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Diiron μ-Vinyliminium Complexes from Acetylene Insertion into a Metal−Aminocarbyne Bond

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The complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; R = Me, **1b**; R = CH_2Ph, **1c**; Xyl = 2,6-$Me_2C_6H_3$), containing a labile NCMe ligand, react under mild conditions with a variety of terminal alkynes $HC{\equiv}CR'$ (R′= $SiMe_3$, Me, Bu^n, Tol, Ph, H; Tol = 4-MeC_6H_4) to give the bridging vinyliminium complexes $[Fe_2\{\mu\text{-}\sigma{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Xyl, R′ = $SiMe_3$, **2a**; R = Me, R′ = $SiMe_3$, **2b**; R = CH_2Ph, R′ = $SiMe_3$, **2c**; R = Xyl, R′ = Me, **3a**; R = R′ = Me, **3b**; R = Xyl, R′ = Bu^n, **4**; R = Xyl, R′ = Tol, **5a**; R = Me, R′ = Tol, **5b**; R = CH_2Ph, R′ = Tol, **5c**; R = Xyl, R′ = Ph, **6**; R = Xyl, R′ = H, **7**). Insertion of the alkyne into the metal−carbyne carbon bond is regiospecific, resulting only in the product containing the R′ group on the carbon bound to Fe. Similarly, insertion of the disubstituted alkynes $R'C{\equiv}CR'$ (R′ = Me, Et) affords the analogous compounds $[Fe_2\{\mu\text{-}\sigma{:}\eta^3\text{-}C(R'){=}C(R')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Xyl, R′ = Me, **8a**; R = R′= Me, **8b**; R = CH_2Ph, R′ = Me, **8c**; R = Xyl, R′ = Et, **9a;** R = Me, R′ = Et, **9b**). The molecular structure of complex **2a** has been elucidated by an X-ray diffraction study.

Introduction

The reactions of alkynes with carbon-bridged dinuclear transition-metal complexes provide a facile pathway to C−C bond formation by insertion of the alkynes into the metal−μ-ligands. Examples include the photochemical reactions of μ-alkylidenes $[M_2(\mu\text{-}CHR)(\mu\text{-}CO)(CO)_2(Cp)_2]$ (M = Fe, Ru) with alkynes ($R'CCR''$), to give the μ-η^1:η^3-allyl $[M_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CR'CR''CHR)(\mu\text{-}CO)(CO)(Cp)_2]$[1] and the insertion into the metal−bridging carbonyl of $[M_2(\mu\text{-}CO)_2(CO)_2(Cp)_2]$ (M = Fe, Ru), affording the dimetallacyclopentenone $[M_2(\mu\text{-}\eta^1{:}\eta^3\text{-}CR'CR''CO)(\mu\text{-}CO)(CO)(Cp)_2]$.[2] Irradiation is required to promote CO dissociation and the π-coordination of the allyl ligand. Analogous reactions have been observed with the methylidene complex $[Fe_2(\mu\text{-}CH_2)(CO)_8]$[3] and the μ-ethenylidene $[Fe_2(\mu\text{-}C{=}CH_2)(\mu\text{-}CO)(CO)_2(Cp)_2]$.[4] Acetylenes (RCCR, R = Me, Ph) also insert into the cationic methylidyne complexes $[Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$, leading to the formation of the vinylketene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^4\text{-}CHC(R)C(R)CO\}(\mu\text{-}CO)(CO)(Cp)_2]^+$.[5]

As a part of our interest in C−C bond formation[6] and ongoing investigations on the reactivity of diiron μ-aminoalkylidyne complexes,[7] we have studied the reactions of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; R = Me, **1b**; R = CH_2Ph, **1c**; Xyl = 2,6-$Me_2C_6H_3$) with acetylenes. Here we report the regiospecific insertion of acetylenes into the metal−μ-carbon bond of **1**, yielding novel bridging vinyliminium diiron complexes.

Results and Discussion

The reactions of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (**1a**−**c**) with a variety of monosubstituted acetylenes ($HC{\equiv}CR'$; R′ = $SiMe_3$, Me, Bu^n, Tol, Ph, H) in CH_2Cl_2 solution heated at refluxing temperature for 4 h afford the complexes $[Fe_2\{\mu\text{-}\sigma{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**2**−**7**) (Scheme 1). Unlike the alkyne insertion reactions mentioned in the Introduction, which require photolytic

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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) 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. (c) Colburn, R. E.; Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1989**, 1799. (d) Knox, S. A. R. *J. Organomet. Chem.* **1990**, *400*, 255.

(2) (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 409. (b) Davies, D. L.; Dyke, A. F.; Knox, S. A. R.; Morris, M. J. *J. Organomet. Chem.* **1981**, *215*, C30−C32. (c) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982,** 1297. (d) Gracey, B. P.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1985**, 1935.

(3) Sumner, C. E.. Jr.; Collier, J. A.; Pettit, R. *Organometallics* **1982**, *1*, 1350.

(4) Casey, C. P.; Miles, W. H.; Fagan, P. J.; Haller, K. J. *Organometallics* **1985**, *4*, 559.

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

(6) (a) Bordoni, S.; Busetto, L.; Camiletti, C.; Zanotti, V.; Albano, V. G.; Monari, M.; Prestopino, F. *Organometallics* **1997**, *16*, 1224. (b) Albano, V. G.; Bordoni, S.; Busetto, L.; Camiletti, C.; Monari, M.; Palazzi, A.; Prestopino, F.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1997**, 4665. (c) Albano, V. G.; Busetto, L.; Camiletti, C.; Castellari, C.; Monari, M.; Zanotti, V. *J. Chem. Soc., Dalton Trans.* **1997**, 4671. (d) Albano, V. G.; Busetto, L.; Camiletti, C.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **1998,** *563* 153.

(7) (a) Albano, V. G.; Busetto, L.; Marchetti, F.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2002,** *649*, 64. (b) Albano, V. G.; Busetto, L.; Monari, M.; Zanotti, V. *J. Organomet. Chem.* **2000**, *606*, 163.

