

SUPPORTING INFORMATION

Metal-Ligand Cooperativity in Iron Dinitrogen Complexes: Proton Coupled Electron Transfer Disproportionation and an Anionic Fe(0)N₂ Hydride

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General. Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry nitrogen or argon in flame-dried glassware or in a nitrogen or argon filled MBraun glovebox. All solvents described in the procedures were dried before use, unless stated otherwise. Anhydrous solvents were freshly distilled from appropriate drying agents (CH_2Cl_2 over CaH_2 , THF over Na/benzophenone, EtOH over Na) or dried over activated alumina columns (M. Braun SPS 800 - Et_2O , hexane, toluene, methanol) and were transferred under Argon. $(^{\text{tBu}}\text{PNN})\text{FeBr}_2^1$ and NaBMe_3H^2 were prepared according to literature known procedures.

NMR spectroscopy ^1H , ^2H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded using a Bruker Avance VIII-400 or Bruker Avance III HD 600 MHz spectrometer. Deuterated solvents were distilled from the appropriate drying agents, degassed by three freeze-pump-thaw cycles and stored over 4 Å molecular sieves prior to use. ^1H NMR spectra (400.1 MHz or 600.1 MHz) were referenced to the residual protons of the deuterated solvent used. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Where appropriate, resonances were assigned using 2D NMR homo- and heterocorrelation (COSY, HMBC, HSQC) techniques. Chemical shifts (δ) are given in ppm, relative to TMS, coupling constants (J) in Hz.

IR: ATR (solid state) measurements were performed in a nitrogen filled glovebox (SylaTech Y05G) using an Agilent Cary 630 FTIR spectrometer equipped with a diamond ATR unit.

Elemental Analyses were carried out on a Elementar vario MICRO cube in the Microanalysis Laboratory of the Heidelberg Chemistry Department.

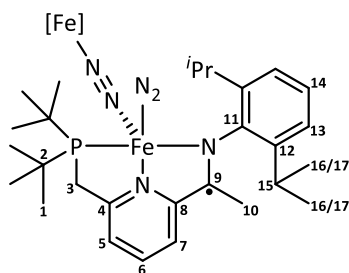
Continuous-wave X-band EPR spectra (ca. 9 GHz) were measured on a Bruker Biospin Elexsys E500 EPR spectrometer fitted with super high Q cavity. The magnetic field and the microwave frequency were calibrated with a Bruker ER 041XK Teslameter and a Bruker microwave frequency counter. The temperature of the sample was adjusted using a flow-through cryostat in conjunction with a Eurotherm (B-VT-2000) variable temperature controller. EPR spectra simulations were carried out using the EasySpin module run through Matlab R2019b.

¹ (a) Butschke, B.; Fillman, K. L.; Bendikov, T.; Shimon, L. J.; Diskin-Posner, Y.; Leitun, G.; Gorelsky, S. I.; Neidig, M. L.; Milstein, D., How Innocent are Potentially Redox Non-Innocent Ligands? Electronic Structure and Metal Oxidation States in Iron-PNN Complexes as a Representative Case Study. *Inorg Chem* **2015**, 54 (10), 4909-26. (b) Du, X.; Zhang, Y.; Peng, D.; Huang, Z., Base-Metal-Catalyzed Regiodivergent Alkene Hydrosilylations. *Angew Chem. Int. Ed.* **2016**, 55 (23), 6671-6675.

² Bell, N. A.; Coates, G. E.; Heslop, J. A., Sodium hydridotrimethylboronate and its ether solvate. Study of hydridotrialkylboronates as reagents for the preparation of beryllium hydrides. *J. Organomet. Chem.* **1987**, 329, 287-291.

Preparation of metal complexes

[[^tBuPNN)Fe(N₂)]₂(μ-N₂) (2**).** In a nitrogen filled glovebox (^tBuPNN)FeBr₂ (**1**) (2.00 g, 3.06 mmol, 1.0 eq.) was added to a 500 mL one necked flask, suspended in -40 °C cold Et₂O (250 mL) and NaBEt₃H (1 M in toluene, 6.00 mL, 6.00 mmol, 1.96 eq.) was added slowly. The mixture was stirred at r.t. for 1.5 h during which the blue suspension turned dark green. The reaction mixture was filtered over a Celite® plug and rinsed with Et₂O until the solution was colorless. The volatile components were removed *in vacuo* and the green/black solid was triturated with Et₂O (3x) to remove residual BEt₃ and toluene. This crude product, usually obtained in quantitative yield, is spectroscopically pure (as judged by ¹H, ³¹P, ¹¹B NMR) and can be directly used for further reactions. If needed, the crude solid can be repeatedly recrystallized from Et₂O/Pentane (3:1 to 1:1 mixtures) at -40 °C to yield dark green crystals of **2** (1.14 g, 69 %). Slow evaporation of a concentrated solution of **2** in Et₂O at r.t. afforded crystals suitable for single crystal X-ray diffraction.



¹H NMR (600 MHz, C₆D₆, 295 K) δ[ppm] = 7.31 (br s, 4H, H13/14), 7.22 (br s, 2H, H13/14), 7.04 (br s, 2H, H5/6/7), 6.98 (br s, 2H, H5/6/7), 6.83 (br s, 2H, H5/6/7), 3.36 (br m, 4H, H3), 3.13 (br s, 2H, H15), 2.53 (br s, 2H, H15), 1.67 (br s, 6H, H16/17), 1.31 (br s, 6H, H10), 1.26 (br s, 6H, H16/17), 1.22 (br s, 6H, H16/17), 1.00 (br s, 6H, H16/17), 0.80 (br d, 18H, H1), 0.70 (br s, 18H, H1). **¹³C{¹H} NMR** (151 MHz, C₆D₆, 295 K)

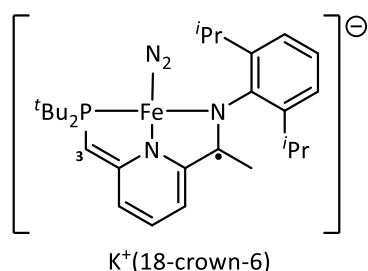
δ [ppm] = 164.0 (br s, C_q), 151.3 (br s, C_q), 146.3 (br s, C_q), 143.9 (br s, C_q), 140.5 (br d, J = 9.7 Hz, C_q), 125.7 (s, CH, C13/14), 124.5 (br s, CH, C5/6/7), 123.8 (br s, CH, C13/14), 123.0 (br s, CH, C13/14), 119.2 (br s, CH, C5/6/7), 109.1 (br s, CH, C5/6/7), 38.7 (br s, C_q), 35.6 (br s, C_q), 34.8 (br d, J = 14.4 Hz, CH₂, C3), 30.2 (br s, CH, C1), 28.2 (br s, CH, C1), 27.7 (br s, CH, C15), 27.4 (br s, CH, C15), 26.3 (br s, CH, C16/17), 24.8 (br s, CH, C16/17), 24.5 (br s, CH, C16/17), 24.3 (br s, CH, C16/17), 17.3 (br s, CH, C10).

³¹P{¹H} NMR (243 MHz, C₆D₆, 295 K) δ [ppm] = 113.7. **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 2060 (ν_{sym} terminal N₂), 2039 (ν_{asym} terminal N₂), 1959 (ν bridging N₂). Anal. Calcd. for C₅₆H₈₆Fe₂N₁₀P₂ [%]: C: 62.68, H: 8.08, N: 13.05; found: C: 62.69, H: 8.26, N: 12.48. Even after multiple attempts the nitrogen content was always too low most likely due to the lability of the coordinated N₂.

Deprotonation:

(**K⁺@18-crown-6**)[(^{*t*}BuPNN-H⁺)Fe(N₂)] (**3b**). In a nitrogen filled glovebox [(^{*t*}BuPNN)Fe(N₂)₂(μ-N₂) (**2**) (20 mg, 18.6 μmol, 1.0 eq.) was dissolved in THF-d₈ (400 μL) and added to a precooled Young NMR tube (-40 °C). KHMDS (7.4 mg, 37.3 μmol, 2.0 eq.) and 18-crown-6 (9.9 mg, 37.3 μmol, 2.0 eq.) were dissolved in a separate vial in THF-d₈ (200 μL). Both solutions were cooled to -40 °C in a cold-dwell

inside the glovebox. The solution of KHMDS was added dropwise to **2** and the mixture was carefully shaken. No obvious color change was observed except where the solution came in contact with warm glass it turned brown. The mixture was directly transferred to a pre-cooled NMR spectrometer (-40 °C) and measured. ^{31}P NMR indicates quantitative conversion to the title compound. *Due to the instability of the compound it was not possible to obtain single-crystals for xray structure determination.*



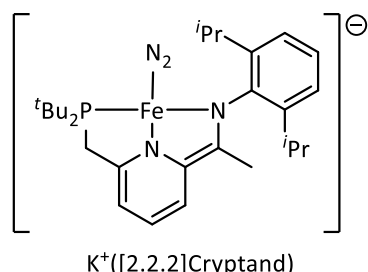
^1H NMR (600 MHz, THF- d_8 , 233 K) δ [ppm] = 7.05 (br s, 3H), 6.22 (br s, 1H), 5.90–5.83 (br m, 2H), 3.58 (overlapping w/ THF- d_7 , 18-crown-6), 3.38 (overlapping, br s), 3.18 (br s), 2.99 (br s), 1.44 (br s), 1.12 (br s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, THF- d_8 , 233 K) δ [ppm] = 173.8 (d, J = 22.4 Hz), 152.4 (br s), 149.6 (br s), 141.6 (br s), 138.5 (br s), 125.8 (br s), 123.7 (br s), 122.5 (br s), 96.6 (br s), 95.4 (br d, J = 13.0 Hz),

71.2 (br s), 54.6 (d, J = 49.4 Hz, C3), 38.9 (br s), 30.7 (br s), 27.3 (br s), 25.8 (br s), 24.7 (br s), 17.6 (br s), 15.7 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, THF- d_8 , 233 K) δ [ppm] = 97.0. *For this compound no 2D NMR spectra could be recorded after several attempts due to the sensitivity of the compound.* IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 1908(ν N_2). *Due to the sensitivity of the compound no clean IR spectrum could be obtained.*

Reduction:

($\text{K}^+ @ [2.2.2]\text{Cryptand}$)[($^t\text{BuPNN}$) $\text{Fe}(\text{N}_2)$] (4a**). [($^t\text{BuPNN}$) $\text{Fe}(\text{N}_2)$] $(\mu\text{-N}_2)$ (**2**) (110 mg, 103 μmol , 1.0 eq.), [2.2.2]Cryptand (81.1 mg, 215 μmol , 2.1 eq.) were weighed into a screw-capped vial and dissolved in precooled Et_2O (-40 °C, 10.0 mL). KC_8 (27.7 mg, 205 μmol , 2.0 eq.) was added slowly and the mixture was stirred at r.t. for 4 days. The reaction mixture was filtered using a frit and the solid was washed with Et_2O (1x 10.0 mL) and pentane (2x 10.0 mL). The product was extracted with THF (2x 10.0 mL) and the solvent removed *in vacuo*. The title compound was obtained as a brown solid (140 mg, 72 %). Layering a concentrated solution of **4a** in THF with HMDSO at r.t. afforded crystals suitable for single crystal X-ray diffraction.**



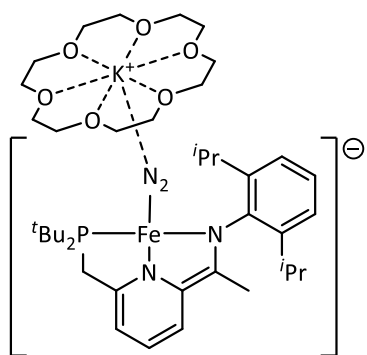
^1H NMR (400 MHz, THF- d_8 , 295 K) δ [ppm] = 10.99 (br s, 1H), 8.82 (s, 1H), 6.42 (br s, 2H), 5.39 (s, 2H), 3.27 (br s, 24H, [2.2.2]Cryptand), 2.28 (br s, 12H, [2.2.2]Cryptand), -1.62 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), -3.02 (br s, 18H, $\text{C}(\text{CH}_3)_3$), -5.25 (br s, 3H, imine CH_3), -6.82 (br s, 6H, $\text{CH}(\text{CH}_3)_2$), -15.11 (br s, 2H), -29.41 (br s, 2H). IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 1927(ν N_2). Anal.

Calcd. for $\text{C}_{46}\text{H}_{79}\text{FeKN}_6\text{O}_6\text{P}$ [%]: C: 58.90, H: 8.49, N: 8.96; found: C:

59.25, H: 8.56, N: 8.43. Despite multiple attempts, the nitrogen content was always too low most likely due to the lability of the coordinated N_2 .

Reduction:

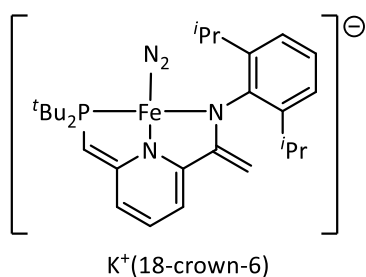
(K⁺@18-crown-6)[(^tBuPNN)Fe(N₂)] (4b). In a nitrogen filled glovebox [(^tBuPNN)Fe(N₂)]₂(μ-N₂) (**2**) (100 mg, 93.2 μmol, 1.0 eq.) and 18-crown-6 (50.0 mg, 189 μmol, 2.0 eq.) were weighed into a vial and dissolved in precooled Et₂O (-40 °C, 10.0 mL) and placed at -40 °C for 10 min. Under vigorous stirring solid K₂C₈ (25.0 mg, 185 μmol, 2.0 eq.) was added slowly and the mixture was stirred at r.t. for 2 days. Pentane (5 mL) was added and the brown reaction mixture was filtered using a frit. The solid was washed with pentane (2x 10 mL), the product extracted with THF (5 mL) until the filtrate was colorless. The solvent was removed *in vacuo* to obtain the title compound as a brown solid (108 mg, 70 %). Layering a concentrated solution of **4b** in THF with hexane at r.t. afforded crystals suitable for single crystal X-ray diffraction.



¹H NMR (600 MHz, THF-d₈, 295 K) δ[ppm] = 11.24 (br s, 1H), 8.77 (s, 1H), 6.46–6.39 (br m, 2H), 5.36 (s, 2H), -1.73 (s, 6H, CH(CH₃)₂), -3.04 (br s, 18H, C(CH₃)₃), -5.31 (br s, 3H, imine CH₃), -6.83 (br s, 6H, CH(CH₃)₂), -15.19 (br s, 2H), -29.91 (br s, 2H). **Magnetic susceptibility** (Evans, THF-d₈, 295 K) μ_{eff} [μ_B] = 2.5(2). **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 1912(ν N₂). Anal. Calcd. for C₄₀H₆₇FeKN₄O₆P [%]: C: 58.17, H: 8.18, N: 6.78; found: C: 59.02, H: 8.36, N: 5.70. Despite multiple attempts, the nitrogen content was always too low most likely due to the lability of the coordinated N₂.

Disproportionation:

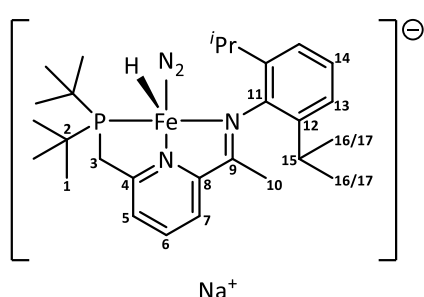
(K⁺@18-crown-6)[(^tBuPNN)Fe(N₂)] (4b) & (K⁺@18-crown-6)[(^tBuPNN-2H⁺)Fe(N₂)] (5b). In a nitrogen filled glovebox [(^tBuPNN)Fe(N₂)]₂(μ-N₂) (**2**) (100 mg, 93.2 μmol, 1.0 eq.) and 18-crown-6 (50.0 mg, 189 μmol, 2.0 eq.) were weighed into a vial and dissolved in THF (3.00 mL). KHMDS (37.2 mg, 186 μmol, 2.0 eq.) was weighed into a separate vial and dissolved in THF (1.00 mL). The solution of KHMDS was added dropwise to **2** and the vial was rinsed with additional THF (1.00 mL). The color of the solution changed instantly from green to dark brown. The mixture was stirred for 1 h at r.t. The solvent was removed *in vacuo* and the residue triturated with Et₂O (2x 10.0 mL). The solid was washed with Et₂O (10.0 mL) and pentane (2x 10.0 mL). After drying under high vacuum 127 mg of a brown solid was obtained containing the two title components. The reduced species **4b** can be identified in ¹H NMR as well as IR, X-ray quality single crystals of the doubly deprotonated compound **5b** were crystallized from the mixture by layering a concentrated THF solution with hexane at r.t. A small amount of a third component, **3b**, is only visible in ¹H and ³¹P{¹H} NMR at low temperature (233 K) and its amount decreases over time.



¹H NMR (600 MHz, THF-d₈, 295 K) δ[ppm] = 27.04 (s), 20.91 (s), 18.10 (s), 8.32 (s), 4.05 (br s, 18-crown-6), 3.37 (s), 1.10 (s), -7.80 (s), -9.69 (br s), -10.00 (br s), -24.89 (s), -34.94 (s), -53.72 (br s), -55.85 (br s) [**5b**]. **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 1937(ν N₂ of **5b**), 1920 (ν N₂ of **4b**).

