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Regio- and Stereoselective Hydride Addition at μ-Vinyliminium Ligands in Cationic Diiron Complexes

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The vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta HC_\alpha{=}NMe_2\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ ($R' = $ Tol, **2a**; $SiMe_3$, **2b**; Me, **2c**; CH_2OH, **2d**) undergo hydride addition at the iminium carbon (C_α), upon treatment with $NaBH_4$, affording the corresponding μ-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')CH{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R' = $ Tol, **5a**; $SiMe_3$, **5b**; Me, **5c**; CH_2OH, **5d**). Similarly, the complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta HC_\alpha{=}N(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ ($R' = $ Tol, **4a**; $SiMe_3$, **4b**; COOMe, **4c**) react with $NaBH_4$ at the C_α, yielding $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R')C_\beta H{=}C_\alpha(H)N(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R' = $ Tol, **7a**; $SiMe_3$, **7b**; COOMe, **7c**). By contrast, the reactions of $NaBH_4$ with $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta HC_\alpha{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R' = $ Tol, **3a**; $SiMe_3$, **3b**; Me, **3c**; CH_2OH, **3d**; Ph, **3e**; COOMe, **3f**; Bu^n, **3g**; H, **3h**), in which the substituent at the iminium nitrogen is the more sterically hindered Xyl group (Xyl $=$ 2,6-$Me_2C_6H_3$), lead to the formation of the bis-alkylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(R')CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R' = $ Tol, **6a**; $SiMe_3$, **6b**; Me, **6c**; CH_2OH, **6d**; Ph, **6e**; COOMe, **6f**; Bu^n, **6g**; H, **6h**). Compounds **6a**−**h** result from regioselective hydride addition at the C_β, presumably because of the steric protection exerted by the Xyl group on the C_α carbon. All the new compounds have been investigated by IR and NMR spectroscopy, and the molecular structures of complexes **5a** and **6f** have been elucidated by X-ray diffraction studies. $LiHBEt_3$ selectively attacks the C_α carbon, despite the presence of the Xyl substituent; therefore $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta HC_\alpha{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ ($R' = $ Me, **3c**; COOMe, **3f**) are converted into the corresponding μ-vinylalkylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')CH{=}CHN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R' = $ Me, **8a**; COOMe, **8b**).

Introduction

We have recently reported that a variety of alkynes ($R'C{\equiv}CR''$; $R'' = $ H; $R' = $ H, Me, Bu^n, Ph, Tol, $SiMe_3$, CH_2OH, COOMe; $R' = R'' = $ Me, Et, COOMe) insert into the metal−carbon bond of diiron μ-aminocarbynes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(MeCN)(Cp)_2][SO_3CF_3]$ (R $=$ Xyl, **1a**; CH_2Ph, **1b**; Me, **1c**; Xyl $=$ 2,6-$Me_2C_6H_3$), affording the corresponding μ-vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta(R'')C_\alpha{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$.[1] The reaction requires the presence of a labile ligand (MeCN) in the parent compound, suggesting that alkyne coordination is a preliminary step. Analogously, alkyne insertion takes place, even more efficiently, in the chloride complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$, upon Cl^- removal, by treatment with Ag^+. In particular it has been found that the insertion of primary alkynes is regiospecific and C−C bond formation selectively occurs between the μ-carbyne carbon and the CH moiety of the alkyne.

The above reactions, which are part of our studies on the formation of carbon−carbon bonds in dinuclear μ-carbyne complexes,[2] allow the synthesis of vinyliminium ligands in an unusual coordination mode (μ-η^1:η^3). In fact bridging coordination is rare,[3] and vinyliminium ligands have been found mostly in mononuclear complexes, adopting different coordination geometries, i.e., σ-coordinated through the iminium carbon (C_α),[4] η^2-coordinated by the vinyl end,[5] and coordinated via both C_α and C_γ.[6] Information on the reactivity of the ligand is even more limited and includes the hydride addition

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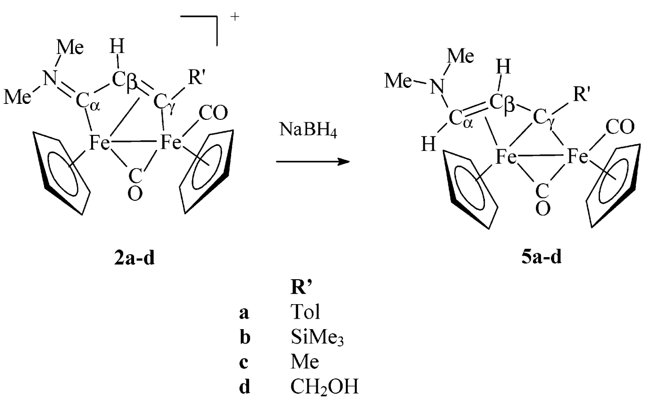
Scheme 1



at the iminium carbon in [Tp′(CO)$_2$Mo{η^2-C(Ph)=C(H)C(H)=N(Bu^t)(Me)}][BF$_4$] [Tp′ = hydridotris(pyrazolyl)borate][5] and the deprotonation of the vinyl end of the ligand in [Ru(Cp){C(=NEt$_2$)CH=CPh$_2$}(CO)(PPr$^i_3$)][BF$_4$] to form the amino allenyl derivative [Ru(Cp){C(NEt$_2$)=C=CPh$_2$)}(CO)(PPr$^i_3$)].[4a]

This work was aimed at investigating the reactivity of the vinyliminium ligand in the complexes [Fe$_2${μ-η^1:η^3-C$_\gamma$(R′)=C$_\beta$HC$_\alpha$=N(Me)(R)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] toward hydride addition and at determining which site of the ligand (C$_\alpha$ or C$_\beta$) was preferentially attacked. Different substituents at the iminium nitrogen (R = Me, **2**; Xyl, **3**; CH$_2$Ph, **4**) and at the C$_\gamma$ position (R′ = Tol, SiMe$_3$, Me, CH$_2$OH, Ph, COOMe, H) have been considered in order to evaluate electronic and steric factors that influence the regiochemistry of the reaction.

Results and Discussion

The reaction of [Fe$_2${μ-η^1:η^3-C(R′)=CHC=NMe$_2$}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] **2a**−**d** (R′ = Tol, **2a**, Tol = 4-MeC$_6$H$_4$; R = SiMe$_3$, **2b**; R = Me, **2c**; R = CH$_2$OH, **2d**) with NaBH$_4$, in tetrahydrofuran solution, results in the formation of the corresponding μ-vinylalkylidene complexes [Fe$_2${μ-η^1:η^3-C(R′)CH=CHNMe$_2$}(μ-CO)(CO)(Cp)$_2$] (R′ = Tol, **5a**; R = SiMe$_3$, **5b**; R = Me, **5c**; R = CH$_2$OH, **5d**) (Scheme 1), in good yields (70−90%).

Complexes **5a**−**d** have been isolated by column chromatography on alumina and fully characterized by spectroscopy and elemental analysis. The structure of **5a**, ascertained by an X-ray diffraction experiment, is shown in Figure 1, and relevant bond lengths and angles are reported in Table 1.

