

Synthesis and reactivity with amines of new diiron alkynyl methoxy carbene complexes

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Abstract

The new diiron alkynyl methoxy carbene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})\text{C}\equiv\text{CR}'\}(\text{Cp})_2]^+$ (R = 2,6-Me₂C₆H₃ (Xyl), R' = Tol, **3a**; R = Xyl, R' = Ph, **3b**; R = Xyl, R' = Buⁿ, **3c**; R = Xyl, R' = SiMe₃, **3d**; R = Me, R' = Tol, **3e**; R = Me, R' = Ph, **3f**) are obtained in two steps by addition of R'C≡CLi (R' = Tol, Ph, Buⁿ, SiMe₃) to the carbonyl aminocarbene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2]^+$ (R = Xyl, **1a**; Me, **1b**), followed by methylation of the resulting alkynyl acyl compounds $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{O})\text{C}\equiv\text{CR}'\}(\text{Cp})_2]$ (R = Xyl, R' = Tol, **2a**; R = Xyl, R' = Ph, **2b**; R = Xyl, R' = Buⁿ, **2c**; R = Xyl, R' = SiMe₃, **2d**; R = Me, R' = Tol, **2e**; R = Me, R' = Ph, **2f**). Complexes **3** react with secondary amines (*i.e.* Me₂NH, C₅H₁₀NH) to give the 4-amino-1-metalla-1,3-dienes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{R}')(\text{NMe}_2)\}(\text{Cp})_2]^+$ (R = Xyl, R' = Tol, **4a**; R = Xyl, R' = Ph, **4b**; R = Me, R' = Ph, **4c**) and $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{Tol})(\text{NC}_5\text{H}_{10})\}(\text{Cp})_2]^+$, **5**. The addition occurs stereo-selectively affording only the E configured products. Analogously, addition of primary amines R'NH₂ (R' = Ph, Et, Prⁱ) affords the 4-(NH-amino)-1-metalla-1,3-diene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{R})(\text{NHR}')\}(\text{Cp})_2]^+$ (R = Ph, **6a**; Et, **6b**; Prⁱ, **6c**). In the case of **6a**, only the E isomer is formed, whereas a mixture of the E and Z isomers is present in the case of **6b,c**, with prevalence of the latter. Moreover, the two isomeric forms exist under dynamic equilibrium conditions, as shown by VT NMR studies. Complexes **6** are deprotonated by strong bases (*e.g.* NaH) resulting in the formation of the neutral vinyl imine complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})=\text{CHC}(=\text{NR})(\text{Tol})\}(\text{Cp})_2]$ (R = Ph, **7a**; Et, **7b**; Prⁱ, **7c**); the reaction can be reverted by addition of strong acids. X-Ray crystal structures have been determined for **3a**[CF₃SO₃]·Et₂O, **4c**[CF₃SO₃], **6a**[BF₄]·CH₂Cl₂, **6c**[CF₃SO₃]·0.5Et₂O and **7a**·CH₂Cl₂.

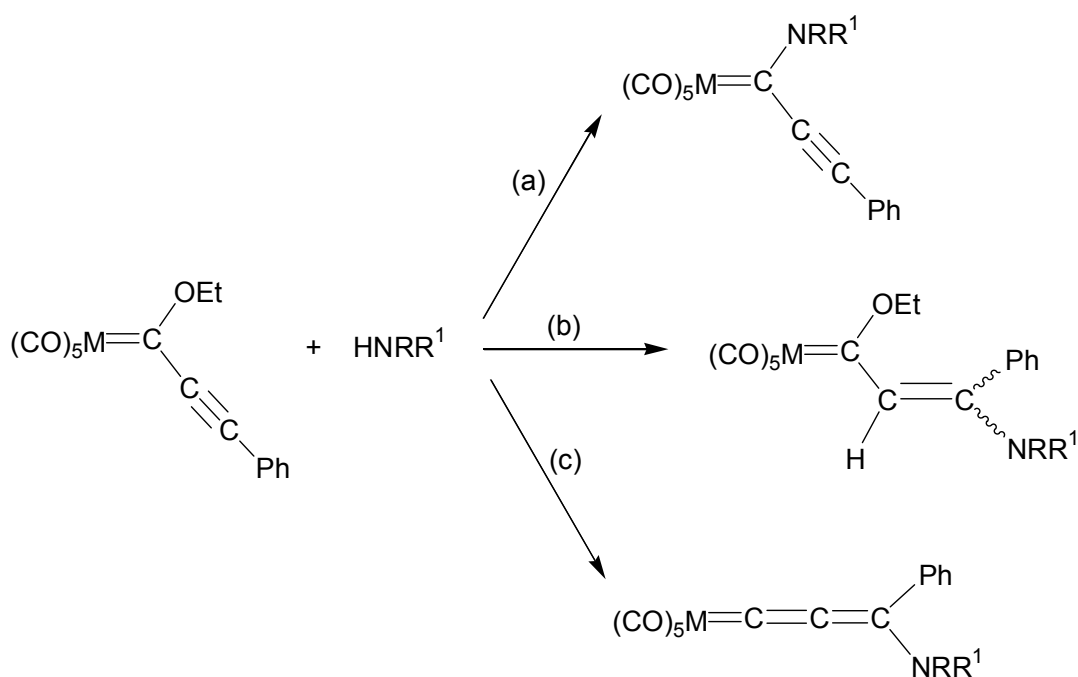
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1. Introduction

Mononuclear alkynylcarbene complexes of the type $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{C}\equiv\text{CR}$ ($\text{M} = \text{Cr}, \text{W}$) have attracted great interest as important reagents in synthetic organic chemistry [1]. They are, in fact, very versatile molecules, which can either react as ester analogues or participate in reactions not related to ester chemistry [2]. In particular, they result very activated substrates in [3+2] cycloadditions with 1,3-dipole [3] and in [4+2] and [2+2] cycloaddition reactions [4,5] together with 4-additions of different substrates such as enamines [6,7], enaminones [8], and enol ethers [9]. Alkynylcarbenes undergo, also, to Micheal additions with a large variety of protic nucleophiles (*e.g.* amines, imines, hydrazine, phosphanes, alcohols, thiols, carboxylic acids) [1a]. In particular, the aminolysis of alkynylcarbene was investigated as early as 1972 [10], but only after long studies it has been possible to establish the presence of three competing reaction paths (Scheme 1) [1a, 11]: (a) the 1-substitution to 1-aminocarbene complexes; (b) the 3-addition to (2-aminoalkenyl)carbene complexes; (c) the 3,1-substitution to (3-amino)allenylidene complexes. Regarding the stereochemistry of these reactions, particular attention has been given to the 3-addition (path b): it has been shown that, in general, secondary alkyl amines $\text{HN}(\text{Alkyl})_2$ at room temperature produce 4-amino-1-metalla-1,3-dienes $(\text{CO})_5\text{M}=\text{C}(\text{OEt})\text{CH}=\text{CR}[\text{N}(\text{Alkyl})_2]$, which have an E-configured $\text{C}=\text{C}(\text{N})$ double bond in virtually quantitative yield, whereas primary aryl amines H_2NAr result selectively in products with Z-configuration [12].

Scheme 1



Coordination of the alkynylcarbene ligand to dinuclear complexes could, in theory, further expand its chemistry, as widely illustrated for other classes of carbene ligands [13,14]. It is, thus, surprising that very little has appeared on dinuclear alkynylcarbene complexes containing a direct M-M bond [1c,13]. Herein, we report the synthesis of a variety of new diiron alkynyl methoxy carbene complexes of the type $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{OMe})\text{C}\equiv\text{CR}'\}(\text{Cp})_2]^+$ (R= 2,6-Me₂C₆H₃ (Xyl), R'= Tol, **3a**; R= Xyl, R'= Ph, **3b**; R= Xyl, R'= Buⁿ, **3c**; R= Xyl, R'= SiMe₃, **3d**; R= Me, R'= Tol, **3e**; R= Me, R'= Ph, **3f**), together with the study of their reactivity towards primary and secondary amines. This represents a further step of our ongoing investigation on the chemistry of diiron complexes, particularly devoted to the study of the formation of new C-C bonds involving terminal and/or bridging ligands [15].

2. Experimental

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. ESI MS spectra were recorded on a Waters Micromass ZQ 4000 with samples dissolved in CH₃CN. All NMR measurements were performed on Varian Gemini 300 and Mercury Plus 400 instruments. The chemical shifts for ¹H and ¹³C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ¹H, ¹³C correlation through gs-HSQC and gs-HMBC experiments [16]. NOE measurements were recorded using the DPGSE-NOE sequence [17]. All chemicals were used as received from Aldrich Co., except $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}(\mu\text{-CO})(\text{CO})_2(\text{Cp})_2][\text{SO}_3\text{CF}_3]$ (R= Xyl, **1a**[SO₃CF₃]; Me, **1b**[SO₃CF₃]) [18] and $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})_2\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{O})\text{C}\equiv\text{CR}'\}(\text{Cp})_2]$ (R'= Tol, **2e**; Ph, **2f**) [19] which were prepared by published methods. The acetylides R'C≡CLi (R'= Tol, Ph, Buⁿ) were prepared just before use from the reaction of the appropriate alkyne R'C≡CH in THF at -50 °C with BuⁿLi (alkyne: BuⁿLi= 1.2).

2.1 Synthesis of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{Xyl})\}(\mu\text{-CO})(\text{CO})\{\text{C}(\text{O})\text{C}\equiv\text{CR}'\}(\text{Cp})_2]$ (R'= Tol, **2a**; Ph, **2b**; Buⁿ, **2c**; SiMe₃, **2d**).

R'C≡CLi (0.567 mmol in THF) was added dropwise to a solution of **1a**[SO₃CF₃] (0.378 mmol) in THF (6 mL) at -50 °C and the resulted solution was stirred at room temperature for 30 minutes. The solution, then, was filtered through an Al₂O₃ pad in order to remove non-reacted R'C≡CLi. Thus, the filtrate was evaporated to dryness and the residue dissolved in CH₂Cl₂ (5 mL)

and chromatographed on an Al₂O₃ column. The final product was obtained as a green fraction using THF as eluent.

2a Yield 124.4 mg (56 %). Anal. Calcd. For C₃₂H₂₉Fe₂NO₃: C, 65.45; H, 4.98; N, 2.39. Found: C, 65.12; H, 5.09; N, 2.51. IR (CH₂Cl₂, 293 K): $\nu(\text{C}\equiv\text{C})$ 2163w; $\nu(\text{CO})$ 1971vs, 1791s, 1605w; $\nu(\text{CN})$ 1526m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.44-7.10 (m, 7H, *Xyl* + *Tol*), 4.94, 4.27 (s, 10H, *Cp*), 4.23 (s, 3H, *NMe*), 2.55, 2.39, (s, 6H, C₆H₃Me₂) 2.33 (s, 3H, *p-MeC*₆H₄) . ¹³C{¹H} NMR (CDCl₃, 293 K): δ 336.9 (μ -CN), 264.9 (μ -CO), 252.2 (COC \equiv), 213.7 (CO), 148.1 (Cipso *Xyl*), 138.9 (C-Me *Tol*), 134.9, 132.9 (C-Me *Xyl*), 132.1, 130.0, 129.0, 128.0, 127.8 (CH arom), 119.7 (Cipso *Tol*), 91.3, 88.5 (C \equiv C), 90.3, 86.1 (*Cp*), 51.8 (N-*Me*), 21.6 (*p-MeC*₆H₄), 18.4, 17.5 (C₆H₃Me₂).

2b Yield 112.7 mg (52 %). Anal. Calcd. For C₃₁H₂₇Fe₂NO₃: C, 64.95; H, 4.75; N, 2.44. Found: C, 64.71; H, 4.92; N, 2.23. IR (CH₂Cl₂, 293 K): $\nu(\text{C}\equiv\text{C})$ 2164w; $\nu(\text{CO})$ 1971vs, 1791s, 1596w; $\nu(\text{CN})$ 1526m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.55-7.19 (m, 8H, *Xyl* + *Ph*), 4.97, 4.28 (s, 10H, *Cp*), 4.24 (s, 3H, *NMe*), 2.55, 2.40 (s, 6H, C₆H₃Me₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 337.0 (μ -CN), 265.1 (μ -CO), 252.6 (COC \equiv), 213.8 (CO), 148.0 (Cipso *Xyl*), 134.8, 132.9 (C-Me *Xyl*), 132.1, 130.0, 128.6, 128.5, 128.0, 127.8 (CH arom), 122.8 (Cipso *Ph*), 91.4, 88.5 (C \equiv C), 90.3, 86.1 (*Cp*), 51.7 (N-*Me*), 18.3, 17.4 (C₆H₃Me₂).