(Na⁺)[(^tBuPNN)FeH(N₂)] (6a**).** In a nitrogen filled glovebox [(^tBuPNN)Fe(N₂)]₂(μ-N₂) (**2**) (100 mg, 93.2 μmol, 1.0 eq.) was weighed into a screwcapped vial, dissolved in cold THF (-40 °C, 4.00 mL) and placed in the freezer (-40 °C) for 30 min. A stock solution of NaBMe₃H (75.0 mg) in cold THF (-40 °C, 1.00 mL) was prepared and stored in the freezer. The solution of **2** was stirred vigorously and the first portion of NaBMe₃H stock solution (400 μL, 375 μmol, 4.0 eq.) was added dropwise. The mixture was stirred at r.t. for 40 min before all volatile components were removed *in vacuo*. The residue was redissolved in cold THF (-40 °C, 4.00 mL) and placed in the freezer (-40 °C) for 30 min. A second portion of NaBMe₃H stock solution (400 μL, 375 μmol, 4.0 eq.) was added dropwise. The mixture was stirred at r.t. for 30 min before all volatile components were removed *in vacuo*. Et₂O (10.0 mL) was added and stirred for 30 min (at first the compound seems to dissolve but after a few minutes a forest green precipitate is visible). The product was collected on a frit, washed with Et₂O (4x 15.0 mL) to remove any boron sideproducts and dried in a stream of N₂. Compound **6a** was obtained as a forest green powder (68.2 mg, 66 %). Recrystallization at r.t. via vapour diffusion of Et₂O into a concentrated THF solution of **6a** afforded crystals suitable for single crystal X-ray diffraction.

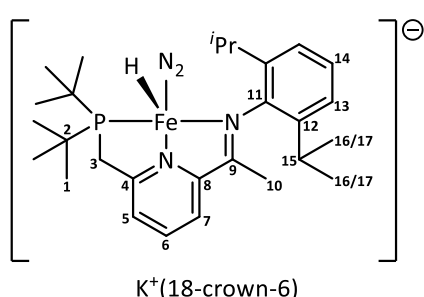
Please note that NMR experiments (¹H and ³¹P NMR) indicate that the conversion of **2** to **6a** is quantitative but due to the partial solubility of **6a** in Et₂O some product is lost during purification.



¹H NMR (600 MHz, THF-d₈, 295 K) δ[ppm] = 7.10 (br s, 1H, H13/14), 7.02 (br s, 2H, H13/14), 6.28 (d, J = 8.0 Hz, 1H, H7), 5.92 (br t, 1H, H6), 5.62 (br s, 1H, H5), 3.57 (overlapping w/ THF-d₇, 1H, H15), 3.39–3.29 (m, AB spin system, 2H, H3), 2.72 (br m, 1H, H15), 1.72 (overlapping w/ THF-d₇, 3H, H10), 1.34–1.29 (overlapping, m, 12H, H1 + H16/17), 1.07–1.03 (overlapping, m, 15H, H1 + 2x H16/17), 0.92 (d, J = 6.2 Hz, 3H, H16/17), -24.25 (d, J = 49.5 Hz, 1H, Fe–H). **¹³C{¹H} NMR** (151 MHz, THF-d₈, 295 K) δ[ppm] = 161.9 (d, J = 7.7 Hz, C_q, C4), 154.2 (s, C_q), 143.5 (s, C_q), 141.6 (s, C_q), 133.2 (d, J = 5.8 Hz, C_q), 126.4 (s, C_q), 123.1 (s, CH, C13/14), 122.4 (s, CH, C13/14), 122.0 (s, CH, C13/14),

117.0 (s, CH, C6), 115.4 (s, CH, C7), 98.5 (d, $J = 9.6$ Hz, CH, C5), 39.9 (s, C_q , C2), 36.2 (d, $J = 16.5$ Hz, CH_2 , C3), 35.0 (d, $J = 6.3$ Hz, C_q , C2), 31.8 (d, $J = 2.7$ Hz, CH_3 , C1), 29.0 (d, $J = 5.3$ Hz, CH_3 , C1), 28.2 (s, CH, C15), 27.7 (s, CH, C15), 25.4³ (s, CH_3 , C16/17), 25.0³ (s, CH_3 , C16/17), 24.2 (s, CH_3 , C16/17), 24.1 (s, CH_3 , C16/17), 14.8 (s, CH_3 , C10). **³¹P{¹H} NMR** (243 MHz, THF- d_8 , 295 K) δ [ppm] = 138.6. **IR** (ATR) $\tilde{\nu}$ [cm^{-1}] = 1934(ν N_2), 1702(ν Fe—H). Anal. Calcd. for $C_{28}H_{44}FeN_4NaP$ [%]: C: 61.54, H: 8.12, N: 10.25; found: C: 61.45, H: 8.26, N: 9.76. Despite multiple attempts, the nitrogen content was always too low most likely due to the lability of the coordinated N_2 .

(K⁺@18-crown-6)[(^{*t*}BuPNN)FeH(N_2)] (6b). Method A: In a nitrogen filled glovebox [^{*t*}BuPNN)Fe(N_2)]₂(μ - N_2) (**2**) (20 mg, 18.6 μ mol, 1.0 eq.) was dissolved in THF- d_8 (400 μ L) and added to a precooled NMR pressure tube (-40 °C). KHMDS (7.4 mg, 37.3 μ mol, 2.0 eq.) and 18-crown-6 (9.9 mg, 37.3 μ mol, 2.0 eq.) were dissolved in a separate vial in THF- d_8 (200 μ L). Both solutions were cooled to -40 °C in a cold-dwell inside the glovebox. The solution of KHMDS was added dropwise to **2** and the mixture was carefully shaken. The tube was pressurized with H_2 (5 bar) and directly transferred to a pre-cooled NMR spectrometer (-40 °C) and measured. The temperature was kept at -10 °C for 17 h and then 1 h at +5 °C. ¹H and ³¹P NMR showed full conversion to the target compound. Method B: (K⁺@18-crown-6)[(^{*t*}BuPNN)Fe(N_2)] (**4b**) (15.0 mg, 18.2 μ mol, 1.0 eq.) was weighed into a vial, dissolved in THF- d_8 (500 μ L) and transferred into a pressure tube. The NMR tube was pressurized with H_2 (5 bar). After 23 h at r.t. the ¹H NMR showed no remaining signals of the starting material indicating full conversion to the title compound. Method C: The title compound can also be obtained by deprotonating [^{*t*}BuPNN)Fe(N_2)]₂(μ - N_2) (**2**) with KHMDS and 18-crown-6 at r.t. (see compound **5b**) and then pressurizing this mixture with H_2 . In this method full conversion is only achieved after prolonged reaction times (1 week).

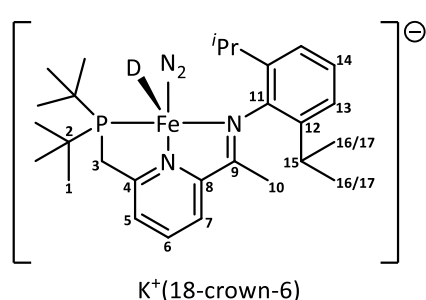


¹H NMR (600 MHz, THF- d_8 , 295 K) δ [ppm] = 7.00 (d, $J = 7.1$ Hz, 1H, H13), 6.96 (d, $J = 7.1$ Hz, 1H, H13), 6.91 (t, $J = 7.2$ Hz, 1H, H14), 6.07 (d, $J = 8.7$ Hz, 1H, H7), 5.67 (t, $J = 7.0$ Hz, 1H, H6), 5.29 (d, $J = 4.9$ Hz, 1H, H5), 3.51 (overlapping, br s, 18-crown-6 + H15), 3.21–3.10 (overlapping, m, 3H, H3 + H15), 1.73 (overlapping w/ THF- d_7 , 3H, H10), 1.28 (d, $J = 9.4$ Hz, 9H, H1), 1.23 (d, $J = 6.0$ Hz, 3H, H16/17), 1.08–1.06 (m, 12H, H1 + H16/17), 0.98 (m, 6H, 2x H16/17), -21.97 (d, $J = 63.1$ Hz, 1H, Fe—H). **¹³C{¹H} NMR** (151 MHz, THF- d_8 , 295 K) δ [ppm] = 161.5 (d, $J = 8.5$ Hz, C_q), 155.3 (s, C_q), 143.0 (d, $J = 15.4$ Hz, C_q), 132.9 (d, $J = 6.0$ Hz, C_q), 123.3 (s, C_q), 122.1 (s, CH, C14), 121.8 (s, CH, C13), 121.5 (s, CH, C13), 115.5 (s, CH, C6), 114.5 (s, CH, C7), 94.8 (d, $J = 9.0$ Hz, CH, C5), 71.0 (br s, CH_2 ,

³ Overlaps with the signals of THF- d_8 in ¹³C NMR; only visible in ¹H-¹³C HSQC and DEPT.

18-crown-6), 39.4 (s, C_q, C2), 36.1 (d, J = 16.6 Hz, CH₂, C3), 35.1 (d, J = 6.5 Hz, C_q, C2), 31.7 (s, CH₃, C1), 29.1 (d, J = 4.7 Hz, CH₃, C1), 27.6 (s, CH, C15), 27.3 (s, CH, C15), 25.4⁴ (s, CH₃, C16/17), 25.3⁴ (s, CH₃, C16/17), 24.3 (s, CH₃, C16/17), 24.2 (s, CH₃, C16/17), 15.0 (s, CH₃, C10). **³¹P{¹H} NMR** (243 MHz, THF-d₈, 295 K) δ[ppm] = 136.8. **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 1941(ν N₂), 1778(ν Fe—H).

(K⁺@18-crown-6)[(^tBuPNN)FeD(N₂)] (6b-D). Method B: (K⁺@18-crown-6)[(^tBuPNN)Fe(N₂)] (**4b**) (15.0 mg, 18.2 μmol, 1.0 eq.) was weighed into a vial, dissolved in THF-d₈ (500 μL) and transferred into a pressure tube. The NMR tube was pressurized with D₂ (5 bar). After 19 h at r.t. the ¹H NMR showed no remaining signals of the starting material indicating full conversion to the title compound.

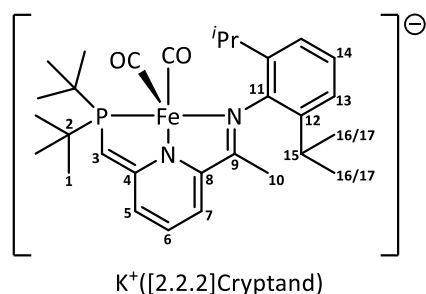


²H NMR (92 MHz, THF-d₈, 295 K) δ[ppm] = -21.87 (d, J = 9.5 Hz, Fe—D). **¹³C{¹H} NMR** (151 MHz, THF-d₈, 295 K) δ[ppm] = 161.1 (s), 155.6 (s), 143.4 (d, J = 12.0 Hz), 133.1 (s), 123.5 (s), 122.1 (s), 121.8 (s), 121.4 (s), 115.3 (s), 114.6 (s), 94.8 (s), 70.9 (br s), 39.4 (s), 36.3 (d, J = 15.3 Hz, C3), 35.4 (s), 31.7 (s), 29.4 (s), 27.7 (s), 27.3 (s), 26.2 (s), 25.6 (s), 24.3 (s), 24.2 (s), 14.8 (s). **³¹P{¹H} NMR**

(243 MHz, THF-d₈, 295 K) δ[ppm] = 138.9. **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 1944(ν N₂).

Deprotonation:

(K⁺@[2.2.2]Cryptand)[(^tBuPNN-H⁺)Fe(CO)₂] (7a). (^tBuPNN)Fe(CO)₂ (**8**) (150 mg, 272 μmol, 1.0 eq.), KHMDS (54.4 mg, 272 μmol, 1.0 eq.) and [2.2.2]Cryptand (108 mg, 286 μmol, 1.1 eq.) were weighed into a screw-capped vial. THF (6.00 mL) was added quickly to the stirring solids to give a green solution. The mixture was stirred at r.t. for 1 h. The volatile components were removed *in vacuo* and the resulting solid was washed with pentane (3x 10 mL) to give the title complex as a dark green powder (266 mg, quant.). Layering a concentrated solution of **7a** in THF with hexane at r.t. afforded crystals suitable for single crystal X-ray diffraction.



¹H NMR (600 MHz, THF-d₈, 295 K) δ[ppm] = 7.05–7.04 (m, 2H, H13), 7.02–6.99 (m, 1H, H14), 6.34 (dt, J = 7.6, 1.3 Hz, 1H, H6), 5.92 (d, J = 7.4 Hz, 1H, H7), 5.66 (d, J = 7.6 Hz, 1H, H5), 3.49–3.39 (s, 24H, [2.2.2]Cryptand), 3.39 (s, 1H, H3), 3.16 (sept, J = 6.9 Hz, 2H, H15), 2.46 (s, 12H, [2.2.2]Cryptand), 1.67 (s, 3H, H10), 1.24 (d, J = 6.7 Hz, 6H, H16/17), 1.15 (d, J = 11.6 Hz, 18H, H1), 1.01 (d,

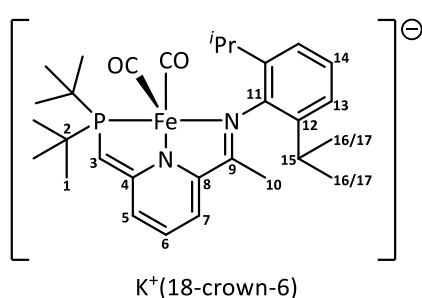
J = 6.9 Hz, 6H, H16/17). **¹³C{¹H} NMR** (151 MHz, THF-d₈, 295 K) δ[ppm] = 222.4 (d, J = 13.8 Hz, CO),

⁴ Overlaps with the signals of THF-d₈ in ¹³C NMR; only visible in ¹H-¹³C HSQC and DEPT.

171.4 (d, $J = 21.8$ Hz, C_q , C4), 154.3 (s, C_q , C11), 147.7 (d, $J = 5.2$ Hz, C_q , C8), 141.7 (s, C_q , C12), 141.1 (s, C_q , C9), 125.1 (d, $J = 2.0$ Hz, CH, C6), 124.0 (s, CH, C14), 122.7 (s, CH, C13), 98.3 (s, CH, C7), 95.4 (d, $J = 17.2$ Hz, CH, C5), 70.9 (s, CH_2 , [2.2.2]Cryptand), 68.1 (s, CH_2 , [2.2.2]Cryptand), 56.8 (d, $J = 49.3$ Hz, CH, C3), 54.5 (s, CH_2 , [2.2.2]Cryptand), 38.9 (d, $J = 14.9$ Hz, C_q , C2), 30.7 (d, $J = 4.7$ Hz, CH_3 , C1), 27.2 (s, CH, C15), 25.8 (s, CH_3 , C16/17), 24.8 (s, CH_3 , C16/17), 16.4 (s, CH_3 , C10). $^{31}P\{^1H\}$ NMR (243 MHz, THF- d_8 , 295 K) δ [ppm] = 119.6. IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 1883(ν_{sym} CO), 1825(ν_{asym} CO). Anal. Calcd. for $C_{48}H_{78}FeKN_4O_8P$ [%]: C: 59.74, H: 8.15, N: 5.81; found: C: 58.05, H: 8.14, N: 5.67.

Deprotonation:

(K^+ @18-crown-6)[($^{tBu}PNN-H^+$)Fe(CO) $_2$] (7b). (^{tBu}PNN)Fe(CO) $_2$ (**8**) (150 mg, 272 μ mol, 1.0 eq.), KHMDS (54.4 mg, 272 μ mol, 1.0 eq.) and 18-crown-6 (75.6 mg, 286 μ mol, 1.1 eq.) were weighed into a screw-capped vial. THF (6.00 mL) was added quickly to the stirring solids to give a green solution. The mixture was stirred at r.t. for 2 h. The volatile components were removed *in vacuo*. The oily residue was triturated with pentane to give a solid. The crude compound was washed with pentane (3x 10 mL) and dried *in vacuo* to give the title complex as a dark green powder (184 mg, 79 %).

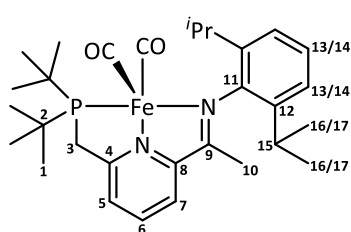


1H NMR (600 MHz, THF- d_8 , 295 K) δ [ppm] = 7.06–7.04 (m, 2H, H13), 7.02–6.99 (m, 1H, H14), 6.32 (dt, $J = 7.5$, 1.1 Hz, 1H, H6), 5.92 (d, $J = 7.4$ Hz, 1H, H7), 5.66 (d, $J = 7.6$ Hz, 1H, H5), 3.51 (s, 24H, 18-crown-6), 3.39 (s, 1H, H3), 3.14 (sept, $J = 6.8$ Hz, 2H, H15), 1.67 (s, 3H, H10), 1.24 (d, $J = 6.7$ Hz, 6H, H16/17), 1.15 (d, $J = 11.6$ Hz, 18H, H1), 1.01 (d, $J = 6.9$ Hz, 6H, H16/17). $^{13}C\{^1H\}$

NMR (151 MHz, THF- d_8 , 295 K) δ [ppm] = 222.5 (d, $J = 13.8$ Hz, CO), 171.3 (d, $J = 21.8$ Hz, C_q , C4), 154.3 (s, C_q , C11), 147.7 (d, $J = 5.3$ Hz, C_q , C8), 141.7 (s, C_q , C12), 141.2 (d, $J = 1.0$ Hz, C_q , C9), 125.1 (d, $J = 1.9$ Hz, CH, C6), 124.1 (s, CH, C14), 122.7 (s, CH, C13), 98.2 (s, CH, C7), 95.3 (d, $J = 17.2$ Hz, CH, C5), 70.9 (s, CH_2 , 18-crown-6), 56.9 (d, $J = 49.0$ Hz, CH, C3), 38.9 (d, $J = 14.9$ Hz, C_q , C2), 30.6 (d, $J = 4.6$ Hz, CH_3 , C1), 27.2 (s, CH, C15), 25.7 (s, CH_3 , C16/17), 24.7 (s, CH_3 , C16/17), 16.4 (s, CH_3 , C10). $^{31}P\{^1H\}$ NMR (243 MHz, THF- d_8 , 295 K) δ [ppm] = 119.7.

