Hydride addition at μ-vinyliminium ligand obtained from disubstituted alkynes

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Abstract

New μ-vinylalkylidene complexes *cis*-[Fe$_2${μ-η^1:η^3-C$_\gamma$(R’)C$_\beta$(R’’)=C$_\alpha$HN(Me)(R)}(μ-CO)(CO)(Cp)$_2$] (R = Me, R’= R’’= Me, **3a**; R = Me, R’= R’’= Et, **3b**; R = Me, R’= R’’= Ph, **3c**; R = CH$_2$Ph, R’= R’’= Me, **3d**; R = CH$_2$Ph, R’= R’’= COOMe, **3e**; R = CH$_2$Ph, R’= SiMe$_3$, R’’= Me, **3f**) have been obtained by reacting the corresponding vinyliminium complexes [Fe$_2${μ-η^1:η^3-C$_\gamma$(R’)=C$_\beta$(R’’)C$_\alpha$=N(Me)(R)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (**2a-f**) with NaBH$_4$. The formation of **3a-f** occurs *via* selective hydride addition at the iminium carbon (C$_\alpha$) of the precursors **2a-f**. By contrast, the vinyliminium *cis*-[Fe$_2${μ-η^1:η^3-C$_\gamma$(R’)=C$_\beta$(R’’)C$_\alpha$=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (R’ = R’’ = COOMe, **4a**; R’= R’’ = Me, **4b**; R’ = Pr^n, R’’ = Me, **4c**; Pr^n = CH$_2$CH$_2$CH$_3$, Xyl = 2,6-Me$_2$C$_6$H$_3$) undergo H$^-$ addition at the adjacent C$_\beta$, affording the bis-alkylidene complexes *cis*-[Fe$_2${μ-η^1:η^2-C(R’)C(H)(R’’)CN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$], (**5a-c**). The *cis* and *trans* isomers of [Fe$_2${μ-η^1:η^3-C$_\gamma$(Et)=C$_\beta$(Et)C$_\alpha$=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (**4d**) react differently with NaBH$_4$: the former reacts at C$_\alpha$ yielding *cis*-[Fe$_2${μ-η^1:η^3-C$_\gamma$(Et)C$_\beta$(Et)=C$_\alpha$HN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$], **6a,** whereas the hydride attack occurs at C$_\beta$ of the latter, leading to the formation of the bis alkylidene *trans*-[Fe$_2${μ-η^1:η^2-C(Et)C(H)(Et)CN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$] (**5d**). The structure of **5d** has been determined by an X-ray diffraction study. Other μ-vinylalkylidene complexes *cis*-[Fe$_2${μ-η^1:η^3-C$_\gamma$(R’)C$_\beta$(R’’)=C$_\alpha$HN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$], (R’= R’’= Ph, **6b**; R’= R’’= Me, **6c**) have been prepared, and the structure of **6c** has been determined by X-ray diffraction. Compound **6b** results from treatment of *cis*-[Fe$_2${μ-η^1:η^3-C$_\gamma$(Ph)=C$_\beta$(Ph)C$_\alpha$=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (**4e**) with NaBH$_4$, whereas **6c** has been obtained by reacting **4b** with LiHBEt$_3$. Both *cis*-**4d** and *trans*-**4d** react with LiHBEt$_3$ affording *cis*-**6a**.

Keywords: vinyliminium, alkylidene, aminocarbene, diiron complexes, crystal structure

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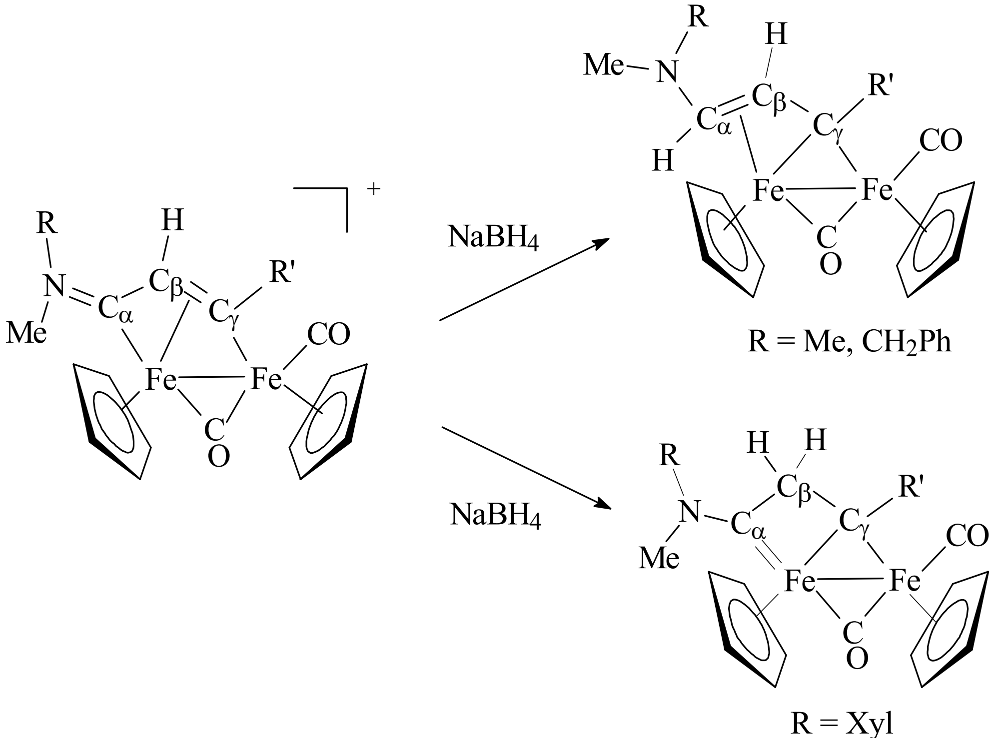
1. Introduction

Insertion of primary alkynes (HC≡CR') into the metal-carbyne bond of the diiron species $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; CH_2Ph, **1b**; Xyl, **1c**; Xyl = 2,6-$Me_2C_6H_3$) provides an efficient route to the synthesis of a new class of bridging vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')\text{=}C(H)C\text{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [1]. Also disubstituted alkynes (R'C≡CR'') insert into the metal-carbyne bond, generating μ-vinyliminium complexes [2], however the latter compounds exhibit some differences compared to those obtained from HCCR', due to steric reasons: i) complexes formed from disubstituted alkynes show *trans* and *cis* isomers, whereas those derived from primary alkynes are exclusively *cis* (*cis-trans* is referred to the mutual Cp position); ii) the insertion of unsymmetrically disubstituted acetylenes can occur in two possible modes (*i.e.* head-head or head-tail), whereas that of primary alkynes is regiospecific; iii) *E-Z* isomers, due to the orientation of Me and Xyl substituents at the iminium moiety, are generally observed, and complexes derived from the insertion of primary alkynes are mainly *E* (Me pointing far from C_β), while those obtained from internal alkynes preferably adopt the opposite *Z* geometry.

Investigations on the reactivity of the μ-vinyliminium complexes obtained from the insertion of primary alkynes, with $NaBH_4$, have revealed that the bridging ligand undergoes selective hydride addition at the iminium carbon, or at the adjacent C_β carbon, depending on the substituents at the iminium nitrogen (Scheme 1). When R = Me or CH_2Ph, hydride attack occurs at the iminium carbon, affording the vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')CH\text{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$. By contrast, when the iminium carbon (C_α) is sterically protected by the more hindering Xyl substituent, H^- addition is directed to C_β, yielding the bis-alkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(R')CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [3].

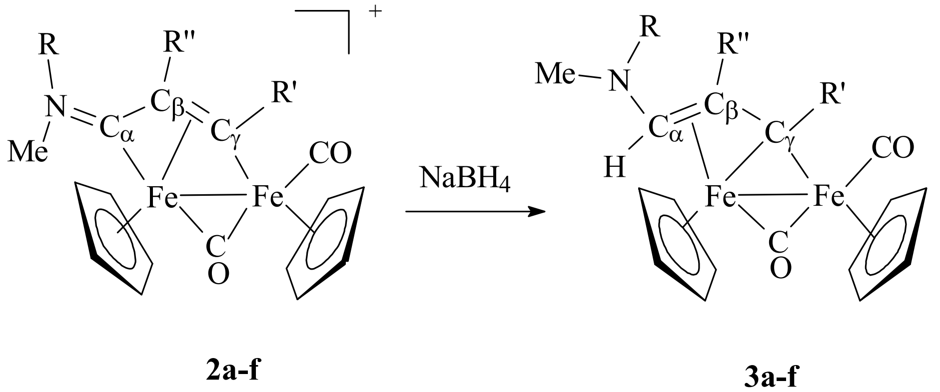


Scheme 1.

