Formation of C–C Bonds in Diiron Complexes by Addition of Carbanions to Alkynyl(methoxy)carbene Ligands

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Addition of cyanide ions to the alkynyl(methoxy)carbene complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta{\equiv}C_\gamma R'\}(Cp)_2]^+$ (R = Xyl, R′ = Tol, **1a**; R = Xyl, R′ = Ph, **1b**; R = Xyl, R′ = Me_3Si, **1c**; R = Me, R′ = Tol, **1d**; R = Me, R′ = Ph, **1e**) occurs selectively at C_α to afford the 1,1-disubstituted σ-propargyl complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C(OMe)(CN)(C{\equiv}CR')\}(Cp)_2]$ (R = Xyl, R′ = Tol, **2a**; R = Xyl, R′ = Ph, **2b**; R = Xyl, R′ = Me_3Si, **2c**; R = Me, R′ = Tol, **2d**; R = Me, R′ = Ph, **2e**). Conversely, the stabilised carbanaions $[CH(R)_2]^-$ (R = CN, CO_2Me) add at the C_γ position with subsequent hydrogen migration to C_β to give the 1-σ-buta-1,3-dienyl complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe){=}C_\beta HC_\gamma(Tol){=}C_\delta(R)_2\}(Cp)_2]$ (R = CN, **3a**; CO_2Me, **3b**). No migration is possible in the absence of hydrogen atoms at C_δ, therefore addition of $[C(Me)(CO_2Me)_2]^-$ to **1a** results in the formation of the σ-allenyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe){=}C_\beta{=}C_\gamma(Tol)C_\delta(Me)(CO_2Me)_2\}(Cp)_2]$ (**4**). Protonation of the neutral complexes **3b** and **4** affords the vinyl(methoxy)carbene complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)C_\delta(R)(CO_2Me)_2\}]^+$ (R = H, **5**; Me, **6**), which exist in solution as mixtures of (*E*)- and (*Z*)-isomers in dynamic equilibrium, as shown by VT NMR studies. The cationic complex **6** shows electrophilic behaviour. Thus, addition of CN^- results in the σ-allyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)(CN)\text{-}[C_\beta H{=}C_\gamma(Tol)C_\delta(Me)(CO_2Me)_2]\}(Cp)_2]$ (**7**), whereas the reaction with Me_2NH affords the vinyl acyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(O)C_\beta H{=}C_\gamma(Tol)C_\delta(Me)(CO_2Me)_2\}(Cp)_2]$ (**8**). The crystal structures of **2b** and **3a·CH₂Cl₂** have been determined.

Introduction

Alkynyl(alkoxy)carbenes represent a quite important class of organometallic complexes, since they are potentially useful reagents for the synthesis of organic compounds.[1] Most of the studies that have appeared to date concern mononuclear chromium and tungsten compounds of the type $(CO)_5M{=}C(OEt)C{\equiv}CR$. Their reactivity includes addition of protic nucleophiles (amines, imines, alcohols, thiols, phosphanes, carboxylic acids)[2–4] and carbon nucleophiles (alkynes, enamines, enaminones, enol ethers),[5–7] together with a large variety of cyclisation reactions.[8–10] We have recently reported the synthesis and the reactivity towards amines of the diiron alkynyl(methoxy)carbene complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta{\equiv}C_\gamma R'\}(Cp)_2]^+$ (R = Xyl, R′ = Tol, **1a**; R = Xyl, R′ = Ph, **1b**; R = Xyl, R′ = Me_3Si, **1c**; R = Me, R′ = Tol, **1d**; R = Me, R′ = Ph, **1e**).[11] The addition of amines to **1** was found to be completely regioselective at C_γ, whereas in the case of the mononuclear species $(CO)_5M{=}C(OEt)C{\equiv}CR$, addition at the carbene carbon C_α has also been observed.[1] The different regiochemistry observed could be due to either steric and/or electronic factors. In order to shed more light on this point, we decided to study the reactivity of **1** with other nucleophiles, and here we report some reactions involving **1** and different carbanions, such as CN^-, $[CH(R)_2]^-$ (R = CN, CO_2Me) and $[CMe(CO_2Me)_2]^-$. These reactions represent a direct way to form new C–C bonds in a diiron complex and, therefore, are potentially interesting in order to build new coordinated organic species.

Results and Discussion

The reaction of the alkynyl(methoxy)carbene complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta{\equiv}C_\gamma R'\}(Cp)_2]^+$ (R = Xyl, R′ = Tol, **1a**; R = Xyl, R′ = Ph, **1b**; R = Xyl, R′ = Me_3Si, **1c**; R = Me, R′ = Tol, **1d**; R = Me, R′ = Ph, **1e**) with $(nBu_4N)(CN)$ in CH_2Cl_2 solution (Scheme 1) results in the selective addition of the cyanide ion to the carbene carbon to give the 1,1-disubstituted σ-propargyl complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C(OMe)(CN)(C{\equiv}CR')\}(Cp)_2]$ (R = Xyl, R′ = Tol, **2a**; R = Xyl, R′ = Ph, **2b**; R = Xyl, R′ = Me_3Si, **2c**; R = Me, R′ = Tol, **2d**; R = Me, R′ = Ph, **2e**) in good yields (70–80%). The reaction can be completely reversed by addition of CF_3SO_3Me.

The IR spectra of **2** show, as expected,[12] ν(CO) at around 1970 and 1790 cm^{-1} for the terminal and bridging carbonyls, respectively, and a weak ν(CN) absorption (at

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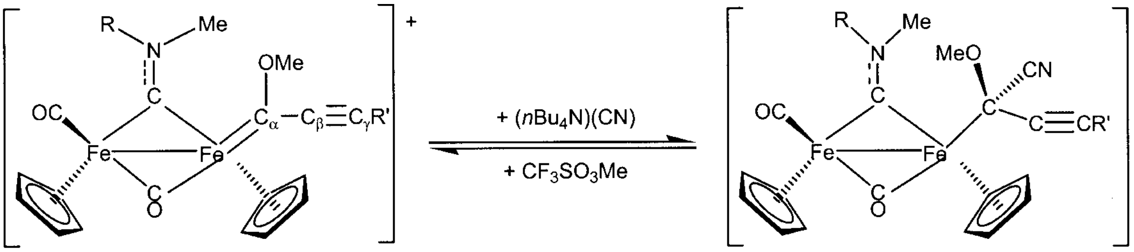


R	R'	
Xyl	Tol	**1a**
Xyl	Ph	**1b**
Xyl	$SiMe_3$	**1c**
Me	Tol	**1d**
Me	Ph	**1e**

R	R'	
Xyl	Tol	**2a**
Xyl	Ph	**2b**
Xyl	$SiMe_3$	**2c**
Me	Tol	**2d**
Me	Ph	**2e**

Scheme 1.

2190 cm^{-1} for **2a**) that is shifted to 2142 cm^{-1} in $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C(OMe)(^{13}CN)(C\equiv CTol)\}(Cp)_2]$ (prepared from the reaction of **1a** with $K^{13}CN$) because of an isotope effect. The NMR spectra of **2** evidence the presence in solution of one single isomer. This is interesting, since complexes **1** are chiral and the addition of CN^- produces a second chiral centre, thus making possible the presence of diastereomeric species. The fact that only one form is present in solution indicates that the cyanide addition is regio- and stereoselective, occurring at one specific face of the plane containing the alkynyl(methoxy)carbene ligand; therefore, a racemic mixture of one single diastereomer is selectively formed.

Three low-field resonances in the ^{13}C NMR spectra are attributable to the bridging carbyne ($\delta \approx 335$ ppm), and to the bridging and the terminal carbonyls ($\delta \approx 270$ and 215 ppm, respectively). The CN carbon resonates at $\delta \approx 126$ ppm, whereas the C≡C group shows two distinct signals at $\delta = 94$–105 and 89–99 ppm. Finally, the sp^3 propargylic carbon resonates in the high-field region of the spectra, as expected for a metal-bound alkyl ($\delta \approx 50$ ppm).

The molecular structure of complex **2b** has been determined by single-crystal X-ray analysis (Figure 1 and Table 1). The molecule contains a terminal C(OMe)(CN)(C≡CPh) ligand bound to $Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$, which shows a *cis* geometry of the Cp ligands with the Xyl group placed in the opposite side of the

Table 1. Selected bond lengths [Å] and angles [°] for complex **2b**.