(^{tBu}PNN)Fe(CO) $_2$ (8**).** Method A: In a nitrogen filled glovebox [$(^{tBu}PNN)Fe(N_2)_2(\mu-N_2)$] (**2**) (60 mg, 55.9 μ mol, 1.0 eq.) was weighed into a vial, dissolved in THF- d_8 (800 μ L) and filtered into a Young tube. The solution was frozen in liquid N_2 , the atmosphere removed *in vacuo* and backfilled with CO (1 bar). After shaking thoroughly 1H and ^{31}P NMR spectra were recorded to ensure quantitative conversion to the target compound **8**. Inside a glovebox the solution was poured into a vial and the solvent was removed *in vacuo* to obtain **8** as a purple powder (60.9 mg, 99 %). Method B: In a 100 mL schlenk flask (^{tBu}PNN)FeBr $_2$ (**1**) (1.00 g, 1.53 mmol, 1.0 eq.) was weighed in, THF (30.0 mL) was added and the

mixture was subjected to multiple freeze-pump-thaw cycles. The system was backfilled with CO and a cooling bath (-78 °C, acetone/dry ice) was placed under the flask. While stirring a solution of NaBEt₃H (1 M in toluene, 3.00 mL, 1.96 eq.) was added slowly and the reaction was stirred for 10 min at -78 °C before stirring at r.t. for 1 h. The solvent was removed *in vacuo* and the residue dried under high vacuum at 40 °C for 2 h. The purple solid was dissolved in Et₂O (20 mL), filtered via cannula filtration and the solvent was removed *in vacuo*. The crude product was washed with HMDSO (2x 5.00 mL) and dried under high vacuum at 50 °C for 3 h to obtain the title compound as a purple powder (583 mg, 69 %). Slow evaporation of a solution of **4b** in benzene/pentane at r.t. afforded crystals suitable for single crystal X-ray diffraction.



¹H NMR (600 MHz, THF-d₈, 295 K) δ[ppm] = 7.28 (d, J = 8.6 Hz, 1H, H7), 7.19 (s, 3H, H13/14), 6.97 (dd, J = 8.5 Hz, 1H, H6), 6.67 (d, J = 6.6 Hz, 1H, H5), 3.83 (d, J = 8.3 Hz, 2H, H3), 2.87 (sept, J = 6.8 Hz, 2H, H15), 1.86 (s, 3H, H10), 1.25 (d, J = 6.8 Hz, 6H, H16/17), 1.18 (d, J = 12.5 Hz, 18H, H1), 1.04 (d, J = 6.9 Hz, 6H, H16/17). **¹³C{¹H} NMR** (151 MHz, THF-d₈, 295 K) δ[ppm] = 221.2 (d, J = 10.2 Hz, CO), 160.0 (d, J = 7.6 Hz, C_q, C4), 152.5 (s, C_q, C11), 145.7 (s, C_q, C9), 145.1 (d, J = 5.1 Hz, C_q, C8), 141.0 (s, C_q, C12), 125.9 (s, CH, C13/14), 125.2 (s, CH, C6), 123.6 (s, CH, C13/14), 121.1 (s, CH, C7), 109.4 (d, J = 9.4 Hz, CH, C5), 38.6 (d, J = 11.2 Hz, C_q, C2), 35.9 (d, J = 18.0 Hz, CH₂, C3), 29.5 (d, J = 3.9 Hz, CH, C1), 27.8 (s, CH, C15), 25.3⁵ (s, CH₃, C16/17), 24.3 (s, CH₃, C16/17), 15.8 (s, CH₃, C10). **³¹P{¹H} NMR** (243 MHz, THF-d₈, 295 K) δ[ppm] = 137.1. **IR** (ATR) $\tilde{\nu}$ [cm⁻¹] = 1933(ν_{sym} CO), 1874(ν_{asym} CO). Anal. Calcd. for C₃₀H₄₃FeN₂O₂P [%]: C: 65.45, H: 7.87, N: 5.09; found: C: 65.19, H: 7.99, N: 5.29.

⁵ Overlaps with the signals of THF-d₈ in ¹³C NMR; only visible in ¹H-¹³C HSQC and DEPT.

Supporting Crystallographic Information

Crystal data and details of the structure determinations are compiled in Tables S1 - S4. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- or Cu- K_{α} radiation, microfocus X-ray tubes, multilayer mirror optics). Detector frames (typically ω -, occasionally ϕ -scans, scan width 0.5...1°) were integrated by profile fitting.^{6,7} Data were corrected for air and detector absorption, Lorentz and polarization effects⁷ and scaled essentially by application of appropriate spherical harmonic functions.^{7,8,9} Absorption by the crystal was treated with a semiempirical multiscan method (as part of the scaling procedure), and augmented by a spherical correction,⁷⁻⁹ or numerically (Gaussian grid).^{8,10} For datasets collected with the microfocus tube(s) an illumination correction was performed as part of the numerical absorption correction.⁸

The structures were solved by ab initio dual space methods (SHELXD, compound **7a** or VLD procedure, compound **8**),^{11,12} by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors (compounds **4b** and **5a**),¹³ or by the charge flip procedure (all other compounds).¹⁴ Refinement was carried out by full-matrix least

⁶ Kabsch, K.; in: Rossmann, M. G.; Arnold, E. (eds.) *"International Tables for Crystallography" Vol. F*, Ch. 11.3, Kluwer Academic Publishers, Dordrecht, The Netherlands, **2001**.

⁷ *CrysAlisPro*, Agilent Technologies UK Ltd., Oxford, England, UK, **2011-2014** and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wrocław, Poland, **2015-2021**.

⁸ *SCALE3 ABSPACK*, *CrysAlisPro*, Agilent Technologies UK Ltd., Oxford, England, UK, **2011-2014** and Rigaku Oxford Diffraction, Rigaku Polska Sp.z o.o., Wrocław, Poland, **2015-2021**.

⁹ Blessing, R. H. An empirical correction for absorption anisotropy. *Acta Cryst.* **1995**, *A51*, 33-38

¹⁰ Busing, W. R.; Levy, H. A. High-speed computation of the absorption correction for single-crystal diffraction measurements. *Acta Cryst.* **1957**, *10*, 180-182.

¹¹ (a) G. M. Sheldrick, *SHELXD*, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany, 2000-2013; (b) G. M. Sheldrick, H. A. Hauptman, C. M. Weeks, R. Miller, I. Usón, *Ab initio phasing*, in: M. G. Rossmann, E. Arnold (eds.) *International Tables for Crystallography*, Vol. F, pp. 333-351, IUCr and Kluwer Academic Publishers, Dordrecht, The Netherlands, 2001.

¹² (a) Burla, M. C.; Giacovazzo, C.; Polidori, G.; From a random to the correct structure: the VLD algorithm. *J. Appl. Cryst.* **2010**, *43*, 825-836. (b) Burla, M. C.; Caliendo, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G.; Siliqi, D. *SIR2019*, CNR IC, Bari, Italy, **2019**. (c) Burla, M. C.; Caliendo, R.; Carrozzini, B.; Cascarano, G. L.; Cuocci, C.; Giacovazzo, C.; Mallamo, M.; Mazzone, A.; Polidori, G. Crystal structure determination and refinement via *SIR2014*. *J. Appl. Cryst.* **2015**, *48*, 306-309.

¹³ (a) P. T. Beurskens, G. Beurskens, R. de Gelder, J. M. M. Smits, S. Garcia-Granda, R. O. Gould, *DIRDIF-2008*, Radboud University Nijmegen, The Netherlands, 2008; (b) P. T. Beurskens, in: G. M. Sheldrick, C. Krüger, R. Goddard (eds.), *Crystallographic Computing 3*, Clarendon Press, Oxford, England, UK, 1985, p. 216

¹⁴ (a) (a) Palatinus, L. *SUPERFLIP*, EPF Lausanne, Switzerland and Fyzikální ústav AV ČR, v. v. i., Prague, Czech Republic, **2007-2014**. (b) Palatinus, L.; Chapuis, G. *SUPERFLIP* - a computer program for the solution of crystal structures by charge flipping in arbitrary dimensions. *J. Appl. Cryst.* **2007**, *40*, 786-790. (c) Palatinus, L.; The charge-flipping algorithm in crystallography. *Acta Cryst.* **2013**, *B69*, 1-16.

squares methods based on F^2 against all unique reflections.¹⁵ All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model.¹⁶ When justified by the quality of the data the positions of some chemically important hydrogen atoms (those of the arene CH groups in contact with Na and the hydride ligand in **6a**, and, in some cases, those on C6) were taken from difference Fourier syntheses and refined. Split atom models were used to refine disordered groups and/or solvent molecules. When found necessary, suitable geometry and adp restraints or constraints were applied.^{16,17}

Due to severe disorder, electron density attributed to solvent of crystallization (toluene and/or *n*-pentane and/or diethylether) was removed from the structure of **2** with the BYPASS procedure,¹⁸ as implemented in PLATON (squeeze/hybrid).¹⁹ Partial structure factors from the solvent masks were included in the refinement as separate contributions to F_{calc} .

In the structure of **5a**, we note an elongation of the displacement ellipsoid of C6 perpendicular to the P1C6C5 plane, which could be interpreted as disorder of C6 across that plane. This could be indicative of the additional presence of a tautomer of **3a**, namely **3a'**, where a hydrogen atom moved from the methyl group (corresponding to C16 in the present structure) to give a methylene group (C-6)H₂ (Scheme S1). Refinement of the model **5a+3a'**, where the hydrogens on C6 had to be restrained to prevent unrealistic C-H distances, gave a ratio **5a:3a'** of about 0.7:0.3. However, as we do not have any spectroscopic evidence for **3a'** and the bond lengths P1-C6 and C5-C6 are more consistent with **5a** we prefer the non-disordered model.

¹⁵ (a) Sheldrick, G. M. *SHELXL-20xx*, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany, **2012-2018**. (b) Robinson, W.; Sheldrick, G. M. in: Isaaks, N. W.; Taylor, M. R. (eds.) „*Crystallographic Computing 4*“, Ch. 22, IUCr and Oxford University Press, Oxford, England, UK, **1988**. (c) Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112. (d) Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst.* **2015**, C71, 3-8.

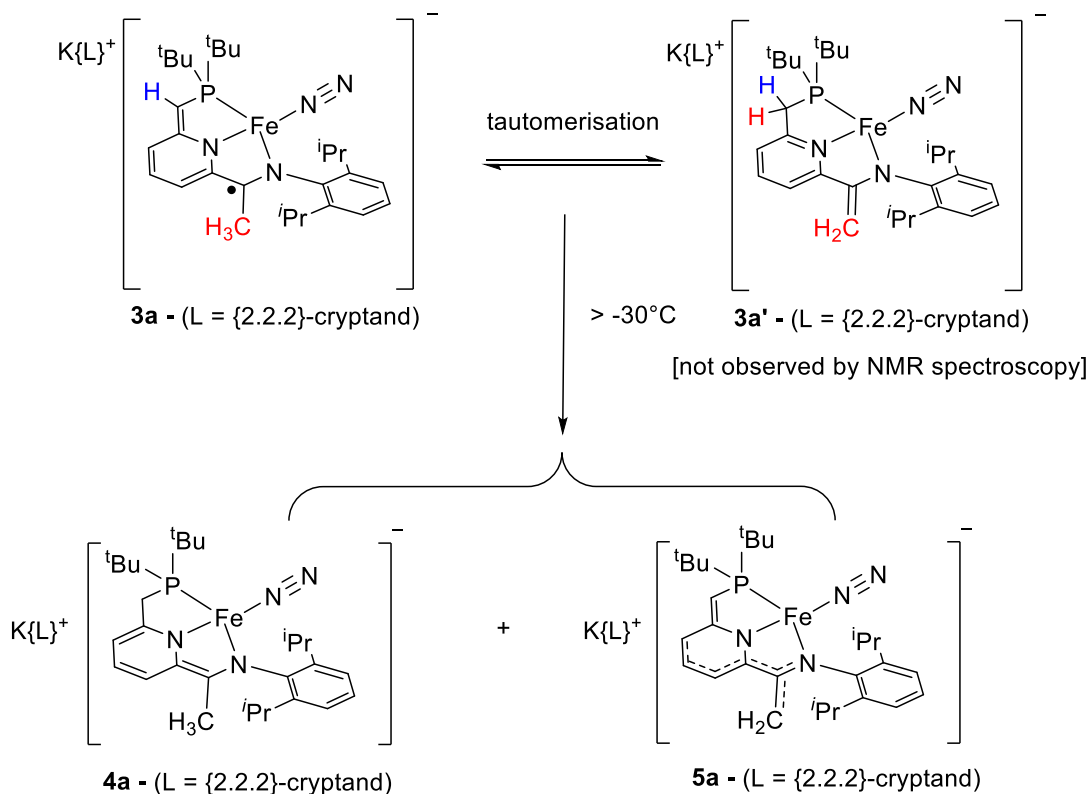
¹⁶ (a) Rollett, J. S. in: Ahmed, F. R.; Hall, S. R.; Huber, C. P. (eds.) „*Crystallographic Computing*“ p. 167, Munksgaard, Copenhagen, Denmark, **1970**. (b) Watkin, D. in: Isaaks, N. W.; Taylor, M. R. (eds.) „*Crystallographic Computing 4*“, Ch. 8, IUCr and Oxford University Press, Oxford, England, UK, **1988**. (c) Müller, P.; Herbst-Irmer, R.; Spek, A. L.; Schneider, T. R.; Sawaya, M. R. in: Müller, P. (ed.) „*Crystal Structure Refinement*“, Ch. 5, Oxford University Press, Oxford, England, UK, **2006**. (d) Watkin, D. Structure refinement: some background theory and practical strategies. *J. Appl. Cryst.* **2008**, 41, 491-522.

¹⁷ Thorn, A.; Dittrich, B.; Sheldrick, G. M. Enhanced rigid-bond restraints. *Acta Cryst.* **2012**, A68, 448-451.

¹⁸ v. d. Sluis, P.; Spek, A. L. BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions. *Acta Cryst.* **1990**, A46, 194-201. (b) Spek, A. L. PLATON SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst.* **2015**, C71, 9-18.

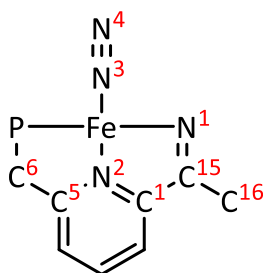
¹⁹ Spek, A. L. PLATON, Utrecht University, The Netherlands. (b) Spek, A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Cryst.* **2003**, 36, 7-13.

CCDC 2118029 - 2118036 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via <https://www.ccdc.cam.ac.uk/structures/>.



Scheme S1. Disproportionation of **3a** to give **4a** and **5a**. The presence of tautomer **3a'** could not be established experimentally.

Overview: Metric parameters of the X-ray structures



No.	N ¹ –C ¹⁵	C ¹⁵ –C ¹⁶	C ¹⁵ –C ¹	C ¹ –N ²
LFeCl ₂ ^a	1.302(8)	1.490(9)	1.492(9)	1.342(8)
2	1.347(3)	1.509(3)	1.403(3)	1.385(3)
	1.352(3)	1.498(3)	1.408(4)	1.392(3)
4a	1.394(4)	1.494(5)	1.367(4)	1.426(4)
4b	1.3859(10)	1.4909(12)	1.3797(11)	1.4205(10)
5a	1.3791(15)	1.4097(18)	1.4398(16)	1.3823(14)
6a	1.380(2)	1.503(2)	1.380(2)	1.425(2)
7a	1.345(3)	1.490(4)	1.415(4)	1.372(3)
8	1.3423(18)	1.5028(19)	1.408(2)	1.3804(18)

No.	N ² –C ⁵	C ⁵ –C ⁶	C ⁶ –P	Fe–N ³	N ³ –N ⁴
LFeCl ₂ ^a	1.339(9)	1.510(9)	1.851(7)	-	-
2	1.366(3)	1.488(3)	1.847(3)	1.804(2)	1.121(3)
	1.367(3)	1.499(3)	1.850(2)	1.808(2)	1.114(3)
4a	1.370(4)	1.510(5)	1.837(3)	1.753(3)	1.144(4)
4b	1.3693(11)	1.5016(13)	1.8368(9)	1.7462(8)	1.1405(12)
5a	1.3816(15)	1.421(2)	1.7790(15)	1.7579(12)	1.1118(17)
6a	1.381(2)	1.506(2)	1.8470(17)	1.7509(16)	1.139(2)
7a [§]	1.392(3)	1.393(14)	1.738(6)	–	–
8 [§]	1.3713(18)	1.494(2)	1.8482(15)	–	–

^a – L = PNN; Data are taken from *Angew. Chem. Int. Ed.* **2013**, 52, 3676-3680

4a and **4b** show no meaningful differences in bond lengths, although in **4b** the K⁺(18-crown-6) coordinates to the N₂ whereas in **4a** the K⁺[2.2.2]Cryptand is separated from the complex anion.

