

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

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The  $C_{\beta}$ -H hydrogen in the diiron vinyliminium complexes  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^3\text{-C}_7(\text{R}')\text{=C}_{\beta}\text{HC}_{\alpha}\text{=N(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$  (R = Me, **1**; R = Bz, **2** (Bz =  $\text{CH}_2\text{Ph}$ ); 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  $[\text{Fe}_2\{\mu\text{-}\eta^1\text{-}\eta^2\text{-C(R')\text{-CCN(Me)(R)}\}\{\mu\text{-CO(CO)(Cp)}_2\}_2]$  (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' =  $\text{SiMe}_3$ , **1d**; R = Me, R' = Tol, **1e**; R = Bz, R' =  $\text{SiMe}_3$ , **2b**; R = Bz, R' = Tol, **2c** (Tol = 4- $\text{MeC}_6\text{H}_4$ ); R = Xyl, R' =  $\text{SiMe}_3$ , **3a**; R = Xyl, R' = Tol, **3b**; R = Xyl, R' = Ph, **3c**) leads to the selective formation of the corresponding  $\mu$ -aminocarbyne alkynyl complexes  $[\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}\{\mu\text{-CO(CO)(C}\equiv\text{CR')}\text{(Cp)}_2\}]$  (R = Me, R' =  $\text{SiMe}_3$ , **5a**; R = Me, R' = Tol, **5b**; R = Bz, R' =  $\text{SiMe}_3$ , **5c**; R = Bz, R' = Tol, **5d**; R = Xyl, R' =  $\text{SiMe}_3$ , **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' =  $\text{SiMe}_3$ , **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' =  $\text{Bu}^n$ , **1c**; R = Xyl, R' = Me, **3d**; R = Xyl, R' = COOMe, **3e**; R = Xyl, R' =  $\text{CMe}_2\text{OH}$ , **3f**) with NaH afford the 1-metalla-2-aminocyclopenta-1,3-dien-5-one species  $[\text{Fe}(\text{Cp})(\text{CO})\{\text{CN(Me)(R)CHC(R')C(O)}\}]$  (R = Me, R' =  $\text{Bu}^n$ , **7a**; R = Xyl, R' = Me, **7b**; R = Xyl, R' = COOMe, **7c**; R = Xyl, R' =  $\text{CMe}_2\text{OH}$ , **7d**). The molecular structures of **4a**· $\text{CH}_2\text{Cl}_2$ , **4b**, **5e**, and **7b** have been determined by X-ray diffraction studies.

## Introduction

Insertions of alkynes into the metal–carbon bond of bridging alkylidene<sup>1</sup> and alkylidyne<sup>2</sup> 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  $\mu$ -aminocarbynes  $[\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}\{\mu\text{-CO(CO)(NCMe)(Cp)}_2\}[\text{SO}_3\text{CF}_3]]$  (R = Me,  $\text{CH}_2\text{Ph}$  (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**)).<sup>3</sup> Since the reactivity of vinyliminium ligands has been largely unexplored,<sup>4</sup> we have started to investigate the reactions of **1–3** with nucleophiles. In particular, we have found that  $\text{NaBH}_4$  adds  $\text{H}^-$  at the  $\mu$ -vinyliminium ligand to form neutral derivatives, whose nature depends on the steric hindrance of the iminium nitrogen substituents.<sup>5</sup> Indeed, the sterically demanding Xyl group inhibits hydride attack at the iminium carbon and directs the addition to the  $C_{\beta}$  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  $\text{CH}_2\text{Ph}$  substituent,

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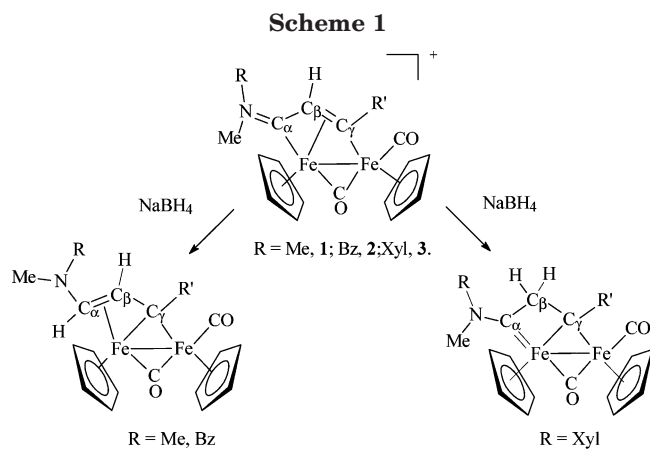
(1) (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 803. (b) Sumner Jr., C. E.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350. (c) Colborn, R. E.; Dyke, A. F.; Knox, S. A. R.; Macpherson, K.; Orpen, A. G. *J. Organomet. Chem.* **1982**, *239*, C15. (d) Adams, P. Q.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1983**, 222. (e) Colborn, R. E.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Orpen, A. G.; Guerschais, J. E.; Roué, J. *J. Chem. Soc., Dalton Trans.* **1989**, 1799. (f) Akita, M.; Hua, R.; Nakanishi, S.; Tanaka, M.; Moro-oka, Y. *Organometallics* **1997**, *16*, 5572. (g) Rowsell, B. D.; McDonald, R.; Ferguson, M. J.; Cowie, M. *Organometallics* **2003**, *22*, 2944. (h) Kaneko, Y.; Suzuki, T.; Isobe, K.; Maitlis, P. M. *J. Organomet. Chem.* **1998**, *554*, 155.

(2) Casey, C. P.; Woo, L. K.; Fagan, P. J.; Palermo, R. E.; Adams, B. R. *Organometallics* **1987**, *6*, 447.

(3) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *Organometallics* **2003**, *22*, 1326. (b) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2004**, *689*, 528.

(4) (a) Bernard, D. J.; Esteruelas, M. A.; Lopez, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995. (b) Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693.

(5) (a) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *Organometallics* **2004**, *23*, 3348. (b) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2005**, *690*, 837.



**Chart 1. Vinyliminium Complexes Investigated in This Paper**

|           | R   | R'                    |
|-----------|-----|-----------------------|
| <b>1a</b> | Me  | COOMe                 |
| <b>1b</b> | Me  | Me                    |
| <b>1c</b> | Me  | Bu <sup>n</sup>       |
| <b>1d</b> | Me  | SiMe <sub>3</sub>     |
| <b>1e</b> | Me  | Tol                   |
| <b>2a</b> | Bz  | COOMe                 |
| <b>2b</b> | Bz  | SiMe <sub>3</sub>     |
| <b>2c</b> | Bz  | Tol                   |
| <b>3a</b> | Xyl | SiMe <sub>3</sub>     |
| <b>3b</b> | Xyl | Tol                   |
| <b>3c</b> | Xyl | Ph                    |
| <b>3d</b> | Xyl | Me                    |
| <b>3e</b> | Xyl | COOMe                 |
| <b>3f</b> | Xyl | C(Me) <sub>2</sub> OH |

the reaction with NaBH<sub>4</sub> occurs selectively at the iminium carbon, yielding the vinylalkylidene complexes [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(R')=CHC(H)N(Me)(R)}(μ-CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (Scheme 1).

