Unprecedented Zwitterionic Iminium−Chalcogenide Bridging Ligands in Diiron Complexes

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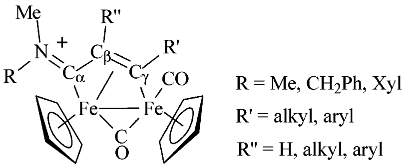
The diiron vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R′ = Me, **1a**; R = Xyl, R′ = Tol, **1b**; R = Xyl, R′ = CO_2Me, **1c**; R = Xyl, R′ = CH_2OH, **1d**; R = Xyl, R′ = Bu^n, **1e**; R = Me, R′ = Me, **1f**; R = Me, R′ = Tol, **1g**; R = Me, R′ = CO_2Me, **1h**; R = Me, R′ = Bu^n, **1i**; R = Me, R′ = CH_2OH, **1l**; R = p-C_6H_4-CN, R′ = Tol, **1m**; R = p-C_6H_4-OMe, R′ = Me, **1n**; Tol = 4-C_6H_4-Me; Xyl = 2,6-$Me_2C_6H_3$] react with elemental sulfur or selenium, in the presence of NaH, to give the zwitterionic vinyliminium compounds $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}C(E)C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R = Xyl, R′ = Me, E = S, **2a**; R = Xyl, R′ = Tol, E = S, **2b**; R = Xyl, R′ = CO_2Me, E = S, **2c**; R = Xyl, R′ = CH_2OH, E = S, **2d**; R = Xyl, R′ = Bu^n, E = S, **2e**; R = Xyl, R′ = Me, E = Se, **3a**; R = Xyl, R′ = Tol, E = Se, **3b**; R = Me, R′ = Me, E = Se, **3c**; R = Me, R′ = Tol, E = Se, **3d**; R = Me, R′ = CO_2Me, E = Se, **3e**; R = Me, R′ = Bu^n, E = Se, **3f**; R = Me, R′ = CH_2OH, E = Se, **3g**]. Similarly, the reaction of **1a** with Me_3NO/NaH results in the formation of $[Fe_2\{\mu\text{-}C(Me)C(O)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**4**), in which the bridging ligand is better described as a bis-alkylidene. The reactions of **1a**,**c** with S_8/NaH afford also the five-membered metallacycles $[Fe(Cp)(CO)\{C_\alpha(NMe(Xyl))C_\beta(H)C_\gamma(R')S\}]$ [R′ = Me, **6a**; R′ = CO_2Me, **6b**], as secondary products, in about 15% yield. Conversely, complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$, **1f**−**h**,**m**,**n**, react with S_8/NaH, giving selectively the five-membered metallacycles $[Fe(Cp)(CO)\{C(R')C(H)C\{N(Me)(R)\}S\}]$ [R = Me, R′ = Me, **7a**; R = Me, R′ = Tol, **7b**; R = Me, R′ = CO_2Me, **7c**; R = p−C_6H_4−CN, R′ = Tol, **7d**; R = p-C_6H_4-OMe, R′ = Me, **7e**]. The molecular structures of **2b**·CH_2Cl_2, **3a**, **4**, **6a**, and **7b** have been determined by X-ray diffraction studies.

Introduction

Dinuclear transition metal complexes, providing multisite interactions between the metal aggregate and coordinated molecules, offer unique possibilities of substrate activation, which cannot be expected in mononuclear complexes.[1] In particular, complexes with two adjacent metal atoms are particularly effective in the activation and transformation of C_3-bridged fragments, including μ-allyls[2] and μ-allenyls.[3] Our interest in the area has been focused on the chemistry of bridging vinyliminium complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}C(R'')C{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (Chart 1)[4] and of their diruthenium counterparts.[5]

Chart 1



It has been evidenced that the bridging vinyliminium ligand is a versatile substrate, accessible to a variety of transformations, obtained by reaction with nucleophiles, including hydride,[6] acetylides,[7] and organolithium reagents.[8] Further possible transformations of the bridging C_3 unit have been found, owing

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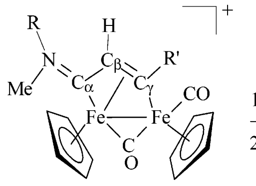
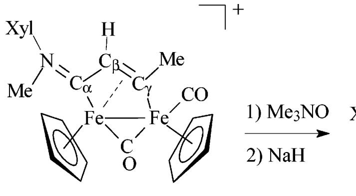
10.1021/om060550r CCC: \$33.50

Scheme 1



	R	R'	E	
1a	Xyl	Me	S	**2a**
1b	Xyl	Tol	S	**2b**
1c	Xyl	CO_2Me	S	**2c**
1d	Xyl	CH_2OH	S	**2d**
1e	Xyl	Bu^n	S	**2e**
1a	Xyl	Me	Se	**3a**
1b	Xyl	Tol	Se	**3b**
1f	Me	Me	Se	**3c**
1g	Me	Tol	Se	**3d**
1h	Me	CO_2Me	Se	**3e**
1i	Me	Bu^n	Se	**3f**
1l	Me	CH_2OH	Se	**3g**

Scheme 2



1a **4**

to the acidic character of the C_β-H in the vinyliminium ligand.[9] Proton removal generates reactive intermediates, which rearrange, resulting in the formation of mono-, di-, or tetranuclear complexes. The former have been identified as metalla-2-aminocyclopenta-1,3-dien-5-one and σ-alkynyl μ-aminocarbyne diiron complexes, respectively, whereas the tetranuclear compounds are generated by dimerization of the parent complexes, involving C−C bond formation between the C_β positions of two μ-vinyliminium ligands.[9]

Herein we report on the successful attempt to trap the reactive deprotonated intermediates by reactions with elemental sulfur or selenium, or with Me_3NO, resulting in the functionalization of the C_β position with a group 16 heteroatom.

Results and Discussion

The diiron vinyliminium complexes [$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R'){=}CHC{=}N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1a**−**l**) react with elemental sulfur or selenium, in the presence of NaH in THF solution, generating the zwitterionic vinyliminium complexes **2a**−**e** and **3a**−**g**, respectively (Scheme 1).

The analogous complex [$Fe_2\{\mu\text{-}C(Me)C(O)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$] (**4**) (Scheme 2), containing oxygen instead of sulfur or selenium, has been obtained, albeit in modest yields (30%), by reacting **1a** with NaH in the presence of Me_3NO.

The compounds **2**, **3**, and **4** have been purified by chromatography and characterized by IR and NMR spectroscopy and elemental analysis. Moreover, the molecular structures of **2b**, **3a**, and **4** have been determined by X-ray diffraction studies: the ORTEP molecular diagrams are shown in Figures 1−3, whereas relevant bond lengths and angles are reported in Table 1, where they are compared to those of the cationic vinyliminium complex *cis*-[$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me){=}C(Me)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]^+$ (**5**).[4b] The three complexes **2b**, **3a**, and **4** display a bridging [μ-C(R′)C(E)CN(Me)(Xyl)] ligand, which can be better discussed by considering two alternative structures (Chart 2). In the first (**A**), the ligand is described as a zwitterionic vinyliminium, which is $\mu\text{-}\eta^1{:}\eta^3$ coordinated. This type of

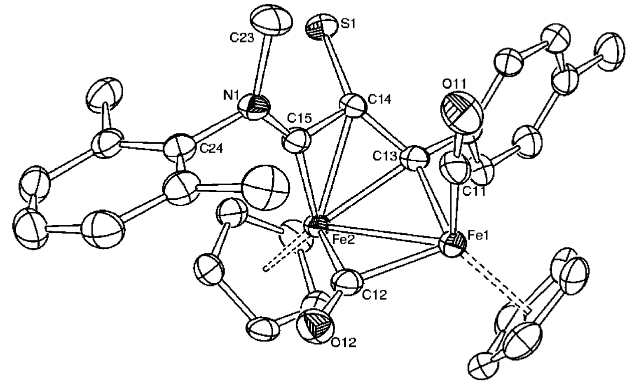


Figure 1. Molecular structure of [$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Tol){=}C(S)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$] (**2b**), with key atoms labeled (all H atoms have been omitted). Displacement ellipsoids are at the 30% probability level. Only the main image of the disordered Tol group is reported.

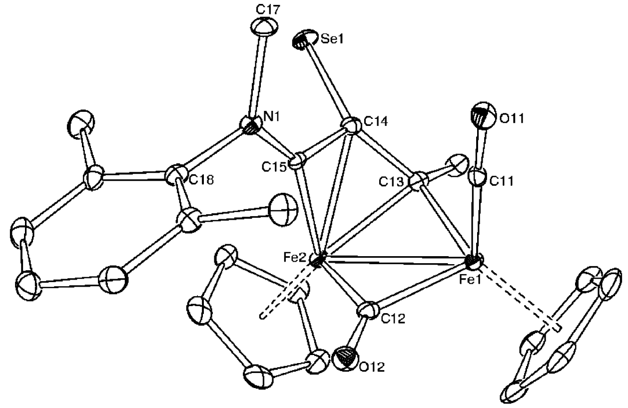


Figure 2. Molecular structure of [$Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me){=}C(Se)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$] (**3a**), with key atoms labeled (all H atoms have been omitted). Displacement ellipsoids are at the 30% probability level.