Since steric factors play a strong influence on the reactivity of the bridging vinyliminium ligands, those derived by the insertion of disubstituted alkynes could exhibit, in the reactions with H^-,□ a more complex behaviour than that described in Scheme 1. In order to clear up the point, we have studied the reactions of the complexes [Fe_2{μ-η^1:η^3-C(R')=C(R'')C=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3], with $NaBH_4$, and here we report the results of these investigations.

2. Results and discussion

The reactions of *cis*-[Fe_2{μ-η^1:η^3-C(R')=C(R'')C=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (**2a-f**) with $NaBH_4$, in tetrahydrofurane solution, lead to the formation of the corresponding μ-vinylalkylidene complexes [Fe_2{μ-η^1:η^3-C(R')C(R'')=CHN(Me)(R)}(μ-CO)(CO)$(Cp)_2$] (**3a-f**) (Scheme 2) in good yields (70-90%).



2a-f

3a-f

	R	R’	R’’
a	Me	Me	Me
b	Me	Et	Et
c	Me	Ph	Ph
d	CH_2Ph	Me	Me
e	CH_2Ph	COOMe	COOMe
f	CH_2Ph	$SiMe_3$	Me

Scheme 2.

Complexes **3a-f** have been isolated by column chromatography on alumina and fully characterized by spectroscopy and elemental analysis.

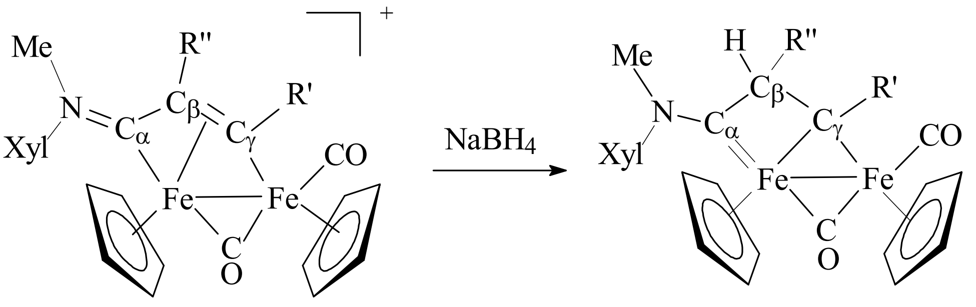
The IR spectra of **3a-f** show two ν(CO) absorptions (*e.g.* at 1935 and 1762 cm^{-1} for **3a,** in CH_2Cl_2 solution), due to the terminal and the bridging CO, respectively. The NMR spectra of **3a-f** reveal the presence, in solution, of one isomer, indicating that hydride addition is regioselective. Attack occurs exclusively at the iminium carbon (C_α), as indicated, in the ^1H NMR spectra of **3a-f**, by the high-field resonance (in the –0.88 ÷ 1.07 ppm range) due to the $C_\alpha H$, which is consistent with our previous findings [3]. The two N-bonded methyl groups in **3a-c** give rise to a single resonance in both ^1H and ^{13}C NMR spectra (*e.g.* for **3a** at 2.33 ppm and 47.0 ppm, respectively). Their equivalence, due to fast rotation, in the NMR time scale, around the C_α-N bond, evidences the loss of double bond character, consequent to the conversion of **2a-c** into **3a-c**.

The μ-vinylalkylidene ligands in **3a-f** act as four electron donor and can be alternatively described as bridging allylidene (η^1:η^3- coordinated), a coordination quite common among dinuclear complexes [4], including diiron compounds [5]. Bridging vinylalkylidene ligands are usually obtained by alkyne insertion into metal- μ-methylidene bond [4,5].

It is worth noting that H^- addition at C_α could occur either on the same side of C_β-R or in the opposite position, generating two isomers (*E, Z*). Since only one isomer has been observed, we conclude that the addition is stereoselective, although we have not been able, so far, to precisely determine which isomer is formed.

The formation of **3a-f** well parallels the previously reported hydride addition at the C_α of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')\text{=}C(H)C\text{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Me or CH_2Ph) [3]. Conversely, reactions of $NaBH_4$ with $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')\text{=}C(R'')C\text{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**4a-c**) appear more difficult to predict: the Xyl group is expected to exert some ‘steric protection’ on the C_α; on the other hand the C_β-R’’ position is presumably less sterically accessible than the corresponding C_β-H of complexes obtained from primary alkynes. Moreover, since complexes **4a-c** exist in both *cis* and *trans* isomeric forms, the different geometries might also affect the regiochemistry of the hydride addition.

Treatment of **4a-c** with $NaBH_4$, in THF solution, results in the formation of the bis-alkylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(R')C(H)(R'')CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**5a-c**) in good yields (Scheme 3).



4a-c

5a-c

	R’	**R’’**
a	COOMe	COOMe
b	Me	Me
c	Pr^n	Me

Scheme 3.

Complexes **5a-c** display the usual ν(CO) band pattern, consisting of two absorptions (*e.g.* at 1930 and 1771 cm^{-1} for **5a**). Relevant NMR data include the proton resonance due to C_β-H, in the range 4.31 ÷ 5.00 ppm, and the ^{13}C NMR signals attributable to C_α and C_γ (*e.g.* at 275.0 ppm and 131.7 ppm for **5a**), in good agreement with their amino-alkylidene and μ-alkylidene character, respectively. No trace of addition to C_α (iminium carbon) has been detected.

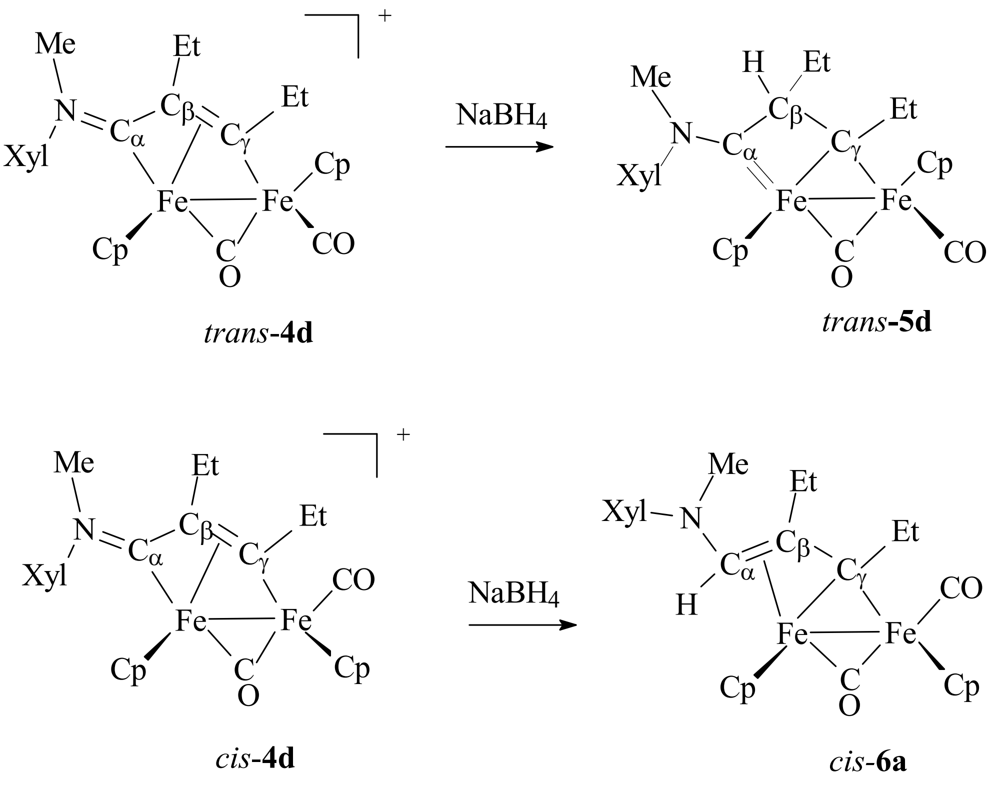
NOE experiments, which allow to distinguish between *cis* and *trans* isomers [2], evidence that the reactions do not involve any *trans-cis* isomerization. Thus, **5a-c** maintain the same mutual Cp position found in their precursors **4a-c**. Indeed the reactions reported in Scheme **3** were performed on *cis*-**4a**, whereas samples of **4b-c** consisted of mixtures of *cis* and *trans* isomers (*cis* : *trans* ratio about 1:3). The same isomeric composition was found in the corresponding products **5a-c**.

The bridging ligand in **5a-c** can be described as bis-alkylidene, because it contains one alkylidene unit bridging the two Fe atoms, and an aminocarbene moiety, terminally bonded to one

Fe centre. This coordination mode is expected to provide great stabilization. Indeed, in dinuclear complexes, alkylidene ligands generally occupy bridging positions, with few exceptions [6], and aminocarbenes are more stable when terminally bonded [7]. Although very stable, the coordination mode adopted by the bridging ligand in **5a-c** appears rather unique: other bridging bis-alkylidene ligands are known, but they generally coordinate two metal atoms without a direct M-M interaction [8].