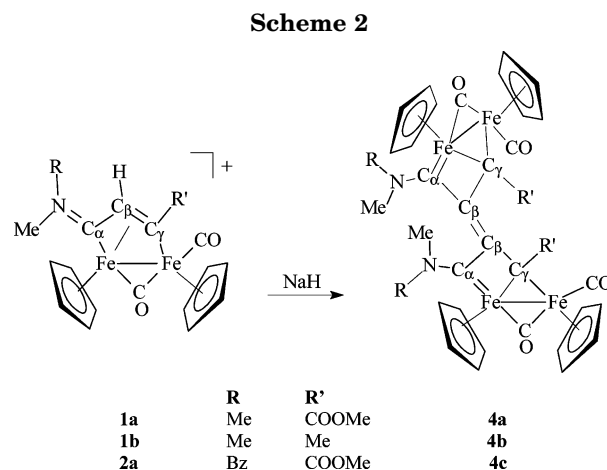
In addition to nucleophilic additions, the reactivity of the bridging vinyliminium ligand in **1–3** could be further extended by the removal of the C<sub>β</sub>–H proton. This possibility is suggested by the mononuclear complex [Ru(Cp){C(=NET<sub>2</sub>)CH=CPh<sub>2</sub>}(CO)(PPR<sup>i</sup><sub>3</sub>)] [BF<sub>4</sub>], to form the aminoallenyl derivative [Ru(Cp){C(=NET<sub>2</sub>)=C=CPh<sub>2</sub>}(CO)(PPR<sup>i</sup><sub>3</sub>)].<sup>4a</sup> Moreover, the Fe–C<sub>α</sub> interaction in the μ-vinyliminium species **1–3** displays some Fisher-type aminocarbene character,<sup>3</sup> and adjacent C–H hydrogens, in Fisher carbenes, are known to be acidic.<sup>6</sup>

These considerations led us to determine to what extent C<sub>β</sub>–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 [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>3</sup>-C(R')=CHC(H)N(Me)(R)}(μ-CO)(CO)(Cp)<sub>2</sub>]-

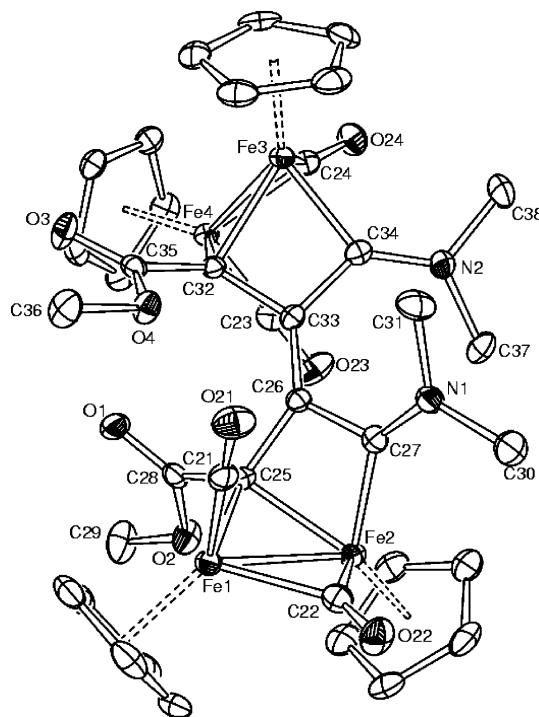
(6) (a) Fischer, H.; Kreissel, F. R.; Schubert, U.; Hoffman, P.; Dotz, K. H.; Weiss, K. In *Transition Metal Carbene Complexes*; VCH: Weinheim, Germany, 1983. (b) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390. (c) Casey, C. P.; Anderson, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 1230. (d) Casey, C. P.; Brunsvold, W. R. *J. Organomet. Chem.* **1976**, *118*, 309. (e) Bernasconi, C. F. *Chem. Soc. Rev.* **1997**, *26*, 299. (f) Plantevin, V.; Wojcicki, A. *J. Organomet. Chem.* **2004**, *689*, 2000.



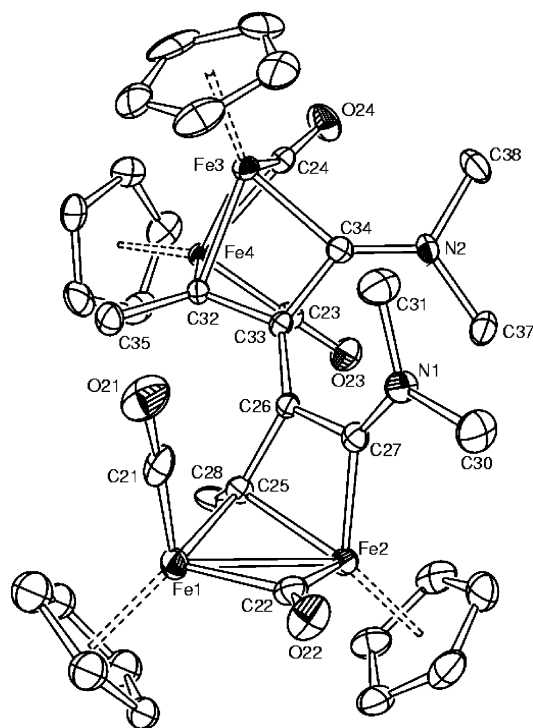
[SO<sub>3</sub>CF<sub>3</sub>] (R = Me, R' = COOMe, **1a**; R = R' = Me, **1b**; R = Bz, R' = COOMe, **2a**) react with NaH in THF solution, affording the novel tetrairon complexes [Fe<sub>2</sub>{μ-η<sup>1</sup>:η<sup>2</sup>-C(R')CCN(Me)(R)}(μ-CO)(CO)(Cp)<sub>2</sub>]<sub>2</sub> (R = Me, R' = COOMe, **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 [Fe<sub>2</sub>{μ-C(R')CCN(Me)<sub>2</sub>}(μ-CO)(CO)(Cp)<sub>2</sub>] (R' = CO<sub>2</sub>Me, **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 [Fe<sub>2</sub>{μ-C(COOMe)CCN(Me)<sub>2</sub>}(μ-CO)(CO)(Cp)<sub>2</sub>]<sub>2</sub> (**4a**). All H atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.



