

Deprotonation of μ -Vinyliminium Ligands in Diiron Complexes: A Route for the Synthesis of Mono- and Polynuclear Species Containing Novel Multidentate Ligands

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The C_{β} –H hydrogen in the diiron vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}_\gamma(\text{R}')\text{=C}_\beta\text{HC}_\alpha\text{=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$ (R = Me, **1**; R = Bz, **2** (Bz = CH_2Ph); R = Xyl, **3** (Xyl = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$)) is easily removed by sodium hydride; different products are consequently formed, depending on the nature of the substituents R and R'. Thus, deprotonation of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(R')=CHC=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$ (R = Me, R' = COOMe, **1a**; R = Me, R' = Me, **1b**; R = Bz, R' = COOMe, **2a**) yields the tetranuclear complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^2\text{-C(R')-CCN(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}_2]$ (R = Me, R' = COOMe, **4a**; R = Me, R' = Me, **4b**; R = Bz, R' = COOMe, **4c**). Conversely, treatment with NaH of the vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(R')=CHC=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$ (R = Me, R' = SiMe₃, **1d**; R = Me, R' = Tol, **1e**; R = Bz, R' = SiMe₃, **2b**; R = Bz, R' = Tol, **2c** (Tol = 4- MeC_6H_4); R = Xyl, R' = SiMe₃, **3a**; R = Xyl, R' = Tol, **3b**; R = Xyl, R' = Ph, **3c**) leads to the selective formation of the corresponding μ -aminocarbyne alkynyl complexes $[\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}\{\mu\text{-CO(CO)(C}\equiv\text{CR')-(Cp)}_2\}]$ (R = Me, R' = SiMe₃, **5a**; R = Me, R' = Tol, **5b**; R = Bz, R' = SiMe₃, **5c**; R = Bz, R' = Tol, **5d**; R = Xyl, R' = SiMe₃, **5e**; R = Xyl, R' = Tol, **5f**; R = Xyl, R' = Ph, **5g**). Compounds **5c,d** react with methyl iodide to give the vinyliminium cations $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(R')=C(Me)C=N(Me)(Bz)}\}\{\mu\text{-CO(CO)(Cp)}_2\}^+]$ (R' = SiMe₃, **6a**; R' = Tol, **6b**). Finally, the reactions of $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(R')=CHC=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$ (R = Me, R' = Buⁿ, **1c**; R = Xyl, R' = Me, **3d**; R = Xyl, R' = COOMe, **3e**; R = Xyl, R' = CMe₂OH, **3f**) with NaH afford the 1-metalla-2-aminocyclopenta-1,3-dien-5-one species $[\text{Fe(Cp)(CO)}\{\text{CN(Me)(R)CHC(R')C(O)}\}]$ (R = Me, R' = Buⁿ, **7a**; R = Xyl, R' = Me, **7b**; R = Xyl, R' = COOMe, **7c**; R = Xyl, R' = CMe₂OH, **7d**). The molecular structures of **4a**·CH₂Cl₂, **4b**, **5e**, and **7b** have been determined by X-ray diffraction studies.

Introduction

Insertions of alkynes into the metal–carbon bond of bridging alkylidene¹ and alkylidyne² dinuclear complexes provide a synthetic pathway to the C–C bond formation in dinuclear transition-metal complexes. The alkyne (R'CCR'') insertion reaction, extended to the diiron μ -aminocarbynes $[\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}\{\mu\text{-CO(CO)(NCMe)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$ (R = Me, CH₂Ph (Bz), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (Xyl)), provided access to the novel bridging

vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(R')=C(R'')C=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$ (R = Me (**1**), Bz (**2**), Xyl (**3**)).³ Since the reactivity of vinyliminium ligands has been largely unexplored,⁴ we have started to investigate the reactions of **1–3** with nucleophiles. In particular, we have found that NaBH₄ adds H[–] at the μ -vinyliminium ligand to form neutral derivatives, whose nature depends on the steric hindrance of the iminium nitrogen substituents.⁵ Indeed, the sterically demanding Xyl group inhibits hydride attack at the iminium carbon and directs the addition to the C_{β} position, affording the bis-alkylidene complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^2\text{-C(R')CH}_2\text{CN(Me)(Xyl)}\}\{\mu\text{-CO(CO)(Cp)}_2\}]$. In contrast, with the less hindered Me or CH₂Ph substituent,

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Scheme 1

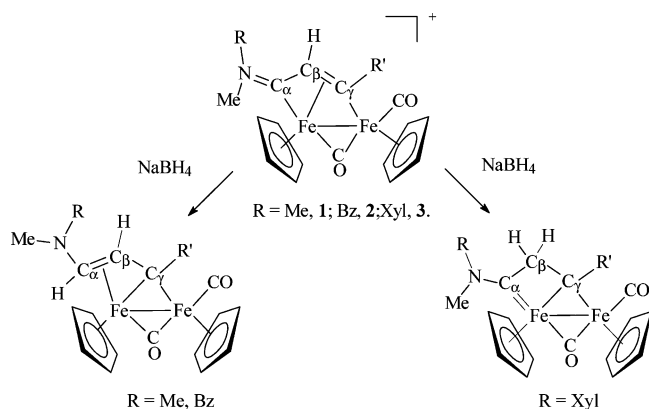


Chart 1. Vinyliminium Complexes Investigated in This Paper

	R	R'
1a	Me	COOMe
1b	Me	Me
1c	Me	Bu ^a
1d	Me	SiMe ₃
1e	Me	Tol
2a	Bz	COOMe
2b	Bz	SiMe ₃
2c	Bz	Tol
3a	Xyl	SiMe ₃
3b	Xyl	Tol
3c	Xyl	Ph
3d	Xyl	Me
3e	Xyl	COOMe
3f	Xyl	C(Me) ₂ OH

the reaction with NaBH₄ occurs selectively at the iminium carbon, yielding the vinylalkylidene complexes [Fe₂{μ-η¹:η³-C(R')=CHC(H)N(Me)₂}(μ-CO)(CO)(Cp)₂]-[SO₃CF₃] (Scheme 1).

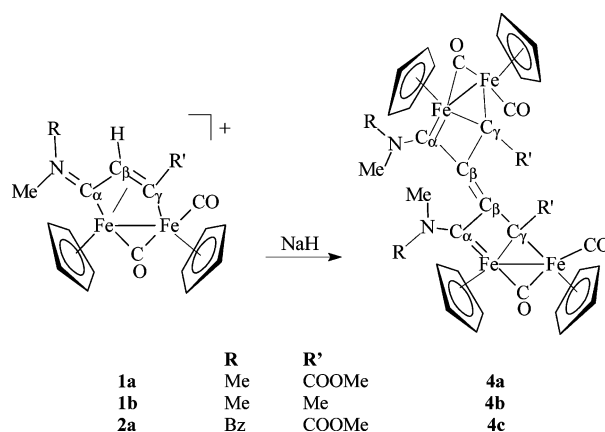
In addition to nucleophilic additions, the reactivity of the bridging vinyliminium ligand in 1–3 could be further extended by the removal of the C_β–H proton. This possibility is suggested by the deprotonation of the vinyliminium ligand, described for the mononuclear complex [Ru(Cp){C(=NET₂)CH=CPh₂}(CO)(PPR₃)] [BF₄], to form the aminoallenyl derivative [Ru(Cp){C(=NET₂)=C=CPh₂}(CO)(PPR₃)].^{4a} Moreover, the Fe–C_α interaction in the μ-vinyliminium species 1–3 displays some Fischer-type aminocarbene character,³ and adjacent C–H hydrogens, in Fischer carbenes, are known to be acidic.⁶

These considerations led us to determine to what extent C_β–H is susceptible to deprotonation, with the aim of exploring the opportunities that this would eventually offer. Here, we present the results of these investigations, which have been performed on a variety of vinyliminium complexes (Chart 1), to elucidate possible steric and electronic effects due to the nature of the substituents R and R'.

Results

Synthesis of Tetrairon Complexes. Compounds [Fe₂{μ-η¹:η³-C(R')=CHC(H)N(Me)(R)}(μ-CO)(CO)(Cp)₂]-

Scheme 2



[SO₃CF₃] (R = Me, R' = COOMe, 1a; R = R' = Me, 1b; R = Bz, R' = COOMe, 2a) react with NaH in THF solution, affording the novel tetrairon complexes [Fe₂{μ-η¹:η²-C(R')CCN(Me)(R)}(μ-CO)(CO)(Cp)₂]₂ (R = Me, R' = COOMe, 4a; R = R' = Me, 4b; R = Bz, R' = COOMe, 4c) (Scheme 2).

Compounds 4a–c have been obtained in 60–70% yield, after purification by column chromatography on alumina, and characterized by IR and NMR spectra and ESI-MS analyses.

The structures of 4a,b have been determined by X-ray diffraction: the ORTEP molecular diagrams are shown in Figures 1 and 2, whereas relevant bond lengths and angles are reported in Tables 1 and 2, respectively. Molecules 4a,b each have two [Fe₂{μ-C(R')CCN(Me)₂}(μ-CO)(CO)(Cp)₂] (R' = CO₂Me, 4a; R' = Me, 4b) moieties, with the Fe(1)–Fe(2) and Fe(3)–Fe(4) axes nearly orthogonal (Fe(1)–Fe(2)–Fe(3)–Fe(4) dihedral angles –89.18(2) and –84.07(4)°, respectively). Each

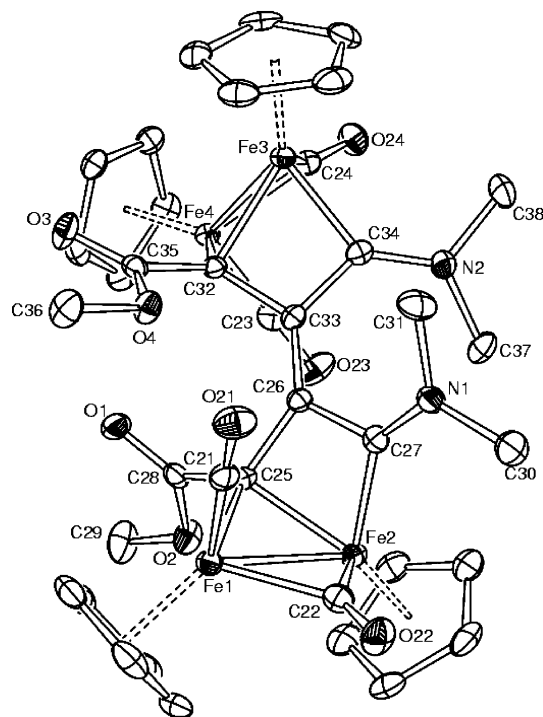


Figure 1. ORTEP drawing of [Fe₂{μ-C(COOMe)CCN(Me)₂}(μ-CO)(CO)(Cp)₂]₂ (4a). All H atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

