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Supplemental Information

Fe(IV) alkylidenes via protonation of Fe(II) vinyl chelates and a comparative Mössbauer spectroscopic study

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I. Experimental Procedures

A. General

All manipulations were performed using either glovebox or high vacuum line techniques. Hydrocarbon solvents containing 1-2 mL of added tetraglyme, and ethereal solvents were distilled under nitrogen from purple sodium benzophenone ketyl and vacuum transferred from same prior to use. Benzene-d_6 was dried over sodium, vacuum transferred and stored under N_2. THF-d_8 was dried over sodium benzophenone ketyl. *cis*-$Me_2Fe(PMe_3)_4$[a], cinnamylamine,[b] and $[(Et_2O)_2H][(3,5\text{-}(CF_3)_2C_6H_3)_4B]$ ($H[BAr^F{}_4]$)[c] were prepared according to literature procedures. All other chemicals were commercially available and used as received. All glassware was oven dried.

NMR spectra were obtained using Mercury-300, INOVA 400, 500 and 600 MHz spectrometers. Chemical shifts are reported relative to benzene-d_6 (^{1}H δ 7.16; $^{13}C\{^1H\}$ δ 128.39) and THF-d_8 (^{1}H δ 3.58; $^{13}C\{^1H\}$ δ 67.57). Infrared spectra were recorded on a Nicolet Avatar 370 DTGX spectrophotometer interfaced to an IBM PC (OMNIC software). Elemental analyses were performed by Complete Analysis Laboratories, Inc., Parsippany, New Jersey.

B. 2-(chloromethyl)pyridine.

This procedure is a modification of the Yamamori *et. al* procedure.[d] Aqueous sodium hydroxide (1.953 g in 20 mL H_2O, 48.8 mmol) was slowly added to a solution of 2-(chloromethyl)pyridine hydrochloride (8.00 g, 48.8 mmol) in water (10 mL). The brown mixture was extracted with Et_2O (4 x10 mL), and the combined extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure to yield 2-(chloromethyl)pyridine as a yellow liquid (5.36g, 88%). 2-(chloromethyl)pyridine slowly decomposes at 23° C and is prepared and used immediately in the next step. ^{1}H NMR ($CDCl_3$): δ 4.64 (s, CH_2, 2H), 7.20 (ddd, $^3J = 7.6$ Hz, $^3J = 4.7$ Hz $^4J = 1.2$ Hz, $^5C_{py}H$, 1H), 7.43 (d, $^3J = 8.0$ Hz, $^3C_{py}H$, 1H), 7.68 (td, $^3J = 8.0$ Hz, $^4J_{HH} = 1.8$ Hz, $^4C_{py}H$, 1H), 8.54 (d, $^3J = 4.5$ Hz, $^6C_{py}H$, 1H).

C. 2-diethylpyridin-2-yl-methylphosphonate.

This procedure is a modification of the Yamamori *et. al.* procedure.[d] Diethyl phosphite (4.35 mL, 33.7 mmol) was added dropwise to a suspension of sodium pieces (775 mg, 33.7 mmol) in benzene (50 mL) at 20 °C. After heating at reflux for 4 h, freshly prepared 2-(chloromethyl)pyridine (4.3 g, 33.7 mmol) was added dropwise at reflux. The solution was heated at reflux for an additional 2 h. The reaction flask was cooled and allowed to stir at 20 °C for 12 h. Water (10 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (3 x10 mL) and CH_2Cl_2 (2 x10 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure to yield the product as a yellow oil (5.50 g, 71%). ^{1}H NMR (C_6D_6): δ 0.97 (t, $^3J = 7.1$ Hz, CH_3, 6H), 3.37 (d, $^2J_{HP} = 22.0$ Hz, CH_2P, 2H), 3.90 (dq, $^3J = 7.2$ Hz, $^3J_{HP} = 7.2$, OCH_2, 4H), 6.61 (m, $^5C_{py}H$, 1H), 7.06 (t, $^3J_{HH} = 7.4$ Hz, $^4C_{py}H$, 1H), 7.27 (d, $^3J_{HH} = 7.4$ Hz, $^3C_{py}H$, 1H), 8.38 (br, $^6C_{py}H$, 1H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 16.43 (d, $^3J_{CP} = 5.9$ Hz, CH_3), 37.22 (d, $^1J_{CP} = 134.7$ Hz, CH_2P), 61.83 (d, $^2J_{CP} = 6.2$ Hz, OCH_2), 121.66 (d, $^4J_{CP} = 3.0$ Hz, $^5C_{py}$), 124.50 (d, $^3J_{CP} = 4.6$ Hz, $^3C_{py}$), 135.97 (d, $^5J_{CP} = 3.0$ Hz, $^4C_{py}$), 149.89 (d, $^4J_{CP} = 2.2$ Hz, $^6C_{py}$), 153.91 (d, $^2J_{CP} = 7.7$ Hz, $^2C_{py}$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 24.78 (s).

D. di-1,2-(*E*-2-(pyridin-2-yl)vinyl)benzene ((bdvp)H_2)

A lithium hexamethyldisilazide (1.46 g, 8.73 mmol) solution in ether (10 mL) was added drop wise to a 2-diethylpyridin-2-yl-methylphosphonate (2.00 g, 8.73 mmol) solution in ether (10 mL) at 20 °C. The yellow solution was stirred for 30 min prior to the addition of o-phthalaldehyde (530 mg, 3.95 mmol) via a solid addition tube. The mixture was stirred at 20 °C for 12 h. Water (10 mL) was added and the layers separated. The aqueous layer was extracted with Et_2O (3 x10 mL) and CH_2Cl_2 (2 x10 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The resulting solid was recrystallized from a (1:10) ether/hexane mixture to yield (bdvp)H_2 as a colorless crystalline solid (413 mg, 37%). ^{1}H NMR ($CDCl_3$): δ 7.09 (d, $^3J = 16.0$ Hz, =CHpy, 2H), 7.16 (dd, $^3J = 4.6$ Hz, $^3J = 7.6$ Hz, $^5C_{py}H$ 2H), 7.34 (dd, $^3J = 6.0$ Hz, $^4J = 3.4$ Hz, $^2C_{Ph}H$, 2H,), 7.44 (d, $^3J = 8.0$ Hz, $^3C_{py}H$, 2H), 7.67 (m, $^4C_{py}H$, $^3C_{PhH}$, 4H), 8.05 (d, $^3J = 16.0$ Hz, =CHPh, 2H), 8.62 (d, $^3J_{HH} = 4.7$ Hz, $^6C_{py}H$, 2H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 121.96 ($^5C_{py}$), 122.17 ($^3C_{py}$), 127.36 ($^2C_{Ph}H$), 128.48 ($^3C_{Ph}$), 130.72 (=CHPh), 131.50 (=CHpy), 136.05 ($^4C_{py}$), 136.55 ($^1C_{Ph}$), 150.10 ($^6C_{py}$), 156.13 ($^2C_{py}$).

E. (E)-1-phenyl-N-(3-phenylpropyl)methanimine ((pipp)H_2)

This procedure is in accordance with that reported by Würthwein *et. al.*[e] To a 100 mL flask charged with CH_2Cl_2 (40 mL) and activated 4Å molecular sieves at 0 °C was added cinnamylamine[b] (1.25 g, 9.39 mmol) and benzaldehyde (1.05 mL, 10.3 mmol). The solution was stirred for 12 h before filtering through celite. The filtrate was concentrated under reduced pressure and dried under vacuum for an hour to remove residual benzaldehyde. Ligand precursor (pipp)H_2 was obtained as yellow oil (1.82 g, 88%), and its NMR data were consistent the literature report.

F. 2-propynylaniline

A 50 mL flask was charged with 2-iodoaniline (2.190 g, 10.0 mmol), CuI (0.190 g, 0.998 mmol), and $PdCl_2(PPh_3)_2$ (0.281 g, 0.400 mmol).[f] NEt_3 (25 mL) was transferred to the flask, resulting in a yellow suspension upon warming to 20 °C. The flask was opened to a 1 L flask containing 2-propyne (490 mm Hg, 26.8 mmol). Within minutes, the formation of a black precipitate was evident, and the mixture was stirred for at 20 °C for 48 hr. The volatiles were removed in vacuo to give a black oily residue. Ethyl acetate (75 mL) was added to the residue, and the black suspension was filtered through Celite to give a yellow solution. Volatiles were removed in vacuo and the product was vacuum distilled (50 °C) as a light yellow oil (1.01 g, 77 % yield). ^{1}H NMR ($CDCl_3$): δ 2.11 (s, CH_3), 4.16 (br s, NH_2), 6.66 (td, 7.5 Hz, 1 Hz, 1H), 6.68 (d, 8 Hz, IH), 7.08 (td, 8 Hz, 1 Hz, 1H), 7.24 (dd, 7.5 Hz, 1 Hz, 1H).