2c Yield 100.4 mg (48 %). Anal. Calcd. For C₂₉H₃₁Fe₂NO₃: C, 62.96; H, 5.65; N, 2.53. Found: C, 63.27; H, 5.37; N, 2.79. IR (CH₂Cl₂, 293 K): $\nu(\text{C}\equiv\text{C})$ 2174w; $\nu(\text{CO})$ 1970vs, 1790s; $\nu(\text{CN})$ 1534m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.27-7.20 (m, 3H, *Xyl*), 4.90, 4.28 (s, 10H, *Cp*), 4.21 (s, 3H, *NMe*), 2.56, 2.41 (s, 6H, C₆H₃Me₂), 2.40 (t, ³J_{HH} = 7.1 Hz, α -CH₂), 1.64-1.42 (m, 4H, β + γ -CH₂), 0.94 (t, ³J_{HH} = 7.1 Hz, 3H, δ -CH₃). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 337.1 (μ -CN), 265.2 (μ -CO), 253.3 (COC \equiv), 213.9 (CO), 148.1 (Cipso *Xyl*), 135.0, 132.9 (C-Me *Xyl*), 130.0, 128.0, 127.8 (CH arom), 91.3, 88.5 (C \equiv C), 90.3, 86.0 (*Cp*), 51.7 (N-*Me*), 30.7 (α -CH₂), 22.2, 18.8 (β + γ -CH₂), 18.4, 17.4 (C₆H₃Me₂), 13.6 (δ -CH₃).

2d Yield 92.5 mg (43 %). Anal. Calcd. For C₂₈H₃₁Fe₂NO₃Si: C, 59.07; H, 5.49; N, 2.46. Found: C, 58.89; H, 5.61; N, 2.32. IR (CH₂Cl₂, 293 K): $\nu(\text{CO})$ 1970vs, 1790s, 1591w; $\nu(\text{CN})$ 1532m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.27-7.09 (m, 3H, *Xyl*), 4.88, 4.26 (s, 10H, *Cp*), 4.16 (s, 3H, *NMe*), 2.53, 2.38 (s, 6H, C₆H₃Me₂), 0.22 (s, 9H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 337.5 (μ -CN), 264.5 (μ -CO), 253.3 (COC \equiv), 213.8 (CO), 148.1 (Cipso *Xyl*), 135.1, 133.0 (C-Me *Xyl*), 130.2, 128.1, 127.9 (CH arom), 104.8, 92.0 (C \equiv C), 90.7, 86.1 (*Cp*), 51.8 (N-*Me*), 18.4, 17.4 (C₆H₃Me₂), 0.1 (SiMe₃).

2.2 Synthesis of $[Fe_2\{\mu-CN(Me)(R)\}(\mu-CO)(CO)\{C(OMe)C\equiv CR'\}(Cp)_2]^+$ ($R = Xyl$, $R' = Tol$, **3a**; $R = Xyl$, $R' = Ph$, **3b**; $R = Xyl$, $R' = Bu^i$, **3c**; $R = Xyl$, $R' = SiMe_3$, **3d**; $R = Me$, $R' = Tol$, **3e**; $R = Me$, $R' = Ph$, **3f**).

CF₃SO₃CH₃ (0.047 mL, 0.416 mmol) was added at room temperature to a stirred CH₂Cl₂ (6 mL) solution of **2a-f** (0.320 mmol). The colour immediately turned from green to red and the complete conversion of **2a-f** into **3a-f** was monitored *via* IR. After 15 min, the solvent was removed under reduced pressure and the residue washed with Et₂O (2x10 mL); the final product was further purified by filtration through celite using CH₂Cl₂ as solvent.

3a[SO₃CF₃] Yield 228.4 mg (95 %). Anal. Calcd. For C₃₄H₃₂F₃Fe₂NO₆S: C, 54.35; H, 4.29; N, 1.86. Found: C, 54.61; H, 4.09; N, 1.91. IR (CH₂Cl₂, 293 K): $\nu(C\equiv C)$ 2154s; $\nu(CO)$ 1996vs, 1824s; $\nu(CN)$ 1524m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.58-7.28 (m, 7H, *Xyl* + *Tol*), 5.30, 4.61 (s, 10H, *Cp*), 4.20 (s, 3H, *NMe*), 3.89 (s, 3H, *OMe*), 2.61, 2.21, (s, 6H, C₆H₃Me₂), 2.43 (s, 3H, *p-MeC*₆H₄) . ¹³C{¹H} NMR (CDCl₃, 293 K): δ 332.2 (μ -CN), 281.4 (Fe=C), 258.1 (μ -CO), 211.8 (CO), 147.3-127.6 (arom), 116.7, 92.3 (C \equiv C), 94.1, 88.6 (*Cp*), 63.5 (*OMe*), 54.2 (*N-Me*), 22.0 (*p-MeC*₆H₄), 18.6, 16.9 (C₆H₃Me₂).

3b[SO₃CF₃] Yield 221.8 mg (94 %). Anal. Calcd. For C₃₃H₃₀F₃Fe₂NO₆S: C, 53.75; H, 4.10; N, 1.90. Found: C, 53.58; H, 4.31; N, 1.77. IR (CH₂Cl₂, 293 K): $\nu(C\equiv C)$ 2161s; $\nu(CO)$ 1997vs, 1827s; $\nu(CN)$ 1524m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.68-7.25 (m, 8H, *Xyl* + *Ph*), 5.29, 4.60 (s, 10H, *Cp*), 4.17 (s, 3H, *NMe*), 3.89 (s, 3H, *OMe*), 2.56, 2.22, (s, 6H, C₆H₃Me₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 332.0 (μ -CN), 281.7 (Fe=C), 257.8 (μ -CO), 211.4 (CO), 147.0 (*Cipso Xyl*), 133.0, 132.2 (*C-Me Xyl*), 132.4, 131.8, 129.8, 128.9 (*CH arom*), 125.9 (*Cipso Ph*), 119.6, 91.6 (C \equiv C), 93.8, 88.4 (*Cp*), 63.5 (*OMe*), 53.9 (*N-Me*), 18.2, 16.5 (C₆H₃Me₂).

3c[SO₃CF₃] Yield 208.9 mg (91 %). Anal. Calcd. For C₃₁H₃₄F₃Fe₂NO₆S: C, 51.90; H, 4.78; N, 1.95. Found: C, 51.77; H, 4.92; N, 2.09. IR (CH₂Cl₂, 293 K): $\nu(C\equiv C)$ 2180s; $\nu(CO)$ 1995vs, 1826s; $\nu(CN)$ 1524m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.37-7.27 (m, 3H, *Xyl*), 5.21, 4.58 (s, 10H, *Cp*), 4.17 (s, 3H, *NMe*), 3.79 (s, 3H, *OMe*), 2.78, 2.76 (m *AA'X*₂, ²J_{HH} = 17.8 Hz, ³J_{HH} = 7.7 Hz, 2H, α -CH₂), 2.58, 2.19, (s, 6H, C₆H₃Me₂), 1.73 (quintet, ³J_{HH} = 7.7 Hz, 2H, β -CH₂), 1.51 (sestet, ³J_{HH} = 7.7 Hz, 2H, γ -CH₂), 0.99 (t, ³J_{HH} = 7.7 Hz, 3H, δ -CH₃). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 332.5 (μ -CN), 285.9 (Fe=C), 258.2 (μ -CO), 211.9 (CO), 147.4 (*Cipso Xyl*), 133.3, 132.4 (*C-Me Xyl*), 129.1, 128.7, 128.1 (*CH arom*), 114.1, 93.2 (C \equiv C), 93.9, 88.5 (*Cp*), 63.5 (*OMe*), 54.1 (*N-Me*), 29.9, 22.2, 20.8 (α + β + γ -CH₂), 18.5, 16.8 (C₆H₃Me₂), 13.4 (δ -CH₃).

3d[SO₃CF₃] Yield 218.3 mg (93 %). Anal. Calcd. For C₃₀H₃₄F₃Fe₂NO₆SSi: C, 49.13; H, 4.67; N, 1.91. Found: C, 49.31; H, 4.39; N, 1.72. IR (CH₂Cl₂, 293 K): $\nu(CO)$ 1998vs, 1830s; $\nu(CN)$ 1523m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.40-7.06 (m, 3H, *Xyl*), 5.23, 4.62 (s, 10H, *Cp*), 4.14 (s, 3H,

NMe), 3.79 (s, 3H, OMe), 2.60, 2.20, (s, 6H, C₆H₃Me₂), 0.39 (s, 3H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 331.7 (μ-CN), 283.7 (Fe=C), 257.3 (μ-CO), 211.7 (CO), 147.3 (Cipso Xyl), 133.6, 132.4 (C-Me Xyl), 130.1, 129.2, 129.0 (CH arom), 103.7, 91.6 (C≡C), 94.9, 88.2 (Cp), 63.6 (OMe), 54.4 (N-Me), 18.7, 16.8 (C₆H₃Me₂), -0.7 (SiMe₃).

3e[SO₃CF₃] Yield 194.7 mg (92 %). Anal. Calcd. For C₂₇H₂₆F₃Fe₂NO₆S: C, 49.04; H, 3.96; N, 2.12. Found: C, 49.31; H, 3.75; N, 2.01. IR (CH₂Cl₂, 293 K): ν(C≡C) 2157s; ν(CO) 1992vs, 1822s; ν(CN) 1594m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.48-7.29 (m, 4H, Tol), 5.20, 5.14 (s, 10H, Cp), 4.19, 4.02 (s, 6H, NMe₂), 3.79 (s, 3H, OMe), 2.42 (s, 3H, p-MeC₆H₄). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 323.2 (μ-CN), 280.5 (Fe=C), 260.1 (μ-CO), 211.6 (CO), 143.2 (Cipso Tol), 132.5-130.0 (CH Tol), 125.5 (C-Me Tol), 116.9, 94.3 (C≡C), 93.8, 88.8 (Cp), 63.4 (OMe), 53.1, 52.9 (N-Me₂), 21.9 (p-MeC₆H₄).

3f[SO₃CF₃] Yield 194.7 mg (94 %). Anal. Calcd. For C₂₆H₂₄F₃Fe₂NO₆S: C, 48.25; H, 3.74; N, 2.16. Found: C, 48.51; H, 3.42; N, 2.33. IR (CH₂Cl₂, 293 K): ν(C≡C) 2161s; ν(CO) 1994vs, 1822s; ν(CN) 1594m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.61-7.48 (m, 5H, Ph), 5.18, 5.13 (s, 10H, Cp), 4.17, 4.00 (s, 6H, NMe₂), 3.80 (s, 3H, OMe). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 323.2 (μ-CN), 280.6 (Fe=C), 259.4 (μ-CO), 211.1 (CO), 132.2, 131.7, 129.0 (CH Ph), 124.1 (Cipso Ph), 111.8, 91.3 (C≡C), 93.6, 88.7 (Cp), 63.6 (OMe), 52.7, 52.6 (N-Me₂).

2.3 Synthesis of [Fe₂{μ-CN(Me)(R)}{μ-CO}(CO){C(OMe)CH=C(R')(NMe₂)}(Cp)₂]⁺ (R = Xyl, R' = Tol, **4a; R = Xyl, R' = Ph, **4b**; R = Me, R' = Ph, **4c**).**

Me₂NH (0.180 mL, 2.0 M in THF, 0.360 mmol) was added to a solution of **3** (0.120 mmol) in THF (6 mL). After stirring 1 hour at room temperature, the solvent was removed *in vacuo* and the residue dissolved in CH₂Cl₂ (5 mL) and chromatographed through Al₂O₃. Some impurities were eliminated using THF as eluent and, then, the final product was obtained as an orange fraction using CH₃CN.

4a[SO₃CF₃] Yield 66.9 mg (70 %). Anal. Calcd. For C₃₆H₃₉F₃Fe₂N₂O₆S: C, 54.29; H, 4.94; N, 3.52. Found: C, 54.61; H, 4.62; N, 3.87. IR (CH₂Cl₂, 293 K): ν(CO) 1973vs, 1794s; ν(CN) 1513m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.30-7.17 (m, 7H, Xyl + Tol), 6.13 (s, 1H, =CH), 4.94, 4.37 (s, 10H, Cp), 4.38 (s, 3H, NMe), 3.13 (s, 6H, NMe₂), 2.96 (s, 3H, OMe), 2.60, 2.16, (s, 6H, C₆H₃Me₂), 2.34 (s, 3H, p-MeC₆H₄). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 335.5 (μ-CN), 277.8 (Fe=C), 266.0 (μ-CO), 213.4 (CO), 159.1 (=C(NMe₂)Tol), 148.0 (Cipso Xyl), 142.3 (Cipso Tol), 133.2, 133.0 (C-Me Xyl), 131.6 (C-Me Tol), 129.9, 129.7, 128.7, 128.6 (CH arom), 114.5 (CH=), 90.5, 87.5 (Cp), 64.2 (OMe), 53.4 (N-Me), 43.2 (NMe₂), 21.6 (p-MeC₆H₄), 18.7, 17.4 (C₆H₃Me₂). MS (ESI): ES⁺ *m/z* 647.