It is worth noting that the C_β carbon in **5a-c** is a stereogenic centre and hydride addition can in principle generate two diastereoisomers. The NMR spectra, showing the presence of a single isomer, indicate that the H^- addition is stereospecific. The observed selectivity is presumably a consequence of a preferential side of attack for the incoming hydride, as already outlined by NOE studies on complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Me)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ and its deuterated counterpart $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Me)C(H)(D)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [3].

By contrast with the above described reactions, the *cis* and *trans* isomers of the complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et){=}C(Et)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**4d**) give different products upon treatment with $NaBH_4$. The isomer *trans*-**4d** selectively reacts at the C_β position, as expected, affording *trans*-$[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Et)C(H)(Et)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**5d**), whereas *cis*-**4d** generates *cis*-$[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et)C(Et){=}CHN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**6a**) because of addition at C_α (Scheme 4).



trans-**4d**

trans-**5d**

cis-**4d**

cis-**6a**

Scheme 4

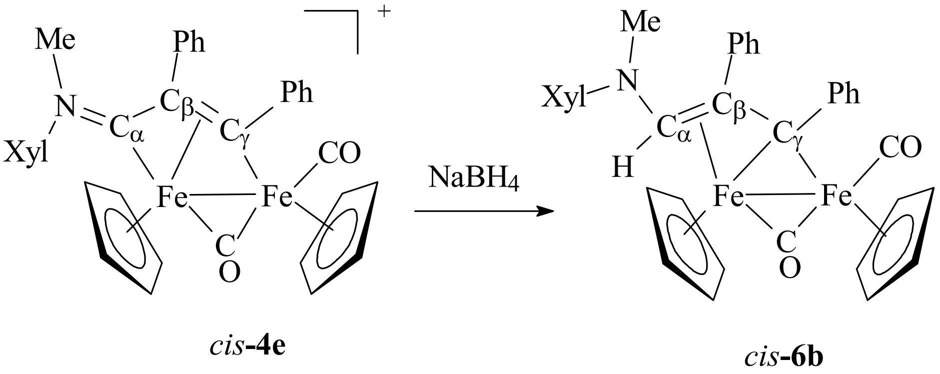
Complexes **5d** and **6a,** obtained in 68 and 60% yield, respectively, have been characterized by spectroscopy, and the structure of **5d** has been determined by X-ray diffraction. The ORTEP molecular diagram of **5d** is shown in Figure 1 and relevant bond lengths and angles are reported in Table 1. The molecule is asymmetric and two chiral centres are present: C_{γ} [C(3)] and C_{β} [C(4)]. The bond parameters in this bis-alkylidene species are strictly comparable to those found in *cis*-$[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(COOMe)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [3], in which the C_{α}-C_{β}-C_{γ} grouping is equivalent to the present one. Compounds $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(COOMe)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ and **5d** present opposite configurations both of the Cp ligands (*cis* in the former, *trans* in the latter) and of the N-substituents, *i.e.* Me and Xyl (*E* in the former, *Z* in the latter). However, these differences do not significantly affect the bonding mode.

On the other hand, the different arrangements adopted by the Cp ligands produce some effect on the spatial conformation of the bis-alkylidene ligand. In fact, in the complex *cis*-$[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(COOMe)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$, a folding of the C(1)Fe(1)C(3)Fe(2) diamond [dihedral angles between the Fe(1)Fe(2)C(1) and Fe(1)Fe(2)C(3) planes 34.0(1)°] is necessary to avoid steric repulsion between the Cp rings and the COOMe group; conversely, in **5d**, the mutual *trans* position of the cyclopentadienyls makes the C(1)Fe(1)C(3)Fe(2) diamond approximately flat [11.4(2)°]. A comparison with the cation *trans*-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)=C(Me)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ [2], that differs from the precursor *trans*-**4d** only for the presence of methyl instead of ethyl groups at C(3) and C(4), respectively, expectedly shows significant variations of the relevant bond values, in agreement with the transformation of a μ-vinyliminum into a bis-alkylidene, and in spite of the similar configuration of the Cp and N(Me)(Xyl) groups.

NMR data and NOE investigations indicate that the geometry of **5d,** in chlorinated solvents, corresponds to that found in the solid state, with the Cp ligands *trans* and the Xyl substituent opposite to C_{β} (*Z* orientation).

The spectroscopic data of **6a** resemble those of **3a-f**; in particular, C_{α}-H resonances are observed at 0.24 ppm and 96.2 ppm, in the ^{1}H and ^{13}C NMR spectra, respectively.

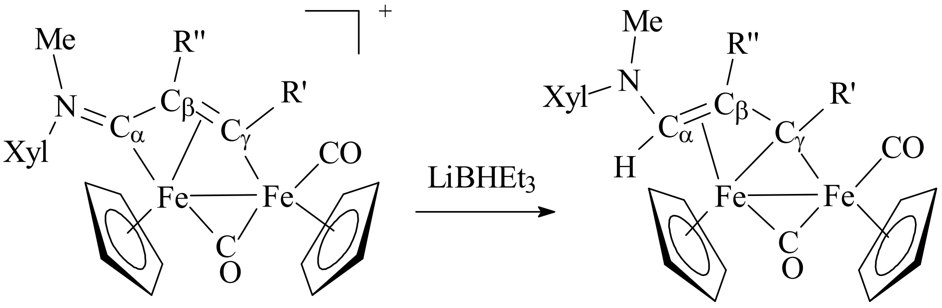
The different outcome of the reactions involving *cis*-**4d** and *trans*-**4d** is remarkable, because the mutual orientation of ancillary ligands (*cis* or *trans*), in dinuclear complexes, rarely exerts a comparable regioselective influence [9]. It is also to be outlined the different behaviour of $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)=C(Me)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**4b**) and **4d**: the former, in both *cis* and *trans* forms, undergoes H^- addition at C_β, whereas *trans*-**4d** and *cis*-**4d** react at C_β and C_α, respectively. The different reactivity is generated by apparently minor differences (replacement of Me with Et groups on the bridging ligand). This again evidences that the regiochemistry of these nucleophilic additions is largely influenced by steric factors, which are the result of combined effects of the substituents at the vinyliminium ligand and the mutual Cp position. In particular, our results suggest that sterically demanding substituents at C_β and C_γ positions, together with a *cis*-geometry of the Cp ligands, make attack at C_β very unfavourable, thus H^- addition occurs exclusively at the iminium carbon (C_α), in spite of the presence of the Xyl 'protecting group'. Support to this idea comes from the reaction of $NaBH_4$ with *cis*-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Ph)=C(Ph)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**4e**), in which phenyl groups are the substituents at the vinyliminium ligand; this reaction affords, selectively, the vinylalkylidene complex *cis*-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Ph)C(Ph)=CHN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**6b**) (Scheme 5). Again, the site of attack is C_α, in spite of the presence of the Xyl group.



Scheme 5

Compound **6b** has been characterized by IR and NMR spectroscopic methods, and elemental analysis. NOE experiments indicate that **6b** adopts *cis* geometry and suggest that C_α–H points to the opposite side of C_β-Ph, similarly to what previously found in $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Tol)C(H)=CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [3].

Previous investigations have shown that, beside steric factors, the nucleophilic character of the hydride reagent can also influence the site of attack on the bridging vinyliminium ligand. In particular, the more nucleophilic $LiHBEt_3$ was found to attack exclusively the iminium carbon (C_α). Now, we have found that **4b** and **4d**, both consisting of mixtures of *trans* and *cis* isomers in about 3:1 ratio, react with superhydride affording *cis*-**6c** and cis-**6a** (Scheme 6). Complex **6a** has been identified by comparison of its spectroscopic properties with those of the compound obtained from *cis*-**4d** and $NaBH_4$ (Scheme 4), and **6c** has been characterized by IR and NMR spectroscopy, and X ray diffraction.



	R'	**R''**	
cis- trans **4d**	Et	Et	*cis*-**6a**
cis- trans **4b**	Me	Me	*cis*-**6c**

Scheme 6.

The ORTEP molecular diagram of **6c** is shown in Figure 2 and relevant bond parameters are reported in Table 1. The hydride addition at C_α exhibits bond effects strictly equivalent to those already discussed for *cis*-$[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Tol)CH{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [3] and corresponding bond distances in the two species are equal within experimental errors. The hydrogen bound to C_α [H(5)] is located *trans* to the C_β-*Me* group, coherently with what found in solution for the analogous compound *cis*-$[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Ph)C(Ph){=}CHN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**6b**) (see above). Moreover, the solid-state structure of **6c** shows that the cumbersome xylyl group is orientated far from the Cp ligands, probably in order to avoid close contacts.

