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Reactions of Diazo Compounds at μ-Vinyliminium Ligands: Synthesis of Novel Dinuclear Azine−Bis(alkylidene) Complexes

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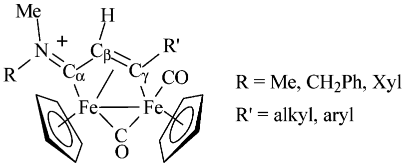
The vinyliminium complexes $[M_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta HC_\alpha{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1a−f**) react with ethyl diazoacetate in the presence of NaH, affording the azine−bis(alkylidene) $[M_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C_\gamma(R')C_\beta\{{=}NN{=}C_\delta(COOMe)H\}C_\alpha N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (M = Fe, R = 2,6-$Me_2C_6H_3$ (Xyl), R′ = Me (**2a**), p-C_6H_4Me (Tol) (**2b**), CO_2Me (**2c**), Bu^n (**2d**); M = Fe, R = R′ = Me (**2e**); M = Ru, R = Xyl, R′ = Me (**2f**)) in 70÷77% yields. Analogous reactions with N_2CPh_2 lead to the formation of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C_\gamma(R')C_\beta({=}NN{=}C_\delta Ph_2)C_\alpha N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = Me (**3a**), COOMe (**3b**)). The azine−bis(alkylidene) ligand easily undergoes electrophilic addition, affording the cationic hydrazone−vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R')C_\beta\{N(E)N{=}C_\delta(R'')(R''')\}C_\alpha{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ (R′ = Me, R″ = CO_2Et, R‴ = E = H, **4a**; R′ = Me, R″ = COOEt, R‴ = H, E = Me, **4b**; R′ = Bu^n, R″ = COOEt, R‴ = H, E = Me, **4c**; R′ = Me, R″ = R‴ = Ph, E = Me, **4d**). Reactions of **4b**,**d** with $NaBH_4$ result in the addition of hydride at the C_α of the vinyliminium moiety, generating the bridging allylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(Me)C_\beta\{N(Me)N{=}C_\delta(R'')(R''')\}C_\alpha(H)N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R″ = CO_2Et, R‴ = H, **5a**; R″ = R‴ = Ph, **5b**), respectively. The X-ray molecular structures of **2a** and **4c**$[CF_3SO_3]\cdot CH_2Cl_2$ have been determined.

Introduction

Binuclear complexes provide potential possibilities of cooperative reactivity which, in combination with activation effects due to bridging coordination, should open new perspectives in the field of metal-assisted transformation of small organic molecules.[1] Our interest in this area has been focused on the chemistry of μ-vinyliminium diiron complexes of the type $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R'){=}C_\beta(H)C_\alpha{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1**: R′ = alkyl, aryl; R = Me, CH_2Ph, Xyl; Xyl = 2,6-$Me_2C_6H_3$) (Chart 1)[2] and of their diruthenium counterparts.[3]The C_3-bridged organic frame in **1** can be expanded by exploiting its remarkable reactivity toward nucleophiles. Indeed, it has been shown that the vinyliminium (azoniabutadienyl) ligands undergo nucleophilic attack by hydride ($NaBH_4$),[4] cyanide,[5] and acetylides.[6] The additions can be directed selectively to the C_α or to the adjacent C_β position to generate new allylidene and bis(alkylidene) ligands.

Chart 1



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More recently, a new approach to the functionalization of the bridged organic frame in **1** has been evidenced. The C_β−H proton of the vinyliminium ligand is acidic, and its removal (by NaH) creates a reactive intermediate which can be "trapped" with appropriate reagents.[7] Thus, deprotonation in the presence of group 16 elements (O, S, Se) results in the formation of the corresponding zwitterionic vinyliminium compounds $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}C(E)C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (E = O, S, Se) (Scheme 1).[8]

Herein we present an extension of these studies, which concerns the deprotonation of the vinyliminium ligands in the presence of diazo compounds, aimed at introducing new functionalities on the central carbon atom of the C_3 bridging frame. Diazoalkanes are valuable reagents for the synthesis of C−C double bonds, and several reactions are known in which

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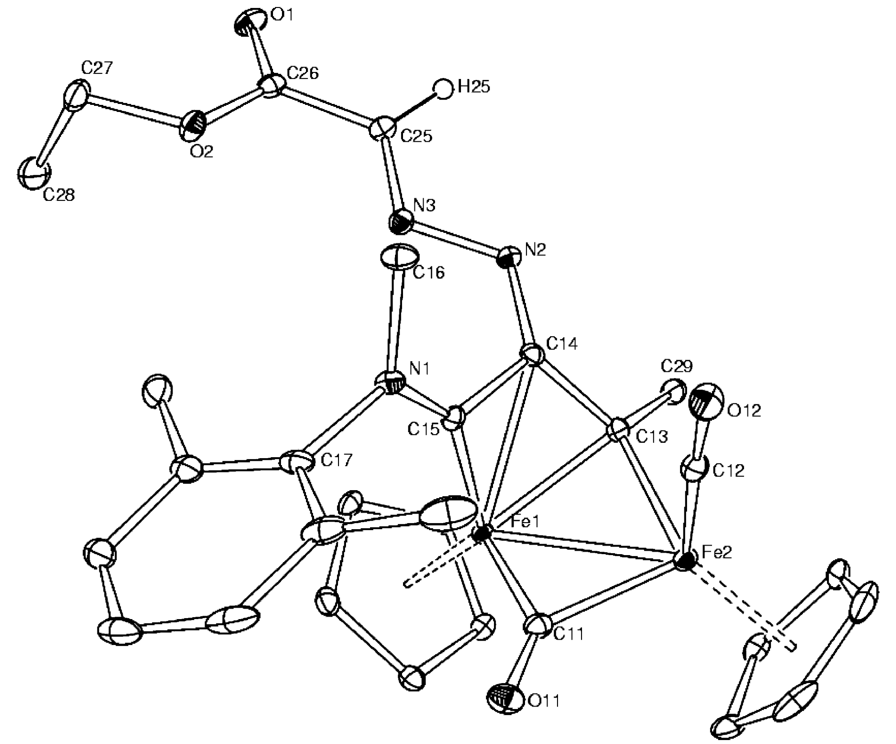
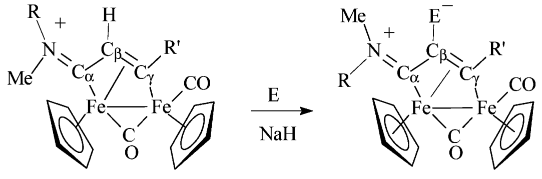


Figure 1. ORTEP drawing of [$Fe_2\{\mu$-η^1:η^2-C(Me)C{=NN=C(H)(CO_2Et)}CN(Me)(Xyl)}(μ-CO)(CO)($Cp)_2$] (**2a**). All H atoms, except H(25), have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

Scheme 1



1

E = O, S, Se

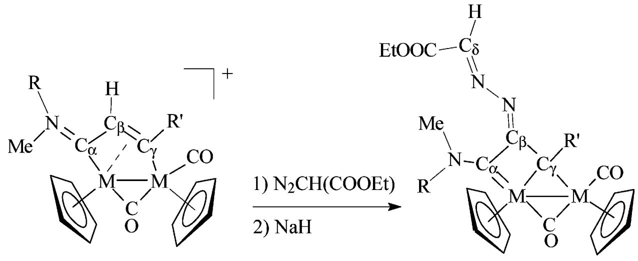
they react with bridging ligands, including μ-alkylidenes[9] and μ-alkylidynes,[10] leading to the extension of the bridging hydrocarbyl chain. Furthermore, diazoalkanes exhibit a rich coordination chemistry,[11] with particular regard to dinuclear complexes.[12] Therefore, they appear to be good candidates to accomplish transformations of the bridging vinyliminium ligand in **1**.