4b[SO₃CF₃] Yield 62.0 mg (66 %). Anal. Calcd. For C₃₅H₃₇F₃Fe₂N₂O₆S: C, 53.73; H, 4.77; N, 3.58. Found: C, 53.95; H, 4.39; N, 3.28. IR (CH₂Cl₂, 293 K): ν (CO) 1974vs, 1795s; ν (CN) 1519m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.48-7.25 (m, 8H, *Xyl* + *Ph*), 6.14 (s, 1H, =CH), 4.95, 4.37 (s, 10H, *Cp*), 4.38 (s, 3H, *NMe*), 3.13 (s, 6H, *NMe*₂), 2.99 (s, 3H, *OMe*), 2.59, 2.16, (s, 6H, C₆H₃Me₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 335.2 (μ -CN), 279.2 (Fe=C), 265.5 (μ -CO), 213.1 (CO), 158.2 (=C(NMe₂)Ph), 147.7 (Cipso *Xyl*), 134.5 (Cipso *Ph*), 133.0, 132.7 (C-Me *Xyl*), 131.3, 129.7, 129.4, 128.9, 128.6, 128.4 (CH arom), 114.5 (CH=), 90.4, 87.5 (*Cp*), 64.1 (*OMe*), 53.2 (N-Me), 43.0 (*NMe*₂), 18.6, 17.3 (C₆H₃Me₂).

4c[SO₃CF₃] Yield 55.7 mg (67 %). Anal. Calcd. For C₂₈H₃₁F₃Fe₂N₂O₆S: C, 48.58; H, 4.51; N, 4.05. Found: C, 48.21; H, 4.74; N, 3.89. IR (CH₂Cl₂, 293 K): ν (CO) 1971vs, 1793s; ν (CN) 1521m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.41-6.90 (m, 5H, *Ph*), 5.36 (s, 1H, =CH), 4.99, 4.83 (s, 10H, *Cp*), 4.38, 4.30 (s, 6H, μ -CNMe₂), 3.32 (s, 3H, *OMe*), 2.91 (s, 6H, *NMe*₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 330.1 (μ -CN), 279.3 (Fe=C), 267.1 (μ -CO), 213.1 (CO), 158.2 (=C(NMe₂)Ph), 135.3 (Cipso *Ph*), 129.8, 128.5, 127.9 (CH arom), 114.9 (CH=), 89.2, 88.2 (*Cp*), 62.9 (*OMe*), 54.0, 51.8 (μ -CNMe₂), 42.1 (*NMe*₂).

2.4 Synthesis of [Fe₂{ μ -CN(Me)(*Xyl*)}(μ -CO)(CO){C(*OMe*)CH=C(*Tol*)(NC₅H₁₀)}(*Cp*)₂]⁺, **5**.

C₅H₁₀NH (0.1 mL, 1.011 mmol) was added to a solution of **3a** (150 mg, 0.200 mmol) in THF (6 mL). After stirring 15 min at room temperature, the solvent was removed *in vacuo* and the residue washed with Et₂O (3x10 mL). The final product **5**[SO₃CF₃] was further purified by filtration through celite using CH₂Cl₂ as solvent. Yield 86.1 mg (87 %). Anal. Calcd. For C₃₈H₄₃F₃Fe₂N₂O₆S: C, 55.35; H, 5.26; N, 3.40. Found: C, 55.12; H, 5.41; N, 3.72. IR (CH₂Cl₂, 293 K): ν (CO) 1974vs, 1793s cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.35-7.03 (m, 7H, *Xyl* + *Tol*), 6.21 (s, 1H, =CH), 4.92, 4.36 (s, 10H, *Cp*), 4.34 (s, 3H, *NMe*), 3.42 (br, 4H, α -CH₂), 2.91 (s, 3H, *OMe*), 2.57, 2.11, (s, 6H, C₆H₃Me₂), 2.38 (s, 3H, *p-MeC*₆H₄), 1.74 (br, 4H, β -CH₂), 1.57 (br, 2H, γ -CH₂). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 334.9 (μ -CN), 278.8 (Fe=C), 265.8 (μ -CO), 213.0 (CO), 157.6 (=C(NC₅H₁₀)*Tol*), 147.6 (Cipso *Xyl*), 142.4 (Cipso *Tol*), 133.0, 132.6 (C-Me *Xyl*), 131.6 (C-Me *Tol*), 129.9-128.4 (CH arom), 114.2 (CH=), 90.2, 87.4 (*Cp*), 64.1 (*OMe*), 53.0 (N-Me), 51.9 (α -CH₂), 26.2 (β -CH₂), 23.6 (γ -CH₂), 21.5 (*p-MeC*₆H₄), 18.6, 17.4 (C₆H₃Me₂).

2.5 Synthesis of [Fe₂{ μ -CN(Me)(*Xyl*)}(μ -CO)(CO){C(*OMe*)CH=C(*Tol*)(*NHR*)}(*Cp*)₂]⁺ (R= *Ph*, **6a**; *Et*, **6b**; *Pr*^{*i*}, **6c**).

RNH₂ (0.600 mmol) was added to a solution of **3a** (150.0 mg, 0.200 mmol) in CH₂Cl₂ (6 mL). After stirring 10 min at room temperature, the solvent was removed *in vacuo* and the residue

washed with Et₂O (3x10 mL). The final product was further purified by filtration through celite using CH₂Cl₂ as solvent.

6a[SO₃CF₃] Yield 138.5 mg (82 %). Anal. Calcd. For C₄₀H₃₉F₃Fe₂N₂O₆S: C, 56.89; H, 4.65; N, 3.32. Found: C, 56.52; H, 4.93; N, 3.21. IR (CH₂Cl₂, 293 K): ν (CO) 1984vs, 1793s; ν (CN) 1549m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 9.96 (br, 1H, NH), 7.36-6.68 (m, 12H, Xyl + Tol + Ph), 5.93 (s, 1H, =CH), 5.00, 4.44 (s, 10H, Cp), 4.48 (s, 3H, NMe), 3.65 (s, 3H, OMe), 2.59, 2.28, (s, 6H, C₆H₃Me₂), 2.38 (s, 3H, p-MeC₆H₄). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 334.7 (μ -CN), 282.6 (Fe=C), 249.7 (μ -CO), 212.3 (CO), 155.8 (=C(NHPh)Tol), 148.1 (Cipso Xyl), 141.9, 139.1 (Cipso Tol + Cipso Ph), 133.2, 132.9 (C-Me Xyl), 131.7 (C-Me Tol), 130.1-122.5 (CH arom), 114.0 (CH=), 90.7, 88.0 (Cp), 62.9 (OMe), 53.5 (N-Me), 21.5 (p-MeC₆H₄), 18.7, 17.3 (C₆H₃Me₂).

6b[SO₃CF₃] Yield 137.0 mg (86 %). Anal. Calcd. For C₃₆H₃₉F₃Fe₂N₂O₆S: C, 54.29; H, 4.94; N, 3.52. Found: C, 54.43; H, 4.74; N, 3.87. IR (CH₂Cl₂, 293 K): ν (CO) 1977vs, 1793s; ν (CN) 1562m cm⁻¹. IR (KBr, 293 K): ν (NH) 3290br cm⁻¹. ¹H NMR (CDCl₃, 238 K) Isomer Z: δ 9.24 (br, 1H, NH), 7.35-7.01 (m, 7H, Xyl + Tol), 4.98 (s, 1H, =CH), 4.93, 4.30 (s, 10H, Cp), 4.52 (s, 3H, OMe), 4.43 (s, 3H, NMe), 3.18 (m, 2H, CH₂CH₃), 2.58, 1.54, (s, 6H, C₆H₃Me₂), 2.36 (s, 3H, p-MeC₆H₄), 1.14 (t, ³J_{HH} = 7.1 Hz, 3H, CH₂CH₃); Isomer E: 8.07 (br, 1H, NH), 7.35-7.01 (m, 7H, Xyl + Tol), 6.21 (s, 1H, =CH), 4.91, 4.34 (s, 10H, Cp), 4.34 (s, 3H, NMe), 3.41 (m, 2H, CH₂CH₃), 2.76 (s, 3H, OMe), 2.58, 2.17, (s, 6H, C₆H₃Me₂), 2.36 (s, 3H, p-MeC₆H₄), 1.43 (t, ³J_{HH} = 6.8 Hz, 3H, CH₂CH₃). Z : E = 1:0.4. ¹³C{¹H} NMR (CDCl₃, 238 K) Isomer Z: δ 338.7 (μ -CN), 268.0 (μ -CO), 263.7 (Fe=C), 213.0 (CO), 156.6 (=C(NHEt)Tol), 147.8 (Cipso Xyl), 146.1 (C-Me Tol), 133.0-126.5 (CH arom + C-Me Xyl + Cipso Tol), 116.1 (CH=), 88.7, 87.9 (Cp), 62.4 (OMe), 52.5 (N-Me), 41.0 (CH₂CH₃), 21.4 (p-MeC₆H₄), 18.9, 16.9 (C₆H₃Me₂), 15.5 (CH₂CH₃); Isomer E: δ 335.7 (μ -CN), 271.5 (Fe=C), 265.9 (μ -CO), 212.0 (CO), 159.2 (=C(NHEt)Tol), 146.4 (Cipso Xyl), 140.1 (C-Me Tol), 133.0-126.5 (CH arom + C-Me Xyl + Cipso Tol), 107.9 (CH=), 89.9, 87.2 (Cp), 64.8 (OMe), 53.1 (N-Me), 41.0 (CH₂CH₃), 21.6 (p-MeC₆H₄), 18.5, 17.0 (C₆H₃Me₂), 13.2 (CH₂CH₃)

6c[SO₃CF₃] Yield 131.3 mg (81 %). Anal. Calcd. For C₃₇H₄₁F₃Fe₂N₂O₆S: C, 54.83; H, 5.10; N, 3.46. Found: C, 54.51; H, 5.38; N, 3.12. IR (CH₂Cl₂, 293 K): ν (CO) 1978vs, 1793s; ν (CN) 1558w cm⁻¹. IR (KBr, 293 K): ν (NH) 3249br cm⁻¹. ¹H NMR (CDCl₃, 218 K) Isomer Z: δ 9.00 (br, 1H, NH), 7.31-6.83 (m, 7H, Xyl + Tol), 4.95, 4.32 (s, 10H, Cp), 4.92 (s, 1H, =CH), 4.45 (s, 3H, OMe), 4.40 (s, 3H, NMe), 3.52 (m, 1H, CHMe₂), 2.58, 1.59, (s, 6H, C₆H₃Me₂), 2.36 (s, 3H, p-MeC₆H₄), 1.21, 1.19 (d, ³J_{HH} = 6.3 Hz, 6H, CHMe₂); Isomer E: δ 7.51 (br, 1H, NH), 7.31-6.83 (m, 7H, Xyl + Tol), 6.29 (s, 1H, =CH), 4.93, 4.33 (s, 10H, Cp), 4.29 (s, 3H, NMe), 3.95 (m, 1H, CHMe₂), 2.65 (s, 3H, OMe), 2.58, 2.14, (s, 6H, C₆H₃Me₂), 2.35 (s, 3H, p-MeC₆H₄), 1.49, 1.36 (d, ³J_{HH} = 6.4 Hz, 6H, CHMe₂). Z : E = 1:0.2. ¹³C{¹H} NMR (CDCl₃, 218 K) Isomer Z: δ 337.4 (μ -CN), 269.1 (μ -CO),

264.2 (Fe=C), 211.7 (CO), 154.3 (=C(NHPrⁱ)Tol), 147.4 (Cipso Xyl), 139.9 (C-Me Tol), 132.7, 132.6 (C-Me Xyl), 131.1 (Cipso Tol), 129.9-125.8 (CH arom), 115.9 (CH=), 88.6, 87.8 (Cp), 61.7 (OMe), 52.2 (N-Me), 47.9 (CHMe₂), 23.3, 23.0 (CHMe₂), 21.3 (p-MeC₆H₄), 18.7, 16.6 (C₆H₃Me₂); Isomer E: δ 334.4 (μ -CN), 272.9 (Fe=C), 268.4 (μ -CO), 212.8 (CO), 146.8 (Cipso Xyl), 142.9 (C-Me Tol), 132.5, 132.3 (C-Me Xyl), 131.2 (Cipso Tol), 129.9-125.8 (CH arom), 107.2 (CH=), 89.7, 87.1 (Cp), 64.9 (OMe), 53.6 (N-Me), 47.0 (CHMe₂), 21.5 (p-MeC₆H₄), 21.2, 20.8 (CHMe₂), 18.3, 16.7 (C₆H₃Me₂)

2.6 Synthesis of [Fe₂{ μ -CN(Me)(Xyl)}(μ -CO)(CO){C(OMe)=CHC(=NR)(Tol)}(Cp)₂] (R= Ph, **7a; Et, **7b**; Prⁱ, **7c**).**

NaH (19.2 mg, 0.800 mmol) was added to a solution of **6** (0.200 mmol) in THF (6 mL). The solution immediately turned from red to brown and it was further stirred for 10 min. Hence, the solvent was removed *in vacuo* and the residue dissolved in CH₂Cl₂ (5 mL) and chromatographed through Al₂O₃. The final product was obtained as a brown solution using THF as eluent.