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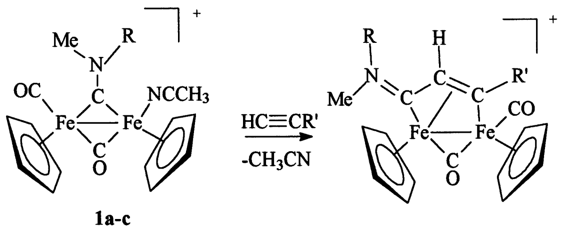
Scheme 1



1a-c

	R	R'
2a	Xyl	$SiMe_3$
2b	Me	$SiMe_3$
2c	CH_2Ph	$SiMe_3$
3a	Xyl	Me
3b	Me	Me
4	Xyl	Bu^n
5a	Xyl	Tol
5b	Me	Tol
5c	CH_2Ph	Tol
6	Xyl	Ph
7	Xyl	H

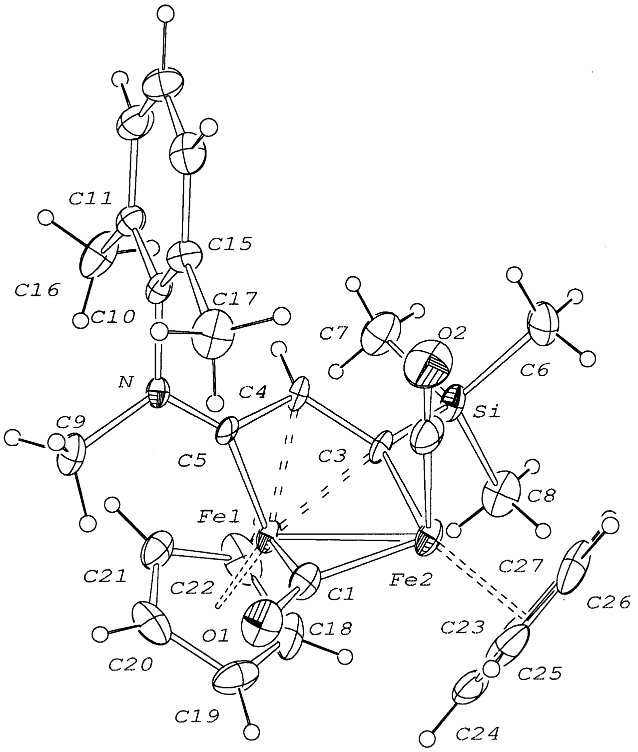


Figure 1. ORTEP drawing of the cation $[Fe_2\{\mu\text{-}\sigma\text{:}\eta^3\text{C-}(SiMe_3)=CHC=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ (**2a**) (thermal ellipsoids at the 30% probability level).

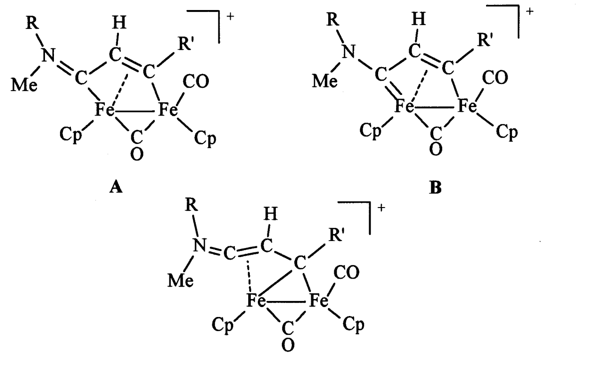


Figure 2.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $[Fe_2\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(SiMe_3)=CHC=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (2a)

Fe(1)−Fe(2)	2.557(1)	Fe(2)−C(2)	1.736(8)
Fe(1)−C(1)	1.976(7)	C(1)−O(1)	1.167(7)
Fe(2)−C(1)	1.878(7)	C(2)−O(2)	1.155(8)
Fe(1)−C(5)	1.844(6)	N−C(5)	1.320(7)
Fe(1)−C(3)	2.028(6)	N−C(9)	1.485(7)
Fe(2)−C(3)	1.970(6)	N−C(10)	1.426(7)
Fe(1)−C(4)	2.052(7)	Si−C(7)	1.885(7)
C(3)−C(4)	1.412(8)	Si−C(8)	1.871(7)
C(4)−C(5)	1.406(8)	Si−C(3)	1.905(6)
Si−C(6)	1.846(7)	Fe(2)−C(cp)(av)	2.126
Fe(1)−C(cp)(av)	2.109		
C(5)−N−C(10)	121.5(5)	C(10)−N−C(9)	118.5(5)
C(5)−N-C(9)	120.0(5)	N−C(5)−C(4)	134.7(6)
C(3)−C(4)−C(5)	117.9(6)	Fe(2)−C(3)−C(4)	119.4(5)
Fe(1)−C(5)−C(4)	77.0(4)		

conditions, the syntheses of **2**−**7** are readily accomplished under mild thermal conditions. A possible explanation is that the insertion requires as an initial step alkyne coordination, which is more easily accomplished by removing the labile MeCN rather than a CO ligand.

Compounds **2**−**7** have been obtained in good yields (60−85%) as their $[SO_3CF_3]^-$ salts after purification by column chromatography on alumina and characterized by spectroscopy and elemental analyses. Compounds **3a**,**b** and **7**, whose synthesis requires the use of volatile alkynes, are better prepared from the chloride complexes $[Fe_2(\mu\text{-}CN(Me)(R)(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$ (R = Xyl, Me) treated with $AgSO_3CF_3$ in the presence of the appropriate alkyne.

The complex $[Fe_2\{\mu\text{-}\sigma\text{:}\eta^3\text{-}C(SiMe_3)=CHC=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**2a**) has been structurally characterized by X-ray diffraction. The molecular diagram of the cation is shown in Figure 1, and relevant bond lengths and angles are reported in Table 1. The stereogeometry can be conveniently described with reference to two moieties: the preexisting core and the new C_3 ligand. The more conventional part comprises the (Cp)Fe(μ-CO)Fe(Cp)(CO) unit, whose cis stereogeometry is that expected from the structure of the precursor $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2]^+$ (**1a**). The $C(SiMe_3)CHCN(Me)(Xyl)$ ligand generated by insertion of the alkyne $HC\equiv CSiMe_3$ into the Fe−C bond of the bridging aminocarbyne ligand μ-CN(Me)(Xyl) is attached to the diiron core in a multiply bridging $\mu\text{-}\sigma\text{:}\eta^3$ fashion. Bond distances and spectroscopic features (see below) indicate that, to adequately describe the bonding of the multiply bridging ligand, at least three resonance forms have to be invoked (Figure 2), as has been done for the similar complexes $[Fe_2\{\mu\text{-}C(R')=C(R'')C=O\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′, R″ = Ph, H, Me).[2c] Two Fe−C(sp^2) interactions are present: Fe(1)−C(5) (1.844(6) Å) and Fe(2)−C(3) (1.970(6) Å). These figures indicate an almost pure σ bond for the latter and some double bond nature for the former (Figure 2, resonance form **B**). In the C(3)−C(4)−C(5)−N sequence C(5)−N (1.320(7) Å) has the character of a double bond. Lack of conjugation of C(5)−N with the C(5)−C(4)−C(3) chain can be assumed because of the significant twisting between the N(Me)(Xyl) unit and C(3)−C(4)−C(5) (42.6(7)°). C(3)−C(4) and C(4)−C(5), on the other hand, are almost identical (1.412(8) and 1.406-

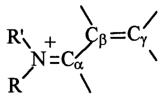


Figure 3.