Results and Discussion

1. Reactions with Diazo Compounds. The reaction of complexes **1a**−**e** with NaH, in the presence of ethyl diazoacetate, resulted in the formation of the azine−bis(alkylidene) compounds **2a**−**e**, in good yields (Scheme 2).

Compounds **2a**−**f** were moderately air sensitive and were characterized by IR and NMR spectroscopy and elemental analysis. Moreover, the structure of **2a** was determined by low-temperature (100 K) X-ray diffraction studies: the ORTEP molecular diagram is shown in Figure 1, and relevant bond lengths and angles are reported in Table 1.

Scheme 2



	M	R		R'	
1a	Fe	Xyl	(2,6-$Me_2C_6H_3$)	Me	**2a**
1b	Fe	Xyl		Tol	**2b**
1c	Fe	Xyl		COOMe	**2c**
1d	Fe	Xyl		Bu^n	**2d**
1e	Fe	Me		Me	**2e**
1f	Ru	Xyl		Me	**2f**

The molecule is composed of a *cis*-[$Fe_2(Cp)_2(\mu$-CO)(CO)] unit to which a bridging azine−bis(alkylidene) ligand is coordinated in a μ-η^1:η^2 fashion. The latter can be described by taking into consideration the two limiting formulas reported in Chart 2, as previously found for the zwitterionic vinyliminium complexes shown in Scheme 1.[8] The Fe(1)−C(15) (1.854(2) Å), Fe(1)−C(13) (2.026(2) Å), and Fe(2)−C(13) (1.971(2) Å) interactions are typical for a terminal aminocarbene (C_α, C(15)) and a bridging alkylidene (C_γ, C(13)).[13] In agreement with the aminocarbene nature of the ligand, the C(15)−N(1) (1.306(3) Å) interaction maintains partial double-bond character, as in the parent vinyliminium species **1b**. However, the orientation

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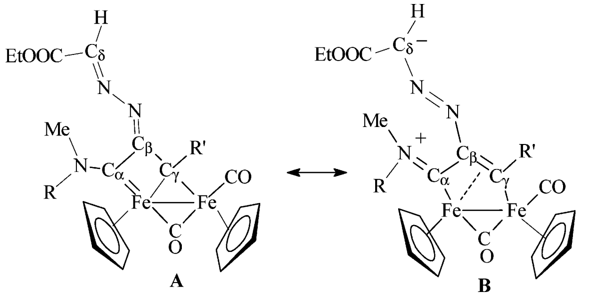
Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C\{=NN=C(H)(CO_2Et)\}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (2a)

Fe(1)−Fe(2)	2.5292(7)	C(13)−C(29)	1.511(3)
Fe(1)−C(11)	1.896(2)	C(15)−N(1)	1.306(3)
Fe(2)−C(11)	1.939(2)	C(14)−N(2)	1.362(2)
Fe(2)−C(12)	1.755(2)	N(2)−N(3)	1.360(2)
Fe(1)−C(13)	2.026(2)	N(3)−C(25)	1.301(2)
Fe(2)−C(13)	1.971(2)	C(25)−C(26)	1.460(3)
Fe(1)−C(14)	2.2179(19)	C(26)−O(1)	1.223(2)
Fe(1)−C(15)	1.854(2)	C(26)−O(2)	1.349(3)
C(13)−C(14)	1.447(3)	C(14)−C(15)	1.458(3)
Fe(2)−C(13)−C(14)	122.71(44)	C(14)−N(2)−N(3)	113.36(16)
C(13)−C(14)−C(15)	109.57(16)	N(2)−N(3)−C(25)	113.53(17)
C(14)−C(15)−Fe(1)	83.16(12)	N(3)−C(25)−C(26)	121.52(19)
C(15)−N(1)−C(16)	122.49(17)	C(25)−C(26)−O(1)	122.7(2)
C(15)−N(1)−C(17)	120.19(17)	C(25)−C(26)−O(2)	113.77(17)
C(16)−N(1)−C(17)	117.22(16)	O(1)−C(26)−O(2)	123.54(19)

Chart 2



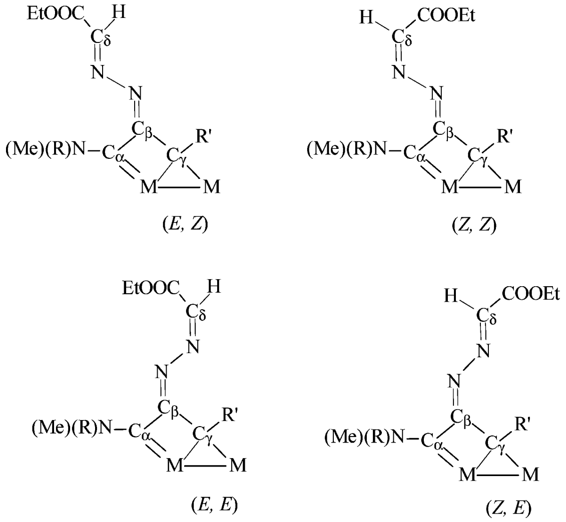
of the Me and Xyl substituents is opposite in the two species: in **2b** the Xyl group points far from the C_β (*Z* configuration), whereas the precursor **1a** adopts the *E* configuration. This is in full agreement with previous observations:[2b] the increased steric demand at the C_β position, due to the replacement of the C_β−H hydrogen, forces the Xyl group far apart in order to minimize steric repulsions.

The C(25)−N(3) (1.301(2) Å) interaction is an almost pure C═N double bond, whereas N(2)−N(3) (1.360(2) Å) and C(14)−N(2) (1.362(2) Å) are intermediate between a double and a single bond, even though the latter is quite elongated and similar to the C−N bond found in formamide (1.38 Å). This suggests some delocalization inside the s-trans [C═NNC═N] azine group; in agreement with this, C(14), N(2), N(3), C(25), C(26), O(1), and O(2) are almost coplanar (mean deviation from the plane 0.0795 Å). Moreover, the Fe(1)−C(14) distance (2.2179(19) Å) is intermediate between that found in $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(CO_2Me)CH_2CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (2.589(1) Å),[4a] where there is no bond, and the bonding distance found in vinyliminium complexes (e.g., 2.080(7) Å in $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me)═C(Me)C═N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$).[2b] This suggests the presence of some bonding interaction between Fe(1) and C(14). Therefore, in addition to the most representative resonance form **A**, also the zwitterionic μ-η^1:η^3-vinyliminium form **B** (Chart 2) has to be considered; this also explains the observed lengthening of C(14)−N(2). In agreement with this, both C(13)−C(14) (1.447(3) Å) and C(14)−C(15) (1.458(3) Å) are basically single bonds,[13] as expected for form **A**, even though the former is sensibly shorter as in **B**.

The IR spectra of complexes **2a**−**f** (in CH_2Cl_2 solution) present absorptions in the carbonyl region attributable to the terminal and the bridging carbonyls and the carboxylate, respectively (e.g., at 1951, 1784, and 1686 cm^{-1} for **2a**).

For complexes **2a**−**f** several isomeric forms are in theory feasible, due to the presence of three different C−N interactions displaying double-bond character. Indeed, for unsymmetric azines four configurations, *E*,*E*, *E*,*Z*, *Z*,*E*, and *Z*,*Z*, are possible (Chart 3). Further isomeric forms should arise from the orientation of the Me and Xyl substituents of the C_α═N(Me)(Xyl) moiety. Finally, isomers should be due also to the conformation of the N−N bond, although azines usually exhibit the s-trans conformation.[14] In spite of these possibilities, the NMR spectra of **2a**−**f** clearly indicate that these complexes exist in a single isomeric form which, presumably, has the same geometry observed in the solid state. In fact, NMR investigations, carried on **2a**,**b**, revealed significant NOE effects between one Cp ligand and the methyls of the xylyl group and between N−*Me* and CO_2CH_2−C*H*$_3$. The formation of a single isomer is presumably due to steric reasons, and the observed geometry corresponds to the most favorable *E*,*Z* configuration.

Chart 3. Configurational Isomers for 2a−f[a]



[a] Cp and CO ligands are omitted.

