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Olefin–aminocarbyne coupling in diiron complexes: Synthesis of new bridging aminoallylidene complexes

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Abstract

The bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; Xyl, **1b**; 4-C_6H_4OMe, **1c**; Xyl = 2,6-$Me_2C_6H_3$) react with acrylonitrile or methyl acrylate, in the presence of Me_3NO and NaH, to give the corresponding μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)(R))C_\beta(H)C_\gamma(H)(R')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = Me, R′ = CN, **3a**; R = Xyl, R′ = CN, **3b**; R = 4-C_6H_4OMe, R′ = CN, **3c**; R = Me, R′ = CO_2Me, **3d**; R = 4-C_6H_4OMe, R′ = CO_2Me, **3e**). Likewise, **1a** reacts with styrene or diethyl maleate, under the same reaction conditions, affording the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = H, R″ = C_6H_5, **3f**; R′ = R″ = CO_2Et, **3g**). The corresponding reactions of $[Ru_2\{\mu\text{-}CN(Me)(CH_2Ph)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1d**) with acrylonitrile or methyl acrylate afford the complexes $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)(CH_2Ph))C_\beta(H)C_\gamma(H)(R')\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R′ = CN, **3h**; CO_2Me, **3i**), respectively.

The coupling reaction of olefin with the carbyne carbon is regio- and stereospecific, leading to the formation of only one isomer. C–C bond formation occurs selectively between the less substituted alkene carbon and the aminocarbyne, and the C_β–H, C_γ–H hydrogen atoms are mutually *trans*.

The reactions with acrylonitrile, leading to **3a**–**c** and **3h** involve, as intermediate species, the nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NC\text{–}CH{=}CH_2)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Me, **4a**; M = Fe, R = Xyl, **4b**; M = Fe, R = 4-C_6H_4OMe, **4c**; M = Ru, R = $CH_2C_6H_5$, **4d**).

Compounds **3a**, **3d** and **3f** undergo methylation (by $CH_3SO_3CF_3$) and protonation (by HSO_3CF_3) at the nitrogen atom, leading to the formation of the cationic complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)_3)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **5a**; R = CO_2Me, **5b**; R = C_6H_5, **5c**) and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(H)(Me)_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **6a**; R = CO_2Me, **6b**; R = C_6H_5, **6c**), respectively.

Complex **3a**, adds the fragment $[Fe(CO)_2(THF)(Cp)]^+$, through the nitrile functionality of the bridging ligand, leading to the formation of the complex $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CNFe(CO)_2Cp)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**9**).

In an analogous reaction, **3a** and $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$, in the presence of Me_3NO, are assembled to give the tetrameric species $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)(CN[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(Cp)_2])\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = Me, **10a**; R = Xyl, **10b**; R = 4-C_6H_4OMe, **10c**).

The molecular structures of **3a** and **3b** have been determined by X-ray diffraction studies.

Keywords: Aminocarbyne; Dinuclear complexes; Allylidene; Coupling reactions; C–C bond formation

1. Introduction

Coupling reactions between bridging alkylidyne or alkylidene ligands (C_1 ligands) with small organic molecules (typically alkynes and, at a lower extent, alkenes) provide valuable routes to the C–C bond formation in dinuclear complexes [1]. These reactions, which take advantage of distinct reactivity patterns due to the bridging coordination, lead to synthesis of new multisite-bound hydrocarbyl ligands otherwise unattainable [2], and also offer helpful models for investigating the C–C bond

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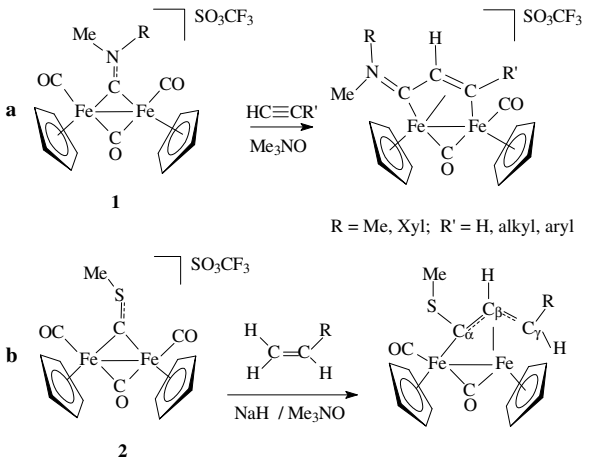


Scheme 1.

formation steps relevant to the hydrocarbon chain growth in the Fischer Tropsch chemistry [3].

Our work in the field has been focused on the reactions of bridging amino- and thiocarbyne complexes with alkynes and alkenes. In particular, we have investigated the coupling between alkynes and the μ-aminocarbyne ligand in **1**, leading to the formation of μ-vinyliminium (azoniabutadienyl) complexes (Scheme 1a) [4]. Consequent studies revealed that the vinyliminium ligand can be further modified by the addition of carbon nucleophiles like acetylides [5] or cyanide [6], generating bridged fragments of increased complexity.

More recently we have described the coupling between the bridging thiocarbyne ligand in complex **2** and activated olefins, leading to the formation of new bridging thiomethylallylidene complexes (Scheme 1b) [7].

In these coupling reactions alkynes and alkenes behave differently: the reaction of **1** with alkynes simply consists of the alkyne insertion in the metal carbyne–carbon bond (Scheme 1a), whereas the coupling of the thiocarbyne ligand with olefins requires a deprotonation step (Scheme 1b).

The nature of the heteroatom (S or N) on the μ-carbyne ligand also exerts some influence on the reactivity. In general, bridging thio- and aminocarbyne ligands display similar properties, in that both contain a π donor heteroatom which provides stabilization to the adjacent carbyne carbon. However, the extent of π-interaction is different in the two ligands and this leads, in some cases, to different reaction profiles [8]. As an example, the alkyne insertion in **1** shown in Scheme 1a, does not take place on the thiocarbyne complex **2**, neither on its acetonitrile derivative. Thereby, predictions of the reactivity of **1** based upon the reactions observed for **2**, or vice versa, are often unreliable.

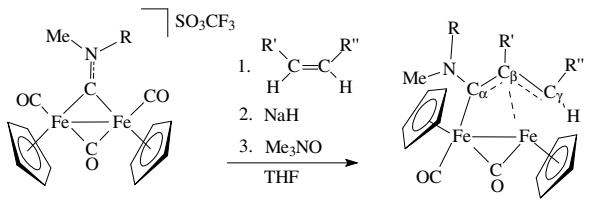
Herein we report on the successful attempt to extend the coupling reaction with olefins to the aminocarbyne complexes **1** and on further modifications of the bridging ligand consequently formed.

2. Results and discussion

The bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; Xyl, **1b**; 4-C_6H_4OMe, **1c**; Xyl = 2,6-$Me_2C_6H_3$) react with olefins (methyl acrylate, acrylonitrile, styrene, diethyl maleate), in THF solution at room temperature, in the presence of Me_3NO/NaH, to give the corresponding μ-allylidene complexes **3a**–**g** in 70–80% yields (Scheme 2).

The reaction parallels that of the thiocarbyne complex **2** with olefins: in both cases the carbyne–alkene coupling requires the displacement of a CO ligand and the presence of NaH in order to remove a proton from the olefin. However, significant differences have been evidenced in the stereochemistry of the reaction products, which concern the mutual orientation of the Cp ligands and will be discussed later.

Compounds **3a**–**g** were purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structures of **3a** and **3b** have been determined by X-ray diffraction. The ORTEP diagrams are shown in Figs. 1 and 2, while the main bond lengths and angles are reported in Table 1. The bonding parameters of the bridging ligand can be evaluated with respect to other C_3-bridging ligands present in closely related diiron complexes (Table 2). In particular, **3a**–**b** are to be compared with the μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(Tol)CH{=}CHNMe_2\}(\mu\text{-}CO)(CO)(Cp)_2]$ [9] (Chart 1, **I**), and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C(SMe)C(H)C(H)(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ [7] (Chart 1, **II**). This analysis points out a close similarity in the bonding situation of **3a**–**b**, **I**, and **II** indicating that the μ-η^1:η^3-C(N(Me)(R))C(H)C(H)(CN) [R = Me, **3a**; Xyl, **3b**] ligand acts mainly as a bridging allylidene, as inferable also from the fact that both the C–C bonds within the ligand [C_α–C_β 1.434(4) Å, C_β–C_γ 1.432(4) Å in **3a**; C_α–C_β 1.416(3) Å, C_β–C_γ 1.435(3) Å in **3b**] and the Fe–C interactions between the ligand and the diiron frame [Fe(2)–C(13) 2.094(3), Fe(2)–C(14) 2.012(3), Fe(2)–C(15) 2.051(3) in **3a**; Fe(2)–C(13) 2.179(2), Fe(2)–C(14) 2.023(2), Fe(2)–C(15) 2.058(2) in **3b**] are very similar. It is noteworthy that in **3a**–**b** the two hydrogen atoms



	R	R'	R"	
1a	Me	H	CN	**3a**
1b	Xyl	H	CN	**3b**
1c	4-C_6H_4OMe	H	CN	**3c**
1a	Me	H	CO_2Me	**3d**
1c	4-C_6H_4OMe	H	CO_2Me	**3e**
1a	Me	H	C_6H_5	**3f**
1a	Me	CO_2Et	CO_2Et	**3g**

Scheme 2.

