**Reactions of Diiron μ-Aminocarbyne Complexes Containing Nitrile Ligands.**

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**Abstract**

The acetonitrile ligand in the μ-aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (R = Me, **2a**, $CH_2Ph$, **2b**, Xyl, **2c**) (Xyl = 2,6-$Me_2C_6H_3$) is readily displaced by halides and cyanide anions affording the corresponding neutral species $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(X)(Cp)_2]$ (X = Br, I, CN). Complexes **2** undergo deprotonation and rearrangement of the coordinated MeCN upon treatment with organolithium reagents. Trimethylacetonitrile, that does not contain acidic α hydrogens has been used in place of MeCN to form the complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCCMe_3)(Cp)_2][SO_3CF_3]$ (**7a-c**). Attempts to replace the nitrile ligand in **3** with carbon nucleophiles (by reaction with RLi) failed, resulting in decomposition products. However the reaction of **7c** with LiC≡CTol (Tol = $C_6H_4Me$), followed by treatment with $HSO_3CF_3$, yielded the imino complex $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)\{N(H)C(C{\equiv}CC_6H_4Me\text{-}4)CMe_3\}(Cp)_2][SO_3CF_3]$ (**8**), obtained *via* acetilyde addition at the coordinated $NCCMe_3$.

Keywords: Acetonitrile, Nitrile activation, Carbyne complexes, dinuclear complexes, C-C bond formation

## 1. Introduction

The formation of C-C bonds in dinuclear transition metal complexes, by coupling reactions of coordinated hydrocarbon ligands, attracts considerable attention because these reactions can act as models for the surface species involved in heterogeneously catalyzed processes.[1] Among the complexes studied, those containing μ-methylidene and μ-methylidyne ligands are of particular interest since they are supposed to play an important role in the Fischer -Tropsch processes.[2]

In recent years we have found that the formation of C-C bond in bridging aminocarbyne complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, **1a**; $CH_2Ph$; **1b**; Xyl, **1c**) (Xyl = 2,6-$Me_2C_6H_3$) can be achieved by addition of carbon nucleophiles ($R'^-$) which occurs selectively at different ligands: organocuprates and acetylides attack the carbonyl carbon to form the acyl complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(COR')(Cp)_2]$, whereas organolithium or Grignard reagents give preferentially addition to the $C_5H_5$ ring yielding the dienyl complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)(C_5H_5R')]$.[3]

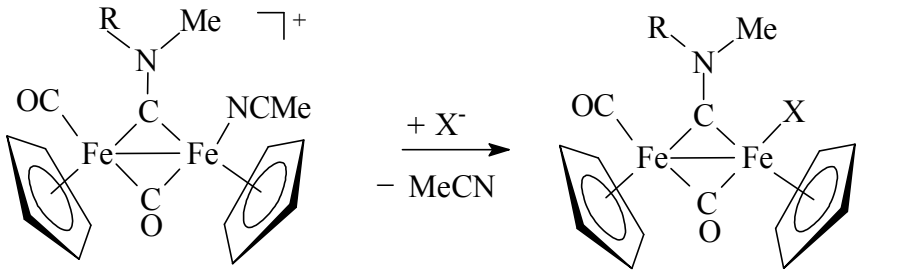
Surprisingly, none of the above nucleophilic additions involve the μ-C of the aminocarbyne ligand, which appears rather unreactive, particularly if compared with the powerful electrophilic character of the μ-methylidyne carbon in the related complex $[Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$.[4] Only cyanide (from $Nbu_4CN$) has been found to react at the carbyne carbon to yield the aminocarbene complex $[Fe_2\{\mu\text{-}C(CN)N(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]$.[5] A possible explanation of such inertness resides in the strong π-interaction between nitrogen and the carbyne carbon, which suggests a large contribution of the μ-iminium structure (μ-C=NRR').[6]

The bridging methylidene ligand in $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(Cp)_2]$ is also rather unreactive. However the corresponding acetonitrile complex $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(CNR)(Cp)_2]$ has been found to undergo C-C coupling reactions with unsaturated hydrocarbons and diazoalkanes,[7] demonstrating that the presence of a labile ligand is crucial for allowing coordination of hydrocarbyl fragments, and promoting their intramolecular coupling with the $\mu\text{-}CH_2$.