7a Yield 94.4 mg (68 %). Anal. Calcd. For C₃₉H₃₈Fe₂N₂O₃: C, 67.45; H, 5.52; N, 4.03. Found: C, 67.12; H, 5.79; N, 4.25. IR (CH₂Cl₂, 293 K): ν (CO) 1958vs, 1783s; ν (CN) 1579w, 1548m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.61-6.67 (m, 12H, Xyl + Tol + Ph), 4.79 (s, 1H, =CH), 4.62, 4.23 (s, 10H, Cp), 3.93 (s, 3H, NMe), 3.19 (s, 3H, OMe), 2.55, 2.09, (s, 6H, C₆H₃Me₂), 2.32 (s, 3H, p-MeC₆H₄) . ¹³C{¹H} NMR (CDCl₃, 293 K): δ 337.9 (μ -CN), 266.1 (μ -CO), 214.9 (CO), 204.0 (Fe-C), 165.8 (C=N), 154.0 (Cipso Ph), 148.2, 139.2, 137.6, 134.1, 133.0 (Cipso Tol + Cipso Xyl + C-Me Xyl + C-Me Tol), 129.8-115.0 (CH arom), 117.0 (=CH), 88.4, 86.3 (Cp), 59.8 (OMe), 51.4 (N-Me), 21.3 (p-MeC₆H₄), 18.4, 17.8 (C₆H₃Me₂).

7b Yield 93.1 mg (72 %). Anal. Calcd. For C₃₅H₃₈Fe₂N₂O₃: C, 65.03; H, 5.93; N, 4.33. Found: C, 65.34; H, 5.68; N, 4.02. IR (CH₂Cl₂, 293 K): ν (CO) 1959vs, 1781s; ν (CN) 1591w, 1562m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.64, 7.06 (d, ³J_{HH} = 7.7 Hz, 4H, Tol), 7.24 (m, 3H, Xyl), 5.22 (s, 1H, =CH), 4.78, 4.24 (s, 10H, Cp), 4.40 (s, 3H, NMe), 3.28, 3.22 (dq ABX₃, ²J_{HH} = 14.3 Hz, ³J_{HH} = 7.0 Hz, 2H, CH₂CH₃), 2.92 (s, 3H, OMe), 2.60, 2.19, (s, 6H, C₆H₃Me₂), 2.29 (s, 3H, p-MeC₆H₄), 1.24 (t, ³J_{HH} = 7.0 Hz, 3H, CH₂CH₃). ¹³C{¹H} NMR (CDCl₃, 293 K): δ 337.0 (μ -CN), 267.5 (μ -CO), 214.5 (CO), 205.8 (Fe-C), 165.7 (C=N), 148.5 (Cipso Xyl), 138.3, 134.0, 133.0 (Cipso Tol + C-Me Xyl + C-Me Tol), 129.8, 128.3, 127.9 (CH arom), 112.9 (=CH), 88.6, 86.3 (Cp), 58.8 (OMe), 51.7 (N-Me), 47.3 (CH₂CH₃), 21.4 (p-MeC₆H₄), 18.7, 17.7 (C₆H₃Me₂), 16.4 (CH₂CH₃).

7c Yield 81.9 mg (62 %). Anal. Calcd. For C₃₆H₄₀Fe₂N₂O₃: C, 65.47; H, 6.10; N, 4.24. Found: C, 65.72; H, 5.93; N, 4.47. IR (CH₂Cl₂, 293 K): ν (CO) 1959vs, 1781s; ν (CN) 1590w, 1559m cm⁻¹. ¹H NMR (CDCl₃, 293 K): δ 7.67, 7.05 (d, ³J_{HH} = 7.9 Hz, 4H, Tol), 7.25 (m, 3H, Xyl), 5.20 (s, 1H,

=CH), 4.81, 4.26 (s, 10H, *Cp*), 4.41 (s, 3H, *NMe*), 3.84 (septet, $^3J_{\text{HH}} = 6.3$ Hz, ^1H , *CHMe*₂), 3.04 (s, 3H, *OMe*), 2.63, 2.22, (s, 6H, *C*₆*H*₃*Me*₂), 2.31 (s, 3H, *p-MeC*₆*H*₄), 1.18, 1.10 (d, $^3J_{\text{HH}} = 6.3$ Hz, 3H, *CHMe*₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 293 K): δ 337.3 ($\mu\text{-CN}$), 267.8 ($\mu\text{-CO}$), 214.7 (*CO*), 190.5 (*Fe-C*), 164.4 (*C=N*), 148.5 (*Cipso Xyl*), 139.1, 138.0, 133.9, 133.0 (*Cipso Tol + C-Me Xyl + C-Me Tol*), 129.8, 128.3, 128.2, 128.0, 127.9 (*CH arom*), 113.1 (=CH), 88.4, 86.2 (*Cp*), 58.5 (*OMe*), 51.6 (*CHMe*₂), 51.4 (*N-Me*), 23.3 (*CHMe*₂), 21.2 (*p-MeC*₆*H*₄), 18.5, 17.5 (*C*₆*H*₃*Me*₂).

2.7 Crystallography

Compounds **3a**[CF_3SO_3] $\cdot\text{Et}_2\text{O}$, **4c**[CF_3SO_3], **6a**[BF_4] $\cdot\text{CH}_2\text{Cl}_2$ and **6c**[CF_3SO_3] $\cdot 0.5\text{Et}_2\text{O}$ were crystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$, whereas **7a** $\cdot\text{CH}_2\text{Cl}_2$ was crystallized from CH_2Cl_2 /petroleum ether. Crystal data were collected at 293(2) K on a Bruker AXS SMART 2000 CCD diffractometer using Mo- $K\alpha$ radiation. Intensity data were measured over full diffraction spheres using 0.3° wide ω scans, crystal-to-detector distance 5.2 cm. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 20 exposures collected in three different ω regions and eventually refined against all reflections. The software SMART [20] was used for collecting frames of data, indexing reflections and determinations of lattice parameters. The collected frames were then processed for integration by the software SAINT and empirical absorption corrections were applied with SADABS [21]. The structure was solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [22]. Crystal data are listed in Table 1. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except positions of H(2n) in **6a**[BF_4] $\cdot\text{CH}_2\text{Cl}_2$ and **6c**[CF_3SO_3] $\cdot 0.5\text{Et}_2\text{O}$ which were located in the Fourier map. H-atom 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-atoms.

3a[CF_3SO_3] $\cdot\text{Et}_2\text{O}$: The *Cp* ligand bound to Fe(2) in the cation, the oxygen and fluorine atoms of the anion CF_3SO_3^- and the Et_2O molecule are disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

4c[CF_3SO_3]: The crystal is racemically twinned with a refined Flack parameter of 0.48(4) [23], and it was, therefore, refined using the TWIN refinement routine of SHELXTL. The *Cp* ligand bound to Fe(2) in the cation and the oxygen and fluorine atoms of the anion CF_3SO_3^- are disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

6a[BF₄]·CH₂Cl₂: The phenyl group bound to N(2) is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter for the disordered group.

6c[CF₃SO₃]·0.5Et₂O: There is half a molecule of Et₂O in the asymmetric unit which is disordered over two positions. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter for the disordered group.

7a·CH₂Cl₂: The CH₂Cl₂ molecule is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter for the disordered group.

Table 1

Crystal data and experimental details.

<i>Complex</i>	3a[CF₃SO₃]·Et₂O	4c[CF₃SO₃]	6a[BF₄]·CH₂Cl₂	6c[CF₃SO₃]·0.5Et₂O	7a·CH₂Cl₂
Formula	C ₃₈ H ₄₂ F ₃ Fe ₂ NO ₇ S	C ₂₈ H ₃₁ F ₃ Fe ₂ N ₂ O ₆ S	C ₄₀ H ₄₁ BCl ₂ F ₄ Fe ₂ N ₂ O ₃	C ₃₉ H ₄₆ F ₃ Fe ₂ N ₂ O _{6.5} S	C ₄₀ H ₄₀ Cl ₂ Fe ₂ N ₂ O ₃
<i>F</i> _w	825.49	692.31	867.16	847.54	779.34
<i>λ</i> , Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
<i>a</i> , Å	16.730(3)	9.1753(18)	13.985(3)	14.443(3)	10.501(2)
<i>b</i> , Å	14.021(3)	10.259(2)	16.952(3)	16.838(3)	33.058(7)
<i>c</i> , Å	16.792(3)	31.755(6)	17.258(4)	16.508(3)	11.391(2)
<i>β</i> , °	94.83(3)	90	94.34(3)	90.77(3)	103.62(3)
Cell Volume, Å ³	3924.8(14)	2989.2(10)	4079.9(14)	4014.1(14)	3842.9(13)
<i>Z</i>	4	4	4	4	4
<i>D</i> _c , g cm ⁻³	1.397	1.538	1.412	1.402	1.347
<i>μ</i> , mm ⁻¹	0.854	1.103	0.899	0.836	0.932
<i>F</i> (000)	1712	1424	1784	1764	1616
Crystal size, mm	0.23x0.18x0.14	0.22x0.18x 0.12	0.29x0.24x0.15	0.30x0.25x0.16	0.28x0.26x0. 16
<i>θ</i> limits, °	1.22-24.11	1.28-25.02	1.46-25.03	1.41-25.03	1.23-23.12
Reflections collected	31404	26561	35696	34786	22010

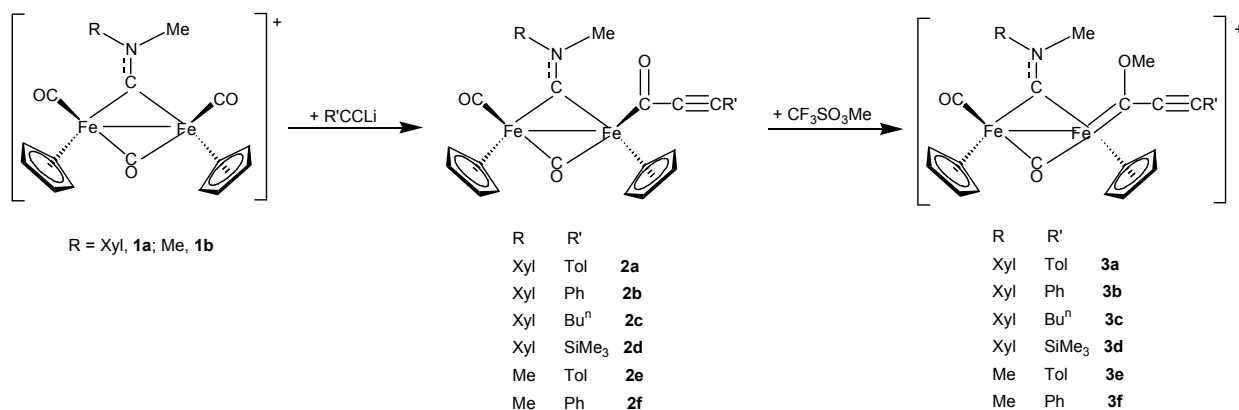
Independent reflections	6242 [$R_{\text{int}} = 0.1175$]	5273 [$R_{\text{int}} = 0.0876$]	7206 [$R_{\text{int}} = 0.0954$]	7086 [$R_{\text{int}} = 0.0520$]	5429 [$R_{\text{int}} = 0.1475$]
Data / restraints / parameters	6242 / 138 / 457	5273 / 86 / 372	7206 / 215 / 446	7086 / 60 / 514	5429 / 11 / 446
Goodness on fit on F^2	0.938	1.009	0.987	1.034	0.935
R_1 ($I > 2\sigma(I)$)	0.0698	0.0574	0.0743	0.0467	0.0803
wR_2 (all data)	0.2220	0.1613	0.2455	0.1363	0.2411
Largest diff. peak and hole, $e \text{ \AA}^{-3}$	0.643 / -0.567	0.497 / -0.656	0.672 / -0.922	0.631 / -0.400	0.672 / -0.587

3. Results and Discussion

3.1 Synthesis and characterisation of $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}(\text{CO})\}\{\text{C}(\text{OMe})\text{C}\equiv\text{CR}'\}\{\text{Cp}\}_2]^+$ ($\text{R} = \text{Xyl}, \text{R}' = \text{Tol}, \mathbf{3a}$; $\text{R} = \text{Xyl}, \text{R}' = \text{Ph}, \mathbf{3b}$; $\text{R} = \text{Xyl}, \text{R}' = \text{Bu}^n, \mathbf{3c}$; $\text{R} = \text{Xyl}, \text{R}' = \text{SiMe}_3, \mathbf{3d}$; $\text{R} = \text{Me}, \text{R}' = \text{Tol}, \mathbf{3e}$; $\text{R} = \text{Me}, \text{R}' = \text{Ph}, \mathbf{3f}$).