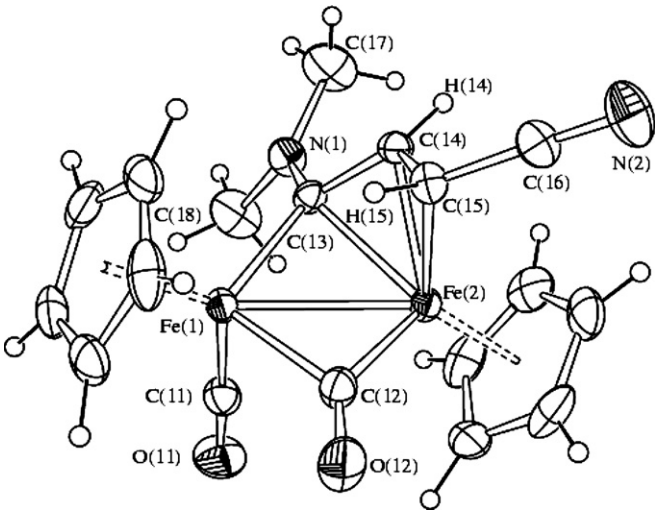


Fig. 1. Molecular structure of **3a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level.

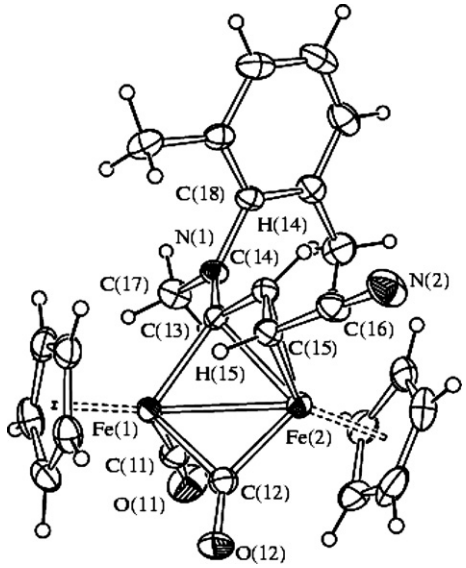


Fig. 2. Molecular structure of **3b**, with key atoms labelled. Displacement ellipsoids are at 30% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for **3a** and **3b**

	3a	3b
Fe(1)–Fe(2)	2.5602(5)	2.5812(5)
Fe(1)–C(11)	1.731(3)	1.733(3)
Fe(1)–C(12)	1.959(3)	1.991(2)
Fe(2)–C(12)	1.884(3)	1.867(2)
Fe(2)–C(13)	2.094(3)	2.179(2)
Fe(1)–C(13)	1.971(3)	1.967(2)
Fe(2)–C(14)	2.012(3)	2.023(2)
Fe(2)–C(15)	2.051(3)	2.058(2)
C(11)–O(11)	1.156(3)	1.155(3)
C(12)–O(12)	1.170(3)	1.173(3)
C(13)–C(14)	1.434(4)	1.416(3)
C(14)–C(15)	1.432(4)	1.435(3)
C(15)–C(16)	1.435(4)	1.440(3)
C(16)–N(2)	1.149(4)	1.137(3)
C(13)–N(1)	1.368(3)	1.375(3)
Fe(1)–C(12)–Fe(2)	83.54(11)	83.93(10)
Fe(1)–C(13)–Fe(2)	78.01(9)	76.82(8)
Fe(1)–C(13)–C(14)	118.09(19)	118.53(16)
C(13)–C(14)–C(15)	120.7(3)	121.5(2)
C(14)–C(15)–C(16)	117.8(3)	117.6(2)
C(15)–C(16)–N(2)	178.2(4)	178.6(3)
C(13)–N(1)–C(17)	122.7(3)	123.17(19)
C(13)–N(1)–C(18)	121.2(3)	121.34(19)
C(17)–N(1)–C(18)	115.1(3)	115.39(19)

Table 2
Comparison between the bonding parameters (Å) of C_3 units in different diiron complexes (numbering I and II refers to Chart 1)[a]

	3a	3b	I	II
Fe_a–C^b_{bridge}	1.971(3)	1.967(2)	1.977(6)	1.955(3)
Fe_b–C_α	2.094(3)	2.179(2)	2.299(6)	2.049(3)
Fe_b–C_β	2.012(3)	2.023(2)	2.070(6)	2.026(3)
Fe_b–C_γ	2.051(3)	2.058(2)	1.979(6)	2.068(3)
C_α–C_β	1.434(4)	1.416(3)	1.408(9)	1.415(4)
C_β–C_γ	1.432(4)	1.435(3)	1.441(8)	1.422(4)
C_α–X[c]	1.368(3)	1.375(3)	1.375(8)	1.758(3)

[a] **I** = [Fe_2 {μ-η^1:η^3- C(Tol)CH=CHNMe$_2$}(μ-CO)(CO)(Cp)$_2$] [9]; **II** = [Fe_2{μ-η^1:η^3- C(SMe)C(H)C(H)(CO$_2$Me)}(μ-CO)(CO)(Cp)$_2$] [7].
[b] $C_{bridge} = C_\alpha$ in **3a-b** and **II**; $C_{bridge} = C_\gamma$ in **I**.
[c] X = N in **3a**–**b** and **I**; X = S in **II**.

within the ligand, *i.e.* H(14) and H(15), are in mutual *trans* position.

One of the most striking features of the complexes **3a**–**b** is that the Cp ligand are mutually *trans*, whereas most of analogous dinuclear complexes (including the μ-allylidene complexes **I** and **II**) are *cis*, with few exceptions [10].

Steric arguments offer a possible explanation for the observed differences. In complexes **3a**–**b** the C_α carbon displays a significant bridging alkylidene character (as emphasized in Chart 2), which forces the steric demanding N(Me)(R) substituent to reside closer to the metal centres than in the species **I**. In these latter, the C_γ assumes a μ-alkylidene character, leaving the N(Me)(R) moiety far apart. Thereby, when the steric demanding N(Me)(R) is closer to the dimetal centre (like in **3a**–**b**) a *trans* configuration for the Cp ligands is favoured.

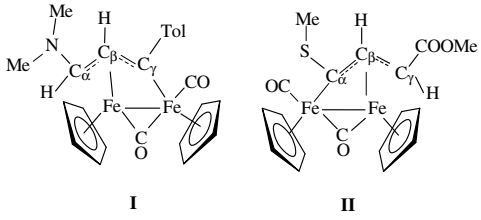


Chart 1.

Analogous considerations can be drawn comparing **3a**–**b** with the bridging thiomethylallylidene complexes (Chart 2, **II**). The coordination mode of the bridging ligand is the same, but the nature of the C_α substituents is different in the two cases [N(Me)(R) or SMe]. Presumably, the steric

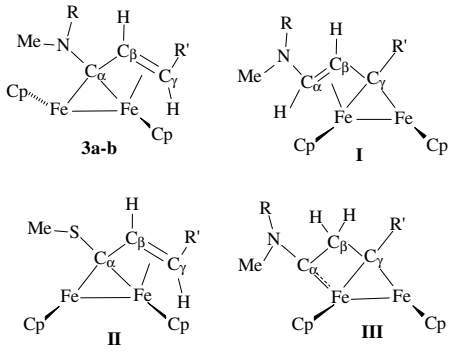


Chart 2. CO ligands are omitted for seek of clarity.

demand of the thiomethyl is not so relevant to force the Cp ligands to assume a *trans* configuration.

It should also be noted that the species **3a**–**b** and **I** exhibit the same hydrocarbyl chain: (Me)(R)N–C_α–C_β(H)–C_γ(R′) plus an hydrogen atom, which is bonded to C_γ or C_α, respectively. A third possibility, in which the H atom is bonded to the C_β carbon, corresponds to the previously reported bis-alkylidene complexes [$Fe_2\{\mu$-η^1:η^2-C(R)CH_2-CN(Me)(Xyl)}(μ-CO)(CO)$(Cp)_2$] (Chart 2 **III**) [9]. These species are not true isomers, since R and R′ are different, however they evidence that the dinuclear $Fe_2(CO)_2Cp_2$ frame is very effective and flexible in accommodating C_3 bridging organic molecules of different nature. One of the reasons for this adaptability is the simplicity in which ancillary ligands can rearrange their coordination geometry around the dimetal centre to respond to different steric demands of the bridging organic frame.