Please note that for **7a** because of positional disorder only data for one unit is given and for **8** only data for one of the two molecules in the asymmetric unit is presented here.

[§] For the bonds involving C⁶ the values given refer to those in the major disordered component. [§] Only data for one of the two molecules in the asymmetric unit is presented here.

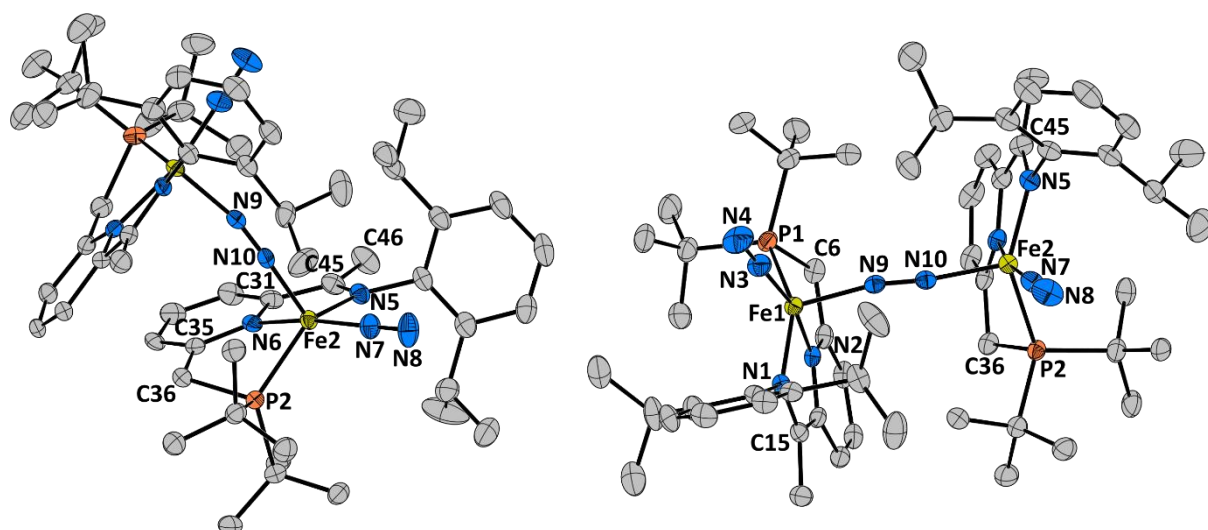


Figure S1. Two views of the molecular structure of **2** with displacement ellipsoids drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond distances [Å]: Fe1—P1 2.2443(7), Fe1—N1 1.9273(19), Fe1—N2 1.920(2), Fe1—N3 1.804(2), Fe1—N9 1.885(2), N3—N4 1.121(3), N1—C15 1.347(3), P1—C6 1.847(3), N9—N10 1.134(3), Fe2—P2 2.2507(7), Fe2—N5 1.921(2), Fe2—N6 1.912(2), Fe2—N7 1.808(2), Fe2—N10 1.882(2), N7—N8 1.114(3), N5—C45 1.352(3), P2—C36 1.850(2), C35—C36 1.499(3), N6—C35 1.367(3), N6—C31 1.392(3), C31—C45 1.408(4), C45—C46 1.498(3). Selected angles [°]: N3—Fe1—N2 167.16(10), N7—Fe2—N6 169.58(10), N3—Fe1—N9 99.69(10), N7—Fe2—N10 98.01(9), N10—N9—Fe1 167.91(18), N9—N10—Fe2 169.50(18), N9—N10—Fe2 169.50(18).

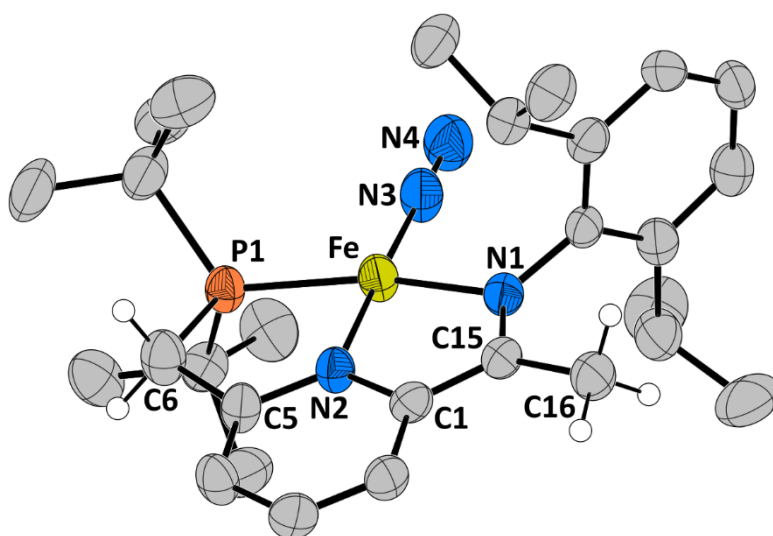


Figure S2. Molecular structure of **4a** with displacement ellipsoids drawn at 50% probability. Most hydrogen atoms and (K⁺@[2.2.2]Cryptand) are omitted for clarity. Selected bond distances [Å]: Fe—P1 2.1856(10), Fe—N1 1.926(3), Fe—N2 1.913(3), Fe—N3 1.753(3), N3—N4 1.144(4), N1—C15 1.394(4), P1—C6 1.837(3), C5—C6 1.510(5), N2—C5 1.370(4), N2—C1 1.426(4), C1—C15 1.367(4), C15—C16 1.494(5). Selected angles [°]: N3—Fe—N2 178.27(13), N4—N3—Fe 177.9(3).

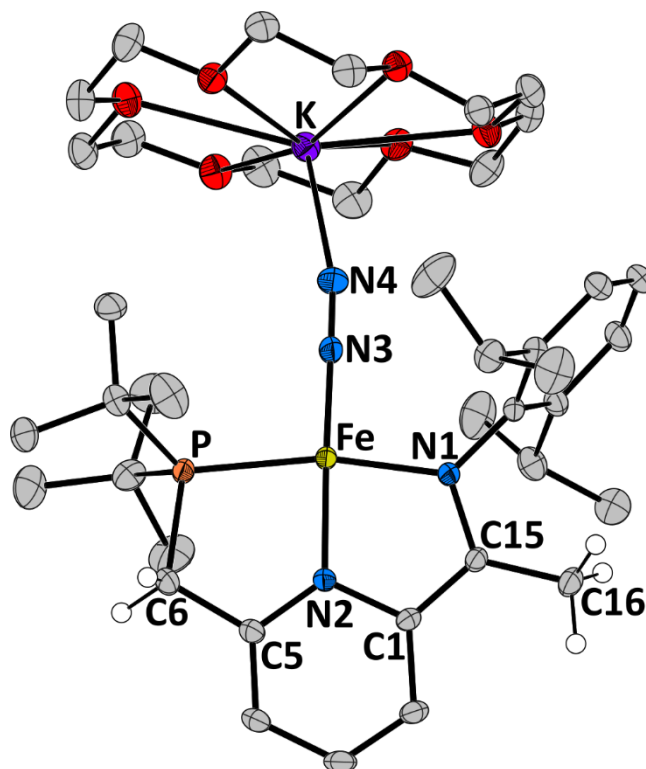


Figure S3. Molecular structure of **4b** with displacement ellipsoids drawn at 50% probability. Most hydrogen atoms are omitted for clarity. Selected bond distances [Å]: Fe—P 2.1833(2), Fe—N1 1.9061(7), Fe—N2 1.9057(7), Fe—N3 1.7462(8), N3—N4 1.1405(12), K—N4 2.8507(9), N1—C15 1.3859(10), P—C6 1.8368(9), C5—C6 1.5016(13), N2—C5 1.3693(11), N2—C1 1.4205(10), C1—C15 1.3797(11), C15—C16 1.4909(12). Selected angles [°]: N3—Fe—N2 173.59(4), N4—N3—Fe 176.38(10).

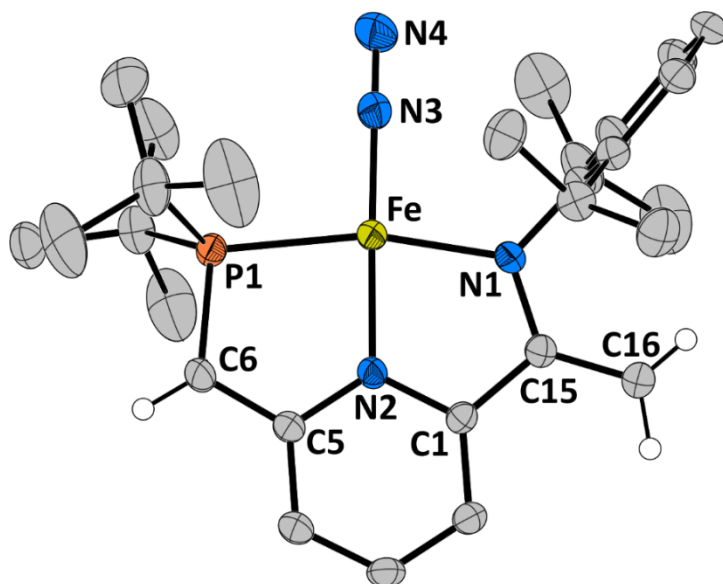


Figure S4. Molecular structure of **5a** with displacement ellipsoids drawn at 50% probability. Most hydrogen atoms and (K⁺@[2.2.2]Cryptand) are omitted for clarity. Selected bond distances [Å]: Fe—P1 2.2308(3), Fe—N1 1.9321(10), Fe—N2 1.9339(10), Fe—N3 1.7578(12), N3—N4 1.1120(17), N1—C15 1.3786(15), P1—C6 1.7790(15), C5—C6 1.421(2), N2—C5 1.3816(15), N2—C1 1.3823(14), C1—C15 1.4398(16), C15—C16 1.4097(18). Selected angles [°]: N3—Fe—N2 177.74(5), N4—N3—Fe 178.79(13).

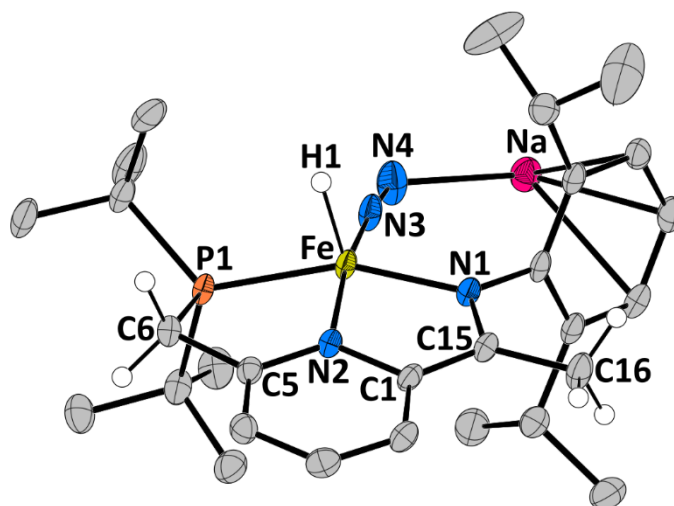


Figure S5. Molecular structure of **6a** with displacement ellipsoids drawn at 50% probability. *Most* hydrogen atoms are omitted for clarity. Only one monomeric unit of the coordination polymer is displayed. Selected bond distances [Å]: Fe—H1 1.49(2), Fe—P1 2.1937(5), Fe—N1 1.9127(14), Fe—N2 1.9081(14), Fe—N3 1.7509(16), N3—N4 1.139(2), N1—C15 1.380(2), P1—C6 1.8470(17), C5—C6 1.506(2), N2—C5 1.381(2), N2—C1 1.425(2), C1—C15 1.380(2), C15—C16 1.503(2). Selected angles [°]: N3—Fe—N2 167.69(7), N4—N3—Fe 174.48(15).

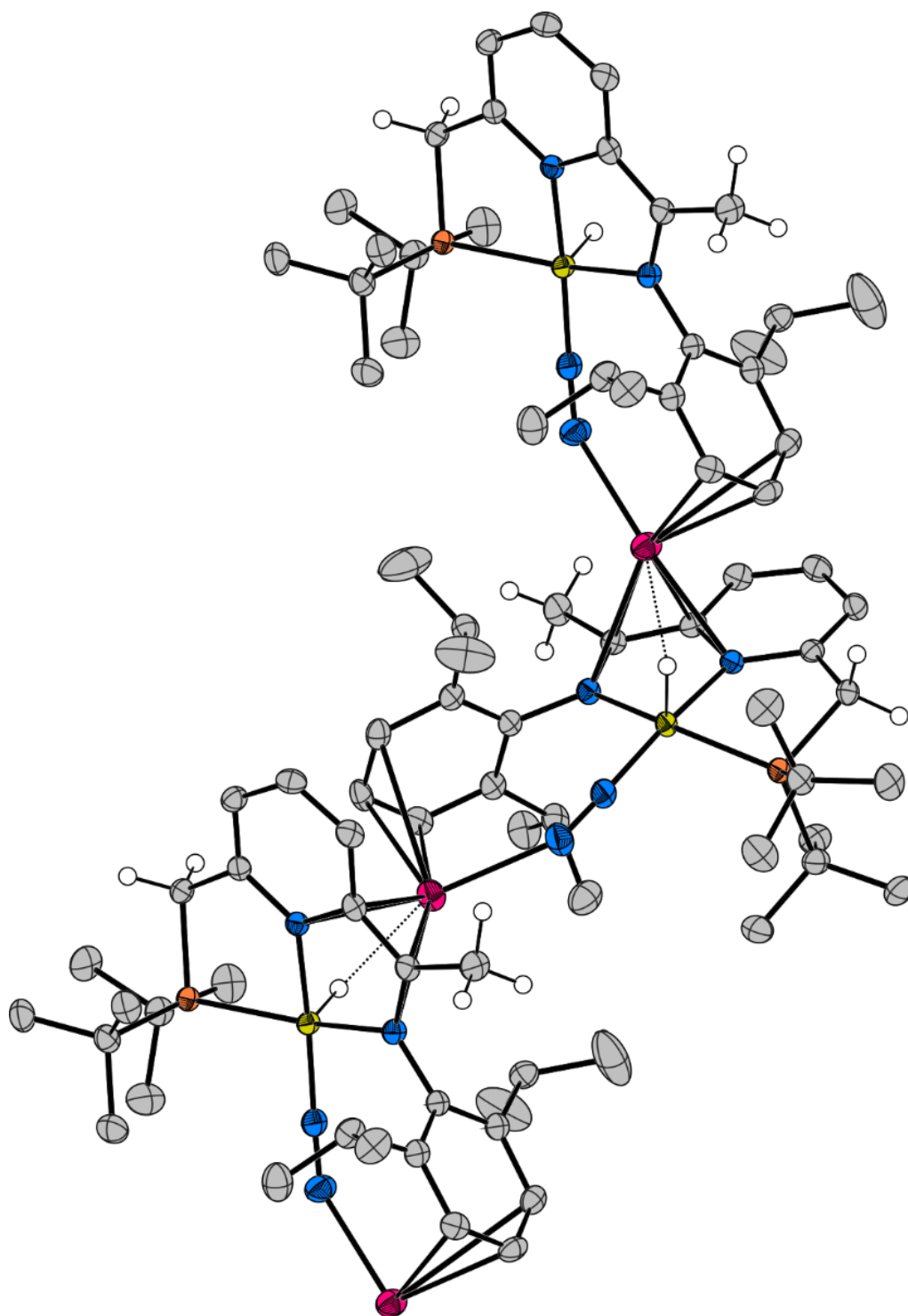


Figure S6. Molecular structure of the coordination polymer **6a** with displacement ellipsoids drawn at 50% probability. Most hydrogen atoms are omitted for clarity.

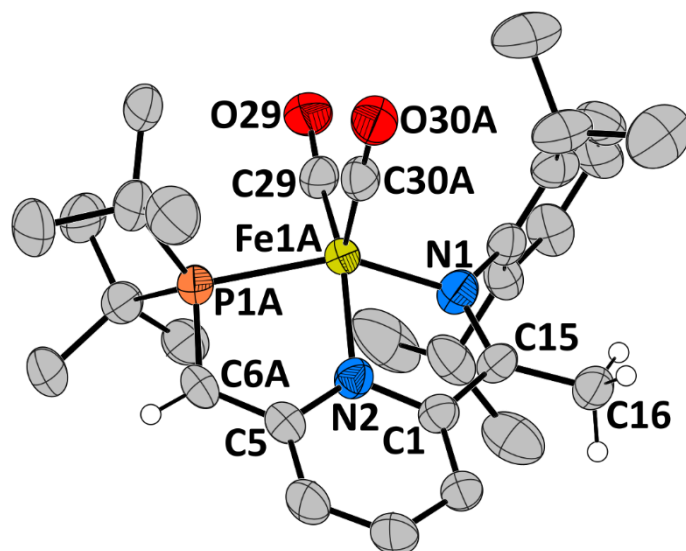


Figure S7. Molecular structure of **7a** with displacement ellipsoids drawn at 50% probability. Most hydrogen atoms, ($K^+@[2.2.2]$ Cryptand) and the minor set of the disordered components of the molecule (Fe, axial CO, P, C6 and the *tert*-butyl groups) are omitted for clarity. Selected bond distances [Å]: Fe1A—P1A 2.268(7), Fe1A—N1 1.922(2), Fe1A—N2 1.969(2), Fe1A—C29 1.708(3), Fe1A—C30A 1.746(4), C29—O29 1.164(3), C30A—O30A 1.178(4), N1—C15 1.345(3), P1A—C6A 1.738(6), C5—C6A 1.393(14), N2—C5 1.392(3), N2—C1 1.372(3), C1—C15 1.415(4), C15—C16 1.490(4).