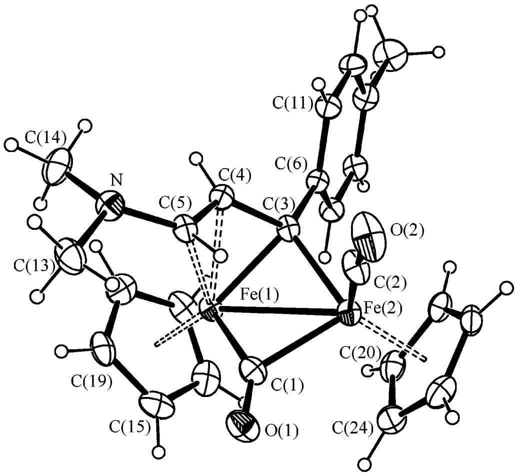


Figure 1. ORTEP drawing of the complex [Fe$_2${μ-η^1:η^3-C(Tol)CH=CHNMe$_2$}(μ-CO)(CO)(Cp)$_2$] (**5a**) (thermal ellipsoids at the 30% probability level).

Table 1. Comparison of Relevant Bond Parameters in 5a and 6f and Related Vinyliminium Complexes[a]

	I	II	III	5a	6f
Fe(1)−Fe(2)	2.557(1)	2.549(1)	2.562(1)	2.555(1)	2.521(1)
Fe(1)−C(1)	1.976(7)	1.954(7)	1.944(8)	1.849(7)	1.842(3)
Fe(2)−C(1)	1.878(7)	1.929(7)	1.894(8)	2.012(6)	2.019(3)
C(1)−O(1)	1.167(7)	1.155(8)	1.181(9)	1.183(7)	1.172(3)
Fe(2)−C(2)	1.736(8)	1.750(9)	1.750(9)	1.729(6)	1.736(3)
C(2)−O(2)	1.155(8)	1.137(9)	1.150(9)	1.157(7)	1.147(3)
Fe(2)−C(3)	1.970(6)	1.954(6)	1.955(7)	1.977(6)	1.990(2)
Fe(1)−C(3)	2.028(6)	2.017(6)	2.035(7)	1.979(6)	1.969(2)
Fe(1)−C(4)	2.052(7)	2.081(6)	2.080(7)	2.070(6)	
Fe(1)−C(5)	1.844(6)	1.843(6)	1.839(7)	2.299(6)	1.874(2)
C(3)−C(6)		1.492(9)ph	1.54(1)		1.472(3)
C(3)−C(4)	1.412(8)	1.396(8)	1.39(1)	1.441(8)	1.535(3)
C(4)−C(5)	1.406(8)	1.421(8)	1.43(1)	1.408(9)	1.489(3)
N−C(5)	1.320(7)	1.289(7)	1.314(8)	1.375(8)	1.317(3)

[a] **I** = [Fe$_2${μ-σ:η^3-C(SiMe$_3$)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (ref 1a); **II** = [Fe$_2${μ-σ:η^3-C(CO$_2$Me)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (ref 1b); **III** = *cis*-[Fe$_2${μ-σ:η^3-C(Me)=C(Me)C=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (ref 1b).

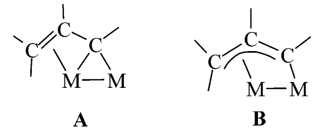


Figure 2. Description as vinylalkylidene (**A**) and bridging allylidene (**B**) of the CCC fragment in type **5** compounds.

Relevant features of the molecular structure are the bond effects produced by the H$^-$ addition at C$_\alpha$ [C(5) in Figure 1], which has been attacked from the less hindered side opposite the Cp ligands (see also further on). They can be appreciated by a comparison with the corresponding structural parameters in the cationic precursors [Fe$_2${μ-η^1:η^3-C(SiMe$_3$)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$]$^+$,[1a] [Fe$_2${μ-η^1:η^3-C(CO$_2$Me)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$]$^+$,[1b] and [Fe$_2${μ-η^1:η^3-C(Me)=C(Me)C=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$]$^+$,[1b] reported in Table 1. The C(5)−C(4) interaction [1.408(9) Å] retains some double-bond character, while some lengthening of the N−C(5) bond [1.375(8) Å] indicates a loss of multiple-bond character as the N atom turns from iminium to enamine. Some pyramidalization of the geometry around N is also detectable [distance of N from the plane of the pertinent carbons, 0.222(7) Å]. The C(5)−Fe(1) interaction [2.299(6) Å] is 0.46 Å longer than in the cationic precursors, as expected, because of the transformation from a σ- to a π-interaction. The electronic structure of the Fe−C−C−C−Fe grouping is not a simple one, and the C(3)−C(4)−C(5) unit is a mix of vinyl and allyl contributions (structures **A** and **B**, respectively, in Figure 2); however the distances C(4)−C(5) [1.408(9) Å] and C(3)−C(4) [1.441(8) Å] clearly identify the structure **A** as the more appropriate description. Therefore C(3) can be described as a bridging alkylidene [C(3)−Fe(1) 1.979(6), C(3)−Fe(2) 1.977(6) Å] and C(4)−C(5) [1.408(9) Å] as a coordinated double bond (dotted lines in Figure 1).

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The bridging carbonyl ligand [C(1)−O(1)] adopts a markedly asymmetric geometry [C(1)−Fe(1) 1.849(7), C(1)−Fe(2) 2.012(6) Å], suggesting a semibridging character. The bond asymmetry is opposite and more pronounced than that found in the cationic precursor. The change should be ascribed to the disappearance of the net charge, formally located at the iminium nitrogen in the cations, that allows a better donation to Fe(1) and, as a consequence, more π back-donation from Fe(1) to the bridging carbonyl ligand.

The infrared spectra of **5a**−**d** in CH_2Cl_2 show the usual ν(CO) band pattern consisting of two strong absorptions (e.g., at 1929 and 1747 cm^{-1} for **5a**), attributable to the terminal and bridging CO, respectively. The absorptions are about 60 cm^{-1} lower with respect to those of the parent complexes **2a**−**d**.

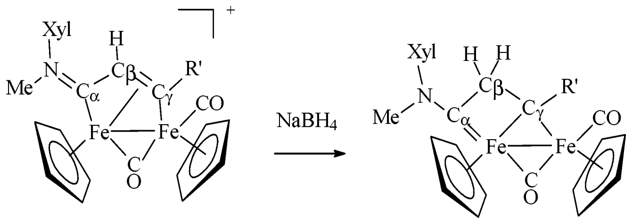
The NMR spectra of **5a**−**d**, in $CDCl_3$ solution, show the presence of one single isomer, indicating that the hydride addition is regio- and stereospecific. The ^1H NMR spectra exhibit an upfield shifted resonance (in the 1.5−1.9 ppm range) assigned to the $C_\alpha H$, which appears as a doublet because of the coupling with $C_\beta H$. The coupling constant of about 10 Hz indicates that $C_\alpha H$ and $C_\beta H$ are mutually *trans*, in accord with the X-ray diffraction structure (Figure 1). The two N-bonded methyl groups give rise to a single resonance in both ^1H and ^{13}C NMR spectra (for **5a** at 2.41 and 40.8 ppm) as a result of fast rotation (on the NMR time scale) at room temperature, around the C_α−N bond. Correspondingly, in the parent cations **2a**−**d**, two resonances are observed because of the double-bond character of the C_α−N(iminium) interaction.

The ^{13}C NMR spectra of **5a**−**d** show resonances attributable to the C_α, C_β, and C_γ carbons in the expected range (e.g., for **5a** at 105.6, 64.8, and 181.5 ppm, respectively). In particular, the C_γ resonance appears downfield shifted, in accord with its μ-alkylidene character.