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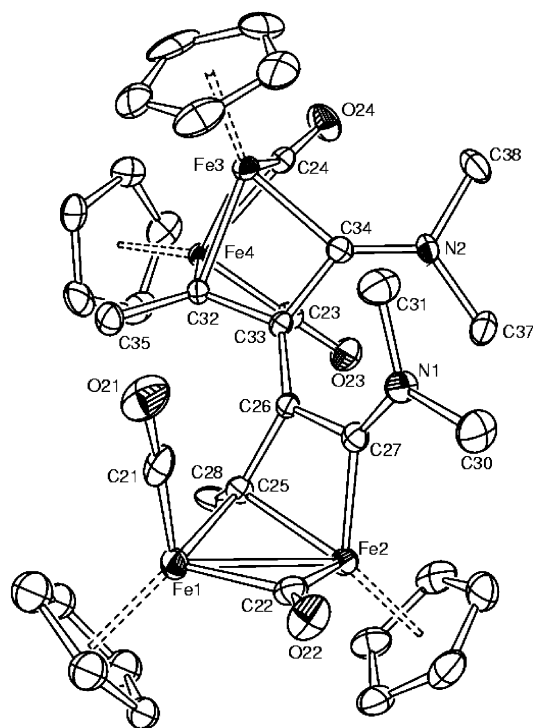


Figure 2. ORTEP drawing of $[\text{Fe}_2\{\mu\text{-C}(\text{Me})\text{CCN}(\text{Me})_2\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]_2$ (**4b**). All H atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level. Only the main image of the disordered Cp ligand bonded to Fe(1) is reported.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4a

Fe(1)–Fe(2)	2.5251(8)	Fe(3)–Fe(4)	2.5299(9)
Fe(1)–C(21)	1.753(4)	Fe(4)–C(23)	1.746(4)
Fe(1)–C(22)	1.976(4)	Fe(4)–C(24)	1.975(4)
Fe(2)–C(22)	1.846(4)	Fe(3)–C(24)	1.859(4)
Fe(1)–C(25)	2.014(3)	Fe(4)–C(32)	1.990(3)
Fe(2)–C(25)	2.031(3)	Fe(3)–C(32)	1.999(3)
Fe(2)–C(26)	2.477(3)	Fe(3)–C(33)	2.506(3)
Fe(2)–C(27)	1.901(4)	Fe(3)–C(34)	1.889(3)
C(21)–O(21)	1.150(5)	C(23)–O(23)	1.155(5)
C(22)–O(22)	1.191(5)	C(24)–O(24)	1.184(4)
C(25)–C(26)	1.471(5)	C(32)–C(33)	1.493(5)
C(26)–C(27)	1.446(5)	C(33)–C(34)	1.448(5)
N(1)–C(27)	1.305(5)	N(2)–C(34)	1.325(5)
N(1)–C(30)	1.460(5)	N(2)–C(37)	1.454(5)
N(1)–C(31)	1.477(5)	N(2)–C(38)	1.467(5)
C(25)–C(28)	1.497(5)	C(32)–C(35)	1.499(5)
C(28)–O(1)	1.205(4)	C(35)–O(3)	1.211(4)
C(28)–O(2)	1.351(4)	C(35)–O(4)	1.353(4)
C(29)–O(2)	1.446(4)	C(36)–O(4)	1.440(4)
C(26)–C(33)	1.408(5)	O(1)–C(35)	2.750(45)

Fe(1)–C(25)–Fe(2)	77.25(12)	Fe(4)–C(32)–Fe(3)	78.74(12)
C(25)–C(26)–C(27)	100.2(3)	C(32)–C(33)–C(34)	99.5(3)
C(26)–C(27)–Fe(2)	94.5(2)	C(33)–C(34)–Fe(3)	96.5(2)
C(26)–C(27)–N(1)	127.0(3)	C(33)–C(34)–N(2)	128.6(3)
Fe(2)–C(27)–N(1)	137.9(3)	Fe(3)–C(34)–N(2)	134.6(3)
C(25)–C(26)–C(33)	130.3(3)	C(32)–C(33)–C(26)	129.1(3)
C(27)–C(26)–C(33)	128.1(3)	C(34)–C(33)–C(26)	130.8(3)

moiety contains an $\text{Fe}_2(\mu\text{-CO})(\text{CO})(\text{Cp})_2$ core and a bridging $\mu\text{-C}(\text{R})\text{CCN}(\text{Me})_2$ ligand. The former adopts a cis arrangement of the Cp ligands as in the parent compounds **1a,b**. The bridging ligand resembles the bis-alkylidene present in $[\text{Fe}_2\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$.^{5a} The iron atoms show a nearly pure σ interaction with the bridging carbon atoms in the two moieties (Fe(1)–C(25) = 2.014(3) and 1.981(5) Å, Fe(2)–C(25) = 2.031(3) and 2.001(5) Å, Fe(4)–C(32)

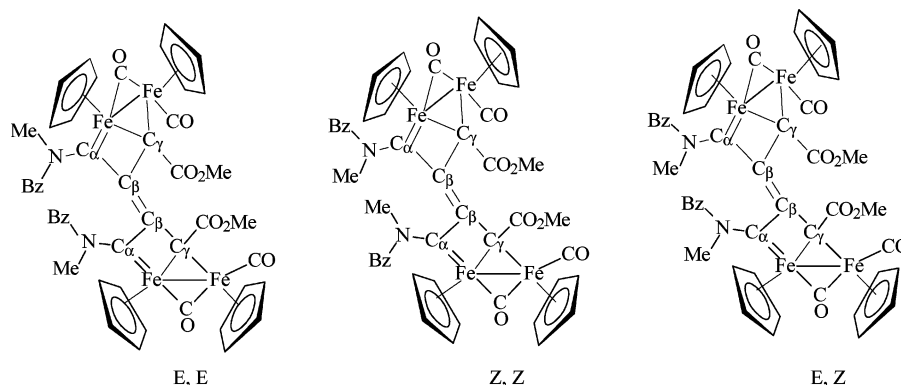
Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4b

Fe(1)–Fe(2)	2.514(7)	Fe(3)–Fe(4)	2.5132(11)
Fe(1)–C(21)	1.716(7)	Fe(4)–C(23)	1.730(6)
Fe(1)–C(22)	1.964(6)	Fe(4)–C(24)	1.982(6)
Fe(2)–C(22)	1.847(6)	Fe(3)–C(24)	1.822(6)
Fe(1)–C(25)	1.981(5)	Fe(4)–C(32)	1.989(5)
Fe(2)–C(25)	2.001(5)	Fe(3)–C(32)	2.001(5)
Fe(2)–C(26)	2.456(5)	Fe(3)–C(33)	2.454(5)
Fe(2)–C(27)	1.886(5)	Fe(3)–C(34)	1.892(5)
C(21)–O(21)	1.164(7)	C(23)–O(23)	1.150(6)
C(22)–O(22)	1.188(7)	C(24)–O(24)	1.189(7)
C(25)–C(26)	1.473(7)	C(32)–C(33)	1.467(7)
C(26)–C(27)	1.451(7)	C(33)–C(34)	1.435(7)
N(1)–C(27)	1.313(7)	N(2)–C(34)	1.313(7)
N(1)–C(30)	1.466(7)	N(2)–C(37)	1.467(7)
N(1)–C(31)	1.462(7)	N(2)–C(38)	1.457(7)
C(25)–C(28)	1.525(7)	C(32)–C(35)	1.528(7)
C(26)–C(33)	1.425(7)		

Fe(1)–C(25)–Fe(2)	78.32(19)	Fe(4)–C(32)–Fe(3)	78.08(19)
C(25)–C(26)–C(27)	101.7(4)	C(32)–C(33)–C(34)	101.8(4)
C(26)–C(27)–Fe(2)	93.9(3)	C(33)–C(34)–Fe(3)	94.0(3)
C(26)–C(27)–N(1)	127.8(5)	C(33)–C(34)–N(2)	129.2(5)
Fe(2)–C(27)–N(1)	138.2(4)	Fe(3)–C(34)–N(2)	136.6(4)
C(25)–C(26)–C(33)	125.3(5)	C(32)–C(33)–C(26)	124.1(4)
C(27)–C(26)–C(33)	131.7(5)	C(34)–C(33)–C(26)	133.1(5)

= 1.990(3) and 1.989(5) Å, Fe(3)–C(32) = 1.999(3) and 2.001(5) Å for **4a,b**, respectively), as expected for a bridging alkylidene. Conversely, the Fe(2)–C(27) (1.901(4) and 1.886(5) Å) and Fe(3)–C(34) (1.889(3) and 1.892(5) Å) interactions as well as N(1)–C(27) (1.305(5) and 1.313(7) Å) and N(2)–C(34) (1.325(5) and 1.313(7) Å) show some double-bond character, typical for a terminal aminocarbene ligand. The two $[\text{Fe}_2\{\mu\text{-C}(\text{R})\text{CCN}(\text{Me})_2\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ units in **4a,b** are joined by the C(26)–C(33) interaction (1.408(5) and 1.425(7) Å), which shows some double-bond character. The C(26) and C(33) atoms adopt an almost perfect sp^2 hybridization (sum of angles $358.6(5)$ and $359.4(5)^\circ$ for **4a** and $358.7(8)$ and $359.0(8)^\circ$ for **4b**), and the C(25)–C(26)–C(27)–C(32)–C(33)–C(34) unit is nearly planar (mean deviation from the C(25)–C(26)–C(27)–C(32)–C(33)–C(34) least-squares plane 0.1619 and 0.1878 Å, for **4a,b**, respectively). Relative to this plane, the CpFe(2) and CpFe(3) fragments lay on opposite sides, to minimize steric repulsions. The sp^2 hybridization of C(26) and C(33) in the bridging bis-alkylidene ligands generates some important differences between these ligands and that present in $[\text{Fe}_2\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$, where C_β has sp^3 hybridization. First, the Fe(2)–C(26) (2.477(3) and 2.456(5) Å) and Fe(3)–C(33) (2.506(3) and 2.454(5) Å) distances in **4a,b** are significantly shorter than the corresponding distance in $[\text{Fe}_2\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (2.589(2) Å), suggesting some interactions between the metal and C_β in the former. This fact, together with steric repulsions between the two units, can account for the lengthening of the C(26)–C(33) interaction compared to a pure double bond. Second, both C(25)–C(26) (1.471(5) and 1.473(7) Å), C(32)–C(33) (1.493(5) and 1.467(7) Å) and C(26)–C(27) (1.446(5) and 1.451(7) Å), C(33)–C(34) (1.448(5) and 1.435(7) Å) interactions are shorter than the corresponding interactions in $[\text{Fe}_2\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ (1.535(3) and 1.489(3) Å, respectively), indicating also some delocalization in the C(25)–C(26)–C(27) and C(32)–C(33)–C(34) systems and suggesting an allylidene contribution to the bonding. Finally, it is worth noting

