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Nitrile ligands activation in dinuclear aminocarbyne complexes

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Abstract

The diiron complexes $[Fe(Cp)(CO)\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C[N(Me)(R)]N{=}C(C_6H_3R')C{=}CH(Tol)\}Fe(Cp)(CO)]$ (R = Xyl, R′ = H, **3a**; R = Xyl, R′ = Br, **3b**; R = Xyl, R′ = OMe, **3c**; R = Xyl, R′ = CO_2Me, **3d**; R = Xyl, R′ = CF_3, **3e**; R = Me, R′ = H, **3f**; R = Me, R′ = CF_3, **3g**) are obtained in good yields from the reaction of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(p\text{-}NCC_6H_4R')(Cp)_2]^+$ (R = Xyl, R′ = H, **2a**; R = Xyl, R′ = Br, **2b**; R = Xyl, R′ = OMe, **2c**; R = Xyl, R′ = CO_2Me, 2d; R = Xyl, R′ = CF_3, **2e**; R = Me, R′ = H, 2f; R = Me, R′ = CF_3, **2g**) with TolC≡CLi. The formation of **3** involves addition of the acetylide at the coordinated nitrile and C–N coupling with the bridging aminocarbyne together with orthometallation of the *p*-substituted aromatic ring and breaking of the Fe–Fe bond. Complexes **3a**–**e** which contain the N(Me)(Xyl) group exist in solution as mixtures of the *E-trans* and *Z-trans* isomers, whereas the compounds **3f,g**, which posses an exocyclic NMe_2 group, exist only in the *Z-cis* form. The crystal structures of *Z-trans*-**3b**, *E-trans*-**3c**, *Z-trans*-**3e** and *Z-cis*-**3g** have been determined by X-ray diffraction experiments.

Keywords: Nitrile; Acetylide addition; Aminocarbyne; Diiron complexes; Crystal structure

1. Introduction

Activation of nitriles by coordination to transition metals is a very important issue in organometallic chemistry and plays a fundamental role in organic synthesis [1]. Depending on the nature of the organometallic frame, coordinated nitriles can react with both nucleophiles and electrophiles or display increased α-CH acidity [2]. Activation towards nucleophilic addition can result in enhancement of the reaction rate from 10^6 to 10^{10} and occasionally to 10^{18} [3]. Nucleophilic additions to metal coordinated nitriles mostly involve protic nucleophiles such as amines [4], alcohols [5] and water [6], leading to the formation of the corresponding amidines, imidoesters and amidates. Additions of carbon nucleophiles are also known, although less common [7].

We have recently investigated the reactivity of diiron and diruthenium aminocarbyne complexes containing nitriles, i.e., $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCCR')(Cp)_2]^+$ (M = Fe, Ru; R = Xyl, Bz, Me; R′ = Me, CMe_3). Although acetonitrile is readily displaced, in the above complexes, by a variety of ligands including amines, imines, phosphines, isocyanides, cyanide, hydride and halides [8], it has been found that treatment with NaH or LiR removes a proton from the coordinated MeCN, and consequently promotes its rearrangement to cyanomethyl ligand [9]. Dinuclear complexes containing trimethylacetonitrile, $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCCCMe_3)(Cp)_2]^+$ [M = Fe, Ru; R = Xyl, Me], lack of acidic α-CH. Their reactions with acetylides proceed via LiCCR′ addition to the nitrile affording, after protonation, the alkynyl imino complexes $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N(H){=}C(CMe_3)(C{\equiv}CR')\}(Cp)_2]^+$ [8b,10]. In the case of the diiron complexes, the reaction can further proceed via coupling between the azavinylidene intermediate and the bridging

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aminocarbyne resulting, upon addition of CF_3SO_3H, in the formation of the μ-allenyl-diaminocarbene complex $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C(Tol)=C=C(CMe_3)N(H)CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(Cp_2)]^+$ [10]. The latter reaction represents an interesting example in which the diiron aminocarbyne frame acts as a template for the preparation of new ligands via formation of new C–C and C–N bonds.

With the aim of extending our knowledge on the activation of nitriles by dinuclear aminocarbyne complexes, we have investigated the reactions of diiron aminocarbyne complexes containing aryl nitriles, with TolC≡CLi. The results of these studies are the object of this paper.

2. Results and discussion

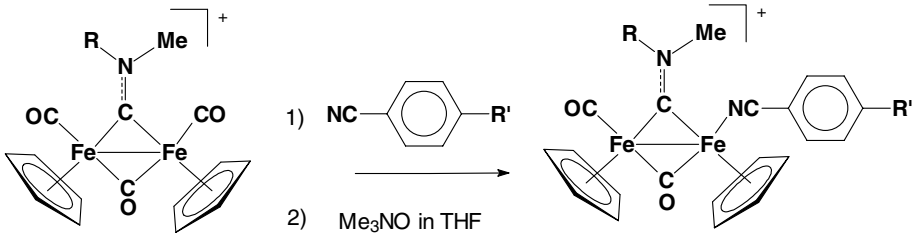
The nitrile complexes $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(p\text{-}NCC_6H_4R')(Cp)_2]^+$ (R = 2,6-$Me_2C_6H_3$ (Xyl), R′ = H, **2a**; R = Xyl, R′ = Br, **2b**; R = Xyl, R′ = OMe, **2c**; R = Xyl, R′ = CO_2 Me, **2**d; R = Xyl, R′ = CF_3, **2e**; R = Me, R′ = H, **2f**; R = Me, R′ = CF_3, **2g**) can be obtained in high yield by Me_3NO assisted replacement of a CO ligand of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; Me, **1b**) in THF (Scheme 1), following the same procedure previously reported for the analogous acetonitrile and trimethylacetonitrile complexes [8a]. Complexes **2** have been fully characterised by spectroscopic methods (NMR and IR) and elemental analyses (see Section 4).

The reaction of **2** with TolC≡CLi (Tol = *p*-MeC_6H_4) in THF at low temperature, followed by stirring at room temperature for 1 h affords the new diiron complexes $[Fe(Cp)(CO)\{\mu\text{-}\eta^2{:}\eta^2\text{-}C[N(Me)(R)]N=C(C_6H_3R')C=CH(Tol)\}Fe(Cp)(CO)]$ (R = Xyl, R′ = H, **3a**; R = Xyl, R′ = Br, **3b**; R = Xyl, R′ = OMe, **3c**; R = Xyl, R′ = CO_2 Me, **3d**; R = Xyl, R′ = CF_3, **3e**; R = Me, R′ = H, **3f**; R = Me, R′ = CF_3, **3g**), which are obtained in good yields (ca. 60%) after column chromatography (Scheme 2).

The crystal structures of **3b**, **3c**, **3e** and **3g** have been determined by X-ray diffraction studies. Their molecular structures are shown in Figs. 1–4, whereas the most relevant bond lengths and bond angles are reported in Tables 1 and 2.

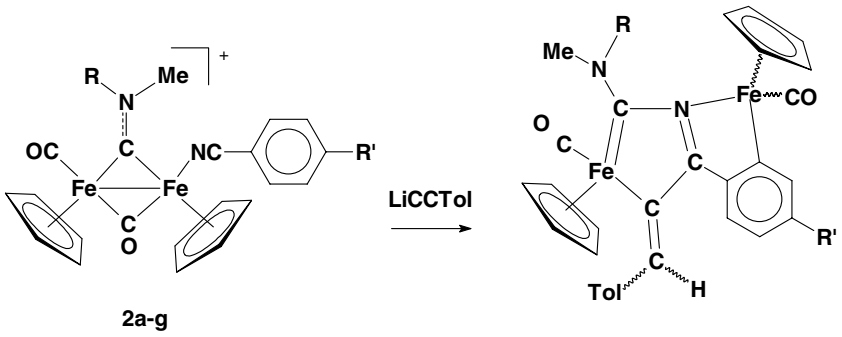
Two independent molecules are present in the asymmetric unit of **3c** · **0.5C_5H_{12}**. All the molecules **3b**, **3c**, **3e** and **3g** are composed by two five member metallacycles, fused on an edge formed by a C–N bond. Both iron atoms show a tetrahedral geometry, with two coordination sites occupied by a Cp and a CO ligand, respectively. The coordination sphere of Fe(1) is completed by a diaminocarbene and a vinyl ligand. In agreement with this, both Fe(1)–C(13) [1.916(7)–1.926(6) Å] and C(13)–N(2) [1.310(7)–1.341(7) Å] show some double bond character, whereas Fe(1)–C(15) [1.952(7)–1.986(7) Å] is essentially a pure Fe–C(sp^2) single bond. In agreement with the vinyl nature of the latter ligand, C(15)–C(16) [1.320(8)–1.366(9) Å] is an almost pure double bond. Interestingly, the C(13)–N(1) interaction [1.384(7)–1.407(2) Å] has mainly the character of a single bond and, thus, the diaminocarbene carbon exhibits a considerably asymmetry in the bonding with the exo- and endo-cyclic nitrogen, probably because the latter is involved in the coordination to Fe(2) and also because of delocalisation involving C(14). Some π-interaction is present also in the bond between Fe(2) and the metallated aromatic ring [Fe(2)–C(25) 1.926(7)–1.9447(19) Å].

