Supporting information for:

Directed C-H Activation with Iron Carbene Complexes

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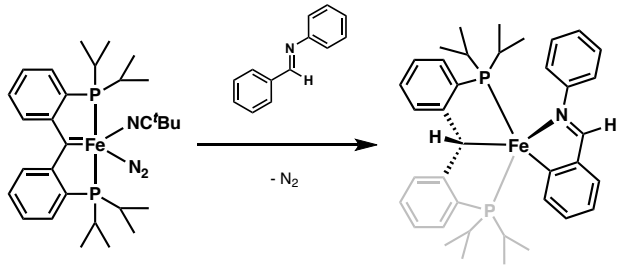
1. Experimental

1.1 General Remarks

All experiments were performed under an inert atmosphere of N_2 using standard glovebox techniques unless otherwise specified. Solvents: hexanes, *n*-pentane, diethyl ether, toluene were dried by passing through a column of activated alumina and stored in the glovebox over 3 Å molecular sieves. Hexamethyldisiloxane was degassed under N_2 and then brought into the glovebox and stored over 3 Å molecular sieves. Deuterated solvents: C_6D_6 and $C_6D_5CD_3$ were dried over calcium hydride followed by filtration and stored in the glovebox over 3 Å molecular sieves. Compounds [{PC(sp^2)P}Fe(NC^{t}Bu)(N_2)] (**1-NC^{t}Bu**),[1] and [{PC(sp^2)P}Fe(PMe_3)(N_2)] (**1-PMe_3**)[1] were prepared according to previously reported procedures. Benzophenone and *N*-benzylideneaniline were received from commercial vendors and recrystallized from diethyl ether at -35 °C prior to use. Azobenzene was used as received. All other reagents are commonly available and were used without additional purification. ^{1}H, ^{13}C{H}, ^{31}P{H}, COSY, HSQC, and HMBC spectra were recorded on a Bruker AVANCE DRX 400/500/800 or Varian DirectDrive 600 spectrometers. All chemical shifts are reported in δ units with references to residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, or to external 85% phosphoric acid for phosphorous chemical shifts.

1.2 Synthesis of [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (2)



1-NC^{t}Bu 2

1-NC^{t}Bu (27 mg, 0.05 mmol, 1.0 eq.) dissolved in 3 mL diethyl ether was added to a 20 mL scintillation vial equipped with a stir bar. *N*-benzylideneaniline (10 mg, 0.055 mmol, 1.1 eq.) dissolved in 2 mL diethyl ether was added to the stirring solution, and precipitation of a green solid was observed immediately. The resulting mixture was stirred at ambient temperature for 10 minutes, before the volatile components were removed under reduced pressure. The green solid was triturated with diethyl ether (10 mL) and then the remaining green solid was dissolved in benzene (10 mL) and filtered through a pad of Celite. The solution was concentrated under reduced pressure, and the concentrated solution was layered with hexanes and analytically pure **2** was obtained after two days at ambient temperature. Yield: 9 mg, 29%.

Data for **2**: μ_{eff} = 5.22 μ_B (Evans).

^{1}H NMR (400 MHz, C_6D_6, 295 K): δ 69.7 ($\nu_{1/2}$ = 157 Hz), 62.0 ($\nu_{1/2}$ = 50.0 Hz), 35.0 ($\nu_{1/2}$ = 15.0 Hz), 19.9 ($\nu_{1/2}$ = 46.7 Hz), 19.7 ($\nu_{1/2}$ = 22.6 Hz), 15.0 ($\nu_{1/2}$ = 20.0 Hz), 11.3 ($\nu_{1/2}$ = 20.0 Hz), -0.2

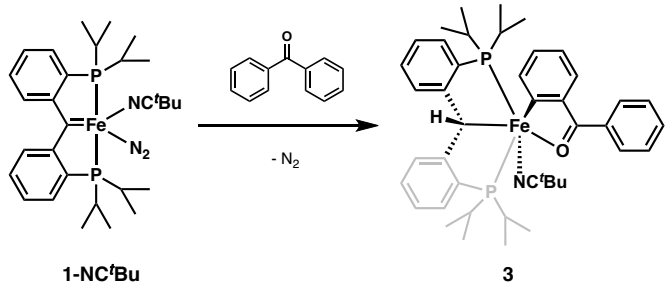
($\nu_{1/2}$ = 194 Hz), -1.3 ($\nu_{1/2}$ = 37.8 Hz), -1.8 ($\nu_{1/2}$ = 70.1 Hz), -2.4 ($\nu_{1/2}$ = 16.4 Hz), -5.1 ($\nu_{1/2}$ = 181 Hz), -6.1 ($\nu_{1/2}$ = 15.4 Hz), -7.5 ($\nu_{1/2}$ = 97.2 Hz), -17.2 ($\nu_{1/2}$ = 155 Hz), -107.0 ($\nu_{1/2}$ = 112 Hz).

Anal. (%) Calcd. For $C_{38}H_{47}FeNP_2$: C, 71.81; H, 7.45; N, 2.20. Found: C, 71.55; H 8.12; N, 1.89.

X-ray crystal structure [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (2)

Single crystals were obtained as dark green prisms from a concentrated benzene solution layered with hexamethyldisiloxane at ambient temperature. Crystal and refinement data for **2**: $C_{38}H_{47}FeNP_2$; M_r = 635.55; Triclinic; space group P-1; *a* = 9.9760(3) Å; *b* = 10.2625(3) Å; *c* = 18.1605(5) Å; α = 85.7430(10)°; β = 77.0530(10)°; γ = 63.3690(10)°; V = 1619.02(8) Å^3; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 0.592 mm^{-1}; d_{calc} = 1.304 g.cm^{-3}; 57485 reflections collected; 8034 unique (R_{int} = 0.0262); giving R_1 = 0.0250, wR_2 = 0.0655 for 7558 data with [I>2σ(I)] and R_1 = 0.0268, wR_2 = 0.0664 for all 8034 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.380/-0.279.

1.3 Synthesis of [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (3)



1-NC^{t}Bu 3

To a 20 mL scintillation vial equipped with a stir bar containing **1-NC^{t}Bu** (72 mg, 0.13 mmol, 1.0 eq.), and 3 mL diethyl ether was added a solution of benzophenone (23 mg, 0.13 mmol, 1.0 eq.) in 2 mL diethyl ether. The resulting solution was stirred at ambient temperature for 10 minutes, before the volatile components were removed under reduced pressure. *n*-pentane (10 mL) was added to the resulting residue, and the mixture was stirred for five minutes before removal of the volatile components to yield a blue-green solid. The solid was extracted with *n*-pentane (5 mL) and filtered through a pad of Celite. The solution was concentrated to *ca.* 1 mL, and stored at -35 °C from which analytically pure **3** was obtained overnight. Yield: 36 mg, 39%.

Data for **3**: μ_{eff} = 4.82 μ_B (Evans).

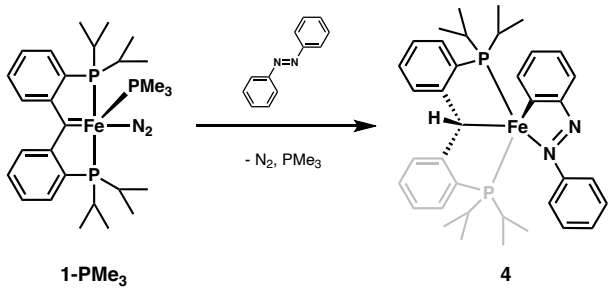
^{1}H NMR (400 MHz, C_6D_6, 295 K): δ 71.1 ($\nu_{1/2}$ = 75 Hz), 69.6 ($\nu_{1/2}$ = 227 Hz), 29.8 ($\nu_{1/2}$ = 40 Hz), 27.8 ($\nu_{1/2}$ = 33 Hz), 26.1 ($\nu_{1/2}$ = 62 Hz), 25.8 ($\nu_{1/2}$ = 61 Hz), 25.6 ($\nu_{1/2}$ = 13 Hz), 24.7 ($\nu_{1/2}$ = 57 Hz), 23.0 ($\nu_{1/2}$ = 44 Hz), 19.3 ($\nu_{1/2}$ = 68 Hz), 10.3 ($\nu_{1/2}$ = 41 Hz), 0.32 ($\nu_{1/2}$ = 75 Hz), -0.43 ($\nu_{1/2}$ = 220Hz), -1.4 ($\nu_{1/2}$ = 80 Hz), -1.7 ($\nu_{1/2}$ = 187 Hz), -2.2 ($\nu_{1/2}$ = 161 Hz), -4.7 ($\nu_{1/2}$ = 52 Hz), -7.9 ($\nu_{1/2}$ = 127 Hz), -10.7 ($\nu_{1/2}$ = 65 Hz), -22.7 ($\nu_{1/2}$ = 220 Hz), -86.0 ($\nu_{1/2}$ = 277 Hz).

Anal. (%) Calcd. For $C_{45}H_{55}FeNOP_2$: C, 71.76; H, 7.70; N, 1.95. Found: C, 72.38; H 8.05; N, 2.14.

X-ray crystal structure of [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (3).

Single crystals were obtained as dark green blocks from a concentrated diethyl ether solution at ambient temperature. Crystal and refinement data for **3**: $C_{43}H_{55}FeNOP_2$; M_r = 719.67; Triclinic; space group P-1; *a* = 9.5332(2) Å; *b* = 12.0978(2) Å; *c* = 16.7258(3) Å; α = 86.9350(10)°; β = 87.9500(10)°; γ = 77.4270(10)°; V = 1879.47(6) Å^3; Z = 2; T = 296(2) K; λ = 1.54178 Å; μ = 4.271 mm^{-1}; d_{calc} = 1.272 g.cm^{-3}; 43252 reflections collected; 7091 unique (R_{int} = 0.0382); giving R_1 = 0.0563, wR_2 = 0.1544 for 6769 data with [I>2σ(I)] and R_1 = 0.0584, wR_2 = 0.1565 for all 7091 data. Residual electron density (e$^-$.Å^{-3}) max/min: 1.089/-0.747.

1.4 Synthesis of [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (4)



1-PMe$_3$ **4**

To **1-PMe$_3$** (30 mg, 0.054 mmol, 1.0 eq.) dissolved in 2 mL diethyl ether in a 20 mL scintillation vial was added azobenzene (10 mg, 0.55 mmol, 1.0 eq.) in 2 mL diethyl ether. The resulting solution was stirred at ambient temperature for four hours, and then the volatile components were removed under reduced pressure. To the purple residue was added *n*-pentane (10 mL) and the volatile components were removed under reduced pressure to yield a blue solid, which was redissolved in hexamethyldisiloxane (5 mL) and filtered through a pad of Celite. The solution was concentrated under reduced pressure, and the concentrated solution was stored at -35° C, from which analytically pure **4** was isolated after one day. Yield: 19 mg, 55%.

Data for **4**: μ_{eff} = 5.12 μ_B (Evans).

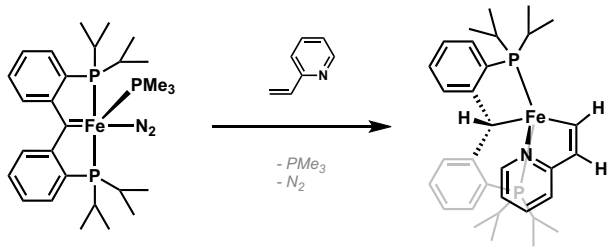
^{1}H NMR (400 MHz, C_6D_6, 295 K): δ 18.4 ($\nu_{1/2}$ = 263 Hz), 10.3 ($\nu_{1/2}$ = 39 Hz), 9.6 ($\nu_{1/2}$ = 31 Hz), 9.0 ($\nu_{1/2}$ = 31 Hz), 8.7 ($\nu_{1/2}$ = 25 Hz), 8.5 ($\nu_{1/2}$ = 22 Hz), 5.1 ($\nu_{1/2}$ = 31 Hz), 3.2 (overlapping signals, $\nu_{1/2}$ = 51 Hz), 0.6 ($\nu_{1/2}$ = 42 Hz), -0.9 ($\nu_{1/2}$ = 45 Hz), -3.0 ($\nu_{1/2}$ = 120 Hz).

Anal. (%) Calcd. For $C_{37}H_{46}FeN_2P_2$: C, 69.81; H, 7.28; N, 4.40. Found: C, 70.06; H 7.51; N, 5.05.

X-ray crystal structure of [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (4)

Single crystals were obtained as dark purple blocks from a concentrated hexamethyldisiloxane solution at ambient temperature. Crystal and refinement data for **4**: $C_{37}H_{46}FeN_2P_2$; M_r = 636.55; Triclinic; space group P-1; *a* = 10.0838(4) Å; *b* = 10.1841(6) Å; *c* = 17.5352(7) Å; α = 89.243(2)°; β = 88.0700(10)°; γ = 65.7090(10)°; V = 1640.41(13) Å^3; Z = 2; T = 120(2) K; λ = 1.54178 Å; μ = 4.811 mm^{-1}; d_{calc} = 1.289 g.cm^{-3}; 29692 reflections collected; 6481 unique (R_{int} = 0.0296); giving R_1 = 0.0272, wR_2 = 0.0729 for 6384 data with [I>2σ(I)] and R_1 = 0.0275, wR_2 = 0.0732 for all 6481 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.364/-0.225.

1.5 Synthesis of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (5)



1-PMe$_3$ **5**

A J-Young NMR tube was charged with [{PC(sp^2)P}Fe(PMe$_3$)(N$_2$)] (55 mg, 0.10 mmol, 1.0 eq.), C_6D_6 (0.7 mL), and 2-vinylpyridine (12 µL, 0.11 mmol, 1.1 eq.). The tube was sealed and heated for two hours in an oil bath, over which time the dark red solution became a dark pink. After the reaction was complete by NMR analysis, the tube was brought back into the drybox, and the contents were transferred to a 20 mL scintillation vial with a stir bar. The volatile components were removed under reduced pressure, and *n*-pentane (10 mL) was added to the pink residue, stirred for five minutes at ambient temperature, and volatile components removed under reduced pressure to yield a pink solid. The solid was dissolved in hexamethyldisiloxane and filtered through a pad of Celite, and concentrated to *ca*. 1 mL under reduced pressure. This concentrated solution was stored at -35 °C overnight, and single crystals of analytically pure **5** were obtained. Yield: 36 mg, 65%.

Data for **5**: μ_{eff} = 2.98 μ_B (Evans).

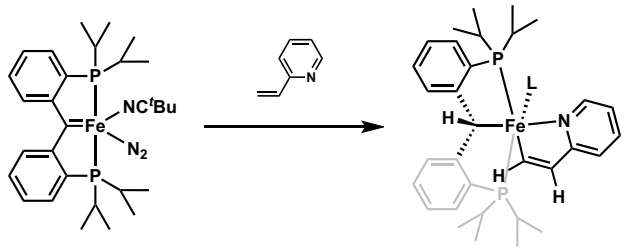
^{1}H NMR (600 MHz, C_6D_6, 295 K): δ 56.9 ($\nu_{1/2}$ = 17.8 Hz), 52.6 ($\nu_{1/2}$ = 23.1 Hz), 52.4 ($\nu_{1/2}$ = 17.0 Hz), 23.7 ($\nu_{1/2}$ = 82 Hz), 3.60 ($\nu_{1/2}$ = 188 Hz), -0.34 ($\nu_{1/2}$ = 186 Hz), -2.59 ($\nu_{1/2}$ = 53 Hz), -4.32 ($\nu_{1/2}$ = 143 Hz), -9.66 ($\nu_{1/2}$ = 105 Hz), -24.1 ($\nu_{1/2}$ = 165 Hz), -33.3 ($\nu_{1/2}$ = 205 Hz).
X-ray crystal structure of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (5).

Anal. (%) Calcd. For $C_{32}H_{43}FeNP_2$: C, 68.70; H, 7.75; N, 2.50. Found: C, 69.12; H 7.33; N, 3.02.

X-ray crystal structure of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (5).

Single crystals were obtained as dark pink rhomboids from a concentrated *n*-pentane solution at -35 °C. Crystal and refinement data for **5**: $C_{32}H_{43}FeNP_2$; M_r = 559.46; Monoclinic; space group $P2_1/c$; *a* = 9.7026(3) Å; *b* = 19.8324(7) Å; *c* = 15.2623(7) Å; α = 90°; β = 93.4120(10)°; γ = 90°; V = 2931.66(19) Å^3; Z = 4; T = 120(2) K; λ = 1.54178 Å; µ = 5.299 mm^{-1}; d_{calc} = 1.268 g.cm^{-3}; 72837 reflections collected; 5783 unique (R_{int} = 0.0443); giving R_1 = 0.0230, wR_2 = 0.0589 for 5542 data with [I>2σ(I)] and R_1 = 0.0244, wR_2 = 0.0601 for all 5783 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.296/-0.186.

1.6 Synthesis of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(L)] (6)



1-NC^{t}Bu **6**

In a 20 mL scintillation vial with a stir bar, **1-NC^{t}Bu** (38 mg, 0.067 mmol, 1.0 eq.) was dissolved in diethyl ether (5 mL). NC^{t}Bu (10 µL, 0.09 mmol, 1.3 eq.) was added to the stirring solution, and the mixture was stirred for one minute before addition of 2-vinylpyridine (7 µL, 0.065 mmol, 1.0 eq.). The solution became dark cherry-red immediately, alongside concomitant effervescence. The solution was stirred at ambient temperature for 15 minutes, before the volatile components were removed under reduced pressure to yield a red residue. *n*-pentane (10 mL) was added to the residue, and the resulting solution stirred at ambient temperature for five-minutes, before removal of the volatile components to yield a cherry-red solid. The solid was redissolved in *n*-pentane, filtered through a pad of Celite, and concentrated under reduced pressure. This concentrated solution was stored at -35° C, from which a 95:5 mixture of **6-NC^{t}Bu** and **6-N$_2$** was obtained. Yield: 32 mg, 74%.

Data for **6-NC^{t}Bu**: ^{1}H NMR (800 MHz, C_6D_6, 295 K): δ 11.1 (br. s, 1H, -C(sp^2)*H*-C(sp^2)H-Py), 9.23 (br. s, 1H, Py*H*), 7.72 (br. s, 1H, Ar*H*), 7.64 (br. s, 1H, -C(sp^2)H-C(sp^2)*H*-Py), 7.08 (br. s, 6H, Ar*H*), 6.93 (br. s, 3H, Ar*H*), 6.49 (br. s, 1H, Ar*H*), 5.21 (br. s, 1H, -C(sp^3)*H*-), 2.46 (br. s, 4H, -C*H*(CH$_3$)$_2$), 1.16 (br. s, 6H, -CH(C*H*$_3$)$_2$), 1.08 (br. s, 6H-CH(C*H*$_3$)$_2$), 0.93 (br. s, 6H, -CH(C*H*$_3$)$_2$), 0.87 (t, *J* = 7.3 Hz, 9H, -NC(C*H*$_3$)$_3$), 0.71 (obscured, 6H, -CH(C*H*$_3$)$_2$).

^{31}P{H} NMR (162 MHz, C_6D_6, 295 K): δ 65.4 (s, 2P).

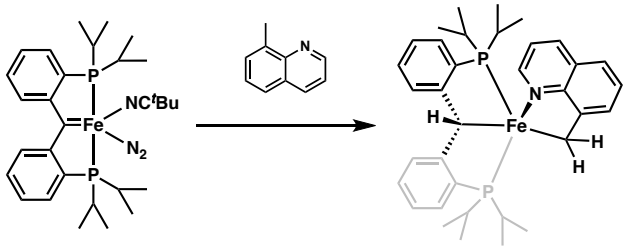
^{13}C{H} NMR (151 MHz, C_6D_6, 295 K): δ 233.7 (t, *J* = 28.5 Hz, -*C*(sp^2)H-C(sp^2)H-Py), 172.2 (s, Ar*C*), 164.6 (t, *J* = 18.2 Hz, Ar*C*), 152.8 (s, Ar*C*), 138.7 (t, *J* = 16.1 Hz, Ar*C*), 133.6 (s, Ar*C*), 130.3 (overlapping signals: -C(sp^2)H-*C*(sp^2)H-Py & Ar*C*), 129.2 (s, Ar*C*), 128.9 (s, Ar*C*), 126.8 (s, Ar*C*), 125.2 (s, Ar*C*), 121.0 (s, Ar*C*), 117.6 (s, Ar*C*), 112.6 (s, Ar*C*), 34.0 (s, Ar*C*), 28.0 (s, Ar*C*), 26.2 (s, Ar*C*), 20.6 (s, Ar*C*), 19.4 (s, Ar*C*), 18.8 (s, Ar*C*), 17.7 (s, Ar*C*).

Anal. (%) Calcd. For $C_{37}H_{52}FeN_2P_2$: C, 69.15; H, 8.16; N, 4.36. Found: C, 69.56; H 7.82; N, 4.12.

X-ray crystal structure of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (6-NC^{t}Bu).

Single crystals were obtained as dark cherry-red blocks from a concentrated diethyl ether solution at ambient temperature. Crystal and refinment data for **6-NC^{t}Bu**: $C_{37}H_{52}FeN_2P_2$; M_r = 642.59; Monoclinic; space group $P2_1/n$; *a* = 11.2139(8) Å; *b* = 16.5390(12) Å; *c* = 18.2256(13) Å; α = 90°; β = 94.244(3)°; γ = 90°; V = 3371.0(4) Å^3; Z = 4; T = 120(2) K; λ = 1.54178 Å; µ = 4.683 mm^{-1}; d_{calc} = 1.266 g.cm^{-3}; 79139 reflections collected; 6880 unique (R_{int} = 0.0613); giving R_1 = 0.0257, wR_2 = 0.0619 for 6319 data with [I>2σ(I)] and R_1 = 0.0295, wR_2 = 0.0645 for all 6880 data. Residual electron density (e$^-$.Å^{-3}) max/min: 0.303/-0.257.

1.7 Synthesis of [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (7).



1-NC^{t}Bu **7**

In a 20 mL scintillation vial equipped with a stir bar, 8-methylquinoline (15 mg, 0.10 mmol, 1.1 eq.) in 1 mL diethyl ether was added to **1-NC^{t}Bu** (62 mg, 0.11 mmol, 1.0 eq.) dissolved in 2 mL diethyl ether. The resulting solution was stirred at ambient temperature for ten minutes, over which time the dark brown solution became red. The volatile components were removed under reduced pressure, and the dark brown residue was extracted with *n*-pentane (5 mL) and filtered through a pad of Celite. The volatile components were removed under reduced pressure, to yield a brown residue which was recrystallized from a 1:1 *n*-pentane/diethyl ether solution at -35 °C from which **7** was obtained. Despite extensive recrystallization attempts, a small amount of an unidentified paramagnetic product is observed in the ^{1}H NMR spectrum even of single crystals. Yield: 34 mg, 57%.

Data for **7**: μ_{eff} = 3.06 μ_B

^{1}H NMR (800 MHz, C_6D_6, 295 K): δ 63.6 ($\nu_{1/2}$ = 72 Hz), 30.6 ($\nu_{1/2}$ = 78 Hz), 27.4 ($\nu_{1/2}$ = 64 Hz), 24.0 ($\nu_{1/2}$ = 110 Hz), 10.3 ($\nu_{1/2}$ = 59 Hz), 9.5 ($\nu_{1/2}$ = 33 Hz), 3.9 ($\nu_{1/2}$ = 39 Hz), 1.7 ($\nu_{1/2}$ = 192 Hz),-1.3 ($\nu_{1/2}$ = 311 Hz), -3.2 ($\nu_{1/2}$ = 114 Hz), -6.0 ($\nu_{1/2}$ = 255 Hz), -6.8 ($\nu_{1/2}$ = 208 Hz), -8.0 ($\nu_{1/2}$ = 365 Hz), -8.4 ($\nu_{1/2}$ = 180 Hz),-9.6 ($\nu_{1/2}$ = 82 Hz), -10.1 ($\nu_{1/2}$ = 197 Hz), -12.0 ($\nu_{1/2}$ = 156.6 Hz), -17.3 ($\nu_{1/2}$ = 137 Hz), -19.4 ($\nu_{1/2}$ = 122 Hz), -29.1 ($\nu_{1/2}$ = 830 Hz).

Anal. (%) Calcd. for $C_{35}H_{45}FeNP_2 \cdot Et_2O$: C, 69.74; H, 8.25; N, 2.09. Found: C, 69.03; H 8.51; N, 1.34.

X-ray crystal structure of [PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (7)

Single crystals were obtained as red blocks from a concentrated 1:1 *n*-pentane/diethyl ether solution at ambient temperature. Crystal and refinement data for **7**: $C_{35}H_{45}FeNP_2$; M_r = 597.51; Monoclinic; space group $P2_1/n$; *a* = 9.9076(17) Å; *b* = 9.9398(19) Å; *c* = 31.847(6) Å; α = 90°; β = 96.767(6)°; γ = 90°; V = 3114.4(10) Å^3; Z = 4; T = 229(2) K; λ = 0.71073 Å; μ = 0.611 mm^{-1}; d_{calc} = 1.274 g.cm^{-3}; 95297 reflections collected; 7755 unique (R_{int} = 0.1011); giving R_1 = 0.0539, wR_2 = 0.1272 for 6060 data with [I>2σ(I)] and R_1 = 0.0724, wR_2 = 0.1386 for all 7755 data. Residual electron density (e$^-$.Å^{-3}) max/min: 1.516/-0.815.

2. NMR Spectra

2.1 NMR Spectrum for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (2)

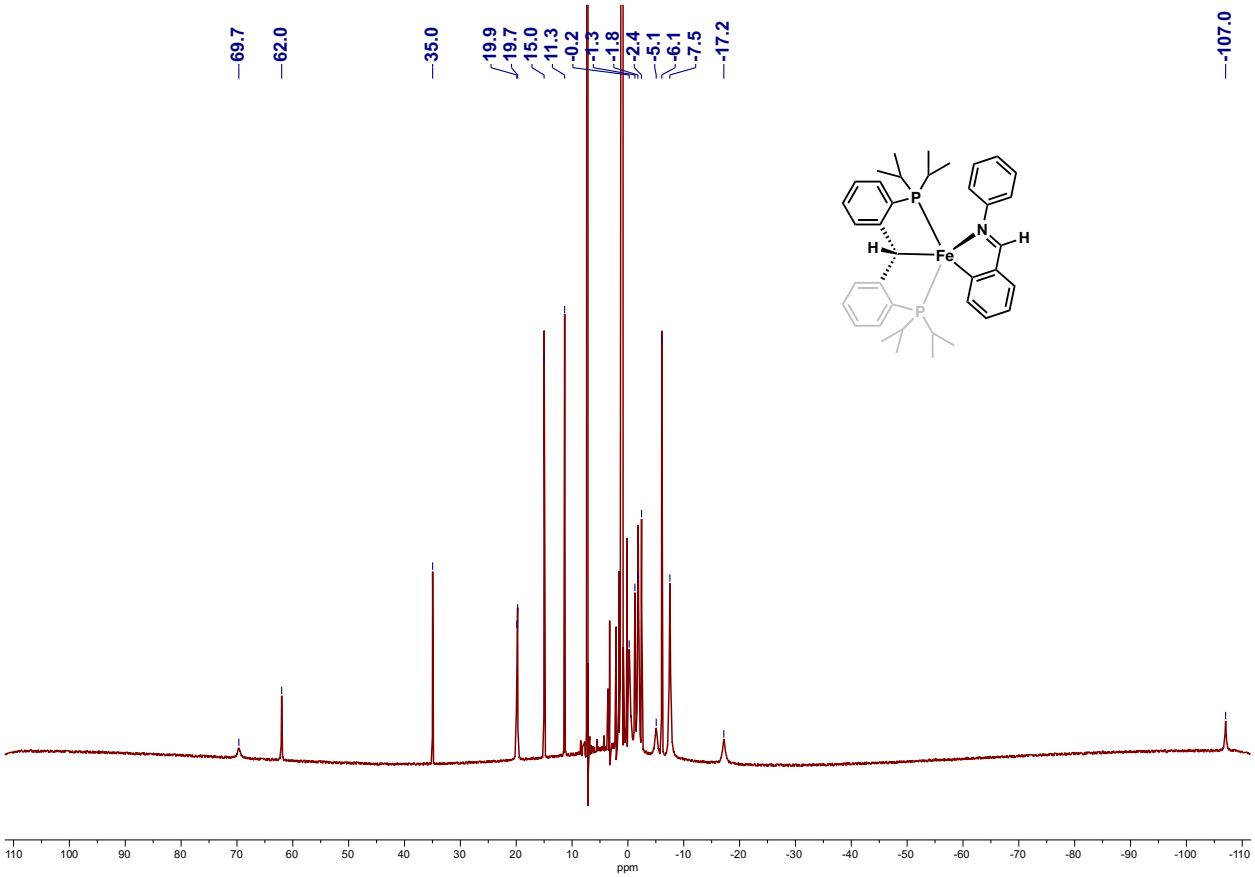


Figure S1. ^{1}H NMR (400 MHz, C_6D_6, 295 K) spectrum of [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**).