On the light of these considerations, we decided to investigate the reactivity of diiron aminocarbyne complexes containing a nitrile ligand, towards nucleophiles, including carbon nucleophiles, with the aim of testing the possibility of C-C bond formation.

## 2. Results and discussion

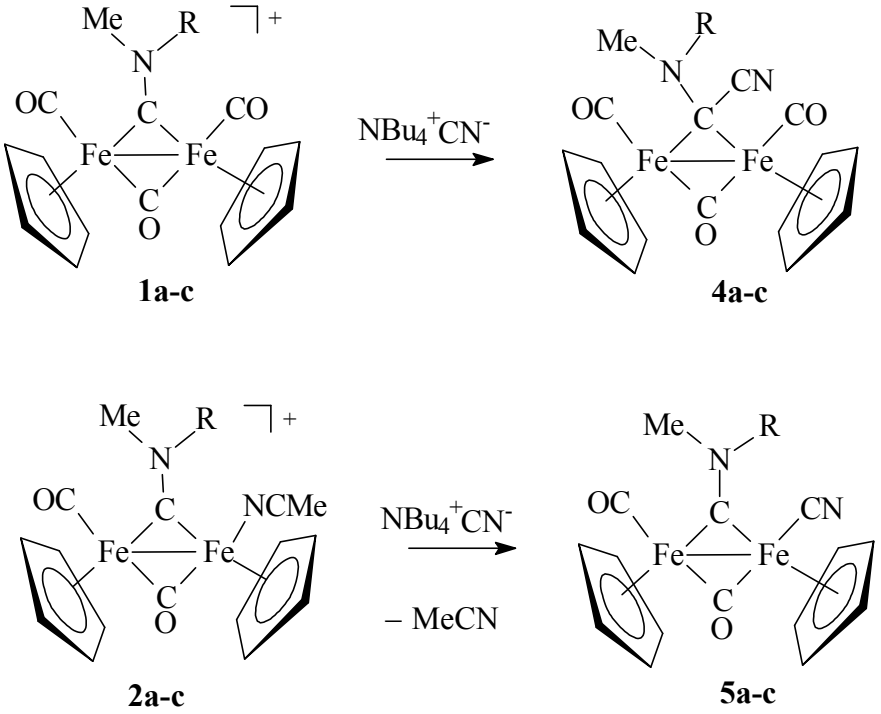
A terminal carbonyl ligand in $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ **1a-c** is readily displaced by MeCN upon treatment with $Me_3NO$ in refluxing acetonitrile, affording $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (R = Me, **2a**; $CH_2Ph$; **2b**; Xyl, **2c**).[8] Nitrile-containing complexes have been often considered equivalent for the coordinatively unsaturated species because of the substitution lability that nitrile ligands usually exhibits.[9] As expected, the complexes **2a-c** undergo displacement of MeCN by a variety of ligands which include phosphines isocyanides, halides and cyanides. Most of these substitution reactions have been previously described.[8,10] In the experimental part are given details about the preparation and spectroscopic properties of the novel halide complexes $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)(X)(Cp)_2]$ ( X= Br, **3a**; I, **3b**); scheme 1.