Finally, it should be outlined that the different, but strictly related C_3 bridged frames (in **3a**–**b**, **I** and **III**) do not interconvert, and are exclusively obtained by distinct reaction routes: **3a**–**b** derive from μ-aminocarbyne–alkene coupling plus proton abstraction (Scheme 2), whereas **I** and **II** result from aminocarbyne–alkyne coupling (Scheme 1a), followed by hydride addition, which can be selectively directed to the C_α or C_β carbon, respectively [9].

The spectroscopic data of **3a**–**f** are consistent with the structures observed in the solid. In particular, the NMR data of **3a**, **3c**–**e** and **3g** reveal the presence, in solution, of a single isomeric form, in which the Cp ligands are mutually *trans*. Conversely, both *cis* and *trans* isomers of **3b** and **3f** are observed, with prevalence of the *trans* isomers. The presence of an isomeric mixture in the case of **3b** and **3f** was clearly indicated, in the NMR spectra, by the presence of two sets of resonances, and in the IR spectra (in CH_2Cl_2 solution) by the observation of two absorptions due to the terminally bonded CO ligand (*e.g.* at 1958 and 1932 cm^{-1} for *cis*-**3b** and *trans*-**3b**, respectively). The *cis* and *trans* isomeric forms were identified by NMR, since NOE effect is detected between the Cp resonances for the *cis* isomers, but not for the *trans* (*e.g.* for cis-**3b** NOE effect was revealed between the Cp signals at δ 4.71 and 4.41 ppm).

Interestingly, both *cis*-**3b** and *cis*-**3f** are quantitatively converted into the corresponding *trans* isomers upon heating for *ca.* 4 h in refluxing toluene. On the other hand, solutions containing only the *trans* forms are stable upon heating in refluxing toluene. This behavior,which is opposite to previously observed *trans* to *cis* isomerizations [10], indicates that the *trans* isomer is, in this case, thermodynamically more stable, and that the *cis* isomer is a kinetic product rather that being in equilibrium with the *trans*.

Concerning the stereochemistry of this reaction it has to be emphasized that beside *cis* and *trans* no other isomeric form was observed in solution. This leads to the important conclusion that the aminocarbyne–olefin coupling reactions are regio- and stereospecific. Indeed, the incorporation of asymmetric olefins should generate, in theory, two regioisomers. Conversely, the ^{1}H NMR spectra of **3a**–**g** evidence that the C–C bond formation occurs selectively between the less substituted alkene carbon and the aminocarbyne ligand. Likewise, the C_βH and C_γH protons of the bridging ligand in **3a**–**f** result placed exclusively on opposite sides of the C_β–C_γ double bond interaction (*E* isomer). This is evidenced, in the ^{1}H NMR spectra, by the occurrence of two doublets, attributable to the C_βH and C_γH protons, respectively, with a coupling constant that corresponds to *trans* olefin hydrogen atoms (*e.g.* 8.0 Hz for **3a**). Moreover, C_γH proton resonance is shifted to low frequencies (*e.g.* −0.92 ppm for **3a**), accordingly to the proximity and the shielding effect exerted by the metal centre. Thus, the structure of the complexes in solution is the same of that observed in the solid (X-ray structure of **3a**–**b**). Moreover, the regio- and stereoselective character of the olefin–aminocarbyne coupling is almost identical to that found in the corresponding reaction with thiocarbyne (Scheme 1b) [7].

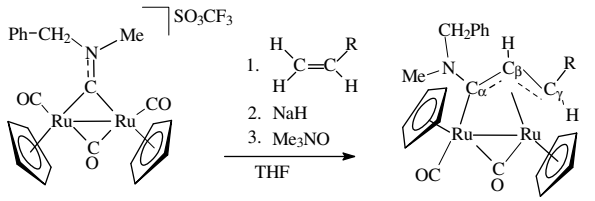
The ^{13}C NMR spectra show the resonances due to the C_α, C_β and C_γ of the bridging allylidene (*e.g.* for **3a**, at 203.9, 59.8 and 21.5 ppm, respectively).

Finally, for complexes **3a**, **d**, **f** and **g** the *N*-methyls give rise to a single resonance in both ^{1}H and ^{13}C NMR spectra (*e.g.* for **3a**, at 3.62 ppm and 46.5 ppm, respectively). The equivalence of the *N*-methyls is consistent with the loss of double bond character in the C_α–N interaction consequent to the aminocarbyne–alkene coupling.

The aminocarbyne–olefin coupling has not a general character. The reaction is limited to olefins activated by electron withdrawing groups, which favour the deprotonation step. The conformation of the olefin is also important, in that **1a** react with diethyl maleate but not with diethyl fumarate.

The nature of the N(Me)R substituents in the μ-aminocarbyne ligand also exhibits some influence on the reaction rate. We observed that **1a** (R = Me) and **1c** (R = 4-C_6H_4OMe) display comparable reactivity, whereas **1b** (R = Xyl) is significantly less reactive and only with acrylonitrile it gives appreciable yields.

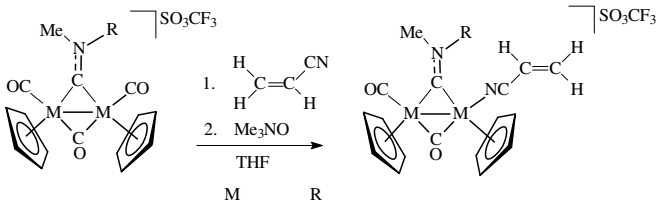
Finally, the reactions involving the diruthenium complex **1d**, analogue to **1a**–**c**, do not evidence any effect due



1d R
1d CN
1d CO_2Me

3h
3i

Scheme 3.



	M	R	
1a	Fe	Me	**4a**
1b	Fe	Xyl	**4b**
1c	Fe	4-C_6H_4OMe	**4c**
1d	Ru	$CH_2C_6H_5$	**4d**

Scheme 4.

to the nature of the metal atoms. The presence of ruthenium in the place of iron does not produce any relevant change in the reaction path. Thus, reactions with acrylonitrile or methyl acrylate afford the corresponding bridging allylidene complexes **3h** and **3i**, respectively (Scheme 3).

Under the same reaction conditions, **1d** is less reactive than the diiron compounds **1a** and **1c** and the reactions yields are consequently lower. Moreover, the reaction products consist of a mixture of the *cis* and *trans* isomers, with predominance of the *trans*. Also in this case, the *cis* isomer is converted into the *trans* upon heating at reflux in THF.

As expected, the spectroscopic data of the diruthenium complexes **3h** and **3i** closely resemble those of the analogous diiron species described above, and do not deserve further comments.

The reaction described in Schemes 1–3 are among the few examples of coupling between bridging carbyne ligands and olefins [11]. Among these, the most remarkable reactivity was exhibited by the μ-methylidyne complex $[Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$, in which the methylidyne–olefin coupling was described as 'hydrocarbation reaction', because of the analogies with the hydroboration reaction [11c,11d,11e,11f,11g]. Less reactive bridging carbyne ligands, like the μ-ethylidyne complex $[Ru_2(\mu\text{-}CMe)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ [11a] and the thiocarbyne complex **2**, mentioned in the introduction, undergo coupling with olefins but require the presence of a base in order to remove a proton from the olefin.