2.2 NMR Spectrum for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (3)

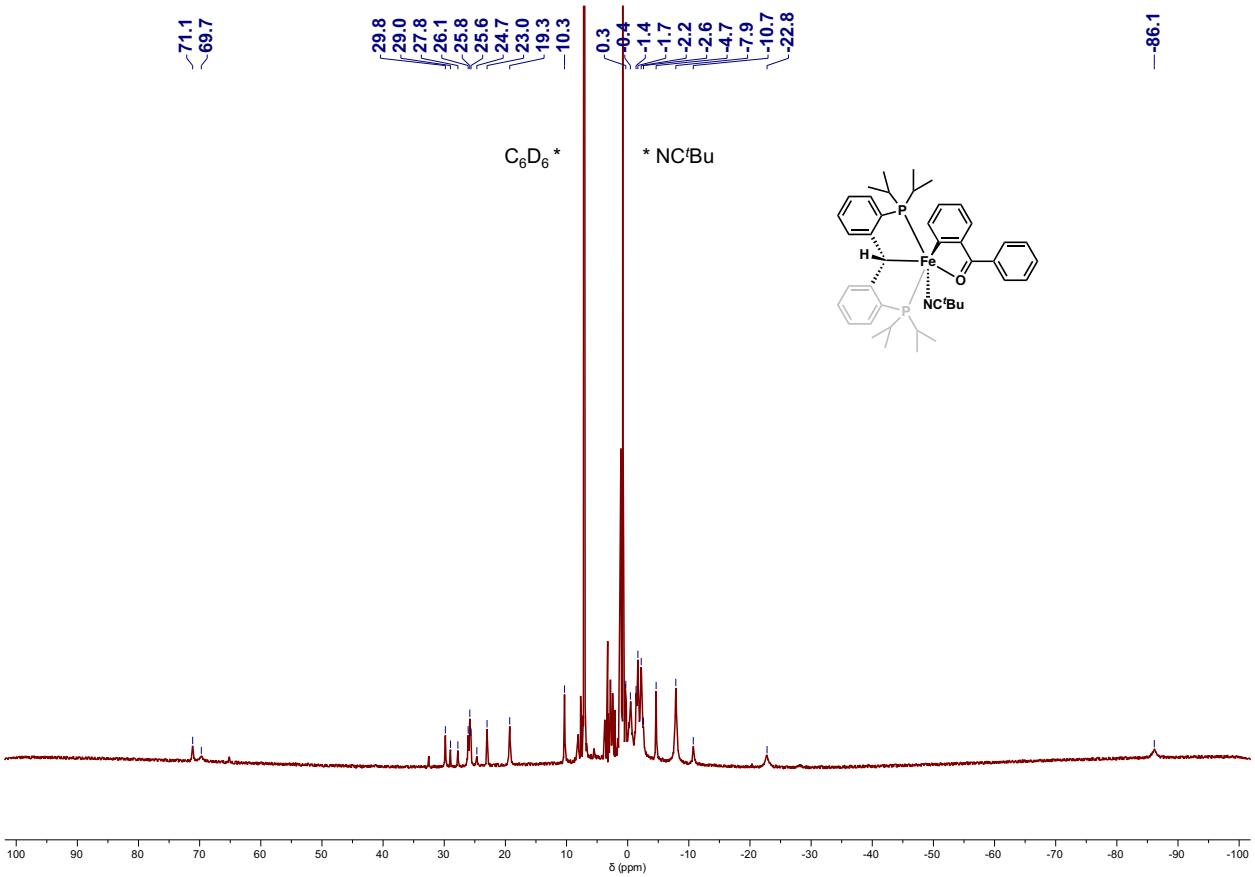


Figure S2. ^{1}H NMR (400 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O)(NC^{t}Bu)] (**2**).

2.3 NMR Spectrum for [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (4)

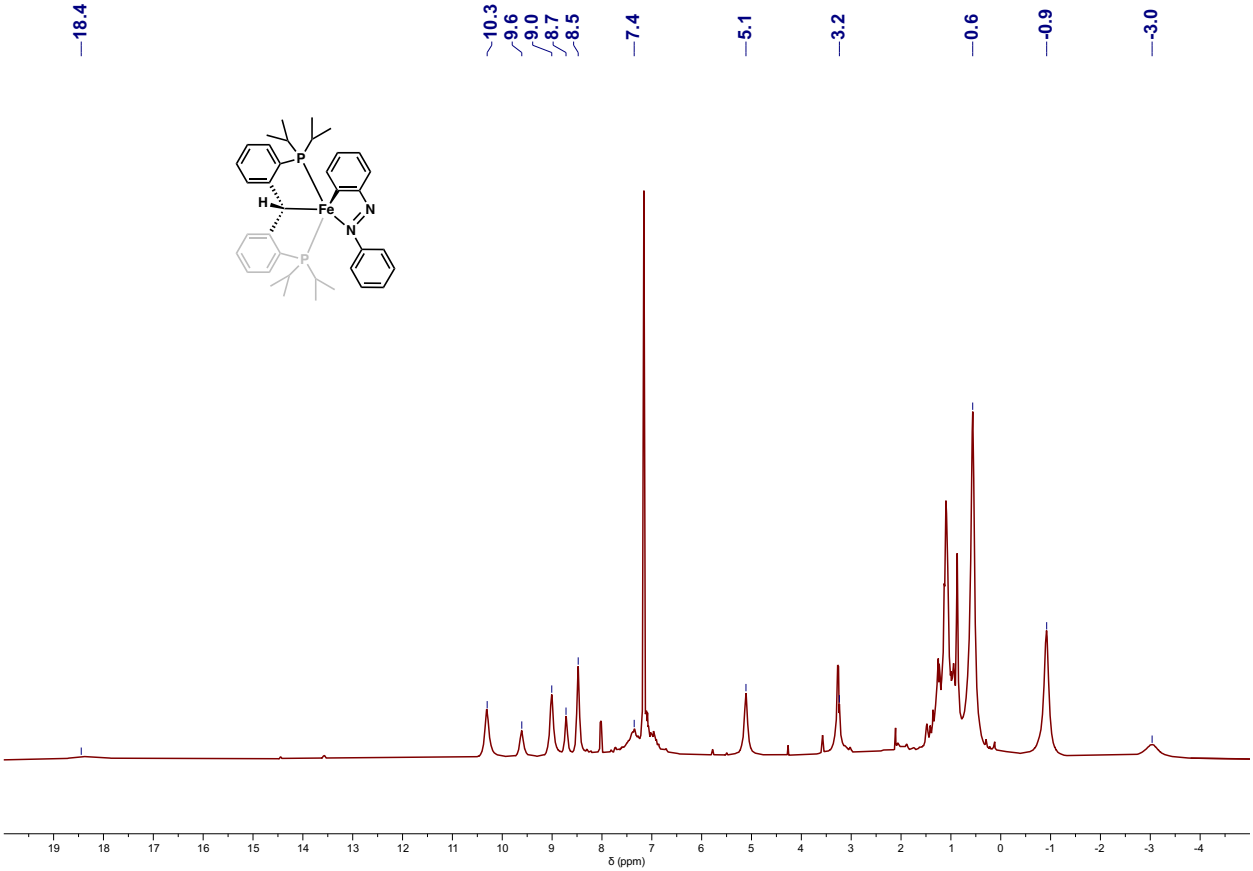


Figure S3. ^{1}H NMR (400 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh-)] (**4**).

2.4 NMR Spectrum for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (5)

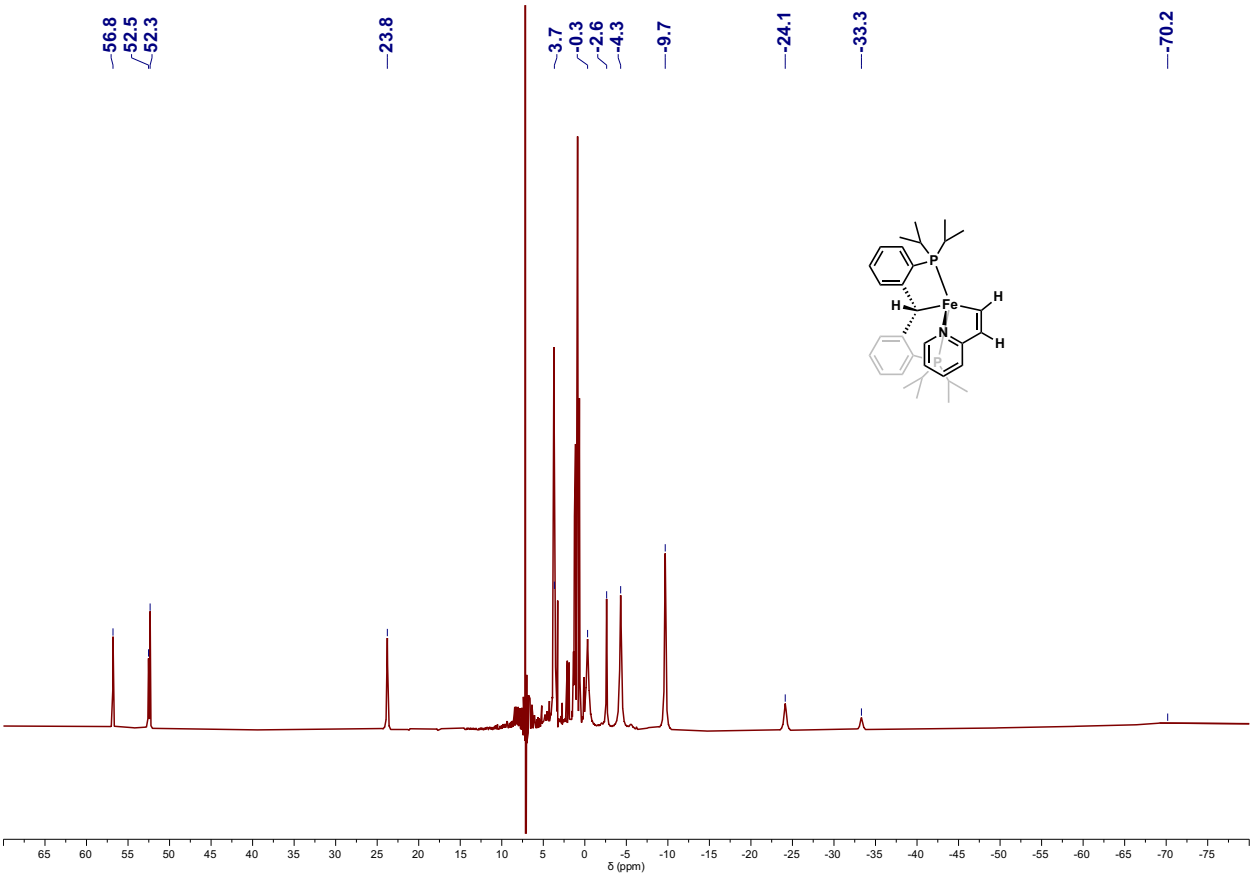


Figure S4. ^{1}H NMR (400 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**).

2.5 NMR Spectra for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (6-NC^{t}Bu)

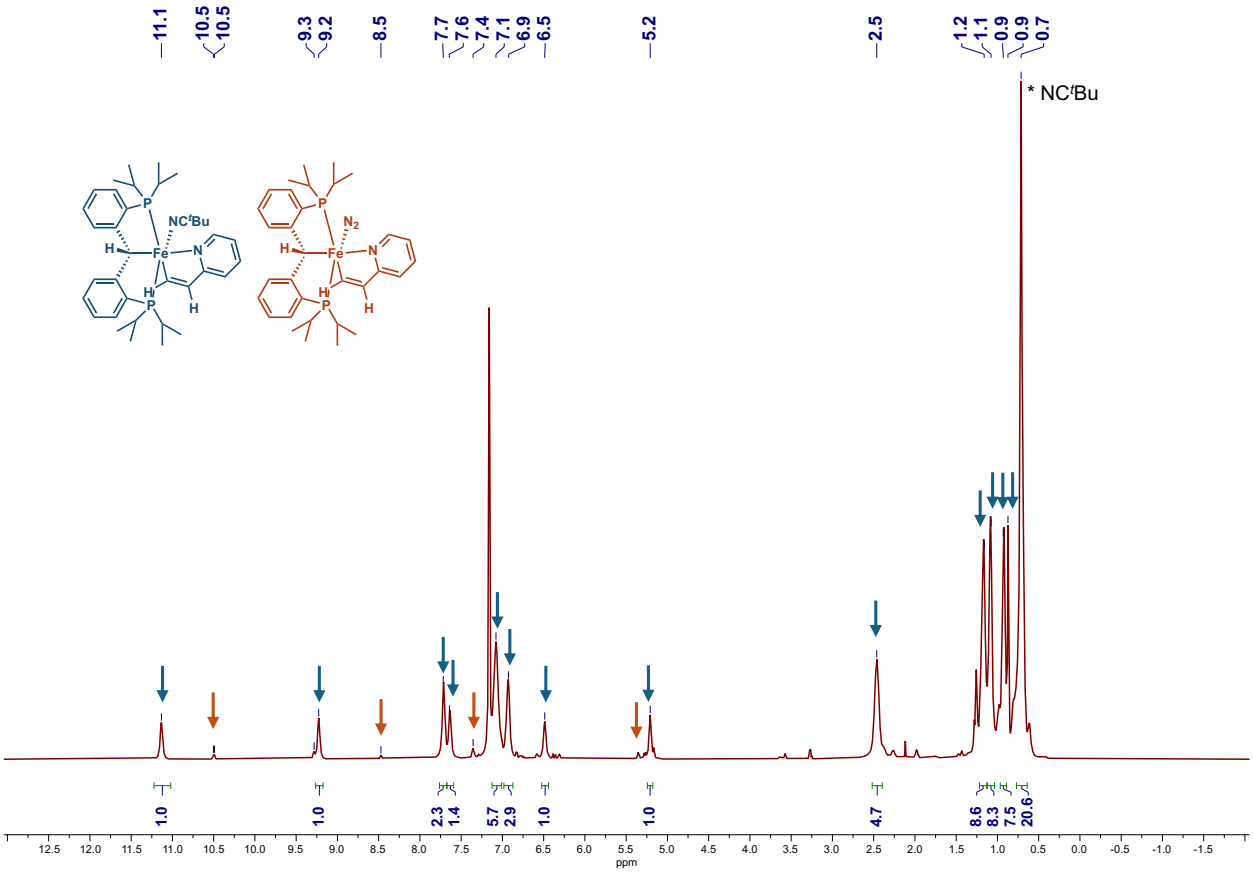


Figure S5. ^{1}H NMR (600 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(L)] (**6-L**). Some signals of **6-N$_2$** are obscured and cannot be assigned.

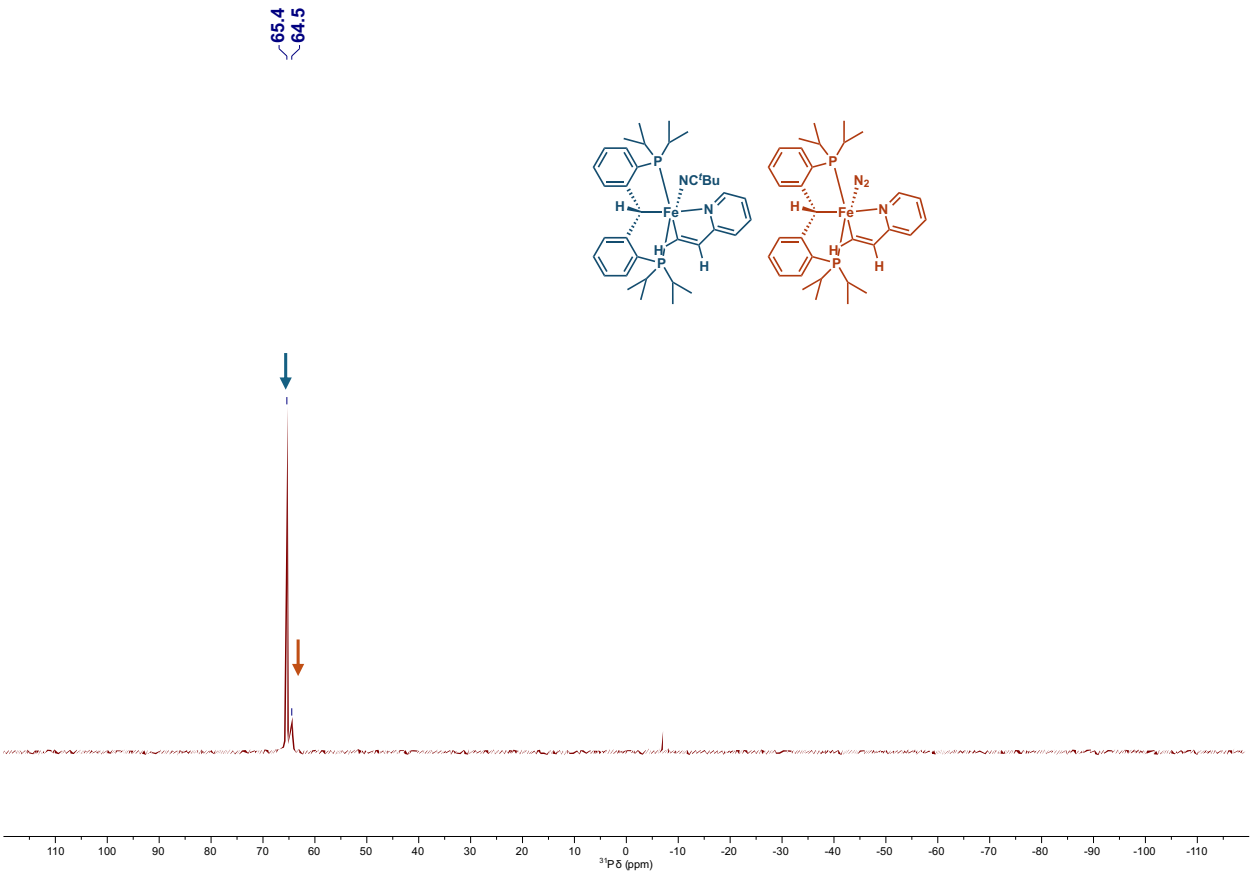


Figure S6. $^{31}P\{H\}$ NMR spectrum (162 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(L)] (**6-L**).

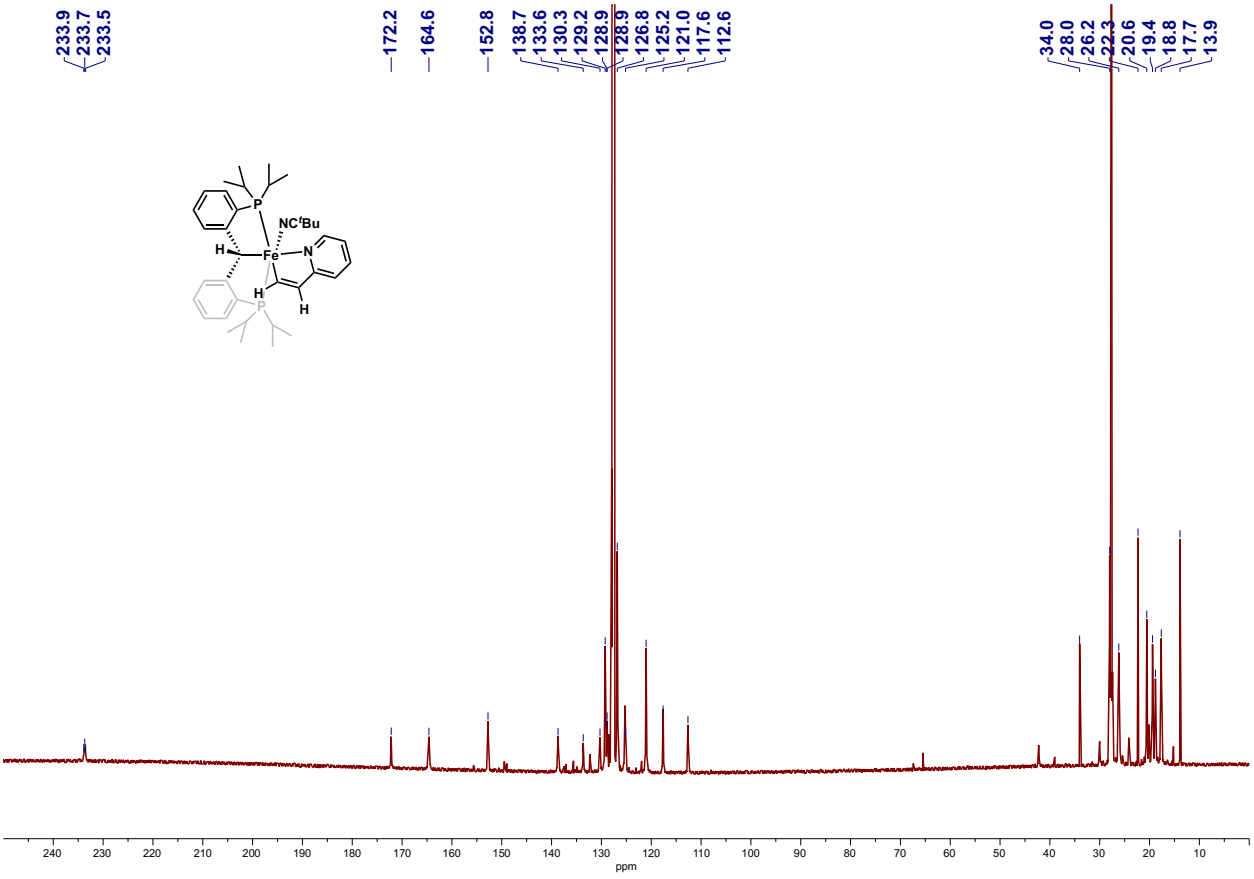


Figure S7. $^{13}C\{H\}$ NMR (151 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

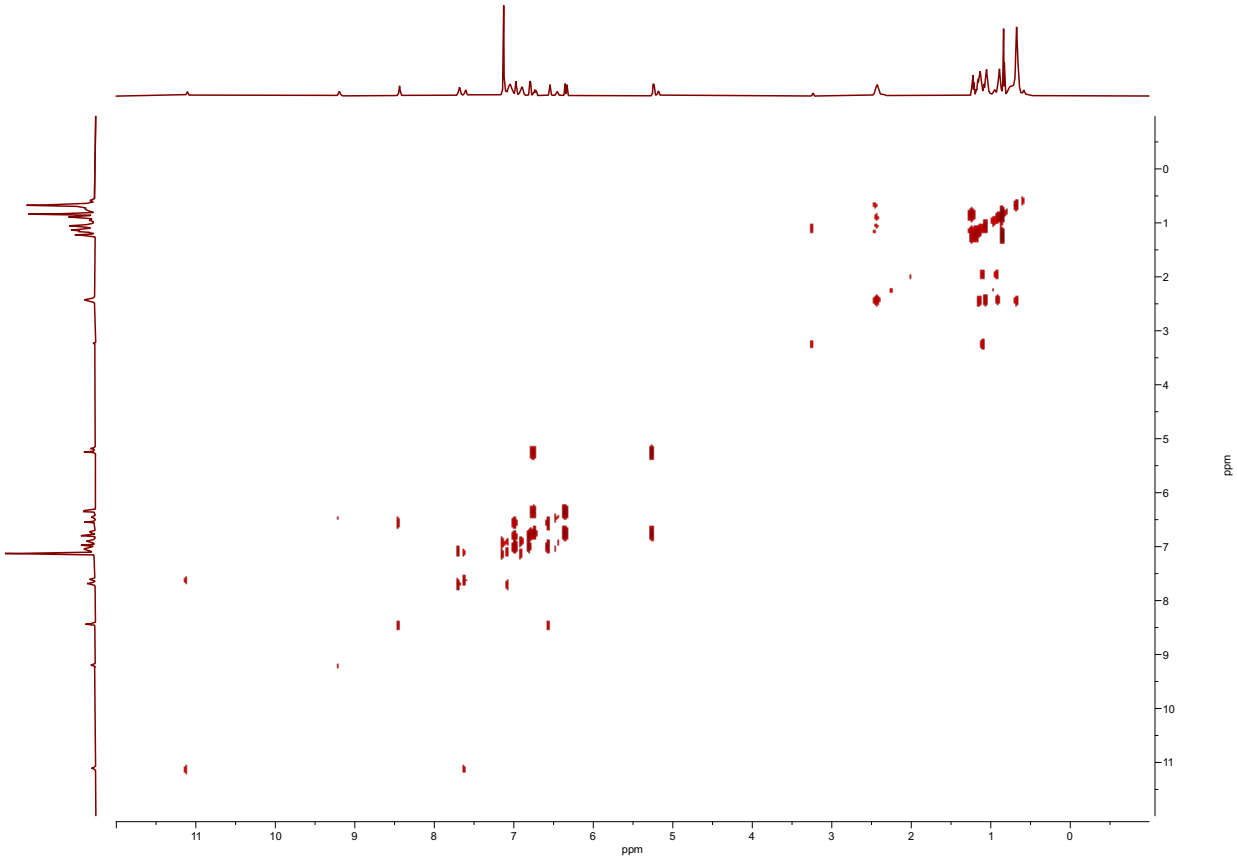


Figure S8. COSY NMR spectrum (800 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

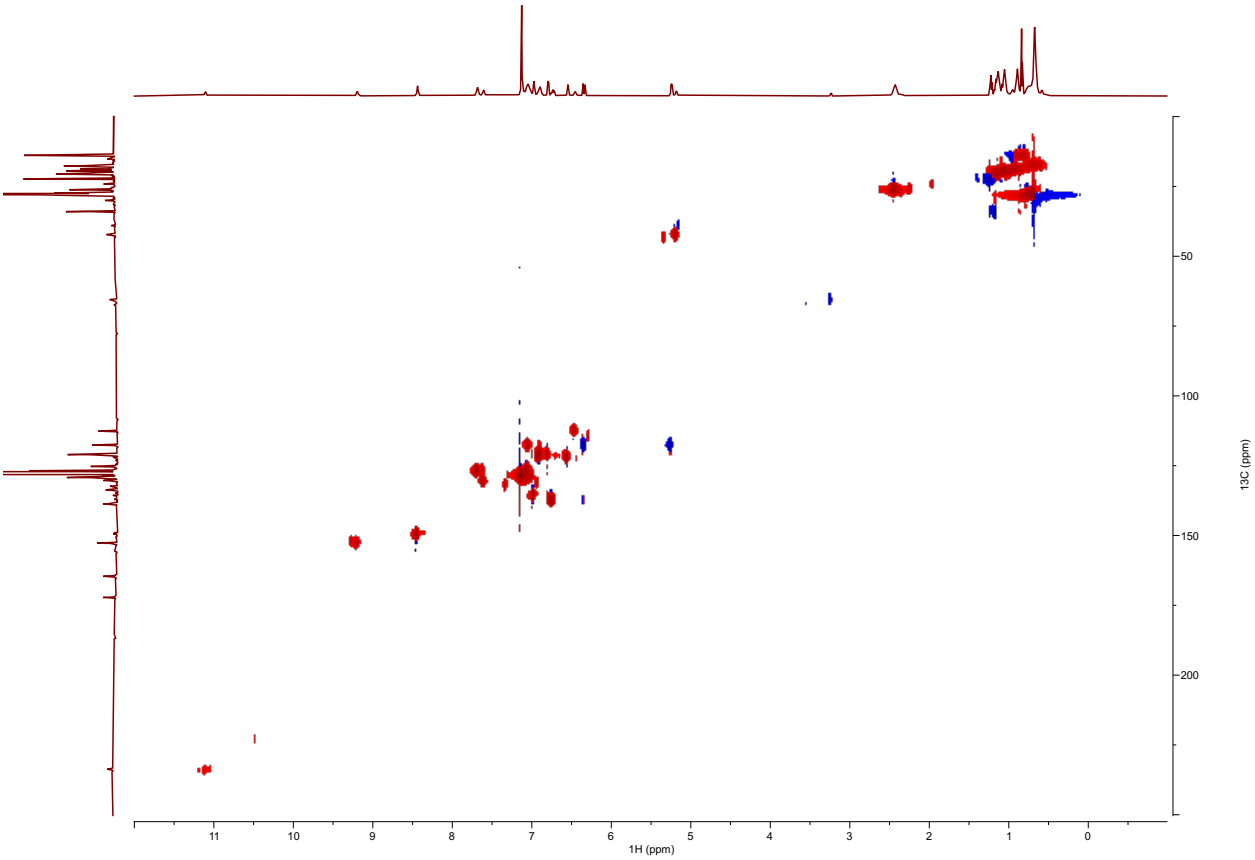


Figure 9. HSQC NMR spectrum (800 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

2.6. NMR Spectra for [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (7)

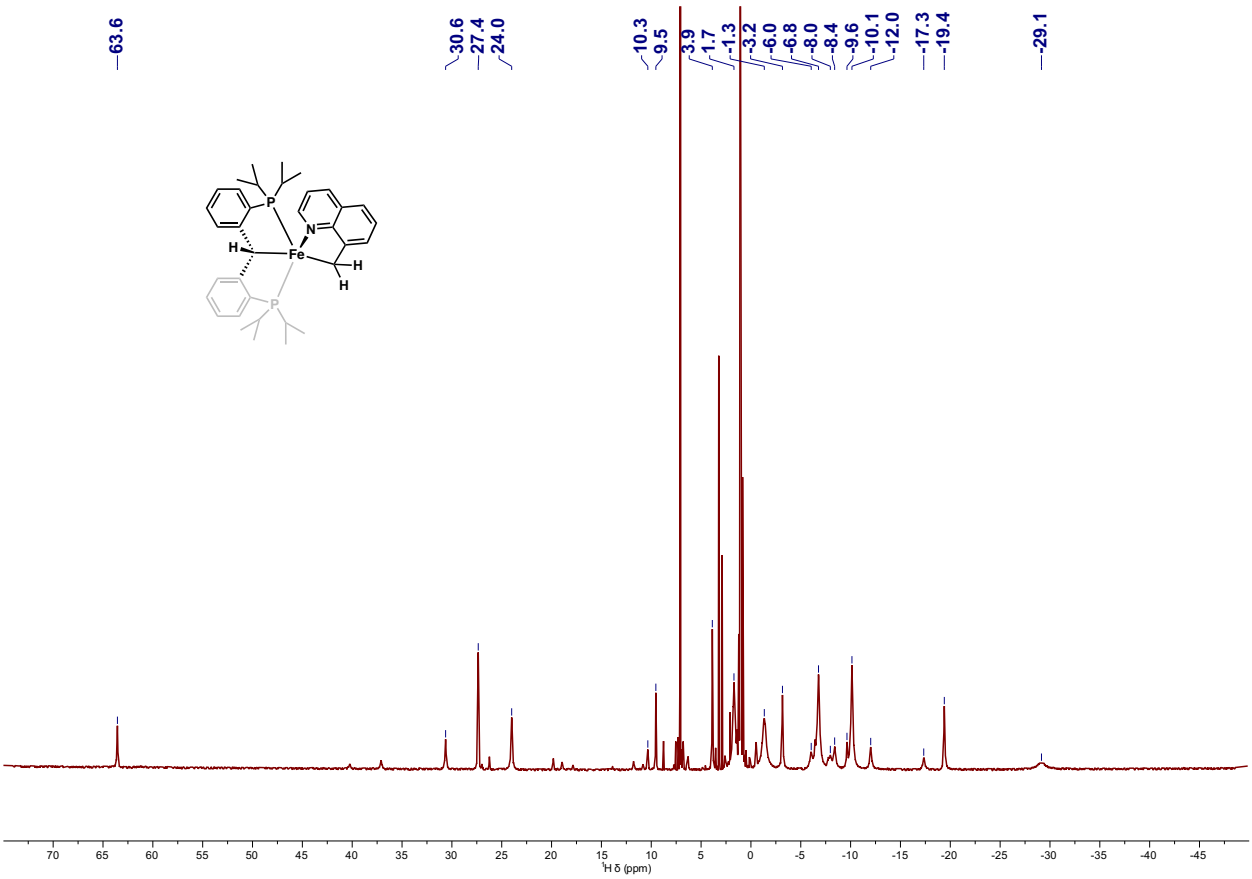


Figure S10. ^{1}H NMR spectrum (800 MHz, C_6D_6, 295 K) of [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**).