**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)  |

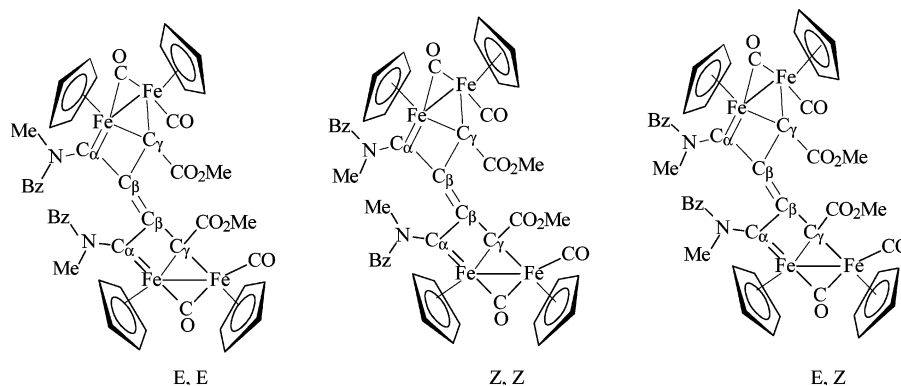
moiety contains an  $\text{Fe}_2(\mu\text{-CO})(\text{CO})(\text{Cp})_2$  core and a bridging  $\mu\text{-C}(\text{R})\text{CCN}(\text{Me})_2$  ligand. The former adopts a cis arrangement of the Cp ligands as in the parent compounds **1a,b**. The bridging ligand resembles the bis-alkylidene present in  $[\text{Fe}_2\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2]$ .<sup>5a</sup> The iron atoms show a nearly pure  $\sigma$  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  $\text{sp}^2$  hybridization (sum of angles 358.6(5) and 359.4(5)° for **4a** and 358.7(8) and 359.0(8)° 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  $\text{sp}^2$  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  $\text{C}_\beta$  has  $\text{sp}^3$  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  $\text{C}_\beta$  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**

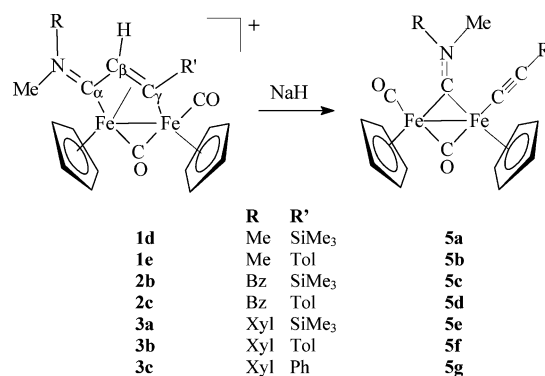
that the two moieties composing **4b** are completely identical, whereas they differ only in the orientation of the carboxylate groups in **4a**. In particular, the C(35)–O(3)–O(4)–C(36) group in **4a** is nearly coplanar with Fe(4)–C(32)–C(33) (Fe(4)–C(32)–C(35)–O(3) dihedral angle  $-15.3(5)^\circ$ ), 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  $^1\text{H}$  NMR spectrum of **4a**, recorded at 233 K, shows a unique set of resonances for the two  $\text{Fe}_2$  frames: thus, two Cp resonances are observed (at  $\delta$  4.84 and 4.35 ppm) and one signal is found for the COOMe groups (at  $\delta$  4.00 ppm). The main feature in the  $^{13}\text{C}$  NMR spectrum, recorded at 233 K, consists of the typical low-field resonance attributable to the aminocarbene carbons  $\text{C}_\alpha$  ( $\delta$  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.<sup>7</sup> 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).

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

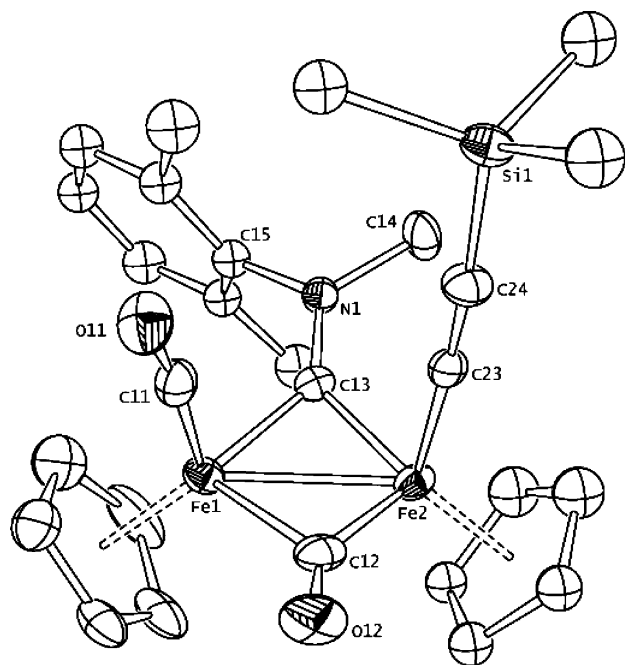
Scheme 3



**Synthesis and Reactivity of  $\sigma$ -Coordinated Acetylide Diiron Complexes.** The reaction of **1d,e**, **2b,c**, and **3a–c** with NaH results in formation of the  $\sigma$ -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' = SiMe<sub>3</sub>, **5a**; R = Me, R' = Tol, **5b**; R = Bz, R' = SiMe<sub>3</sub>, **5c**; R = Bz, R' = Tol, **5d**; R = Xyl, R' = SiMe<sub>3</sub>, **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,<sup>8</sup> 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  $\sigma$ -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) =

(8) (a) Boss, K.; Cox, M. G.; Dowling, C.; Manning, A. R. *J. Organomet. Chem.* **2000**, *612*, 18. (b) Albano, V. G.; Busetto, L.; Camiletti, C.; Castellari, C.; Monari, M.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1997**, 4671. (c) Albano, V. G.; Busetto, L.; Camiletti, C.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **1998**, *563*, 153. (d) Albano, V. G.; Busetto, L.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2000**, *606*, 163.