In spite of the fact that the molecules present similar bond lengths and bond angles, some stereochemical differences are to be outlined. First, the Cp rings adopt a pseudo *trans* arrangement in **3b**, **3c** and **3e**, whereas they can be considered *cis* in **3g**. Other differences consist in



	R	R'
2a	Xyl	H
2b	Xyl	Br
2c	Xyl	OMe
2d	Xyl	COOMe
2e	Xyl	CF_3
2f	Me	H
2g	Me	CF_3

Scheme 1.



2a-g

	R	R'
3a	Xyl	H
3b	Xyl	Br
3c	Xyl	OMe
3d	Xyl	COOMe
3e	Xyl	CF_3
3f	Me	H
3g	Me	CF_3

Scheme 2.

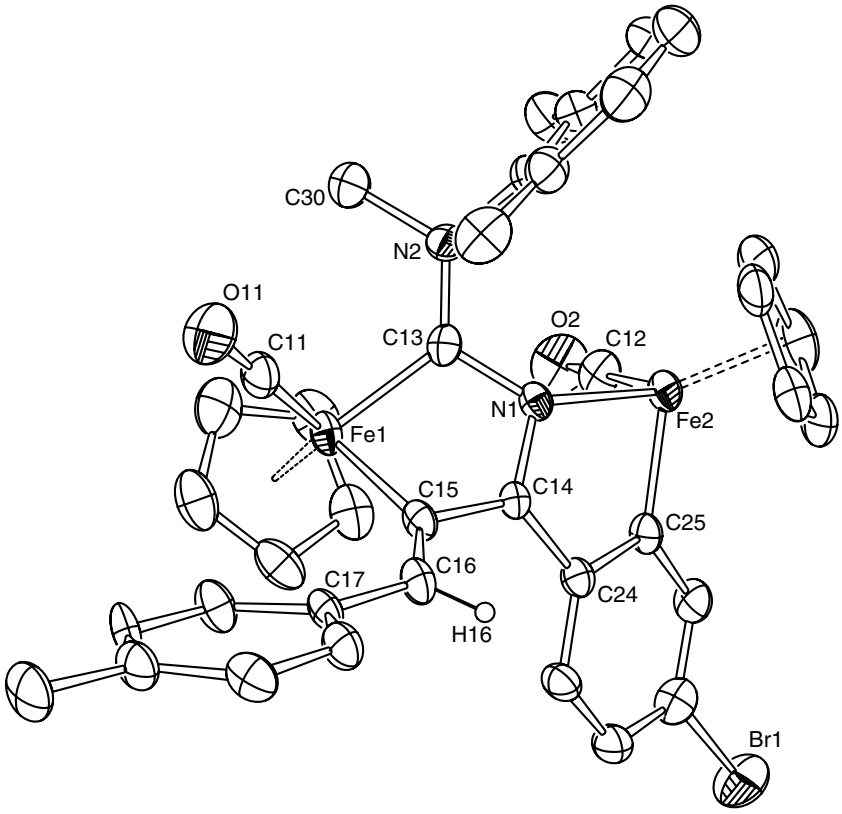


Fig. 1. Molecular structure of **3b** (all H atoms, apart from H16, have been omitted). Displacement ellipsoids are at 30% probability level.

the configuration of the exocyclic C(15)=C(16) bond, which adopts a *Z* configuration in **3b**, **3e** and **3g** whereas it is *E* in **3c**. Therefore the compounds shown in Figs. 1–4 should be appropriately described as *Z-trans*-**3b**, *E-trans*-**3c**, *Z-trans*-**3e** and *Z-cis*-**3g**. The different configurations of C(15)=C(16) do not affect sensibly the rest of the molecule, whereas the different geometries of the Cp ligands have important effects on the conformation of the two condensed metallacycles. Thus, the ring comprising Fe(2) is almost planar in all the four complexes and, in fact, Fe(2), C(25), C(24), C(14) and N(1) show a very small deviation from their mean squares plane

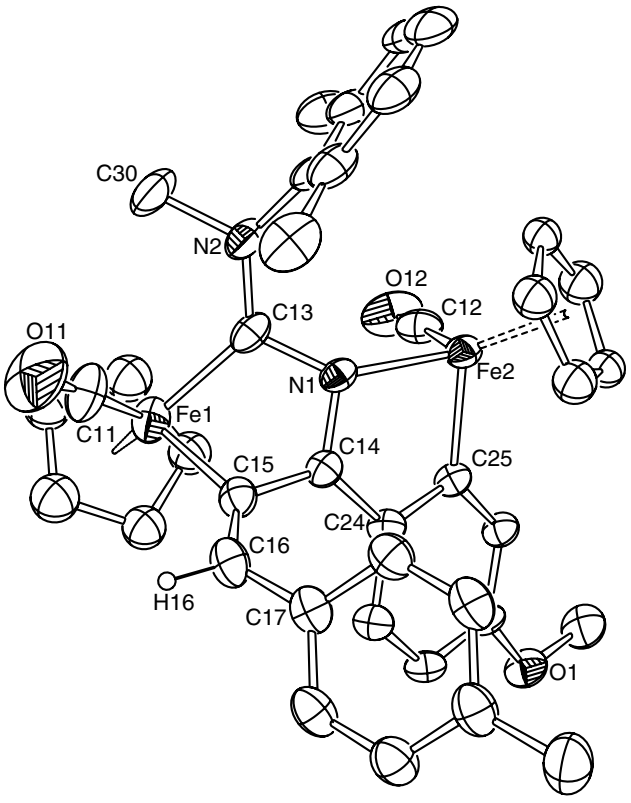


Fig. 2. Molecular structure of **3c** (all H atoms, apart from H16, have been omitted). Only one of the two independent molecules is represented. Displacement ellipsoids are at 30% probability level.

of 0.0225 Å in *Z-cis*-**3g** and 0.0812–0.0948 Å in the *trans* complexes. In the case of *Z-cis*-**3g** both C(15) and C(13) lay very close to this plane [torsion angles C(15)–C(14)–C(24)–C(25) −179.9(7)°, C(24)–C(14)–N(1)–C(13) 168.4(5)°], whereas they are considerably out of the plane in *Z-trans*-**3b**, *E-trans*-**3c** and *Z-trans*-**3e** [torsion angles C(15)–C(14)–C(24)–C(25) −166.02(16)° to −169.6(6)°, C(24)–C(14)–N(1)–C(13) 141.3(5)–149.5(6)°]. These differences in the conformation of the two five member cycles seems to affect the C(14)–N(1) bond length, which lays on the edge shared by the two rings and appears shorter for *Z-cis*-**3g** [1.331(7) Å] compared to *Z-trans*-**3b**, *E-trans*-**3c** and *Z-trans*-**3e** [1.355(8)–1.373(7) Å]. Moreover, in all the complexes the C(14)–N(1) interaction is longer than a pure C=N double bond and N(1) shows some pyramidalisation [sum angles 352.5(8)–356.1(8)° in *Z-trans*-**3b**, *E-trans*-**3c** and *Z-trans*-**3e**; 358.9(8)° in *Z-cis*-**3g**]. The Fe(2)–N(1) interaction [2.028(5)–2.0395(15) Å in *Z-trans*-**3b**, *E-trans*-**3c** and *Z-trans*-**3e**; 2.011(5) Å in *Z-cis*-**3g**] is also slightly longer than expected for a coordinated imine, e.g. 1.964(3) Å in $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)\{N(H)C(C{\equiv}CTol)CMe_3\}(Cp)_2]^+$ [10]. Delocalisation effects seem to have only a minor contribution to the lengthening of C(14)–N(1), even though they should be considered. Thus, both C(14)–C(15) [1.427(8)–1.472(8) Å] and C(14)–C(24) [1.435(8)–1.454(2) Å] are sensibly shorter than a single $C(sp^2)$–$C(sp^2)$ bond. On the basis of all these considerations, these complexes can be also described as a 1-metalla-2-amino-3-aza-5-alkylidencyclopenta-1,3-diene which acts a chelating ligand on Fe(2) via the endocyclic nitrogen and an orthometallated aromatic ring.

