Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information.

Experimental preparations and spectroscopic and analytical data for the new compounds.

Strongly Donor Metalla-N-Heterocyclic Carbenes

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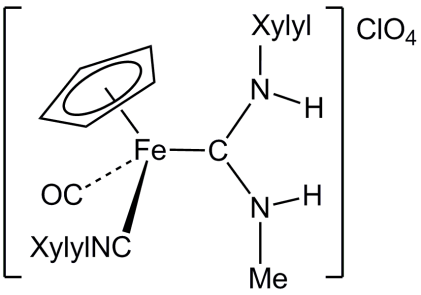
Experimental

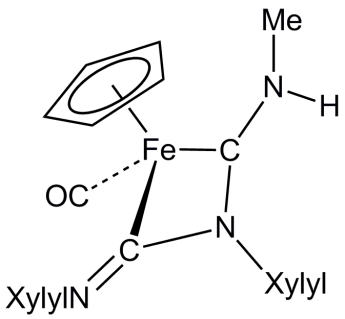
General Considerations

All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with Perkin-Elmer Spectrum 100 and Paragon 1000 spectrophotometers. The C, H, and N analyses were performed on a Perkin-Elmer 240B elemental analyzer. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Coupling constants *J* are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, hp = heptet, m = multiplet, br = broad. Chemical shifts of the NMR spectra were referenced to internal $SiMe_4$ (^1H and ^{13}C) or external H_3PO_4 (^{31}P). Assignments are based on $^1H,^1H$-COSY, $^1H,^{13}C$-HMBC, $^1H,^{13}C$-HSQC and DEPT experiments. All reagents were obtained commercially and used without further purification.

Synthesis and characterization of the new compounds



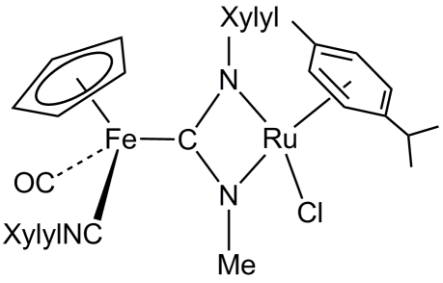
Synthesis of Compound [**2**](ClO_4): Through a solution of compound [**1**](ClO_4) (0.10 g, 0. 19 mmol) in dichloromethane (12 mL) NH_2CH_3 was bubbled for 5 min and the resulting mixture stirred for 1 h. The solution was then concentrated to 2 mL and hexane (5 mL) added to obtain a yellow precipitate, which was washed with hexane (3 x 5 mL) and dried under vacuum. Yield 99 mg (93%). ^1H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 8.47 (s, 1H, N*H*-Xylyl), 7.32-7.09 (6H, H_{arom}-Xylyl), 6.24 (q, $^3J_{HH}$ = 4.9 Hz, 1H, N*H*-Me), 5.17 (s, 5H, Cp), 3.15 (d, $^3J_{HH}$ = 4.9 Hz, 3H, NCH_3), 2.44 (s, 6H, $CNC_6H_3(CH_3)_2$), 2.23 (s, 3H, CH_3-Xylyl), 2.15 ppm (s, 3H, CH_3-Xylyl); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 215.9 (s, CO), 209.7 (s, $C_{carbene}$), 170.6 (s, *C*NXylyl), 137.0, 136.8, 135.5, 134,9, 134.2 (s, C_{ipso} and C_{ortho}-Xylyl), 129.8, 129.7, 129.2, 128.6 (s, C_{meta} and C_{para}-Xylyl), 85.3 (s, C_5H_5), 36.5 (s, NCH_3), 19.1 (s, $CNC_6H_3(CH_3)_2$), 18.5 (s, CH_3-Xylyl), 18.4 ppm (s, CH_3-Xylyl); IR (THF): ν(CO) 1976 (vs), ν(CN) 2130 cm^{-1} (vs). Anal. Calcd for $C_{25}H_{28}ClFeN_3O_5$: C, 55.42; H, 5.21; N, 7.76. Found: C, 55.09; H, 5.30; N, 7.82.