(8) Å, respectively) and reveal extensive π bond delocalization. On the basis of the geometric evidence the electronic structure of this region of the molecule can be described in two alternative ways: (i) the similarity of the C(3)−C(4)−C(5) distances points to the presence of an allyl unit (Figure 2, forms **A** and **C**) and (ii) the nonequivalence of the Fe−C interactions, with Fe(1)−C(5) shorter (1.844(6) Å) and Fe(1)−C(4,3) longer and almost equivalent (2.028(6) and 2.052(7) Å, respectively), makes the description as a vinyliminium group appropriate (Figure 2, form **A**).

Vinyliminium ligands, otherwise indicated as azoniabutadienyls (Figure 3), have been previously reported. They have been found in a variety of coordinative situations, i.e. σ-coordinated through the iminium carbon (C_α) in $[RuCp\{C({=}NR'R'')CH{=}CPh_2\}(CO)(PPr^i_3)][BF_4]$ ($R' = R'' =$ Et, $R' =$ H, $R'' =$ Ph, Pr^i)[8] and $[Re\{C({=}NHR)CH{=}CPh_2\}(CO)_2(triphos)][SO_3CF_3]$ (R = H, Ph, $CH_2{-}C{\equiv}CH$),[9] η^2-coordinated by the vinyl end as in $[Tp'(CO)_2Mo\{\eta^2\text{-}C(Ph){=}C(H)C(H){=}N(Me)(Bu^t)\}][BF_4]$[10] (Tp′ = hydridotris(pyrazolyl)borate), and coordinated via both C_α and C_γ in the iminium metallacyclobutene complexes $[Mo\{C(Ph){=}C(Ph)C{=}N(H)(Xyl)\}(CNXyl)_3Cp^*][BF_4]_2$.[11] Examples of bridging coordination are $[HRu_3(\mu_3\text{-}\eta^3\text{-}Et_2NCCHCMe)(CO)_8(PPh_3)]$[12] and two isomers of $[Ru_3H\{C(Me)CC(H)NMe_2\}(CO)_9]$.[13] The bond distances in the C−C−C fragment of these ligands show significant variations, depending on their coordination modes, but the $-C{=}NR_2$ terminal unit always exhibits an almost localized double bond and therefore a formal positive charge at the nitrogen atom, as in **2a**.

Complexes **2**−**7** exhibit, in their infrared spectra in CH_2Cl_2 solution, two absorptions due to the terminal and bridging carbonyls (e.g. for **2a** at 2001 and 1813 cm^{-1}, respectively). In addition, a ν(CN) band around 1630 cm^{-1} accounts for the double-bond character of the $C_\alpha{-}N$ interaction. Analogous absorptions have been observed for the propyneiminium ligand ($C_4H_8N{=}C(Me){-}C{\equiv}CMe$) coordinated to a dicobalt hexacarbonyl fragment.[14]

A downfield-shifted ^{13}C carbon resonance (e.g. at 231.2 ppm for **2a**) is assigned to C_α (C(5) in Figure 1). Similar resonances have been attributed to the α-carbon of the azoniabutadienyl ligand in the complexes $[RuCp\{C({=}NR'R'')CH{=}CPh_2\}(CO)(PPr^i_3)][BF_4]$.[9] The signals fall at lower field than expected for an iminium carbon[15] and are closer to the range typical for an aminocarbene carbon,[16] suggesting a contribution of the carbene resonance form **B,** in accord with the structural evidence (vide supra). The other two carbons of the $N{-}C_\alpha{-}C_\beta{-}C_\gamma$ chain, originating from the inserted alkyne (corresponding to C(3) and C(4) in Figure 1), show large shift differences (e.g. for **2a** signals are observed at 207.3 and 56.3 ppm). The high-field resonance is attributable to C_β and is typical for a coordinated olefinic carbon, whereas the low-field signal reveals the alkylidene character of C_γ (C(3) in Figure 1). The assignments of C_β and C_γ resonances, in the ^{13}C NMR spectra of **2**−**6**, have been fully confirmed by DEPT experiments.

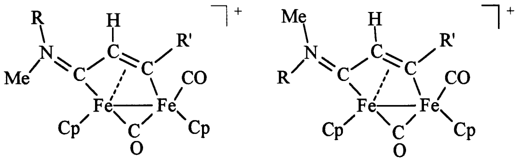


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Figure 4. Isomeric forms for **3a** (R = Xyl, R′ = Me), **5a** (R = Xyl, R′ = Tol), **6** (R = Xyl, R′ = Ph), **7** (R = Xyl, R′ = H), **2c** (R = CH_2Ph, R′= $SiMe_3$), and **5c** (R = CH_2Ph, R′ = Tol).

The insertion of a monosubstituted acetylene into the metal−carbon bond should, in principle, generate two isomeric forms, as a result of the head-to-head or head-to-tail insertion modes. However, the NMR spectra of complexes **2a**,**b**, **3b**, **4**, and **5b** show the presence, in solution, of just one isomer. The NMR data of **2a** are consistent with the geometry shown in the solid-state structure. The CH portion of the inserted $HC{\equiv}CSiMe_3$ generates a ^1H NMR resonance at 4.30 ppm, which is in the range expected for $C_\beta{-}H$. [2] The alternative isomer would present a C_γ −H proton whose resonance is expected to be in the typical low-field range of methylidene protons, at about 11 ppm. An explanation of the exclusive binding of the unsubstituted acetylenic carbon (C(4) in Figure 1) to the aminocarbene carbon (C(5)) is in terms of steric hindrance of both aminocarbene and acetylenic substituents.

Like **2a,** the complexes **2**−**6** exhibit a resonance at about 4−5 ppm, attributable to $C_\beta{-}H$, whereas no signal is observed around 11 ppm, indicating that the insertions are regiospecific. This point is clearly illustrated by the ^1H NMR of $[Fe_2\{\mu\text{-}C(H){=}CHC{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**7**), obtained by acetylene insertion, where both $C_\gamma{-}H$ and $C_\beta{-}H$ are present. Their resonances are observed at 12.73, 12.57 and 5.49, 4.59 ppm, respectively. Two doublets, of similar intensity for each hydrogen of the inserted acetylene, indicate the presence of two isomers in comparable amounts. These isomeric forms could be attributed to different orientations of the Me and Xyl groups in the iminium moiety (isomers **I** and **II** in Figure 4). Restricted rotation around the C=N(iminium) bond does not allow interconversion of **I** and **II**.

Two isomeric forms are also observed for the complexes **2c**, **3a**, **5a**,**c**, and **6** and are similarly attributed

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[8] Bernard, D. J.; Esteruelas, M. A.; Lopez, A. M.; Modrego, J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4995.

[9] Mantovani, N.; Marvelli, L.; Rossi, R.; Bertolasi, V.; Bianchini, C.; de los Rios, I.; Peruzzini, M. *Organometallics* **2002** *21*, 2382.

[10] Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 693.

[11] Adams, C. J.; Anderson, K. M.; Bartlett, I. M.; Connelly, N. G.; Orpen, A. G.; Paget, T. J.; Phetmung, H.; Smith, D. W. *J. Chem. Soc., Dalton Trans.* **2001**, 1284.

