Supplemental Information

Neutral Fe(IV) alkylidenes, including some that bind dinitrogen

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Department of Chemistry and Chemical Biology Baker Laboratory Cornell University Ithaca, NY 14853 USA **General Considerations.** All manipulations were performed using either glovebox or high vacuum line techniques. All glassware was oven dried. THF and ether were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from the same prior to use. Hydrocarbon solvents were treated in the same manner with the addition of 1-2 mL/L tetraglyme. Benzene- d_6 and was dried over sodium, vacuum transferred and stored over sodium. THF- d_8 was dried over sodium and vacuum transferred from sodium benzophenone ketyl prior to use. **1**[BAr^F₄] was prepared according to literature procedure.^a

NMR spectra were obtained using an INOVA 400 MHz and 500 MHz spectrometers. Chemical shifts are reported relative to benzene- d_6 (¹H δ 7.16; ¹³C{¹H} δ 128.39) or THF- d_8 (¹H δ 3.58; ¹³C{¹H} δ 67.57). Multidimensional techniques were conducted using INOVA software affiliated with the spectrometers.

Procedures. 1. (2-picolyl)lithium.^b A flask was charged with 2-picoline (3.0 mL, 30 mmol). 25 mL Et₂O was transferred and the colorless solution was cooled to -25 °C under Ar. ⁿBuLi was added dropwise, resulting in a bright orange solution. Within minutes, an orange precipitate was apparent. The mixture was stirred at -25 °C for 45 min, cooled to -60 °C, and filtered. The orange precipitate was triturated with 10 mL pentane to give a fine bright yellow powder (1.56 g, 52 % yield). ¹H NMR (THF-*d*₈): δ 2.46 (1H, s), 2.49 (1H, s), 4.51 (1H, t, 5 Hz), 5.43 (1H, d, 9 Hz), 5.80 (1H, t, 7 Hz), 6.63 (1H, d, 5 Hz).

2. (dimethylphosphino)methyllithium, Me₂PCH₂Li.^c A solution of PMe₃ (2.0 mL, 20 mmol) in 6 mL hexanes was added dropwise under Ar to a flask containing 'BuLi (11.0 mL, 1.7 M in pentane, 18.7 mmol), resulting in a colorless solution with some precipitate. The mixture was stirred for 24 h, cooled to -78 °C, filtered, and washed once with pentane to give an off-white solid (0.737 g, 48 %). ¹H NMR (THF-*d*₈): δ -0.92 (2H, s, CH₂Li), 0.74 ppm (6H, s, Me). ³¹P NMR (THF-*d*₈): δ -40.70 ppm (s).

3. (methylphenylphosphino)methyllithium, MePhPCH₂Li.^c A solution of ^tBuLi (9.0 mL, 1.7 M in pentane, 15 mmol) was added to a 50 mL flask. Dimethylphenylphosphine (2.11 g, 15.3 mmol) was added dropwise under Ar, resulting in a yellow solution. The mixture was stirred at 23 °C for 24 h to afford a yellow precipitate, which was collected by filtration and washed with pentane (2 x 5 mL) to give the product as a white solid. ¹H NMR (THF-*d*₈): δ -0.65 (2H, s, C*H*₂Li), 1.02 (3H, d, Me), 6.86 (1H, t, 7 Hz, Ph CH), 7.03 (2H, t, 7 Hz, Ph CH), 7.48 ppm (2H, m, Ph CH). ³¹P NMR (THF-*d*₈): δ -18.86 ppm (s).

4. (diphenylphosphino)methyllithium, Ph₂PCH₂Li.^d A solution of ^tBuLi (5.0 mL, 1.7 M in pentane, 8.5 mmol) was added to a 50 mL flask. Methyldiphenylphosphine (1.73 g, 8.62 mmol) was added dropwise under Ar, resulting in a pale yellow solution. The mixture was stirred at 23 °C for 2 d, resulting in the formation of a white precipitate, which was collected by filtration and washed with pentane (2 x 10 mL) to give the desired product as a white solid. ¹H NMR (THF-*d*₈): δ -0.38 (2H, s, CH₂Li), 6.89 (2H, m, Ph CH), 7.01 (4H, m, Ph CH), 7.46 ppm (4H, m, Ph CH). ³¹P NMR (THF-*d*₈): δ 3.46 ppm (s).