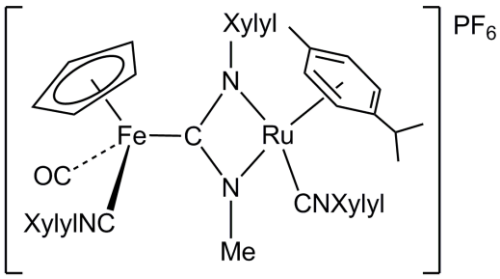
Synthesis of Compound **3**: To a solution of compound [**2**](ClO_4) (0.10 g, 0.18 mmol) in dichloromethane (12 mL) was added an excess of KOH (0.20 g, 3.56 mmol) and the resulting mixture stirred for 30 min at room temperature. The solution was then filtered and the solvent evaporated to dryness to obtain a yellow residue, which was extracted with hexane (3 x 5 mL). The resulting solution was filtered and then evaporated to dryness yielding a yellow solid. Yield 77 mg (95%). ^1H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 7.24-6.93 (5H, H_{arom}-Xylyl), 6.79 (t, $^3J_{HH}$ = 7.4 Hz, 1H, H_{para}-Xylyl), 6.14 (br, 1H, N*H*-Me), 4.31 (s, 5H, Cp), 3.11 (s, 3H, NCH_3), 2.32 (s, 3H, CH_3-Xylyl), 2.25 (s, 3H, CH_3-

Xylyl), 2.19 (s, 3H, CH_3-Xylyl), 2.18 ppm (s, 3H, CH_3-Xylyl); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 223.9 (s, $C_{carbene}$), 213.5 (s, CO), 176.9 (s, *C*=NXylyl), 150.6, 137.7, 137.5, 134.0 (s, C_{ipso} and C_{ortho}-Xylyl), 129.3, 128.9, 128.7, 128.2, 127.4 (s, C_{meta} and C_{para}-Xylyl), 80.3 (s, C_5H_5), 35.4 (s, NCH_3), 19.4, 19.3, 18.8, 18.5 ppm (s, CH_3-Xylyl); IR (THF): ν(CO) 1919 cm^{-1} (vs). Anal. Calcd for $C_{25}H_{27}FeN_3O$: C, 68.03; H, 6.17; N, 9.52. Found: C, 67.78; H, 6.31; N, 9.56.