Fe(1)–Fe(2)	2.5271(10)	C(13)–N(1)	1.317(5)
Fe(2)–C(11)	1.763(6)	C(14)–N(1)	1.468(6)
Fe(1)–C(12)	1.856(5)	C(23)–O(1)	1.430(5)
Fe(2)–C(12)	1.992(5)	C(24)–O(1)	1.426(5)
Fe(1)–C(13)	1.839(4)	C(23)–C(25)	1.463(7)
Fe(2)–C(13)	1.897(4)	C(25)–N(2)	1.144(6)
Fe(1)–C(23)	2.091(5)	C(23)–C(26)	1.470(7)
C(11)–O(11)	1.140(6)	C(26)–C(27)	1.188(6)
C(12)–O(12)	1.172(5)	C(27)–C(28)	1.437(7)
Fe(1)–C(23)–O(1)	110.9(3)	C(23)–C(26)–C(27)	174.8(5)
Fe(1)–C(23)–C(25)	108.0(3)	C(26)–C(27)–C(28)	176.5(5)
Fe(1)–C(23)–C(26)	107.3(3)	O(1)–C(23)–C(25)	108.6(4)
C(23)–C(25)–N(2)	177.5(6)	O(1)–C(23)–C(26)	111.2(4)

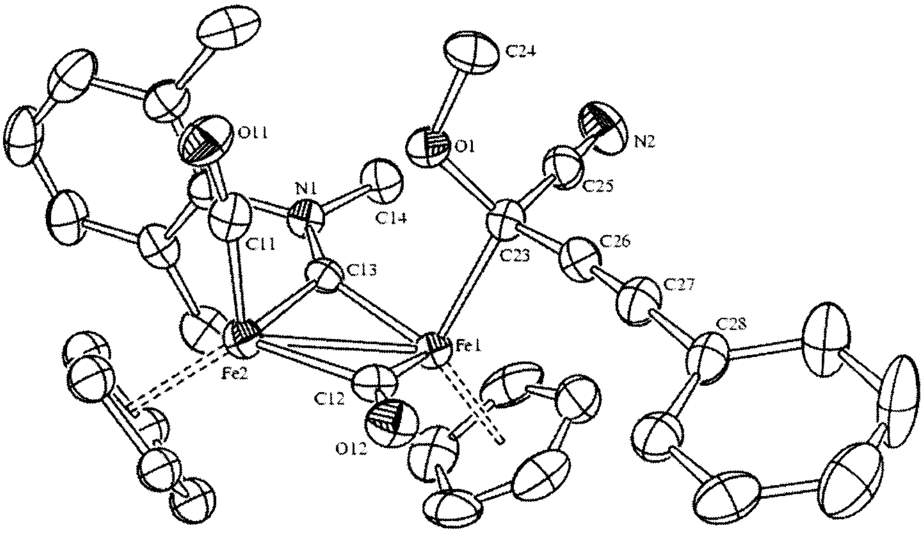
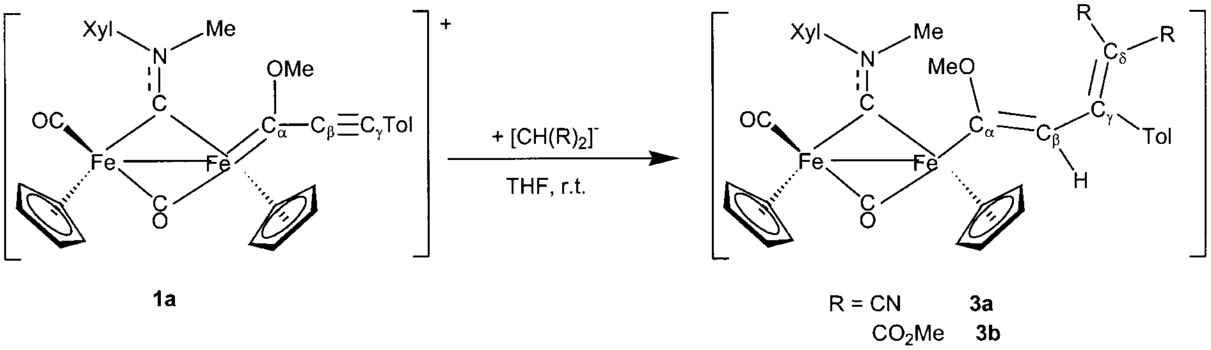


Figure 1. Molecular structure of **2b**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Cp bound to Fe(2) is drawn.



Scheme 2.

σ-propargyl, as previously found in analogous diiron and diruthenium complexes.[13,14] As in **1a**,[11] the C(13)–N(1) interaction [1.317(5) Å] suggests some double-bond character, and thus the aminocarbyne ligand can be alternatively described as a bridging iminium ion.

The bridging CO shows a marked asymmetry [Fe(1)–C(12) = 1.856(5) and Fe(2)–C(12) = 1.992(5) Å] as consequence of the different electronic properties of the terminal ligands [i.e. the σ-propargyl and CO]. Similarly, the bridging aminocarbyne is also asymmetric, although to a lesser extent [Fe(1)–C(13) = 1.839(4) and Fe(2)–C(13) = 1.897(4) Å]; an analogous behaviour has been observed previously in other diiron complexes containing bridging aminocarbyne and bridging carbonyl ligands.[12b,12c,13b,13c,15] The Fe(1)–C(23) distance [2.091(5) Å] is that of a pure Fe–C(sp^3) σ-bond and is similar to that found in the cyanomethyl complex [Fe_2\{μ-CN(Me)$_2$\}(μ-CO)(CO)(CH_2CN)-(Cp)$_2$] [2.068(3) Å].[15] The propargylic nature of the ligand is indicated by the fact that the C(23)–C(26) interaction [1.470(7) Å] is a single bond whereas C(26)–C(27) [1.188(6) Å] is a triple bond; moreover, the C(23)–C(26)–C(27)–C(28) chain is almost linear [C(23)–C(26)–C(27) = 174.8(5)°; C(26)–C(27)–C(28) = 176.5(5)°]. The C(25)–N(2) interaction [1.144(6) Å] is typical for the triple bond in organic nitriles, and C(25) shows sp hybridisation [C(23)–C(25)–N(2) = 177.5(6)°].

Table 2. Selected bond lengths [Å] and angles [°] for complex **3a**.

Fe(1)–Fe(2)	2.5110(9)	C(13)–N(1)	1.318(4)
Fe(2)–C(11)	1.758(4)	C(23)–O(1)	1.348(4)
Fe(1)–C(12)	1.859(3)	C(23)–C(25)	1.413(5)
Fe(2)–C(12)	2.008(3)	C(25)–C(26)	1.406(5)
Fe(1)–C(13)	1.834(3)	C(26)–C(27)	1.411(5)
Fe(2)–C(13)	1.894(3)	C(27)–C(28)	1.421(5)
Fe(1)–C(23)	1.936(3)	C(28)–N(2)	1.158(4)
C(11)–O(11)	1.153(4)	C(27)–C(29)	1.440(7)
C(12)–O(12)	1.178(4)	C(29)–N(3)	1.149(5)
Fe(1)–C(23)–O(1)	116.6(2)	C(26)–C(27)–C(28)	122.5(3)
Fe(1)–C(23)–C(25)	121.9(2)	C(26)–C(27)–C(29)	121.6(3)
O(1)–C(23)–C(25)	121.5(3)	C(28)–C(27)–C(29)	115.9(3)
C(23)–C(25)–C(26)	132.6(3)	C(27)–C(28)–N(2)	179.6(4)
C(25)–C(26)–C(27)	124.5(3)	C(27)–C(29)–N(3)	179.2(4)

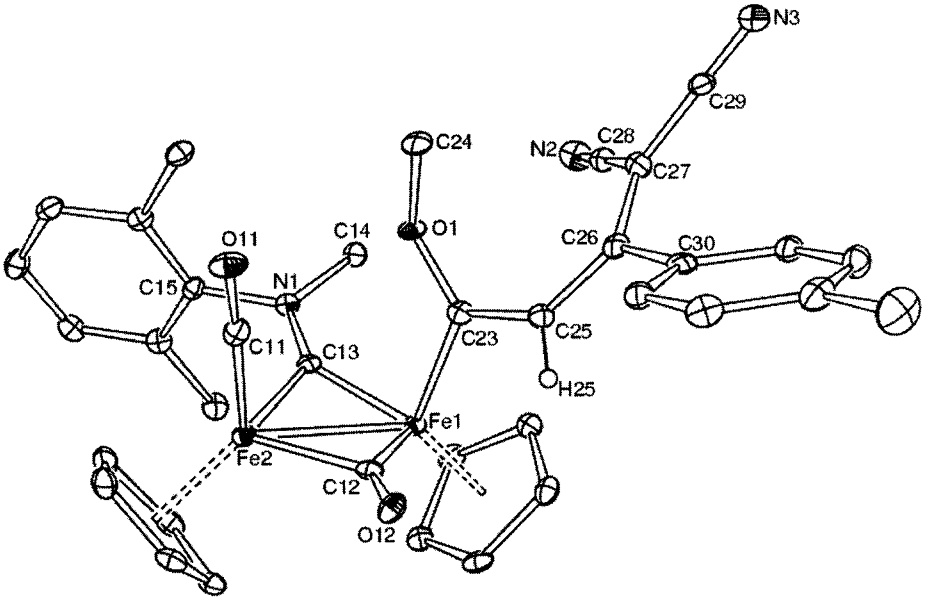
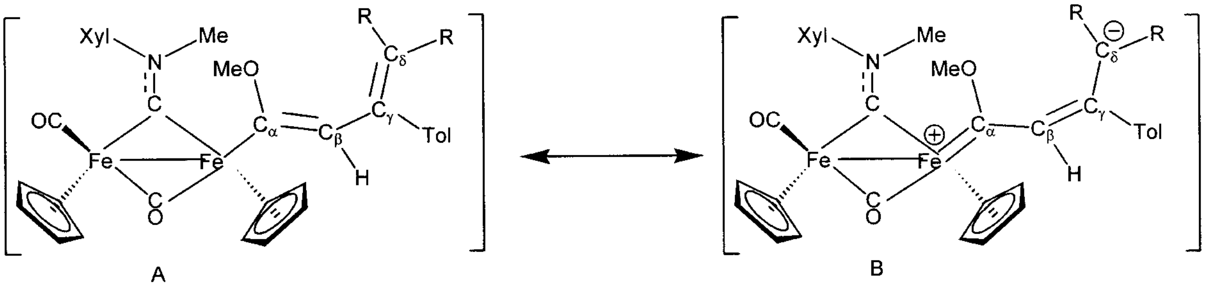


Figure 2. Molecular structure of **3a**, with key atoms labelled [all H atoms, except H(25), have been omitted]. Displacement ellipsoids are at 30% probability level.



