Supporting Information for

Ketone Hydrogenation Catalyzed by a New Iron(II)-PNN Complex

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1. General Considerations

All reactions were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques. All solvents were reagent grade or better. Tetrahydrofuran (THF), diethyl ether, benzene, toluene, and pentane were refluxed over sodium and distilled under a nitrogen atmosphere. Acetonitrile and ethanol were refluxed for several hours over calcium hydride and magnesium, respectively, and were distilled under nitrogen. Methylene chloride (DCM) as well as the deuterated solvents were purged with argon and stored in the glove box over 3 Å molecular sieves. All commercially available reagents were used as received. $[Fe(H)(CO)_2L_{PNN}](BF_4)$ (**1**) and $[FeBr_2L_{PNN}]$ (**7**) were prepared according to previously reported procedures.[1] NMR spectra were recorded using Bruker Avance III 300 and Avance III 400 spectrometers. Chemical shifts were referenced to the residual solvent peaks (^{1}H,

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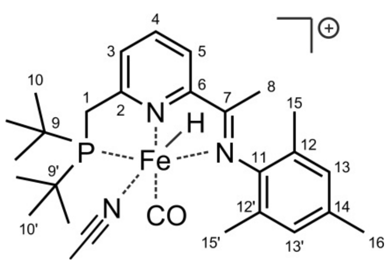
^{13}C),[2] as well as to the external standards phosphoric acid (85% solution in D_2O) at 0.0 ppm (^{31}P) and neat perfluorobenzene at -164.9 ppm (^{19}F). Chemical shifts are reported in ppm and coupling constants (*J*) in Hz. NMR assignments were assisted by ^{1}H-^{1}H-COSY, ^{1}H-^{31}P-HMQC, ^{1}H-^{13}C-HSQC, ^{1}H-^{13}C-HMBC, and ^{13}C-DEPTQ NMR spectroscopy, as required. IR spectra were recorded on a Nicolet FT-IR spectrophotometer. ESI-MS spectra were recorded on a Micromass ZQ V4.1 by the Chemical Research Support Unit of the Weizmann Institute of Science. Elemental analyses were performed on a Thermo Finnigan Italia SpA (Flash EA 1112) CHN elemental analyzer by the Chemical Research Support Unit of the Weizmann Institute of Science. Note that some complexes gave unsatisfactory carbon analyses but acceptable hydrogen and nitrogen content because of a combustion problem due to the tetrafluoroborate anion,[3] and discrepancies of similar magnitude have been previously reported in such complexes.[4]

2. Complex Synthesis

[Fe(H)(CO)(MeCN)L_{PNN}](BF_4) (1)

Typically, ca. 100 mg [Fe(H)$(CO)_2L_{PNN}$](BF_4) (**3**, 0.1680 mmol) were dissolved in 5 ml MeCN, and the solution was refluxed under nitrogen for 6 h. Afterwards, the solvent was removed under reduced pressure, and the residue was dissolved in ca. 1 ml dichloromethane (DCM). After filtration over celite, the product was precipitated by dropwise addition of the DCM solution to ca. 20 ml pentane while stirring vigorously. After removal of the supernatant and repeated washings with pentane, [Fe(H)(CO)(MeCN)L_{PNN}](BF_4) (**1**) was obtained as a purple powder. Yield 97 mg, 95 %.

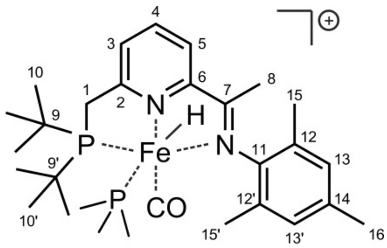
Note that the product usually contains ca. 2 – 5% starting material under these optimized conditions. While upon scaling up the reaction this value further increases, the yield decreases when the reaction time is increased, and higher amounts of paramagnetic impurities are formed. Note further, that the amount of paramagnetic impurities further increases when the concentration of **3** in the reaction mixture is decreased.



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = -17.23 (d, 1H, $^{2}J_{HP}$ = 65.2 Hz, Fe–*H*), 1.16 (d, 9H, $^{3}J_{HP}$ = 13.2 Hz, H_{10}'),1.35 (d, 9H, $^{3}J_{HP}$ = 13.4 Hz, H_{10}), 2.08 (s, 3H, H_{15}'), 2.09 (s, 3H, CH_3CN), 2.17 (s, 3H, H_{15}), 2.20 (s, 3H, H_8), 2.35 (s, 3H, H_{16}), 3.83 (s, 1H, H_1'), 3.85 (d, 1H, $^{2}J_{HP}$ = 4.0 Hz, H_1), 7.00 (s, 1H, H_{13}'), 7.05 (s, 1H, H_{13}), 7.84 (d, 1H, $^{3}J_{HH}$ = 7.8 Hz, H_3), 7.93 (d, 1H, $^{3}J_{HH}$ = 7.8 Hz, H_5), 8.09 (vt, 1H, $^{3}J_{HH}$ = 7.8 Hz, H_4) ppm. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = -17.31 (d, 1H, $^{2}J_{HP}$ = 64.9 Hz, Fe–*H*), 1.15 (d, 9H, $^{3}J_{HP}$ = 13.0 Hz, H_{10}'), 1.36 (d, 9H, $^{3}J_{HP}$ = 13.3 Hz, H_{10}), 2.08 (s, 3H, H_{15}'), 2.14 (s, 3H, CH_3CN), 2.17 (s, 3H, H_{15}), 2.20 (s, 3H, H_8), 2.33 (s, 3H, H_{16}), 3.81 (dd, 1H, $^{2}J_{HP}$ = 13.2 Hz, $^{2}J_{HH}$ = 17.7 Hz, H_1'), 4.08 (dd, 1H, $^{2}J_{HP}$ = 5.5 Hz, $^{2}J_{HH}$ = 17.8 Hz, H_1), 6.95 (s, 1H, H_{13}'), 7.00 (s, 1H, H_{13}), 7.87 (d, 1H, $^{3}J_{HH}$ = 7.8 Hz, H_3), 7.90 (d, 1H, $^{3}J_{HH}$ = 8.0 Hz, H_5), 8.04 (vt, 1H, $^{3}J_{HH}$ = 7.4 Hz, H_4) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 298 K): δ = 4.2 (s, *C*H_3CN), 17.5 (s, C_8), 18.3 (s, C_{15}'), 18.5 (s, C_{15}), 20.9 (s, C_{16}), 27.8 (s, C_{10}'), 29.8 (d, $^{2}J_{CP}$ = 2.9 Hz, C_{10}), 36.3 (d, $^{1}J_{CP}$ = 12.9 Hz, C_1), 37.3 (d, $^{1}J_{CP}$ = 22.1 Hz, C_9'), 37.4 (d, $^{1}J_{CP}$ = 11.9 Hz, C_9), 124.2 (s, C_5), 125.4 (d, $^{3}J_{CP}$ = 8.5 Hz, C_3), 127.5 (d, $^{3}J_{CP}$ = 5.8 Hz, CH_3*C*N), 127.85 (s, C_{12}), 127.94 (s, C_{12}'), 129.7 (s, C_{13}), 130.1 (s, C_{13}'), 136.3 (s, C_{14}), 138.3 (s, C_4), 147.5 (s, C_{11}), 155.6 (d, J_{CP} = 4.9 Hz, C_6), 163.2 (d, $^{2}J_{CP}$ = 6.4 Hz, C_2), 172.2 (s, C_7), 217.4 (d, $^{2}J_{CP}$ = 21.8 Hz, *C*O) ppm. **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$, 298 K): δ = 4.2 (s, *C*H_3CN), 17.4 (s, C_8), 18.2 (s, C_{15}'), 18.4 (s, C_{15}), 20.9 (s, C_{16}), 27.8 (s, C_{10}'), 29.7 (d, $^{2}J_{CP}$ = 2.3 Hz, C_{10}'), 36.2 (d, $^{1}J_{CP}$ = 15.8 Hz, C_1), 36.9 (d, $^{1}J_{CP}$ = 22.0 Hz, C_9'), 37.1 (d, $^{1}J_{CP}$ = 10.8 Hz, C_9), 123.9 (s, C_5), 125.5 (d, $^{3}J_{CP}$ = 8.4 Hz, C_3), 127.3 (s, C_{12}'), 127.5 (s, C_{12}), 129.6 (s, C_{13}), 129.8 (s, C_{13}'), 135.8 (s, C_{14}), 138.0 (s, C_4), 147.2 (s, C_{11}), 154.9 (d, J_{CP} = 5.1 Hz, C_6), 163.1 (d, $^{2}J_{CP}$ = 6.4 Hz, C_2), 171.5 (s, C_7), 216.9 (d, $^{2}J_{CP}$ = 21.6 Hz, *C*O) ppm. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 298 K): δ = 114.0 (s) ppm. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, 298 K): δ = 113.9 (s) ppm. **^{19}F{^{1}H} NMR** (377 MHz, CD_2Cl_2, 298 K): δ = -146.2 (s, BF_4^-) ppm. **IR(NaCl):** $\tilde{\nu}$ = 1924 cm^{-1} (ν_{CO}). **Anal. calcd.** for $C_{28}H_{41}BF_4FeN_3OP$: C, 55.20; H, 6.78; N, 6.90; Found: C, 53.89; H, 6.64; N, 6.42. **MS** (ESI, acetonitrile, m/z^+): 481.3 $[M\text{-}CH_3CN\text{-}BF_4]^+$ = $[C_{26}H_{38}FeN_2OP]^+$; (ESI, acetonitrile, m/z^-): 87.0 $[BF_4]^-$. **Crystal Data:** $C_{28}H_{41}FeN_3OP$ + BF_4, black plate, 0.50 x 0.30 x 0.10 mm^3, Monoclinic *P2₁/c*, a = 17.8880(11) Å, b = 8.6252(5) Å, c = 21.0338(13) Å, β = 111.094(2)°, from 30° of data, T = 100(2) K, V = 3027.8(3) Å^3, Z = 4, fw = 609.27, D_c=1.337 Mg·m^{-3}, μ = 0.601 mm^{-1}; structure deposited CCDC-1438624.

[Fe(H)(CO)(PMe$_3$)L$_{PNN}$](BF$_4$) (5a)

To a solution of 51.1 mg [Fe(H)(CO)(MeCN)L$_{PNN}$](BF$_4$) (**1**) (0.0839 mmol) in 4.5 ml DCM, 0.1 ml PMe_3 (73.5 mg, 0.9661 mmol) were added via a microliter syringe, and the solution was stirred for 30 min. at room temperature. All volatiles were removed by vacuum, and the residue was taken up in a small amount of DCM. After filtration over celite, the product was precipitated by dropwise addition of the DCM solution to ca. 20 ml Et_2O while stirring vigorously, and the precipitate was washed twice with Et_2O. After drying in vacuum, $[Fe(H)(CO)(PMe_3)L_{PNN}](BF_4)$ (**5a**) was obtained as a red-brown powder. Yield 47.6 mg, 88 %.



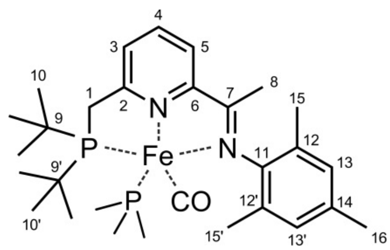
^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = -10.35 (dd, 1H, $^2J_{HP}$ = 33.1, 82.0 Hz, Fe–*H*), 1.06 (d, 9H, $^2J_{HP}$ = 6.7 Hz, P(C*H*$_3$)$_3$), 1.18 (br, d, 9H, $^3J_{HP}$ = 12.6 Hz, H_{10}'), 1.32 (d, 9H, $^3J_{HP}$ = 13.8 Hz, H_{10}), 1.95 (s, 3H, H_{15}), 2.25 (d, 3H, J_{HP} = 2.6 Hz, H_8), 2.33 (s, 3H, H_{16}), 2.35 (s, 3H, H_{15}'), 3.48 (dd, 1H, $^2J_{HP}$ = 4.6 Hz, $^2J_{HH}$ = 18.4 Hz, H_1), 3.86 (dd, 1H, $^2J_{HP}$ = 13.5 Hz, $^2J_{HH}$ = 18.3 Hz, H_1'), 7.00 (s, 1H, H_{13}), 7.01 (s, 1H, H_{13}'), 7.79 (d, 1H, $^3J_{HH}$ = 7.7 Hz, H_3), 7.99 (d, 1H, $^3J_{HH}$ = 7.9 Hz, H_5), 8.06 (dvt, 1H, J_{HP} = 2.1 Hz, $^3J_{HH}$ = 7.8 Hz, H_4) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2, 298 K): δ = 14.9 (d, $^1J_{CP}$ = 20.5 Hz, P(*C*H$_3$)$_3$), 18.2 (s, C_8), 18.5 (s, C_{15}), 20.7 (s, C_{16}), 21.2 (d, J_{CP} = 1.1 Hz, C_{15}'), 27.5 (s, C_{10}'), 30.6 (d, $^2J_{CP}$ = 3.9 Hz, C_{10}), 35.7 (d, $^1J_{CP}$ = 9.9 Hz, C_9), 37.1 (d, $^1J_{CP}$ = 11.0 Hz, C_1), 39.8 (dd, $^3J_{CP}$ = 7.7 Hz, $^1J_{CP}$ = 26.6 Hz, C_9'), 124.0 (dd, J_{CP} = 2.8 Hz, $^3J_{CP}$ = 8.4 Hz, C_3), 124.8 (d, J_{CP} = 2.3 Hz, C_5), 128.5 (s, C_{12}'), 128.6 (s, C_{12}), 130.2 (s, C_{13}'), 130.6 (s, C_{13}), 137.0 (s, C_{14}), 137.6 (d, J_{CP} = 3.1 Hz, C_4), 148.5 (s, C_{11}), 155.3 (dd, J_{CP} = 2.5, 5.5 Hz, C_6), 162.5 (dd, J_{CP} = 4.0, 6.8 Hz, C_2), 171.0 (d, J_{CP} = 2.1 Hz, C_7), 218.5 (dd, $^2J_{CP}$ = 1.9, 15.3 Hz, *C*O) ppm. **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2, 298 K): δ = -5.5 (d, $^2J_{PP}$ = 14.9 Hz, *P*(CH$_3$)$_3$), 120.9 (d, $^2J_{PP}$ = 15.2 Hz, *P*NN) ppm. **^{19}F{^{1}H} NMR** (377 MHz, CD_2Cl_2, 298 K): δ = -148.0 (s, B*F*$_4^-$) ppm. **IR(NaCl):** $\tilde{\nu}$ = 1926 cm^{-1}. **MS** (ESI, acetonitrile, *m*/*z*$^+$): 481.2 $[M\text{-}BF_4\text{-}CH_3CN]^+$ = $[C_{26}H_{38}FeN_2OP]^+$; (ESI, acetonitrile, *m*/*z*$^-$): 87.0 $[BF_4]^-$.