[12] Churchill, M. R.; Lake, C. H.; Lashewycz-Rubycz, R. A.; Yao, H.; McCargar, R. D.; Keister, J. B. *J. Organomet. Chem.* **1993**, *452*, 151.

[13] Aime, S.; Osella, D.; Deeming, A. J.; Arce, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1459.

[14] Maas, G.; Rahm, R.; Mayer, D.; Baumann, W. *Organometallics* **1995**, *14*, 1061.

[15] Rabiller, C.; Renou, J. P.; Martin, G. J. *J. Chem. Soc., Perkin Trans.* **1977**, *2*, 536.

[16] 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.

to the different orientations of the nitrogen substituents. Support for this explanation is the observation that complexes **2b**, **3b**, and **5b,** containing the $\mathrm{NMe_2}$ group in place of the unsymmetrically substituted N(Me)(Xyl) or $\mathrm{N(Me)(CH_2Ph)}$, consist of a single isomer. Alternative explanations based upon the cis–trans arrangements of the Cp ligands appear less realistic, in view of the predominance of the cis stereogeometry and the structural data described above.

Complexes containing the N(Me)(Xyl) group are predominantly (**3a**, **5a**, **6**, **7**) or exclusively (**2a, 4**) one isomer, indicating that one of the two orientations of the N substituents (**I** and **II**) is largely preferred. Presumably, the favored isomer is the one found in the solid state for **2a** (Figure 1), corresponding to **I** (Figure 4), with the Xyl group far from the Cp ligand, to minimize contacts. The isomers show distinct ^{1}H NMR signals; in particular, resonances due to N–Me and to C_β–H differ significatively for **I** and **II**. The N–Me resonance of the predominant isomers falls in the range 3.8–4.3 ppm, whereas the corresponding signal of the minor isomers is shifted about 0.7 ppm upfield (3.1–3.6 ppm). Likewise, the C_β–H resonance is shifted about 1 ppm upfield for the major isomers. Assuming that the structure of **2a** is that found in the crystal (isomer **I**), a comparison of its NMR data with those of the more abundant isomers of **3a**, **5a**, **6**, and **7** suggests that also the latter have structures of type **I**.

Alkyne insertions are not limited to monosubstituted acetylenes: 2-butyne and 3-hexyne also insert into the metal–carbyne bond of **1a**–**c**, yielding the complexes $[\mathrm{Fe_2}\{\mu\text{-}\sigma{:}\eta^3\text{-C(R')=C(R')C=N(Me)(R)}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cp})_2]$-$[\mathrm{SO_3CF_3}]$ (R = Xyl, R′ = Me, **8a**; R = R′= Me, **8b**; R = $\mathrm{CH_2Ph}$, R′ = Me, **8c**; R = Xyl, R′ = Et, **9a**; R = Me, R′ = Et, **9b**). However, yields are very low, due to the volatility of 2-butyne and the higher steric demand of the disubstituted acetylenes. As for **3a**,**b** and **7**, better yields (65–80%) have been obtained by reacting acetylenes with the chloride complexes $[\mathrm{Fe_2}\{\mu\text{-CN(Me)(R)}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cl})(\mathrm{Cp_2})]$ (R = Xyl, Me, $\mathrm{CH_2Ph}$) treated in situ with $\mathrm{AgSO_3CF_3}$.

Complexes **8a**,**b** and **9a**,**b** exhibit, in their NMR spectra, the presence of a single isomer. In contrast, **8c** exhibits two isomers, which are again attributable to the different orientations of the nitrogen substituents. These isomeric species are present in comparable amounts, as found in the vinyliminium complexes **2c** and **5c**, which contain the $\mathrm{N(Me)CH_2Ph}$ group. The spectroscopic properties of **8a**–**c** and **9a**,**b** are similar to those of the complexes obtained by insertion of monosubstituted acetylenes. C_α, C_β, and C_γ resonances, in the ^{13}C NMR spectra, fall in the expected range (e.g. for **8b** at 224.8, 65.9, and 200.7 ppm, respectively).

Further studies on the insertion reactions of mono- and disubstituted acetylenes are in progress to gain a better understanding of the insertion mechanism, stereochemistry, and reactivity of the vinyliminium complexes.

Experimental Section

General Data. All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin-Elmer 983-G spectrophotometer and ^{1}H and ^{13}C NMR spectra on a Varian Gemini 300. Unless otherwise stated, NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. All the reagents were commercial products (Aldrich) of the highest purity available and were used as received. $[\mathrm{Fe_2(CO)_4(Cp)_2}]$ was purchased from Strem and used as received. The compounds $[\mathrm{Fe_2}\{\mu\text{-CN(Me)R}\}$-$(\mu\text{-CO})(\mathrm{CO})_2(\mathrm{Cp})_2]\mathrm{SO_3CF_3}$ (R = 2,6-$\mathrm{Me_2C_6H_3}$, Me, $\mathrm{CH_2Ph}$)[17] and their derivatives $[\mathrm{Fe_2}\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{NCMe})(\mathrm{Cp})_2]$-$[\mathrm{SO_3CF_3}]$ and $[\mathrm{Fe_2}\{\mu\text{-CN(Me)R}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cl})(\mathrm{Cp})_2]$[7b] were prepared as described in the literature.

Synthesis of $[\mathrm{Fe_2}\{\mu\text{-}\sigma{:}\eta^3\text{-C(SiMe}_3\text{)=CHC=N(Me)(R)}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cp})_2][\mathrm{SO_3CF_3}]$ (R = Xyl, 2a; R = Me, 2b; R = $\mathrm{CH_2Ph}$, 2c). Compound **1a** (507 mg, 0.80 mmol) and $\mathrm{HCCSiMe_3}$ (118 mg, 1.2 mmol) in $\mathrm{CH_2Cl_2}$ solution (20 mL) were heated at reflux temperature for 4 h. Then the solvent was removed under reduced pressure and the residue filtered on an alumina pad with a mixture of MeCN and THF (1:1) as eluent. Crystallization at −20 °C from THF solution layered with diethyl ether gave dark brown crystals of **2a** (487 mg, 88%). Anal. Calcd for $\mathrm{C_{28}H_{32}Fe_2F_3NO_5SSi}$: C, 48.64; H, 4.66. Found: C, 48.59; H 4.55. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 2001 (vs), 1813 (s); ν(CN) 1631 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.21–6.92 (m, 3 H, $\mathrm{Me_2C_6}H_3$); 5.44, 5.20 (s, 10 H, Cp); 4.30 (s, 1 H, C_βH); 4.25 (s, 3 H, NMe); 2.27, 1.77 (s, 6 H, $Me_2\mathrm{C_6H_3}$); 0.55 (s, 9 H, $\mathrm{SiMe_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 254.0 (μ-CO); 231.2 (C_α); 209.4 (CO); 207.3 (C_γ); 145.0 (ipso $\mathrm{Me_2C_6H_3}$); 131.4, 131.1, 129.5, 129.4, 129.3 ($\mathrm{Me_2}C_6\mathrm{H_3}$); 90.0, 87.0 (Cp); 56.3 (C_β); 45.8 (NMe); 17.9, 17.2 ($Me_2\mathrm{C_6H_3}$); 2.6 ($\mathrm{SiMe_3}$).