**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.

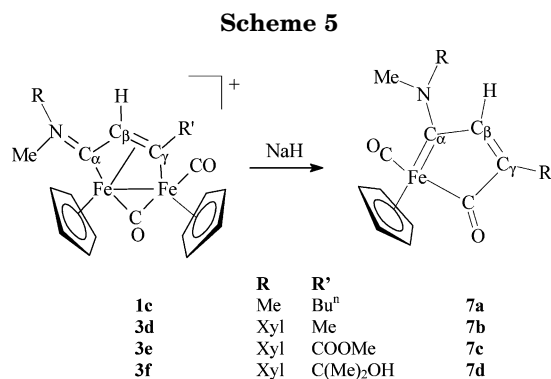
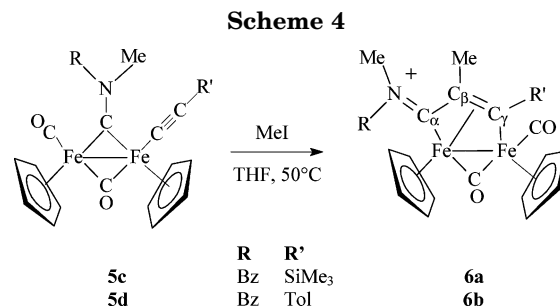
**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for **5e**

|                   |            |                  |           |
|-------------------|------------|------------------|-----------|
| 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  $\pi$  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).<sup>9</sup>

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, CH<sub>2</sub>CN, CN, Cl; R = Xyl, Bz).<sup>8</sup> These isomers are due to the different orientations that the nonequivalent nitrogen substituents (Me and CH<sub>2</sub>Ph, or Me and Xyl) can assume with respect to the  $\mu$ -CN interaction, which exhibits partial double-bond character. A characteristic downfield <sup>13</sup>C NMR resonance accounts for the presence of the aminocarbene carbon (e.g. at  $\delta$  330.5 ppm for **5a**).

Finally, attempts to transform the  $\sigma$ -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 HSO<sub>3</sub>CF<sub>3</sub> 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' = SiMe<sub>3</sub>, **5c**; R' = Tol, **5d**) with an excess of methyl iodide in refluxing



THF, followed by exchange of I<sup>−</sup> with SO<sub>3</sub>CF<sub>3</sub><sup>−</sup>, 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' = SiMe<sub>3</sub>, **6a**; R' = Tol, **6b**) (Scheme 4).

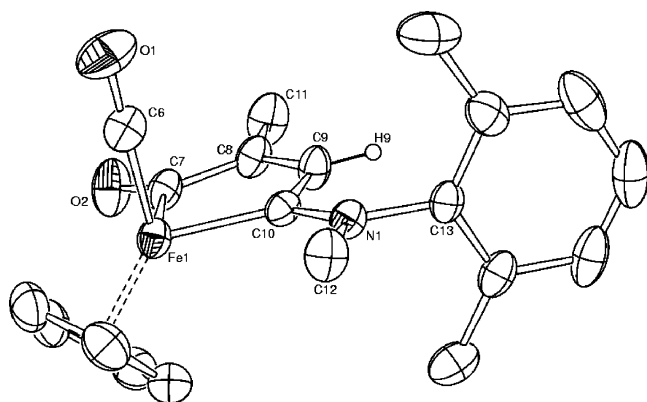
Complex **6a** has been previously obtained by insertion of MeC≡CSiMe<sub>3</sub> into the Fe–aminocarbene bond of  $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Bz})\}(\mu\text{-CO})(\text{NCMe})(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ .<sup>5b</sup> The spectroscopic properties of **6b** are those expected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

**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  $\pi$  back-bonding, whereas the former is mainly a  $\sigma$  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 <sup>13</sup>C NMR spectra of **7a–d**, typical low-field resonances have been found for the acyl carbon (e.g. at  $\delta$  270.7 ppm for **7b**) and for the aminocarbene carbon

(9) Simonetta, M.; Gavezzotti, A. In *The Chemistry of the Carbon–Carbon Triple Bond*; Wiley: New York, 1978.

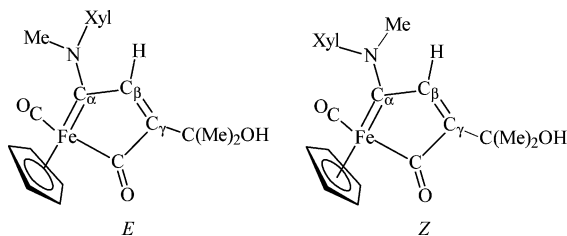


**Figure 4.** ORTEP drawing of  $[\text{Fe}(\text{Cp})(\text{CO})\{\text{CN}(\text{Me})(\text{Xyl})\text{CHC}(\text{Me})\text{C}(\text{O})\}]$  (**7b**). All H atoms, except H(9), have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

**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****



$\text{C}_\alpha$  (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).

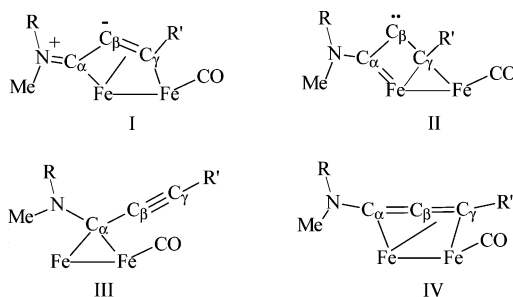
Examples of 1-metallacyclopent-3-ene-2,5-dione<sup>10</sup> and 1-metallacyclopent-3-en-2-one complexes<sup>11</sup> have been reported in the literature. Interestingly, complex **7b** represents, to our knowledge, the first 1-metallacyclopent-1,3-dien-5-one ring structurally characterized.

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

(10) (a) Elarraoui, A.; Ros, J.; Yáñez, R.; Solans, X.; Font-Bardia, M. *J. Organomet. Chem.* **2002**, *642*, 107. (b) Mao, T.; Zhang, Z.; Washington, J.; Takats, J.; Jordan, R. B. *Organometallics* **1999**, *18*, 2331.

(11) (a) Kayan, A.; Gallucci, J. C.; Wojcicki, A. *J. Organomet. Chem.* **2001**, *630*, 44. (b) Huffman, M. A.; Liebeskind, L. S. *Organometallics* **1992**, *11*, 255.

**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,<sup>12</sup> 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).<sup>13</sup>

## 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  $\text{C}_\beta$  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  $\text{C}_\beta$ , no longer coordinated to the metals, displays a “carbene character”. Other rearrangements are also possible, leading to a bridging alkynylaminocarbene (III),<sup>14</sup> or a coordinated allene-1,3-diyne (IV).<sup>15</sup>

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”.<sup>16</sup> 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

(12) Busetto, L.; Camiletti, C.; Zanotti, V.; Albano, V. G.; Sabatino, P. *J. Organomet. Chem.* **2000**, *593*, 335.

(13) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V.; Zoli, E. *J. Organomet. Chem.*, in press.

(14) Davis, J. H.; Lukehart, C. M.; Sacksteder, L. *Organometallics* **1987**, *6*, 50.

(15) (a) Clarke, L. P.; Davies, J. E.; Raithby, P. R.; Shields, G. P. *Dalton* **2000**, 4527. (b) Akita, M.; Chung, M. C.; Terada, M.; Miyauti, M.; Tanaka, M.; Moro-oka, Y. *J. Organomet. Chem.* **1998**, *565*, 49.

(16) (a) Rabier, A.; Lugan, N.; Mathieu, R.; Geoffroy, G. L. *Organometallics* **1994**, *13*, 4676. (b) Rabier, A.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **2001**, *617–618*, 681. (c) Lattuada, L.; Licandro, E.; Maiorana, S.; Molinari, H.; Papagni, A. *Organometallics* **1991**, *10*, 807.