Bridging vinylalkylidene ligands in **5a**−**d** are presumably the result of a simple (direct) hydride addition at the iminium carbon, rather than the outcome of a more complex reaction pattern, involving addition at the C_β followed by intramolecular hydrogen migration.[7] This is clearly evidenced by the reaction of **2a** with $NaBD_4$, which leads to the formation of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Tol)CH{=}C(D)NMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$. The ^{13}C NMR spectrum shows a triplet for the C_α ($^1J_{CD}$ = 25.8 Hz), at 105.6 ppm. The ^1H NMR shows a broad singlet for the $C_\beta H$, together with the disappearance of the $C_\alpha H$ resonance, whereas the other signals remain unchanged with respect to **5a**.

Four-electron-donor μ-vinylalkylidene ligands ($\eta^1{:}\eta^3$-coordinated) are common among dinuclear complexes, including diiron,[8] diruthenium,[9] and dirhodium[10] compounds. In complexes **5a**−**d**, the vinyl end of the bridging ligand bears the NMe_2 substituent; therefore, it can be described also as an enamine. Compounds **5a**−**d** can be compared to $[Mn_2(CO)_8(\mu\text{-}\eta^2C_3H_3NEt_2)]$,[11] $[Re_2(CO)_8(\mu\text{-}\eta^2C_3H_3NMe_2)]$,[12] and $[Mn_2(CO)_7(\mu\text{-}\eta^4C_3H_3\text{-}NEt_2)]$,[11] where the bridging C_3H_3 unit is bonded to a NR_2 groups. These complexes, obtained from coordination of ynamines, have been described as metalated μ-aminoallyls.

Scheme 2



3a-h **6a-h**

	R'
a	Tol
b	$SiMe_3$
c	Me
d	CH_2OH
e	Ph
f	COOMe
g	Bu^n
h	H

Treatment of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, **3a**−**h** (R′ = Tol, **3a**; $SiMe_3$, **3b**; Me, **3c**; CH_2OH, **3d**; Ph, **3e**; COOMe, **3f**; Bu^n, **3g**; H, **3h**), with $NaBH_4$, in tetrahydrofuran solution, under conditions similar to those above described for the synthesis of **5**, results in the formation of the corresponding bis-alkylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(R')CH_2\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = Tol, **6a**; $SiMe_3$, **6b**; Me, **6c**; CH_2OH, **6d**; Ph, **6e**; COOMe, **6f**; Bu^n, **6g**; H, **6h**) (Scheme 2).

Complexes **6a**−**h** have been characterized by spectroscopic methods and elemental analyses. A detailed description of the structure of **6f** has been obtained by X-ray diffraction. The molecular model is illustrated in Figure 3, and relevant bond parameters are reported in Table 1. An inspection of the geometry immediately shows that the steric hindrance of the Xyl group exerts a protective effect on C_α [C(5)], while C_β [C(4)] appears to be more accessible. The transformation of C(4) in a saturated tetracoordinate carbon [bond lengths C(4)−C(3) 1.535(3), C(4)−C(5) 1.489(3) Å] breaks off the π-bond connection between the bridging alkylidene C(3) and the terminal alkylidene C(5). The effect on the iron−carbon interactions in comparison to **5a** is negligible for the bridging C(3) [Fe(1)−C(3) 1.969(2), Fe(2)−C(3) 1.990(2) Å] but substantial for C(5) [Fe(1)−C(5) 1.874(2) Å]. This molecule is therefore a genuine bis-alkylidene species in which the terminal alkylidene function is stabilized by significant π-bond delocalization involving the nitrogen atom [N−C(5) 1.317(3), C(5)−Fe(1) 1.874(2) Å]. The C(1)−O(1) bridging ligand exhibits bonding asymmetry very similar to that just discussed for **5a** [C(1)−Fe(1) 1.842, C(1)−Fe(2) 2.019(3) Å].

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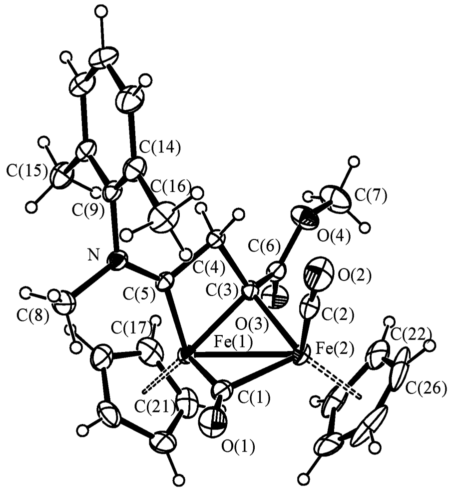
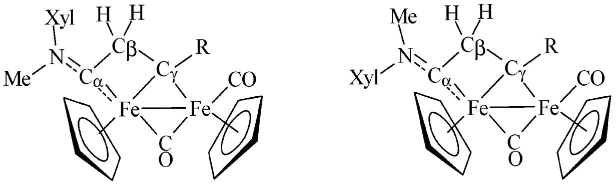


Figure 3. ORTEP drawing of the complex [$Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(COOMe)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$] (**6f**) (thermal ellipsoids at the 30% probability level).



E *Z*

Figure 4. *E*−*Z* isomers for **6a**−**h**.

Compounds **6a**−**h** display the usual ν(CO) band pattern consisting of two absorptions attributable to the terminal and bridging CO (e.g., for **6a** at 1922 and 1738 cm^{-1}).

The NMR spectra of **6a**−**h**, in $CDCl_3$ solution, reveal the presence of two isomers, in about 2−1.5:1 ratio, as observed for their precursors **3a**−**h**. In particular, the ^1H NMR spectra show two signals, for each isomer, attributable to the nonequivalent geminal $C_\beta H_2$ protons (e.g., for **6a** at 3.74, 3.45 ppm and 4.64, 4.45 ppm, respectively). The isomers arise from the orientations of the Me and Xyl group around the C_α−N interaction, whose double-bond character (see Figure 4) has already been discussed for **6f**.

NOE experiments performed on **6f** and comparison of the NMe chemical shifts of the two isomeric forms for each of the complexes **6a**−**h** indicate that the preferred orientation is *E*, corresponding to the geometry observed in the solid (Figure 3); indeed irradiation of the N-Me resonance (3.57 ppm) of the major isomer of complex **6f** has resulted in significant NOE enhancements of the resonances due to one Cp ligand (4.63 ppm) and the two methyl groups on the Xyl ring (2.04 and 1.83 ppm), whereas no effect has been detected on the resonance due to the $C_\beta H$. On the other hand, by irradiating the N-Me resonance (2.97 ppm) of the minor isomer, remarkable enhancements of the resonances due to $C_\beta H$ (4.59 and 3.86 ppm) and COOMe (3.89 ppm) have been detected.

It is worth noting that the precursors **3a**−**h** also present *E*, *Z* isomers, as a consequence of the different orientation of the iminium substituents (Me, Xyl), with predominance of the *E* isomer, which exhibits the Xyl group facing the $C_\beta H$.