Major features in the ^{13}C NMR spectra of **2a**−**f** are the C_α and C_γ resonances, which fall in the typical ranges for aminocarbene and alkylidene carbons, respectively (e.g., for **2a** at 243.1 and 185.5 ppm). In addition, the C_β resonance (e.g., at 125.7 ppm for **2a**) results in a significant downfield shift with respect to the corresponding precursors (at 52.7 ppm for **1a**), as a consequence of the imine character assumed by the C_β carbon.

The reaction shown in Scheme 2 deserves some further comments. Deprotonation of **1** in the presence of ethyl diazoacetate was originally investigated with the aim of forming a C−C double bond at the C_β position. Indeed, the proton abstraction from **1** was expected to give intermediates potentially able to react with the carbenes generated by the diazoacetate. Conversely, the reaction which occurred without release of N_2 represents one of the rare examples of incorporation of the intact diazoalkane into a bridging ligand.[15] In our case, the addition of diazoacetate led to the formation of a C═N double bond, generating an azine functionality at the C_β position. Azine formation via addition of diazo compounds to carbene or carbenoid species in not entirely unprecedented. Examples include the addition of diazofluorene to 1,3-dimesitylimidazol-2-ylidene.[16] Moreover, azines are known to be formed in rhodium(II)-catalyzed decompositions of alkyl- and aryldiazo-

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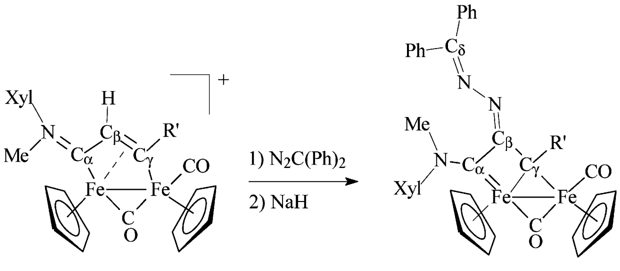
Scheme 3



	R’	
1a	Me	**3a**
1c	COOMe	**3b**

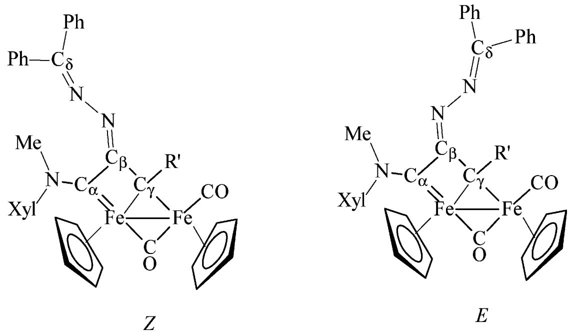
methanes, and these reactions are believed to occur via the initial formation of a carbenoid which subsequently adds the diazoalkane.[17] Likewise, catalytic olefinations of carbonyl compounds with diazo reagents are often accompanied by the formation of azine compounds as secondary products.[18]

A second point to be outlined is that the reaction provides a highly functionalized C_3 bridging frame by trapping the deprotonated intermediate with diazoacetate. The overall result is the replacement of the C_β−H proton in the vinyliminium ligand with a diazoacetate group. In comparison to the related reactions of **1** with NaH in the presence of group 16 elements, shown in Scheme 1, the addition of diazoacetate appears less sensitive to the nature of the substituents on the vinyliminium ligands. Indeed, for some vinyliminium complexes the addition of sulfur was observed to involve the C_α or C_γ carbon, instead of the C_β carbon, producing the fragmentation of the dinuclear complexes, whereas the reaction with diazoacetate takes place exclusively at the C_β carbon. Likewise, the reaction is not affected by the presence of ruthenium in place of iron. In fact, the diruthenium complex **1f** was found to react with ethyl diazoacetate exactly like its diiron counterpart **1a** (Scheme 1) and the properties of the corresponding products **2f** and **2a** are similar.

In order to establish whether the reaction described above could be extended to other diazo reagents, the complexes **1a**,**c** were treated with diphenyldiazomethane in the presence of NaH. Again, the reactions occurred by addition of the diazo reagent at the C_β carbon of the bridging ligand, affording **3a**,**b**, respectively (Scheme 3).

Compounds **3a**,**b** were readily characterized by IR and NMR spectroscopy and elemental analysis. The NMR spectra of **3a**,**b**, at room temperature, show some broadening of the signals, suggesting the occurrence of an exchange process. Spectra recorded at 243 K indicate the presence of two isomers. NOE investigations on **3b** (at 243 K) suggest a possible explanation: the isomers might result from different orientations of the [N=$C_\delta(Ph)_2$] unit, with respect to the C_β=N bond (Chart 4). In particular, the major isomer of **3b** did not show any NOE between the N−*Me* and phenyl resonances, whereas this effect was observed for the minor isomer. Moreover, the isomers mainly differ in the chemical shift of the C_γ−R′ group, which is influenced by the orientation of the N=$C_\delta(Ph)_2$ group. This hypothesis does not exclude an alternative explanation based on the exchange between the N−Me and N−Xyl positions, although fluxionality of the aminocarbene ligand (C_αN(Me)(Xyl)) has never been observed in any of the related bis(alkylidene) complexes investigated so far.

Chart 4. Isomers for Complexes 3a,b



The addition of diazo reagents cannot be considered of general character, since the reactions of **1a**,**c** with N_2CH_2 or $N_2CH(SiMe_3)$, in the presence of NaH, failed to produce the expected azine−bis(alkylidene) ligand. In particular, the products observed in the reaction with $N_2CH(SiMe_3)$ were the metallacyclopentadiene complexes which are known to be formed when **1a**,**c** are treated with NaH in the absence of trapping reagents.[7] Therefore, the reaction seems to be facilitated by electron-withdrawing diazo compounds.

2. Reactions of the Azine−Bis(alkylidene) Ligand. The bridging organic frame in **2a**−**e** is highly functionalized, in that it contains an azine (2,3-diazabutadiene) moiety and is anchored to the metal atoms through a bridging alkylidene and a terminally bonded aminoalkylidene. It is worth mentioning that the presence of an azine functionality might induce new photochromic properties[19] or provide further possibilities of metal coordination.[20] This has been the case of the ferrocenyl-substituted azines, which have revealed peculiar electro- and photochromic activity,[21] with potential applications in the field of chemical sensors.[22]

In our complexes, the presence of an azine group, not directly coordinated to the metal centers, should provide routes to possible modifications and further extension of the bridging frame. Specifically, we have investigated the reactions of **2a**,**d** and **3a** with HSO_3CF_3 and $MeSO_3CF_3$, aimed at determining which of the potential electrophilic sites of the ligand would be more reactive. The methylation (or protonation) reactions occur selectively at the N atom bound to C_β, affording the novel hydrazone−vinyliminium complexes **4a**−**d** in high yields (Scheme 4).

Complexes **4a**−**d** were characterized by spectroscopy and elemental analysis. Moreover, the molecular structure of **4c**[CF_3SO_3]·CH_2Cl_2 was elucidated by X-ray diffraction: the ORTEP molecular diagram is shown in Figure 2, whereas relevant bond lengths and angles are reported in Table 2.