The IR spectra of **3** show the presence of a single band at 1915–1930 cm^{-1} for both the CO ligands. The NMR spectra of **3a**–**e** indicate the presence in solution of two isomers in ca. 2–1:1 ratio, whereas a single species in present in the case of **3f,g**. On the basis of the solid state structures, it is possible to assume that the two species present in the case of **3a**–**e** are the *E-trans* and *Z-trans* isomers, whereas the complexes **3f,g** maintain a *Z-cis* structure (Scheme 3). NMR measurements on the crystalline materials, dissolved in $CDCl_3$, confirm this hypothesis and have helped on the assignment of the NMR data to all the different isomers.

The *Z* isomers are characterized by the ^{13}C vinyl resonance due to Fe(1)–*C*(15) at δ 200–206 ppm, whereas it is shifted at lower frequencies for the *E* isomers (δ 177–194 ppm). Moreover, the ^1H C(16)–*H*(16) proton resonates always at higher frequencies for the *Z* isomers than for the *E* isomer. Other important features in the ^{13}C NMR spectra are the high frequencies resonances due to Fe(1)=*C*(13) (249–269 ppm) and *C*(14)=N(1) (δ 198–208 ppm); the former falls within the typical range for iron diaminocarbenes. The carbon of the orthometallated aromatic ring *C*(25) resonates at δ 150–168 ppm, whereas the exocyclic vinyl *C*(16)–H(16) shows a resonance at δ 130–144 ppm. Finally, it is noteworthy that in the ^1H NMR spectra of **3f,g** the protons of both Cp ligands resonante at distinct but similar frequencies (δ ca. 4.5 ppm), whereas they are separate by 0.5–0.6 ppm in the complexes **3a**–**e** which contain the Xyl group on the diaminocarbene. NOE studies indicate that the Cp at higher frequencies [δ 4.2–4.4 ppm] is the one close to the N(2)–Me substituent [thus bound to Fe(1)], whereas the Xyl group shields the Fe(2)–Cp protons [δ 3.7–3.8 ppm]. Similar results have been obtained on both the isomers of **3a**–**e**, confirming that they differ only for the configuration of the exocyclic C(15)=C(16) bond, whereas they maintain the *trans* arrangement of the Cp and the *E* configuration of C(13)–N(2).

The mechanism for the formation of **3** from **2** seems to be quite complex and presumably proceeds through several steps. Attempts to isolate or identify intermediate species failed. However, on the basis of previous considerations on the analogous reactions of $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(NCCMe_3)(Cp)_2]^+$ [M = Fe, Ru; R = Xyl, Bz, Me] [8b,10] with R′C≡CLi, it appears reasonable that the reaction occurs via nucleophilic attack of TolC≡CLi on the nitrile carbon of **2**, generating

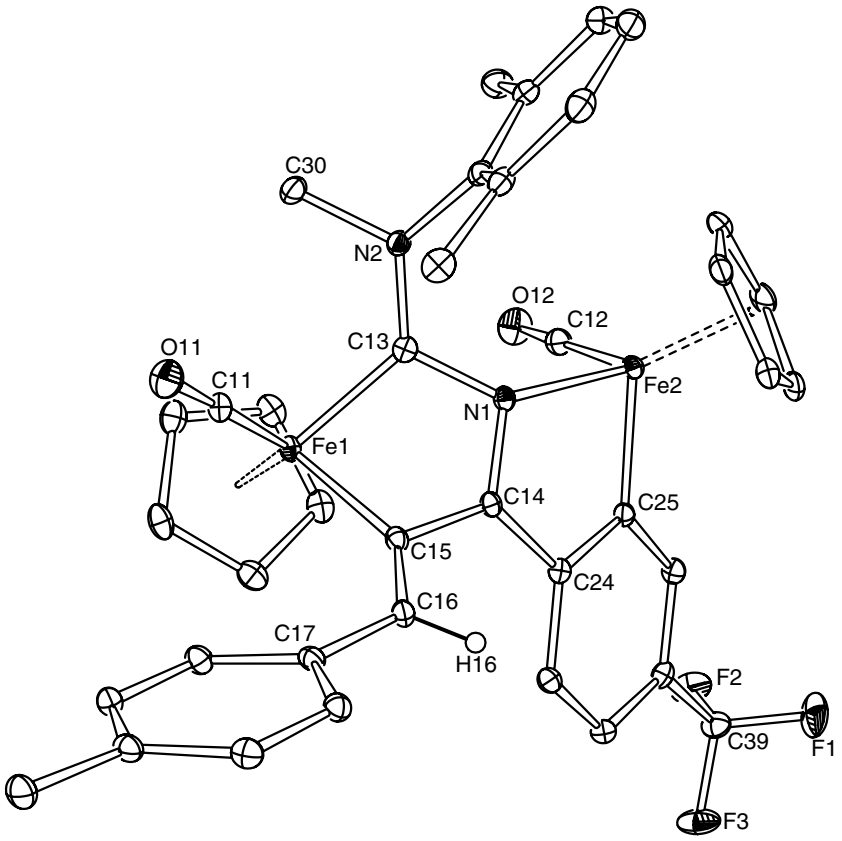


Fig. 3. Molecular structure of **3e** (all H atoms, apart from H16, have been omitted). Displacement ellipsoids are at 30% probability level.

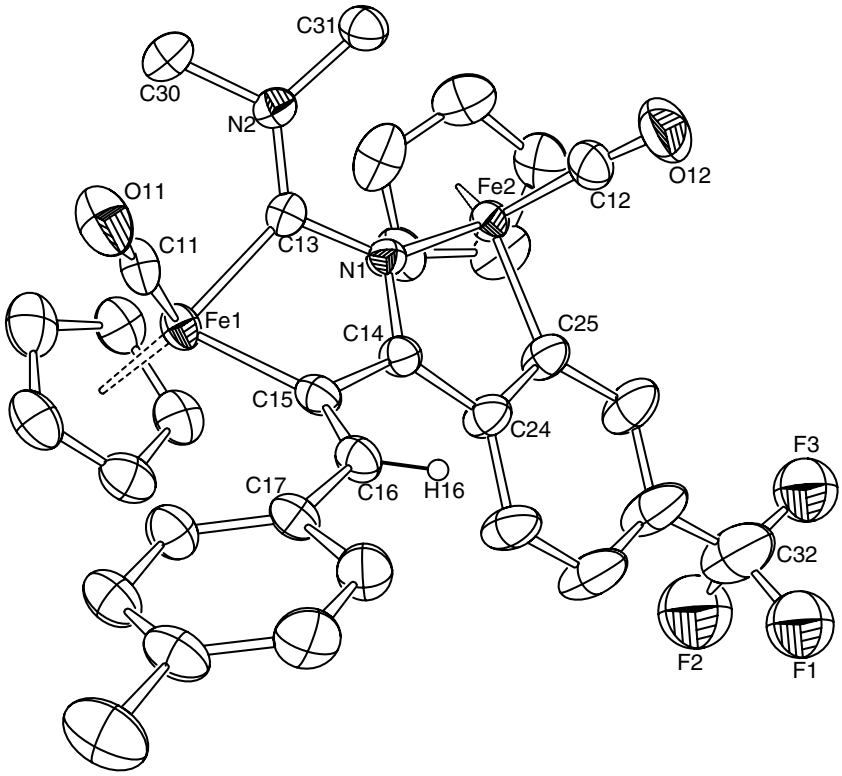


Fig. 4. Molecular structure of **3g** (all H atoms, apart from H16, have been omitted). Displacement ellipsoids are at 30% probability level.