Moreover, the reaction of **3c** with $NaBD_4$ affords the expected complex [$Fe_2\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(Me)C(HD)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$], which is the partially deuterated counterpart of **6c** and displays a stereogenic center at C_β. The corresponding ^1H NMR spectrum suggests that deuteride addition is stereospecific: in fact, both *E* and *Z* isomers exhibit one single $C_\beta H$ resonance (at 3.56 and 4.21 ppm, respectively). A possible explanation of the stereospecific character of the reaction is that nucleophilic attack at C_β is hampered by the more hindered Cp side of the precursor **3c**. Support for this hypothesis comes from a NOE experiment on the more abundant *E* isomer of **6c**, which has allowed the assignment of the resonances of the $C_\beta H_2$ protons. The signal at 3.56 ppm, which is also observed in the deuterated counterpart of **6c**, corresponds to the hydrogen pointing toward the Cp ligands. Therefore C_β-D is on the opposite side, where we believe the approach of the nucleophile is favored.

Concerning the ^{13}C NMR data of **6a**−**h**, the most noticeable resonances are those that evidence the peculiarity of the bridging ligand, consisting of both a bridging and a terminal alkylidene. Indeed the μ-alkylidene carbon (C_γ) resonance falls in the expected range, around 130−180 ppm. The C_β resonance occurs at higher field (e.g., for **6a** at 73.1 ppm), while the aminoalkylidene nature of the C_α is evidenced by the corresponding low-field resonance (at about 280 ppm), well within the typical range of terminally bonded diiron aminocarbene complexes.[13]

The hydride addition to complexes **3a**−**h** is reversible, and the parent compounds can be regenerated in good yields upon treatment of **6a**−**h** with HSO_3CF_3.

Comparison of the reactions shown in Schemes 1 and 2 evidences the regioselective character of the hydride addition, which occurs at C_α and C_β, respectively. This remarkable regioselectivity is originated by structural differences in the precursors **2a**−**d** and **3a**−**h**, i.e., the presence in the latter complexes of a Xyl substituent in place of a methyl at the iminium nitrogen. The sterically demanding Xyl group protects the adjacent C_α from nucleophilic attack and redirects hydride addition to the less hindered C_β position. The observed attack at C_β indicates that electronic effects are not relevant, Xyl being more electron-withdrawing than Me.

To further investigate the steric effects on the iminium reactivity, we have examined the reaction of $NaBH_4$ with [$Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2$][$SO_3CF_3$] (R′ = Tol, **4a**; $SiMe_3$, **4b**; COOMe, **4c**), in which the iminium substituents are Me and CH_2Ph. The benzyl group is less sterically demanding than Xyl, and complexes **4a**−**c** consist of a mixture of *E* and *Z* isomers, in almost equivalent amount.

The reactions of **4a**−**c** with $NaBH_4$ take place as described for compounds **2a**−**d**, and hydride addition occurs exclusively at the iminium carbon (C_α), yielding the vinylalkylidene complexes [$Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R')CH{=}CHN(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2$] (R′ = Tol, **7a**; $SiMe_3$, **7b**; COOMe, **7c**) (Scheme 3). Complexes **7a**,**b** display spectroscopic properties similar to those of the analogous compounds **5a** and **5b**, respectively. Only one

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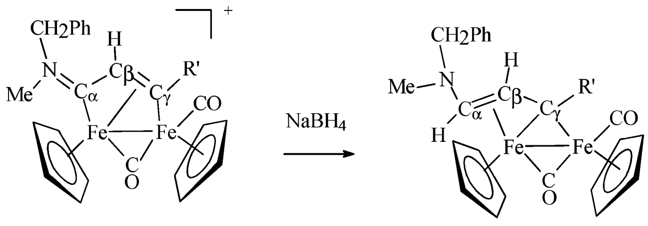
[13] Zanotti, V.; Bordoni, S.; Busetto, L.; Carlucci, L.; Palazzi, A.; Serra, R.; Albano, V. G.; Monari, M.; Prestopino, F.; Laschi, F.; Zanello, P. *Organometallics* **1995**, *14*, 5232.

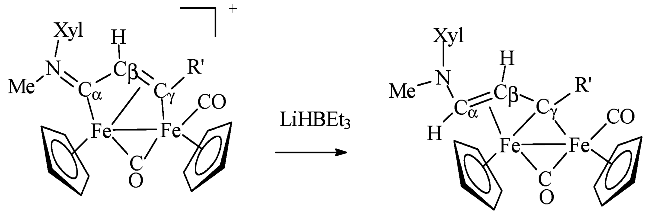
Scheme 3



4a-c **7a-c**

	R'
a	Tol
b	SiMe$_3$
c	COOMe

Scheme 4



	R'
3c	Me
3f	COOMe

	R'
8a	Me
8b	COOMe

isomer is observed, and hydride addition is exclusively *trans* to C$_\beta$-H. Therefore, only the Xyl group, among the substituents investigated, prevents attack of NaBH$_4$ at the iminium carbon (C$_\alpha$).

It should be noted that the above considerations concern the use of NaBH$_4$ and that a different hydride source could, in principle, lead to a different result. To investigate this point, we have studied the reactivity of [Fe$_2${μ-η^1:η^3-C(R′)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (R′ = Me, **3c**; COOMe, **3f**) with LiHBEt$_3$ (superhydride). By contrast with the corresponding reactions with NaBH$_4$, hydride addition selectively occurs at the iminium carbon C$_\alpha$, with the formation of the corresponding vinylalkylidene complexes [Fe$_2${μ-η^1:η^3-C(R′)CH=CHN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$] (R′ = Me, **8a**; COOMe, **8b**) (Scheme 4). No traces of compounds **6c** and **6f**, expected from attack at the C$_\beta$, have been detected.

The spectroscopic properties of **8a**,**b** resemble those of the complexes of type **5**. Their ^{1}H MMR spectra show two doublets (e.g., at 1.78 and 3.96 ppm for **8a**), assigned to C$_\alpha$H and C$_\beta$H, respectively: the coupling constant (10.4 Hz) indicates that they are mutually *trans*, as observed for the analogous μ-vinylalkylidenes **5a**−**d** and **7a**−**c**. The bridging alkylidene carbon gives rise to the expected low-field ^{13}C NMR resonance (at 184.6 ppm for **8a**).

The different behavior of BH$_4^-$ and HBEt$_3^-$ toward these substrates is interesting in several respects. It confirms the intuitive feeling that the C$_\alpha$ carbons are more acidic sites than C$_\beta$. The reaction with the more nucleophilic LiHBEt$_3$ appears to be governed by electronic rather than steric factors. By contrast, steric control dominates the regiochemistry in the case of the weaker nucleophile NaBH$_4$.

It should be remarked that **8a**,**b** and the corresponding complexes **6c**,**f** are isomers, resulting from hydride additions at C$_\alpha$ and C$_\beta$, respectively. Attempts to interconvert these species, upon heating in THF solution at reflux temperature, were unsuccessful.

Finally, reaction of **3c** with LiDBEt$_3$ places the deuterium exclusively on the C$_\alpha$, indicating that no hydrogen migration occurs between C$_\beta$ and C$_\alpha$ sites.

Conclusions

We have described the reactivity of bridging vinyliminium ligands in diiron complexes toward NaBH$_4$ and the factors controlling its regio- and stereoselectivity. The iminium carbon C$_\alpha$ is apparently the preferential site of attack, and in the absence of encumbering substituents at the nitrogen, hydride addition yields stable μ-vinylalkylidene products. However, H$^-$ addition is directed at C$_\beta$, with formation of bis-alkylidene complexes, when a Xyl group replacing a Me group (at the iminium nitrogen) makes C$_\alpha$ less accessible. We have evidenced that also other factors, including the strength of the nucleophile, are to be considered. The regioselectivity is accompanied by the stereoselectivity generated by the steric hindrance of the Cp ligands that permit the attack only from the less crowded terminal CO side (of the molecule), irrespective of the carbon atom undergoing hydride addition.