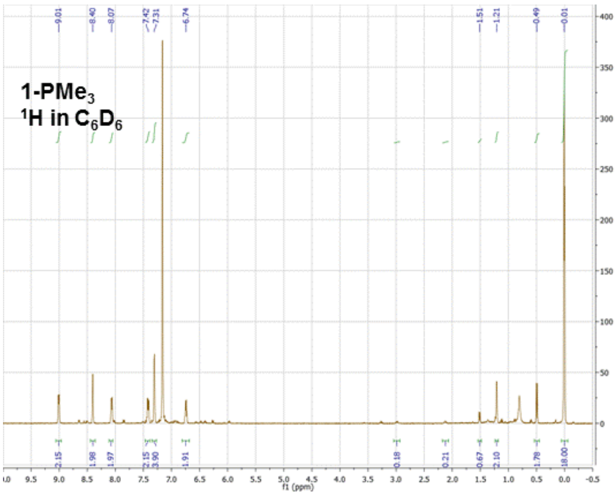
G. N-benzylidene-2-propynylaniline.

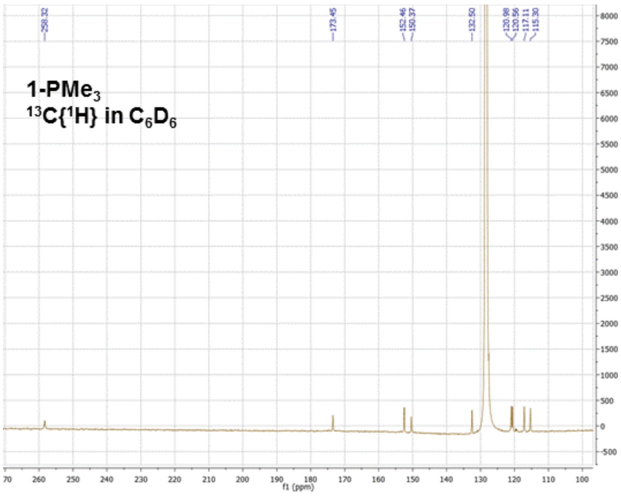
A 25 mL flask was charged with 2-propynylaniline (250 mg, 1.91 mmol), benzaldehyde (202 mg, 1.90 mmol), CH_2Cl_2 (6 mL), and 4 Å molecular sieves. The mixture was stirred for 36 hr, filtered, and washed with dry CH_2Cl_2 (3 x 10 mL). The volatiles were removed in vacuo to afford the product as a yellow oil (345 mg, 83 % yield). ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H), 7.01 (dd, 8 Hz, 1 Hz, 1H), 7.12 (td, 8 Hz, 1 Hz, 1H), 7.29 (td, 8 Hz, 2 Hz, 1H), 7.46 (m, 2H), 7.49 (m, 2H), 7.95 (m, 2H), 8.46 (s, Im C-H, 1H).

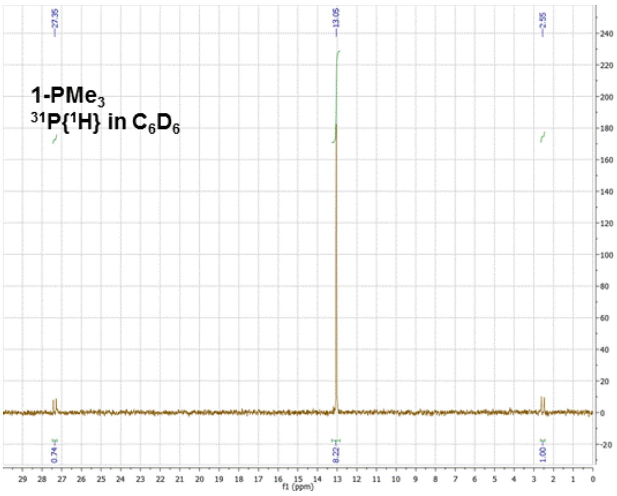
^{13}C NMR (C_6D_6): δ 4.32, 78.37, 90.22, 117.79, 119.98, 125.19, 128.62, 128.86, 129.30, 131.44, 133.45, 137.00, 154.77, 161.72.

H. *trans*-(bdvp)Fe(PMe$_3$)$_2$ (1-PMe$_3$)

A 50 mL round bottom flask was charged with (bdvp)H_2 (51 mg, 0.179 mmol) and Fe(PMe$_3$)$_4$Me$_2$^{a} (70 mg, 0.179 mmol). Toluene (25 mL) was transferred under vacuum at –78 °C and the solution was slowly warmed to –20 °C and stirred at –20 °C for 10 h before warming to 23 °C. The solution was concentrated under reduced pressure to yield **1**-PMe$_3$ as a purple microcrystalline solid (51 mg, 84%). Recrystallization upon slow evaporation at -40 °C in toluene yielded crystals suitable for single-crystal X-ray diffraction. ^{1}H NMR (C_6D_6): δ 0.00 (t, $^2J_{HP}$ = 7.0 Hz, PMe$_3$, 18H), 6.75 (q, $^3J_{HH}$ = 4.7 Hz, $^5C_{py}$H, 2H), 7.31 (m, $^3C_{py}$H, $^4C_{py}$H, 4H), 7.42 (m, $^3C_{Ph}$H, 2H), 8.07 (m, $^2C_{Ph}$H, 2H), 8.40 (s, =CHpy, 2H), 9.01 (d, $^3J_{HH}$ = 5.2 Hz, $^6C_{py}$H, 2H). ^{13}C{^{1}H} NMR (C_6D_6): δ 11.36 (PMe$_3$), 115.30 ($^5C_{py}$), 117.12 ($^2C_{Ph}$), 120.57 (=CHpy), 120.98 ($^3C_{py}$), 132.51 ($^4C_{py}$), 150.37 ($^1C_{Ph}$), 152.46 ($^6C_{py}$), 173.45 ($^2C_{py}$), 258.32 (t, $^2J_{CP}$ = 22.8 Hz, =C(H)Fe). ^{31}P{^{1}H} NMR (C_6D_6): δ 13.04 (s). Anal. Calc. for $C_{26}H_{32}FeN_2P_2$: C, 63.69; H, 6.58; N, 5.71. Found: C, 63.76; H, 6.63; N, 5.34.