The methylation of the nitrogen atom completely reestablishes the vinyliminium character of the bridging μ-η^1:η^3 ligand, as indicated by the Fe(1)−C(13) (2.042(4) Å), Fe(1)−C(14) (2.077(4) Å), Fe(1)−C(15) (1.845(4) Å), and Fe(2)−C(13) (1.977(4) Å) interactions, which are very similar to those found in other β-substituted vinyliminium complexes, as for instance *cis*-[$Fe_2\{\mu$-η^1:η^3-C(Me)=C(Me)C=N(Me)(Xyl)$\}(\mu$-CO)(CO)$(Cp)_2]^+$ (2.035(7), 2.080(7), 1.839(7), and 1.855(7) Å, respectively).[2b]

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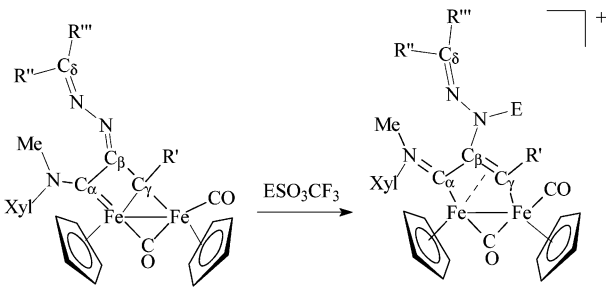
Scheme 4



	R'	R''	R'''	E	
2a	Me	CO_2Et	H	H	**4a**
2a	Me	CO_2Et	H	Me	**4b**
2d	Bu^n	CO_2Et	H	Me	**4c**
3a	Me	Ph	Ph	Me	**4d**

Table 2. Selected Bond Lengths (Å) and Angles (°) for $[Fe_2\{\mu$-η^1:η^3-C(Bu^n)C{N(Me)N=C(CO_2Et)(H)}C=N(Me)-(Xyl)}(μ-CO)(CO)$(Cp)_2][SO_3CF_3]$ (4c).

Fe(1)−Fe(2)	2.5588(11)	C(15)−N(1)	1.294(5)
Fe(1)−C(11)	1.968(4)	C(14)−N(2)	1.432(5)
Fe(2)−C(11)	1.899(4)	N(2)−N(3)	1.332(5)
Fe(2)−C(12)	1.750(4)	N(3)−C(25)	1.286(5)
Fe(1)−C(13)	2.042(4)	C(25)−C(26)	1.464(7)
Fe(2)−C(13)	1.977(4)	C(26)−O(1)	1.200(6)
Fe(1)−C(14)	2.077(4)	C(26)−O(2)	1.332(7)
Fe(1)−C(15)	1.845(4)	N(2)−C(29)	1.449(6)
C(13)−C(30)	1.514(5)		

Fe(2)−C(13)−C(14)	119.0(3)	C(14)−N(2)−N(3)	117.4(3)
C(13)−C(14)−C(15)	115.8(3)	C(14)−N(2)−C(29)	120.5(3)
C(14)−C(15)−Fe(1)	77.4(7)	C(29)−N(2)−N(3)	121.6(3)
C(15)−N(1)−C(16)	121.8(3)	N(3)−C(25)−C(26)	119.1(5)
C(15)−N(1)−C(17)	121.7(3)	C(25)−C(26)−O(1)	122.7(6)
C(16)−N(1)−C(17)	116.4(3)	C(25)−C(26)−O(2)	113.4(4)
N(2)−N(3)−C(25)	119.2(4)	O(1)−C(26)−O(2)	123.9(5)

The iminium N(Me)(Xyl) group adopts a *Z* configuration because of the presence of a β-substituent, which is essentially a hydrazone. Thus, C(14)−N(2) (1.432(5) Å) is a single bond, whereas the N(3)−C(25) distance (1.286(5) Å) is typical for a double bond.[13]

The observed selective methylation of the C_β−N nitrogen atom is most probably related to the change described above in the coordination mode of the bridging C_3 frame. In other words, the methylation and consequently the loss of double-bond character of the C_β=N interaction, which would leave an unsaturated C_β carbon, becomes possible since C_β happens to be coordinated to the Fe atom, producing the observed change in the coordination mode. Conversely, if methylation had occurred on the C_δ=N moiety, a similar stabilization could not be extended to the C_δ carbon.

The IR spectra (in CH_2Cl_2 solution) of **4a**−**d** exhibit the typical pattern of bridging vinyliminium complexes:[3] i.e., two CO absorptions at ca. 1985 and 1815 cm^{-1} and a band due to the C_α−N interaction (e.g., at 1614 cm^{-1} for **4a**). In addition, one band for a partial C−N double-bond interaction (C_δ-N) is observed (e.g., at 1580 cm^{-1} for **4a**). The ^1H NMR spectra of **4a**−**c**, recorded at room temperature, show the presence of a single isomeric form, as do their corresponding precursors. NOE studies carried on complex **4b** indicated that both E (E = Me), which gives rise to a singlet at δ 3.59 ppm, and C_γ−*Me* (at 3.84 ppm) lie opposite to C_αN−*Me* (at 3.16 ppm). These features are consistent with the configuration observed in the solid for **4c**. In the ^{13}C NMR spectra the resonances of the C_α, C_β, and C_γ carbons (e.g., at δ 227.1, 91.1, and 204.8 ppm for **4b**) are consistent with the data previously reported for μ-vinyliminium ligands.[3]

Finally, it is worth mentioning that the protonation reaction, which leads to **4a**, is completely reversed upon treatment with NaH in THF solution.

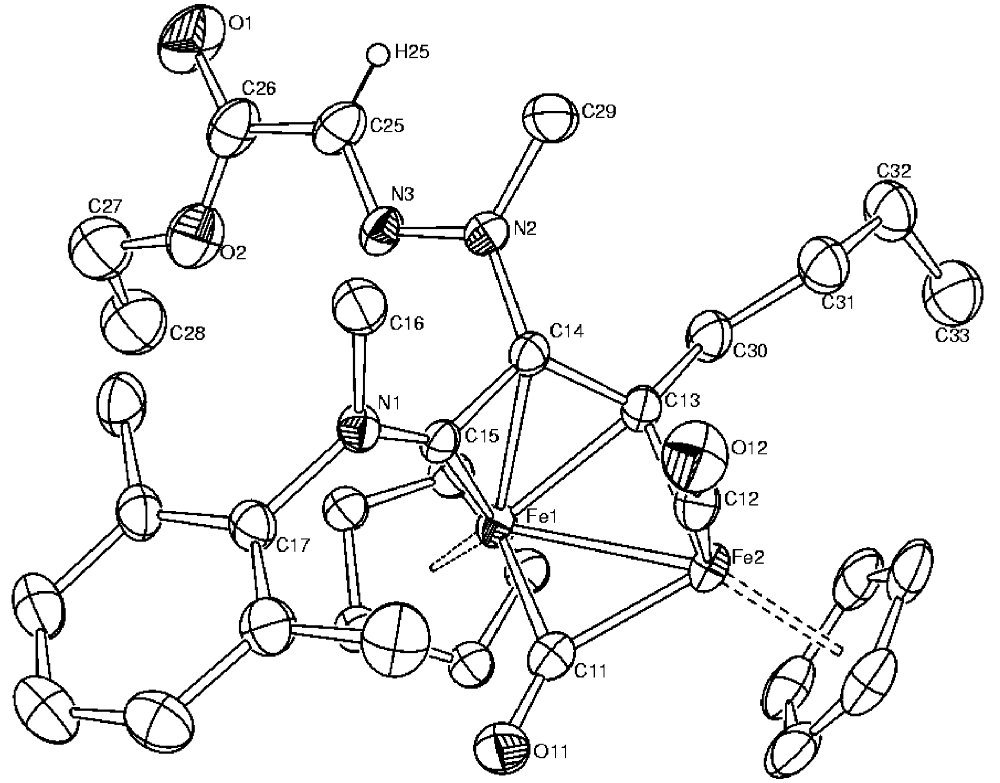
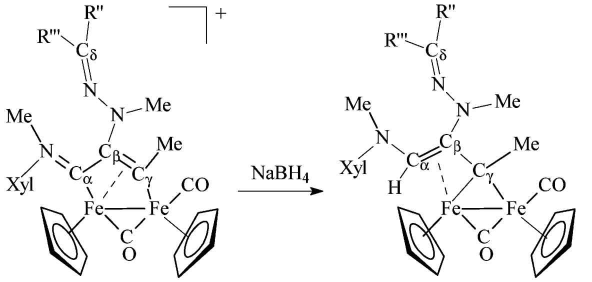


Figure 2. ORTEP drawing of the cation $[Fe_2\{\mu$-η^1:η^3-C(Bu^n)C{N(Me)N=C(CO_2Et)(H)}C=N(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2]^+$ (**4c**). All H atoms, except H(25), have been omitted for clarity. Only the main images of the disordered Cp bound to Fe(1) and of the ethyl group bound to O(2) are given. Thermal ellipsoids are at the 30% probability level.

