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Carbon Monoxide-Isocyanide Coupling Promoted by Acetylide Addition at a Diiron Complex

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General experimental details.

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Unless otherwise stated, solvents were distilled immediately before use under nitrogen from appropriate drying agents. Once isolated, the metal products were conserved under nitrogen. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). The reaction vessels were oven dried at 150°C prior to use, evacuated (10^{-2} mmHg) and then filled with nitrogen. Infrared spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer. Elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. ESI MS spectrum was recorded on a Waters Micromass ZQ 4000 on a sample dissolved in CH₃CN. NMR spectra were recorded on a Mercury Plus 400 instruments. The chemical shifts for ¹H and ¹³C were referenced to the non-deuterated aliquot of the solvent. The ¹H and ¹³C NMR spectra were assigned with assistance of ¹H.¹³C correlation measured through gs-HSOC and gs-HMBC experiments.¹ NOE measurements were recorded using the DPFGSE-NOE sequence.² The organic reactants were commercial products (Sigma Aldrich) of the highest purity available used as received. [Fe₂{ μ -CN(Me)(Xyl)}(μ -CO)(CO)(CNXyl)(Cp)₂][SO₃CF₃] (Xyl = 2,6- $C_6H_3Me_2$) was prepared according to the literature.³

X-ray crystallography.

Crystal data and collection details for $1a \cdot CH_2Cl_2$ and $1b \cdot 0.5Et_2O$ are reported in Table S1. The diffraction experiments were respectively carried out on a Bruker SMART 2000 diffractometer ($1a \cdot CH_2Cl_2$) and on a Bruker Apex II diffractometer ($1b \cdot 0.5Et_2O$), equipped with a CCD detector using Mo-K α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).⁴ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using $F^{2.5}$ Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, apart from the Et₂O molecule in $1b \cdot 0.5Et_2O$. The Cp ligand bonded to Fe(1) in $1a \cdot CH_2Cl_2$ is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar *U* restraints and one occupancy parameter per disordered group.

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² K. Stott, J. Stonehouse, J. Keeler, T. L. Hwang and A. J. Shaka, J. Am. Chem. Soc., 1995, 117, 4199.

³ F. Marchetti, S. Zacchini, and V. Zanotti, Organometallics, 2014, 33, 3990.

⁴ G. M. Sheldrick, SADABS, *Program for empirical absorption correction*, University of Göttingen, Göttingen, Germany, 1996.

⁵ G. M. Sheldrick, SHELX97, University of Göttingen, Göttingen, Germany, 1997.

Complex	$1a \cdot CH_2Cl_2$	$1b \cdot 0.5Et_2O$
Formula	$C_{40}H_{38}Cl_2Fe_2N_2O_2$	$C_{42}H_{43}Fe_2N_2O_{2.5}$
Formula weight	761.32	727.48
Т, К	293(2)	293(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_{1}/c$
<i>a</i> , Å	10.271(2)	16.505(3)
b, Å	20.397(4)	14.661(3)
<i>c</i> , Å	17.702(4)	17.918(3)
β, °	105.15(3)	111.590(2)
Cell volume, Å ³	3579.6(12)	4031.9(13)
Z	4	4
$D_{\rm c},{\rm g~cm}^{-3}$	1.413	1.198
μ , mm ⁻¹	0.997	0.755
F(000)	1576	1524
Crystal size, mm	0.24×0.21×0.15	0.25×0.20×0.15
θ limits, °	1.55-25.55	1.92-25.03
Reflections collected	32914	35762
Independent reflections	$6692 [R_{int} = 0.0385]$	7111 [$R_{int} = 0.0894$]
Data/restraints/parameters	6692/ 146 / 479	7111 / 9 / 442
Goodness on fit on F ²	1.144	1.091
$R_1 (I > 2\sigma(I))$	0.0592	0.0868
wR_2 (all data)	0.1446	0.2820
Largest diff. peak and hole, e.Å ⁻³	1.148 / -0.664	0.623 / -0.642

Table S1. Crystal data and experimental details for $1a \cdot CH_2Cl_2$ and $1b \cdot 0.5Et_2O$.