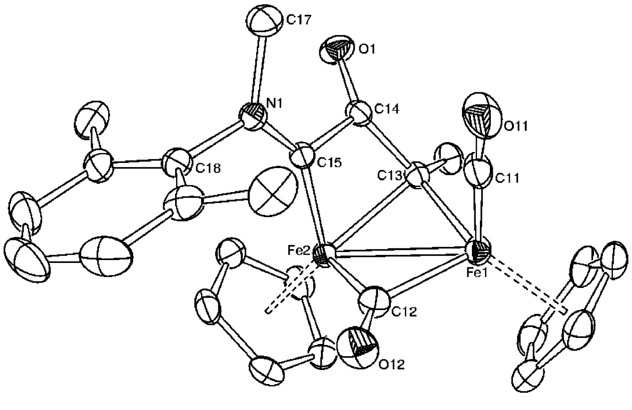


Figure 3. Molecular structure of [$Fe_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me)C(O)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$], (**4**), with key atoms labeled (all H atoms have been omitted). Displacement ellipsoids are at the 30% probability level.

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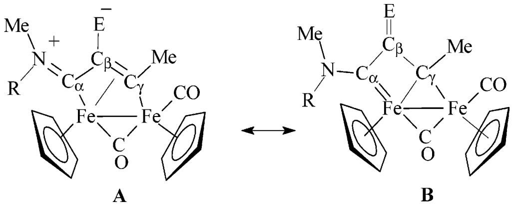
[9] Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Organometallics* **2005**, *24*, 2297.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2b, 3a, and 4, Compared to *cis*-[$Fe_2\{\mu$-η^1:η^3-C(Me)=C(Me)C=N(Me)(Xyl)$\}(\mu$-CO)(CO)$(Cp)_2]^+$ (5)

	2b	3a	4	5[a]
Fe(1)−Fe(2)	2.5489(9)	2.5409(12)	2.5403(8)	2.562(1)
Fe(1)−C(11)	1.744(5)	1.752(4)	1.747(3)	1.750(9)
Fe(1)−C(12)	1.916(5)	1.911(4)	1.953(3)	1.894(8)
Fe(2)−C(12)	1.918(4)	1.921(4)	1.882(3)	1.944(8)
Fe(1)−C(13)	1.988(4)	1.966(4)	1.979(2)	1.955(7)
Fe(2)−C(13)	2.040(4)	2.034(4)	2.017(2)	2.035(7)
Fe(2)−C(14)	2.151(4)	2.158(3)	2.330(2)	2.080(7)
Fe(2)−C(15)	1.860(4)	1.864(3)	1.874(2)	1.839(7)
C(11)−O(11)	1.155(6)	1.150(4)	1.147(3)	1.150(9)
C(12)−O(12)	1.182(6)	1.181(4)	1.172(3)	1.181(9)
C(13)−C(14)	1.430(6)	1.435(5)	1.446(3)	1.39(1)
C(14)−C(15)	1.440(6)	1.431(5)	1.487(3)	1.43(1)
C(15)−N(1)	1.307(5)	1.307(4)	1.310(3)	1.314(8)
C(14)−X	1.736(4)	1.899(3)	1.254(3)	1.52(1)
Fe(1)−C(13)−C(14)	121.3(3)	120.3(3)	129.03(16)	121.8(5)
C(13)−C(14)−C(15)	111.8(3)	112.6(3)	106.31(18)	115.5(6)
C(14)−C(15)−Fe(2)	80.2(3)	80.7(2)	86.97(13)	77.9(4)
C(14)−C(15)−N(1)	129.9(4)	132.4(3)	126.03(19)	131.3(7)

[a] See ref 4b.

Chart 2



coordination has been discussed in previous publications[4] and shows analogies to the closely related dinuclear propargyl iron derivatives described by Knox.[10] The positive charge is delocalized over the whole vinyliminium, whereas the negative charge is localized on the heteroatom E. Alternatively, the ligand can be viewed as bridging bis-alkylidene μ-η^1:η^2 coordinated (**B**); in this case, C$_\beta$ is not bonded to the metal and C$_\beta$=E has a double-bonded character. The bonding parameters for both **2b** and **3a** are very similar to those of the vinyliminium **5**, and therefore, they can be mainly represented by the zwitterionic form (**A**). In agreement with this, all three carbon atoms C(13), C(14), and C(15) (C$_\gamma$, C$_\beta$, and C$_\alpha$, respectively) are bonded to Fe(2) [Fe(2)−C(13) 2.040(4) and 2.034(4) Å; Fe(2)−C(14) 2.151(4) and 2.158(3) Å; Fe(2)−C(15) 1.860(4) and 1.864(3) Å, for **2b** and **3a**, respectively]. Moreover, both C(13)−C(14) [1.430(6) and 1.435(5) Å, for **2b** and **3a**, respectively] and C(14)−C(15) [1.440(6) and 1.431(5) Å] interactions show some double-bond character, whereas C(14)−S(1) [1.736(4) Å] and C(14)−Se(1) [1.899(3) Å] are essentially single bonds. Conversely, the structure of **4** is better represented by the bis-alkylidene form (**B**), even though some contribution of the zwitterionic structure (**A**) has to be considered. In particular, the Fe(2)−C(14) distance [2.330(2) Å] is considerably elongated with respect to **2b** and **3a**, suggesting a very weak interaction that better agrees with a μ-η^1:η^2 coordination. Also the C(13)−C(14) [1.446(3) Å] and C(14)−C(15) [1.487(3) Å] interactions are slightly longer than in **2b** and **3a**, indicating a reduced double-bond character. Conversely, the C(14)−O(1) interaction [1.254(3) Å] is an almost pure C(sp^2)=O double bond, as found in organic ketones.

The IR spectra (in dichloromethane solution) of **2** and **3** exhibit two bands due to the terminal and bridging carbonyls (e.g., for **2a** at 1961 and 1790 cm^{-1}, respectively). These ν-(CO) occur at higher frequencies compared to those of **4** (at 1945 and 1777 cm^{-1}). Finally, ν(C$_\beta$O) is found for **4** (in KBr) at 1465 cm^{-1}, in agreement with its partial double-bond character.

The NMR spectra of **2** and **3** indicate the presence in solution of single species, although several isomers might exist owing to the mutual positions of the Cp ligands (*cis*−*trans*) and to the orientation of the N substituents, when these are not equivalent (*E*−*Z* isomers). NOE investigations indicate that all the compounds are *cis* and that complexes **2** and **3a**,**b**, in which the N substituents are Me and Xyl, adopt a *Z* configuration (Xyl pointing far from C$_\beta$), as found in the solid state for **2b**, **3a**, and **4**. This indicates that the formation of **2**, **3**, and **4** from **1** is accompanied by inversion of the configuration at the nitrogen center, since the parent complexes **1** exist in solution mainly in the *E* form.[4a] It is worth noting that the *Z* configuration is preferred when the C$_\beta$ substituent is more sterically demanding than H: indeed, *Z* is the dominant configuration in the vinyliminium complexes [$Fe_2\{\mu$-η^1:η^3-C(R′)=C(R′)C=N(Me)-(Xyl)$\}(\mu$-CO)(CO)$(Cp)_2]^+$ (R′ = alkyl or aryl).[4b] In a similar manner, the presence of a heteroatom (O, S, Se) on the C$_\beta$ induces the iminium substituents to assume a *Z* configuration.

The C$_\alpha$ resonance, in the ^{13}C NMR spectra of the complexes containing S or Se, is found at δ ca. 230 ppm, as expected for a μ-vinyliminium complex. For the same species, the C$_\gamma$ carbon resonates in the range δ 179−207 ppm, in accordance with its alkylidene character. The resonance of C$_\beta$ is observed at δ ca. 110 ppm in the sulfides **2**, whereas it is upfield shifted (i.e., δ ca. 90 ppm) in the selenides **3**. The ^{13}C NMR spectrum of **4** is significantly different from those of **2** and **3**, in agreement with the prevalence of the bis-alkylidene form (**B**, Chart 2). In particular, C$_\alpha$ is downfield shifted (δ 258.9 ppm), as expected for a terminal aminocarbene; also C$_\beta$ resonates at lower field (δ 156.9 ppm), because of its carbonyl nature.

The formation of **2**−**4** presumably proceeds via deprotonation of C$_\beta$−H of the vinyliminium ligand. Although deprotonated intermediate species have been not identified, it appears reasonable that proton removal would leave an electron-rich C$_\beta$ carbon, susceptible to oxidation by elemental sulfur or selenium or by Me_3NO. It has to be remarked that, in the absence of any of these reagents, the treatment with NaH produces rearrangements of the vinyliminium complexes, affording binuclear alkynyl products or mononuclear and tetranuclear derivatives, previously described.[9] Since none of these compounds have been detected among the reaction products, it is evident that sulfur, selenium, or Me_3NO efficiently traps the reactive intermediates generated by C$_\beta$−H deprotonation.

Hydrogen replacement, in the μ-vinyliminium ligand, by a group 16 element (O, S, Se), described above, deserves some further comments. The bridging ligand evidences a dipolar character, particularly in complexes containing S and Se. The observed charge separation suggests a description of the ligand as a betaine. Mesoionic betaines are usually stabilized by a large delocalization of both positive and negative charge in the cyclic aromatic structures in which they are embedded.[11] Conversely, in **2** and **3**, stabilization to the dipolar organic frame is provided by metal coordination, according to the bridging modes described above (Chart 2). It is worth noting that dipolar iminium thiolates of the type [(R^{I})(R^{II})N=C$_\alpha$(R)C$_\beta$(S)=C$_\gamma$(R^{III})-

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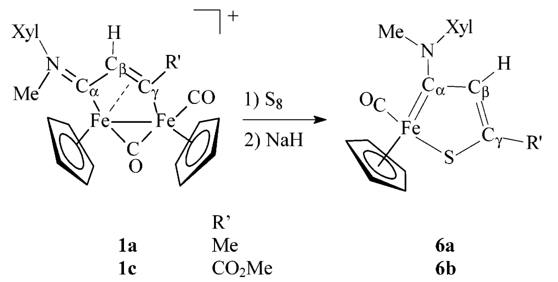
[10] (a) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. *J. Chem. Soc., Chem. Commun.* **1980**, 409. (b) Dyke, A. F.; Knox, S. A. R.; Naish, P. J.; Taylor, G. E. J. *Chem. Soc., Dalton Trans.* **1982** 1297.