Scheme 3.

The molecular structure of **2b** indicates that cyanide addition has occurred stereoselectively from a single side of the plane containing the alkynyl(methoxy)carbene ligand, thus explaining the observed formation of a single isomer.

The addition of stabilised carbanions of the type $[CH(R)_2]^-$ (R = CN, CO_2Me) to **1a** occurs differently (Scheme 2) and results in the formation of the 1-σ-buta-1,3-dienyl complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)=C_\beta HC_\gamma(Tol)=C_\delta(R)_2\}(Cp)_2]$ (R = CN, **3a**; CO_2Me, **3b**) in good yields (60–70%). Compounds **3** have been fully characterised spectroscopically and, moreover, the crystal structure of **3a** has been determined by X-ray diffraction (Figure 2 and Table 2).

The molecule retains the $Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2$ core present in the parent compound **1a**, to which the new terminal 1-σ-buta-1,3-dienyl ligand $C_\alpha(OMe)=C_\beta HC_\gamma(Tol)=C_\delta(CN)_2$ is bound. The almost equal C(23)–C(25) [1.413(5) Å], C(25)–C(26) [1.406(5) Å] and C(26)–C(27) [1.411(5) Å] distances indicate a strong delocalisation inside the butadienyl ligand, probably because of the presence of the strongly electron-withdrawing cyano groups. It is noteworthy that σ-butadienyl ligands usually show an alternating trend of the C–C bonds as, for example in $[Fe(Cp)(CO)_2(CH=CHCH=CHBr)]$ [1.341(4), 1.426(4) and 1.320(4) Å].[16] The delocalisation in the ligand causes some π-back-donation from the metal and, in fact, the Fe(1)–C(23) bond length [1.936(3) Å] is shorter than a pure Fe–C(sp^2) σ-interaction; for instance, 1.971(3) Å in $[Fe(Cp)(CO)_2(CH=CHCH=CHBr)]$[16] and 1.956(7) Å in the vinyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C(OMe)=CHC(=NPh)(Tol)\}(Cp)_2]$.[11] For comparison, the Fe=C(carbene) distance in the parent compound **1a** is 1.849(7) Å.[11] These data suggest that the1-σ-buta-1,3-dienyl complex **3a** can be alternatively described as a zwitterionic vinyl carbene (resonance form B in Scheme 3), although the first form prevails.

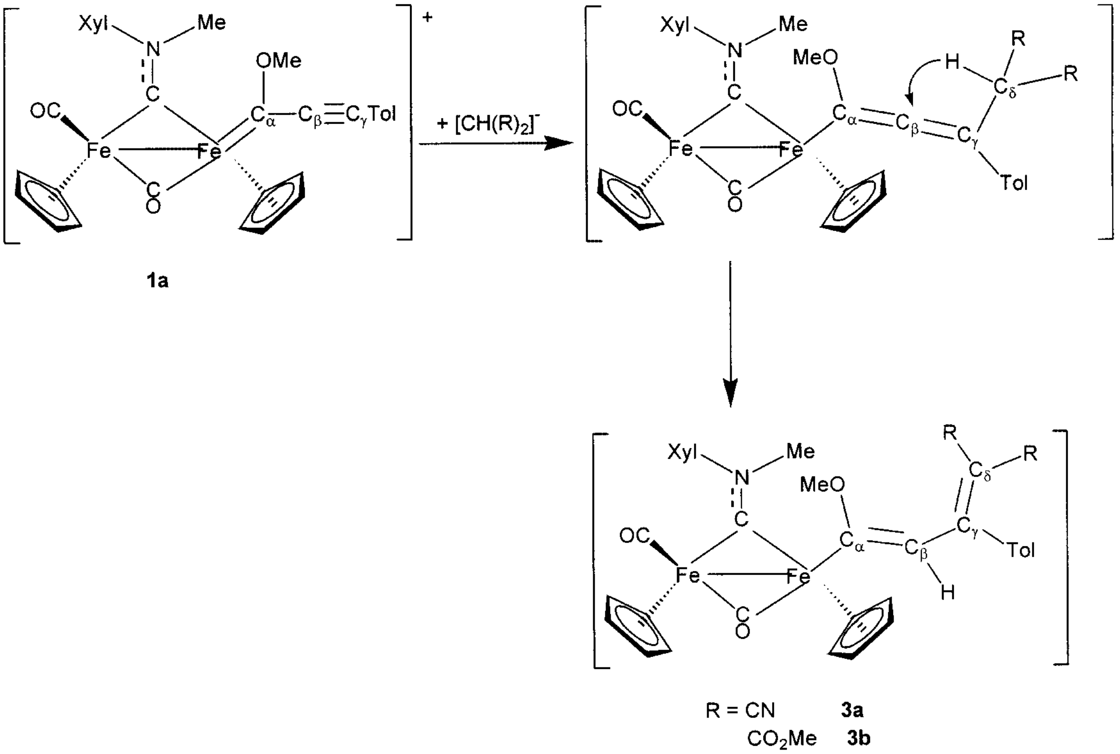
From a stereochemical point of view, the C(23)=C(25) bond possesses an *E* configuration, whereas the ligand adopts an *s-cis* conformation about C(25)–C(26); the fact that the latter has a partial double-bond character also makes this conformation rigid in solution. This is fully confirmed by NOE experiments, which show a strong enhancement of the Tol protons after irradiation of H(25).

The NMR spectra of **3** show the presence of a single species in solution, therefore the reactions are completely regio- and stereoselective. The main feature of the ^1H NMR spectra is represented by the resonances at δ = 5.98 (**3a**) and 5.43 ppm (**3b**) attributable to C_β-H. The C_β and C_γ carbons of the 1-σ-buta-1,3-dienyl ligand appear at similar chemical shifts in both **3a** and **3b** [δ = 118.9 and 121.4 ppm (C_β) and 134.9 and 133–138 ppm (C_γ)], whereas the resonances of C_α and C_δ differ considerably [δ = 262.8 and 221.8 ppm (C_α) and 59.7 and 114.8 ppm (C_δ)]. The latter is directly influenced by the different substituents at C_δ, and this also has some important effects on the nature of the ligand. In fact, the low-field value of δ_{C_α} for **3a** (δ = 262.8 ppm) suggests the presence of some methoxy carbene character; for example, in the parent alkynyl(methoxy)carbene complex **1a**, we have δ_{C_α} = 281.4 ppm. Conversely, the value of δ_{C_α} for **3b** (δ = 221.8 ppm) is typical for an Fe–C(sp^2) single bond as found in σ-vinyl and σ-butadienyl complexes; for instance, the related complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)=C_\beta HC_\gamma(Tol)=NPh\}(Cp)_2]$,[11] which contains a 1-σ-4-azabuta-1,3-dienyl ligand, has δ_{C_α} at δ = 204.0 ppm. This indicates that **3b** can be mainly described by the 1-σ-buta-1,3-dienyl form (A), whereas the zwitterionic form (B) becomes more important in the case of **3a**, as also indicated by its crystal structure.

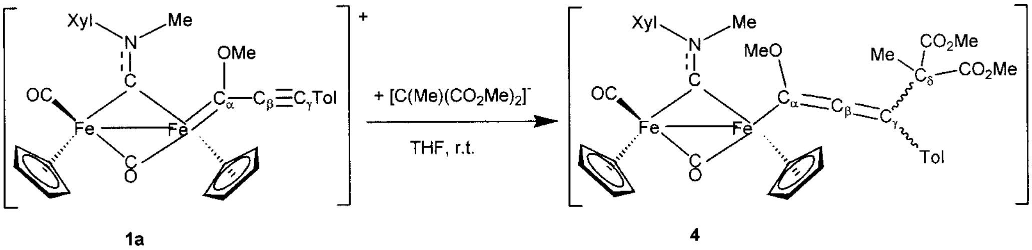
The formation of **3** very likely proceeds by addition of $[CH(R)_2]^-$ to C_γ of **1a** to give a σ-allenyl intermediate, followed by hydrogen migration from C_δ to C_β (Scheme 4); an example of the latter process has been described for the formation of the zwitterionic η^3-allyl complex $[Pt\{\eta^3\text{-}CH_2C[C(CO_2Me)_2]CHPh\}(PPh_3)_2]$ from $[Pt(\eta^3\text{-}CH_2CCH)(PPh_3)_2]^+$ and $[CH(CO_2Me)_2]^-$.[17]

In order to confirm this, we studied the reaction between **1a** and $[C(Me)(CO_2Me)_2]^-$ (Scheme 5). As expected, no methyl migration is observed and, thus, the σ-allenyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)=C_\beta=C_\gamma(Tol)C_\delta(Me)(CO_2Me)_2\}(Cp)_2]$ (**4**) can be isolated in good yield (78%).