Synthesis of $[Fe_2\{\mu-CN(Me)(Xyl)\}(\mu-CO)\{\mu-C(O)N(Xyl)C(C=CR)\}(Cp)_2]$ (R = Ph, 1a; R = Tol, 1b; R = SiMe₃, 1c). The synthesis of 1a is described in detail; 1b-c were very similar procedures from $[Fe_2{\mu-CN(Me)(Xyl)}(\mu$ prepared with CO)(CO)(CNXyl)(Cp)₂][SO₃CF₃] and the appropriate lithium acetylide. A solution of LiC=CPh in THF (5.0 mL, 0.29 mmol), freshly prepared from equimolar amounts of HC=CPh and BuLi, was added to a solution of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-$ CO)(CO)(CNXyl)(Cp)₂][SO₃CF₃] (250 mg, 0.345 mmol) in THF (20 mL). The mixture was heated at reflux temperature for 12 hours, then it was cooled to room temperature and eliminated of the volatile materials under vacuum. The resulting residue was dissolved in CH₂Cl₂ (10 mL) and charged on an alumina column. A red fraction was collected by using a mixture of CH_2Cl_2 and THF (3:1 v/v) as eluent, thus 1a was isolated as a red solid upon removal of the volatiles under vacuum. Crystals suitable for X ray analysis were obtained as follows: for 1a, from a dichloromethane solution layered with pentane and settled aside at -40 °C; for 1b, from a concentrated diethyl ether solution settled aside at -20 °C.

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO){μ-C(O)N(Xyl)C(C=CPh)}(Cp)₂], 1a. Yield 163 mg, 70%. Anal. Calcd. for C₃₉H₃₆Fe₂N₂O₂: C, 69.25; H, 5.36; N, 5.36. Found: C, 69.31; H, 5.28; N, 5.41. IR (CH₂Cl₂): $v_{C=C} = 2167w$, $v_{CO} = 1769vs$, 1606s, $v_{\mu CN} = 1510m$ cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.25$ -6.79 (11 H, *arom* CH); 5.03, 4.43 (s, 10 H, Cp); 4.23 (s, 3 H, NMe); 2.57, 2.09, 2.02, 1.80 ppm (s, 12 H, C₆H₃*Me*₂). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 348.7$ (μ-CN); 277.6 (μ-CO); 239.7 (Fe=C); 225.6 (C=O); 147.4, 143.3 (*ipso*-C₆H₃Me₂); 134.5-125.2 (*aromatics*); 119.6, 117.3 (C=C); 91.4, 90.9 (Cp); 51.4 (NMe); 18.8, 18.7 ppm (C₆H₃*Me*₂).

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO){μ-C(O)N(Xyl)C(C=CTol)}(Cp)₂], 1b. Red solid, 71% yield. Anal. Calcd. for C₄₀H₃₈Fe₂N₂O₂: C, 69.58; H, 5.55; N, 4.06. Found: C, 69.54; H, 5.50; N, 4.11. IR (CH₂Cl₂): $v_{C=C} = 2163w$, $v_{CO} = 1769vs$, 1603s, $v_{\mu-CN} = 1509m$ cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.25$ -6.79 (10 H, *arom* CH); 5.01, 4.42 (s, 10 H, Cp); 4.22 (s, 3 H, NMe); 2.56, 2.08, 2.01, 1.85 (s, 12 H, C₆H₃*Me*₂); 2.28 ppm (s, 3 H, C₆H₄*Me*). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 348.8$ (μ-CN); 277.7 (μ-CO); 239.9 (Fe=C); 225.6 (C=O); 147.3, 143.7, 139.6, 135.1, 134.5, 133.6, 131.5, 129.5, 129.1, 128.7, 128.3, 127.5, 126.8, 126.5 (*aromatics*); 119.7, 117.9 (C=C); 91.3, 90.7 (Cp); 51.3 (NMe); 21.5 (C₆H₄*Me*); 18.7, 18.6, 18.5 ppm (C₆H₃*Me*₂).