$[\text{Fe}_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(R')=CHC=N(Me)(Xyl)\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2\text{-}[\text{SO}_3\text{CF}_3]$  ( $\text{R}' = \text{Me}$ , **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  $\sigma$  coordinated to an Fe atom.

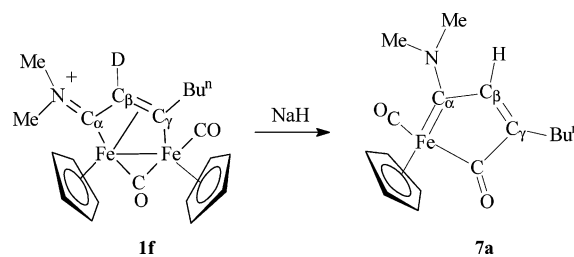
It is not obvious why deinsertion is observed for the reactions of **1d,e**, **2b,c**, and **3a-c**, rather than dimerization or fragmentation. This behavior is related to the nature of the substituent at  $\text{C}_\gamma$ , since the sterically demanding  $\text{SiMe}_3$  and aryl substituents are thought to prevent the dimerization. Moreover, (trimethylsilyl)- and arylacetylides are among the most stable  $\sigma$ -alkynyl ligands, and this may also favor the formation of **5a-g**.

Interestingly, the deinsertion reaction affords  $\sigma$ -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.<sup>17</sup> Even when the nitriles do not contain acidic protons (e.g.  $\text{NCCMe}_3$ , aryl nitriles) the reactions with acetylides proceed via nucleophilic addition at the nitrile ligands, instead of producing its replacement.<sup>13,18</sup>

Complexes **5a-g** are interesting compounds for several reasons. They contain a  $\sigma$ -coordinated alkynyl ligand,<sup>19</sup> whereas, in binuclear complexes, alkynyl ligands are more commonly found in bridging positions.<sup>20</sup> Moreover, metal-alkynyl complexes represent an area of growing interest<sup>21</sup> for potential applications in nonlinear optics,<sup>22</sup> as luminescent materials,<sup>23</sup> and as molecular devices.<sup>24</sup>

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  $\text{H}^+$ , 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  $\text{NEt}_3$ , sodium naphthalenide ( $\text{NaNaph}$ ), and  $\text{KOH}$ , under conditions similar to those used in the reactions with NaH. Investigations were not conclusive, because both  $\text{NaNaph}$  and  $\text{KOH}$  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  $\text{NEt}_3$  failed to produce any transformation.

Moreover, the reaction with NaH has been carried out on the  $\text{C}_\beta$ -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  $\text{C}_\beta$  (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  $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{Ph}$  and to the presence of relatively small R' groups ( $\text{COOMe}$ , Me) at  $\text{C}_\gamma$ . 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  $\sigma$ -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  $\text{NaBH}_4$ ,<sup>5</sup> evidence that

(17) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2002**, *649*, 64.

(18) Albano, V. G.; Bordoni, S.; Busetto, L.; Marchetti, F.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2003**, *684*, 37.

(19) Hurst, S. K.; Ren, T. *J. Organomet. Chem.* **2003**, *670*, 188.

(20) (a) Lang, H.; George, D. S. A.; Rheinwald, G. *Coord. Chem. Rev.* **2000**, *206-207*, 101. (b) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89. (c) Cherkas, A. A.; Randall, L. H.; Taylor, N. J.; Mott, G. N.; Yule, J. E.; Guinamant, J. L.; Carty, A. J. *Organometallics* **1990**, *9*, 1677. (d) Darren, S. A.; McDonald, R.; Cowie, M. *Organometallics* **1998**, *17*, 2553. (e) Hogarth, G.; Redmond, S. P. *J. Organomet. Chem.* **1997**, *534*, 221. (f) Smith, W. F.; Yule, J.; Taylor, N. J.; Paik, H. N.; Carty, A. *J. Inorg. Chem.* **1977**, *16*, 1593.

(21) Long, N. J.; Williams, C. K.; *Angew. Chem., Int. Ed.* **2003**, *42*, 2586.

(22) (a) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291. (b) Whittall, I. R.; McDonagh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1999**, *43*, 349.

(23) Yam V. W. W. *Acc. Chem. Res.* **2002**, *35*, 555.

(24) (a) Ziessel, R.; Hissler, M.; El-Ghayoury, A.; Harriman, A. *Coord. Chem. Rev.* **1998**, *180*, 1251. (b) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178-180*, 431.

the reaction products strongly depend on the nature of the hydride reagent: NaH acts exclusively as a base, whereas the nucleophile NaBH<sub>4</sub> provides H<sup>-</sup> 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<sub>β</sub>-H in  $\mu$ -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 CH<sub>3</sub>CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for <sup>1</sup>H and <sup>13</sup>C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and <sup>1</sup>H, <sup>13</sup>C correlations measured using gs-HSQC and gs-HMBC experiments.<sup>25</sup> 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.<sup>26</sup> All the reagents were commercial products (Aldrich) of the highest purity available and were used as received. [Fe<sub>2</sub>(CO)<sub>4</sub>(Cp)<sub>2</sub>] was purchased from Strem and used as received. The compounds [Fe<sub>2</sub>{ $\mu$ -CN(Me)(R)}( $\mu$ -CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>]<sup>sd</sup> (R = Me, Xyl) and [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C(R')=CHC=N(Me)(R)}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**1a**, **b**, **d**, **e**; **2a-c**; **3a-e**) were prepared as described in the literature.<sup>3</sup>

**Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C<sub>7</sub>(Bu<sup>n</sup>)=C<sub>β</sub>HC<sub>α</sub>=N(Me)<sub>2</sub>}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**1c**) and [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C<sub>7</sub>(Bu<sup>n</sup>)=C<sub>β</sub>DC<sub>α</sub>=N(Me)<sub>2</sub>}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**1f**).** HC≡CBu<sup>n</sup> (0.068 mL, 0.59 mmol) was added to a solution of [Fe<sub>2</sub>{ $\mu$ -CN(Me)<sub>2</sub>}( $\mu$ -CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (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 CH<sub>2</sub>Cl<sub>2</sub> solution, layered with diethyl ether, gave crystals of **1c**. Yield: 248 mg, 90%. Anal. Calcd for C<sub>22</sub>H<sub>26</sub>F<sub>3</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 45.15; H, 4.48; N, 2.39. Found: C, 44.99; H, 4.52; N, 2.29. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 1990 (vs), 1805 (s),  $\nu$ (C<sub>α</sub>N) 1682 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.16, 4.99 (s, 10 H, Cp); 4.52 (s, 1 H, C<sub>β</sub>H); 4.14, 3.74 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>); 3.83, 3.25 (s, 6 H, NMe); 2.05, 1.86 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.67 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>); 1.10 (t, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.32 Hz, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  257.0 ( $\mu$ -CO); 225.6 (C<sub>α</sub>); 212.8 (C<sub>γ</sub>); 209.6 (CO); 89.6, 87.3 (Cp); 54.7 (C<sub>γ</sub>CH<sub>2</sub>); 51.3 (C<sub>β</sub>); 50.9, 44.7 (NMe); 37.7 (C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>); 22.8 (C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 14.1 (C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>).