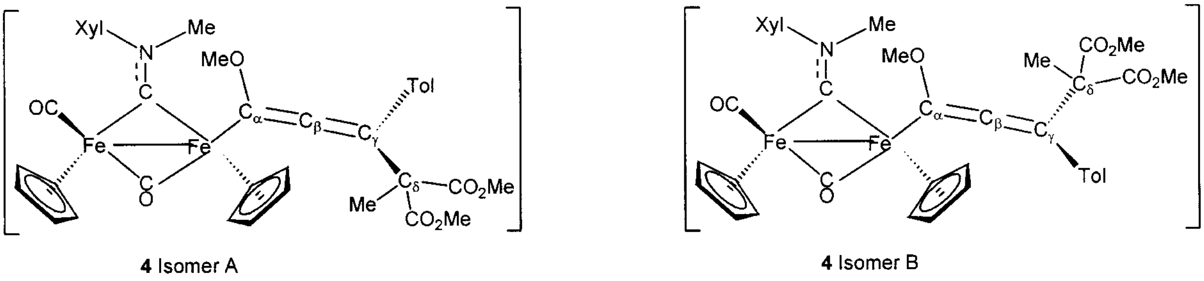
The IR spectrum of **4** shows ν(CO) at 1963 and 1787 cm^{-1} for the terminal and bridging carbonyls, respectively, and ν(CO_2Me) at 1734 cm^{-1}. The NMR spectra indicate the presence in solution of two isomers in a 2:1 ratio, with similar but distinct resonances. This suggests that the addition of $[C(Me)(CO_2Me)_2]^-$ to **1a** is not stereoselective, but can occur on both sides of the plane containing the alkynyl(methoxy)carbene ligand (Scheme 6). Therefore, the two isomers differ only in the relative orientation of the Tol and $C_\delta(Me)(CO_2Me)_2$ substituents; in particular, in one isomer (A), the Tol group points towards the μ-



Scheme 4.



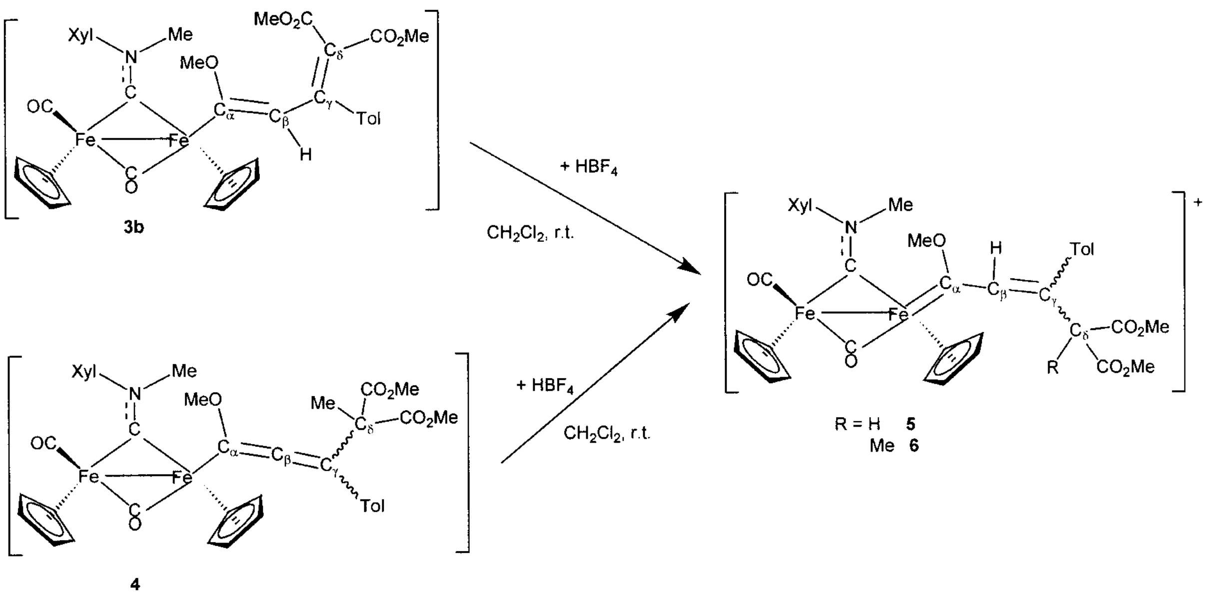
Scheme 5.



Scheme 6.

CN(Me)(Xyl) ligand, whereas in the other (B) it is directed to the same side as μ-CO.

It is quite interesting to compare this reaction with the addition of CN^- reported in Scheme 1. The latter is completely stereoselective, probably because it involves a site of the alkynyl(methoxy)carbene ligand (C_α) which is very close to the diiron core of the molecule and, thus, is sterically protected by the other ligands. Conversely, C_γ is sterically free and therefore very little control of the stereochemistry of the addition is possible. Some steric control is probably exerted also on the regiochemistry of these nucleophilic additions. In fact, the small CN^- ion can easily access C_α,



Scheme 7.

whereas the more cumbersome $[CH(R)_2]^-$ and $[C(Me)(CO_2Me)_2]^-$ add to C_γ.

The σ-allenyl ligand in **4** shows characteristic resonances in the ^{13}C NMR spectrum[18] at δ = 144–147, 195 and 104 ppm for C_α, C_β and C_γ, respectively. The aliphatic C_δ atoms resonate at $\delta \approx 59$ ppm, whereas its Me group resonates at $\delta \approx 22$ ppm.

Both complexes **3b** and **4** react quantitatively with strong acids to afford the cationic vinyl(methoxy)carbene complexes $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta H{=}C_\gamma(Tol)C_\delta(R)(CO_2Me)_2\}]^+$ (R = H, **5**; Me, **6**; Scheme 7). Conversely, the reaction of **3a** and **2a–e** with acids results in a complex mixture of decomposition products.

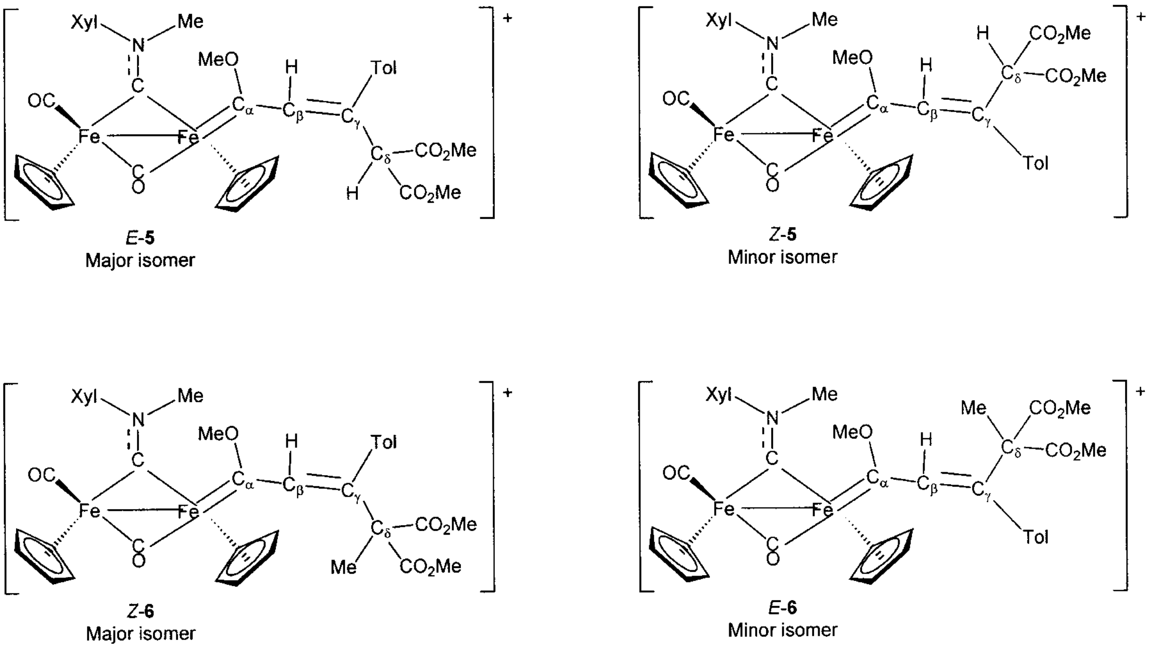
The regiochemistry of the protonation reactions is quite interesting as complex **3b** adds H^+ selectively at the C_δ carbon of the 1-σ-buta-1,3-dienyl ligand in order to favour the delocalisation of the positive charge along the entire ligand and the diiron frame. The same result is obtained in the case of the reaction of **4** by selective protonation of C_β.

The reactivity of σ-allenyl complexes towards nucleophiles has been widely studied, whereas data on reactions with electrophiles are quite scarce.[18] It is, however, been reported that electrophiles usually react at C_γ and not C_β. For instance, the protonation of $[Re(Cp)(NO)(PPh_3)(\sigma\text{-}CH{=}C{=}CH_2)]$ with HBF_4 results in the formation of $[Re(Cp)(NO)(PPh_3)(\eta^2\text{-}CH{\equiv}CCH_3)]^+$ by addition of H^+ to C_γ.[19] Thus, the reaction reported here represents a rare case of electrophilic attack at C_β of a σ-allenyl complex.