Diiron aminocarbene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}(\text{CO})_2(\text{Cp})_2\}]^+$ ($\text{R} = \text{Xyl}, \mathbf{1a}$; $\text{Me}, \mathbf{1b}$) react with acetylides $\text{R}'\text{C}\equiv\text{CLi}$ ($\text{R}' = \text{Tol}, \text{Ph}, \text{Bu}^n, \text{SiMe}_3$) in THF at -50°C to give $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}(\text{CO})\}\{\text{C}(\text{O})\text{C}\equiv\text{CR}'\}\{\text{Cp}\}_2]$ ($\text{R} = \text{Xyl}, \text{R}' = \text{Tol}, \mathbf{2a}$; $\text{R} = \text{Xyl}, \text{R}' = \text{Ph}, \mathbf{2b}$; $\text{R} = \text{Xyl}, \text{R}' = \text{Bu}^n, \mathbf{2c}$; $\text{R} = \text{Xyl}, \text{R}' = \text{SiMe}_3, \mathbf{2d}$; $\text{R} = \text{Me}, \text{R}' = \text{Tol}, \mathbf{2e}$; $\text{R} = \text{Me}, \text{R}' = \text{Ph}, \mathbf{2f}$) in good yields (40 – 60 %) [19]. The reaction of **2** with $\text{CF}_3\text{SO}_3\text{Me}$ in CH_2Cl_2 results in their nearly quantitative conversion into the diiron alkynyl methoxy carbene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}(\text{CO})\}\{\text{C}(\text{OMe})\text{C}\equiv\text{CR}'\}\{\text{Cp}\}_2]^+$ ($\text{R} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (Xyl), $\text{R}' = \text{Tol}, \mathbf{3a}$; $\text{R} = \text{Xyl}, \text{R}' = \text{Ph}, \mathbf{3b}$; $\text{R} = \text{Xyl}, \text{R}' = \text{Bu}^n, \mathbf{3c}$; $\text{R} = \text{Xyl}, \text{R}' = \text{SiMe}_3, \mathbf{3d}$; $\text{R} = \text{Me}, \text{R}' = \text{Tol}, \mathbf{3e}$; $\text{R} = \text{Me}, \text{R}' = \text{Ph}, \mathbf{3f}$) (Scheme 2).

Scheme 2



Type **2** and **3** compounds have been spectroscopically characterised whereas **3a** has been also structurally studied by X-ray diffraction. Its molecular structure is shown in Figure 1 and the main bond lengths and bond angles are reported in Table 2.

Figure 1

Molecular structure of the cation **3a**, with key atoms labelled (all H atoms have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Cp ligand bound to Fe(2) is drawn.

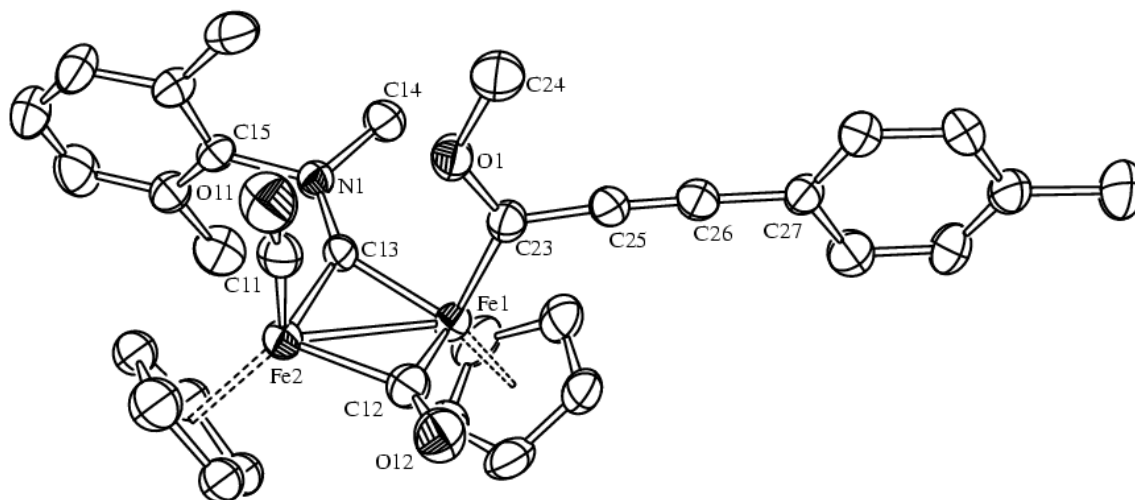


Table 2

Selected bond lengths (Å) and angles (°) for complex **3a**.

Fe(1)-Fe(2)	2.5248(14)	N(1)-C(13)	1.311(8)
Fe(2)-C(11)	1.750(8)	N(1)-C(14)	1.495(6)
Fe(1)-C(12)	1.924(8)	N(1)-C(15)	1.465(8)
Fe(2)-C(12)	1.925(7)	C(23)-O(1)	1.325(8)
Fe(1)-C(13)	1.846(6)	C(24)-O(1)	1.474(9)

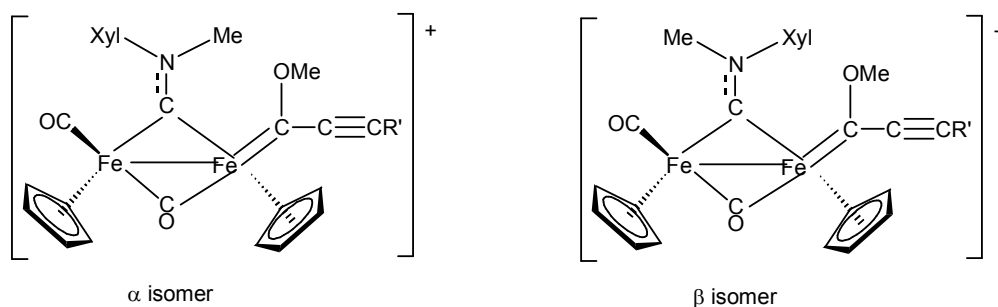
Fe(2)-C(13)	1.869(6)	C(23)-C(25)	1.408(10)
Fe(1)-C(23)	1.849(7)	C(25)-C(26)	1.204(9)
C(11)-O(11)	1.144(8)	C(26)-C(27)	1.444(10)
C(12)-O(12)	1.173(8)		
Fe(1)-C(13)-Fe(2)	85.6(3)	C(23)-C(25)-C(26)	174.8(8)
Fe(1)-C(23)-O(1)	121.8(5)	C(25)-C(26)-C(27)	178.6(8)
Fe(1)-C(23)-C(25)	122.5(5)	C(13)-N(1)-C(14)	123.0(5)
O(1)-C(23)-C(25)	115.7(6)	C(13)-N(1)-C(15)	121.4(5)

The $\text{Fe}_2\{\mu\text{-CN(Me)(Xyl)}\}(\mu\text{-CO})(\text{CO})(\text{Cp})_2$ core of **3a** shows a *cis* geometry of the Cp ligands respect to the plane determined by the two Fe and $\mu\text{-C}$ atoms. The Fe(1)-Fe(2) interaction [2.5248(14) Å] indicates the presence of a single bond between the two metals, whereas the C(13)-N(1) interaction [1.311(8) Å] shows a considerably double bond character; thus, the μ -aminocarbyne can be alternatively described as a bridging iminium ligand. In agreement, N(1) shows an almost perfect sp^2 hybridisation [sum angle at N(1) 360.0(9)°] and the N(Me)(Xyl) unit is nearly coplanar with $\text{Fe}_2(\mu\text{-C})$ [dihedral angles Fe(2)-C(13)-N(1)-C(14) 169.7(6)° and Fe(1)-C(13)-N(1)-C(15) 169.8(5)°]. The Xyl group lays on the opposite side of the bulky alkynyl methoxy carbene ligand in order to minimize steric repulsions, as previously found in analogous diiron and diruthenium asymmetrically substituted μ -aminocarbyne complexes [15b,24]. The Fe(1)-C(23) interaction [1.849(7) Å] shows a considerable π -character, greater than in analogous terminal aminocarbene ligands [15f,25] and similar to the one found in Fe-isocyanide complexes, *e.g.* 1.830(6) Å in $[\text{Fe}_2\{\mu\text{-CN(Me)}_2\}(\mu\text{-CO})(\text{CO})(\text{CNMe})(\text{Cp})_2]^+$ [26]. As a consequence of the strong π -character of the alkynyl methoxy carbene ligand, the electron densities on the two Fe atoms are similar and, thus, the Fe(1)-C(12) [1.924(8) Å] and Fe(2)-C(12) [1.925(7) Å] interactions are identical within experimental errors. It has been in fact shown that the asymmetry of $\mu\text{-CO}$ in complexes containing the (L)Fe(1)(Cp)($\mu\text{-CO}$)Fe(2)(Cp)(CO) unit is very sensitive to the different electron densities on Fe(1) and Fe(2) [15b, 15d, 15f, 19, 26]. For instance, when L is a pure σ -donor such as the cyanomethyl ligand in $[\text{Fe}_2\{\mu\text{-CN(Me)}_2\}(\mu\text{-CO})(\text{CO})(\text{CH}_2\text{CN})(\text{Cp})_2]$ [27], the Fe(1)-($\mu\text{-CO}$) and Fe(2)-($\mu\text{-CO}$) interactions are considerably different [1.852(3) and 2.003(3) Å, respectively], whereas they are almost identical when L is a strong π -acceptor such as CNMe in $[\text{Fe}_2\{\mu\text{-CN(Me)}_2\}(\mu\text{-CO})(\text{CO})(\text{CNMe})(\text{Cp})_2]^+$ [26] [1.909(5) and 1.967(6) Å, respectively]. C(23) shows an almost perfect sp^2 hybridisation [sum angle 360.0(9)°], and the C(23)-O(1) [1.325(8) Å] and C(23)-C(25) [1.408(10) Å] interactions indicate the presence of some π -interaction also

between the carbene carbon and both the methoxy and alkynyl substituents. The atoms of the alkynyl methoxy carbene unit, *i.e.* Fe(1), C(23), O(1), C(24), C(25), C(26) and C(27), are almost in the same plane [mean deviation from the least-squares plane 0.0185 Å], and this is nearly parallel to the Fe(1)-Fe(2) vector [dihedral angle Fe(2)-Fe(1)-C(23)-C(25) 159.1(5)°]. The methoxy group points towards the carbon of the bridging aminocarbene and the O(1)...C(13) distance [2.769(15) Å] suggests the presence of a weak interaction.

The IR spectra of **3a-f** show the presence of bands typical for terminal and bridging $\nu(\text{CO})$ and $\nu(\text{C}\equiv\text{C})$. In the case of complexes **3e,f** which contain a symmetrically substituted bridging aminocarbene ligand, the NMR spectra show the presence in solution of only one species, whereas in the case of **3a-d**, which contain the asymmetric $\mu\text{-CN}(\text{Me})(\text{Xyl})$, a main species is present together with traces (< 5%) of a second isomer, as found also in the parent compounds **2a-d**. In analogy to what reported in previous studies [15b,24], it is possible to assign to the main species the α -form (Scheme 3), which is also the one found in the solid state, and the β -form to the minor isomer. The fact that the α -isomer largely predominates is mainly due to the bulkiness of the Xyl group, which directs $\text{R}'\text{C}\equiv\text{CLi}$ attack preferentially to the CO opposite to Xyl and this configuration is fully maintained after methylation. The β -forms of **2a-d** can be separated by column chromatography and, thus, pure α -**3a-d** can be obtained after methylation. Therefore, only the α -isomers of **3a-d** will be considered in the rest of the paper.

Scheme 3



3.2 Reactivity $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}\}(\text{CO})\{\text{C}(\text{OMe})\text{C}\equiv\text{CR}'\}\{\text{Cp}\}_2]^+$ with secondary amines.

Complexes **3** react with Me_2NH (3-10 equivalents) in THF at room temperature to give $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}\}(\text{CO})\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{R}')(\text{NMe}_2)\}\{\text{Cp}\}_2]^+$ (R= Xyl, R'= Tol, **4a**; R= Xyl, R'= Ph, **4b**; R= Me, R'= Ph, **4c**) in good yields (66-70 %, after column chromatography) (Scheme 4). The same products can be also obtained by reacting **3** with Me_3NO under similar

conditions. Probably, partial decomposition of Me₃NO to Me₂NH and CH₂O in agreement with the Polonovski reaction occurs [28], and, then, the amine reacts with **3** to give the observed product. In a similar way, the complex [Fe₂{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(OMe)CH=C(Tol)(NC₅H₁₀)}(Cp)₂]⁺, **5**, has been obtained from the reaction of **3a** with piperidine (C₅H₁₀NH) (Scheme 4). Compounds **4** and **5** are the only products observed in these reactions, and changes in the experimental conditions (*i.e.* different T and different solvent) do not affect the reactions. This should be compared with what reported for analogous mononuclear alkynyl alkoxy chromium and tungsten complexes, where different products were observed depending on the experimental conditions [1a, 11]. Compounds **4** and **5** have been spectroscopically characterised *via* IR and NMR. The derivative **4c** has been also structurally characterised by X-ray diffraction and its molecular structure is shown in Figure 2, whereas the main bond lengths and bond angles are reported in Table 3.