Table 1
Selected bond lengths (Å) for complexes **3b**, **3c**, **3e** and **3g**

	3b	**3c**		**3e**	**3g**
		Molecule 1[a]	Molecule 2[a]		
Fe(1)–C(11)	1.712(8)	1.704(9)	1.704(8)	1.7423(19)	1.693(7)
Fe(2)–C(12)	1.718(9)	1.707(7)	1.725(8)	1.753(2)	1.727(8)
Fe(1)–C(13)	1.917(7)	1.916(7)	1.926(6)	1.9167(18)	1.923(6)
Fe(1)–C(15)	1.977(7)	1.952(7)	1.986(7)	1.9858(19)	1.957(7)
Fe(2)–N(1)	2.031(5)	2.038(5)	2.028(5)	2.0395(15)	2.011(5)
Fe(2)–C(25)	1.926(7)	1.933(6)	1.935(6)	1.9447(19)	1.929(6)
C(11)–O(11)	1.171(9)	1.163(9)	1.162(7)	1.158(2)	1.179(8)
C(12)–O(12)	1.157(9)	1.175(8)	1.149(8)	1.156(2)	1.149(9)
C(13)–N(1)	1.398(8)	1.396(7)	1.384(7)	1.407(2)	1.405(7)
C(13)–N(2)	1.334(8)	1.341(7)	1.345(7)	1.338(2)	1.310(7)
C(14)–N(1)	1.355(8)	1.366(7)	1.373(7)	1.355(2)	1.331(7)
C(14)–C(15)	1.439(8)	1.427(8)	1.431(8)	1.446(2)	1.472(8)
C(14)–C(24)	1.446(9)	1.436(8)	1.435(8)	1.454(2)	1.442(9)
C(15)–C(16)	1.329(9)	1.348(8)	1.320(8)	1.344(3)	1.366(9)
C(16)–C(17)	1.463(9)	1.455(9)	1.462(9)	1.470(2)	1.459(8)
C(24)–C(25)	1.407(9)	1.394(8)	1.405(8)	1.416(2)	1.410(8)

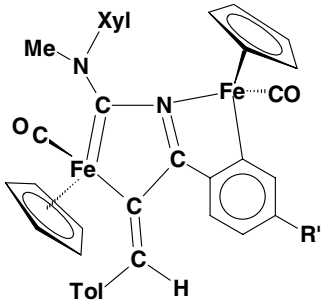
[a] Two independent molecules are present in the unite cell.

Table 2
Selected bond angles (°) for complexes **3b**, **3c**, **3e** and **3g**

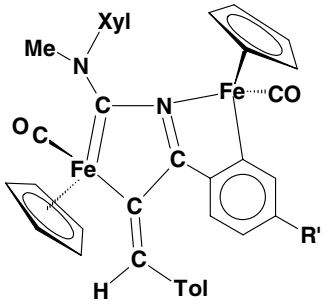
	3b	**3c**		**3e**	**3g**
		Molecule 1[a]	Molecule 2[a]		
C(13)–Fe(1)–C(15)	79.4(3)	79.1(3)	79.3(2)	79.30(7)	78.9(2)
Fe(1)–C(13)–N(1)	111.8(5)	112.6(4)	111.0(4)	111.96(12)	112.6(4)
C(13)–N(1)–C(14)	108.1(5)	106.7(5)	106.8(5)	107.45(14)	109.2(5)
N(1)–C(14)–C(15)	117.1(6)	116.9(5)	116.8(5)	117.68(15)	117.0(5)
C(14)–C(15)–Fe(1)	99.2(4)	99.8(4)	95.3(4)	98.66(11)	103.8(4)
N(1)–Fe(2)–C(25)	81.3(2)	81.9(2)	81.6(2)	81.47(7)	81.8(2)
Fe(2)–C(25)–C(24)	115.6(5)	113.3(4)	113.9(4)	114.07(13)	114.3(5)
C(25)–C(24)–C(14)	111.8(6)	115.2(5)	114.3(5)	113.61(15)	114.2(6)
C(24)–C(14)–N(1)	116.6(6)	114.8(5)	114.9(5)	115.27(15)	114.8(5)
C(14)–N(1)–Fe(2)	111.8(4)	110.9(4)	111.9(4)	112.71(11)	114.5(4)
C(14)–C(15)–C(16)	121.2(6)	124.8(6)	132.5(6)	121.47(16)	116.4(6)
Fe(1)–C(15)–C(16)	139.4(5)	135.4(5)	132.1(5)	139.76(14)	139.5(5)
C(15)–C(16)–C(17)	129.6(7)	126.7(6)	130.8(6)	128.74(16)	129.8(6)
N(1)–C(13)–N(2)	120.5(6)	119.1(6)	120.1(5)	120.15(15)	118.1(5)
Fe(1)–C(13)–N(2)	127.7(5)	128.2(5)	128.8(4)	127.82(13)	129.3(4)

[a] Two independent molecules are present in the unite cell.

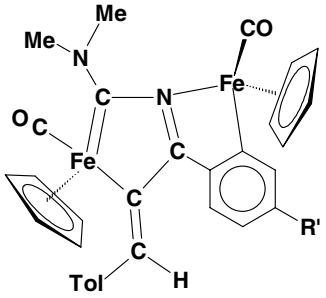
a η^1-azavinylidene intermediate of the type $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)\{N{=}C(p\text{-}NCC_6H_4R')(C{\equiv}CR')\}(Cp)_2]$. Then, the azavynilidene ligand is supposed to migrate and couple with the bridging aminocarbyne. These two initial steps accounts for the formation of the C(14)–C(15) and C(13)–N(1) bond, observed in **3**. Further rearrangements must then take place in order to explain the formation of the final product **3**. A reasonable sequence of intermediate species involved in this process can be hardly traced out, in the absence of further evidences. However some considerations can be drown: the sequence must include an orthometallation reaction, which, to the best of our knowledge, has never been described in the case of diiron complexes bridged by carbyne or carbene ligands. In general, the orthometallation reaction has been known for a long time [11], and compounds that contain an orthometallated ligand continue to be of interest for the generation of catalysts [12], compounds with interesting material properties [13], and antitumor agents [14]. A second consideration concern the fragmentation of the diiron frame $Fe_2Cp_2(\mu\text{-}CO)$ which usually appears very robust and is unaffected even by strong rearrangements, occurring on the coordinated ligands [8–10,15]. Breaking of the Fe–Fe bond has been previously observed only in the reaction of $[M_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (M = Fe, Ru) with KH and acetonitrile, to form a metallapyrrole ring [16].



Z-trans-**3a-e**



E-trans-**3a-e**



Z-cis-**3f-g**

Scheme 3.

3. Conclusions

The results obtained demonstrate very well the capability of diiron aminocarbyne complexes of activating coordinated nitriles with respect to the addition of acetilydes. Nucleophilic attack at the coordinated nitrile is accompanied by coupling with the bridging aminicarbyne ligand, resulting in C–N bond formation.

Further rearrangements take place depending on the nature of the nitrile ligand, and different products are correspondingly formed (Scheme 4). Complexes containing the trimethylacetonitrile ligand afford the allene-amminocarbene compound [10], whereas aryl-nitriles, causes the fragmentation of the Fe–Fe bond.

In all of the cases, it is to be outlined the role of the two adjacent metal centres in promoting intramolecular couplings of coordinated ligands, and building-up organic fragments. The metal atoms also provide stabilization to these species, through a variety of coordination modes.

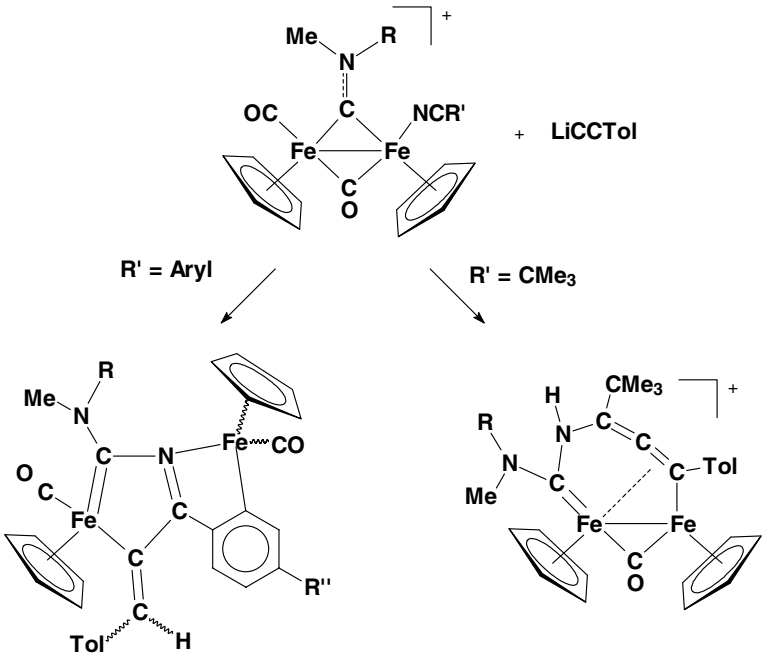
4. Experimental

4.1. General

All reactions were carried out routinely under nitrogen using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Infrared spectra were recorded on a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed on Varian Gemini 300 and Varian Mercury Plus 400 instruments. The chemical shifts were referenced to internal TMS for ^{1}H and ^{13}C, and to external CCl_3F for ^{19}F. The spectra were fully assigned via $^{1}H,^{13}C$ correlation measured using gs-HSQC and gs-HMBC experiments [17]. Monodimensional NOE measurements were recorded using the DPFGSE-NOE sequence [18]. All chemicals were used as received from Aldrich Co., except $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Xyl, **1a**; Me, **1b**) [19] which were prepared by published methods. TolC≡CLi was prepared just before use from the reaction of TolC≡CH with Bu^{n}Li in THF at −50 °C (molar ratio 1.2:1).