[11] Sakai, N.; Funabashi, M.; Hamada, T.; Minakata, S.; Ilhyong Ryu, I.; Komatsu, M. *Tetrahedron* **1999**, *55*, 13703, and references therein.

Scheme 3



	R'	
1a	Me	**6a**
1c	CO_2Me	**6b**

(R^{IV})] are rare,[12] and to our knowledge, none have been found coordinated to metallic centers. A comparison between the ligand present in **2b** and the organic zwitterion PhC[=N^+(CH_2CH_2)$_2$O]C(S^-)=C(Ph)(Ph_2P=S) (**C**)[12a] shows some analogies but also some interesting differences. In both cases, the zwitterionic nature of the molecule is evidenced by the fact that C_α=N is essentially a double bond [1.307(5) Å in **2b**, 1.310(2) Å in **C**], whereas C_β−S is a single bond [1.736(4) Å in **2b**, 1.715(2) Å in **C**], in agreement with charge separation. Conversely, the C_α−C_β [1.440(6) Å in **2b**, 1.488(3) Å in **C**] and C_β−C_γ [1.430(6) Å in **2b**, 1.354(3) Å in **C**] interactions indicate an alternating bonding situation in **C** [C_α−C_β single, C_β=C_γ double], whereas there is an almost perfect delocalization in **2b**, as a consequence of the coordination to the diiron frame. Thus, the ligand possesses some allylic character, in agreement with our previous findings for similar vinyliminium ligands.[4]

Interestingly, the reactions of **1a**,**c** with S_8/NaH do not afford **2a**,**c** as unique reaction products. Chromatography allowed the isolation of the mononuclear complexes [Fe(Cp)(CO){C_α(NMe(Xyl))C_β(H)C_γ(R′)S}] [R′ = Me, **6a**; R′ = CO_2Me, **6b**], as minor products (15−20% yield) (Scheme 3).

Complexes **6a**,**b** have been characterized by spectroscopy (IR and NMR) and elemental analysis. Moreover, the molecular structure of **6a** has been ascertained by X-ray diffraction: the ORTEP molecular diagram is shown in Figure 4, whereas relevant bond angles and lengths are listed in Table 2.

The molecule can be described as a five-membered 1-metalla-5-thiacyclopenta-1,3-diene, containing a pseudo-tetrahedrally coordinated Fe atom. The C(8)−C(9) (C_β−C_γ) interaction [1.326(11) Å] is very short, suggesting an almost pure double-bond character. Nonetheless, both C(7)−C(8) [1.440(10) Å] and C(9)−S(1) [1.711(8) Å] show some shortening compared to single bonds, indicating some π-delocalization in the ring, which is, in fact, almost planar [mean deviation from the Fe(1)−S(1)−C(9)−C(8)−C(7) least-squares plane 0.032 Å]. N(1) adopts a nearly perfect sp^2 hybridization [sum of angles 360.0(11)°], and the N(1)−C(7) interaction [1.328(9) Å] shows some double-bond character; relative to the latter, the N(Me)(Xyl) group adopts the *E* configuration. Finally, the Fe(1)−C(7) interaction [1.953(7) Å] is elongated with respect to a pure terminal amino−carbene bond, showing some vinyl character.[13]

The IR spectra of **6a**,**b** (in CH_2Cl_2 solution) show a band due to the carbonyl ligand (e.g., for **6a** at 1932 cm^{-1}) and an absorption attributed to the C_β−C_γ interaction, at ca. 1515 cm^{-1}. In the ^1H NMR spectra, the C_β−H proton is found at relatively low fields (e.g., for **6a** at δ 5.83 ppm). NOE studies have outlined that complex **6b** exists in solution as a mixture of *E* and *Z* isomers, with prevalence of the former. Most relevant features of the ^{13}C NMR spectra are given by the resonances related to C_α, C_β, and C_γ. The first falls at ca. 250 ppm, at a value typical for an aminocarbene carbon; the second is found at ca. 135 ppm, consistent with the olefinic nature of the C_β carbon; finally, C_γ resonates at lower fields (e.g., for **6a** at δ 198.0 ppm), because of the closeness to the sulfur atom.

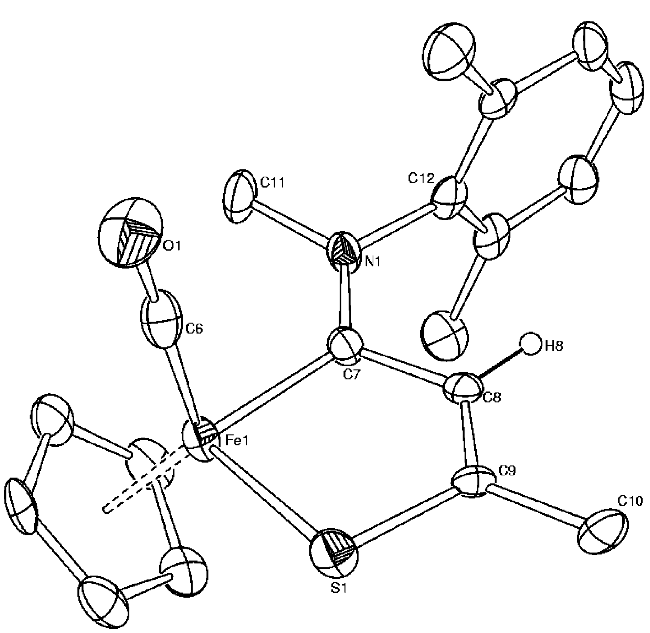


Figure 4. Molecular structure of [Fe(Cp)(CO){C_α(NMe(Xyl))C_β(H)C_γ(Me)S}] (**6a**), with key atoms labeled (all H atoms, except H(8), have been omitted). Displacement ellipsoids are at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Fe(Cp)(CO){C_α(NMe(Xyl))C_β(H)C_γ(Me)S}] (6a)

Fe(1)−C(6)	1.736(11)	C(7)−C(8)	1.440(10)
C(6)−O(1)	1.147(11)	C(8)−C(9)	1.326(11)
Fe(1)−S(1)	2.253(3)	C(7)−Fe(1)	1.953(7)
S(1)−C(9)	1.711(8)	C(7)−N(1)	1.328(9)
N(1)−C(12)	1.446(10)	N(1)−C(11)	1.467(10)
S(1)−Fe(1)−C(7)	86.3(2)	C(8)−C(7)−Fe(1)	115.8(6)
Fe(1)−S(1)−C(9)	98.7(3)	C(7)−N(1)−C(11)	124.9(7)
S(1)−C(9)−C(8)	118.5(6)	C(7)−N(1)−C(12)	122.6(6)
C(7)−C(8)−C(9)	120.4(8)	C(11)−N(1)−C(12)	112.5(6)
S(1)−C(9)−C(10)	118.3(6)	N(1)−C(7)−C(8)	117.7(7)
C(8)−C(9)−C(10)	123.2(7)	Fe(1)−C(7)−N(1)	126.5(6)

The formation of **6a**,**b** is peculiar to **1a** and **1c**, and in the reactions of **1b**,**d**,**e** with S_8/NaH, the corresponding metallacycle products have not been observed. Compounds **6a**,**b** resemble the analogous 1-metalla-2-aminocyclopenta-1,3-dien-5-one complexes [Fe(Cp)(CO){CN(Me)(Xyl)CHC(R′)C(O)}] [R′ = Me, CO_2Me], obtained by simple treatment of **1a** with NaH, which differ from **6**, having a CO group in the place of S within the metallacycle.[9] In both cases, the metallacycles are originated by the fragmentation of the dinuclear frame, promoted by reaction with NaH. A further analogy consists in the fact that the parent vinyliminium ligands remain intact along with their conversion into the observed metallacycles. Since the C_β−H is still present in the final products, it is not clear whether proton removal takes place at some stage of the reaction or NaH acts mainly as a reducing agent, favoring the fragmentation in the dinuclear parent compound.

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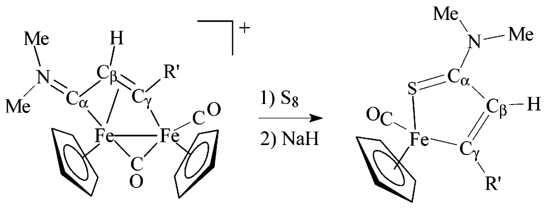
[13] (a) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V.; Zoli, E. *J. Organomet. Chem.* **2005**, *690*, 348. (b) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V.; Zoli, E. *J. Organomet. Chem.* **2005**, *690*, 1959.