Synthesis of Compound **4**: To a solution of compound **3** (0.10 g, 0.23 mmol) in THF (12 mL) was added $[Ru(p\text{-cym})Cl_2]_2$ (69 mg, 0.11 mmol) and $LiN(SiMe_3)_2$ (0.227 mL, 1 M in hexane) and the resulting mixture stirred for 1 h at room temperature, yielding an orange solution. The solvent was then evaporated to dryness and the residue extracted with hexane (3 x 5 mL). The solution was filtered and then the solvent evaporated under vacuum to obtain an orange solid. Yield 145 mg (90%). The complex was obtained as a mixture of two diastereomers (A and B), most probably resulting from the presence of two stereogenic centers (Fe and Ru), in an approximate ratio of 1:1. Isomer A: ^1H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 7.05 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H_{meta}-Xylyl), 6.80-6.70 (3H, H_{arom}-Xylyl), 6.59 (t, $^3J_{HH}$ = 7.3 Hz, 1H, H_{para}-Xylyl), 6.43 (d, $^3J_{HH}$ = 7.3 Hz, 1H, H_{meta}-Xylyl), 4.81 (d, $^3J_{HH}$ = 5.4 Hz, 1H, *p*-cym), 4.71-4.68 (2H, *p*-cym), 4.66 (s, 5H, Cp), 4.41 (d, $^3J_{HH}$ = 5.4 Hz, 1H, *p*-cym), 3.47 (s, 3H, NCH_3), 2.66 (s, 3H, CH_3-Xylyl), 2.60 (hp, $^3J_{HH}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.37 (s, 3H, CH_3-Xylyl), 1.98 (s, 6H, $CNC_6H_3(CH_3)_2$), 1.63 (s, 3H, CH_3-*p*-cym), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.11 ppm (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 219.0 (s, $C_{carbene}$), 205.5 (s, CO), 178.6 (s, *C*NXylyl), 150.9, 135.9, 135.4, 133.8, 130.0 (s, C_{ipso} and C_{ortho}-Xylyl), 128.3, 127.7, 137.3, 126.4, 123.1 (s, C_{meta} and C_{para}-Xylyl), 100.7, 93.8 (s, C_{ipso}-*p*-cym), 86.5 (s, C_5H_5), 80.4, 79.2 (s, CH_{arom}-*p*-cym), 41.5 (s, NCH_3), 31.3 (s, $CH(CH_3)_2$), 23.5, 22.4 (s, CH_3-Xylyl), 21.1, 21.0 (s, $CH(CH_3)_2$), 18.6 (s, $CNC_6H_3(CH_3)_2$), 17.7 ppm (s, CH_3-*p*-cym); Isomer B: ^1H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 7.30-7.25 (3H, H_{arom}-Xylyl), 6.82-6.70 (3H, H_{arom}-Xylyl), 4.87 (d, $^3J_{HH}$ = 5.5 Hz, 1H, *p*-cym), 4.76-4.72 (2H, *p*-cym), 4.62 (s, 5H, Cp), 4.53 (d, $^3J_{HH}$ = 5.6 Hz, 1H, *p*-cym), 3.41 (s, 3H, NCH_3), 2.70 (s, 3H, CH_3-Xylyl), 2.63 (hp, $^3J_{HH}$ = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.50 (s, 3H, CH_3-Xylyl), 2.21 (s, 6H, $CNC_6H_3(CH_3)_2$), 1.72 (s, 3H, CH_3-*p*-cym), 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.12 ppm (d, $^3J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 217.9 (s, $C_{carbene}$), 208.2 (s, CO), 181.2 (s, *C*NXylyl), 150.6, 136.5, 135.9, 134.4, 130.2 (s, C_{ipso} and C_{ortho}-Xylyl), 130.0-123.0 (C_{meta} and C_{para}-Xylyl), 100.5, 93.3 (s, C_{ipso}-*p*-cym), 85.9 (s, C_5H_5), 80.4, 79.9, 79.6, 79.4 (s, CH_{arom}-*p*-cym), 41.6 (s, NCH_3), 31.4 (s, $CH(CH_3)_2$), 23.4, 22.5 (s, CH_3-Xylyl), 21.2, 20.7 (s, $CH(CH_3)_2$), 18.8 (s, $CNC_6H_3(CH_3)_2$), 18.0 ppm (s, CH_3-*p*-cym); IR (THF): ν(CO) 1953 (vs), ν(CN) 2097 cm^{-1} (vs). Anal. Calcd for $C_{35}H_{40}ClFeN_3ORu$: C, 59.12; H, 5.67; N, 5.91. Found: C, 58.51; H, 5.97; N, 5.87.

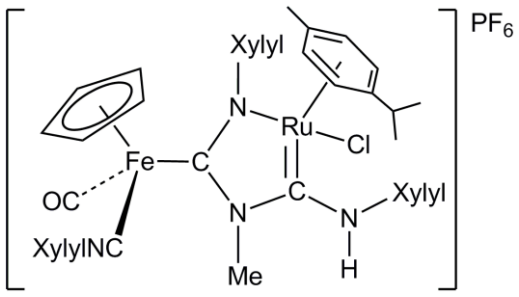


Synthesis of Compound [**5**](PF_6): To a solution of compound **4** (0.10 g, 0.14 mmol) in THF (12 mL) was added CNXylyl (18 mg, 0.14 mmol) and $TlPF_6$ (49 mg, 0.14 mmol) and the resulting mixture stirred for 15 min at room temperature. The solution was



