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Alkyne−Isocyanide Coupling in $[Fe_2(CNMe)(CO)_3(Cp)_2]$: A New Route to Diiron μ-Vinyliminium Complexes[†]

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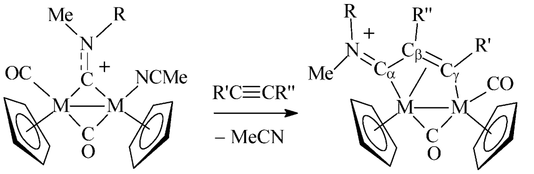
Alkynes (RC≡CR′) insert into the metal−isocyanide bond of $[Fe_2(CNMe)(CO)_3(Cp)_2]$ (**1**), under UV irradiation, affording the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R)C(R')C{=}N(Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = R′= Ph, **2a**; R = R′ = Me, **2b**; R = R′ = Et, **2c**; R = Ph, R′ = H, **2d**; R = Tol, R′ = H, **2e**; R = $SiMe_3$, R′ = H, **2f**; R = Me, R′ = H, **2g**; R = CH_2OH, R′ = H, **2h**; Tol = 4-MeC_6H_4), with displacement of one CO ligand. Compounds **2b**,**c** exist as a mixture of cis and trans isomers (with reference to the mutual Cp position), whereas **2a**,**d**−**h** exclusively have the cis geometry. The insertion of terminal alkynes is regioselective, since C−C bond formation occurs selectively between the isocyanide and the nonsubstituted carbon of HC≡CR. Compound **1** reacts with 2 equiv of $HC{\equiv}CCO_2Me$ under UV irradiation, affording $[Fe_2\{\mu\text{-}\eta^2\text{:}\eta^4\text{-}C(OH)C(CO_2Me)C(H)CN(Me)(CH{=}CHCO_2Me\}(CO)(Cp)_2]$ (**4**). Complexes **2a**,**c** undergo electrophilic addition at the N atom by treatment with HSO_3CF_3, allyl iodide ($ICH_2CH{=}CH_2$), and methyl chloroformate (ClCOOMe), affording the corresponding vinyliminium cations $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R){=}C(R)C{=}N(Me)(E)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ (R = Ph, E = H, **5a**; R = Et, E = H, **5b**; R = Ph, E = $CH_2CH{=}CH_2$, **6**; R = Ph, E = CO_2Me, **7**). The reactions of **6** with $NaBH_4$ and NBu_4CN afford $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Ph)C(Ph){=}C(H)N(Me)(CH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**8**) and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Ph)C(Ph)C(CN)N(Me)(CH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**9**), respectively. The molecular structures of *cis*-**2c**, $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et){=}C(Et)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**3**), **4**, and **5a** have been established by X-ray diffraction studies.

Introduction

The transition-metal-promoted conversion of C_1 ligands into organic compounds remains a major goal in organometallic chemistry. In this context, the insertion of alkynes into the metal−carbon bond of bridging CO,[1] μ-alkylidenes,[2] and μ-alkylidynes[3] provides an efficient route to the C−C bond formation in dinuclear complexes. These reactions, which generally result in the formation of C_3-bridged species, have attracted great attention because of the implications with the carbon−carbon chain growth in the Fischer−Tropsch (FT) process.[4]

Our work in this area has shown that the coupling of C_1 (aminocarbyne) and C_2 (alkyne) units affords C_3 bridging vinyliminium species (Scheme 1).[5,6]

Scheme 1



R = Me, Xyl, CH_2Ph
R' and R'' = alkyl, aryl, H
M= Fe, Ru

These latter species have been further modified and have grown in complexity by introduction of new functionalities, under regio- and stereoselective conditions. Indeed, we have reported that the bridging vinyliminium ligands undergo a variety of transformations upon addition of hydride,[7] cyanide,[8] acetylides,[9] and organolithium reagents.[10] Further modifications

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[†] Dedicated to Professor Robert J. Angelici on the occasion of his 70th birthday.

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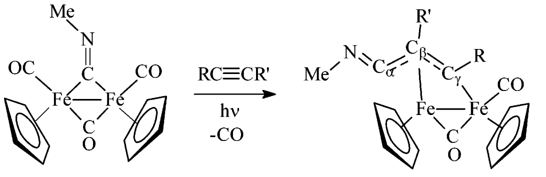
Scheme 2



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R	R'	
Ph	Ph	**2a**
Me	Me	**2b**
Et	Et	**2c**
Ph	H	**2d**
Tol	H	**2e**
$SiMe_3$	H	**2f**
Me	H	**2g**
CH_2OH	H	**2h**

of the bridging vinyliminium ligand have also been found, owing to the acidic character of the C_β-H.[11]

Herein we report on the extension of these studies to the alkyne−isocyanide coupling in the diiron complex $[Fe_2(CNMe)(CO)_3(Cp)_2]$ (**1**). To the best of our knowledge, the reactivity of **1** toward alkynes is still unexplored, in spite of the fact that the chemistry of isocyanide complexes has been extensively investigated in the past.[12]

Results and Discussion

Alkyne Insertion into the Metal−Isocyanide Bond. The complex $[Fe_2(CNMe)(CO)_3(Cp)_2]$ (**1**) consists of an isomeric mixture of terminal and bridging isocyanide, with a large prevalence of the second form.[13] The reactions of **1** with mono- and disubstituted alkynes RC≡CR′, under UV irradiation in Et_2O solution, result in the formation of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R)C(R')C{=}N(Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2a**−**h**) in about 60% yield (Scheme 2).

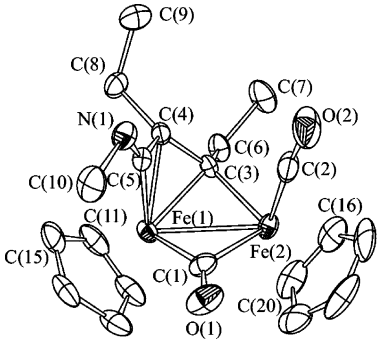


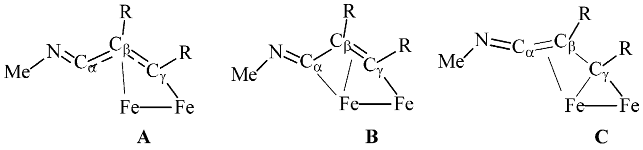
Figure 1. ORTEP drawing of *cis*-$[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et)C(Et)C{=}N(Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2c**). Hydrogen atoms are omitted for clarity; thermal ellipsoids are given at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2c, 3, and 5a

	2c	**3**	**5a**[a]
Fe(1)−C(1)	1.866(3)	1.949(4)	1.962(6) [1.981(6)]
Fe(2)−C(1)	1.949(3)	1.896(4)	1.867(6) [1.887(6)]
Fe(1)−C(3)	2.029(2)	2.030(4)	2.059(5) [2.047(5)]
Fe(2)−C(3)	1.967(2)	1.976(4)	1.960(5) [1.973(5)]
Fe(1)−C(4)	2.056(3)	2.073(4)	2.105(4) [2.103(5)]
Fe(1)−C(5)	1.952(3)	1.853(4)	1.832(5) [1.841(5)]
C(1)−O(1)	1.186(3)	1.163(5)	1.177(6) [1.166(6)]
Fe(1)−Fe(2)	2.5249(7)	2.5532(8)	2.560(1) [2.554(1)]
C(2)−O(2)	1.135(4)	1.130(6)	1.132(7) [1.138(7)]
C(3)−C(4)	1.427(4)	1.410(6)	1.430(7) [1.424(7)]
C(4)−C(5)	1.431(4)	1.444(5)	1.421(7) [1.428(7)]
C(5)−N(1)	1.237(4)	1.292(5)	1.289(6) [1.27886)]
C(10)−N(1)	1.470(4)		
C(6)−N(1)		1.484(5)	1.468(7) [1.466(7)]
C(9)−N(1)		1.455(5)	
Fe(1)−C(Cp) (av)	2.094	2.099	2.096 [2.103]
Fe(2)−C(Cp) (av)[b]	2.115	2.116	2.119 [2.136]
C(3)−C(4)−C(5)	117.1(2)	114.9(3)	114.3(4) [114.3(4)]
N(1)−C(5)−C(4)	137.1(2)	132.7(3)	131.7(5) [133.4(5)]
C(5)−N(1)−C(10)	120.0(3)		
C(5)−N(1)−C(9)		121.1(3)	
C(5)−N(1)−C(6)		122.0(4)	124.5(5) [124.8(5)]
C(6)−N(1)−C(9)		116.8(3)	
C(5)−N(1)−H(1)			116(4) [118(4)]

[a] Data for the second conformer of **5a** are given in brackets. [b] Main image of the Cp ligand.