Scheme 1

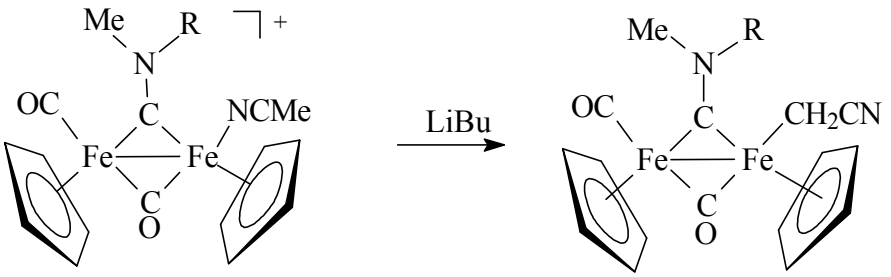
The spectroscopic properties of **3a** are similar to those of the chloride complex $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)(Cl)(Cp)_2]$ previously reported.[8] Both chloride and bromide complexes show the presence, in $CDCl_3$ solution, of only the *cis* isomer as usually found in di-iron μ-aminocarbyne complexes [3, 11] (*cis* and *trans* are referred to the mutual position of the Cp rings with respect to the Fe-Fe bond). By contrast, the iodide complex **3b** consists of two isomers. A possible explanation is that, due to bulkiness of the iodide ligand, both *cis* and *trans* isomers are present.

The reactions of **2a-c** with cyanide well illustrate the change in the reactivity pattern induced by the presence of the acetonitrile ligand. In fact, whereas the addition of cyanide occurs at the carbyne carbon of **1a-c** to form the alkylidene compounds $[Fe_2\{\mu\text{-}C(CN)N(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2]$ (**4a-c**),[5] the corresponding acetonitrile complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (**2a-c**) react with $CN^-$ leading to the formation of $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(CN)(Cp)_2]$ (**5a-c**) (scheme 2).[8]




Scheme 2

Therefore the MeCN ligand in **2a-c** seems able to direct selectively the nuclephilic attack at the metal atom. In order to determine whether this would apply to carbon nucleophiles like organolithium or organocopper reagents, the reactions of **2a-c** with LiR have been studied. The results reported in scheme 3 show that organolithium reagents behave towards **2a-c** like strong bases rather than nucleophiles, determining the deprotonation of the coordinated MeCN instead of giving its displacement, and yielding the cyano methyl complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(CH_2CN)(Cp)_2]$ (**6a-c**).[12] Proton abstraction from coordinated acetonitrile is not surprising, and its enhanced acidity has been exploited to catalyze MeCN condensation with carbonyl compounds.[13] However the rearrangement to cyanomethyl ligand is rather unusual and has been previously observed only in the case of $[RhOs(CH_2CN)(CO)_3(dppm)_2]$.[14]




**2a-c** R = Me a, $CH_2Ph$ b, Xyl c **6**a-c

Scheme 3

Since the acetonitrile ligand in compounds **2a-c** can not be displaced by organolithium reagents, we have examined the synthesis and reactivity of diiron complexes containing trimetylacetonitrile in place of MeCN. The absence of acidic α-C-H in $NCCMe_3$ should allow the treatment with carbon nucleophiles, providing access to dinuclear complexes with hydrocarbyl ligands of the type $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(R')(Cp)_2]$, (R' = alkyl, aryl, vinyl or alkynyl).

The synthesis and the spectroscopic properties of the trimeylacetonitrile complexes $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)(NCCMe_3)(Cp)_2][SO_3CF_3]$ (R = Me, 7a; $CH_2Ph$; **7b**; Xyl, **7c**) well parallel those of **2a-c**. They have been obtained upon treatment of **1a-c** with a slight excess of $Me_3CCN$ in THF solution in the presence of $Me_3NO$.

The IR spectra of **7a-c**, in $CH_2Cl_2$ solution, exhibit one terminal and one bridging carbonyl absorption (e.g. at 1982 and 1815 $cm^{-1}$ for **7a**). The $^1H$ and $^{13}C$ NMR spectra show two signals of the same intensity for the non-equivalent Cp groups (for **7a** at 5.01, 4.85 and 89.0 87.5 ppm, respectively). Likewise each of the N-bonded methyl groups in **7a** gives rise to a singlet resonance. The NMR spectra of **7b**, which contain the asymmetrically substituted

μ-C=N(Me)($CH_2$Ph) show the presence of two isomers in solution. These isomeric forms, which are usually found in complexes of the type [$Fe_2${μ-CN(Me)R}(μ-CO)(CO)(L)$(Cp)_2$] and indicated as α and β isomers,[3a, 10, 11, 15] are due to the different orientation of R and Me with respect to the non equivalent Fe atoms (figure 1). Compound **7c** consist of only one of the two possible α and β isomers. This is presumably due to the large difference of steric demand of the Me and Xyl groups, which inhibits the formation of more hindered isomer. It should be reminded that interconvertion of the α and β isomers *via* rotation around the μ-C–N bond is not possible due to the double bond character of this interaction.