3. Crystallographic Tables

3.1 Crystal data for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (2).

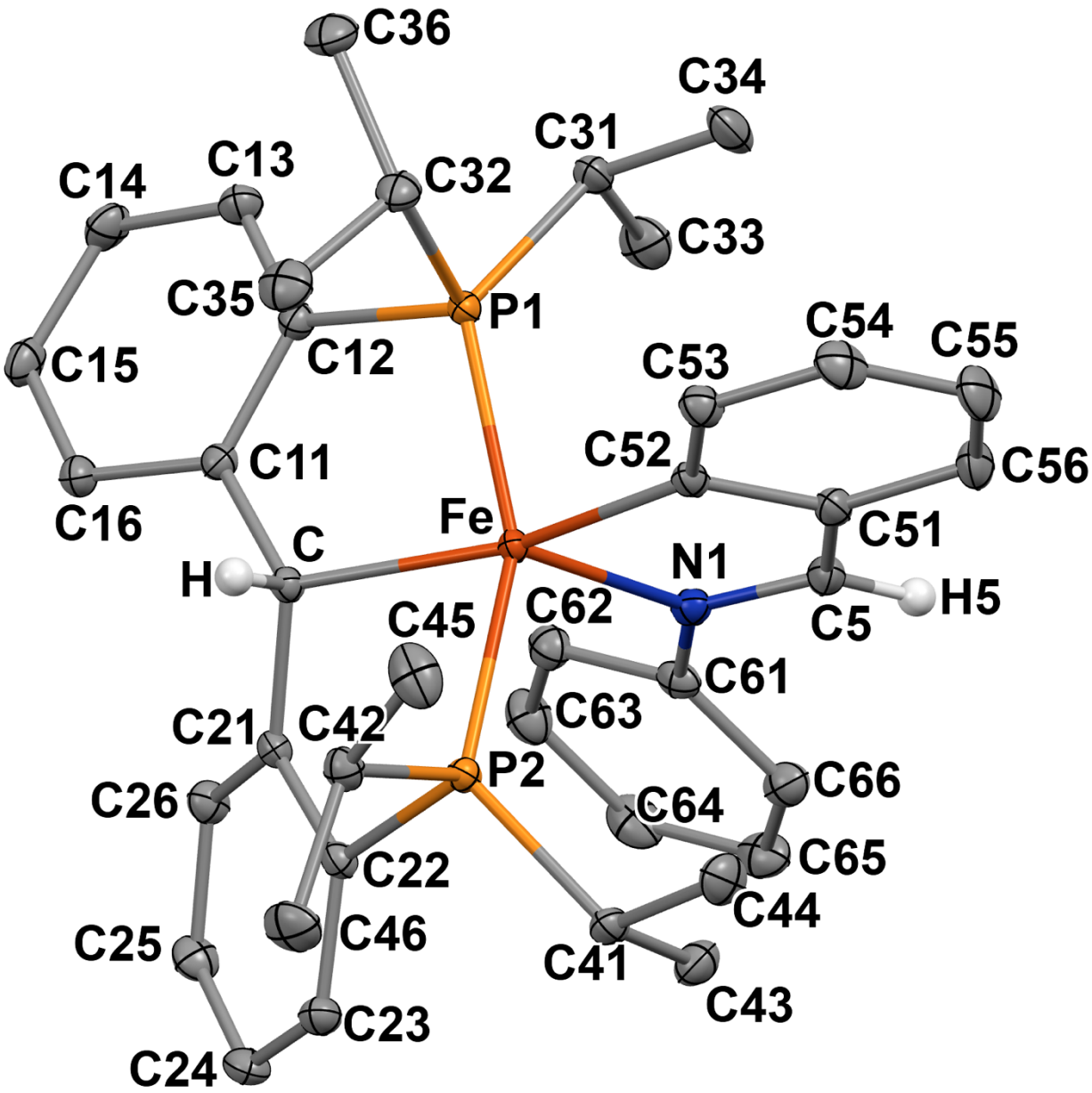


Figure S11. Thermal ellipsoid representation of [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**) at the 50% probability level. Most hydrogen atoms omitted for clarity.

Table S1. Crystal data and structural refinement for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**).

Identification code	ZL_VI_102_a
Empirical formula	$C_{38}H_{47}FeNP_2$
Formula weight	635.55
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a	9.9760(3) Å
b	10.2625(3) Å
c	18.1605(5) Å
α	85.7430(10)°
β	77.0530(10)°
γ	63.3690(10)°
Volume	1619.02(8) Å^3
Z	2
Density (calculated)	1.304 g.cm^{-3}
Absorption coefficient (μ)	0.592 mm^{-1}
F(000)	676
Crystal size	0.362 × 0.240 × 0.226 mm^3
θ range for data collection	2.221 to 28.301°
Index ranges	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -23 ≤ l ≤ 24
Reflections collected	57485
Independent reflections	8034 [R_{int} = 0.0262]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7002
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8034 / 0 / 390
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R_1 = 0.0250, wR_2 = 0.0655
R indices (all data)	R_1 = 0.0268, wR_2 = 0.0664
Extinction coefficient	n/a
Largest diff. peak and hole	0.380 and -0.279 e$^-$.Å^{-3}

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
C(11)	0.32991(12)	0.60041(12)	0.34524(6)	0.012(1)
C(15)	0.11688(14)	0.55292(13)	0.41286(7)	0.017(1)
Fe	0.55383(2)	0.72902(2)	0.26635(2)	0.009(1)
P(1)	0.39472(3)	0.81670(3)	0.37676(2)	0.010(1)
N(1)	0.44817(11)	0.89597(10)	0.19305(5)	0.012(1)
C	0.47526(12)	0.56547(12)	0.28520(6)	0.011(1)
P(2)	0.73633(3)	0.55536(3)	0.18150(2)	0.010(1)
C(12)	0.27201(12)	0.72419(12)	0.39278(6)	0.012(1)
C(13)	0.13619(13)	0.76363(13)	0.44785(7)	0.016(1)
C(14)	0.05642(14)	0.68026(14)	0.45644(7)	0.018(1)
C(16)	0.25316(13)	0.51210(13)	0.35917(6)	0.015(1)
C(21)	0.48680(12)	0.50454(11)	0.20964(6)	0.011(1)
C(22)	0.62456(12)	0.47297(12)	0.15550(6)	0.012(1)
C(23)	0.65412(13)	0.40283(13)	0.08669(6)	0.015(1)
C(24)	0.54441(14)	0.37099(13)	0.06751(7)	0.016(1)
C(25)	0.40370(14)	0.41356(13)	0.11739(7)	0.017(1)
C(26)	0.37496(13)	0.47894(12)	0.18739(6)	0.014(1)
C(5)	0.49913(13)	0.99398(12)	0.18635(6)	0.014(1)
C(31)	0.26052(13)	1.00970(12)	0.40406(7)	0.015(1)
C(32)	0.50052(14)	0.75585(13)	0.45483(6)	0.016(1)
C(33)	0.14789(15)	1.07566(14)	0.35146(8)	0.023(1)
C(34)	0.34772(15)	1.09930(14)	0.40661(8)	0.023(1)
C(35)	0.61523(15)	0.59453(14)	0.44150(7)	0.022(1)
C(36)	0.39992(16)	0.78400(15)	0.53458(7)	0.022(1)
C(41)	0.83688(13)	0.59165(12)	0.08903(6)	0.014(1)
C(42)	0.88816(13)	0.40171(12)	0.22099(6)	0.014(1)
C(43)	0.72029(14)	0.69641(14)	0.04431(7)	0.019(1)
C(44)	0.94445(14)	0.65535(14)	0.09870(7)	0.020(1)
C(45)	0.98022(15)	0.45046(14)	0.25978(8)	0.024(1)
C(46)	0.99387(15)	0.27581(14)	0.16435(8)	0.024(1)
C(51)	0.61350(13)	0.97557(12)	0.22760(6)	0.014(1)
C(52)	0.66141(12)	0.84943(12)	0.27282(6)	0.012(1)
C(53)	0.76878(13)	0.83768(13)	0.31519(7)	0.015(1)

C(54)	0.82409(14)	0.94076(14)	0.31254(7)	0.020(1)
C(55)	0.77450(15)	1.06281(14)	0.26776(8)	0.023(1)
C(56)	0.66920(14)	1.08052(13)	0.22512(7)	0.019(1)
C(61)	0.33882(13)	0.90704(12)	0.15140(6)	0.013(1)
C(62)	0.23562(13)	0.85122(12)	0.18328(7)	0.016(1)
C(63)	0.12821(14)	0.85596(14)	0.14466(7)	0.020(1)
C(64)	0.12496(15)	0.91381(14)	0.07315(8)	0.022(1)
C(65)	0.22804(15)	0.96893(14)	0.04079(7)	0.021(1)
C(66)	0.33469(14)	0.96626(13)	0.07948(7)	0.017(1)
H(15)	0.0648	0.4935	0.4198	0.020
H	0.5586(17)	0.4926(16)	0.3067(8)	0.016
H(13)	0.0985	0.8478	0.4795	0.019
H(14)	-0.0387	0.7100	0.4918	0.021
H(16)	0.2953	0.4227	0.3313	0.018
H(23)	0.7502	0.3765	0.0526	0.018
H(24)	0.5655	0.3211	0.0212	0.020
H(25)	0.3255	0.3979	0.1036	0.020
H(26)	0.2777	0.5066	0.2206	0.017
H(5)	0.4618	1.0753	0.1551	0.017
H(31)	0.1995	1.0118	0.4562	0.019
H(32)	0.5619	0.8117	0.4514	0.019
H(33A)	0.0710	1.1737	0.3704	0.035
H(33B)	0.0967	1.0141	0.3497	0.035
H(33C)	0.2038	1.0815	0.3005	0.035
H(34A)	0.2743	1.2015	0.4192	0.034
H(34B)	0.4151	1.0926	0.3572	0.034
H(34C)	0.4096	1.0611	0.4452	0.034
H(35A)	0.6738	0.5630	0.4815	0.032
H(35B)	0.6857	0.5812	0.3923	0.032
H(35C)	0.5596	0.5362	0.4421	0.032
H(36A)	0.4653	0.7447	0.5716	0.033
H(36B)	0.3328	0.7361	0.5392	0.033
H(36C)	0.3372	0.8892	0.5440	0.033
H(41)	0.8994	0.4973	0.0595	0.016
H(42)	0.8329	0.3612	0.2616	0.017
H(43A)	0.7736	0.7020	-0.0073	0.028
H(43B)	0.6678	0.7935	0.0689	0.028

H(43C)	0.6448	0.6608	0.0427	0.028
H(44A)	0.9829	0.6871	0.0497	0.030
H(44B)	1.0310	0.5808	0.1182	0.030
H(44C)	0.8883	0.7390	0.1344	0.030
H(45A)	1.0458	0.3685	0.2865	0.036
H(45B)	0.9095	0.5308	0.2959	0.036
H(45C)	1.0443	0.4833	0.2217	0.036
H(46A)	1.0573	0.1919	0.1909	0.036
H(46B)	1.0603	0.3060	0.1263	0.036
H(46C)	0.9319	0.2487	0.1395	0.036
H(53)	0.8045	0.7564	0.3466	0.018
H(54)	0.8969	0.9280	0.3417	0.024
H(55)	0.8127	1.1329	0.2666	0.027
H(56)	0.6345	1.1629	0.1943	0.023
H(62)	0.2387	0.8096	0.2318	0.019
H(63)	0.0567	0.8195	0.1672	0.024
H(64)	0.0524	0.9156	0.0465	0.026
H(65)	0.2257	1.0087	-0.0081	0.025
H(66)	0.4047	1.0046	0.0571	0.021

Table S3. Anisotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(11)	0.0121(5)	0.0129(5)	0.0103(5)	0.0010(4)	-0.0022(4)	-0.0063(4)
C(15)	0.0183(5)	0.0211(6)	0.0159(5)	0.0033(4)	-0.0025(4)	-0.0141(5)
Fe	0.0097(1)	0.0086(1)	0.0094(1)	-0.0003(1)	-0.0013(1)	-0.0051(1)
P(1)	0.0122(1)	0.0100(1)	0.0098(1)	-0.0011(1)	-0.0008(1)	-0.0059(1)
N(1)	0.0116(4)	0.0123(4)	0.0111(4)	-0.0003(3)	-0.0015(3)	-0.0043(4)
C	0.0110(5)	0.0110(5)	0.0106(5)	-0.0009(4)	-0.0011(4)	-0.0061(4)
P(2)	0.0095(1)	0.0100(1)	0.0108(1)	-0.0011(1)	-0.0005(1)	-0.0050(1)
C(12)	0.0124(5)	0.0126(5)	0.0110(5)	0.0009(4)	-0.0018(4)	-0.0066(4)
C(13)	0.0156(5)	0.0153(5)	0.0153(5)	-0.0019(4)	0.0008(4)	-0.0069(4)
C(14)	0.0147(5)	0.0215(6)	0.0161(5)	0.0011(4)	0.0015(4)	-0.0097(5)
C(16)	0.0184(5)	0.0155(5)	0.0133(5)	-0.0002(4)	-0.0016(4)	-0.0105(4)
C(21)	0.0130(5)	0.0090(5)	0.0116(5)	-0.0004(4)	-0.0022(4)	-0.0055(4)
C(22)	0.0122(5)	0.0104(5)	0.0131(5)	-0.0007(4)	-0.0025(4)	-0.0059(4)
C(23)	0.0153(5)	0.0150(5)	0.0133(5)	-0.0024(4)	0.0001(4)	-0.0070(4)
C(24)	0.0211(6)	0.0159(5)	0.0137(5)	-0.0030(4)	-0.0037(4)	-0.0089(5)
C(25)	0.0175(5)	0.0186(6)	0.0180(5)	-0.0008(4)	-0.0065(4)	-0.0102(5)
C(26)	0.0126(5)	0.0155(5)	0.0158(5)	-0.0010(4)	-0.0022(4)	-0.0074(4)
C(5)	0.0165(5)	0.0115(5)	0.0128(5)	0.0010(4)	-0.0007(4)	-0.0054(4)
C(31)	0.0175(5)	0.0116(5)	0.0155(5)	-0.0028(4)	0.0016(4)	-0.0067(4)
C(32)	0.0204(6)	0.0192(6)	0.0121(5)	0.0006(4)	-0.0050(4)	-0.0115(5)
C(33)	0.0217(6)	0.0150(6)	0.0250(6)	-0.0004(5)	-0.0042(5)	-0.0020(5)
C(34)	0.0243(6)	0.0155(6)	0.0281(7)	-0.0085(5)	0.0045(5)	-0.0112(5)
C(35)	0.0226(6)	0.0224(6)	0.0185(6)	0.0036(5)	-0.0092(5)	-0.0073(5)
C(36)	0.0294(7)	0.0274(7)	0.0122(5)	-0.0003(5)	-0.0035(5)	-0.0152(6)
C(41)	0.0138(5)	0.0148(5)	0.0124(5)	-0.0020(4)	0.0016(4)	-0.0079(4)
C(42)	0.0130(5)	0.0118(5)	0.0164(5)	0.0002(4)	-0.0029(4)	-0.0043(4)
C(43)	0.0210(6)	0.0220(6)	0.0140(5)	0.0031(4)	-0.0023(4)	-0.0115(5)
C(44)	0.0171(6)	0.0244(6)	0.0223(6)	-0.0012(5)	0.0013(5)	-0.0140(5)
C(45)	0.0210(6)	0.0194(6)	0.0346(7)	0.0040(5)	-0.0155(5)	-0.0083(5)
C(46)	0.0218(6)	0.0152(6)	0.0244(6)	-0.0030(5)	-0.0030(5)	0.0011(5)
C(51)	0.0144(5)	0.0126(5)	0.0139(5)	-0.0014(4)	0.0009(4)	-0.0072(4)
C(52)	0.0118(5)	0.0120(5)	0.0122(5)	-0.0026(4)	0.0010(4)	-0.0065(4)
C(53)	0.0144(5)	0.0158(5)	0.0163(5)	-0.0018(4)	-0.0019(4)	-0.0077(4)
C(54)	0.0186(6)	0.0240(6)	0.0226(6)	-0.0043(5)	-0.0038(5)	-0.0136(5)

C(55)	0.0259(6)	0.0220(6)	0.0280(6)	-0.0025(5)	-0.0021(5)	-0.0186(5)
C(56)	0.0229(6)	0.0153(5)	0.0212(6)	0.0006(4)	-0.0004(5)	-0.0124(5)
C(61)	0.0122(5)	0.0106(5)	0.0140(5)	-0.0012(4)	-0.0038(4)	-0.0021(4)
C(62)	0.0179(5)	0.0139(5)	0.0161(5)	0.0016(4)	-0.0055(4)	-0.0066(4)
C(63)	0.0199(6)	0.0179(6)	0.0259(6)	0.0013(5)	-0.0088(5)	-0.0096(5)
C(64)	0.0223(6)	0.0191(6)	0.0261(6)	0.0001(5)	-0.0141(5)	-0.0063(5)
C(65)	0.0234(6)	0.0184(6)	0.0163(5)	0.0014(4)	-0.0085(5)	-0.0044(5)
C(66)	0.0165(5)	0.0158(5)	0.0156(5)	0.0011(4)	-0.0027(4)	-0.0044(4)

Table S4. Distances [Å] for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**).

atom-atom	distance	atom-atom	distance
C(11)-C(16)	1.4046(15)	C(11)-C(12)	1.4052(15)
C(11)-C	1.5177(15)	C(15)-C(14)	1.3895(17)
C(15)-C(16)	1.3895(16)	C(15)-H(15)	0.9500
Fe-C(52)	1.9899(11)	Fe-N(1)	2.1188(9)
Fe-C	2.1266(10)	Fe-P(1)	2.2160(3)
Fe-P(2)	2.2599(3)	P(1)-C(12)	1.8236(11)
P(1)-C(31)	1.8527(12)	P(1)-C(32)	1.8607(12)
N(1)-C(5)	1.3029(15)	N(1)-C(61)	1.4216(14)
C-C(21)	1.5097(14)	C-H	0.974(15)
P(2)-C(22)	1.8226(11)	P(2)-C(41)	1.8581(11)
P(2)-C(42)	1.8635(11)	C(12)-C(13)	1.4005(15)
C(13)-C(14)	1.3873(16)	C(13)-H(13)	0.9500
C(14)-H(14)	0.9500	C(16)-H(16)	0.9500
C(21)-C(26)	1.3992(15)	C(21)-C(22)	1.4153(15)
C(22)-C(23)	1.3944(15)	C(23)-C(24)	1.3909(16)
C(23)-H(23)	0.9500	C(24)-C(25)	1.3861(17)
C(24)-H(24)	0.9500	C(25)-C(26)	1.3925(16)
C(25)-H(25)	0.9500	C(26)-H(26)	0.9500
C(5)-C(51)	1.4379(16)	C(5)-H(5)	0.9500
C(31)-C(33)	1.5285(17)	C(31)-C(34)	1.5316(16)
C(31)-H(31)	1.0000	C(32)-C(36)	1.5294(16)
C(32)-C(35)	1.5316(17)	C(32)-H(32)	1.0000
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
C(41)-C(44)	1.5298(16)	C(41)-C(43)	1.5300(16)
C(41)-H(41)	1.0000	C(42)-C(46)	1.5262(16)
C(42)-C(45)	1.5310(16)	C(42)-H(42)	1.0000
C(43)-H(43A)	0.9800	C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800	C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800	C(44)-H(44C)	0.9800
C(45)-H(45A)	0.9800	C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800	C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800	C(46)-H(46C)	0.9800
C(51)-C(56)	1.4102(15)	C(51)-C(52)	1.4290(16)
C(52)-C(53)	1.4121(15)	C(53)-C(54)	1.3891(16)
C(53)-H(53)	0.9500	C(54)-C(55)	1.3959(19)
C(54)-H(54)	0.9500	C(55)-C(56)	1.3815(18)
C(55)-H(55)	0.9500	C(56)-H(56)	0.9500
C(61)-C(62)	1.3913(16)	C(61)-C(66)	1.4003(16)
C(62)-C(63)	1.3883(16)	C(62)-H(62)	0.9500
C(63)-C(64)	1.3882(18)	C(63)-H(63)	0.9500

C(64)-C(65)	1.3872(19)	C(64)-H(64)	0.9500
C(65)-C(66)	1.3900(17)	C(65)-H(65)	0.9500
C(66)-H(66)	0.9500		

Table S5. Angles [°] for [{PC(sp^3)HP}Fe(-C^{Ar}-CH=NPh-)] (**2**).

atom-atom-atom	angle	atom-atom-atom	angle
C(16)-C(11)-C(12)	117.36(10)	C(16)-C(11)-C	123.98(1)
C(12)-C(11)-C	118.58(9)	C(14)-C(15)-C(16)	120.36(11)
C(14)-C(15)-H(15)	119.8	C(16)-C(15)-H(15)	119.8
C(52)-Fe-N(1)	81.61(4)	C(52)-Fe-C	162.61(4)
N(1)-Fe-C	115.67(4)	C(52)-Fe-P(1)	92.21(3)
N(1)-Fe-P(1)	101.46(3)	C-Fe-P(1)	82.72(3)
C(52)-Fe-P(2)	99.70(3)	N(1)-Fe-P(2)	100.59(3)
C-Fe-P(2)	79.81(3)	P(1)-Fe-P(2)	156.229(13)
C(12)-P(1)-C(31)	104.22(5)	C(12)-P(1)-C(32)	104.10(5)
C(31)-P(1)-C(32)	102.70(5)	C(12)-P(1)-Fe	105.48(4)
C(31)-P(1)-Fe	127.55(4)	C(32)-P(1)-Fe	110.55(4)
C(5)-N(1)-C(61)	120.07(10)	C(5)-N(1)-Fe	111.84(7)
C(61)-N(1)-Fe	128.05(7)	C(21)-C-C(11)	118.00(9)
C(21)-C-Fe	108.67(7)	C(11)-C-Fe	116.57(7)
C(21)-C-H	107.1(9)	C(11)-C-H	105.8(9)
Fe-C-H	98.4(9)	C(22)-P(2)-C(41)	103.68(5)
C(22)-P(2)-C(42)	103.79(5)	C(41)-P(2)-C(42)	105.42(5)
C(22)-P(2)-Fe	100.59(4)	C(41)-P(2)-Fe	124.88(4)
C(42)-P(2)-Fe	115.62(4)	C(13)-C(12)-C(11)	120.97(10)
C(13)-C(12)-P(1)	125.84(9)	C(11)-C(12)-P(1)	113.14(8)
C(14)-C(13)-C(12)	120.24(11)	C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9	C(13)-C(14)-C(15)	119.42(11)
C(13)-C(14)-H(14)	120.3	C(15)-C(14)-H(14)	120.3
C(15)-C(16)-C(11)	121.32(11)	C(15)-C(16)-H(16)	119.3
C(11)-C(16)-H(16)	119.3	C(26)-C(21)-C(22)	117.05(10)
C(26)-C(21)-C	126.87(10)	C(22)-C(21)-C	116.07(9)
C(23)-C(22)-C(21)	120.91(10)	C(23)-C(22)-P(2)	126.24(8)
C(21)-C(22)-P(2)	112.32(8)	C(24)-C(23)-C(22)	120.69(10)
C(24)-C(23)-H(23)	119.7	C(22)-C(23)-H(23)	119.7
C(25)-C(24)-C(23)	118.62(10)	C(25)-C(24)-H(24)	120.7
C(23)-C(24)-H(24)	120.7	C(24)-C(25)-C(26)	121.11(10)
C(24)-C(25)-H(25)	119.4	C(26)-C(25)-H(25)	119.4
C(25)-C(26)-C(21)	121.17(10)	C(25)-C(26)-H(26)	119.4
C(21)-C(26)-H(26)	119.4	N(1)-C(5)-C(51)	118.08(10)
N(1)-C(5)-H(5)	121.0	C(51)-C(5)-H(5)	121.0
C(33)-C(31)-C(34)	111.53(10)	C(33)-C(31)-P(1)	110.98(8)
C(34)-C(31)-P(1)	111.14(8)	C(33)-C(31)-H(31)	107.7
C(34)-C(31)-H(31)	107.7	P(1)-C(31)-H(31)	107.7
C(36)-C(32)-C(35)	111.07(10)	C(36)-C(32)-P(1)	115.34(9)
C(35)-C(32)-P(1)	109.22(8)	C(36)-C(32)-H(32)	106.9
C(35)-C(32)-H(32)	106.9	P(1)-C(32)-H(32)	106.9
C(31)-C(33)-H(33A)	109.5	C(31)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
C(31)-C(34)-H(34A)	109.5	C(31)-C(34)-H(34B)	109.5