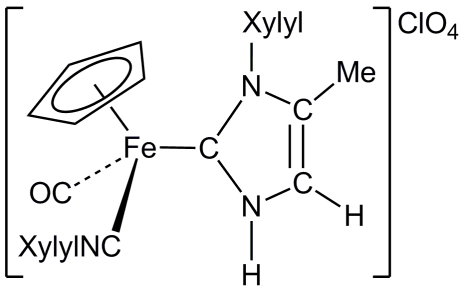
then filtered and concentrated to 2 mL. Addition of hexane (10 mL) causes the formation of an orange solid, corresponding of a mixture of two diastereomers in an approximate ratio 1:1. Yield 123 mg (92%). Isomer A: ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 7.30-6.85 (9H, H_{arom}-Xylyl), 5.71 (d, $^{3}J_{HH}$ = 6.1 Hz, 1H, *p*-cym), 5.67 (d, $^{3}J_{HH}$ = 6.1 Hz, 1H, *p*-cym), 5.39 (d, $^{3}J_{HH}$ = 6.3 Hz, 1H, *p*-cym), 5.32 (d, $^{3}J_{HH}$ = 6.3 Hz, 1H, *p*-cym), 4.70 (s, 5H, Cp), 3.27 (s, 3H, NCH_3), 2.44 (hp, $^{3}J_{HH}$ = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 2.39 (s, 6H, $CNC_6H_3(CH_3)_2$), 2.35 (s, 3H, CH_3-Xylyl), 2.20 (s, 3H, CH_3-Xylyl), 2.08 (s, 6H, $CNC_6H_3(CH_3)_2$), 1.97 (s, 3H, CH_3-*p*-cym), 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.11 ppm (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$); $^{13}C\{^{1}H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 216.4 (s, $C_{carbene}$), 215.3 (s, CO), 175.4 (s, *C*NXylyl), 148.8, 135.6, 135.0, 134.6, 134.3 (s, C_{ipso} and C_{ortho}-Xylyl), 129.9-125.3 (C_{meta} and C_{para}-Xylyl), 111.7, 105.5 (s, C_{ipso}-*p*-cym), 90.5, 90.3, 89.9, 89.2 (s, *C*H_{arom}-*p*-cym), 85.0 (s, C_5H_5), 44.2 (s, NCH_3), 31.3 (s, *C*$H(CH_3)_2$), 22.6, 21.2, 20.4 (s, CH_3-Xylyl), 19.8, 19.7 (s, $CNC_6H_3(CH_3)_2$), 19.5 (s, $CH(CH_3)_2$), 19.0 (s, $CH(CH_3)_2$), 18.9 ppm (s, CH_3-*p*-cym); Isomer B: ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 7.37-6.82 (9H, H_{arom}-Xylyl), 5.71 (dd, $^{3}J_{HH}$ = 6.2 Hz, $^{3}J_{HH}$ = 3.5 Hz, 1H, *p*-cym), 5.67 (d, $^{3}J_{HH}$ = 6.4 Hz, 1H, *p*-cym), 5.29 (m, 2H, *p*-cym), 4.68 (s, 5H, Cp), 3.25 (s, 3H, NCH_3), 2.57 (s, 6H, $CNC_6H_3(CH_3)_2$), 2.43 (s, 3H, CH_3-Xylyl), 2.28 (s, 6H, $CNC_6H_3(CH_3)_2$), 2.10 (s, 3H, CH_3-Xylyl), 1.94 (s, 3H, CH_3-*p*-cym), 1.16 (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$), 1.09 ppm (d, $^{3}J_{HH}$ = 6.9 Hz, 3H, $CH(CH_3)_2$); $^{13}C\{^{1}H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 217.3 (s, $C_{carbene}$), 215.5 (s, CO), 174.6 (s, *C*NXylyl), 158.4, 148.6, 135.7, 135.3, 134.8, 134.8 (s, C_{ipso} and C_{ortho}-Xylyl), 130.0-125.4 (s, C_{meta} and C_{para}-Xylyl), 111.4, 105.4 (s, C_{ipso}-*p*-cym), 90.5, 90.3, 89.9, 89.4 (s, *C*H_{arom}-*p*-cym), 84.8 (s, C_5H_5), 44.1 (s, NCH_3), 31.7 (s, *C*$H(CH_3)_2$), 19.3 (s, $CNC_6H_3(CH_3)_2$), 23.4, 22.6 (s, CH_3-Xylyl), 20.8 (s, $CH(CH_3)_2$), 20.3 (s, $CH(CH_3)_2$), 19.0 (s, $CNC_6H_3(CH_3)_2$), 18.6 ppm (s, CH_3-*p*-cym); IR (THF): ν(CO) 1963 (vs), ν(CN) 2114 cm^{-1} (m). Anal. Calcd for $C_{44}H_{49}F_6FeN_4OPRu$: C, 55.53; H, 5.19; N, 5.89. Found: C, 55.69; H, 4.99; N, 5.86.