The $^{13}$C NMR spectra of **7a-c**, exhibit the characteristic low field signal of the bridging carbyne carbon (e.g. at 339.0 ppm for **7c**).

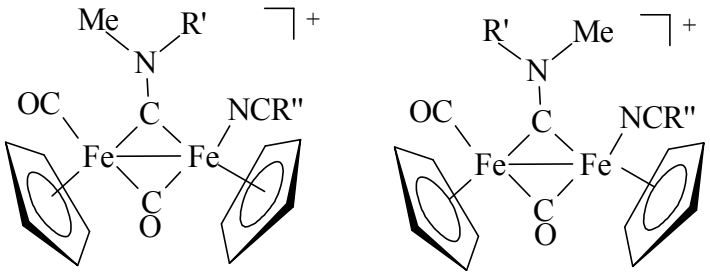
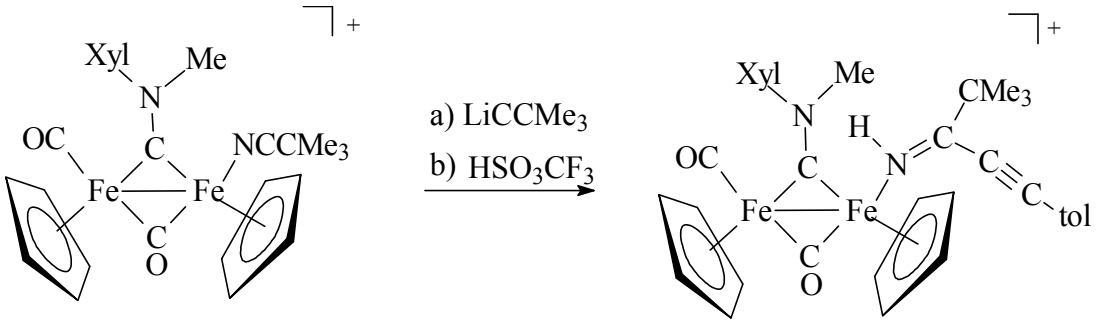



Figure1. α and β isomeric forms

The reactions of [$Fe_2${μ-CN(Me)Xyl}(μ-CO)(CO)($NCCMe_3$)$(Cp)_2$][$SO_3CF_3$] **7c** with several organo lithium RLi, (R = Me, Bu, C≡CPh), reagents have been investigated. The expected displacement of the nitrile ligand by the carbon nucleophile does not take place and the reaction mixtures contain unidentified decomposition products. On the other hand organo-lithium regents are also strong reducing agent and since it is known [16] that the aminocarbyne

complexes **1b** can be reduced to the unstable radical $[Fe_2\{\mu\text{-}CN(Me)CH_2Ph\}(\mu\text{-}CO)(CO)_2(Cp)_2]^{\bullet}$, it is likely that the above reactions of **7c** proceed through a radical mechanism. A remarkable exception to this general trend is represented by the reaction with LiCCtol: treatment of **7c** with tolylacetylide followed by addition of $HSO_3CF_3$ results in the formation of the imine complex $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)\{N(H)C(C{\equiv}CC_6H_4Me\text{-}4)CMe_3\}(Cp)_2]$ $[CF_3SO_3]$ (**8**), scheme 4.




7c **8**

Scheme 4

Compound **8** has been characterized by elemental analyses and IR and NMR spectroscopy.