5. Mesityllithium, MesLi.^e A 100 mL flask was charged with Et₂O (35 mL) and bromomesitylene (3.805 g, 19.1 mmol). The colorless solution was cooled to -78 °C. ⁿBuLi (12.0 mL, 1.6 M, 19.2 mmol) was added dropwise. The mixture was allowed to warm to 23 °C over the course of 2.5 h. The mixture was stirred at 23 °C for 17 h, resulting in a pale yellow solution with white solid. The mixture was filtered and the filter cake washed twice with pentane to give the product as a white solid. ¹H NMR (C₆D₆/THF): δ 2.38 (3H, s), 2.78 (6H, s), 6.98 ppm (2H, s). 6. (3); mer-{ κ -C,N,C-(C₆H₄-yl-2-CH(Me)N(2-C₆H₄-C(ⁱPr))Fe{trans-(PMe₃)₂}N₂. A flask was charged with [mer-{k-C,N,C-(C₆H₄-yl-2-CH=N(2-C₆H₄-C(^{i}Pr)}Fe{(PMe₃)₃][B(3,5-(CF₃)₂-C₆H₃] (2) (100 mg, 0.072 mmol) and 4 mL Et₂O, affording a dark red solution. The solution was cooled to -78 °C under an Ar atmosphere. A solution of MeLi (0.36 mL, 0.20 M in Et₂O, 0.072 mmol) was added dropwise, resulting in no apparent color change. The solution was allowed to slowly warm to 23 °C and was stirred for 12 h, giving a red-brown solution. The solvent was removed in vacuo and the resulting residue triturated with pentane ($2 \times 5 \text{ mL}$). Under a N₂ atmosphere, 5 mL pentane was added to the residue and the resulting mixture filtered through Celite and stripped to a red residue (25 mg, 72 % yield). ¹H NMR (C_6D_6): δ 0.31 (9H, d, 8 Hz, PMe₃), 0.57 (9H, d, 8 Hz, PMe₃), 1.47 (3H, d, 6.5 Hz, NCHCH₃), 1.55 (3H, d, 7 Hz, ⁱPr Me), 1.73 (3H, d, 7 Hz, ⁱPr Me), 4.60 (1H, sept, 7 Hz, ⁱPr CH), 4.96 (1H, m, NCH), 6.29 (1H, dd, 8 Hz, 6.5 Hz, Ar), 6.70 (1H, d, 9 Hz, Ar), 6.84 (1H, t, 7.5 Hz, Ar), 7.05 (1H, d, 7.5 Hz, Ar), 7.26 (1H, t, 7 Hz, Ar), 7.35 (1H, t, 7 Hz, Ar), 7.40 (1H, d, 9 Hz, Ar), 8.13 (1H, d, 6.5 Hz, Ar). ¹³C NMR (C₆D₆): δ 13.92 (d, 24 Hz), 15.33 (d, 23 Hz), 24.73 (d, 28 Hz), 24.95, 44.12, 64.44, 110.45, 114.36 (t, 3.5 Hz), 119.66, 121.36 (t, 3 Hz), 122.91 (t, 3 Hz), 125.30 (t, 3 Hz), 130.37, 136.84, 148.63, 157.02, 168.09, 181.03 (t, 29 Hz), 313.77 (t, 14 Hz, Fe=C). ³¹P NMR (C₆D₆): δ 12.98 (1P, d, 125 Hz), 15.08 (1P, d, 125 Hz). IR: $v_{N2}(C_6D_6) = 2058 \text{ cm}^{-1}$. Anal. Calc. for C₂₄H₃₇FeN₃P₂: C, 59.39; H, 7.68; N, 8.66. Found: C, 59.95; H, 7.97; N, 7.61.