Scheme 4



	R'	
1f	Me	**7a**
1g	Tol	**7b**
1h	CO_2Me	**7c**

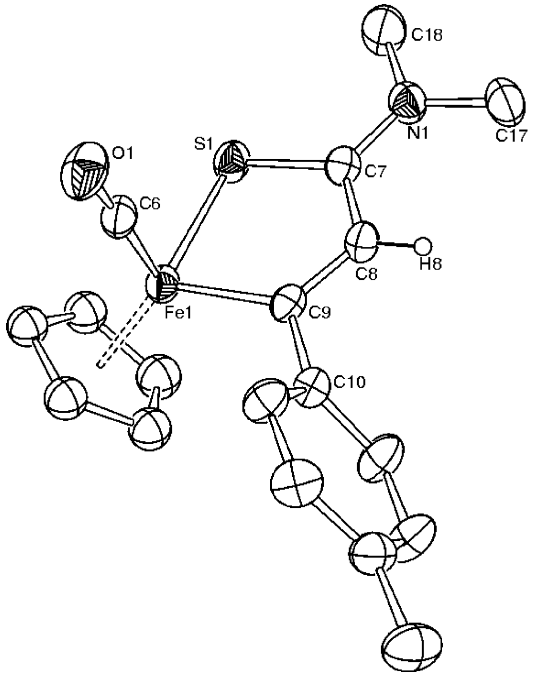


Figure 5. Molecular structure of [Fe(Cp)(CO){C(Tol)C(H)C-(NMe_2)S}] (**7b**), with key atoms labeled (all H atoms, except H(8), have been omitted). Displacement ellipsoids are at the 30% probability level. Only the main image of the disordered Cp ligand is reported.

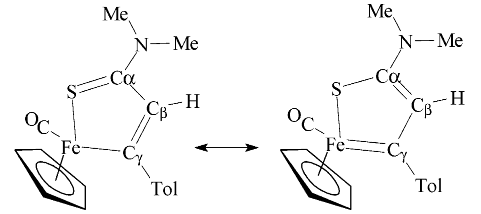
Completely different pathways are observed by reacting the complexes **1f**−**h** with elemental sulfur, in the presence of sodium hydride. In fact, the mononuclear species [Fe(Cp)(CO)C-(R′)C(H)C{N(Me)(R)}S] (R = Me, R′ = Me, **7a**; R = Me, R′ = Tol, **7b**; R = Me, R′ = CO_2Me, **7c**) are formed (Scheme 4).

Compounds **7a**−**c** have been characterized on the basis of spectroscopic data, and the molecular structure of **7b** has been determined by X-ray crystallography (Figure 5 and Table 3). The iron atom is pseudo-tetrahedrally coordinated to a Cp, a CO, and a chelating vinyl thiopropargylamide ligand, and the resulting five-membered ring can be described as a 1-metalla-5-thiacyclopenta-2,4-diene. In agreement with this, both C(7)−S(1) [1.706(2) Å] and C(8)−C(9) [1.361(3) Å] interactions show a considerable double-bond character. The Fe(1)−C(9) interaction [1.937(2) Å] is shorter than a pure vinyl σ-Fe−C(sp^2) bond and suggests some π-back-donation from the metal. Taking this into consideration, the molecule can be alternatively described as a 1-metalla-5-thiacyclopenta-1,3-diene (Chart 3); in agreement with this, also the C(7)−C(8) interaction [1.426(3) Å] displays some double-bond character. The ring is perfectly planar [mean deviation from the Fe(1)−S(1)−C(7)−C(8)−C(9) least-squares plane 0.0084 Å] and also the NMe_2 group lies in this plane [dihedral angles C(8)−C(7)−N(1)−C(17) −1.3(4)° and C(8)−C(7)−N(1)−C(18) −179.0(3)°]. The observed coplanarity as well as the perfect sp^2 hybridization of N(1) [sum of angles 359.9(3)°] indicates some π-interaction between the five-membered ring and NMe_2 [C(7)−N(1) 1.338(3) Å]. All these data indicate that the five-membered ring is essentially aromatic.

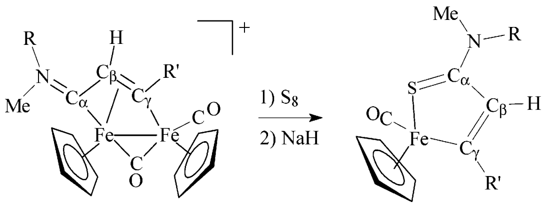
Table 3. Selected Bond Lengths (Å) and Angles (deg) for [Fe(Cp)(CO){C(Tol)C(H)C(NMe_2)S}] (7b)

Fe(1)−C(6)	1.724(2)	C(7)−C(8)	1.426(3)
C(6)−O(1)	1.155(3)	C(8)−C(9)	1.361(3)
Fe(1)−S(1)	2.2489(9)	C(9)−Fe(1)	1.937(2)
S(1)−C(7)	1.706(2)	C(7)−N(1)	1.338(3)
N(1)−C(17)	1.459(4)	N(1)−C(18)	1.460(4)
S(1)−Fe(1)−C(9)	84.68(7)	C(8)−C(9)−Fe(1)	120.73(16)
Fe(1)−S(1)−C(7)	100.63(8)	C(7)−N(1)−C(17)	122.3(2)
S(1)−C(7)−C(8)	115.23(17)	C(7)−N(1)−C(18)	121.1(2)
C(7)−C(8)−C(9)	118.7(2)	C(17)−N(1)−C(18)	116.5(2)
S(1)−C(7)−N(1)	121.73(18)	N(1)−C(7)−C(8)	123.0(2)
C(8)−C(9)−C(10)	116.40(19)	Fe(1)−C(9)−C(10)	122.87(15)

Chart 3. Resonance Forms for 7b



Scheme 5



	R	R'	
1m	4-C_6H_4-CN	Tol	**7d**
1n	4-C_6H_4-OMe	Me	**7e**

It is not obvious why, for **7a**−**c**, sulfur addition occurs at the C_α instead of at the C_β carbon, as in the complexes of types **2** and **3**. A possible explanation is related to the presence of less sterically demanding iminium substituents, in place of Xyl. The latter has been demonstrated to act as a "protecting group" and inhibits addition at the iminium carbon (C_α) for steric reasons. To evidence possible electronic effects, in addition to steric effects, the investigation has been extended to the complexes **1m** and **1n** (Scheme 5), displaying the *para*-methoxy and *para*-cyano phenyl substituent, respectively. Since **1m** and **1n** are novel compounds, details on their syntheses, from the corresponding isocyanide diiron precursors, are given in the Experimental Section.

Again, both **1m** and **1n** react with NaH/S_8, generating the corresponding metallacycles (Scheme 5). Therefore, steric effects are dominant, and only the Xyl substituent prevents the reaction from taking place at the iminium carbon. However, it has to be remarked that the reactions of **1f**−**l** with selenium occur exclusively at the C_β carbon (Scheme 1, compounds **3c**−**g**), despite the presence of methyls as substituents at the iminium nitrogen. This observation indicates that the nature of the heteroatom also affects the reaction outcome.

Finally, the reactions outlined in Schemes 3, 4, and 5 represent interesting and versatile syntheses of five-membered thiametallacycles containing iron; to the best of our knowledge, only a few of these molecules have been structurally characterized.[14]

Conclusions

The reactions of diiron vinyliminium complexes, containing an acidic C_β−H hydrogen, with NaH in the presence of elemental S or Se or with Me_3NO, respectively, provide a general entry to the hydrogen replacement with the corresponding group 16 element, affording complexes of the type $[Fe_2\{\mu\text{-}C(R')C(E)CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2]$. The bridging ligand in the latter can be described either as a zwitterionic μ-η^1:η^3 vinyliminium or as a μ-η^1:η^2 bis-alkylidene (Chart 3, structures **A** and **B**, respectively). The zwitterionic form better describes the vinyliminium ligand containing S or Se, whereas the bis-alkylidene form prevails when the oxygen atom is present.

On the other hand, the study has evidenced that the iminium carbon (C_α) and the C_γ of the vinyliminium ligand are also susceptible to reacting with sulfur, leading to the fragmentation of the dinuclear complexes and the formation of five-membered metallacycles, which include the vinyliminium ligand and a S atom.

Whereas C_γ−S bond formation appears rather limited and unpredictable, the addition of sulfur to the iminium carbon (C_α) occurs selectively, when the C_α position is not sterically protected by the presence of the Xyl substituent.

Finally, the results herein presented reinforce our findings on the very rich chemistry of bridging diiron vinyliminium complexes. In particular, the preparation of the new zwitterionic iminium thiolate (selenolate) ligands promises further developments in the synthesis of new highly functionalized organic frames, bridging Fe atoms.