Chart 1



The synthesis of **2a**−**h** is the result of alkyne insertion into the metal−isocyanide bond of **1**, promoted by photochemical loss of a CO ligand. All the compounds have been purified by column chromatography on alumina and characterized by IR and NMR spectroscopy and elemental analysis. The structure of **2c** has been determined by X-ray diffraction. The ORTEP molecular diagram is shown in Figure 1, and relevant bond lengths and angles are reported in Table 1. This is the first structural study for this family of compounds in which the multibridging ligand bears an imine fragment. The electronic structure of the $N{-}C_\alpha{-}C_\beta{-}C_\gamma$ unit can be schematized in three different ways: (**A**) allylimine, (**B**) enimine (azabutadienyl), and (**C**) ketenimine. As a consequence, the ligand−metal bonding interactions can be described differently, as shown in Chart 1. An analysis of the bond parameters is necessary in order to find out the best representation of the electronic structure of this

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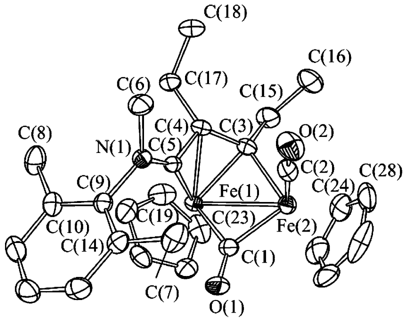

Figure 2. ORTEP drawing of the cation of (*cis*,*Z*)-[$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Et){=}C(Et)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (**3**). Hydrogen atoms are omitted for clarity; thermal ellipsoids are given at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Fe(Cp){$\boldsymbol{\eta^5}$-Fe(Cp)(CO){$\boldsymbol{\mu\text{-}\eta^2}$-C{N(Me)(CH═CHCO$_2$Me)}-CHC(CO$_2$Me)C(OH)}] (4)

Fe(1)−Fe(2)	2.5561(13)	C(5)−C(1)	1.415(9)
Fe(1)−C(1)	2.017(6)	C(5)−C(6)	1.469(9)
Fe(2)−C(1)	1.907(7)	C(6)−O(3)	1.311(9)
Fe(2)−C(3)	1.988(6)	O(3)−C(7)	1.441(8))
Fe(1)−C(3)	1.986(6)	N(1)−C(9)	1.365(9)
Fe(1)−C(4)	2.014(6)	C(9)−C(10)	1.35(1)
Fe(1)−C(5)	2.022(7)	C(11)−O(6)	1.35(1)
Fe(2)−C(2)	1.737(7)	O(6)−C(12)	1.47(1)
C(1)−O(1)	1.379(8)	C(11)−O(5)	1.18(1)
C(2)−O(2)	1.149(9)	N(1)−C(8)	1.441(8)
C(3)−N(1)	1.412(8)	Fe(1)−C(Cp) (av)	2.063
C(3)−C(4)	1.459(9)	Fe(2)−C(Cp) (av)	2.111
C(4)−C(5)	1.430(9)		

Fe(1)−C(1)−O(1)	128.6(5)	C(3)−N(1)−C(9)	118.8(5)
Fe(2)−C(1)−O(1)	122.8(4)	C(4)−C(5)−C(6)	121.8(6)
C(4)−C(3)−N(1)	117.9(5)	C(8)−N(1)−C(9)	119.3(6)
C(1)−Fe(2)−C(3)	82.0(3)	C(4)−C(5)−C(1)	113.5(6)
Fe(2)−C(3)−C(4)	111.8(4)	C(5)−C(1)−Fe(2)	115.8(5)
C(3)−C(4)−C(5)	112.6(5)		

unconventional NC_3Fe_2 grouping. The C(5)−N(imine) interaction (1.237(4) Å) indicates a localized double bond. (Compare this value with the genuine single bond N−C(10)(methyl) = 1.470(4) Å.) The torsion angle in the chain $C_\gamma-C_\beta-C_\alpha-N$ (C(3)−C(4)−C(5)−N = 39.0(3)°) is high for an efficient π-bond delocalization, as required by structures **A** and **C**. Therefore, a good approximation of the electronic structure of the NC_3 fragment is as azabutadienyl (**B**) and its interaction with the Fe_2 core is η^1 to Fe(2) and $\eta^1{:}\eta^2$ to Fe(1). The degree of nonequivalence of the iron atoms in this asymmetric molecule is assessed by the bonding asymmetry of the bridging carbonyl (Fe(1)−C(1) = 1.866(3) Å, Fe(2)−C(1) = 1.949(3) Å). The shorter distance from Fe(1) indicates greater donation to this atom to which C_α (C(5)) acts essentially as a one-electron donor, its p_z orbital being primarily engaged in the localized π bond to N. The quite long Fe(1)−C(5) distance (1.952(3) Å) is in accord with this interpretation.

The bridging ligand in the neutral complex **2c** is strictly related to the analogous grouping present in the cationic [$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Et){=}C(Et)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**3**).[5b] Complex **3** is formally derived from **2c** by addition of a Xyl^+ fragment at the nitrogen atom. In order to ascertain the structural effects of a second substituent of the nitrogen atom, we have now determined the X-ray structure of **3.** The molecular diagram is shown in Figure 2, and relevant bond lengths and angles are given in Table 2. Expectedly, we find that the bond parameters in **3** are comparable, within experimental error, to those already reported for [$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me){=}C(Me)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$.[5b] A comparison with **2c** reveals the effects of changing the nature of the nitrogen from imine to iminium. The bonding interactions of C_γ (C(3)) and C_β (C(4)) are substantially unaffected, while C_α (C(5)) exhibits significant variations. The C_α−N bond is lengthened with respect to **2c** (1.292(5) vs 1.237(4) Å). This lengthening is accompanied by a shortening of the C_α−Fe bond (C(5)−Fe(1): 1.853(4) vs 1.952(3) Å). These figures indicate that the p_z orbital on C_α is less involved in π bonding to N and more involved in bonding to Fe(1). The result is a higher electron donation to the metal with respect to **2c**. This rationalization is confirmed by the inversion of the asymmetry of the bridging carbonyl, which is now farther from Fe(1) (Fe(1)−C(1) = 1.949(4) Å and Fe(2)−C(1) = 1.896(4) Å vs 1.866(3) and 1.949(3) Å in **2c**), while the other bond interactions of Fe(1) are slightly (but not significantly) lengthened. The electronic structure of the $N-C_\alpha-C_\beta-C_\gamma$ grouping is not significantly changed with respect to the neutral species **2c**, and the system can still be described as azabutadienyl with a torsion angle along the chain N−C(5)−C(4)−C(3) (34.7(4)° in **3** vs 39.0(3)° in **2c**).

The IR spectra (in CH_2Cl_2 solution) of **2a**−**h** exhibit a weak absorption in the range 1714−1740 cm^{-1}, attributable to the imine C_α−N bond and the usual ν(CO) band pattern (e.g., for **2a** at 1972 and 1788 cm^{-1}).

Several isomeric forms are, in theory, possible for **2a**−**h** due to the mutual Cp position (cis and trans isomers) or to the two possible orientations of the N−Me group in the imine moiety (*E* and *Z* isomers). Nonetheless, NOE studies, carried out on compounds **2a**−**c,** indicate that these species adopt a *Z* configuration in solution, in agreement with the geometry found in the solid state. Moreover, **2a** exists only in the cis form, whereas both cis and trans isomers are present in the case of **2b**,**c**. Mixtures of **2b**,**c** as the cis and trans isomers have been completely converted into the more stable *cis*-**2b** and *cis*-**2c,** upon heating at reflux temperature in toluene for 2 h.