7. (4); mer-{ κ -C,N,C-(C₆H₄-yl-2-CH(2-pic)N(2-C₆H₄-C(ⁱPr))Fe{trans-(PMe₃)₂N₂. A 25 mL flask was charged with 2 (250 mg, 0.181 mmol) and 6 mL Et₂O, affording a dark red solution. The solution was cooled to -78 °C under Ar. A solution of 2-picolyllithium (18 mg, 0.18 mmol) in 2 mL thf was added dropwise, resulting in a red-orange solution. The solution was allowed to warm to 23 °C and was stirred for 12 h. Solvent was removed and the resultant residue triturated with pentane (2 x 8 mL) to give a red solid. The product was extracted with 10 mL hexanes under N₂ and filtered through Celite. The resultant dark red solution was stripped to give an oily red-orange solid (63 mg, 62 % yield). ¹H NMR (C₆D₆): δ 0.28 (9H, d, 8 Hz, PMe₃), 0.70 (9H, d, 8 Hz, PMe₃), 1.59 (3H, d, 7 Hz, ⁱPr Me), 1.77 (3H, d, 7 Hz, ⁱPr Me), 2.82 (1H, dd, 13 Hz, 10 Hz, pvCH₂), 3.89 (1H, d, 13 Hz, pvCH₂), 4.65 (1H, sept, 7 Hz, ⁱPr CH), 6.05 (1H, t, 7.5 Hz, NCH), 6.31 (1H, t, 7 Hz, Ar), 6.59 (1H, d, 7 Hz, Ar), 6.69 (1H, t, 6 Hz, Ar), 6.77 (1H, d, 7 Hz, Ar), 6.99 (1H, t, 7.5 Hz, Ar), 7.03 (1H, t, 7 Hz, Ar), 7.08 (1H, t, 7 Hz, Ar), 7.30 (1H, t, 7 Hz, Ar), 7.43 (1H, d, 8.5 Hz, Ar), 7.89 (1H, d, 9 Hz, Ar), 8.17 (1H, d, 6.5 Hz, Ar), 8.69 ppm (1H, d, 4 Hz, Ar). ¹³C NMR (C₆D₆): δ 13.82 (d, 23 Hz), 15.66 (d, 23 Hz), 24.73, 24.97, 44.22, 46.16, 69.79, 111.01, 115.24 (t, 4 Hz), 119.69, 121.23, 121.59 (t, 3 Hz), 122.50 (t, 3 Hz), 124.84, 125.38 (t, 3.5 Hz), 130.98, 135.75, 137.04, 148.60, 150.26, 156.17, 160.99, 168.40 (dd, 6 Hz, 3 Hz), 181.81 (t, 28 Hz), 313.95 (t, 13 Hz). ³¹P NMR (C₆D₆): δ 13.04 (d, 124 Hz), 15.02 (d, 124 Hz). IR: v_{N2} $(C_6D_6) = 2056 \text{ cm}^{-1}$. Anal. Calc. for $C_{29}H_{40}FeN_4P_2$: C, 61.93; H, 7.17; N, 9.96. Found: C, 62.21; H, 7.17; N, 9.06.