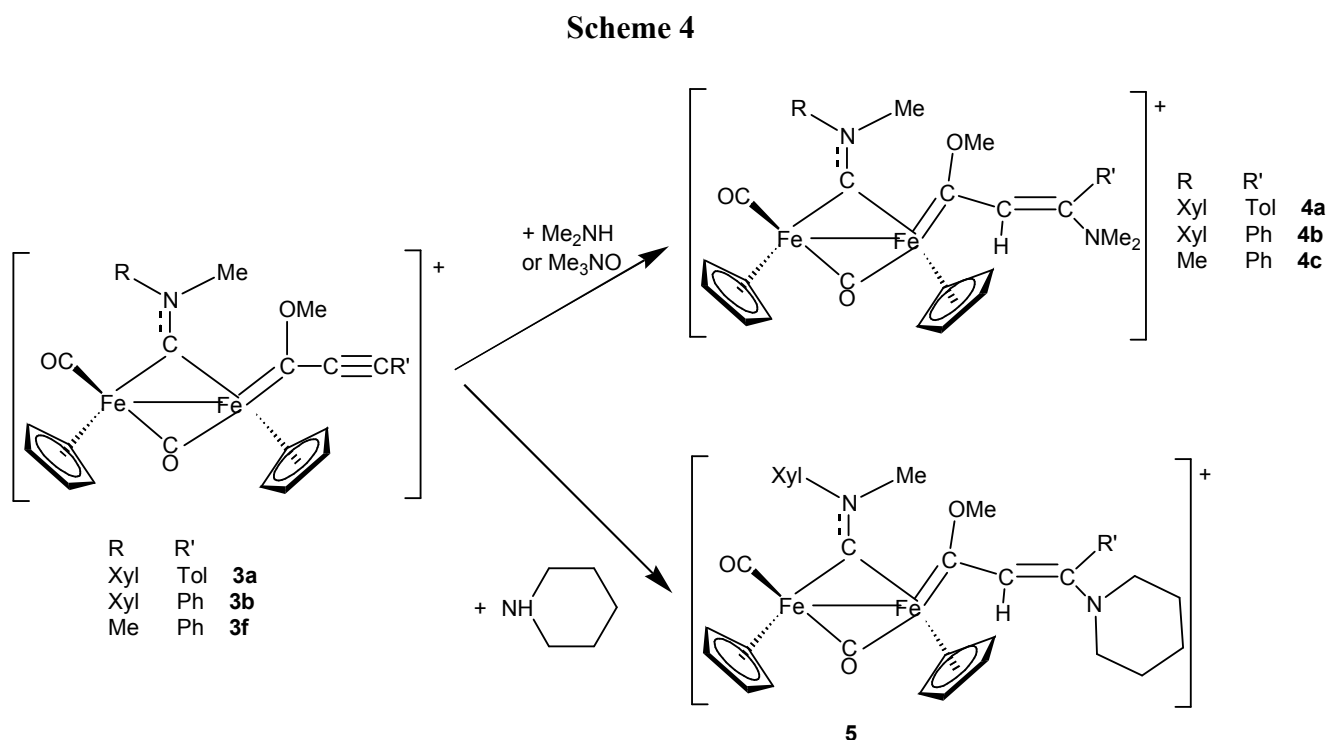


Figure 2

Molecular structure of the cation **4c**, with key atoms labelled (all H atoms, except H(18), have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Cp ligand bound to Fe(2) is drawn.

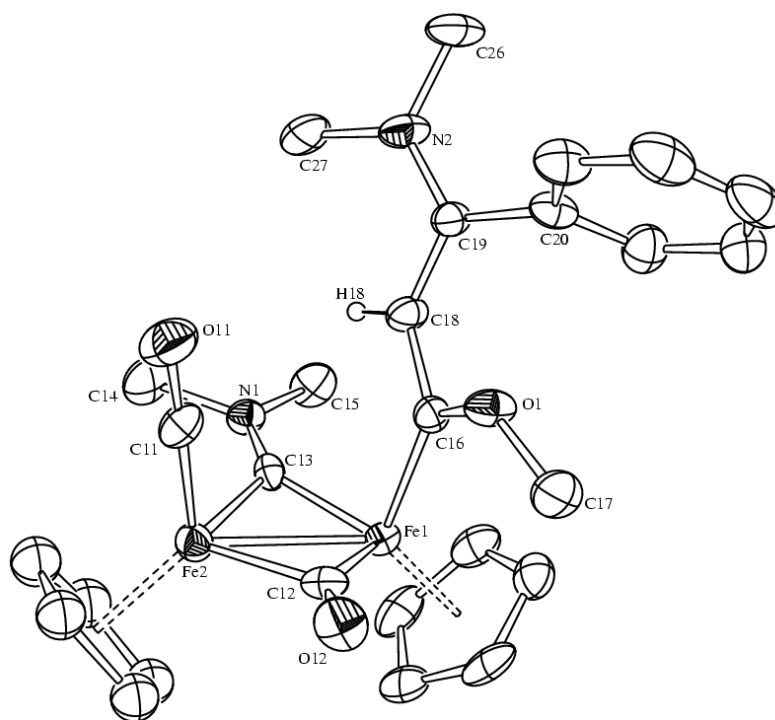


Table 3

Selected bond lengths (Å) and angles (°) for complex **4c**.

Fe1(1)-Fe(2)	2.5167(13)	C(13)-N(1)	1.301(8)
Fe(2)-C(11)	1.729(8)	C(16)-O(1)	1.324(8)
Fe(2)-C(12)	1.989(8)	O(1)-C(17)	1.414(9)
Fe(1)-C(12)	1.870(7)	C(16)-C(18)	1.413(9)
Fe(2)-C(13)	1.881(6)	C(18)-C(19)	1.382(9)
Fe(1)-C(13)	1.851(6)	C(19)-C(20)	1.483(9)
Fe(1)-C(16)	1.951(6)	C(19)-N(2)	1.341(9)
C(11)-O(11)	1.181(9)	N(2)-C(26)	1.449(10)
C(12)-O(12)	1.165(8)	N(2)-C(27)	1.440(10)
Fe(1)-C(16)-O(1)	126.8(5)	C(18)-C(19)-N(2)	119.9(6)
Fe(1)-C(16)-C(18)	123.6(5)	N(2)-C(19)-C(20)	118.1(6)
O(1)-C(16)-C(18)	109.5(5)	C(19)-N(2)-C(26)	123.9(7)
C(16)-C(18)-C(19)	128.8(6)	C(19)-N(2)-C(27)	121.0(6)
C(18)-C(19)-C(20)	122.0(6)	C(26)-N(2)-C(27)	114.6(6)

The structure of **4c** can be discussed as composed by two moieties, *i.e.* the $\text{Fe}_2\{\mu\text{-CN(Me)}_2\}(\mu\text{-CO})(\text{CO})(\text{Cp}_2)$ unit and the enamino methoxy carbene ligand

C(OMe)CH=C(Ph)(NMe₂). The former resembles the analogous unit present in **3a**, except for the presence of two Me groups instead of one Me and one Xyl. The Fe(1)-C(16) interaction [1.951(6) Å] suggests that C(OMe)CH=C(Ph)(NMe₂) is a weaker π -acceptor than the parent alkynyl methoxy carbene ligand C(OMe)C \equiv C(R); in agreement with this, the μ -CO ligand in **4c** shows an appreciable asymmetry [Fe(1)-C(12) 1.870(7) Å, Fe(2)-C(12) 1.989(8) Å]. The C(16)-C(18) [1.413(9) Å] and C(18)-C(19) [1.382(9) Å] interactions are considerably different, the latter having a nearly pure double bond character and the former being closer to the C-C interaction in alternating dienes. Thus, the terminal ligand of the molecule can be described by the 4-amino-1-metalla-1,3-diene structure Fe=C(OMe)-CH=C(Ph)(NMe₂), whereas the zwitterionic structure (–)Fe-C(OMe)=CH-C(Ph)(=N⁺Me₂) gives only a limited contribution (the negative charge has to be intended delocalised over the whole Fe₂{ μ -CN(Me)₂}(μ -CO)(CO)(Cp₂) unit). This should be contrasted with the structure of analogous mononuclear Cr and W 4-amino-1-metalla-1,3-diene complexes (OC)₅M=C(OEt)-CH=CPh(NHR) [12a] for which the zwitterionic structures (–OC)₅M-C(OEt)=CH-CPh(=N⁺HR) are very important, as clearly demonstrated by the almost equalized C-C interactions [*e.g.* 1.408(8) and 1.406(8) Å, respectively, for M=W, R=CH₂Ph]. The C(18)=C(19) bond possesses an E-configuration, as consequence of a *cis* addition of the amine, whereas the Fe(1),C(16),C(18),C(19)[N(2)Me₂] backbone adopts an almost planar *s-trans* conformation [dihedral angles Fe(1)-C(16)-C(18)-C(19) –168.8(9)°, C(16)-C(18)-C(19)-N(2) –166.2(7)°]. Delocalisation is, hence, possible all along the ligand, involving the metal, the three C atoms, the NMe₂ and OMe group, but not the Tol ring [C(19)-C(20) 1.483(9) Å; C(18)-C(19)-C(20)-C(25) 62.8(10)°]. Finally, the plane on which the C(OMe)CH=C(Ph)(NMe₂) ligand lays, is almost perpendicular to the Fe(1)-Fe(2) vector [dihedral angle Fe(2)-Fe(1)-C(16)-C(18) –74.8(6)°], with the C(18)-H(18) vector pointing towards the μ -CNMe₂ ligand.

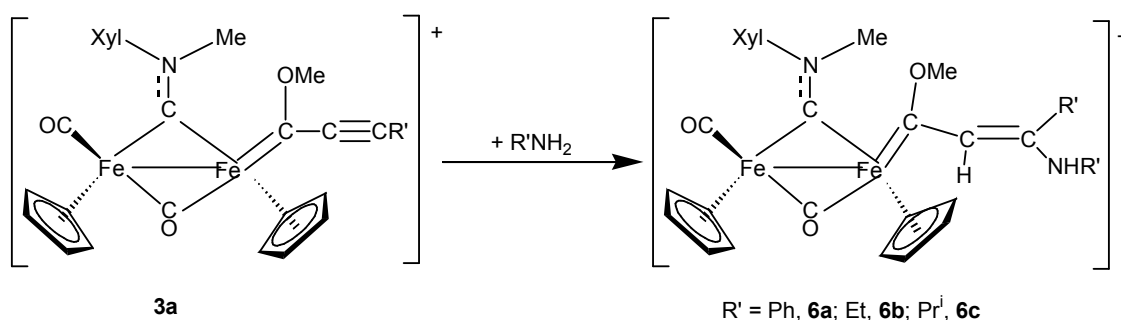
Both terminal and bridging ν (CO) bands in the IR spectra of **4,5** are at 20-30 cm⁻¹ below the ones on the parent compounds **3**, as a consequence of the lower π -acidity of C(OMe)CH=C(R')(NR₂) compared to C(OMe)C \equiv C(R'). The three C-atoms of the enamino methoxy carbene ligand resonate in the ¹³C NMR spectra at 277-280 [Fe=C], 114-115 [CH=] and 157-160 ppm [=C(N)], whereas the olefinic proton resonates at 5.4-6.2 ppm in the ¹H spectra. Only one species is present in the NMR spectra, as a result of a complete regio- and stereo-selective addition of the amines to **3**. NOE has been detected in all species **4,5** between the olefinic CH and the protons of the NR₂ groups [R₂ = Me₂, C₃H₁₀], indicating that the E-configuration of the double bond is fully retained in solution. Irradiation of =CH in **4,5** generates NOE also on the protons of OMe, the methyl group of μ -CN(Me)(R) and one Cp ligand. The solid state structure of **4c** shows that the distance between the olefinic CH proton and the methyl group of μ -CN(Me)(R) is less than

2.5 Å, whereas the one with the closer Cp ligand is *ca.* 3.6 Å, and the OMe is at more than 4.5 Å. Therefore, free rotation in solution around the Fe=C and C-OMe bonds has to be assumed in order to bring the CH closer to OMe and Cp and, hence, to fully explain the NOE experiments (see next Section for further details).

3.3 Reactivity $[Fe_2\{\mu-CN(Me)(R)\}(\mu-CO)(CO)\{C(OMe)C\equiv CR'\}(Cp)_2]^+$ with primary amines.

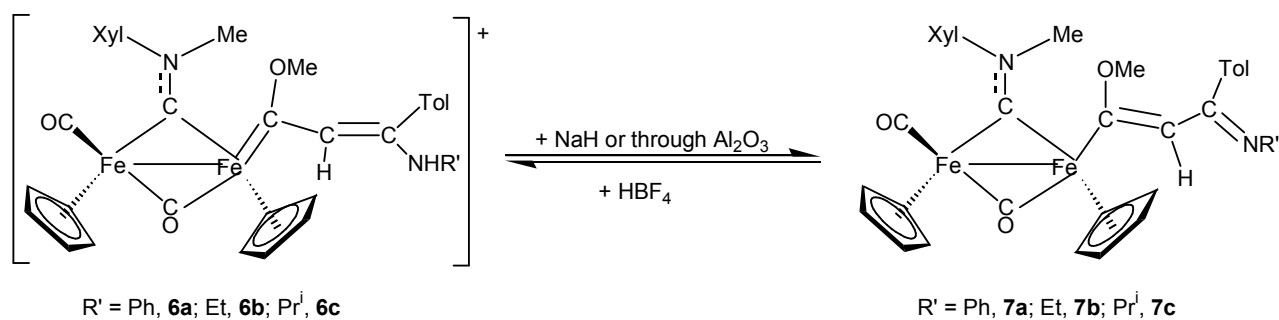
Similarly to what reported in the previous Section, complex **3a** adds primary amines $R'NH_2$, both aromatic ($R' = Ph$) and aliphatic ($R' = Et, Pr^i$), to give 4-(*NH*-amino)-1-metalla-1,3-diene complexes $[Fe_2\{\mu-CN(Me)(Xyl)\}(\mu-CO)(CO)\{C(OMe)CH=C(R)(NHR')\}(Cp)_2]^+$ ($R = Ph$, **6a**; Et , **6b**; Pr^i , **6c**), in very good yields (81-86 %) (Scheme 5).