Chart 2. Possible Isomers for the Complex 4c

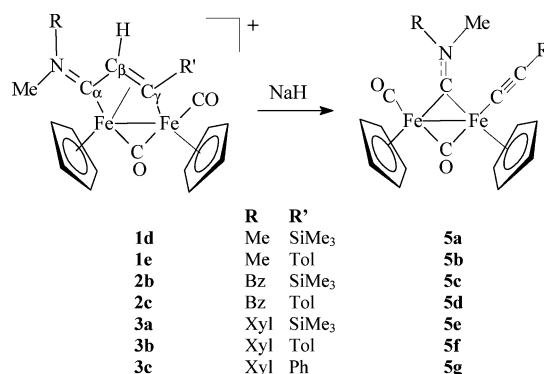


that the two moieties composing **4b** are completely identical, whereas they differ only in the orientation of the carboxylate groups in **4a**. In particular, the C(35)–O(3)–O(4)–C(36) group in **4a** is nearly coplanar with Fe(4)–C(32)–C(33) (Fe(4)–C(32)–C(35)–O(3) dihedral angle $-15.3(5)^\circ$), whereas C(28)–O(1)–O(2)–C(29) is almost orthogonal to the plane determined by Fe(1)–C(25)–C(26) (Fe(1)–C(25)–C(28)–O(1) dihedral angle $90.0(4)^\circ$). This orientation of the COOMe groups allows extra stabilization of the molecule via a weak interaction between O(1) and C(35) (O(1)⋯C(35) = 2.750(45) Å), which is significantly shorter than the sum of the van der Waals radii of carbon and oxygen (i.e. 3.15 Å).

The ^1H NMR spectrum of **4a**, recorded at 233 K, shows a unique set of resonances for the two Fe_2 frames: thus, two Cp resonances are observed (at δ 4.84 and 4.35 ppm) and one signal is found for the COOMe groups (at δ 4.00 ppm). The main feature in the ^{13}C NMR spectrum, recorded at 233 K, consists of the typical low-field resonance attributable to the aminocarbene carbons C_α (δ 247.3 ppm). At room temperature, the spectra show some broadening and a single resonance for the four Cp ligands, indicating the occurrence of an exchange process. The latter requires exchange between the aminocarbene ligand and the terminally bonded CO. Fluxionality within the $\text{Cp}_2\text{Fe}_2(\text{CO})_2$ frame is favored by the fact that both aminocarbene and CO can easily switch between bridging and terminal coordination positions. A related fluxional behavior has been observed in diiron aminocarbene complexes of the type $[\text{Fe}_2(\mu\text{-CO})_2\{\text{CH}(\text{NR}_2)\}(\text{CO})(\text{Cp})_2]$, in which exchange between terminally bonded aminocarbene and CO ligands resulted in the equivalence of the Cp ligands, on the NMR time scale.⁷ Compound **4c** behaves similarly to **4a** and shows fluxionality, whereas **4b** does not exhibit any exchange process at room temperature, suggesting that the fluxionality observed for **4a,c** is related to the presence of the COOMe groups.

The NMR spectra of **4c**, recorded at 233 K, indicate the presence of one isomer, although several isomeric forms are possible, due to the different orientations that the nonequivalent nitrogen substituents (Me and Bz) can assume, and because of the hindered rotation around the N–C(carbene) bond. The observed isomer is, presumably, the Z,Z form, in which steric repulsions between the benzyl groups are minimized (Chart 2).

Scheme 3



Synthesis and Reactivity of σ -Coordinated Acetylide Diiron Complexes. The reaction of **1d,e**, **2b,c**, and **3a–c** with NaH results in formation of the σ -alkynyl complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})(\text{C}\equiv\text{CR}')(\text{Cp})_2]$ (R = Me, R' = SiMe₃, **5a**; R = Me, R' = Tol, **5b**; R = Bz, R' = SiMe₃, **5c**; R = Bz, R' = Tol, **5d**; R = Xyl, R' = SiMe₃, **5e**; R = Xyl, R' = Tol, **5f**; R = Xyl, R' = Ph, **5g**), in about 90% yield (Scheme 3). The molecular structure of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{C}\equiv\text{CSiMe}_3)(\text{Cp})_2]$ (**5e**) has been established by X-ray diffraction analysis (Figure 3 and Table 3).

The $\text{Fe}_2(\mu\text{-CO})(\text{CO})(\text{Cp})_2$ core in **5e** shows a cis arrangement of the Cp ligands, as in the parent compound **3a**. The N(1)–C(13) interaction (1.307(7) Å) falls within the range found previously for other aminocarbene species,⁸ and it shows some significant double-bond character, also indicating the iminium nature of the bridging ligand. The Xyl group is on the side opposite to $\text{C}\equiv\text{CSiMe}_3$, to minimize steric repulsions. A comparison of Fe(1)–C(12) (2.021(6) Å) and Fe(2)–C(12) (1.843(7) Å) shows the remarkable asymmetry of $\mu\text{-CO}$, and this is due to the different electronic properties of the terminal ligands present on Fe(1) and Fe(2). In particular, $\mu\text{-CO}$ shows a longer interaction with Fe(1), which is bonded to an acidic terminal CO, whereas Fe(2) is bonded to a stronger σ -donor such as $\text{C}\equiv\text{CSiMe}_3$. The latter adopts an almost linear geometry, in agreement with the sp hybridizations of C(23) and C(24) (Fe(2)–C(23)–C(24) = $177.2(5)^\circ$ and C(23)–C(24)–Si(1) =

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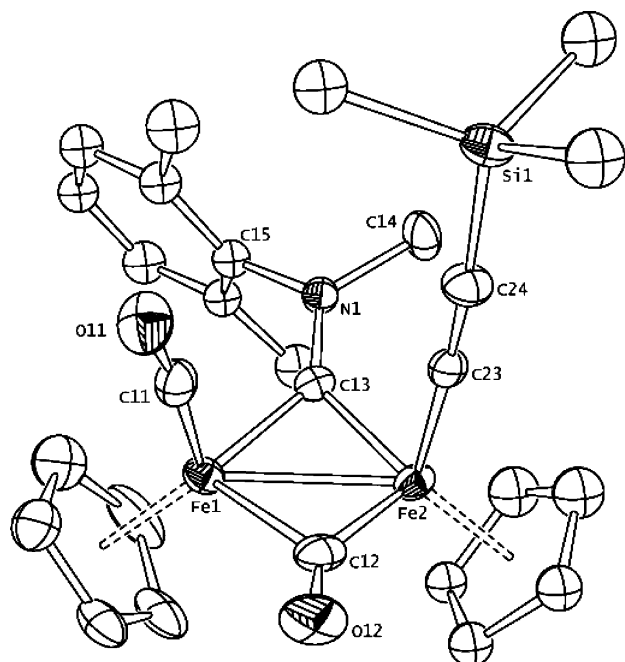


Figure 3. ORTEP drawing of the main image of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{C}\equiv\text{CSiMe}_3)(\text{Cp})_2]$ (**5e**). All H atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level. Only the main images of the disordered groups are reported.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **5e**

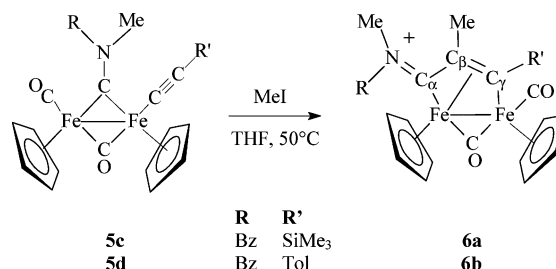
Fe(1)–Fe(2)	2.5069(13)	C(11)–O(11)	1.140(7)
Fe(1)–C(11)	1.757(6)	C(12)–O(12)	1.168(7)
Fe(1)–C(12)	2.021(6)	N(1)–C(13)	1.307(7)
Fe(2)–C(12)	1.843(7)	N(1)–C(14)	1.494(7)
Fe(1)–C(13)	1.875(5)	N(1)–C(15)	1.462(12)
Fe(2)–C(13)	1.824(5)	C(23)–C(24)	1.240(7)
Fe(2)–C(23)	1.889(5)	C(24)–Si(1)	1.806(6)
Fe(1)–C(13)–Fe(2)	85.3(2)	C(13)–N(1)–C(14)	122.6(5)
Fe(2)–C(23)–C(24)	177.2(5)	C(13)–N(1)–C(15)	121.8(8)
C(23)–C(24)–Si(1)	173.7(5)	C(14)–N(1)–C(15)	115.1(8)

173.7(5)°). The Fe(2)–C(23) distance (1.889(5) Å) reveals some π interaction between the metal and the acetylide, and this causes a slight lengthening of the C(23)–C(24) bond (1.240(7) Å) compared to a pure C≡C triple bond (e.g. 1.18 Å in HC≡CH).⁹

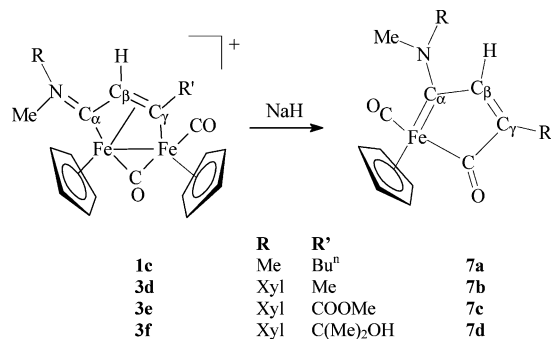
Compounds **5c–g** exist in solution as mixtures of two isomers, as usually found in complexes of the type $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})(\text{L})(\text{Cp})_2]$ (L = C(O)R, CH₂CN, CN, Cl; R = Xyl, Bz).⁸ These isomers are due to the different orientations that the nonequivalent nitrogen substituents (Me and CH₂Ph, or Me and Xyl) can assume with respect to the μ -CN interaction, which exhibits partial double-bond character. A characteristic downfield ¹³C NMR resonance accounts for the presence of the aminocarbene carbon (e.g. at δ 330.5 ppm for **5a**).