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 Waters Micromass ZQ 4000 with samples dissolved in CH_3CN. All NMR measurements were performed at 298 K on a Mercury Plus 400 instrument. NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned via ^1H,^{13}C correlation measured using gs-HSQC and gs-HMBC experiments.[15] NOE measurements were recorded using the DPFGSE-NOE sequence.[16] All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. **1a**−**l** were prepared by published methods.[4]

Synthesis of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = 4-C_6H_4CN, R = 4-C_6H_4OMe). The isocyanide CN(4-C_6H_4-CN) (154 mg, 1.20 mmol) and $[Fe_2(CO)_2(\mu\text{-}CO)_2(Cp)_2]$ (650 mg, 1.84 mmol) were dissolved in MeCN (35 mL). The solution was stirred at boiling temperature for 8 h. Then, the solvent was removed and the residue was dissolved in CH_2Cl_2 (25 mL) and treated with $CF_3SO_3CH_3$ (1.30 mmol). The resulting solution was stirred at room temperature for 4 h. Chromatography on an alumina column, with MeOH as eluent, afforded $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4CN)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$. Yield: 371 mg, 50%. Anal. Calcd for $C_{23}H_{17}F_3Fe_2N_2O_6S$: C, 44.69; H, 2.77; N, 4.53. Found: C, 44.71; H, 2.82; N, 4.55. IR (CH_2Cl_2): ν(C≡N) 2122 (m), ν(CO) 2023 (vs), 1992 (s), 1840 (s), ν(μ-CN) 1552 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.97−7.71 (m, 4 H, C_6H_4); 5.49, 4.80 (s, 10 H, Cp); 4.59 (s, 3 H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 326.8 (μ-C); 252.7 (μ-CO); 208.5, 207.2 (CO); 152.8, 134.6, 126.7 (C_6H_4); 120.9 (C_6H_4*C*N); 90.5, 90.1 (Cp); 57.2 (NMe).

Complex $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4OMe)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ was prepared by the same procedure described for $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4CN)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$, by using CN(4-$C_6H_4$OMe) and $[Fe_2(CO)_2(\mu\text{-}CO)_2(Cp)_2]$. Yield: 86%. Anal. Calcd for $C_{23}H_{20}F_3Fe_2NO_7S$: C, 44.33; H, 3.23; N, 2.25. Found: C, 44.25; H, 3.18; N, 2.19. IR (CH_2Cl_2): ν(CO) 2022 (vs), 1991 (s), 1837 (s), ν(μ-CN) 1537 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.90−7.08 (m, 4 H, C_6H_4); 5.50, 4.83 (s, 10 H, Cp); 4.58 (s, 3 H, NMe); 3.90 (s, 3 H, OMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 324.3 (μ-C); 254.5 (μ-CO); 208.6, 207.6 (CO); 159.6, 143.8, 126.4, 115.1 (C_6H_4); 90.3, 90.0 (Cp); 57.4 (NMe); 55.6 (OMe).

Synthesis of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ [R = 4-C_6H_4CN, 4-C_6H_4OMe]. Complex $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4CN)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (200 mg, 0.324 mmol) was dissolved in MeCN (15 mL) and treated with Me_3NO (32 mg, 0.427 mmol). The resulting solution was stirred for 20 min and filtered on a Celite pad. Solvent removal, under reduced pressure, gave a brown residue of $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4CN)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$. Yield: 153 mg, 75%. Anal. Calcd for $C_{24}H_{20}F_3Fe_2N_3O_5S$: C, 45.67; H, 3.19; N, 6.66. Found: C, 45.75; H, 3.12; N, 6.68. IR (CH_2Cl_2): ν(C≡N) 2118 (m), ν(CO) 1984 (vs), 1820 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.98−7.28 (m, 4 H, C_6H_4); *5.11*, 4.97, 4.43 (s, 10 H, Cp); 4.60 (s, 3 H, NMe); 1.98 (s, 3 H, NCMe). Isomer ratio (*E*/*Z*) 3:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 338.4 (μ-C); 264.3 (μ-CO); 211.3 (CO); 145.4−127.2 (C_6H_4 and N*C*Me); 117.8 (C_6H_4*C*N); *89.0*, 88.5, 87.4, *86.9* (Cp); *56.3*, 53.7 (NMe); 4.92, 4.18 (NC*Me*).

Complex $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4OMe)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ was prepared by the same procedure described for $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4CN)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$, by reacting $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4OMe)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ with Me_3NO in MeCN. Yield: 80%. Anal. Calcd for $C_{24}H_{23}F_3Fe_2N_2O_6S$: C, 45.31; H, 3.64; N, 4.40. Found: C, 45.22; H, 3.61; N, 4.17. IR (CH_2Cl_2): ν(CO) 1985 (vs), 1817 (s), ν(μ-CN) 1527 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.65−7.06 (m, 4 H, C_6H_4); 5.08, 4.94, 4.45, 4.29 (s, 10 H, Cp); 4.87, 4.57 (s, 3 H, NMe); 3.90, 3.89 (s, 3 H, OMe); 2.01, 1.99 (s, 3 H, NCMe). Isomer ratio (*E*/*Z*) 1:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 336.4, 336.3 (μ-C); 265.9, 265.8 (μ-CO); 211.7, 210.9 (CO); 159.3, 159.1, 144.1, 143.6, 126.4, 115.0, 114.9 (C_6H_4); 130.2, 129.7 (N*C*Me); 88.6, 88.3, 87.0, 86.7 (Cp); 56.5, 55.7 (NMe); 55.6, 55.5 (OMe); 3.91 (NC*Me*).

Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(R')=C_\beta(H)C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = 4-C_6H_4-CN, R′ = Tol, 1m; R = 4-C_6H_4-OMe, R′ = Me, 1n; Tol = 4-C_6H_4-Me]. Complex $[Fe_2\{\mu\text{-}CN(Me)(4\text{-}C_6H_4\text{-}CN)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (150 mg, 0.238 mmol) was dissolved in CH_2Cl_2 (20 mL) and treated with HC≡CTol (0.40 mmol). The solution was stirred at reflux temperature for 4 h. Chromatography on an alumina column, with

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MeOH as eluent, afforded **1m**. Yield: 134 mg, 80%. Anal. Calcd for $C_{31}H_{25}F_3Fe_2N_2O_5S$: C, 52.72; H, 3.57; N, 3.97. Found: C, 52.66; H, 3.66; N, 4.01. IR (CH_2Cl_2): ν(C≡N) 2119 (s), ν(CO) 1994 (vs), 1814 (s), ν(C_αN) 1601 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.95−7.11 (m, 8 H, C_6H_4CN and C_6H_4Me); *5.32*, 5.30, 5.09, *4.90* (s, 10 H, Cp); 4.50 (s, 1 H, C_βH); 4.39, *3.69* (s, 3 H, NMe); *2.45*, 2.42 (s, 3 H, C_6H_4*Me*). *E*/*Z* ratio 4:1. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 253.5 (μ-CO); 232.6 (C_α); 209.4 (CO); 206.3 (C_γ); 153.1 (ipso-C_6H_4Me); 148.0 (ipso-C_6H_4CN); 137.6−122.2 (C_6H_4CN and C_6H_4Me); 117.4 (C_6H_4*C*N); 91.9, *91.7*, *88.0*, 88.4 (Cp); 55.1 (C_β); *55.4*, 45.9 (NMe); 21.1 (C_6H_4*Me*).

Compound **1n** was prepared by reacting [Fe_2{μ-CN(Me)(*p*-C_6H_4-OMe)}(μ-CO)(CO)(NCMe)$(Cp)_2$][SO_3CF_3] (150 mg, 0.236 mmol) with a large excess of HC≡CMe, at room temperature for 12 h.

1n (yield: 79%). Anal. Calcd for $C_{25}H_{24}F_3Fe_2NO_6S$: C, 47.27; H, 3.81; N, 2.21. Found: C, 47.39; H, 3.97; N, 2.15. IR (CH_2Cl_2): ν(CO) 1991 (vs), 1812 (s), ν(C_αN) 1640 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.52−6.77 (m, 4 H, C_6H_4OMe); 5.31, *5.25*, 5.11, *4.77* (s, 10 H, Cp); *4.97*, 4.53 (s, 1 H, C_βH); 4.24, *3.57* (s, 3 H, NMe); *3.91*, 3.75 (s, 3 H, OMe); *3.89*, 3.81 (s, 3 H, C_γMe). *E*/*Z* ratio 2:1. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 255.9 (μ-CO); 230.0, *229.1* (C_α); *209.9*, 209.5 (CO); 208.4 (C_γ); *159.8*, 159.5 (ipso-C_6H_4OMe); 153.1 (ipso-C_6H_4Me); 139.1, *136.2*, 126.0, 122.6, *114.5*, 114.3 (C_6H_4OMe); 90.4, *90.3*, 88.0, *87.8* (Cp); 55.4 (OMe); *54.0*, 53.8 (C_β); *53.7*, 46.5 (NMe); 42.4, *42.2* (C_γ*Me*).

Synthesis of [Fe_2{μ-η^1:η^3-C(R′)=C(E)C=N(Me)(R)}(μ-CO)(CO)$(Cp)_2$] (R = Xyl, R′ = Me, E = S, 2a; R = Xyl, R′ = Tol, E = S, 2b; R = Xyl, R′ = CO_2Me, E = S, 2c; R = Xyl, R′ = CH_2OH, E = S, 2d; R = Xyl, R′ = Bu^n, E = S, 2e; R = Xyl, R′ = Me, E = Se, 3a; R = Xyl, R′ = Tol, E = Se, 3b; R = Me, R′ = Me, E = Se, 3c; R = Me, R′ = Tol, E = Se, 3d; R = Me, R′ = CO_2Me, E = Se, 3e; R = Me, R′ = Bu^n, E = Se, 3f; R = Me, R′ = CH_2OH, E = Se, 3g). A mixture of **1a** (202 mg, 0.319 mmol) and S_8 (300 mg, 1.17 mmol) in THF (20 mL) was treated with NaH (38 mg, 1.60 mmol). The mixture was stirred for 30 min, then it was filtered on an alumina pad. Solvent removal gave a residue that was dissolved in CH_2Cl_2 and chromatographed on alumina: the band corresponding to **2a** was collected using THF as eluent. The product was obtained as a green powder upon solvent removal. Yield: 118 mg, 72%. Anal. Calcd for $C_{25}H_{25}Fe_2NO_2S$: C, 58.28; H, 4.89; N, 2.72. Found: C, 58.24; H, 4.96; N, 2.71. IR (CH_2Cl_2): ν(CO) 1961 (vs), 1790 (s), ν(C_αN) 1602 (w) cm^{-1}. IR (KBr pellets): ν(CS) 689 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38−7.21 (m, 3 H, $Me_2C_6H_3$); 4.97, 4.29 (s, 10 H, Cp); 4.03 (s, 3 H, C_γMe); 3.59 (s, 3 H, NMe); 2.61, 2.11 (s, 6 H, $Me_2C_6H_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 264.0 (μ-CO); 234.6 (C_α); 212.0 (CO); 199.6 (C_γ); 142.2 (ipso-$Me_2C_6H_3$); 135.5, 134.5, 128.9, 128.8, 128.4 ($Me_2C_6H_3$); 113.1 (C_β); 89.7, 89.3 (Cp); 45.7 (NMe); 38.9 (C_γ*Me*); 18.4, 17.9 ($Me_2C_6H_3$).