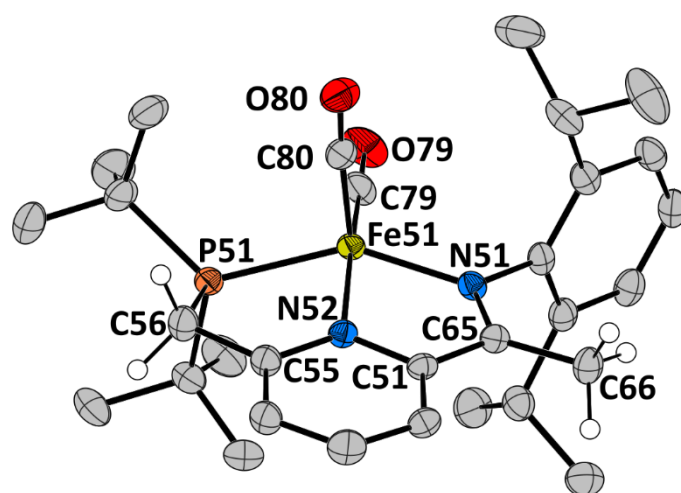


Figure S8. Molecular structure of **8** with displacement ellipsoids drawn at 50% probability. Most hydrogen atoms are omitted for clarity. One of the two independent molecules shown. Co-crystallized solvent (benzene) omitted for clarity. Values in brackets correspond to the second independent molecule. Selected bond distances [Å]: Fe51—P51 2.2355(4)[2.2317(4)], Fe51—N51 1.9273(12)[1.9201(11)], Fe51—N52 1.9232(11)[1.9243(12)], Fe51—C79 1.7581(15)[1.7606(16)], Fe51—C80 1.7712(15)[1.7730(16)], C79—O79 1.1592(19)[1.1588(19)], C80—O80 1.1571(19)[1.1588(19)], N51—C65 1.3423(18)[1.3469(18)], P51—C56 1.8482(15)[1.8465(15)], C55—C56 1.494(2)[1.491(2)], N52—C55 1.3713(18)[1.3722(18)], N52—C51 1.3804(18)[1.3780(17)], C51—C65 1.408(2)[1.406(2)], C65—C66 1.5028(19)[1.5031(19)].

Table S1. Details of crystal structure determinations of **2 · solv** and **4a**.

	2 · solv	4a
formula	C ₅₆ H ₈₆ Fe ₂ N ₁₀ P ₂	C ₄₆ H ₇₉ FeKN ₆ O ₆ P
crystal system	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> bca
<i>a</i> /Å	10.54417(10)	21.0956(2)
<i>b</i> /Å	22.0336(3)	20.4391(3)
<i>c</i> /Å	30.3189(3)	23.6545(2)
<i>V</i> /Å ³	7043.87(14)	10199.25(19)
<i>Z</i>	4	8
<i>M_r</i>	1072.98	938.07
<i>F</i> ₀₀₀	2296	4040
<i>d_c</i> /Mg·m ⁻³	1.012	1.222
<i>μ</i> /mm ⁻¹	4.008	3.791
max., min. transmission factors	1.000, 0.816 ^a	1.000, 0.726 ^a
X-radiation, <i>λ</i> /Å	Cu K _α , 1.54184	Cu K _α , 1.54184
data collect. temperatur. /K	120(1)	120(1)
<i>θ</i> range /°	2.5 to 71.2	3.5 to 67.3
index ranges <i>h,k,l</i>	-12 ... 12, -26 ... 23, -37 ... 37	-25 ... 25, -24 ... 22, -28 ... 28
reflections measured	191892	286579
unique [<i>R</i> _{int}]	13527 [0.058]	9026 [0.165]
observed [<i>I</i> ≥ 2σ(<i>I</i>)]	12815	5649
data / restraints / parameters	13527 / 0 / 653	9026 / 0 / 561
absolute structure parameter	0.0000(12)	
GooF on <i>F</i> ²	1.036	1.014
<i>R</i> indices [<i>F</i> > 4σ(<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0272, 0.0606	0.0527, 0.1159
<i>R</i> indices (all data) <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0304, 0.0617	0.1091, 0.1415
largest residual peaks /e·Å ⁻³	0.225, -0.229	0.400, -0.580
CCDC deposition number	2118029	2118030

^a numerical absorption correction.

Table S2. Details of crystal structure determinations of **4b** and **5a**.

	4b	5a ^b (5a) _{0.7} + (3') _{0.3} ^c
formula	C ₄₀ H ₆₇ FeKN ₄ O ₆ P	C ₄₆ H ₇₇ FeKN ₆ O ₆ P ^b C ₄₆ H _{77.3} FeKN ₆ O ₆ P ^c
crystal system	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> <i>bca</i>
<i>a</i> /Å	13.77975(8)	21.13782(18)
<i>b</i> /Å	15.47696(9)	20.21592(15)
<i>c</i> /Å	20.95850(12)	23.78326(19)
β /°	90.7035(5)	
<i>V</i> /Å ³	4469.45(4)	10163.07(14)
<i>Z</i>	4	8
<i>M</i> _r	825.89	936.05 ^b 936.36 ^c
<i>F</i> ₀₀₀	1772	4024 ^b 4026 ^c
<i>d</i> _c /Mg·m ⁻³	1.227	1.224
μ /mm ⁻¹	0.512	0.460
max., min. transmission factors	1.000, 0.933 ^a	1.000, 0.911 ^a
X-radiation, λ /Å	Mo <i>K</i> _α , 0.71073	Mo <i>K</i> _α , 0.71073
data collect. temperatur. /K	120(1)	120(1)
θ range /°	2.3 to 34.2	2.3 to 34.3
index ranges <i>h,k,l</i>	-21 ... 21, -23 ... 24, -33 ... 32	-33 ... 33, -31 ... 31, -37 ... 37
reflections measured	362985	607282
unique [<i>R</i> _{int}]	18268 [0.055]	20803 [0.084]
observed [<i>I</i> ≥ 2σ(<i>I</i>)]	16186	15737
data / restraints / parameters	18268 / 0 / 489	20803 / 0 / 572
GooF on <i>F</i> ²	1.035	1.020 ^b 1.023 ^c
<i>R</i> indices [<i>F</i> > 4σ(<i>F</i>)] <i>R</i> (<i>F</i>), w <i>R</i> (<i>F</i> ²)	0.0351, 0.0865	0.0440, 0.1006 ^b 0.0440, 0.1005 ^c
<i>R</i> indices (all data) <i>R</i> (<i>F</i>), w <i>R</i> (<i>F</i> ²)	0.0418, 0.0897	0.0681, 0.1103 ^b 0.0681, 0.1101 ^c
largest residual peaks /e·Å ⁻³	1.054, -0.828	0.793, -0.434 ^b 0.793, -0.435 ^c
CCDC deposition number	2118031	2118032 ^b 2118033 ^c

^a empirical absorption correction. ^b "non-disordered" model. ^c "disordered" model.

Table S3. Details of crystal structure determinations of **6a** and **7a**.

	6a	7a
formula	C ₂₈ H ₄₄ FeN ₄ NaP	C ₄₈ H ₇₈ FeKN ₄ O ₈ P
crystal system	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P bca</i>
<i>a</i> /Å	12.79918(13)	21.2230(3)
<i>b</i> /Å	13.56920(16)	20.2791(3)
<i>c</i> /Å	16.37913(14)	23.8369(3)
β /°	101.4730(9)	
<i>V</i> /Å ³	2787.80(5)	10259.0(2)
<i>Z</i>	4	8
<i>M</i> _r	546.48	965.06
<i>F</i> ₀₀₀	1168	4144
<i>d</i> _c /Mg·m ⁻³	1.302	1.250
μ /mm ⁻¹	5.202	3.803
max., min. transmission factors	1.000, 0.793 ^a	1.000, 0.787 ^b
X-radiation, λ /Å	Cu <i>K</i> _α , 1.54184	Cu <i>K</i> _α , 1.54184
data collect. temperatur. /K	120(1)	120(1)
θ range /°	4.0 to 70.5	3.5 to 67.1
index ranges <i>h,k,l</i>	-15 ... 15, -16 ... 16, -19 ... 19	-22 ... 25, -23 ... 22, -26 ... 28
reflections measured	108398	228669
unique [<i>R</i> _{int}]	5323 [0.052]	8967 [0.130]
observed [<i>I</i> ≥ 2σ(<i>I</i>)]	4886	5856
data / restraints / parameters	5323 / 0 / 343	8967 / 687 / 857
GooF on <i>F</i> ²	1.023	1.013
<i>R</i> indices [<i>F</i> > 4σ(<i>F</i>)] <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0313, 0.0782	0.0467, 0.0942
<i>R</i> indices (all data) <i>R</i> (<i>F</i>), <i>wR</i> (<i>F</i> ²)	0.0355, 0.0807	0.0927, 0.1116
largest residual peaks /e·Å ⁻³	0.357, -0.282	0.276, -0.276
CCDC deposition number	2118034	2118035

^a numerical absorption correction; ^b empirical absorption correction.

Table S4. Details of crystal structure determinations of **8·0.5 C₆H₆**.

	8·0.5 C₆H₆
formula	C ₃₃ H ₄₆ FeN ₂ O ₂ P
crystal system	monoclinic
space group	<i>P</i> 2 ₁ /n
<i>a</i> /Å	21.3248(2)
<i>b</i> /Å	10.36360(10)
<i>c</i> /Å	28.6298(3)
<i>α</i> /°	90
<i>β</i> /°	93.9318(9)
<i>γ</i> /°	90
<i>V</i> /Å ³	6312.36(11)
<i>Z</i>	8
<i>M_r</i>	589.54
<i>F</i> ₀₀₀	2520
<i>d_c</i> /Mg·m ⁻³	1.241
<i>μ</i> /mm ⁻¹	4.541
max., min. transmission factors	1.000, 0.580 ^a
X-radiation, <i>λ</i> /Å	Cu <i>K</i> _α , 1.54184
data collect. temperatur. /K	120(1)
<i>θ</i> range /°	2.5 to 70.3
index ranges <i>h,k,l</i>	-25 ... 26, -12 ... 12, -34 ... 34
reflections measured	147115
unique [<i>R</i> _{int}]	11982 [0.042]
observed [<i>I</i> ≥ 2σ(<i>I</i>)]	11042
data / restraints / parameters	11982 / 79 / 759
GooF on <i>F</i> ²	1.043
<i>R</i> indices [<i>F</i> > 4σ(<i>F</i>)] <i>R</i> (<i>F</i>), w <i>R</i> (<i>F</i> ²)	0.0275, 0.0723
<i>R</i> indices (all data) <i>R</i> (<i>F</i>), w <i>R</i> (<i>F</i> ²)	0.0311, 0.0744
largest residual peaks /e·Å ⁻³	0.306, -0.293
CCDC deposition number	2118036

^a numerical absorption correction.

NMR Spectra

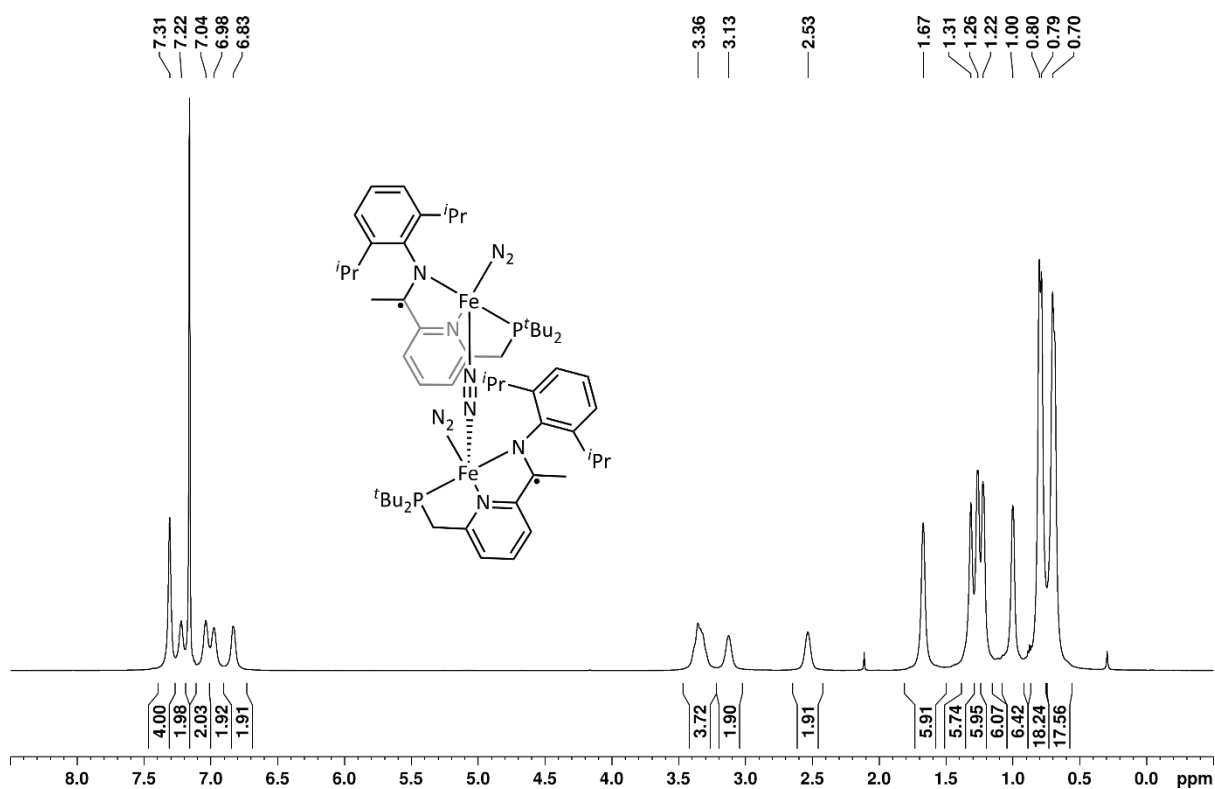


Figure S9. ¹H NMR spectrum of **2** (600 MHz, C₆D₆, 295 K).

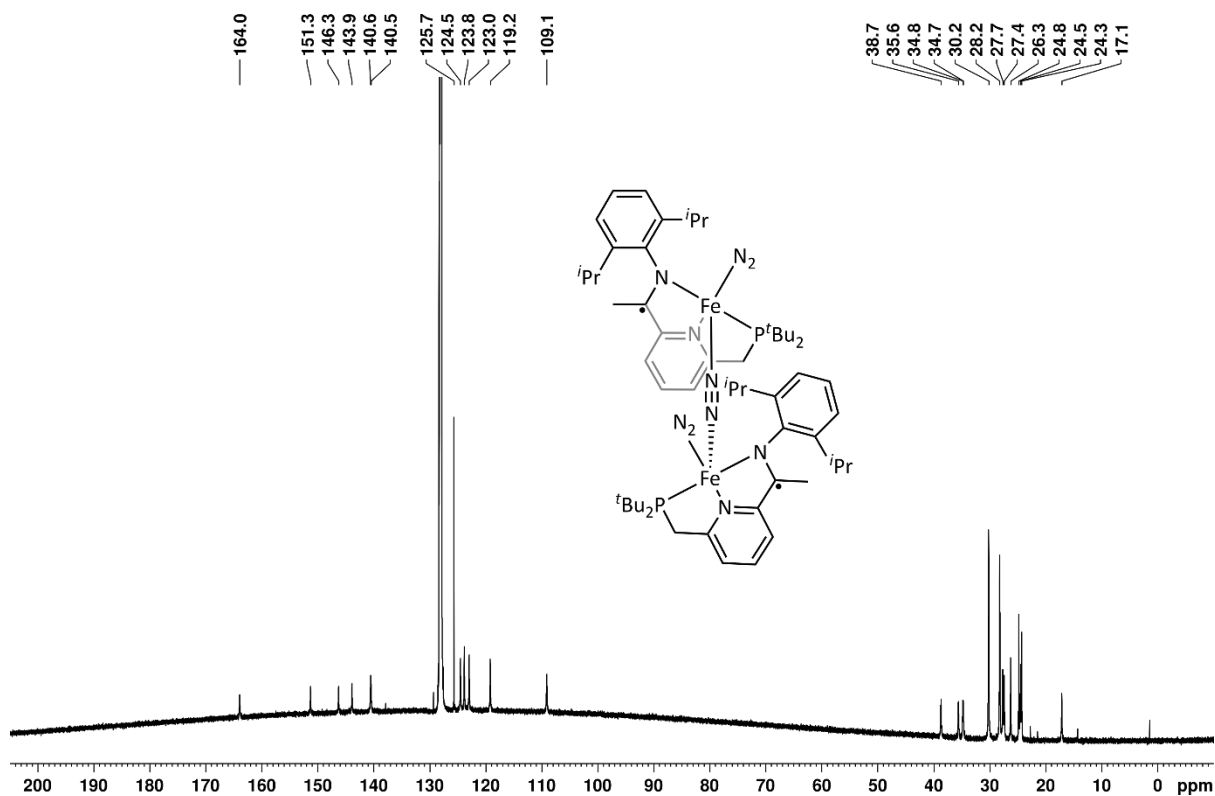


Figure S10. ¹³C{¹H} NMR spectrum of **2** (151 MHz, C₆D₆, 295 K).