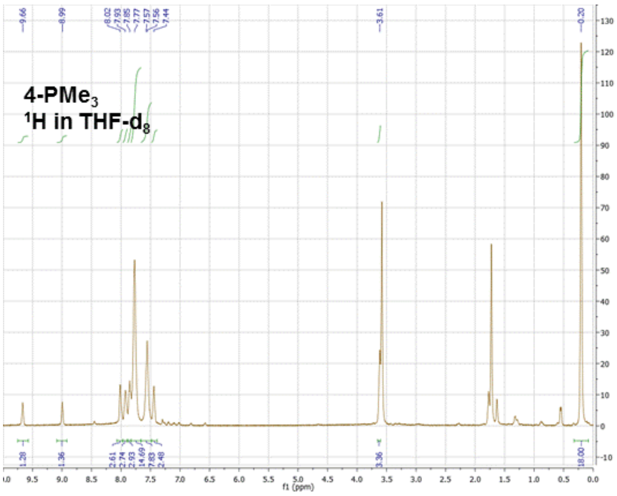


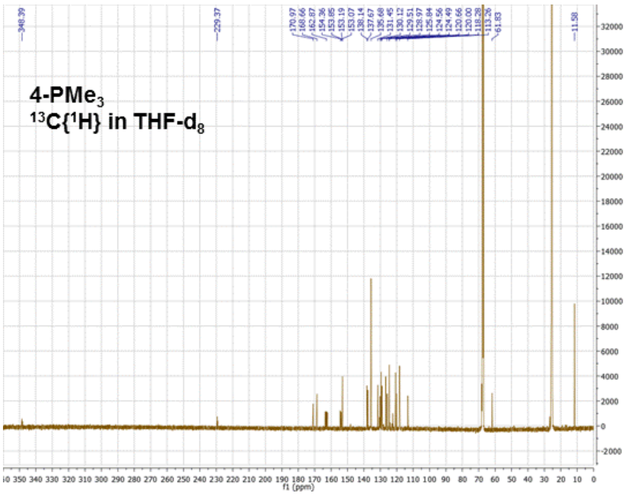


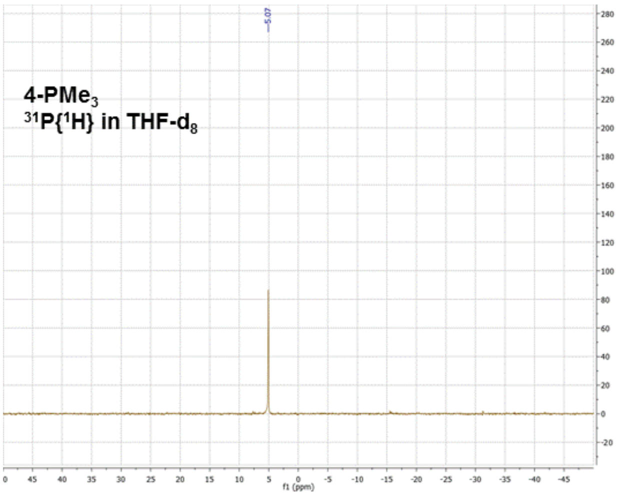


I. [(bavp)Fe(PMe$_3$)$_2$][BAr$^F{}_4$] (4-PMe$_3$)

A 10 mL round bottom flask was charged with **1**-PMe$_3$ (10 mg, 0.020 mmol) and HBAr$^F{}_4$^{c} (20.6 mg, 0.020 mmol). THF (25 mL) was transferred under vacuum at –78 °C resulting in an immediate color change from purple to orange. The reaction was slowly warmed to 23 °C, stirred for 4 h and concentrated under reduced pressure to yield **4**-PMe$_3$ as an orange powder (22 mg, 80%). Recrystallization upon slow evaporation at –40 °C in THF/toluene (1:1) yielded crystals suitable for single-crystal X-ray diffraction. ^{1}H NMR (THF-d$_8$): δ 0.21 (t, $^2J_{HP}$ = 8.0 Hz, PMe$_3$ 18H), 3.62 (br, CH$_2$, 2H), 7.45, 7.75, 7.77, 7.94 (m, $^2C_{Ph}$H-$^5C_{Ph}$H, 4H), 7.45 (m, $^5C_{py}$H, 1H), 7.56 (s, BAr^F, 4H), 7.59 (br, $^{5'}C_{py}$H, 1H), 7.78 (s, BAr^F, 8H), 7.85 (m, $^{3'}C_{py}$H, 1H), 7.87 (m, ^{3}CH, 1H), 7.92 (m, $^4C_{py}$H, 1H), 8.01 (m, $^{4'}C_{py}$H, 1H), 8.02 (br, =CHpy', 1H), 9.00, (d, $^3J_{HH}$ = 5.1 Hz, $^6C_{py}$H, 1H), 9.67 (d, $^3J_{HH}$ = 5.1 Hz, $^{6'}C_{py}$H, 1H). ^{13}C{^{1}H} NMR (THF-d$_8$): δ 11.58 (t, $^2J_{CP}$ = 24.7 Hz, PMe$_3$), 61.83 (br, CH$_2$), 113.26, 120.66, 128.97, 131.43 ($^2C_{Ph}$-$^5C_{Ph}$), 118.28 (BAr^F), 120.00 ($^{5'}C_{py}$), 124.49 ($^3C_{py}$), 124.56 ($^5C_{py}$), 125.60 (q, $^1J_{CF}$ = 272.6 Hz, BAr^F), 125.84 ($^{3'}C_{py}$), 129.51 (=CHpy'), 130.08 (q, $^2J_{CF}$ = 31.0 Hz, BAr^F), 135.67 (BAr^F), 137.69 ($^{4'}C_{py}$), 138.12 ($^4C_{py}$), 153.07 ($^6C_{py}$), 153.19 ($^{6'}C_{py}$), 153.85 ($^6C_{Ph}$), 154.36 ($^1C_{Ph}$), 162.91 (q, $^1J_{CF}$ = 49.6 Hz, BAr^F), 168.69 ($^1C_{py}$), 170.95 ($^{1'}C_{py}$), 229.37 (t, $^2J_{HP}$ = 23.6 Hz, C-Fe), 348.39 (t, $^2J_{HP}$ = 31.0 Hz, C=Fe). ^{31}P{^{1}H} NMR (THF-d$_8$): δ 5.08 (s). Anal. Calc. for $C_{58}H_{45}BF_{24}FeN_2P_2$: C, 51.43; H, 3.35; N, 2.07. Found: C, 51.61; H, 3.52; N, 2.31.





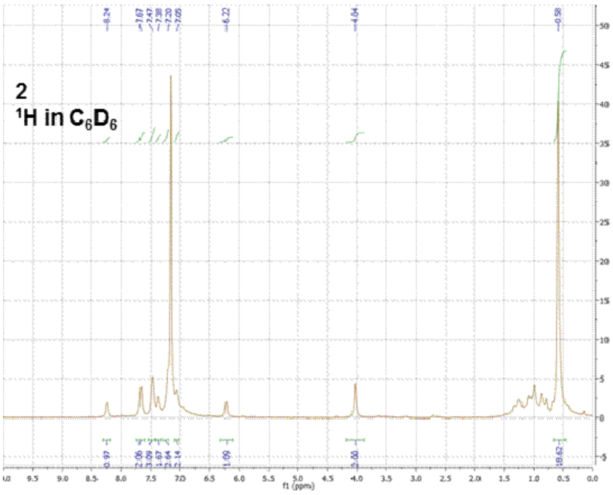


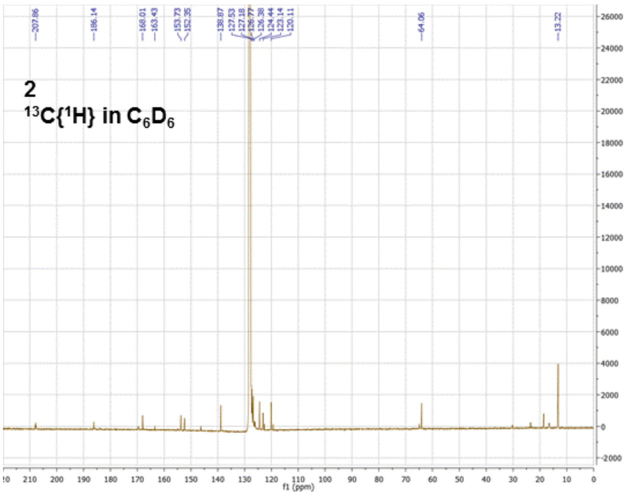
J. [(bavp)Fe(PMe$_2$Ph)$_2$][BAr$^F_4$] (4-PMe$_2$Ph)