8. (5); mer-{ κ -C,N,C-(C₆H₄-yl-2-CH(Bn)N(2-C₆H₄-C(ⁱPr))Fe{trans-(PMe₃)₂N₂. A 25 mL flask was charged with 1[BAr^F₄] (404 mg, 0.292 mmol) and benzyl potassium (38 mg, 0.292 mmol). 10 mL Et₂O was transferred to the flask, resulting in a red-purple solution. The mixture was allowed to warm to 23 °C and was stirred for 5 h. The solvent was removed to give a purple solid. 8 mL pentane was transferred to the flask and the resultant mixture was filtered. The filter cake was extracted with pentane until extract was no longer red. The filtrate was stripped to a purple solid. In the glovebox, 8 mL Et₂O was added to the solid. The resulting red-orange solution was stirred for 30 min, then stripped to a red-brown solid (126 mg, 76.7 % yield). X-ray quality crystals were grown by slow evaporation of a concentrated pentane solution. ¹H NMR (C₆D₆): δ 0.27 (9H, d, 8 Hz, PMe₃), 0.69 (9H, d, 8 Hz, PMe₃), 1.58 (3H, d, 7 Hz, ⁱPr CH₃), 1.76 (3H, d, 7 Hz, ⁱPr CH₃), 2.57 (1H, dd, 13 Hz, 11 Hz, Ph-CH₂), 3.67 (1H, d, 13 Hz, Ph-CH₂), 4.65 (1H, sept, 7 Hz, ⁱPr CH), 5.39 (1H, m, N-CH(Bn)), 6.33 (1H, t, 7 Hz, Ar), 6.50 (1H, d, 7 Hz, Ar), 6.94 (1H, m, Ar), 6.97 (1H, m, Ar), 7.10 (1H, d, 9 Hz, Ar), 7.19 (1H, m, Ar), 7.27 (3H, m, Ar), 7.35 (2H, d, 7 Hz, Ar), 7.44 (1H, d, 8 Hz, Ar), 8.13 ppm (br d, 7 Hz, Ar). 13 C NMR (C₆D₆): δ 13.77 (d, 23 Hz, PMe₃), 15.80 (d, 24 Hz, PMe₃), 24.69, 24.92, 43.15, 44.35, 70.95, 110.69, 113.87 (t, 4 Hz), 119.80, 122.28 (t, 3 Hz), 122.70 (t, 3 Hz), 125.55 (t, 4 Hz), 126.57, 128.78, 130.25, 130.74 (t, 2 Hz), 136.95 (t, 3 Hz), 140.45, 148.69 (d, 2 Hz), 154.60 (t, 2 Hz), 167.75 (dd, 6 Hz, 3 Hz), 181.37 (t, 28 Hz, Fe-C_{arvl}), 315.55 ppm (t, 14 Hz, Fe=C). ³¹P NMR (C₆D₆): δ 12.70 (d, 127 Hz), 15.06 ppm (d, 127 Hz). IR: $v(N_2) = 2058 \text{ cm}^{-1}$. Anal. Calc. for $C_{30}H_{41}\text{Fe}N_3P_2$: C, 64.23; H, 7.43; N, 7.18. Found: C, 64.18; H, 7.36; N, 7.48.





9. (6); mer-{k-C,N,C-(C₆H₄-yl-2-CH(Bn)N(2-C₆H₄-C(ⁱPr)}Fe(PMe₃)₃. A 25 mL flask was charged with $1[BArF_4]$ (117 mg, 0.0847 mmol) and benzyl potassium (11 mg, 0.084 mmol). 5 mL Et₂O was transferred to the flask. The mixture was allowed to slowly warm from -78 °C to 23 °C and was stirred for 12 h, resulting in a red-purple solution. The solvent was removed in vacuo to give a dark red-purple solid. 8 mL pentane was transferred to the flask and the mixture was filtered. The filter cake was washed with pentane (4 x 8 mL) until extracts were no longer red. The solvent was removed to give a magenta solid (44 mg, 86 % yield). C_6D_6 (0.5 mL) was transferred to the flask and the resultant solution was added under Ar to a J-Young tube. ¹H NMR (C₆D₆): δ 0.20 (9H, d, 7 Hz, PMe₃), 0.74 (9H, d, 7 Hz, PMe₃), 1.22 (9H, d, 5 Hz, PMe₃), 1.66 (3H, d, 7 Hz, ⁱPr CH₃), 1.71 (3H, d, 7 Hz, ⁱPr CH₃), 2.59 (1H, "t", 12 Hz, Bn CH₂), 3.97 (1H, "t", 12 Hz, Bn CH₂), 4.76 (1H, sept, 7 Hz, ⁱPr CH), 5.37 (1H, m, NCHBn), 6.37 (1H, t, 7 Hz, Ar), 6.50 (1H, d, 7 Hz, Ar), 6.98 (1H, t, 6.5 Hz, Ar), 7.07 (1H, t, 6.5 Hz, Ar), 7.22-7.35 (4H, m, Ar), 7.44 (2H, d, 7 Hz, Ar), 7.59 (1H, d, 8.5 Hz, Ar), 7.97 ppm (1H, "d", 7 Hz, Ar). ¹³C NMR (C₆D₆): δ 18.94 (d, 19 Hz), 19.58 (d, 21 Hz), 23.54 (d, 15 Hz), 23.69, 24.00, 44.14, 47.47 (d, 4 Hz), 72.02, 108.45, 113.20, 119.93, 121.48 (t, 3 Hz), 121.67 (t, 3 Hz), 124.51 (t, 3 Hz), 126.29, 128.86, 128.97, 130.46, 141.19, 142.51, 150.85 (d, 5 Hz), 156.30, 169.36, 180.61 (td, 26 Hz, 13 Hz), 313.17 ppm (td, 23 Hz, 12 Hz, Fe=C). ³¹P NMR (C₆D₆): δ 7.54 (dd, 92 Hz, 70 Hz), 9.34 (dd, 70 Hz, 53 Hz), 12.36 ppm (dd, 92 Hz, 53 Hz).