Complexes **2b**,**c** have been obtained by the same procedure described for the synthesis of **2a** by reacting $\mathrm{HCCSiMe_3}$ with **1b**,**c**, respectively.

2b. Yield: 72%. Anal. Calcd for $\mathrm{C_{21}H_{26}Fe_2F_3NO_5SSi}$: C, 41.95; H, 4.36. Found: C, 41.98; H, 4.40. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1990 (vs), 1807 (s); ν(CN) 1685 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 5.21, 4.93 (s, 10 H, Cp); 5.21 (s, 1H, C_βH); 3.77, 3.17 (s, 6H, NMe); 0.54 (s, 9 H, $\mathrm{SiMe_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 256.2 (μ-CO); 224.5 (C_α); 209.4 (CO); 202.7 (C_γ); 88.9, 86.2 (Cp); 56.2 (C_β); 51.1, 44.0 (NMe); 2.58 ($\mathrm{SiMe_3}$).

2c. Yield: 88%. Anal. Calcd for $\mathrm{C_{27}H_{30}Fe_2F_3NO_5SSi}$: C, 47.88; H, 4.46. Found: C, 47.67; H, 4.55. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 1990 (vs), 1806 (s); ν(CN) 1663 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.46–7.07 (m, 5 H, $\mathrm{C_6H_5}$); *5.67*, 4.91, 4.59, *5.41* (d, 2 H, $^2J_{\mathrm{HH}}$ = 14 Hz, $\mathrm{C}H_2\mathrm{Ph}$); *5.30*, 5.28, *5.08*, 5.06 (s, 10 H, Cp); *5.20*, 4.85 (s, 1 H, C_βH); 3.77, *3.06* (s, 3 H, N–Me); *0.67*, 0.61 (s, 9 H, $\mathrm{SiMe_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ *257.5*, 256.0 (μ-CO); 225.2, *225.1* (C_α); 209.8, *209.5* (CO); *204.4*, 203.7 (C_γ); 132.1–128.9 (Ph); 89.2, 86.6 (Cp); 67.5, *61.0* ($C\mathrm{H_2Ph}$); *56.6*, 56.0 (C_β); *47.9*, 42.2 (NMe); *2.8*, 2.7 ($\mathrm{SiMe_3}$).

Synthesis of $[\mathrm{Fe_2}\{\mu\text{-}\sigma{:}\eta^3\text{-C(Me)=CHC=N(Me)(R)}\}(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cp})_2][\mathrm{SO_3CF_3}]$ (R = Xyl, 3a; R = Me, 3b). An excess of HC≡CMe was bubbled through a solution of $[\mathrm{Fe_2}(\mu\text{-CN(Me)(Xyl)})(\mu\text{-CO})(\mathrm{CO})(\mathrm{Cl})(\mathrm{Cp})_2]$ (140 mg, 0.30 mmol) in $\mathrm{CH_2Cl_2}$ (15 mL), and then $\mathrm{AgSO_3CF_3}$ (108 mg, 0.42 mmol) was added. The mixture, which immediately became green, was stirred for 10 min; then it was filtered through an alumina pad. Elution with MeCN and crystallization from a $\mathrm{CH_2Cl_2}$–$\mathrm{Et_2O}$ mixture gave **3a** (52 mg, 56%). Anal. Calcd for $\mathrm{C_{26}H_{26}Fe_2F_3NO_5S}$: C, 49.31; H, 4.14. Found: C, 49.30; H, 4.18. IR ($\mathrm{CH_2Cl_2}$): ν(CO) 2000 (vs), 1815 (s); ν(CN) 1632 (m) $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.42–6.91 (m, 3 H, $\mathrm{Me_2C_6}H_3$); 5.39, *5.28*, 5.16, *4.72* (s, 10 H, Cp); *5.23*, 3.99 (s, 1 H, C_βH); 4.16, *3.48* (s, 3 H, NMe); *3.99*, 3.82 (s, 3 H, CγMe); *2.53*, 2.28, *1.96*, 1.75 (s, 6 H, $Me_2\mathrm{C_6H_3}$); isomer ratio 2:1. ^{13}C NMR ($\mathrm{CDCl_3}$): δ 254.6 (μ-CO); 233.4, *230.9* (C_α); *211.6*, 211.4 (C_γ); 210.6, *209.7* (CO); 144.8, *141.1* (ipso Ph); 134.0–129.0 (Ph); 91.0, *90.7*, 87.8, *87.6* (Cp);

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[17] (a) Cox, G.; Dowling, C.; Manning, A. R.; McArdle, P.; Cunningham, D. *J. Organomet. Chem.* **1992**, *438*, 143. (b) Boss, K.; Dowling, C.; Manning, A. R. *J. Organomet. Chem.* **1996**, *509*, 19.

53.5, 52.7 (C$_\beta$); *52.1*, 46.0 (NMe); 42.7, *42.3* (Cγ-*Me*); *17.9*, 17.8, *17.7*, 17.2 (*Me*$_2$C$_6$H$_3$).

Compound **3b** was obtained by reaction of [Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)(Cl)(Cp)$_2$] with HCCMe as described for the synthesis of **3a**.

3b. Yield: 72%. Anal. Calcd for C$_{19}$H$_{20}$Fe$_2$F$_3$NO$_5$S: C, 42.02; H, 3.71. Found: C, 39.95; H, 3.67. IR (CH$_2$Cl$_2$): ν(CO) 1990 (vs), 1806 (s); ν(CN) 1684 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.16, 4.99 (s, 10 H, Cp); 4.73 (s, 1 H, C$_\beta$H); 3.86, 3.84 (s, 6 H, NMe and C$_\gamma$Me); 3.29 (s, 3 H, NMe).