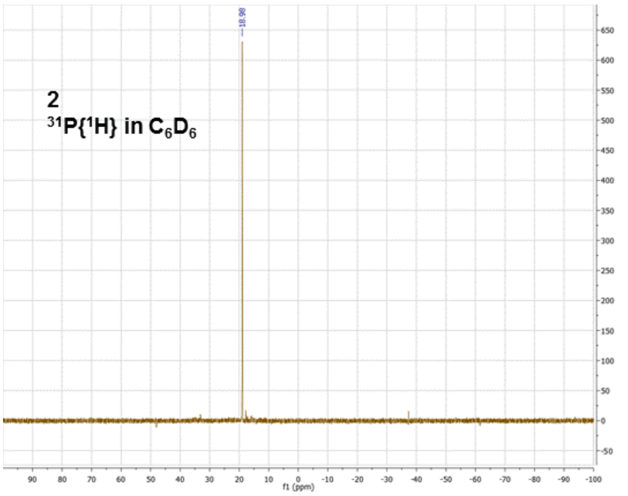
A 50 mL round bottom flask was charged with **1**-PMe$_3$ (76 mg, 0.155 mmol) and PMe$_2$Ph (214 mg, 1.55 mmol). Toluene (20 mL) was transferred under vacuum at –78 °C and the solution was refluxed for 24 h. The flask was cooled down to 23 °C and concentrated under reduced pressure to remove PMe$_3$. Toluene was again back transferred under vacuum at –78 °C and the resulting solution was refluxed for an additional 12 h. The flask was cooled down to 23 °C and concentrated under reduced pressure resulting in an oily mixture. HBAr$^F_4$^{c} (110 mg, 0.109 mmol) was added to the purple residue and THF (20 mL) was back transferred under vacuum at –78 °C. The reaction flask was allowed to warm to 23 °C and stirred for 4 h. The orange solution was concentrated under reduced pressure to result in a waxy orange solid. Pentane (20 mL) was transferred under vacuum at -78 °C to result in a suspension. Filtration and drying yielded **4**-PMe$_2$Ph as an orange solid (145 mg, 94%). ^{1}H NMR (THF-d$_8$): δ 0.51 (d, $^2J_{HP}$ = 8.0 Hz, PMe$_2$, 12H), 3.04 (t, $^3J_{HP}$ = 7.6 Hz, CH$_2$, 2H), 6.40; 6.94; 7.11 (br, PPh, 10H), (br, 7.50-7.90 (br m, ^{2}C$_{Ph}$H-^{5}C$_{Ph}$H, ^{3}C$_{py}$H, $^{3'}$C$_{py}$H, ^{5}C$_{py}$H, $^{5'}$C$_{py}$H, 8H), 7.58 (s, BAr^F 4H), 7.79 (s, BAr^F, 8H), 7.90-7.94 (m, ^{4}C$_{py}$H, $^{4'}$C$_{py}$, 2H), 8.04 (br, =CH-, 1H), 8.47, (d, ^{6}C$_{py}$H, 1H), 9.34 (br, $^{6'}$C$_{py}$H, 1H). ^{13}C{^{1}H} NMR (THF-d$_8$): δ 10.03 (t, $^2J_{CP}$ = 28.2 Hz, P(CH$_3$)$_2$), 61.62 (CH$_2$), 113.63, 120.78, 129.71, 131.42 (^{2}C$_{Ph}$-^{5}C$_{Ph}$), 118.32 (BAr^F), 120.26 ($^{5'}$C$_{py}$), 123.50 (d, PPh-*ipso*, $^2J_{CP}$ = 37.5 Hz), 124.12 (^{3}C$_{py}$), 124.38 (^{5}C$_{py}$), 125.63 (q, $^1J_{CF}$ = 274.6 Hz, BAr^F), 125.93 ($^{3'}$C$_{py}$), 128.70 (t, PPh, $^3J_{CP}$ = 8.2 Hz), 129.30 (t, PPh, $^3J_{CP}$ = 8.4 Hz) 129.091 (=CH-), 130.21 (q, $^2J_{CF}$ = 36.7 Hz, BAr^F), 132.86 (br, PPh), 135.62 (BAr^F), 137.39 ($^{4'}$C$_{py}$), 137.47 (^{4}C$_{py}$), 152.92 (^{6}C$_{py}$), 153.47 ($^{6'}$C$_{py}$), 154.05 (^{6}C$_{Ph}$), 154.18 (^{1}C$_{py}$), 162.97 (q, $^1J_{CB}$ = 51.7 Hz, BAr^F), 168.02 (^{2}C$_{py}$), 170.66 ($^{2'}$C$_{py}$), 228.15 (t, $^2J_{HP}$ = 22.1 Hz, C-Fe), 350.59 (t, $^2J_{HP}$ = 28.5 Hz, C=Fe). ^{31}P{^{1}H} NMR (THF-d$_8$): δ 15.29 (s). Anal. Calc. for $C_{68}H_{49}BF_{24}FeN_2P_2$: C, 55.23; H, 3.34; N, 1.89. Found: C, 55.24; H, 3.15; N, 1.92.

K. *trans*-(pipp)Fe(PMe$_3$)$_2$N$_2$ (2)

To a 50 mL flask charged with (pipp)H$_2$ (148 mg, 0.669 mmol) and cis-Fe(PMe$_3$)$_4$Me$_2$^{a} (261 mg, 0.669 mmol) was added THF (25 mL) at -78 °C. The solution was slowly warmed to 23 °C and stirred for 12 h. The resulting brown solution was concentrated under reduced pressure to yield a purple solid. The solid was then dissolved in THF (10 mL) and stirred under N$_2$ for 4 h to afford a brown solution. Volatiles were removed under reduced pressure to yield **2** as a brown solid (201 mg, 63%). ^{1}H NMR (C$_6$D$_6$): δ 0.58 (br, PMe$_3$, 18H), 4.03 (br, CH$_2$, 2H), 6.22 (br, =C*H*(CH$_2$), 1H), 7.05; 7.20 (m, ^{5}C$_{Ph}$H, *p*-CH, 2H), 7.35-7.30; 7.45-7.49 (m, *o*-CH, *m*-CH, ^{4}C$_{Ph}$H, 5H) 7.66-7.68 (br, =CHN, ^{6}C$_{Ph}$H, 2H), 8.26 (d, $^3J_{HH}$ = 6.8 Hz, ^{3}C$_{Ph}$H, 1H). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 13.22 (t, PMe$_3$, $^1J_{CP}$ = 22.6 Hz), 64.06 (CH$_2$), 120.11 (*o*-C), 123.14; 124.44; 126.77; 127.18; 127.53 (*m*-C, *p*-C, $^{4-6}$C$_{Ph}$) 138.87 (^{3}C$_{Ph}$), 152.42 (^{1}C$_{Ph}$), 153.73 (*ipso*-C), 168.06 (=CHN), 186.14 (t, $^2J_{CP}$ = 22.5 Hz, ^{2}C$_{Ph}$Fe), 207.86 (t, $^2J_{CP}$ = 18.4 Hz, Fe*C*(Ph)=CH). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 18.95 (s). IR (C$_6$D$_6$): ν(N$_2$) 2048 cm^{-1}. Anal. Calc. for $C_{22}H_{31}FeN_3P_2$: C, 58.04; H, 6.86; N, 9.23. Found: C, 58.03; H, 6.80; N, 7.29.