For complexes **2d**−**h,** obtained by insertion of unsymmetric alkynes, a third type of isomerism is possible, due to the insertion mode of the primary alkynes. Interestingly, the ^1H NMR spectra of **2d**−**h** exhibit a single set of resonances, indicating that the insertion reaction is regioselective. In particular, the ^1H NMR spectra show that the CH portion of the inserted HCCR generates a resonance at about δ_H 2.85−3.19 ppm, as expected for C_β−H. In contrast, the alternative isomer (C_γ−H) would resonate in the higher frequency range of methylidene protons. NOE experiments confirm that the bridging chain sequence is $N-C_\alpha-C_\beta(H)-C_\gamma(R)$ and give further information on the geometry of the complexes in solution: the Cp ligands are mutually cis and the imine N−*Me* group is in the *Z* configuration, as found in the solid state for **2c**.

Major features of the ^{13}C NMR spectra of **2a**−**h** include the C_α carbon resonance at about 195 ppm and the C_γ resonance in the 180−200 ppm range, which are consistent with their iminoacyl and alkylidene nature. Conversely, the C_β resonance is found at ca. δ 50 ppm.

The reaction described in Scheme 2 deserves further comment. Metal-assisted coupling reactions between alkynes and isocyanides are known for both mononuclear[14] and dinuclear complexes of Mn,[15] Os,[16] and Rh.[17] Among these examples only the dirhodium complex [$Rh_2Cp_2(CO)\{\mu\text{-}C(NR)C(CF_3)C(CF_3)\}$]

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(14) (a) Adams, C. J.; Anderson, K. M.; Bartlett, I. M.; Connelly, N. G.; Orpen, A. G.; Paget, T. J. *Organometallics* **2002**, *21*, 3454. (b) Barnea, E.; Andrea, T.; Kapon, M.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 10860. (c) Werner, H.; Heinemann, A.; Windmueller, B.; Steinert, P. *Chem. Ber.* **1996**, *129*, 903.

(15) Adams, R. D.; Mingsheng, H.; *Organometallics*, **1995**, *14*, 506.

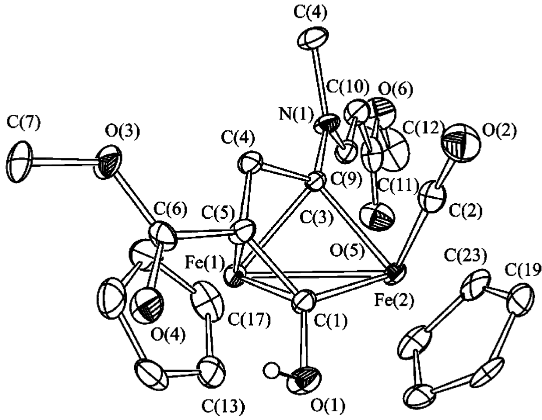
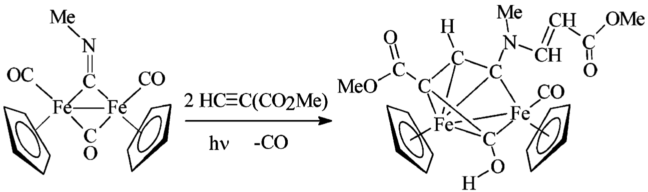


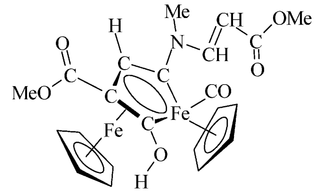
Figure 3. ORTEP drawing of [$Fe_2\{\mu$-η^2:η^4-C(OH)C(CO_2Me)C(H)CN(Me)(CH═CHCO$_2$Me)}(CO)(Cp)$_2$] (**4**). Only the hydrogen atom bound to O(1) is shown. Thermal ellipsoids are given at the 30% probability level.

Scheme 3



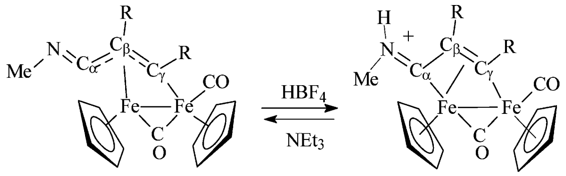
1 **4**

Chart 2



4

Scheme 4



	R	
2a	Ph	**5a**
2c	Et	**5b**

has a bridging enimine ligand with a structure and coordination mode similar to that found in **2a**−**h**.[17] Indeed, alkyne−isocyanide couplings present a variety of outcomes, mostly as a consequence of multiple insertions, rearrangements, or inclusion of other molecular fragments. Moreover, the μ-η^1:η^3 coordination described above is not the only way for an enimine (azabutadienyl) fragment to bridge two metal centers.[18] According to the variety of possible combinations between alkynes and isocyanides, not all the reactions that we have investigated proceed as described in Scheme 2. This is the case of the reaction of **1** with methyl propiolate, which under the same reaction conditions as for **2a**−**h** affords complex **4**, with no trace of the expected analogue of **2a**−**h** (Scheme 3). Even when the reaction was performed with 1 equiv of HC≡CCO$_2$Me, instead of a large excess, compound **4** was the only identified product, although formed in lower yield. Complex **4** has been isolated by chromatography and characterized by spectroscopy and X-ray diffraction. The ORTEP molecular diagram is shown in Figure 3, whereas relevant bond lengths and angles are reported in Table 2.

The reaction sequence leading to the formation of **4** is far from being understood and involves displacement of one CO ligand from **1**, combination of two HC≡CCO$_2$Me molecules with the isocyanide and the bridging CO ligand, and the addition of two hydrogen atoms. One propiolate molecule is terminally added to the nitrogen atom, giving the dangling chain that does not interact with the metal core. The other propiolate molecule undergoes further rearrangements which involve addition to the carbon atoms of the bridging ligands: i.e., the isocyanide (C(3)) and bridging carbonyl (C(1)). The resulting fragment is engaged in η^4 coordination to one metal atom (Fe(1)). Compound **4** can be described as being composed of a [$Fe_2(Cp)_2$(CO)] moiety coordinated by a bridging μ-η^2:η^4-{C(OH)═C(CO$_2$Me)C(H)═CN(Me)(CH═CHCO$_2$Me)} ligand (Scheme 3). A more appealing rationalization of the molecular architecture can be inferred from the following geometrical features: the atoms C(3)−C(4)−C(5)−C(1)−Fe(2) form a five-membered ring described as metallacyclopentadienyl (deviations from the average plane in the range −0.06 to +0.12 Å, C−C distances in the range 1.42−1.46(1) Å, C(1,3)−Fe(2) distances 1.91 and 1.99(1) Å). The metalla ring is almost parallel to the Cp ring (C(13)−C(17)) bound to Fe(1) (dihedral angle 10.3(4)°). In conclusion, the molecule can be viewed as a ferrocene analogue, in which one ring incorporates one metal atom (Fe(2)) and has different substituents containing heteroatoms (Chart 2).

The IR spectrum of **4** (in CH$_2$Cl$_2$ solution) shows one terminal ν(CO) absorption, at 1965 cm^{-1}, together with two absorptions attributable to the carboxylate groups (at 1686 and 1672 cm^{-1}) and a band due to ν(C═C) at 1601 cm^{-1}. The ^{1}H NMR spectrum exhibits two separate resonances for the inequivalent Cp rings (at δ 4.94 and 4.31 ppm). Four singlets (at δ_H 10.00, 5.24, 3.74, and 3.31 ppm) are attributable to the O*H*, C$_\beta$*H*, carboxylate methyl, and N-bound methyl, respectively. Moreover, the protons of the enamine moiety resonate as doublets at 8.35 and 4.90 ppm. Finally, the carbon atoms of the metallacyclopentadienyl ring resonate, in the ^{13}C NMR spectrum, at 179.0 (C$_\alpha$), 79.3 (C$_\beta$), 67.2 (C$_\gamma$), and 216.6 (COH) ppm, respectively.

