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Acetylide Addition to Bridging Vinyliminium Ligands in Dinuclear Complexes

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The (vinyliminium)diiron complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\gamma(R')=C_\beta(R')C_\alpha=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ [R = Xyl, R′ = Me (**1a**); R = Xyl, R′ = Et (**1b**); R = R′ = Me (**1c**); R = Me, R′ = Et (**1d**); R = CH_2Ph, R′ = Me (**1e**); Xyl = 2,6-$Me_2C_6H_3$] undergo regio- and stereoselective addition by lithium acetylides. Addition of LiC≡CR′′ (R′′ = Tol, Ph, $SiMe_3$; Tol = 4-MeC_6H_4) to *trans*-**1a** occurs at the C_β atom of the vinyliminium ligand and results in the formation of the bis(alkylidene) complexes *cis*-$[Fe_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me)C(Me)(C{\equiv}CR'')CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R′′ = Tol (**2a**), Ph (**2b**), $SiMe_3$ (**2c**)]. The molecular structure of **2a** has been determined by X-ray diffraction. Similarly, the diruthenium complex $[Ru_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)=C(Me)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**3**) reacts with LiC≡CTol to give the bis(alkylidene) compound $[Ru_2\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(Me)C(Me)(C{\equiv}CTol)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**4**). Conversely, **1c** and **1d** undergo acetylide attack at the C_α atom of the vinyliminium ligand to yield the allylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(R')C(R')C(C{\equiv}CR'')N(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R′ = Me, R′′ = Tol (**5a**); R′ = Me, R′′ = Ph (**5b**); R′ = Me, R′′ = $SiMe_3$ (**5c**); R′ = Me, R′′ = *n*Bu (**5d**); R′ = Me, R′′ = C(Me)=CH_2 (**5e**); R′ = Me, R′′ = H (**5f**); R′ = Et, R′′ = Tol (**5g**); R′ = Et, R′′ = Ph (**5h**); R′ = Et, R′′ = $SiMe_3$ (**5i**); R′ = Et, R′′ = C(Me)=CH_2 (**5j**)]. Analogously, the reaction of **1e** with LiC≡CPh affords $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)C(Me)C(C{\equiv}CPh)N(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**6**). The molecular structure of **5h** has been determined by X-ray diffraction. Finally, **1b**, in both its *cis* and *trans* forms, undergoes acetylide attack at the C_α atom of the vinyliminium ligand to give the complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Et)C(Et)C(C{\equiv}CR'')N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R′′ = $SiMe_3$ (**7a**), H (**7b**)].
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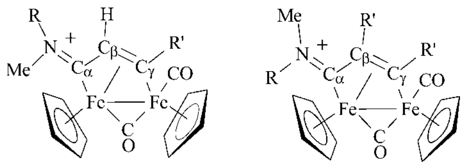
Introduction

Dinuclear complexes are expected to provide new reactivity patterns that are distinct from those of similar monometallic complexes and open novel perspectives in the field of homogeneous catalysis and metal-assisted organic synthesis.[1] Our interest in this area has been focused on the chemistry of the vinyliminium-bridged diiron complexes **I** and **II** (Figure 1), which are obtained by the insertion of primary and secondary alkynes, respectively, into the metal–carbyne bond of $[Fe_2\{CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$.[2]

The carbon skeleton of the bridging framework in **I** and **II** should be able to be expanded by addition of appropriate carbon nucleophiles by taking advantage of the electrophilic character of the vinyliminium ligand. Thus, it has been found that the addition of CN^- can be selectively directed to the iminium carbon atom (C_α) or to the adjacent C_β atom to afford μ-$\eta^1{:}\eta^3$-vinylalkylidene and μ-$\eta^1{:}\eta^2$-bis(alkylidene) ligands, respectively,[3] in a similar way to that reported for hydride addition.[4] However, the acidity of the C_β-H proton in complexes of type **I** represents a serious limitation to the addition of carbon nucleophiles. Indeed, reactions with organolithium reagents result in C_β-H proton removal rather than nucleophilic addition.[5] To overcome this limitation, further studies have been restricted to vinyliminium complexes of type **II**, which do not contain C_β-H protons. Nevertheless, organolithium reagents (LiMe, LiPh) have been found to attack the C_5H_5 ring instead of the bridging ligand. This initial attack is followed by hydride migration from the C_5H_5R ring to the iminium carbon atom (C_α).[6]



R = Me, CH_2Ph, Xyl
R′ = alkyl, aryl

Figure 1. μ-Vinyliminium complexes.

Moreover, we have recently communicated that the reaction of *cis*-$[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Me)=C(Me)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ with acetylides occurs at the carbonyl group with cleavage of the carbon–oxygen bond.[7] The three-carbon-atom chain of the bridging frame grows

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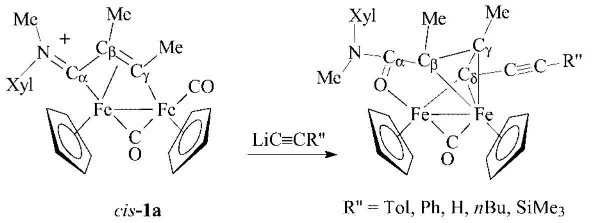
by several units due to the inclusion of both the alkynyl (C≡CR′′) and the $C_δ$ atom, which originates from the CO ligand (Scheme 1).

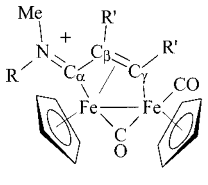


Scheme 1.

Herein we report on an extension of these studies, the aim of which was to establish whether the reaction reported above has a general character or if other reaction paths are available. A number of μ-vinyliminium complexes containing different substituents on the bridging ligand and displaying *cis* or *trans* geometry were examined in order to determine possible steric and electronic effects.

Results and Discussion

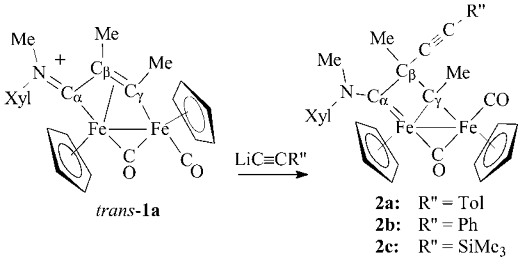
The vinyliminium complexes investigated in this work are shown in Figure 2. They were obtained by insertion of the appropriate disubstituted alkyne into the Fe–aminocarbyne bond of the complexes $[Fe_2\{μ\text{-}CN(Me)(R)\}(μ\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ and $[Fe_2\{μ\text{-}CN(Me)(R)\}(μ\text{-}CO)(CO)(Cl)(Cp)_2]$ according to published methods.[2] It should be remembered that compounds **1a** and **1b** assume a *trans* geometry when they are obtained from the aminocarbyne complexes $[Fe_2\{μ\text{-}CN(Me)(R)\}(μ\text{-}CO)(CO)(Cl)(Cp)_2]$ by chloride abstraction in the presence of the appropriate alkyne, and that they can be converted into the corresponding *cis* isomers by heating in refluxing thf. Conversely, complexes **1c**–**e** are only isolated as their *cis* isomers.[2b]



	R	R'
1a	Xyl	Me
1b	Xyl	Et
1c	Me	Me
1d	Me	Et
1e	CH_2Ph	Me

Figure 2. Vinyliminium complexes examined in this work.

Complex *trans*-**1a** reacts with LiC≡CR′′ (R′′ = Tol, Ph, $SiMe_3$; Tol = 4-MeC_6H_4) in thf solution to afford the corresponding acetylene-functionalised bis(alkylidene) complexes $[Fe_2\{μ\text{-}η^1\text{:}η^2\text{-}C(Me)C(Me)(C≡CR'')CN(Me)(Xyl)\}(μ\text{-}CO)(CO)(Cp)_2]$ (**2a**–**c**) as a consequence of nucleophilic addition at the $C_β$ atom of the vinyliminium ligand (Scheme 2).