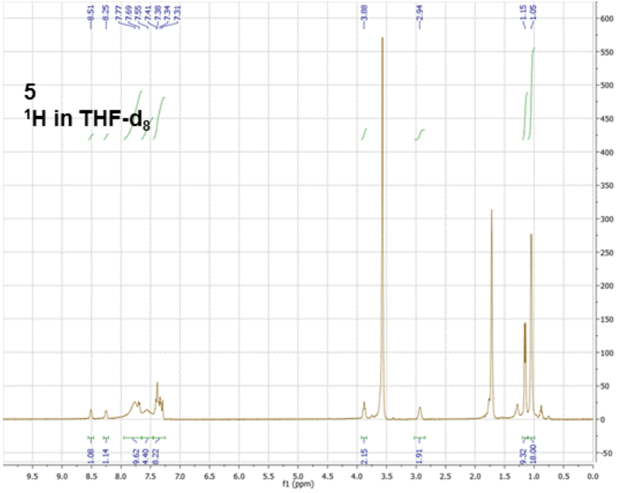


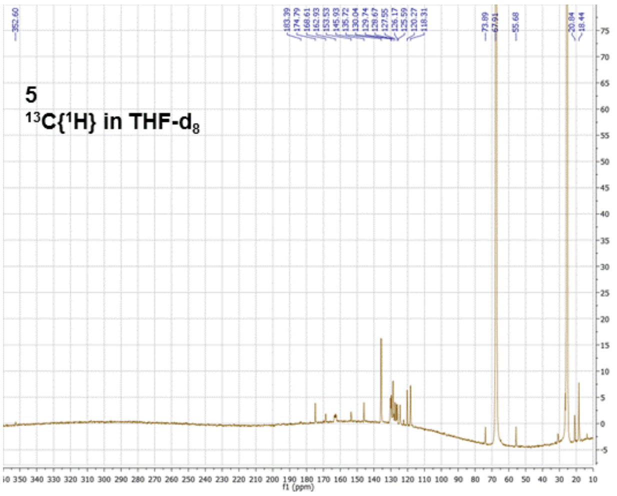


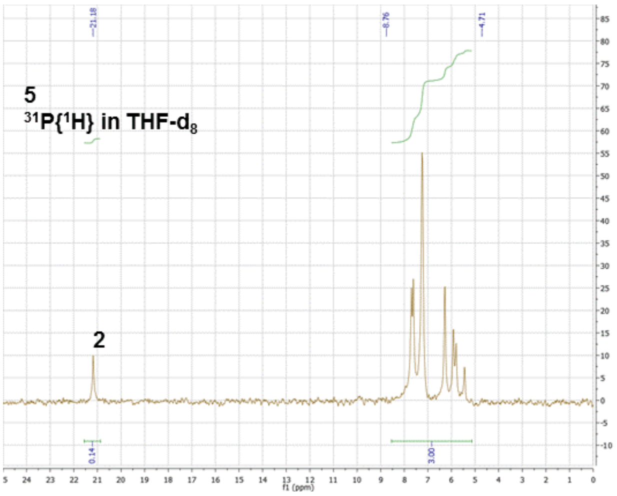


L. [(piap)Fe(PMe$_3$)$_3$][BAr$^F{}_4$] (5)

To a 50 mL flask charged with **2** (60 mg, 0.132 mmol) and HBAr$^F{}_4$[c] (133 mg, 0.131 mmol) was added PMe$_3$ (10.0 mg, 0.132 mmol) at -195 °C, followed by 20 mL THF. The liquid nitrogen dewar was replaced with a -78 °C bath and the mixture was stirred and allowed to warm to 23 °C over 12 h. The volatiles were removed under reduced pressure resulting in a yellow solid. Pentane (20 mL) was transferred at -78 °C and the flask was allowed to warm to 23 °C. The resulting suspension was filtered and dried under vacuum to yield **5** as light yellow powder (130 mg, 72%). Recrystallization upon slow evaporation at -40 °C in THF/Et$_2$O/Hex (1:1:1) yielded crystals suitable for single-crystal X-ray diffraction. ^{1}H NMR (THF-d$_8$): δ 1.06 (2, $^2J_{HP}$ = 7.1 Hz, PMe$_3$, 18H), 1.16 (t, $^2J_{HP}$ = 7.0 Hz, PMe$_3$, 9H), 2.94 (br m, CH$_2$C=Fe, 2H), 3.88 (t, $^3J_{HH}$ = 7.1 Hz, NCH$_2$, 2H), 7.32 (br, ^{5}C$_{Ph}$H, *p*-CH, 2H), 7.36 (br, ^{4}C$_{Ph}$H, 1H), 7.38 (br, *o*-CH, 2H), 7.41 (br, *m*-CH, 2H), 7.55 (s, BAr^F, 4H), 7.70 (br, ^{6}C$_{Ph}$H, 1H), 7.77 (s, BAr^F, 8H), 8.26 (br, ^{3}C$_{Ph}$H, 1H), 8.51 (br, =CHN, 1H). ^{13}C{^{1}H} NMR (THF-d$_8$): δ 18.44 (t, $^2J_{CP}$ = 27.0 Hz, PMe$_3$), 21.93 (d, $^2J_{CP}$ = 21.1 Hz, PMe$_3$), 55.68 (NCH$_2$), 73.87 (*C*H$_2$C=Fe), 118.26 (BAr^F), 120.28 (*o*-C), 125.60 (q, $^1J_{CF}$ = 272.5 Hz, BAr^F), 126.17 (^{5}C$_{Ph}$), 127.55 (*p*-C), 128.67 (*m*-C), 128.96 (^{6}C$_{Ph}$), 129.73 (^{4}C$_{Ph}$), 130.09 (q, $^2J_{CF}$ = 33.8 Hz, BAr^F), 135.69 (BAr^F), 145.92 (^{3}C$_{Ph}$), 153.57 (^{1}C$_{Ph}$), 162.87 (q, $^1J_{CB}$ = 49.6 Hz, BAr^F), 168.63 (*ipso*-C), 174.79 (=CHN), 183.37 (td, $^2J_{CP}$ = 40.9 Hz, $^2J_{CP}$ = 10.0 Hz, ^{2}C$_{Ph}$), 352.61 (q, $^2J_{CP}$ = 20.9 Hz, Fe=C). ^{31}P{^{1}H} NMR (THF-d$_8$): δ 5.87 ("t", $^2J_{PP}$ = 62 Hz), 7.44 ("d", $^2J_{PP}$ = 62 Hz). Anal. Calc. for C$_{57}$H$_{53}$BF$_{24}$FeNP$_3$: C, 50.06; H, 3.91; N, 1.02. Found: C, 50.02; H, 3.89; N, 1.10.

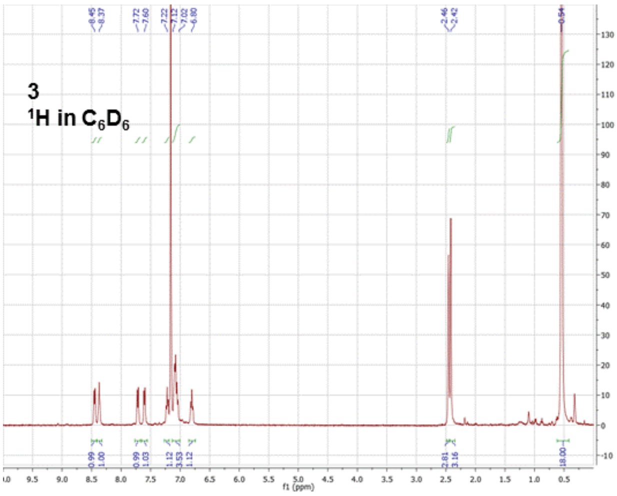


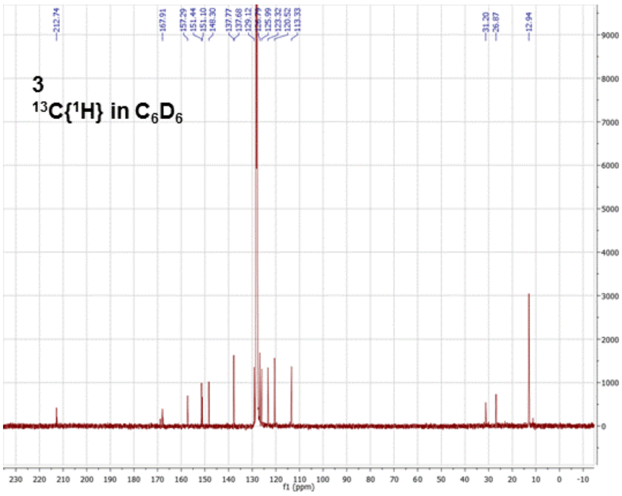


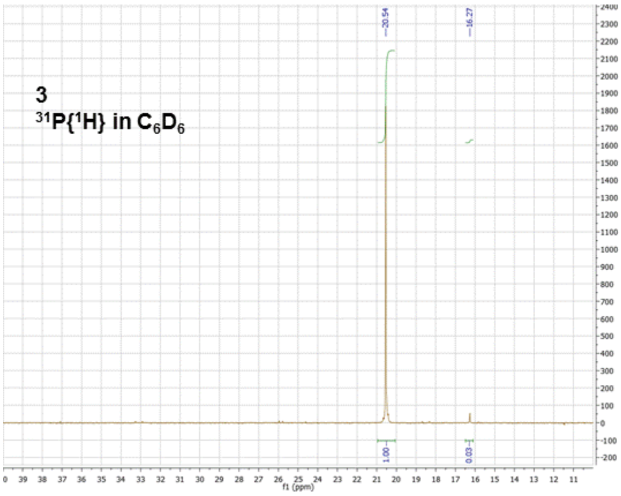


M. *trans*-(pipvd)Fe(PMe$_3$)$_2$N$_2$ (3)

Under an N$_2$ atmosphere, FeMe$_2$(PMe$_3$)$_4$[a] (178 mg, 0.456 mmol) was added to a solution of N-benzylidene-2-propynylaniline (100 mg, 0.456 mmol) in benzene (6 mL). The resultant dark red-brown solution was stirred for 6 hr, then stripped to a sticky dark residue. The residue was triturated twice with hexanes to afford a green powder (157 mg, 73 % yield). ^{1}H NMR (C_6D_6): δ 0.54 (br s, 18H), 2.42 (s, CH_3, 3H), 2.46 (s, CH_3, 3H), 6.80 (t, 7.5 Hz, Ph, 1H), 7.02-7.12 (m, Ph, 3H), 7.22 (t, 7 Hz, Ph, 1H), 7.60 (d, 7.5 Hz, Ph, 1H), 7.72 (d, 8 Hz, Ph, 1H), 8.37 (t, $^4J_{HP}$ = 5 Hz, NCH, 1H), 8.45 (d, 7 Hz, Ph, 1H). ^{13}C NMR (C_6D_6): δ 12.94 (t, $^2J_{CP}$, PMe$_3$), 26.87 (CH_3), 31.20 (CH_3), 113.33 (Ph *C*H), 120.52 (Ph *C*H), 123.32 (Ph *C*H), 125.99 (Ph *C*H), 126.79 (Ph *C*H), 128.59 (Ph *C*H), 129.12 (Ph *C*H), 137.68 (t, $^3J_{CP}$ = 3 Hz, Ph), 137.77 (Ph *C*H), 148.30 (h), 151.10 (Ph), 151.44 (=*C*Me$_2$), 157.29 (t, $^3J_{CP}$ = 4 Hz, *C*=N), 167.91 (t, $^2J_{CP}$ = 24 Hz, vinyl *C*-Fe), 212.74 (t, $^2J_{CP}$ = 17 Hz, aryl *C*-Fe). ^{31}P NMR (C_6D_6): δ 20.56. IR (C_6D_6): ν(N_2) = 2046 cm^{-1}. Anal. for $C_{23}H_{33}FeN_3P_2$ (calc.) C 58.86, H 7.09, N 8.95; (found) C 58.62, H 7.15, N 8.96.