Scheme 5



	R''	R'''	
4b	CO_2Et	H	**5a**
4d	Ph	Ph	**5b**

Since treatment with $CH_3SO_3CF_3$ restores the μ-vinyliminium character of the bridging frame, it is expected to give reactions typical of the vinyliminium ligand, including the addition of hydride. This would promote further rearrangements of the bridging ligand and demonstrate that, through a step-by-step addition procedure, it is possible to generate coordinated organic frames of increasing complexity. Therefore, we examined the reactions of **4b**,**d** with $NaBH_4$. The reactions, performed in THF at room temperature, afforded the amino−hydrazone−allylidene complexes **5a**,**b** in high yields (Scheme 5).

Hydride addition occurs selectively at the C_α carbon of the vinyliminium ligand, in agreement with previous results on the reactions of $NaBH_4$ with similar μ-vinyliminium complexes.[4b] Compounds **5a**,**b** were identified by spectroscopic methods: their IR and NMR spectra closely resemble those of analogous diiron bridging allylidene complexes.[4] The IR spectra present two carbonylic absorptions at lower wavenumbers with respect to the precursors **4b**,**d** (e.g., for **5a** at 1926 and 1755 cm^{-1}). The ^{13}C NMR spectra show resonances due to C_α, C_γ, and C_β (in the case of **5a**, at 97.9, 180.8, and 99.4 ppm, respectively), which are consistent with the μ-allylidene nature of the C_3 bridging chain.

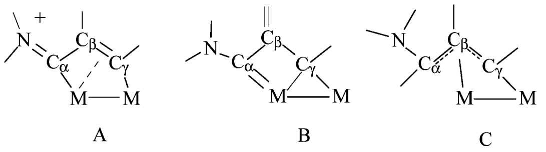
The most relevant ^1H NMR feature is the resonance attributable to $C_\alpha H$, which falls in the typical high-field range (e.g., at δ 1.23 ppm for **5a**). In particular, the signal is almost identical with that of the complex $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C_\gamma(Ph)C_\beta(Ph)C_\alpha(H)N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (δ 1.24 ppm for $C_\alpha-H$), previously reported.[4b] In view of these similarities, and since in all of the previously reported μ-allylidene complexes the $C_\alpha-H$ hydrogen is placed on the opposite site with respect to $C_\beta-R$, we assume that also **5a**,**b** adopt the same configuration (*Z* configuration), as shown in Scheme 5.

Conclusions

Our findings bring further evidence that deprotonation of the bridging vinyliminium ligands generates reactive intermediates which can be exploited for introducing functionalities on the C_β position. In particular, ethyl diazoacetate and diphenyldiazomethane proved to act as efficient trapping reagents, resulting in the formation of C═N double bonds. The novel bridging frame, consequently created, is coordinated to the dimetallic core through a bridging alkylidene and terminal aminoalkylidene groups and contains an azine functionality. This latter group, in turn, can be transformed into a hydrazone group by methylation (or protonation) of the N atom, affording new cationic complexes.

A second point outlined herein is the role of the rather flexible bridging coordination in supporting the transformations performed on the bridging organic frame. Each of the substitution and electrophilic or nucleophilic addition reactions involving the bridging ligand are accompanied by changes in the bridging coordination mode: rearrangements from vinyliminium (Chart 5, **A**) to bis(alkylidene) (**B**) and to allylidene (**C**).

Chart 5



Moreover, these reactions are stereo- and regio-specific, since they occur at definite sites of the ligand and generate specific configurations. Thereby, μ-vinyliminium ligands are found to be good candidates for creating bridging organic frames of increasing complexity on a dinuclear transition-metal core.

Experimental Section

General Data. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer, and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. ESI MS spectra were recorded on a Waters Micromass ZQ 4000 instrument with samples dissolved in CH_3CN. All NMR measurements were performed on a Varian Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and $^1H,^{13}C$ correlations measured through gs-HSQC and gs-HMBC experiments.[23] Unless otherwise stated, 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 given in italics. NOE measurements were recorded using the DPFGSE-NOE sequence.[24] All of the reagents were commercial products (Aldrich) of the highest purity available and were used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. $[M_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')═C(H)C═N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1a**−**f**)[2,3] were prepared by published methods.

Synthesis of $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C_\gamma(R')C_\beta\{═NN═C_\delta(H)(CO_2Et)\}C_\alpha N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Xyl, R′ = Me, 2a; R = Xyl, R′ = Tol, 2b; R = Xyl, R′ = CO_2Me, 2c; R = Xyl, R′ = Bu^n, 2d; R = Me, R′ = Me, 2e). A THF solution of **1a** (98 mg, 0.155 mmol) was treated with $N_2CH(COOEt)$ (1.60 mmol) and then with NaH (30 mg, 1.25 mmol). The mixture was stirred for 20 min, and then it was filtered on alumina. Removal of the volatile material and chromatography of the residue on an alumina column, with THF as eluent, gave a green band corresponding to **2a**. Yield: 71 mg, 77%. Crystals of **2a**, 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 $C_{29}H_{31}Fe_2N_3O_4$: C, 58.32; H, 5.23; N, 7.04. Found: C, 58.38; H, 5.19; N, 7.02. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1951 (vs), 1784 (s), 1686 (m); ν(C═N) 1571 (w), 1525 (w). ^1H NMR ($CDCl_3$; δ): 7.69 (s, 1 H, $C_\delta H$); 7.33−7.17 (m, 3 H, $Me_2C_6H_3$); 4.92, 4.34 (s, 10 H, Cp); 4.22, 4.17 (dq, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, CO_2CH_2); 3.86 (s, 3 H, $C_\gamma Me$); 3.28 (s, 3 H, NMe); 2.67, 2.09 (s, 6 H, $Me_2C_6H_3$); 1.26 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 267.7 (μ-CO); 243.1 (C_α); 213.9 (CO); 185.5 (C_γ); 165.7 (CO_2Et); 143.4 (*ipso*-$Me_2C_6H_3$); 136.0, 134.2, 128.8, 128.6, 128.4 ($Me_2C_6H_3$); 134.4

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(C_δ); 125.7 (C_β); 89.0, 87.2 (Cp); 59.6 (CO_2CH_2); 50.8 (NMe); 38.1 ($C_\gamma Me$); 18.8, 18.6 ($Me_2C_6H_3$); 14.5 ($CO_2CH_2CH_3$).

Compounds **2b**−**e** were prepared by the same procedure described for **2a**, by reacting $N_2CH(COOEt)$/NaH with **1b**−**e**, respectively.

2b: yield 70%; dark green. Anal. Calcd for $C_{35}H_{35}Fe_2N_3O_4$: C, 62.43; H, 5.24; N, 6.24. Found: C, 62.45; H, 5.38; N, 6.18. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1953 (vs), 1785 (s), 1681 (m); ν(C=N) 1575 (w), 1523 (w). ^1H NMR ($CDCl_3$; δ): 7.55−7.19 (m, 7 H, $Me_2C_6H_3$ and C_6H_4Me); 7.47 (s, 1 H, $C_\delta H$); 4.60, 4.51 (s, 10 H, Cp); 4.15, 4.14 (dq, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, CO_2CH_2); 3.39 (s, 3 H, NMe); 2.71, 2.14 (s, 6 H, $Me_2C_6H_3$); 2.43 (s, 3 H, C_6H_4Me); 1.21 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 268.0 (μ-CO); 243.7 (C_α); 214.5 (CO); 181.8 (C_γ); 165.6 (CO_2Et); 153.7 (ipso-C_6H_4Me); 143.2 (ipso-$Me_2C_6H_3$); 136.0, 134.5, 133.9, 128.7, 128.4, 128.3 (C_6H_4Me and $Me_2C_6H_3$); 135.0 (C_δ); 124.4 (C_β); 90.4, 86.9 (Cp); 59.4 (CO_2CH_2); 51.2 (NMe); 21.2 (C_6H_4Me); 19.1, 18.6 ($Me_2C_6H_3$); 14.5 ($CO_2CH_2CH_3$).