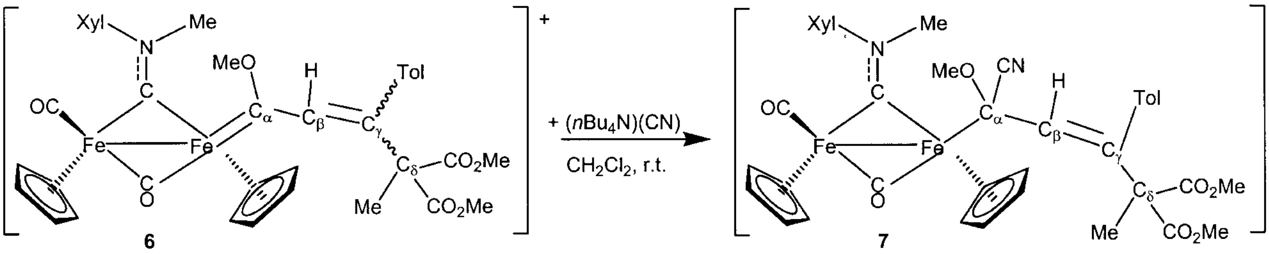
Complexes **5** and **6** were fully characterised spectroscopically. Their IR spectra show ν(CO) shifted by about 30 cm^{-1} towards higher frequencies with respect to the parent complexes **3b** and **4**, as expected for cationic compounds. The NMR spectra at room temperature indicate the presence of an exchange process, which can be frozen-out at 243 K. Under these conditions, two species can clearly be distinguished in solution in ratios of 1.3:1 for **5** and 1.5:1 for **6**. These were fully characterised by gs-HSQC and gs-HMBC experiments[20] at 243 K, and their stereochemistry assigned by NOE measurements conducted at 218 K to avoid saturation-transfer effects.[21] The two species are isomers which differ only in the configuration of the vinyl double bond $C_\beta{=}C_\gamma$ (Scheme 8). In both cases the major isomer is the one in which the C_β-H hydrogen is *cis* to the Tol group; because of the different nature of the substituents on C_δ, this possesses an (*E*)-configuration in **5** and a (*Z*)-configuration in **6**. Therefore, the minor isomers have the configuration (*Z*)-**5** and (*E*)-**6**. The two isomers can be easily distinguished from the ^1H chemical shift of C_β-H, which resonates at lower field in the major isomers [(*E*)-**5**: δ = 6.69 ppm; (*Z*)-**6**: δ = 6.53 ppm), than in the minor isomers [(*Z*)-**5**: δ = 6.49 ppm; (*E*)-**6**: δ = 6.24 ppm)], where it is *trans* to Tol. For example, NOE studies on **6** show that irradiation of the C_β-H resonance in the minor isomer (δ = 6.24 ppm) generates a strong enhancement of the C_δ-*Me* resonance, in agreement with the proposed (*E*)-configuration. The carbene nature of the ligand is supported by the typical ^{13}C chemical shift of C_α ($\delta \approx 315$ ppm); conversely, C_β and C_γ resonate at values characteristic of olefinic protons ($\delta \approx 140$ and 135 ppm, respectively).

The reaction of the vinyl(methoxy)carbene complex **6** with CN^- was then studied (Scheme 9). As in the case of the analogous reaction of **1**, the cyanide ion selectively adds to the carbene carbon to afford the σ-allyl complex $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)(CN)[C_\beta H{=}C_\gamma(Tol)C_\delta(Me)(CO_2Me)_2]\}(Cp)_2]$ (**7**) in good yield (68 %). This reaction is also completely regio- and stereoselective, resulting in the formation of a single species whose spectroscopic and NOE data suggest a (*Z*)-configuration of the double bond.

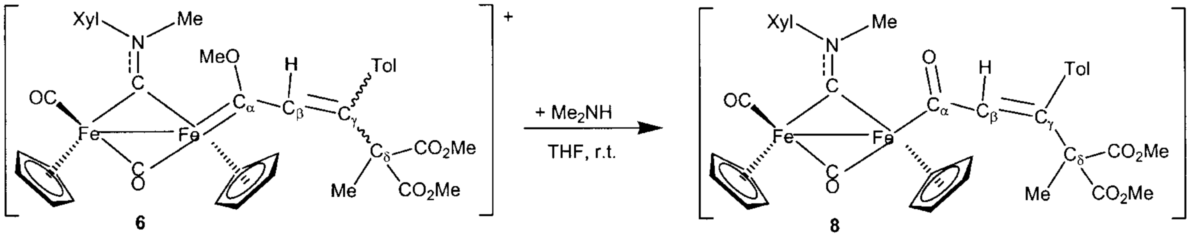
Finally, the reactivity of **6** with a neutral nucleophile such as Me_2NH was considered (Scheme 10). This results in the formation of the neutral organometallic species $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(O)C_\beta H{=}C_\gamma(Tol)C_\delta(Me)\text{-}$



Scheme 8.



Scheme 9.



Scheme 10.

$(CO_2Me)_2\}(Cp)_2]$ (**8**), which can be recovered in good yield (76%) after column chromatography. The same species can also be obtained by direct chromatography of **6** through an Al_2O_3 column (previously treated with 4% water) with CH_2Cl_2/THF (1:1) as eluent. In the case of the reaction of **6** with Me_2NH, IR spectroscopy clearly indicates that **8** is already present in solution before chromatography. Complex **8** contains a vinylacyl ligand, as clearly indicated by its NMR spectra. In particular, the acyl carbon resonates at δ = 265.8 ppm, and the vinyl atoms show characteristic resonances (i.e. C_γ: δ = 125.6 ppm; C_β: δ = 143.3 ppm (^{13}C NMR) and C_β-H: δ = 6.45 ppm (^1H NMR). A single species is present in solution, for which, on the basis of its spectroscopic features, we can assume a (*Z*)-configuration for the double bond.

Conclusions

The results reported in this paper indicate that the alkynyl(methoxy)carbene ligand in **1** contains two different sites available for nucleophilic attack, i.e. C_α and C_γ. The regiochemistry of the reactions studied is mainly controlled by steric factors; thus, the small CN^- ion adds at C_α, whereas the bulkier $[CH(R)_2]^-$ and $[C(Me)(CO_2Me)_2]^-$ react selectively at C_γ. In the same way, it can be considered that the addition of amines to **1** is also mainly sterically controlled and therefore it occurs at C_γ, as observed previously.[11] Electronic factors must also be considered, and they point to the same conclusions. Thus, the hard CN^- nucleophile attacks in a 1,2 manner, accordingly to the HSAB theory, whereas the softer $[CH(R)_2]^-$ and $[C(Me)(CO_2Me)_2]^-$ anions react in a 1,4 manner.

The addition of carbanions to **1** results in the formation of new C–C bonds and, hence, different types of ligands are formed. In particular, addition at C_α generates 1,1-disubstituted σ-propargyl compounds, whereas σ-allenyl complexes are formed in the case of reaction at C_γ. The latter species can evolve further when a hydrogen is present on C_δ, resulting eventually in the formation of 1-σ-buta-1,3-dienyl complexes. All the ligands formed are terminally coordinated to the diiron frame, even though they are known to be able to act also as bridging ligands in different coordination modes.[18,22]

Finally, we have shown that the neutral complexes **3** and **4** can react with electrophiles and that the resultant cationic products can be further modified by nucleophilic additions. This represents an interesting step-by-step sequence for the building up of highly functionalised ligands in diiron species.

Experimental Section

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Infrared spectra were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed on Varian Gemini 300 and Varian Mercury 400 instruments. The chemical shifts for ^1H and ^{13}C are referenced to internal TMS. The spectra were fully assigned by ^1H,^{13}C correlation measured using gs-HSQC and gs-HMBC experiments.[20] Monodimensional NOE measurements were recorded using the DPFGSE-NOE sequence.[23] All chemicals were used as received from Aldrich Co., except $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe)C_\beta{\equiv}C_\gamma R'\}(Cp)_2][SO_3CF_3]$ (R = Xyl, R′ = Tol, **1a**; R = Xyl, R′ = Ph, **1b**; R = Xyl, R′ = Me_3Si, **1c**; R = Me, R′ = Tol, **1d**; R = Me, R′ = Ph, **1e**)[11] which were prepared by published methods. The anions $Na[CH(CN)_2]$, $Na[CH(CO_2Me)_2]$ and $Na[C(Me)(CO_2Me)_2]$ were prepared just before use by the reaction of Na with $CH_2(CN)_2$, $CH_2(CO_2Me)_2$ and $CH(Me)(CO_2Me)_2$, respectively, in THF.

Synthesis of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{C(OMe)(CN)(C{\equiv}CR'')\}(Cp)_2]$ (R = Xyl, R′ = Tol, 2a; R = Xyl, R′ = Ph, 2b; R = Xyl, R′ = Me_3Si, 2c; R = Me, R′ = Tol, 2d; R = Me, R′ = Ph, 2e): $(nBu_4N)(CN)$ (110.0 mg, 0.417 mmol) was added to a solution of **1** (0.220 mmol) in CH_2Cl_2 (15 mL) and the mixture stirred at room temperature for 20 min; during this time, the solution changed from red to brown. The solvent was then removed under reduced pressure and the residue dissolved in CH_2Cl_2 (5 mL) and chromatographed through Al_2O_3. The final product was obtained as a brown fraction using CH_2Cl_2 as eluent.

2a: $C_{34}H_{32}Fe_2N_2O_3$ (628.32): calcd. C 64.99, H 5.13, N 4.46; found C 65.11, H 5.01, N 4.21. Yield 110.6 mg (80%). ^1H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 2.34 (s, 3 H, $p\text{-}C_6H_4\mathit{Me}$), 2.13, 2.62 (s, 6 H, $C_6H_3\mathit{Me}_2$), 2.86 (s, 3 H, O*Me*), 4.28, 4.64 (s, 10 H, Cp), 4.71 (s, 3 H, N*Me*), 7.12–7.50 (m, 7 H, arom). $^{13}C\{^1H\}$ NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 17.6, 18.3 ($C_6H_3\mathit{Me}_2$), 21.2 ($p\text{-}C_6H_4\mathit{Me}$), 50.8 (Fe-*C*), 50.9 (N-*Me*), 52.7 (O*Me*), 86.5, 89.4 (Cp), 89.7, 94.5 ($C{\equiv}C$), 121.2 (C_{ipso} Tol), 126.2 ($C{\equiv}N$), 127.9, 128.0, 128.7, 129.8, 131.0, (*C*-H arom), 132.3, 134.0, 137.3 (*C*-Me Xyl + Tol), 149.4 (C_{ipso} Xyl), 215.0 (*C*O), 266.5 (μ-*C*O), 338.3 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$ = 2192(s) (CN), 1970(vs) (CO), 1791(s) cm^{-1} (μ-CO).