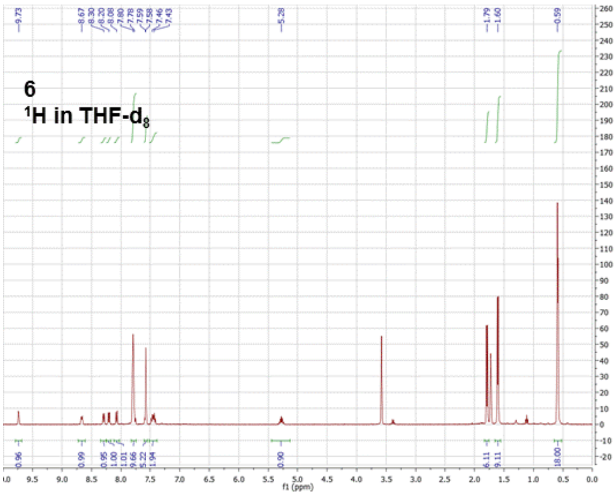


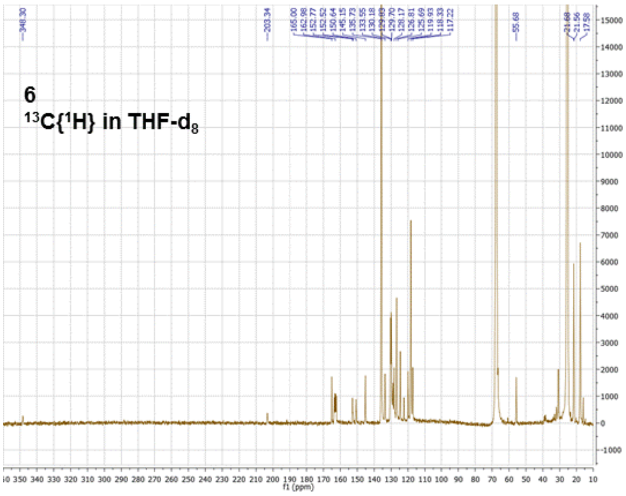


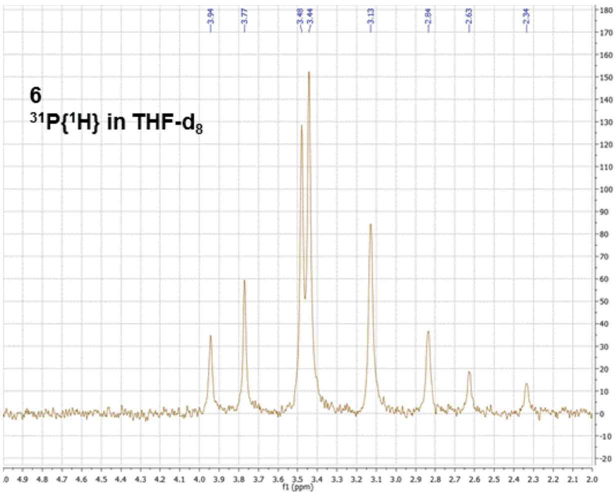


N. [(pipad)Fe(PMe$_3$)$_3$][BAr$^F{}_4$] (6)

To a 25 mL flask containing **3** (100 mg, 0.213 mmol) and HBAr$^F{}_4{}^c$ (216 mg, 0.216 mmol) and equipped with a 30.5 mL gas bulb were added PMe$_3$ (128 mm Hg) and Et$_2$O (10 mL) at 77 K. The flask was warmed to -78 °C, then slowly allowed to warm to 20 °C and stirred for 12 hr, resulting in a color change from green to dark red. The solvent was removed in vacuo to give a red residue. Pentane (8 mL) was transferred and the resultant suspension filtered and washed with pentane (3 x 5mL) to afford a dark red solid (217 mg, 74 % yield). Slow evaporation of a hexanes/Et$_2$O solution resulted in dark red crystals suitable for single-crystal X-ray diffraction. ^{1}H NMR (thf-d$_8$): δ 0.60 ppm (t, $^2J_{HP}$ = 4 Hz, PMe$_3$, 18H), 1.61 (d, $^2J_{HP}$ = 6 Hz, PMe$_3$, 9H), 1.79 (d, 7 Hz, ^{i}Pr C*H*$_3$, 6H), 5.28 (sept, 7 Hz, ^{i}Pr C*H*, 1H), 7.43 (t, 7 Hz, Ph, 1H), 7.46 (t, 7 Hz, Ph, 1H), 7.58 (br s, BAr^F, 4H), 7.59 (m, Ph, 1H), 7.78 (t, 8 Hz, Ph, 1H), 7.80 (br s, BAr^F, 8H), 8.08 (d, 8 Hz, Ph, 1H), 8.20 (d, 8 Hz, Ph, 1H), 8.30 (d, 7.5 Hz, Ph, 1H), 8.67 (d, 8 Hz, Ph, 1H), 9.73 (br s, Im C-*H*, 1H). ^{13}C NMR (thf-d$_8$): δ 17.65 (t, $^2J_{CP}$ = 13 Hz, PMe$_3$), 21.67 (m, PMe$_3$), 21.74 (^{i}Pr *C*H$_3$), 55.70 (d, $^3J_{CP}$ = 8 Hz, ^{i}Pr *C*H), 117.26 (Ph *C*H), 118.37 (BAr^F), 120.03 (Ph *C*H), 125.68 (q, $^1J_{CF}$ = 272 Hz, BAr^F), 126.78 (Ph *C*H), 128.21 (t, $^3J_{CP}$ = 3 Hz, Ph *C*H), 129.74 (Ph *C*H), 129.88 (Ph *C*H), 130.21 (q, $^2J_{CF}$ = 32 Hz, BArF), 133.61 (Ph *C*H), 135.78 (BAr^F), 145.22 (Ph *C*H), 150.68 (dt, $^3J_{CP}$ = 6, 2 Hz, Ph), 152.52 (Ph), 152.82 (Ph), 162.98 (q, $^1J_{CB}$ = 49 Hz, BAr^F), 165.07 (C=N), 203.38 (td, $^2J_{CP}$ = 31, 14 Hz), 348.4 (C=Fe). ^{31}P NMR (thf-d$_8$): δ 4.13-5.84 (m). Anal. for $C_{58}H_{55}BF_{24}FeNP_3$ (calc.) C 50.42, H 4.01, N 1.01; (found) C 52.17, H 4.51, 1.13.







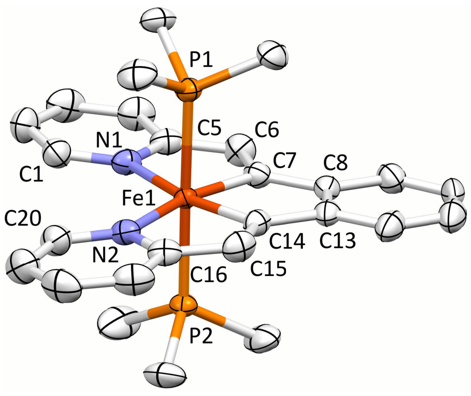
II. X-ray Crystal Structures

Single crystal X-ray diffraction studies were conducted on a Siemens P4 SMART CCD area detector; the structures were solved by direct methods (SHELXS).

A. 1. *trans*-(bdvp)Fe(PMe$_3$)$_2$ (1-PMe$_3$)

Crystal data for **1**-PMe$_3$: C$_{26}$H$_{32}$N$_2$P$_2$Fe, M = 490.33, triclinic, P-1, a = 10.2138(8), b = 10.6014(8), c = 12.4208(10) Å, α = 88.674(4)° β = 67.062(3)°, γ = 89.687(4)°, V = 1238.24(17) Å^3, T = 203(2), λ = 0.71073 Å, Z = 2, R_{int} = 0.0311, 22420 reflections, 6098 independent, R_1(all data) = 0.0663, wR_2 = 0.1766, GOF = 1.077, CCDC-1057831.

2. Fig. S1.

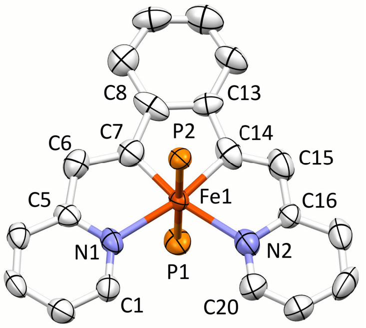


Molecular view of (bdvp)Fe(PMe$_3$)$_2$ (**1**-PMe$_3$). Interatomic distances (Å) and angles (°): Fe-N1, 2.057(3); Fe-N2, 2.062 (3); Fe-C7, 1.877(3); Fe-C14, 1.888(3); Fe-P1, 2.2285(8); Fe-P2, 2.2280(8); N1-Fe-C7, 81.10(13); N1-Fe-C14, 166.62(13); N1-Fe-N2, 112.43(11); N1-Fe-P1, 89.45(8); N1-Fe-P2, 91.17(8); C7-Fe-C14, 85.61(14); C7-Fe-N2, 166.35(13); C7-Fe-P1, 90.06(10); C7-Fe-P2, 89.61(10); C14-Fe-N2, 80.91(13); C14-Fe-P1, 89.03(9); C14-Fe-P2, 90.26(9); N2-Fe-P1, 91.84(8); N2-Fe-P2, 88.32(8); P1-Fe-P2, 179.24(3).