Scheme 5



Attempts to further purify **6** by alumina column chromatography resulted in their partial deprotonation to give the neutral vinyl imine complexes $[Fe_2\{\mu-CN(Me)(Xyl)\}(\mu-CO)(CO)\{C(OMe)=CHC(=NR)(Tol)\}(Cp)_2]$ ($R = Ph$, **7a**; Et , **7b**; Pr^i , **7c**). Compounds **7** can be more efficiently obtained by deprotonation of **6** with NaH in THF (yields 62-72 % after column chromatography) (Scheme 6). The IR spectra of **7** show $\nu(CO)$ at *ca.* 1958 (terminal) and 1780 (bridging) cm^{-1} , frequencies typical for neutral complexes, and two $\nu(CN)$ at 1580-1590 and 1548-1562 cm^{-1} , attributable to the imine $C=N$ and aminocarbonyne $\mu-CN(Me)(Xyl)$ stretchings, respectively. Only one species is present in the NMR spectra, which show a typical olefinic CH at δ_H *ca.* 4.8-5.2 ppm and δ_C *ca.* 113-117 ppm. The imine carbon resonates in the ^{13}C NMR at *ca.* 165 ppm, whereas the Fe-bound vinyl carbon resonates at 190-205 ppm.

Scheme 6



The molecular structure of **7a** is shown in Figure 3, whereas the main bond lengths and bond angles are reported in Table 4. The Fe(1)-C(23) distance [1.956(7) Å] indicates the presence of an almost pure σ -Fe-C(sp²) interaction with only a very minor π -interaction, as expected for a metal-vinyl bond. Thus, the electron density is greater on Fe(1) than in Fe(2) (bound to CO) and consequently μ -CO shows a strong asymmetry [Fe(1)-C(12) 1.818(11), Fe(2)-C(12) 1.968(9) Å]. The C(23)-C(25) interaction [1.353(10) Å] is typical for a C=C double bond, whereas C(25)-C(26) [1.492(10) Å] is an almost pure single bond, indicating lack of conjugation between the vinyl and imine group, and, in fact, the two π -system are considerably tilted [C(23)-C(25)-C(26)-N(2) dihedral angle 147.8(9)°]. The C(26)-N(2) [1.285(10) Å] and C(23)-O(1) [1.387(9) Å] interactions are typical for an imine and an enol ether, respectively [29]. The C(23)=C(25) bond possesses an E-configuration, as well as the C(26)=N(2) bond, whereas the ligand adopts a *s-trans* conformation around the C(25)-C(26) single bond. The vinyl ligand is tilted respect to the Fe(1)-Fe(2) vector [Fe(2)-Fe(1)-C(23)-C(25) dihedral angle -52.6(9)°] with the C(25)-H(25) vector pointing at the bridging aminocarbene carbon.

Figure 3

Molecular structure of **7a**, with key atoms labelled (all H atoms, except H(25), have been omitted).

Displacement ellipsoids are at 30% probability level.

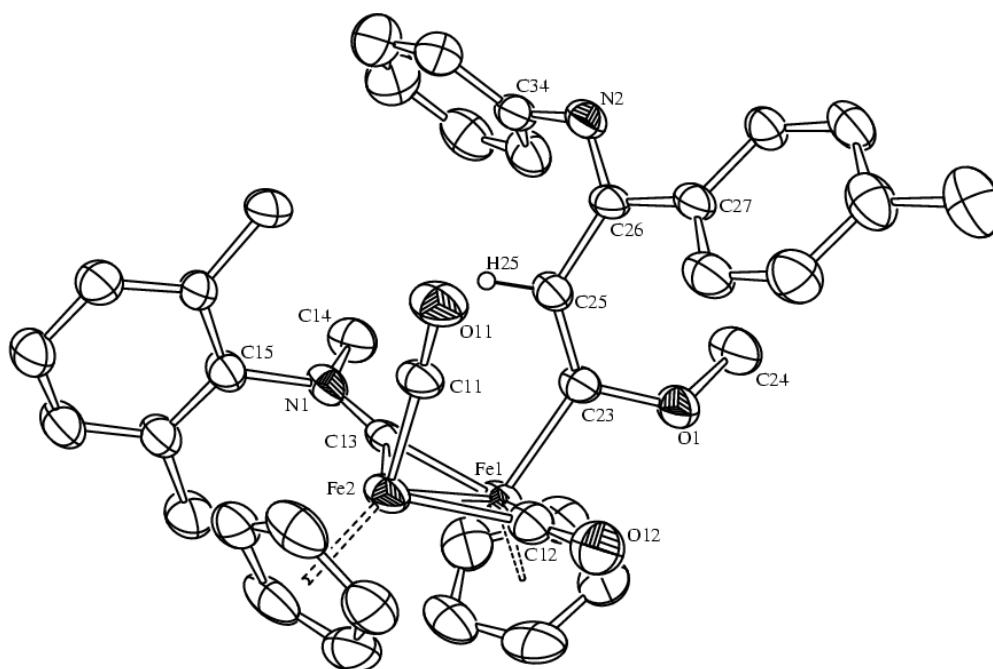


Table 4

Selected bond lengths (Å) and angles (°) for complex **7a**.

Fe(1)-Fe(2)	2.5058(16)	C(13)-N(1)	1.304(10)
Fe(2)-C(11)	1.734(8)	C(23)-O(1)	1.387(9)
Fe(1)-C(12)	1.818(11)	O(1)-C(24)	1.440(10)
Fe(2)-C(12)	1.968(9)	C(23)-C(25)	1.353(10)
Fe(1)-C(13)	1.812(8)	C(25)-C(26)	1.492(10)
Fe(2)-C(13)	1.882(9)	C(26)-C(27)	1.459(12)
Fe(1)-C(23)	1.956(7)	C(26)-N(2)	1.285(10)
C(11)-O(11)	1.155(8)	N(2)-C(34)	1.393(11)
C(12)-O(12)	1.183(10)	N(1)-C(15)	1.465(10)
Fe(1)-C(23)-O(1)	111.6(5)	C(25)-C(26)-C(27)	121.6(8)
Fe(1)-C(23)-C(25)	129.0(6)	C(25)-C(26)-N(2)	122.0(8)
O(1)-C(23)-C(25)	119.0(6)	C(27)-C(26)-N(2)	116.2(7)
C(23)-C(25)-C(26)	131.4(7)	C(26)-N(2)-C(34)	121.6(7)

Protonation of **7** with HBF_4 in CH_2Cl_2 yields quantitatively the cationic parent compounds **6** (Scheme 6), indicating that the protonation/deprotonation of complexes **7** and **6** is completely reversible. Moreover, the spectroscopic data of **6** do not depend on how they have been obtained, suggesting that anion-cation interactions are not very important in solution.

The solid state structures of **6a**[BF₄] \cdot CH₂Cl₂ and **6c**[CF₃SO₃] \cdot 0.5Et₂O have been determined by X-ray analyses (see Figures 4 and 5, and Table 5). A hydrogen bond between the enaminic proton N(2)H(2n) of the cation and the BF₄⁻ anion exists in the structure of **6a**[BF₄] \cdot CH₂Cl₂ [N(2)...F(3) 3.154(10) Å, N(2)-H(2n)...F(3) 170(8)°]. In a similar way, there is a hydrogen bond between the enaminic group and the CF₃SO₃⁻ anion in **6c**[CF₃SO₃] \cdot 0.5Et₂O [N(2)...O(20) 2.954(5) Å, N(2)-H(2n)...O(20) 166(4)°]. The molecular structures of the cations **6a** and **6c** are both composed by a Fe₂{ μ -CN(Me)(Xyl)}(μ -CO)(CO)(Cp₂) unit with a *cis*- α structure (see previous Sections) and an enamino methoxy carbene ligand C(OMe)CH=C(Tol)(NHR).

Figure 4

Molecular structure of the cation **6a**, with key atoms labelled (all H atoms, except H(25) and H(2n), have been omitted). Displacement ellipsoids are at 30% probability level. Only the main image of the disordered Ph group bound to N(2) is drawn.

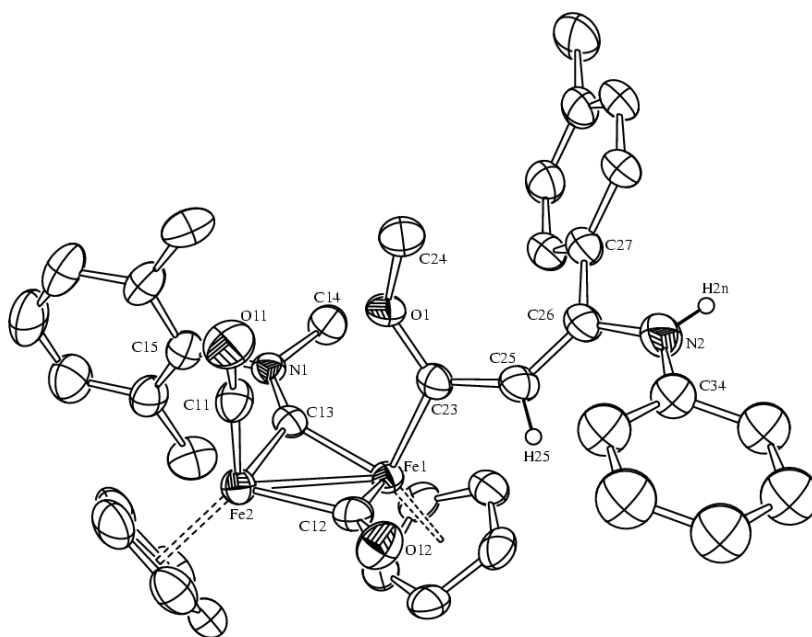


Figure 5

Molecular structure of the cation **6c**, with key atoms labelled (all H atoms, except H(25) and H(2n), have been omitted). Displacement ellipsoids are at 30% probability level.

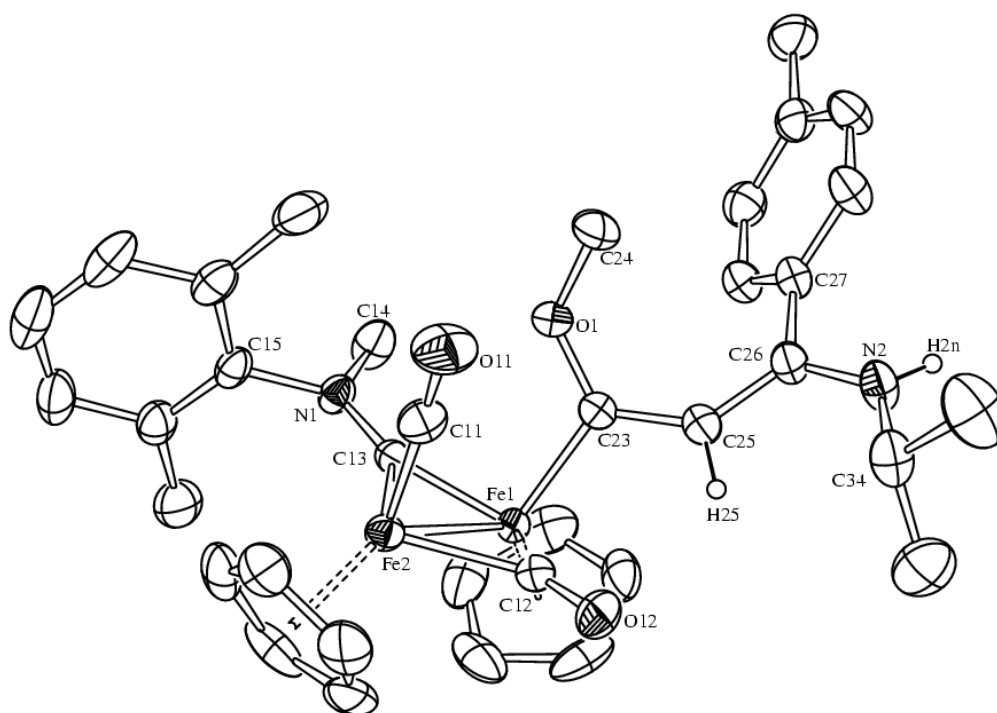


Table 5

Selected bond lengths (Å) and angles (°) for complexes **6a** and **6c**.