Significant differences are present between the bond values in **6c** and **5d,** consistent with the rehybridization effects produced by hydride attack at different atoms. While hydride addition at C_β [C(4)] in **5d** generates a genuine sp^3 carbon that breaks off conjugation in the C_α-C_β-C_γ grouping and put C(4) out of reach of the iron orbitals [Fe(1)…C(4) 2.591(3) Å], hydride addition at C_α [C(5)] in **6c** leaves C_β in a state intermediate between sp^3 and sp^2, and some C_α-C_β-C_γ electron delocalisation is evident [C(3)-C(4) 1.433(3), C(4)-C(5) 1.413(4) Å]. This is a truly non-conventional bond situation.

Both **6a** and **6c** display *cis* geometry, in spite of the fact that their parent complexes are mixtures of *cis* and *trans* isomers, with predominance of the *trans*. Thus, hydride addition, in this case, must be accompanied by *trans* to *cis* isomerization. Analogous *trans-cis* isomerizations are commonly observed in complexes containing the [Fe_2(μ-CO)Cp_2] frame, and *cis*-isomers are generally more stable [10].

Also of interest is the observation that complexes **6c** and **5b** are isomers, originated by H^- addition at different sites of [Fe_2{μ-η^1:η^3-C(Me)=C(Me)C=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (**4b**). In other words, it is possible to selectively attack C_α or C_β in **4b**, by appropriate choice of the hydride source (*i.e.*, $LiBHEt_3$ or $NaBH_4$). Finally, since interconversion of **6c** and **5b** would be possible in theory, by intramolecular hydrogen migration, each of the two complexes has been heated in THF, at refluxing temperature for several hours, with the aim of promoting the rearrangement. Nevertheless, neither **6c** nor **5b** showed any isomerization under these conditions.

3. Conclusions

Bridging-vinyliminium complexes [Fe_2{μ-η^1:η^3-C_γ(R')=C_β(R'')C_α=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$] [SO_3CF_3] undergo regioselective hydride addition at C_α or C_β , upon treatment with $NaBH_4$. The preferential site of addition is largely determined by steric factors, that can be summarized as follows: i) sterically demanding Xyl substituent on the iminium moiety disfavours addition at C_α; ii) increasing steric hindrance of the C_β substituents directs the attack at C_α; iii) *cis* arrangement of the Cp ligands hamper the addition at the C_β with respect to the corresponding *trans* isomer.

Beside steric factors, the nucleophilic character of the hydride source plays a role. Indeed the more nucleophilic $LiHBEt_3$ selectively attacks C_α. These results indicate that it is possible to control the regiochemistry of the bridging vinyliminium ligand by appropriate choice of the hydride reagent and of the ligand substituents. Extension of these investigations to other nucleophiles will be the subject of future communications.

4. Experimental section

4.1 General

Reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ^{1}H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and $^{1}H,^{13}C$ correlation measured using gs-HSQC and gs-HMBC experiments [11]. 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 italicised. NOE measurements were recorded using the DPFGSE-NOE sequence [12]. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Compounds $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ [13] and their derivatives $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (**1a-c**) [14] were prepared as described in the literature. Complexes **2a, 2b, 2d, 4d** [1] and **2e, 4a 4b** [2] were prepared as previously reported.

*4.2. Synthesis of cis-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')=C_\beta(R'')C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Me, R' = R''= Ph, **2c**; R = CH_2Ph, R' = $SiMe_3$, R'' = Me, **2f**; R = Xyl, R' = R'' = Ph, **4e**).*

Compound $[Fe_2\{\mu\text{-}CNMe_2\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1a**) (220 mg, 0.414 mmol) in THF (15 mL), was stirred with PhC≡CPh (155 mg, 0.871 mmol) and anhydrous Me_3NO (68 mg, 0.907 mmol) for 60 min. Removal of the solvent and chromatography on an alumina column with MeOH as eluent gave a brown fraction which was collected. Crystallization from CH_2Cl_2 solution, layered with diethyl ether, afforded **2c**. Yield: 228 mg, 81 %. Anal. Calcd. for $C_{30}H_{26}F_3Fe_2NO_5S$: C, 52.89; H, 3.85; N, 2.06. Found: C, 52.79; H, 3.79; N, 2.10. IR (CH_2Cl_2): ν(CO) 1994 (vs), 1813 (s), ν($C_\alpha N$) 1663 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.59-6.88 (m, 10 H, Ph); 5.25, 4.96 (s, 10 H, Cp); 3.91, 2.63 (s, 6 H, NMe_2). ^{13}C NMR (CD_2Cl_2): δ 254.9 (μ-CO); 224.9 (C_α); 203.9, 202.0 (C_γ and CO); 154.0-124.1 (Ph); 93.0, 89.2 (Cp); 73.5 (C_β); 49.2, 46.6 (NMe_2).

Complexes **2f** and **4e** were obtained by the same procedure described for **2c**, by reacting **1b** with $MeC\equiv CSiMe_3/Me_3NO$ and **1c** with $PhC\equiv CPh/Me_3NO$, respectively.

2f (79 %, green). Anal. Calcd. for $C_{28}H_{32}F_3Fe_2NO_5SSi$: C, 48.64; H, 4.67; N, 2.03. Found: C, 48.55; H, 4.62; N, 2.05. IR (CH_2Cl_2) ν(CO) 1982 (vs), 1815 (s), ν($C_\alpha N$) 1652 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$)

δ 7.48-7.18 (m, 5 H, Ph); 5.77, 5.72, *4.77*, *4.67* (d, $^2J_{\mathrm{HH}}$ = 14Hz, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{Ph}$); 5.00, *4.99*, 4.53, *4.50* (s, 10 H, Cp); *3.96*, 3.16 (s, 3 H, NMe); *2.23*, 2.14 (s, 3 H, $\mathrm{C}_\beta\mathrm{Me}$); 0.70, *0.67* (s, 9 H, $\mathrm{SiMe_3}$); *Z*/*E* ratio 2 :1. ^{13}C NMR ($\mathrm{CDCl_3}$) δ 254.6, *253.1* (μ-CO); *222.3*, 221.1 (C_α); 208.5 (CO); 195.2 (C_γ); 132.4-128.9 (Ph); *89.0*, 88.9, *88.4*, 88.2 (Cp); 70.6 (C_β); *65.2*, 62.3 ($\mathit{C}\mathrm{H_2Ph}$); 45.4, *43.4* (NMe); *20.6*, 20.2 ($\mathrm{C}_\beta\mathit{Me}$); 4.1 ($\mathrm{SiMe_3}$).

4e (60 %, red-brown). Anal. Calcd. for $\mathrm{C_{37}H_{32}F_3Fe_2NO_5S}$: C, 57.61; H, 4.18; N, 1.82. Found: C, 57.51; H, 4.09; N, 1.90. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1998 (vs), 1825 (s), ν(C_αN) 1604 (m) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.52-6.41 (m, 13 H, Ph and $\mathrm{Me_2C_6}\mathit{H}_3$); *5.62*, *5.17*, 5.00, 4.48 (s, 10 H, Cp); *4.32*, 2.69 (s, 3 H, NMe); 2.35, 2.01, *1.79*, *1.35* (s, 6 H, $\mathit{Me}_2\mathrm{C_6H_3}$); *Z*/*E* ratio 2:1. ^{13}C NMR ($\mathrm{CDCl_3}$): δ *252.9*, 251.1 (μ-CO); *228.5*, 226.8 (C_α); 211.0, *210.9* (CO); 207.0, *206.9* (C_γ); 153.0 (ipso-Ph); *143.3*, 141.3 (ipso-$\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 134.2-119.2 (Ph and $\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); *93.0*, 92.9, 88.0, *87.9* (Cp); 76.1, *75.0* (C_β); 49.2, *47.0* (NMe); 18.2, *17.7*, 17.4, *17.2* ($\mathit{Me}_2\mathrm{C_6H_3}$).

*4.3. Synthesis of cis-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')C_\beta(R'')=C_\alpha HN(R)(Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Me, R' = R''= Me, **3a**; R = Me, R' = R'' = Et, **3b**; R = Me, R' = R'' = Ph, **3c**; R = CH_2Ph, R' = R'' = Me, **3d**; R = CH_2Ph, R' = R'' = COOMe, **3e**; R = CH_2Ph, R' = $SiMe_3$, R'' = Me, **3f**).*

Complex $[\mathrm{Fe_2}\{\mu\text{-}\eta^1:\eta^3\text{-C(Me)=C(Me)C=NMe_2}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cp})_2][\mathrm{SO_3CF_3}]$ (**2a**) (100 mg, 0.180 mmol), was treated with an excess of $\mathrm{NaBH_4}$ (35 mg, 0.921 mmol), in THF solution (10 mL). The mixture was stirred at room temperature for 15 minutes. Then, the solvent was removed and the brown residue filtered on an alumina pad, using $\mathrm{CH_2Cl_2}$ as eluent. Solvent removal gave a microcrystalline residue. Yield: 51 mg, 69 %. Anal. Calcd. for $\mathrm{C_{19}H_{23}Fe_2NO_2}$: C, 55.78; H, 5.67; N, 3.42. Found: C, 55.84; H, 5.65; N, 3.48. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1935 (vs), 1762 (s) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 4.70, 4.31 (s, 10 H, Cp); 3.82 (s, 3 H, $\mathrm{C}_\gamma\mathrm{Me}$); 2.33 (s, 6 H, $\mathrm{NMe_2}$); 2.03 (s, 3 H, $\mathrm{C}_\beta\mathrm{Me}$); −0.75 (s, 1 H, $\mathrm{C}_\alpha\mathrm{H}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 273.7 (μ-CO); 217.2 (CO); 187.8 (C_γ); 93.4 (C_α); 87.9 (C_β); 87.6, 84.4 (Cp); 47.0 ($\mathrm{NMe_2}$); 37.3 ($\mathrm{C}_\gamma\mathit{Me}$); 16.7 ($\mathrm{C}_\beta\mathit{Me}$).