Synthesis of [Fe$_2${μ-σ:η^3-C(Bu^n)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (4). Complex **4** has been obtained by following the same procedure described for the synthesis of **2a** by reacting **1a** with HCCBu^n. Yield: 71%. Anal. Calcd for C$_{29}$H$_{32}$Fe$_2$F$_3$NO$_5$S: C, 51.58; H, 4.78. Found: C, 51.90; H, 4.82. IR (CH$_2$Cl$_2$): ν(CO) 2001 (vs), 1815 (s); ν(CN) 1634 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.37–6.91 (m, 3 H, Me$_2$C$_6$*H*$_3$); 5.36, 5.15 (s, 10 H, Cp); 4.17 (s, 3 H, NMe); 3.88 (s,1 H, C$_\beta$H); 3.70 (m, 2 H, C$_\gamma$C*H*$_2$CH$_2$CH$_2$CH$_3$); 2.26, 1.73 (s, 6 H, *Me*$_2$C$_6$H$_3$); 1.90 (m, 2 H, CγCH$_2$C*H*$_2$CH$_2$CH$_3$); 1.59 (m, 2 H, CγCH$_2$CH$_2$C*H*$_2$CH$_3$); 1.01 (t, $^3J_{\mathrm{HH}}$ = 7 Hz, 3 H, CγCH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 254.8 (μ-CO); 233.1 (C$_\alpha$); 217.3 (C$_\gamma$); 209.6 (CO); 144.8 (ipso Me$_2$*C*$_6$H$_3$); 131.5, 130.9, 129.4, 129.2 (Me$_2$*C*$_6$H$_3$); 90.7, 87.8 (Cp); 55.6 (C$_\gamma$*C*H$_2$); 51.1 (C$_\beta$); 46.0 (NMe); 37.9 (C$_\gamma$CH$_2$*C*H$_2$CH$_2$CH$_3$); 22.7 (C$_\gamma$CH$_2$CH$_2$*C*H$_2$CH$_3$); 17.9, 17.0 (*Me*$_2$C$_6$H$_3$); 14.0 (CγCH$_2$CH$_2$CH$_2$*C*H$_3$).

Synthesis of [Fe$_2${μ-σ:η^3-C(Tol)=CHC=N(Me)(R)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (R = Xyl, 5a; R = Me, 5b; R = CH$_2$Ph, 5c). Complexes **5a**–**c** have been obtained by the same procedure described for the synthesis of **2a**–**c** by reacting HCCTol with **1a**–**c**, respectively.

5a. Yield: 69%. Anal. Calcd for C$_{32}$H$_{30}$Fe$_2$F$_3$NO$_5$S: C, 54.18; H, 4.26. Found: C, 54.09; H, 4.35. IR (CH$_2$Cl$_2$): ν(CO) 2002 (vs), 1818 (s); ν(CN) 1630 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.62–6.93 (m, 7 H, Me$_2$C$_6$*H*$_3$ and MeC$_6$*H*$_4$); 5.34, 5.15, *5.09*, *4.85* (s, 10 H, Cp); *4.92*, 3.90 (s, 1 H, C$_\beta$H); 4.25, *3.58* (s, 3 H, N–Me); *2.51*, 2.20, *2.00*, 1.79 (6 H, s, *Me*$_2$C$_6$H$_3$); *2.45*, 2.42 (s, 3 H, *Me*C$_6$H$_4$); isomer ratio 3:1. ^{13}C NMR (CDCl$_3$): δ 253.5 (μ-CO); 232.2, *230.6* (C$_\alpha$); *210.4*, 209.7 (CO); 208.1, *207.6* (C$_\gamma$); 153.1, 145.1 (ipso Me$_2$*C*$_6$H$_3$ and Me*C*$_6$H$_4$); 137.4–126.4 (Me$_2$C$_6$H$_3$ and MeC$_6$H$_4$); 92.2, *92.1*, 88.0, *87.8* (Cp); 53.5, *53.4* (C$_\beta$); *52.4*, 45.9 (NMe); *21.2*, 21.1, (*Me*C$_6$H$_4$); *17.9*, 17.8, 17.2 (*Me*$_2$C$_6$H$_3$).

5b. Yield: 84%. Anal. Calcd for C$_{25}$H$_{24}$Fe$_2$F$_3$NO$_5$S: C, 45.49; H, 3.91. Found: C, 45.60; H, 3.94. IR (CH$_2$Cl$_2$): ν(CO) 1992 (vs), 1807 (s); ν(CN) 1684 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48, 7.34 (d, 2 H, $^3J_{\mathrm{HH}}$ = 6 Hz, C$_6$H$_4$); 5.21, 4.97 (s, 10 H, Cp); 4.68 (s, 1 H, C$_\beta$H); 3.96, 3.41 (s, 6H, NMe); 2.50 (s, 3 H, *Me*C$_6$H$_4$). ^{13}C NMR (CDCl$_3$): δ 257.2 (μ-CO); 225.3 (C$_\alpha$); 209.9 (CO); 204.6 (C$_\gamma$); 153.3 (ipso C$_6$H$_4$); 137.5, 129.4, 127.1 (C$_6$H$_4$); 91.1, 87.7 (Cp); 52.5 (C$_\beta$); 51.6, 44.5 (NMe); 21.0 (*Me*C$_6$H$_4$).

5c. Yield: 91%. Anal. Calcd for C$_{31}$H$_{28}$Fe$_2$F$_3$NO$_5$S: C, 53.55; H, 4.06. Found: C, 54.04; H, 4.20. IR (CH$_2$Cl$_2$): ν(CO) 1991 (vs), 1807 (s); ν(CN) 1667 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.52–7.10 (m, 9 H, C$_6$H$_5$ and MeC$_6$*H*$_4$); 5.69, 5.44, *4.91*, *4.65* (d, 2 H, $^2J_{\mathrm{HH}}$ = 14 Hz, C*H*$_2$Ph); 5.21, *5.20*, 5.02, *5.00* (s, 10 H, Cp); 4.70, *4.48*, (s, 1 H, C$_\beta$H); *3.81*, 3.10 (s, 3 H, N–Me); 2.45 (s, 3 H, *Me*C$_6$H$_4$); isomer ratio 6:5. ^{13}C NMR (CDCl$_3$): δ 258.2 (μ-CO); *225.5*, 225.2 (C$_\alpha$); *209.9*, 209.7 (CO); 205.7, *205.3* (C$_\gamma$); 153.3–126.9 (Ph); *91.4*, 91.3, 87.9 (Cp); *68.3*, 61.5 (*C*H$_2$Ph); *52.7*, 52.5 (C$_\beta$); 48.2, *42.5* (NMe); 21.1 (*Me*C$_6$H$_4$).