Complex [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C<sub>7</sub>(Bu<sup>n</sup>)=C<sub>β</sub>DC<sub>α</sub>=N(Me)<sub>2</sub>}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**1f**) was synthesized by the same procedure

described for **1c**, by reacting [Fe<sub>2</sub>{ $\mu$ -CN(Me)<sub>2</sub>}( $\mu$ -CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] with DC≡CBu<sup>n</sup>. The latter was prepared treating HC≡CBu<sup>n</sup> in THF solution at -40 °C, with an equimolar amount of Bu<sup>n</sup>Li, followed by treatment with D<sub>2</sub>O. Yield: 88%. Color: green. Anal. Calcd for C<sub>22</sub>H<sub>27</sub>F<sub>3</sub>Fe<sub>2</sub>NO<sub>5</sub>S: C, 45.08; H, 4.64; N, 2.39. Found: C, 45.11; H, 4.61; N, 2.35. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 1990 (vs), 1805 (s),  $\nu$ (C<sub>α</sub>N) 1682 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.23, 5.07 (s, 10 H, Cp); 4.18, 3.75 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>); 3.87, 3.29 (s, 6 H, NMe); 2.05, 1.87 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.69 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.11 (t, 3 H, <sup>3</sup>J<sub>HH</sub> = 7.32 Hz, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

**Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^3$ -C<sub>7</sub>(CMe<sub>2</sub>OH)=C<sub>β</sub>HC<sub>α</sub>=N(Me)(Xyl)}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (**3f**).** A solution of the complex [Fe<sub>2</sub>{ $\mu$ -CN(Me)(Xyl)}( $\mu$ -CO)(CO)(NCMe)(Cp)<sub>2</sub>][SO<sub>3</sub>CF<sub>3</sub>] (210 mg, 0.331 mmol), in CH<sub>2</sub>Cl<sub>2</sub>, was treated with HC≡C(Me)<sub>2</sub>OH (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 CH<sub>2</sub>Cl<sub>2</sub> solution, layered with diethyl ether, afforded brown crystals of **3f**. Yield: 191 mg, 85%. Anal. Calcd for C<sub>28</sub>H<sub>30</sub>F<sub>3</sub>Fe<sub>2</sub>NO<sub>6</sub>S: C, 49.65; H, 4.46; N, 2.07. Found: C, 49.82; H, 4.38; N, 2.13. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 1998 (vs), 1806 (s),  $\nu$ (C<sub>α</sub>N) 1632 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.07-6.73 (m, 3 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 5.44, 5.29, 5.22, 4.68 (s, 10 H, Cp); 4.95 (s, 1 H, C<sub>β</sub>H); 4.15 (s, 3 H, NMe); 2.40, 2.20, 1.92, 1.73 (s, 6 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 1.51 (s, 6 H, CMe<sub>2</sub>OH); *E:Z* ratio 5:1. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  255.6 ( $\mu$ -CO); 231.1 (C<sub>α</sub>); 210.3 (CO); 209.6 (C<sub>γ</sub>); 144.5 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 139.7, 136.6, 132.9, 131.0, 129.3 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 90.8, 89.5, 88.3, 87.0 (Cp); 70.0 (CMe<sub>2</sub>OH); 48.7 (C<sub>β</sub>); 45.8 (NMe); 32.0, 31.4 (CMe<sub>2</sub>OH); 17.6, 17.0 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

**Synthesis of [Fe<sub>2</sub>{ $\mu$ - $\eta^1$ : $\eta^2$ -C<sub>7</sub>(R')C<sub>β</sub>C<sub>α</sub>N(Me)(R)}( $\mu$ -CO)(CO)(Cp)<sub>2</sub>] (R = Me, R' = COOMe, **4a**; R = Me, R' = Me, **4b**; R = CH<sub>2</sub>Ph, 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 CH<sub>2</sub>Cl<sub>2</sub> and THF (4:1) as eluent, afforded a dark gray band, which was collected. Crystallization at -20 °C from CH<sub>2</sub>Cl<sub>2</sub> solution layered with petroleum ether (bp 40-60 °C) gave crystals of **4a**. Yield: 66 mg, 60%. Anal. Calcd for C<sub>38</sub>H<sub>38</sub>Fe<sub>4</sub>N<sub>2</sub>O<sub>8</sub>: C, 52.22; H, 4.38; N, 3.20. Found: C, 52.26; H, 4.41; N, 3.20. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 1939 (s), 1751 (vs), 1741 (vs), 1688 (w), 1659 (w),  $\nu$ (C<sub>α</sub>N) 1568 (w), 1541 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 233 K):  $\delta$  4.84, 4.35 (s, 20 H, Cp); 4.00 (s, 6 H, CO<sub>2</sub>Me); 3.32, 2.26 (s, 12 H, NMe). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 233K):  $\delta$  278.4 ( $\mu$ -CO); 247.3 (C<sub>α</sub>); 216.0 (CO); 181.8 (CO<sub>2</sub>Me); 151.4 (C<sub>γ</sub>); 87.4, 87.3 (Cp); 71.6 (C<sub>β</sub>); 51.5 (CO<sub>2</sub>Me); 47.1, 43.1 (NMe). ESI-MS (ES<sup>+</sup>): *m/z* 874 [M<sup>+</sup>, 11%], 437 [M/2<sup>+</sup>, 100%], 409 [M/2<sup>+</sup> - 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 C<sub>36</sub>H<sub>38</sub>Fe<sub>4</sub>N<sub>2</sub>O<sub>8</sub>: C, 55.01; H, 4.87; N, 3.56. Found: C, 55.07; H, 4.92; N, 3.63. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 1921 (s), 1740 (s-sh), 1728 (vs),  $\nu$ (C<sub>α</sub>N) 1603 (w), 1558 (wm) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.84, 4.48 (s, 20 H, Cp); 3.71, 3.48 (s, 12 H, NMe); 1.85 (s, 6 H, C<sub>γ</sub>Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  272.0 ( $\mu$ -CO); 262.4 (C<sub>α</sub>); 221.9 (CO); 172.6 (C<sub>γ</sub>); 86.8, 84.7 (Cp); 79.2 (C<sub>β</sub>); 51.4, 42.8 (NMe); 13.2 (C<sub>γ</sub>Me).