Note that the PMe_3 ligand is located *trans* to the hydride ligand as indicated by the ^{1}H-NMR data. The hydride signal splits into a doublet of doublets with two different $^2J_{HP}$ coupling constants of 33.1 and 82.0 Hz, thus indicating that one phosphorus donor must be *trans* and another *cis* to the hydride ligand.

[Fe(CO)(PMe$_3$)L$_{PNN}$] (4a)

Method a: To a solution of 20.0 mg [Fe(H)(CO)(PMe$_3$)L$_{PNN}$](BF$_4$) (**5a**, 0.0310 mmol) in 5 ml C_6H_6, 6.2 mg KHMDS (0.0311 mmol) were added, and the mixture was stirred for 30 min. at room temperature. After filtration through a pad of silica, the solvent was removed in vacuum for several hours. Yield: 14.7 mg (0.0264 mmol, 85%)

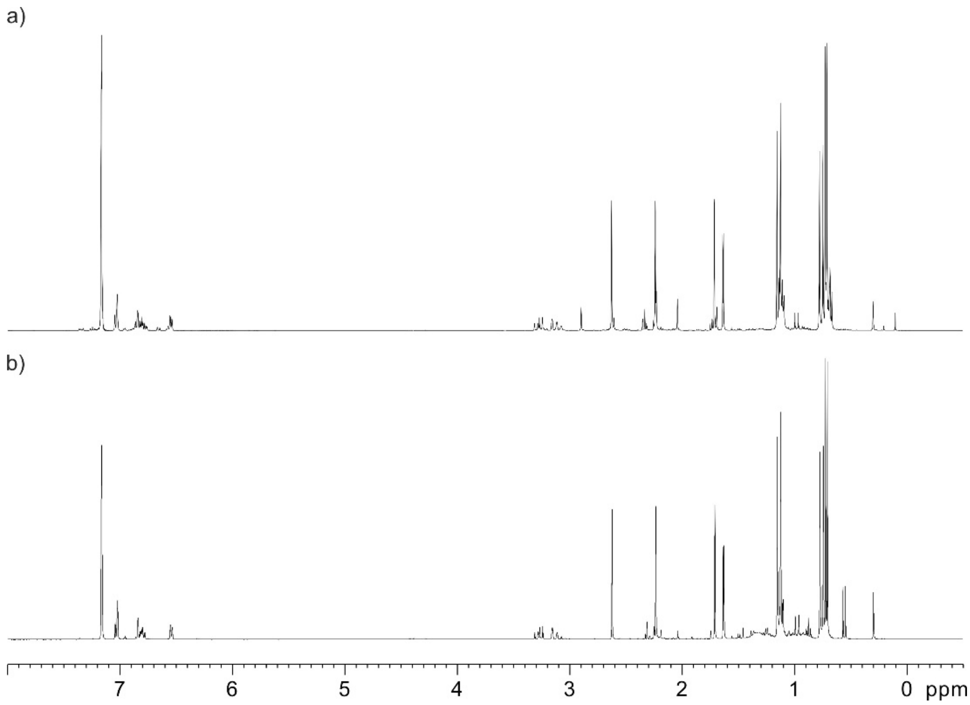
Method b: For this experiment, a stock solution of [Fe(PMe$_3$)$_2$L$_{PNN}$] (**8**) was used, which was prepared as follows: A suspension of 200.0 mg [FeBr$_2$L$_{PNN}$] (**7**) (0.3267 mmol) in 25 ml Et$_2$O was cooled to -30°C, and 0.65 ml of a 1M solution of NaHBEt$_3$ in THF were added. The mixture was stirred for 1 h at room temperature and filtered through a syringe filter. Presumably, [Fe(N$_2$)$_2$L$_{PNN}$] (**8**) is formed.[5] While this compound could not be isolated even after several attempts, [Fe(CO)$_2$L$_{PNN}$] is cleanly generated when CO is added to this solution, and this observation strongly indicates the generation of [Fe(N$_2$)$_2$L$_{PNN}$] (**8**).[5] To this solution, 200 µl PMe$_3$ (147 mg, 1.9322 mmol) were added, and the mixture was kept at room temperature for several days, during which first [Fe(PMe$_3$)(N$_2$)L$_{PNN}$] (**12**) and then [Fe(PMe$_3$)$_2$L$_{PNN}$] (**13**) were formed according to NMR studies. 1.4 ml of this solution (containing ca. 18.30 µmol [Fe]) were filled into a screw-cap NMR tube with a septum cap, and after the addition of 440 µl CO (ca. 19.6 µmol) via a gas-tight syringe, the tube was shaken immediately and kept at room temperature overnight. The solvent was removed in vacuum, first at room temperature until the major amount of solvent was evaporated, then for 30 min. at 50°C and for 60 min. at 70°C. Yield: 7.3 mg, 13.1 mmol, 72%.



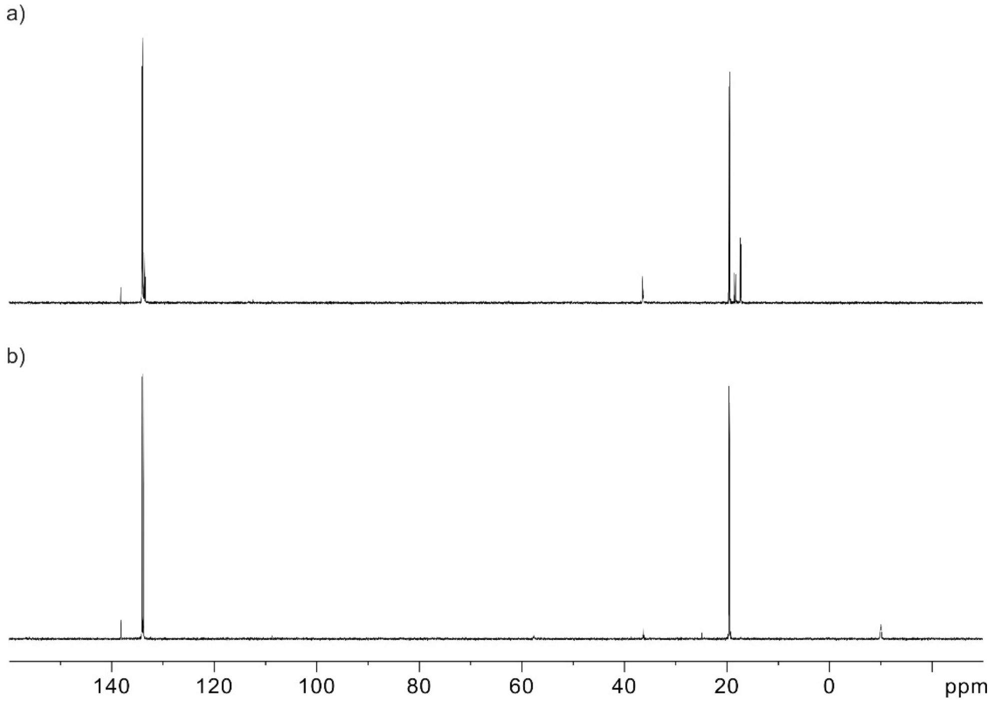
^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 0.71 (d, 9H, $^2J_{HP}$ = 6.7 Hz, P(CH_3)$_3$), 0.76 (d, 9H, $^3J_{HP}$ = 11.8 Hz, H$_{10'}$), 1.13 (d, 9H, $^3J_{HP}$ = 12.2 Hz, H$_{10}$), 1.63 (d, 3H, J_{HP} = 2.6 Hz, H$_8$), 1.71 (s, 3H, H$_{15'}$), 2.23 (s, 3H, H$_{16}$), 2.62 (s, 3H, H$_{15}$), 3.13 (br, d, 1H, $^2J_{HH}$ = 16.9 Hz, H$_1$), 3.27 (dd, 1H, $^2J_{HP}$ = 11.3 Hz, $^2J_{HH}$ = 16.9 Hz, H$_{1'}$), 6.54 (br, d, 1H, $^3J_{HH}$ = 6.5 Hz, H$_3$), 6.80 (m, 1H, H$_4$), 6.84 (br, s, 1H, H$_{13'}$), 7.02 (br, s, 1H, H$_{13}$), 7.03 (br, d, 1H, $^3J_{HH}$ = 6.4 Hz, H$_5$) ppm. **^{13}C{^{1}H} NMR** (101 MHz, C_6D_6, 298 K): δ = 14.8 (s, C$_8$), 15.6 (d, $^1J_{CP}$ = 19.0 Hz, P(CH$_3$)$_3$), 19.6 (s, C$_{15'}$), 20.9 (s, C$_{16}$), 21.9 (d, J_{CP} = 1.4 Hz, C$_{15}$), 28.4 (d, $^2J_{CP}$ = 5.1 Hz, C$_{10'}$), 30.6 (d, $^2J_{CP}$ = 4.2 Hz, C$_{10}$), 33.9 (d, $^1J_{CP}$ = 11.3 Hz, C$_9$), 36.2 (d, $^1J_{CP}$ = 10.6 Hz, C$_1$), 40.2 (dd, $^3J_{CP}$ =

6.1 Hz, ${}^{1}J_{CP}$ = 9.8 Hz, C_9'), 107.2 (d, ${}^{3}J_{CP}$ = 8.5 Hz, C_3), 118.7 (d, J_{CP} = 3.4 Hz, C_5), 124.2 (dd, J_{CP} = 1.0, 3.1 Hz, C_4), 127.9 (C_{12}, overlapping with C_6D_6), 129.1 (s, C_{13}'), 129.6 (s, C_{13}), 130.9 (d, J_{CP} = 2.4 Hz, C_{12}'), 132.2 (s, C_{14}), 140.0 (s, C_7), 143.3 (dd, J_{CP} = 3.6, 5.4 Hz, C_6), 154.3 (d, J_{CP} = 2.3 Hz, C_{11}), 161.0 (d, ${}^{2}J_{CP}$ = 10.0 Hz, C_2), 222.3 (dd, ${}^{2}J_{CP}$ = 7.4, 26.1 Hz, *C*O) ppm. **${}^{31}P\{{}^{1}H\}$ NMR** (162 MHz, C_6D_6, 298 K): δ = 19.4 (d, ${}^{2}J_{PP}$ = 36.7 Hz, *P*(CH_3)$_3$), 133.9 (d, ${}^{2}J_{PP}$ = 36.6 Hz, *P*NN) ppm. **IR(NaCl):** $\tilde{\nu}$ = 1860 cm^{-1}.

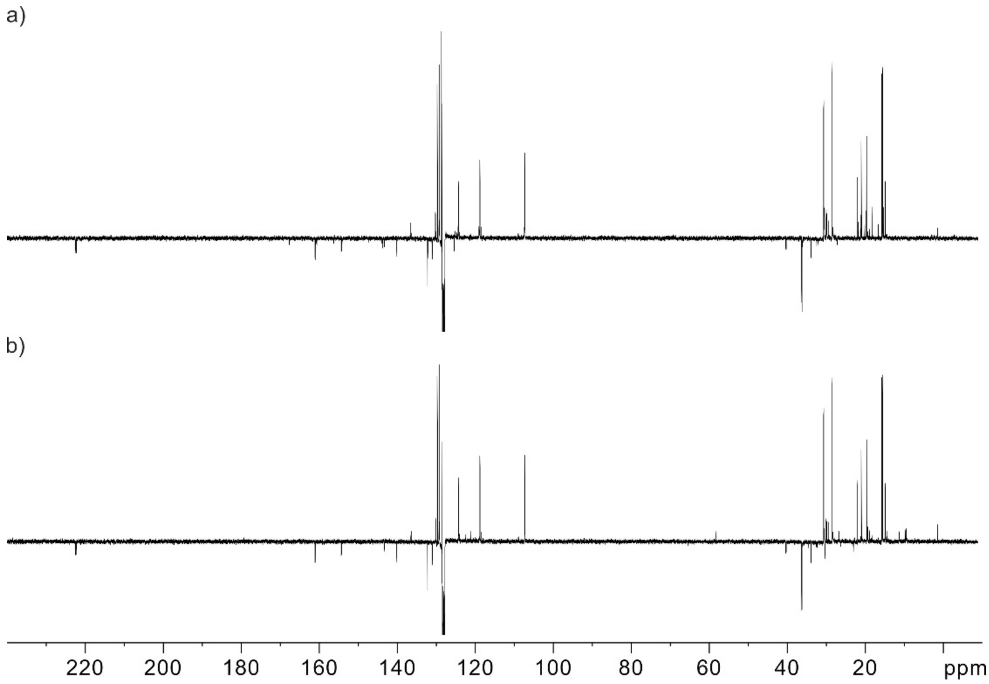
Note that the characterization is given for the material generated via Method b. However, the NMR and IR spectral data of the products obtained by both methods are essentially identical and thus confirm the formation of [Fe(CO)(PMe_3)L_{PNN}] (**4a**) (see Figures SI 1 – 5).