H(34A)-C(34)-H(34B)	109.5	C(31)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(32)-C(35)-H(35A)	109.5	C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
C(32)-C(36)-H(36A)	109.5	C(32)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	C(32)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
C(44)-C(41)-C(43)	109.42(10)	C(44)-C(41)-P(2)	111.83(8)
C(43)-C(41)-P(2)	110.28(8)	C(44)-C(41)-H(41)	108.4
C(43)-C(41)-H(41)	108.4	P(2)-C(41)-H(41)	108.4
C(46)-C(42)-C(45)	111.30(10)	C(46)-C(42)-P(2)	113.78(8)
C(45)-C(42)-P(2)	113.31(8)	C(46)-C(42)-H(42)	105.9
C(45)-C(42)-H(42)	105.9	P(2)-C(42)-H(42)	105.9
C(41)-C(43)-H(43A)	109.5	C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5	C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5	H(43B)-C(43)-H(43C)	109.5
C(41)-C(44)-H(44A)	109.5	C(41)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5	C(41)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(42)-C(45)-H(45A)	109.5	C(42)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5	C(42)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5	H(45B)-C(45)-H(45C)	109.5
C(42)-C(46)-H(46A)	109.5	C(42)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5	C(42)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
C(56)-C(51)-C(52)	122.74(11)	C(56)-C(51)-C(5)	120.95(11)
C(52)-C(51)-C(5)	116.26(10)	C(53)-C(52)-C(51)	114.93(10)
C(53)-C(52)-Fe	132.80(9)	C(51)-C(52)-Fe	112.20(8)
C(54)-C(53)-C(52)	122.33(11)	C(54)-C(53)-H(53)	118.8
C(52)-C(53)-H(53)	118.8	C(53)-C(54)-C(55)	121.14(11)
C(53)-C(54)-H(54)	119.4	C(55)-C(54)-H(54)	119.4
C(56)-C(55)-C(54)	119.21(11)	C(56)-C(55)-H(55)	120.4
C(54)-C(55)-H(55)	120.4	C(55)-C(56)-C(51)	119.63(11)
C(55)-C(56)-H(56)	120.2	C(51)-C(56)-H(56)	120.2
C(62)-C(61)-C(66)	119.33(10)	C(62)-C(61)-N(1)	117.64(10)
C(66)-C(61)-N(1)	122.99(10)	C(63)-C(62)-C(61)	120.37(11)
C(63)-C(62)-H(62)	119.8	C(61)-C(62)-H(62)	119.8
C(64)-C(63)-C(62)	120.22(12)	C(64)-C(63)-H(63)	119.9
C(62)-C(63)-H(63)	119.9	C(65)-C(64)-C(63)	119.75(11)
C(65)-C(64)-H(64)	120.1	C(63)-C(64)-H(64)	120.1
C(64)-C(65)-C(66)	120.39(11)	C(64)-C(65)-H(65)	119.8
C(66)-C(65)-H(65)	119.8	C(65)-C(66)-C(61)	119.94(11)
C(65)-C(66)-H(66)	120.0	C(61)-C(66)-H(66)	120.0

3.2 Crystal data for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (3).

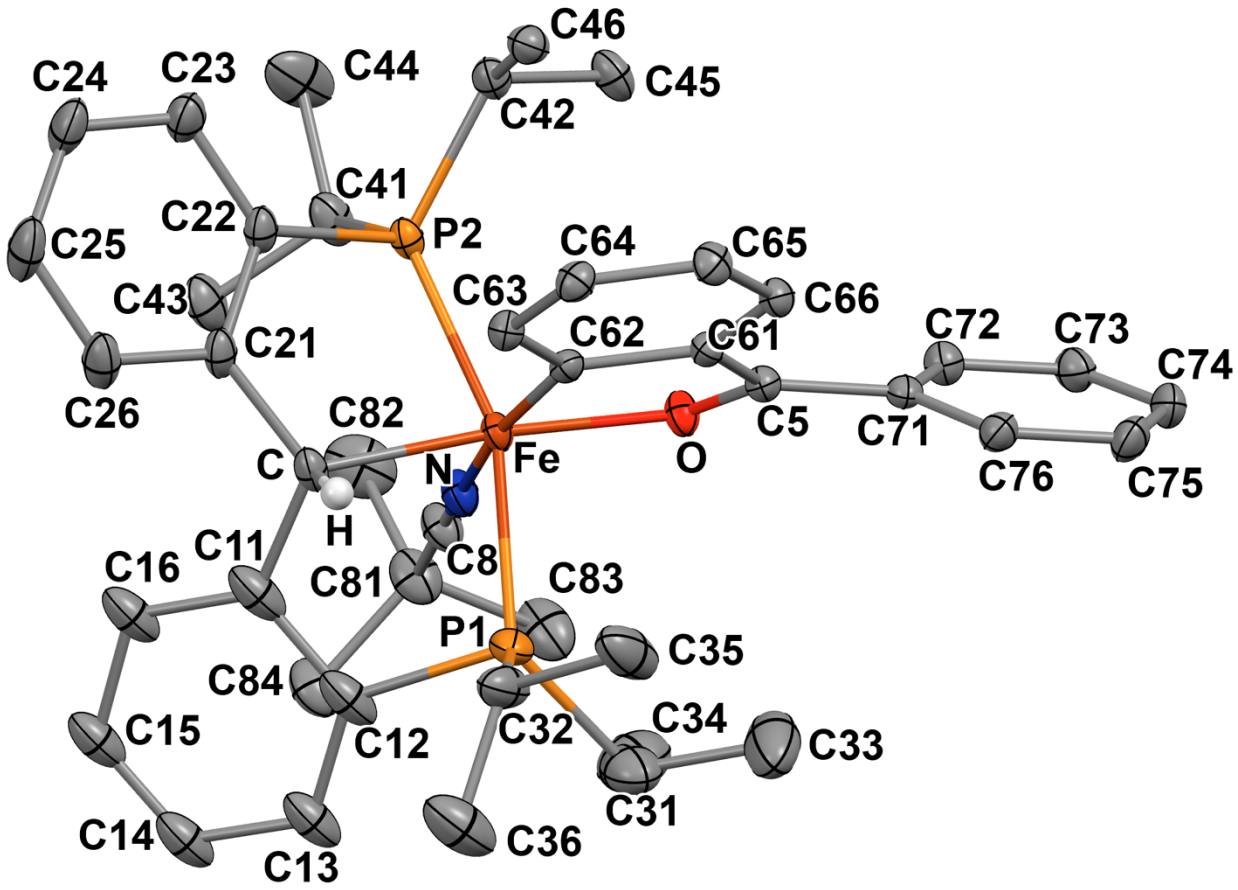


Figure S12. Thermal ellipsoid representation of [PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu) (**3**) at the 50% probability level. Most hydrogen atoms omitted for clarity.

Table S6. Crystal data and structural refinement for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (**3**).

Identification code	ZL_VI_013_a
Empirical formula	$C_{43}H_{55}FeNOP_2$
Formula weight	719.67
Temperature	296(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
a	9.5332(2) Å
b	12.0978(2) Å
c	16.7258(3) Å
α	86.9350(10)°
β	87.9500(10)°
γ	77.4270(10)°
Volume	1879.47(6) Å^3
Z	2
Density (calculated)	1.272 g.cm^{-3}
Absorption coefficient (μ)	4.271 mm^{-1}
F(000)	768
Crystal size	0.192 × 0.153 × 0.114 mm^3
θ range for data collection	2.646 to 72.038°
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -19 ≤ l ≤ 20
Reflections collected	43252
Independent reflections	7091 [R_{int} = 0.0382]
Completeness to θ = 67.679°	96.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7535 and 0.5981
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7091 / 0 / 417
Goodness-of-fit on F^2	1.106
Final R indices [I>2σ(I)]	R_1 = 0.0563, wR_2 = 0.1544
R indices (all data)	R_1 = 0.0584, wR_2 = 0.1565
Extinction coefficient	n/a
Largest diff. peak and hole	1.089 and -0.747 e$^-$.Å^{-3}

Table S7. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (**3**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Fe	0.27591(4)	0.74344(3)	0.25182(2)	0.021(1)
P(1)	0.12189(10)	0.64591(7)	0.31683(5)	0.036(1)
O	0.3786(2)	0.76648(16)	0.34784(12)	0.025(1)
N	0.4142(3)	0.5999(2)	0.24184(16)	0.029(1)
C	0.1385(3)	0.7230(3)	0.16084(17)	0.025(1)
P(2)	0.38678(7)	0.82056(6)	0.15108(4)	0.022(1)
C(5)	0.3221(3)	0.8523(2)	0.38773(16)	0.022(1)
C(8)	0.4989(3)	0.5165(3)	0.2377(2)	0.032(1)
C(11)	0.1301(4)	0.6004(3)	0.1610(3)	0.045(1)
C(12)	0.1133(4)	0.5490(3)	0.2380(3)	0.045(1)
C(13)	0.1017(4)	0.4362(3)	0.2478(3)	0.045(1)
C(14)	0.1086(4)	0.3708(3)	0.1812(3)	0.045(1)
C(15)	0.1256(4)	0.4186(3)	0.1071(3)	0.045(1)
C(16)	0.1370(4)	0.5339(3)	0.0953(3)	0.045(1)
C(21)	0.1524(3)	0.7859(3)	0.08128(17)	0.028(1)
C(22)	0.2591(3)	0.8487(3)	0.07081(17)	0.027(1)
C(23)	0.2682(4)	0.9164(3)	0.00110(19)	0.036(1)
C(24)	0.1720(4)	0.9207(4)	-0.0595(2)	0.044(1)
C(25)	0.0656(4)	0.8585(4)	-0.0501(2)	0.045(1)
C(26)	0.0548(3)	0.7926(3)	0.01942(19)	0.038(1)
C(31)	0.1566(5)	0.5602(4)	0.4127(3)	0.059(1)
C(32)	-0.0786(4)	0.7192(3)	0.3280(2)	0.044(1)
C(33)	0.1480(9)	0.6356(5)	0.4860(3)	0.090(2)
C(34)	0.2994(6)	0.4886(5)	0.4080(4)	0.076(2)
C(35)	-0.1136(5)	0.8121(4)	0.3897(3)	0.064(1)
C(36)	-0.1775(5)	0.6379(4)	0.3400(4)	0.065(1)
C(41)	0.5425(3)	0.7246(3)	0.0995(2)	0.035(1)
C(42)	0.4570(3)	0.9515(3)	0.15735(18)	0.026(1)
C(43)	0.4880(4)	0.6384(3)	0.0512(2)	0.038(1)
C(44)	0.6381(4)	0.7828(4)	0.0446(3)	0.060(1)
C(45)	0.5732(3)	0.9310(3)	0.2210(2)	0.035(1)
C(46)	0.3414(3)	1.0580(2)	0.17307(18)	0.028(1)
C(61)	0.2026(3)	0.9299(2)	0.35140(16)	0.020(1)

C(62)	0.1615(3)	0.8894(2)	0.27830(16)	0.020(1)
C(63)	0.0456(3)	0.9643(2)	0.23905(16)	0.022(1)
C(64)	-0.0204(3)	1.0681(2)	0.26793(17)	0.025(1)
C(65)	0.0253(3)	1.1057(2)	0.33886(18)	0.027(1)
C(66)	0.1359(3)	1.0366(2)	0.37995(17)	0.023(1)
C(71)	0.3821(3)	0.8608(2)	0.46698(17)	0.023(1)
C(72)	0.5285(3)	0.8180(3)	0.47790(18)	0.028(1)
C(73)	0.5898(3)	0.8234(3)	0.55107(19)	0.031(1)
C(74)	0.5057(4)	0.8712(3)	0.61457(18)	0.032(1)
C(75)	0.3592(4)	0.9104(3)	0.60561(19)	0.034(1)
C(76)	0.2971(3)	0.9056(3)	0.53209(17)	0.028(1)
C(81)	0.6028(4)	0.4061(3)	0.2319(2)	0.038(1)
C(82)	0.7219(4)	0.4172(4)	0.1705(3)	0.057(1)
C(83)	0.6649(5)	0.3700(3)	0.3158(3)	0.052(1)
C(84)	0.5207(4)	0.3195(3)	0.2050(3)	0.045(1)
H	0.045(4)	0.763(3)	0.184(2)	0.037
H(13)	0.0894	0.4047	0.2988	0.053
H(14)	0.1016	0.2953	0.1873	0.053
H(15)	0.1299	0.3747	0.0628	0.053
H(16)	0.1490	0.5643	0.0439	0.053
H(23)	0.3390	0.9586	-0.0044	0.043
H(24)	0.1785	0.9647	-0.1063	0.053
H(25)	0.0008	0.8611	-0.0907	0.054
H(26)	-0.0180	0.7524	0.0251	0.045
H(31)	0.0859	0.5125	0.4204	0.070
H(32)	-0.1038	0.7587	0.2761	0.053
H(33A)	0.1471	0.5896	0.5345	0.135
H(33B)	0.0617	0.6938	0.4838	0.135
H(33C)	0.2300	0.6698	0.4848	0.135
H(34A)	0.3075	0.4277	0.4480	0.114
H(34B)	0.3694	0.5325	0.4170	0.114
H(34C)	0.3158	0.4580	0.3558	0.114
H(35A)	-0.2146	0.8455	0.3895	0.097
H(35B)	-0.0602	0.8695	0.3760	0.097
H(35C)	-0.0877	0.7793	0.4421	0.097
H(36A)	-0.2754	0.6790	0.3364	0.098
H(36B)	-0.1629	0.5999	0.3919	0.098

H(36C)	-0.1571	0.5830	0.2995	0.098
H(41)	0.6034	0.6815	0.1415	0.042
H(42)	0.5037	0.9646	0.1056	0.032
H(43A)	0.5682	0.5818	0.0332	0.057
H(43B)	0.4368	0.6767	0.0058	0.057
H(43C)	0.4249	0.6027	0.0846	0.057
H(44A)	0.7101	0.7265	0.0192	0.089
H(44B)	0.6838	0.8289	0.0756	0.089
H(44C)	0.5807	0.8296	0.0045	0.089
H(45A)	0.6161	0.9958	0.2213	0.052
H(45B)	0.6458	0.8652	0.2087	0.052
H(45C)	0.5305	0.9192	0.2727	0.052
H(46A)	0.3843	1.1230	0.1702	0.042
H(46B)	0.2987	1.0504	0.2254	0.042
H(46C)	0.2688	1.0674	0.1335	0.042
H(63)	0.0129	0.9424	0.1919	0.027
H(64)	-0.0961	1.1138	0.2402	0.031
H(65)	-0.0186	1.1763	0.3576	0.032
H(66)	0.1670	1.0605	0.4269	0.028
H(72)	0.5859	0.7854	0.4355	0.033
H(73)	0.6876	0.7947	0.5575	0.037
H(74)	0.5474	0.8772	0.6631	0.039
H(75)	0.3019	0.9399	0.6489	0.040
H(76)	0.1987	0.9324	0.5264	0.033
H(82A)	0.7897	0.3460	0.1680	0.086
H(82B)	0.7700	0.4743	0.1861	0.086
H(82C)	0.6809	0.4384	0.1189	0.086
H(83A)	0.7308	0.2978	0.3136	0.079
H(83B)	0.5880	0.3643	0.3533	0.079
H(83C)	0.7146	0.4256	0.3325	0.079
H(84A)	0.5851	0.2467	0.2019	0.067
H(84B)	0.4813	0.3433	0.1533	0.067
H(84C)	0.4442	0.3141	0.2430	0.067

Table S8. Anisotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0234(2)	0.0177(2)	0.0214(2)	-0.0050(2)	-0.0026(2)	-0.0030(2)
P(1)	0.0532(5)	0.0281(4)	0.0316(4)	0.0012(3)	-0.0033(4)	-0.0213(4)
O	0.0290(10)	0.0208(9)	0.0254(10)	-0.0054(8)	-0.0063(8)	-0.0009(8)
N	0.0329(13)	0.0244(12)	0.0305(13)	-0.0070(10)	-0.0070(11)	-0.0040(11)
C	0.0216(13)	0.0311(14)	0.0233(14)	-0.0109(11)	0.0001(11)	-0.0075(11)
P(2)	0.0195(3)	0.0258(3)	0.0225(3)	-0.0084(3)	0.0003(3)	-0.0049(3)
C(5)	0.0249(13)	0.0210(13)	0.0197(13)	-0.0013(10)	-0.0008(11)	-0.0068(10)
C(8)	0.0319(15)	0.0248(15)	0.0372(17)	-0.0064(12)	-0.0070(13)	-0.0025(13)
C(11)	0.0310(7)	0.0368(8)	0.0700(10)	-0.0260(7)	0.0038(7)	-0.0118(6)
C(12)	0.0310(7)	0.0368(8)	0.0700(10)	-0.0260(7)	0.0038(7)	-0.0118(6)
C(13)	0.0310(7)	0.0368(8)	0.0700(10)	-0.0260(7)	0.0038(7)	-0.0118(6)
C(14)	0.0310(7)	0.0368(8)	0.0700(10)	-0.0260(7)	0.0038(7)	-0.0118(6)
C(15)	0.0310(7)	0.0368(8)	0.0700(10)	-0.0260(7)	0.0038(7)	-0.0118(6)
C(16)	0.0310(7)	0.0368(8)	0.0700(10)	-0.0260(7)	0.0038(7)	-0.0118(6)
C(21)	0.0233(13)	0.0399(16)	0.0198(14)	-0.0113(12)	0.0020(11)	-0.0056(12)
C(22)	0.0258(14)	0.0358(15)	0.0191(13)	-0.0084(11)	0.0010(11)	-0.0057(12)
C(23)	0.0357(16)	0.053(2)	0.0228(15)	-0.0047(14)	0.0018(13)	-0.0149(15)
C(24)	0.046(2)	0.068(2)	0.0192(15)	-0.0012(15)	-0.0030(14)	-0.0129(18)
C(25)	0.0346(17)	0.079(3)	0.0231(16)	-0.0076(16)	-0.0065(14)	-0.0120(18)
C(26)	0.0265(15)	0.062(2)	0.0278(16)	-0.0121(15)	-0.0010(13)	-0.0140(15)
C(31)	0.076(3)	0.044(2)	0.061(3)	0.0129(19)	-0.017(2)	-0.024(2)
C(32)	0.059(2)	0.0364(18)	0.041(2)	-0.0135(15)	0.0227(17)	-0.0217(17)
C(33)	0.164(7)	0.060(3)	0.053(3)	0.010(2)	-0.033(4)	-0.038(4)
C(34)	0.088(4)	0.066(3)	0.072(3)	0.013(3)	0.005(3)	-0.016(3)
C(35)	0.073(3)	0.063(3)	0.069(3)	-0.034(2)	0.033(2)	-0.039(2)
C(36)	0.048(2)	0.052(2)	0.103(4)	-0.032(3)	0.014(2)	-0.020(2)
C(41)	0.0256(14)	0.0371(17)	0.0434(19)	-0.0191(15)	0.0064(13)	-0.0061(13)
C(42)	0.0243(13)	0.0306(15)	0.0260(14)	-0.0068(11)	0.0013(11)	-0.0082(11)
C(43)	0.0358(17)	0.0401(18)	0.0395(18)	-0.0215(15)	0.0047(14)	-0.0059(14)
C(44)	0.045(2)	0.060(2)	0.079(3)	-0.035(2)	0.041(2)	-0.0210(19)
C(45)	0.0275(15)	0.0377(17)	0.0422(18)	-0.0120(14)	-0.0051(13)	-0.0113(13)
C(46)	0.0298(14)	0.0262(14)	0.0291(15)	-0.0031(11)	0.0025(12)	-0.0094(12)
C(61)	0.0236(12)	0.0200(12)	0.0181(13)	-0.0015(10)	0.0015(10)	-0.0065(10)

C(62)	0.0227(12)	0.0209(12)	0.0180(13)	-0.0004(10)	0.0025(10)	-0.0072(10)
C(63)	0.0221(12)	0.0241(13)	0.0197(13)	-0.0020(10)	-0.0011(10)	-0.0037(10)
C(64)	0.0257(13)	0.0251(14)	0.0240(14)	0.0007(11)	-0.0010(11)	-0.0021(11)
C(65)	0.0304(14)	0.0212(13)	0.0268(15)	-0.0051(11)	0.0017(12)	-0.0012(11)
C(66)	0.0267(13)	0.0221(13)	0.0219(13)	-0.0039(10)	0.0007(11)	-0.0060(11)
C(71)	0.0292(14)	0.0193(12)	0.0217(14)	0.0012(10)	-0.0030(11)	-0.0090(11)
C(72)	0.0287(14)	0.0284(14)	0.0261(15)	-0.0037(11)	-0.0017(12)	-0.0065(12)
C(73)	0.0295(15)	0.0335(15)	0.0302(16)	0.0008(12)	-0.0070(12)	-0.0102(12)
C(74)	0.0399(17)	0.0401(17)	0.0213(14)	0.0003(12)	-0.0073(13)	-0.0168(14)
C(75)	0.0382(17)	0.0450(18)	0.0188(14)	-0.0008(13)	0.0024(12)	-0.0119(14)
C(76)	0.0291(14)	0.0325(15)	0.0220(14)	0.0009(11)	-0.0001(11)	-0.0091(12)
C(81)	0.0339(16)	0.0262(15)	0.052(2)	-0.0082(14)	-0.0073(15)	0.0045(13)
C(82)	0.0364(19)	0.043(2)	0.087(3)	-0.010(2)	0.006(2)	0.0051(16)
C(83)	0.051(2)	0.0337(18)	0.069(3)	-0.0013(18)	-0.026(2)	0.0016(16)
C(84)	0.048(2)	0.0290(16)	0.056(2)	-0.0126(16)	-0.0078(17)	-0.0006(15)

Table S9. Distances [Å] for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (**3**).

atom-atom	distance	atom-Atom	distance
Fe-C(62)	1.927(3)	Fe-N	1.950(3)
Fe-O	1.973(2)	Fe-C	2.102(3)
Fe-P(2)	2.2272(9)	Fe-P(1)	2.2876(9)
P(1)-C(12)	1.826(4)	P(1)-C(31)	1.862(4)
P(1)-C(32)	1.931(4)	O-C(5)	1.272(3)
N-C(8)	1.150(4)	C-C(11)	1.502(4)
C-C(21)	1.514(4)	C-H	0.99(4)
P(2)-C(22)	1.813(3)	P(2)-C(42)	1.858(3)
P(2)-C(41)	1.887(3)	C(5)-C(61)	1.439(4)
C(5)-C(71)	1.480(4)	C(8)-C(81)	1.485(4)
C(11)-C(16)	1.388(5)	C(11)-C(12)	1.419(6)
C(12)-C(13)	1.393(5)	C(13)-C(14)	1.392(5)
C(13)-H(13)	0.9300	C(14)-C(15)	1.358(6)
C(14)-H(14)	0.9300	C(15)-C(16)	1.425(5)
C(15)-H(15)	0.9300	C(16)-H(16)	0.9300
C(21)-C(22)	1.397(4)	C(21)-C(26)	1.404(4)
C(22)-C(23)	1.400(5)	C(23)-C(24)	1.384(5)
C(23)-H(23)	0.9300	C(24)-C(25)	1.388(6)
C(24)-H(24)	0.9300	C(25)-C(26)	1.387(5)
C(25)-H(25)	0.9300	C(26)-H(26)	0.9300
C(31)-C(34)	1.448(7)	C(31)-C(33)	1.555(7)
C(31)-H(31)	0.9800	C(32)-C(36)	1.505(5)
C(32)-C(35)	1.542(5)	C(32)-H(32)	0.9800
C(33)-H(33A)	0.9600	C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600	C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600	C(34)-H(34C)	0.9600
C(35)-H(35A)	0.9600	C(35)-H(35B)	0.9600
C(35)-H(35C)	0.9600	C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600	C(36)-H(36C)	0.9600
C(41)-C(44)	1.523(5)	C(41)-C(43)	1.538(4)
C(41)-H(41)	0.9800	C(42)-C(46)	1.530(4)
C(42)-C(45)	1.535(4)	C(42)-H(42)	0.9800
C(43)-H(43A)	0.9600	C(43)-H(43B)	0.9600
C(43)-H(43C)	0.9600	C(44)-H(44A)	0.9600
C(44)-H(44B)	0.9600	C(44)-H(44C)	0.9600
C(45)-H(45A)	0.9600	C(45)-H(45B)	0.9600
C(45)-H(45C)	0.9600	C(46)-H(46A)	0.9600
C(46)-H(46B)	0.9600	C(46)-H(46C)	0.9600
C(61)-C(66)	1.410(4)	C(61)-C(62)	1.439(4)
C(62)-C(63)	1.423(4)	C(63)-C(64)	1.379(4)
C(63)-H(63)	0.9300	C(64)-C(65)	1.410(4)
C(64)-H(64)	0.9300	C(65)-C(66)	1.375(4)
C(65)-H(65)	0.9300	C(66)-H(66)	0.9300
C(71)-C(72)	1.395(4)	C(71)-C(76)	1.395(4)
C(72)-C(73)	1.385(4)	C(72)-H(72)	0.9300

C(73)-C(74)	1.381(5)	C(73)-H(73)	0.9300
C(74)-C(75)	1.385(5)	C(74)-H(74)	0.9300
C(75)-C(76)	1.393(4)	C(75)-H(75)	0.9300
C(76)-H(76)	0.9300	C(81)-C(82)	1.527(6)
C(81)-C(84)	1.531(5)	C(81)-C(83)	1.546(5)
C(82)-H(82A)	0.9600	C(82)-H(82B)	0.9600
C(82)-H(82C)	0.9600	C(83)-H(83A)	0.9600
C(83)-H(83B)	0.9600	C(83)-H(83C)	0.9600
C(84)-H(84A)	0.9600	C(84)-H(84B)	0.9600
C(84)-H(84C)	0.9600		

Table S10. Angles [°] for [{PC(sp^3)HP}Fe(-C^{Ar}-C^{Bz}=O-)(NC^{t}Bu)] (**3**).

atom-atom-atom	angle	atom-atom-atom	angle
C(62)-Fe-N	169.07(11)	C(62)-Fe-O	81.59(10)
N-Fe-O	87.52(9)	C(62)-Fe-C	93.36(11)
N-Fe-C	97.56(11)	O-Fe-C	171.32(10)
C(62)-Fe-P(2)	91.62(8)	N-Fe-P(2)	90.20(9)
O-Fe-P(2)	104.38(7)	C-Fe-P(2)	82.72(9)
C(62)-Fe-P(1)	93.58(8)	N-Fe-P(1)	88.48(9)
O-Fe-P(1)	96.26(7)	C-Fe-P(1)	76.93(9)
P(2)-Fe-P(1)	159.25(3)	C(12)-P(1)-C(31)	107.8(2)
C(12)-P(1)-C(32)	100.51(16)	C(31)-P(1)-C(32)	102.8(2)
C(12)-P(1)-Fe	97.51(13)	C(31)-P(1)-Fe	125.84(16)
C(32)-P(1)-Fe	118.78(12)	C(5)-O-Fe	116.33(17)
C(8)-N-Fe	177.6(3)	C(11)-C-C(21)	118.7(3)
C(11)-C-Fe	108.8(2)	C(21)-C-Fe	117.08(19)
C(11)-C-H	106(2)	C(21)-C-H	104(2)
Fe-C-H	100(2)	C(22)-P(2)-C(42)	106.11(14)
C(22)-P(2)-C(41)	99.96(14)	C(42)-P(2)-C(41)	101.31(14)
C(22)-P(2)-Fe	105.06(10)	C(42)-P(2)-Fe	124.35(10)
C(41)-P(2)-Fe	117.08(12)	O-C(5)-C(61)	115.9(2)
O-C(5)-C(71)	117.4(2)	C(61)-C(5)-C(71)	126.7(2)
N-C(8)-C(81)	177.3(3)	C(16)-C(11)-C(12)	117.7(3)
C(16)-C(11)-C	127.4(4)	C(12)-C(11)-C	114.9(3)
C(13)-C(12)-C(11)	121.5(3)	C(13)-C(12)-P(1)	127.2(4)
C(11)-C(12)-P(1)	111.2(3)	C(14)-C(13)-C(12)	120.0(4)
C(14)-C(13)-H(13)	120.0	C(12)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	119.1(4)	C(15)-C(14)-H(14)	120.4
C(13)-C(14)-H(14)	120.4	C(14)-C(15)-C(16)	122.1(4)
C(14)-C(15)-H(15)	119.0	C(16)-C(15)-H(15)	119.0
C(11)-C(16)-C(15)	119.5(4)	C(11)-C(16)-H(16)	120.2
C(15)-C(16)-H(16)	120.2	C(22)-C(21)-C(26)	117.8(3)
C(22)-C(21)-C	119.1(2)	C(26)-C(21)-C	122.9(3)
C(21)-C(22)-C(23)	121.2(3)	C(21)-C(22)-P(2)	112.5(2)
C(23)-C(22)-P(2)	126.1(2)	C(24)-C(23)-C(22)	120.0(3)
C(24)-C(23)-H(23)	120.0	C(22)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	119.4(3)	C(23)-C(24)-H(24)	120.3
C(25)-C(24)-H(24)	120.3	C(26)-C(25)-C(24)	120.8(3)
C(26)-C(25)-H(25)	119.6	C(24)-C(25)-H(25)	119.6
C(25)-C(26)-C(21)	120.8(3)	C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6	C(34)-C(31)-C(33)	108.5(5)
C(34)-C(31)-P(1)	108.6(4)	C(33)-C(31)-P(1)	112.3(3)
C(34)-C(31)-H(31)	109.1	C(33)-C(31)-H(31)	109.1
P(1)-C(31)-H(31)	109.1	C(36)-C(32)-C(35)	110.8(3)
C(36)-C(32)-P(1)	113.8(3)	C(35)-C(32)-P(1)	115.5(3)
C(36)-C(32)-H(32)	105.2	C(35)-C(32)-H(32)	105.2
P(1)-C(32)-H(32)	105.2	C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5