The IR spectra, in $CH_2Cl_2$ solution, exhibit one terminal and one bridging carbonyl at 1977 and 1817 $cm^{-1}$, respectively. Evidence of the imine coordination is given by the IR spectra, ν(N-H) at 3314 (in KBr pellets) and by $^1H$ NMR resonace at 6.12 ppm due to the N-H proton. Major features, in the $^{13}C$ NMR spectra of **8** include the expected low-field resonance of the μ-aminocarbyne carbon (at 340.1 ppm), which indicates that the carbyne ligand has been unaffected by the reaction, and the signal attributable to the imine carbon at 186.7 ppm.

The formation of complex **8** is the result of a nucleophilic attack at the coordinated $NCCMe_3$, which presumably form the azavinylidene intermediate $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)\{N{=}C(C{\equiv}CC_6H_4Me\text{-}4)CMe_3\}(Cp_2)]$ (**9**). In spite of the fact that several azavinylidene complexes are known, [17] the intermediate **9** appears too unstable in our hands to be characterized even by spectroscopy. However nitrogen protonation transform the azavinyldene into the more stable imine complex **8**.

Nucleophilic addition at coordinated nitriles is not a rare occurrence, in spite of the fact that they usually behave as labile ligands.[18] However additions generally involve water, alcohols, amines and only at very low extent, carbon nucleophiles with formation of imine ligands.[19]

Finally it should be underlined that the formation of **9** from the nitrile precursor **7c,** as well as the synthesis of the cyanomethyl **6a-c**, indicate that nitrile ligands are strongly activated by coordination to the diiron μ-aminocarbyne frame, and that, far from behaving exclusivly as labile ligands, they show a remarkable reactivity.

## 3. Experimental details

### *3.1. 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. Glassware was oven-dried before use. Infrared spectra were recorded on a Perkin-Elmer 983-G spectrophotometer, $^1H$ and $^{13}C$ NMR spectra on a Varian Gemini 300. Unless otherwise stated, NMR signals due to trace amounts of second isomeric form 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 from Strem and used as received. Compounds

$[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me **2a** R=$CH_2Ph$ **2b,** $Me_2C_6H_3$ **2c**) [3a, 11] were prepared as described in the literature.

*3.2. Syntheses of $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)(Br)(Cp)_2]$ (**3a**) and $[Fe_2\{\mu\text{-}CN(Me)Xyl\}(\mu\text{-}CO)(CO)(I)(Cp)_2]$ (**3b**)*

Potassium bromide (445 mg, 3.71 mmol) was added to a solution of $[Fe_2\{\mu\text{-}CN(Me)(Xyl)\}(\mu\text{-}CO)(CO)(NCMe)(Cp)_2][SO_3CF_3]$ (**2c**) (170 mg, 0.26 mmol) in THF (15 mL) and the mixture was heated at refluxing temperature for 30 min. Removal of the solvent gave a brown residue that was chromatographed on alumina using THF and diethyl ether (1:1) as eluent. Crystallization from $CH_2Cl_2$ and $Et_2O$ afforded **3a** (120 mg, 85%). Analysis. Found: C, 50.41; H, 4.25%. $C_{22}H_{22}BrFe_2NO_2$ requires: C, 50.42; H, 4.23%. IR ($CH_2Cl_2$) $\nu_{max}(cm^{-1})$ 1979vs and 1797s (CO). NMR: $\delta_H$ ($CDCl_3$): 7.39-7.20 (3 H, m $C_6H_4$), 4.90 (3 H, s, NMe), 4.75 (5 H, s, Cp), 4.30 (5 H, s, Cp), 2.75 and 2.22 (6 H, s, $Me_2C_6H_3$). $\delta_C$ ($CDCl_3$): 342.8 ($\mu$-C), 267.5 ($\mu$-CO), 214.0 (CO), 149.3 (ipso- $Me_2C_6H_3$), 135.1-128.9 ($Me_2C_6H_3$), 87.1 (Cp); 53.8 (N-Me), 19.3 and 18.3 ($Me_2C_6H_3$).

Compound **3b** was obtained from 2c and KI following the same procedure described for the synhesis of **3a**.