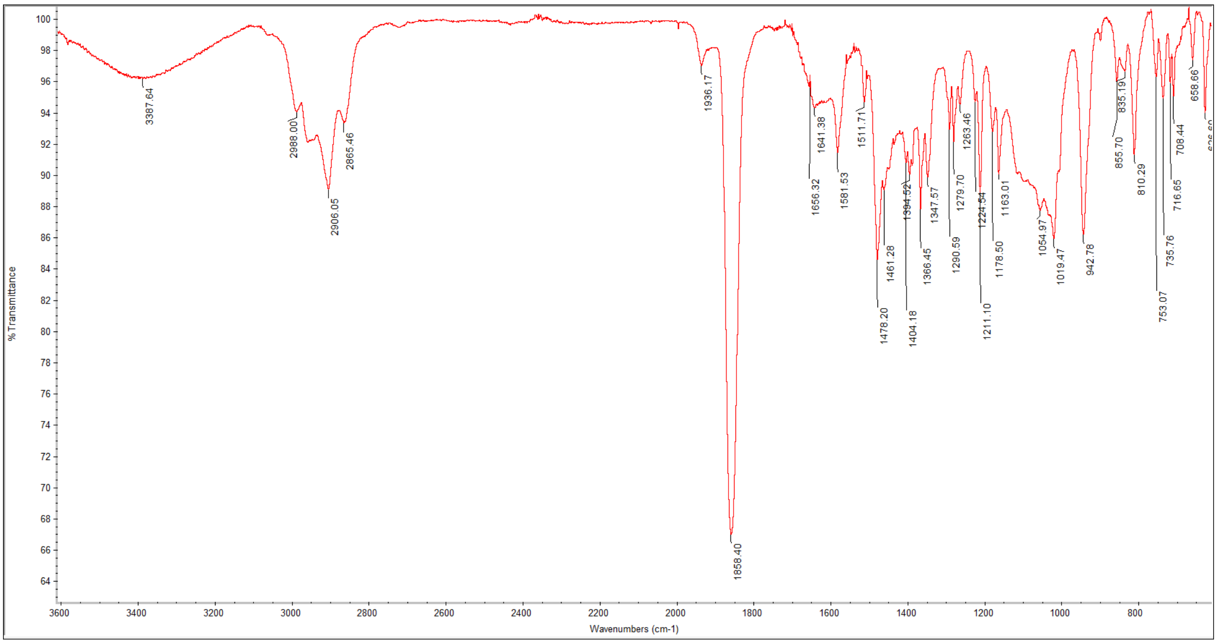
SI 1. ^{1}H-NMR spectra of [Fe(CO)(PMe_3)L_{PNN}] (**4a**) as synthesized via a) Method a and b) Method b.



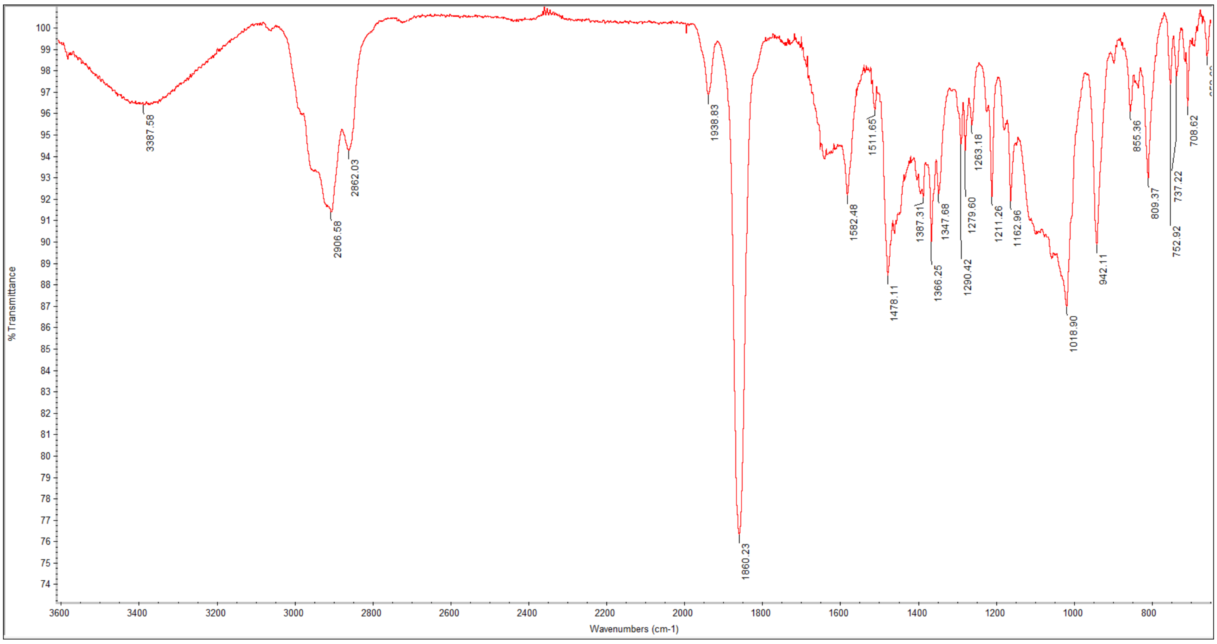
SI 2. $^{31}P\{^{1}H\}$-NMR spectra of [Fe(CO)(PMe$_3$)L$_{PNN}$] (**4a**) as synthesized via a) Method a and b) Method b.



SI 3. $^{13}C\{^{1}H\}$-NMR spectra of [Fe(CO)(PMe$_3$)L$_{PNN}$] (**4a**) as synthesized via a) Method b and b) Method b.



SI 4. IR spectrum of [Fe(CO)(PMe_3)L_{PNN}] (**4a**) as synthesized via Method a.

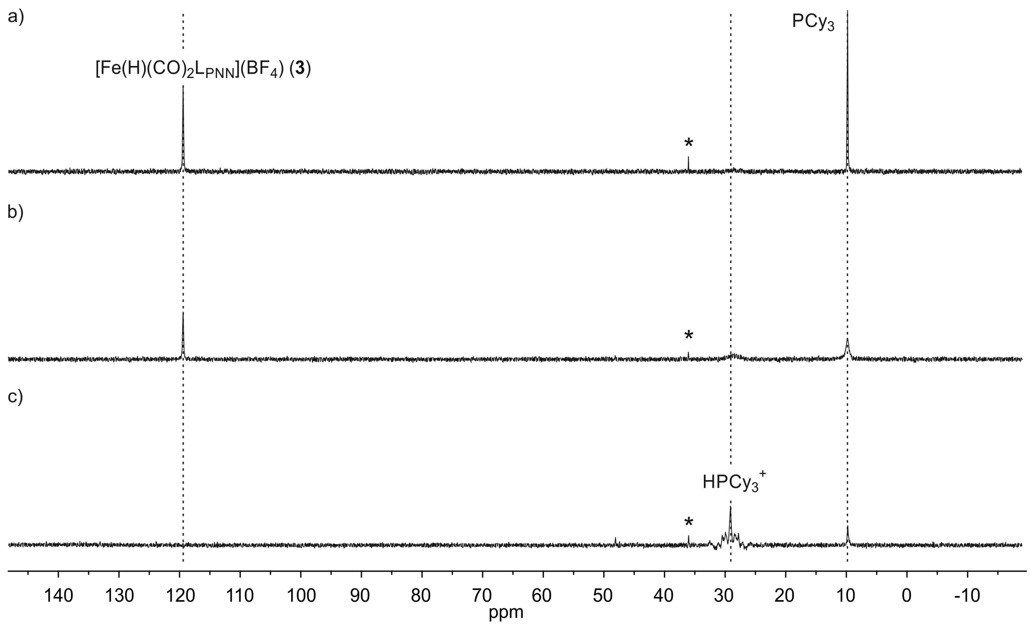


SI 5. IR spectrum of [Fe(CO)(PMe_3)L_{PNN}] (**4a**) as synthesized via Method b.

3. Estimation of the Acidity of [Fe(H)(CO)$_2$$L_{PNN}$]($BF_4$) (3)

In order to estimate the acidity of the hydride complex [Fe(H)(CO)$_2$$L_{PNN}$]($BF_4$) (**3**) in methylene chloride as a solvent, 6.6 mg [Fe(H)(CO)$_2$$L_{PNN}$]($BF_4$) (0.0111 mmol) and 4.2 mg PCy_3 (0.0150 mmol) were dissolved in 0.7 ml CH_2Cl_2, and ^{31}P-NMR spectra were recorded at different times (see SI 1). The signal at 29.5 ppm is characteristic for the formation of $HPCy_3^+$

and thus for the proton transfer from **3** to PCy_3.[6] This experiment allows to estimate the pK_a value of $[Fe(H)(CO)_2L_{PNN}](BF_4)$ (**3**) in CH_2Cl_2 to be lower than 9.7.[6]

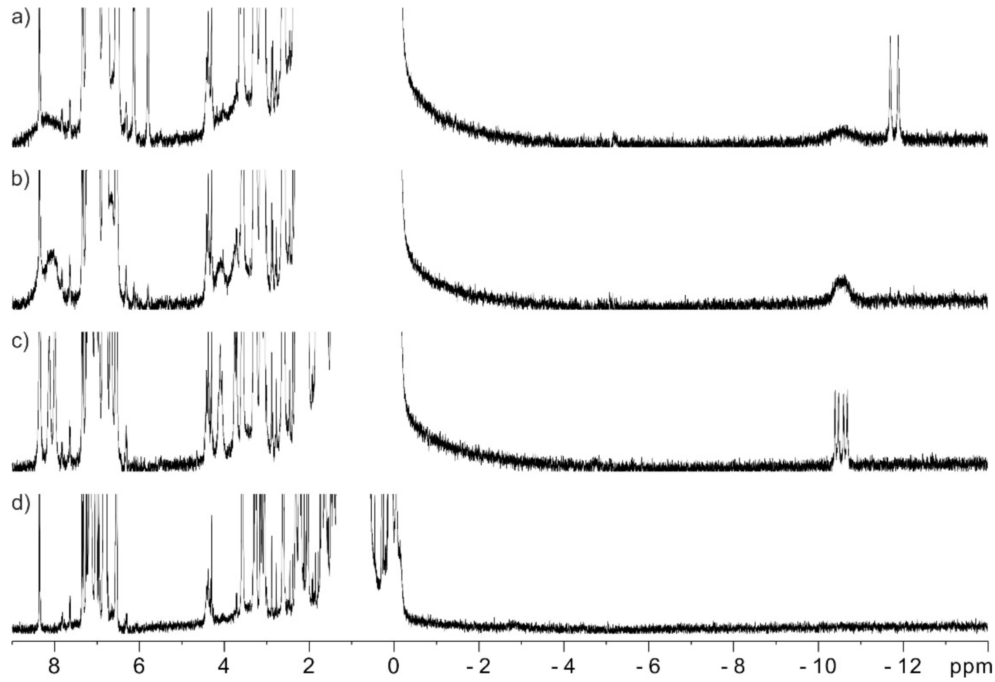


SI 6. ^{1}H NMR spectra of the reaction of $[Fe(H)(CO)_2L_{PNN}](BF_4)$ (**3**) and PCy_3 in CH_2Cl_2 a) after mixing, b) after 1.5 h at room temperature, and c) after 24 hours at room temperature. The signal marked with an asterisk indicates trace amounts of free PNN ligand. The coupling pattern around the signal for $HPCy_3^+$ is caused by the ^{1}H decoupler pulse being put to -4.5 ppm.

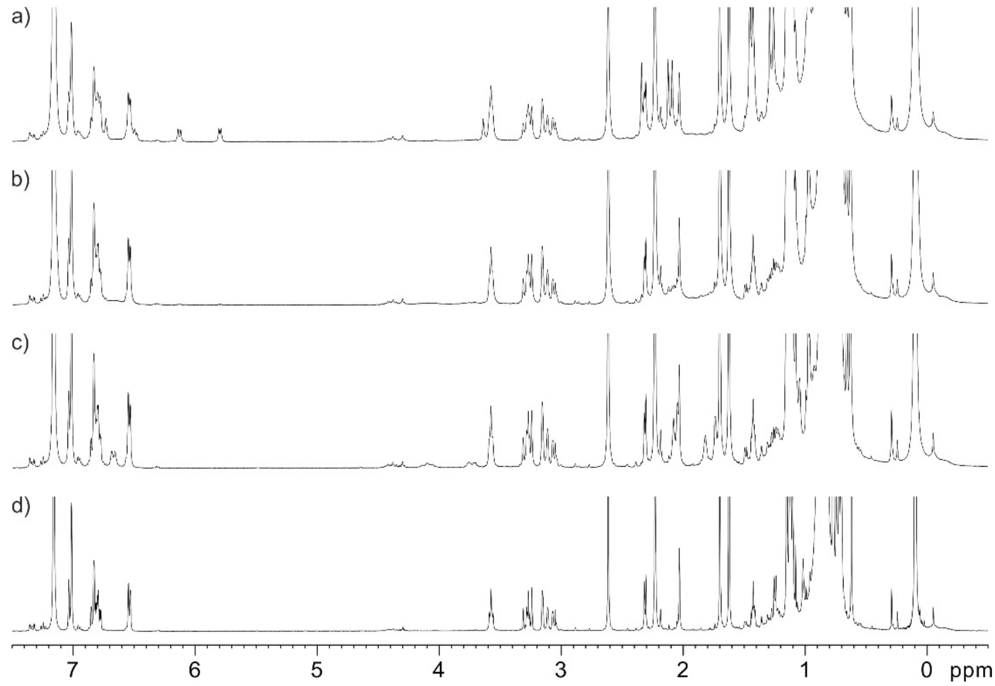
4. Additional Details for the Catalytic Reactions

Note that in the catalytic experiment employing 100 eq KHMDS (Table 3, entry 6 in the main text) small amounts of a white solid (less than 20 mg, for ca. 400 mg acetophenone) are found after the reaction. After hydrolysis of the white solid with methanol and evaporation of the solvent, the residue is identified as acetophenone by ^{1}H-NMR spectroscopy. Thus, the solid formed during the reaction presumably corresponds to the potassium salt of the starting compound.