C(31)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5	C(31)-C(34)-H(34A)	109.5
C(31)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(31)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(32)-C(35)-H(35A)	109.5
C(32)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	C(32)-C(36)-H(36A)	109.5
C(32)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
C(32)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	C(44)-C(41)-C(43)	108.5(3)
C(44)-C(41)-P(2)	116.3(2)	C(43)-C(41)-P(2)	110.2(2)
C(44)-C(41)-H(41)	107.2	C(43)-C(41)-H(41)	107.2
P(2)-C(41)-H(41)	107.2	C(46)-C(42)-C(45)	111.3(2)
C(46)-C(42)-P(2)	114.3(2)	C(45)-C(42)-P(2)	108.9(2)
C(46)-C(42)-H(42)	107.3	C(45)-C(42)-H(42)	107.3
P(2)-C(42)-H(42)	107.3	C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.5	H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.5	H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5	C(41)-C(44)-H(44A)	109.5
C(41)-C(44)-H(44B)	109.5	H(44A)-C(44)-H(44B)	109.5
C(41)-C(44)-H(44C)	109.5	H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5	C(42)-C(45)-H(45A)	109.5
C(42)-C(45)-H(45B)	109.5	H(45A)-C(45)-H(45B)	109.5
C(42)-C(45)-H(45C)	109.5	H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5	C(42)-C(46)-H(46A)	109.5
C(42)-C(46)-H(46B)	109.5	H(46A)-C(46)-H(46B)	109.5
C(42)-C(46)-H(46C)	109.5	H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5	C(66)-C(61)-C(62)	122.4(2)
C(66)-C(61)-C(5)	125.3(2)	C(62)-C(61)-C(5)	112.3(2)
C(63)-C(62)-C(61)	114.5(2)	C(63)-C(62)-Fe	132.2(2)
C(61)-C(62)-Fe	113.33(19)	C(64)-C(63)-C(62)	122.8(3)
C(64)-C(63)-H(63)	118.6	C(62)-C(63)-H(63)	118.6
C(63)-C(64)-C(65)	120.9(3)	C(63)-C(64)-H(64)	119.5
C(65)-C(64)-H(64)	119.5	C(66)-C(65)-C(64)	119.0(3)
C(66)-C(65)-H(65)	120.5	C(64)-C(65)-H(65)	120.5
C(65)-C(66)-C(61)	120.4(3)	C(65)-C(66)-H(66)	119.8
C(61)-C(66)-H(66)	119.8	C(72)-C(71)-C(76)	118.7(3)
C(72)-C(71)-C(5)	118.6(3)	C(76)-C(71)-C(5)	122.7(3)
C(73)-C(72)-C(71)	120.8(3)	C(73)-C(72)-H(72)	119.6
C(71)-C(72)-H(72)	119.6	C(74)-C(73)-C(72)	120.2(3)
C(74)-C(73)-H(73)	119.9	C(72)-C(73)-H(73)	119.9
C(73)-C(74)-C(75)	119.7(3)	C(73)-C(74)-H(74)	120.1
C(75)-C(74)-H(74)	120.1	C(74)-C(75)-C(76)	120.3(3)
C(74)-C(75)-H(75)	119.8	C(76)-C(75)-H(75)	119.8
C(75)-C(76)-C(71)	120.2(3)	C(75)-C(76)-H(76)	119.9
C(71)-C(76)-H(76)	119.9	C(8)-C(81)-C(82)	110.0(3)
C(8)-C(81)-C(84)	107.8(3)	C(82)-C(81)-C(84)	109.6(3)

C(8)-C(81)-C(83)	108.2(3)	C(82)-C(81)-C(83)	111.0(3)
C(84)-C(81)-C(83)	110.1(3)	C(81)-C(82)-H(82A)	109.5
C(81)-C(82)-H(82B)	109.5	H(82A)-C(82)-H(82B)	109.5
C(81)-C(82)-H(82C)	109.5	H(82A)-C(82)-H(82C)	109.5
H(82B)-C(82)-H(82C)	109.5	C(81)-C(83)-H(83A)	109.5
C(81)-C(83)-H(83B)	109.5	H(83A)-C(83)-H(83B)	109.5
C(81)-C(83)-H(83C)	109.5	H(83A)-C(83)-H(83C)	109.5
H(83B)-C(83)-H(83C)	109.5	C(81)-C(84)-H(84A)	109.5
C(81)-C(84)-H(84B)	109.5	H(84A)-C(84)-H(84B)	109.5
C(81)-C(84)-H(84C)	109.5	H(84A)-C(84)-H(84C)	109.5
H(84B)-C(84)-H(84C)	109.5		

3.3 Crystal data for [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (4).

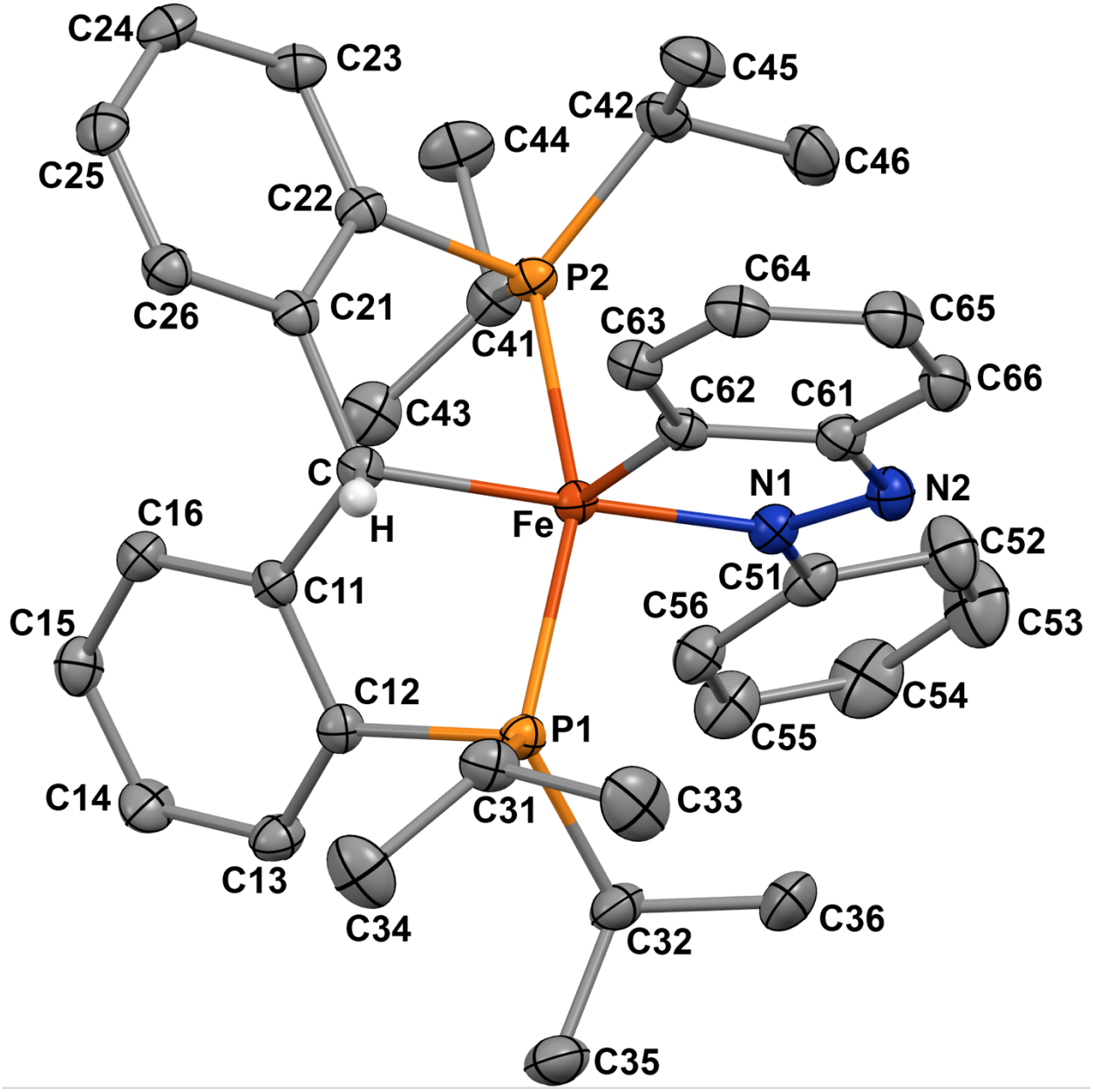


Figure S13. Thermal ellipsoid representation of [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (**4**) at the 50% probability level. Most hydrogen atoms omitted for clarity.

Table S11. Crystal data and structural refinement [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (**4**).

Identification code	ZL_V_215_a
Empirical formula	$C_{37}H_{46}FeN_2P_2$
Formula weight	636.55
Temperature	120(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
a	10.0838(4) Å
b	10.1841(6) Å
c	17.5352(7) Å
α	89.243(2)°
β	88.0700(10)°
γ	65.7090(10)°
Volume	1640.41(13) Å^3
Z	2
Density (calculated)	1.289 g.cm^{-3}
Absorption coefficient (μ)	4.811 mm^{-1}
F(000)	676
Crystal size	0.223 × 0.172 × 0.170 mm^3
θ range for data collection	2.521 to 72.399°
Index ranges	$-12 \le h \le 12$, $-12 \le k \le 12$, $-21 \le l \le 21$
Reflections collected	29692
Independent reflections	6481 [R_{int} = 0.0296]
Completeness to θ = 67.679°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.379
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6481 / 0 / 390
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R_1 = 0.0272, wR_2 = 0.0729
R indices (all data)	R_1 = 0.0275, wR_2 = 0.0732
Extinction coefficient	n/a
Largest diff. peak and hole	0.364 and -0.225 e$^-$.Å^{-3}

Table S12. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (**4**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Fe	0.70075(2)	0.36028(2)	0.25171(2)	0.015(1)
P(1)	0.63793(3)	0.23494(3)	0.16538(2)	0.017(1)
P(2)	0.84256(3)	0.44974(3)	0.30737(2)	0.017(1)
N(1)	0.62062(12)	0.31727(12)	0.34341(6)	0.019(1)
N(2)	0.49299(12)	0.40767(13)	0.37030(6)	0.022(1)
C	0.78508(14)	0.41364(14)	0.15130(7)	0.017(1)
C(11)	0.88304(14)	0.26563(14)	0.12336(7)	0.017(1)
C(12)	0.82339(14)	0.16162(14)	0.12518(7)	0.018(1)
C(13)	0.91059(15)	0.01831(15)	0.10790(8)	0.022(1)
C(14)	1.05718(15)	-0.02416(15)	0.08786(8)	0.025(1)
C(15)	1.11563(14)	0.07734(15)	0.08379(8)	0.023(1)
C(16)	1.02990(14)	0.22078(15)	0.10111(7)	0.020(1)
C(21)	0.86325(14)	0.51066(13)	0.15897(7)	0.018(1)
C(22)	0.90713(14)	0.53225(14)	0.23091(7)	0.019(1)
C(23)	0.98884(15)	0.61366(15)	0.23874(8)	0.023(1)
C(24)	1.02693(15)	0.67427(15)	0.17533(8)	0.024(1)
C(25)	0.98066(15)	0.65633(14)	0.10362(8)	0.023(1)
C(26)	0.89919(15)	0.57627(14)	0.09562(8)	0.021(1)
C(31)	0.51278(15)	0.33649(15)	0.08904(8)	0.023(1)
C(32)	0.60128(15)	0.07529(15)	0.19206(8)	0.024(1)
C(33)	0.35331(16)	0.3773(2)	0.11279(10)	0.038(1)
C(34)	0.54910(18)	0.26985(19)	0.00940(9)	0.036(1)
C(35)	0.57755(18)	-0.01034(18)	0.12628(10)	0.032(1)
C(36)	0.47699(18)	0.11205(19)	0.25194(9)	0.034(1)
C(41)	1.00689(15)	0.30560(15)	0.34883(8)	0.022(1)
C(42)	0.77945(15)	0.58739(16)	0.38422(8)	0.024(1)
C(43)	1.08698(15)	0.18976(16)	0.28912(9)	0.027(1)
C(44)	1.11407(17)	0.35636(18)	0.38468(10)	0.033(1)
C(45)	0.65861(17)	0.72969(17)	0.35926(9)	0.031(1)
C(46)	0.73328(18)	0.52765(19)	0.45603(8)	0.032(1)
C(51)	0.69058(15)	0.19395(15)	0.39048(8)	0.022(1)
C(52)	0.64991(19)	0.18888(18)	0.46691(9)	0.034(1)
C(53)	0.7251(2)	0.0663(2)	0.50950(10)	0.043(1)

C(54)	0.8396(2)	-0.05020(19)	0.47700(10)	0.039(1)
C(55)	0.88054(17)	-0.04560(17)	0.40127(10)	0.031(1)
C(56)	0.80625(15)	0.07705(16)	0.35805(8)	0.025(1)
C(61)	0.44042(14)	0.52599(14)	0.32278(7)	0.020(1)
C(62)	0.52859(14)	0.52797(14)	0.25772(7)	0.018(1)
C(63)	0.47505(15)	0.65320(15)	0.21218(8)	0.021(1)
C(64)	0.34521(15)	0.76819(15)	0.23085(8)	0.024(1)
C(65)	0.26140(15)	0.76387(16)	0.29573(9)	0.027(1)
C(66)	0.30809(15)	0.64315(16)	0.34135(8)	0.025(1)
H	0.706(2)	0.4592(19)	0.1138(10)	0.026
H(13)	0.8700	-0.0509	0.1098	0.026
H(14)	1.1169	-0.1225	0.0770	0.030
H(15)	1.2152	0.0486	0.0690	0.028
H(16)	1.0713	0.2893	0.0978	0.024
H(23)	1.0183	0.6274	0.2878	0.027
H(24)	1.0842	0.7278	0.1805	0.029
H(25)	1.0051	0.6992	0.0601	0.028
H(26)	0.8673	0.5657	0.0466	0.026
H(31)	0.5230	0.4299	0.0845	0.028
H(32)	0.6906	0.0071	0.2177	0.029
H(33A)	0.2903	0.4508	0.0779	0.057
H(33B)	0.3354	0.4156	0.1649	0.057
H(33C)	0.3321	0.2918	0.1107	0.057
H(34A)	0.4879	0.3391	-0.0278	0.054
H(34B)	0.5309	0.1825	0.0086	0.054
H(34C)	0.6518	0.2452	-0.0037	0.054
H(35A)	0.4814	0.0442	0.1052	0.049
H(35B)	0.5833	-0.1033	0.1454	0.049
H(35C)	0.6528	-0.0265	0.0863	0.049
H(36A)	0.3849	0.1747	0.2291	0.050
H(36B)	0.4956	0.1618	0.2950	0.050
H(36C)	0.4710	0.0231	0.2700	0.050
H(41)	0.9715	0.2586	0.3903	0.027
H(42)	0.8644	0.6083	0.3976	0.029
H(43A)	1.0193	0.1537	0.2683	0.041
H(43B)	1.1674	0.1102	0.3129	0.041
H(43C)	1.1256	0.2311	0.2479	0.041

H(44A)	1.1502	0.4048	0.3459	0.049
H(44B)	1.1960	0.2731	0.4047	0.049
H(44C)	1.0646	0.4237	0.4264	0.049
H(45A)	0.6881	0.7610	0.3110	0.046
H(45B)	0.6413	0.8031	0.3985	0.046
H(45C)	0.5691	0.7160	0.3523	0.046
H(46A)	0.6503	0.5053	0.4449	0.047
H(46B)	0.7053	0.5996	0.4969	0.047
H(46C)	0.8147	0.4398	0.4723	0.047
H(52)	0.5715	0.2686	0.4896	0.041
H(53)	0.6976	0.0624	0.5616	0.052
H(54)	0.8902	-0.1335	0.5067	0.047
H(55)	0.9590	-0.1257	0.3788	0.037
H(56)	0.8348	0.0808	0.3062	0.030
H(63)	0.5293	0.6586	0.1678	0.025
H(64)	0.3122	0.8514	0.1993	0.029
H(65)	0.1728	0.8440	0.3081	0.032
H(66)	0.2515	0.6390	0.3850	0.030

Table S13. Anisotropic displacement parameters ($Å^2$) for [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0128(1)	0.0146(1)	0.0166(1)	0.0004(1)	-0.0016(1)	-0.0049(1)
P(1)	0.0139(2)	0.0172(2)	0.0200(2)	-0.0012(1)	-0.0011(1)	-0.0064(1)
P(2)	0.0170(2)	0.0186(2)	0.0168(2)	0.0012(1)	-0.0033(1)	-0.0078(1)
N(1)	0.0175(5)	0.0195(5)	0.0198(5)	0.0016(4)	-0.0023(4)	-0.0072(4)
N(2)	0.0190(5)	0.0230(6)	0.0216(5)	-0.0002(4)	0.0006(4)	-0.0078(5)
C	0.0165(6)	0.0173(6)	0.0177(6)	0.0000(5)	-0.0015(5)	-0.0064(5)
C(11)	0.0176(6)	0.0180(6)	0.0143(5)	0.0013(5)	-0.0024(4)	-0.0064(5)
C(12)	0.0153(6)	0.0187(6)	0.0180(6)	0.0009(5)	-0.0019(4)	-0.0059(5)
C(13)	0.0197(6)	0.0172(6)	0.0291(7)	0.0007(5)	-0.0014(5)	-0.0077(5)
C(14)	0.0200(6)	0.0160(6)	0.0332(7)	-0.0004(5)	0.0008(5)	-0.0025(5)
C(15)	0.0155(6)	0.0243(7)	0.0261(7)	0.0006(5)	0.0009(5)	-0.0048(5)
C(16)	0.0188(6)	0.0207(6)	0.0214(6)	0.0015(5)	-0.0006(5)	-0.0095(5)
C(21)	0.0157(6)	0.0139(6)	0.0214(6)	-0.0005(5)	-0.0003(5)	-0.0034(5)
C(22)	0.0177(6)	0.0159(6)	0.0218(6)	0.0013(5)	-0.0016(5)	-0.0057(5)
C(23)	0.0239(7)	0.0207(7)	0.0249(7)	0.0011(5)	-0.0056(5)	-0.0099(5)
C(24)	0.0244(7)	0.0190(6)	0.0323(7)	0.0023(5)	-0.0035(5)	-0.0115(5)
C(25)	0.0250(7)	0.0172(6)	0.0259(7)	0.0033(5)	0.0015(5)	-0.0081(5)
C(26)	0.0232(6)	0.0194(6)	0.0200(6)	-0.0002(5)	-0.0005(5)	-0.0075(5)
C(31)	0.0182(6)	0.0220(7)	0.0278(7)	-0.0008(5)	-0.0062(5)	-0.0053(5)
C(32)	0.0218(7)	0.0229(7)	0.0321(7)	0.0005(6)	0.0000(5)	-0.0131(6)
C(33)	0.0171(7)	0.0444(10)	0.0443(9)	-0.0052(7)	-0.0074(6)	-0.0035(7)
C(34)	0.0325(8)	0.0405(9)	0.0253(7)	-0.0009(6)	-0.0082(6)	-0.0054(7)
C(35)	0.0308(8)	0.0294(8)	0.0431(9)	-0.0059(7)	0.0001(6)	-0.0187(7)
C(36)	0.0301(8)	0.0410(9)	0.0377(8)	-0.0019(7)	0.0049(6)	-0.0234(7)
C(41)	0.0201(6)	0.0254(7)	0.0223(6)	0.0067(5)	-0.0062(5)	-0.0098(5)
C(42)	0.0234(7)	0.0282(7)	0.0226(6)	-0.0068(5)	-0.0018(5)	-0.0117(6)
C(43)	0.0199(7)	0.0260(7)	0.0314(7)	0.0045(6)	-0.0047(5)	-0.0048(6)
C(44)	0.0267(7)	0.0351(8)	0.0378(8)	0.0069(7)	-0.0160(6)	-0.0134(7)
C(45)	0.0291(8)	0.0259(7)	0.0350(8)	-0.0098(6)	-0.0024(6)	-0.0085(6)
C(46)	0.0321(8)	0.0436(9)	0.0212(7)	-0.0069(6)	0.0007(6)	-0.0179(7)
C(51)	0.0222(6)	0.0223(7)	0.0227(6)	0.0056(5)	-0.0050(5)	-0.0107(5)
C(52)	0.0366(8)	0.0328(8)	0.0250(7)	0.0050(6)	0.0009(6)	-0.0059(7)

C(53)	0.0509(11)	0.0441(10)	0.0263(8)	0.0145(7)	-0.0019(7)	-0.0105(8)
C(54)	0.0397(9)	0.0338(9)	0.0399(9)	0.0195(7)	-0.0108(7)	-0.0100(7)
C(55)	0.0239(7)	0.0259(7)	0.0392(8)	0.0081(6)	-0.0048(6)	-0.0055(6)
C(56)	0.0220(7)	0.0253(7)	0.0268(7)	0.0054(5)	-0.0016(5)	-0.0101(6)
C(61)	0.0177(6)	0.0202(6)	0.0212(6)	-0.0013(5)	-0.0019(5)	-0.0075(5)
C(62)	0.0167(6)	0.0169(6)	0.0191(6)	-0.0019(5)	-0.0033(5)	-0.0058(5)
C(63)	0.0220(6)	0.0198(6)	0.0207(6)	0.0003(5)	-0.0031(5)	-0.0075(5)
C(64)	0.0244(7)	0.0176(6)	0.0281(7)	0.0018(5)	-0.0075(5)	-0.0048(5)
C(65)	0.0173(6)	0.0211(7)	0.0353(8)	-0.0047(6)	-0.0014(5)	-0.0016(5)
C(66)	0.0190(6)	0.0262(7)	0.0275(7)	-0.0038(6)	0.0024(5)	-0.0078(6)

Table S14. Distances [Å] for [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (**4**).

atom-atom	distance	atom-atom	distance
Fe-C(62)	1.8693(13)	Fe-N(1)	1.9015(11)
Fe-C	2.0911(13)	Fe-P(2)	2.2399(4)
Fe-P(1)	2.2589(4)	P(1)-C(12)	1.8243(13)
P(1)-C(31)	1.8595(14)	P(1)-C(32)	1.8606(14)
P(2)-C(22)	1.8135(13)	P(2)-C(42)	1.8559(14)
P(2)-C(41)	1.8658(14)	N(1)-N(2)	1.3122(16)
N(1)-C(51)	1.4280(17)	N(2)-C(61)	1.3802(18)
C-C(11)	1.4999(18)	C-C(21)	1.5058(18)
C-H	1.004(18)	C(11)-C(16)	1.4012(18)
C(11)-C(12)	1.4165(18)	C(12)-C(13)	1.3903(19)
C(13)-C(14)	1.3923(19)	C(13)-H(13)	0.9500
C(14)-C(15)	1.385(2)	C(14)-H(14)	0.9500
C(15)-C(16)	1.389(2)	C(15)-H(15)	0.9500
C(16)-H(16)	0.9500	C(21)-C(22)	1.4001(18)
C(21)-C(26)	1.4016(18)	C(22)-C(23)	1.3993(19)
C(23)-C(24)	1.383(2)	C(23)-H(23)	0.9500
C(24)-C(25)	1.396(2)	C(24)-H(24)	0.9500
C(25)-C(26)	1.386(2)	C(25)-H(25)	0.9500
C(26)-H(26)	0.9500	C(31)-C(34)	1.527(2)
C(31)-C(33)	1.530(2)	C(31)-H(31)	1.0000
C(32)-C(36)	1.533(2)	C(32)-C(35)	1.538(2)
C(32)-H(32)	1.0000	C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800	C(33)-H(33C)	0.9800
C(34)-H(34A)	0.9800	C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800	C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800	C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800	C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800	C(41)-C(43)	1.527(2)
C(41)-C(44)	1.531(2)	C(41)-H(41)	1.0000
C(42)-C(45)	1.531(2)	C(42)-C(46)	1.532(2)
C(42)-H(42)	1.0000	C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800	C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800	C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800	C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800	C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800	C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800	C(51)-C(56)	1.390(2)
C(51)-C(52)	1.395(2)	C(52)-C(53)	1.388(2)
C(52)-H(52)	0.9500	C(53)-C(54)	1.383(3)
C(53)-H(53)	0.9500	C(54)-C(55)	1.383(2)
C(54)-H(54)	0.9500	C(55)-C(56)	1.392(2)
C(55)-H(55)	0.9500	C(56)-H(56)	0.9500
C(61)-C(66)	1.4076(19)	C(61)-C(62)	1.4276(18)
C(62)-C(63)	1.4112(18)	C(63)-C(64)	1.383(2)
C(63)-H(63)	0.9500	C(64)-C(65)	1.405(2)

C(64)-H(64)	0.9500	C(65)-C(66)	1.377(2)
C(65)-H(65)	0.9500	C(66)-H(66)	0.9500

Table S15. Angles [°] for [{PC(sp^3)HP}Fe(-C^{Ar}-N=NPh)] (**4**).

atom-atom-atom	angle	atom-atom-atom	angle
C(62)-Fe-N(1)	81.78(5)	C(62)-Fe-C	96.72(5)
N(1)-Fe-C	178.41(5)	C(62)-Fe-P(2)	96.83(4)
N(1)-Fe-P(2)	96.48(3)	C-Fe-P(2)	83.13(4)
C(62)-Fe-P(1)	99.86(4)	N(1)-Fe-P(1)	101.23(3)
C-Fe-P(1)	79.54(4)	P(2)-Fe-P(1)	157.156(15)
C(12)-P(1)-C(31)	108.14(6)	C(12)-P(1)-C(32)	105.30(6)
C(31)-P(1)-C(32)	108.93(6)	C(12)-P(1)-Fe	89.92(4)
C(31)-P(1)-Fe	118.34(5)	C(32)-P(1)-Fe	122.41(5)
C(22)-P(2)-C(42)	104.44(6)	C(22)-P(2)-C(41)	106.74(6)
C(42)-P(2)-C(41)	102.43(6)	C(22)-P(2)-Fe	105.39(4)
C(42)-P(2)-Fe	124.37(5)	C(41)-P(2)-Fe	112.20(5)
N(2)-N(1)-C(51)	114.11(11)	N(2)-N(1)-Fe	120.19(9)
C(51)-N(1)-Fe	125.64(9)	N(1)-N(2)-C(61)	108.85(11)
C(11)-C-C(21)	112.98(11)	C(11)-C-Fe	99.84(8)
C(21)-C-Fe	116.95(9)	C(11)-C-H	108.6(10)
C(21)-C-H	107.8(10)	Fe-C-H	110.3(10)
C(16)-C(11)-C(12)	118.17(12)	C(16)-C(11)-C	125.21(12)
C(12)-C(11)-C	116.46(11)	C(13)-C(12)-C(11)	120.38(12)
C(13)-C(12)-P(1)	127.14(10)	C(11)-C(12)-P(1)	111.83(9)
C(12)-C(13)-C(14)	120.30(13)	C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9	C(15)-C(14)-C(13)	119.79(13)
C(15)-C(14)-H(14)	120.1	C(13)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	120.51(12)	C(14)-C(15)-H(15)	119.7
C(16)-C(15)-H(15)	119.7	C(15)-C(16)-C(11)	120.80(12)
C(15)-C(16)-H(16)	119.6	C(11)-C(16)-H(16)	119.6
C(22)-C(21)-C(26)	118.39(12)	C(22)-C(21)-C	119.54(11)
C(26)-C(21)-C	122.02(12)	C(23)-C(22)-C(21)	120.58(12)
C(23)-C(22)-P(2)	126.48(10)	C(21)-C(22)-P(2)	112.92(10)
C(24)-C(23)-C(22)	120.27(13)	C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9	C(23)-C(24)-C(25)	119.57(13)
C(23)-C(24)-H(24)	120.2	C(25)-C(24)-H(24)	120.2
C(26)-C(25)-C(24)	120.37(13)	C(26)-C(25)-H(25)	119.8
C(24)-C(25)-H(25)	119.8	C(25)-C(26)-C(21)	120.77(13)
C(25)-C(26)-H(26)	119.6	C(21)-C(26)-H(26)	119.6
C(34)-C(31)-C(33)	111.91(12)	C(34)-C(31)-P(1)	116.11(10)
C(33)-C(31)-P(1)	111.76(11)	C(34)-C(31)-H(31)	105.3
C(33)-C(31)-H(31)	105.3	P(1)-C(31)-H(31)	105.3
C(36)-C(32)-C(35)	109.91(12)	C(36)-C(32)-P(1)	112.13(10)
C(35)-C(32)-P(1)	116.78(11)	C(36)-C(32)-H(32)	105.7
C(35)-C(32)-H(32)	105.7	P(1)-C(32)-H(32)	105.7
C(31)-C(33)-H(33A)	109.5	C(31)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
C(31)-C(34)-H(34A)	109.5	C(31)-C(34)-H(34B)	109.5