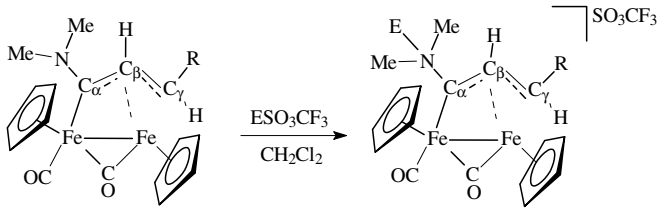
Concerning the reaction mechanism, the conclusions we can draw are very similar to those reported for the olefin–carbyne coupling reactions involving the μ-ethylidyne complex $[Ru_2(\mu\text{-}CMe)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$ [11a] or the thiocarbyne complex **2** [7]. The reaction sequence should include, as preliminary step, the η^2-olefin coordination at the site made available by CO removal. This is accomplished, in our case, by the use of Me_3NO. Without this reagent the reaction does not take place. Subsequent steps include intramolecular coupling, which might entail a metallacyclobutane ring, and deprotonation. Unfortunately, none of the supposed intermediates have detected. Even the initial η^2-olefin intermediate appears very elusive. Only in one case, namely in the reactions with acrylonitrile, it was possible to isolate intermediate species which were identified as the nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NC\text{–}CH{=}CH_2)(Cp)_2][SO_3CF_3]$ (M = Fe, R = Me, **4a**; M = Fe, R = Xyl, **4b**; M = Fe, R = 4-C_6H_4OMe, **4c**; M = Ru, R = $CH_2C_6H_5$, **4d**) (Scheme 4). Coordination of acrylonitrile through the nitrile, rather than with the olefin functionality, is in a good agreement with the demonstrated reactivity of type **1** complexes towards nitriles [12]. Obviously, the nitrile complexes **4a**–**d** can be obtained in better yields upon treatment of **1a**–**d** with acrylonitrile and Me_3NO without NaH. The observation that the nitrile complexes **4a**–**d** are transformed into **3a**–**c** and **3h**, respectively, upon treatment with NaH, indicate that they are effective reaction intermediates.

Compounds **4a**–**d** have been characterized by IR and NMR spectroscopy, and elemental analysis (see Section 4). Their spectroscopic data closely resemble those of analogous diiron and diruthenium nitrile complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCR')(Cp)_2][SO_3CF_3]$ reported in the literature [12,13]. In particular these compounds are characterized, in the ^{13}C NMR spectra, by the typical low field resonance of the bridging aminocarbyne carbon, in the 330–340 ppm range (*e.g.* at 331.0 ppm for **4a**). Also consistent is the observation that **4a**, in which the substituents at the N atom are both methyls, displays a single isomeric form, whereas complexes **4b**–**d** are a mixture of two isomers. These are due to the different orientations that Me and R (R = Xyl, 4-C_6H_4OMe, $CH_2C_6H_5$) can assume with respect to the non-equivalent metal atoms, and are consequence of the double bond character of the μ-C=N interaction (*E* and *Z* isomerism).

The reactivity of complexes of type **3** was then investigated. In particular, we have found that compounds **3a**, **d** and **f** undergo methylation (by $CH_3SO_3CF_3$) and protonation (by HSO_3CF_3) at the NMe_2 group, affording, in nearly quantitative yields, the cationic species $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)_3)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **5a**; R = CO_2Me, **5b**; R = C_6H_5, **5c**) and $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(H)(Me)_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CN, **6a**; R = CO_2Me, **6b**; R = C_6H_5, **6c**), respectively (Scheme 5). The reactions were carried out in CH_2Cl_2 solution at room temperature.

Compounds **5** and **6** have been purified by filtration on celite and characterized by IR and NMR spectroscopy, and elemental analysis.

The IR spectra (in CH_2Cl_2 solution) of **5a**–**c** exhibit absorptions due to the terminal and bridging carbonyls



	R	E	
3a	CN	CH_3^+	**5a**
3d	CO_2Me	CH_3^+	**5b**
3f	C_6H_5	CH_3^+	**5c**
3a	CN	H^+	**6a**
3d	CO_2Me	H^+	**6b**
3f	C_6H_5	H^+	**6c**

Scheme 5.

(*e.g.* at 1986 and 1815 cm^{-1} for **5a**). Additional bands are observed for **5a**, due to the CN group (at 2205 cm^{-1}), and for **5b**, attributable to the CO_2Me (at 1710 cm^{-1}). As expected, the CO bands are shifted to higher frequencies (ca. 30 cm^{-1}) compared to the parent complexes, as effect of the positive charge in **5a–c**.

Analogous considerations concern the protonation reaction. In addition, the IR spectra of **6a–c** (in KBr pellets) show the typical NH absorption around 3200 cm^{-1} (*e.g.* at 3215 cm^{-1} for **6a**).

The ^1H NMR spectra (in CD_3CN solution) of compounds **5** and **6** indicate the presence of a single isomer, since only one set of resonances is observed. In particular, the *N*-methyls give rise to one singlet signal in both ^1H and ^{13}C NMR spectra (*e.g.* for **5a** at 3.12 and 58.8 ppm, respectively), indicating free rotation around the C_α–NMe_3 bond. Moreover, NOE investigations revealed that **5–6** retain the *trans* configuration of the Cp ligands, shown by their parent species **3**.

The electrophilic addition at the aminic nitrogen atom does not modify significantly the ^{13}C NMR resonance pattern for the C_3 bridging ligand: C_α gives rise to a low frequency resonance (180 ppm for **5a**), whereas C_β and C_γ signals occur in 80–20 ppm range.

The protonation reactions, which lead to **6a–c** are reversible and the parent complexes are restored upon treatment with bases (*e.g.* NaH), whereas methylation reactions are not.

The complexes **5a–c** present several similarities with the ammonium and the sulphonium complexes **7** [14] and **8** [7] (Chart 3), previously published.

Also **7** and **8** were obtained by methylation (with $MeSO_3CF_3$) of the heteroatom in their corresponding neutral precursors. The main difference between the ammonium complexes **5** and **7** with respect to the sulphonium **8** is that the SMe_2 group can be displaced by nucleophiles like hydride ($NaBH_4$) and cyanide (NBu_4CN) [7], whereas, under similar reaction conditions, neither **7** nor **5** release the NMe_3 group. Thereby, the ammonium allylidene ligand in **5** fails to become the precursor of other bridging C_3 frames via NMe_3 displacement.

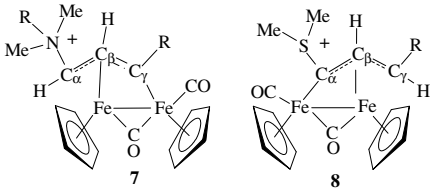


Chart 3.

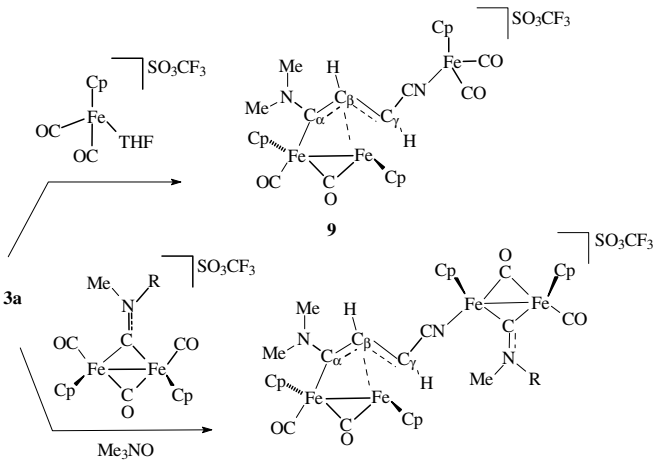
Beside the protonation and methylation reactions, the presence of nitrogen functional groups (NMe_2 and CN), potential able to act as ligands, could be exploited to coordinate further metal complexes. Thereby, we have investigated the reaction of **3a** with $[Fe(CO)_2(THF)(Cp)]^+$, generated by treatment of $[Fe_2(CO)_4(Cp)_2]$ with $AgSO_3CF_3$. The reaction, carried out in THF, leads to the formation of the trinuclear complex **9** in good yields (Scheme 6).

Likewise, the reaction of **3a** with $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; Xyl, **1b**; 4-C_6H_4OMe, **1c**) affords the corresponding tetranuclear adducts **10a–c**, respectively, in about 70% yield (Scheme 6). The reaction requires the presence of Me_3NO in order to generate a vacant coordination site on the aminocarbyne complexes and promote the nitrile coordination.

By contrast with the methylation and protonation, which occur at the NMe_2 group of **3a**, the addition of the iron frame takes place selectively through the nitrile coordination. The preference for the nitrile coordination is consistent with previous observations which evidenced that nitriles, better than amines, displace the CO ligand in the aminocarbyne complexes **1a–c** [12].

Compounds **9** and **10a–c** have been isolated by chromatography on alumina and characterized by IR and NMR spectroscopy and elemental analysis.

The IR spectra of **10a–c** (in CH_2Cl_2 solution) show two absorptions for the terminal carbonyls (*e.g.* at 1981 cm^{-1} and 1940 cm^{-1} for **10a**) and two for the bridging ones



R = Me, **10a**; Xyl, **10b**; 4-C_6H_4OMe **10c**

Scheme 6.

(*e.g.* at 1812 cm^{-1} and 1785 cm^{-1} for **10a**). Moreover, the μ-CN band is observed (*e.g.* at 1586 cm^{-1} for **10a**).