 $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){\mu-C(O)N(Xyl)C(C=CSiMe_3)}(Cp)_2]$, 1c. Red solid, 70% yield. Anal. Calcd. for C₃₆H₄₀Fe₂N₂O₂Si: C, 64.30; H, 6.00; N, 4.17. Found: C, 64.29; H, 5.94; N, 4.22. IR (CH₂Cl₂): $v_{C=C} = 2102w$, $v_{CO} = 1965vs$, 1778s, $v_{\mu-CN} =$ 1504m cm⁻¹. ¹H NMR (CDCl₃, 298 K): δ = 7.28-6.69 (m, 6 H, C₆H₃Me₂); 4.98, 4.42 (s, 10 H, Cp); 4.19 (s, 3 H, NMe); 2.63, 2.31, 1.97, 1.82 (s, 12 H, C₆H₃Me₂); 0.05 (s, 9 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 298 K): δ = 347.4 (µ-CN); 278.5 (µ-CO); 236.0 (Fe=C); 224.2 (C=O); 133.2-125.4 (*aromatics*); 123.9 (C=C); 91.9, 90.2 (Cp); 51.5 (NMe); 19.2, 18.9, 18.7 (C₆H₃Me₂); -0.67 ppm (SiMe₃).

Figure S1. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){\mu-C(O)N(Xyl)C(C=CPh)}(Cp)_2]$, 1a.



Figure S2. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){\mu-C(O)N(Xyl)C(C=CPh)}(Cp)_2]$, 1a.



Figure S3. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2\{\mu-CN(Me)(Xyl)\}(\mu-CO)\{\mu-C(O)N(Xyl)C(C=CTol)\}(Cp)_2]$, 1b.



Figure S4. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){\mu-C(O)N(Xyl)C(C=CTol)}(Cp)_2]$, 1b.



Figure S5. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){\mu-C(O)N(Xyl)C(C=CSiMe_3)}(Cp)_2]$, 1c.



Figure S6. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){\mu-C(O)N(Xyl)C(C=CSiMe_3)}(Cp)_2]$, 1c.



Synthesis of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CR}(CNXyl)(Cp)_2]$ (R = Ph, 2a; R = Tol, 2b; R = SiMe₃, 2c; Tol = 1,4-C₆H₄Me). The synthesis of 2a is described in detail; 2b-c were prepared with very similar procedures from $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO)(CNXyl)(Cp)_2][SO_3CF_3]$ and the appropriate lithium acetylide. A solution of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO)(CNXyl)(Cp)_2][SO_3CF_3]$ (150 mg, 0.207 mmol) in THF (15 mL) was cooled to -20 °C and then treated with a solution of LiC=CPh in THF (5.0 mL, 0.29 mmol), which was freshly prepared from equimolar amounts of HC=CPh and BuLi. The mixture was allowed to warm to room temperature and stirred for additional 30 minutes. The final solution was filtered on a short alumina pad, thus the solvent was removed under reduced pressure. The residue was dissolved in diethyl ether (10 mL) and charged on an alumina column. A green band was collected by using neat Et₂O as eluent: complex 2a was isolated as a pale-green solid upon removal of the volatiles under vacuum.

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO){C(O)C=CPh}(CNXyl)(Cp)₂], 2a. Yield 102 mg, 73%. Anal. Calcd. for C₃₉H₃₆Fe₂N₂O₂: C, 69.25; H, 5.36; N, 5.36. Found: C, 69.44; H, 5.22; N, 5.38. IR (CH₂Cl₂): $v_{C=N} = 2082vs$, $v_{CO} = 1766s$, 1598m, $v_{\mu-CN} = 1526m$ cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.60-6.89$ (11 H, arom CH); 4.94, 4.25 (s, 10 H, Cp); 4.34 (s, 3 H, NMe); 2.64, 2.34, 2.15 ppm (s, 12 H, C₆H₃Me₂). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 340.5$ (μ-CN); 273.7 (μ-CO); 257.7 (C=O); 176.5 (C=N); 148.4 (*ipso*-C₆H₃Me₂); 135.2-125.9 (*aromatics*); 91.8, 77.2 (C=C); 89.5, 85.4 (Cp); 51.4 (NMe); 18.6, 18.2, 17.4 ppm (C₆H₃Me₂).