H(34A)-C(34)-H(34B)	109.5	C(31)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(32)-C(35)-H(35A)	109.5	C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
C(32)-C(36)-H(36A)	109.5	C(32)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	C(32)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
C(43)-C(41)-C(44)	109.64(12)	C(43)-C(41)-P(2)	110.27(9)
C(44)-C(41)-P(2)	115.80(10)	C(43)-C(41)-H(41)	106.9
C(44)-C(41)-H(41)	106.9	P(2)-C(41)-H(41)	106.9
C(45)-C(42)-C(46)	111.40(13)	C(45)-C(42)-P(2)	112.93(10)
C(46)-C(42)-P(2)	110.50(10)	C(45)-C(42)-H(42)	107.2
C(46)-C(42)-H(42)	107.2	P(2)-C(42)-H(42)	107.2
C(41)-C(43)-H(43A)	109.5	C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5	C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5	H(43B)-C(43)-H(43C)	109.5
C(41)-C(44)-H(44A)	109.5	C(41)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5	C(41)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(42)-C(45)-H(45A)	109.5	C(42)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5	C(42)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5	H(45B)-C(45)-H(45C)	109.5
C(42)-C(46)-H(46A)	109.5	C(42)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5	C(42)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
C(56)-C(51)-C(52)	119.79(13)	C(56)-C(51)-N(1)	117.48(12)
C(52)-C(51)-N(1)	122.71(13)	C(53)-C(52)-C(51)	119.40(15)
C(53)-C(52)-H(52)	120.3	C(51)-C(52)-H(52)	120.3
C(54)-C(53)-C(52)	120.71(16)	C(54)-C(53)-H(53)	119.6
C(52)-C(53)-H(53)	119.6	C(53)-C(54)-C(55)	120.11(15)
C(53)-C(54)-H(54)	119.9	C(55)-C(54)-H(54)	119.9
C(54)-C(55)-C(56)	119.68(15)	C(54)-C(55)-H(55)	120.2
C(56)-C(55)-H(55)	120.2	C(51)-C(56)-C(55)	120.30(14)
C(51)-C(56)-H(56)	119.8	C(55)-C(56)-H(56)	119.8
N(2)-C(61)-C(66)	120.15(12)	N(2)-C(61)-C(62)	117.73(12)
C(66)-C(61)-C(62)	122.02(12)	C(63)-C(62)-C(61)	116.41(12)
C(63)-C(62)-Fe	132.13(10)	C(61)-C(62)-Fe	111.43(9)
C(64)-C(63)-C(62)	121.32(13)	C(64)-C(63)-H(63)	119.3
C(62)-C(63)-H(63)	119.3	C(63)-C(64)-C(65)	121.03(13)
C(63)-C(64)-H(64)	119.5	C(65)-C(64)-H(64)	119.5
C(66)-C(65)-C(64)	119.80(13)	C(66)-C(65)-H(65)	120.1
C(64)-C(65)-H(65)	120.1	C(65)-C(66)-C(61)	119.42(13)
C(65)-C(66)-H(66)	120.3	C(61)-C(66)-H(66)	120.3

3.4 Crystal data for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (5).

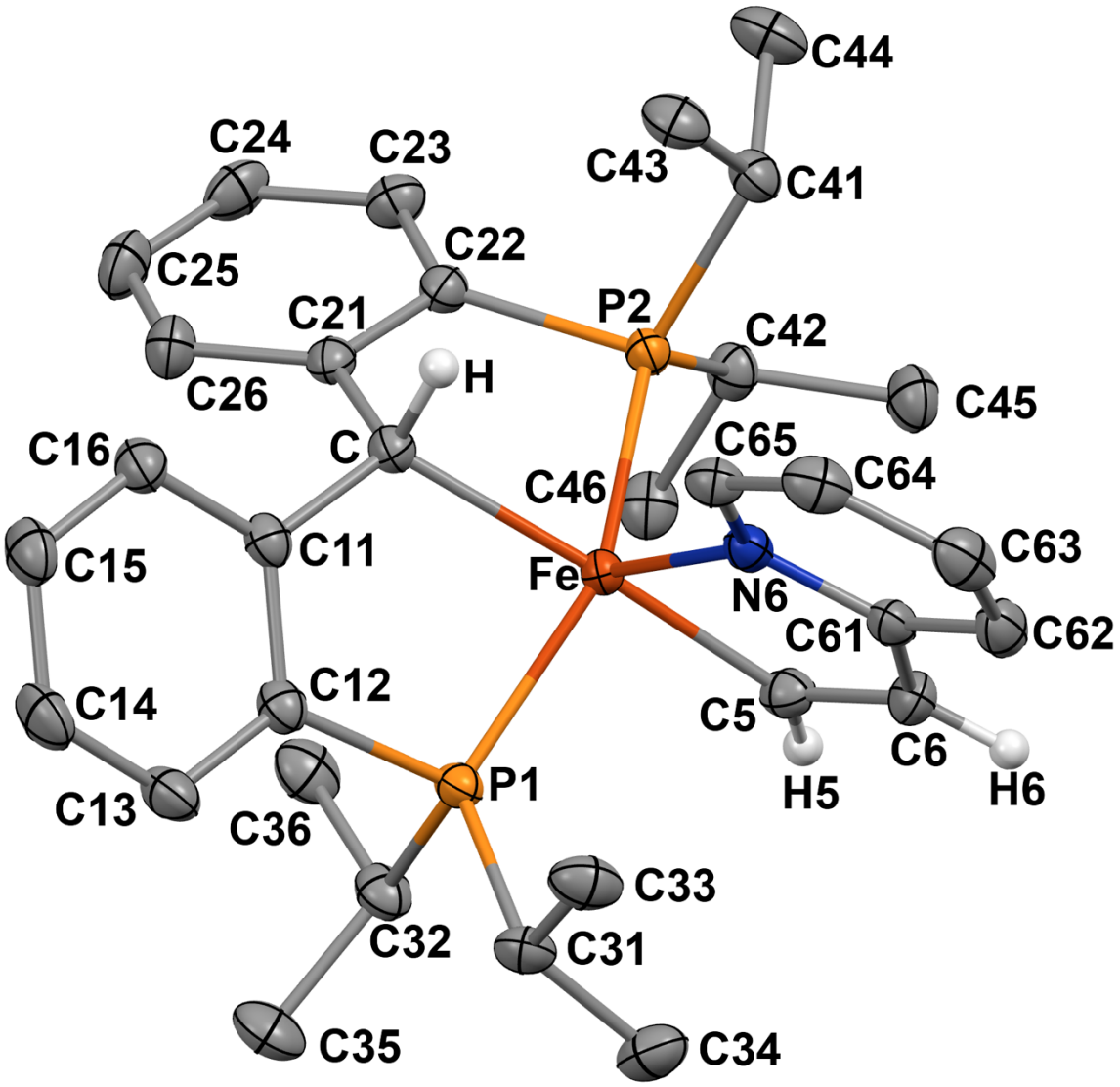


Figure S14. Thermal ellipsoid representation of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**) at the 50% probability level. Most hydrogen atoms omitted for clarity.

Table S16. Crystal data and structural refinement for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**).

Identification code	ZL_V_271_a
Empirical formula	$C_{32}H_{43}FeNP_2$
Formula weight	559.46
Temperature	120(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a	9.7026(3) Å
b	19.8324(7) Å
c	15.2623(7) Å
α	90°
β	93.4120(10)°
γ	90°
Volume	2931.66(19) $Å^3$
Z	4
Density (calculated)	1.268 $g.cm^{-3}$
Absorption coefficient (μ)	5.299 mm^{-1}
F(000)	1192
Crystal size	0.192 × 0.173 × 0.112 mm^3
θ range for data collection	3.658 to 72.427°
Index ranges	$-12 \leq h \leq 10$, $-24 \leq k \leq 24$, $-18 \leq l \leq 18$
Reflections collected	72837
Independent reflections	5783 [R_{int} = 0.0443]
Completeness to θ = 67.679°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.4755
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5783 / 0 / 339
Goodness-of-fit on F^2	1.033
Final R indices [I>2σ(I)]	R_1 = 0.0230, wR_2 = 0.0589
R indices (all data)	R_1 = 0.0244, wR_2 = 0.0601
Extinction coefficient	n/a
Largest diff. peak and hole	0.296 and -0.186 $e^-.Å^{-3}$

Table S17. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
Fe	0.67970(2)	0.61515(2)	0.31850(2)	0.015(1)
P(1)	0.87633(3)	0.56361(2)	0.28983(2)	0.018(1)
C	0.77601(12)	0.69924(6)	0.26440(8)	0.018(1)
P(2)	0.55830(3)	0.69579(2)	0.38425(2)	0.017(1)
C(5)	0.60205(13)	0.53835(6)	0.38025(8)	0.021(1)
N(6)	0.54614(10)	0.57834(5)	0.21781(7)	0.018(1)
C(6)	0.50430(13)	0.50262(6)	0.33256(9)	0.023(1)
C(11)	0.90197(12)	0.68543(6)	0.21311(8)	0.019(1)
C(12)	0.96460(13)	0.62181(6)	0.21926(8)	0.021(1)
C(13)	1.07974(14)	0.60735(7)	0.17127(9)	0.027(1)
C(14)	1.13238(14)	0.65583(8)	0.11713(10)	0.031(1)
C(15)	1.07030(14)	0.71896(8)	0.10982(9)	0.029(1)
C(16)	0.95677(13)	0.73352(7)	0.15749(9)	0.024(1)
C(21)	0.79216(12)	0.75476(6)	0.33166(8)	0.019(1)
C(22)	0.68416(12)	0.76436(6)	0.38824(8)	0.019(1)
C(23)	0.69051(14)	0.81583(6)	0.45038(9)	0.024(1)
C(24)	0.80668(15)	0.85638(7)	0.46180(9)	0.028(1)
C(25)	0.91563(15)	0.84587(7)	0.40900(10)	0.030(1)
C(26)	0.90839(14)	0.79644(7)	0.34419(9)	0.025(1)
C(31)	0.89071(13)	0.48058(6)	0.23440(9)	0.024(1)
C(32)	0.99286(13)	0.55457(7)	0.39055(8)	0.024(1)
C(33)	0.80443(15)	0.48028(7)	0.14701(9)	0.030(1)
C(34)	0.84821(17)	0.42281(7)	0.29344(10)	0.033(1)
C(35)	1.13669(14)	0.52616(8)	0.37618(10)	0.034(1)
C(36)	1.00367(15)	0.62226(7)	0.43826(9)	0.030(1)
C(41)	0.39461(12)	0.73054(7)	0.33233(9)	0.023(1)
C(42)	0.51956(13)	0.68609(6)	0.50130(8)	0.022(1)
C(43)	0.41743(14)	0.75535(7)	0.23945(9)	0.029(1)
C(44)	0.32966(15)	0.78670(8)	0.38497(10)	0.034(1)
C(45)	0.39766(14)	0.63805(7)	0.51118(9)	0.028(1)
C(46)	0.64826(14)	0.66231(7)	0.55521(9)	0.026(1)
C(61)	0.47466(12)	0.52272(6)	0.24281(8)	0.020(1)
C(62)	0.38638(13)	0.48838(7)	0.18120(9)	0.026(1)

C(63)	0.37314(14)	0.51034(7)	0.09541(10)	0.029(1)
C(64)	0.44730(14)	0.56659(7)	0.07055(9)	0.027(1)
C(65)	0.53139(13)	0.59854(6)	0.13371(8)	0.022(1)
H	0.6996(17)	0.7130(8)	0.2207(11)	0.027
H(5)	0.6216(18)	0.5235(9)	0.4395(12)	0.032
H(6)	0.4575	0.4659	0.3575	0.027
H(13)	1.1218	0.5641	0.1759	0.033
H(14)	1.2108	0.6460	0.0850	0.037
H(15)	1.1057	0.7521	0.0722	0.034
H(16)	0.9153	0.7769	0.1524	0.028
H(23)	0.6143	0.8233	0.4854	0.029
H(24)	0.8113	0.8908	0.5052	0.034
H(25)	0.9964	0.8727	0.4171	0.036
H(26)	0.9836	0.7908	0.3078	0.031
H(31)	0.9896	0.4737	0.2215	0.028
H(32)	0.9472	0.5224	0.4302	0.029
H(33A)	0.8199	0.4380	0.1159	0.045
H(33B)	0.8318	0.5184	0.1110	0.045
H(33C)	0.7064	0.4843	0.1582	0.045
H(34A)	0.8586	0.3798	0.2629	0.049
H(34B)	0.7517	0.4287	0.3074	0.049
H(34C)	0.9072	0.4229	0.3478	0.049
H(35A)	1.1889	0.5218	0.4329	0.050
H(35B)	1.1855	0.5567	0.3382	0.050
H(35C)	1.1276	0.4817	0.3483	0.050
H(36A)	1.0567	0.6166	0.4945	0.045
H(36B)	0.9109	0.6387	0.4488	0.045
H(36C)	1.0504	0.6549	0.4021	0.045
H(41)	0.3266	0.6927	0.3270	0.027
H(42)	0.4932	0.7313	0.5239	0.026
H(43A)	0.3296	0.7712	0.2117	0.043
H(43B)	0.4531	0.7183	0.2049	0.043
H(43C)	0.4842	0.7925	0.2422	0.043
H(44A)	0.2417	0.8004	0.3553	0.051
H(44B)	0.3923	0.8255	0.3893	0.051
H(44C)	0.3133	0.7702	0.4440	0.051
H(45A)	0.3795	0.6338	0.5734	0.043

H(45B)	0.4201	0.5936	0.4877	0.043
H(45C)	0.3155	0.6560	0.4787	0.043
H(46A)	0.6285	0.6603	0.6174	0.040
H(46B)	0.7241	0.6940	0.5475	0.040
H(46C)	0.6746	0.6174	0.5353	0.040
H(62)	0.3360	0.4501	0.1988	0.031
H(63)	0.3139	0.4873	0.0536	0.035
H(64)	0.4402	0.5825	0.0118	0.032
H(65)	0.5818	0.6370	0.1168	0.026

Table S18. Anisotropic displacement parameters ($Å^2$) for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0133(1)	0.0151(1)	0.0169(1)	0.0004(1)	0.0004(1)	-0.0006(1)
P(1)	0.0154(1)	0.0188(1)	0.0194(2)	0.0013(1)	0.0007(1)	0.0025(1)
C	0.0155(5)	0.0183(5)	0.0204(6)	0.0013(4)	0.0003(4)	-0.0004(4)
P(2)	0.0143(1)	0.0172(1)	0.0184(1)	-0.0006(1)	0.0015(1)	-0.0004(1)
C(5)	0.0226(6)	0.0197(6)	0.0212(6)	0.0030(5)	0.0027(5)	0.0024(5)
N(6)	0.0166(5)	0.0181(5)	0.0198(5)	-0.0017(4)	0.0010(4)	0.0019(4)
C(6)	0.0215(6)	0.0190(6)	0.0277(6)	0.0032(5)	0.0047(5)	-0.0019(5)
C(11)	0.0157(5)	0.0235(6)	0.0187(6)	0.0000(5)	-0.0010(4)	-0.0008(4)
C(12)	0.0174(6)	0.0245(6)	0.0198(6)	0.0018(5)	0.0000(5)	0.0004(5)
C(13)	0.0197(6)	0.0322(7)	0.0302(7)	0.0026(5)	0.0040(5)	0.0066(5)
C(14)	0.0191(6)	0.0423(8)	0.0314(7)	0.0032(6)	0.0088(5)	0.0030(6)
C(15)	0.0220(6)	0.0368(7)	0.0276(7)	0.0073(6)	0.0058(5)	-0.0031(5)
C(16)	0.0198(6)	0.0264(6)	0.0250(6)	0.0046(5)	0.0012(5)	0.0000(5)
C(21)	0.0182(5)	0.0170(5)	0.0209(6)	0.0032(4)	-0.0011(4)	-0.0003(4)
C(22)	0.0182(6)	0.0179(5)	0.0209(6)	0.0012(4)	-0.0010(4)	-0.0004(4)
C(23)	0.0276(6)	0.0210(6)	0.0244(6)	-0.0012(5)	0.0019(5)	0.0006(5)
C(24)	0.0375(7)	0.0191(6)	0.0275(7)	-0.0038(5)	-0.0028(6)	-0.0047(5)
C(25)	0.0297(7)	0.0258(7)	0.0340(7)	0.0000(6)	-0.0022(6)	-0.0116(5)
C(26)	0.0227(6)	0.0259(6)	0.0279(7)	0.0008(5)	0.0023(5)	-0.0058(5)
C(31)	0.0232(6)	0.0215(6)	0.0262(6)	-0.0010(5)	0.0025(5)	0.0062(5)
C(32)	0.0198(6)	0.0298(7)	0.0229(6)	0.0047(5)	-0.0021(5)	0.0025(5)
C(33)	0.0328(7)	0.0270(7)	0.0289(7)	-0.0067(5)	-0.0019(6)	0.0082(5)
C(34)	0.0418(8)	0.0203(6)	0.0363(8)	0.0011(6)	0.0051(6)	0.0038(6)
C(35)	0.0233(7)	0.0416(8)	0.0346(8)	0.0012(6)	-0.0058(6)	0.0099(6)
C(36)	0.0254(7)	0.0381(8)	0.0263(7)	-0.0030(6)	-0.0061(5)	0.0021(6)
C(41)	0.0166(6)	0.0244(6)	0.0274(6)	-0.0001(5)	-0.0010(5)	0.0020(5)
C(42)	0.0223(6)	0.0232(6)	0.0207(6)	-0.0009(5)	0.0049(5)	-0.0013(5)
C(43)	0.0252(6)	0.0323(7)	0.0273(7)	0.0023(5)	-0.0035(5)	0.0069(5)
C(44)	0.0280(7)	0.0383(8)	0.0357(8)	-0.0017(6)	0.0024(6)	0.0139(6)
C(45)	0.0240(6)	0.0322(7)	0.0300(7)	0.0029(6)	0.0080(5)	-0.0045(5)
C(46)	0.0281(7)	0.0317(7)	0.0194(6)	0.0010(5)	-0.0001(5)	-0.0037(5)
C(61)	0.0161(5)	0.0187(6)	0.0263(6)	-0.0027(5)	0.0026(5)	0.0017(4)
C(62)	0.0203(6)	0.0231(6)	0.0339(7)	-0.0065(5)	0.0007(5)	-0.0022(5)

C(63)	0.0241(6)	0.0313(7)	0.0317(7)	-0.0117(6)	-0.0052(5)	0.0014(5)
C(64)	0.0291(7)	0.0298(7)	0.0217(6)	-0.0039(5)	-0.0031(5)	0.0064(5)
C(65)	0.0225(6)	0.0209(6)	0.0211(6)	-0.0010(5)	0.0015(5)	0.0031(5)

Table S19. Distances [Å] for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**).

atom-atom	distance	atom-atom	distance
Fe-C(5)	1.9648(12)	Fe-N(6)	2.0824(10)
Fe-C	2.1043(12)	Fe-P(1)	2.2305(3)
Fe-P(2)	2.2568(3)	P(1)-C(12)	1.8264(13)
P(1)-C(31)	1.8604(13)	P(1)-C(32)	1.8620(13)
C-C(21)	1.5073(17)	C-C(11)	1.5150(16)
C-H	1.005(17)	P(2)-C(22)	1.8263(12)
P(2)-C(42)	1.8573(13)	P(2)-C(41)	1.8643(13)
C(5)-C(6)	1.3598(18)	C(5)-H(5)	0.960(18)
N(6)-C(65)	1.3441(16)	N(6)-C(61)	1.3692(16)
C(6)-C(61)	1.4391(18)	C(6)-H(6)	0.9500
C(11)-C(12)	1.4012(17)	C(11)-C(16)	1.4024(18)
C(12)-C(13)	1.4015(18)	C(13)-C(14)	1.385(2)
C(13)-H(13)	0.9500	C(14)-C(15)	1.391(2)
C(14)-H(14)	0.9500	C(15)-C(16)	1.3862(19)
C(15)-H(15)	0.9500	C(16)-H(16)	0.9500
C(21)-C(26)	1.4021(17)	C(21)-C(22)	1.4099(17)
C(22)-C(23)	1.3923(18)	C(23)-C(24)	1.3872(19)
C(23)-H(23)	0.9500	C(24)-C(25)	1.383(2)
C(24)-H(24)	0.9500	C(25)-C(26)	1.391(2)
C(25)-H(25)	0.9500	C(26)-H(26)	0.9500
C(31)-C(34)	1.5294(19)	C(31)-C(33)	1.5319(18)
C(31)-H(31)	1.0000	C(32)-C(36)	1.528(2)
C(32)-C(35)	1.5327(18)	C(32)-H(32)	1.0000
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
C(41)-C(43)	1.5290(19)	C(41)-C(44)	1.5309(19)
C(41)-H(41)	1.0000	C(42)-C(46)	1.5285(18)
C(42)-C(45)	1.5332(18)	C(42)-H(42)	1.0000
C(43)-H(43A)	0.9800	C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800	C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800	C(44)-H(44C)	0.9800
C(45)-H(45A)	0.9800	C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800	C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800	C(46)-H(46C)	0.9800
C(61)-C(62)	1.4092(18)	C(62)-C(63)	1.378(2)
C(62)-H(62)	0.9500	C(63)-C(64)	1.392(2)
C(63)-H(63)	0.9500	C(64)-C(65)	1.3794(18)
C(64)-H(64)	0.9500	C(65)-H(65)	0.9500

Table S20. Angles [°] for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}] (**5**).

atom-atom-atom	angle	atom-atom-atom	angle
C(5)-Fe-N(6)	80.95(5)	C(5)-Fe-C	174.00(5)
N(6)-Fe-C	105.05(4)	C(5)-Fe-P(1)	95.50(4)
N(6)-Fe-P(1)	101.34(3)	C-Fe-P(1)	83.18(3)
C(5)-Fe-P(2)	96.36(4)	N(6)-Fe-P(2)	104.96(3)
C-Fe-P(2)	82.45(3)	P(1)-Fe-P(2)	152.515(14)
C(12)-P(1)-C(31)	103.93(6)	C(12)-P(1)-C(32)	105.35(6)
C(31)-P(1)-C(32)	103.41(6)	C(12)-P(1)-Fe	105.23(4)
C(31)-P(1)-Fe	125.66(4)	C(32)-P(1)-Fe	111.51(4)
C(21)-C-C(11)	115.44(10)	C(21)-C-Fe	110.02(8)
C(11)-C-Fe	116.76(8)	C(21)-C-H	107.2(9)
C(11)-C-H	107.0(9)	Fe-C-H	98.5(9)
C(22)-P(2)-C(42)	102.60(6)	C(22)-P(2)-C(41)	106.85(6)
C(42)-P(2)-C(41)	103.36(6)	C(22)-P(2)-Fe	100.19(4)
C(42)-P(2)-Fe	119.68(4)	C(41)-P(2)-Fe	121.80(4)
C(6)-C(5)-Fe	114.98(9)	C(6)-C(5)-H(5)	115.9(10)
Fe-C(5)-H(5)	129.1(10)	C(65)-N(6)-C(61)	118.64(11)
C(65)-N(6)-Fe	128.79(8)	C(61)-N(6)-Fe	112.34(8)
C(5)-C(6)-C(61)	117.30(11)	C(5)-C(6)-H(6)	121.3
C(61)-C(6)-H(6)	121.3	C(12)-C(11)-C(16)	118.32(11)
C(12)-C(11)-C	119.22(11)	C(16)-C(11)-C	122.44(11)
C(11)-C(12)-C(13)	120.35(12)	C(11)-C(12)-P(1)	113.07(9)
C(13)-C(12)-P(1)	126.53(10)	C(14)-C(13)-C(12)	120.23(13)
C(14)-C(13)-H(13)	119.9	C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	119.97(12)	C(13)-C(14)-H(14)	120.0
C(15)-C(14)-H(14)	120.0	C(16)-C(15)-C(14)	119.95(13)
C(16)-C(15)-H(15)	120.0	C(14)-C(15)-H(15)	120.0
C(15)-C(16)-C(11)	121.18(12)	C(15)-C(16)-H(16)	119.4
C(11)-C(16)-H(16)	119.4	C(26)-C(21)-C(22)	117.26(11)
C(26)-C(21)-C	125.01(11)	C(22)-C(21)-C	117.70(10)
C(23)-C(22)-C(21)	120.79(11)	C(23)-C(22)-P(2)	124.83(10)
C(21)-C(22)-P(2)	113.51(9)	C(24)-C(23)-C(22)	120.89(12)
C(24)-C(23)-H(23)	119.6	C(22)-C(23)-H(23)	119.6
C(25)-C(24)-C(23)	118.89(12)	C(25)-C(24)-H(24)	120.6
C(23)-C(24)-H(24)	120.6	C(24)-C(25)-C(26)	120.84(12)
C(24)-C(25)-H(25)	119.6	C(26)-C(25)-H(25)	119.6
C(25)-C(26)-C(21)	121.23(12)	C(25)-C(26)-H(26)	119.4
C(21)-C(26)-H(26)	119.4	C(34)-C(31)-C(33)	110.95(12)
C(34)-C(31)-P(1)	111.41(9)	C(33)-C(31)-P(1)	110.33(9)
C(34)-C(31)-H(31)	108.0	C(33)-C(31)-H(31)	108.0
P(1)-C(31)-H(31)	108.0	C(36)-C(32)-C(35)	110.73(11)
C(36)-C(32)-P(1)	109.26(9)	C(35)-C(32)-P(1)	115.50(10)
C(36)-C(32)-H(32)	107.0	C(35)-C(32)-H(32)	107.0
P(1)-C(32)-H(32)	107.0	C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5

H(33B)-C(33)-H(33C)	109.5	C(31)-C(34)-H(34A)	109.5
C(31)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(31)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(32)-C(35)-H(35A)	109.5
C(32)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	C(32)-C(36)-H(36A)	109.5
C(32)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
C(32)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	C(43)-C(41)-C(44)	109.83(11)
C(43)-C(41)-P(2)	110.27(9)	C(44)-C(41)-P(2)	114.38(9)
C(43)-C(41)-H(41)	107.4	C(44)-C(41)-H(41)	107.4
P(2)-C(41)-H(41)	107.4	C(46)-C(42)-C(45)	111.44(11)
C(46)-C(42)-P(2)	110.13(9)	C(45)-C(42)-P(2)	111.12(9)
C(46)-C(42)-H(42)	108.0	C(45)-C(42)-H(42)	108.0
P(2)-C(42)-H(42)	108.0	C(41)-C(43)-H(43A)	109.5
C(41)-C(43)-H(43B)	109.5	H(43A)-C(43)-H(43B)	109.5
C(41)-C(43)-H(43C)	109.5	H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5	C(41)-C(44)-H(44A)	109.5
C(41)-C(44)-H(44B)	109.5	H(44A)-C(44)-H(44B)	109.5
C(41)-C(44)-H(44C)	109.5	H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5	C(42)-C(45)-H(45A)	109.5
C(42)-C(45)-H(45B)	109.5	H(45A)-C(45)-H(45B)	109.5
C(42)-C(45)-H(45C)	109.5	H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5	C(42)-C(46)-H(46A)	109.5
C(42)-C(46)-H(46B)	109.5	H(46A)-C(46)-H(46B)	109.5
C(42)-C(46)-H(46C)	109.5	H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5	N(6)-C(61)-C(62)	120.08(12)
N(6)-C(61)-C(6)	114.36(11)	C(62)-C(61)-C(6)	125.48(12)
C(63)-C(62)-C(61)	119.98(12)	C(63)-C(62)-H(62)	120.0
C(61)-C(62)-H(62)	120.0	C(62)-C(63)-C(64)	119.43(12)
C(62)-C(63)-H(63)	120.3	C(64)-C(63)-H(63)	120.3
C(65)-C(64)-C(63)	118.12(13)	C(65)-C(64)-H(64)	120.9
C(63)-C(64)-H(64)	120.9	N(6)-C(65)-C(64)	123.74(12)
N(6)-C(65)-H(65)	118.1	C(64)-C(65)-H(65)	118.1