Finally, attempts to transform the σ -alkynyl species **5a–g** into the parent vinyliminium compounds **1–3**, or into new vinylidene ligands ($\text{Fe}_2\{\text{C}=\text{CH}(\text{R}')\}$), by treatment with HSO₃CF₃ failed, resulting in extensive decomposition. Conversely, the reaction of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Bz})\}(\mu\text{-CO})(\text{CO})(\text{C}\equiv\text{CR}')(\text{Cp})_2]$ (R' = SiMe₃, **5c**; R' = Tol, **5d**) with an excess of methyl iodide in refluxing

Scheme 4



Scheme 5



THF, followed by exchange of I[−] with SO₃CF₃[−], yielded the vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}(\text{R}')=\text{C}(\text{Me})\text{C}=\text{N}(\text{Me})(\text{Bz})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (R' = SiMe₃, **6a**; R' = Tol, **6b**) (Scheme 4).

Complex **6a** has been previously obtained by insertion of MeC≡CSiMe₃ into the Fe–aminocarbene bond of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Bz})\}(\mu\text{-CO})(\text{NCMe})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$.^{5b} The spectroscopic properties of **6b** are those expected for a bridging vinyliminium diiron complex.³

Synthesis of 1-Metalla-2-aminocyclopenta-1,3-dien-5-one Complexes. The vinyliminium complexes **1c** and **3d–f** react with NaH to give the corresponding 1-metalla-2-aminocyclopenta-1,3-dien-5-one complexes **7a–d**, in about 70–80% yield (Scheme 5).

Complexes **7a–d** have been purified by chromatography and fully characterized by spectroscopy and elemental analysis. Moreover, the X-ray structure of $[\text{Fe}(\text{Cp})(\text{CO})\{\text{CN}(\text{Me})(\text{Xyl})\text{CHC}(\text{Me})\text{C}(\text{O})\}]$ (**7b**) has been determined: the ORTEP molecular diagram is shown in Figure 4, and relevant bond lengths and angles are reported in Table 4. The five atoms constituting the 1-metalla-2-aminocyclopenta-1,3-dien-5-one ring are essentially coplanar (mean deviation from the Fe(1)–C(7)–C(8)–C(9)–C(10) least-squares plane 0.0116 Å). The Fe(1)–C(7) (1.940(3) Å) and Fe(1)–C(10) (1.910(3) Å) interactions are typical for a metal–acyl and a metal–aminocarbene; the latter shows a strong π back-bonding, whereas the former is mainly a σ interaction. Accordingly, the C(7)–O(2) interaction (1.216(3) Å) is an almost pure double bond, and also the aminocarbene C(10)–N(1) interaction (1.328(3) Å) shows a partial double-bond character. The C–C interactions present an alternating behavior; thus, C(8)–C(9) (1.332(4) Å) is an almost pure double bond, whereas C(7)–C(8) (1.508(4) Å) and C(9)–C(10) (1.467(4) Å) are essentially single bonds.

In the ¹³C NMR spectra of **7a–d**, typical low-field resonances have been found for the acyl carbon (e.g. at δ 270.7 ppm for **7b**) and for the aminocarbene carbon

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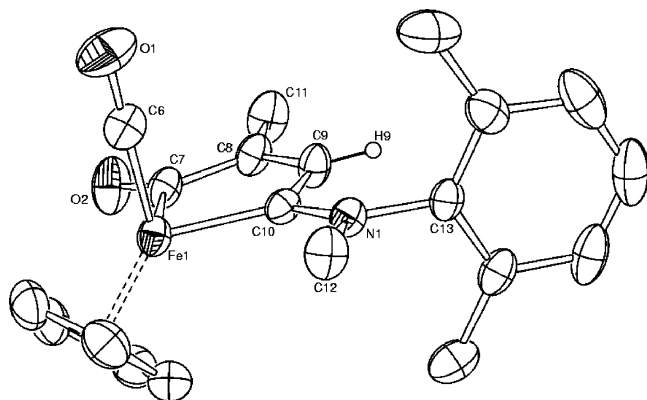
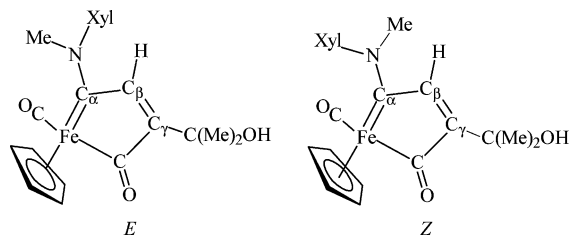


Figure 4. ORTEP drawing of $[\text{Fe}(\text{Cp})(\text{CO})\{\text{CN}(\text{Me})(\text{Xyl})\text{CHC}(\text{Me})\text{C}(\text{O})\}]$ (**7b**). All H atoms, except H(9), have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **7b**

Fe(1)–C(6)	1.727(3)	C(9)–C(10)	1.467(4)
Fe(1)–C(7)	1.940(3)	C(7)–O(2)	1.216(3)
Fe(1)–C(10)	1.910(3)	C(8)–C(11)	1.501(4)
C(6)–O(1)	1.138(4)	C(10)–N(1)	1.328(3)
C(7)–C(8)	1.508(4)	N(1)–C(12)	1.471(3)
C(8)–C(9)	1.332(4)	N(1)–C(13)	1.441(3)
C(10)–Fe(1)–C(7)	82.92(12)	C(8)–C(9)–C(10)	115.0(3)
Fe(1)–C(7)–C(8)	113.4(2)	C(9)–C(10)–Fe(1)	115.27(19)
C(7)–C(8)–C(9)	113.3(3)		

Chart 3. *E/Z* Isomers for Complex **7d**

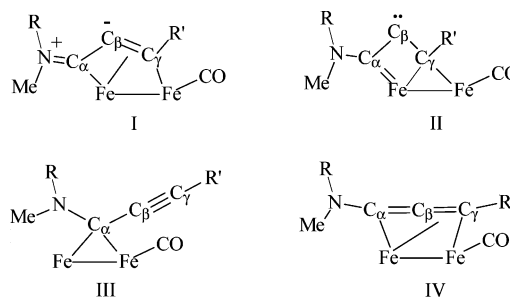


C_α (e.g. at 266.2 ppm for **7b**). NOE investigations have outlined that the nitrogen substituents of both **7b** and **7c** adopt in solution the *E* arrangement, in agreement with what is observed in the solid state. Conversely, complex **7d** exists in solution as mixture of two isomeric forms, which have been identified as *E* and *Z*, with a prevalence of the former (Chart 3).

Examples of 1-metallacyclopent-3-ene-2,5-dione¹⁰ and 1-metallacyclopent-3-en-2-one complexes¹¹ have been reported in the literature. Interestingly, complex **7b** represents, to our knowledge, the first 1-metallacyclopent-1,3-dien-5-one ring structurally characterized.

The formation of **7a–d** is the result of an intramolecular rearrangement, which requires coupling of the vinyliminium with a CO ligand and fragmentation of the diiron assembly. It should be remarked that the diiron frame $\text{Fe}_2\text{Cp}_2(\mu\text{-CO})$ is usually very robust and is unaffected even by strong rearrangements, occurring

Chart 4



on the coordinated ligands. Fragmentation has been observed only in a few cases, which include the reaction of $[\text{M}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ ($\text{M} = \text{Fe}, \text{Ru}$) with KH and acetonitrile, to form a metallapyrrole ring,¹² and acetylide addition at coordinated nitrile in $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})(\text{p-NCC}_6\text{H}_4\text{R}')(\text{Cp})_2]^+$, yielding a five-membered metallacycle (1-metalla-2-amino-3-aza-5-alkylidenecyclopenta-1,3-diene).¹³

Discussion

Reactions of the vinyliminium complexes with NaH selectively form three different types of products, resulting from dimerization of the dinuclear compounds (**4a–c**), fragmentation (**7a–d**), or alkyne deinsertion (**5a–g**). Since $\text{C}_\beta\text{–H}$ proton abstraction is presumably the initial step in all of these reactions, the different outcomes could be related to the nature of the deprotonated intermediates (Chart 4). The simple proton abstraction would leave a zwitterionic intermediate (Chart 4, I), bearing a negative charge on the C_β and a positive charge placed on the iminium moiety. However, proton removal, generating an highly unsaturated organic fragment, can be accompanied by changes in the coordination mode: the bridging ligand might assume a bis-alkylidene coordination mode (II), in which the C_β , no longer coordinated to the metals, displays a “carbene character”. Other rearrangements are also possible, leading to a bridging alkynylaminocarbene (III),¹⁴ or a coordinated allene-1,3-diyne (IV).¹⁵

The formation of the tetranuclear complexes **4a–c** (Scheme 2) is well explained by the dimerization of type II intermediates (Chart 4). Similar dimerizations have been reported for the deprotonated forms of some alkoxy- and aminocarbene complexes, which undergo oxidative coupling to give bridging bis-carbene complexes in an overall sequence described as “dehydrodimerization”.¹⁶ The formation of **4a–c** is presumably related to the smallness of both R and R' substituents, which do not oppose steric hindrance to the dimerization. In agreement with this, the complexes

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$[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(R')=CHC=N(Me)(Xyl)\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2\text{-}[\text{SO}_3\text{CF}_3]$ ($\text{R}' = \text{Me}$, **3d**; $\text{R}' = \text{COOMe}$, **3e**), which differ from **1a,b** for the presence of the more hindered Xyl substituent, do not dimerize upon treatment with NaH.

The deinsertion of the acetylide unit (Scheme 5), which represents a different type of reaction path, consequent to $\text{C}_\beta\text{-H}$ proton abstraction, should be better explained by the formation of an aminoalkylidene intermediate of type III (Chart 4).