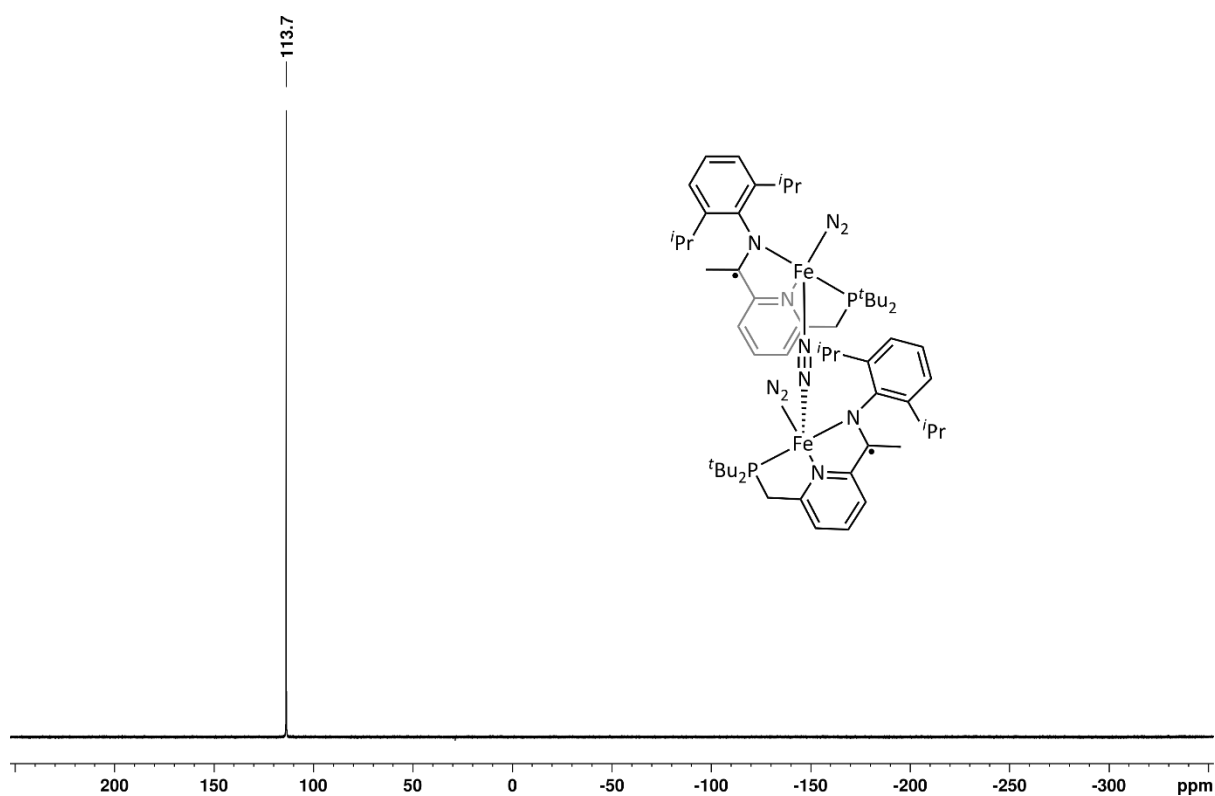


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** (243 MHz, C_6D_6 , 295 K).

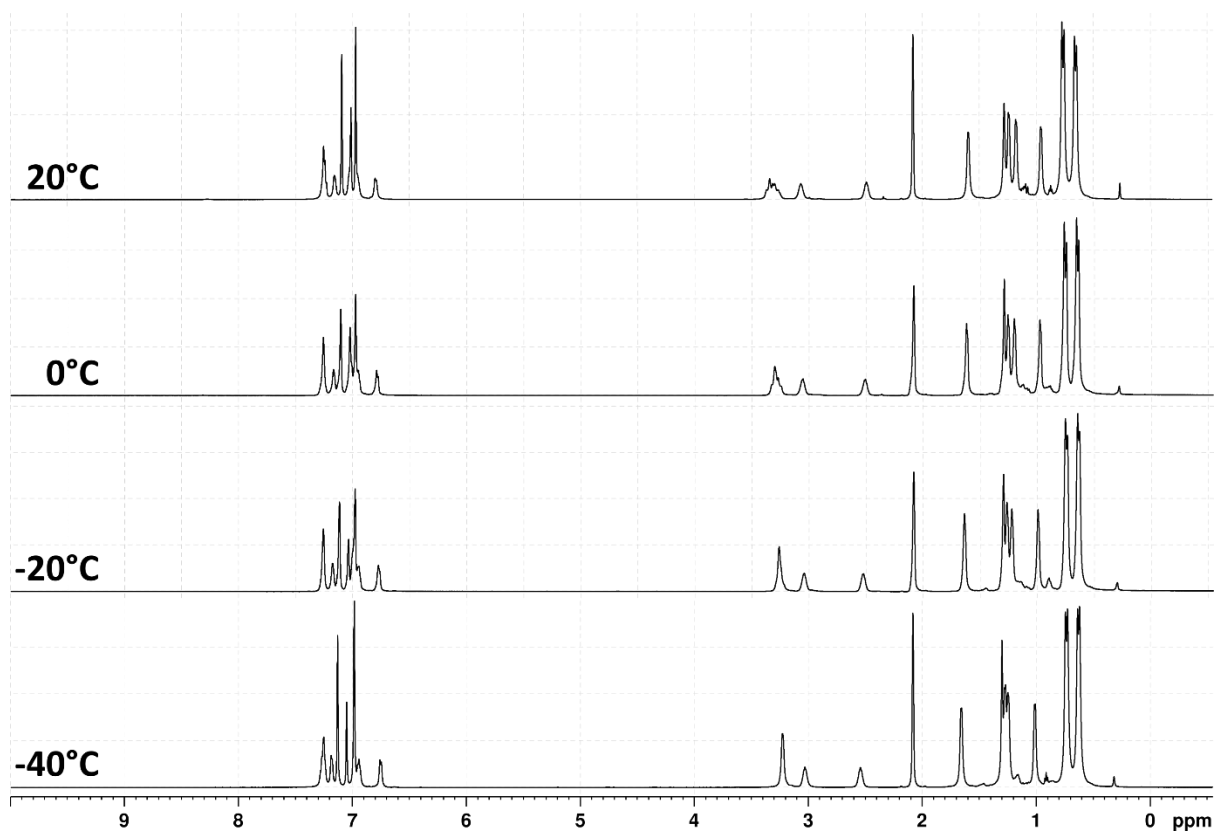


Figure S12. Variable temperature ^1H NMR spectra of **2** (600 MHz, toluene- d_8 , 233 K–293 K).

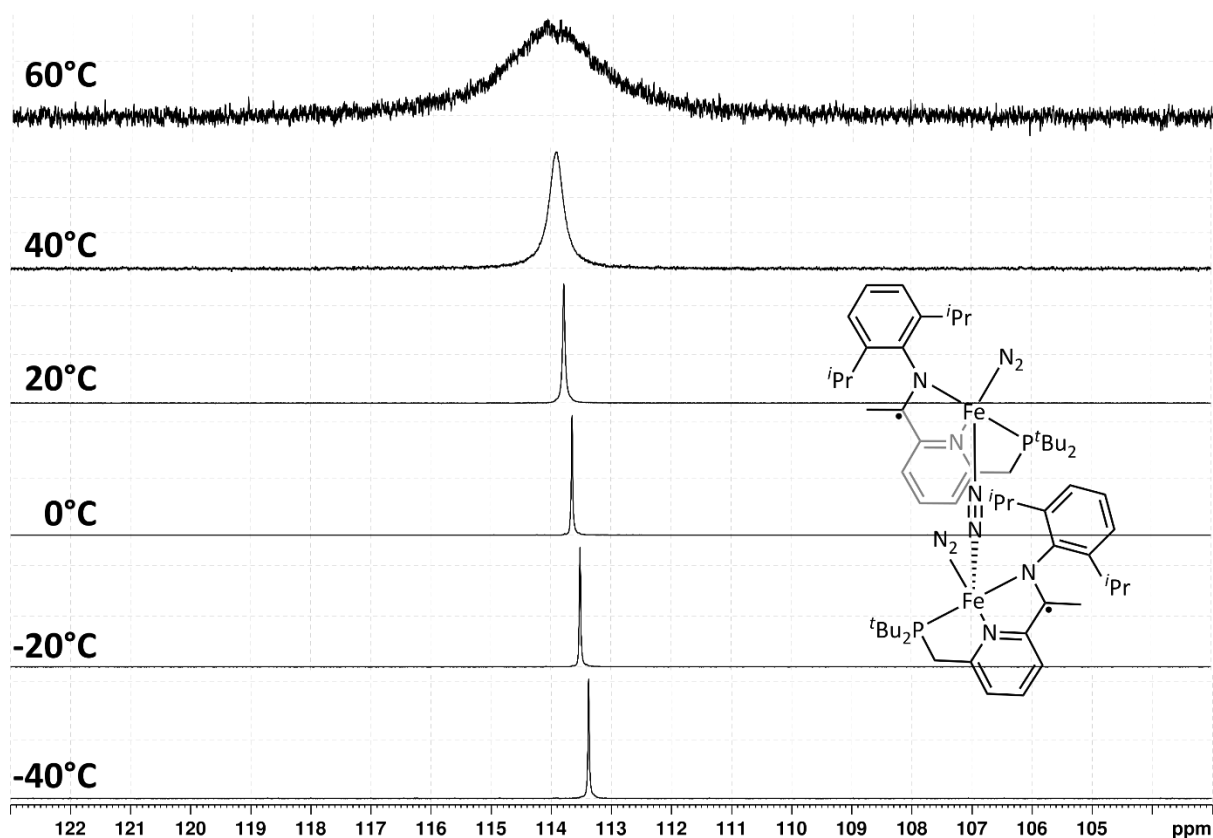


Figure S13. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** (243 MHz, toluene- d_8 , 233 K–333 K).

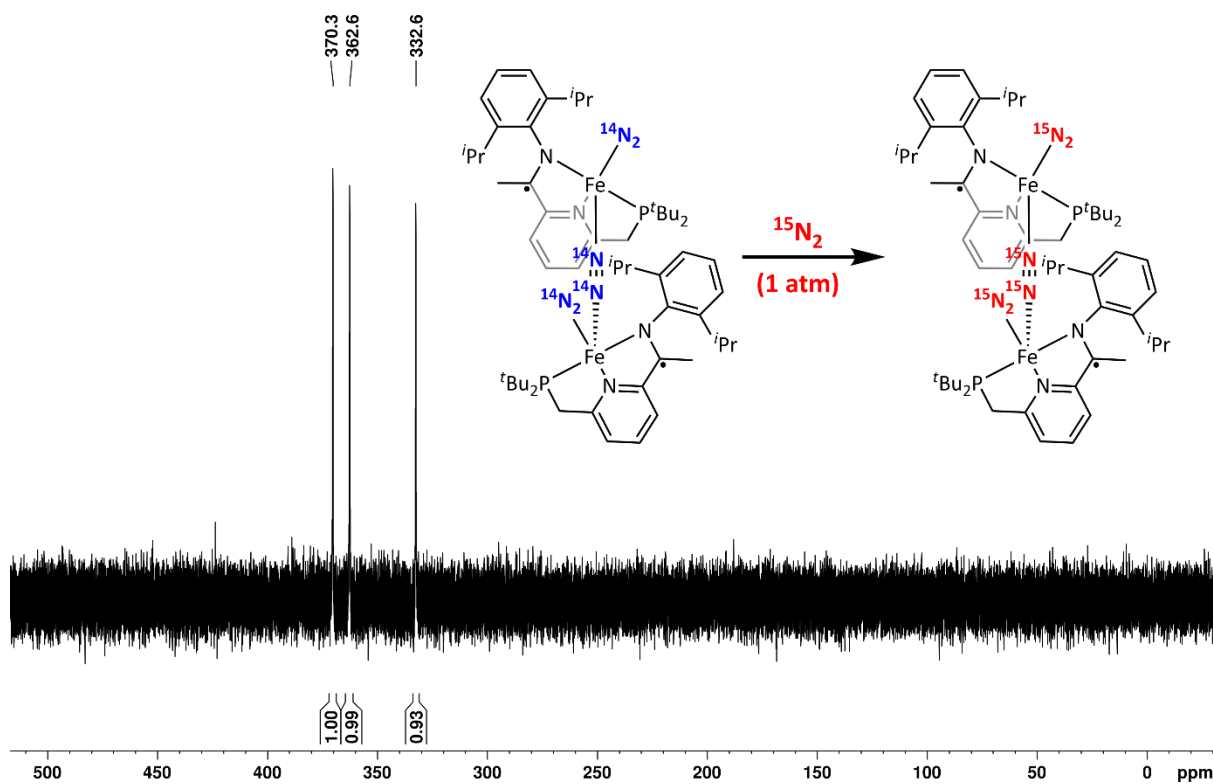


Figure S14. $^{15}\text{N}_2$ exchange experiment: ($^{14}\text{N}_2$)-**2** dissolved under Ar atmosphere, 1 atm of $^{15}\text{N}_2$ added, directly measured ^{15}N NMR spectrum (60.8 MHz, C_6D_6 , 295 K).

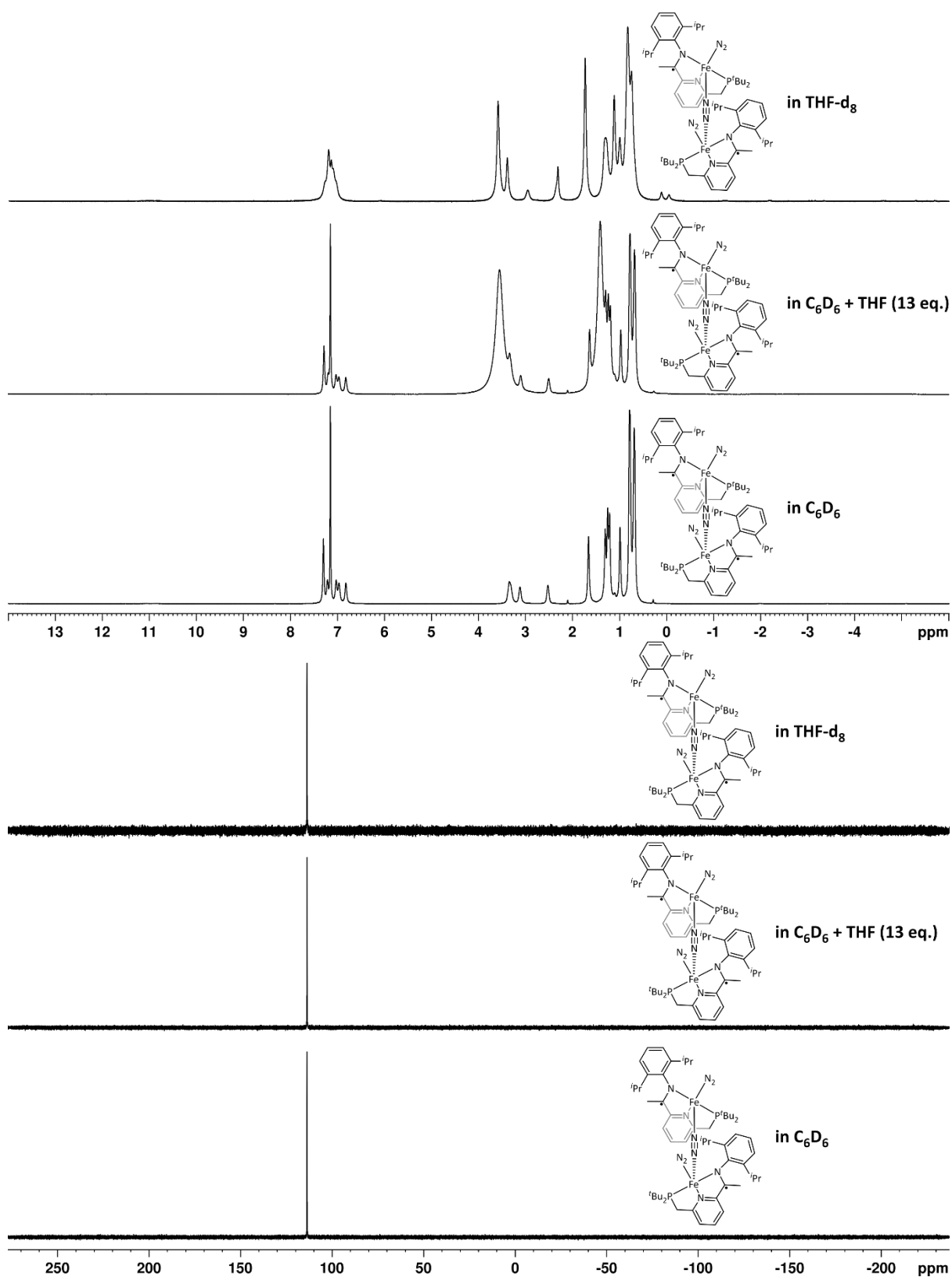


Figure S15. Prove of stability of the coordinated N_2 in **2** by addition of various amounts of THF. Top: 1H NMR (600 MHz, 295 K), bottom: $^{31}P\{^1H\}$ NMR (243 MHz, 295 K).