**3b**: (88%). Analysis. Found: C, 46.31; H, 3.90%. $C_{22}H_{22}Fe_2INO_2$ requires: C, 46.27; H, 3.88%. Signals due to a second isomeric form (in about 0.8 ratio) are italicized IR ($CH_2Cl_2$) $\nu_{max}(cm^{-1})$ *1974*vs, 1953vs and 1797s (CO). NMR $\delta_H$ ($CDCl_3$): 7.39-7.20 (3 H, m $C_6H_4$), 4.94, *4.82* (3 H, s, NMe), *4.77*, 4.75, *4.30*, 4.26, (10 H, s, Cp), *2.74*, 2.57, 2.48, and *2.26* (6 H, s, $Me_2C_6H_3$). $\delta_C$ ($CDCl_3$): *344.1*, 341.5 ($\mu$-C), 267.9, *266.1* ($\mu$-CO), 215.7, *214.6* (CO), *149.8*, 149.4 (ipso-$C_6H_3Me_2$), 135.3-128.9 ($C_6H_3Me_2$), *90.4*, *88.1*, 87.2, 86.9, (Cp), 55.5, *55.3* (N-Me); 19.3, *18.5* and 18.3 ($C_6H_3Me_2$).

*3.3. Synthesis of [$Fe_2$($\mu$-$CNMe_2$)($\mu$-CO)(CO)($NCCMe_3$)($Cp)_2$][$SO_3CF_3$] (**7a**), [$Fe_2${$\mu$-CN(Me)($CH_2Ph$)}($\mu$-CO)(CO)($NCCMe_3$)($Cp)_2$][$SO_3CF_3$] (**7b**), [$Fe_2${$\mu$-CN(Me)(Xyl)}($\mu$-CO)(CO)($NCCMe_3$)($Cp)_2$][$SO_3CF_3$] (**7c**),*

Compound **1a** (320 mg, 0.60 mmol) and trimethylacetonitrile (100 mg, 1.20 mmol) in THF (10 mL) was treated with anhydrous $Me_3NO$ (45 mg, 0.60 mmol) and the mixture was stirred for 120 min. Filtration on a Celite pad and removal of the solvent gave a brown residue that was whashed with petroleum ether (bp. 40-60 °C) and crystallized from $CH_2Cl_2$ layered with n-pentane at –20 °C yielding **7a** as a brown microcrystalline solid (253 mg mg, 72%). Analysis. Found: C, 43.31; H, 4.36%. $C_{21}H_{25}F_3Fe_2N_2O_5S$ requires: C, 43.03; H, 4.30%. IR ($CH_2Cl_2$) $\nu_{max}$($cm^{-1}$) 1982vs and 1815s (CO). NMR $\delta_H$ ($CDCl_3$): 5.01 (5 H, s, Cp), 4.85 (5 H, s, Cp), 4.62 (3 H, s, NMe), 4.31 (3 H, s, NMe), and 1.03 (9 H, C*Me*$_3$). $\delta_C$ ($CDCl_3$): 329.9 (μ-*C*), 267.3 (μ-CO), 211.9 (CO), 139.2 (N*C*$CMe_3$), 89.0, 87.5 (Cp), 54.2, 53.3 ($NMe_2$), 31.3, and 28.2 (NC*Me*$_3$).

Compounds **7b** and **7c** were obtained from **2b** and **2c**, respectively, following the same procedure above described.

**7b**: (77%) Analysis. Found: C, 48.91; H, 4.47%. $C_{27}H_{29}F_3Fe_2N_2O_5S$ requires: C, 48.96; H, 4.41%. IR ($CH_2Cl_2$) $\nu_{max}$($cm^{-1}$) 1981vs and 1815s (CO). NMR (α isomer): $\delta_H$ ($CDCl_3$): 7.41-7.22 (8 H, m, $C_6H_5$ and $Me_2C_6H_3$), 5.95, 5.78 (2 H, d, J = 19 Hz, C$H_2$Ph), 4.97 (5 H, s, Cp), 4.92 (5 H, s, Cp), 4.45 (3 H, s, NMe), and 1.03 (9 H, s, C*Me*$_3$); (β isomer): $\delta_H$ ($CDCl_3$): 7.41-7.22 (8 H, m, $C_6H_5$ and $Me_2C_6H_3$), 6.42, 6.36 (2 H, d, J = 19 Hz, C$H_2$Ph), 5.05 (5 H, s, Cp), 4.85 (5 H, s, Cp), 4.18 (3 H, s, NMe), and 1.03 (9 H, s, C*Me*$_3$); (α:β ratio = 0.9)