Since the vinyliminium complexes have been obtained by alkyne insertion into Fe-aminocarbyne, the sequence shown in Scheme 3 can be considered the corresponding reverse reaction, although the acetylide fragment remains σ coordinated to an Fe atom.

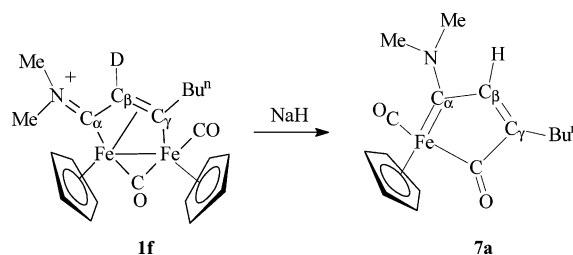
It is not obvious why deinsertion is observed for the reactions of **1d,e**, **2b,c**, and **3a-c**, rather than dimerization or fragmentation. This behavior is related to the nature of the substituent at C_γ , since the sterically demanding SiMe_3 and aryl substituents are thought to prevent the dimerization. Moreover, (trimethylsilyl)- and arylacetylides are among the most stable σ -alkynyl ligands, and this may also favor the formation of **5a-g**.

Interestingly, the deinsertion reaction affords σ -alkynyl complexes, which are not otherwise available. Attempts to generate the alkynyl complexes **5** by simple replacement of the labile nitrile ligand in $[\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{NCR}')(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ ($\text{R}' = \text{Me}$, aryl) with $\text{LiC}\equiv\text{CR}''$ have been unsuccessful. In fact, acetylides cause the deprotonation of the coordinated acetonitrile and subsequent rearrangement to cyanomethyl.¹⁷ Even when the nitriles do not contain acidic protons (e.g. NCCMe_3 , aryl nitriles) the reactions with acetylides proceed via nucleophilic addition at the nitrile ligands, instead of producing its replacement.^{13,18}

Complexes **5a-g** are interesting compounds for several reasons. They contain a σ -coordinated alkynyl ligand,¹⁹ whereas, in binuclear complexes, alkynyl ligands are more commonly found in bridging positions.²⁰ Moreover, metal-alkynyl complexes represent an area of growing interest²¹ for potential applications in nonlinear optics,²² as luminescent materials,²³ and as molecular devices.²⁴

The third type of rearrangement observed, as a consequence of the treatment with NaH, consists of the fragmentation of the dinuclear precursor with formation of the metallacyclic complexes **7a-d**. Again, steric and

Scheme 6



electronic factors related to the nature of the substituents R and R' in the parent complexes **1c** and **3d-f** seem to produce the observed fragmentation rather than dimerization or deinsertion. The process is presumably initiated by removal of the acidic $\text{C}_\beta\text{-H}$. However, since the stoichiometry of the reaction requires loss of $[\text{CpFe}]^+$ rather than H^+ , we cannot exclude the possibility that the initial step consists of one-electron reduction. To investigate this point, compounds **1c** and **3d-f** have been treated with different bases, including NEt_3 , sodium naphthalenide (NaNaph), and KOH , under conditions similar to those used in the reactions with NaH. Investigations were not conclusive, because both NaNaph and KOH reacted, leading to the formation of the corresponding metallacyclopentenone complexes **7** in lower, but still comparable, yields with respect to those obtained with NaH, whereas NEt_3 failed to produce any transformation.

Moreover, the reaction with NaH has been carried out on the C_β -deuterated vinyliminium complex $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C(Bu}^n\text{)=C(D)C=N(Me)}_2\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (**1f**). The reaction affords the metallacyclic ring **7a**, with loss of deuterium at C_β (Scheme 6).

This result is in agreement with the hypothesis that removal of the $\text{C}_\beta\text{-H}$ proton in the vinyliminium complexes **1c** is the initial step of the process; however, it is not conclusive evidence, because the $\text{C}_\beta\text{-H}$ in **7a** is expected to be acidic as well, and deuterium-hydrogen exchange could take place on the metallacycle **7**, during the workup.

Conclusions

The $\text{C}_\beta\text{-H}$ hydrogen in the vinyliminium complexes $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}_\gamma(\text{R}')\text{=C}_\beta\text{HC}_\alpha\text{=N(Me)(R)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2\text{-}[\text{SO}_3\text{CF}_3]$ (**1-3**) is efficiently removed by NaH. The resulting neutral species are not stable and rapidly evolve to give tetra-, di-, or mononuclear complexes, depending on the properties of the substituents R and R' on the ligand. The formation of tetrairon species is limited to $\text{R} = \text{Me}$, CH_2Ph and to the presence of relatively small R' groups (COOMe , Me) at C_γ . When the steric demand of R and/or R' increases, the Fe-Fe bond can be broken, resulting in mononuclear 1-metalla-2-aminocyclopenta-1,3-dien-5-one compounds. Finally, in the presence of substituents $\text{R}' = \text{SiMe}_3$, Ph, Tol, which can generate stable σ -alkynyl ligands ($\text{-C}\equiv\text{CR}'$), the reaction provides cleavage of the $\text{C}_\alpha\text{-C}_\beta$ bond, independent of the nature of R, affording diiron amino-carbyne complexes having a terminal alkynyl ligand. These reactions are very selective and do not form mixtures of products.

The results reported here, compared with previous findings on the reactions with NaBH_4 ,⁵ evidence that

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the reaction products strongly depend on the nature of the hydride reagent: NaH acts exclusively as a base, whereas the nucleophile NaBH₄ provides H[−] addition.

Moreover, these results indicate that the bridging vinyliminium ligand can generate new and reactive organic fragments, which are stabilized through coordination to the metal centers, yielding a variety of new and interesting mono- and polymetallic species. Exploitation of the acidic character of C_β–H in μ -vinyliminium ligands, for generating new C–C and C–heteroatom bonds, is currently under investigation and will be the matter of future reports.

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. ESI MS spectra were recorded on a Waters Micromass ZQ 4000 with samples dissolved in CH₃CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ¹H and ¹³C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and ¹H, ¹³C correlations measured using gs-HSQC and gs-HMBC experiments.²⁵ Unless otherwise specified, NMR spectra were recorded at 298 K; NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. NOE measurements were recorded using the DPGSE-NOE sequence.²⁶ All the reagents were commercial products (Aldrich) of the highest purity available and were used as received. [Fe₂(CO)₄(Cp)₂] was purchased from Strem and used as received. The compounds [Fe₂{ μ -CN(Me)(R)}(μ -CO)(CO)(NCMe)(Cp)₂][SO₃CF₃]^{8d} (R = Me, Xyl) and [Fe₂{ μ - η^1 : η^3 -C(R')=CHC=N(Me)(R)}(μ -CO)(CO)(Cp)₂][SO₃CF₃] (**1a,b,d,e**; **2a–c**; **3a–e**) were prepared as described in the literature.³

Synthesis of [Fe₂{ μ - η^1 : η^3 -C₇(Buⁿ)=C_βHC_α=N(Me)₂}(μ -CO)(CO)(Cp)₂][SO₃CF₃] (1c**) and [Fe₂{ μ - η^1 : η^3 -C₇(Buⁿ)=C_βDC_α=N(Me)₂}(μ -CO)(CO)(Cp)₂][SO₃CF₃] (**1f**).** HC≡CBuⁿ (0.068 mL, 0.59 mmol) was added to a solution of [Fe₂{ μ -CN(Me)₂}(μ -CO)(CO)(NCMe)(Cp)₂][SO₃CF₃] (250 mg, 0.471 mmol), in THF (20 mL). The mixture was stirred at boiling temperature for 60 min, and then the solvent was removed under reduced pressure and the residue chromatographed on an alumina column. Elution with MeOH afforded a green band, which was collected and evaporated to dryness. Crystallization from a CH₂Cl₂ solution, layered with diethyl ether, gave crystals of **1c**. Yield: 248 mg, 90%. Anal. Calcd for C₂₂H₂₆F₃Fe₂NO₅S: C, 45.15; H, 4.48; N, 2.39. Found: C, 44.99; H, 4.52; N, 2.29. IR (CH₂Cl₂): ν (CO) 1990 (vs), 1805 (s), ν (C_αN) 1682 (m) cm^{−1}. ¹H NMR (CDCl₃): δ 5.16, 4.99 (s, 10 H, Cp); 4.52 (s, 1 H, C_βH); 4.14, 3.74 (m, 2 H, C_γCH₂); 3.83, 3.25 (s, 6 H, NMe); 2.05, 1.86 (m, 2 H, C_γCH₂CH₂); 1.67 (m, 2 H, C_γCH₂CH₂CH₂); 1.10 (t, 3 H, ³J_{HH} = 7.32 Hz, C_γCH₂CH₂CH₂CH₃). ¹³C NMR (CDCl₃): δ 257.0 (μ -CO); 225.6 (C_α); 212.8 (C_γ); 209.6 (CO); 89.6, 87.3 (C_β); 54.7 (C_γCH₂); 51.3 (C_β); 50.9, 44.7 (NMe); 37.7 (C_γCH₂CH₂); 22.8 (C_γCH₂CH₂CH₂); 14.1 (C_γCH₂CH₂CH₂CH₃).

Complex [Fe₂{ μ - η^1 : η^3 -C₇(Buⁿ)=C_βDC_α=N(Me)₂}(μ -CO)(CO)(Cp)₂][SO₃CF₃] (**1f**) was synthesized by the same procedure

described for **1c**, by reacting [Fe₂{ μ -CN(Me)₂}(μ -CO)(CO)(NCMe)(Cp)₂][SO₃CF₃] with DC≡CBuⁿ. The latter was prepared treating HC≡CBuⁿ in THF solution at −40 °C, with an equimolar amount of BuⁿLi, followed by treatment with D₂O. Yield: 88%. Color: green. Anal. Calcd for C₂₂H₂₇F₃Fe₂NO₅S: C, 45.08; H, 4.64; N, 2.39. Found: C, 45.11; H, 4.61; N, 2.35. IR (CH₂Cl₂): ν (CO) 1990 (vs), 1805 (s), ν (C_αN) 1682 (m) cm^{−1}. ¹H NMR (CDCl₃): δ 5.23, 5.07 (s, 10 H, Cp); 4.18, 3.75 (m, 2 H, C_γCH₂); 3.87, 3.29 (s, 6 H, NMe); 2.05, 1.87 (m, 2 H, C_γCH₂CH₂); 1.69 (m, 2 H, C_γCH₂CH₂CH₂); 1.11 (t, 3 H, ³J_{HH} = 7.32 Hz, C_γCH₂CH₂CH₂CH₃).