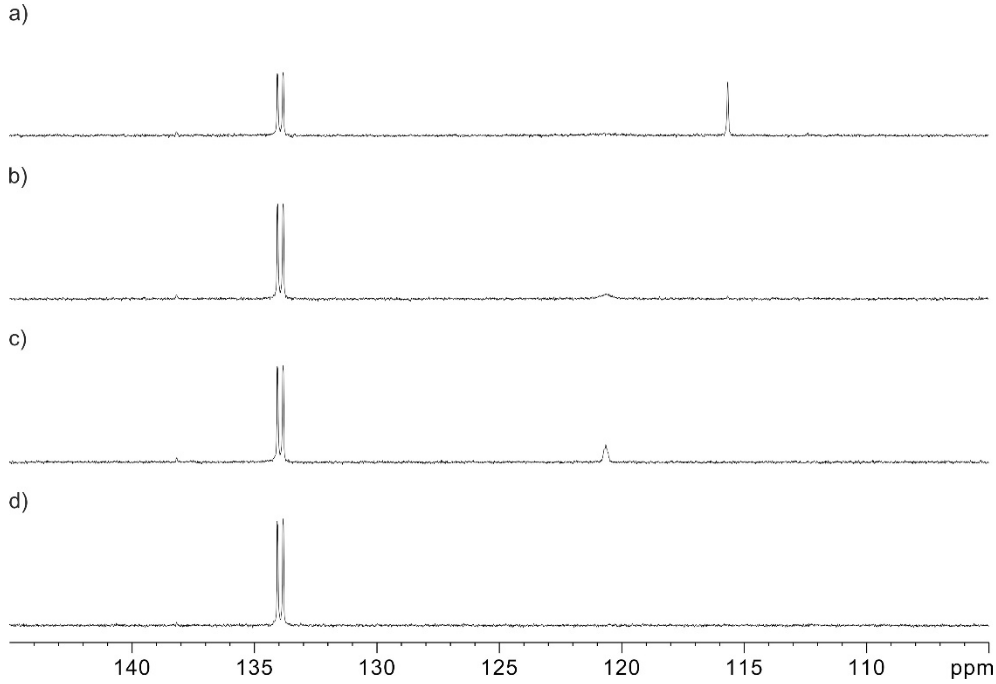
5. NMR-Deprotonation Experiments at Room Temperature



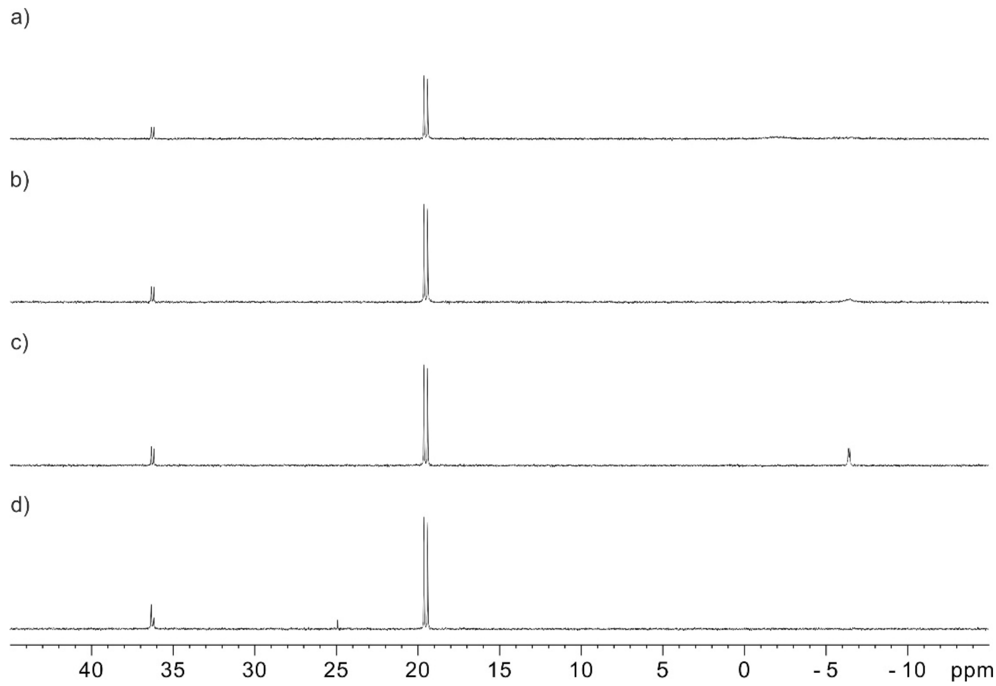
SI 7. ^{1}H NMR spectra of the reaction of a mixture of **1** and 20 eq. PMe_3 with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min. b) t = 1.0 h, c) t = 2.5 h, and d) t = 6 d; magnified hydride region.



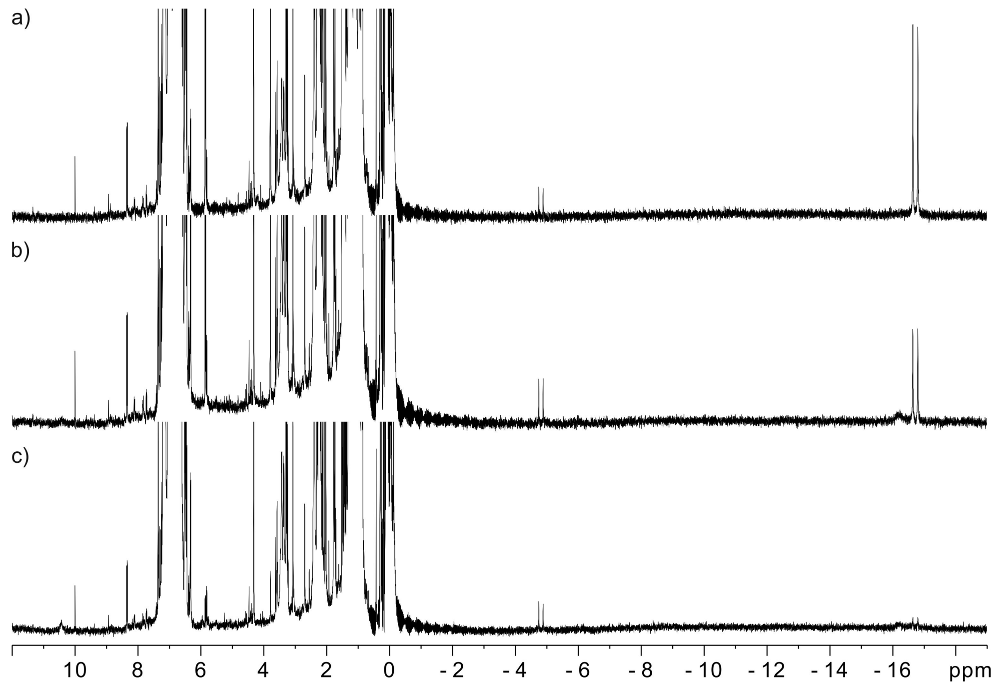
SI 8. ^{1}H NMR spectra of the reaction of a mixture of **1** and 20 eq. PMe_3 with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min. b) t = 1.0 h, c) t = 2.5 h, and d) t = 6 d; aliphatic and aromatic region.



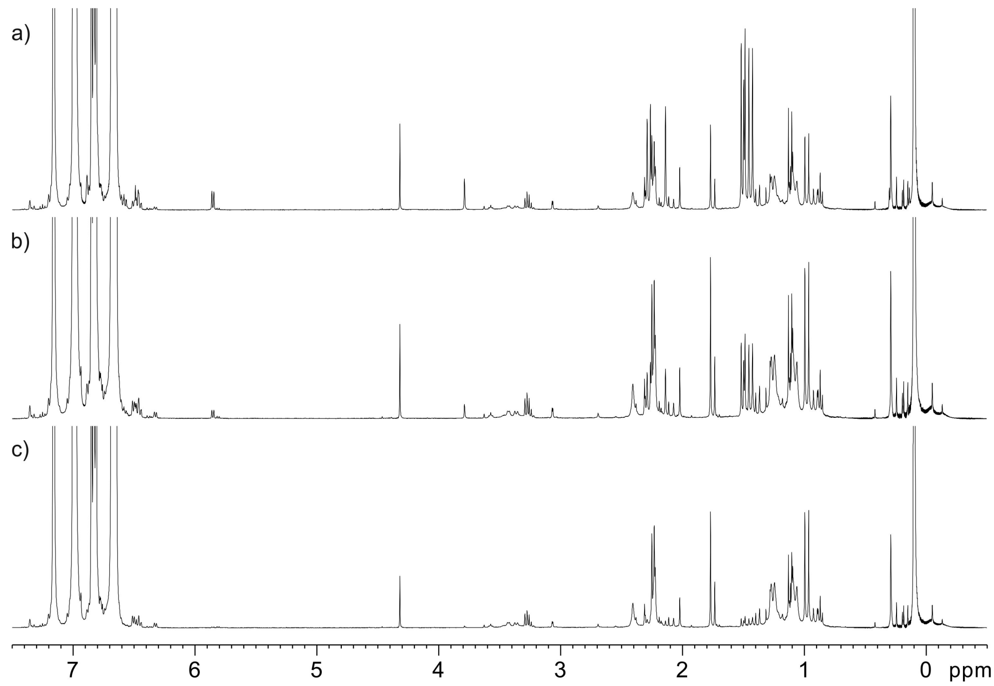
SI 9. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of a mixture of **1** and 20 eq. PMe_3 with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min. b) t = 1.0 h, c) t = 2.5 h, and d) t = 6 d; region 1.



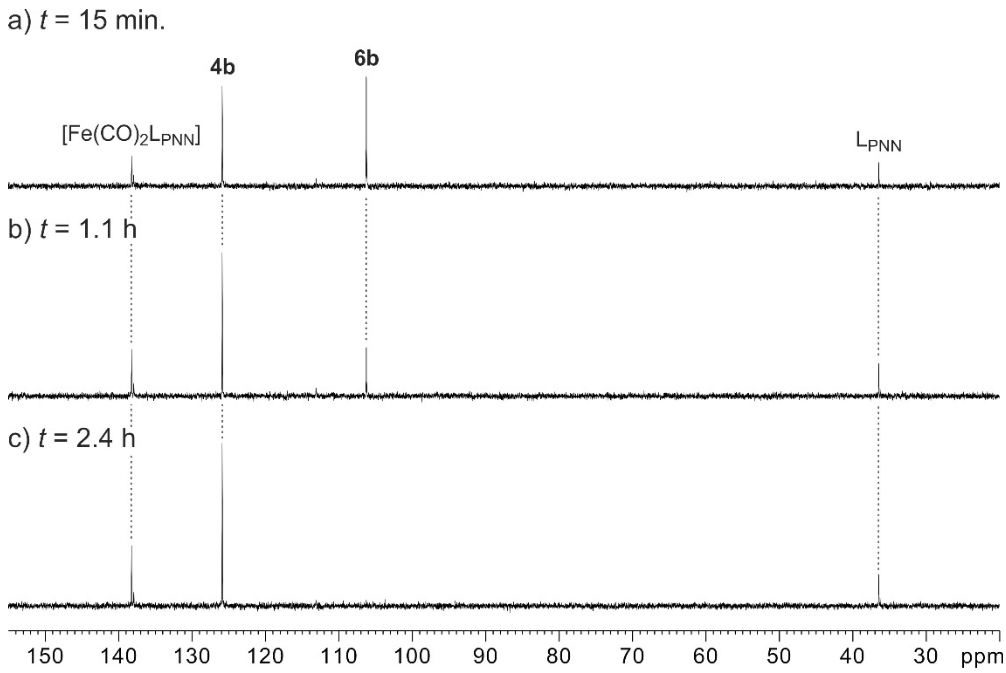
SI 10. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of a mixture of **1** and 20 eq. PMe_3 with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min. b) t = 1.0 h, c) t = 2.5 h, and d) t = 6 d; region 2.



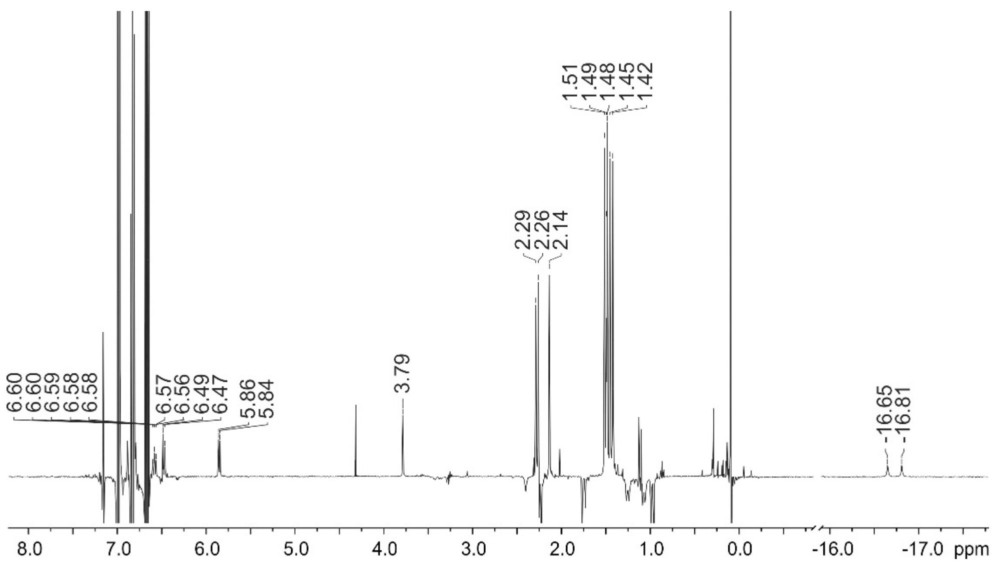
SI 11. ^{1}H NMR spectra of the reaction of a mixture of **1** and 20 eq. PhCN with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min., b) t = 1.1 h, c) t = 2.4 h; magnified hydride region.



SI 12. ^{1}H NMR spectra of the reaction of a mixture of **1** and 20 eq. PhCN with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min., b) t = 1.1 h, c) t = 2.4 h; aliphatic and aromatic region.



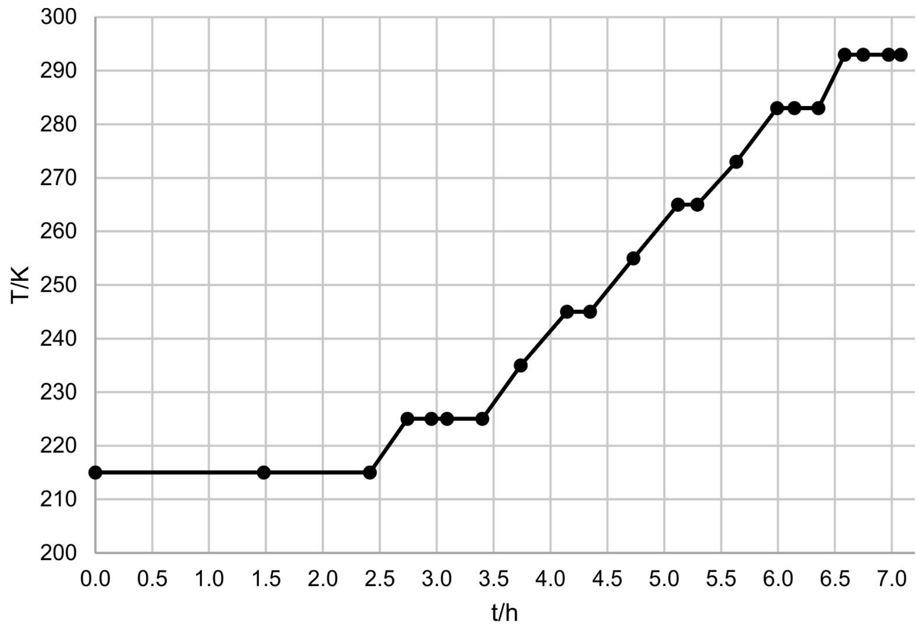
SI 13 $^{31}P\{^{1}H\}$-NMR spectra of the reaction of a mixture of **1** and 20 eq. PhCN with 1 eq. KHMDS in C_6D_6 after KHMDS addition (t = 0): a) t = 15 min., b) t = 1.1 h, c) t = 2.4 h. For structural details of **4b** and **6b** see Fig. 5 in the main text. Note that both [$Fe(CO)_2L_{PNN}$] and L_{PNN} are accompanied by unidentified signals located slightly up-field.