4.2. Synthesis of $[Fe_2\{\mu\text{-}CN(Me)(R)\}(\mu\text{-}CO)(CO)(p\text{-}NCC_6H_4R')(Cp)_2]$ (R = Xyl, R′ = H, **2a**; R = Xyl, R′ = Br, **2b**; R = Xyl, R′ = OMe, **2c**; R = Xyl, R′ = CO_2Me, **2d**; R = Xyl, R′ = CF_3, **2e**; R = Me, R′ = H, **2f**; R = Me, R′ = CF_3, **2g**)

p-R′C_6H_4CN (0.700 mmol) and Me_3NO (52.5 mg, 0.700 mmol) were added to a solution of **1** (0.350 mmol) in THF (10 ml), and the solution stirred at room temperature for 3 h. The solvent was, then, removed in vacuo



Scheme 4.

and the residue washed with Et_2O (2 × 10 ml) and petroleum ether (2 × 10 ml). The product was, therefore, further purified by filtration through celite using CH_2Cl_2 as solvent.

2a: Yield: 231.5 mg (95%). Anal. Calc. for $C_{30}H_{27}F_3Fe_2N_2O_5S$: C, 51.75; H, 3.91; N, 4.02. Found: C, 51.54; H, 4.11, N, 4.21%. IR (in CH_2Cl_2, 293 K): ν(CO) 1985 (vs), 1823 (s); ν(CN) 1587 (m), 1519 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.41–7.04 (m, 8H, *arom*), 5.00, 4.22 (s, 10H, *Cp*), 4.35 (s, 3H, N*Me*), 2.51, 1.85 (s, 6H, $Me_2C_6H_3$); Isomer β: δ 7.41–7.04 (m, 8H, *arom*), 5.10, 4.31 (s, 10H, *Cp*), 4.61 (s, 3H, N*Me*), 2.51, 1.85 (s, 6H, $Me_2C_6H_3$). Isomer ratio α:β = 3:1. ^{13}C NMR ($CDCl_3$, 293 K) Isomer α: δ 336.8 (μ-*C*), 264.2 (μ-*C*O), 210.6 (*C*O), 147.8 (*C*-ipso Xyl), 133.6, 133.2 (*C*–Me Xyl), 132.6–128.8 (*C*H arom), 118.6 (*C*N), 109.8 (*C*-ipso Ph), 88.8, 86.6 (*Cp*), 53.3 (N*Me*), 18.4, 17.3 ($Me_2C_6H_3$); Isomer β: δ 337.2 (μ-*C*), 263.4 (μ-*C*O), 211.2 (*C*O), 147.7 (*C*-ipso Xyl), 133.5, 132.9 (*C*–Me Xyl), 132.6–128.8 (*C*H arom), 118.5 (*C*N), 109.7 (*C*-ipso Ph), 88.0, 87.5 (*Cp*), 53.7 (N*Me*), 18.2, 16.9 ($Me_2C_6H_3$).

2b: Yield: 249.6 mg (92%). Anal. Calc. for $C_{30}H_{26}BrF_3Fe_2N_2O_5S$: C, 46.48; H, 3.38; N, 3.61. Found: C, 46.12; H, 3.01, N, 3.89%. IR (in CH_2Cl_2, 293 K): ν(CO) 1986 (vs), 1822 (s); ν(CN) 1587 (m), 1519 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.58–7.08 (m, 7H, *arom*), 5.13, 4.36 (s, 10H, *Cp*), 4.44 (s, 3H, N*Me*), 2.64, 1.96 (s, 6H, $Me_2C_6H_3$); Isomer β: δ 7.58–7.08 (m, 7H, *arom*), 5.06, 4.48 (s, 10H, *Cp*), 4.73 (s, 3H, N*Me*), 2.63, 1.98 (s, 6H, $Me_2C_6H_3$). Isomer ratio α:β = 2:1. ^{13}C NMR ($CDCl_3$, 293 K) Isomer α: δ 337.4 (μ-*C*), 264.6 (μ-*C*O), 211.3 (*C*O), 148.4 (*C*-ipso Xyl), 134.0–128.2 (*C*H arom + *C*–Me Xyl + *C*–Br), 118.3 (*C*N), 109.2 (*C*–CN), 89.4, 87.4 (*Cp*), 55.5 (N*Me*), 19.0, 17.8 ($Me_2C_6H_3$); Isomer β: δ 338.1 (μ-*C*), 263.9 (μ-*C*O), 211.9 (*C*O), 148.3 (*C*-ipso Xyl), 134.0–128.2 (*C*H arom + *C*–Me Xyl + *C*–Br), 119.5 (*C*N), 109.1 (*C*–CN), 88.5, 88.2 (*Cp*), 54.4 (N*Me*), 18.8, 17.4 ($Me_2C_6H_3$).

2c: Yield: 228.8 mg (90%). Anal. Calc. for $C_{31}H_{29}F_3Fe_2N_2O_6S$: C, 51.27; H, 4.02; N, 3.86. Found: C, 51.52; H, 3.79, N, 4.08%. IR (in CH_2Cl_2, 293 K): (CO) 1986 (vs), 1821 (s); ν(CN) 1603 (m), 1509 (ms). ^{1}H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.50–6.77 (m, 7H, *arom*), 5.11, 4.33 (s, 10H, *Cp*), 4.44 (s, 3H, N*Me*), 3.73 (s, 3H, O*Me*), 2.65, 1.98 (s, 6H, $Me_2C_6H_3$); Isomer β: δ 7.50–6.77 (m, 7H, *arom*), 5.02, 4.47 (s, 10H, *Cp*), 4.74 (s, 3H, N*Me*), 3.72 (s, 3H, O*Me*), 2.64, 1.99 (s, 6H, $Me_2C_6H_3$). Isomer ratio α:β = 1.4:1. ^{13}C NMR ($CDCl_3$, 293 K) Isomer α: δ 337.8 (μ-*C*), 265.1 (μ-*C*O), 211.3 (*C*O), 164.0 (*C*–OMe), 148.4 (*C*-ipso Xyl), 134.3, 115.4 (*C*H NCC_6H_4OMe), 133.8, 132.9 (*C*–Me Xyl), 130.2, 129.4, 129.3 (*C*H Xyl), 119.5 (*C*N), 101.7 (*C*–CN), 89.3, 87.1 (*Cp*), 55.9 (O*Me*), 55.3 (N*Me*), 19.0, 17.9 ($Me_2C_6H_3$); Isomer β: δ 338.7 (μ-*C*), 264.3 (μ-*C*O), 211.9 (*C*O), 163.9 (*C*–OMe), 148.3 (*C*-ipso Xyl), 134.6, 115.3 (*C*H NCC_6H_4OMe), 133.5, 132.4 (*C*–Me Xyl), 130.3, 129.3, 129.2 (*C*H Xyl), 122.7 (*C*N), 101.6 (*C*–CN), 88.4, 87.9 (*Cp*), 56.0 (O*Me*), 54.2 (N*Me*), 18.8, 17.4 ($Me_2C_6H_3$).

2d: Yield: 232.3 mg (88%). Anal. Calc. for $C_{32}H_{29}F_3Fe_2N_2O_7S$: C, 50.96; H, 3.88; N, 3.71. Found: C, 51.13; H, 3.52, N, 3.44%. IR (in CH_2Cl_2, 293 K):

(CO) 1985 (vs), 1822 (s); *ν*(COOMe) 1730 (s); *ν*(CN) 1519 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.91–7.03 (m, 7H, *arom*), 5.14, 4.38 (s, 10H, *Cp*), 4.44 (s, 3H, N*Me*), 3.80 (s, 3H, COO*Me*), 2.63, 1.95 (s, 6H, $Me_2C_6H_3$); Isomer β: δ 7.91–7.03 (m, 7H, *arom*), 5.08, 4.48 (s, 10H, *Cp*), 4.74 (s, 3H, N*Me*), 3.79 (s, 3H, COO*Me*), 2.63, 1.97 (s, 6H, $Me_2C_6H_3$). Isomer ratio α:β = 1.4:1. ^{13}C NMR ($CDCl_3$, 293 K) Isomer α: δ 337.2 (μ-*C*), 264.3 (μ-*C*O), 211.3 (*C*O), 165.1 (*C*OOMe), 148.4 (*C*-ipso Xyl), 134.6 (*C*–COOMe), 133.7, 132.8 (*C*–Me Xyl), 132.4–129.2 (*C*H arom), 118.2 (*C*N), 114.2 (*C*-CN), 89.5, 87.4 (*Cp*), 55.5 (N*Me*), 52.9 (COO*Me*), 19.0, 17.8 ($Me_2C_6H_3$); Isomer β: δ 337.9 (μ-*C*), 263.6 (μ-*C*O), 211.9 (*C*O), 165.2 (*C*OOMe), 148.3 (*C*-ipso Xyl), 134.4 (*C*-COOMe), 133.4, 132.7 (*C*–Me Xyl), 132.4–129.2 (*C*H arom), 118.2 (*C*N), 114.1 (*C*–CN), 88.6, 88.3 (*Cp*), 54.4 (N*Me*), 52.9 (COO*Me*), 18.7, 17.4 ($Me_2C_6H_3$).