Synthesis of [Fe$_2${μ-σ:η^3-C(Ph)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (6). Complex **6** has been obtained by the same procedure described for the synthesis of **2a** by reacting **1a** with HCCPh. Yield: 67%. Anal. Calcd for C$_{31}$H$_{28}$Fe$_2$F$_3$NO$_5$S: C, 53.55; H, 4.06. Found: C, 53.58; H, 4.00. IR (CH$_2$Cl$_2$): ν(CO) 2003 (vs), 1819 (s); ν(CN) 1629 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.71–6.96 (m, 8 H, Me$_2$C$_6$*H*$_3$ and C$_6$*H*$_5$); 5.37, 5.14, *5.08*, *4.88* (s, 10 H, Cp); *4.97*, 3.94 (s, 1 H, C$_\beta$H); 4.25, *3.58* (s, 3 H, N–Me); *2.51*, *2.01*, 2.20, 1.79 (6 H, s, *Me*$_2$C$_6$H$_3$); isomer ratio 3:1. ^{13}C NMR (CDCl$_3$): δ 253.2 (μ-CO); 231.9, *230.4* (C$_\alpha$); *210.3*, 209.6 (CO); 207.6, *207.1* (C$_\gamma$); *155.8*, 155.6, 145.1, *140.8* (ipso C$_6$H$_5$ and ipso Me$_2$C$_6$H$_3$); 134.9–126.4 (*C*$_6$H$_3$Me$_2$ and *C*$_6$H$_4$Me); 92.2, *92.1*, 88.0, *87.9* (Cp); 53.6, *53.4* (C$_\beta$); *52.5*, 45.9 (NMe); *18.7*, 18.0, *17.9*, 17.2 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe$_2${μ-σ:η^3-C(H)=CHC=N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (7). Complex **7** has been obtained by the same procedure described for the synthesis of **2a** by treating **1a** with AgSO$_3$CF$_3$ in the presence of HCCH. Yield: 61%. Anal. Calcd for C$_{25}$H$_{24}$Fe$_2$F$_3$NO$_5$S: C, 48.49; H, 3.91. Found: C, 48.47; H, 3.92. IR (CH$_2$Cl$_2$): ν(CO) 2005 (vs), 1820 (s); ν(CN) 1628 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ *12.73*, 12.57 (d, 1 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, C$_\gamma$H); 7.44–6.92 (m, 3 H, Me$_2$C$_6$*H*$_3$); *5.49*, 4.59 (d, 1 H, $^3J_{\mathrm{HH}}$ = 7.1 Hz, C$_\beta$H); 5.43, *5.36*, *4.74*, 5.16 (s, 10 H, Cp); 4.15, *3.50* (NMe); *2.51*, 2.28, 1.71, *1.93* (*Me*$_2$C$_6$H$_3$); isomer ratio 6:5. ^{13}C NMR (CDCl$_3$): δ *253.3*, 253.2 (μ-CO); *233.9*, 232.1 (C$_\alpha$); 209.7, *208.9* (CO); *189.1*, 188.0 (C$_\gamma$); 144.7, *141.2* (ipso Me$_2$*C*$_6$H$_3$); 133.6–129.0 (Me$_2$*C*$_6$H$_3$); *90.1*, 89.9, *87.0*, 86.5 (Cp); *53.2*, 52.2 (C$_\beta$); *52.1*, 46.1 (NMe); *17.9*, 17.7, *17.5*, 16.9 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe$_2${μ-σ:η^3-C(Me)=C(Me)C=N(Me)(R)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (R = Xyl, 8a; R = Me, 8b; R = CH$_2$Ph, 8c). Complexes **8a**,**b** have been obtained by the same procedure described for the synthesis of **3a**,**b** by reacting 2-butyne with [Fe$_2$(μ-CN(Me)(R))(μ-CO)(CO)(Cl)(Cp)$_2$] (R = Xyl, Me, CH$_2$Ph, respectively).

8a. Yield: 80%. Anal. Calcd for C$_{27}$H$_{28}$Fe$_2$F$_3$NO$_5$S: C, 50.10; H, 4.36. Found: C, 50.16; H, 4.33. IR (CH$_2$Cl$_2$): ν(CO) 1986 (vs), 1826 (s); ν(CN) 1608 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48–6.91 (m, 3 H, Me$_2$C$_6$*H*$_3$); 4.73, 4.47 (s, 10 H, Cp); 3.91, (s, 3 H, C$_\gamma$Me); 3.61 (s, 3 H, NMe); 2.48 (s, 3 H, *Me*$_2$C$_6$H$_3$); 2.15, 2.08 (s, 6 H, *Me*$_2$C$_6$H$_3$ and C$_\beta$Me). ^{13}C NMR (CDCl$_3$): δ 251.4 (μ-CO); 230.0 (C$_\alpha$); 208.8 (CO); 204.4 (C$_\gamma$); 141.8 (ipso Me$_2$*C*$_6$H$_3$); 133.9–128.9 (Me$_2$*C*$_6$H$_3$); 89.4, 88.4 (Cp); 69.4 (C$_\beta$); 49.9 (NMe); 37.9 (C$_\gamma$Me); 18.1, 17.8 (*Me*$_2$C$_6$H$_3$); 16.5 (C$_\beta$Me).

8b. Yield: 73%. Anal. Calcd for C$_{20}$H$_{22}$Fe$_2$F$_3$NO$_5$S: C, 43.12; H, 3.98. Found: C, 43.12; H, 4.02. IR (CH$_2$Cl$_2$): ν(CO) 1987 (vs), 1806 (s); ν(CN) 1665 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.18, 4.94 (s, 10 H, Cp); 3.87, 3.77, 3.17 (s, 9H, NMe + C$_\beta$Me); 1.94 (s, 3 H, C$_\beta$Me). ^{13}C NMR (CDCl$_3$): δ 257.7 (μ-CO); 224.8 (C$_\alpha$); 210.0 (CO); 200.7 (C$_\gamma$); 90.3, 88.1 (Cp); 65.9 (C$_\beta$); 49.1, 45.1 (NMe); 37.1 (C$_\gamma$*Me*); 15.4 (C$_\beta$*Me*).

8c. Yield: 84%. Anal. Calcd for C$_{26}$H$_{26}$Fe$_2$F$_3$NO$_5$S: C, 49.31; H, 4.14. Found: C, 49.25; H, 4.24. IR (CH$_2$Cl$_2$): ν(CO) 1987 (vs), 1806 (s); ν(CN) 1653 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.45–7.08 (m, 5 H, C$_6$H$_5$); *5.27*, 5.26, 4.98, *4.95* (s, 10 H, Cp); *5.06*, *4.94*, 4.82, 4.28 (d, 2 H, $^2J_{\mathrm{HH}}$ = 14 Hz, C*H*$_2$Ph); 3.80, *3.79* (s, 3 H, C$_\gamma$Me); 3.62, *2.88* (s, 3 H, NMe); 1.96, *1.93* (s, 3 H, C$_\beta$Me); isomer ratio 5:4. ^{13}C NMR (CDCl$_3$): δ *258.5*, 257.0 (μ-CO); 227.1, *225.8* (C$_\alpha$); 210.2, *209.7* (CO); 202.1, *202.0* (C$_\gamma$); 132.3–128.6 (Ph); 90.6, 87.9, *87.8* (Cp); 65.6, *61.1* (*C*H$_2$Ph); *65.0*, 64.8 (C$_\beta$); *45.2*, 41.5 (NMe); 37.1, *36.9* (C$_\gamma$*Me*); *15.8*, 15.5 (C$_\beta$*Me*).