**4c.** Yield: 68%. Color: dark gray. Anal. Calcd for C<sub>50</sub>H<sub>46</sub>Fe<sub>4</sub>N<sub>2</sub>O<sub>8</sub>: C, 58.52; H, 4.52; N, 2.73. Found: C, 58.43; H, 4.60; N, 2.77. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (CO) 1939 (s), 1752 (vs), 1742 (vs), 1687 (w), 1659 (w),  $\nu$ (C<sub>α</sub>N) 1568 (w), 1537 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 233 K):  $\delta$  7.45-6.91 (m, 10 H, Ph); 4.87, 4.40 (s, 20 H, Cp); 4.81, 4.52 (d, 4 H, <sup>2</sup>J<sub>HH</sub> = 13.7 Hz, CH<sub>2</sub>Ph); 4.03 (s, 6 H, CO<sub>2</sub>Me); 2.07 (s, 6 H, NMe). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 233 K):  $\delta$  278.6 ( $\mu$ -CO); 246.8 (C<sub>α</sub>); 216.1 (CO); 181.7 (CO<sub>2</sub>Me); 151.4 (C<sub>γ</sub>);

(25) Wilker, W.; Leibfritz, D.; Kerssebaum, R.; Beimele, W. *Magn. Reson. Chem.* 1993, **31**, 287.

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



135.2–127.8 (Ph); 87.7, 87.3 (Cp); 70.8 (C $\beta$ ); 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 $_2$ { $\mu$ -CN(Me)(R)}( $\mu$ -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 $_2$ ):  $\nu$ (C $\equiv$ C) 2011 (vs),  $\nu$ (CO) 1972 (vs), 1794 (s),  $\nu$ ( $\mu$ -CN) 1534 (w) cm $^{-1}$ .  $^1$ H NMR (CDCl $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  330.5 ( $\mu$ -C); 263.9 ( $\mu$ -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 $_2$ ):  $\nu$ (C $\equiv$ C) 2011 (vs),  $\nu$ (CO) 1972 (vs), 1794 (s),  $\nu$ ( $\mu$ -CN) 1534 (w) cm $^{-1}$ .  $^1$ H NMR (CDCl $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  333.6 ( $\mu$ -C); 263.6, 263.2 ( $\mu$ -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 $_2$ ):  $\nu$ (C $\equiv$ C) 2012 (vs),  $\nu$ (CO) 1973 (vs), 1792 (s),  $\nu$ ( $\mu$ -CN) 1506 (w) cm $^{-1}$ .  $^1$ H NMR (CDCl $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  337.2 ( $\mu$ -C); 263.6 ( $\mu$ -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 $_2$ { $\mu$ -CN(Me)(R)}( $\mu$ -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):  $\nu$ (C $\equiv$ C) 2087 (s),  $\nu$ (CO) 1963 (vs), 1788 (s) cm $^{-1}$ .  $^1$ H NMR (C $_6$ D $_5$ CD $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  331.0 ( $\mu$ -C); 261.0 ( $\mu$ -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):  $\nu$ (C $\equiv$ C) 2090 (s),  $\nu$ (CO) 1970 (vs), 1805 (s) cm $^{-1}$ .  $^1$ H NMR (C $_6$ D $_5$ CD $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  334.1, 333.7 ( $\mu$ -C); 260.9, 260.6 ( $\mu$ -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 $_2$ ):  $\nu$ (C $\equiv$ C) 2087 (m),  $\nu$ (CO) 1971 (vs), 1792 (s),  $\nu$ (CN) 1505 (w) cm $^{-1}$ .  $^1$ H NMR (C $_6$ D $_5$ CD $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  338.5 ( $\mu$ -C); 259.3 ( $\mu$ -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 $_2$ ):  $\nu$ (C $\equiv$ C) 2086 (m),  $\nu$ (CO) 1971 (vs), 1792 (s),  $\nu$ (CN) 1504 (w) cm $^{-1}$ .  $^1$ H NMR (C $_6$ D $_5$ CD $_3$ ):  $\delta$  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 $_3$ ):  $\delta$  338.3 ( $\mu$ -C); 260.0 ( $\mu$ -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 $_2$ { $\mu$ - $\eta^1$ : $\eta^3$ -C $_6$ (R')=C $\beta$ (Me)C $_6$ =N(Me)(Bz)}( $\mu$ -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 $_5$ SSi: C, 48.64; H, 4.67; N, 2.03. Found: C, 48.55; H, 4.62; N, 2.05. IR (CH $_2$ Cl $_2$ ):  $\nu$ (CO) 1982 (vs), 1815 (s),  $\nu$ (CN) 1652 (m) cm $^{-1}$ .  $^1$ H NMR (CDCl $_3$ ):  $\delta$  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 $\beta$ Me); 0.70, 0.67 (s, 9 H, SiMe $_3$ ); *Z:E* ratio 2:1.  $^{13}$ C NMR (CDCl $_3$ ):  $\delta$  254.6, 253.1 ( $\mu$ -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 $\beta$ ); 65.2, 62.3 (CH $_2$ Ph); 45.4, 43.4 (NMe); 20.6, 20.2 (C $\beta$ 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 $_2$ ):  $\nu$ (CO) 1989 (vs), 1807 (s),  $\nu$ (CN) 1655 (m) cm $^{-1}$ .  $^1$ H NMR (CDCl $_3$ ):  $\delta$  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 $\beta$ Me); *Z:E* ratio 3:1.  $^{13}$ C NMR (CDCl $_3$ ):  $\delta$  258.1 ( $\mu$ -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 $\beta$ ); 45.9, 41.9 (NMe); 21.2 (C $_6$ H $_4$ Me); 18.3, 18.1 (C $\beta$ Me).

**Synthesis of [Fe(Cp)(CO){C $_6$ N(Me)(R)C $\beta$ HC $_7$ (R)C(O)}-] (R = Me, R' = Bu $^n$ , **7a**; R = Xyl, R' = Me, **7b**; R = Xyl, R' = COOMe, **7c**; R = Xyl, R' = CM $_2$ 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 $_2$ ):  $\nu$ (CO) 1911