Complexes **3b-f** were obtained following the same procedure described for the synthesis of **3a**, by reacting **2b-f** with $\mathrm{NaBH_4}$.

3b (90 %, brown). Anal. Calcd. for $\mathrm{C_{21}H_{27}Fe_2NO_2}$: C, 57.70; H, 6.23; N, 3.20. Found: C, 57.81; H, 6.12; N, 3.31. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1940 (vs), 1769 (s) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 4.72, 4.34 (s, 10 H, Cp); 4.40, 4.01 (m, 2 H, $\mathrm{C}_\gamma\mathrm{CH_2}$); 2.39 (s, 6 H, $\mathrm{NMe_2}$); 2.70, 2.14 (m, 2 H, $\mathrm{C}_\beta\mathrm{CH_2}$); 1.68 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, $\mathrm{C}_\gamma\mathrm{CH_2C}\mathit{H}_3$); 1.28 (t, 3 H, $^3J_{\mathrm{HH}}$ = 7.7 Hz, $\mathrm{C}_\gamma\mathrm{CH_2C}\mathit{H}_3$); −0.88 (s, 1 H, $\mathrm{C}_\alpha\mathrm{H}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 274.5 (μ-CO); 216.7 (CO); 197.1 (C_γ); 94.3 (C_α); 93.7 (C_β); 87.3, 84.2 (Cp); 47.7 ($\mathrm{NMe_2}$); 42.6 ($\mathrm{C}_\gamma\mathit{C}\mathrm{H_2}$); 23.7 ($\mathrm{C}_\beta\mathit{C}\mathrm{H_2}$); 21.1 ($\mathrm{C}_\gamma\mathrm{CH_2}\mathit{C}\mathrm{H_3}$); 16.7 ($\mathrm{C}_\gamma\mathrm{CH_2}\mathit{C}\mathrm{H_3}$).

3c (91 %, green). Anal. Calcd. for $C_{29}H_{27}Fe_2NO_2$: C, 65.32; H, 5.10; N, 2.63. Found: C, 65.45; H, 5.12; N, 2.55. IR (CH_2Cl_2): ν(CO) 1934 (vs), 1756 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.21-6.69 (m, 10 H, Ph); 4.91, 4.34 (s, 10 H, Cp); 2.18 (s, 6 H, NMe_2); 0.86 (s, 1 H, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 278.3 (μ-CO); 217.8 (CO); 185.6 (C_γ); 156.5-122.2 (Ph); 98.2 (C_α); 88.5, 81.5 (Cp); 77.5 (C_β); 42.8 (NMe_2).

3d (89 %, brown). Anal. Calcd. for $C_{25}H_{27}Fe_2NO_2$: C, 61.89; H, 5.61; N, 2.89. Found: C, 61.97; H, 5.52; N, 2.93. IR (CH_2Cl_2): ν(CO) 1938 (vs), 1763 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.58-7.10 (m, 5 H, Ph); 4.73, 4.35 (s, 10 H, Cp); 3.97, 3.51 (d, 2 H, $^2J_{HH}$ = 14.3 Hz, CH_2Ph); 3.87 (s, 3 H, $C_\gamma Me$); 2.21, 2.14 (s, 6 H, NMe and $C_\beta Me$); −0.45 (s, 1 H, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 273.5 (μ-CO); 217.1 (CO); 187.8 (C_γ); 139.3-126.5 (Ph); 92.5 (C_α); 87.6, 84.5 (Cp); 86.9 (C_β); 63.1 (CH_2Ph); 43.1 (NMe); 37.2 ($C_\gamma Me$); 16.9 ($C_\beta Me$).

3e (88 %, ochre yellow). Anal. Calcd. for $C_{27}H_{27}Fe_2NO_6$: C, 56.58; H, 4.75; N, 2.44. Found: C, 56.52; H, 4.70; N, 2.54. IR (CH_2Cl_2): ν(CO) 1941 (vs), 1768 (s), 1717 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.47-6.78 (m, 5 H, Ph); 4.74, 4.63 (s, 10 H, Cp); 3.99, 3.88 (d, 2 H, $^2J_{HH}$ = 14.7 Hz, CH_2Ph); 3.98, 3.72 (s, 6 H, CO_2Me); 2.16 (s, 3 H, NMe); 1.07 (s, 1 H, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 271.0 (μ-CO); 216.4 (CO); 179.8 (C_γ-CO_2Me); 170.9 (C_β-CO_2Me); 142.6 (C_γ); 136.7, 128.9, 128.4, 128.0, 127.5 (Ph); 100.8 (C_α); 87.4, 83.3 (Cp); 66.8 (C_β); 61.4 (CH_2Ph); 52.1, 51.8 (CO_2Me); 38.1 (NMe).

3f (84 %, brown). Anal. Calcd. for $C_{27}H_{33}Fe_2NO_2Si$: C, 59.69; H, 6.12; N, 2.58. Found: C, 59.76; H, 6.14; N, 2.61. IR (CH_2Cl_2): ν(CO) 1929 (vs), 1772 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.38-7.23 (m, 5 H, Ph); 4.48, 4.32 (s, 10 H, Cp); 3.98, 3.61 (d, 2H, $^2J_{HH}$ = 14.3 Hz, CH_2Ph); 2.30, 2.24 (s, 6 H, $C_\beta Me$ and NMe); 0.69 (s, 9 H, $SiMe_3$); 0.21 (s, 1 H, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 274.9 (μ-CO); 214.3 (CO); 176.4 (C_γ); 138.9-126.8 (Ph); 93.3 (C_α); 87.3, 84.8 (Cp); 63.0 (CH_2Ph); 43.3 (NMe); 22.1 ($C_\beta Me$); 5.0 ($SiMe_3$).

4.4. Synthesis of $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C_\gamma(R')C_\beta(H)(R'')C_\alpha N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ *(R' = R'' =* CO_2Me*, **5a**; R' = R''= Me, **5b**; R'=* Pr^n*, R''= Me, **5c**; R' = R''= Et, **5d**).*

Complex *cis*-**4a** (105 mg, 0.143 mmol) was treated with an excess of $NaBH_4$ (19 mg, 0.500 mmol), in THF solution (10 mL). The mixture was stirred at room temperature for 15 minutes, then the solvent was removed under reduced pressure and the residue was filtered on alumina. A red band, corresponding to *cis*-**5a**, was collected using THF as eluent. Yield: 60 mg, 71 %. Anal. Calcd. for $C_{28}H_{29}Fe_2NO_6$: C, 57.27; H, 4.98; N, 2.39. Found: C, 57.38; H, 4.81; N, 2.29. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1771 (s), 1725 (s), 1677 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.25-7.03 (m, 3 H, $Me_2C_6H_3$); 5.00 (s, 1 H, $C_\beta H$); 4.60, 4.20 (s, 10 H, Cp); 3.87, 3.81 (s, 6 H, CO_2Me); 3.00 (s, 3 H, NMe); 2.14

(s, 6 H, $\mathit{Me}_2\mathrm{C_6H_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 275.0 ($\mathrm{C_\alpha}$); 264.0 (μ-CO); 216.9 (CO); 172.8 ($\mathrm{C_\gamma}$-$\mathit{C}\mathrm{O_2Me}$); 145.0 (ipso-$\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 143.8 ($\mathrm{C_\beta}$-$\mathit{C}\mathrm{O_2Me}$); 134.2, 133.4, 129.3, 128.2, 128.1 ($\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 131.7 ($\mathrm{C_\gamma}$); 87.6, 86.4 (Cp); 84.7 ($\mathrm{C_\beta}$); 51.6, 50.5 ($\mathrm{CO_2}\mathit{Me}$); 42.7 (NMe); 18.0, 17.2 ($\mathit{Me}_2\mathrm{C_6H_3}$).