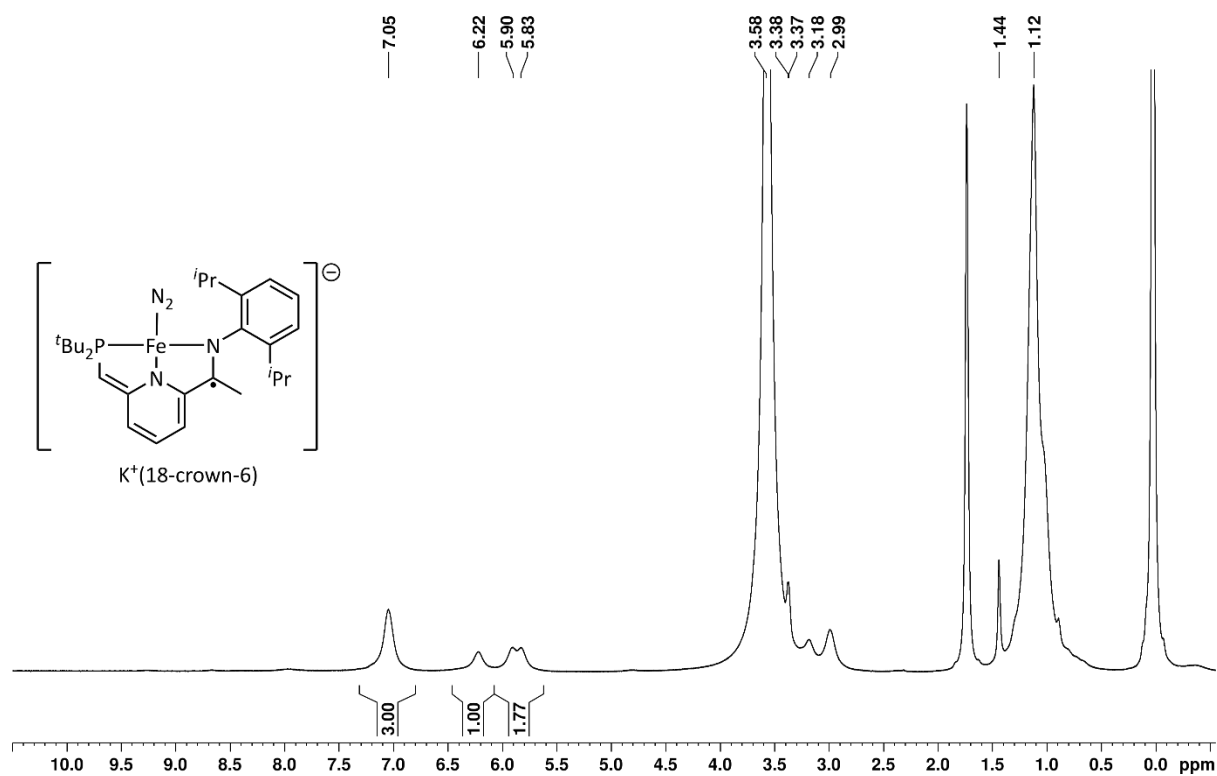


Figure S16. ¹H NMR spectrum of **3b** (600 MHz, THF-d₈, 233 K).

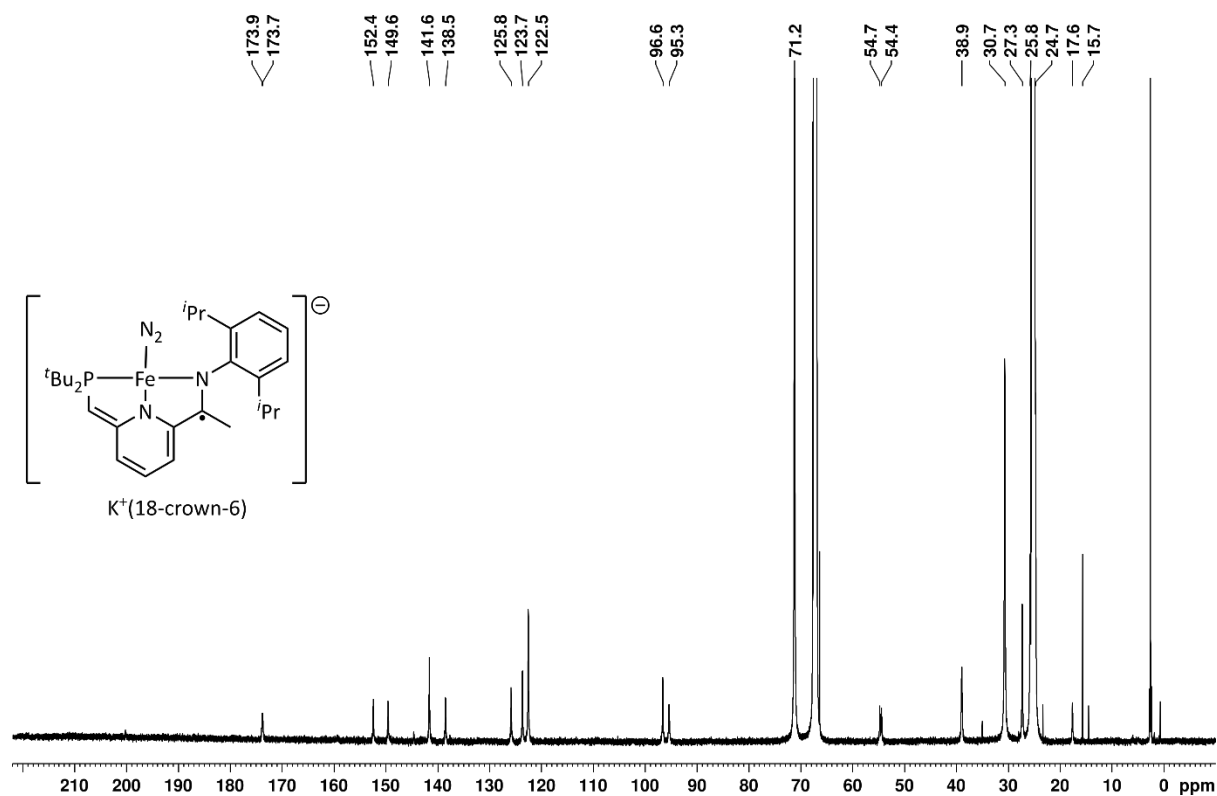


Figure S17. ¹³C{¹H} NMR spectrum of **3b** (151 MHz, THF-d₈, 233 K).

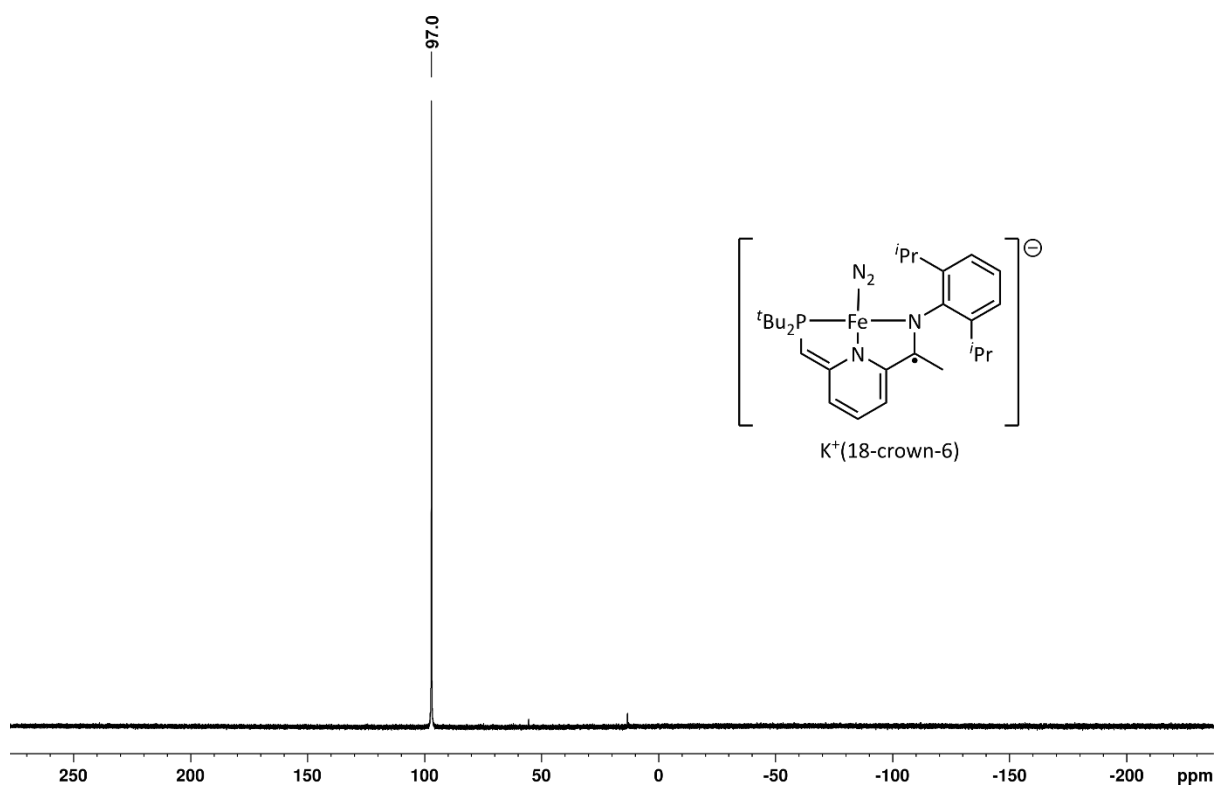


Figure S18. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3b** (243 MHz, THF-d_8 , 233 K).

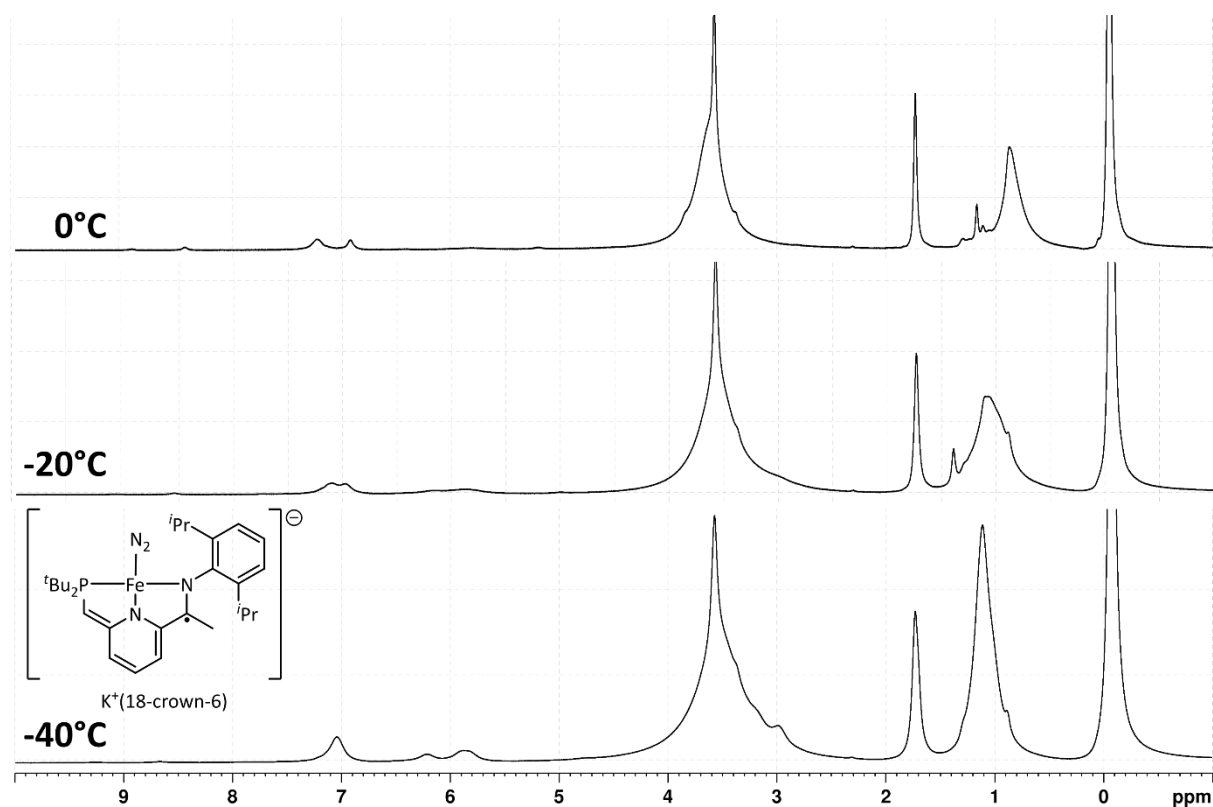


Figure S19. Variable temperature ^1H NMR spectra of **3b** (600 MHz, THF-d_8 , 233 K–273 K).

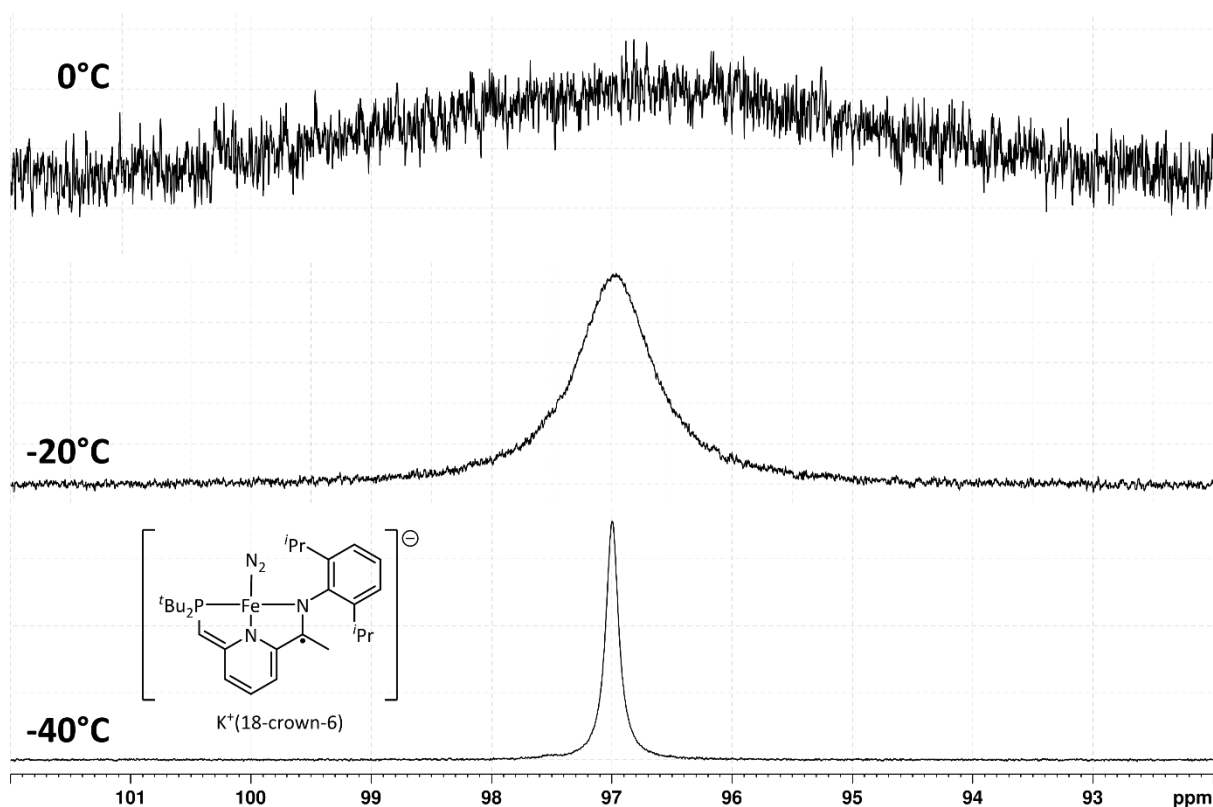


Figure S20. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3b** (243 MHz, THF-d_8 , 233 K–273 K).