	6a	6c
Fe(1)-Fe(2)	2.5028(13)	2.5112(8)
Fe(2)-C(11)	1.731(8)	1.750(4)
Fe(1)-C(12)	1.850(7)	1.866(3)
Fe(2)-C(12)	1.969(7)	1.979(3)
Fe(1)-C(13)	1.840(6)	1.847(3)
Fe(2)-C(13)	1.886(6)	1.892(3)
Fe(1)-C(23)	1.903(6)	1.934(3)
C(11)-O(11)	1.160(8)	1.150(4)
C(12)-O(12)	1.195(7)	1.170(4)
C(13)-N(1)	1.307(8)	1.308(4)
C(23)-O(1)	1.350(7)	1.337(4)
O(1)-C(24)	1.461(8)	1.455(4)
C(23)-C(25)	1.425(9)	1.400(4)
C(25)-C(26)	1.356(9)	1.403(5)
C(26)-C(27)	1.472(9)	1.476(5)
C(26)-N(2)	1.375(9)	1.335(4)

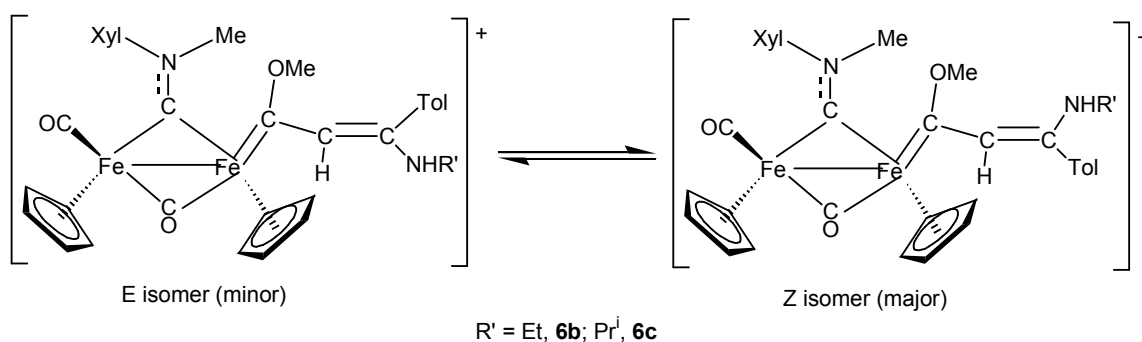
N(2)-C(34)	1.419(9)	1.463(5)
Fe(1)-C(23)-O(1)	117.2(4)	116.9(2)
Fe(1)-C(23)-C(25)	121.8(5)	120.5(2)
O(1)-C(23)-C(25)	120.9(5)	122.6(3)
C(23)-C(25)-C(26)	130.7(6)	133.7(3)
C(25)-C(26)-C(27)	125.2(6)	123.9(3)
C(25)-C(26)-N(2)	120.6(6)	119.9(3)
C(27)-C(26)-N(2)	113.7(6)	116.1(3)
C(26)-N(2)-C(34)	125.0(7)	125.2(3)

The Fe(1)-C(23) interactions [1.903(6) and 1.934(3) Å for **6a** and **6c**, respectively] suggest a π -character of the bond halfway between the ones found in **3a** and **7a**; also the μ -CO asymmetry assumes an intermediate value [Fe(1)-C(12) 1.850(7) and 1.866(3), Fe(2)-C(12) 1.969(7) and 1.979(3) Å for **6a** and **6c**, respectively]. Comparison of the C(23)-C(25) [1.425(9) Å **6a**, 1.400(4) Å **6c**], C(25)-C(26) [1.326(9) Å **6a**, 1.403(5) Å **6c**] and C(26)-N(2) [1.375(9) Å **6a**, 1.335(4) Å **6c**] interactions indicates that the terminal ligand in **6a**, as in **4c**, can be mainly described by the 4-(*NH*-amino)-1-metalla-1,3-diene structure Fe=C(OMe)-CH=C(Tol)(NHR), whereas for **6c** the zwitterionic structure (\ominus)Fe-C(OMe)=CH-C(Tol)(=N $^+$ HR) becomes more important; the lengthening of the Fe(1)-C(23) passing from **6a** to **6c** interaction is in perfect agreement with this hypothesis. In both **6a** and **6c**, the C(23)=C(25) bonds possess an E-configuration as in **4c**, whereas the Fe(1),C(23),C(25),C(26)[N(2)HR] backbone adopts a tilted and not a planar *s-trans* conformation [dihedral angles Fe(1)-C(23)-C(25)-C(26) 144.1(7) and $-152.0(4)^\circ$, C(23)-C(25)-C(26)-N(2) 173.3(7) and $-164.1(4)^\circ$ for **6a** and **6c**, respectively]. Finally, the C(OMe)CH=C(Tol)(NHR) ligand in **6a** and **6c** adopts a different orientation respect to the Fe(1)-Fe(2) vector [dihedral angles Fe(2)-Fe(1)-C(23)-C(25) 130.1(5) and $-112.2(3)^\circ$ for **6a** and **6c**, respectively], compared to **4c**. In fact, it is now the OMe group which points towards μ -CN(Me)(Xyl), whereas the C(25)-H(25) vector points on the opposite direction. Moreover, the C-OMe group is now rotated with the methyl pointing on the opposite side of the Fe₂(μ -C)₂ plane, bringing in this way its protons closer to the olefinic CH. The differences in the orientation of C(OMe)CH=C(Tol)(NHR) in **6a** and **6c** compared to the orientation of C(OMe)CH=C(Ph)(NMe₂) are probably due to packing effects. It is very likely that in solution there is free rotation around the Fe=C and C-OMe bonds and, hence, the solution structures for complexes **4-6** should be an average of the solid state structures of **4c**, **6a** and **6c**, as

demonstrated by NOE studies. In fact, only in this way the olefinic CH proton can be, in average, close enough to μ -CN(Me)(R), Cp and OMe to generate NOE.

In the case of **6a**, the ^1H and ^{13}C NMR spectra show the presence in solution at room temperature of only one species; the NMR data and, in particular, NOE data clearly indicate that the solid state structure is completely retained in solution as well as the E-configuration of the double bond. Conversely, the ^1H and ^{13}C NMR spectra at room temperature indicate the presence of an exchange process in the case of **6b,c**, which is frozen below 238 K. At these temperatures, two species are present in solution in the ratio 1 : 0.4 (**6b**) and 1 : 0.2 (**6c**), identified as Z-**6b,c** (major species) and E-**6b,c** (minor species) (Scheme 7). Their NMR spectra have been fully assigned by gs-HSQC and gs-HMBC [16] at low temperature (see Experimental). The olefinic CH protons resonate at δ_{H} ca. 6.2 ppm for E-**6b,c**, as in **4** which have all the E-configuration, whereas they are upfield shifted for Z-**6b,c** (δ_{H} ca. 5 ppm) because of the shielding effect of the *cis* Tol group. Conversely, the NH resonances appear to resonate at higher fields in E-**6b,c** (δ_{H} ca. 7.5-8.0 ppm) than in Z-**6b,c** (δ_{H} ca. 9.2-10 ppm), and this is due to the formation of an intra-molecular hydrogen bond in Z-**6b,c** between NH and the OMe group, as found in analogous mononuclear complexes [12a]. NOE studies on **6b,c** have been satisfactorily performed at 198 K, since at higher temperatures saturation transfer effects are interfering. These studies have confirmed the E-configuration for the minor isomers of **6b,c** and have demonstrated that also at low temperature there is still rotation around the Fe=C and C-OMe bonds. For instance, irradiation of the CH resonance of the minor isomer of **6b** generates NOE on one Cp ligand, the aminocarbyne NMe, the OMe and the Et groups.

Scheme 7



A full line shape analysis of the ^1H VT NMR spectra of **6b,c** has allowed the calculation of the activation parameters for the E-Z conversion. The Arrhenius plot gives $E_a = 48.2 \pm 1.4 \text{ KJ mol}^{-1}$ for **6b**, and $E_a = 53.3 \pm 1.7 \text{ KJ mol}^{-1}$ for **6c**, whereas the use of the Eyring equation allows the calculation of both ΔH^\ddagger (45.9 ± 1.4 and $50.9 \pm 1.7 \text{ KJ mol}^{-1}$ for **6b** and **6c**, respectively) and ΔS^\ddagger (-48.7 ± 3.4 and $-42.0 \pm 4.3 \text{ J K}^{-1} \text{ mol}^{-1}$ for **6b** and **6c**, respectively). These data indicate that the

process is slightly slower for **6c** than **6b**. Moreover, the fact that ΔS^\ddagger is negative is probably due to the fact that **Z-6b,c** but not **E-6b,c** contain an intra-molecular hydrogen bond and, thus, they have a different capability of interacting with the solvent.

The different behaviour in solution of **6b,c** compared to **6a** correlates quite well with the different C(25)-C(26) bond order determined in the solid state. Thus, in **6a** C(25)=C(26) shows a double bond character and, in fact, no exchange has been detected even at high temperature. Conversely, the C(25)-C(26) bond order is reduced in **6b,c**, probably because of the more electron donating character of Et and Prⁱ compared to Ph, and, hence, the dynamic conversion between the E and Z isomers occurs in solution.

4. Conclusions

The reaction of diiron alkynyl methoxy carbene complexes **3** with both primary and secondary amines appears to be completely regioselective, and results in the exclusive formation of 4-amino-1-metalla-1,3-diene compounds **4-6**. This should be contrasted with the reaction of mononuclear chromium and tungsten alkynyl alkoxy carbene compounds with amines, which can afford also 1-aminocarbene and (3-amino)allenylidene complexes [1a, 11]. Probably, the different electronic properties of the moieties bearing the carbene ligands, *i.e.* $\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}\{\mu\text{-CO}\}\text{(CO)(Cp)}_2$ and M(CO)_5 (M = Cr, W), are mainly responsible for the different distribution of products in the two reactions. Moreover, the reaction of **3** with amines (both primary and secondary) is also completely stereoselective, resulting in the formation of only the E-isomer (*cis* addition), the only exceptions being the addition of EtNH₂ and PrⁱNH₂ which results in a mixture of E and Z isomers. Conversely, the reaction of the mononuclear complexes $\text{(CO)}_5\text{M=C(OEt)C}\equiv\text{CR}$ (M = Cr, W) gives usually products with E-configuration in the case of secondary amines and Z-isomers with primary aromatic amines. Thus, the replacement of the mono-metallic M(CO)_5 (M = Cr, W) fragment with the dinuclear $\text{Fe}_2\{\mu\text{-CN(Me)(R)}\}\{\mu\text{-CO}\}\text{(CO)(Cp)}_2$ unit affects both the regio- and stereo-chemistry of the reaction of the alkynyl alkoxy ligand with amines. In the case of primary aliphatic amines (EtNH₂ and PrⁱNH₂), since exchange between the E and Z isomers is observed, is impossible to say whether the addition is just not stereo-selective, or if a *cis* addition occurs also in this case, followed by partial isomerisation of the original E-product.

The results reported in this paper show that diiron alkynyl methoxy carbene complexes **3** can easily undergo to Micheal-type additions as previously found in analogous mononuclear complexes, but, at the same time, some important differences in the regio- and stereo-chemistry have been highlighted. Further work will be devoted to fully understand the analogies and the differences between the mononuclear and dinuclear systems, with the aim of exploiting the latter for

organic synthesis. For this purpose, it is very important to note that iron, differently from chromium, is completely non toxic.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 243230 for **3a**[CF₃SO₃]·Et₂O, 243231 for **7a**·CH₂Cl₂, 2432332 for **6a**[BF₄]·CH₂Cl₂, 243233 for **4c**[CF₃SO₃] and 243234 for **6c**[CF₃SO₃]·0.5Et₂O. 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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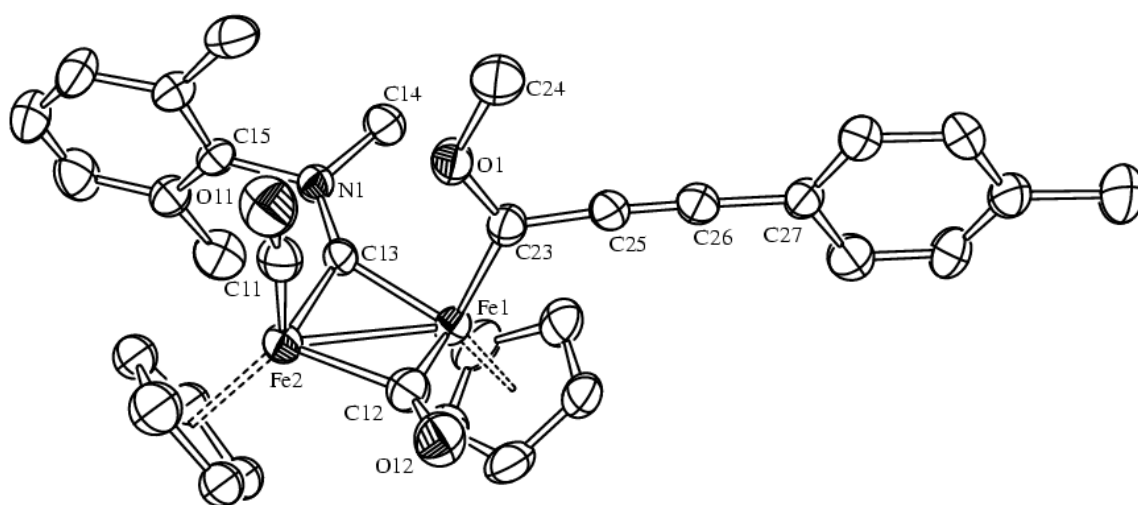
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Graphical abstract



The new diiron alkynyl methoxy carbene complexes $[\text{Fe}_2\{\mu\text{-CN}(\text{Me})(\text{R})\}\{\mu\text{-CO}\}(\text{CO})\{\text{C}(\text{OMe})\text{C}\equiv\text{CR}'\}\{\text{Cp}\}_2]^+$ have been obtained following the traditional “Fischer synthesis”. These add amines selectively at the $\text{C}\equiv\text{C}$ triple bond affording dinuclear species containing an enamino methoxy carbene ligand. When a proton is present on the enamino nitrogen, this can be reversibly removed to give a neutral vinyl imine complex.