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO){C(O)C=CTol}(CNXyl)(Cp)₂], 2b. Pale-green solid, 74% yield; chromatography: CH₂Cl₂. Anal. Calcd. for C₄₀H₃₈Fe₂N₂O₂: C, 69.58; H, 5.55; N, 4.06. Found: C, 69.66; H, 5.44; N, 3.98. IR (CH₂Cl₂): $v_{C=C} = 2159w$, $v_{C=N} = 2080vs$, $v_{CO} = 1766s$, 1591m, $v_{\mu+CN} = 1508m$ cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.51$ -6.90 (10 H, *arom* CH); 4.95, 4.26 (s, 10 H, Cp); 4.35 (s, 3 H, NMe); 2.66, 2.34, 2.15 (s, 12 H, C₆H₃Me₂); 2.38 ppm (s, 3 H, C₆H₄Me). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 340.6$ (μ-CN); 273.6 (μ-CO); 256.9 (C=O); 176.6 (C=N); 148.4 (*ipso-C*₆H₃Me₂); 138.2-125.1 (*aromatics*); 92.0, 78.0 (C=C); 90.4, 86.3 (Cp); 51.5 (NMe); 21.5 (C₆H₄Me); 19.6, 18.6, 17.6 ppm (C₆H₃Me₂).

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO){C(O)C=CSiMe₃}(CNXyl)(Cp)₂], 2c. Bright-green solid, 61% yield; chromatography: Et₂O. Anal. Calcd. for C₃₆H₄₀Fe₂N₂O₂Si: C, 64.30; H, 6.00; N, 4.17. Found: C, 64.20; H, 5.89; N, 4.15. IR (CH₂Cl₂): $v_{C=N} = 2080vs$, $v_{CO} = 1773s$, 1590w, $v_{\mu-CN} = 1530m$ cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.19$ -6.90 (6 H, C₆H₃Me₂); 4.86, 4.22 (s, 10 H, Cp); 4.25 (s, 3 H, NMe); 2.64, 2.29, 2.10 (s, 12 H,

C₆H₃*Me*₂); 0.26 ppm (s, 9 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 298 K): δ = 340.9 (µ-CN); 273.0 (µ-CO); 258.0 (C=O); 176.5 (C=N); 148.5 (*ipso*-C₆H₃Me₂); 135.5, 134.5, 133.5, 129.5, 127.8, 127.3, 126.0 (*aromatics*); 105.5, 93.2 (C=C); 90.0, 85.4 (Cp); 51.6 (NMe); 18.8, 18.4, 17.5 ppm (C₆H₃*Me*₂); 0.00 (SiMe₃). ESI-MS (ES⁺): 672 [M⁺, 52%], 575 m/z [M⁺ – CCSiMe₃, 100%]. Figure S7. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CPh}(CNXyl)(Cp)_2]$, 2a.



Figure S8. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CPh}(CNXyl)(Cp)_2]$, 2a.



Figure S9. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CTol}(CNXyl)(Cp)_2]$, 2b.



Figure S10. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CSiMe_3}(CNXyl)(Cp)_2]$, 2c.



Figure S11. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CSiMe_3}(CNXyl)(Cp)_2]$, 2c.



Synthesis of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CR)=NXyl}(Cp)_2]$ (R = Ph, 3a; R = Tol, 3b; R = SiMe₃, 3c). The synthesis of 3a is described in detail; 3b-c were prepared with very similar procedures from 2b-c. A solution of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO){C(O)C=CPh}(CNXyl)(Cp)_2]$, 2a (100 mg, 0.148 mmol), in CH₂Cl₂ (20 mL) was stirred at reflux temperature for 12 hours. Then the mixture was allowed to cool to room temperature, and charged on an alumina column. A red band was collected by using neat THF as eluent, thus 3a was isolated as a brown-red solid upon removal of the volatiles under vacuum.

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(C=CPh)=NXyl}(Cp)₂], 3a. Yield 61 mg, 61%. Anal. Calcd. for C₃₉H₃₆Fe₂N₂O₂: C, 69.25; H, 5.36; N, 5.36. Found: C, 69.29; H, 5.35; N, 5.29. IR (CH₂Cl₂): $v_{C=C} = 2167w$, $v_{CO} = 1965vs$, 1773s, $v_{\mu-CN} = 1505m$ cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.30$ -6.82 (11 H, *arom* CH); 5.03, 4.33 (s, 10 H, Cp); 4.33 (s, 3 H, NMe); 2.62, 2.31, 1.95, 1.91 ppm (s, 12 H, C₆H₃*Me*₂). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 342.5$ (μ-CN); 271.3 (μ-CO); 219.0 (C=N); 211.0 (CO); 147.7 (*ipso*-C₆H₃Me₂); 135.1-123.4 (*aromatics*); 117.3, 105.7 (C=C); 90.6, 88.1 (Cp); 52.5 (NMe); 18.9, 18.6, 18.5, 18.3 ppm (C₆H₃Me₂).