3.5 Crystal data for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (6-NC^{t}Bu).

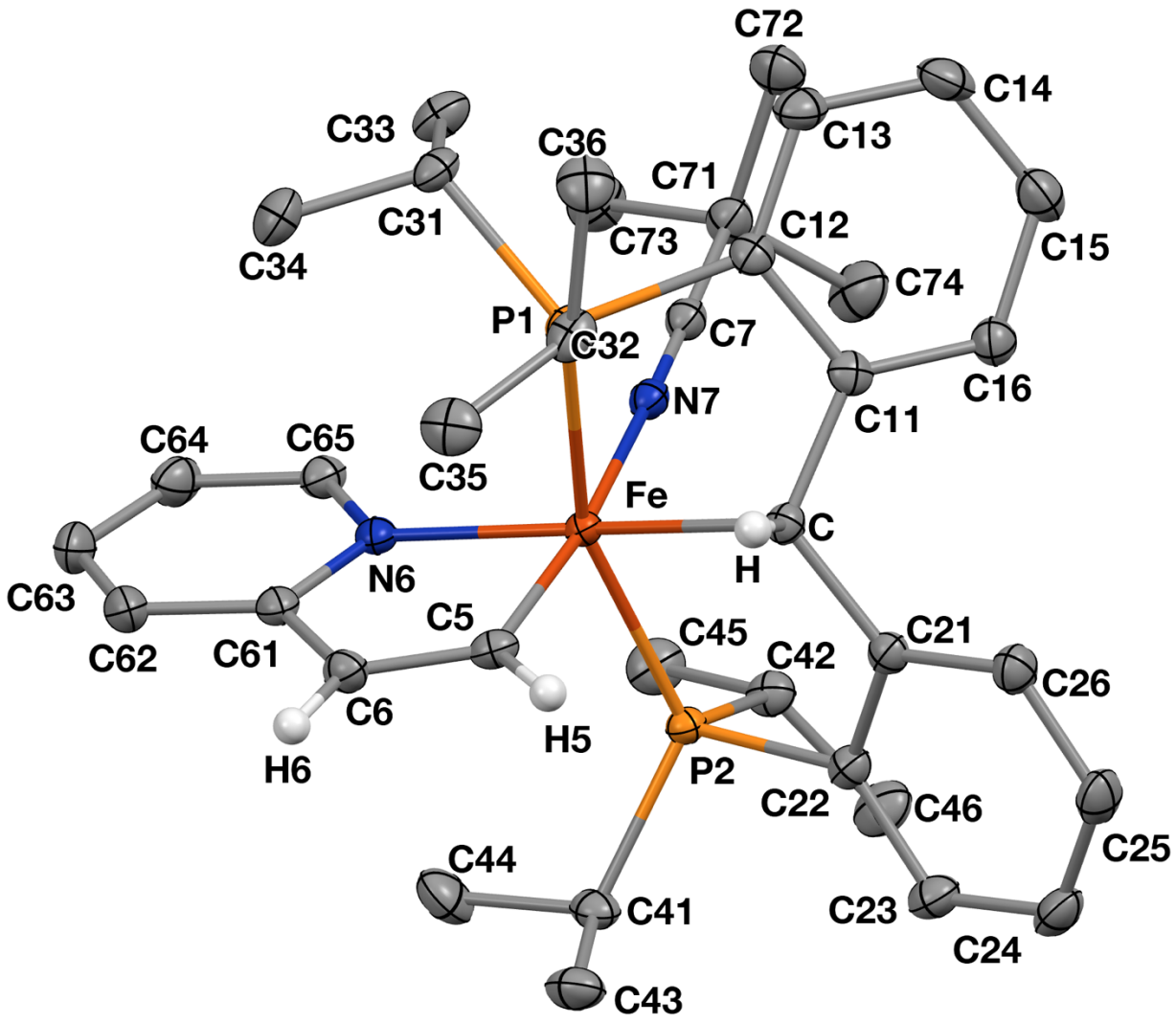


Figure S15. Thermal ellipsoid representation of [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

Table S21. Crystal data and refinement for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

Identification code	ZL_V_281_a
Empirical formula	$C_{37}H_{52}FeN_2P_2$
Formula weight	642.59
Temperature	120(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a	11.2139(8) Å
b	16.5390(12) Å
c	18.2256(13) Å
α	90°
β	94.244(3)°
γ	90°
Volume	3371.0(4) Å^3
Z	4
Density (calculated)	1.266 g.cm^{-3}
Absorption coefficient (μ)	4.683 mm^{-1}
F(000)	1376
Crystal size	0.149 × 0.060 × 0.053 mm^3
θ range for data collection	3.613 to 74.465°
Index ranges	$-14 \leq h \leq 13$, $-20 \leq k \leq 20$, $-22 \leq l \leq 22$
Reflections collected	79139
Independent reflections	6880 [R_{int} = 0.0613]
Completeness to θ = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.640
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6880 / 0 / 396
Goodness-of-fit on F^2	1.021
Final R indices [I>2σ(I)]	R_1 = 0.0257, wR_2 = 0.0619
R indices (all data)	R_1 = 0.0295, wR_2 = 0.0645
Extinction coefficient	n/a
Largest diff. peak and hole	0.303 and -0.257 e$^-$.Å^{-3}

Table S22. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U(eq)
P(1)	0.07925(3)	0.70203(2)	0.47144(2)	0.014(1)
C	0.28441(11)	0.64240(7)	0.53758(7)	0.014(1)
C(5)	0.30453(11)	0.70763(8)	0.39174(7)	0.016(1)
N(6)	0.24528(9)	0.85246(6)	0.41775(6)	0.015(1)
C(6)	0.28977(12)	0.75517(8)	0.33051(7)	0.018(1)
N(7)	0.22293(9)	0.81373(6)	0.56884(6)	0.015(1)
C(7)	0.19282(11)	0.84905(8)	0.61890(7)	0.016(1)
C(11)	0.19197(11)	0.64060(7)	0.59276(7)	0.015(1)
C(12)	0.07570(11)	0.66465(7)	0.56580(7)	0.016(1)
C(13)	-0.01866(12)	0.66316(8)	0.61118(8)	0.022(1)
C(14)	0.00174(13)	0.64070(9)	0.68517(8)	0.026(1)
C(15)	0.11612(14)	0.62093(9)	0.71257(8)	0.025(1)
C(16)	0.21111(12)	0.62058(8)	0.66716(7)	0.019(1)
C(21)	0.40775(11)	0.61334(7)	0.56311(7)	0.016(1)
C(22)	0.50553(11)	0.66256(7)	0.55285(7)	0.016(1)
C(23)	0.62230(12)	0.63330(8)	0.56778(8)	0.021(1)
C(24)	0.64134(13)	0.55525(9)	0.59426(8)	0.024(1)
C(25)	0.54354(13)	0.50623(8)	0.60587(8)	0.024(1)
C(26)	0.42833(13)	0.53449(8)	0.59021(7)	0.021(1)
C(31)	-0.05751(11)	0.76454(8)	0.45177(8)	0.019(1)
C(32)	0.04140(12)	0.60467(8)	0.42094(7)	0.020(1)
C(33)	-0.05982(13)	0.83866(8)	0.50170(8)	0.024(1)
C(34)	-0.06664(13)	0.79182(9)	0.37117(8)	0.025(1)
C(35)	0.06458(13)	0.60095(9)	0.33923(8)	0.026(1)
C(36)	-0.08537(13)	0.57472(9)	0.43262(8)	0.026(1)
Fe	0.26851(2)	0.75450(2)	0.48301(2)	0.012(1)
C(41)	0.58334(11)	0.79032(8)	0.45919(7)	0.019(1)
C(42)	0.50050(12)	0.82499(8)	0.60520(7)	0.018(1)
C(43)	0.60432(13)	0.72448(9)	0.40240(8)	0.025(1)
C(44)	0.55748(15)	0.87078(9)	0.41947(9)	0.030(1)
C(45)	0.48188(13)	0.91602(8)	0.59264(8)	0.024(1)
C(46)	0.62323(13)	0.81011(9)	0.64529(8)	0.027(1)
C(61)	0.25441(11)	0.83653(8)	0.34419(7)	0.017(1)

C(62)	0.23047(12)	0.89686(9)	0.29074(8)	0.022(1)
C(63)	0.20262(13)	0.97427(9)	0.31145(8)	0.026(1)
C(64)	0.19790(12)	0.99106(8)	0.38624(8)	0.023(1)
C(65)	0.21849(11)	0.92905(8)	0.43650(7)	0.018(1)
C(71)	0.15681(12)	0.89730(8)	0.68224(7)	0.019(1)
C(72)	0.04181(13)	0.86222(9)	0.71032(8)	0.025(1)
C(73)	0.13703(15)	0.98523(9)	0.65666(9)	0.028(1)
C(74)	0.25774(15)	0.89323(11)	0.74364(8)	0.032(1)
P(2)	0.46266(3)	0.76341(2)	0.51998(2)	0.013(1)
H	0.2580(15)	0.6048(11)	0.4982(10)	0.021
H(5)	0.3300(16)	0.6507(11)	0.3858(10)	0.025
H(6)	0.3020	0.7357	0.2826	0.022
H(13)	-0.0969	0.6774	0.5920	0.026
H(14)	-0.0626	0.6391	0.7162	0.031
H(15)	0.1304	0.6074	0.7631	0.030
H(16)	0.2892	0.6067	0.6870	0.023
H(23)	0.6886	0.6670	0.5597	0.026
H(24)	0.7204	0.5355	0.6044	0.029
H(25)	0.5560	0.4531	0.6247	0.029
H(26)	0.3623	0.5003	0.5978	0.025
H(31)	-0.1289	0.7304	0.4601	0.022
H(32)	0.0960	0.5632	0.4452	0.024
H(33A)	-0.1350	0.8681	0.4911	0.036
H(33B)	0.0076	0.8741	0.4927	0.036
H(33C)	-0.0535	0.8213	0.5533	0.036
H(34A)	-0.1375	0.8260	0.3617	0.038
H(34B)	-0.0732	0.7443	0.3390	0.038
H(34C)	0.0050	0.8226	0.3612	0.038
H(35A)	0.0482	0.5462	0.3206	0.038
H(35B)	0.1482	0.6148	0.3331	0.038
H(35C)	0.0121	0.6395	0.3117	0.038
H(36A)	-0.0946	0.5190	0.4148	0.039
H(36B)	-0.1439	0.6095	0.4053	0.039
H(36C)	-0.0985	0.5766	0.4852	0.039
H(41)	0.6592	0.7969	0.4911	0.023
H(42)	0.4409	0.8088	0.6407	0.022
H(43A)	0.6704	0.7406	0.3732	0.038

H(43B)	0.5316	0.7172	0.3698	0.038
H(43C)	0.6244	0.6735	0.4278	0.038
H(44A)	0.6278	0.8874	0.3944	0.044
H(44B)	0.5390	0.9122	0.4554	0.044
H(44C)	0.4891	0.8642	0.3833	0.044
H(45A)	0.4751	0.9430	0.6400	0.037
H(45B)	0.4085	0.9249	0.5610	0.037
H(45C)	0.5502	0.9383	0.5688	0.037
H(46A)	0.6340	0.8463	0.6879	0.040
H(46B)	0.6858	0.8207	0.6117	0.040
H(46C)	0.6286	0.7538	0.6620	0.040
H(62)	0.2335	0.8842	0.2401	0.027
H(63)	0.1870	1.0154	0.2756	0.031
H(64)	0.1808	1.0442	0.4023	0.028
H(65)	0.2135	0.9410	0.4872	0.022
H(72A)	0.0207	0.8926	0.7537	0.038
H(72B)	0.0547	0.8053	0.7236	0.038
H(72C)	-0.0233	0.8663	0.6716	0.038
H(73A)	0.1120	1.0179	0.6977	0.042
H(73B)	0.0748	0.9868	0.6160	0.042
H(73C)	0.2117	1.0070	0.6400	0.042
H(74A)	0.2357	0.9253	0.7858	0.048
H(74B)	0.3314	0.9150	0.7256	0.048
H(74C)	0.2706	0.8369	0.7588	0.048

Table S23. Anisotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P(1)	0.0115(1)	0.0139(1)	0.0164(1)	-0.0001(1)	-0.0007(1)	-0.0001(1)
C	0.0146(6)	0.0134(5)	0.0146(5)	0.0005(4)	0.0007(4)	0.0002(4)
C(5)	0.0122(6)	0.0179(6)	0.0192(6)	-0.0025(5)	0.0010(4)	0.0009(4)
N(6)	0.0113(5)	0.0168(5)	0.0168(5)	0.0021(4)	0.0008(4)	-0.0004(4)
C(6)	0.0167(6)	0.0230(6)	0.0142(6)	-0.0017(5)	0.0015(5)	0.0013(5)
N(7)	0.0123(5)	0.0147(5)	0.0165(5)	0.0012(4)	-0.0005(4)	-0.0001(4)
C(7)	0.0144(6)	0.0164(6)	0.0175(6)	0.0013(5)	-0.0006(5)	0.0004(4)
C(11)	0.0167(6)	0.0112(5)	0.0186(6)	-0.0007(4)	0.0020(5)	-0.0023(4)
C(12)	0.0154(6)	0.0145(5)	0.0181(6)	-0.0001(4)	0.0007(5)	-0.0025(4)
C(13)	0.0157(6)	0.0226(6)	0.0282(7)	0.0016(5)	0.0041(5)	-0.0013(5)
C(14)	0.0238(7)	0.0278(7)	0.0280(7)	0.0023(6)	0.0132(6)	-0.0014(6)
C(15)	0.0311(8)	0.0259(7)	0.0195(6)	0.0028(5)	0.0073(6)	0.0008(6)
C(16)	0.0210(6)	0.0188(6)	0.0183(6)	0.0018(5)	0.0013(5)	0.0007(5)
C(21)	0.0166(6)	0.0171(6)	0.0135(5)	-0.0011(4)	0.0008(4)	0.0021(5)
C(22)	0.0157(6)	0.0168(6)	0.0162(6)	-0.0014(4)	-0.0001(5)	0.0017(5)
C(23)	0.0152(6)	0.0251(7)	0.0236(6)	-0.0017(5)	-0.0007(5)	0.0027(5)
C(24)	0.0202(7)	0.0278(7)	0.0240(7)	-0.0011(5)	-0.0017(5)	0.0108(5)
C(25)	0.0293(7)	0.0200(6)	0.0227(6)	0.0025(5)	0.0019(5)	0.0100(5)
C(26)	0.0230(7)	0.0183(6)	0.0208(6)	0.0025(5)	0.0027(5)	0.0027(5)
C(31)	0.0124(6)	0.0181(6)	0.0245(7)	0.0007(5)	-0.0020(5)	0.0010(5)
C(32)	0.0195(6)	0.0158(6)	0.0226(6)	-0.0025(5)	-0.0043(5)	-0.0016(5)
C(33)	0.0186(7)	0.0236(7)	0.0299(7)	-0.0036(5)	-0.0013(5)	0.0058(5)
C(34)	0.0230(7)	0.0257(7)	0.0261(7)	0.0024(5)	-0.0054(5)	0.0042(5)
C(35)	0.0259(7)	0.0260(7)	0.0244(7)	-0.0076(5)	-0.0008(5)	-0.0048(5)
C(36)	0.0245(7)	0.0236(7)	0.0286(7)	-0.0010(5)	-0.0023(6)	-0.0084(5)
Fe	0.0102(1)	0.0121(1)	0.0122(1)	0.0001(1)	0.0007(1)	0.0006(1)
C(41)	0.0133(6)	0.0252(6)	0.0192(6)	-0.0001(5)	0.0028(5)	-0.0029(5)
C(42)	0.0170(6)	0.0200(6)	0.0181(6)	-0.0027(5)	0.0004(5)	-0.0009(5)
C(43)	0.0185(7)	0.0339(7)	0.0238(7)	-0.0041(6)	0.0066(5)	0.0006(6)
C(44)	0.0345(8)	0.0273(7)	0.0284(7)	0.0061(6)	0.0119(6)	-0.0046(6)
C(45)	0.0247(7)	0.0196(6)	0.0288(7)	-0.0043(5)	-0.0003(6)	-0.0025(5)
C(46)	0.0227(7)	0.0315(7)	0.0244(7)	-0.0060(6)	-0.0055(6)	0.0010(6)
C(61)	0.0123(6)	0.0220(6)	0.0167(6)	0.0023(5)	0.0011(4)	0.0000(5)

C(62)	0.0190(6)	0.0290(7)	0.0186(6)	0.0059(5)	0.0026(5)	0.0028(5)
C(63)	0.0230(7)	0.0267(7)	0.0280(7)	0.0129(6)	0.0035(6)	0.0054(5)
C(64)	0.0219(7)	0.0181(6)	0.0307(7)	0.0042(5)	0.0037(5)	0.0039(5)
C(65)	0.0149(6)	0.0174(6)	0.0217(6)	0.0009(5)	0.0014(5)	0.0007(5)
C(71)	0.0202(6)	0.0206(6)	0.0164(6)	-0.0028(5)	0.0002(5)	0.0036(5)
C(72)	0.0271(7)	0.0278(7)	0.0214(6)	-0.0016(5)	0.0066(5)	0.0029(6)
C(73)	0.0337(8)	0.0189(6)	0.0322(8)	-0.0031(6)	0.0050(6)	0.0040(6)
C(74)	0.0286(8)	0.0451(9)	0.0204(7)	-0.0080(6)	-0.0056(6)	0.0067(7)
P(2)	0.0112(1)	0.0144(1)	0.0145(1)	0.0000(1)	0.0008(1)	0.0000(1)

Table S24. Distances [Å] for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

atom-atom	distance	atom-atom	distance
P(1)-C(12)	1.8307(13)	P(1)-C(31)	1.8622(13)
P(1)-C(32)	1.8875(13)	P(1)-Fe	2.2882(4)
C-C(11)	1.4970(17)	C-C(21)	1.5050(17)
C-Fe	2.1054(12)	C-H	0.979(18)
C(5)-C(6)	1.3651(19)	C(5)-Fe	1.9053(13)
C(5)-H(5)	0.993(18)	N(6)-C(65)	1.3517(17)
N(6)-C(61)	1.3776(17)	N(6)-Fe	2.0152(11)
C(6)-C(61)	1.4300(18)	C(6)-H(6)	0.9500
N(7)-C(7)	1.1547(17)	N(7)-Fe	1.9459(11)
C(7)-C(71)	1.4837(17)	C(11)-C(16)	1.3968(18)
C(11)-C(12)	1.4159(18)	C(12)-C(13)	1.3907(19)
C(13)-C(14)	1.401(2)	C(13)-H(13)	0.9500
C(14)-C(15)	1.381(2)	C(14)-H(14)	0.9500
C(15)-C(16)	1.397(2)	C(15)-H(15)	0.9500
C(16)-H(16)	0.9500	C(21)-C(22)	1.3894(18)
C(21)-C(26)	1.4074(18)	C(22)-C(23)	1.4036(18)
C(22)-P(2)	1.8247(13)	C(23)-C(24)	1.389(2)
C(23)-H(23)	0.9500	C(24)-C(25)	1.393(2)
C(24)-H(24)	0.9500	C(25)-C(26)	1.384(2)
C(25)-H(25)	0.9500	C(26)-H(26)	0.9500
C(31)-C(33)	1.5281(19)	C(31)-C(34)	1.5329(19)
C(31)-H(31)	1.0000	C(32)-C(35)	1.5318(19)
C(32)-C(36)	1.5351(19)	C(32)-H(32)	1.0000
C(33)-H(33A)	0.9800	C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800	C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800	C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800	C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800	C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800	C(36)-H(36C)	0.9800
Fe-P(2)	2.2357(4)	C(41)-C(44)	1.532(2)
C(41)-C(43)	1.5323(19)	C(41)-P(2)	1.8653(13)
C(41)-H(41)	1.0000	C(42)-C(46)	1.5297(19)
C(42)-C(45)	1.5348(19)	C(42)-P(2)	1.8793(13)
C(42)-H(42)	1.0000	C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800	C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800	C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800	C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800	C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800	C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800	C(61)-C(62)	1.4064(19)
C(62)-C(63)	1.377(2)	C(62)-H(62)	0.9500
C(63)-C(64)	1.396(2)	C(63)-H(63)	0.9500
C(64)-C(65)	1.3831(19)	C(64)-H(64)	0.9500
C(65)-H(65)	0.9500	C(71)-C(74)	1.5332(19)
C(71)-C(72)	1.536(2)	C(71)-C(73)	1.5381(19)

C(72)-H(72A)	0.9800	C(72)-H(72B)	0.9800
C(72)-H(72C)	0.9800	C(73)-H(73A)	0.9800
C(73)-H(73B)	0.9800	C(73)-H(73C)	0.9800
C(74)-H(74A)	0.9800	C(74)-H(74B)	0.9800
C(74)-H(74C)	0.9800		

Table S25. Angles [°] for [{PC(sp^3)HP}Fe{-C(sp^2)H-CH-Py-}(NC^{t}Bu)] (**6-NC^{t}Bu**).

atom-atom-atom	angle	atom-atom-atom	angle
C(12)-P(1)-C(31)	107.07(6)	C(12)-P(1)-C(32)	98.64(6)
C(31)-P(1)-C(32)	103.15(6)	C(12)-P(1)-Fe	97.24(4)
C(31)-P(1)-Fe	123.52(4)	C(32)-P(1)-Fe	122.82(4)
C(11)-C-C(21)	116.89(10)	C(11)-C-Fe	107.23(8)
C(21)-C-Fe	118.10(8)	C(11)-C-H	107.0(10)
C(21)-C-H	104.2(10)	Fe-C-H	101.7(10)
C(6)-C(5)-Fe	117.30(9)	C(6)-C(5)-H(5)	118.4(10)
Fe-C(5)-H(5)	124.2(10)	C(65)-N(6)-C(61)	117.33(11)
C(65)-N(6)-Fe	128.73(9)	C(61)-N(6)-Fe	113.89(8)
C(5)-C(6)-C(61)	114.70(12)	C(5)-C(6)-H(6)	122.6
C(61)-C(6)-H(6)	122.6	C(7)-N(7)-Fe	178.17(10)
N(7)-C(7)-C(71)	177.69(14)	C(16)-C(11)-C(12)	118.35(12)
C(16)-C(11)-C	126.33(12)	C(12)-C(11)-C	115.27(11)
C(13)-C(12)-C(11)	120.68(12)	C(13)-C(12)-P(1)	129.43(10)
C(11)-C(12)-P(1)	109.72(9)	C(12)-C(13)-C(14)	119.99(13)
C(12)-C(13)-H(13)	120.0	C(14)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	119.47(13)	C(15)-C(14)-H(14)	120.3
C(13)-C(14)-H(14)	120.3	C(14)-C(15)-C(16)	121.03(13)
C(14)-C(15)-H(15)	119.5	C(16)-C(15)-H(15)	119.5
C(15)-C(16)-C(11)	120.34(13)	C(15)-C(16)-H(16)	119.8
C(11)-C(16)-H(16)	119.8	C(22)-C(21)-C(26)	118.66(12)
C(22)-C(21)-C	119.18(11)	C(26)-C(21)-C	121.83(12)
C(21)-C(22)-C(23)	120.40(12)	C(21)-C(22)-P(2)	112.86(9)
C(23)-C(22)-P(2)	126.74(10)	C(24)-C(23)-C(22)	120.33(13)
C(24)-C(23)-H(23)	119.8	C(22)-C(23)-H(23)	119.8
C(23)-C(24)-C(25)	119.43(13)	C(23)-C(24)-H(24)	120.3
C(25)-C(24)-H(24)	120.3	C(26)-C(25)-C(24)	120.38(13)
C(26)-C(25)-H(25)	119.8	C(24)-C(25)-H(25)	119.8
C(25)-C(26)-C(21)	120.78(13)	C(25)-C(26)-H(26)	119.6
C(21)-C(26)-H(26)	119.6	C(33)-C(31)-C(34)	109.37(11)
C(33)-C(31)-P(1)	112.38(9)	C(34)-C(31)-P(1)	110.09(9)
C(33)-C(31)-H(31)	108.3	C(34)-C(31)-H(31)	108.3
P(1)-C(31)-H(31)	108.3	C(35)-C(32)-C(36)	110.33(11)
C(35)-C(32)-P(1)	117.39(9)	C(36)-C(32)-P(1)	112.63(10)
C(35)-C(32)-H(32)	105.1	C(36)-C(32)-H(32)	105.1
P(1)-C(32)-H(32)	105.1	C(31)-C(33)-H(33A)	109.5
C(31)-C(33)-H(33B)	109.5	H(33A)-C(33)-H(33B)	109.5
C(31)-C(33)-H(33C)	109.5	H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5	C(31)-C(34)-H(34A)	109.5
C(31)-C(34)-H(34B)	109.5	H(34A)-C(34)-H(34B)	109.5
C(31)-C(34)-H(34C)	109.5	H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5	C(32)-C(35)-H(35A)	109.5
C(32)-C(35)-H(35B)	109.5	H(35A)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5	H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5	C(32)-C(36)-H(36A)	109.5

C(32)-C(36)-H(36B)	109.5	H(36A)-C(36)-H(36B)	109.5
C(32)-C(36)-H(36C)	109.5	H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5	C(5)-Fe-N(7)	172.72(5)
C(5)-Fe-N(6)	80.70(5)	N(7)-Fe-N(6)	92.27(4)
C(5)-Fe-C	92.18(5)	N(7)-Fe-C	94.68(5)
N(6)-Fe-C	171.70(5)	C(5)-Fe-P(2)	91.45(4)
N(7)-Fe-P(2)	91.86(3)	N(6)-Fe-P(2)	101.85(3)
C-Fe-P(2)	82.48(4)	C(5)-Fe-P(1)	91.17(4)
N(7)-Fe-P(1)	88.16(3)	N(6)-Fe-P(1)	99.90(3)
C-Fe-P(1)	75.82(4)	P(2)-Fe-P(1)	158.227(14)
C(44)-C(41)-C(43)	109.34(12)	C(44)-C(41)-P(2)	111.57(9)
C(43)-C(41)-P(2)	112.71(9)	C(44)-C(41)-H(41)	107.7
C(43)-C(41)-H(41)	107.7	P(2)-C(41)-H(41)	107.7
C(46)-C(42)-C(45)	109.68(11)	C(46)-C(42)-P(2)	116.60(9)
C(45)-C(42)-P(2)	112.86(9)	C(46)-C(42)-H(42)	105.6
C(45)-C(42)-H(42)	105.6	P(2)-C(42)-H(42)	105.6
C(41)-C(43)-H(43A)	109.5	C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5	C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5	H(43B)-C(43)-H(43C)	109.5
C(41)-C(44)-H(44A)	109.5	C(41)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5	C(41)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(42)-C(45)-H(45A)	109.5	C(42)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5	C(42)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5	H(45B)-C(45)-H(45C)	109.5
C(42)-C(46)-H(46A)	109.5	C(42)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5	C(42)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
N(6)-C(61)-C(62)	120.96(12)	N(6)-C(61)-C(6)	113.02(11)
C(62)-C(61)-C(6)	126.02(12)	C(63)-C(62)-C(61)	120.34(13)
C(63)-C(62)-H(62)	119.8	C(61)-C(62)-H(62)	119.8
C(62)-C(63)-C(64)	118.58(12)	C(62)-C(63)-H(63)	120.7
C(64)-C(63)-H(63)	120.7	C(65)-C(64)-C(63)	118.86(13)
C(65)-C(64)-H(64)	120.6	C(63)-C(64)-H(64)	120.6
N(6)-C(65)-C(64)	123.84(13)	N(6)-C(65)-H(65)	118.1
C(64)-C(65)-H(65)	118.1	C(7)-C(71)-C(74)	108.40(11)
C(7)-C(71)-C(72)	109.85(11)	C(74)-C(71)-C(72)	109.44(12)
C(7)-C(71)-C(73)	108.31(11)	C(74)-C(71)-C(73)	110.17(12)
C(72)-C(71)-C(73)	110.63(11)	C(71)-C(72)-H(72A)	109.5
C(71)-C(72)-H(72B)	109.5	H(72A)-C(72)-H(72B)	109.5
C(71)-C(72)-H(72C)	109.5	H(72A)-C(72)-H(72C)	109.5
H(72B)-C(72)-H(72C)	109.5	C(71)-C(73)-H(73A)	109.5
C(71)-C(73)-H(73B)	109.5	H(73A)-C(73)-H(73B)	109.5
C(71)-C(73)-H(73C)	109.5	H(73A)-C(73)-H(73C)	109.5
H(73B)-C(73)-H(73C)	109.5	C(71)-C(74)-H(74A)	109.5
C(71)-C(74)-H(74B)	109.5	H(74A)-C(74)-H(74B)	109.5
C(71)-C(74)-H(74C)	109.5	H(74A)-C(74)-H(74C)	109.5
H(74B)-C(74)-H(74C)	109.5	C(22)-P(2)-C(41)	103.18(6)