B. 1. [(bavp)Fe(PMe$_3$)$_2$][BAr^F$_4$] (4-PMe$_3$)

Crystal data for **4**-PMe$_3$: C$_{58}$H$_{45}$N$_2$F$_{24}$BP$_2$Fe, M = 1354.56, monoclinic, P2$_1$/c, a = 19.6517(7), b = 12.5655(4), c = 25.3645(7) Å, β = 109.7450(10)°, V = 5895.1(3) Å^3, T = 203(2), λ = 0.71073 Å, Z = 4, R_{int} = 0.0365, 49817 reflections, 12059 independent, R_1(all data) = 0.0958, wR_2 = 0.1782, GOF = 1.012, CCDC-1057830. The structure contains eight disordered CF$_3$ groups, all of which were modeled accordingly.

2. Fig. S2.

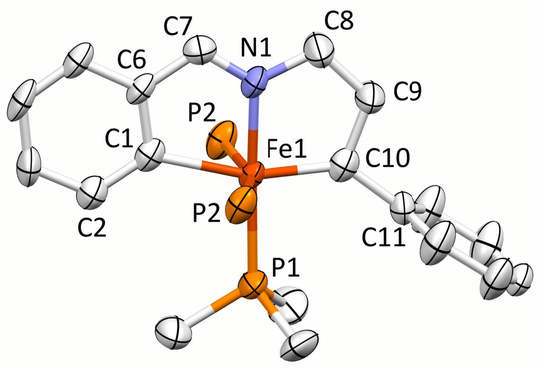


Molecular view of the cation pertaining to [(bavp]Fe(PMe$_3$)$_2$][BAr^F$_4$] (**4**-PMe$_3$); the PMe$_3$ methyl groups have been removed for clarity. Interatomic distances (Å) and angles (°): Fe-N1, 2.083(3); Fe-N2, 2.129 (4); Fe-C7, 1.809(4); Fe-C14, 1.858(4); Fe-P1, 2.2671(11); Fe-P2, 2.2725(11); N1-Fe-C7, 81.47(17); N1-Fe-C14, 168.31(19); N1-Fe-N2, 110.98(14); N1-Fe-P1, 88.53(9); N1-Fe-P2, 91.32(9); C7-Fe-C14, 86.9(2); N2-Fe-C7, 167.48(17); C7-Fe-P1, 91.87(13); C7-Fe-P2, 87.81(13); N2-Fe-C14, 80.71(18); C14-Fe-P1, 91.49(13); C14-Fe-P2, 88.60(13); N2-Fe-P1, 89.89(10); N2-Fe-P2, 90.44(10); P1-Fe-P2, 179.66(5).

C. 1. [(piap)Fe(PMe$_3$)$_3$][BAr^F$_4$] (5)

Crystal data for **5**(THF): $C_{61}H_{60}NOF_{24}BP_3Fe$, M = 1438.67, monoclinic, C2/m, a = 19.963(5), b = 17.492(6), c = 19.586(6) Å, β = 93.869(14)°, V = 6824(4) Å^3, T = 203(2), λ = 0.71073 Å, Z = 4, R_{int} = 0.0579, 21278 reflections, 5076 independent, R_1(all data) = 0.0899, wR_2 = 0.1923, GOF = 1.155, CCDC-1057829.

2. Fig. S3.

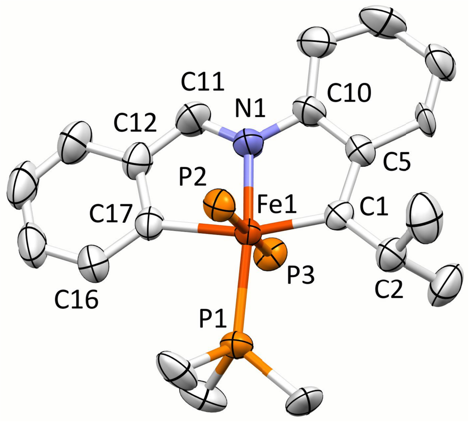


Molecular view of the cation pertaining to [(piap)Fe(PMe$_3$)$_3$][BAr^F$_4$] (**5**); the methyl groups of the *trans*-PMe$_3$ ligands have been removed for clarity. Interatomic distances (Å) and angles (°): Fe-C1, 2.106(6); Fe-N1, 1.949(6); Fe-C10, 1.867(7); Fe-P1, 2.281(2); Fe-P2, 2.2733(16); C1-C6, 1.396(10); C6-C7, 1.417(10); C7-N1, 1.307(9); N1-C8, 1.452(10); C8-C9, 1.441(12); C9-C10, 1.494(11); C10-C11, 1.512(10); C1-Fe-N1, 78.4(3); C1-Fe-C10, 161.6(3); C1-Fe-P1, 103.7(2); N1-Fe-C10, 83.2(3); N1-Fe-P1, 177.94(17); C10-Fe-P1, 94.8(2); C1-Fe-P2, 79.47(4); N1-Fe-P2, 88.54(5); C10-Fe-P2, 100.20(4); P1-Fe-P2, 91.83(5); P2-Fe-P2, 158.89(8); Fe-C1-C2, 133.8(5); Fe-C1-C6, 110.4(5); C1-C6-C7, 116.5(6); C6-C7-N1, 113.8(6); C7-N1-C8, 121.4(6); Fe-N1-C7, 121.0(5); Fe-N1-C8, 117.6(5); N1-C8-C9, 109.2(7); C8-C9-C10, 114.3(6); C9-C10-C11, 107.9(6); Fe-C10-C9, 115.7(5); Fe-C10-C11, 136.4(5).

D. 1. [(pipad)Fe(PMe$_3$)$_3$][BAr^F$_4$] (6)

Crystal data for **6**: $C_{58}H_{55}NF_{24}BP_3Fe$, M = 1381.60, monoclinic, P2$_1$/c, a = 18.4232(6), b = 13.0618(4), c = 25.9802(8) Å, β = 99.5300(10)°, V = 6165.6(3) Å^3, T = 233(2), λ = 0.71073 Å, Z = 4, R_{int} = 0.0393, 35706 reflections, 9178 independent, R_1(all data) = 0.0780, wR_2 = 0.1273, GOF = 1.050, CCDC-1057828. All PMe$_3$ methyl groups and six CF$_3$ groups were disordered and modeled accordingly.

2. Fig. S4.



Molecular view of the cation pertaining to [(pipad)Fe(PMe$_3$)$_3$][BAr^F$_4$] (**6**); the methyl groups of the *trans*-PMe$_3$ ligands have been removed for clarity. Interatomic distances (Å) and angles (°): Fe-C1, 1.899(3); Fe-N1, 1.933(3); Fe-C17, 2.059(3); Fe-P1, 2.317(2); Fe-P2, 2.226(3); Fe-P3, 2.367(3); C12-C17, 1.415(5); C11-C12, 1.402(6); N1-C11, 1.307(5); N1-C10, 1.392(5); C5-C10, 1.394(5); C1-C5, 1.465(5); C1-C2, 1.525(5); N1-Fe-C17, 80.04(14); C1-Fe-C17, 163.36(15); C17-Fe-P1, 92.03(12); C17-Fe-P2, 88.28(13); C17-Fe-P3, 87.16(12); N1-Fe-C1, 83.34(14); N1-Fe-P1, 167.04(14); N1-Fe-P2, 96.52(16); N1-Fe-P3, 79.34(14); C1-Fe-P1, 104.46(12); C1-Fe-P2, 92.87(12); C1-Fe-P3, 90.53(13); P1-Fe-P2, 93.45(14); P1-Fe-P3, 90.11(13); P2-Fe-P3, 174.32(13); Fe-C17-C16, 136.0(3); Fe-C17-C12, 110.8(3); C17-C12-C11, 114.3(3); N1-C11-C12, 116.4(4); C10-N1-C11, 125.5(3); Fe-N1-C10, 116.1(2); Fe-N1-C11, 118.4(3); N1-C10-C5, 112.6(3); C1-C5-C10, 114.9(3); C2-C1-C5, 116.0(3); Fe-C1-C5, 112.8(2); Fe-C1-C2, 131.0(3).