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(C=CTol)=NXyl}(Cp)₂], 3b. Brown-red solid, 68% yield. Anal. Calcd. for C₄₀H₃₈Fe₂N₂O₂: C, 69.58; H, 5.55; N, 4.06. Found: C, 69.64; H, 5.58; N, 4.15. IR (CH₂Cl₂): $v_{C=C} = 2164w$, $v_{CO} = 1964vs$, 1773s, $v_{\mu-CN} = 1509m \text{ cm}^{-1}$. ¹H NMR (CDCl₃, 298 K): $\delta = 7.31$ -6.83 (10 H, *arom* CH); 5.01, 4.31 (s, 10 H, Cp); 4.28 (s, 3 H, NMe); 2.60, 2.28, 1.89 (s, 12 H, C₆H₃*Me*₂); 2.29 ppm (s, 3 H, C₆H₄*Me*). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 343.6$ (μ-CN); 272.5 (μ-CO); 220.0 (C=N); 210.9 (CO); 150.0 (*ipso*-C₆H₄Me); 147.7 (*ipso*-C₆H₃Me₂); 139.8-120.5 (*aromatics*); 118.0, 108.1 (C=C); 90.8, 88.4 (Cp); 52.6 (NMe); 21.5 (C₆H₄*Me*); 18.9, 18.7, 18.6, 18.4 ppm (C₆H₃*Me*₂).

[Fe₂{μ-CN(Me)(Xyl)}(μ-CO)(CO){C(C=CSiMe₃)=NXyl}(Cp)₂], 3c. Brown-red solid, 70% yield. Anal. Calcd. for C₃₆H₄₀Fe₂N₂O₂Si: C, 64.30; H, 6.00; N, 4.17. Found: C, 64.38; H, 6.06; N, 4.09. IR (CH₂Cl₂): $v_{C=C} = 2102w$, $v_{CO} = 1965vs$, 1778s, $v_{\mu-CN} =$ 1504m cm⁻¹. ¹H NMR (CDCl₃, 298 K): $\delta = 7.30$ -6.70 (6 H, *arom* CH); 4.91, 4.29 (s, 10 H, Cp); 4.28 (s, 3 H, NMe); 2.59, 2.29, 1.85 (s, 12 H, C₆H₃*Me*₂); -0.08 ppm (s, 9 H, SiMe₃). ¹³C{¹H} NMR (CDCl₃, 298 K): $\delta = 342.4$ (μ-CN); 270.7 (μ-CO); 218.6 (C=N); 210.0 (C=O); 151.3 (*ipso*-Ph); 147.7 (*ipso*-C₆H₃Me₂); 135.2, 133.6, 130.0, 128.2, 127.4, 126.8, 123.2 (*aromatics*); 121.8, 109.5 (C=C); 90.9, 87.9 (Cp); 51.7 (NMe); 18.8, 18.7, 18.5, 18.3 (C₆H₃*Me*₂); -0.37 ppm (SiMe₃).

Figure S12. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CPh)=NXyl}(Cp)_2]$, 3a.



Figure S13. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CPh)=NXyl}(Cp)_2]$, **3a**.



Figure S14. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CTol)=NXyl}(Cp)_2]$, 3b.



Figure S15. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CTol)=NXyl}(Cp)_2]$, **3b**.



Figure S16. ¹H NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CSiMe_3)=NXyl}(Cp)_2]$, 3c.



Figure S17. ¹³C NMR spectrum (CDCl₃, 400 MHz) of $[Fe_2{\mu-CN(Me)(Xyl)}(\mu-CO)(CO){C(C=CSiMe_3)=NXyl}(Cp)_2]$, 3c.