Compounds **2b**−**e** and **3a**−**g** were prepared by the same procedure described for **2a**, by reacting S (or Se) and NaH with **1b**−**l**, respectively. Crystals of **2b** and **3a** suitable for X-ray analysis were obtained by CH_2Cl_2 solutions layered with petroleum ether (bp 40−60 °C), at −20 °C.

2b (yield 80%; color: green). Anal. Calcd for $C_{31}H_{29}Fe_2NO_2S$: C. 62.97; H. 4.94, N 2.37. Found: C. 63.01; H. 4.90, N 2.29. IR (CH_2Cl_2): ν(CO) 1963 (vs), 1790 (s), ν(CN) 1599 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.59−7.24 (7 H, MeC_6H_4 and $Me_2C_6H_3$); 4.59, 4.55 (s, 10 H, Cp); 3.69 (s, 3 H, NMe); 2.65, 2.16 (s, 3 H, $Me_2C_6H_3$); 2.45 ppm (s, 3 H, MeC_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 264.3 (μ-CO); 235.3 (C_α); 212.7 (CO); 196.1 (C_γ); 153.9 (ipso-MeC_6H_4); 142.2 (ipso-$Me_2C_6H_3$); 135.6−126.2 (MeC_6H_4 and $Me_2C_6H_3$); 112.8 (C_β); 90.5 89.3 (Cp); 45.6 (NMe); 21.3 (MeC_6H_4); 18.5 17.9 ppm ($Me_2C_6H_3$).

2c (yield: 75%; color: green). Anal. Calcd for $C_{26}H_{25}Fe_2NO_4S$: C, 55.84; H, 4.51; N, 2.50. Found: C, 55.91; H, 4.37; N, 2.52. IR (CH_2Cl_2): ν(CO) 1972 (vs), 1799 (s), 1701 (m), ν(C_αN) 1599 (w) cm^{-1}. IR (KBr pellets): ν(CS) 687 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.39−7.22 (m, 3 H, $Me_2C_6H_3$); 4.91, 4.54 (s, 10 H, Cp); 4.19 (s, 3 H, CO_2Me); 3.64 (s, 3 H, NMe); 2.60, 2.08 (s, 6 H, $Me_2C_6H_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 261.7 (μ-CO); 236.5 (C_α); 211.6 (CO); 180.3, 179.0 (*C*O_2Me and C_γ); 142.4 (ipso-$Me_2C_6H_3$); 135.3, 134.3, 129.2, 129.1, 128.6 ($Me_2C_6H_3$); 115.4 (C_β); 90.6, 89.1 (Cp); 52.2 (CO_2*Me*); 46.0 (NMe); 18.2, 17.8 ($Me_2C_6H_3$).

2d (yield: 80%; color: green). Anal. Calcd for $C_{25}H_{25}Fe_2NO_3S$: C, 56.52; H, 4.74; N, 2.64. Found: C, 56.51; H, 4.83; N, 2.50. IR (CH_2Cl_2): ν(CO) 1967 (vs), 1789 (s), ν(C_αN) 1599 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.39−7.24 (m, 3 H, $Me_2C_6H_3$); 6.85 (dd, $^3J_{HH}$ = 4.76 Hz, 1 H, OH); 6.02, 5.95 (dd, $^2J_{HH}$ = 12.99 Hz, $^3J_{HH}$ = 4.76 Hz, 2 H, CH_2OH); 4.99, 4.52 (s, 10 H, Cp); 3.57 (s, 3 H, NMe); 2.57, 2.10 (s, 6 H, $Me_2C_6H_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 262.6 (μ-CO); 236.5 (C_α); 212.1 (CO); 201.2 (C_γ); 141.2 (ipso-$Me_2C_6H_3$); 135.5−128.7 ($Me_2C_6H_3$); 88.9, 88.8 (Cp); 73.0 (CH_2); 45.7 (NMe); 18.1, 17.7 ($Me_2C_6H_3$).

2e (yield: 77%; color: green). Anal. Calcd for $C_{28}H_{31}Fe_2NO_2S$: C, 60.34; H, 5.61; N, 2.51. Found: C, 60.26; H, 5.54; N, 2.48. IR (CH_2Cl_2): ν(CO) 1961 (vs), 1789 (s), ν(C_αN) 1604 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.37−7.20 (m, 3 H, $Me_2C_6H_3$); 4.97, 4.32 (s, 10 H, Cp); 3.77, 2.77 (m, 2 H, $C_\gamma CH_2$); 1.85, 1.72 (m, 4 H, $C_\gamma CH_2CH_2CH_2$); 3.57 (s, 3 H, NMe); 2.62, 2.09 (s, 6 H, $Me_2C_6H_3$); 1.18 (m, 3 H, $C_\gamma CH_2CH_2CH_2CH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 264.5 (μ-CO); 233.7 (C_α); 212.3 (CO); 206.7 (C_γ); 142.1 (ipso-$Me_2C_6H_3$); 135.6, 134.7, 128.9, 128.5 ($Me_2C_6H_3$); 109.9 (C_β); 89.8, 89.0 (Cp); 51.7, 33.6, 23.9 (CH_2); 45.6 (NMe); 18.3, 17.9 ($Me_2C_6H_3$); 14.4 ($C_\gamma CH_2CH_2CH_2CH_3$).

3a (yield: 85%, color: green). Anal. Calcd for $C_{25}H_{25}Fe_2NO_2Se$: C, 53.42; H, 4.48; N, 2.49. Found: C, 53.36; H, 4.47; N, 2.52. IR (CH_2Cl_2): ν(CO) 1965 (vs), 1793 (s), ν(C_αN) 1604 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.36−7.21 (m, 3 H, $Me_2C_6H_3$); 4.99, 4.30 (s, 10 H, Cp); 4.13 (s, 3 H, C_γMe); 3.57 (s, 3 H, NMe); 2.67, 2.10 (s, 6 H, $Me_2C_6H_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 262.7 (μ-CO); 228.9 (C_α); 211.8 (CO); 202.1 (C_γ); 141.7 (ipso-$Me_2C_6H_3$); 135.9, 134.6, 128.9, 128.6 ($Me_2C_6H_3$); 90.7 (C_β); 90.5, 89.4 (Cp); 46.6 (NMe); 41.5 (C_γ*Me*); 18.3, 18.1 ($Me_2C_6H_3$).

3b (yield: 85%, color: red). Anal. Calcd for $C_{31}H_{29}Fe_2NO_2Se$: C, 58.34; H, 4.58; N, 2.19. Found: C, 58.36; H, 4.47; N, 2.31. IR (CH_2Cl_2): ν(CO) 1967 (vs), 1793 (s), ν(C_αN) 1605 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.54−7.21 (m, 7 H, $Me_2C_6H_3$ and C_6H_4Me); 4.59, 4.54 (s, 10 H, Cp); 3.65 (s, 3 H, NMe); 2.69, 2.12 (s, 6 H, $Me_2C_6H_3$); 2.43 (s, 3 H, C_6H_4*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 262.6 (μ-CO); 229.5 (C_α); 212.3 (CO); 199.2 (C_γ); 154.7 (ipso-C_6H_4Me); 141.7 (ipso-$Me_2C_6H_3$); 135.9, 134.8, 134.4, 129.1, 129.0, 128.8, 128.7, 125.7 ($Me_2C_6H_3$ and C_6H_4Me); 90.6, 90.2 (Cp); 89.6 (C_β); 46.9 (NMe); 21.3 (C_6H_4*Me*); 18.5, 18.1 ($Me_2C_6H_3$).

3c (yield: 82%, color: green). Anal. Calcd for $C_{18}H_{19}Fe_2NO_2Se$: C, 45.80; H, 4.06; N, 2.97. Found: C, 45.77; H, 4.12; N, 3.03. IR (CH_2Cl_2): ν(CO) 1968 (vs), 1783 (s), ν(C_αN) 1657 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.99, 4.56 (s, 10 H, Cp); 4.02 (s, 3 H, C_γ-Me); 3.76, 3.33 (s, 6 H, NMe). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 265.9 (μ-CO); 226.1 (C_α); 211.0 (CO); 199.7 (C_γ); 91.2 (C_β); 90.4, 89.0 (Cp); 45.1, 44.6 (NMe); 41.1 (C_γ*Me*).