Synthesis of [Fe₂{ μ - η^1 : η^3 -C₇(CMe₂OH)=C_βHC_α=N(Me)(Xyl)}(μ -CO)(CO)(Cp)₂][SO₃CF₃] (3f**).** A solution of the complex [Fe₂{ μ -CN(Me)(Xyl)}(μ -CO)(CO)(NCMe)(Cp)₂][SO₃CF₃] (210 mg, 0.331 mmol), in CH₂Cl₂, was treated with HC≡CC(Me)₂OH (0.041 mL, 0.42 mmol). The mixture was stirred at boiling temperature for 4 h and then filtered on a Celite pad. Removal of the solvent gave a residue that was washed with diethyl ether (2 × 20 mL). Crystallization from a CH₂Cl₂ solution, layered with diethyl ether, afforded brown crystals of **3f**. Yield: 191 mg, 85%. Anal. Calcd for C₂₈H₃₀F₃Fe₂NO₆S: C, 49.65; H, 4.46; N, 2.07. Found: C, 49.82; H, 4.38; N, 2.13. IR (CH₂Cl₂): ν (CO) 1998 (vs), 1806 (s), ν (C_αN) 1632 (m) cm^{−1}. ¹H NMR (CDCl₃): δ 8.07–6.73 (m, 3 H, Me₂C₆H₃); 5.44, 5.29, 5.22, 4.68 (s, 10 H, Cp); 4.95 (s, 1 H, C_βH); 4.15 (s, 3 H, NMe); 2.40, 2.20, 1.92, 1.73 (s, 6 H, Me₂C₆H₃); 1.51 (s, 6 H, CMe₂OH); *E:Z* ratio 5:1. ¹³C NMR (CDCl₃): δ 255.6 (μ -CO); 231.1 (C_α); 210.3 (CO); 209.6 (C_γ); 144.5 (ipso-Me₂C₆H₃); 139.7, 136.6, 132.9, 131.0, 129.3 (Me₂C₆H₃); 90.8, 89.5, 88.3, 87.0 (Cp); 70.0 (CMe₂OH); 48.7 (C_β); 45.8 (NMe); 32.0, 31.4 (CMe₂OH); 17.6, 17.0 (Me₂C₆H₃).

Synthesis of [Fe₂{ μ - η^1 : η^2 -C₇(R')C_βC_αN(Me)(R)}(μ -CO)(CO)(Cp)₂]₂ (R = Me, R' = COOMe, **4a; R = Me, R' = Me, **4b**; R = CH₂Ph, R' = COOMe, **4c**).** Compound **1a** (148 mg, 0.252 mmol), in THF solution (10 mL), was treated with NaH (35 mg, 1.46 mmol). The mixture was stirred for 20 min and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with a mixture of CH₂Cl₂ and THF (4:1) as eluent, afforded a dark gray band, which was collected. Crystallization at −20 °C from CH₂Cl₂ solution layered with petroleum ether (bp 40–60° C) gave crystals of **4a**. Yield: 66 mg, 60%. Anal. Calcd for C₃₈H₃₈Fe₄N₂O₈: C, 52.22; H, 4.38; N, 3.20. Found: C, 52.26; H, 4.41; N, 3.20. IR (CH₂Cl₂): ν (CO) 1939 (s), 1751 (vs), 1741 (vs), 1688 (w), 1659 (w), ν (C_αN) 1568 (w), 1541 (w) cm^{−1}. ¹H NMR (CDCl₃, 233 K): δ 4.84, 4.35 (s, 20 H, Cp); 4.00 (s, 6 H, CO₂Me); 3.32, 2.26 (s, 12 H, NMe). ¹³C NMR (CDCl₃, 233 K): δ 278.4 (μ -CO); 247.3 (C_α); 216.0 (CO); 181.8 (CO₂Me); 151.4 (C_γ); 87.4, 87.3 (Cp); 71.6 (C_β); 51.5 (CO₂Me); 47.1, 43.1 (NMe). ESI-MS (ES⁺): *m/z* 874 [M⁺, 11%], 437 [M/2⁺, 100%], 409 [M/2⁺ − CO, 68%].

Complexes **4b,c** were prepared by following the same procedure described for the synthesis of **4a**, by reacting NaH with **1b** and **2a**, respectively. Crystals of **4b** suitable for X-ray analysis were collected by a dichloromethane solution layered with *n*-pentane, at −20 °C.

4b. Yield: 70%. Color: blue-grey. Anal. Calcd for C₃₆H₃₈Fe₄N₂O₈: C, 55.01; H, 4.87; N, 3.56. Found: C, 55.07; H, 4.92; N, 3.63. IR (CH₂Cl₂): ν (CO) 1921 (s), 1740 (s-sh), 1728 (vs), ν (C_αN) 1603 (w), 1558 (wm) cm^{−1}. ¹H NMR (CDCl₃): δ 4.84, 4.48 (s, 20 H, Cp); 3.71, 3.48 (s, 12 H, NMe); 1.85 (s, 6 H, C_γMe). ¹³C NMR (CDCl₃): δ 272.0 (μ -CO); 262.4 (C_α); 221.9 (CO); 172.6 (C_γ); 86.8, 84.7 (Cp); 79.2 (C_β); 51.4, 42.8 (NMe); 13.2 (C_γMe).

4c. Yield: 68%. Color: dark gray. Anal. Calcd for C₅₀H₄₆Fe₄N₂O₈: C, 58.52; H, 4.52; N, 2.73. Found: C, 58.43; H, 4.60; N, 2.77. IR (CH₂Cl₂): ν (CO) 1939 (s), 1752 (vs), 1742 (vs), 1687 (w), 1659 (w), ν (C_αN) 1568 (w), 1537 (w) cm^{−1}. ¹H NMR (CDCl₃, 233 K): δ 7.45–6.91 (m, 10 H, Ph); 4.87, 4.40 (s, 20 H, Cp); 4.81, 4.52 (d, 4 H, ²J_{HH} = 13.7 Hz, CH₂Ph); 4.03 (s, 6 H, CO₂Me); 2.07 (s, 6 H, NMe). ¹³C NMR (CDCl₃, 233 K): δ 278.6 (μ -CO); 246.8 (C_α); 216.1 (CO); 181.7 (CO₂Me); 151.4 (C_γ);

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135.2–127.8 (Ph); 87.7, 87.3 (Cp); 70.8 (C β); 63.3 (CH $_2$ Ph); 51.4 (CO $_2$ Me); 39.8 (NMe). ESI-MS (ES $^+$): m/z 1026 [M $^+$, 7%], 513 [M/2 $^+$, 100%], 485 [M/2 $^+$ – CO, 37%].

Synthesis of [Fe $_2$ { μ -CN(Me)(R)}(μ -CO)(CO)(C $\equiv$ CSiMe $_3$)(Cp) $_2$] (R = Me, **5a; R = Bz, **5c**; R = Xyl, **5e**).** Compound **1d** (100 mg, 0.166 mmol), was dissolved in THF (15 mL) and treated with NaH (21 mg, 0.875 mmol). The mixture was stirred for 30 min, and then the solvent was removed. The residue was washed with petroleum ether (2 $\times$ 20 mL), dissolved in CH $_2$ Cl $_2$, and filtered on a Celite pad. Crystallization at –20 °C from CH $_2$ Cl $_2$ solution, layered with petroleum ether, gave brown crystals of **5a**. Yield: 70 mg, 93%. Anal. Calcd for C $_{20}$ H $_{25}$ Fe $_2$ NO $_2$ Si: C, 53.24; H, 5.58; N, 3.10. Found: C, 53.27; H, 5.50; N, 3.11. IR (CH $_2$ Cl $_2$): ν (C $\equiv$ C) 2011 (vs), ν (CO) 1972 (vs), 1794 (s), ν (μ -CN) 1534 (w) cm $^{-1}$. 1 H NMR (CDCl $_3$): δ 4.71, 4.68 (s, 10 H, Cp); 4.16, 4.02 (s, 6 H, NMe); –0.23 (s, 9 H, SiMe $_3$). 13 C NMR (CDCl $_3$): δ 330.5 (μ -C); 263.9 (μ -CO); 212.3 (CO); 133.6, 117.6 (C $\equiv$ C); 87.2, 85.7 (Cp); 52.1, 50.8 (NMe); 1.53 (SiMe $_3$).

Complexes **5c,e** were prepared by following the same procedure described for the synthesis of **5a**, by reacting NaH with **2b** and **3a**, respectively. Crystals of **5e** suitable for X-ray analysis were collected from a CH $_2$ Cl $_2$ solution layered with petroleum ether, at –20 °C.

5c. Yield: 95%. Color: ochre yellow. Anal. Calcd for C $_{26}$ H $_{29}$ Fe $_2$ NO $_2$ Si: C, 59.22; H, 5.54; N, 2.66. Found: C, 59.12; H, 5.70; N, 2.69. IR (CH $_2$ Cl $_2$): ν (C $\equiv$ C) 2011 (vs), ν (CO) 1972 (vs), 1794 (s), ν (μ -CN) 1534 (w) cm $^{-1}$. 1 H NMR (CDCl $_3$): δ 7.57–7.38 (m, 5 H, Ph); 6.19, 5.74, 5.55, 5.36 (d, 2 H, $^2J_{\text{HH}} = 15$ Hz, CH $_2$ Ph); 4.80, 4.77, 4.72, 4.65 (s, 10 H, Cp); 4.06, 3.91 (s, 3 H, NMe); –0.14, –0.17 (s, 9 H, SiMe $_3$); isomer ratio 3:2. 13 C NMR (CDCl $_3$): δ 333.6 (μ -C); 263.6, 263.2 (μ -CO); 212.4, 212.2 (CO); 136.2–126.9 (Ph and C $\equiv$ C); 118.0, 117.5 (C $\equiv$ C); 87.6, 87.4, 86.0, 85.9 (Cp); 69.8, 69.0 (CH $_2$ Ph); 49.6, 48.1 (NMe); 1.64, 1.60 (SiMe $_3$).