10. (8-Me₂); { κ -C,N,C,P-(C₆H₄-yl-2-CH(CH₂PMe₂)N(2-C₆H₄-C(ⁱPr))Fe{cis-(PMe₃)₂}. a. From Me₂PCH₂Li. A 50 mL flask was charged with 2 (338 mg, 0.245 mmol) and Me₂PCH₂Li (20 mg, 0.24 mmol). 10 mL Et₂O was transferred to the flask, resulting in a red-purple solution. The solution was allowed to slowly warm to 23 °C and stirred for 6 h. Solvent was removed to give a magenta residue. Pentane (10 mL) was transferred and the mixture was filtered. The filter cake was extracted with pentane until extracts were colorless. The filtrate was stripped to a magenta solid (91 mg, 75 % yield). X-ray quality crystals were grown at -30 °C from a concentrated pentane solution. ¹H NMR (C_6D_6): $\delta 0.39$ (3H, d, 8 Hz, CH₂PMe₂), 0.54 (12H, d, 6 Hz, PMe₃ + CH₂PMe₂), 1.20 (9H, d, 6 Hz, PMe₃), 1.62 (3H, d, 7 Hz, ⁱPr Me), 1.70 (1H, dt, 11.5 Hz, 4.5 Hz, Me₂PCH₂), 1.86 (3H, d, 7 Hz, ⁱPr Me), 4.62 (1H, sept, 7 Hz, ⁱPr CH), 5.53 (1H, dd, 25 Hz, 4.5 Hz, NCH), 6.38 (1H, m, Ar), 7.03 (2H, m, Ar), 7.25 (3H, m, Ar), 7.66 (1H, d, 9 Hz, Ar), 7.97 ppm (1H, m, Ar). ¹³C NMR (C₆D₆): δ 17.09 (d, 22.5 Hz), 19.29 (d, 24 Hz), 20.19 (d, 16 Hz), 22.81, 23.08 (d, 16 Hz), 23.46, 41.99 (dd, 47 Hz, 6 Hz), 47.54 (9.5 Hz), 66.94 (4.5 Hz), 109.83, 111.63, 118.60 (t, 3 Hz), 120.35, 123.14 (t, 3 Hz), 124.06 (t, 3 Hz), 127.19, 144.90 (d, 5 Hz), 148.35 (d, 6 Hz), 157.11 (dd, 9 Hz, 3 Hz), 166.71, 177.67 (td, 38 Hz, 7 Hz, Fe-C_{arvl}), 305.79 (td, 18 Hz, 11 Hz, Fe=C). ³¹P NMR (C₆D₆): δ 12.97 (dd, 92 Hz, 57 Hz), 21.62 (dd, 57 Hz, 53 Hz), 39.52 (dd, 92 Hz, 53 Hz). b. From MesLi. A 25 mL flask was charged with 2 (120 mg, 0.0869 mmol) and MesLi (11 mg, 0.087 mmol). 5 mL Et₂O was transferred and the resultant red solution was allowed to warm to 23 °C and stirred for 12 h. The solvent was removed in vacuo and pentane (8 mL) was transferred to the flask. The mixture was filtered and stripped to an oily red residue. The ¹H NMR spectrum showed mesitylene (δ 2.16 (9H, s) and 6.72 (3H, s) in C_6D_6), with 8-Me₂ as the dominant Fe-containing product.