3d (yield: 88%, color: green). Anal. Calcd for $C_{24}H_{23}Fe_2NO_2Se$: C, 52.59; H, 4.23; N, 2.56. Found: C, 52.62; H, 4.18; N, 2.62. IR (CH_2Cl_2): ν(CO) 1970 (vs), 1783 (s), ν(C_αN) 1657 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.52, 7.38 (d, 4 H, $^3J_{HH}$ = 6.0 Hz, MeC_6H_4); 4.81, 4.60 (s, 10 H, Cp); 3.81, 3.38 (s, 6 H, NMe); 2.41 (s, 3 H, MeC_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 265.8 (μ-CO); 227.0 (C_α); 211.3 (CO); 196.9 (C_γ); 154.5 (ipso-MeC_6H_4); 134.4, 129.2, 128.6, 128.5, 125.2 (MeC_6H_4); 90.8 (C_β); 90.2, 90.0 (Cp); 45.0, 44.8 (NMe); 21.2 (MeC_6H_4).

3e (yield: 82%, color: brown). Anal. Calcd for $C_{19}H_{19}Fe_2NO_4Se$: C, 44.23; H, 3.71; N, 2.71. Found: C, 44.30; H, 3.67; N, 2.65. IR (CH_2Cl_2): ν(CO) 1978 (vs), 1793 (s), 1701 (m), ν(C_αN) 1654 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.90, 4.78 (s, 10 H, Cp); 4.14 (s,

Table 4. Crystal Data and Experimental Details for 2b·CH$_2$Cl$_2$, 3a, 4, 6a, and 7b

	2b·CH$_2$Cl$_2$	**3a**	**4**	**6a**	**7b**
formula	$C_{32}H_{31}Cl_2Fe_2NO_2S$	$C_{25}H_{25}Fe_2NO_2Se$	$C_{25}H_{25}Fe_2NO_3$	$C_{19}H_{21}FeNOS$	$C_{18}H_{19}FeNOS$
fw	676.24	562.12	499.16	367.28	353.25
T, K	293(2)	100(2)	296(2)	295(2)	293(2)
λ, Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	monoclinic	orthorhombic	triclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	*Pbca*	$P\bar{1}$
a, Å	8.4612(17)	8.3952(17)	10.498(2)	12.947(3)	9.5043(19)
b, Å	16.310(3)	8.8375(18)	13.149(3)	16.041(4)	10.032(2)
c, Å	22.242(4)	17.233(3)	16.805(3)	17.013(5)	10.085(2)
α, deg	90	76.57(3)	90	90	113.79(3)
β, deg	98.27(3)	82.09(3)	101.91(3)	90	102.08(3)
γ, deg	90	61.98(3)	90	90	95.94(3)
cell volume, Å^3	3037.6(11)	1097.2(4)	2269.8(8)	3533.3(16)	841.2(3)
Z	4	2	4	8	2
D_c, g cm^{-3}	1.479	1.701	1.461	1.381	1.395
μ, mm^{-1}	1.230	3.003	1.304	0.975	1.021
F(000)	1392	568	1032	1536	368
cryst size, mm	0.22 × 0.18 × 0.13	0.26 × 0.22 × 0.15	0.23 × 0.18 × 0.14	0.18 × 0.14 × 0.11	0.31 × 0.25 × 0.18
θ limits, deg	1.55−25.03	1.22−30.51	1.98−30.51	2.35−25.00	2.24−27.88
no. of reflns collected	26 500	13 026	300 582	23 768	9469
no. of indep reflns	5358 [$R_{int} = 0.0831$]	6670 [$R_{int} = 0.0685$]	6919 [$R_{int} = 0.0669$]	3119 [$R_{int} = 0.1638$]	4009 [$R_{int} = 0.0256$]
no. of data/restraints/ params	5358/271/458	6670/146/284	6919/0/284	3119/1/215	4009/46/201
goodness on fit on F^2	0.977	0.987	1.001	1.325	1.040
R_1 ($I > 2\sigma(I)$)	0.0498	0.0536	0.0435	0.1156	0.0425
wR_2 (all data)	0.1409	0.1448	0.1188	0.2183	0.1201
largest diff peak and hole, e Å^{-3}	0.563/−0.476	1.671/−1.173	0.582/ −0.484	0.718/ −0.505	0.563/−0.506

3 H, CO$_2$Me); 3.71, 3.37 (s, 6 H, NMe). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 262.9 (μ-CO); 227.6 (C$_\alpha$); 210.3 (CO); 181.1 (C$_\gamma$); 178.4 (*C*O$_2$Me); 92.8 (C$_\beta$); 91.6, 88.8 (Cp); 52.2 (CO$_2$*Me*); 45.4, 44.8 (NMe).

3f (yield: 83%, color: brown). Anal. Calcd for $C_{21}H_{25}Fe_2NO_2Se$: C, 49.06; H, 4.90; N, 2.72. Found: C, 49.12; H, 4.85; N, 2.78. IR (CH$_2$Cl$_2$): ν(CO) 1965 (vs), 1782 (s), ν(C$_\alpha$N) 1654 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 5.01, 4.61 (s, 10 H, Cp); 3.74, 2.79 (m, 2 H, C$_\gamma$CH$_2$); 3.68, 3.35 (s, 6 H, NMe); 1.80, 1.70 (m, 4 H, C$_\gamma$CH$_2$C*H*$_2$C*H*$_2$); 1.21 (m, 3 H, C$_\gamma$CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 264.9 (μ-CO); 226.8 (C$_\alpha$); 211.3 (CO); 199.1 (C$_\gamma$); 91.9 (C$_\beta$); 89.5, 89.1 (Cp); 51.5, 33.9, 24.6 (CH$_2$); 45.4, 43.9 (NMe); 13.7 (C$_\gamma$CH$_2$CH$_2$CH$_2$*C*H$_3$).

3g (yield: 76%, color: green). Anal. Calcd for $C_{18}H_{19}Fe_2NO_2Se$: C, 45.80; H, 4.06; N, 2.97. Found: C, 44.69; H, 3.99; N, 2.90. IR (CH$_2$Cl$_2$): ν(CO) 1973 (vs), 1787 (s), ν(C$_\alpha$N) 1654 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.13 (m, 1 H, OH); 5.92, 5.65 (m, 2 H, C*H*$_2$OH); 4.93, 4.65 (s, 10 H, Cp); 3.66, 3.18 (s, 6 H, NMe). ^{13}C{^{1}H} NMR (CDCl$_3$) δ 263.1 (μ-CO); 225.4 (C$_\alpha$); 214.0 (CO); 200.2 (C$_\gamma$); 90.1 (C$_\beta$); 89.4, 88.5 (Cp); 69.4 (CH$_2$); 45.1, 44.5 (NMe).

Synthesis of [Fe$_2${μ-η^1:η^3-C$_\gamma$(Me)C$_\beta$(O)C$_\alpha$N(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$] (4). A THF solution (20 mL) of **1a** (250 mg, 0.395 mmol) was treated with Me$_3$NO (148 mg, 1.97 mmol) and NaH (96 mg, 4.00 mmol). The mixture was stirred for 1 h, then it was filtered on an alumina pad. Solvent removal and chromatography on alumina gave a green band corresponding to **4**, collected by using a mixture of THF and MeOH as eluent (19:1, v:v). Yield: 58 mg, 29%. Crystals suitable for X-ray analysis were collected by a diethyl ether solution layered with petroleum ether (bp 40−60 °C), at −20 °C. Anal. Calcd for $C_{25}H_{25}Fe_2NO_3$: C, 60.15; H, 5.05; N, 2.81. Found: C, 60.18; H, 4.93; N, 2.87. IR (CH$_2$Cl$_2$): ν(CO) 1945 (vs), 1777 (s), ν(C$_\alpha$N) 1550 (m) cm^{-1}. IR (KBr pellets): ν(C$_\beta$O) 1465 (m) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.33−7.10 (m, 3 H, Me$_2$C$_6$*H*$_3$); 4.88, 4.22 (s, 10 H, Cp); 3.59 (s, 3 H, C$_\gamma$Me); 3.44 (s, 3 H, NMe); 2.34, 2.10 (s, 6 H, *Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 275.7 (μ-CO); 258.9 (C$_\alpha$); 219.2 (CO); 184.5 (C$_\gamma$); 156.9 (C$_\beta$); 143.2 (ipso-Me$_2$*C*$_6$H$_3$); 138.7, 136.0, 129.3, 128.7, 128.1 (Me$_2$*C*$_6$H$_3$); 88.5, 86.6 (Cp); 46.3 (NMe); 35.0 (C$_\gamma$*Me*); 18.1, 17.5 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe(Cp)(CO){C$_\alpha${N(Me)(Xyl)}C$_\beta$(H)C$_\gamma$(R′)S}] (R′ = Me, 6a; R′ = CO$_2$Me, 6b). Compound **6a** was obtained as secondary product in the reaction of **1a** with S$_8$/NaH described above and isolated by chromatography as an orange band by using CH$_2$Cl$_2$ as eluent. Yield: 18 mg, 15%. Crystals suitable for X-ray analysis were obtained by a CDCl$_3$ solution layered with *n*-pentane, at −20 °C. Anal. Calcd for $C_{19}H_{21}FeNOS$: C, 62.13; H, 5.76; N, 3.81. Found: C, 62.22; H, 5.84; N, 3.72. IR (CH$_2$Cl$_2$): ν(CO) 1932 (vs), ν(C$_\beta$C$_\gamma$) 1516 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.17−7.10 (3 H, Me$_2$C$_6$*H*$_3$); 5.83 (s, 1 H, C$_\beta$H); 4.69 (s, 5 H, Cp); 3.61 (s, 3 H, NMe); 2.24 (s, 3 H, C$_\gamma$Me); 2.24, 2.03 (s, 6 H, *Me*$_2$C$_6$H$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 249.6 (C$_\alpha$); 217.3 (CO); 198.0 (C$_\gamma$); 145.3 (ipso-Me$_2$*C*$_6$H$_3$); 133.2, 132.9, 129.0, 128.6, 127.5 (Me$_2$*C*$_6$H$_3$); 131.6 (C$_\beta$); 82.9 (Cp); 47.3 (NMe); 26.0 (C$_\gamma$*Me*); 19.6 (*Me*$_2$C$_6$H$_3$).