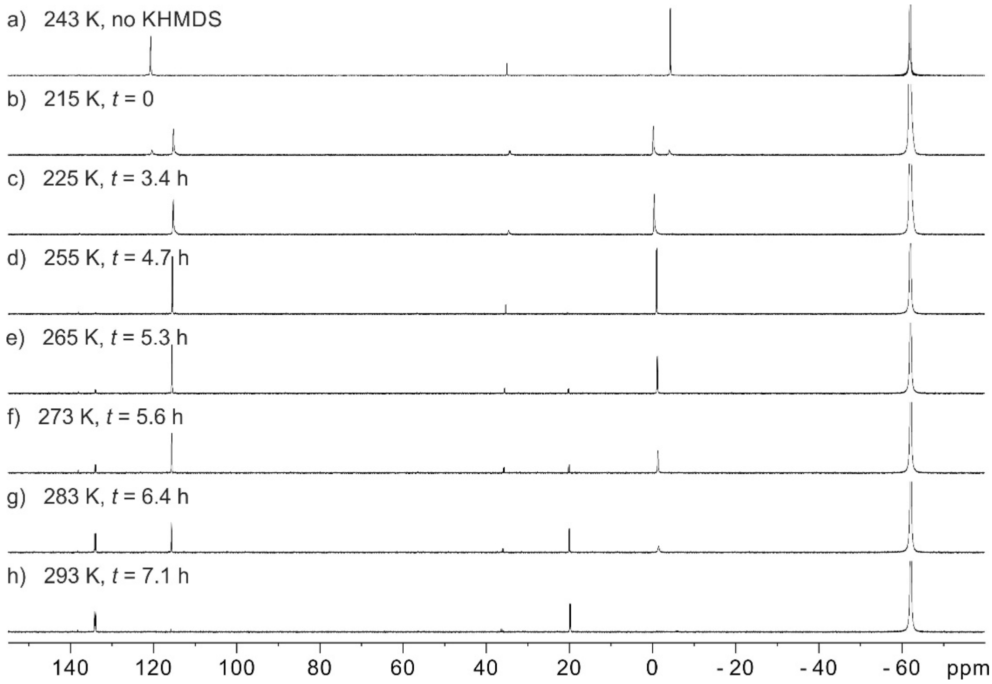
SI 14. ^{1}H-NMR spectrum of the species at 106.2 ppm, i.e. **6b**, in the ^{31}P-NMR spectrum (see SI 13a and 13b in the main text) as derived by subtraction of the ^{1}H-NMR spectra for t = 15 min. and t = 2.4 h (see SI 11 and SI 12). The relevant resonances are identified based on the stepwise disappearance of these signals in the complete set of ^{1}H-NMR spectra.

Obviously, the species at 106.2 ppm in the ^{31}P-NMR spectrum is a hydride complex as indicated by a doublet at -16.73 ppm (d, $^{2}J_{HP}$ = 63.6 Hz) in the difference spectrum, and in the ^{31}P-^{1}H HMQC spectrum, a cross peak for the signals at 106.2 and -16.73 ppm in the ^{31}P and ^{1}H-NMR spectra, respectively, can be identified. Two sets of doublets for the ^{t}Bu groups are located at 1.44 (d, $^{3}J_{HP}$ = 12.2 Hz) and 1.50 ppm (d, $^{3}J_{HP}$ = 12.4 Hz), and four methyl resonances at 1.49, 2.14, 2.26, and 2.29 ppm can be identified. In the aromatic region, the three resonances at 5.85 ppm (d, $^{3}J_{HH}$ = 6.6 Hz), 6.48 ppm (d, $^{3}J_{HH}$ = 8.8 Hz), and 6.58 ppm (ddd, $^{3}J_{HH}$ = 8.4, 6.7 Hz, J_{HP} = 1.6 Hz) are indicative of the pyridine protons. These signals are significantly shifted up-field when compared with the parent compound **3**, and this behavior is typical for dearomatized complexes.[7,8] Further, a singlet at 3.79 ppm most probably corresponds to the deprotonated methylene arm.[7] Only the aromatic signals for the PhCN ligand are overlapping with other signals. However, these observations are only indirect evidence for the formation of a dearomatized species upon deprotonation with KHMDS, and all attempts to isolate the presumably formed Fe^{0} complex [Fe(CO)(PhCN)L_{PNN}] (**4a**) have been unsuccessful; after complete evaporation of the solvent, the ^{31}P{^{1}H}-NMR spectrum in fresh C_6D_6 shows only signals for [Fe(CO)$_2$$L_{PNN}$] (**1**) and free L_{PNN}.

6. VT-NMR Experiments

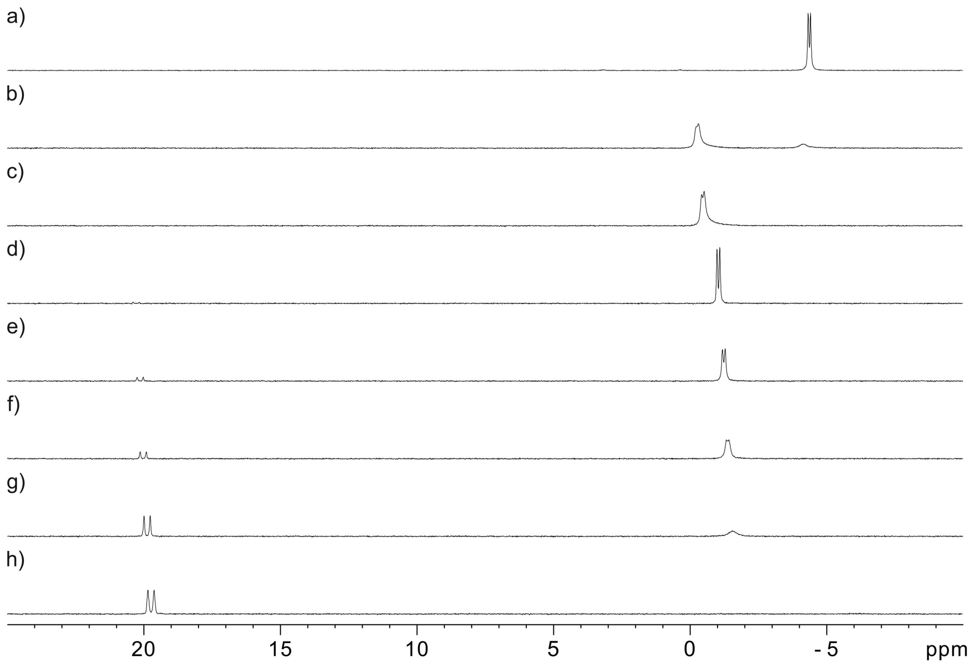


SI 15. Temperature program in the VT-NMR experiment of the system [Fe(H)(CO)(MeCN)(L_{PNN})](BF_4)/PMe_3/KHMDS in toluene-d_8 as described in the main text. Each dot represents a ^{31}P-NMR measurement.

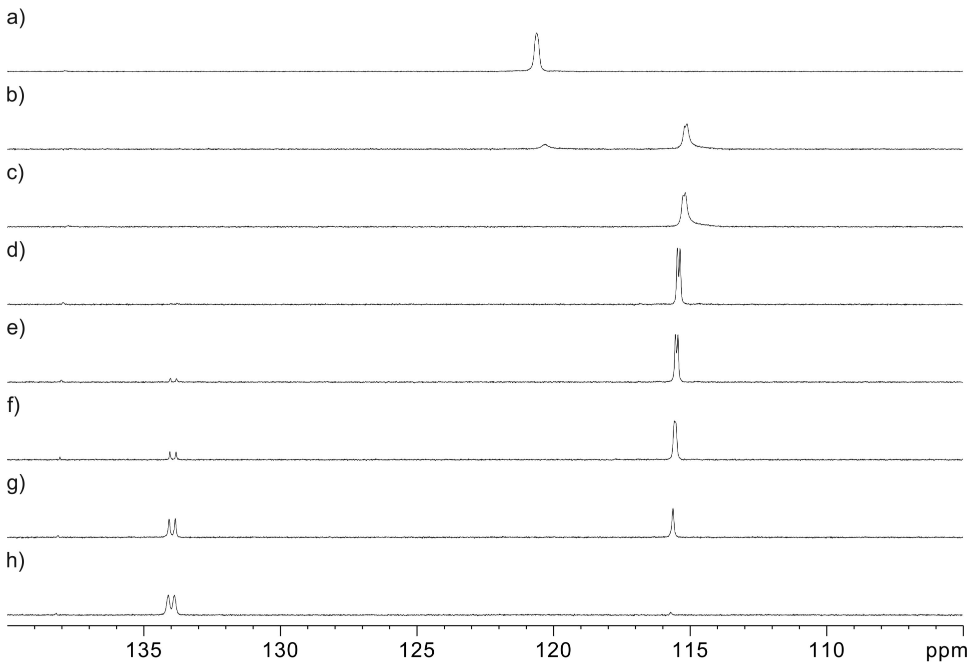


SI 16. VT-NMR experiment: $^{31}P\{^{1}H\}$-NMR spectra a) before the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3, at 243 K; b) immediately after the addition of KHMDS, t = 0 at 215 K, c) t = 3.4 h at 225 K, d) t = 4.7 h at 255 K, e) t = 5.3 h at 265 K, f) t = 5.6 h at 273 K, and g) t = 6.4 h at 283 K, h) t = 7.1 h at 293 K.

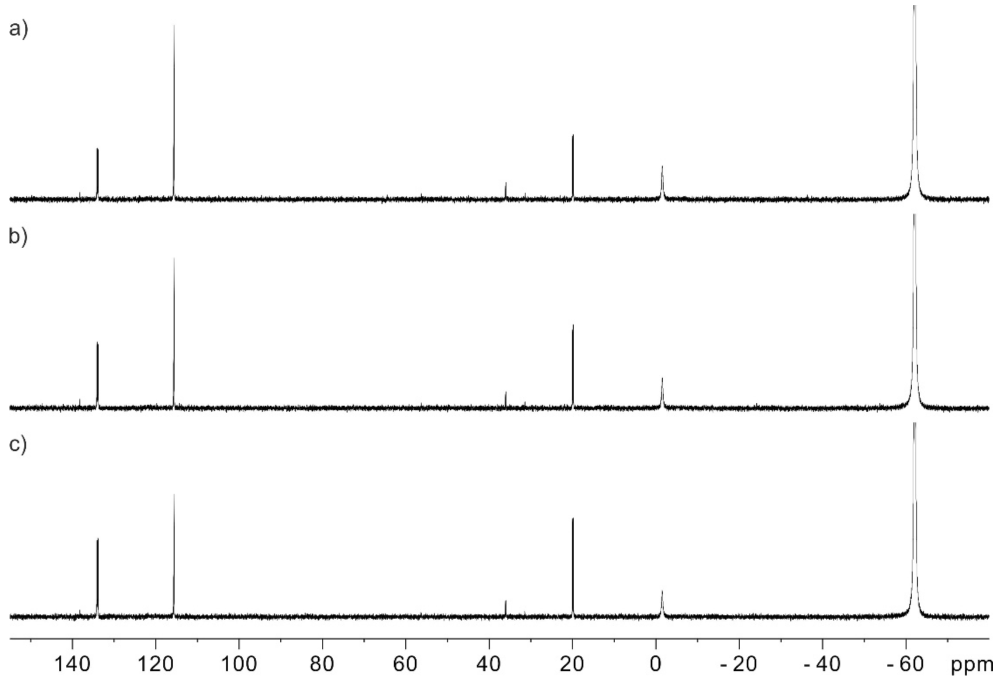
To a solution of **1** in toluene-d_8 in a sealed screw-cap NMR tube with a septum cap, 20 eq. PMe_3 were added at room temperature with a microliter syringe, and a $^{31}P\{^{1}H\}$-NMR spectrum was recorded after cooling to 243 K in order to make sure that the formation of $[Fe(H)(CO)(PMe_3)L_{PNN}](BF_4)$ (**5a**) is complete (SI 16a; for a more detailed representation of the spectra, see SI 17 and SI 18). While the signals at -62.0 and 34.9 ppm correspond to free PMe_3 free L_{PNN}, respectively, the signals at -4.4 ppm (d, $^{2}J_{PP}$ = 14.2 Hz) and 120.5 ppm (s) indicate the formation of $[Fe(H)(CO)(PMe_3)L_{PNN}](BF_4)$ (**5a**) (see also the ^{1}H-NMR spectra in SI 21 – 23 and compare the characterization data for **5a**). The fact that the signal at 120.5 ppm corresponds to a singlet instead of a doublet might be due to a decoalescence process occurring at decreased temperature. Afterwards, the sample was cooled down in an acetone/dry-ice bath, and a solution of 1 eq. KHMDS in toluene-d_8 was carefully added with a syringe (step 2 in Figure 9). After mixing the two solutions at -78°C, the NMR tube was put into a 400 MHz NMR spectrometer, which had been cooled down to 215 K. Small amounts of unreacted $[Fe(H)(CO)(PMe_3)L_{PNN}](BF_4)$ (**5a**) are still visible under these conditions, and a new set of broad signals appears at -0.3 and 115.1 ppm (SI 16b). In the ^{1}H-NMR spectra, a new broad signal appears at -11.64 ppm. We assign these signals to dearomatized $[Fe(H)(CO)(PMe_3)(L_{PNN} – H)]$ (**6a**) as outlined above. Even after 2.4 h at 215 K, significant changes could not be detected in the ^{31}P-NMR spectrum. Upon warming the sample to 225 K, residual **5a** is completely converted to **6a**, and the latter species is stable under these conditions for at least 1 h (SI 16c). Upon warming to 255 K, the signals for [Fe(H)(CO)(PMe$_3$)(L$_{PNN}$ – H)] (**6a**) become sharper and two doublets are resolved at -1.1 ppm (d, $^2J_{PP}$ = 16.3 Hz) and 115.4 ppm (d, $^2J_{PP}$ = 16.0 Hz) in the ^{31}P-NMR spectrum (SI 16d). In the ^{1}H-NMR spectrum at 255 K, a sharp doublet of doublets at 11.76 ppm (dd, $^2J_{HP}$ = 73.1, 44.6 Hz) is well in agreement with the presence of species **6a**. When the mixture is warmed to 265 K (SI 16e), two new doublets appear at 20.1 and 133.9 ppm, which correspond to [Fe(CO)(PMe$_3$)L$_{PNN}$] (**4a**), and the signals for **6a** begin to broaden again. Upon gradual heating to 293 K, **6a** is completely converted to **4a**. At 283 and 293 K this process occurs within few minutes (SI 19 and 20). In the ^{1}H-NMR spectrum (SI 20 and 21), hydride species are not observed, which is consistent with the formation of [Fe(CO)(PMe$_3$)L$_{PNN}$] (**4a**).