Scheme 2.

Thus, the reaction of *trans*-**1a** has a completely different outcome to that of the corresponding *cis* isomer (Scheme 1). Compounds **2a**–**c** were obtained in good yields (ca. 70%) after purification by column chromatography on alumina and were characterised by IR and NMR spectroscopy.

The structure of **2a** was determined by X-ray diffraction: the ORTEP molecular diagram is shown in Figure 3 and relevant bond lengths and angles are listed in Table 1.

The bridging ligand is coordinated to the Fe atoms through a bridging alkylidene carbon atom ($C_γ$) and an aminocarbene moiety. The main bond lengths and angles are similar to those of the analogous bis(alkylidene) complex $[Fe_2\{μ\text{-}η^1\text{:}η^2\text{-}C(CO_2Me)CH_2CN(Me)(Xyl)\}(μ\text{-}CO)(CO)(Cp)_2]$, which was obtained by hydride addition to $C_β$ of the vinyliminium ligand in *cis*-$[Fe_2\{μ\text{-}η^1\text{:}η^3\text{-}C(CO_2Me)=C(H)C=N(Me)(Xyl)\}(μ\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$.[4a] In particular, both the N(1)–C(15) [1.321(7) Å] and the Fe(1)–C(15) [1.899(6) Å] interactions show some double-bond character, which is typical for a terminal aminocarbene ligand.[8] In agreement with this, both C(15) and N(1) adopt a nearly perfect sp^2 hybridisation [sum of angles: 360.1(8)° and 360.0(8)°, respectively]. Moreover, the iron atoms are bound through nearly pure σ-interactions to the $C_γ$ atom [Fe(1)–C(13) 1.970(6), Fe(2)–C(13) 1.992(5) Å], as expected for a bridging alkylidene. Finally, the C(13)–C(14) [1.562(8) Å] and C(14)–C(15) [1.510(7) Å] interactions are typical for pure C–C single bonds, in agreement with the sp^3 hybridisation assumed by C(14); conversely, the C(17)–C(18) interaction [1.189(8) Å] exhibits a triple-bond character and the C(14)–C(17)–C(18)–C(19) unit is almost perfectly linear, as expected for an alkynyl group [C(14)–C(17)–C(18) 172.6(6), C(17)–C(18)–C(19) 179.6(7)°].

The spectroscopic data for **2a**–**c** are consistent with the structure of **2a**. The IR spectra (in CH_2Cl_2 solution) exhibit absorptions for a terminal and a bridging carbonyl group (1919 and 1749 cm^{-1} for **2a**), and a band attributable to the $C_α$–N interaction at about 1510 cm^{-1}. The ^{13}C NMR spectra contain a low-field resonance due to the aminocarbene carbon atom $C_α$ ($δ$ = 268.8 ppm for **2a**) and the $C_γ$ resonance ($δ$ = 181.5 ppm for **2a**), in the range typical for alkylidene carbon atoms. Moreover, NOE experiments indicate that **2a**–**c** adopt the same geometry in solution as in the solid, with the Cp ligands mutually *cis* and a (*Z*) configuration for the Me and Xyl groups. Therefore, the acetylide addition is accompanied by *trans*/*cis* isomerisation.[9] The

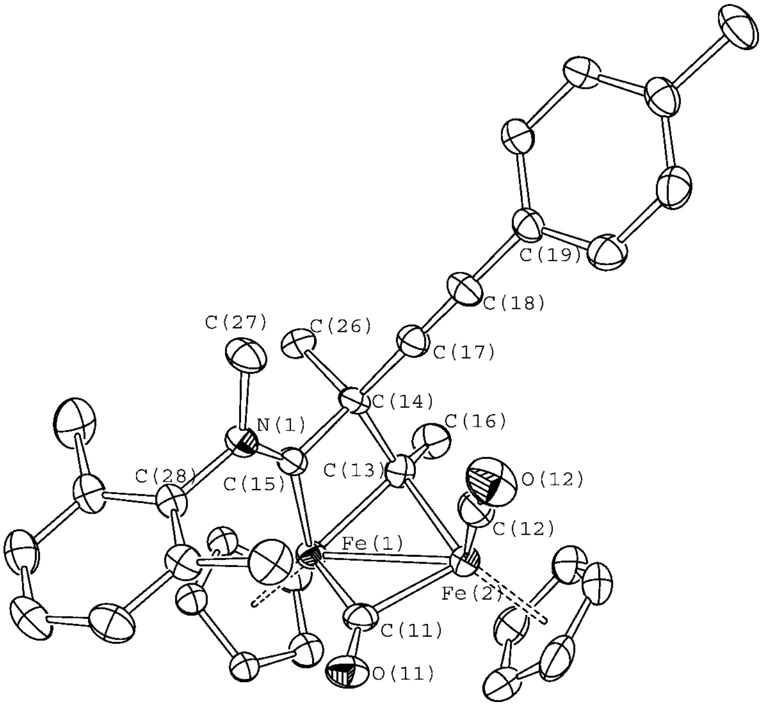


Figure 3. ORTEP drawing of $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C(Me)(C{\equiv}CTol)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2a**). All H atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C(Me)(C{\equiv}CTol)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**2a**).

Fe(1)–Fe(2)	2.5085(12)	C(13)–C(14)	1.562(8)
Fe(2)–C(12)	1.747(8)	C(14)–C(15)	1.510(7)
Fe(1)–C(11)	1.832(6)	C(13)–C(16)	1.512(8)
Fe(2)–C(11)	1.965(6)	C(14)–C(17)	1.479(8)
Fe(1)–C(13)	1.970(6)	C(17)–C(18)	1.189(8)
Fe(2)–C(13)	1.992(5)	C(18)–C(19)	1.430(8)
Fe(1)–C(15)	1.899(6)	C(14)–C(26)	1.551(8)
C(11)–O(11)	1.198(7)	C(15)–N(1)	1.321(7)
C(12)–O(12)	1.155(8)	C(27)–N(1)	1.471(7)
Fe(2)–C(13)–Fe(1)	78.6(2)	C(14)–C(15)–Fe(1)	97.8(4)
Fe(2)–C(13)–C(14)	118.2(4)	C(14)–C(17)–C(18)	172.6(6)
C(13)–C(14)–C(15)	94.5(4)	C(17)–C(18)–C(19)	179.6(7)
C(15)–N(1)–C(27)	124.2(5)	C(27)–N(1)–C(28)	114.8(5)
C(15)–N(1)–C(28)	121.0(4)	Fe(1)–C(11)–Fe(2)	82.6(3)
C(14)–C(15)–N(1)	124.2(5)	N(1)–C(15)–Fe(1)	138.1(4)

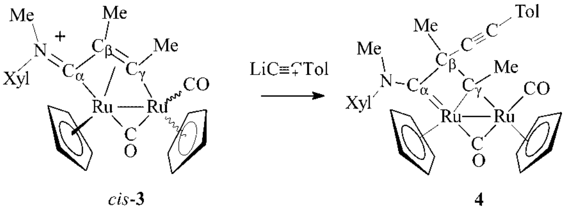
NMR spectra of **2a**–**c** also show that only one isomer is present in solution, thereby indicating that the acetylide addition, which generates a stereogenic centre at C_β, is stereospecific. Thus, we assume that the acetylene fragment is exclusively placed on the opposite side to the sterically demanding Cp ligands, as shown by the structure of **2a** in the solid.