The corresponding NMR spectra (in $CDCl_3$) exhibit resonances consistent with those of the parent compounds **3a** and **1a–c**. In particular, the ^1H NMR spectra show the $C_\gamma H$ proton resonance, shifted to low frequencies (*e.g.* −1.35 ppm for **10a**), accordingly to the shielding effect exerted by the metal centre. On the other hand, the ^{13}C NMR spectra exhibit the signals due to the C_α, C_β and C_γ of the bridging allylidene (*e.g.* for **10a**, at 203.1, 53.1 and 19.6 ppm, respectively) and the typical downfield resonance of the bridging aminocarbyne carbon, (*e.g.* at 331.2 ppm for **10a**). Interestingly, each of the compounds **10a–c** exists as in a single isomeric form. In particular, NOE investigations pointed out that the Cp rings of the aminocarbyne fragment are mutually *cis*, whereas those of the allylidene moiety are *trans*, as in their parent species **1a–c** and **3a**, respectively.

3. Conclusions

The bridging aminocarbyne complexes **1a–d** reacts with olefins generating bridging allylidene ligands. This result, together with those previously reported on related thiocarbyne complexes, show that the coupling between activated olefin and heteroatom substituted μ-carbynes has a general character, and that the reactions proceed as well with diiron and diruthenium complexes characterized by the $M_2(CO)_2(Cp)_2$ frame. This latter effectively supports the bridging allylidene ligand, in that it can easily arrange the coordination geometry of the ancillary CO and Cp (*e.g. cis trans* isomers) to better respond to the steric requirements of the bridging ligand.

Olefin incorporation into the aminocarbyne ligand is regio- and stereospecific. It represents a valuable example of bridging hydrocarbyl transformation (specifically: C_1–C_3 chain growth). Further modifications of the bridging frame are feasible due to the presence nitrogen functional groups. These reactions include electrophilic additions at the NR_2 functional group, or assembling with unsaturated organometallic iron complexes through the nitrile functionality.

4. Experimental details

4.1. General

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. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^1H,^{13}C correlation through gs-HSQC and gs-HMBC experiments [15]. NOE measurements were recorded using the DPFGSE-NOE sequence [16]. NMR signals due to a second isomeric form (where it has been possible to detect and/or resolve them) are italicized. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compounds **1a**,**b** [17], **1c** [18] and **1d** [19] were prepared by published methods.

4.2. Synthesis of $[M_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)(R))C_\beta(R')\text{-}C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($M = Fe$, $R = Me$, $R' = H$, $R'' = CN$, **3a**; $M = Fe$, $R = Xyl$, $R' = H$, $R'' = CN$, **3b**; $M = Fe$, $R = 4\text{-}C_6H_4OMe$, $R' = H$, $R'' = CN$, **3c**; $M = Fe$, $R = Me$, $R' = H$, $R'' = CO_2Me$, **3d**; $M = Fe$, $R = 4\text{-}C_6H_4OMe$, $R' = H$, $R'' = CO_2Me$, **3e**; $M = Fe$, $R = Me$, $R' = H$, $R'' = C_6H_5$, **3f**; $M = Fe$, $R = Me$, $R' = CO_2Et$, $R'' = CO_2Et$, **3g**; $M = Ru$, $R = CH_2C_6H_5$, $R' = H$, $R'' = CN$, **3h**; $M = Ru$, $R = CH_2C_6H_5$, $R' = H$, $R'' = CO_2Me$, **3i**)*

To a solution of **1a** (531 mg, 1.0 mmol) in THF (20 mL) were successively added: acrylonitrile (0.4 mL, 10 mmol), NaH (120 mg, 5.0 mmol), and Me_3NO (110 mg, 1.5 mmol). The mixture was stirred at room temperature for 2 h and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, afforded a green solid, corresponding to **3a**. Yield: 78%. Anal. Calc. for $C_{18}H_{18}Fe_2N_2O_2$: C, 53.20; H, 4.47; N, 6.90. Found: C, 53.09; H, 4.44; N, 6.96%. IR (CH_2Cl_2) *ν*(CN) 2204 (w); *ν*(CO) 1933 (vs), 1777 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 4.60 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.49 (s, 5H, Cp); 4.32 (s, 5H, Cp); 3.62 (s, 6H, NMe_2); −0.92 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 269.3 (μ-CO); 213.0 (CO); 203.9 (C_α); 126.3 (C≡N); 89.4 (Cp); 86.5 (Cp); 59.8 (C_β); 46.5 (NMe_2); 21.5 (C_γ).

Compounds **3b–i** were prepared with the same procedure described for **3a**, by reacting **1a–d** with NaH, Me_3NO and the appropriate olefin.

Compound **3b** (yield: 38%). Anal. Calc. for $C_{25}H_{24}Fe_2N_2O_2$: C, 60.48; H, 4.88; N, 5.65. Found: C, 60.40; H, 4.92; N, 5.67%. IR (CH_2Cl_2) *ν*(CN) 2204 (w), *ν*(CO) 1958 (vs), 1932 (vs), 1791 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.34–6.86 (m, 3H, $C_6H_3Me_2$); 4.71, *4.65* (s, 5H, Cp); 4.67, *4.17* (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); *4.44*, 4.41 (s, 5H, Cp); *3.83*, 3.55 (s, 3H, NMe); 2.63, *2.61* (s, 3H, C_6H_3Me); *2.23*, 2.19 (s, 3H, C_6H_3Me); *−0.80*, −0.92 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). *trans*/*cis* Ratio 2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* *265.4*, 265.0 (μ-CO); *213.1*, 213.0 (CO); *205.9*, 203.8 (C_α); 148.4, *148.3* ($C_{ipso\ Xyl}$); *129.0*, 126.5 (C≡N); 134.0–128.6 (C_{arom}); *88.2*, 87.7, 85.2, *84.9* (Cp); *59.0*, 58.3 (C_β); *48.3*, 46.1 (NMe); *20.2*, 19.3 (C_γ); *18.4*, 17.9 ($Me_2C_6H_3$); *17.5*, 17.2 ($Me_2C_6H_3$).

Compound **3c** (yield: 75%). Anal. Calc. for $C_{24}H_{22}Fe_2N_2O_3$: C, 57.83; H, 4.45; N, 5.62. Found: C, 57.75; H, 4.52; N, 5.67%. IR (CH_2Cl_2) *ν*(CN) 2203 (w), *ν*(CO) 1935 (vs), 1779 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.36–6.78 (m, 4H, C_6H_4OMe); 4.68 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.49 (s, 5H, Cp); 4.43 (s, 5H, Cp); 3.85 (s, 3H, NMe); 3.75 (s, 3H, $C_6H_4O\mathit{Me}$); -0.92 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 265.0 (μ-CO); 213.0 (CO); 205.0 (C_α); 150.0, 128.5, 128.0, 115.0, 114.1 (C_{arom}); 126.0 (C≡N); 88.0, 85.8 (Cp); 59.6 (C_β); 56.1 ($C_6H_4O\mathit{Me}$); 46.6 (NMe); 21.5 (C_γ).

Compound **3d** (yield: 80%). Anal. Calc. for $C_{19}H_{21}Fe_2NO_4$: C, 51.93; H, 4.82; N, 3.19. Found: C, 51.87; H, 4.75; N, 3.28%. IR (CH_2Cl_2) *ν*(CO) 1933 (vs), 1777 (s), 1693 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 4.97 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.34 (br s, 10H, Cp); 3.64 (s, 9H, $NMe_2 + CO_2Me$); −0.29 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 261.5 (μ-CO); 213.7 (CO); 204.6 (C_α); 175.9 ($\mathit{C}O_2Me$); 87.6, 84.2 (Cp); 60.2 (C_β); 51.3 ($CO_2\mathit{Me}$); 46.7 (NMe_2); 43.1 (C_γ).

Compound **3e** (yield: 78%). Anal. Calc. for $C_{25}H_{25}Fe_2NO_5$: C, 56.49; H, 4.74; N, 2.64. Found: C, 56.59; H, 4.75; N, 2.56%. IR (CH_2Cl_2) *ν*(CO) 1930 (vs), 1773 (s), 1694 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.41–6.82 (m, 4H, C_6H_4OMe); 5.02 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.46 (s, 5H, Cp); 4.37 (s, 5H, Cp); 3.88 (s, 6H, NMe + $C_6H_4O\mathit{Me}$); 3.57 (s, 3H, CO_2Me); −0.32 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 265.1 (μ-CO); 212.9 (CO); 204.1 (C_α); 176.0 ($\mathit{C}O_2Me$); 150.0, 128.5, 128.0, 115.0, 114.1 (C_{arom}); 89.1 (Cp); 87.7, 68.5 (C_β); 56.1 ($C_6H_4O\mathit{Me}$); 51.4 ($CO_2\mathit{Me}$); 46.5 (NMe); 43.3 (C_γ).