2b: $C_{33}H_{30}Fe_2N_2O_3$ (614.29): calcd. C 64.52, H 4.92, N 4.56; found C 64.68, H 5.11, N 4.28. Yield 102.7 mg (76%). ^1H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 2.15, 2.64 (s, 6 H, $C_6H_3\mathit{Me}_2$), 2.88 (s, 3 H, O*Me*), 4.30, 4.69 (s, 10 H, Cp), 4.72 (s, 3 H, N*Me*), 7.20–7.59 (m, 8 H, arom) ppm. $^{13}C\{^1H\}$ NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 16.6, 18.2 ($C_6H_3\mathit{Me}_2$), 50.4 (Fe-*C*), 50.8 (N-*Me*), 52.7 (O*Me*), 86.5, 89.3 (Cp), 90.4, 94.3 ($C{\equiv}C$), 124.2 (C_{ipso} Tol), 126.0 ($C{\equiv}N$), 127.2, 127.8, 127.9, 129.7, 130.9 (*C*-H arom), 132.2, 133.9 (*C*-Me Xyl), 149.2 (C_{ipso} Xyl), 214.9 (*C*O), 266.5 (μ-*C*O), 338.1 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$ = 2192(s) (CN), 1970(vs) (CO), 1790(s) cm^{-1} (μ-CO).

2c: $C_{33}H_{30}Fe_2N_2O_3Si$ (642.38): calcd. C 61.70, H 4.71, N 4.36; found C 61.43, H 4.95, N 4.29. Yield 92.2 mg (72%). ^1H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 0.29 (s, 9 H, Me_3Si), 2.13, 2.65 (s, 6 H, $C_6H_3\mathit{Me}_2$), 2.83 (s, 3 H, O*Me*), 4.30, 4.65 (s, 10 H, Cp), 4.72 (s, 3 H, N*Me*), 7.24–7.34 (m, 3 H, arom) ppm. $^{13}C\{^1H\}$ NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 1.1 (Me_3Si), 17.0, 18.7 ($C_6H_3\mathit{Me}_2$), 51.2 (N-*Me*), 52.8 (O*Me*), 86.7, 89.8 (Cp), 99.0, 105.6 ($C{\equiv}C$), 126.4 ($C{\equiv}N$), 128.0, 130.1 (*C*-H arom), 132.3, 138.5 (*C*-Me Xyl), 149.7 (C_{ipso} Xyl), 215.1 (*C*O), 264.8 (μ-*C*O), 338.4 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$: 2193(s) (CN), 1969(vs) (CO), 1793(s) cm^{-1} (μ-CO).

2d: $C_{27}H_{26}Fe_2N_2O_3$ (538.20): calcd. C 60.25, H 4.87, N 5.21; found C 60.07, H 4.93, N 5.05. Yield 82.9 mg (70%). ^1H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 2.42 (s, 3 H, $p\text{-}C_6H_4\mathit{Me}$), 2.89 (s, 3 H, O*Me*), 4.14, 4.58 (s, 6 H, $N\mathit{Me}_2$), 4.66, 4.80 (s, 10 H, Cp), 7.20–7.53 (m, 4 H, arom) ppm. $^{13}C\{^1H\}$ NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 21.4 ($p\text{-}C_6H_4\mathit{Me}$), 50.4 (Fe-*C*), 50.1, 53.9, ($N\mathit{Me}_2$), 53.6 (O*Me*), 86.6, 89.4, (Cp), 94.4 ($C{\equiv}C$), 121.6 (C_{ipso} Tol), 127.0 ($C{\equiv}N$), 128.9 (*C*-Me Tol), 128.7–131.5 (*C*-H arom), 214.6 (*C*O), 276.0 (μ-*C*O), 333.3 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$ = 2192(m) (CN), 1969(vs) (CO), 1790(s) cm^{-1} (μ-CO).

2e: $C_{26}H_{24}Fe_2N_2O_3$ (524.17): calcd. C 59.56, H 4.62, N 5.34; found C 59.23, H 4.59, N 5.52. Yield 88.8 mg (77%). ^1H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 2.84 (s, 3 H, O*Me*), 4.10, 4.53 (s, 6 H, $N\mathit{Me}_2$), 4.60, 4.76 (s, 10 H, Cp), 7.30–7.530 (m, 5 H, arom) ppm. $^{13}C\{^1H\}$ NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 49.9 (Fe-*C*), 49.8, 53.3 (O*Me* + $N\mathit{Me}_2$), 86.6, 89.1 (Cp), 90.6, 94.2 ($C{\equiv}C$), 124.3 ($C{\equiv}N$), 125.6 (C_{ipso} Ph), 127.1–130.8 (*C*-H arom), 214.7 (*C*O), 267.9 (μ-*C*O), 332.3 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$ = 2192(m) (CN), 1969(vs) (CO), 1789(s) cm^{-1} (μ-CO).

Synthesis of $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{C_\alpha(OMe){=}C_\beta HC_\gamma(Tol){=}C_\delta(R)_2\}(Cp)_2]$ (R = CN, 3a; CO_2Me, 3b): $Na[CH(R)_2]$ (0.500 mmol in 7 mL of THF) was added to a solution of **1a** (200.0 mg, 0.260 mmol) in THF (10 mL) and the mixture stirred at room temperature for 5 min. It was then filtered through an Al_2O_3 pad and the solvent removed from the filtrate under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and chromatographed through Al_2O_3. The final product was obtained as a brown fraction using THF as eluent.

3a: $C_{36}H_{33}Fe_2N_3O_3$ (667.36): calcd. C 64.79, H 4.98, N 6.30; found C 64.58, H 4.75, N 6.09. Yield 121.4 mg (70%). ^1H NMR

(399.939 MHz, CDCl$_3$, 293 K): δ = 2.34 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.37, 2.55 (s, 6 H, C$_6$H$_3$*Me*$_2$), 3.30 (s, 3 H, O*Me*), 4.47 (s, 3 H, N*Me*), 4.29, 4.79 (s, 10 H, Cp), 5.98 (s, 1 H, =C$_\beta$*H*), 7.14–7.34 (m, 7 H, arom) ppm. ^{13}C{^{1}H} NMR (100.575 MHz, CDCl$_3$, 293 K): δ = 17.5, 18.5 (C$_6$H$_3$*Me*$_2$), 21.4 (*p*-C$_6$H$_4$*Me*), 53.1 (N-*Me*), 59.7 (*C*$_\delta$), 63.6 (O*Me*), 86.9, 90.2 (Cp), 118.0 (*C*$_\beta$H), 118.9 (*C*≡N), 128.4, 128.5, 128.8, 129.6, 130.0 (*C*-H arom), 132.9, 133.6 (*C*-Me Xyl), 134.9 (*C*$_\gamma$), 140.7 (*C*-Me Tol), 148.1 (*C*$_{ipso}$ Xyl), 158.8 (*C*$_{ipso}$ Tol), 213.4 (*C*O), 262.8 (Fe-*C*$_\alpha$), 266.2 (μ-*C*O), 336.3 (μ-*C*) ppm. IR (CH$_2$Cl$_2$, 293 K): $\tilde{\nu}$ = 2199(s) (CN), 1968(vs) (CO), 1791(s) cm^{-1} (μ-CO).