11. (8-MePh); { κ -C,N,C,P-(C₆H₄-yl-2-CH(CH₂PMePh)N(2-C₆H₄-C(ⁱPr))Fe{cis-(PMe₃)₂}. A 25 mL flask was charged with 2 (296 mg, 0.214 mmol) and 8 mL Et₂O. The dark red solution was cooled to -78 °C. A solution of PhMePCH₂Li (31 mg, 0.069 mmol) in 2 mL THF was added dropwise, resulting in a dark red-purple solution. The mixture was allowed to slowly warm to 23 °C overnight, then was stripped to a dark red solid. 8 mL pentane was transferred to the flask and the resultant mixture was filtered. The filter cake was extracted with pentane until extracts were colorless. The filtrate was stripped to a dark red residue. NMR spectra showed a mixture of isomers in a 1.4:1 ratio. Crystallization from pentane afforded the major isomer in > 90 % purity as a red-purple crystalline solid (65 mg, 52 % yield). ¹H NMR (C_6D_6): δ 0.55 (9H, d, 8 Hz, PMe₃), 0.90 (3H, d, 7 Hz, ⁱPr Me), 0.97 (3H, d, 8 Hz, PMePh), 1.20 (9H, d, 6 Hz, PMe₃), 1.59 (1H, dd, 12 Hz, 8 Hz, MePhPCH₂), 1.79 (3H, d, 7 Hz, ⁱPr Me), 2.35 (1H, dd, 12 Hz, 5 Hz, MePhPCH₂), 4.50 (1H, sept, 7 Hz, ⁱPr CH), 5.68 (1H, dd, 26 Hz, 5 Hz, NCH), 6.42 (1H, t, 7 Hz, Ar), 6.51 (2H, t, 8 Hz, Ar), 6.81 (3H, m, Ar), 7.05 (2H, m, Ar), 7.27 (3H, m, Ar), 7.66 (1H, d, 8.5 Hz, Ar), 8.06 ppm (1H, m, Ar). ¹³C NMR (C₆D₆): δ 14.66 (d, 23 Hz), 19.44 (d, 25 Hz), 22.23, 23.09 (d, 17 Hz), 23.43, 44.81 (dd, 45 Hz, 5 Hz), 48.03 (d, 10 Hz), 66.85 (d, 5 Hz), 109.68, 111.39, 118.65 (t, 3 Hz), 120.81, 123.40 (t, 2.5 Hz), 127.69, 127.79, 131.04 (d, 8 Hz), 144.71 (d, 24 Hz), 145.28 (d, 5 Hz), 148.94 (d, 6 Hz), 157.87 (dd, 9 Hz, 3 Hz), 167.27, 178.16 (td, 37 Hz, 7 Hz), 306.48 ppm (td, 20 Hz, 12 Hz, Fe=C). ³¹P NMR (C₆D₆): δ 12.45 (dd, 87 Hz, 58 Hz, minor), 13.84 (dd, 87 Hz, 59 Hz, major), 19.25 (dd, 58 Hz, 49 Hz, minor), 20.10 (dd, 59 Hz, 48 Hz, major), 40.49 (dd, 87 Hz, 48 Hz, major), 41.69 ppm (dd, 87 Hz, 49 Hz, minor).