Experimental Section

General Data. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Unless otherwise stated, solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer, and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K 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. 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.[14] 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 **2a**−**d**, **3a**−**h**, and **4a**−**c** were prepared as described in the literature.[1]

Syntheses of [Fe$_2${μ-η^1:η^3-C$_\gamma$(R′)C$_\beta$(H)=C$_\alpha$(H)NMe$_2$}(μ-CO)(CO)(Cp)$_2$] (R′ = Tol, 5a; SiMe$_3$, 5b; Me, 5c; CH$_2$OH, 5d). Complex **2a** (60 mg, 0.0969 mmol) was treated with an excess of NaBH$_4$ (11 mg, 0.289 mmol) in THF solution (10 mL). The mixture was stirred at room temperature for 15 min, then the solvent was removed under reduced pressure and the residue filtered on an alumina pad, using a mixture of CH$_2$Cl$_2$ and petroleum ether (1:1) as eluent. Green crystals of **5a**, suitable for X-ray analysis, were obtained by crystallization at −20 °C from a CH$_2$Cl$_2$ solution layered with petroleum ether. Yield: 40 mg, 87%. Anal. Calcd for C$_{24}$H$_{25}$Fe$_2$NO$_2$: C, 61.18; H, 5.35; N, 2.97. Found: C, 61.23; H, 5.24; N, 3.01. IR (CH$_2$Cl$_2$): ν(CO) 1929 (vs), 1747 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.75, 7.28 (d, 4 H, $^3J_{HH}$ = 7 Hz, C$_6$*H*$_4$-Me); 4.62, 4.42 (s, 10 H, Cp); 3.93 (d, 1 H, $^3J_{HH}$ = 9.5 Hz, C$_\beta$H); 2.45 (s, 3 H, C$_6$H$_4$*Me*); 2.41 (s, 6 H, NMe); 1.86 (d, 1 H, $^3J_{HH}$ = 9.5 Hz, C$_\alpha$H). ^{13}C NMR (CDCl$_3$) δ 278.1 (μ-CO); 217.4 (CO); 181.5 (C$_\gamma$); 157.3 (ipso-*C*$_6$H$_4$Me); 134.3, 128.8, 128.3 (*C*$_6$H$_4$Me); 105.6 (C$_\alpha$); 87.6, 81.1 (Cp); 64.8 (C$_\beta$); 40.8 (NMe); 21.1 (C$_6$H$_4$*Me*).

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(14) Stott, K.; Stonehouse, J.; Keeler, J.; Hwang, T. L.; Shaka, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 4199.

Complexes **5b**,**c** were obtained following the same procedure described for the synthesis of **5a**, by reacting **2b**,**c** with $NaBH_4$, respectively.

5b. Yield: 93%. Anal. Calcd for $C_{20}H_{27}Fe_2NO_2Si$: C, 53.00; H, 6.00; N, 3.09. Found: C, 53.12; H, 5.91; N, 3.08. IR (CH_2Cl_2): ν(CO) 1928 (vs), 1751 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.69, 4.52 (s, 10 H, Cp); 4.15 (d, 1 H, $^3J_{HH}$ = 9.5 Hz, $C_\beta H$); 2.37 (s, 6 H, NMe); 1.66 (d, 1 H, $^3J_{HH}$ = 9.5 Hz, $C_\alpha H$); 0.62 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 277.5 (μ-CO); 217.4 (CO); 173.3 (C_γ); 108.1 (C_α); 85.5, 79.3 (Cp); 67.7 (C_β); 40.7 (NMe); 3.4 ($SiMe_3$).

5c. Yield: 84%. Anal. Calcd for $C_{18}H_{21}Fe_2NO_2$: C, 54.73; H, 5.36; N, 3.55. Found: C, 54.76; H 5.32; N, 3.52. IR (CH_2Cl_2): ν(CO) 1928 (vs), 1754 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): 4.65, 4.42 (s, 10 H, Cp); 3.96 (d, 1 H, $^3J_{HH}$ = 10 Hz, $C_\beta H$); 3.85 (s, 3 H, $C_\gamma Me$); 2.35 (s, 6 H, NMe); 1.49 (d, 1 H, $^3J_{HH}$ = 10 Hz, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): δ 275.9 (μ-CO); 217.6 (CO); 185.2 (C_γ); 102.4 (C_α); 86.5, 80.9 (Cp); 68.2 (C_β); 42.0 (NMe); 41.1 ($C_\gamma\mathit{Me}$).

Complex **5d** was obtained following the same procedure described for the synthesis of **5a**, by reacting **2d** with $NaBH_4$ and using THF as eluent in the column chromatography.

5d. Yield: 68%. Anal. Calcd for $C_{18}H_{21}Fe_2NO_3$: C, 52.60; H, 5.15; N, 3.41. Found: C, 52.49; H 5.16; N, 3.44. IR (CH_2Cl_2): ν(CO) 1929 (vs), 1755 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.57 (br, 1 H, OH); 5.99, 5.74 (m, 2 H, $C\mathit{H}_2OH$); 4.69, 4.47 (s, 10 H, Cp); 4.15 (d, 1 H, $^3J_{HH}$ = 10 Hz, $C_\beta H$); 2.34 (s, 6 H, NMe); 1.64 (d, 1 H, $^3J_{HH}$ = 10 Hz, $C_\alpha H$). ^{13}C NMR ($CDCl_3$): 273.7 (μ-CO); 217.5 (CO); 182.0 (C_γ); 105.6 (C_α); 85.7, 80.2 (Cp); 67.9 (CH_2OH); 66.7 (C_β); 40.9 (NMe).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(R')CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = Tol, 6a; $SiMe_3$, 6b; Me, 6c; CH_2OH, 6d; Ph, 6e; COOMe, 6f; Bu^n, 6g; H, 6h). Complex $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Tol){=}CHC{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, **3a** (90 mg, 0.127 mmol), was treated with an excess of $NaBH_4$ (26 mg, 0.684 mmol) in THF solution (10 mL). The mixture was stirred at room temperature for 15 min, then the solvent was removed under reduced pressure and the residue filtered on an alumina pad, using CH_2Cl_2 as eluent. Crystallization at −20 °C from a CH_2Cl_2 solution layered with *n*-hexane afforded **6a**. Yield: 54 mg, 76%. Anal. Calcd for $C_{31}H_{31}Fe_2NO_2$: C, 66.34; H, 5.57; N, 2.50. Found: C, 66.38; H, 5.55, N, 2.51. IR (CH_2Cl_2): ν(CO) 1922 (vs), 1738 (s), ν(CN) 1512 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.47−6.91 (m, 7 H, $Me_2C_6\mathit{H}_3$ and $C_6\mathit{H}_4Me$); 4.69, 4.38, *4.36*, *4.04* (s, 10 H, Cp); *4.64*, *4.45*, 3.74, 3.45 (d, 2 H, $^2J_{HH}$ = 19 Hz, $C_\beta H_2$); 3.67, *3.02* (s, 3 H, NMe); *2.39*, 2.35 (s, 3 H, $C_6H_4\mathit{Me}$); *2.24*, *2.17*, 1.97, 1.92 (s, 6 H, $\mathit{Me}_2C_6H_3$); *E*/*Z* ratio 3:1. ^{13}C NMR ($CDCl_3$): δ 283.4, *282.8* (C_α); 271.0, *270.1* (μ-CO); 219.0, *218.3* (CO); *162.8*, 162.4, 161.5, *160.8* (C_γ and ipso-C_6H_4Me); 142.5 (ipso-$Me_2\mathit{C}_6H_3$); 135.3−124.7 ($Me_2C_6\mathit{H}_3$ and C_6H_4Me); *88.6*, 88.3, 85.3, *85.1* (Cp); *75.5*, 73.1 (C_β); 45.3, *40.9* (NMe); 21.1 ($C_6H_4\mathit{Me}$); *18.3*, *18.2*, 17.8, 17.1 ($\mathit{Me}_2C_6H_3$).