2c: yield 72%; dark green. Anal. Calcd for $C_{30}H_{31}Fe_2N_3O_6$: C, 56.19; H, 4.87; N, 6.55. Found: C, 56.22; H, 4.99; N, 6.59. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1962 (vs), 1794 (s), 1697 (m), 1598 (w); ν(C=N) 1577 (w). ^1H NMR ($CDCl_3$; δ): 7.64 (s, 1 H, $C_\delta H$); 7.35−7.19 (m, 3 H, $Me_2C_6H_3$); 4.83, 4.57 (s, 10 H, Cp); 4.20 (m, 2 H, CO_2CH_2); 4.14 (s, 3 H, COOMe); 3.37 (s, 3 H, NMe); 2.64, 2.08 (s, 6 H, $Me_2C_6H_3$); 1.27 (t, 3 H, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 268.3 (μ-CO); 244.2 (C_α); 213.6 (CO); 180.6 (COOMe); 165.5 (CO_2Et); 161.6 (C_γ); 143.7 (ipso-$Me_2C_6H_3$); 137.6 (C_δ); 135.8, 134.2, 129.2, 129.0, 128.7 ($Me_2C_6H_3$); 126.0 (C_β); 89.1, 88.0 (Cp); 60.1 (CO_2CH_2); 52.1 (CO_2Me); 51.2 (NMe); 18.9, 18.6 ($Me_2C_6H_3$); 14.7 ($CO_2CH_2CH_3$).

2d: yield 75%; dark green. Anal. Calcd for $C_{32}H_{37}Fe_2N_3O_4$: C, 60.12; H, 5.83; N, 6.57. Found: C, 59.98; H, 5.79; N, 6.69. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1951 (vs), 1784 (s), 1677 (m); ν(C=N) 1572 (w), 1525 (w). ^1H NMR ($CDCl_3$; δ): 7.64 (s, 1 H, $C_\delta H$); 7.30−7.13 (m, 3 H, $Me_2C_6H_3$); 4.90, 4.35 (s, 10 H, Cp); 4.57 (m, 2 H, $C_\gamma CH_2$); 4.17, 4.14 (m, 2 H, CO_2CH_2); 3.27 (s, 3 H, NMe); 2.65, 2.05 (s, 6 H, $Me_2C_6H_3$); 2.61 (m, 2 H, $C_\gamma CH_2CH_2$); 1.79, 1.69 (m, 2 H, $C_\gamma CH_2CH_2CH_2$); 1.22 (m, 3 H, $CO_2CH_2CH_3$); 1.15 (m, 3 H, $C_\gamma CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 267.6 (μ-CO); 242.6 (C_α); 213.9 (CO); 193.2 (C_γ); 165.7 (CO_2Et); 143.1 (ipso-$Me_2C_6H_3$); 135.8, 134.2, 128.6, 128.5, 128.3 ($Me_2C_6H_3$); 133.5 (C_δ); 121.6 (C_β); 88.7, 87.2 (Cp); 59.3 (CO_2CH_2); 51.7 ($C_\gamma CH_2$); 50.7 (NMe); 34.7 ($C_\gamma CH_2CH_2$); 23.9 ($C_\gamma CH_2CH_2CH_2$); 18.7, 18.5 ($Me_2C_6H_3$); 14.5 ($CO_2CH_2CH_3$); 14.4 ($C_\gamma CH_2CH_2CH_2CH_3$).

2e: yield 72%; dark green. Anal. Calcd for $C_{22}H_{25}Fe_2N_3O_4$: C, 52.10; H, 4.97; N, 8.29. Found: C, 52.03; H, 4.90; N, 8.34. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1954 (vs), 1774 (s), 1678 (m); ν(C=N) 1642 (w), 1529 (w). ^1H NMR ($CDCl_3$; δ): 7.56 (s, 1 H, $C_\delta H$); 4.90, 4.57 (s, 10 H, Cp); 4.22, 4.14 (dq, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 6.95 Hz, 2 H, CO_2CH_2); 3.77 (s, 3 H, $C_\gamma Me$); 3.72, 3.00 (s, 6 H, NMe); 1.28 (t, $^3J_{HH}$ = 6.95 Hz, 3 H, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 252.5 (μ-CO); 237.6 (C_α); 212.9 (CO); 182.0 (C_γ); 165.7 (CO_2Et); 132.8 (C_δ); 125.5 (C_β); 88.5, 87.1 (Cp); 59.6 (CO_2CH_2); 49.3, 45.5 (NMe); 37.2 ($C_\gamma Me$); 14.4 ($CO_2CH_2CH_3$).

Synthesis of [$Ru_2\{\mu$-η^1:η^2-C_γ(Me)$C_\beta\{$=NN=C_δ(H)(CO_2Et)$\}$-C_αN(Me)(Xyl)$\}$(μ-CO)(CO)$(Cp)_2$] (2f). This product was prepared by the same procedure described for **2a**, by reacting **1f** with $N_2CH(COOEt)$ and NaH. **2f**: yield 72%; purple. Anal. Calcd for $C_{29}H_{31}N_3O_4Ru_2$: C, 50.65; H, 4.54; N, 6.11. Found: C, 50.68; H, 4.41; N, 6.00. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1944 (vs), 1787 (s), 1686 (m); ν(C=N) 1605 (w), 1572 (w). ^1H NMR ($CDCl_3$; δ): 7.66 (s, 1 H, $C_\delta H$); 7.29−7.13 (m, 3 H, $Me_2C_6H_3$); 5.31, 4.71 (s, 10 H, Cp); 4.22, 4.20 (dq, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, CO_2CH_2); 3.45, 3.44 (s, 6 H, C_γMe and NMe); 2.55, 2.15 (s, 6 H, $Me_2C_6H_3$); 1.26 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 241.4 (μ-CO); 232.7 (C_α); 202.2 (CO); 165.3 (CO_2Et); 160.5 (C_γ); 144.2 (*ipso*-$Me_2C_6H_3$); 143.8 (C_β); 136.6 (C_δ); 136.0, 133.5, 128.9, 128.3, 128.1 ($Me_2C_6H_3$); 90.3, 87.8 (Cp); 59.9 (CO_2CH_2); 49.3 (NMe); 39.1 ($C_\gamma Me$); 18.8, 18.6 ($Me_2C_6H_3$); 14.4 ($CO_2CH_2CH_3$).

Synthesis of [$Fe_2\{\mu$-η^1:η^2-C_γ(R′)$C_\beta\{$=NN=$C_\delta(Ph)_2\}C_\alpha$N(Me)(Xyl)$\}$(μ-CO)(CO)$(Cp)_2$] (R′ = Me, 3a; R′ = COOMe, 3b). Compounds **3a**,**b** were prepared by the same procedure described for **2a**, by reacting **1a**,**c** with $N_2C(Ph)_2$/NaH.

3a: yield 65%; dark green. Anal. Calcd for $C_{38}H_{35}Fe_2N_3O_2$: C, 67.38; H, 5.21; N, 6.20. Found: C, 67.42; H, 5.18; N, 6.20. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1934 (vs), 1769 (s); ν(C=N) 1546 (w). ^1H NMR ($CDCl_3$, 243 K; δ): 7.84−7.13 (m, 13 H, $Me_2C_6H_3$ and Ph); 4.82, *4.78*, 4.30, *4.11* (s, 10 H, Cp); *3.88*, 3.61 (s, 3 H, C_γ-Me); 3.35, 2.*87* (s, 3 H, NMe); 2.29, 2.20, *2.10*, *2.02* (s, 6 H, $Me_2C_6H_3$); *Z/E* ratio 2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 243 K; δ): *277.7*, 273.9 (μ-CO); *254.8*, 252.6 (C_α); 215.6, *215.2* (CO); 184.1, *171.2* (C_γ); *162.5*, 157.8 (C_δ); 145.1−127.4 (C_β, Ph and $Me_2C_6H_3$); 88.3, *87.9*, 86.2, *86.1* (Cp); 50.6, *46.2* (NMe); *43.4*, 38.5 ($C_\gamma Me$); 19.0, *18.1*, 17.9, *17.5* ($Me_2C_6H_3$). ESI-MS (ES^+): *m*/*z* 677 [M^+].