2e: Yield: 246.1 mg (92%). Anal. Calc. for $C_{31}H_{26}F_6Fe_2N_2O_5S$: C, 48.72; H, 3.43; N, 3.67. Found: C, 48.39; H, 3.44, N, 3.80%. IR (in CH_2Cl_2, 293 K): (CO) 1985 (vs), 1822 (s); *ν*(CN) 1520 (ms). ^{1}H NMR ($CDCl_3$, 293 K) Isomer α: δ 7.75–7.19 (m, 7H, *arom*), 5.13, 4.39 (s, 10H, *Cp*), 4.44 (s, 3H, N*Me*), 2.63, 1.97 (s, 6H, $Me_2C_6H_3$); Isomer β: δ 7.75–7.19 (m, 7H, *arom*), 5.08, 4.49 (s, 10H, *Cp*), 4.73 (s, 3H, N*Me*), 2.63, 1.99 (s, 6H, $Me_2C_6H_3$). Isomer ratio α:β = 1.2:1. ^{13}C NMR ($CDCl_3$, 293 K) Isomer α: δ 337.2 (μ-*C*), 264.2 (μ-*C*O), 211.3 (*C*O), 148.4 (*C*-ipso Xyl), 135.1–126.4 (*C*H arom + *C*–Me Xyl + *C*–CF_3), 123.0 (q, $^1J_{CF}$ = 273.6 Hz, C_3), 117.7 (*C*N), 114.0 (*C*–CN), 89.4, 87.5 (*Cp*), 55.5 (N*Me*), 18.9, 17.8 ($Me_2C_6H_3$); Isomer β: δ 337.9 (μ-*C*), 263.6 (μ-*C*O), 211.9 (*C*O), 148.3 (*C*-ipso Xyl), 135.1–126.4 (*C*H arom + *C*–Me Xyl + *C*–CF_3), 123.1 (q, $^1J_{CF}$ = 273.6 Hz, C_3), 117.7 (*C*N), 114.0 (*C*–CN), 88.6, 88.3 (*Cp*), 54.4 (N*Me*), 18.7, 17.4 ($Me_2C_6H_3$). ^{19}F NMR ($CDCl_3$, 293 K) Isomer α: δ −64.04; Isomer β: δ −63.91.

2f: Yield: 180.3 mg (85%). Anal. Calc. for $C_{23}H_{21}F_3Fe_2N_2O_5S$: C, 45.58; H, 3.49; N, 4.62. Found: C, 45.64; H, 3.23, N, 4.85%. IR (in CH_2Cl_2, 293 K): (CO) 1982 (vs), 1816 (s); *ν*(CN) 1589 (m). ^{1}H NMR ($CDCl_3$, 293 K): δ 7.52–7.19 (m, 5H, *Ph*), 4.98, 4.91(s, 10H, *Cp*), 4.65, 4.24 (6H, s, NMe_2).

2g: Yield: 219.4 mg (93%). Anal. Calc. for $C_{24}H_{20}F_6Fe_2N_2O_5S$: C, 42.76; H. 2.99; N, 4.16. Found: C, 42.98; H, 2.72, N, 4.34%. IR (in CH_2Cl_2, 293 K): (CO) 1981 (vs), 1816 (s); *ν*(CN) 1589 (ms). ^{1}H NMR ($CDCl_3$, 293 K):δ 8.10–7.71 (m, 4H, *arom*), 5.29, 5.21 (s, 10H, *Cp*), 4.77, 4.43 (s, 6H, NMe_2). ^{13}C NMR ($CDCl_3$, 293 K): δ 329.3 (μ-*C*), 266.6 (μ-*C*O), 212.9 (*C*O), 134.8 (q, $^2J_{CF}$ = 8.4 Hz, *C*–CF_3), 135.0, 134.7 (*C*H *o*-$NCC_6H_4CF_3$), 127.8, 127.6 (q, $^3J_{CF}$ = 4.2 and 3.4 Hz, *C*H *m*-$NCC_6H_4CF_3$), 124.7 (q, $^1J_{CF}$ = 272.3 Hz, C_3), 123.0 (q, $^1J_{CF}$ = 321.8 Hz, *C*$F_3SO_3^-$), 118.8 (*C*N), 117.6 (*C*–CN), 90.4, 89.0 (*Cp*), 54.8, 54.0 (NMe_2).

*4.3. Synthesis of [Fe(Cp)(CO){μ-η^2:η^2-C[N(Me)-(R)]N=C(C_6H_3R')C=CH(Tol)}Fe(Cp)(CO)] (R = Xyl, R′ = H, **3a**; R = Xyl, R′ = Br, **3b**; R = Xyl, R′ = OMe, **3c**; R = Xyl, R′ = CO_2Me, **3d**; R = Xyl, R′ = CF_3, **3e**; R = Me, R′ = H, **3f**; R = Me, R′ = CF_3, **3g**)*

A solution of TolCCLi (1.45 mmol) was prepared by addition at −50 °C of Bu^{n}Li (0.580 ml, 2.5 M in hexane, 1.45 mmol) to TolCCH (0.200 ml, 1.58 mmol) dissolved in THF (5 ml), and the mixture stirred at room temperature for 1 h. This solution was, then, added at −50 °C to **2** (0.720 mmol) dissolved in THF (10 ml), and the mixture stirred at room temperature for 1 h. The resulting red solution was, therefore, filtered through Al_2O_3 in order to remove the excess of TolCCLi, and the solvent removed from the filtrated under reduced pressure. The residue was, then, dissolved in CH_2Cl_2 (3 ml) and chromatographed through Al_2O_3–. The final product was obtained as a red fraction using CH_2Cl_2 as eluent.

3a: Yield: 290.9 mg (61%). Anal. Calc. for $C_{38}H_{34}Fe_2N_2O_2$: C, 68.90; H, 5.17; N, 4.23. Found: C, 68.59; H, 5.36, N, 4.01%. IR (in CH_2Cl_2, 293 K): *ν*(CO) 1915 (vs); *ν*(CN) 1572 (w), 1508 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.77–6.69 (m, 11H, *arom*), 7.26 (s, 1H, =C*H*), 4.24, 3.72 (s, 10H, *Cp*), 3.40 (s, 3H, N*Me*), 2.69, 2.17 (s, 6H, $Me_2C_6H_3$), 2.39 (s, 3H, *Me*C_6H_4); Isomer *Z*: δ 7.77–6.69 (m, 11H, *arom*), 7.61 (s, 1H, =C*H*), 4.39, 3.76 (s, 10H, *Cp*), 3.54 (s, 3H, N*Me*), 2.47, 2.26 (s, 6H, $Me_2C_6H_3$), 2.37 (s, 3H, *Me*C_6H_4). Isomer ratio *E*:*Z* = 10:9.5. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*:δ 253.9 (Fe=*C*), 223.1, 222.5 (*C*O), 203.4 (*C*=N), 189.7 (Fe–*C*=CH), 168.6 (Fe–*C*C_6H_4), 145.1 (*C*-ipso Tol), 144.3 (*C*-ipso Xyl), 136.0 (=*C*H), 135.3, 134.8 (*C*–Me Xyl), 136.8 (*C*–Me Tol), 133.9 (*C*-ipso C_6H_4), 132.7–122.5 (*C*H arom), 84.9, 82.3 (*Cp*), 50.2 (N*Me*), 21.7 (*Me*C_6H_4), 19.4, 19.2 ($Me_2C_6H_3$); Isomer *Z*: δ 256.4 (Fe=*C*), 221.8, 221.5 (*C*O), 203.6 (*C*=N), 201.0 (Fe–*C*=CH), 166.6 (Fe–*C*C_6H_4), 145.4 (*C*-ipso Tol), 144.5 (*C*-ipso Xyl), 139.3 (=*C*H), 135.4, 134.5 (*C*–Me Xyl), 137.1 (*C*–Me Tol), 139.8 (*C*-ipso C_6H_4), 132.7–122.5 (*C*H arom), 85.2, 82.5 (*Cp*), 51.0 (N*Me*), 22.0 (*Me*C_6H_4), 20.1, 19.8 ($Me_2C_6H_3$).