Complexes **6b**−**h** were obtained following the same procedure described for the synthesis of **6a**, by reacting complexes **3b**−**h** with $NaBH_4$, respectively.

6b. Yield: 76%. Anal. Calcd for $C_{27}H_{33}Fe_2NO_2Si$: C, 59.69; H, 6.12, N, 2.58. Found: C, 59.77; H, 6.04; N, 2.56. IR (CH_2Cl_2): ν(CO) 1921 (vs), 1739 (s), ν(CN) 1511 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.30−6.90 (m, 3 H, $Me_2C_6\mathit{H}_3$); 4.77, *4.72*, 4.61, *3.99* (s, 10 H, Cp); *4.62*, *4.04*, 3.90, 2.82 (d, 2 H, $^2J_{HH}$ = 20 Hz, $C_\beta H_2$); 3.61, *2.94* (s, 3 H, NMe); *2.21*, *2.20*, 2.03, 1.85 (s, 6 H, $\mathit{Me}_2C_6H_3$); *0.51*, 0.41 (s, 9 H, $SiMe_3$); *E*/*Z* ratio 2:1. ^{13}C NMR ($CDCl_3$): δ 281.3, *282.2* (C_α); 269.2, *268.0* (μ-CO); 219.0, *218.5* (CO); 160.1, *159.4* (C_γ); *146.1*, 142.6 (ipso-$Me_2\mathit{C}_6H_3$); 135.2−127.9 ($Me_2\mathit{C}_6H_3$); *85.6*, 85.5, 84.1, *83.7* (Cp); *70.6*, 67.5 (C_β); 45.1, *40.8* (NMe); *18.1*, *18.0*, 17.4, 16.9 ($\mathit{Me}_2C_6H_3$); 2.9, *2.8* ($SiMe_3$).

6c. Yield: 85%. Anal. Calcd for $C_{25}H_{27}Fe_2NO_2$: C, 61.89; H, 5.61, N, 2.89. Found: C, 61.89; H, 5.58, N, 2.90. IR (CH_2Cl_2): ν(CO) 1915 (vs), 1736 (s), ν(CN) 1512 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.24−6.89 (m, 3 H, $Me_2C_6\mathit{H}_3$); 4.64, *4.59*, 4.46, *3.91* (s, 10 H, Cp); *4.42*, *4.21*, 3.56, 3.34 (d, 2 H, $^2J_{HH}$ = 20 Hz, $C_\beta H_2$); *3.65*, 3.56 (s, 3 H, $C_\gamma Me$); 3.62, *2.97* (s, 3 H, NMe); *2.22*, *2.16*, 2.07, 1.85 (s, 6 H, $\mathit{Me}_2C_6H_3$); *E*/*Z* ratio 3:2. ^{13}C NMR ($CDCl_3$): δ 282.2, *281.8* (C_α); 273.0, *271.6* (μ-CO); 218.9, *218.4* (CO); 172.6, *172.2* (C_γ); *146.3*, 142.2 (ipso-$Me_2\mathit{C}_6H_3$); 135.2−127.8 ($Me_2\mathit{C}_6H_3$); *87.0*, *86.7*, 86.6, 85.3 (Cp); *78.5*, 76.1 (C_β); *47.5*, 47.3 ($C_\gamma\mathit{Me}$); 45.9, *40.9* (NMe); *18.0*, *17.9*, 17.6, 17.0 ($\mathit{Me}_2C_6H_3$).

6d. Yield: 77%. Anal. Calcd for $C_{25}H_{27}Fe_2NO_3$: C, 59.91; H, 5.43, N, 2.73. Found: C, 60.06; H, 5.40; N, 2.79. IR (CH_2Cl_2): ν(CO) 1916 (vs), 1733 (s), ν(CN) 1511 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.04−6.82 (m, 3 H, $Me_2C_6\mathit{H}_3$); 5.24 (br, 1 H, OH); 4.60, *4.55*, *4.48*, 4.43 (s, 10 H, Cp); 3.59 (s, 3 H, NMe); 3.64, 3.52 (d, 2 H, $^2J_{HH}$ = 12 Hz, $C\mathit{H}_2OH$); 3.53, 3.29 (d, 2 H, $^2J_{HH}$ = 20 Hz, $C_\beta H_2$); 2.04, 1.82 (s, 6 H; $\mathit{Me}_2C_6H_3$); *E*/*Z* ratio 15:1. ^{13}C NMR ($CDCl_3$) δ 282.1 (C_α); 273.0 (μ-CO); 218.8 (CO); 172.5 (C_γ); 142.2 (ipso-$Me_2\mathit{C}_6H_3$); 132.7, 131.6, 128.9, 128.2, 128.0 ($Me_2\mathit{C}_6H_3$); 86.6, 85.3 (Cp); 76.1 (C_β); 47.2 (CH_2OH); 45.9 (NMe); 17.5, 16.9 ($\mathit{Me}_2C_6H_3$).

6e. Yield: 79%. Anal. Calcd for $C_{30}H_{29}Fe_2NO_2$: C, 65.84; H, 5.34; N, 2.56. Found: C, 65.91; H, 5.27; N, 2.54. IR (CH_2Cl_2): ν(CO) 1922 (vs), 1743 (s), ν(CN) 1513 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.74−6.92 (m, 8 H, $Me_2C_6\mathit{H}_3$ and Ph); 4.71, 4.38, *4.35*, *4.05* (s, 10 H, Cp); *4.63*, *4.47*, 3.75, 3.45 (d, 2 H, $^2J_{HH}$ = 21 Hz, $C_\beta H_2$); 3.68, *3.03* (s, 3 H, NMe); *2.24*, *2.18*, 1.98, 1.92 (s, 6 H, $\mathit{Me}_2C_6H_3$); *E*/*Z* ratio 2:1. ^{13}C NMR ($CDCl_3$): δ 282.9, *282.3* (C_α); 270.8, *269.9* (μ-CO); 218.9, *218.3* (CO); *165.3*, 164.9 (C_γ); 160.9, *160.2* (ipso-Ph); *146.0*, 142.4 (ipso-$Me_2\mathit{C}_6H_3$); 135.3−122.7 ($Me_2\mathit{C}_6H_3$ and Ph); *88.5*, 88.2, 85.3, *85.1* (Cp); *75.3*, 72.9 (C_β); 45.3, *40.9* (NMe); *18.3*, 17.8, 17.1 ($\mathit{Me}_2C_6H_3$).