Compound **6b** was obtained as secondary product in the reaction of **1c** with S$_8$/NaH described above and isolated by chromatography as a gray band by using diethyl ether as eluent. Yield: 17%. Anal. Calcd for $C_{20}H_{21}FeNO_3S$: C, 58.40; H, 5.15; N, 3.41. Found: C, 58.30; H, 5.02; N, 3.51. IR (CH$_2$Cl$_2$): ν(CO) 1946 (vs), 1712 (m), ν(C$_\beta$C$_\gamma$) 1512 (w) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ *7.81*, 6.79 (s, 1 H, C$_\beta$H); 7.18−7.10 (3 H, Me$_2$C$_6$*H*$_3$); 4.77, *4.14* (s, 5 H, Cp); *3.85*, 3.71 (s, 3 H, CO$_2$Me); 3.69, *3.53* (s, 3 H, NMe); *2.37*, *2.32*, 2.24, 2.00 (s, 6 H, *Me*$_2$C$_6$H$_3$). *E*/*Z* ratio 2:1. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 253.0, *248.3* (C$_\alpha$); 215.7 (CO); 179.1 (C$_\gamma$); 164.0 (*C*O$_2$Me); *149.1*, 141.5 (ipso-Me$_2$*C*$_6$H$_3$); 136.8−127.8 (Me$_2$*C*$_6$H$_3$); 135.6, *134.7* (C$_\beta$); 83.4, *82.9* (Cp); *52.6*, 52.5 (CO$_2$*Me*); 48.2, *43.8* (NMe); *18.4*, *18.0*, 17.7, 17.3 (*Me*$_2$C$_6$H$_3$).

Synthesis of [Fe(Cp)(CO){C(R′)C(H)C{N(Me)(R)}S}] (R = Me, R′ = Me, 7a; R = Me, R′ = Tol, 7b; R = Me, R′ = CO$_2$Me, **7c; R = *p*-C$_6$H$_4$-CN, R′ = Tol, 7d; R = 4-C$_6$H$_4$OMe, R′ = Me, 7e).** Compound **1f** (75 mg, 0.137 mmol) was dissolved in THF (10 mL), and S$_8$ (450 mg, 1.76 mmol) was added. The mixture was treated with NaH (33 mg, 1.38 mmol) and stirred for 45 min. Then, the mixture was filtered on alumina. Solvent removal and chromatography on alumina, with CH$_2$Cl$_2$ as eluent, afforded **7a** as a red fraction. Yield: 37 mg, 84%. Anal. Calcd for $C_{12}H_{15}FeNOS$: C, 57.00; H, 5.45; N, 5.05. Found: C, 57.12; H, 5.39; N, 5.11. IR (CH$_2$Cl$_2$): ν(CO) 1924 (vs), ν(C═C) 1527 (s) cm^{-1}. ^{1}H NMR (acetone-*d*$_6$): δ 7.10 (s, 1 H, C$_\beta$H); 4.58 (s, 5 H, Cp); 3.40, 3.32 (s, 6 H, NMe); 2.79 (s, 3 H, C$_\gamma$Me). ^{13}C{^{1}H} NMR (acetone-*d*$_6$): δ 247.2 (C$_\gamma$); 218.0 (CO); 200.3 (C$_\alpha$); 134.3 (C$_\beta$); 82.9 (Cp); 41.7, 41.6 (NMe); 38.4 (C$_\gamma$*Me*). ESI-MS (ES$^+$): 277 *m*/*z*.

Complexes **7b**−**e** were obtained by the same procedure described for **7a**, by reacting S_8/NaH with **1g**, **1h**, **1m**, and **1n**, respectively. Crystals of **7b** suitable for X-ray analysis were obtained by a diethyl ether solution, layered with *n*-pentane, at −20 °C.

7b (yield: 85%; color: orange). Anal. Calcd for $C_{18}H_{19}FeNOS$: C, 61.20; H, 5.42; N, 3.96. Found: C, 61.25; H, 5.44; N, 4.02. IR (CH_2Cl_2): ν(CO) 1925 (vs), ν(C=C) 1526 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.25, 7.11 (d, 4 H, $^3J_{HH}$ = 8.05 Hz, MeC$_6$*H*$_4$); 7.11 (s, 1 H, C_βH); 4.41 (s, 5 H, Cp); 3.48, 3.31 (s, 6 H, NMe); 2.35 (s, 3 H, *Me*C$_6$H$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 244.3 (C_γ), 217.5 (CO), 199.7 (C_α), 153.9 (ipso-Me*C*$_6$H$_4$); 136.0, 128.1, 124.8 (Me*C*$_6$H$_4$); 133.8 (C_β); 83.5 (Cp); 43.2, 42.6 (NMe); 21.1 (*Me*C$_6$H$_4$).

7c (yield: 88%; color: orange). Anal. Calcd for $C_{13}H_{15}FeNO_3S$: C, 48.62; H, 4.71; N, 4.36. Found: C, 48.71; H, 4.69; N, 4.25. IR (CH_2Cl_2): ν(CO) 1944 (vs), 1693 (m), ν(C=C) 1536 (s) cm^{-1}. ^{1}H NMR (acetone-*d*$_6$): δ 7.22 (s, 1 H, C_βH); 4.58 (s, 5 H, Cp); 3.73 (s, 3 H, CO$_2$Me); 3.47, 3.40 (s, 6 H, NMe). ^{13}C{^{1}H} NMR (acetone-*d*$_6$): δ 221.7 (C_γ); 216.9 (CO); 201.2 (C_α); 179.3 (*C*O$_2$Me); 134.0 (C_β); 82.8 (Cp); 50.6 (CO$_2$*Me*); 43.0, 42.5 (NMe).

7d (yield: 75%; color: orange). Anal. Calcd for $C_{24}H_{20}FeN_2OS$: C, 65.46; H, 4.58; N, 6.36. Found: C, 65.57; H, 4.62; N, 6.28. IR (CH_2Cl_2): ν(C≡N) 2217 (w), ν(CO) 1934 (vs), ν(C=C) 1604 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.66−7.03 (m, 8 H, CNC$_6$*H*$_4$ and MeC$_6$*H*$_4$); 6.88 (s, 1 H, C_βH); 4.44 (s, 5 H, Cp); 3.74 (s, 3 H, NMe); 2.29 (s, 3 H, *Me*C$_6$H$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 249.9 (C_γ), 216.5 (CO), 200.6 (C_α), 153.4 (ipso-Me*C*$_6$H$_4$); 150.0 (ipso-CN*C*$_6$H$_4$); 135.9 (C_β); 133.5, 128.1, 126.3, 124.7 (Me*C*$_6$H$_4$); 118.0 (C$_6$H$_4$*C*N); 83.8 (Cp); 43.3 (NMe); 21.0 (*Me*C$_6$H$_4$).

7e (yield: 76%; color: brown). Anal. Calcd for $C_{18}H_{19}FeNO_2S$: C, 58.55; H, 5.19; N, 3.79. Found: C, 58.57; H, 5.22; N, 3.66. IR (CH_2Cl_2): ν(CO) 1926 (vs), ν(C=C) 1607 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.10, 6.90 (m, 4 H, C$_6$*H*$_4$); 6.69 (s, 1 H, C_βH); 4.61 (s, 5 H, Cp); 3.82 (s, 3 H, OMe); 3.65 (s, 3 H, NMe); 2.79 (s, 3 H, C_γMe). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 249.0 (C_γ); 217.1 (CO); 201.5 (C_α); 158.5, 139.6 (ipso-*C*$_6$H$_4$OMe); 136.5 (C_β); 126.7, 114.5 (*C*$_6$H$_4$OMe); 82.8 (Cp); 55.4 (OMe); 43.5 (NMe); 38.9 (C_γ*Me*).

X-ray Crystallography. Crystal data and collection details for **2b**·CH$_2$Cl$_2$, **3a**, **4**, **6a**, and **7b** are reported in Table 4. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer (for **2b**·CH$_2$Cl$_2$, **3a**, **4**, and **7b**) and on a Bruker Apex II diffractometer (for **6a**), equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[17] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[18] Non-H atoms were refined anisotropically, unless otherwise stated. H atoms were placed in calculated positions, except H(8) in **6a** and **7b**, which were located in the Fourier map. H atoms were treated isotropically using the 1.2-fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5-fold U_{iso} value of the parent C atom. The Tol group and the CH$_2$Cl$_2$ molecule in **2b**·CH$_2$Cl$_2$ and Cp ligand in **7b** are disordered. Disordered atomic positions were split and refined using one occupancy parameter per disordered group.

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Supporting Information Available: Crystallographic data for compounds **2b**·CH$_2$Cl$_2$, **3a**, **4**, **6a**, and **7b** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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