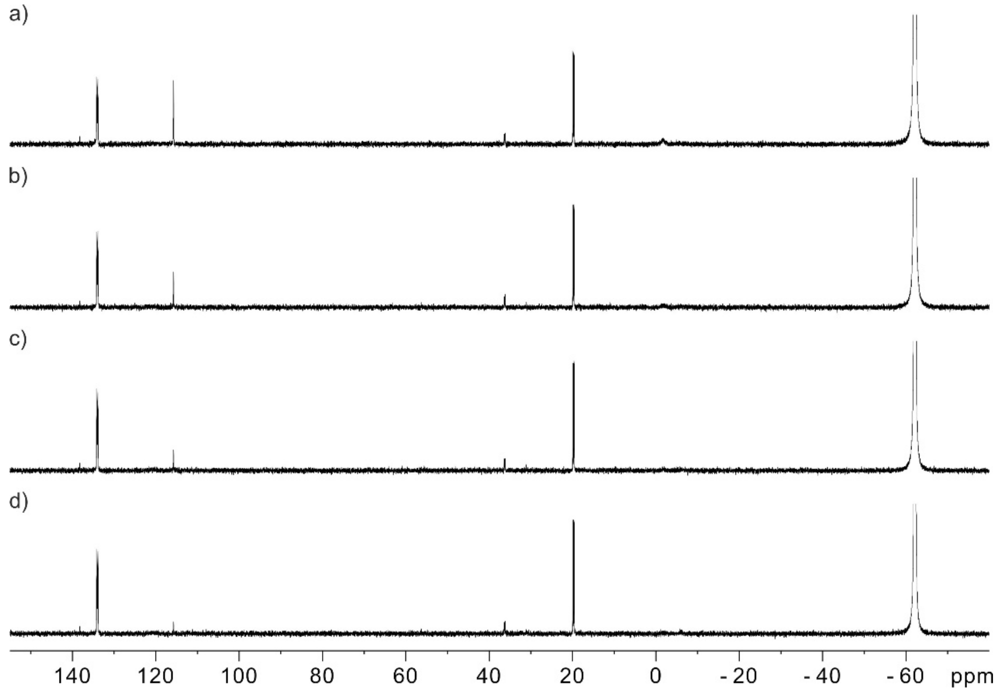
SI 17. ^{31}P{^{1}H} NMR spectra a) before the addition of KHMDS to a toluene-d$_8$ solution of **1** and 20 eq. PMe$_3$ at 243 K; b) immediately after the addition of KHMDS, t = 0 at 215 K, c) t = 3.4 h at 225 K, d) t = 4.7 h at 255 K, e) t = 5.3 h at 265 K, f) t = 5.6 h at 273 K, and g) t = 6.4 h at 283 K, h) t = 7.1 h at 293 K; region 1.



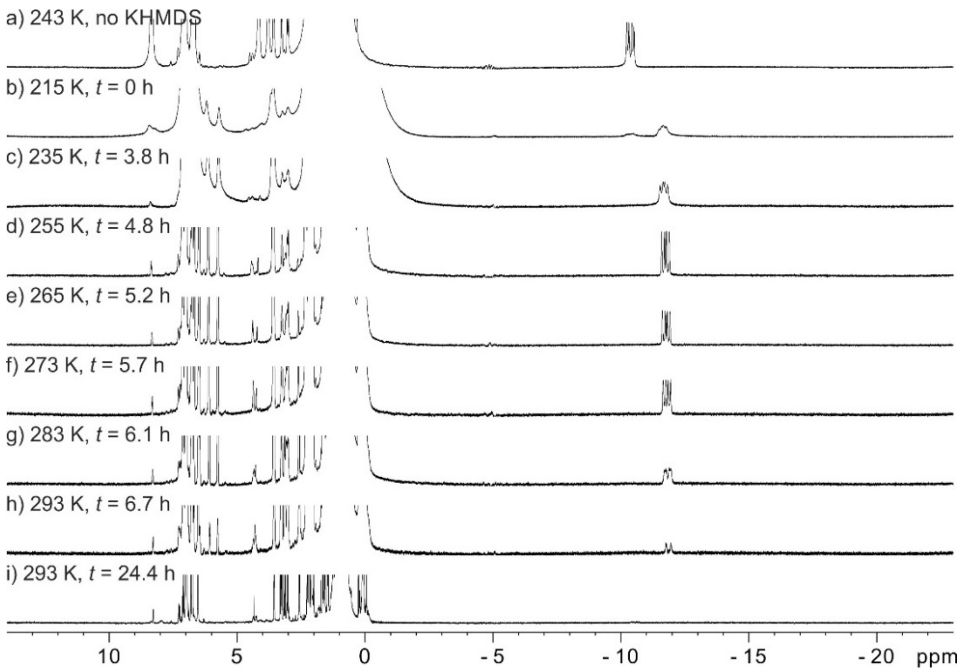
SI 18. $^{31}P\{^{1}H\}$ NMR spectra a) before the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3 at 243 K; b) immediately after the addition of KHMDS, $t = 0$ at 215 K, c) $t = 3.4$ h at 225 K, d) $t = 4.7$ h at 255 K, e) $t = 5.3$ h at 265 K, f) $t = 5.6$ h at 273 K, and g) $t = 6.4$ h at 283 K, h) $t = 7.1$ h at 293 K; region 2.



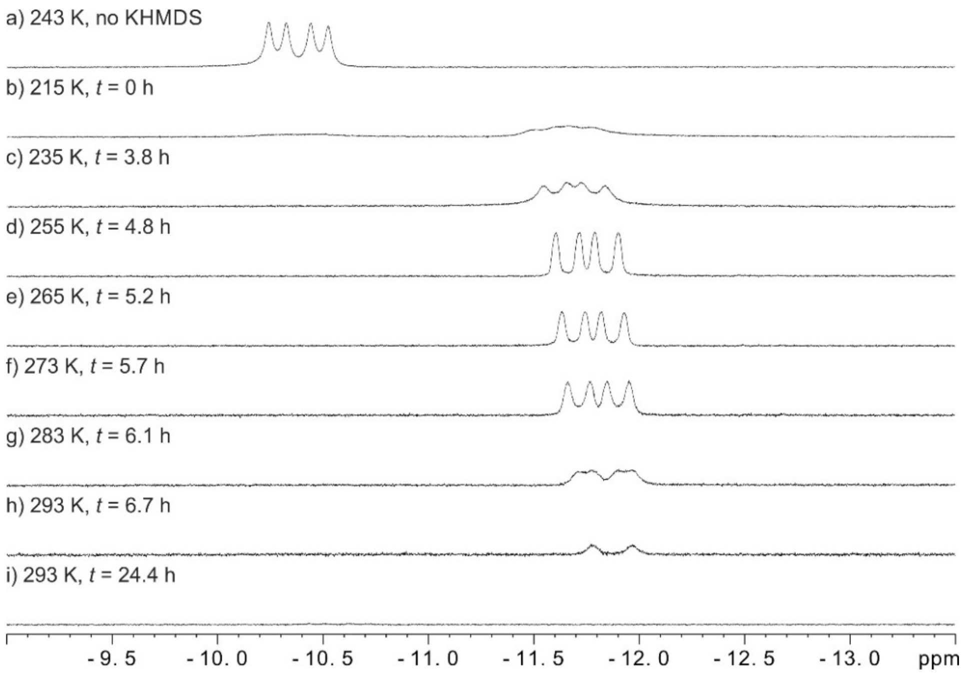
SI 19. $^{31}P\{^{1}H\}$ NMR spectra after the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3; spectra are given for 283 K for a) $t = 6.0$ h, b) $t = 6.1$ h, c) $t = 6.4$ h.



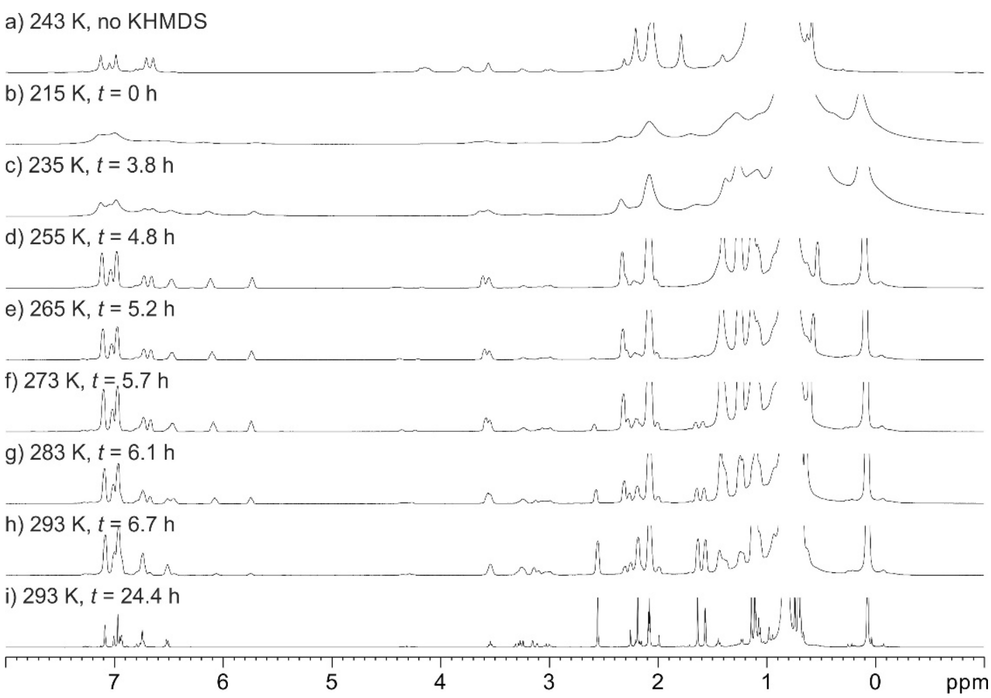
SI 20. $^{31}P\{^1H\}$ NMR spectra after the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3; spectra are given for 293 K for a) t = 6.6 h, b) t = 6.7 h, c) t = 7.0 h, d) t = 7.1 h.



SI 21. ^1H NMR spectra a) before the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3 at 243 K; b) immediately after the addition of KHMDS, t = 0 at 215 K, c) t = 3.8 h at 235 K, d) t = 4.8 h at 255 K, e) t = 5.2 h at 265 K, f) t = 5.7 h at 273 K, and g) t = 6.1 h at 283 K, h) t = 6.7 h at 293 K, i) t = 24.4 h at 293 K; magnified hydride region.



SI 22. ^{1}H NMR spectra a) before the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3 at 243 K; b) immediately after the addition of KHMDS, $t = 0$ at 215 K, c) $t = 3.8$ h at 235 K, d) $t = 4.8$ h at 255 K, e) $t = 5.2$ h at 265 K, f) $t = 5.7$ h at 273 K, and g) $t = 6.1$ h at 283 K, h) $t = 6.7$ h at 293 K, i) $t = 24.4$ h at 293 K; magnified hydride region (enlarged).



SI 23. ^{1}H NMR spectra a) before the addition of KHMDS to a toluene-d_8 solution of **1** and 20 eq. PMe_3 at 243 K; b) immediately after the addition of KHMDS, $t = 0$ at 215 K, c) $t = 3.8$ h at 235 K, d) $t = 4.8$ h at 255 K, e) $t = 5.2$ h at 265 K, f) $t = 5.7$ h at 273 K, and g) $t = 6.1$ h at 283 K, h) $t = 6.7$ h at 293 K, i) $t = 24.4$ h at 293 K; aromatic and aliphatic region.