**Table 5. Crystal Data and Experimental Details for 4a·CH<sub>2</sub>Cl<sub>2</sub>, 4b, 5e, and 7b**

|   | 4a·CH <sub>2</sub> Cl <sub>2</sub>  | 4b  | 5e   | 7b  |
|---|---|---|--|---|
| formula                                       | C <sub>39</sub> H <sub>40</sub> Cl <sub>2</sub> Fe <sub>4</sub> N <sub>2</sub> O <sub>8</sub> | C <sub>36</sub> H <sub>38</sub> Fe <sub>4</sub> N <sub>2</sub> O <sub>4</sub> | C <sub>27</sub> H <sub>31</sub> Fe <sub>2</sub> NO <sub>2</sub> Si | C <sub>20</sub> H <sub>21</sub> FeNO <sub>2</sub> |
| fw  | 959.03  | 786.08  | 541.32   | 363.23  |
| T, 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                                   | P2 <sub>1</sub> /n  | P2 <sub>1</sub> /c  | Aba2   | P2 <sub>1</sub> /c                                |
| a, Å  | 18.032(4)   | 12.735(3)   | 9.920(2)   | 9.3991(19)  |
| b, Å  | 10.346(2)   | 27.480(6)   | 34.927(7)  | 19.964(4)   |
| c, 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 <sup>3</sup>                      | 3861.2(13)  | 3292.8(11)  | 5144.6(18)   | 1788.5(6)   |
| Z   | 4   | 4   | 8  | 4   |
| D <sub>c</sub> , g cm <sup>-3</sup>           | 1.650   | 1.586   | 1.398  | 1.349   |
| μ, mm <sup>-1</sup>                           | 1.667   | 1.770   | 1.198  | 0.854   |
| F(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> <sub>int</sub> = 0.0771)  | 5811 ( <i>R</i> <sub>int</sub> = 0.1083)                                      | 4551 ( <i>R</i> <sub>int</sub> = 0.0769)                           | 4625 ( <i>R</i> <sub>int</sub> = 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> <sup>2</sup>      | 1.062   | 1.054   | 1.050  | 0.963   |
| R1 ( <i>I</i> > 2σ( <i>I</i> ))               | 0.0502  | 0.0564  | 0.0478   | 0.0494  |
| wR2 (all data)                                | 0.1416  | 0.1398  | 0.1212   | 0.1452  |
| largest diff peak and hole, e Å <sup>-3</sup> | 2.190/−1.385  | 0.572/−0.629  | 0.514/−0.340   | 0.350/−0.519                                      |

(vs), ν(C<sub>α</sub>N) 1625 (w sh), ν(acyl) 1599 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.29 (s, 1 H, C<sub>β</sub>H); 4.48 (s, 5 H, Cp); 3.71, 3.49 (s, 6 H, NMe); 2.25 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>); 1.41 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.31 (m, 2 H, C<sub>γ</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 0.89 (t, <sup>3</sup>J<sub>HH</sub> = 7.32 Hz, CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 272.0 (C=O); 262.3 (C<sub>α</sub>); 221.9 (CO); 177.1 (C<sub>γ</sub>); 145.5 (C<sub>β</sub>); 84.8 (Cp); 51.4, 42.8 (NMe); 30.3, 27.0, 22.6 (CH<sub>2</sub>); 13.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

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 CH<sub>2</sub>Cl<sub>2</sub> solution layered with *n*-pentane, at −20 °C.

**7b.** Yield: 73%. Color: orange. Anal. Calcd for C<sub>20</sub>H<sub>21</sub>-FeNO<sub>2</sub>: C, 66.13; H, 5.83; N, 3.86. Found: C, 66.29; H, 5.74; N, 3.90. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 1916 (vs), ν(C<sub>α</sub>N) 1627 (m), ν(acyl) 1597 (s) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.27–7.16 (m, 3 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 6.54 (s, 1 H, C<sub>β</sub>H); 4.62 (s, 5 H, Cp); 3.82 (s, 3 H, NMe); 2.19, 2.10 (s, 6 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 1.70 (s, 3 H, C<sub>γ</sub>Me). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 270.7 (C=O); 266.2 (C<sub>α</sub>); 221.3 (CO); 173.2 (C<sub>γ</sub>); 148.0 (C<sub>β</sub>); 145.3 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 132.6, 132.1, 129.2, 128.8, 128.6 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 84.8 (Cp); 48.7 (NMe); 17.6, 17.4 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 13.1 (C<sub>γ</sub>Me). ESI-MS (ES<sup>+</sup>): *m/z* 363 [M<sup>+</sup>].

**7c.** Yield: 67%. Color: orange. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>-FeNO<sub>4</sub>: C, 61.94; H, 5.20; N, 3.44. Found: C, 62.01; H, 5.17; N, 3.45. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 1935 (vs), 1724 (s), ν(C<sub>α</sub>N) 1624 (m), ν(acyl) 1610 (ms) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.34–7.08 (m, 3 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 7.03 (s, 1 H, C<sub>β</sub>H); 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, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 267.5 (C<sub>α</sub>); 241.3 (C=O); 221.9 (CO); 164.2 (COOMe); 151.7 (C<sub>β</sub>); 145.1 (ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 132.3, 132.7, 129.5, 129.0, 128.7 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 85.3 (Cp); 52.0 (COOMe); 49.6 (NMe); 17.6, 17.4 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

**7d.** Yield: 88%. Color: brown. Anal. Calcd for C<sub>22</sub>H<sub>25</sub>-FeNO<sub>3</sub>: C, 61.94; H, 5.20; N, 3.44. Found: C, 62.00; H, 5.20; N, 3.32. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CO) 1926 (vs), ν(C<sub>α</sub>N) 1620 (m), ν(acyl) 1578 (ms) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.42, 6.47 (s, 1 H, C<sub>β</sub>); 7.29–7.16 (m, 3 H, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 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, Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 1.44, 1.43, 1.19, 1.18 (s, 6 H, CMe<sub>2</sub>OH); *E:Z* ratio 2:1. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 278.3, 276.8 (C=O); 265.7, 263.8 (C<sub>α</sub>); 223.8, 220.8 (CO); 177.5, 174.8 (C<sub>γ</sub>); 149.0, 144.9

(ipso-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 145.0, 143.5 (C<sub>β</sub>); 133.6, 133.0, 132.2, 131.8, 129.2, 129.1, 129.0, 128.9, 128.7, 128.1 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>); 85.4, 84.9 (Cp); 71.5, 71.1 (CMe<sub>2</sub>OH); 49.0, 44.6 (NMe); 29.8, 29.6, 28.9, 28.4 (CMe<sub>2</sub>OH); 18.3, 17.5, 17.2 (Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>).

**X-ray Crystallography.** Crystal data and collection details for **4a·CH<sub>2</sub>Cl<sub>2</sub>**, **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 Kα radiation. Data were corrected for Lorentz–polarization and absorption effects (empirical absorption correction SADABS).<sup>27</sup> Structures were solved by direct methods and refined by full-matrix least squares based on all data using *F*<sup>2</sup>.<sup>28</sup> 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).<sup>29</sup> Disorder was found for one Cp ligand in **4b** and **5e**, and the Xyl and the SiMe<sub>3</sub> 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·CH<sub>2</sub>Cl<sub>2</sub>**, **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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(27) Sheldrick, G. M. SADABS, program for empirical absorption correction; University of Göttingen, Göttingen, Germany, 1996.

(28) Sheldrick, G. M. SHELX97, program for crystal structure determination; University of Göttingen, Göttingen, Germany, 1997.

(29) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876.