Synthesis of Compound [**6**](PF_6): To a solution of compound [**5**](PF_6) (0.10 g, 0.11 mmol) in THF (12 mL) was added an aqueous solution of HCl (38 mL, 10%, 0.11 mmol). The mixture was stirred at room temperature for 1 d. The solution was filtered and then concentrated to 3 mL. Addition of hexane (6 mL) gave an orange solid, which was filtered and washed with hexane (2 x 5 mL). The solid was dissolved in THF (3 mL) and then hexane (4 mL) and diethyl ether (4 mL) added to afford an orange precipitate, which was filtered and dried under vacuum. Crystals of [**6**](PF_6) suitable for X-ray analysis were formed by slow diffusion of hexane into a solution of the compound in THF. Yield 62 mg (60%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 8.35 (s, 1H, N*H*-Xylyl), 7.45-6.94 (9H, H_{arom}-Xylyl), 4.89 (m, 2H, *p*-cym), 4.87 (s, 5H, Cp), 4.17 (s, 3H, NCH_3), 4.00 (d, $^{3}J_{HH}$ = 4.7 Hz, 1H, *p*-cym), 3.91 (d, $^{3}J_{HH}$ = 5.4 Hz, 1H, *p*-cym), 2.61 (s, 3H, CH_3-Xylyl), 2.56 (m, 1H, C*H*$(CH_3)_2$), 2.51 (s, 3H, CH_3-Xylyl), 2.41 (s, 3H, CH_3-*p*-cym), 2.40 (s, 6H, $CNC_6H_3(CH_3)_2$), 1.72 (s, 6H, CH_3-Xylyl), 1.12 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, $CH(CH_3)_2$), 1.03 ppm (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, $CH(CH_3)_2$); $^{13}C\{^{1}H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 219.8 (s, $C_{carbene}$), 219.0 (s, $C_{carbene}$), 213.1 (s, CO), 172.5 (s, *C*NXylyl), 157.5, 139.6, 138.5, 138.2, 135.5, 134.3 (s, C_{ipso} and C_{ortho}-Xylyl), 130.6-127.5 (C_{meta} and C_{para}-Xylyl), 127.3, 91.2 (s, C_{ipso}-*p*-cym), 87.3, 86.1, 85.4, 84.8 (s, *C*H_{arom}-*p*-cym), 86.5 (s, C_5H_5), 39.8 (s, NCH_3), 32.1 (s, *C*$H(CH_3)_2$), 23.2 (s, $CH(CH_3)_2$), 22.2 (s, $CH(CH_3)_2$), 20.8, 20.7, 19.7, 19.6 (s, CH_3-Xylyl), 19.1 (s,



$CNC_6H_3(CH_3)_2$), 18.3 ppm (s, CH_3-*p*-cym); IR (THF): ν(CO) 1975 (vs), ν(CN) 2114 cm^{-1} (m). Anal. Calcd for $C_{44}H_{50}ClF_6FeN_4OPRu$: C, 53.48; H, 5.10; N, 5.67. Found: C, 53.27; H, 5.17; N, 5.65.