Synthesis of [Fe$_2${μ-σ:η^3-C(Et)=C(Et)C=N(Me)(R)}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] (R = Xyl, 9a; R = Me, 9b). Complexes **9a**,**b** have been obtained by the same procedure described for the synthesis of **8a**,**b** by reacting 3-hexyne with [Fe$_2$(μ-CN(Me)(Xyl))(μ-CO)(CO)(Cl)(Cp)$_2$] and [Fe$_2$(μ-CNMe$_2$)(μ-CO)(CO)(Cl)(Cp)$_2$], respectively.

9a. Yield: 67%. Anal. Calcd for C$_{29}$H$_{32}$Fe$_2$F$_3$NO$_5$S: C, 51.58; H, 4.78. Found: C, 51.70; H, 4.81. IR (CH$_2$Cl$_2$): ν(CO) 1986 (vs), 1828 (s); ν(CN) 1605 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.48–7.23 (m, 3 H, Me$_2$C$_6$*H*$_3$); 4.73, 4.49 (s, 10 H, Cp); 4.24, 4.11 (m, 2 H, C$_\gamma$C*H*$_2$CH$_3$); 3.63 (s, 3 H, NMe); 2.80, 1.84 (m, 2H, C$_\beta$C*H*$_2$CH$_3$); 2.50, 2.13 (s, 6 H, *Me*$_2$C$_6$H$_3$), 1.85 (t, $^3J_{\mathrm{HH}}$ = 7 Hz, 3H, C$_\gamma$–CH$_2$C*H*$_3$); 1.63 (t, $^3J_{\mathrm{HH}}$ = 7 Hz, 3H, C$_\beta$–CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 251.7 (μ-CO); 230.0 (C$_\alpha$); 213.1, 209.2 (CO and C$_\gamma$); 140.5–129.0 (Me$_2$*C*$_6$H$_3$); 89.4, 89.0 (Cp); 67.9 (C$_\beta$); 51.1 (NMe); 43.4 (C$_\gamma$*C*H$_2$CH$_3$); 26.0 (Cβ*C*H$_2$CH$_3$); 20.0 (C$_\gamma$CH$_2$*C*H$_3$); 18.4 (*Me*$_2$C$_6$H$_3$); 14.9 (C$_\beta$CH$_2$*C*H$_3$).

9b. Yield: 77%. Anal. Calcd for C$_{22}$H$_{26}$Fe$_2$F$_3$NO$_5$S: C, 45.15; H, 4.48. Found: C, 45.09; H, 4.50. IR (CH$_2$Cl$_2$): ν(CO) 1987 (vs), 1805 (s); ν(CN) 1669 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.20, 4.96 (s, 10 H, Cp); 4.13, 4.10 (dq, $^3J_{\mathrm{HH}}$ = 7 Hz, $^2J_{\mathrm{HH}}$ = 13 Hz,

Table 2. Crystal Data and Experimental Details for [$Fe_2\{\mu$-σ:η^3-C($SiMe_3$)=CHC=N(Me)(Xyl)$\}$-(μ-CO)(CO)($Cp)_2$][SO_3CF_3] (2a)

formula	$C_{28}H_{32}F_3Fe_2NO_5SSi$
fw	691.40
T, K	298(2)
λ(Mo Kα), Å	0.710 73
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	10.6504(6)
b, Å	21.938(1)
c, Å	13.1721(7)
β, deg	99.265(2)
V, Å^3	3037.5(3)
Z	4
D(calcd), Mg m^{-3}	1.512
μ(Mo Kα), mm^{-1}	1.119
F(000)	1424
cryst size, mm	0.23 × 0.14 × 0.10
θ limits, deg	2.5−26
no. of rflns collected	30 455 ($\pm h$, $\pm k$, $\pm l$)
no. of unique obsd rflns ($I > 2\sigma(I)$)	5957
goodness of fit on F^2	0.937
R1(F),[a] wR2(F^2)[b] ($I > 2\sigma(I)$)	0.0596, 0.1339
largest diff peak, hole, e Å^{-3}	0.68, −0.63

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

2 H, C_γ−CH_2CH$_3$); 3.90, 3.16 (s, 6H, NMe); 2.47, 2.23 (dq, $^3J_{HH}$ = 7 Hz, $^2J_{HH}$ = 15 Hz, 2 H, C_β−CH_2CH$_3$); 1.63 (t, $^3J_{HH}$ = 7 Hz, 3 H, C_γ−CH$_2$CH_3); 1.09 (t, $^3J_{HH}$ = 7 Hz, 3 H, C_β−CH$_2$CH_3). ^{13}C NMR (CDCl$_3$): δ 257.7 (μ-CO); 225.9 (C_α); 210.2, 209.8 (CO and C_γ); 90.3, 87.5 (Cp); 69.5 (C_β); 49.7, 45.3 (NMe); 43.0 ($C_\gamma$$CH_2CH_3$); 22.5 ($C_\beta$$CH_2CH_3$); 19.0 ($C_\gamma$CH$_2$$CH_3$); 13.1 ($C_\beta$CH$_2$$CH_3$).

X-ray Crystallography. The X-ray intensity data for **2a** were collected on a Bruker AXS SMART 2000 diffractometer equipped with a CCD detector using graphite-monochromated Mo Kα radiation at room temperature. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in 3 different ω regions and eventually refined against all reflections. A full sphere of reciprocal space was scanned by 0.3° ω steps, with the detector kept 5.0 cm from the sample. Intensity decay was monitored by re-collecting the initial 50 frames at the end of the data collection and analyzing the duplicate reflections. The software SMART[18] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT,[18] and an empirical absorption correction was applied with SADABS.[19] The structure was solved by direct methods (SIR97)[20] and subsequent Fourier syntheses in the space group $P2_1/n$ and refined with full-matrix least squares on F^2 using SHELXTL.[21] The hydrogen atoms were added in idealized positions, except the one attached to the C_β carbon (C(4)), which was located in the Fourier map and refined isotropically. The final refinement on F^2 proceeded by full-matrix least-squares calculations using anisotropic thermal parameters for all the non-hydrogen atoms. The methyl, xylyl, and cyclopentadienyl hydrogen atoms were assigned isotropic thermal parameters of the pertinent carbon atoms: $U(H) = 1.5[U_{eq}(C(Me))]$, $U(H) = 1.2[U_{eq}(C)]$, and $U(H) = 1.2[U_{eq}(C)]$, respectively. Crystallographic data and structure refinement details for **2a** are given in Table 2.

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Supporting Information Available: Tables giving all crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **2a**; these crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) *SMART & SAINT Software Reference Manuals, Version 5.051 (Windows NT Version)*; Bruker Analytical X-ray Instruments: Madison, WI, 1998.

(19) Sheldrick, G. M., SADABS, Program for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 1996.

(20) Altomare, A.; Cascarano, C.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Burna, M. C.; Polidori, G.; Camalli, M.; Spagna, R. *SIR97*: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(21) Sheldrick, G. M. SHELXTLplus Version 5.1 (Windows NT Version) Structure Determination Package; Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.