Interestingly, the observed nucleophilic addition at the C_β position of the bridging ligand does not correspond to the reactivity expected for a non-coordinated vinyliminium functionality, which should react at the iminium carbon atom (C_α) or at the conjugated C_γ position. This unusual reactivity shown by the bridging C_3 frame presumably originates from the stability of the bis(alkylidene) coordination mode, which is assumed to be a consequence of the nucleophilic addition and C–C bond formation at C_β.

The most relevant feature of the reactions described above is the completely different outcome of the acetylide addition for *cis*-**1a** and *trans*-**1a**. The mutual arrangement of ancillary ligands in dinuclear complexes rarely exerts any relevant influence on the reactivity of adjacent ligands,[10] although the results reported above are not entirely unexpected. In a very similar and previously reported reaction, the *cis* and *trans* isomers of **1b** were found to react with $NaBH_4$ in different ways: the *cis* isomer was found to undergo hydride addition at C_α, whereas the *trans* isomer reacts at C_β.[4b] This seems to indicate that the *trans* arrangement of the Cp ligands is more favourable than the *cis* one for addition at the C_β position.

A second point to be noted is that neither *cis*-**1a** nor *trans*-**1a** undergo acetylide attack at the iminium carbon atom (C_α), in spite of its strongly electrophilic character. This can be explained in terms of restricted access to the C_α position due to the presence of the sterically demanding Xyl group.

Since (μ-vinyliminium)diruthenium complexes analogous to **1a**–**e** are known, and their chemistry generally parallels that of their diiron counterparts,[11] we extended the investigation to the diruthenium species in order to detect possible effects due to the nature of the metal atom. Thus, we studied the reactions of the *trans* and *cis* isomers of the diruthenium complex $[Ru_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(Me){=}C(Me)C{=}N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**3**), which is an analogue of **1a**, with lithium acetylides. Surprisingly, both *trans* and *cis* isomers react in the same way to give the acetylene-functionalised bis(alkylidene) compound [Ru$_2${μ-η^1:η^2-C(Me)C(Me)(C≡CTol)CN(Me)(Xyl)}(μ-CO)(CO)(Cp)$_2$] (**4**; Scheme 3).



cis-**3**
trans-**3**

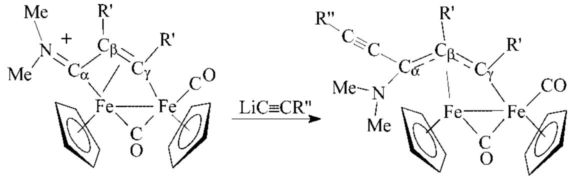
4

Scheme 3.

Complex **4**, which is an analogue of the diiron compound **2a**, was characterised by spectroscopy and elemental analysis. In particular, its NMR spectroscopic data well parallel those of **2a** (see Experimental Section), thereby suggesting that the two compounds adopt identical geometries.

Further investigations concerned the complexes [Fe$_2${μ-η^1:η^3-C(R′)=C(R′)C=N(Me)$_2$}(μ-CO)(CO)(Cp)$_2$][SO$_3$CF$_3$] [R′ = Me (**1c**), Et (**1d**)], which exist only as *cis* isomers. Compounds **1c** and **1d** differ from **1a** in that they contain a methyl group instead of a Xyl group in the iminium moiety. Therefore, in the absence of steric protection due to the Xyl group, the iminium carbon atom is expected to be the preferential site of addition. Accordingly, the reactions of **1c** and **1d** with a series of lithium acetylides LiC≡CR″ [R″ = H, Ph, Tol, SiMe$_3$, C(Me)=CH$_2$] resulted in the formation of the novel bridging acetylene-functionalised allylidene complexes **5a**–**j**, as reported in Scheme 4.

Compounds **5a**–**j** were obtained in good yields after purification by column chromatography on alumina and were characterised by IR and NMR spectroscopy. The structure of **5h** was determined by X-ray diffraction; the ORTEP molecular diagram is shown in Figure 4 and selected bond lengths and angles are listed in Table 2.



	R'	R"	
1c	Me	Tol	**5a**
1c	Me	Ph	**5b**
1c	Me	SiMe$_3$	**5c**
1c	Me	*n*Bu	**5d**
1c	Me	C(Me)=CH$_2$	**5e**
1c	Me	H	**5f**
1d	Et	Tol	**5g**
1d	Et	Ph	**5h**
1d	Et	SiMe$_3$	**5i**
1d	Et	C(Me)=CH$_2$	**5j**

Scheme 4.

Table 2. Selected bond lengths [Å] and angles [°] for [Fe$_2${μ-η^1:η^3-C(Et)C(Et)C(C≡CPh)N(Me)$_2$}(μ-CO)(CO)(Cp)$_2$] (**5h**).

Fe(1)–Fe(2)	2.5362(8)	C(13)–C(14)	1.425(4)
Fe(2)–C(12)	1.750(4)	C(14)–C(15)	1.463(4)
Fe(1)–C(11)	1.903(3)	C(13)–C(16)	1.520(4)
Fe(2)–C(11)	1.946(3)	C(14)–C(18)	1.528(4)
Fe(1)–C(13)	2.010(3)	C(15)–C(22)	1.452(4)
Fe(2)–C(13)	1.987(3)	C(22)–C(23)	1.199(4)
C(11)–O(11)	1.168(4)	C(23)–C(24)	1.438(4)
C(12)–O(12)	1.137(4)	C(15)–N(1)	1.455(4)
Fe(1)–C(14)	2.040(3)	Fe(1)–C(15)	2.098(3)
Fe(2)–C(13)–Fe(1)	78.77(11)	C(14)–C(15)–N(1)	119.8(2)
Fe(1)–C(11)–Fe(2)	82.43(13)	C(14)–C(15)–C(22)	117.8(2)
Fe(2)–C(13)–C(14)	126.1(2)	C(15)–C(22)–C(23)	169.0(3)
C(13)–C(14)–C(15)	120.1(2)	C(22)–C(23)–C(24)	176.1(4)

The C$_3$-bridged coordination framework exhibits some changes as a consequence of acetylide addition, although it remains σ-bound to Fe(2) [Fe(2)–C(13) 1.987(3) Å] and η^3-coordinated to Fe(1) [Fe(1)–C(13) 2.010(3), Fe(1)–C(14) 2.040(3), Fe(1)–C(15) 2.098(3) Å]. The usual description for this bonding mode is a mix of vinylalkylidene and allylidene

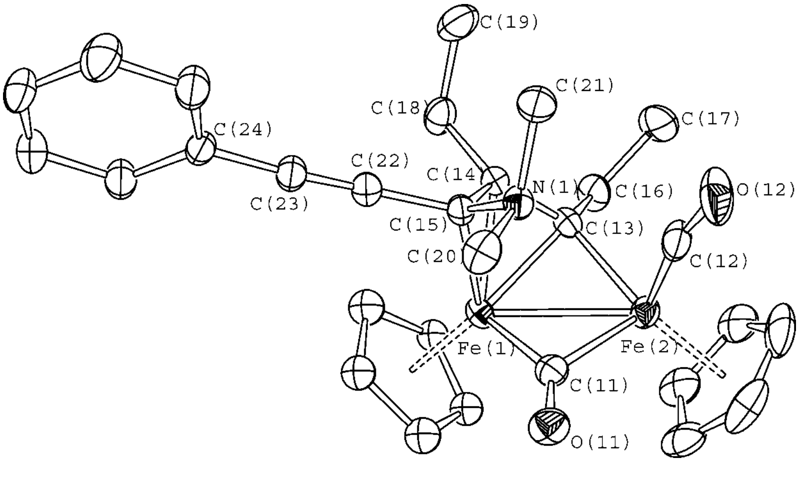


Figure 4. ORTEP drawing of [Fe$_2${μ-η^1:η^3-C(Et)C(Et)C(C≡CPh)N(Me)$_2$}(μ-CO)(CO)(Cp)$_2$] (**5h**). All H atoms have been omitted for clarity. Thermal ellipsoids are at the 30% probability level.