Compound **3f** (yield: 56%). Anal. Calc. for $C_{23}H_{23}Fe_2NO_2$: C, 60.39; H, 5.07; N, 3.06. Found: C, 60.46; H, 5.00; N, 3.05%. IR (CH_2Cl_2) *ν*(CO) 1958 (vs), 1938 (vs), 1767 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.43–6.95 (m, 5H, C_6H_5); 4.85, *4.45* (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.74, *4.70* (s, 5H, Cp); *4.66*, 4.64 (s, 5H, Cp); *3.95*, 3.65 (s, 6H, NMe_2); −0.87, *−1.13* (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). *trans*/*cis* Ratio 1.5:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 265.0, *264.1* (μ-CO); 213.0, *212.2* (CO); 206.0, *204.0* (C_α); 131.5–125.2 (C_{arom}); *90.1*, 89.6, 87.0, *86.6* (Cp); *60.1*, 58.3 (C_β); *52.6*, 51.4 (NMe_2); *21.7*, 21.0 (C_γ).

Compound **3g** (yield: 74%). Anal. Calc. for $C_{23}H_{27}Fe_2NO_6$: C, 52.57; H, 5.18; N, 2.67. Found: C, 52.49; H, 5.24; N, 2.65%. IR (CH_2Cl_2) *ν*(CO) 1939 (vs), 1780 (s), 1716 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 4.90 (s, 5H, Cp); 4.83 (s, 5H, Cp); 4.30–3.60 (m, 4H, $CO_2\mathit{CH}_2CH_3$); 3.70 (s, 6H, NMe_2); 1.50–1.08 (m, 6H, $CO_2CH_2\mathit{CH}_3$); −0.56 (s, 1H, $C_\gamma\mathit{H}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 265.0 (μ-CO); 213.0 (CO); 199.3 (C_α); 170.4 ($\mathit{C}O_2CH_2CH_3$); 90.1, 88.0 (Cp); 68.5 (C_β); 59.9, 58.0 ($CO_2\mathit{C}H_2CH_3$); 46.4 (NMe_2); 33.8 (C_γ); 14.5, 14.1 ($CO_2CH_2\mathit{C}H_3$).

Compound **3h** (yield: 41%). Anal. Calc. for $C_{24}H_{22}N_2O_2Ru_2$: C, 50.18; H, 3.86; N, 4.88. Found: C, 50.08; H, 3.91; N, 4.83%. IR (CH_2Cl_2) *ν*(CN) 2202 (w), *ν*(CO) 1960, (vs), 1931 (vs), 1762 (s) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.49–7.18 (m, 5H, $CH_2C_6\mathit{H}_5$); 5.23, *5.11* (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.98, *4.89* (s, 5H, Cp); *4.75*, 4.66 (s, 5H, Cp); 3.73–3.55 (m, 2H, $C\mathit{H}_2C_6H_5$); 3.75, *3.69* (s, 3H, NMe); *1.32*, 1.19 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). *trans*/*cis* Ratio 1.2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 246.0, *245.8* (μ-CO); 206.1, *205.5* (CO); *170.1*, 168.9 (C_α); 140.5–127.0 (C_{arom} + C≡N); 96.0, *94.7* (C_γ); 88.8, *88.2 85.6*, 84.1 (Cp); 68.1, *67.5* (C_β); *61.2*, 61.0 ($\mathit{C}H_2C_6H_5$); 48.3, *47.1* (NMe).

Compound **3i** (yield: 36%). Anal. Calc. for $C_{25}H_{25}NO_4Ru_2$: C, 49.42; H, 4.15; N, 2.31. Found: C, 49.51; H, 4.66; N, 2.33%. IR (CH_2Cl_2) *ν*(CO) 1932 (vs), 1765 (s), 1695 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* (ppm): 7.55–7.11 (m, 5H, $CH_2C_6\mathit{H}_5$); 5.23, *5.02* (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.91, *4.82* (s, 5H, Cp); *4.65*, 4.59 (s, 5H, Cp); 3.99–3.49 (m, 2H, $C\mathit{H}_2C_6H_5$); 3.77, *3.72* (s, 3H, NMe); 3.67, *3.59* (s, 3H, CO_2Me); *1.74*, 1.39 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). *trans*/*cis* Ratio 1.3:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 246.2, *245.8* (μ-CO); 206.6, *205.8* (CO); 177.5, *175.9* ($\mathit{C}O_2Me$); 170.9, *169.5* (C_α); 140.5–127.0 (C_{arom}); *88.6*, 88.0, 84.9, *84.1* (Cp); 68.8, *67.3* (C_β); 61.4, *60.9* ($\mathit{C}H_2C_6H_5$); 47.6, *46.5* (NMe).

*4.3. Synthesis of [M₂{μ-CN(Me)(R)}(μ-CO)(CO)(NC–CH=CH₂)(Cp)₂][SO₃CF₃] (M = Fe, R = Me, **4a**; M = Fe, R = Xyl, **4b**; M = Fe, R = 4-C₆H₄OMe, **4c**; M = Ru, R = CH₂C₆H₅, **4d**)*

To a solution of **1a** (531 mg, 1.0 mmol) in THF (20 mL) were successively added acrylonitrile (0.4 mL, 10 mmol) and Me_3NO (110 mg, 1.5 mmol). The mixture was stirred at room temperature for 15 min, and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with methanol as eluent, afforded a brown solid, corresponding to **4a**. Yield: 94%. Anal. Calc. for $C_{19}H_{19}F_3Fe_2N_2O_5S$: C, 41.01; H, 3.44; N, 5.04. Found: C, 40.96; H, 3.47; N, 5.05%. IR (CH_2Cl_2) *ν*(CO) 1983 (vs), 1814 (s), *ν*(CN) 1585 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 5.78 (d, 1H, $^3J_{HH} = 12.0$ Hz, NCCH=CH_2); 5.68 (d, 1H, $^3J_{HH} = 16.0$ Hz, NCCH=CH_2); 5.42 (dd, 1H, NCCH=CH$_2$); 4.90 (s, 5H, Cp); 4.78 (s, 5H, Cp); 4.46 (s, 3H, NMe); 4.16 (s, 3H, NMe). $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 331.0 (μ-CN); 265.8 (μ-CO); 211.0 (CO); 140.1 (NCCH=CH_2); 129.3 (NCCH=CH_2); 106.5 (NCCH=CH_2); 88.7, 87.3 (Cp); 54.0, 53.3 (NMe).

Compounds **4b**–**d** were prepared with the same procedure described for **4a**, by reacting **1b**–**d** with acrylonitrile and Me_3NO.

Compound **4b** (yield: 95%). Anal. Calc. for $C_{26}H_{25}F_3Fe_2N_2O_5S$: C, 48.30; H, 3.90; N, 4.34. Found: C, 48.26; H, 3.91; N, 4.35%. IR (CH_2Cl_2) *ν*(CO) 1985 (vs), 1815 (s), *ν*(CN) 1521 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.37–7.23 (m, 3H, $C_6\mathit{H}_3Me_2$); 5.97–5.86 (m, 2H, NCCH=CH_2); 5.78-5.69 (m, 1H, NCCH=CH$_2$); 5.10, *5.03* (s, 5H, Cp); 4.85, *4.80* (s, 3H, NMe); 4.50, *4.43* (s, 5H, Cp); 2.69, *2.65* (s, 3H, $C_6H_3\mathit{Me}$); 2.14, *2.08* (s, 3H, $C_6H_3\mathit{Me}$). *E*:*Z* ratio 1.3:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 338.8, *338.6* (μ-CN); 264.5, *263.8* (μ-CO); 211.6, *211.4* (CO); 148.4, *148.3*

($C_{ipso\ Xyl}$); 140.3, *140.1* (NCCH=*C*H_2); 134.3-128.5 (C_{arom}); 129.4, *129.3* (N*C*CH=CH_2); 107.3, *107.1* (NC*C*H=CH_2); 88.6, *88.5* (Cp); 88.4, *88.3* (Cp); 54.6, *54.4* (NMe); 18.5, *18.2*, 17.6, *17.3* (*Me*$_2C_6H_3$).