**7c**: (89%). Analysis. Found: C, 50.01; H, 4.69%. $C_{28}H_{31}F_3Fe_2N_2O_5S$ requires: C, 49.72; H, 4.62%. IR ($CH_2Cl_2$) $\nu_{max}$($cm^{-1}$) 1987vs and 1821s (CO). NMR $\delta_H$ ($CDCl_3$): 7.42-

7.04 (8 H, m, $C_6H_5$ and $Me_2C_6H_3$), 4.98 (5 H, s, Cp), 4.47 (5 H, s, Cp), 4.78 (3 H, s, NMe), 2.68, 2.14 (6 H, s, $Me_2C_6H_3$), and 1.11 (9 H, $CMe_3$). $\delta_C$ ($CDCl_3$): 339.0 (μ-*C*), 265.2 (μ-CO), 212.5 (CO), 148.8 (N*C*$CMe_3$), 141.1-129.7 ( $Me_2C_6H_3$), 88.8, 88.4 (Cp), 56.1 (NMe), 31.5, 28.3(NC*Me*$_3$), 19.5 and 18.2 ($Me_2C_6H_3$).

*3.4. Synthesis of [$Fe_2${μ-CN(Me)(Xyl)}(μ-CO)(CO){NHC(C≡$CC_6H_4$Me-4)$CMe_3$}$(Cp)_2$][$SO_3CF_3$] (**8**).*

A solution of LiC≡$CC_6H_4$Me-4, (freshly prepared from n-butyllithium and 4-ethynyltoluene 0.50 mmol) in THF (10 mL), was added to a stirred solution of **7c** (320 mg, 0.47 mmol), in THF (7 mL), at -30°C. The mixture was stirred for 15 min. and the color changed to brownish-green. Then $HSO_3CF_3$ (0.045 mL, 0.51 mmol) was added dropwise and the mixture turned immediately dark yellow.The mixture was warmed to room temperature filtered on a celite pad. Solvent removal and chromatography on an alumina column, with a mixture of THF and $CH_3CN$ (1:1/v:v) as eluent gave a brown band that was collected. Crystallization of **4a** from $CH_2Cl_2$ layered with diethyl ether gave dark brown crystals (191 mg, 51%).

Anal. Calcd for $C_{37}H_{39}F_3Fe_2N_2O_5S$: C, 56.07; H, 4.96. Found: C, 56.21; H, 5.01. IR $\nu_{max}$($cm^{-1}$) (KBr pellets) 3314 (N-H); ($CH_2Cl_2$): 2200 m (C≡C), 1977 vs and 1817 s (CO). NMR $\delta_H$ ($CDCl_3$): 7.78-7.31 (7 H, m, $Me_2C_6H_3$ and $MeC_6H_4$), 6.12 (1 H, s, N-*H*), 5.06, 4.44 (10 H, s, Cp), 4.94 (3 H, s, NMe), 2.71, 2.48 (6 H, s, $Me_2C_6H_3$), 2.19 (3 H, s, $MeC_6H_4$), 0.96 (s, 9 H, $CMe_3$). $\delta_C$ ($CDCl_3$): 339.9 (μ-C), 263.9 (μ-CO), 212.6 (CO), 186.7 (N≡*C*), 148.4, 141.8 (*ipso*-$Me_2C_6H_3$ and *ipso*-$MeC_6H_3$); 133.2-128.9 ($Me_2C_6H_3$ and $MeC_6H_3$), 117.4, 107.1 (C≡C), 88.2 (Cp), 53.8 (NMe), 44.2, 26.6 ($CMe_3$), 21.8 ($MeC_6H_4$), 18.6, 17.6 ($Me_2C_6H_3$).

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