5e. Yield: 90%. Color: ochre yellow. Anal. Calcd for C $_{27}$ H $_{31}$ Fe $_2$ NO $_2$ Si: C, 59.91; H, 5.77; N, 2.59. Found: C, 59.94; H, 5.77; N, 2.50. IR (CH $_2$ Cl $_2$): ν (C $\equiv$ C) 2012 (vs), ν (CO) 1973 (vs), 1792 (s), ν (μ -CN) 1506 (w) cm $^{-1}$. 1 H NMR (CDCl $_3$): δ 7.34–7.16 (m, 3 H, Me $_2$ C $_6$ H $_3$); 4.81, 4.29 (s, 10 H, Cp); 4.43 (s, 3 H, NMe); 2.67, 2.26 (s, 6 H, Me $_2$ C $_6$ H $_3$); –0.17 (s, 9 H, SiMe $_3$). 13 C NMR (CDCl $_3$): δ 337.2 (μ -C); 263.6 (μ -CO); 212.8 (CO); 148.4 (ipso-Me $_2$ C $_6$ H $_3$); 134.3, 133.2, 129.9, 128.1, 128.0 (Me $_2$ C $_6$ H $_3$); 131.0, 118.3 (C $\equiv$ C); 87.6, 85.7 (Cp); 51.5 (NMe); 18.5, 17.9 (Me $_2$ C $_6$ H $_3$); 1.5 (SiMe $_3$).

Synthesis of [Fe $_2$ { μ -CN(Me)(R)}(μ -CO)(CO)(C $\equiv$ CR')-(Cp) $_2$] (R = Me, R' = Tol, **5b; R = Bz, R' = Tol, **5d**; R = Xyl, R' = Tol, **5f**; R = Xyl, R' = Ph, **5g**).** A solution of **1e** (145 mg, 0.234 mmol) in THF (15 mL) was treated with NaH (27 mg, 1.17 mmol), and the mixture was stirred for 30 min. Then, the solvent was removed, the residue dissolved in a 1:1 mixture of toluene and diethyl ether, and this solution filtered on a Celite pad. Solvent removal afforded a brown powder of **5b**. Yield: 100 mg, 91%. Anal. Calcd for C $_{24}$ H $_{23}$ Fe $_2$ NO $_2$: C, 61.44; H, 4.94; N, 2.99. Found: C, 61.47; H, 4.95; N, 3.06. IR (THF): ν (C $\equiv$ C) 2087 (s), ν (CO) 1963 (vs), 1788 (s) cm $^{-1}$. 1 H NMR (C $_6$ D $_5$ CD $_3$): δ 7.48, 7.34 (d, 4 H, $^3J_{\text{HH}} = 6.3$ Hz, C $_6$ H $_4$ Me); 4.55, 4.29 (s, 10 H, Cp); 4.07, 4.00 (s, 3 H, NMe); 2.22 (s, 3 H, C $_6$ H $_4$ Me). 13 C NMR (C $_6$ D $_5$ CD $_3$): δ 331.0 (μ -C); 261.0 (μ -CO); 213.7 (CO); 156.9 (ipso-C $_6$ H $_4$ Me); 137.9, 129.0, 126.1 (C $_6$ H $_4$ Me); 120.2, 107.8 (C $\equiv$ C); 87.9, 85.0 (Cp); 51.4, 50.0 (NMe); 21.3 (C $_6$ H $_4$ Me).

Complexes **5d,f,g** were prepared by following the same procedure described for the synthesis of **5b**, by reacting NaH with **2c** and **3b,c**, respectively.

5d. Yield: 88%. Color: ochre yellow. Anal. Calcd for C $_{30}$ H $_{27}$ Fe $_2$ NO $_2$: C, 66.09; H, 4.99; N, 2.57. Found: C, 66.01; H, 4.83; N, 2.53. IR (THF): ν (C $\equiv$ C) 2090 (s), ν (CO) 1970 (vs), 1805 (s) cm $^{-1}$. 1 H NMR (C $_6$ D $_5$ CD $_3$): δ 7.56–6.80 (m, 9 H, C $_6$ H $_4$ Me and Ph); 5.48, 5.22 (d, $^2J_{\text{HH}} = 14$ Hz, CH $_2$ Ph); 4.59, 4.55, 4.54, 4.34 (s, 10 H, Cp); 3.99, 3.98 (s, 3 H, NMe); 2.22, 2.19 (s, 3 H,

C $_6$ H $_4$ Me); isomer ratio 3:2. 13 C NMR (C $_6$ D $_5$ CD $_3$): δ 334.1, 333.7 (μ -C); 260.9, 260.6 (μ -CO); 213.7, 213.2 (CO); 157.4–124.4 (C $_6$ H $_4$ Me and Ph); 119.2, 119.1, 107.3, 106.8 (C $\equiv$ C); 87.6, 86.0, 85.8, 82.2 (Cp); 69.4, 68.8 (CH $_2$ Ph); 48.1, 47.3 (NMe); 21.1 (C $_6$ H $_4$ Me).

5f. Yield: 90%. Color: ochre yellow. Anal. Calcd for C $_{31}$ H $_{29}$ Fe $_2$ NO $_2$: C, 66.58; H, 5.23; N, 2.50. Found: C, 66.48; H, 5.21; N, 2.55. IR (CH $_2$ Cl $_2$): ν (C $\equiv$ C) 2087 (m), ν (CO) 1971 (vs), 1792 (s), ν (CN) 1505 (w) cm $^{-1}$. 1 H NMR (C $_6$ D $_5$ CD $_3$): δ 7.17–6.79 (m, 7 H, C $_6$ H $_4$ Me and Me $_2$ C $_6$ H $_3$); 4.60, 4.53, 4.32, 3.98 (s, 10 H, Cp); 4.08, 4.05 (s, 3 H, NMe); 2.28, 2.12 (s, 6 H, Me $_2$ C $_6$ H $_3$); 2.22 (s, 3 H, C $_6$ H $_4$ Me); isomer ratio 7:1. 13 C NMR (C $_6$ D $_5$ CD $_3$): δ 338.5 (μ -C); 259.3 (μ -CO); 214.2 (CO); 158.1–124.0 (C $_6$ H $_4$ Me and Me $_2$ C $_6$ H $_3$); 120.1, 106.2 (C $\equiv$ C); 87.8, 86.7, 86.1, 82.2 (Cp); 51.3 (NMe); 21.2 (C $_6$ H $_4$ Me); 18.3, 17.8 (Me $_2$ C $_6$ H $_3$). ESI-MS (ES $^+$): m/z 559 [M $^+$].

5g. Yield: 87%. Color: ochre yellow. Anal. Calcd for C $_{30}$ H $_{27}$ Fe $_2$ NO $_2$: C, 66.09; H, 4.99; N, 2.57. Found: C, 66.00; H, 5.05; N, 2.56. IR (CH $_2$ Cl $_2$): ν (C $\equiv$ C) 2086 (m), ν (CO) 1971 (vs), 1792 (s), ν (CN) 1504 (w) cm $^{-1}$. 1 H NMR (C $_6$ D $_5$ CD $_3$): δ 7.57–6.72 (m, 8 H, Ph and Me $_2$ C $_6$ H $_3$); 4.56, 4.54, 4.31, 3.95 (s, 10 H, Cp); 4.07, 4.04 (s, 3 H, NMe); 2.24, 2.19 (s, 6 H, Me $_2$ C $_6$ H $_3$); isomer ratio 9:1. 13 C NMR (C $_6$ D $_5$ CD $_3$): δ 338.3 (μ -C); 260.0 (μ -CO); 214.4 (CO); 161.7–125.0 (Ph and Me $_2$ C $_6$ H $_3$); 117.8, 106.2 (C $\equiv$ C); 87.6, 85.4 (Cp); 52.1 (NMe); 18.4, 17.7 (Me $_2$ C $_6$ H $_3$).

Synthesis of [Fe $_2$ { μ - η^1 : η^3 -C $_6$ (R')=C $_6$ (Me)C $_6$ =N(Me)(Bz)}-(μ -CO)(CO)(Cp) $_2$][SO $_3$ CF $_3$] (R' = SiMe $_3$, **6a; R' = Tol, **6b**).** To a THF solution (15 mL) of **5c** (120 mg, 0.228 mmol) was added MeI (0.9 mL, 14.5 mmol), and the resulting mixture was stirred at about 50 °C for 20 min. The solution was cooled to room temperature, and then AgCF $_3$ SO $_3$ (88 mg, 0.344 mmol) was added; subsequent chromatography on alumina, using a 1:1 mixture of THF and MeCN as eluent, afforded a green band, corresponding to **6a**. Yield: 68 mg, 43%. Anal. Calcd for C $_{28}$ H $_{32}$ F $_3$ Fe $_2$ NO $_5$ Si: C, 48.64; H, 4.67; N, 2.03. Found: C, 48.55; H, 4.62; N, 2.05. IR (CH $_2$ Cl $_2$): ν (CO) 1982 (vs), 1815 (s), ν (CN) 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, $^2J_{\text{HH}} = 14$ Hz, 2 H, CH $_2$ 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, C $_6$ Me); 0.70, 0.67 (s, 9 H, SiMe $_3$); *Z:E* ratio 2:1. 13 C NMR (CDCl $_3$): δ 254.6, 253.1 (μ -CO); 222.3, 221.1 (C $_6$); 208.5 (CO); 195.2 (C $_7$); 132.4–128.9 (Ph); 89.0, 88.9, 88.4, 88.2 (Cp); 70.6 (C $_6$); 65.2, 62.3 (CH $_2$ Ph); 45.4, 43.4 (NMe); 20.6, 20.2 (C $_6$ Me); 4.1 (SiMe $_3$).

Complex **6b** was prepared by following the same procedure described for the synthesis of **6a**, by reacting **5d** with MeI and AgCF $_3$ SO $_3$.