Formation of Vinyliminium Complexes. The reactivity of the bridging enimine (azabutadienyl) ligand in **2a**−**h** was then investigated. Conversion of **2a**−**h** into the corresponding vinyliminium species [$Fe_2\{\mu$-η^1:η^3-C(R)═C(R′)C═N(Me$_2$)}(μ-CO)(CO)(Cp)$_2$][CF$_3$SO$_3$] appears to be possible simply via N-methylation. For instance, **2e** reacts with 1 equiv of CF$_3$SO$_3$CH$_3$, in dichloromethane solution, to give the known vinyliminium complex [$Fe_2\{\mu$-η^1:η^3-C(Tol)═C(H)C═N(Me)$_2$}(μ-CO)(CO)(Cp)$_2$][CF$_3$SO$_3$][5a] in almost quantitative yield. Likewise, the reactions of **2a** and (*cis* + *trans*)-**2c** with HBF$_4$ result in the formation of the new vinyliminium species [$Fe_2\{\mu$-η^1:η^3-C(R)═C(R)C═N(Me)(H)}(μ-CO)(CO)(Cp)$_2$][BF$_4$] (R = Ph, **5a**; R = Et, **5b**) (Scheme 4). The reaction is completely reversible, and the parent complexes are recovered after treatment of **5a**,**b** with Et$_3$N.

It should be noted that vinyliminium complexes of type **5** are not otherwise obtainable, because the usual approach, consisting of alkyne insertion into the aminocarbyne complex,

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(16) Huang, J.-Y.; Lin, J.-J.; Chi, K.-M.; Lu, K.-L. *J. Chem. Soc., Dalton Trans.* **1997**, 15.

(17) Dickson, R. S.; Fallon, G. D.; Nesbit, R. J.; Pateras, H. *Organometallics* **1987**, *6*, 2517.

(18) Lemke, F. R.; Szalda, D. J.; Bullock, R. M. *Organometallics* **1992**, *11*, 876.

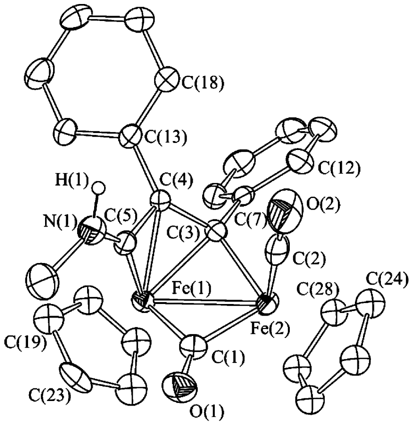


Figure 4. ORTEP drawing of the cation of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Ph){=}C(Ph)C{=}N(Me)(H)\}(\mu\text{-}CO)(CO)(Cp)_2][BF_4]$ (**5a**). Only the hydrogen atom bound to N(1) is shown. Thermal ellipsoids are given at the 30% probability level.

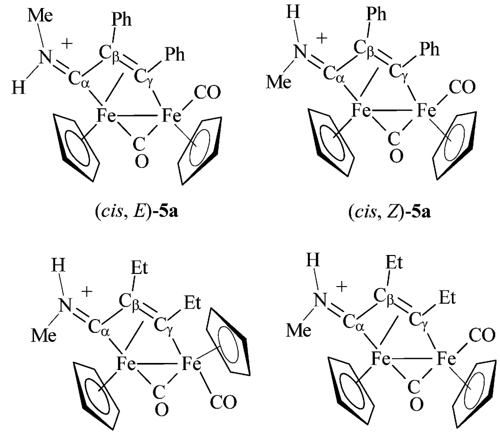
is unsuccessful in the case of $[Fe_2\{\mu\text{-}CN(Me)(H)\}(\mu\text{-}CO)(CO)_2(Cp)_2]^+$.[19] Indeed, this latter species, upon treatment with alkynes in the presence of Me_3NO, undergoes deprotonation rather than alkyne insertion.

Complex **5a** has been structurally characterized by X-ray crystallography (Figure 4, and Table 1). In the crystal two conformers of the cation of $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Ph){=}C(Ph)C{=}N(Me)(H)\}(\mu\text{-}CO)(CO)(Cp)_2][BF_4]$ (**5a**) are present. Since the difference between the two conformers resides in the mutual orientation of the phenyl rings, only the stereogeometry of one is represented in Figure 4, whereas relevant bond lengths and angles for both are reported in Table 1. The molecular structure of **5a** closely resembles those of the related vinyliminium complexes $[M_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}C(R'')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$,[5] as can be inferred by a comparison of the corresponding bond distances and angles. The iminium group presents a *Z* conformation, with the N−Me group pointing in the opposite direction with respect to the C_β−Ph group.

The IR spectrum of **5a** (in CH_2Cl_2 solution) exhibits two bands due to the terminal and bridging carbonyls, at 2004 and 1804 cm^{-1}, respectively. Moreover, a sharp band, due to ν(NH), is observed at 3246 cm^{-1} (in KBr pellets). The ^1H NMR spectrum of **5a** reveals the presence of two isomers in solution, in an 8:5 ratio. These have been identified as (*cis*,*E*)-**5a** and (*cis*,*Z*)-**5a** (Chart 3), on the basis of NOE investigations. The NH proton gives rise to a broad resonance at low field (10.37 ppm). Relevant ^{13}C NMR features include the resonances of C_α, C_β, and C_γ (at δ 226.5, 71.8, and 200.8 ppm, respectively, for (*cis*,*E*)-**5a**), in the range typical for vinyliminium ligands.[5] Conversely, the IR spectrum of **5b** (in CH_2Cl_2 solution) suggests the presence of a mixture of cis and trans isomers: the carbonyl absorptions related to the cis isomer are found at 2000 and 1807 cm^{-1}, and those of the trans isomer are at 1978 and 1789 cm^{-1}.

The presence of an isomeric mixture is well evidenced in the ^1H NMR spectrum of **5b,** which exhibits two sets of resonances in a 6:1 ratio. NOE studies indicate that the major isomer is (*trans*,*Z*)-**5b**, whereas the minor species is (*cis*,*Z*)-**5b** (Chart 3). The presence of cis and trans isomers is consistent with the fact that the parent compound **2c** also contains a mixture of cis and trans isomers. However, also the reaction of pure *cis*-**2c** with HBF_4 affords a mixture of *cis*-**5b** and *trans*-**5b**, suggesting that the observed isomeric mixture corresponds to an equilibrium composition. This hypothesis is also strengthened by the observation that the isomer ratio does not change upon heating at reflux temperature, in THF, for 120 min. These findings appear in contrast with the behavior of disubstituted vinyliminium complexes of the type $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R){=}C(R)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (R = Me, Et),[5b] in which the trans isomer is easily converted into the cis species by heating at reflux temperature in THF.

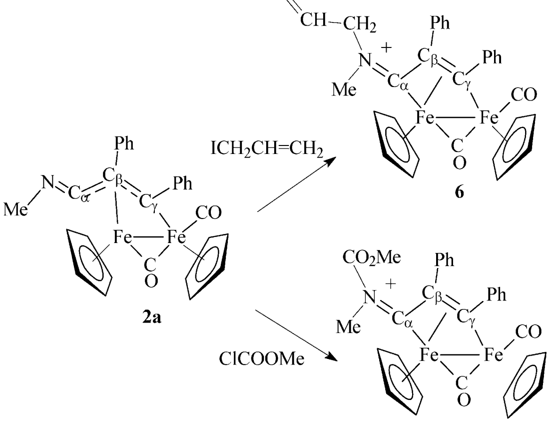
Chart 3



(*cis*, *E*)-**5a** (*cis*, *Z*)-**5a**

(*trans*, *Z*)-**5b** (*cis*, *Z*)-**5b**

Scheme 5



The nucleophilic character of the imine nitrogen in **2** can be further exploited to prepare new N-functionalized vinyliminium complexes. Thus, **2a** reacts with allyl iodide ($ICH_2CH{=}CH_2$) and methyl chloroformate (ClCOOMe), affording the species $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Ph){=}C(Ph)C{=}N(Me)(CH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2][I]$ (**6**) and $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Ph){=}C(Ph)C{=}N(Me)(COOMe)\}(\mu\text{-}CO)(CO)(Cp)_2][Cl]$ (**7**), respectively (Scheme 5). Compounds **6** and **7** have been fully characterized by IR and NMR spectroscopy, elemental analysis, and mass spectrometry (see the Experimental Section). Their properties resemble those of related vinyliminium complexes.[5] Complex **6** exists in solution as mixture of cis,*E* and cis,*Z* isomers, in comparable amounts, as indicated by NOE investigations. In contrast, the ^1H NMR spectrum of complex **7** shows a single set of resonances, but it has not been possible to establish the configuration adopted by the nitrogen substituents.