C(22)-P(2)-C(42)	100.73(6)	C(41)-P(2)-C(42)	103.43(6)
C(22)-P(2)-Fe	105.41(4)	C(41)-P(2)-Fe	124.74(4)
C(42)-P(2)-Fe	116.11(4)		

3.6 Crystal data for [{PC(sp^3))HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (7)

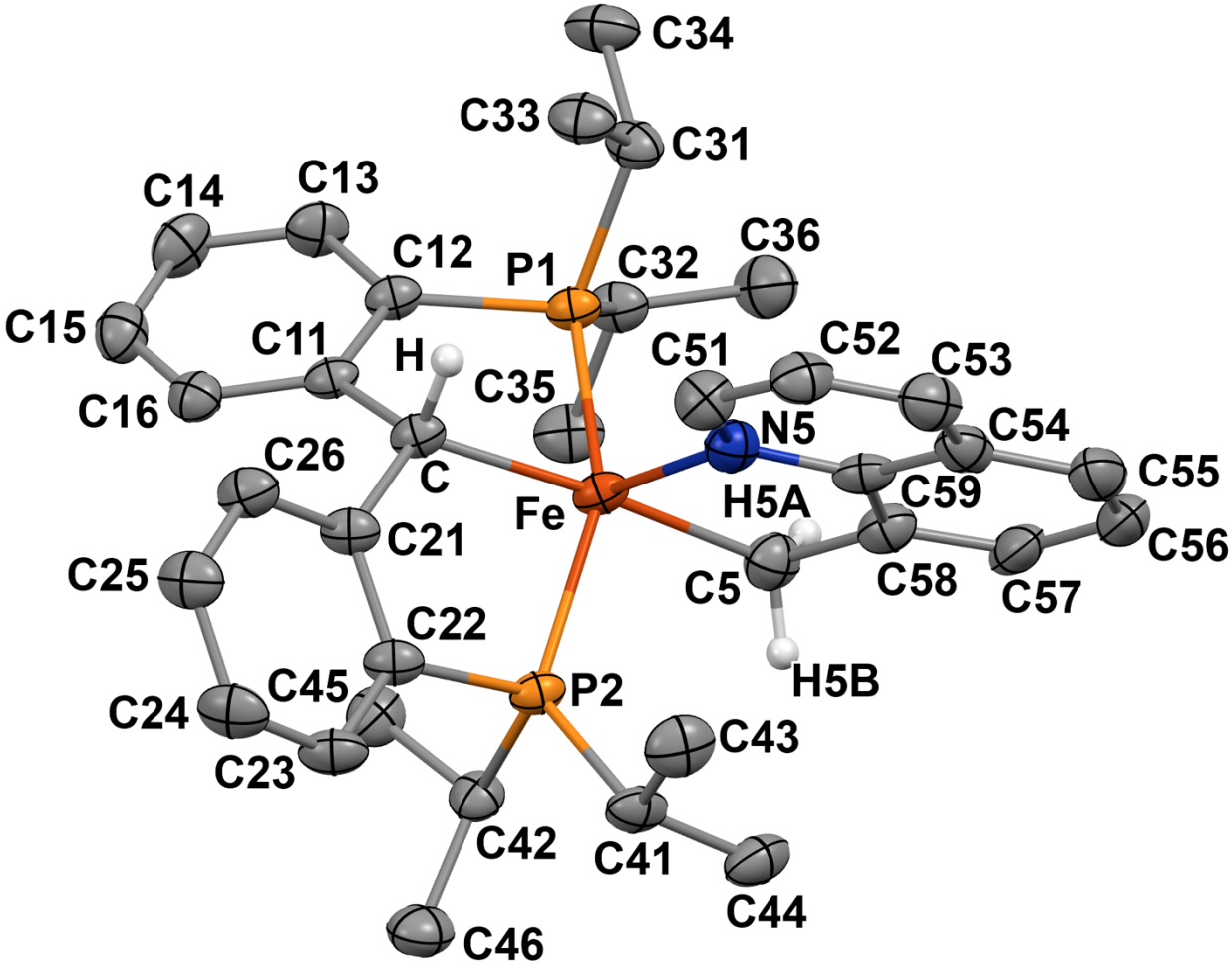


Figure S16. Thermal ellipsoid representation of [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**).

Table S26. Crystal data and structural refinement for {PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**).

Identification code	ZL_VI_145
Empirical formula	$C_{35}H_{45}FeNP_2$
Formula weight	597.51
Temperature	229(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
a	9.9076(17) Å
b	9.9398(19) Å
c	31.847(6) Å
α	90°
β	96.767(6)°
γ	90°
Volume	3114.4(10) Å^3
Z	4
Density (calculated)	1.274 g.cm^{-3}
Absorption coefficient (μ)	0.611 mm^{-1}
F(000)	1272
Crystal size	0.153 × 0.126 × 0.090 mm^3
θ range for data collection	2.094 to 28.305°
Index ranges	$-13 \leq h \leq 11$, $-13 \leq k \leq 13$, $-42 \leq l \leq 42$
Reflections collected	95297
Independent reflections	7755 [R_{int} = 0.1011]
Completeness to θ = 25.000°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7079
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7755 / 0 / 369
Goodness-of-fit on F^2	1.039
Final R indices [I>2σ(I)]	R_1 = 0.0539, wR_2 = 0.1272
R indices (all data)	R_1 = 0.0724, wR_2 = 0.1386
Extinction coefficient	n/a
Largest diff. peak and hole	1.516 and -0.815 e$^-$.Å^{-3}

Table S27. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

atom	x	y	z	U(eq)
Fe	0.28863(4)	0.33581(4)	0.11963(2)	0.024(1)
P(1)	0.14782(7)	0.18032(7)	0.08619(2)	0.024(1)
C	0.4156(3)	0.1688(3)	0.13063(8)	0.024(1)
P(2)	0.48445(7)	0.44913(7)	0.12928(2)	0.025(1)
C(5)	0.1712(3)	0.5048(3)	0.10284(10)	0.035(1)
C(11)	0.4029(3)	0.0753(2)	0.09337(8)	0.024(1)
C(12)	0.2716(3)	0.0576(3)	0.07153(8)	0.025(1)
C(13)	0.2494(3)	-0.0381(3)	0.03918(9)	0.033(1)
C(14)	0.3569(3)	-0.1108(3)	0.02655(9)	0.039(1)
C(15)	0.4874(3)	-0.0859(3)	0.04561(9)	0.035(1)
C(16)	0.5093(3)	0.0048(3)	0.07855(8)	0.029(1)
C(21)	0.5600(3)	0.1957(3)	0.15065(8)	0.027(1)
C(22)	0.6108(3)	0.3267(3)	0.15121(8)	0.027(1)
C(23)	0.7433(3)	0.3534(3)	0.17017(9)	0.034(1)
C(24)	0.8230(3)	0.2520(3)	0.18938(9)	0.038(1)
C(25)	0.7722(3)	0.1218(3)	0.18973(9)	0.036(1)
C(26)	0.6430(3)	0.0945(3)	0.17042(9)	0.033(1)
C(31)	0.0244(3)	0.0851(3)	0.11445(9)	0.031(1)
C(32)	0.0467(3)	0.2192(3)	0.03482(8)	0.030(1)
C(33)	0.0997(3)	0.0212(3)	0.15434(9)	0.036(1)
C(34)	-0.0585(3)	-0.0212(3)	0.08799(11)	0.042(1)
C(35)	0.1335(3)	0.2935(3)	0.00572(9)	0.036(1)
C(36)	-0.0822(3)	0.2986(3)	0.04066(11)	0.043(1)
C(41)	0.5226(3)	0.5976(3)	0.16375(9)	0.032(1)
C(42)	0.5390(3)	0.5024(3)	0.07793(8)	0.030(1)
C(43)	0.5019(4)	0.5653(3)	0.20965(9)	0.040(1)
C(44)	0.4369(4)	0.7195(3)	0.14802(10)	0.039(1)
C(45)	0.5336(3)	0.3802(3)	0.04866(9)	0.034(1)
C(46)	0.6778(3)	0.5708(3)	0.08056(10)	0.041(1)
C(51)	0.2604(3)	0.3087(3)	0.21536(9)	0.035(1)
C(52)	0.2124(3)	0.3459(3)	0.25300(9)	0.035(1)
C(53)	0.1232(3)	0.4481(3)	0.25401(10)	0.040(1)
C(54)	0.0795(3)	0.5155(3)	0.21673(9)	0.034(1)

C(55)	-0.0176(3)	0.6232(3)	0.21394(11)	0.042(1)
C(56)	-0.0549(3)	0.6845(3)	0.17676(12)	0.042(1)
C(57)	0.0054(3)	0.6466(3)	0.13878(11)	0.038(1)
C(58)	0.1001(3)	0.5455(3)	0.13984(9)	0.033(1)
C(59)	0.1316(3)	0.4787(3)	0.17900(8)	0.029(1)
N(5)	0.2225(2)	0.3708(2)	0.17859(7)	0.031(1)
H	0.369(3)	0.124(3)	0.1523(10)	0.036
H(5A)	0.099(4)	0.510(4)	0.0814(12)	0.053
H(5B)	0.213(4)	0.585(4)	0.0953(12)	0.053
H(13)	0.1608	-0.0531	0.0259	0.040
H(14)	0.3414	-0.1764	0.0053	0.046
H(15)	0.5615	-0.1310	0.0361	0.042
H(16)	0.5985	0.0195	0.0913	0.034
H(23)	0.7780	0.4414	0.1697	0.041
H(24)	0.9114	0.2709	0.2022	0.045
H(25)	0.8258	0.0524	0.2031	0.044
H(26)	0.6098	0.0059	0.1705	0.040
H(31)	-0.0407	0.1512	0.1238	0.037
H(32)	0.0183	0.1327	0.0211	0.036
H(33A)	0.1659	-0.0431	0.1463	0.054
H(33B)	0.0351	-0.0246	0.1700	0.054
H(33C)	0.1459	0.0907	0.1719	0.054
H(34A)	-0.1097	0.0215	0.0637	0.063
H(34B)	-0.1208	-0.0645	0.1051	0.063
H(34C)	0.0023	-0.0880	0.0784	0.063
H(35A)	0.2103	0.2376	0.0007	0.055
H(35B)	0.1663	0.3770	0.0190	0.055
H(35C)	0.0792	0.3129	-0.0209	0.055
H(36A)	-0.1311	0.3190	0.0132	0.064
H(36B)	-0.0576	0.3818	0.0556	0.064
H(36C)	-0.1396	0.2453	0.0569	0.064
H(41)	0.6194	0.6211	0.1631	0.038
H(42)	0.4708	0.5678	0.0651	0.036
H(43A)	0.4063	0.5487	0.2115	0.060
H(43B)	0.5322	0.6409	0.2276	0.060
H(43C)	0.5542	0.4860	0.2189	0.060
H(44A)	0.4507	0.7388	0.1190	0.059

H(44B)	0.4641	0.7969	0.1656	0.059
H(44C)	0.3416	0.7003	0.1495	0.059
H(45A)	0.5596	0.4070	0.0214	0.052
H(45B)	0.4420	0.3442	0.0449	0.052
H(45C)	0.5959	0.3119	0.0611	0.052
H(46A)	0.6989	0.5911	0.0523	0.062
H(46B)	0.7466	0.5113	0.0945	0.062
H(46C)	0.6759	0.6536	0.0966	0.062
H(51)	0.3221	0.2368	0.2158	0.042
H(52)	0.2424	0.2993	0.2780	0.042
H(53)	0.0913	0.4733	0.2795	0.048
H(55)	-0.0553	0.6511	0.2382	0.050
H(56)	-0.1209	0.7528	0.1752	0.050
H(57)	-0.0211	0.6920	0.1132	0.046

Table S28. Anisotropic displacement parameters (Å^2) for [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe	0.0296(2)	0.0213(2)	0.0206(2)	0.0007(1)	-0.0033(1)	-0.0038(2)
P(1)	0.0263(3)	0.0234(3)	0.0208(3)	0.0008(2)	-0.0023(2)	-0.0045(3)
C	0.0275(13)	0.0229(12)	0.0209(11)	0.0006(10)	-0.0036(9)	-0.0036(10)
P(2)	0.0311(4)	0.0220(3)	0.0199(3)	-0.0012(2)	0.0003(2)	-0.0056(3)
C(5)	0.0395(17)	0.0337(15)	0.0324(15)	-0.0064(12)	0.0048(12)	-0.0023(13)
C(11)	0.0294(13)	0.0202(11)	0.0206(11)	0.0034(9)	0.0001(10)	-0.0037(10)
C(12)	0.0303(14)	0.0238(12)	0.0215(12)	0.0006(10)	-0.0008(10)	-0.0046(10)
C(13)	0.0362(15)	0.0355(15)	0.0265(13)	-0.0076(11)	-0.0028(11)	-0.0067(12)
C(14)	0.0532(19)	0.0347(16)	0.0277(14)	-0.0103(12)	0.0037(13)	0.0003(14)
C(15)	0.0414(16)	0.0340(15)	0.0299(14)	0.0008(12)	0.0091(12)	0.0050(13)
C(16)	0.0299(14)	0.0284(13)	0.0276(13)	0.0043(11)	0.0021(10)	0.0004(11)
C(21)	0.0286(13)	0.0290(13)	0.0213(12)	0.0013(10)	-0.0029(10)	-0.0058(11)
C(22)	0.0298(13)	0.0288(13)	0.0214(12)	0.0009(10)	-0.0026(10)	-0.0072(11)
C(23)	0.0364(16)	0.0336(15)	0.0305(14)	0.0023(12)	-0.0037(12)	-0.0132(12)
C(24)	0.0305(15)	0.0460(18)	0.0334(15)	0.0042(13)	-0.0098(12)	-0.0097(13)
C(25)	0.0333(15)	0.0399(16)	0.0340(15)	0.0090(13)	-0.0065(12)	-0.0023(13)
C(26)	0.0329(15)	0.0300(14)	0.0339(15)	0.0034(12)	-0.0059(11)	-0.0034(12)
C(31)	0.0295(14)	0.0330(14)	0.0313(14)	0.0069(12)	0.0040(11)	-0.0021(11)
C(32)	0.0307(14)	0.0314(14)	0.0264(13)	0.0028(11)	-0.0061(10)	-0.0047(11)
C(33)	0.0393(16)	0.0365(16)	0.0323(15)	0.0100(12)	0.0027(12)	-0.0066(13)
C(34)	0.0358(17)	0.0414(17)	0.0470(18)	0.0081(14)	-0.0035(13)	-0.0150(14)
C(35)	0.0450(17)	0.0411(16)	0.0215(13)	0.0052(12)	-0.0027(12)	-0.0060(14)
C(36)	0.0353(16)	0.0414(17)	0.0494(19)	0.0082(15)	-0.0062(14)	0.0027(14)
C(41)	0.0373(15)	0.0294(14)	0.0288(14)	-0.0075(11)	0.0040(11)	-0.0112(12)
C(42)	0.0365(15)	0.0280(13)	0.0249(13)	0.0037(11)	0.0057(11)	0.0002(11)
C(43)	0.0536(19)	0.0419(17)	0.0228(13)	-0.0075(12)	0.0004(12)	-0.0077(15)
C(44)	0.059(2)	0.0256(14)	0.0340(15)	-0.0044(12)	0.0103(14)	-0.0079(14)
C(45)	0.0445(17)	0.0354(15)	0.0239(13)	0.0004(12)	0.0057(12)	0.0008(13)
C(46)	0.0470(18)	0.0383(17)	0.0407(17)	0.0021(14)	0.0139(14)	-0.0103(14)
C(51)	0.0388(16)	0.0357(15)	0.0295(14)	0.0008(12)	0.0018(12)	0.0004(13)
C(52)	0.0454(17)	0.0339(15)	0.0261(13)	0.0004(11)	0.0081(12)	-0.0073(13)
C(53)	0.0445(18)	0.0420(17)	0.0360(16)	-0.0078(13)	0.0114(13)	-0.0084(14)
C(54)	0.0309(15)	0.0363(15)	0.0342(15)	-0.0099(12)	0.0070(11)	-0.0099(12)
C(55)	0.0368(17)	0.0377(17)	0.0518(19)	-0.0117(15)	0.0115(14)	-0.0070(13)

C(56)	0.0334(16)	0.0254(14)	0.066(2)	-0.0026(14)	0.0054(15)	0.0001(12)
C(57)	0.0352(16)	0.0207(13)	0.057(2)	-0.0008(13)	-0.0028(14)	0.0001(11)
C(58)	0.0357(15)	0.0280(14)	0.0333(15)	-0.0011(11)	0.0003(12)	-0.0043(12)
C(59)	0.0313(14)	0.0257(13)	0.0281(13)	0.0014(11)	-0.0035(10)	-0.0108(11)
N(5)	0.0345(13)	0.0304(12)	0.0278(12)	-0.0040(9)	0.0046(9)	-0.0029(10)

Table S29. Distances [Å] for [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**).

atom-atom	distance	atom-atom	distance
Fe-C(5)	2.078(3)	Fe-C	2.087(3)
Fe-N(5)	2.090(2)	Fe-P(2)	2.2331(8)
Fe-P(1)	2.2625(8)	P(1)-C(12)	1.829(3)
P(1)-C(32)	1.856(3)	P(1)-C(31)	1.860(3)
C-C(11)	1.501(3)	C-C(21)	1.519(3)
C-H	0.98(3)	P(2)-C(22)	1.825(3)
P(2)-C(41)	1.851(3)	P(2)-C(42)	1.859(3)
C(5)-C(58)	1.498(4)	C(5)-H(5A)	0.93(4)
C(5)-H(5B)	0.94(4)	C(11)-C(16)	1.394(4)
C(11)-C(12)	1.412(4)	C(12)-C(13)	1.400(4)
C(13)-C(14)	1.386(4)	C(13)-H(13)	0.9400
C(14)-C(15)	1.385(4)	C(14)-H(14)	0.9400
C(15)-C(16)	1.381(4)	C(15)-H(15)	0.9400
C(16)-H(16)	0.9400	C(21)-C(22)	1.395(4)
C(21)-C(26)	1.401(4)	C(22)-C(23)	1.404(4)
C(23)-C(24)	1.379(4)	C(23)-H(23)	0.9400
C(24)-C(25)	1.389(4)	C(24)-H(24)	0.9400
C(25)-C(26)	1.381(4)	C(25)-H(25)	0.9400
C(26)-H(26)	0.9400	C(31)-C(34)	1.529(4)
C(31)-C(33)	1.533(4)	C(31)-H(31)	0.9900
C(32)-C(35)	1.527(4)	C(32)-C(36)	1.531(4)
C(32)-H(32)	0.9900	C(33)-H(33A)	0.9700
C(33)-H(33B)	0.9700	C(33)-H(33C)	0.9700
C(34)-H(34A)	0.9700	C(34)-H(34B)	0.9700
C(34)-H(34C)	0.9700	C(35)-H(35A)	0.9700
C(35)-H(35B)	0.9700	C(35)-H(35C)	0.9700
C(36)-H(36A)	0.9700	C(36)-H(36B)	0.9700
C(36)-H(36C)	0.9700	C(41)-C(44)	1.530(4)
C(41)-C(43)	1.533(4)	C(41)-H(41)	0.9900
C(42)-C(46)	1.528(4)	C(42)-C(45)	1.528(4)
C(42)-H(42)	0.9900	C(43)-H(43A)	0.9700
C(43)-H(43B)	0.9700	C(43)-H(43C)	0.9700
C(44)-H(44A)	0.9700	C(44)-H(44B)	0.9700
C(44)-H(44C)	0.9700	C(45)-H(45A)	0.9700
C(45)-H(45B)	0.9700	C(45)-H(45C)	0.9700
C(46)-H(46A)	0.9700	C(46)-H(46B)	0.9700
C(46)-H(46C)	0.9700	C(51)-N(5)	1.338(4)
C(51)-C(52)	1.391(4)	C(51)-H(51)	0.9400
C(52)-C(53)	1.349(5)	C(52)-H(52)	0.9400
C(53)-C(54)	1.387(4)	C(53)-H(53)	0.9400
C(54)-C(59)	1.410(4)	C(54)-C(55)	1.436(4)
C(55)-C(56)	1.344(5)	C(55)-H(55)	0.9400
C(56)-C(57)	1.460(5)	C(56)-H(56)	0.9400
C(57)-C(58)	1.372(4)	C(57)-H(57)	0.9400
C(58)-C(59)	1.415(4)	C(59)-N(5)	1.401(4)

Table S30. Angles [°] for [{PC(sp^3)HP}Fe{-C(sp^3)H$_2$-N^{quin}-}] (**7**).

atom-atom-atom	angle	atom-atom-atom	angle
C(5)-Fe-C	174.01(11)	C(5)-Fe-N(5)	82.59(11)
C-Fe-N(5)	103.20(10)	C(5)-Fe-P(2)	94.51(9)
C-Fe-P(2)	83.17(8)	N(5)-Fe-P(2)	98.72(7)
C(5)-Fe-P(1)	97.80(9)	C-Fe-P(1)	82.06(7)
N(5)-Fe-P(1)	107.18(7)	P(2)-Fe-P(1)	152.49(3)
C(12)-P(1)-C(32)	102.86(13)	C(12)-P(1)-C(31)	106.43(13)
C(32)-P(1)-C(31)	102.42(13)	C(12)-P(1)-Fe	100.44(9)
C(32)-P(1)-Fe	120.76(9)	C(31)-P(1)-Fe	121.59(10)
C(11)-C-C(21)	115.3(2)	C(11)-C-Fe	111.52(17)
C(21)-C-Fe	116.72(18)	C(11)-C-H	105.8(19)
C(21)-C-H	106.4(19)	Fe-C-H	98.9(19)
C(22)-P(2)-C(41)	102.82(13)	C(22)-P(2)-C(42)	105.63(13)
C(41)-P(2)-C(42)	103.55(13)	C(22)-P(2)-Fe	105.18(9)
C(41)-P(2)-Fe	126.66(10)	C(42)-P(2)-Fe	111.13(9)
C(58)-C(5)-Fe	108.5(2)	C(58)-C(5)-H(5A)	100(2)
Fe-C(5)-H(5A)	126(2)	C(58)-C(5)-H(5B)	104(2)
Fe-C(5)-H(5B)	120(2)	H(5A)-C(5)-H(5B)	95(3)
C(16)-C(11)-C(12)	117.4(2)	C(16)-C(11)-C	125.6(2)
C(12)-C(11)-C	117.0(2)	C(13)-C(12)-C(11)	120.2(3)
C(13)-C(12)-P(1)	126.1(2)	C(11)-C(12)-P(1)	113.41(19)
C(14)-C(13)-C(12)	120.6(3)	C(14)-C(13)-H(13)	119.7
C(12)-C(13)-H(13)	119.7	C(15)-C(14)-C(13)	119.3(3)
C(15)-C(14)-H(14)	120.3	C(13)-C(14)-H(14)	120.3
C(16)-C(15)-C(14)	120.3(3)	C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8	C(15)-C(16)-C(11)	121.9(3)
C(15)-C(16)-H(16)	119.1	C(11)-C(16)-H(16)	119.1
C(22)-C(21)-C(26)	118.2(2)	C(22)-C(21)-C	119.3(2)
C(26)-C(21)-C	122.4(2)	C(21)-C(22)-C(23)	120.0(3)
C(21)-C(22)-P(2)	112.79(19)	C(23)-C(22)-P(2)	127.1(2)
C(24)-C(23)-C(22)	120.7(3)	C(24)-C(23)-H(23)	119.7
C(22)-C(23)-H(23)	119.7	C(23)-C(24)-C(25)	119.7(3)
C(23)-C(24)-H(24)	120.1	C(25)-C(24)-H(24)	120.1
C(26)-C(25)-C(24)	119.8(3)	C(26)-C(25)-H(25)	120.1
C(24)-C(25)-H(25)	120.1	C(25)-C(26)-C(21)	121.5(3)
C(25)-C(26)-H(26)	119.2	C(21)-C(26)-H(26)	119.2
C(34)-C(31)-C(33)	110.3(2)	C(34)-C(31)-P(1)	115.2(2)
C(33)-C(31)-P(1)	109.17(19)	C(34)-C(31)-H(31)	107.3
C(33)-C(31)-H(31)	107.3	P(1)-C(31)-H(31)	107.3
C(35)-C(32)-C(36)	111.3(3)	C(35)-C(32)-P(1)	110.56(19)
C(36)-C(32)-P(1)	111.8(2)	C(35)-C(32)-H(32)	107.7
C(36)-C(32)-H(32)	107.7	P(1)-C(32)-H(32)	107.7
C(31)-C(33)-H(33A)	109.5	C(31)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5	C(31)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5	H(33B)-C(33)-H(33C)	109.5
C(31)-C(34)-H(34A)	109.5	C(31)-C(34)-H(34B)	109.5

H(34A)-C(34)-H(34B)	109.5	C(31)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5	H(34B)-C(34)-H(34C)	109.5
C(32)-C(35)-H(35A)	109.5	C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5	C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5	H(35B)-C(35)-H(35C)	109.5
C(32)-C(36)-H(36A)	109.5	C(32)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5	C(32)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5	H(36B)-C(36)-H(36C)	109.5
C(44)-C(41)-C(43)	110.3(3)	C(44)-C(41)-P(2)	111.8(2)
C(43)-C(41)-P(2)	111.0(2)	C(44)-C(41)-H(41)	107.9
C(43)-C(41)-H(41)	107.9	P(2)-C(41)-H(41)	107.9
C(46)-C(42)-C(45)	110.7(2)	C(46)-C(42)-P(2)	115.6(2)
C(45)-C(42)-P(2)	108.51(19)	C(46)-C(42)-H(42)	107.2
C(45)-C(42)-H(42)	107.2	P(2)-C(42)-H(42)	107.2
C(41)-C(43)-H(43A)	109.5	C(41)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5	C(41)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5	H(43B)-C(43)-H(43C)	109.5
C(41)-C(44)-H(44A)	109.5	C(41)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5	C(41)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(42)-C(45)-H(45A)	109.5	C(42)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5	C(42)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5	H(45B)-C(45)-H(45C)	109.5
C(42)-C(46)-H(46A)	109.5	C(42)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5	C(42)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5	H(46B)-C(46)-H(46C)	109.5
N(5)-C(51)-C(52)	122.9(3)	N(5)-C(51)-H(51)	118.6
C(52)-C(51)-H(51)	118.6	C(53)-C(52)-C(51)	120.8(3)
C(53)-C(52)-H(52)	119.6	C(51)-C(52)-H(52)	119.6
C(52)-C(53)-C(54)	118.8(3)	C(52)-C(53)-H(53)	120.6
C(54)-C(53)-H(53)	120.6	C(53)-C(54)-C(59)	119.7(3)
C(53)-C(54)-C(55)	123.5(3)	C(59)-C(54)-C(55)	116.8(3)
C(56)-C(55)-C(54)	120.3(3)	C(56)-C(55)-H(55)	119.8
C(54)-C(55)-H(55)	119.8	C(55)-C(56)-C(57)	121.1(3)
C(55)-C(56)-H(56)	119.5	C(57)-C(56)-H(56)	119.5
C(58)-C(57)-C(56)	120.9(3)	C(58)-C(57)-H(57)	119.5
C(56)-C(57)-H(57)	119.5	C(57)-C(58)-C(59)	116.4(3)
C(57)-C(58)-C(5)	124.2(3)	C(59)-C(58)-C(5)	119.4(3)
N(5)-C(59)-C(54)	120.4(3)	N(5)-C(59)-C(58)	115.2(3)
C(54)-C(59)-C(58)	124.4(3)	C(51)-N(5)-C(59)	117.3(2)
C(51)-N(5)-Fe	128.6(2)	C(59)-N(5)-Fe	113.95(18)

4. References

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