contributions (Figure 5, **A** and **B**, respectively).[12] The structure of **5h** can be compared to that of the related complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(Tol)C_\beta(H)C_\alpha(H)N(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**III**),[4a] $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(SiMe_3)C_\beta(H)C_\alpha(CN)N(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**IV**),[3] and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\gamma(Me)C_\beta(Me)C_\alpha(CN)N(Me)_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ (**V**),[3] which were obtained by hydride or cyanide addition.[3] Compound **III** has a C_α–C_β bond length [1.408(9) Å] shorter than that of C_β–C_γ [1.441(8) Å], and has been described as containing a bridging vinylalkylidene. Conversely, **5h** shows the opposite trend, namely the C_β-C_γ bond length [1.435(4) Å] is shorter than that of C_α–C_β [1.463(4) Å], and because of this closely resembles **IV** and **V** [C_β–C_γ 1.414(3) and 1.419(3), C_α–C_β 1.447(3) and 1.449(3) Å, respectively], which were more appropriately described as allylidene complexes (Figure 5, **B**). This observation, together with the fact that the C(15)–N(1) (C_α–N) [1.455(4) Å] and Fe(1)–C(15) interactions [2.098(3) Å] are almost a single bond and both C(15) and N(1) deviate appreciably from sp^2 hybridisation [sum of angles: 348.5(3) and 334.6(4)°, respectively], suggests that the ligand can also be described in terms of a η^1:η^2-vinyl contribution (Figure 5, **C**), although the most representative description is as an allylidene (**B**).

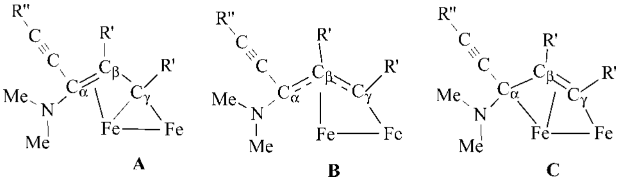


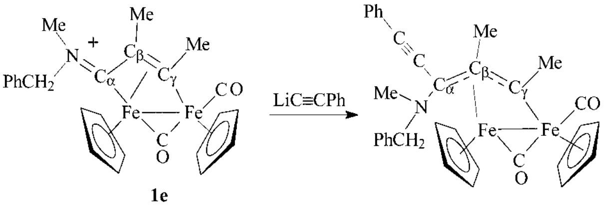
Figure 5. Description of the bridging ligand in complexes of type **5**.

A further difference between **5h** and the complexes derived by hydride addition to C_α (**III**) consists in the orientation of the NMe_2 group. Thus, in the acetylene-functionalised compound **5h** it lies *trans* to the R substituent of C_β whereas it is *cis* in complex **III**.[4a] In this respect **5h** more closely resembles the products obtained by cyanide addition (**IV** and **V**), which display an analogous *trans* orientation.[3]

The spectroscopic data of **5a–j** are fully consistent with the proposed formulation. The IR spectra (in CH_2Cl_2 solution) exhibit the usual ν(CO) band pattern and a weak absorption at 2120–2180 cm^{-1} for the C≡C bond. The ^1H NMR spectra suggest a single isomer in solution, which indicates that the reaction is regio- and stereoselective. In particular, NOE investigations carried out on **5b** show that irradiation of the C_β-*Me* resonance (δ = 2.18 ppm) results in a significant enhancement of the *N*-methyl resonance at δ = 1.64 ppm, whereas no NOE is detected between C_β-*Me* and the other N–*Me* (δ = 2.31 ppm) or between the *N*-bound methyl groups and the Cp ligands. Indeed, looking at the structure of **5h**, the NMe_2 group is placed on the side opposite to the Cp ligand and one *N*-methyl group lies much closer to the C_β substituent than the other.

The major features of the ^{13}C NMR spectra concern the C_α and C_γ resonances: the latter is found downfield (δ = 203.4 ppm for **5h**), whereas the former is shifted upfield (δ = 72.8 ppm for **5h**), with respect to the vinyliminium precursors. These data are consistent with the alkyl nature of C_α and the vinyl character of C_γ. Finally, two signals in the range δ = 89–107 ppm can be assigned to the sp carbon atoms (δ = 92.4 and 91.1 ppm for **5h**).

The reaction of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Me){=}C(Me)C{=}N(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1e**) with LiC≡CPh was also investigated. Compared to **1a** and **1c**, compound **1e** has one benzyl group as an *N*-substituent. The aim of this study was to determine to what extent substituents with a steric hindrance intermediate between Me and Xyl can exert steric protection on the iminium carbon atom (C_α). The addition occurs selectively at C_α and results in the formation of complex **6** (Scheme 5).

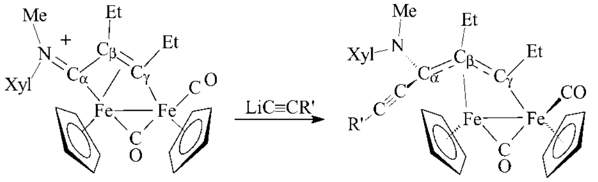


1e **6**

Scheme 5.

The spectroscopic data of **6** are similar to those of **5a–j**. However, by contrast with **5a–j**, complex **6** contains minor amounts of a second isomeric form in solution (isomer ratio about 12:1). These isomers are presumably due to the different orientations that the methyl and benzyl substituents can adopt as a consequence of hindered rotation around the C_α–N bond. NOE experiments on the major isomer suggest that the most favourable geometry is that with the bulkier benzyl group pointing toward the bridging and terminal CO.

Finally, the reactions of compound **1b** with LiC≡CR′ (R′ = $SiMe_3$, H) resulted in the formation of complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Et)C(Et)C(C{\equiv}CR')N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = $SiMe_3$ **7a**, H **7b**) in low yields (20–30%; Scheme 6).



	R'	
1b	SiMe$_3$	**7a**
1b	H	**7b**

Scheme 6.

It is noteworthy that both *cis*- and *trans*-**1b** react in the same way. Unexpectedly, the addition occurs selectively at the iminium carbon atom rather than producing CO cleavage, in spite of the presence of the Xyl group and a *cis* arrangement of the Cp ligands.

Compounds **7a** and **7b** are unstable and decompose in CH_2Cl_2 solution at room temperature after 12 h. Nonetheless, they could be purified by chromatography on alumina and characterised by IR and NMR spectroscopy. Their NMR spectroscopic data, and in particular the C_α, C_β and C_γ resonances (see Experimental Section), are consistent with their acetylene-functionalised allylidene nature. NOE studies were carried out on complex **7b**. Thus, irradiation of the Cp resonance at δ = 3.68 ppm resulted in significant enhancement of the resonances at δ = 4.67 (Cp), 2.62 (N-*Me*) and 1.29 ppm (Xyl-*Me*). This indicates that the Cp ligands adopt a *cis* geometry and the N(Me)(Xyl) is close to one Cp ring. Thus, the geometry of the substituents at the C_α atom seems to be different from that found in **5h**, since the alkynyl moiety in **7b** points toward the CO ligands.