Complexes **6** and **7** are of interest because the vinyliminium complexes so far reported have been limited to species containing the $C_\alpha N(Me)(R)$ fragment, in which R = Me, CH_2Ph, Xyl. In fact the ligand is generated from the bridging aminocarbyne CN(Me)R, which, in turn, is conveniently obtained from available isocyanides (CNR) and strong alkylating agents

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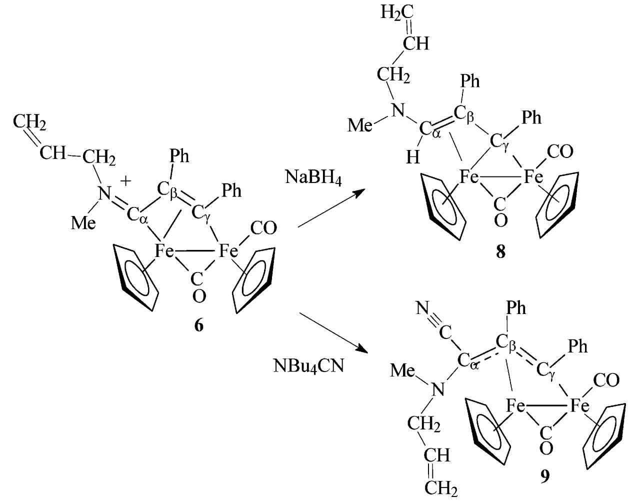
[19] Willis, S.; Manning, A. R.; Stephens, F. S. *J. Chem. Soc., Dalton Trans.* **1979**, 23.

Scheme 6



$(MeSO_3CF_3)$. Thus, the synthesis of **6** and **7** demonstrates that nitrogen functionalization can be extended to a range of different substituents, overcoming the aforementioned limits.

It has been previously shown that the substituents on the iminium nitrogen influence the reactivity of the ligand. Indeed, the Xyl group exerts a "steric protection" on the iminium carbon (C_α), the most reactive site of the ligand, and hinders the addition of hydride or cyanide at that position.[7,8] The syntheses of **6** and **7** provide the opportunity to extend the investigations and observe possible effects due to the allyl or carboxylate groups. Therefore, the reactions of **6** and **7** with $NaBH_4$ and $[(NBu_4)(CN)]$ have been studied. Unexpectedly, the reactions of **7** with H^- or CN^- simply reverse the alkylation step and result in the formation of the parent complex **2a**. The reaction of **6** with $NaBH_4$ affords the enamino−alkylidene compound $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Ph)C(Ph){=}C(H)N(Me)(CH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**8**), while with $(NBu^t{}_4)(CN)$ the result is the formation of the cyano-functionalized allylidene species $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Ph)C(Ph)C(CN)N(Me)(CH_2CH{=}CH_2)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**9**) (Scheme 6). Compounds **8** and **9** have been fully characterized by spectroscopy (see the Experimental Section), and their properties are consistent with those of strictly related compounds.[7,8]

The results shown in Scheme 6 are consistent with the nucleophilic attack at C_α exhibited by the vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R'){=}C(R'')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Me, CH_2Ph; R′ = Me, Tol, $SiMe_3$, COOMe, R″ = H; R′ = R″ = Me, Et, COOMe) in their reactions with $NaBH_4$[7] and $[(NBu_4)(CN)]$.[8]

Conclusions

Photochemical reactions of the diiron isocyanide complex $[Fe_2(CNMe)(CO)_3(Cp)_2]$ with alkynes yield novel bridging enimine complexes by alkyne insertion into the metal−carbon bond of the bridging isocyanide. The reaction takes place with a variety of alkynes, except for $HC{\equiv}C(CO_2Me)$, which yields an unprecedented ferrocene-like complex. The insertion of monosubstituted alkynes is regiospecific, and the C−C bond formation exclusively occurs between the less hindered alkyne carbon and the isocyanide. The N atom in the bridging enimine ligand can be easily protonated or alkylated, providing a route for the synthesis of new functionalized vinyliminium complexes, whose reactivity parallels that of strictly related complexes.

Experimental Section

General Procedures. All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer, and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA instrument. ESI MS spectra were recorded on a Waters Micromass ZQ 4000 instrument with samples dissolved in CH_3CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 spectrometers. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via DEPT experiments and ^1H, ^{13}C correlation through gs-HSQC and gs-HMBC experiments.[20] Unless otherwise stated, all NMR spectra were recorded at 298 K; NMR signals due to a second isomeric form (when it was possible to detect and/or resolve them) are given in italics. NOE measurements were recorded using the DPFGSE-NOE sequence.[21] All of the reagents were commercial products (Aldrich) of the highest purity available and were used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. The compounds $[Fe_2(CNMe)(CO)_3(Cp)_2]$ (**1**)[12] and (*cis*,*Z*)-$[Fe_2\{\mu\text{-}C(Et){=}C(Et)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (**3**) were prepared by published methods.[5b] Crystals of **3** suitable for X-ray analysis were obtained by a CH_2Cl_2 solution layered with diethyl ether, at −20 °C.

Synthesis of (*Z*)-$[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(R)C(R')C{=}N(Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = R′= Ph, 2a; R = R′ = Me, 2b; R = R′ = Et, 2c; R = Ph, R′ = H, 2d; R = C_6H_4Me (Tol), R′ = H, 2e; R = $SiMe_3$, R′ = H, 2f; R = Me, R′ = H, 2g; R = CH_2OH, R′ = H, 2h). A solution of $[Fe_2(CNMe)(CO)_3(Cp)_2]$ (**1**; 310 mg, 0.845 mmol), in diethyl ether (25 mL), was treated with $PhC{\equiv}CPh$ (306 mg, 1.72 mmol) and irradiated by a UV lamp for 6 h. Hence, the mixture was chromatographed on alumina, and a band corresponding to **2a** was collected with THF. The product was obtained as an emerald green powder upon removal of the solvent under reduced pressure. Yield: 245 mg, 56%. Anal. Calcd for $C_{28}H_{23}Fe_2NO_2$: C, 65.03; H, 4.48; N, 2.71. Found: C, 65.13; H, 4.42; N, 2.70. IR (CH_2Cl_2): ν(CO) 1972 (vs), 1778 (s), ν(C=N) 1729 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.10−7.00 (m, 3 H, $Me_2C_6H_3$ and Ph); 4.86, 4.56 (s, 10 H, Cp); 3.85 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 264.8 (μ-CO); 211.9 (CO); 192.5 (C_α); 188.5 (C_γ); 155.7, 136.3 (ipso-Ph); 130.6, 128.5, 127.9, 127.8, 127.7, 126.9, 125.9, 124.8 (Ph); 89.5, 85.3 (Cp); 47.6 (C_β); 41.2 (NMe).

Compounds **2b**−**h** were prepared by the same procedure described for **2a**, by reacting **1** with the appropriate alkyne. The synthesis of **2b** was performed in toluene solution. Conversion of the cis/trans mixtures of **2b**,**c** into the respective neat cis forms were accomplished by heating in boiling toluene solutions, for 2 h. Crystals suitable for X-ray analysis were obtained by a CH_2Cl_2 solution of **2c** layered with *n*-pentane, at −20 °C.

2b (yield 60%; reaction time 4 h; green). Anal. Calcd for $C_{18}H_{19}Fe_2NO_2$: C, 55.01; H, 4.87; N, 3.56. Found: C, 54.09; H, 4.87; N, 3.52. IR (CH_2Cl_2): ν(CO) *1966* (s), 1954 (vs), 1796 (s), ν(C=N) 1714 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ *4.84*, 4.58, *4.54*, 4.37 (s, 10 H, Cp); 3.81, *3.77* (s, 3 H, C_γMe); 3.75, *3.68* (s, 3 H, NMe); *1.59*, 1.46 (s, 3 H, C_βMe). Trans/cis ratio 6:5. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ *266.9*, 265.2 (μ-CO); *211.9*, 211.6 (CO); *197.3*, 193.8 (C_α); 196.0 (C_γ); 88.5, 88.3, *88.0*, *85.0* (Cp); 49.2, *48.9* (C_β); *41.4*, 36.2 (NMe); *35.7*, 35.1 (C_γ*Me*); *16.9*, 15.0 (C_β*Me*).