3b: yield 60%; brown. Anal. Calcd for $C_{39}H_{35}Fe_2N_3O_4$: C, 64.93; H, 4.89; N, 5.82. Found: C, 64.98; H, 4.80; N, 5.77. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1946 (vs), 1777 (s), 1686 (w); ν(C=N) 1546 (w). ^1H NMR ($CDCl_3$, 243 K; δ): 7.81−7.16 (m, 13 H, $Me_2C_6H_3$ and Ph); 4.79, *4.71*, *4.50*, 4.32 (s, 10 H, Cp); *3.67*, 3.63 (s, 3 H, CO_2Me); *3.47*, 3.03 (s, 3 H, NMe); *2.24*, *2.17*, 2.09 (s, 6 H, $Me_2C_6H_3$); *E*/Z ratio 2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 243 K; δ): 272.7, *270.1* (μ-CO); *251.9*, 250.3 (C_α); 251.2, *214.8* (CO); 182.5, *181.3* (CO_2Me); 161.4, 159.9, 159.7 (C_γ and C_δ); 144.3−126.3 (C_β, Ph and $Me_2C_6H_3$); *88.2*, 88.1, *86.8*, 86.5 (Cp); 53.6, 51.6 (CO_2Me); 51.0, *46.7* (NMe); *18.8*, 18.0, *17.6*, 17.5 ($Me_2C_6H_3$).

Synthesis of [$Fe_2\{\mu$-η^1:η^3-C_γ(Me)$C_\beta\{$NHN=C_δ(H)(CO_2Et)$\}$-C_α=N(Me)(Xyl)$\}$(μ-CO)(CO)$(Cp)_2$][BF_4] (4a). Complex **2a** (80 mg, 0.134 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with HBF_4 in a diethyl ether solution (0.20 mmol). The mixture was stirred for 10 min and then filtered on Celite. The product was obtained as a green powder upon solvent removal under reduced pressure. Yield: 64 mg, 80%. Treatment of **4a**, in THF solution (10 mL), with a 5-fold excess of NaH formed **2a** again in about 70% yield. Anal. Calcd for $C_{29}H_{32}BF_4Fe_2N_3O_4$: C, 50.84; H, 4.71; N, 6.13. Found: C, 50.88; H, 4.74; N, 6.09. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1983 (vs), 1814 (s), 1727 (w); ν(C=N) 1614 (m), 1580 (w). ^1H NMR ($CDCl_3$; δ): 8.08 (s, 1 H, $C_\delta H$); 7.40−7.18 (m, 3 H, $Me_2C_6H_3$); 5.11, 4.56 (s, 10 H, Cp); 4.22, 4.20 (dq, $^2J_{HH}$ = 10.9 Hz, $^3J_{HH}$ = 7.3 Hz, 2 H, CO_2CH_2); 4.01 (s, 3 H, C_γMe); 3.37 (s, 3 H, NMe); 2.69, 2.03 (s, 6 H, $Me_2C_6H_3$); 1.28 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, $CO_2CH_2CH_3$); NH not observed. $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 261.3 (μ-CO); 234.0 (C_α); 212.5 (CO); 184.5 (C_γ); 164.6 (CO_2Et); 142.7 (ipso-$Me_2C_6H_3$); 135.8, 134.4, 129.4, 129.3, 129.0 ($Me_2C_6H_3$); 134.0 (C_δ); 105.3 (C_β); 90.4, 88.3 (Cp); 60.5 (CO_2CH_2); 51.7 (NMe); 38.6 ($C_\gamma Me$); 18.9, 18.7 ($Me_2C_6H_3$); 14.7 ($CO_2CH_2CH_3$).

Synthesis of [$Fe_2\{\mu$-η^1:η^3-C_γ(R′)$C_\beta\{$N(Me)N=C_δ(R″)(R‴)$\}$-C_α=N(Me)(Xyl)$\}$(μ-CO)(CO)$(Cp)_2$][SO_3CF_3] (R′ = Me, R″ = COOEt, R‴ = H, 4b; R′ = Bu^n, R″ = COOEt, R‴ = H, 4c; R′ = Me, R″ = R‴ = Ph, 4d). Complex **2a** (104 mg, 0.175 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with $CF_3SO_3CH_3$ (0.030 mL, 0.265 mmol). The solution was stirred for 15 min and then chromatographed on an alumina column. Elution with MeOH afforded a brown band corresponding to **4b**. Yield: 101 mg, 76%. Anal. Calcd for $C_{31}H_{34}F_3Fe_2N_3O_7S$: C, 48.90; H, 4.50; N, 5.52. Found: C, 48.92; H, 4.47; N, 5.40. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1990 (vs), 1826 (s), 1707 (m); ν(C=N) 1607 (m), 1555 (w). ^1H NMR ($CDCl_3$; δ): 7.41−7.17 (m, 3 H, $Me_2C_6H_3$); 6.75 (s, 1 H, $C_\delta H$); 5.49, 4.98 (s, 10 H, Cp); 4.28 (m, CO_2CH_2); 3.84 (s, 3 H, C_γMe); 3.59 (s, 3 H, C_βNMe); 3.16 (s, 3 H, C_αNMe); 2.60, 1.88 (s, 6 H, $Me_2C_6H_3$); 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CO_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 251.8 (μ-CO); 227.1 (C_α); 210.2 (CO); 204.8(C_γ); 163.1 (CO_2Et); 141.1 (ipso-$Me_2C_6H_3$); 134.3, 133.9, 129.4, 129.2, 128.7 ($Me_2C_6H_3$); 122.0 (C_δ); 91.6, 89.1 (Cp); 91.1 (C_β); 60.6 (CO_2CH_2); 49.6 ($C_\alpha NMe$); 39.3 ($C_\beta NMe$); 38.1 ($C_\gamma Me$); 18.0 ($Me_2C_6H_3$); 14.2 ($CO_2CH_2CH_3$).

Compounds **4c**,**d** were prepared by the same procedure described for **4b**, by reacting $CF_3SO_3CH_3$ with **2d** and **3a**, respectively. Crystals of **4c** suitable for X-ray analysis were obtained by crystallization at −20 °C from a CH_2Cl_2 solution layered with diethyl ether.

4c: yield 85%; brown. Anal. Calcd for $C_{34}H_{40}F_3Fe_2N_3O_7S$: C, 50.83; H, 5.02; N, 5.23. Found: C, 50.79; H, 4.92; N, 5.28. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1990 (vs), 1825 (s), 1709 (m); ν(C=N) 1610 (w), 1556 (w). ^1H NMR ($CDCl_3$; δ): 7.33−7.11 (m, 3 H, $Me_2C_6H_3$); 6.65 (s, 1 H, $C_\delta H$); 5.38, 4.94 (s, 10 H, Cp); 4.22 (m, 2 H, CO_2CH_2); 4.00, 3.60 (m, 2 H, $C_\gamma CH_2$); 3.54 (s, 3 H, $C_\beta NMe$); 3.16 (s, 3 H, $C_\alpha NMe$); 2.42, 1.82 (s, 6 H, $Me_2C_6H_3$); 2.11, 2.00 (m, 2 H, $C_\gamma CH_2CH_2$); 1.67 (m, 2 H, $C_\gamma CH_2CH_2CH_2$); 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, $CO_2CH_2CH_3$); 1.07 (m, 3 H, $C_\gamma CH_2CH_2CH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 251.7 (μ-CO); 227.2 (C_α); 212.4 (C_γ); 210.4 (CO); 163.3 (CO_2Et); 140.7 (ipso-$Me_2C_6H_3$); 133.9, 129.4, 129.1, 128.7 ($Me_2C_6H_3$); 121.4 (C_δ); 91.4 (C_β); 91.0, 89.5 (Cp); 60.5 (CO_2CH_2); 50.3 ($C_\alpha NMe$); 49.6 ($C_\gamma CH_2$); 41.0 ($C_\beta NMe$); 37.1 ($C_\gamma CH_2CH_2$); 23.7 ($C_\gamma CH_2CH_2CH_2$); 18.0, 17.7 ($Me_2C_6H_3$); 14.3, 14.1 ($CH_2CH_2CH_2CH_3$ and $CO_2CH_2CH_3$).