6f. Yield: 95%. Anal. Calcd for $C_{26}H_{27}Fe_2NO_4$: C, 59.01; H, 5.14, N, 2.65. Found: C, 59.03; H, 5.11; N, 2.61. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1763 (s), 1664 (w), 1636 (w), ν(CN) 1512 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24−6.85 (m, 3 H, $Me_2C_6\mathit{H}_3$); 4.67, *4.65*, 4.63, *4.04* (s, 10 H, Cp); *4.59*, *3.86*, 3.78, 2.77 (d, 2 H, $^2J_{HH}$ = 20 Hz, $C_\beta H_2$); 3.97, *3.89* (s, 3 H, CO_2Me); 3.57, *2.97* (s, 3 H, NMe); *2.22*, *2.14*, 2.04, 1.83 (s, 6 H, $\mathit{Me}_2C_6H_3$); *E*/*Z* ratio 3:2. ^{13}C NMR ($CDCl_3$): δ 276.1, *276.0* (C_α); 268.8, *267.4* (μ-CO); 217.7, *217.5* (CO); 186.0, *185.5* ($\mathit{C}O_2Me$); *145.9*, 142.0 (ipso-$Me_2\mathit{C}_6H_3$); 134.9−128.0 ($Me_2\mathit{C}_6H_3$); 133.0 (C_γ); *87.3*, 87.1, 86.1, *85.5* (Cp); *69.6*, 67.4 (C_β); *50.9*, 50.8 ($CO_2\mathit{Me}$); 45.8, *41.3* (NMe); *18.1*, 17.7, 16.9 ($\mathit{Me}_2C_6H_3$).

6g. Yield: 92%. Anal. Calcd for $C_{28}H_{33}Fe_2NO_2$: C, 63.78; H, 6.31; N, 2.66. Found: C, 63.80; H, 6.36; N, 2.64. IR (CH_2Cl_2): ν(CO) 1917 (vs), 1735 (s), ν(CN) 1511 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24−6.89 (m, 3 H, $Me_2C_6\mathit{H}_3$); 4.64, *4.60*, 4.49, *3.94* (s, 10 H, Cp); *4.30*, *4.10*, 3.41, 3.23 (d, 2 H, $^2J_{HH}$ = 20 Hz, $C_\beta H_2$); *4.08*, 4.04, 3.80, *3.58* (dt, 2 H, $^2J_{HH}$ = 4 Hz, $^3J_{HH}$ = 13 Hz, $C_\gamma C\mathit{H}_2$); 3.63, *2.97* (s, 3 H, NMe); *2.21*, *2.16*, 2.06, 1.84 (s, 6 H, $\mathit{Me}_2C_6H_3$); 1.81 (m, 2 H, $C_\gamma CH_2C\mathit{H}_2$); *1.70*, 1.59 (m, 2 H, $C_\gamma CH_2CH_2C\mathit{H}_2$); *1.16*, 1.04 (t, 3 H, $^3J_{HH}$ = 7 Hz, $C_\gamma CH_2CH_2CH_2C\mathit{H}_3$); *E*/*Z* ratio 3:2. ^{13}C NMR ($CDCl_3$): δ 282.3 (C_α); 273.8, *272.2* (μ-CO); 219.2, *218.8* (CO); 177.6 (C_γ); 142.3−127.8 ($Me_2\mathit{C}_6H_3$); *86.8*, 86.4, 85.4, *84.8* (Cp); *75.7*, 73.4 (C_β); 60.6 ($C_\gamma\mathit{C}H_2$); 45.9, *40.9* (NMe); *33.3*, 33.2 ($C_\gamma CH_2\mathit{C}H_2$); *23.8*, 23.6 ($C_\gamma CH_2CH_2\mathit{C}H_2$); *18.1*, *17.9*, 17.6, 16.9 ($\mathit{Me}_2C_6H_3$); *14.7*, 14.5 ($C_\gamma CH_2CH_2CH_2\mathit{C}H_3$).

6h. Yield: 88%. Anal. Calcd for $C_{24}H_{25}Fe_2NO_2$: C, 61.18; H, 5.35, N, 2.97. Found: C, 61.10; H, 5.42; N, 2.89. IR (CH_2Cl_2): ν(CO) 1918 (vs), 1740 (s), ν(CN) 1512 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ *11.23*, 11.10 (dd, 1 H, $^3J_{HH}$ = 7 Hz, $^3J_{HH}$ = 2 Hz, $C_\gamma H$); 7.24−6.88 (m, 3 H, $Me_2C_6\mathit{H}_3$); 4.64, *4.61*, 4.52, *3.98* (s, 10 H, Cp); *4.82*, 4.16 (dd, 1 H, $^2J_{HH}$ = 20 Hz, $^3J_{HH}$ = 7 Hz, $C_\beta H$); 3.59, *2.97* (s, 3 H, NMe); *4.19*, 3.07 (dd, 1 H, $^2J_{HH}$ = 20 Hz, $^3J_{HH}$ = 2 Hz, $C_\beta H$); *2.22*, *2.09*, 2.06, 1.80 (s, 6 H, $\mathit{Me}_2C_6H_3$); *E*/*Z* ratio 6:5. ^{13}C NMR ($CDCl_3$): δ *281.0*, 280.9 (C_α); 272.7, *271.4* (μ-CO); 218.1, *218.0* (CO); *149.9*, 149.6 (C_γ); *146.1*, 142.1 (ipso-$Me_2\mathit{C}_6H_3$); 135.1−127.8 ($Me_2\mathit{C}_6H_3$); *85.6*, 85.4, 84.0, *83.5* (Cp); *69.0*, 66.7 (C_β); 45.8, *41.0* (NMe); *17.9*, *17.8*, 17.6, 17.0 ($\mathit{Me}_2C_6H_3$).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')CH{=}CHN(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = Tol, 7a; $SiMe_3$, 7b; COOMe, 7c). Complex **7a** was obtained following the same procedure described for the synthesis of **5a**, by treating **4a** (110 mg, 0.158 mmol) with $NaBH_4$.

7a. Yield: 97%. Anal. Calcd for $C_{30}H_{29}Fe_2NO_2$: C, 65.84; H, 5.34; N, 2.56. Found: C, 65.91; H 5.35; N, 2.55. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1747 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.96−7.27 (m, 9 H, Ph and C_6H_4Me); 4.52, 4.42 (s, 10 H, Cp); 4.01 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_βH); 4.02, 3.87 (d, 2 H, $^2J_{HH}$ = 15 Hz, CH_2Ph); 2.46 (s, 3 H, NMe); 2.24 (s, 3 H, C_6H_4*Me*); 2.08 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_αH). ^{13}C NMR ($CDCl_3$): δ 278.3 (μ-CO); 217.4 (CO); 181.7 (C_γ); 157.4 (ipso-C_6H_4Me); 136.9, 134.2, 128.8, 128.5, 128.3, 127.4 (Ph and C_6H_4Me); 105.6 (C_α); 87.6, 81.6 (Cp); 64.0 (C_β); 60.0 (CH_2Ph); 35.9 (NMe); 21.1 (C_6H_4*Me*).

Complex **7b** and **7c** were obtained following the same procedure described for the synthesis of **5a**, by reacting **4b** and **4c** with $NaBH_4$, respectively.