3b: Yield: 298.9 mg (56%). Anal. Calc. for $C_{38}H_{33}BrFe_2N_2O_2$: C, 61.57; H, 4.49; N, 3.78. Found: C, 61.85; H, 4.09, N, 3.85%. IR (in CH_2Cl_2, 293 K): *ν*(CO) 1918 (vs); *ν*(CN) 1554 (m), 1508 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 7.83 (s, 1H, C*H* *o*-C_6H_3Br), 7.77–6.86 (m, 9H, *arom*), 6.79 (s, 1H, =C*H*), 4.31, 3.78 (s, 10H, *Cp*), 3.42 (s, 3H, N*Me*), 2.73, 2.18 (s, 6H, $Me_2C_6H_3$), 2.40 (s, 3H, *Me*C_6H_4); Isomer *Z*: δ 8.00 (s, 1H, C*H* *o*-C_6H_3Br), 7.77–6.86 (m, 9H, *arom*), 7.61 (s, 1H, =C*H*), 4.44, 3.82 (s, 10H, *Cp*), 3.56 (s, 3H, N*Me*), 2.52, 2.21 (s, 6H, $Me_2C_6H_3$), 2.33 (s, 3H, *Me*C_6H_4). Isomer ratio *E*:*Z* = 10:5.9. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 252.9 (Fe=*C*), 222.8, 222.3 (*C*O),

202.9 (*C*═N), 186.2 (Fe–*C*═CH), 168.4 (Fe–*C*C_6H_3Br), 145.9 (*C*H *o*-C_6H_3Br), 145.0–118.2 (arom), 130.1 (═*C*H), 84.9, 82.2 (*Cp*), 50.2 (N*Me*), 21.9 (*Me*C_6H_4), 19.7, 19.1 ($Me_2C_6H_3$); Isomer *Z*: δ 256.8 (Fe═*C*), 221.7, 221.2 (*C*O), 205.9 (Fe–*C*═CH), 202.0 (*C*═N), 166.5 (Fe–*C*C_6H_3Br), 146.1 (*C*H *o*-C_6H_3Br), 145.0–118.2 (arom), 139.8 (═*C*H), 85.2, 82.4 (*Cp*), 51.1 (N*Me*), 21.7 (*Me*C_6H_4), 20.0, 19.4 ($Me_2C_6H_3$).

3c: Yield: 289.2 mg (58%). Anal. Calc. for $C_{39}H_{36}Fe_2N_2O_3$: C, 67.65; H, 5.24; N, 4.05. Found: C, 67.39; H, 5.47, N, 4.39%. IR (in CH_2Cl_2, 293 K): *v*(CO) 1915 (vs); *v*(CN) 1575 (m), 1509 (m). ^{1}H NMR ($CDCl_3$, 293 K): Isomer *E*: δ 7.86–6.33 (m, 9H, *arom*), 7.60 (s, 1H, C*H* *o*-C_6H_3OMe), 6.71 (s, 1H, ═C*H*), 4.28, 3.78 (s, 10H, *Cp*), 3.82 (s, 3H, O*Me*), 3.47 (s, 3H, N*Me*), 2.59, 2.39 (s, 6H, $Me_2C_6H_3$), 2.30 (s, 3H, *Me*C_6H_4); Isomer *Z*: δ 7.86–6.33 (m, 9H, *arom*), 7.82 (s, 1H, C*H* *o*-C_6H_3OMe), 7.35 (s, 1H, ═C*H*), 4.41, 3.78 (s, 10H, *Cp*), 3.90 (s, 3H, O*Me*), 3.56 (s, 3H, N*Me*), 2.75, 2.16 (s, 6H, $Me_2C_6H_3$), 2.42 (s, 3H, *Me*C_6H_4). Isomer ratio *E*:*Z* = 1:1.04. ^{13}C NMR ($CDCl_3$, 293 K): Isomer *E*: δ 257.0 (Fe═*C*), 223.3, 222.1 (*C*O), 208.0 (*C*═N), 194.3 (Fe–*C*═CH), 168.9 (*C*–OMe), 158.2 (Fe–*C*C_6H_3OMe), 145.4 (*C*-ipso Xyl), 139.8–111.4 (arom + ═*C*H), 84.6, 82.5 (*Cp*), 55.3 (O*Me*), 50.9 (N*Me*), 21.4 (*Me*C_6H_4), 20.0, 19.7 ($Me_2C_6H_3$); Isomer *Z*: δ 256.0 (Fe═*C*), 222.5, 222.2 (*C*O), 206.0 (Fe–*C*═CH), 203.6 (*C*═N), 166.9 (*C*–OMe), 158.4 (Fe–*C*C_6H_3OMe), 145.3 (*C*-ipso Xyl), 139.8–111.4 (arom + ═*C*H), 85.1, 82.3 (*Cp*), 55.5 (O*Me*), 50.2 (N*Me*), 21.7 (*Me*C_6H_4), 19.4, 19.2 ($Me_2C_6H_3$).

3d: Yield: 280.1 mg (54%). Anal. Calc. for $C_{40}H_{36}Fe_2N_2O_4$: C, 66.69; H, 5.04; N, 3.89. Found: C, 66.92; H, 5.29, N, 3.56%. IR (in CH_2Cl_2, 293 K): *v*(CO) 1917 (vs); *v*(COOMe) 1716 (m); *v*(CN) 1508 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 8.15–6.96 (m, 9H, *arom*), 7.67 (s, 1H, C*H* *o*-C_6H_3COOMe), 6.78 (s, 1H, ═C*H*), 4.26, 3.74 (s, 10H, *Cp*), 3.88 (s, 3H, COO*Me*), 3.33 (s, 3H, N*Me*), 2.69, 2.14 (s, 6H, $Me_2C_6H_3$), 2.27 (s, 3H, *Me*C_6H_4); Isomer *Z*: δ 8.22 (s, 1H, C*H* *o*-C_6H_3COOMe), 8.15–6.96 (m, 9H, *arom*), 7.77 (s, 1H, ═C*H*), 4.40, 3.80 (s, 10H, *Cp*), 3.93 (s, 3H, COO*Me*), 3.53 (s, 3H, N*Me*), 2.44, 2.17 (s, 6H, $Me_2C_6H_3$), 2.37 (s, 3H, *Me*C_6H_4). Isomer ratio *E*:*Z* = 5:3. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 249.0 (Fe═*C*), 222.8, 222.3 (*C*O), 197.5 (*C*═N), 177.1 (Fe–*C*═CH), 168.3 (*C*OOMe), 150.2 (Fe–*C*C_6H_3COOMe), 144.7 (*C*-ipso Xyl), 143.9 (═*C*H), 139.7–123.3 (arom), 85.2, 82.1 (*Cp*), 52.2 (COO*Me*), 49.7 (N*Me*), 21.6 (*Me*C_6H_4), 19.6, 19.1 ($Me_2C_6H_3$); Isomer *Z*: δ 255.6 (Fe═*C*), 221.5, 220.8 (*C*O), 201.9 (Fe–*C*═CH), 199.7 (*C*═N), 168.7 (*C*OOMe), 150.9 (Fe–*C*C_6H_3COOMe), 144.3 (*C*-ipso Xyl), 144.0 (═*C*H), 139.7–123.3 (arom), 85.3, 82.4 (*Cp*), 52.4 (COO*Me*), 51.0 (N*Me*), 21.3 (*Me*C_6H_4), 20.0, 19.4 ($Me_2C_6H_3$).