2c (yield 64%; reaction time 3 h; emerald green). Anal. Calcd for $C_{20}H_{23}Fe_2NO_2$: C, 57.05; H, 5.51; N, 3.33. Found: C, 57.12;

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

H, 5.55; N, 3.28. IR (CH$_2$Cl$_2$): ν(CO) 1964 (s), *1940* (vs), *1780* (s), 1773 (m), ν(C=N) 1718 (w), *1715* (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.82, 4.54, *4.52*, *4.38* (s, 10 H, Cp); *4.21*, 4.11 (m, 2 H, C$_\gamma$CH$_2$); *3.74*, 3.70 (s, 3 H, NMe); 2.45, 1.30 (m, 2 H, C$_\beta$CH$_2$); *1.71* (dd, 3 H, $^3J_{HH}$ = 7.32 Hz, $^3J_{HH}$ = 7.69 Hz, C$_\gamma$CH$_2$CH_3); 1.64 (dd, 3 H, $^3J_{HH}$ = 7.32 Hz, $^3J_{HH}$ = 7.32 Hz, C$_\gamma$CH$_2$CH_3); *1.19* (m, 3 H, C$_\beta$CH$_2$CH_3); 1.10 (dd, 3 H, $^3J_{HH}$ = 7.32 Hz, $^3J_{HH}$ = 7.69 Hz, C$_\beta$CH$_2$CH_3). Cis/trans ratio 5:2. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 265.8, *264.2* (μ-CO); *212.6*, 212.1 (CO); 201.6, *198.9* (C$_\gamma$); *195.4*, 192.3 (C$_\alpha$); *88.2*, 87.8, *86.3*, 84.4 (Cp); 54.3, *50.8* (C$_\beta$); *42.7*, 41.7 (NMe); *42.6*, 42.2 (C$_\gamma$CH$_2$); *24.4*, 23.7 (C$_\beta$CH$_2$); 18.8, *18.5* (C$_\gamma$CH$_2$CH$_3$); *12.5*, 12.1 (C$_\beta$CH$_2$CH$_3$).

2d (yield 55%; reaction time 3.5 h; green). Anal. Calcd for C$_{22}$H$_{19}$Fe$_2$NO$_2$: C, 59.91; H, 4.34; N, 3.18. Found: C, 59.98; H, 4.26; N, 3.08. IR (CH$_2$Cl$_2$): ν(CO) 1970 (vs), 1778 (s), ν(C=N) 1732 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.05−7.31 (m, 5 H, Ph); 4.82, 4.64 (s, 10 H, Cp); 3.82 (s, 3 H, NMe); 2.99 (s, 1 H, C$_\beta$H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 264.2 (μ-CO); 211.5 (CO); 196.7 (C$_\gamma$); 192.2 (C$_\alpha$); 157.6 (*ipso*-Ph); 128.0, 127.9, 125.9 (Ph); 88.7, 84.8 (Cp); 41.6 (NMe); 35.0 (C$_\beta$).

2e (yield 60%, reaction time 2.5 h; brownish green). Anal. Calcd for C$_{23}$H$_{21}$Fe$_2$NO$_2$: C, 60.70; H, 4.65; N, 3.08. Found: C, 60.66; H, 4.68; N, 3.12. IR (CH$_2$Cl$_2$): ν(CO) 1969 (vs), 1778 (s), ν(C=N) 1730 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.64, 7.28 (d, 4 H, $^3J_{HH}$ = 8.0 Hz, C$_6H_4$Me); 4.80, 4.64 (s, 10 H, Cp); 3.81 (s, 3 H, NMe); 2.96 (s, 1 H, C$_\beta$H); 2.45 (s, 3 H, C$_6$H$_4$*Me*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 264.5 (μ-CO); 211.6 (CO); 197.0 (C$_\gamma$); 192.6 (C$_\alpha$); 154.9 (ipso-C_6H$_4$Me); 135.5, 129.2, 128.6, 127.9 (C_6H$_4$Me); 88.8, 84.8 (Cp); 41.6 (NMe); 35.0 (C$_\beta$); 21.1 (C$_6$H$_4$*Me*).

2f (yield 60%; reaction time 5 h; brownish green). Anal. Calcd for C$_{19}$H$_{23}$Fe$_2$NO$_2$Si: C, 52.20; H, 5.30; N, 3.20. Found: C, 52.23; H, 5.25; N, 3.26. IR (CH$_2$Cl$_2$): ν(CO) 1974 (vs), 1789 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.02, 4.70 (s, 10 H, Cp); 3.76 (s, 3 H, NMe); 3.19 (s, 1 H, C$_\beta$H); 0.59 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 261.1 (μ-CO); 210.6 (CO); 191.8 (C$_\alpha$); 179.7 (C$_\gamma$); 87.4, 86.1 (Cp); 41.4 (NMe); 38.3 (C$_\beta$); 2.9 (SiMe$_3$).

2g (yield 61%; reaction time 9 h; green). Anal. Calcd for C$_{17}$H$_{17}$Fe$_2$NO$_2$: C, 53.87; H, 4.52; N, 3.70. Found: C, 53.80; H, 4.49; N, 3.74. IR (CH$_2$Cl$_2$): ν(CO) 1972 (vs), 1780 (s), ν(C=N) 1727 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.88, 4.60 (s, 10 H, Cp); 3.85 (s, 3 H, NMe); 3.73 (s, 3 H, C$_\gamma$Me); 2.88 (s, 1 H, C$_\beta$H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 263.2 (μ-CO); 211.9 (CO); 195.8 (C$_\gamma$); 192.0 (C$_\alpha$); 88.0, 86.6 (Cp); 41.0 (NMe); 37.6 (C$_\beta$); 38.9 (C$_\gamma$*Me*).

2h (yield 59%; reaction time 7 h; green). Anal. Calcd for C$_{17}$H$_{17}$Fe$_2$NO$_3$: C, 51.69; H, 4.34; N, 3.55. Found: C, 51.62; H, 4.39; N, 3.58. IR (CH$_2$Cl$_2$): ν(CO) 1978 (vs), 1789 (s), ν(C=N) 1740 (w) cm^{-1}. ^{1}H NMR (CD$_3$CN): δ 6.15, 5.88 (d, 2 H, $^2J_{HH}$ = 14.6 Hz, CH_2OH); 5.14, 4.75 (s, 10 H, Cp); 5.06 (br, 1 H, OH); 3.48 (s, 3 H, NMe); 2.85 (s, 1 H, C$_\beta$H). ^{13}C{^{1}H} NMR (CD$_3$CN): δ 264.2 (μ-CO); 212.1 (CO); 196.7 (C$_\gamma$); 191.9 (C$_\alpha$); 89.3, 88.5 (Cp); 74.9 (CH$_2$OH); 45.6 (NMe); 35.3 (C$_\beta$).

Synthesis of [Fe$_2${μ-η^2:η^4-C(OH)C(CO$_2$Me)C(H)CN(Me)(CH=CHCO$_2$Me}(CO)(Cp)$_2$] (4). This product was prepared by the same procedure described for **2a−h**, by reacting **1** (185 mg, 0.365 mmol) with HC≡CCO$_2$Me (3.6 mmol): reaction time 6 h; green; yield 104 mg (56%). Anal. Calcd for C$_{22}$H$_{23}$Fe$_2$NO$_6$: C, 51.90; H, 4.55; N, 2.75. Found: C, 51.92; H, 4.47; N, 2.60. IR (CH$_2$Cl$_2$): ν(CO) 1965 (vs), 1686 (m), 1672 (m), ν(C=C) 1601 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.00 (s, 1 H, OH); 8.35 (d, 2 H, $^3J_{HH}$ = 13.54 Hz, *H*C=CHCO$_2$Me); 4.90 (d, 2 H, $^3J_{HH}$ = 13.54 Hz, HC=C*H*CO$_2$Me); 5.24 (s, 1 H, C$_\beta$H); 4.94, 4.31 (s, 10 H, Cp); 3.74 (s, 6 H, COOMe); 3.31 (s, 3 H, NMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 218.8 (CO); 216.6 (COH); 179.0 (C$_\alpha$); 176.2, 169.6 (*C*OOMe); 152.5 (H*C*=CHCO$_2$Me); 87.9 (HC=*C*HCO$_2$Me); 84.1, 77.7 (Cp); 79.3 (C$_\beta$); 67.2 (C$_\gamma$); 51.7, 50.8 (COO*Me*); 40.0 (NMe).