6b. Yield: 66%. Color: ochre yellow. Anal. Calcd for C $_{32}$ H $_{30}$ F $_3$ Fe $_2$ NO $_5$ S: C, 54.18; H, 4.26; N, 1.97. Found: C, 54.22; H, 4.39; N, 1.93. IR (CH $_2$ Cl $_2$): ν (CO) 1989 (vs), 1807 (s), ν (CN) 1655 (m) cm $^{-1}$. 1 H NMR (CDCl $_3$): δ 7.56–7.11 (m, 9 H, Ph and C $_6$ H $_4$ Me); 5.74, 5.67, 5.14, 4.44 (d, 2H, $^2J_{\text{HH}} = 15$ Hz, CH $_2$ Ph); 5.26, 5.25, 4.90, 4.89 (s, 10 H, Cp); 3.75, 3.03 (s, 3 H, NMe); 2.47 (s, 3 H, C $_6$ H $_4$ Me); 1.75, 1.73 (s, 3 H, C $_6$ Me); *Z:E* ratio 3:1. 13 C NMR (CDCl $_3$): δ 258.1 (μ -CO); 226.2, 225.0 (C $_6$); 210.6, 210.0 (CO); 202.2 (C $_7$); 150.8 (ipso-C $_6$ H $_4$ Me); 136.4–125.3 (Ph and C $_6$ H $_4$ Me); 91.7, 88.0, 87.9 (Cp); 66.4, 61.5 (CH $_2$ Ph); 65.6, 65.3 (C $_6$); 45.9, 41.9 (NMe); 21.2 (C $_6$ H $_4$ Me); 18.3, 18.1 (C $_6$ Me).

Synthesis of [Fe(Cp)(CO){C $_6$ N(Me)(R)C $_6$ HC $_7$ (R)C(O)}-] (R = Me, R' = Bu n , **7a; R = Xyl, R' = Me, **7b**; R = Xyl, R' = COOMe, **7c**; R = Xyl, R' = CMe $_2$ OH, **7d**).** Complex **1c** (200 mg, 0.342 mmol), was dissolved in THF (20 mL) and treated with NaH (38 mg, 1.58 mmol). The resulting mixture was stirred for 30 min and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on alumina, using a 1:1 mixture of CH $_2$ Cl $_2$ and THF as eluent, afforded a brown band corresponding to **7a**. Yield: 73 mg, 68%. Anal. Calcd for C $_{16}$ H $_{21}$ FeNO $_2$: C, 60.97; H, 6.72; N, 4.44. Found: C, 61.03; H, 6.66; N, 4.48. IR (CH $_2$ Cl $_2$): ν (CO) 1911

Table 5. Crystal Data and Experimental Details for **4a**·CH₂Cl₂, **4b**, **5e**, and **7b**

	4a ·CH ₂ Cl ₂	4b	5e	7b
formula	C ₃₉ H ₄₀ Cl ₂ Fe ₄ N ₂ O ₈	C ₃₆ H ₃₈ Fe ₄ N ₂ O ₄	C ₂₇ H ₃₁ Fe ₂ NO ₂ Si	C ₂₀ H ₂₁ FeNO ₂
fw	959.03	786.08	541.32	363.23
<i>T</i> , K	150(2)	293(2)	293(2)	293(2)
λ , Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Aba</i> 2	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	18.032(4)	12.735(3)	9.920(2)	9.3991(19)
<i>b</i> , Å	10.346(2)	27.480(6)	34.927(7)	19.964(4)
<i>c</i> , Å	21.479(4)	10.206(2)	14.849(3)	10.132(2)
β , deg	105.50(3)	112.80(3)	90	109.83(3)
cell vol, Å ³	3861.2(13)	3292.8(11)	5144.6(18)	1788.5(6)
<i>Z</i>	4	4	8	4
<i>D_c</i> , g cm ⁻³	1.650	1.586	1.398	1.349
μ , mm ⁻¹	1.667	1.770	1.198	0.854
<i>F</i> (000)	1960	1616	256	760
cryst size, mm	0.24 × 0.21 × 0.15	0.19 × 0.16 × 0.11	0.24 × 0.22 × 0.14	0.24 × 0.19 × 0.11
θ limits, deg	1.31–26.37	1.48–25.03	1.17–25.03	2.04–28.70
no. of rflns collected	37 213	26 427	22 038	21 148
no. of indep rflns	7877 (<i>R</i> _{int} = 0.0771)	5811 (<i>R</i> _{int} = 0.1083)	4551 (<i>R</i> _{int} = 0.0769)	4625 (<i>R</i> _{int} = 0.0644)
no. of data/restraints/params	7877/0/502	5811/178/417	4551/85/297	4625/0/221
goodness on fit on <i>F</i> ²	1.062	1.054	1.050	0.963
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0502	0.0564	0.0478	0.0494
w <i>R</i> 2 (all data)	0.1416	0.1398	0.1212	0.1452
largest diff peak and hole, e Å ⁻³	2.190/–1.385	0.572/–0.629	0.514/–0.340	0.350/–0.519

(vs), ν (C_αN) 1625 (w sh), ν (acyl) 1599 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 7.29 (s, 1 H, C_βH); 4.48 (s, 5 H, Cp); 3.71, 3.49 (s, 6 H, NMe); 2.25 (m, 2 H, C_γCH₂); 1.41 (m, 2 H, C_γCH₂CH₂); 1.31 (m, 2 H, C_γCH₂CH₂CH₂); 0.89 (t, ³*J*_{HH} = 7.32 Hz, CH₂CH₂CH₂CH₃). ¹³C NMR (CDCl₃): δ 272.0 (C=O); 262.3 (C_α); 221.9 (CO); 177.1 (C_γ); 145.5 (C_β); 84.8 (Cp); 51.4, 42.8 (NMe); 30.3, 27.0, 22.6 (CH₂); 13.9 (CH₂CH₂CH₂CH₃).

The reaction of **1f** with NaH was performed by the same procedure described for the synthesis of **7a**.

Complexes **7b–d** were prepared by following the same procedure described for the synthesis of **7a**, by reacting NaH with **3d–f**, respectively. Crystals of **7b** suitable for X-ray analysis were obtained by a CH₂Cl₂ solution layered with *n*-pentane, at –20 °C.

7b. Yield: 73%. Color: orange. Anal. Calcd for C₂₀H₂₁FeNO₂: C, 66.13; H, 5.83; N, 3.86. Found: C, 66.29; H, 5.74; N, 3.90. IR (CH₂Cl₂): ν (CO) 1916 (vs), ν (C_αN) 1627 (m), ν (acyl) 1597 (s) cm⁻¹. ¹H NMR (CDCl₃): δ 7.27–7.16 (m, 3 H, Me₂C₆H₃); 6.54 (s, 1 H, C_βH); 4.62 (s, 5 H, Cp); 3.82 (s, 3 H, NMe); 2.19, 2.10 (s, 6 H, Me₂C₆H₃); 1.70 (s, 3 H, C_γMe). ¹³C NMR (CDCl₃): δ 270.7 (C=O); 266.2 (C_α); 221.3 (CO); 173.2 (C_γ); 148.0 (C_β); 145.3 (ipso-Me₂C₆H₃); 132.6, 132.1, 129.2, 128.8, 128.6 (Me₂C₆H₃); 84.8 (Cp); 48.7 (NMe); 17.6, 17.4 (Me₂C₆H₃); 13.1 (C_γMe). ESI-MS (ES⁺): *m/z* 363 [M⁺].

7c. Yield: 67%. Color: orange. Anal. Calcd for C₂₁H₂₁FeNO₄: C, 61.94; H, 5.20; N, 3.44. Found: C, 62.01; H, 5.17; N, 3.45. IR (CH₂Cl₂): ν (CO) 1935 (vs), 1724 (s), ν (C_αN) 1624 (m), ν (acyl) 1610 (ms) cm⁻¹. ¹H NMR (CDCl₃): δ 7.34–7.08 (m, 3 H, Me₂C₆H₃); 7.03 (s, 1 H, C_βH); 4.68 (s, 5 H, Cp); 3.83 (s, 3 H, NMe); 3.69 (s, 3 H, COOMe); 2.19, 2.11 (s, 6 H, Me₂C₆H₃). ¹³C NMR (CDCl₃): δ 267.5 (C_α); 241.3 (C=O); 221.9 (CO); 164.2 (COOMe); 151.7 (C_β); 145.1 (ipso-Me₂C₆H₃); 132.3, 132.7, 129.5, 129.0, 128.7 (Me₂C₆H₃); 85.3 (Cp); 52.0 (COOMe); 49.6 (NMe); 17.6, 17.4 (Me₂C₆H₃).

7d. Yield: 88%. Color: brown. Anal. Calcd for C₂₂H₂₅FeNO₃: C, 61.94; H, 5.20; N, 3.44. Found: C, 62.00; H, 5.20; N, 3.32. IR (CH₂Cl₂): ν (CO) 1926 (vs), ν (C_αN) 1620 (m), ν (acyl) 1578 (ms) cm⁻¹. ¹H NMR (CDCl₃): δ 7.42, 6.47 (s, 1 H, C_β); 7.29–7.16 (m, 3 H, Me₂C₆H₃); 5.27, 5.13 (s, 1 H, OH); 4.64, 3.99 (s, 5 H, Cp); 3.81, 3.67 (s, 3 H, NMe); 2.39, 2.33, 2.19, 2.09 (s, 6 H, Me₂C₆H₃); 1.44, 1.43, 1.19, 1.18 (s, 6 H, CMe₂OH); *E:Z* ratio 2:1. ¹³C NMR (CDCl₃): δ 278.3, 276.8 (C=O); 265.7, 263.8 (C_α); 223.8, 220.8 (CO); 177.5, 174.8 (C_γ); 149.0, 144.9

(ipso-Me₂C₆H₃); 145.0, 143.5 (C_β); 133.6, 133.0, 132.2, 131.8, 129.2, 129.1, 129.0, 128.9, 128.7, 128.1 (Me₂C₆H₃); 85.4, 84.9 (Cp); 71.5, 71.1 (CMe₂OH); 49.0, 44.6 (NMe); 29.8, 29.6, 28.9, 28.4 (CMe₂OH); 18.3, 17.5, 17.2 (Me₂C₆H₃).

X-ray Crystallography. Crystal data and collection details for **4a**·CH₂Cl₂, **4b**, **5e**, and **7b** are reported in Table 5. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo K α radiation. Data were corrected for Lorentz–polarization and absorption effects (empirical absorption correction SADABS).²⁷ Structures were solved by direct methods and refined by full-matrix least squares based on all data using *F*².²⁸ 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. The crystals of **5e** appeared to be racemically twinned with a refined Flack parameter of 0.50(3).²⁹ Disorder was found for one Cp ligand in **4b** and **5e**, and the Xyl and the SiMe₃ groups in **5e** 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: Crystallographic data for compounds **4a**·CH₂Cl₂, **4b**, **5e**, and **7b** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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