Synthesis of Compound [**7**](ClO_4): To a solution of compound [**1**](ClO_4) (50 mg, 0.10 mmol) in THF (10 mL) was added propargylamine (0.26 mL, d = 0.806 g/mL, 4 mmol). The resulting mixture was heated at the refluxing temperature for 4 h. The solvent was then evaporated to dryness to eliminate the excess of amine. The residue was disolved in THF (3 mL) and hexane (8 mL) added to yield an orange solid. Yield 45 mg (82%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 11.49 (s, 1H, NH), 7.35-7.07 (7H, H_{arom}-Xylyl and =CH), 5.02 (s, 5H, Cp), 2.32 (s, 6H, $CNC_6H_3(CH_3)_2$), 1.95 (s, 3H, CH_3-Xylyl), 1.85 (s, 3H, CH_3-Xylyl), 1.82 ppm (d, $^4J_{HH}$ = 0.8 Hz, 3H, =CMe); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 215.0 (s, CO), 171.4 (s, $C_{carbene}$), 137.3, 136.8, 136.6, 135.4 (s, C_{ipso} and C_{ortho}-Xylyl), 132.9 (s, =*C*-CH_3), 130.5, 129.4, 129.3, 129.0, 128.4 (s, C_{meta} and C_{para}-Xylyl), 120.7 (s, =CH), 85.1 (s, C_5H_5), 19.1 (s, $CNC_6H_3(CH_3)_2$), 18.2, 18.1 (s, CH_3-Xylyl), 10.4 ppm (s, =C-CH_3); IR (THF): ν(CO) 1983 (vs), ν(CN) 2132 cm^{-1} (vs). Anal. Calcd for $C_{27}H_{28}ClFeN_3O_5$: C, 57.31; H, 4.99; N, 7.43. Found: C, 57.16; H, 4.91; N, 7.31. Crystals of [**7**](ClO_4) suitable for X-ray analysis were obtained by slow diffusion of hexane into a solution of the compound in THF. The high value of the wR2 in the X-ray refinement (see deposited CIF file) is mainly due to thermal agitation of the perchlorate anion and, particularly, of the solvent (THF), being the structure of the complex cation rather accurately determined.



Synthesis of Compound [**8**]I: To a solution of [**7**](ClO_4) (50 mg, 0.09 mmol) in dichloromethane (10 mL) was added an excess of KOH (0.10 g, 1.78 mmol) and the resulting mixture stirred for 45 min at room temperature. The solution was then filtered and CH_3I (0.01 mL, d = 2.28 g/mL, 0.18 mmol) added. The solution was stirred for 5 min and then the solvent evaporated to dryness. The residue was disolved in THF (5 mL) and hexane (10 mL) added giving a yellow solid. Yield 43 mg (81%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25ºC): δ = 7.46-7.13 (7H, H_{arom}-Xylyl and =CH), 4.98 (s, 5H, Cp), 4.04 (s, 3H, NMe), 2.29 (s, 6H, $CNC_6H_3(CH_3)_2$), 1.93 (s, 3H, CH_3-Xylyl), 1.89 (s, 3H, CH_3-Xylyl), 1.81 ppm (s, 3H, =CMe); $^{13}C\{^1H\}$ NMR (100.61 MHz, CD_2Cl_2, 25ºC): δ = 215.5 (s, CO), 171.7 (s, $C_{carbene}$), 171.5 (s, *C*Xylyl), 137.5, 137.3, 136.8, 135.1 (s, C_{ipso} and C_{ortho}-Xylyl), 132.5 (s, =*C*-CH_3), 129.8, 129.0, 128.9, 128.5, 128.1 (s, C_{meta} and C_{para}-Xylyl), 126.3 (s, =CH), 85.7 (s, C_5H_5), 41.4 (s, NCH_3), 18.7 (s, $CNC_6H_3(CH_3)_2$), 17.9, 17.6 (s, CH_3-Xylyl), 9.6 ppm (s, =C-CH_3); IR (THF): ν(CO) 1980 (vs), ν(CN) 2125 cm^{-1} (vs). Anal. Calcd for $C_{28}H_{30}IFeN_3O$: C, 55.38; H, 4.98; N, 6.92. Found: C, 55.57; H, 4.97; N, 7.02.