Synthesis of [Fe$_2${μ-η^1:η^3-C(R)=C(R)C=N(Me)(H)}(μ-CO)(CO)(Cp)$_2$][BF$_4$] (R = Ph, 5a; R = Et, 5b). A solution of **2a** (100 mg, 0.193 mmol) in CH$_2$Cl$_2$ (10 mL) was treated with HBF$_4$ (0.20 mmol). The mixture was stirred for 10 min, and then the solvent was removed under reduced pressure. The residue was washed with diethyl ether (2 × 10 mL) and dissolved in CH$_2$Cl$_2$, and this solution was filtered on a Celite pad. The product was obtained as dark brown crystals upon removal of the solvent. Yield: 106 mg (91%). Crystals suitable for X-ray analysis were obtained by a CH$_3$CN solution of **5a** layered with diethyl ether, at −20 °C. Anal. Calcd for C$_{28}$H$_{24}$BF$_4$Fe$_2$NO$_2$: C, 55.59; H, 4.00; N, 2.32. Found: C, 55.56; H, 4.08; N, 2.26. IR (KBr pellets): ν(NH) 3246 (m) cm^{-1}. IR (CH$_2$Cl$_2$): ν(CO) 2004 (vs), 1804 (s), ν(C=N) 1674 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.37 (br, 1 H, NH); 7.82−6.81 (m, 10 H, Ph); 5.32, *5.24*, 4.98, *4.91* (s, 10 H, Cp); *3.77*, 2.59 (d, $^3J_{HH}$ = 4.94 ppm, 3 H, NMe). *E*/*Z* ratio 8:5. ^{13}C{^{1}H} NMR (CDCl$_3$): δ *255.4*, 252.6 (μ-CO); 226.5 (C$_\alpha$); 210.2, *208.4* (CO); 200.8, *198.9* (C$_\gamma$); *153.5*, 153.2 (*ipso*-Ph); 132.8−123.7 (Ph); *91.9*, 91.7, 88.6, *87.5* (Cp); 71.8 (C$_\beta$); 39.7, *37.1* (NMe).

Compound **5b** was prepared by the same procedure described for **6a**, by reacting **2c** (88 mg, 0.209 mmol) with HBF$_4$ (0.25 mmol): yield: 98 mg (92%); green. Anal. Calcd for C$_{20}$H$_{24}$BF$_4$Fe$_2$NO$_2$: C, 47.20; H, 4.75; N, 2.75. Found: C, 47.16; H, 4.79; N, 2.83. IR (KBr pellets): ν(NH) 3226 (m) cm^{-1}. IR (CH$_2$Cl$_2$): ν(CO) *2000* (s), 1978 (vs), *1807* (m), 1789 (s), ν(C=N) 1671 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 10.09 (s br, 1 H, NH); *5.15*, *4.84*, 4.75, 4.61 (s, 10 H, Cp); *4.34*, *4.06*, 4.12, 4.02 (m, 2 H, C$_\gamma$CH$_2$); 3.78, *3.24* (s, 3 H, NMe); 2.72, *2.51*, *2.01*, 1.88 (m, 2 H, C$_\beta$CH$_2$); *1.86*, 1.68 (m, 3 H, C$_\gamma$CH$_2$CH_3); *1.20*, 1.18 (m, 3 H, C$_\beta$CH$_2$CH_3). Trans/cis ratio 6:1. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 254.5 (μ-CO); 223.8 (C$_\alpha$); 209.2 (CO); 203.0 (C$_\gamma$); 89.4, 88.0 (Cp); 74.3 (C$_\beta$); 43.5 (NMe); 37.7 (C$_\gamma$-*C*H$_2$); 23.5 (C$_\beta$-*C*H$_2$); 18.2 (C$_\gamma$CH$_2$*C*H$_3$); 12.8 (C$_\beta$CH$_2$*C*H$_3$).

Synthesis of [Fe$_2${μ-η^1:η^3-C(Ph)=C(Ph)C=N(Me)(CH$_2$CH=CH$_2$)}(μ-CO)(CO)(Cp)$_2$][I] (6). CH$_2$CHCH$_2$I (0.70 mmol) was added to a solution of **2a** (90 mg, 0.174 mmol) in CH$_2$Cl$_2$ (10 mL). The mixture was stirred for 20 min, and then the solvent was removed. Chromatography of the residue on alumina, with MeOH as eluent, afforded a red band corresponding to **7**. Yield: 99 mg (83%). Anal. Calcd for C$_{31}$H$_{28}$Fe$_2$INO$_2$: C, 54.34; H, 4.12; N, 2.04. Found: C, 54.32; H, 4.12; N, 2.07. IR (CH$_2$Cl$_2$): ν(CO) 1994 (vs), 1813 (s), ν(C=N) 1653 (m), ν(C=C) 1637 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.64−7.03 (m, 10 H, Ph); 5.94, *5.27* (m, 1 H, NCH$_2$C*H*); 5.51, *5.46*, *5.11*, 5.10 (s, 10 H, Cp); 5.50, *5.28* (m, 2 H, NCH$_2$CHCH_2); 4.97 (m, 1 H, NCH$_2$C*H*); 4.02, *2.63* (s, 3 H, NMe); *3.66*, 3.63, 3.48, *3.44* (m, 2 H, NCH$_2$). *E*/*Z* ratio 6:5. ^{13}C{^{1}H} NMR (CDCl$_3$): δ *254.8*, 254.1 (μ-CO); 224.7, *223.9* (C$_\alpha$); 210.2, *209.9* (CO); 201.1, *201.0* (C$_\gamma$); 152.9 (*ipso*-Ph); 133.0−122.8 (Ph); 123.0, *122.8* (NCH$_2$CHCH_2); 122.9 (NCH$_2$*C*HCH$_2$); *92.1*, 92.0, 88.4, *88.3* (Cp); 72.4, 72.1 (C$_\beta$); 64.8, *61.6* (NCH$_2$); *44.6*, 42.8 (NMe). ESI-MS (ES$^+$): *m*/*z* 558. ESI-MS (ES$^-$): *m*/*z* 127.

Synthesis of [Fe$_2${μ-η^1:η^3-C(Ph)=C(Ph)C=N(Me)(CO$_2$Me)}(μ-CO)(CO)(Cp)$_2$][Cl] (7). ClC(O)OMe (0.90 mmol) was added to a solution of **2a** (95 mg, 0.184 mmol) in CH$_2$Cl$_2$ (15 mL), and the mixture was stirred for 20 min. Removal of the volatile materials gave **7** as a red microcrystalline powder. Yield: 90 mg (80%). Anal. Calcd for C$_{30}$H$_{26}$ClFe$_2$NO$_4$: C, 58.91; H, 4.28; N, 2.29. Found: C, 58.97; H, 4.24; N, 2.25. IR (CH$_2$Cl$_2$): ν(CO) 2007 (vs), 1832 (s), 1774 (s), ν(C=N) 1556 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.10−6.75 (m, 10 H, Ph); 5.19, 5.10 (s, 10 H, Cp); 4.18 (s, 3 H, CO$_2$Me); 3.28 (s, 3 H, NMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 249.2 (μ-CO); 217.0 (C$_\alpha$); 207.9 (CO); 202.5 (C$_\gamma$); 161.3 (*C*O$_2$Me); 152.9 (ipso-Ph); 146.6−124.6 (Ph); 94.2, 91.7 (Cp); 71.9 (C$_\beta$); 55.4 (CO$_2$*Me*); 43.0 (NMe).