Conclusions

Complexes containing bridging vinyliminium ligands are very reactive toward acetylides: they undergo nucleophilic addition with C–C bond formation at the C_3 bridging ligand. Several reaction paths have been evidenced, in addition to the nucleophilic attack to CO and its cleavage, previously communicated. The results evidence that, although several sites of addition are available, the reactions are selective and do not produce mixtures of isomers. The site of addition is largely determined by steric arguments, related to the nature of the substituents on the vinyliminium ligand. Thus, the iminium carbon atom (C_α) appears as the most reactive site, but it is made hardly accessible by the presence of the sterically demanding Xyl substituent. Likewise, nucleophilic addition at the C_β position is hampered when the Cp ligands are mutually *cis*, or in the presence of C_β substituents more sterically demanding than a methyl group. When all these factors operate, the acetylide attack is directed to the CO and is soon followed by an intramolecular rearrangement involving the vinyliminium ligand. Thus, the reactions lack a general character and, in some cases, are difficult to predict. On the other hand, the bridging C_3 moiety displays a variety of possible ways in which it can add an alkynyl group to generate new bridging hydrocarbyl ligands with more complex architectures.

Experimental Section

General: All reactions were routinely carried out under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatographic separations were performed on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. IR spectra were recorded with a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed with a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed with Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned by DEPT experiments and $^1H,^{13}C$ correlation through gs-HSQC and gs-HMBC experiments.[13] All NMR spectra were recorded at 298 K; NMR signals due to a second isomeric form (where it was possible to detect and/or resolve them) are *italicized*. NOE measurements were recorded using the DPFGSE-NOE sequence.[14] All reagents were commercial products (Aldrich) of the highest purity available and were used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Complexes $[Fe_2\{\mu\text{-}\eta^1:\eta^3\text{-}C(R')=C(R')C=N(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**1a**–**e**)[2] and $[Ru_2\{\mu\text{-}C(Me)=C(Me)C=N(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2][CF_3SO_3]$ (**3**)[11] were prepared as described in the literature.

Synthesis of $[Fe_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C(Me)(C{\equiv}CR'')CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [R″ = Tol (2a), Ph (2b), $SiMe_3$ (2c)]: A solution of *trans*-**1a** (201 mg, 0.311 mmol), in thf (8 mL), was treated at room temperature with a thf solution of LiC≡CTol (1.2 mL, 0.620 mmol) freshly prepared from *n*BuLi and HC≡CTol. The mixture was stirred for 30 min, then it was concentrated under reduced pressure. Chromatography of the residue on alumina, using diethyl ether as eluent, afforded a red band corresponding to **2a**. Yield: 137 mg (72%). Crystals suitable for X-ray diffraction were obtained by layering a diethyl ether solution of **2a** with petroleum ether (b.p. 40–60 °C) at –20 °C. $C_{35}H_{35}Fe_2NO_2$ (613.35): calcd. C 68.54, H, 5.75; found C 68.36, H 5.70. IR (CH_2Cl_2): ν(CO) 1919 (vs), 1749 (s); ν(C_αN) 1511 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.64–6.98 (m, 7 H, $Me_2C_6\mathit{H}_3$ and $C_6\mathit{H}_4Me$), 4.58, 3.95 (s, 10 H, Cp), 3.43 (s, 3 H, $C_\gamma Me$), 3.40 (s, 3 H, NMe), 2.32 (s, 3 H, $C_6H_4\mathit{Me}$), 2.25, 2.20 (s, 6 H, $\mathit{Me}_2C_6H_3$), 2.01 (s, 3 H, $C_\beta Me$) ppm. ^{13}C NMR ($CDCl_3$): δ = 283.2 (μ-CO), 268.8 (C_α), 216.5 (CO), 181.5 (C_γ), 146.1 (*ipso*-$Me_2\mathit{C}_6H_3$), 137.3–127.3 ($Me_2\mathit{C}_6H_3$ and C_6H_4Me), 94.1, 85.9 (C≡C), 87.9, 85.2 (Cp), 75.0 (C_β), 43.0 (NMe), 39.3 ($C_\gamma\mathit{Me}$), 27.5 ($C_\beta\mathit{Me}$), 21.4 ($C_6H_4\mathit{Me}$), 18.4, 17.7 ($\mathit{Me}_2C_6H_3$) ppm. Complexes **2b** and **2c** were obtained according to the same procedure described for the synthesis of **2a** by treating *trans*-**1a** (190 mg) with LiC≡CPh and LiC≡CSiMe$_3$, respectively. **2b:** Yield: 124 mg (74%). Colour: red. $C_{34}H_{33}Fe_2NO_2$ (599.32): calcd. C 68.14, H, 5.55; found C 68.21, H 5.62. IR (CH_2Cl_2): ν(CO) 1918 (vs), 1749 (s); ν(C_αN) 1511 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.71–6.39 (m, 8 H, $Me_2C_6\mathit{H}_3$ and Ph), 4.58, 3.95 (s, 10 H, Cp), 3.44 (s, 3 H, $C_\gamma Me$), 3.40 (s, 3 H, NMe), 2.25, 2.20 (s, 6 H, $Me_2C_6\mathit{H}_3$), 2.03 (s, 3 H, $C_\beta Me$) ppm. ^{13}C NMR ($CDCl_3$): δ = 282.3 (μ-CO), 268.4 (C_α), 216.6 (CO), 181.2 (C_γ), 146.7 (*ipso*-$Me_2\mathit{C}_6H_3$), 135.1–125.9 ($Me_2C_6H_3$ and C_6H_5), 94.1, 85.9 (C≡C), 87.9, 85.2 (Cp), 75.0 (C_β), 43.0 (NMe), 39.3 ($C_\gamma\mathit{Me}$), 27.5 ($C_\beta\mathit{Me}$), 18.4, 17.7 ($\mathit{Me}_2C_6H_3$) ppm. **2c:** Yield: 119 mg (68%). Colour: red. $C_{31}H_{37}Fe_2NO_2Si$ (595.41): calcd. C 62.53, H, 6.26; found C 62.55, H 6.20. IR (CH_2Cl_2): ν(CO) 1918 (vs), 1750 (s); ν(C_αN) 1511 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.10–6.80 (m, 3 H, $Me_2C_6\mathit{H}_3$), 4.54, 3.91 (s, 10 H, Cp), 3.37 (s, 3 H, $C_\gamma Me$), 3.36 (s, 3 H, NMe), 2.23, 2.17 (s, 6 H, $\mathit{Me}_2C_6H_3$), 1.92 (s, 3 H, $C_\beta Me$), 0.45 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 282.3 (μ-CO), 266.2 (C_α), 216.5 (CO), 181.1 (C_γ), 147.4 (*ipso*-$Me_2\mathit{C}_6H_3$), 137.2–126.4 ($Me_2\mathit{C}_6H_3$), 113.7, 90.1 (C≡C), 87.8, 85.2 (Cp), 78.8 (C_β), 42.9 (NMe), 39.1 ($C_\gamma\mathit{Me}$), 29.7 ($C_\beta\mathit{Me}$), 18.3, 17.7 ($\mathit{Me}_2C_6H_3$) ppm.