3b: C$_{38}$H$_{39}$Fe$_2$NO$_7$ (733.41): calcd. C 62.23, H 5.36, N 1.91; found C 62.48, H 5.04, N 2.15. Yield 114.4 mg (60%). ^{1}H NMR (399.939 MHz, CDCl$_3$, 293 K): δ = 2.25, 2.58, 2.89 (s, 9 H, C$_6$H$_3$*Me*$_2$ + *p*-C$_6$H$_4$*Me*), 3.15 (s, 3 H, O*Me*), 3.52 (s, 6 H, CO$_2$*Me*), 4.38 (s, 3 H, N*Me*), 4.23, 4.83 (s, 10 H, Cp), 5.54 (s, 1 H, =C$_\beta$*H*), 6.92–7.22 (m, 7 H, arom) ppm. ^{13}C{^{1}H} NMR (100.575 MHz, CDCl$_3$, 293 K): δ = 17.8, 18.7 (C$_6$H$_3$*Me*$_2$), 21.4 (*p*-C$_6$H$_4$*Me*), 51.5 (CO$_2$*Me*), 52.2 (N-*Me*), 61.6 (O*Me*), 86.4, 89.1 (Cp), 114.8 (*C*$_\delta$), 121.4 (*C*$_\beta$H), 127.9, 128.0, 128.3, 128.6, 129.9 (*C*-H arom), 133.0, 134.1, 137.7, 138.5 (*C*-Me Tol + *C*-Me Xyl + *C*$_\gamma$**)**, 148.2 (*C*$_{ipso}$ Xyl), 152.6 (*C*$_{ipso}$ Tol), 168.1 (*C*O$_2$Me), 214.4 (*C*O), 221.8 (Fe-*C*$_\alpha$), 265.4 (μ-*C*O), 337.5 (μ-*C*) ppm. IR (CH$_2$Cl$_2$, 293 K): $\tilde{\nu}$ = 1960(vs) (CO), 1784(s) (μ-CO), 1736(s) cm^{-1} (CO$_2$Me).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){C$_\alpha$(OMe)=C$_\beta$=C$_\gamma$(Tol)C$_\delta$(Me)(CO$_2$Me)$_2$}(Cp)$_2$] (4): Na[C(Me)(CO$_2$Me)$_2$] (0.300 mmol, in 5 mL THF) was added to a solution of **1a** (200.0 mg, 0.260 mmol) in THF (10 mL) and the mixture stirred at room temperature for 5 min. It was then filtered through an Al$_2$O$_3$ pad and the solvent removed from the filtrate under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ (5 mL) and chromatographed through Al$_2$O$_3$. The final product was obtained as a brown fraction using THF as eluent. C$_{39}$H$_{41}$Fe$_2$NO$_7$ (747.44): calcd. C 62.67, H 5.53, N 1.87; found C 62.98, H 5.38, N 1.95. Yield 151.5 mg (78%). ^{1}H NMR (399.939 MHz, CDCl$_3$, 293 K). – Isomer A: δ = 1.66 (s, 3 H, C$_\delta$*Me*), 2.24 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.12, 2.55 (s, 6 H, C$_6$H$_3$*Me*$_2$), 2.95 (s, 3 H, O*Me*), 3.61, 3.84 (s, 6 H, CO$_2$*Me*), 4.16 (s, 3 H, N*Me*), 4.19, 4.63 (s, 10 H, Cp), 6.96–7.30 (m, 7 H, arom) ppm. – Isomer B: δ = 1.76 (s, 3 H, C$_\delta$*Me*), 2.28 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.15, 2.59 (s, 6 H, C$_6$H$_3$*Me*$_2$), 2.88 (s, 3 H, O*Me*), 3.66, 3.68 (s, 6 H, CO$_2$*Me*), 4.28 (s, 3 H, N*Me*), 4.22, 4.66 (s, 10 H, Cp), 6.96–7.30 (m, 7 H, arom) ppm. Isomer ratio: A/B = 2. ^{13}C{^{1}H} NMR (100.575 MHz, CDCl$_3$, 293 K). – Isomer A: δ = 17.0, 18.4 (C$_6$H$_3$*Me*$_2$**)**, 20.9 (*p*-C$_6$H$_4$*Me*), 22.8 (C$_\delta$*Me*), 51.7 (N-*Me*), 52.2, 52.5 (CO$_2$*Me*), 56.3 (O*Me*), 59.5 (*C*$_\delta$), 85.7, 89.1 (Cp), 104.6 (=*C*$_\gamma$), 127.2–129.8 (*C*-H arom), 133.2–138.8 (*C*$_{ipso}$ Tol + *C*-Me Tol + *C*-Me Xyl), 144.7 (Fe-*C*$_\alpha$=), 148.4 (*C*$_{ipso}$ Xyl), 172.6, 173.5 (*C*O$_2$Me), 195.3 (=*C*$_\beta$=), 215.4 (*C*O), 265.3 (μ-*C*O), 339.5 (μ-*C*) ppm. – Isomer B: δ = 16.9, 18.5 (C$_6$H$_3$*Me*$_2$), 20.9 (*p*-C$_6$H$_4$*Me*), 22.3 (C$_\delta$*Me*), 51.7 (N-*Me*), 52.1, 52.3, (CO$_2$*Me*), 55.8 (O*Me*), 59.7 (*C*$_\delta$), 85.7, 89.4, (Cp), 104.5 (=*C*$_\gamma$), 127.2–129.8 (*C*-H arom), 133.2–138.8 (*C*$_{ipso}$ Tol + *C*-Me Tol + *C*-Me Xyl**)**, 147.5 (Fe-*C*$_\alpha$=), 148.3 (*C*$_{ipso}$ Xyl), 173.0, 173.1 (*C*O$_2$Me), 194.5 (=*C*$_\beta$=), 215.8 (*C*O), 265.1 (μ-*C*O), 340.1 (μ-*C*) ppm. IR (CH$_2$Cl$_2$, 293 K): $\tilde{\nu}$ = 1963(vs) (CO), 1787(s) (μ-CO), 1734(s) cm^{-1} (CO$_2$Me).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){C$_\alpha$(OMe)C$_\beta$H=C$_\gamma$(Tol)C$_\delta$H(CO$_2$Me)$_2$}(Cp)$_2$][BF$_4$] (5): HBF$_4$ (0.100 mL, 54 wt.% in Et$_2$O, 0.726 mmol) was added to a solution of **3b** (238.3 mg, 0.325 mmol) in CH$_2$Cl$_2$ (10 mL) and the mixture stirred at room temperature for 5 min until complete formation of the final product. The solvent was then removed under reduced pressure and the residue washed with Et$_2$O (2 × 10 mL) and petroleum ether (2 × 10 mL). C$_{38}$H$_{40}$BF$_4$Fe$_2$NO$_7$ (821.22): calcd. C 55.58, H 4.91, N 1.71; found C 55.21, H 5.04, N 1.98. Yield 241.0 mg (90%). ^{1}H NMR (399.939 MHz, CDCl$_3$, 243 K). – (*E*)-isomer: δ = 2.24 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.36, 2.53 (s, 6 H, C$_6$H$_3$*Me*$_2$), 3.50 (s, 3 H, O*Me*), 3.76, 3.82 (s, 6 H, CO$_2$*Me*), 4.13 (s, 3 H, N*Me*), 4.75 (s, 1 H, C$_\delta$*H*), 4.52, 5.12 (s, 10 H, Cp), 6.69 (s, 1 H, =C$_\beta$*H*), 7.01–7.79 (m, 7 H, arom) ppm. – (*Z*)-Isomer: δ = 2.28 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.33, 2.50 (s, 6 H, C$_6$H$_3$*Me*$_2$), 3.46 (s, 3 H, O*Me*), 3.73, 3.78 (s, 6 H, CO$_2$*Me*), 3.90 (s, 3 H, N*Me*), 4.67 (s, 1 H, C$_\delta$*H*), 4.52, 5.06 (s, 10 H, Cp), 6.49 (s, 1 H, =C$_\beta$*H*), 7.01–7.79 (m, 7 H, arom) ppm. Isomer ratio *E*/*Z* = 1.3. ^{13}C{^{1}H} NMR (100.575 MHz, CDCl$_3$, 243 K). – (*E*)-Isomer: δ = 16.8, 18.4 (C$_6$H$_3$*Me*$_2$), 21.4 (*p*-C$_6$H$_4$*Me*), 52.9 (N-*Me*), 53.7, 53.8 (CO$_2$*Me*), 57.2 (*C*$_\delta$), 63.0 (O*Me*), 88.5, 92.8 (Cp), 126.9–130.1 (*C*-H arom), 132.3–139.7 (*C*$_{ipso}$ Tol + *C*-Me Xyl + *C*$_\gamma$**)**, 140.7 (*C*-Me Tol), 140.9 (*C*$_\beta$H), 147.2 (*C*$_{ipso}$ Xyl), 168.0, 168.5 (*C*O$_2$Me), 212.7 (*C*O), 259.5 (μ-*C*O), 313.6 (Fe=*C*$_\alpha$), 332.7 (μ-*C*) ppm. – (*Z*)-Isomer: δ = 16.7, 18.4 (C$_6$H$_3$*Me*$_2$), 21.3 (*p*-C$_6$H$_4$*Me*), 53.7 (N-*Me*), 53.6, 54.2 (CO$_2$*Me*), 57.0 (*C*$_\delta$),64.5 (O*Me*), 88.8, 92.8 (Cp), 126.9–130.1 (*C*-H arom), 132.3–139.7 (*C*$_{ipso}$ Tol + *C*-Me Xyl + *C*$_\gamma$), 138.2 (*C*$_\beta$H), 139.7 (*C*-Me Tol), 146.8 (*C*$_{ipso}$ Xyl), 167.9, 168.3 (*C*O$_2$Me), 212.1 (*C*O), 261.9 (μ-*C*O), 317.1 (Fe=*C*$_\alpha$)331.2 (μ-*C*) ppm. IR (CH$_2$Cl$_2$, 293 K): $\tilde{\nu}$ = 1991(vs) (CO), 1816(s) (μ-CO), 1755(ms), 1739(s) cm^{-1} (CO$_2$Me).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){C$_\alpha$(OMe)C$_\beta$H=C$_\gamma$(Tol)C$_\delta$(Me)(CO$_2$Me)$_2$}(Cp)$_2$][BF$_4$] (6): HBF$_4$ (0.100 mL, 54 wt.% in Et$_2$O, 0.726 mmol) was added to a solution of **4** (300.0 mg, 0.402 mmol) in CH$_2$Cl$_2$ (10 mL) and the mixture stirred at room temperature for 5 min until complete formation of the final product. The solvent was then removed under reduced pressure and the residue washed with Et$_2$O (2 × 10 mL) and petroleum ether (2 × 10 mL). C$_{39}$H$_{42}$BF$_4$Fe$_2$NO$_7$ (835.25): calcd. C 56.08, H 5.07, N 1.68; found C 55.84, H 5.34, N 1.47. Yield 308.9 mg (92%). ^{1}H NMR (399.939 MHz, CDCl$_3$, 243 K). – (*Z*)-Isomer: δ = 1.58 (s, 3 H, C$_\delta$*Me*), 2.31 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.11, 2.44 (s, 6 H, C$_6$H$_3$*Me*$_2$), 3.56 (s, 3 H, O*Me*), 3.73, 3.75 (s, 6 H, CO$_2$*Me*), 4.07 (s, 3 H, N*Me*), 4.40, 5.11 (s, 10 H, Cp), 6.53 (s, 1 H, =C$_\beta$*H*), 6.82–7.28 (m, 7 H, arom) ppm. (*E*)-Isomer: δ = 1.51 (s, 3 H, C$_\delta$*Me*), 2.26 (s, 3 H, *p*-C$_6$H$_4$*Me*), 2.14, 2.44 (s, 6 H, C$_6$H$_3$*Me*$_2$), 3.50 (s, 3 H, O*Me*), 3.69, 3.87 (s, 6 H, CO$_2$*Me*), 3.71 (s, 3 H, N*Me*), 4.49, 5.06 (s, 10 H, Cp), 6.24 (s, 1 H, =C$_\beta$*H*), 6.82–7.28 (m, 7 H, arom) ppm. Isomer ratio *Z*/*E* = 1.5. ^{13}C{^{1}H} NMR (100.575 MHz, CDCl$_3$, 243 K). – (*Z*)-Isomer: δ = 16.8, 18.3 (C$_6$H$_3$*Me*$_2$), 21.4 (*p*-C$_6$H$_4$*Me*), 22.6 (C$_\delta$*Me*), 53.7, 53.8 (CO$_2$*Me*), 54.4 (N-*Me*), 60.5 (*C*$_\delta$), 63.4 (O*Me*), 88.4, 92.6 (Cp), 127.5–129.9 (*C*-H arom), 132.5, 132.9, 133.1, 134.8 (*C*$_{ipso}$ Tol + *C*-Me Xyl + *C*$_\gamma$**)**,139.9 (*C*-Me Tol), 141.0 (*C*$_\beta$H), 147.1 (*C*$_{ipso}$ Xyl), 171.6, 172.1 (*C*O$_2$Me), 212.3 (*C*O), 258.3 (μ-*C*O), 314.5 (Fe=*C*$_\alpha$),332.6 (μ-*C*) ppm. – (*E*)-Isomer: δ = 16.2, 18.3 (C$_6$H$_3$*Me*$_2$), 21.3 (*p*-C$_6$H$_4$*Me*), 22.3 (C$_\delta$*Me*), 53.7 (N-*Me*), 53.7, 53.8 (CO$_2$*Me*), 60.4 (*C*$_\delta$),64.6 (O*Me*), 88.8, 92.7 (Cp), 127.5–129.9 (*C*-H arom), 132.2, 132.4, 132.6, 133.2 (*C*$_{ipso}$ Tol + *C*-Me Xyl + *C*$_\gamma$**)**, 138.6 (*C*$_\beta$H), 138.8 (*C*-Me Tol), 146.8 (*C*$_{ipso}$ Xyl), 171.6, 171.9 (*C*O$_2$Me), 212.2 (*C*O), 262.1 (μ-*C*O), 316.9 (Fe=*C*$_\alpha$), 331.2 (μ-*C*) ppm. IR (CH$_2$Cl$_2$, 293 K): $\tilde{\nu}$ = 1992(vs) (CO), 1817(s) (μ-CO), 1730(s) cm^{-1} (CO$_2$Me).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){C$_\alpha$(OMe)(CN)[C$_\beta$H=C$_\gamma$(Tol)C$_\delta$(Me)(CO$_2$Me)$_2$]}(Cp)$_2$] (7): (*n*Bu$_4$N)(CN) (110.0 mg, 0.417 mmol) was added to a solution of **6** (200.0 mg, 0.268 mmol) in CH$_2$Cl$_2$ (10 mL) and the mixture stirred at room temperature for 1 h. The solvent was then removed under reduced pressure and the residue dissolved in CH$_2$Cl$_2$ (5 mL) and chromatographed through Al$_2$O$_3$. The final product was obtained as an orange-brown fraction using THF as eluent. C$_{40}$H$_{42}$Fe$_2$N$_2$O$_7$ (774.46): calcd. C 62.03, H 5.47, N 3.62; found C 62.35, H 5.17, N 3.95. Yield