Complexes **5b-d** were obtained following the same procedure described for the synthesis of **5a**, by reacting **4b-d** with $\mathrm{NaBH_4}$. Crystals of **5d** suitable for X ray analysis were obtained by crystallization at -20 °C from a $\mathrm{CH_2Cl_2}$ solution layered with petroleum ether (b.p. 40-60° C)

5b (75 %, green). Anal. Calcd. for $\mathrm{C_{26}H_{29}Fe_2NO_2}$: C, 62.56; H, 5.86; N, 2.81. Found: C, 62.40; H, 5.99; N, 2.84. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1910 (vs), 1740 (s) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.35-6.90 (m, 3 H, $\mathrm{Me_2C_6}\mathit{H}_3$); *4.55*, 4.41, 3.99, *3.96* (s, 10 H, Cp); *4.66*, 4.31 (qq, 1 H, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $^4J_{\mathrm{HH}}$ = 1.5 Hz, $\mathrm{C_\beta H}$); *3.50*, 3.46 (d, 3 H, $^4J_{\mathrm{HH}}$ = 1.5 Hz, $\mathrm{C_\gamma Me}$); 3.02, *2.94* (s, 3 H, NMe); *2.25*, 2.21, 2.15, *2.12* (s, 6 H, $\mathit{Me}_2\mathrm{C_6H_3}$); 1.50, *1.46* (d, 3 H, $^3J_{\mathrm{HH}}$ = 7.0 Hz, $\mathrm{C_\beta Me}$); *trans/cis* ratio 3:1. ^{13}C NMR ($\mathrm{CDCl_3}$) δ 284.0, *282.2* ($\mathrm{C_\alpha}$); *278.3*, 277.9 (μ-CO); *219.0*, 215.1 (CO); 181.2, *179.4* ($\mathrm{C_\gamma}$); 145.6 (ipso-$\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 134.6-127.8 ($\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 88.7, *87.5*, 86.7, *84.8* (Cp); 85.4, *83.7* ($\mathrm{C_\beta}$); *41.2*, 40.6, 40.1 ($\mathrm{C_\gamma}\mathit{Me}$ and NMe); *18.5*, 18.1, *17.5*, 17.4 ($\mathit{Me}_2\mathrm{C_6H_3}$); *16.6*, 16.4 ($\mathrm{C_\beta}\mathit{Me}$).

5c (86 %, green). Anal. Calcd. for $\mathrm{C_{28}H_{33}Fe_2NO_2}$: C, 63.78; H, 6.31; N, 2.66. Found: C, 63.81; H, 6.19; N, 2.71. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1910 (vs), 1743 (s) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.32-6.81 (m, 3 H, $\mathrm{Me_2C_6}\mathit{H}_3$); *4.58*, 4.51, *4.01*, 3.98 (s, 10 H, Cp); 4.39, *4.38* (m, 1 H, $\mathrm{C_\beta H}$); *3.70*, 3.69 (m, 2 H, $\mathrm{C_\gamma C}\mathit{H}_2$); 3.03, *2.91* (s, 3 H, NMe); 2.23, 2.15, *2.12* (s, 6 H, $\mathit{Me}_2\mathrm{C_6H_3}$); 1.90 (m, 2 H, $\mathrm{C_\gamma CH_2C}\mathit{H}_2$); 1.47, *1.44* (d, 3 H, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $\mathrm{C_\beta Me}$); *1.26*, 1.24 (t, $^3J_{\mathrm{HH}}$ = 7.2 Hz, $\mathrm{C_\gamma CH_2CH_2C}\mathit{H}_3$); *trans/cis* ratio 3:1. ^{13}C NMR ($\mathrm{CDCl_3}$) δ 283.4 ($\mathrm{C_\alpha}$); 277.4 (μ-CO); *216.0*, 214.7 (CO); 184.8, *184.0* ($\mathrm{C_\gamma}$); 145.4 (ipso-$\mathrm{Me_2C_6H_3}$); 134.3, 133.1, 129.5, 128.1, 127.9 ($\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 88.2, *87.2,* 86.6, *84.7* (Cp); 84.6 ($\mathrm{C_\beta}$); 57.1, *56.8* ($\mathrm{C_\gamma}\mathit{C}\mathrm{H_2}$); *40.3*, 40.1 (NMe); 25.6, *24.5* ($\mathrm{C_\gamma CH_2}\mathit{C}\mathrm{H_2}$); *18.8,* 18.1, *17.6*, 17.4 ($\mathit{Me}_2\mathrm{C_6H_3}$); 16.9, *15.7* ($\mathrm{C_\beta Me}$); 15.1, *15.0* ($\mathrm{C_\gamma CH_2CH_2}\mathit{C}\mathrm{H_3}$).

(*trans*)-**5d** (68 %, green). Anal. Calcd. for $\mathrm{C_{28}H_{33}Fe_2NO_2}$: C, 63.78; H, 6.31; N, 2.66. Found: C, 63.66; H, 6.25; N, 2.71. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1911 (vs), 1741 (s) cm^{-1}. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 7.32-7.11 (m, 3 H, $\mathrm{Me_2C_6}\mathit{H}_3$); 4.52, 3.97 (s, 10 H, Cp); 4.31 (dd, 1 H, $^3J_{\mathrm{HH}}$ = 9 Hz, $^4J_{\mathrm{HH}}$ = 2 Hz, $\mathrm{C_\beta H}$); 4.09, 3.64 (m, 2 H, $\mathrm{C_\gamma CH_2}$); 3.05 (s, 3 H, NMe); 2.42, 1.41 (m, 2 H, $\mathrm{C_\beta CH_2}$); 2.22, 2.18 (s, 6 H, $\mathit{Me}_2\mathrm{C_6H_3}$); 1.58 (t, 6 H, $^3J_{\mathrm{HH}}$ = 7 Hz, $\mathrm{C_\gamma CH_2C}\mathit{H}_3$); 1.36 (m, 2 H, $\mathrm{C_\beta CH_2C}\mathit{H}_3$). ^{13}C NMR ($\mathrm{CDCl_3}$) δ 284.4 ($\mathrm{C_\alpha}$); 277.2 (μ-CO); 214.5 (CO); 187.9 ($\mathrm{C_\gamma}$); 145.3 (ipso-$\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 134.4, 133.2, 129.5, 128.2, 127.9 ($\mathrm{Me_2}\mathit{C}_6\mathrm{H_3}$); 88.5, 86.8 (Cp); 84.1 ($\mathrm{C_\beta}$); 46.5 ($\mathrm{C_\gamma}\mathit{C}\mathrm{H_2}$); 40.7 (NMe); 27.2 ($\mathrm{C_\beta}\mathit{C}\mathrm{H_2}$); 19.1 ($\mathrm{C_\gamma CH_2}\mathit{C}\mathrm{H_3}$); 18.5, 17.9 ($\mathit{Me}_2\mathrm{C_6H_3}$); 14.4 ($\mathrm{C_\beta CH_2}\mathit{C}\mathrm{H_3}$).

4.5. Synthesis of cis-$[\mathrm{Fe_2}\{\mu\text{-}\eta^1:\eta^3\text{-}\mathrm{C_\gamma(Et)C_\beta(Et){=}C_\alpha(H)N(Me)(Xyl)}\}(\mu\text{-}\mathrm{CO})(\mathrm{CO})(\mathrm{Cp})_2]$ ***(6a).***

A solution of (*trans* + *cis*)-**4d** (115 mg, 0.170 mmol; *trans*/*cis* ratio 3:1), in THF (8 mL), was treated at –30°C with a THF solution of $LiBHEt_3$ (0.22 mL, 0.22 mmol). The mixture was stirred at room temperature for 20 minutes, and then the solvent was removed under reduced pressure. Chromatography on alumina, using CH_2Cl_2 as eluent, afforded a red band. Yield: 54 mg, 60 %. The same product was also prepared in comparable yields by reacting *cis*-**4d** with $NaBH_4$. Anal. Calcd. for $C_{28}H_{33}Fe_2NO_2$: C, 63.76; H, 6.26; N, 2.66. Found: C, 63.66; H, 6.20; N, 2.58. IR (CH_2Cl_2): ν (CO) 1925 (vs), 1751 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.24-6.82 (m, 3 H, $Me_2C_6H_3$); 4.70, 4.40 (s, 10 H, Cp); 4.03 (m, 2H, $C_\gamma CH_2$); 3.00 (s, 3 H, NMe); 2.68, 1.56 (m, 2 H, $C_\beta CH_2$); 2.19, 2.07 (s, 6 H, $Me_2C_6H_3$); 1.65 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, $C_\gamma CH_2CH_3$); 0.56 (t, 3 H, $^3J_{HH}$ = 7.2 Hz, $C_\beta CH_2CH_3$); 0.24 (s, 1 H, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 276.9 (μ-CO); 217.5 (CO); 196.6 (C_γ); 149.0 (ipso-$Me_2C_6H_3$); 135.8, 135.6, 129.6, 128.3, 125.3 ($Me_2C_6H_3$); 96.2 (C_α); 92.5 (C_β); 87.4, 84.0 (Cp); 42.7 ($C_\gamma CH_2$); 42.1 (NMe); 24.8 ($C_\beta CH_2$); 21.1, 20.3, 19.2 ($Me_2C_6H_3$ and $C_\gamma CH_2CH_3$); 14.2 ($C_\beta CH_2CH_3$).