7. Energies and Coordinates for the Calculated Structures

SI 24. Calculated energies in Hartree.

	opt+freq(def2-SVP/BP86)		SP(def2-TZVP/PBE0)
	E(SCF)	E(SCF + chem. pot.)	E(SCF)
2	-2915.5672053	-2915.0643677	-2914.9158703
4a	-3263.2687674	-3262.6665621	-3262.5431552
4b	-3126.5863107	-3126.0030466	-3125.8687639
6a	-3263.2341746	-3262.6353172	-3262.5176100
6b	-3126.5546825	-3125.9746139	-3125.8527192
10	-3183.4465105	-3182.9162877	-3182.7429558
11	-2915.5258089	-2915.0264526	-2914.8861287

$[Fe(CO)_2L_{PNN}]$ (**2**)

```
Fe        -0.18446000   -0.02978000   -0.61850000
P         -2.22757000   -0.54245000    0.04349000
N         -0.80522000    1.77785000   -0.28009000
N          1.45213000    0.78656000   -0.10711000
C         -3.10003000    1.03282000   -0.46880000
C         -2.12202000    2.16371000   -0.28596000
C         -2.49615000    3.48851000   -0.09353000
H         -3.56242000    3.75520000   -0.09107000
C         -1.49077000    4.47769000    0.10355000
H         -1.77174000    5.53204000    0.24191000
C         -0.15941000    4.09275000    0.14043000
H          0.63563000    4.83213000    0.31125000
C          0.18885000    2.72188000   -0.02425000
C          1.47782000    2.12999000    0.07122000
C         -3.25820000   -1.92492000   -0.79877000
C         -4.77425000   -1.63678000   -0.76065000
H         -5.31325000   -2.48170000   -1.24101000
H         -5.04018000   -0.72250000   -1.32720000
H         -5.17205000   -1.53458000    0.26523000
C         -2.80260000   -1.98959000   -2.27160000
H         -1.74403000   -2.29783000   -2.35840000
H         -2.91182000   -1.02232000   -2.80008000
H         -3.42563000   -2.73657000   -2.80862000
C         -2.95566000   -3.28700000   -0.14191000
H         -3.41146000   -4.09324000   -0.75546000
H         -3.38498000   -3.37029000    0.87513000
H         -1.86694000   -3.48538000   -0.08562000
C         -2.41583000   -0.63579000    1.96175000
C         -1.52640000   -1.78263000    2.48665000
H         -1.44962000   -1.70968000    3.59228000
H         -0.50199000   -1.71523000    2.07003000
H         -1.92317000   -2.78511000    2.24663000
```

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C	-1.84985000	0.69199000	2.51577000
H	-2.47411000	1.56721000	2.24880000
H	-0.82480000	0.87844000	2.13944000
H	-1.81092000	0.63231000	3.62414000
C	2.67965000	0.06386000	0.01140000
C	3.05506000	-0.42297000	1.28830000
C	4.24958000	-1.15544000	1.40227000
H	4.54355000	-1.53930000	2.39329000
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C	4.66753000	-0.91582000	-0.96391000
H	5.29692000	-1.10744000	-1.84886000
C	3.47893000	-0.18029000	-1.13059000
C	2.16050000	-0.16321000	2.47312000
H	1.11807000	-0.45081000	2.22495000
H	2.11960000	0.91631000	2.73306000
H	2.48947000	-0.72248000	3.36962000
C	6.33234000	-2.23876000	0.42929000
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H	6.80411000	-2.10216000	1.42331000
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C	3.03855000	0.29931000	-2.49045000
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H	2.59702000	1.31494000	-2.45192000
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C	-0.36874000	-0.00656000	-2.35459000
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H	2.57828000	3.95358000	0.49501000
H	3.27938000	2.47563000	1.22886000
H	-3.31393000	0.89330000	-1.55113000

[Fe(CO)(PMe_3)L_{PNN}] (**4a**)

Fe	0.19052000	0.08302000	0.41981000
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C	2.54592000	2.81143000	-1.81733000
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H	-0.52523000	4.31632000	-2.15582000

C	-0.14971000	2.40901000	-1.15606000
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C	-2.72077000	2.72244000	-1.15070000
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H	-3.33162000	2.85885000	-0.23288000
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H	1.99317000	-1.57828000	2.57962000
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H	1.44135000	-3.50128000	1.03192000
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C	0.51370000	-2.73653000	-1.87889000
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H	-0.32439000	-2.23528000	-1.35302000
H	0.77506000	-3.64272000	-1.30187000
C	2.92695000	-2.49057000	-2.62935000
H	2.67687000	-2.85926000	-3.64812000
H	3.23632000	-3.37162000	-2.03528000
H	3.80035000	-1.81438000	-2.73589000
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H	0.93968000	-1.10410000	-3.97037000
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C	-3.19190000	-0.57717000	-1.30840000
C	-4.39045000	-1.30951000	-1.26371000
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C	-2.39296000	-0.48825000	-2.58223000
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H	-2.73729000	-1.22482000	-3.33318000
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C	-3.01559000	0.63444000	2.33450000
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H	-3.20436000	1.72922000	2.28954000
H	-1.92561000	0.50081000	2.45964000
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C	2.45032000	2.13119000	2.26349000
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H	2.46232000	2.85160000	3.10662000
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C	0.57330000	0.66107000	3.85165000
H	0.66877000	1.46822000	4.60583000
H	-0.41912000	0.17999000	3.94304000
H	1.34308000	-0.10991000	4.04448000
C	-0.22611000	2.87453000	2.17251000
H	-1.30140000	2.63242000	2.19475000
H	0.04062000	3.50505000	3.04444000
H	-0.02698000	3.43361000	1.23763000
P	0.77982000	1.31268000	2.13002000

[Fe(CO)(PhCN)L_{PNN}] (**4b**)

Fe	-0.73785000	0.56185000	-0.25561000
P	0.75292000	2.15050000	0.11462000
O	-1.44281000	1.65441000	-2.87653000
N	-0.41372000	0.17836000	1.61735000
C	-1.19274000	1.21043000	-1.81879000
C	-2.59589000	-0.64195000	1.47199000
C	-1.43691000	-0.50387000	2.27917000
C	-1.23952000	-0.94646000	3.61936000
H	-2.03924000	-1.50886000	4.12154000
C	-0.05549000	-0.65649000	4.27799000
H	0.10338000	-0.98854000	5.31447000
C	0.94917000	0.10061000	3.60627000
H	1.88143000	0.38396000	4.11497000
C	0.73816000	0.49927000	2.29165000
C	1.71037000	1.33920000	1.50377000
C	-0.01174000	3.75082000	0.87245000
C	-0.81515000	3.29274000	2.11140000
H	-1.38535000	4.15774000	2.51187000
H	-0.16577000	2.91340000	2.92517000
H	-1.53335000	2.49131000	1.84848000
C	-1.00852000	4.33778000	-0.14903000
H	-1.68702000	3.55119000	-0.53571000
H	-0.51235000	4.81144000	-1.01511000
H	-1.63085000	5.11301000	0.34629000
C	2.11725000	2.59205000	-1.16026000
C	1.57155000	3.61204000	-2.18000000
H	1.43292000	4.61707000	-1.73680000
H	0.60960000	3.28250000	-2.62012000
H	2.30080000	3.71928000	-3.01117000
C	3.39898000	3.13501000	-0.49289000
H	4.13975000	3.37883000	-1.28467000
H	3.87415000	2.38598000	0.17117000
H	3.22852000	4.05647000	0.09206000
C	0.32959000	-0.71803000	-0.79227000
N	1.05727000	-1.65802000	-1.06013000
C	2.25552000	-2.27597000	-0.76037000
C	2.98419000	-2.95654000	-1.76372000
C	2.76470000	-2.23138000	0.56494000
C	4.20875000	-3.56238000	-1.44902000
H	2.57644000	-2.99057000	-2.78425000
C	3.98815000	-2.84524000	0.86286000

H	2.17471000	-1.72737000	1.34620000
C	4.71898000	-3.51022000	-0.13917000
H	4.77193000	-4.08398000	-2.23829000
H	4.37381000	-2.80612000	1.89357000
H	5.67925000	-3.99055000	0.10127000
N	-2.45081000	-0.08382000	0.24127000
C	-3.55789000	-0.13591000	-0.65968000
C	-4.49433000	0.92659000	-0.64430000
C	-3.69097000	-1.21815000	-1.56367000
C	-5.57316000	0.88375000	-1.54586000
C	-4.78804000	-1.21614000	-2.44444000
C	-5.74107000	-0.17866000	-2.45465000
H	-6.30341000	1.70992000	-1.53852000
H	-4.89929000	-2.05641000	-3.14990000
C	-3.86483000	-1.33123000	1.88741000
H	-3.82073000	-1.67533000	2.93710000
H	-4.74226000	-0.65904000	1.78286000
H	-4.07474000	-2.21258000	1.24479000
C	-4.29899000	2.07217000	0.31555000
H	-4.40296000	1.74856000	1.37334000
H	-3.26601000	2.46665000	0.22462000
H	-5.01911000	2.89222000	0.13184000
C	-6.88535000	-0.18790000	-3.44291000
H	-7.24730000	-1.21727000	-3.64091000
H	-7.74415000	0.41390000	-3.08377000
H	-6.57176000	0.23909000	-4.42057000
C	-2.65329000	-2.31058000	-1.59715000
H	-1.69971000	-1.92182000	-2.01108000
H	-2.40276000	-2.67745000	-0.58114000
H	-2.98322000	-3.16851000	-2.21403000
H	2.27682000	2.04134000	2.14794000
C	2.47066000	1.29162000	-1.91271000
H	2.83235000	0.49114000	-1.23679000
H	1.60514000	0.89304000	-2.47376000
H	3.28673000	1.50596000	-2.63559000
C	1.01826000	4.81081000	1.29599000
H	1.77332000	4.40615000	2.00086000
H	1.54852000	5.25487000	0.43126000
H	0.49610000	5.64145000	1.81840000
H	2.44743000	0.68284000	0.99101000

[Fe(H)(CO)(PMe_3)(L_{PNN} - H)] **(6a)**

Fe	0.12253000	-0.02004000	0.29513000
P	2.12014000	-0.84551000	-0.31425000
N	0.75117000	1.53667000	-0.73335000
N	-1.59028000	0.80951000	-0.14816000
C	2.97644000	0.67085000	-0.70518000
C	2.10677000	1.72647000	-1.01421000
C	2.46954000	2.99655000	-1.59714000
H	3.53025000	3.18475000	-1.81796000
C	1.50219000	3.94689000	-1.89778000
H	1.80452000	4.90541000	-2.34819000
C	0.12836000	3.69109000	-1.65258000
H	-0.65005000	4.42111000	-1.90731000

C	-0.19867000	2.45428000	-1.06950000
C	-1.54808000	1.97517000	-0.78083000
C	3.20728000	-1.88619000	0.89054000
C	4.71014000	-1.69340000	0.60420000
H	5.30275000	-2.29077000	1.33126000
H	5.00559000	-0.63197000	0.72486000
H	5.00497000	-2.01892000	-0.40954000
C	2.92361000	-1.39536000	2.32090000
H	1.87007000	-1.57330000	2.60560000
H	3.15210000	-0.32066000	2.43977000
H	3.56775000	-1.95118000	3.03643000
C	2.81871000	-3.37739000	0.83924000
H	3.35288000	-3.91978000	1.64910000
H	3.09685000	-3.86271000	-0.11450000
H	1.73186000	-3.51987000	1.00545000
C	2.02637000	-1.82062000	-2.01281000
C	1.00800000	-2.97441000	-1.95112000
H	0.86176000	-3.39709000	-2.96895000
H	0.02372000	-2.60973000	-1.59136000
H	1.32597000	-3.80274000	-1.29256000
C	3.40472000	-2.32610000	-2.47546000
H	3.32327000	-2.71739000	-3.51311000
H	3.79850000	-3.15032000	-1.85010000
H	4.15220000	-1.50633000	-2.49233000
C	1.53543000	-0.78814000	-3.05196000
H	2.28105000	0.01189000	-3.22186000
H	0.59334000	-0.30537000	-2.72874000
H	1.34700000	-1.30250000	-4.01866000
C	-2.80414000	0.04293000	-0.14144000
C	-3.22712000	-0.54791000	-1.36628000
C	-4.37213000	-1.36375000	-1.35815000
H	-4.69181000	-1.82744000	-2.30598000
C	-5.11135000	-1.61364000	-0.18671000
C	-4.66458000	-1.01782000	1.00554000
H	-5.21985000	-1.19888000	1.94048000
C	-3.52110000	-0.19894000	1.05456000
C	-2.45072000	-0.33383000	-2.64100000
H	-1.36240000	-0.41227000	-2.44046000
H	-2.62652000	0.67163000	-3.07711000
H	-2.72440000	-1.08258000	-3.40851000
C	-6.31403000	-2.52832000	-0.20636000
H	-6.00387000	-3.59344000	-0.13348000
H	-6.89277000	-2.42345000	-1.14644000
H	-6.99780000	-2.32740000	0.64229000
C	-3.08395000	0.41705000	2.35549000
H	-3.54519000	-0.09049000	3.22375000
H	-3.35732000	1.49288000	2.40911000
H	-1.98467000	0.35438000	2.44912000
O	-0.70590000	-2.35089000	1.81652000
C	-0.38832000	-1.39738000	1.20477000
H	4.03946000	0.72912000	-0.97813000
C	-2.75767000	2.75716000	-1.20182000
H	-2.76268000	3.74196000	-0.68753000
H	-2.74348000	2.96683000	-2.29161000
H	-3.69338000	2.22475000	-0.95152000
H	-0.21309000	-0.85656000	-0.89965000

C	2.26962000	2.23643000	2.16261000
H	2.30665000	2.95390000	1.32077000
H	2.34989000	2.78763000	3.12159000
H	3.12004000	1.54420000	2.03770000
C	0.48334000	0.67366000	3.80685000
H	0.48792000	1.49557000	4.55077000
H	-0.45936000	0.10046000	3.89585000
H	1.32018000	-0.01400000	4.02524000
C	-0.44229000	2.84037000	2.17540000
H	-0.17947000	3.44383000	3.06732000
H	-0.28345000	3.45533000	1.26867000
H	-1.50676000	2.55594000	2.22108000
P	0.64813000	1.33551000	2.08121000

[Fe(H)(CO)(PhCN)(L_{PNN} - H)] (**6b**)

Fe	-0.30910000	0.47525000	-0.20563000
P	1.10519000	2.22294000	-0.35830000
N	0.61334000	0.19555000	1.52861000
N	-1.53816000	-0.78817000	0.64386000
C	2.28004000	1.78975000	0.90965000
C	1.83816000	0.80126000	1.79492000
C	2.54229000	0.34033000	2.97368000
H	3.50588000	0.80896000	3.22125000
C	2.01791000	-0.66638000	3.76961000
H	2.57222000	-1.00087000	4.66063000
C	0.77458000	-1.27460000	3.44587000
H	0.34780000	-2.07815000	4.05873000
C	0.11492000	-0.80405000	2.29975000
C	-1.16975000	-1.30440000	1.79866000
C	2.09363000	2.49168000	-1.98593000
C	3.41885000	3.24159000	-1.73583000
H	3.97763000	3.31660000	-2.69425000
H	4.06291000	2.69269000	-1.02056000
H	3.27539000	4.26961000	-1.35815000
C	2.43870000	1.08756000	-2.52072000
H	1.53037000	0.51933000	-2.79641000
H	2.99870000	0.49864000	-1.76768000
H	3.07553000	1.18802000	-3.42624000
C	1.24285000	3.22686000	-3.03902000
H	1.78357000	3.22815000	-4.01025000
H	1.05613000	4.28452000	-2.76998000
H	0.26617000	2.72921000	-3.20218000
C	0.27935000	3.89350000	0.18509000
C	-1.00763000	4.16163000	-0.61787000
H	-1.49441000	5.08634000	-0.23824000
H	-1.72759000	3.32811000	-0.50153000
H	-0.82363000	4.30264000	-1.69880000
C	1.24675000	5.08570000	0.07501000
H	0.78149000	5.98058000	0.54283000
H	1.47906000	5.35257000	-0.97428000
H	2.19857000	4.89146000	0.61064000
C	-0.09136000	3.70806000	1.67250000
H	0.80854000	3.57662000	2.30468000
H	-0.73790000	2.81912000	1.81689000