Synthesis of $[Ru_2\{\mu\text{-}\eta^1:\eta^2\text{-}C(Me)C(Me)(C{\equiv}CTol)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (4): A solution of **3** (300 mg, 0.407 mmol) in thf (15 mL), was treated at room temperature with a thf solution of LiC≡CTol (1.6 mL, 0.827 mmol) freshly prepared from *n*BuLi and HC≡CTol. The mixture was stirred for 30 min, then the solvent was removed under reduced pressure. Chromatography of the residue on alumina, using diethyl ether as eluent, afforded a red band corresponding to **4**. Yield: 203 mg (71%). $C_{35}H_{35}NO_2Ru_2$ (703.8): calcd. C 59.73, H, 5.01; found C 59.92, H 4.89. IR (CH_2Cl_2): ν(C≡C) 2159 (w); ν(CO) 1918 (vs), 1744 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.67–7.09 (m, 7 H, $Me_2C_6\mathit{H}_3$ and $C_6\mathit{H}_4Me$), 5.12, 4.51 (s, 10 H, Cp), 3.57 (s, 3 H, NMe), 3.08 (s, 3 H, $C_\gamma Me$), 2.34 (s, 3 H, $C_6H_4\mathit{Me}$), 2.24, 2.23 (s, 6 H, $\mathit{Me}_2C_6H_3$), 1.87 (s, 3 H, $C_\beta Me$)

ppm. ^{13}C NMR ($CDCl_3$): δ = 252.1 (C_α), 249.29 (μ-CO), 204.5 (CO), 156.2 (C_γ), 147.0 (*ipso*-$Me_2\mathit{C}_6H_3$), 137.7 (*ipso*-C_6H_4Me), 133.4, 132.6, 132.4, 131.4–128.0 ($Me_2\mathit{C}_6H_3$ and C_6H_4Me), 94.1, 89.0 ($C\equiv C$), 90.0, 86.9 (Cp), 76.3 (C_β), 42.2 (NMe), 40.0 ($C_\gamma\mathit{Me}$), 28.1 ($C_\beta\mathit{Me}$), 21.8 ($C_6H_4\mathit{Me}$), 18.7, 17.9 ($\mathit{Me}_2C_6H_3$) ppm.

Synthesis of [Fe_2\{μ-η^1:η^3-C(Me)C(Me)C($C\equiv CR''$)N($Me)_2$\}(μ-CO)(CO)($Cp)_2$] [R″ = Tol (5a), Ph (5b), $SiMe_3$ (5c), *n*Bu (5d), C(Me)=CH_2 (5e), H (5f)]: A solution of complex **1c** (99 mg, 0.178 mmol), in thf (10 mL) was treated with $LiC\equiv CTol$ (0.552 mmol) according to the same procedure described for the synthesis of **2a–c**. The reaction afforded **5a** as red crystals in 69% yield (64 mg). $C_{28}H_{29}Fe_2NO_2$ (523.22): calcd. C 64.27, H 5.59; found C 64.29, H 5.54. IR (CH_2Cl_2): ν($C\equiv C$) 2181 (w); ν(CO) 1939 (vs), 1769 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.43–7.09 (m, 4 H, $C_6\mathit{H}_4Me$), 4.81, 4.33 (s, 10 H, Cp), 3.86 (s, 3 H, $C_\gamma Me$), 2.34 (s, 3 H, $C_6H_4\mathit{Me}$), 2.29, 1.61 (s, 6 H, NMe), 2.15 (s, 3 H, $C_\beta Me$) ppm. ^{13}C NMR ($CDCl_3$): δ = 275.8 (μ-CO), 214.5 (CO), 193.7 (C_γ), 136.9, 132.3, 130.6, 129.0, 121.8 (C_6H_4Me), 93.1, 91.8 ($C\equiv C$), 89.7 (C_β), 88.4, 87.1 (Cp), 72.9 (C_α), 48.4, 41.1 (NMe), 39.4 ($C_\gamma\mathit{Me}$), 22.8 ($C_\beta\mathit{Me}$), 21.5 ($C_6H_4\mathit{Me}$) ppm. Complexes **5b–f** were obtained analogously by treating **1c** (150 mg) with the appropriate lithium acetylide. **5b:** Yield: 113 mg (82%). Colour: red. $C_{27}H_{27}Fe_2NO_2$ (509.20): calcd. C 63.68, H, 5.34; found C 63.72, H 5.44. IR (CH_2Cl_2): ν($C\equiv C$) 2181 (w); ν(CO) 1940 (vs), 1768 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.56–7.26 (m, 5 H, Ph), 4.82, 4.35 (s, 10 H, Cp), 3.87 (s, 3 H, $C_\gamma Me$), 2.31, 1.64 (s, 6 H, NMe), 2.18 (s, 3 H, $C_\beta Me$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.4 (μ-CO), 214.7 (CO), 194.0 (C_γ), 132.4–124.9 (Ph), 93.0, 92.6 ($C\equiv C$), 89.8 (C_β), 88.4, 87.1 (Cp), 72.5 (C_α), 48.4, 41.1 (NMe), 39.4 ($C_\gamma\mathit{Me}$), 22.6 ($C_\beta\mathit{Me}$) ppm. **5c:** Yield: 119 mg (87%). Colour: red. $C_{24}H_{31}Fe_2NO_2Si$ (505.28): calcd. C 57.05, H, 6.18; found C 57.08, H 6.16. IR (CH_2Cl_2): ν($C\equiv C$) 2118 (m); ν(CO) 1940 (vs), 1769 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.79, 4.25 (s, 10 H, Cp), 3.82 (s, 3 H, $C_\gamma Me$), 2.19 (s, 3 H, $C_\beta Me$), 2.04, 1.54 (s, 6 H, NMe), 0.21 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.4 (μ-CO), 214.6 (CO), 193.9 (C_γ), 107.1, 96.1 ($C\equiv C$), 89.6 (C_β), 88.4, 87.5 (Cp), 72.8 (C_α), 48.1, 40.9 (NMe), 39.3 ($C_\gamma\mathit{Me}$), 22.3 ($C_\beta\mathit{Me}$), 0.78 ($SiMe_3$) ppm. **5d:** Yield: 105 mg (80%). Colour: ochre yellow. $C_{25}H_{31}Fe_2NO_2$ (489.21): calcd. C 61.38, H 6.39; found C 61.44, H 6.35. IR (CH_2Cl_2): ν(CO) 1934 (vs), 1762 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.77, 4.26 (s, 10 H, Cp), 3.83 (s, 3 H, $C_\gamma Me$), 2.32 (m, 2 H, $C\equiv CCH_2$), 2.18 (s, 3 H, $C_\beta Me$), 2.04, 1.52 (s, 6 H, NMe), 1.58–1.32 (m, 4 H, $C\equiv CCH_2C\mathit{H}_2C\mathit{H}_2$), 0.93 (m, 3 H, $C\equiv CCH_2CH_2CH_2C\mathit{H}_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.8 (μ-CO), 214.8 (CO), 193.6 (C_γ), 92.7, 89.2 ($C\equiv C$), 89.2 (C_β), 88.3, 87.2 (Cp), 71.3 (C_α), 48.3, 41.0 (NMe), 39.5 ($C_\gamma\mathit{Me}$), 32.0, 22.2, 19.3 (CH_2), 22.5 ($C_\beta\mathit{Me}$), 13.8 ($CH_2CH_2CH_2\mathit{C}H_3$) ppm. **5e:** Yield: 63 mg (74%). Colour: ochre yellow. $C_{24}H_{27}Fe_2NO_2$ (473.17): calcd. C 60.92, H 5.75; found C 60.99, H 5.67. IR (CH_2Cl_2): ν($C\equiv C$) 2159 (w); ν(CO) 1938 (vs), 1764 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.15, 5.08 (m, 2 H, CH_2), 4.73, 4.22 (s, 10 H, Cp), 3.77 (s, 3 H, $C_\gamma Me$), 2.15 (s, 3 H, $C_\beta Me$), 2.01, 1.49 (s, 6 H, NMe), 1.91 (s, 3 H, $C\equiv CC\mathit{Me}$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.3 (μ-CO), 214.6 (CO), 193.8 (C_γ), 127.9 ($C\equiv C\mathit{C}Me$), 118.3 (CH_2), 94.4, 91.7 ($C\equiv C$), 89.7 (C_β), 88.4, 87.1 (Cp), 72.7 (C_α), 48.3, 41.0 (NMe), 39.4 ($C_\gamma\mathit{Me}$), 24.3 ($C\equiv CC\mathit{Me}$), 22.6 ($C_\beta\mathit{Me}$) ppm. **5f:** Yield: 24 mg (21%). Colour: ochre yellow. $C_{21}H_{23}Fe_2NO_2$ (433.10): calcd. C 58.24, H 5.35; found C 58.30, H 5.34. IR (CH_2Cl_2): ν(CO) 1942 (vs), 1771 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.79, 4.27 (s, 10 H, Cp), 3.83 (s, 3 H, $C_\gamma Me$), 2.64 (s, 1 H, $C\equiv CH$), 2.20 (s, 3 H, $C_\beta Me$), 2.05, 1.54 (s, 6 H, NMe) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.0 (μ-CO), 214.5 (CO), 194.0 (C_γ), 89.7 (C_β), 88.4, 87.3 (Cp), 85.3, 82.1 ($C\equiv C$), 69.9 (C_α), 47.9, 40.9 (NMe), 39.4 ($C_\gamma\mathit{Me}$), 22.1 ($C_\beta\mathit{Me}$) ppm.

