C_\gamma CH_2$$CH_3$); 1.36 (t, 3H, $C_\gamma CH_2$$CH_3$); −1.11 (s, 1H, $C_\alpha$H). $^{13}C\{^1H\}$ NMR ($CDCl_3$) $\delta$ 269.4 (μ-CO); 214.5 (CO); 197.8 ($C_\gamma$); 88.7, 85.0 (Cp); 87.6 ($C_\beta$); 80.5 ($C_\alpha$); 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) · $CH_2Cl_2$ and (6c) · $CH_2Cl_2$*

X-ray intensity data for **5** · $CH_2Cl_2$ and **6c** · $CH_2Cl_2$ 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 $C_\alpha$ 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

Table 2
Crystal data and experimental details for **[5] · $CH_2Cl_2$** and **[6c] · $CH_2Cl_2$**

| Compound | **[5] · $CH_2Cl_2$** | **[6c] · $CH_2Cl_2$** |
|---|---|---|
| Formula | $C_{24}H_{32}F_3Fe_2NO_5S \cdot CH_2Cl_2$ | $C_{23}H_{30}F_3Fe_2NO_5S \cdot CH_2Cl_2$ |
| Fw | 700.19 | 686.17 |
| Temperature (K) | 100 | 100 |
| λ (Å) | 0.71073 | 0.71073 |
| Crystal symmetry | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| *a* (Å) | 7.6268(6) | 11.151(2) |
| *b* (Å) | 21.399(2) | 9.447(2) |
| *c* (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) |
| *Z* | 4 | 4 |
| $D_c$ (mg $m^{-3}$) | 1.645 | 1.664 |
| μ (Mo Kα) ($mm^{-1}$) | 1.346 | 1.388 |
| *F*(000) | 1440 | 1408 |
| Crystal size ($mm^3$) | 0.30 × 0.25 × 0.23 | 0.25 × 0.20 × 0.15 |
| θ Limits (°) | 2.54–26.99 | 1.57–29.86 |
| Reflections collected | 29,267[$R_{int} = 0.0593$)] | 33,297[$R_{int} = 0.0721$)] |
| Unique observed reflections [$F_o > 4\sigma(F_o)$] | 6132 | 7844 |
| Goodness-of-fit-on $F^2$ | 1.077 | 1.076 |
| $R_1$ (*F*)[a], $wR_2$ ($F^2$)[b] | 0.0708, 0.1848 | 0.0605, 0.1488 |
| Largest difference peak and hole (e $Å^{-3}$) | 1.983 and −1.133 | 1.558 and −1.520 |

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

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 1233 336033; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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