4.6. Synthesis of cis-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Ph)C_\beta(Ph)=C_\alpha(H)N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ *(**6b**).*

Complex (*cis*)-**4e** (120 mg, 0.156 mmol) was treated with $NaBH_4$ (25 mg, 0.658 mmol), in THF solution (8 mL). The mixture was stirred at room temperature for 15 minutes, and then the solvent was removed under reduced pressure. Chromatography on alumina, using a mixture of CH_2Cl_2 and diethyl ether (1:1) as eluent, afforded a brown band. Yield: 78 mg, 80 %. Anal. Calcd. for $C_{36}H_{33}Fe_2NO_2$: C, 69.37; H, 5.34; N, 2.25. Found: C, 69.44; H, 5.25; N, 2.24. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1751 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.22-6.53 (m, 13 H, Ph and $Me_2C_6H_3$); 4.95, 4.26 (s, 10 H, Cp); 2.92 (s, 3 H, NMe); 2.23, 2.02 (s, 3 H, $Me_2C_6H_3$); 1.24 ($C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 278.8 (μ-CO); 218.1 (CO); 186.1 (C_γ); 156.9-123.2 (Ph and $Me_2C_6H_3$); 104.1 (C_α); 88.5, 82.2 (Cp); 76.5 (C_β); 38.3 (NMe); 19.8, 19.1 ($Me_2C_6H_3$).

4.7. Synthesis of cis-$[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Me)C_\beta(Me)=C_\alpha(H)N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ *(**6c**).*

This complex was obtained following the same procedure described for the synthesis of **6a**, by reacting (*trans* + *cis*)-**4b** (50 mg, 0.0773 mmol; *trans*/*cis* ratio 3:1) with $LiBHEt_3$. Yield: 28 mg, 73 %. Brown crystals, suitable for X ray analysis, were obtained by crystallization at –20 °C from a CH_2Cl_2 solution layered with n-pentane. Anal. Calcd. for $C_{26}H_{29}Fe_2NO_2$: C, 62.56; H, 5.86; N, 2.81. Found: C, 62.68; H, 5.93; N, 2.88. IR (CH_2Cl_2): ν(CO) 1926 (vs), 1751 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.04-6.92 (m, 3 H, $Me_2C_6H_3$); 4.67, 4.41 (s, 10 H, Cp); 3.86 (s, 3 H, $C_\gamma Me$); 2.86 (s, 3 H, NMe); 2.34, 2.11 (s, 6 H, $Me_2C_6H_3$); 1.80 (s, 3 H, $C_\beta Me$); 0.36 (s, 1 H, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 276.1 (μ-CO); 217.4 (CO); 185.5 (C_γ); 147.8 (ipso-$Me_2C_6H_3$); 135.9, 135.5, 129.1, 128.2, 125.3

($Me_2C_6H_3$); 95.6 (C_α); 88.5 (C_β); 87.4, 86.6 (Cp); 41.3 (NMe); 37.9 ($C_\gamma Me$); 19.8, 18.6, 17.6 ($Me_2C_6H_3$ and $C_\beta Me$).

4.8. Crystallography

The diffraction experiments for **5d** and **6c** were carried out at room temperature on a Bruker AXS SMART 2000 CCD based diffractometer using graphite monochromated Mo-K_α radiation (λ=0.71073 Å). Intensity data were measured over a full diffraction sphere using 0.3° wide ω scans, crystal-to-detector distance 5.0 cm. The software SMART [15] was used for collecting frames of data, indexing reflections and determination of lattice parameters. The collected frames were then processed for integration by software SAINT [15] and an empirical absorption correction was applied with SADABS [16]. The structures were solved by direct methods (SIR97) [17] and subsequent Fourier syntheses, and refined by full-matrix least-squares calculations on F^2 (SHELXTL) [18] attributing anisotropic thermal parameters to all the non-hydrogen atoms. In complex **6c** the Cp ligand bound to Fe(1) was found disordered over two positions and the site occupation factors were refined yielding 0.65 and 0.35, respectively. The methyl, methylene and aromatic hydrogen atoms were placed in calculated positions and refined with idealized geometry, whereas the H atoms from the hydride addition were located in the Fourier map and refined isotropically. Crystal data and experimental details are reported in Table 2.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 244892 for **5d**, and no. 244893 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; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement

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Figures

Figure 1. ORTEP drawing (ellipsoids at 30% probability) of [Fe_2{μ-η^1:η^2-C(Et)C(H)(Et)CN(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$](**5d**)**.** Only the C_β hydrogen [H(4)] is shown.

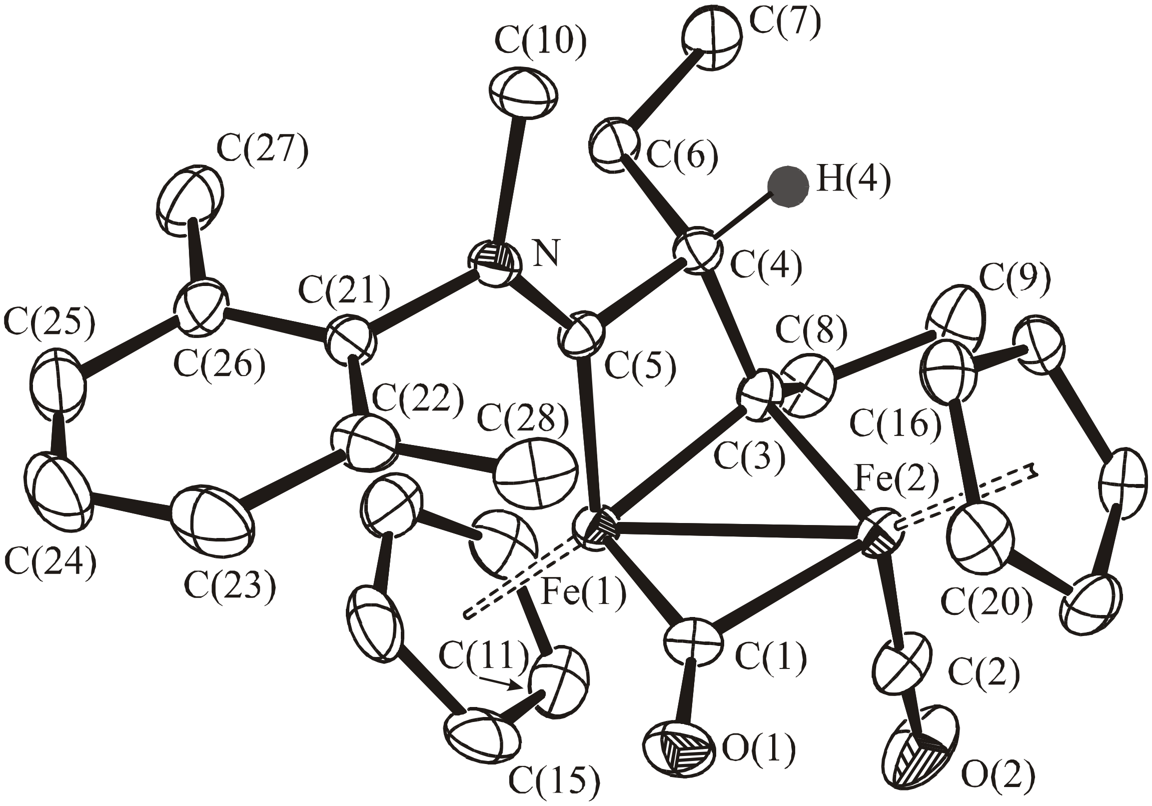

Figure 2. ORTEP drawing (ellipsoids at 30% probability) of [Fe$_2${μ-η^1:η^3-C(Me)C(Me)=CHN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$] (**6c**). Only the vinyl C$_\alpha$ hydrogen [H(5)] is shown.