Table 3. Crystal data and experimental details for **2b** and **3a**·CH_2Cl_2.

Complex	**2b**	**3a**·CH_2Cl_2
Formula	$C_{33}H_{30}Fe_2N_2O_3$	$C_{37}H_{35}Cl_2Fe_2N_3O_3$
Mol. mass	614.29	752.28
T [K]	293(2)	100(2)
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	9.5892(19)	13.561(3)
b [Å]	18.320(4)	28.916(6)
c [Å]	16.215(3)	8.9896(18)
β [°]	96.26(3)	105.73(3)
V [Å^3]	2831.7(10)	3393.2(12)
Z	4	4
D_c [g cm^{-3}]	1.441	1.473
μ [mm^{-1}]	1.062	1.054
F(000)	1272	1552
Crystal size [mm]	0.25 × 0.21 × 0.16	0.23 × 0.18 × 0.12
θ limits [°]	1.65–25.02	1.41–25.55
Reflections collected	24789	31265
Independent reflections	5019 (R_{int} = 0.0992)	6350 (R_{int} = 0.0872)
Data/restraints/parameters	5019/ 38/361	6350/0/429
Goodness on fit on F^2	0.948	1.053
R_1 [$I > 2\sigma(I)$]	0.0528	0.0507
wR_2 (all data)	0.1440	0.1254
Largest diff. peak and hole [e Å^{-3}]	0.439/–0.476	0.594/–1.010

125.9 mg (68%). ^{1}H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 1.44 (s, 3 H, C_δ*Me*), 2.26 (s, 3 H, *p*-C_6H_4*Me*), 2.00, 2.53 (s, 6 H, C_6H_3*Me*$_2$), 2.67 (s, 3 H, O*Me*), 3.76 (s, 6 H, CO_2*Me*), 4.54 (s, 3 H, N*Me*), 4.19, 4.60 (s, 10 H, Cp), 6.07 (s, 1 H, =C_β*H*), 6.91–7.27 (m, 7 H, arom) ppm. ^{13}C{^{1}H} NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 17.2, 18.7 (C_6H_3*Me*$_2$), 21.5 (*p*-C_6H_4*Me*), 22.4 (C_δ*Me*), 51.4 (N-*Me*), 52.7 (O*Me*), 52.8 (CO_2*Me*), 57.6 (Fe-C_α),62.5 (C_δ), 87.1, 89.4 (Cp), 123.5 (*C*N), 127.0 (C_{ipso} Tol), 128.1–130.1 (*C*-H arom), 132.2 (C_γ), 133.2, 134.6 (*C*-Me Xyl), 136.3 (C_βH), 137.3 (*C*-Me Tol), 149.9 (C_{ipso} Xyl), 172.4 (*C*O_2Me), 216.1 (*C*O), 271.8 (μ-*C*O), 337.0 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$ = 2191(m) (CN), 1967(vs) (CO), 1774(s) (μ-CO), 1729(s) cm^{-1} (CO_2Me).

Synthesis of [Fe$_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){C_α(O)C_βH=C_γ(Tol)–C_δ(Me)(CO_2Me)$_2$}(Cp)$_2$] (8): Me_2NH (3.0 mL, 2.0 M in THF, 6.0 mmol) was added to a solution of **6** (200.0 mg, 0.268 mmol) in THF (15 mL), and the mixture stirred at room temperature for 30 min. The solvent was then removed in vacuo and the residue dissolved in CH_2Cl_2 and chromatographed through Al_2O_3. The final product was obtained as a green fraction using CH_2Cl_2/THF (1:1) as eluent. $C_{38}H_{39}Fe_2NO_7$ (733.41): calcd. C 62.23, H 5.36, N 1.91; found C 62.51,; H 5.12, N 1.77. Yield: 149.4 mg (76%). ^{1}H NMR (399.939 MHz, $CDCl_3$, 293 K): δ = 1.42 (s, 3 H, C_δ*Me*), 2.24 (s, 3 H, *p*-C_6H_4*Me*), 2.43, 2.45 (s, 6 H, C_6H_3*Me*$_2$), 3.38 (s, 3 H, N*Me*), 3.71, 3.83 (s, 6 H, CO_2*Me*), 4.22, 4.82, (s, 10 H, Cp), 6.45 (s, 1 H, =C_β*H*), 6.99–7.24 (m, 7 H, arom) ppm. ^{13}C{^{1}H} NMR (100.575 MHz, $CDCl_3$, 293 K): δ = 17.5, 18.5 (C_6H_3*Me*$_2$), 21.3 (*p*-C_6H_4*Me*), 22.2 (C_δ*Me*), 51.0 (N-*Me*), 52.7, 52.9 (CO_2*Me*), 60.6 (C_δ), 86.1, 89.5 (Cp), 125.6 (C_γ), 127.7–131.0 (*C*-H arom + C_γ), 133.4, 134.4, 135.4, 136.6 (*C*-Me Tol + *C*-Me Xyl + C_{ipso} Tol), 143.3 (C_βH), 148.1 (C_{ipso} Xyl), 172.3, 172.5 (*C*O_2Me), 215.4 (*C*O), 265.8 (Fe-C_α), 267.2 (μ-*C*O), 337.5 (μ-*C*) ppm. IR (CH_2Cl_2, 293 K): $\tilde{\nu}$ = 1965(vs) (CO), 1774(s) (μ-CO), 1733(s) cm^{-1} (CO_2Me).

X-ray Crystallographic Study: Compounds **2b** and **3a**·CH_2Cl_2 were crystallised from CH_2Cl_2/pentane. Crystal data and collection details are reported in Table 3. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo-K_α radiation. Data were corrected for Lorentz polarisation and absorption effects (empirical absorption correction SADABS).[24] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[25] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. One Cp ligand in **2b** is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

CCDC-261569 (for **2b**) and CCDC-261570 (for **3a**·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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