Synthesis of [Fe_2\{μ-η^1:η^3-C(Et)C(Et)C($C\equiv CR''$)N($Me)_2$\}(μ-CO)(CO)($Cp)_2$] [R″ = Tol (5g), Ph (5h), $SiMe_3$ (5i), C(Me)=CH_2 (5j)]: Complexes **5g–j** were obtained by the same procedure described for the synthesis of **5a** by treating **1d** (180 mg) with the appropriate lithium acetylide. Crystals of **5h** suitable for X-ray analysis were collected by layering a diethyl ether solution with *n*-pentane at –20 °C. **5g:** Yield: 115 mg (65%). Colour: red. $C_{30}H_{33}Fe_2NO_2$ (551.28): calcd. C 65.36, H, 6.03; found C 65.42, H 6.11. IR (CH_2Cl_2): ν($C\equiv C$) 2180 (w); ν(CO) 1940 (vs), 1769 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.35–6.95 (m, 4 H, $C_6\mathit{H}_4Me$), 4.79, 4.35 (s, 10 H, Cp), 4.46, 4.09 (m, 2 H, $C_\gamma CH_2$), 3.19, 2.18 (m, 2 H, $C_\beta CH_2$), 2.33 (s, 3 H, $C_6H_4\mathit{Me}$), 2.18, 1.59 (s, 6 H, NMe), 1.67 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\gamma CH_2C\mathit{H}_3$), 1.26 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\beta CH_2C\mathit{H}_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.5 (μ-CO), 214.7 (CO), 203.3 (C_γ), 136.8–121.9 (C_6H_4Me), 93.7 (C_β), 91.5, 91.1 ($C\equiv C$), 88.4, 86.5 (Cp), 73.1 (C_α), 49.0, 41.6 (NMe), 44.8 ($C_\gamma\mathit{C}H_2$), 29.5 ($C_\beta\mathit{C}H_2$), 21.5 ($C_6H_4\mathit{Me}$), 20.5 ($C_\gamma CH_2\mathit{C}H_3$), 16.4 ($C_\beta CH_2\mathit{C}H_3$) ppm. **5h:** Yield: 104 mg (60%). Colour: red. $C_{29}H_{31}Fe_2NO_2$ (537.25): calcd. C 64.83, H, 5.82; found C 64.86%; H 5.82. IR (CH_2Cl_2): ν($C\equiv C$) 2180 (w); ν(CO) 1941 (vs), 1768 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.45–7.24 (m, 5 H, Ph), 4.81, 4.38 (s, 10 H, Cp), 4.50, 4.10 (m, 2 H, $C_\gamma CH_2$), 3.22, 2.19 (m, 2 H, $C_\beta CH_2$), 2.21, 1.62 (s, 6 H, NMe), 1.70 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\gamma CH_2C\mathit{H}_3$), 1.28 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\beta CH_2C\mathit{H}_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.3 (μ-CO), 214.6 (CO), 203.4 (C_γ), 130.7, 128.2, 126.8, 125.0 (Ph), 93.8 (C_β), 92.4, 91.1 ($C\equiv C$), 88.4, 86.5 (Cp), 72.8 (C_α), 49.1, 41.6 (NMe), 44.8 ($C_\gamma\mathit{C}H_2$), 29.5 ($C_\beta\mathit{C}H_2$), 20.5 ($C_\gamma CH_2\mathit{C}H_3$), 16.5 ($C_\beta CH_2\mathit{C}H_3$) ppm. **5i:** Yield: 119 mg (69%). Colour: ochre yellow. $C_{26}H_{35}Fe_2NO_2Si$ (533.34): calcd. C 58.55, H 6.61; found C 58.50, H 6.69. IR (CH_2Cl_2): ν($C\equiv C$) 2118 (m), ν(CO) 1940 (vs), 1766 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 4.78, 4.28 (s, 10 H, Cp), 4.43, 4.06 (m, 2 H, $C_\gamma CH_2$), 3.10, 2.19 (m, 2 H, $C_\beta CH_2$), 2.06, 1.52 (s, 6 H, NMe), 1.65 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\gamma CH_2C\mathit{H}_3$), 1.21 (t, $^3J_{H,H}$ = 8 Hz, 3 H, $C_\beta CH_2C\mathit{H}_3$), 0.19 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.6 (μ-CO), 214.8 (CO), 203.5 (C_γ), 106.9, 94.0 ($C\equiv C$), 93.7 (C_β), 88.4, 86.9 (Cp), 72.9 (C_α), 48.8, 41.4 (NMe), 44.7 ($C_\gamma\mathit{C}H_2$), 28.9 ($C_\beta\mathit{C}H_2$), 20.3 ($C_\gamma CH_2\mathit{C}H_3$), 16.1 ($C_\beta CH_2\mathit{C}H_3$), 0.67 ($SiMe_3$) ppm. **5j:** Yield: 134 mg (83%). Colour: ochre yellow. $C_{26}H_{31}Fe_2NO_2$ (501.22): calcd. C 62.30, H, 6.23; found C 62.20, H 6.18. IR (CH_2Cl_2): ν($C\equiv C$) 2160 (w); ν(CO) 1938 (vs), 1764 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 5.20, 5.14 (m, 2 H, CH_2), 4.78, 4.32 (s, 10 H, Cp), 4.46, 4.06 (s, 2 H, $C_\gamma CH_2$), 3.15, 2.05 (s, 2 H, $C_\beta CH_2$), 2.09, 1.54 (s, 6 H, NMe), 1.96 (s, 3 H, $C\equiv CC\mathit{Me}$), 1.66 (dd, $^3J_{H,H}$ = 7.14 Hz, $^3J_{H,H}$ = 7.69 Hz, 3 H, $C_\gamma CH_2C\mathit{H}_3$), 1.23 (dd, $^3J_{H,H}$ = 7.14 Hz, $^3J_{H,H}$ = 7.69 Hz, 3 H, $C_\gamma CH_2C\mathit{H}_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 272.5 (μ-CO), 214.7 (CO), 203.3 (C_γ), 127.9 ($C\equiv C\mathit{C}Me$), 118.2 (CH_2), 93.7 (C_β), 92.4, 91.4 ($C\equiv C$), 88.4, 86.5 (Cp), 72.9 (C_α), 49.0, 41.5 (NMe), 44.8 ($C_\gamma\mathit{C}H_2$), 29.4 ($C_\beta\mathit{C}H_2$), 24.3 ($C\equiv CC\mathit{Me}$), 20.5 ($C_\gamma CH_2\mathit{C}H_3$), 16.4 ($C_\beta CH_2\mathit{C}H_3$) ppm.