Compound **4c** (yield: 92%). Anal. Calc. for $C_{25}H_{23}F_3Fe_2N_2O_6S$: C, 46.30; H, 3.58; N, 4.32. Found: C, 46.33; H, 3.64; N, 4.35%. IR (CH_2Cl_2) *ν*(CO) 1985 (vs), 1817 (s), *ν*(CN) 1527 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.61–7.16 (m, 4H, C_6H_4OMe); 5.94–5.80 (m, 2H, NCCH=CH_2); 5.60 (m, 1H, NCC*H*=CH_2); 5.08, *4.99* (s, 5H, Cp); 4.46, *4.35* (s, 5H, Cp); 4.87, *4.79* (s, 3H, NMe); 3.90, *3.86* (s, 3H, OMe). *E:Z* ratio 1.2:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 336.4, *336.2* (μ-CN); 265.1, *264.8* (μ-CO); 211.7, *211.0* (CO); 159.7, *159.3*, 144.2, *143.6*, 126.5, *125.9*, 115.0, *114.6* (C_{arom}); 140.5, *140.2* (NCCH=*C*H_2); 129.2, *129.1* (N*C*CH=CH_2); 107.0, *106.7* (NC*C*H=CH_2); 88.6, *88.3* (Cp); 87.9, *87.5* (Cp); 56.5, *56.0* (NMe); 55.6, *55.4* (OMe).

Compound **4d** (yield: 90%). Anal. Calc. for $C_{25}H_{23}F_3N_2O_5Ru_2S$: C, 41.44; H, 3.20; N, 3.87. Found: C, 41.50; H, 3.20; N, 3.83%. IR (CH_2Cl_2) *ν*(CO) 1980 (vs), 1817 (s), *ν*(CN) 1574 (m) cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.49–7.30 (m, 5H, $CH_2C_6H_5$); 6.01–5.94 (m, 2H, NCCH=CH_2); 5.80–5.53 (m, 3H, C$H_2C_6H_5$ + NCC*H*=CH_2); 5.28, *5.25* (s, 5H, Cp); 4.98, *4.90* (s, 5H, Cp); 3.88, *3.83* (s, 3H, NMe). *E:Z* ratio 1.5:1. $^{13}C\{^1H\}$ NMR ($CDCl_3$) *δ* 305.0, *304.7* (μ-CN); 238.1, *237.5* (μ-CO); 201.1, *200.3* (CO); 140.5–106.9 (C_{arom} + $C_{acrylonitrile}$); 89.8, 87.9 (Cp); 51.0, *49.9* (NMe).

*4.4. Synthesis of [Fe_2{μ-η^1:η^3-$C_\alpha(N(Me)_3)C_\beta(H)$-$C_\gamma(H)(R)$}(μ-CO)(CO)$(Cp)_2$][$SO_3CF_3$] (R = CN, **5a**; R = CO_2 Me, **5b**; R = C_6 H_5, **5c**)*

$CH_3SO_3CF_3$ (0.13 mL, 1.1 mmol) was added to a solution of **3a** (406 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) and the resulting solution was stirred at room temperature for 4 h. Removal of the volatile material under reduced pressure and chromatography of the residue on an alumina column, with methanol as eluent, afforded a dark brown solid, corresponding to **5a**. Yield: 87%. Anal. Calc. for $C_{20}H_{21}F_3Fe_2N_2O_5S$: C, 42.11; H, 3.71; N, 4.91. Found: C, 42.02; H, 3.66; N, 4.97%. IR (CH_2Cl_2) *ν*(CN) 2205 (w), *ν*(CO) 1986 (vs), 1815 (s) cm^{-1}. ^1H NMR (CD_3CN) *δ* 6.07 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.2$ Hz); 5.15 (s, 5H, Cp); 4.98 (s, 5H, Cp); 3.12 (s, 9H, NMe_3); −0.77 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.2$ Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) *δ* 267.0 (μ-CO); 213.5 (CO); 180.1 (C_α); 126.5 (CN); 87.3, 85.2 (Cp); 75.0 (C_β); 58.8 (NMe_3); 38.7 (C_γ).

Compounds **5b–c** were prepared with the same procedure described for **5a**, by treating **3d** and **3f** with $CH_3SO_3CF_3$ in CH_2Cl_2 solution.

Compound **5b** (yield: 86%). Anal. Calc. for $C_{21}H_{24}F_3Fe_2NO_7S$: C, 41.79; H, 4.01; N, 2.32. Found: C, 41.79; H, 3.96; N, 2.30%. IR (CH_2Cl_2) *ν*(CO) 1988 (vs), 1817 (s), 1710 (m) cm^{-1}. ^1H NMR (CD_3CN) *δ* 6.01 (d, 1H, $C_\beta H$, $^3J_{HH} = 7.8$ Hz); 5.36 (s, 5H, Cp); 5.23 (s, 5H, Cp); 3.62 (s, 3H, CO_2Me); 3.12 (s, 9H, NMe_3); −0.56 (d, 1H, $C_\gamma H$, $^3J_{HH} = 7.8$ Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) *δ* 266.7 (μ-CO); 213.3 (CO); 181.2 (C_α); 174.4 (*C*O_2Me); 89.1, 87.1 (Cp); 71.4 (C_β); 55.4 (NMe_3); 52.4 (CO_2*Me*); 39.1 (C_γ).

Compound **5c** (yield: 87%). Anal. Calc. for $C_{25}H_{26}F_3Fe_2NO_5S$: C, 48.31; H, 4.22; N, 2.25. Found: C, 48.40; H, 4.18; N, 2.24%. IR (CH_2Cl_2) *ν*(CO) 1986 (vs), 1817 (s) cm^{-1}. ^1H NMR (CD_3CN) *δ* 7.41–7.01 (m, 5H, C_6H_5); 5.99 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.2$ Hz); 5.48 (s, 5H, Cp); 5.33 (s, 5H, Cp); 3.10 (s, 9H, NMe_3); -0.74 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.2$ Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) *δ* 266.5 (μ-CO); 213.0 (CO); 179.7 (C_α); 132.0-125.0 (C_{arom}); 89.9 (Cp); 86.0 (Cp); 73.4 (C_β); 56.7 (NMe_3); 35.4 (C_γ).

*4.5. Synthesis of [Fe_2{μ-η^1:η^3-$C_\alpha(N(H)(Me)_2)C_\beta(H)$-$C_\gamma(H)(R)$}(μ-CO)(CO)$(Cp)_2$][$SO_3CF_3$] (R = CN, **6a**; R = CO_2 Me, **6b**; R = C_6 H_5, **6c**)*

A solution of **3a** (406 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) was treated with HSO_3CF_3(0.10 mL, 1.1 mmol). The resulting solution was stirred at room temperature for 1 h. Removal of the volatile material under reduced pressure and filtration of the residue on a celite pad afforded a dark brown solid, corresponding to **6a**. Yield: 90%. Anal. Calc. for $C_{19}H_{19}F_3Fe_2N_2O_5S$: C, 41.01; H, 3.44; N, 5.04. Found: C, 40.90; H, 3.50; N, 4.97%. IR (CH_2Cl_2) *ν*(CN) 2206 (w), *ν*(CO) 1987 (vs), 1814 (s) cm^{-1}. ^1H NMR (CD_3CN) *δ* 6.04 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 5.22 (s, 5H, Cp); 4.85 (s, 5H, Cp); 3.49 (s, 6H, NMe_2); −1.36 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). *NH not observed.* $^{13}C\{^1H\}$ NMR (CD_3CN) *δ* 267.0 (μ-CO); 213.5 (CO); 182.4 (C_α); 125.9 (CN); 88.9, 85.9 (Cp); 78.3 (C_β); 52.3 (NMe_2); 33.4 (C_γ).

Compounds **6b–c** were prepared with the same procedure described for **6a**, by treating **3d** and **3f** with HSO_3CF_3 in CH_2Cl_2 solution.

Compound **6b** (yield: 88%). Anal. Calc. for $C_{20}H_{22}F_3Fe_2NO_7S$: C, 40.75; H, 3.76; N, 2.38. Found: C, 40.79; H, 3.86; N, 2.30%. IR (CH_2Cl_2) *ν*(CO) 1988 (vs), 1816 (s), 1712 (m) cm^{-1}. ^1H NMR (CD_3CN) *δ* 5.91 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 5.41 (s, 5H, Cp); 5.05 (s, 5H, Cp); 3.75 (s, 3H, CO_2Me); 3.43 (s, 6H, NMe_2); −0.61 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). *NH not observed.* $^{13}C\{^1H\}$ NMR (CD_3CN) *δ* 266.5 (μ-CO); 213.1 (CO); 183.7 (C_α); 175.0 (*C*O_2Me); 89.2, 85.8 (Cp); 79.0 (C_β); 51.7 (NMe_2); 51.2 (CO_2*Me*); 43.5 (C_γ).