4d: yield 89%; brown. Anal. Calcd for $C_{40}H_{38}F_3Fe_2N_3O_5S$: C, 57.09; H, 4.55; N, 4.99. Found: C, 57.13; H, 4.55; N, 5.06. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1992 (vs), 1825 (s); ν(C=N) 1606 (w). ^1H NMR ($CDCl_3$; δ): 7.60−7.15 (m, 13 H, $Me_2C_6H_3$ and Ph); 5.44, 4.88 (s, 10 H, Cp); 3.87 (s, 3 H, $C_\gamma Me$); 3.58 (s, 3 H, $C_\beta NMe$); 2.98 (s, 3 H, $C_\alpha NMe$); 2.20, 1.98 (s, 6 H, $Me_2C_6H_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 254.6 (μ-CO); 230.5 (C_α); 211.8 (CO); 198.0 (C_γ); 161.5 (C_δ); 141.8 (ipso-$Me_2C_6H_3$); 138.6−128.0 (Ph and $Me_2C_6H_3$); 100.2 (C_β); 91.4, 88.4 (Cp); 52.0, 46.2 (NMe); 39.7 ($C_\gamma Me$); 18.6, 17.9 ($Me_2C_6H_3$).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(Me)C_\beta\{N(Me)N{=}C_\delta(R'')(R''')\}\text{-}C_\alpha(H)N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R'' = H, R''' = CO_2Et, 5a; R'' = R''' = Ph, 5b). Complex **4b** (100 mg, 0.131 mmol), in THF solution, was treated with $NaBH_4$ (25 mg, 0.658 mmol), stirred for 30 min, and then filtered on alumina. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, gave an orange band corresponding to **5a**. Yield: 64 mg, 80%. Anal. Calcd for $C_{30}H_{35}Fe_2N_3O_4$: C, 58.75; H, 5.75; N, 6.85. Found: C, 58.77; H, 5.82; N, 6.83. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1926 (vs), 1755 (s); ν(C_δN) 1606 (w) cm^{-1}. ^1H NMR ($CDCl_3$; δ): 7.28−7.08 (m, 3 H, $Me_2C_6H_3$); 6.62 (s, 1 H, $C_\delta H$); 5.05, 4.87 (s, 10 H, Cp); 4.49 (q, $^3J_{HH}$ = 7.14 Hz, 2 H, CO_2CH_2); 3.78 (s, 3 H, $C_\gamma Me$); 3.37 (s, 3 H, NNMe); 2.87 (s, 3 H, $C_\alpha NMe$); 2.67, 2.19 (s, 6 H, $Me_2C_6H_3$); 1.54 (t, $^3J_{HH}$ = 7.14 Hz, 3 H, $CO_2CH_2CH_3$); 1.23 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 277.1 (μ-CO); 217.7 (CO); 180.8 (C_γ); 165.5 (CO_2Et); 147.6 (ipso-$Me_2C_6H_3$); 136.4, 136.1, 128.4, 128.3, 126.5 ($Me_2C_6H_3$); 115.8 (C_δ); 99.4 (C_β); 97.9 (C_α); 87.2, 83.8 (Cp); 60.0 (CO_2CH_2); 40.9 (NNMe); 38.9 ($C_\gamma Me$); 34.2 ($C_\alpha NMe$); 19.0, 18.5 ($Me_2C_6H_3$); 14.4 ($CO_2CH_2CH_3$).

Compound **5b** was prepared by the same procedure described for **5a**, by reacting **4d** with $NaBH_4$. **5b**: yield 80%; brown. Anal. Calcd for $C_{39}H_{39}Fe_2N_3O_2$: C, 67.55; H, 5.67; N, 6.06. Found: C, 67.58; H, 5.65; N, 6.02. IR (CH_2Cl_2; cm^{-1}): ν(CO) 1922 (vs), 1745 (s); ν(C_δN) 1604 (w). ^1H NMR ($CDCl_3$; δ): 7.83−6.88 (m, 13 H, Ph and $Me_2C_6H_3$); 4.79, 4.66 (s, 10 H, Cp); 3.98 (s, 3 H, $C_\gamma Me$); 2.96 (s, 3 H, NNMe); 2.87 (s, 3 H, $C_\alpha NMe$); 2.72, 1.89 (s, 6 H, $Me_2C_6H_3$); 1.26 (s, 1 H, $C_\alpha H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 278.0 (μ-CO); 217.2 (CO); 179.1 (C_γ); 147.0 (ipso-$Me_2C_6H_3$); 141.2−126.1 (Ph, $Me_2C_6H_3$ and C_δ); 98.6 (C_β); 97.4 (C_α); 86.8, 82.7 (Cp); 38.3 ($C_\gamma Me$); 38.2 (NNMe); 34.9 ($C_\alpha NMe$); 18.8, 18.2 ($Me_2C_6H_3$).

Table 3. Crystal Data and Experimental Details for 2a and 4c[CF_3SO_3]·CH_2Cl_2

	2a	**4c**[CF_3SO_3]·CH_2Cl_2
formula	$C_{29}H_{31}Fe_2N_3O_4$	$C_{35}H_{42}Cl_2F_3Fe_2N_3O_7S$
fw	597.27	888.38
T, K	100(2)	293(2)
λ, Å	0.710 73	0.710 73
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.0593(18)	11.814(2)
b, Å	11.785(2)	12.577(3)
c, Å	12.541(3)	15.404(3)
α, deg	96.29(3)	107.03(3)
β, deg	95.75(3)	98.26(3)
γ, deg	96.76(3)	110.62(3)
cell vol, Å^3	1312.9(5)	1968.8(7)
Z	2	2
D_c, g cm^{-3}	1.511	1.499
μ, mm^{-1}	1.146	0.989
F(000)	620	916
cryst size, mm	0.25 × 0.21 × 0.14	0.26 × 0.22 × 0.16
θ limits, deg	1.64−28.70	1.44−27.10
no. of rflns collected	15 791	21 139
no. of indep rflns	6761 (R_{int} = 0.0626)	8694 (R_{int} = 0.0370)
no. of data/restraints/ params	6761/0/348	8694/190/478
goodness on fit on F^2	1.065	1.042
R1 ($I > 2\sigma(I)$)	0.0421	0.0607
wR2 (all data)	0.1075	0.1901
largest diff peak/hole, e Å^{-3}	0.562/−0.972	1.276/−1.016

X-ray Crystallography. Crystal data and collection details for **2a** and **4c**[CF_3SO_3]·CH_2Cl_2 are reported in Table 3. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz−polarization and absorption effects (empirical absorption correction SADABS).[25] Structures were solved by direct methods and refined by full-matrix least squares on the basis of all data using F^2.[26] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. One Cp ligand, the ethyl group bound to O(2), and the CH_2Cl_2 molecule in **4c**[CF_3SO_3]·CH_2Cl_2 are disordered. Disordered atomic positions were split and refined isotropically using similar distances and similar U restraints and one occupancy parameter per disordered group.

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Supporting Information Available: CIF files giving crystallographic data for compounds **2a** and **4c**[CF_3SO_3]·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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