Synthesis of [Fe_2\{μ-η^1:η^3-C(Me)C(Me)C($C\equiv CPh$)N(Me)(CH_2Ph)\}(μ-CO)(CO)($Cp)_2$] (6): This complex was obtained according to the same procedure described for the synthesis of **5a** by treating **1e** (120 mg, 0.190 mmol) with $LiC\equiv CPh$. Yield: 80 mg (72%). Colour: ochre yellow. $C_{33}H_{31}Fe_2NO_2$ (585.29): calcd. C 67.72, H 5.34; found C 67.78, H 5.40. IR (CH_2Cl_2): ν($C\equiv C$) 2181 (w); ν(CO) 1953 (vs), 1767 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.54–7.13 (m, 10 H, Ph), 4.86, *4.83*, 4.39, *4.31* (s, 10 H, Cp), 4.53, 3.30 (d, $^2J_{H,H}$ = 12.64 Hz, 2 H, $C\mathit{H}_2Ph$), 3.92, *3.84* (s, 3 H, $C_\gamma Me$), 2.31, *2.27* (s, 3 H, $C_\beta Me$), *2.22*, 1.54 (s, 3 H, NMe) ppm. Isomer ratio 12: 1. ^{13}C NMR ($CDCl_3$): δ = 270.7 (μ-CO), 213.8 (CO), 194.3 (C_γ), 138.8–124.8 (Ph), 93.6, 93.4 ($C\equiv C$), 89.1 (C_β), *88.7*, 88.5, *87.6*, 87.4 (Cp), 73.7 (C_α), *65.4*, 59.7 ($\mathit{C}H_2Ph$), 45.5, *42.1* (NMe), 39.6, *37.7* ($C_\gamma\mathit{Me}$), *23.8*, 23.0 ($C_\beta\mathit{Me}$) ppm.

Syntheses of [Fe_2\{μ-η^1:η^3-C(Et)C(Et)C(C≡CR″)N(Me)(Xyl)\}(μ-CO)(CO)$(Cp)_2$] [R″ = $SiMe_3$ (7a), H (7b)]: A solution of *cis*-**1b** (180 mg, 0.267 mmol) in thf (10 mL) was treated with a thf solution of LiC≡$CSiMe_3$ (0.40 mL, 0.40 mmol) freshly prepared from *n*BuLi and HC≡$CSiMe_3$. Solvent removal and chromatography of the residue on alumina, using CH_2Cl_2 as eluent, afforded a brown band corresponding to **7a** (45 mg, 27 %). $C_{33}H_{41}Fe_2NO_2Si$ (623.46): calcd. C 63.57, H 6.63; found C 63.65, H 6.57. IR (CH_2Cl_2): ν(CO) 1943 (vs), 1762 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.17–6.78 (m, 3 H, $Me_2C_6H_3$), 4.59, 4.35 (s, 10 H, Cp), 4.26, 3.97 (m, 2 H, $C_\gamma CH_2$), 2.89 (s, 3 H, NMe), 2.57, 1.14 (m, 2 H, $C_\beta CH_2$), 1.48, 1.35 (s, 6 H, $Me_2C_6H_3$), 1.31 (m, 3 H, $C_\gamma CH_2CH_3$), 0.85 (m, 3 H, $C_\beta CH_2CH_3$), 0.07 (s, 9 H, $SiMe_3$) ppm. ^{13}C NMR ($CDCl_3$): δ = 273.8 (μ-CO), 212.6 (CO), 202.8 (C_γ), 155.5 (*ipso*-$Me_2C_6H_3$), 134.8–122.7 ($Me_2C_6H_3$), 106.5, 88.6 (C≡C), 97.3 (C_α), 89.4 (C_β), 88.1, 85.8 (Cp), 43.4 ($C_\gamma CH_2$), 39.9 (NMe), 25.4 ($C_\beta CH_2$), 19.5, 19.2 ($Me_2C_6H_3$), 17.3 ($C_\gamma CH_2CH_3$), 14.9 ($C_\beta CH_2CH_3$), 1.34 ($SiMe_3$) ppm. Complex **7b** was obtained according to the same procedure described for the synthesis of **7a** by treating *cis*-**1b** (180 mg) with LiC≡CH. **7b:** Yield: 37 mg (25 %). Colour: brownish green. $C_{30}H_{33}Fe_2NO_2$ (551.28): calcd. C 65.36, H 6.03; found C 65.42, H 6.00. IR (CH_2Cl_2): ν(CO) 1945 (vs), 1762 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.19–6.96 (m, 3 H, $Me_2C_6H_3$), 4.67, 3.68 (s, 10 H, Cp), 3.76 (m, 2 H, $C_\gamma CH_2$), 2.62 (s, 3 H, NMe), 2.18 (s, 1 H, C≡CH), 2.02, 1.68 (m, 2 H, $C_\beta CH_2$), 1.29, 1.26 (s, 6 H, $Me_2C_6H_3$), 1.22 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\gamma CH_2CH_3$), 0.43 (t, $^3J_{H,H}$ = 7 Hz, 3 H, $C_\beta CH_2CH_3$) ppm.

X-ray Crystallography: The X-ray intensity data for **2a** and **5h** were collected at room temperature with a Bruker AXS SMART 2000 CCD diffractometer using Mo-K_α radiation. Intensity data were measured over full diffraction spheres using 0.3°-wide ω-scans and a crystal-to-detector distance of 5.2 cm. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in three sets of 20 exposures collected in three different ω-regions and eventually refined against all reflections. The software SMART[15] was used for collecting frames of data, indexing reflections and determining the lattice parameters. The collected frames were then processed for integration by the software SAINT and empirical absorption corrections were applied with SADABS.[16] The structure was solved by direct methods and refined by full-matrix least squares based on all data using F^2.[17] Crystal data are listed in Table 3. Non-H atoms were refined anisotropically, unless otherwise stated; H atoms were placed in calculated positions and treated isotropically using the 1.2-fold U_{iso} value of the parent atoms, except methyl protons, which were assigned the 1.5-fold U_{iso} value of the parent C atoms. One Cp ligand in both **2a** and **5h** 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-626314 (**2a**) and -626315 (**5h**) 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.

Table 3. Crystal data and experimental details for **2a** and **5h**.

Complex	2a	5h
Empirical formula	$C_{35}H_{35}Fe_2NO_2$	$C_{29}H_{31}Fe_2NO_2$
Formula mass	613.34	537.25
λ [Å]	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a [Å]	14.2068(6)	9.2783(19)
b [Å]	9.1543(4)	11.275(2)
c [Å]	22.3490(10)	12.226(2)
α [°]	90	95.73(3)
β [°]	94.0690(10)	100.61(3)
γ [°]	90	92.50(3)
V [Å^3]	2899.2(2)	1248.3(4)
Z	4	2
D_c [g cm^{-3}]	1.405	1.429
μ [mm^{-1}]	1.033	1.188
F(000)	1280	560
Crystal size [mm]	0.21 × 0.18 × 0.12	0.24 × 0.21 × 0.13
θ limits [°]	1.44–24.11	1.70–26.37
Reflections collected	22967	12447
Independent reflections	4629 (R_{int} = 0.1321)	5099 (R_{int} = 0.0319)
Data/restraints/parameters	4629/26/363	5099/27/309
Goodness on fit on F^2	1.061	1.013
R_1 [$I > 2\sigma(I)$]	0.0696	0.0435
wR_2 (all data)	0.1865	0.1232
Largest diff. peak/hole [e Å^{-3}]	0.550/–1.053	0.526/–0.334

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