7b. Yield: 80%. Anal. Calcd for $C_{26}H_{31}Fe_2NO_2Si$: C, 59.00; H, 5.90; N, 2.65. Found: C, 58.92; H 5.96; N, 2.62. IR (CH_2Cl_2): ν(CO) 1930 (vs), 1751 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.49−7.26 (m, 5 H, Ph); 4.69, 4.40 (s, 10 H, Cp); 4.17 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_βH); 3.97, 3.81 (d, 2 H, $^2J_{HH}$ = 15 Hz, CH_2Ph); 2.20 (s, 3 H, NMe); 1.88 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_αH); 0.60 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 278.4 (μ-CO); 217.6 (CO); 173.8 (C_γ); 136.8, 128.9, 128.5, 128.4, 127.4 (Ph); 108.3 (C_α); 85.6, 79.8 (Cp); 66.8 (C_β); 60.1 (CH_2Ph); 35.8 (NMe); 3.4 ($SiMe_3$).

Complex **7c** was obtained following the same procedure described for the synthesis of **3a**, by reacting **4c** (110 mg, 0.166 mmol) with $NaBH_4$.

7c. Yield: 66%. Anal. Calcd for $C_{25}H_{25}Fe_2NO_4$: C, 58.29; H, 4.89; N, 2.72. Found: C, 58.30; H, 4.83; N, 2.69. IR (CH_2Cl_2): ν(CO) 1936 (vs), 1762 (s), 1689 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.46−7.28 (m, 5 H, Ph); 4.66, 4.43 (s, 10 H, Cp); 4.39 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_βH); 4.05 (s, 3 H, CO_2Me); 3.94, 3.84 (d, 2 H, $^2J_{HH}$ = 14 Hz, CH_2Ph); 2.24 (s, 3 H, NMe); 2.02 (d, 1 H, $^3J_{HH}$ = 9 Hz, C_αH). ^{13}C NMR ($CDCl_3$): δ 271.6 (μ-CO); 217.3 (CO); 172.0 (CO_2Me); 157.8 (C_γ); 136.1, 128.6, 128.5, 127.6 (Ph); 107.6 (C_α); 86.6, 82.0 (Cp); 62.9 (C_β); 60.5 (CH_2Ph); 51.8 (CO_2*Me*); 35.6 (NMe).

Synthesis of [$Fe_2\{\mu$-η^1:η^3-C(R′)CH=CHN(Me)(Xyl)$\}(\mu$-CO)(CO)(Cp)$_2$] (R′ = Me, 8a COOMe, 8b). A THF solution of **3c** (46 mg, 0.0727 mmol), cooled to −30 °C, was treated with a solution of $LiBHEt_3$ in THF (0.10 mmol); the mixture was stirred at room temperature for 30 min, then the solvent was removed. Chromatography of the residue on an alumina column afforded an orange band, corresponding to **8a**, collected using CH_2Cl_2 as eluent. Yield: 20 mg, 57%. Anal. Calcd for $C_{25}H_{27}Fe_2NO_2$: C, 61.89; H, 5.61; N, 2.89. Found: C, 61.93; H 5.68; N, 2.90. IR (CH_2Cl_2): ν(CO) 1922 (vs), 1751 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.24−6.88 (m, 3 H, $Me_2C_6H_3$); 4.61, 4.38 (s, 10 H, Cp); 3.96 (d, 1 H, $^3J_{HH}$ = 10.4 Hz, C_βH); 3.94 (s, 3 H, C_γMe); 2.58, 2.54 (s, 6 H, *Me*$_2C_6H_3$ and NMe); 1.93 (s, 3 H, *Me*$_2C_6H_3$); 1.78 (d, 1 H, $^3J_{HH}$ = 10.4 Hz, C_αH). ^{13}C NMR ($CDCl_3$): δ 278.0 (μ-CO); 217.6 (CO); 184.6 (C_γ); 145.2−126.7 ($Me_2C_6H_3$); 104.7 (C_α); 86.4, 82.1 (Cp); 64.8 (C_β); 42.5 (NMe); 36.3 (C_γMe); 18.9, 17.6 (*Me*$_2C_6H_3$).

Complex **8b** was obtained following the same procedure described for the synthesis of **8a**, by treating **3f** (50 mg, 0.074 mmol) with $LiBHEt_3$.

8b. Yield: 82%. Anal. Calcd for $C_{26}H_{27}Fe_2NO_4$: C, 59.01; H, 5.14; N, 2.65. Found: C, 59.07; H 5.08; N, 2.65. IR (CH_2Cl_2): ν(CO) 1931 (vs), 1769 (s), 1690 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.10−6.92 (m, 3 H, $Me_2C_6H_3$); 4.62, 4.52 (s, 10 H, Cp); 4.41 (d, 1 H, $^3J_{HH}$ = 10.4 Hz, C_βH); 4.09 (s, 3 H, CO_2Me); 2.61, 2.51, 1.93 (s, 9 H, *Me*$_2C_6H_3$ and NMe); 2.05 (d, 1 H, $^3J_{HH}$ = 10.4 Hz, C_αH). ^{13}C NMR ($CDCl_3$): δ 260.5 (μ-CO); 217.1 (CO); 171.2 (CO_2Me); 156.4 (C_γ); 144.6 (ipso-$Me_2C_6H_3$); 136.4−127.2 ($Me_2C_6H_3$); 111.2 (C_α); 86.5, 82.6 (Cp); 61.2 (C_β); 51.9 (CO_2*Me*); 36.6 (NMe); 18.7, 17.6 (*Me*$_2C_6H_3$).

X-ray Crystallography. The diffraction experiments for **5a** and **6f** were carried out at room temperature on a Bruker AXS SMART 2000 CCD based diffractometer using graphite-monochromated Mo Kα 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 the software SAINT,[15] and an empirical absorption correction was applied using 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. The methyl and aromatic hydrogen atoms, although observed in the electron density maps, were placed in calculated positions and allowed to ride the carrier carbons with thermal parameters tied to those of the pertinent atoms. The other H atoms were located and their parameters refined individually. Crystallographic data and structure refinement details for **5a** and **6f** are given in Table 2.

Table 2. Crystal Data and Experimental Details for 5a and 6f

	5a	6f
formula	$C_{24}H_{25}Fe_2NO_2$	$C_{26}H_{27}Fe_2NO_4$
fw	471.15	529.19
T, K	298(2)	298(2)
λ, Å	0.71073	0.71073
cryst symmetry	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	8.1439(8)	10.6352(3)
b, Å	10.349(1)	13.2769(3)
c, Å	12.818(1)	16.3383(4)
α, deg	83.718(3)	90
β, deg	78.364(3)	94.627(1)
γ, deg	79.393(3)	90
cell volume, Å^3	1037.0(2)	2299.5(1)
Z	2	4
D_c, Mg m^{-3}	1.509	1.529
μ(Mo Kα), mm^{-1}	1.419	1.295
F(000)	488	1096
cryst size, mm	0.10 × 0.15 × 0.25	0.20 × 0.25 × 0.28
θ limits, deg	2.59−25.99	1.92−30.04
no. of reflns collected	10 287 (±h, ±k, ±l)	29 796 (±h, ±k, ±l)
no. of unique obsd reflns [$F_o > 4\sigma(F_o)$]	4055 [R(int) = 0.0575]	6718 [R(int) = 0.0792]
goodness-of-fit on F^2	1.019	0.849
R1(F)[a], wR2(F^2)[b]	0.0645, 0.1588	0.0406, 0.0901
largest diff peak and hole, e·Å^{-3}	1.110/−0.739	0.659/−0.508

[a] $R1 = \sum||F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

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Supporting Information Available: Tables giving all crystal data, atomic coordinates, and bond lengths and angles for **5a** and **6f**; these crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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