3e: Yield: 315.5 mg (60%). Anal. Calc. for $C_{39}H_{33}F_3Fe_2N_2O_2$: C, 64.13; H, 4.55; N, 3.84. Found: C, 64.41; H, 4.17, N, 4.01%. IR (in CH_2Cl_2, 293 K): (CO) 1921 (vs); *v*(CN) 1508 (m). ^{1}H NMR ($CDCl_3$, 293 K) Isomer *E*: δ 8.08–6.70 (m, 10H, *arom*), 6.83 (s, 1H, ═C*H*), 4.30, 3.77 (s, 10H, *Cp*), 3.37 (s, 3H, N*Me*), 2.71, 2.17 (s, 6H, $Me_2C_6H_3$), 2.31 (s, 3H, *Me*C_6H_4); Isomer *Z*: δ 8.08–6.70 (m, 10H, *arom*), 7.84 (s, 1H, ═C*H*), 4.45, 3.83 (s, 10H, *Cp*), 3.57 (s, 3H, N*Me*), 2.45, 2.24 (s, 6H, $Me_2C_6H_3$), 2.41 (s, 3H, *Me*C_6H_4). Isomer ratio *E*:*Z* = 3:2. ^{13}C NMR ($CDCl_3$, 293 K) Isomer *E*: δ 249.1 (Fe═*C*), 222.5, 222.0 (*C*O), 198.2 (*C*═N), 177.2 (Fe–*C*═CH), 167.8 (Fe–*C*$C_6H_3CF_3$), 148.5 (*C*-ipso $C_6H_3CF_3$), 144.4 (*C*-ipso Xyl), 140.0–118.8 (arom + C_3), 130.7 (═*C*H), 84.8, 81.8 (*Cp*), 50.8 (N*Me*), 21.3 (*Me*C_6H_4), 19.3, 18.8 ($Me_2C_6H_3$); Isomer *Z*: δ 255.1 (Fe═*C*), 221.1, 220.4 (*C*O), 202.5 (Fe–*C*═CH), 199.6 (*C*═N), 166.2 (Fe–*C*$C_6H_3CF_3$), 149.4 (*C*-ipso $C_6H_3CF_3$), 144.9 (*C*-ipso Xyl), 140.0–118.8 (arom + C_3), 139.1 (═*C*H), 85.0, 82.1 (*Cp*), 49.5 (N*Me*), 21.6 (*Me*C_6H_4), 19.7, 19.1 ($Me_2C_6H_3$). ^{19}F NMR ($CDCl_3$, 293 K) Isomer *E*: δ −62.72; Isomer *Z*: δ −62.75.

3f: Yield: 234.9 mg (57%). Anal. Calc. for $C_{31}H_{28}Fe_2N_2O_2$: C, 65.06; H, 4.93; N, 4.90. Found: C, 65.27; H, 4.69, N, 5.02%. IR (in CH_2Cl_2, 293 K): *v*(CO) 1926 (vs); *v*(CN) 1508 (m). ^{1}H NMR ($CDCl_3$, 293 K): δ 8.06–6.55 (m, 8H, *arom*), 7.87 (s, 1H, ═C*H*), 4.57, 4.49 (s, 10H, *Cp*), 3.63, 3.58 (s, 6H, NMe_2), 2.39 (s, 3H, *Me*C_6H_4). ^{13}C NMR ($CDCl_3$, 293 K): δ 268.3 (Fe═*C*), 220.8, 218.8 (*C*O), 208.5 (*C*═N), 197.1 (Fe–*C*═CH), 163.8 (Fe–*C*C_6H_4), 144.3 (═*C*H), 142.9 (*C*-ipso C_6H_4), 141.1 (*C*-ipso Tol), 138.5 (*C*–Me Tol), 132.6–119.1 (*C*H arom), 84.0, 82.8 (*Cp*), 49.8, 42.6 (NMe_2), 21.6 (*Me*C_6H_4).

3g: Yield: 295.0 mg (64%). Anal. Calc. for $C_{32}H_{27}F_3Fe_2N_2O_2$: C, 60.03; H, 4.25; N, 4.38. Found: C, 60.29; H, 4.02, N, 4.05%. IR (in CH_2Cl_2, 293 K): (CO) 1930 (vs); *v*(CN) 1539 (w), 1507 (m). ^{1}H NMR ($CDCl_3$, 293 K): δ 8.09 (s, 1H, ═C*H*), 7.91–7.15 (m, 7H, *arom*), 4.57, 4.51 (s, 10H, *Cp*), 3.64, 3.58 (s, 6H, NMe_2), 2.38 (s, 3H, *Me*C_6H_4). ^{13}C NMR ($CDCl_3$, 293 K): δ 269.2 (Fe═*C*), 220.5, 218.1 (*C*O), 207.5 (*C*═N), 197.3 (Fe–*C*═CH), 163.7 (Fe–*C*$C_6H_3CF_3$), 146.8 (*C*-ipso $C_6H_3CF_3$), 143.1 (*C*H *o*-$C_6H_3CF_3$), 139.6 (═*C*H), 139.8 (*C*-ipso Tol), 137.3 (*C*–Me Tol), 132.9–118.9 (*C*H arom + C_3 + *C*–CF_3), 84.0, 82.9 (*Cp*), 50.1, 42.8 (NMe_2), 21.6 (*Me*C_6H_4). ^{19}F NMR ($CDCl_3$, 293 K): δ −62.70.

4.4. X-ray structural determinations

Compounds **3b**, **3c** · **0.5C_5H_{12}**, **3e** and **3g** · **C_5H_{12}** were crystallised from CH_2Cl_2/pentane at −20 °C. Crystal data and collection details are reported in Table 3. The diffraction experiments were carried out on a Bruker SMART 2000 diffractometer equipped with a CCD detector using Mo Kα radiation. Data were corrected for Lorentz polarization and absorption effects

Table 3
Crystal data and experimental details for **3b**, **3c** · **0.5C$_5$H$_{12}$**, **3e** and **3g** · **C$_5$H$_{12}$**

Complex	**3b**	**3c** · **0.5C$_5$H$_{12}$**	**3e**	**3g** · **C$_5$H$_{12}$**
Formula	$C_{38}H_{33}BrFe_2N_2O_2$	$C_{41.5}H_{42}Fe_2N_2O_3$	$C_{39}H_{33}F_3Fe_2N_2O_2$	$C_{37}H_{39}F_3Fe_2N_2O_2$
Formula weight	741.27	728.47	730.37	712.40
T (K)	293(2)	293(2)	150(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$C2/c$
a (Å)	14.411(3)	9.988(2)	14.397(3)	33.456(7)
b (Å)	16.116(3)	17.106(3)	16.236(3)	12.717(3)
c (Å)	15.460(3)	22.806(5)	15.189(3)	22.746(5)
α (°)	90	71.26(3)	90	90
β (°)	114.53(3)	88.67(3)	114.50(3)	131.16(3)
γ (°)	90	79.19(3)	90	90
Cell volume (Å^3)	3266.5(11)	3621.6(13)	3230.7(11)	7286(3)
Z	4	4	4	8
D_c (g cm^{-3})	1.507	1.336	1.502	1.299
μ (mm^{-1})	2.148	0.842	0.954	0.844
F(0 0 0)	1512	1524	1504	2960
Crystal size (mm)	0.19 × 0.16 × 0.11	0.24 × 0.21 × 0.13	0.36 × 0.26 × 0.19	0.21 × 0.15 × 0.12
θ limits (°)	1.63–25.03	0.94–25.03	1.64–25.68	1.62–25.02
Reflections collected	28,607	28,638	29,661	31,663
Independent reflections (R_{int})	5773 (0.1301)	12,784 (0.0809)	6134 (0.0520)	6431 (0.0991)
Data/restraints/parameters	5773/0/410	12,784/477/847	6134/0/437	6431/371/455
Goodness-on-fit on F^2	0.911	0.917	1.033	1.065
R_1 [$I > 2\sigma(I)$]	0.0658	0.0660	0.0355	0.0773
wR_2 (all data)	0.1887	0.1947	0.0799	0.2412
Largest differential peak and hole (e Å^{-3})	0.453/−0.901	0.683/−0.399	0.538/−0.847	0.879/−0.877

(empirical absorption correction SADABS) [20]. Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [21]. Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated. The Cp ligands bound to Fe(1), Fe(2) and Fe(3) in **3c** · **0.5C$_5$H$_{12}$** and the CF_3 group in **3g** · **C$_5$H$_{12}$** are disordered over two positions, whereas the C_5H_{12} molecule in **3g** · **C$_5$H$_{12}$** is disordered over four positions. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group. In the case of the C_5H_{12} molecule in **3g** · **C$_5$H$_{12}$** the sum of the occupancy parameters for the four positions was restrained to unit. Two independent molecules are present in the asymmetric unit of **3c** · **0.5C$_5$H$_{12}$**.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 251913 for **3b**, 251914 for **3c** · **0.5C$_5$H$_{12}$**, 251915 for **3e** and 251916 for **3g** · **C$_5$H$_{12}$**. Copies of this information can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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