Compound **6c** (yield: 87%). Anal. Calc. for $C_{24}H_{24}F_3Fe_2NO_5S$: C, 47.45; H, 3.98; N, 2.31. Found: C, 47.40; H, 4.07; N, 2.24%. IR (CH_2Cl_2) *ν*(CO) 1987 (vs), 1815 (s) cm^{-1}. ^1H NMR (CD_3CN) *δ* 7.37–7.03 (m, 5H, C_6H_5); 5.88 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.2$ Hz); 5.51 (s, 5H, Cp); 5.28 (s, 5H, Cp); 3.40 (s, 6H, NMe_2); −0.70 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.2$ Hz). $^{13}C\{^1H\}$ NMR (CD_3CN) *δ* 267.1 (μ-CO); 213.5 (CO); 178.9 (C_α); 132.0-125.0 (C_{arom}); 90.1, 87.3 (Cp); 78.4 (C_β); 52.0 (NMe_2);35.1 (C_γ).

4.6. Synthesis of [$Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(NMe_2)C_\beta(H)C_\gamma(H)\text{-}(CNFe(CO)_2Cp)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (**9**)

A solution of **3a** (406 mg, 1.0 mmol) in THF (20 mL) was treated with $[Fe(CO)_2(THF)(Cp)][SO_3CF_3]$, freshly prepared by treatment of $[Fe_2(CO)_4(Cp)_2]$ (213 mg, 0.6 mmol) with $AgSO_3CF_3$ (180 mg, 0.7 mmol). The mixture was stirred at room temperature for 1 hour and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with methanol as eluent, afforded a green–brown solid, corresponding to **9**. Yield: 76%. Anal. Calc. for $C_{26}H_{23}F_3Fe_3N_2O_7S$: C, 42.63; H, 3.17; N, 3.83. Found: C, 42.71; H, 3.13; N, 3.70%. IR (CH_2Cl_2) ν(CO) 2079 (vs), 2035 (vs), 1939 (vs), 1780 (s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.35 (s, 5H, Cp); 4.56 (s, 5H, Cp); 4.34 (s, 5H, Cp); 4.18 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 3.64 (s, 6H, NMe_2); −1.14 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.8 (μ-CO); 211.9, 210.5, 209.8 (CO); 204.2 (C_α); 125.0 (C≡N); 90.9, 87.9, 85.8 (Cp); 52.0 (C_β); 46.0 (NMe_2); 19.1 (C_γ).

4.7. Synthesis of [$Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)([Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(N(Me)_2)C_\beta(H)C_\gamma(H)(CN)\}(\mu\text{-}CO)(CO)\text{-}(Cp)_2])(Cp)_2][SO_3CF_3]$ (R = Me, **10a**; R = Xyl, **10b**; R = 4-C_6H_4OMe, **10c**)

To a solution of **1a** (531 mg, 1.0 mmol) in THF (20 mL) were successively added **3a** (406 mg, 1.0 mmol) and Me_3NO (110 mg, 1.5 mmol). The mixture was stirred at room temperature for 1 h and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with methanol as eluent, afforded a brown solid, corresponding to **10a**. Yield: 70%. Anal. Calc. for $C_{34}H_{34}F_3Fe_4N_3O_7S$: C, 44.89; H, 3.77; N, 4.62. Found: C, 45.00; H, 3.73; N, 4.60%. IR (CH_2Cl_2) ν(CO) 1981 (vs), 1940 (vs), 1812 (s), 1785 (s), ν(CN) 1586 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.31 (s, 5H, Cp); 5.02 (s, 5H, Cp); 4.51 (s, 5H, Cp); 4.32 (s, 5H, Cp); 4.25 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.67 (s, 3H, NMe); 4.32 (s, 3H, NMe); 3.52 (s, 6H, NMe_2); −1.35 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 331.2 (μ-CN); 266.4 (μ-CO); 265.7 (μ-CO); 213.0 (CO); 211.5 (CO); 203.1 (C_α); 125.3 (C≡N); 90.1 (Cp); 88.9 (Cp); 87.3 (Cp); 86.1 (Cp); 54.0 (NMe); 53.3 (NMe); 53.1 (C_β); 46.5 (NMe_2); 19.6 (C_γ).

Compounds **10b–c** were prepared with the same procedure described for **10a**, by reacting **1b–c** with **3a** and Me_3NO.

Compound **10b** (yield: 66%). Anal. Calc. for $C_{41}H_{40}F_3Fe_4N_3O_7S$: C, 49.25; H, 4.04; N, 4.21. Found: C, 49.30; H, 4.13; N, 4.30%. IR (CH_2Cl_2) ν(CO) 1985 (vs), 1938 (vs), 1819 (s), 1788 (s), ν(CN) 1525 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.40–7.03 (m, 3H, $Me_2C_6H_3$); 5.15 (s, 5H, Cp); 4.89 (s, 5H, Cp); 4.51 (s, 5H, Cp); 4.34 (s, 5H, Cp); 4.27 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.80 (s, 3H, NMe); 3.52 (s, 6H, NMe_2); 2.70 (s, 3H, $Me_2C_6H_3$); 2.20 (s, 3H, $Me_2C_6H_3$); −1.32 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 338.6 (μ-CN); 265.9, 265.0 (μ-CO); 213.0, 212.1 (CO); 203.6 (C_α); 148.0–125.1 (C_{arom} + C≡N); 89.2, 88.7, 87.0, 86.5 (Cp); 54.5 (NMe); 52.8 (C_β); 46.5 (NMe_2); 20.7–18.5 (C_γ + $Me_2C_6H_3$).

Compound **10c** (yield: 73%). Anal. Calc. for $C_{40}H_{38}F_3Fe_4N_3O_8S$: C, 47.95; H, 3.83; N, 4.20. Found: C, 48.03; H, 3.77; N, 4.24%. IR (CH_2Cl_2) ν(CO) 1983 (vs), 1940 (vs), 1819 (s), 1786 (s), ν(CN) 1530 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.60–7.10 (m, 4H, C_6H_4OMe); 5.08 (s, 5H, Cp); 4.86 (s, 5H, Cp); 4.50 (s, 5H, Cp); 4.37 (s, 5H, Cp); 4.30 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.0$ Hz); 4.79 (s, 3H, NMe); 3.90 (s, 3H, C_6H_4OMe); 3.52 (s, 6H, NMe_2); −1.30 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.0$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 336.5 (μ-CN); 265.9, 265.0 (μ-CO); 213.0, 210.9 (CO); 203.5 (C_α); 159.5–115.0 (C_{arom} + C≡N); 89.5, 88.9, 87.4, 87.0 (Cp); 56.5 (NMe); 55.1 (C_6H_4OMe); 53.0 (C_β); 46.5 (NMe_2); 20.1 (C_γ).

4.8. X-ray crystallography for **3a** and **3b**

Crystals of **3a** and **3b** suitable for X ray analysis were obtained by a CH_2Cl_2 solution, layered with petroleum ether, at −20 °C.

Crystal data for **3a** and **3b** were collected at room temperature on a Bruker APEX II CCD diffractometer using graphite monochromated Mo Kα radiation. Structures were solved by direct methods and structures refined by full-matrix least-squares based on all data using F^2 [20]. Crystal data are listed in Table 3. Non-H atoms were refined anisotropically. H-atoms were placed in calculated positions, except position of H(14) and H(15) in both **3a** and **3b** which were located in the Fourier map. H-atoms

Table 3
Crystal data and experimental details for **3a** and **3b**

Complex	**3a**	**3b**
Empirical formula	$C_{18}H_{18}Fe_2N_2O_2$	$C_{25}H_{24}Fe_2N_2O_2$
Formula weight	406.04	496.16
T (K)	293(2)	295(2)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	7.4182(5)	8.0777(5)
b (Å)	14.3307(9)	15.2350(10)
c (Å)	15.8838(10)	18.0168(11)
β (°)	90	101.5300(10)
Cell volume (Å^3)	1688.58(19)	2172.5(2)
Z	4	4
D_c (g cm^{-3})	1.597	1.517
μ (mm^{-1})	1.730	1.360
F(000)	832	1024
Crystal size (mm)	0.22 × 0.16 × 0.13	0.23 × 0.16 × 0.14
θ Limits (°)	1.91–28.69	1.77–27.00
Reflections collected	19654	23749
Independent reflections [R_{int}]	4116 [0.0417]	4728 [0.0462]
Data/restraints/parameters	4116/2/225	4728/2/289
Goodness-on-fit on F^2	1.051	1.018
R_1 ($I > 2\sigma(I)$)	0.0322	0.0342
wR_2 (all data)	0.0675	0.0851
Largest differences in peak and hole (e Å^{-3})	0.417/−0.290	0.420/−0.230

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.

5. Supplementary material

CCDC 661224 and 661225 contains the supplementary crystallographic data for **3a** and **3b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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