III. Mössbauer Procedures and Spectra

A. General

^{57}Fe Mössbauer spectra[g,h] were recorded on a WissEl Mössbauer spectrometer (MRG-500) at 77 K in constant acceleration mode. ^{57}Co/Rh was used as the radiation source. WinNormos for Igor Pro software has been used for the quantitative evaluation of the spectral parameters (least-squares fitting to Lorentzian peaks). The minimum experimental line widths were 0.20 mms^{-1}. The temperature of the samples was controlled by an MBBC-HE0106 MÖSSBAUER He/N$_2$ cryostat within an accuracy of ±0.3 K. Isomer shifts were determined relative to □-iron at 298 K.

B. Table S1

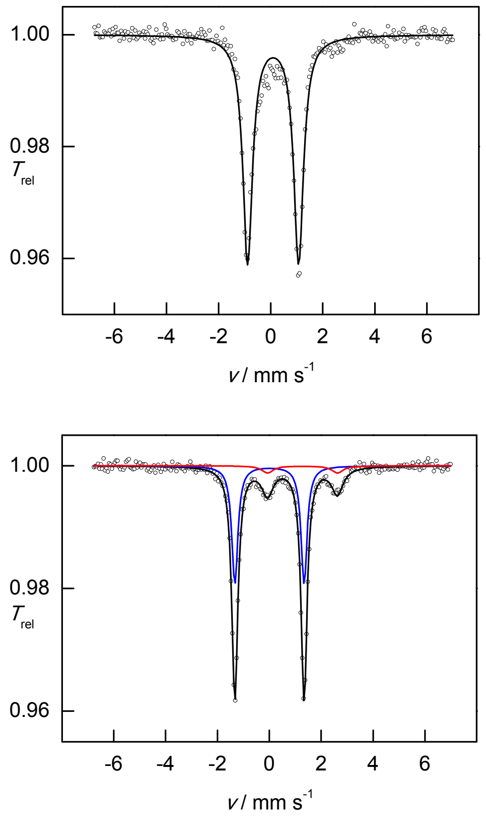
Comparison of Fe(II) and Fe(IV) alkylidene Mössbauer parameters.

Cmpd	δ (mm/s)	ΔE$_Q$ (mm/s)	Γ$_{FWHM}$ (mm/s)
(bdvp)Fe(PMe$_3$)$_2$ (**1**-PMe$_3$)	0.09(1)	1.96(1)	0.45(1)
trans-(pipp)Fe(PMe$_3$)$_2$N$_2$ (**2**)[a]	0.08(1)	2.14(1)	0.31(1)
trans-(pipvd)Fe(PMe$_3$)$_2$N$_2$ (**3**)	0.07(1)	1.97(1)	0.33(1)
[(bavp]Fe(PMe$_3$)$_2$][BAr^F$_4$] (**4**-PMe$_3$)[b]	0.01(1)	2.67(1)	0.28(1)
[(piap)Fe(PMe$_3$)$_3$][BAr^F$_4$] (**5**)[c]	0.06(1)	2.02(1)	0.29(1)
[(pipad)Fe(PMe$_3$)$_3$][BAr^F$_4$] (**6**)	0.07(1)	2.20(1)	0.28(1)

---

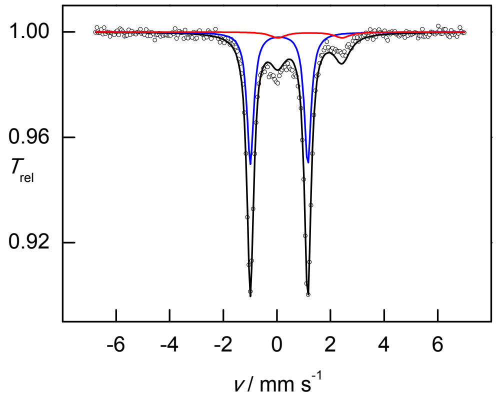
[a] Sample contained 20% of a high spin Fe(II) species: δ = 1.23(1) mm/s, ΔE$_Q$ = 2.40(1) mm/s, Γ$_{FWHM}$ = 0.73(1) mm/s. [b] Sample contained 18% of a high spin Fe(II) species: δ = 1.28(1) mm/s, ΔE$_Q$ = 2.70(1) mm/s, Γ$_{FWHM}$ = 0.54(1) mm/s. [c] Sample contained 35% of a high spin Fe(II) species: δ = 1.25(1) mm/s, ΔE$_Q$ = 2.42(1) mm/s, Γ$_{FWHM}$ = 0.51(1) mm/s.

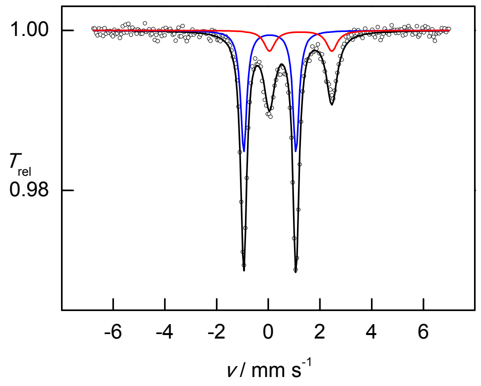
C. Fig. S5.



Mössbauer spectra of *trans*-(bdvp)Fe(PMe$_3$)$_2$ (**1**-PMe$_3$, top: $\delta = 0.09(1)$ mm/s, $\Delta E_Q = 1.96(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.45(1)$ mm/s) and [(bavp)Fe(PMe$_3$)$_2$][BAr$^F{}_4$] (**4**-PMe$_3$, bottom, 82%: $\delta = 0.01(1)$ mm/s, $\Delta E_Q = 2.67(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.28(1)$ mm/s; 18% of a high spin Fe(II) species, δ 1.28(1) mm/s, $\Delta E_Q = 2.70(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.54(1)$ mm/s).

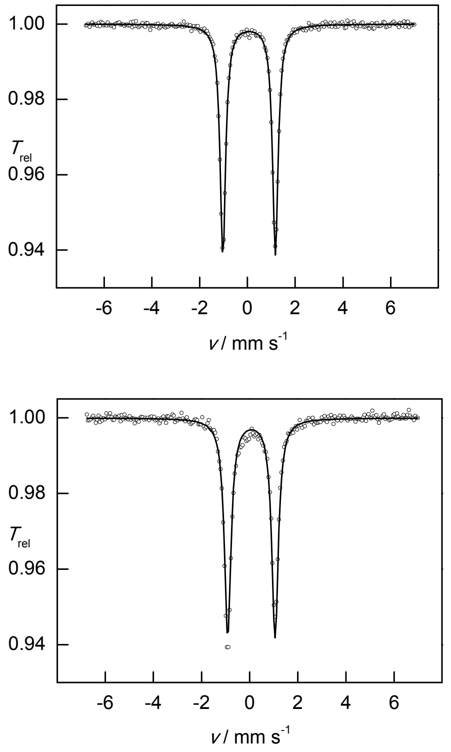
D. Fig. S6.





Mössbauer spectra of *trans*-(pipp)Fe(PMe$_3$)$_2$N$_2$ (**2**, top, 80%: $\delta = 0.08(1)$ mm/s, $\Delta E_Q = 2.14(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.31(1)$ mm/s; 20% of a high spin Fe(II) species, $\delta = 1.23(1)$ mm/s, $\Delta E_Q = 2.40(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.73(1)$ mm/s) and [(piap)Fe(PMe$_3$)$_3$][BAr$^F{}_4$] (**5**, bottom, 65%: $\delta = 0.08(1)$ mm/s, $\Delta E_Q = 2.02(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.29(1)$ mm/s; 35% of a high spin Fe(II) species, δ 1.25(1) mm/s, $\Delta E_Q = 2.42(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.51(1)$ mm/s).

E. Fig. S7.



Mössbauer spectra of *trans*-(pipvd)Fe(PMe$_3$)$_2$N$_2$ (**2**, top: $\delta = 0.07(1)$ mm/s, $\Delta E_Q = 2.20(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.27(1)$ mm/s) and [(pipad)Fe(PMe$_3$)$_3$][BAr$^F{}_4$] (**6**, bottom: $\delta = 0.07(1)$ mm/s, $\Delta E_Q = 1.97(1)$ mm/s, $\Gamma_{\mathrm{FWHM}} = 0.33(1)$ mm/s).

The origin of the impurities in **4**-PMe$_3$, **2** and **5** are unknown. The compounds gave satisfactory analyses, and appeared reasonably thermallly stable, although they are highly air sensitive. We can only conclude that in the shipping and handling upon mailing to collaborators, some degradation was induced.

IV. Notes and references

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