12. (8-Ph₂); { κ -C,N,C,P-(C₆H₄-yl-2-CH(CH₂PPh₂)N(2-C₆H₄-C(ⁱPr)}Fe{*cis*-(PMe₃)₂}. A 25 mL flask was charged with 2 (200 mg, 0.145 mmol) and Ph₂PCH₂Li (30 mg, 0.15 mmol). 6 mL Et₂O was transferred to the flask at -78 °C. The mixture was allowed to warm to 23 °C and was stirred for 12 h. The dark red solution was stripped to a red solid. Hexanes (10 mL) was transferred to the flask and the mixture filtered. The filter cake was washed with hexanes until extracts were colorless. The filtrate was stripped to give an oily red residue. ¹H NMR (C₆D₆): δ 0.50 (9H, d, 8 Hz, PMe₃), 1.18 (9H, d, 6 Hz, PMe₃), 1.43 (3H, d, 7 Hz, ⁱPr Me), 1.87 (3H, d, 7 Hz, ⁱPr Me), 2.06 (1H, dd, 12 Hz, 8 Hz, Ph₂PCH₂), 2.35 (1H, td, 12 Hz, 5 Hz, Ph₂PCH₂), 4.75 (1H, sept, 7 Hz, ⁱPr CH), 5.59 (1H, dd, 26 Hz, 5 Hz, NCH), 6.41 (1H, t, 7 Hz, Ar), 6.77-7.12 (several, Ar), 7.24 (2H, m, Ar) 7.36 (3H, m, Ar), 7.59 (1H, d, 7 Hz, Ar), 7.73 (1H, d, 8.5 Hz, Ar), 8.03 ppm (1H, m, Ar). ³¹P NMR (C₆D₆): δ 13.35 (dd, 86 Hz, 59 Hz), 17.42 (dd, 59 Hz, 43 Hz).





13. (7); *mer*-{**k**-C,**N**,**C**-(**C**₆**H**₄-**yl**-2-C**H**=**N**(2-C₆**H**₄-**C**(ⁱ**Pr**)}**F**e{*trans*-(**PMe**₃)₂}**CH**₃. **2** (50 mg, 0.036 mmol) and Et₂O (2 mL) were added to a 10 mL flask. The resultant dark red solution was cooled to -78 °C and opened to an Ar atmosphere. MeMgCl (0.35 mL, 0.104 M in Et₂O, 0.036 mmol) was added dropwise to the flask. The mixture was allowed to warm to 23 °C and was stirred for 6 h. The resultant red-brown solution was stripped to a red-brown solid. Pentane (2 mL) was added and the mixture was filtered through Celite and stripped to a green residue. ¹H NMR (C₆D₆): δ -0.65 (3H, t, ³J_{HP} = 11 Hz, Fe-CH₃), 0.32 (18H, t, 4 Hz, PMe₃), 1.65 (6H, t, 7 Hz, ⁱPr CH₃), 5.10 (1H, m, ⁱPr CH), 6.95 (1H, t, 7.5 Hz), 7.05 (1H, d, 8 Hz), 7.35 (1H, t, 7.5 Hz), 7.46 (1H, t, 8 Hz), 7.62 (1H, t, 7.5 Hz), 7.96 (1H, d, 8 Hz), 8.19 (1H, d, 8 Hz), 8.52 (1H, d, 7.5 Hz), 9.54 ppm (1H, s, N=CH). ¹³C NMR (C₆D₆): δ -21.88 (t, 35 Hz), 13.95 (t, 11.5 Hz), 17.77 (t, 4 Hz), 52.49 (t, 2 Hz), 112.25 (s), 114.05 (s), 115.36 (t, 3 Hz), 122.45 (t, 2 Hz), 122.94 (t, 4 Hz), 125.05 (t, 3 Hz), 128.89 (s), 129.04 (s), 129.41 (t, 3 Hz), 141.76 (t, 3 Hz), 154.91 (t, 3 Hz), 208.87 (t, 37.5 Hz), 321.15 ppm (t, 30.5 Hz). ³¹P NMR (C₆D₆): δ -1.48 ppm (s).





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