H	-0.64570000	4.60379000	2.02657000
C	-2.83222000	-1.04220000	0.09503000
C	-3.93308000	-0.28754000	0.57150000
C	-5.19059000	-0.50294000	-0.02225000
H	-6.05078000	0.08471000	0.33839000
C	-5.37920000	-1.43839000	-1.05697000
C	-4.25961000	-2.16921000	-1.50094000
H	-4.38333000	-2.90713000	-2.31071000
C	-2.97886000	-1.98354000	-0.95163000
C	-3.73719000	0.72735000	1.66915000
H	-2.86148000	1.37166000	1.43799000
H	-3.52115000	0.24307000	2.64539000
H	-4.63263000	1.36441000	1.79871000
C	-6.73221000	-1.62682000	-1.70401000
H	-6.81523000	-1.02231000	-2.63335000
H	-7.55659000	-1.31217000	-1.03356000
H	-6.90603000	-2.68422000	-1.98926000
C	-1.77989000	-2.73484000	-1.46976000
H	-2.07549000	-3.54379000	-2.16480000
H	-1.18042000	-3.17577000	-0.64703000
H	-1.09668000	-2.04149000	-2.00298000
O	-1.80162000	1.16259000	-2.60525000
C	-1.19137000	0.84938000	-1.65436000
H	3.20114000	2.35338000	1.11132000
C	-1.98352000	-2.29661000	2.57752000
H	-1.40011000	-3.22708000	2.73707000
H	-2.23223000	-1.89610000	3.58225000
H	-2.92074000	-2.55198000	2.05013000
H	-1.16193000	1.53527000	0.42079000
N	0.86992000	-0.88996000	-0.75502000
C	1.64681000	-1.77570000	-0.74342000
C	2.62788000	-2.78001000	-0.52026000
C	3.03597000	-3.67977000	-1.53836000
C	3.20349000	-2.86747000	0.77839000
C	4.00442000	-4.65141000	-1.25718000
H	2.58791000	-3.60507000	-2.53977000
C	4.16919000	-3.84658000	1.03831000
H	2.88428000	-2.16097000	1.55955000
C	4.57244000	-4.73936000	0.02742000
H	4.32061000	-5.34822000	-2.04819000
H	4.61434000	-3.91220000	2.04274000
H	5.33298000	-5.50569000	0.24075000

[Fe(H)(CO)(PhCN)(L_{PNP} - H)] (**9**)

Fe	-0.05723000	0.23585000	-0.11908000
H	-0.87985000	1.40221000	0.45832000
P	-1.96345000	-0.85291000	0.00160000
P	1.79572000	1.38727000	0.37162000
O	-0.61299000	1.65772000	-2.58308000
N	0.09972000	-0.35894000	1.84786000
C	-0.36723000	1.05557000	-1.60592000
C	-2.28966000	-0.79885000	1.82699000
H	-2.74099000	0.19701000	2.02599000
H	-3.00361000	-1.57197000	2.17573000

C	-0.95693000	-0.87918000	2.53093000
C	-0.83438000	-1.42333000	3.81158000
H	-1.71347000	-1.84250000	4.31902000
C	0.44607000	-1.40545000	4.42305000
H	0.58520000	-1.84667000	5.42267000
C	1.51254000	-0.81183000	3.77337000
H	2.50492000	-0.75651000	4.24375000
C	1.34477000	-0.22039000	2.47003000
C	2.35022000	0.49814000	1.80149000
C	-1.97603000	-2.69743000	-0.38698000
H	-1.57611000	-2.74049000	-1.42427000
C	-3.36677000	-3.35045000	-0.34136000
H	-3.27754000	-4.43942000	-0.53930000
H	-4.07035000	-2.93773000	-1.09016000
H	-3.83211000	-3.24296000	0.66117000
C	-0.99605000	-3.43767000	0.54212000
H	-1.39610000	-3.50985000	1.57399000
H	-0.01221000	-2.93792000	0.60396000
H	-0.83320000	-4.47089000	0.17160000
C	-3.51042000	-0.16884000	-0.80521000
H	-4.35258000	-0.74395000	-0.35952000
C	-3.48118000	-0.40543000	-2.32628000
H	-4.42932000	-0.05012000	-2.78109000
H	-3.36521000	-1.47385000	-2.59577000
H	-2.65426000	0.15781000	-2.80123000
C	-3.70449000	1.32127000	-0.48386000
H	-2.89128000	1.93242000	-0.92107000
H	-3.72909000	1.52586000	0.60480000
H	-4.66639000	1.67314000	-0.91207000
C	1.55651000	3.22058000	0.79950000
H	2.57223000	3.67483000	0.74932000
C	1.01606000	3.33377000	2.23195000
H	0.83085000	4.39736000	2.49309000
H	1.71151000	2.90228000	2.97739000
H	0.05268000	2.78752000	2.32099000
C	0.62310000	3.93344000	-0.19109000
H	-0.40074000	3.51389000	-0.11377000
H	0.93864000	3.83176000	-1.24610000
H	0.56696000	5.01731000	0.04520000
C	3.20988000	1.35858000	-0.87109000
H	3.22481000	0.29049000	-1.17322000
C	2.95889000	2.21079000	-2.12372000
H	3.00475000	3.29518000	-1.89323000
H	1.97814000	1.99946000	-2.59162000
H	3.74454000	2.00710000	-2.88163000
C	4.56482000	1.68782000	-0.22583000
H	5.37452000	1.60502000	-0.98158000
H	4.80938000	0.99224000	0.60036000
H	4.59367000	2.72450000	0.17157000
H	3.29433000	0.72080000	2.31911000
C	0.99425000	-1.08839000	-0.73229000
N	1.74211000	-1.93680000	-1.15883000
C	2.96756000	-2.58003000	-1.12090000
C	3.30829000	-3.52850000	-2.11003000
C	3.87946000	-2.27471000	-0.07925000
C	4.55852000	-4.16234000	-2.05968000

H	2.58603000	-3.75217000	-2.90836000
C	5.12238000	-2.91877000	-0.04505000
H	3.58155000	-1.52866000	0.67827000
C	5.46916000	-3.86142000	-1.03145000
H	4.82403000	-4.89937000	-2.83300000
H	5.83028000	-2.68116000	0.76411000
H	6.44853000	-4.36218000	-0.99773000

[Fe(CO)(PhCN)LPNP] (**10**)

Fe	-0.65536000	0.59203000	-0.18502000
P	-2.16795000	-0.96573000	-0.24628000
P	0.95349000	1.93506000	0.42070000
O	-2.15534000	2.48325000	-1.83832000
N	-0.94429000	0.39912000	1.81264000
C	-1.60468000	1.75631000	-1.08218000
C	-3.14217000	-0.48958000	1.27134000
H	-3.68299000	0.43121000	0.95742000
H	-3.87976000	-1.23097000	1.63835000
C	-2.11844000	-0.12352000	2.31172000
C	-2.32799000	-0.30453000	3.68372000
H	-3.28758000	-0.71673000	4.02822000
C	-1.31910000	0.04119000	4.59789000
H	-1.46530000	-0.09341000	5.67938000
C	-0.11374000	0.55277000	4.08977000
H	0.71570000	0.81837000	4.76135000
C	0.05050000	0.71677000	2.70858000
C	1.33675000	1.20521000	2.09927000
C	-1.58337000	-2.73372000	0.05842000
H	-1.11744000	-2.98756000	-0.92094000
C	-2.70667000	-3.73329000	0.36897000
H	-2.29350000	-4.76121000	0.44397000
H	-3.50005000	-3.75591000	-0.40502000
H	-3.18716000	-3.50612000	1.34396000
C	-0.48391000	-2.77382000	1.13186000
H	-0.90708000	-2.62473000	2.14689000
H	0.26327000	-1.97642000	0.95296000
H	0.03406000	-3.75457000	1.11877000
C	-3.35589000	-1.14115000	-1.68502000
H	-3.79131000	-2.16062000	-1.60411000
C	-2.53293000	-1.04794000	-2.98363000
H	-3.17372000	-1.28260000	-3.85906000
H	-1.66957000	-1.74341000	-2.99087000
H	-2.12301000	-0.02663000	-3.10868000
C	-4.50013000	-0.11687000	-1.65398000
H	-4.11586000	0.92194000	-1.64455000
H	-5.16717000	-0.25624000	-0.77929000
H	-5.12393000	-0.23019000	-2.56551000
C	0.57778000	3.73473000	0.83944000
H	1.45809000	4.09983000	1.41504000
C	-0.67217000	3.79795000	1.73334000
H	-0.95876000	4.85449000	1.91772000
H	-0.51471000	3.31580000	2.71861000
H	-1.52307000	3.28459000	1.23953000
C	0.40410000	4.59142000	-0.42454000

H	-0.39072000	4.18399000	-1.08040000
H	1.33650000	4.66311000	-1.01709000
H	0.11024000	5.62458000	-0.14302000
C	2.61748000	1.91268000	-0.44408000
H	2.89116000	0.83942000	-0.33359000
C	2.49131000	2.19561000	-1.95079000
H	2.33317000	3.27301000	-2.15490000
H	1.65394000	1.62917000	-2.40050000
H	3.42532000	1.89172000	-2.46721000
C	3.69372000	2.77658000	0.22780000
H	4.67823000	2.60166000	-0.25498000
H	3.81045000	2.55191000	1.30783000
H	3.46958000	3.85865000	0.12628000
H	1.89808000	1.87310000	2.78451000
C	0.42045000	-0.34226000	-1.16827000
N	1.12776000	-0.95869000	-1.98601000
C	2.24216000	-1.77877000	-1.84121000
C	2.77328000	-2.43672000	-2.97675000
C	2.88304000	-1.96565000	-0.58675000
C	3.90654000	-3.25392000	-2.86022000
H	2.27495000	-2.28580000	-3.94578000
C	4.01585000	-2.78249000	-0.48056000
H	2.46092000	-1.46439000	0.29756000
C	4.53714000	-3.43189000	-1.61511000
H	4.30535000	-3.75762000	-3.75475000
H	4.49806000	-2.91663000	0.50093000
H	5.42870000	-4.07124000	-1.52904000
H	1.98018000	0.32495000	1.87207000

$[Fe(H)(CO)_2(L_{PNN} - H)]$ (**11**)

Fe	-0.15555000	-0.05499000	-0.36593000
P	-2.30296000	-0.51963000	0.15414000
N	-0.76451000	1.81280000	-0.15557000
N	1.57970000	0.87149000	-0.20055000
C	-3.03652000	1.07674000	-0.11873000
C	-2.11849000	2.13364000	-0.13476000
C	-2.44554000	3.54147000	-0.10748000
H	-3.50742000	3.82682000	-0.09228000
C	-1.45198000	4.50693000	-0.08641000
H	-1.72706000	5.57272000	-0.06075000
C	-0.08160000	4.13405000	-0.08808000
H	0.72004000	4.88269000	-0.06561000
C	0.20777000	2.76268000	-0.12578000
C	1.55307000	2.18351000	-0.10823000
C	-3.27917000	-1.80530000	-0.89093000
C	-4.79389000	-1.50664000	-0.86564000
H	-5.31767000	-2.24931000	-1.50572000
H	-5.01096000	-0.50187000	-1.27877000
H	-5.23738000	-1.57202000	0.14354000
C	-2.79753000	-1.66416000	-2.34746000
H	-1.74886000	-1.99569000	-2.46849000
H	-2.87856000	-0.61918000	-2.70531000
H	-3.42916000	-2.30099000	-3.00338000
C	-2.99746000	-3.24403000	-0.41712000

H	-3.45615000	-3.95970000	-1.13291000
H	-3.43103000	-3.45753000	0.57870000
H	-1.91120000	-3.46140000	-0.38024000
C	-2.52843000	-0.92306000	2.04511000
C	-1.60905000	-2.07695000	2.48675000
H	-1.71452000	-2.23378000	3.58220000
H	-0.54674000	-1.83816000	2.28346000
H	-1.84392000	-3.03609000	1.99016000
C	-3.99482000	-1.23087000	2.40030000
H	-4.09722000	-1.29608000	3.50529000
H	-4.34376000	-2.19601000	1.98529000
H	-4.67719000	-0.42772000	2.05428000
C	-2.11287000	0.35927000	2.79771000
H	-2.79143000	1.20492000	2.57306000
H	-1.08348000	0.66936000	2.52614000
H	-2.13890000	0.16597000	3.89153000
C	2.79023000	0.13294000	-0.01661000
C	3.24890000	-0.09035000	1.30641000
C	4.40423000	-0.87456000	1.48480000
H	4.76236000	-1.05807000	2.51098000
C	5.10780000	-1.42765000	0.39967000
C	4.61950000	-1.18190000	-0.89883000
H	5.15485000	-1.60525000	-1.76473000
C	3.46265000	-0.41885000	-1.13425000
C	2.50072000	0.48572000	2.48223000
H	1.40927000	0.31230000	2.36279000
H	2.64043000	1.58487000	2.56327000
H	2.83495000	0.03425000	3.43556000
C	6.34078000	-2.27666000	0.60739000
H	6.15806000	-3.32807000	0.29891000
H	6.65900000	-2.28943000	1.66817000
H	7.19345000	-1.90777000	-0.00005000
C	2.93464000	-0.22215000	-2.53218000
H	3.72314000	-0.39420000	-3.28990000
H	2.51388000	0.79064000	-2.68469000
H	2.10930000	-0.93555000	-2.73752000
O	0.71914000	-2.82961000	-0.24523000
C	0.38100000	-1.71314000	-0.31593000
O	-0.35294000	0.28695000	-3.29290000
C	-0.31809000	0.11517000	-2.14132000
H	-4.11401000	1.27204000	-0.03209000
C	2.77665000	3.04200000	0.02979000
H	2.81745000	3.78022000	-0.79730000
H	2.74207000	3.61964000	0.97650000
H	3.70018000	2.43537000	0.01286000
H	-0.02699000	-0.16817000	1.14889000

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