Synthesis of [Fe$_2${μ-η^1:η^3-C(Ph)C(Ph)=C(H)N(Me)(CH$_2$CH=CH$_2$)}(μ-CO)(CO)(Cp)$_2$] (8). Complex **6** (50 mg, 0.0730 mmol) was dissolved in THF (10 mL) and treated with NaBH$_4$ (14 mg, 0.368 mmol). The mixture was stirred for 15 min, and then it was filtered on alumina. Solvent removal and chromatography of the residue on alumina, with CH$_2$Cl$_2$ as eluent, gave a green band

Table 3. Crystal Data and Experimental Details for 2c, 3, 4·CH$_2$Cl$_2$, and 5a

	2c	**3**	**4**·CH$_2$Cl$_2$	**5a**
formula	$C_{20}H_{23}Fe_2NO_2$	$C_{29}H_{32}F_3Fe_2NO_5S$	$C_{23}H_{25}Cl_2Fe_2NO_6$	$C_{28}H_{24}BF_4Fe_2NO_2$
fw	421.09	675.32	594.04	604.99
T, K	296(2)	296(2)	296(2)	296(2)
λ, Å	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a, Å	9.693(2)	8.2804(3)	9.0847(18)	13.911(3)
b, Å	12.446(3)	12.4402(4)	35.133(7)	22.709(5)
c, Å	15.295(3)	15.0634(5)	8.4489(17)	17.018(3)
α, deg	90	107.4700(10)	90	90
β, deg	91.781(5)	101.8190(10)	115.43(3)	101.16(3)
γ, deg	90	91.7950(10)	90	90
cell vol, Å^3	1844.3(7)	1441.55(8)	2435.4(8)	5274.5(18)
Z	4	2	4	8
D_c, g cm^{-3}	1.517	1.556	1.620	1.524
μ, mm^{-1}	1.585	1.138	1.450	1.155
$F(000)$	872	696	1216	2464
cryst size, mm	0.25 × 0.23 × 0.21	0.28 × 0.25 × 0.23	0.25 × 0.21 × 0.15	0.23 × 0.19 × 0.14
θ limits, deg	2.66−28.70	2.53−28.00	2.55−25.00	1.51−25.03
no. of rflns collected	21 343 ($R_{int} = 0.0610$)	16 496 ($R_{int} = 0.0291$)	18 651 ($R_{int} = 0.1111$)	46 377 ($R_{int} = 0.0740$)
no. of indep rflns	4754	6926	3765	9319
goodness of fit on F^2	1.102	1.042	1.131	1.048
R1 ($I > 2\sigma(I)$)[a]	0.0604	0.0660	0.0817	0.0592
wR2 (all data)[b]	0.1625	0.2112	0.1850	0.1787
largest diff peak and hole, e Å^{-3}	1.103/−1.800	1.264/−0.919	0.997/−0.769	0.880/−0.700

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

corresponding to **8**. Yield: 35 mg (86%). Anal. Calcd for $C_{31}H_{29}Fe_2NO_2$: C, 66.58; H, 5.23; N, 2.50. Found: C, 66.52; H, 5.29; N, 2.58. IR (CH$_2$Cl$_2$): ν(CO) 1933 (vs), 1754 (s), ν(C═C) 1591 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.19−6.65 (m, 10 H, Ph); 5.91 (m, 1 H, NCH$_2$C*H*); 5.15 (m, 2 H, NCH$_2$CHC*H*$_2$); 4.85, 4.32 (s, 10 H, Cp); 3.21 (m, 2 H, NCH$_2$); 1.90 (s, 3 H, NMe); 0.91 (s, 1H, C$_\alpha$H). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 278.7 (μ-CO); 217.8 (CO); 185.8 (C$_\gamma$); 156.7 (*ipso*-*C*$_6$H$_4$Me); 139.7, 134.5, 131.3, 129.2, 128.8, 127.1, 125.6, 123.2 (Ph); 123.3 (NCH$_2$*C*H); 117.9 (NCH$_2$CH*C*H$_2$); 97.3 (C$_\alpha$); 88.6, 81.8 (Cp); 83.7 (C$_\beta$); 59.6 (NCH$_2$); 38.6 (NMe).

Synthesis of [Fe$_2${μ-η^1:η^3-C(Ph)C(Ph)C(CN)N(Me)(CH$_2$CH═CH$_2$)}(μ-CO)(CO)(Cp)$_2$] (9). NBu$^t_4$CN (23 mg, 0.0858 mmol) was added to a solution of **6** (48 mg, 0.0701 mmol) in CH$_2$Cl$_2$ (15 mL). The mixture was stirred for 30 min, and then it was filtered on alumina. The product was obtained as a red powder upon removal of the solvent under reduced pressure. Yield: 36 mg (88%). Anal. Calcd for $C_{32}H_{28}Fe_2N_2O_2$: C, 65.78; H, 4.83; N, 4.79. Found: C, 65.66; H, 4.79; N, 4.88. IR (CH$_2$Cl$_2$): ν(C≡N) 2187 (w), ν(CO) 1972 (vs), 1788 (s), ν(C═C) 1591 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.95−7.02 (m, 10 H, Ph); 5.73, *5.72* (m, 1 H, NCH$_2$C*H*); *5.12*, 5.04 (m, 2 H, NCH$_2$CHC*H*$_2$); *4.82*, 4.80, 4.57 (s, 10 H, Cp); 4.13, *3.10*, *2.99*, 2.80 (dd, 2 H, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 2.9$ Hz, NCH$_2$); *2.48*, 2.05 (s, 3H, NMe). Isomer ratio 6:5. ^{13}C{^{1}H} NMR (CDCl$_3$): δ *264.6*, 264.1 (μ-CO); *213.4*, 213.0 (CO); *197.6*, 197.1 (C$_\gamma$); 157.3, *157.2* (ipso-Ph); *139.6*, 139.4, 135.6, *134.8*, 132.1, 128.2, *128.0*, *127.9*, 127.8, 127.2, 126.9, 126.6 (Ph); *124.1*, 124.0 (NCH$_2$*C*H); *120.2*, 120.0 (C≡N); *118.0*, 117.2 (NCH$_2$CH*C*H$_2$); *90.6*, 90.4, *87.2*, 87.1 (Cp); 96.6, *95.7* (C$_\beta$); *65.8*, 59.3 (NCH$_2$); *64.2*, 63.0 (C$_\alpha$); 45.9, *39.9* (NMe).

X-ray Crystallography. The X-ray intensity data for **2c**, **3**, **4**·CH$_2$Cl$_2$, and **5a** were measured on a Bruker AXS SMART 2000 diffractometer, equipped with a CCD detector. Cell dimensions and the orientation matrix were initially determined from a least-squares refinement on reflections measured in 3 sets of 20 exposures, collected in 3 different ω regions, and eventually refined against all data. For all crystals, a full sphere of reciprocal space was scanned by 0.3° ω steps, with the detector kept at 5.0 cm from the sample. The software SMART[22] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the SAINT program,[22] and an empirical absorption correction was applied using SADABS.[23] The structures were solved by direct methods (SIR 97)[24] and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 (SHELXTL),[25] using anisotropic thermal parameters for all non-hydrogen atoms except the cyclopentadienyl ligands in **4**. In **3**, some disorder was detected for both the fluorine and oxygen atoms of the CF$_3$SO$_3^-$ group, which were refined over two sites, yielding occupation factors of 0.55 and 0.57 for the main images of the F atoms bound to C(39) and O atoms bound to S, respectively. Crystals of **4** were found to contain one CH$_2$Cl$_2$ molecule in the asymmetric unit. In the solid state **5a** is present in two conformers. In both conformers one cyclopentadienyl ring (bound to Fe(2)) is disordered over two positions and the site occupation factors were refined to 0.69 for the main image in both conformers. All hydrogen atoms, except the hydrogen bound to O(1) in **4** and to N(1) in **5a**, which were found in the Fourier map and refined isotropically, were added in calculated positions, included in the final stage of refinement with isotropic thermal parameters, $U(H) = 1.2\ U_{eq}(C)$ ($U(H) = 1.5\ U_{eq}(C-Me)$), and allowed to ride on their carrier carbons. Crystal data and details of the data collection for all structures are reported in Table 3.

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Supporting Information Available: CIF files giving X-ray crystallographic data for the structure determinations of **2c**, **3**, **4**·CH$_2$Cl$_2$, and **5a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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