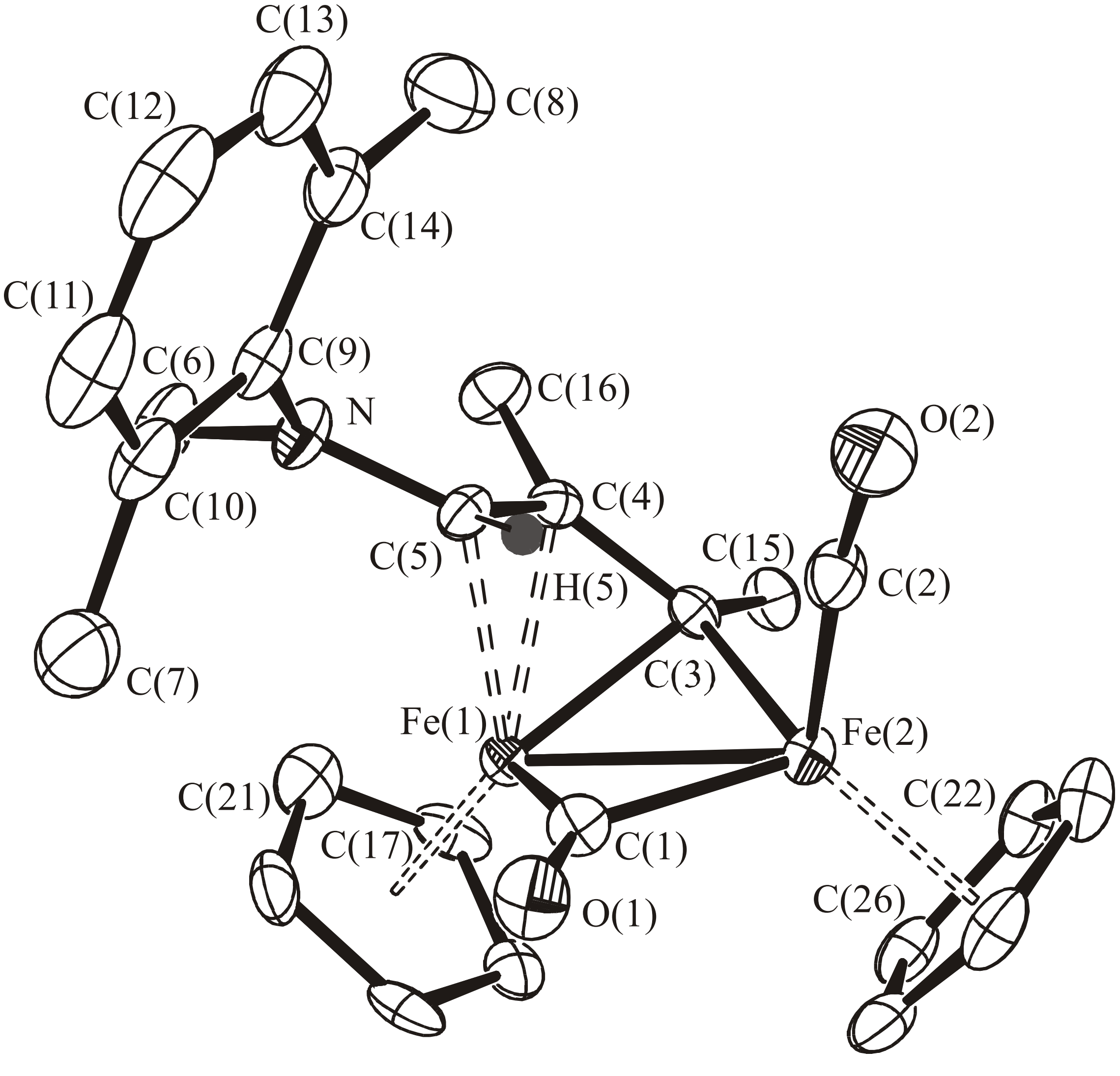

Table 1. Selected bond lengths (Å) and angles (°) for complexes **5d** and **6c.**

Compound	**5d**	**6c**
Fe(1)-Fe(2)	2.5349(5)	2.5260(5)
Fe(1)-C(1)	1.853(3)	1.851(3)
Fe(2)-C(1)	1.991(3)	1.983(3)
Fe(2)-C(2)	1.726(3)	1.733(3)
Fe(1)-C(3)	1.973(3)	1.968(3)
Fe(2)-C(3)	2.000(3)	1.979(2)
Fe(1)-C(4)		2.082(3)
Fe(1)-C(5)	1.893(3)	2.201(3)
N-C(5)	1.312(4)	1.398(3)
C(4)-C(5)	1.506(4)	1.413(4)
C(3)-C(4)	1.546(4)	1.433(4)
N-C(10)/C(6)	1.482(4)	1.442(4)
N-C(21)/C(9)	1.460(4)	1.435(4)
C(1)-O(1)	1.180(4)	1.192(3)
C(2)-O(2)	1.149(4)	1.149(4)
Fe(1)-C(Cp)	2.146	2.125*
Fe(2)-C(Cp)	2.144	2.129
C(3)-C(4)-C(5)	94.3(2)	118.8(2)
N-C(5)-C(4)	122.2(2)	125.8(3)
Fe(1)-C(3)-C(4)	94.1(2)	73.6(2)
Fe(1)-C(5)-C(4)	98.7(2)	66.2(2)
Fe(1)-C(4)-C(5)		75.4(2)
Fe(1)-C(5)-N	138.9(2)	126.1(2)
Fe(2)-C(3)-C(4)	113.2(2)	122.7(2)

* main image of the Cp ligand.

Table 2. Crystal data and experimental details for **5d** and **6c**.

Compound	**5d**	**6c**
Formula	$C_{28}H_{33}Fe_2NO_2$	$C_{26}H_{29}Fe_2NO_2$
Fw	527.25	499.20
T, K	298(2)	298(2)
λ, Å	0.71073	0.71073
Crystal symmetry	Triclinic	Orthorhombic
Space group	$P\ \bar{1}$	$P2_12_12_1$
a, Å	8.8246(3)	7.6954(3)
b, Å	9.4263(3)	14.3285(6)
c, Å	17.1185(5)	20.8168(8)
α, °	82.5733(7)	90
β, °	75.4731(7)	90
γ, °	63.4679(6)	90
Cell volume, $Å^3$	1233.03(7)	2295.3(2)
Z	2	4
D_c, Mg m^{-3}	1.420	1.445
μ(Mo-K_α), mm^{-1}	1.201	1.286
F(000)	552	1040
Crystal size/ mm	0.15 x 0.18 x 0.25	0.20 x 0.25 x 0.25
θ limits, °	2.64-25.00	1.73-30.05
Reflections collected	11067(±h, ±k, ±l)	30026(±h, ±k, ±l)
Unique observed reflections $[F_o > 4\sigma(F_o)]$	4358[R(int) = 0.0649]	6709[R(int) = 0.0720]
Goodness-of-fit-on F^2	1.032	1.002
R_1 (F)[a], wR_2 (F^2)[b]	0.0612, 0.1555	0.0404, 0.0965
Absolute structure parameter		0.04(2)
Largest diff. peak and hole, e. $Å^{-3}$	0.497/ –0.498	0.332/ –0.652

[a] $R_1 = \Sigma||Fo|-|Fc|/\Sigma|Fo|$.

[b] $wR_2 = [\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$ where $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 + 2Fc^2)/3$

Graphical contents entry

Hydride addition at μ-vinyliminium ligand obtained from disubstituted alkynes

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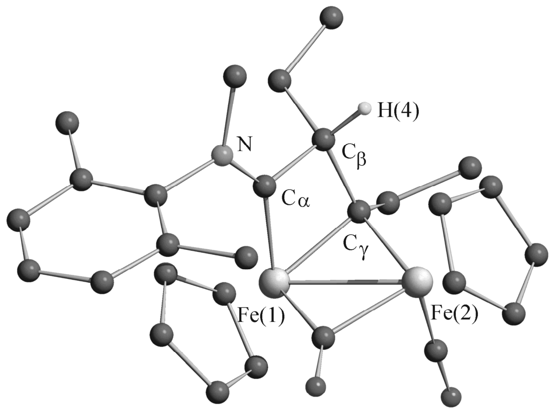
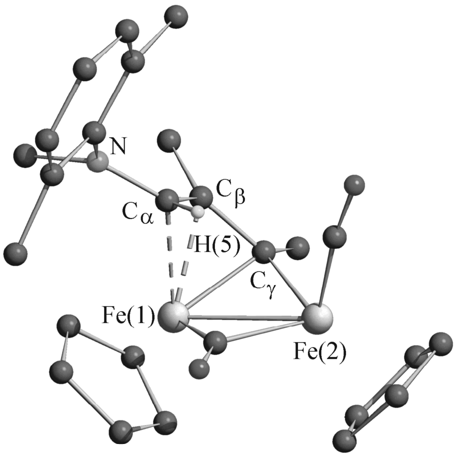
$NaBH_4$ gives addition at the bridging vinyliminium ligand in the diiron complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(R')=C_\beta(R'')C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R' and R'' = alkyl or aryl substituents, R = Me, CH_2Ph or Xyl). Depending on the nature of these substituents and on the geometry of the parent complexes (*cis* or *trans*), H^- addition occurs selectively at the iminium carbon (C_α) or at the adjacent C_β position, affording complexes of the type **5d** or **6a**, respectively.



5d



6c