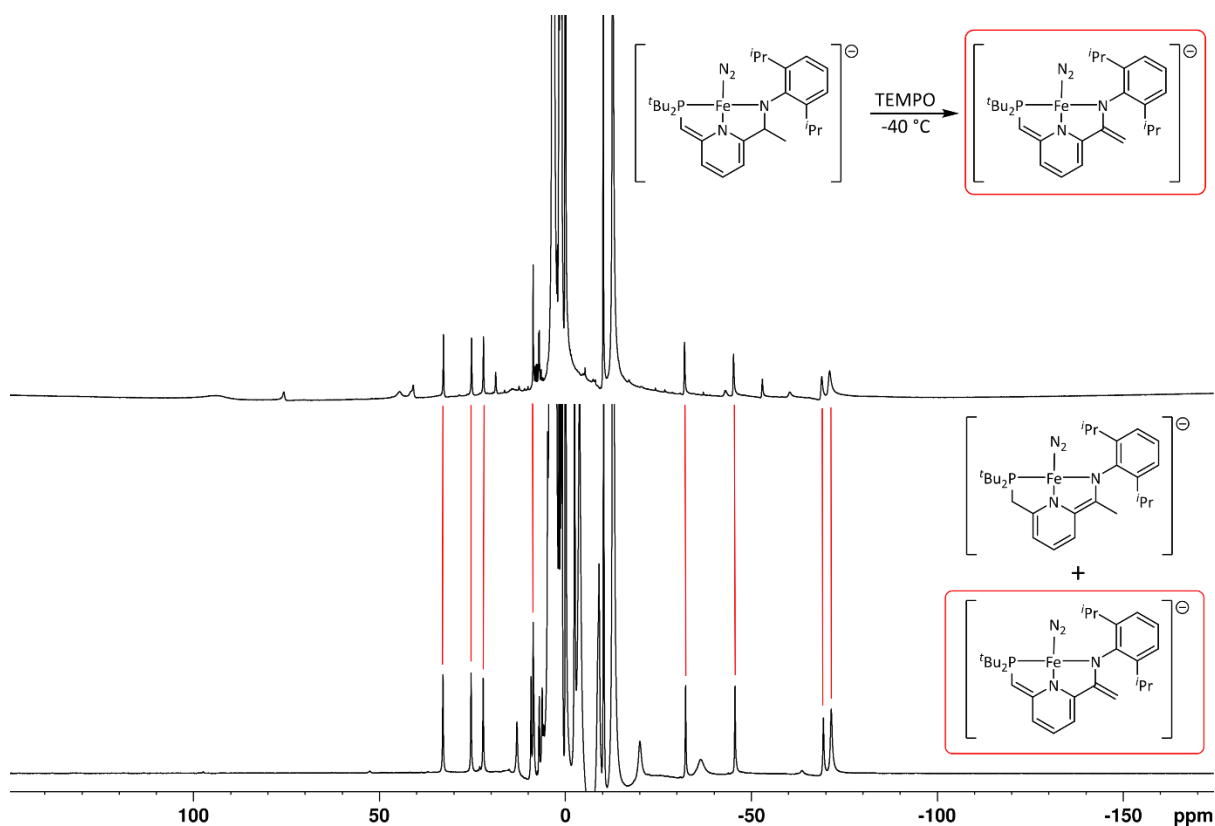


Figure S21. ^1H para NMR spectra (400 MHz, THF-d_8 , 233 K). Top: reaction of **3** with TEMPO (1 eq.) to (mainly) **5**, bottom: comparison with disproportionation products, **5** highlighted in red.



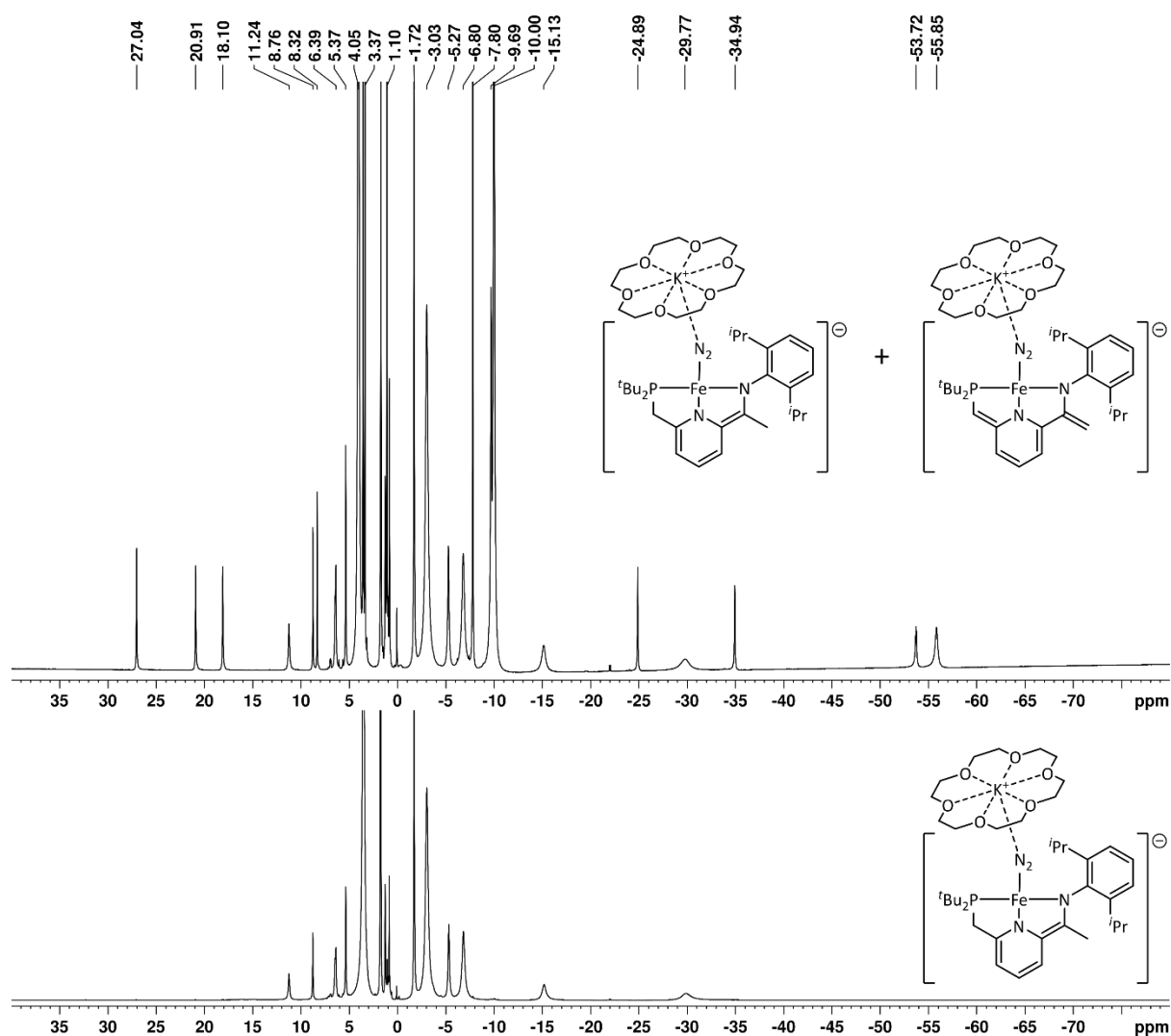
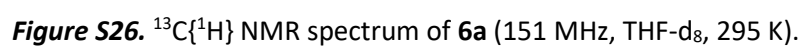
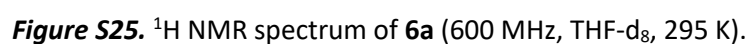


Figure S24. ^1H paramagnetic NMR spectrum of the disproportionation into **4b** and **5b** (top) (600 MHz, THF-d_8 , 295 K). Reference spectrum of **4b** for comparison (bottom).



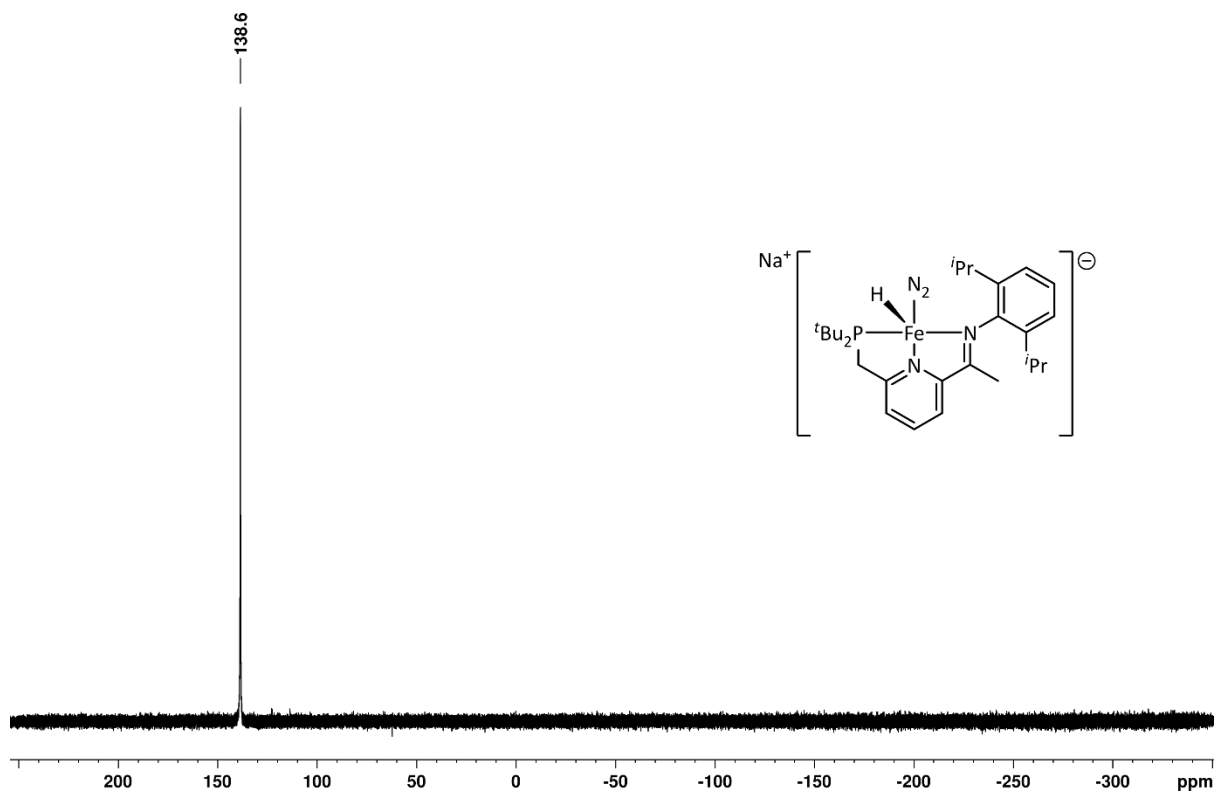


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6a** (243 MHz, THF-d_8 , 295 K).

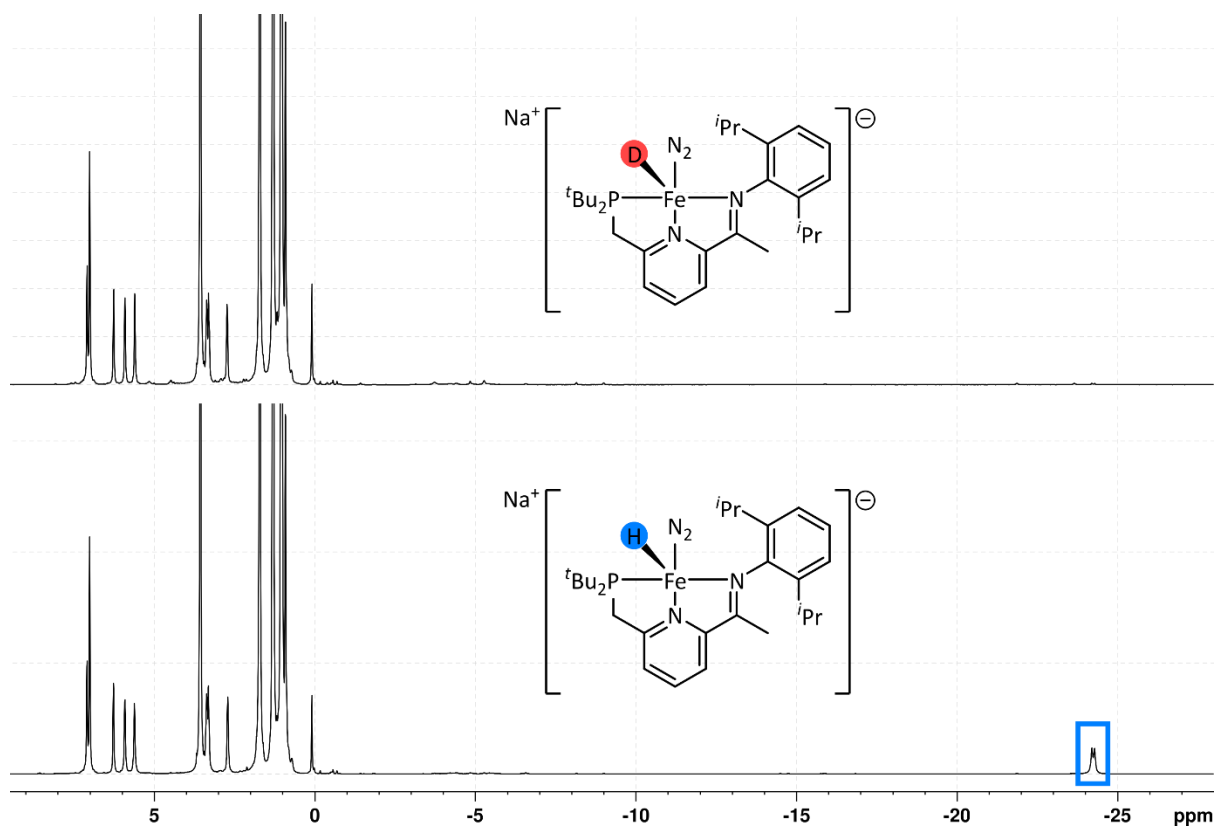


Figure S28. ^1H NMR spectra of **6a** (bottom) and **6a-D** (top); (600 MHz, THF-d_8 , 295 K).

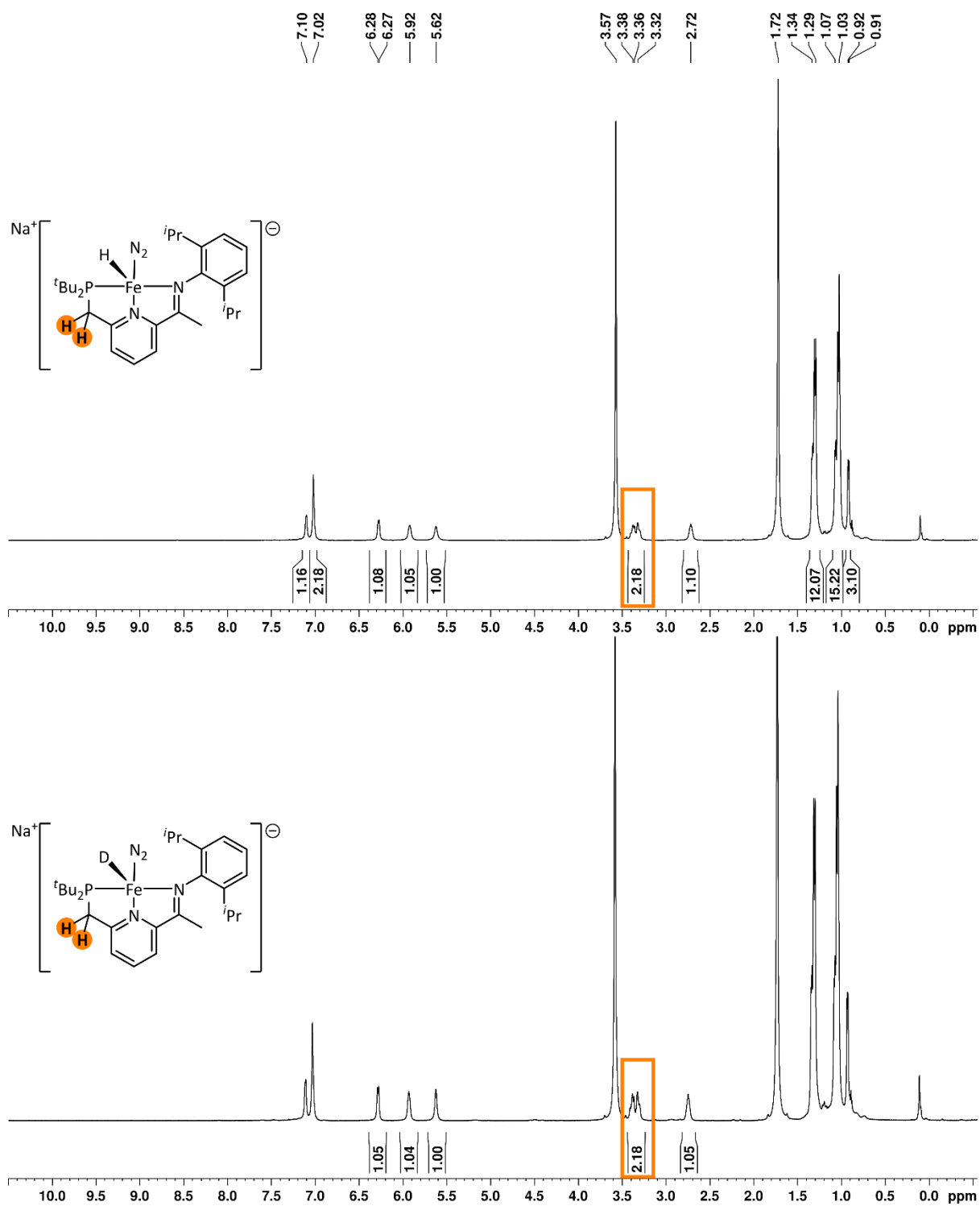


Figure S29. ^1H NMR spectra of **6a** (top) and **6a-D** (bottom) (600 MHz, THF-d_8 , 295 K). Highlighted in orange are the integrals of the benzylic CH_2 -groups to show that no deuterium is incorporated in this position. Reaction conditions: **6a** was pressurized with D_2 (7 bar) in a pressure tube.

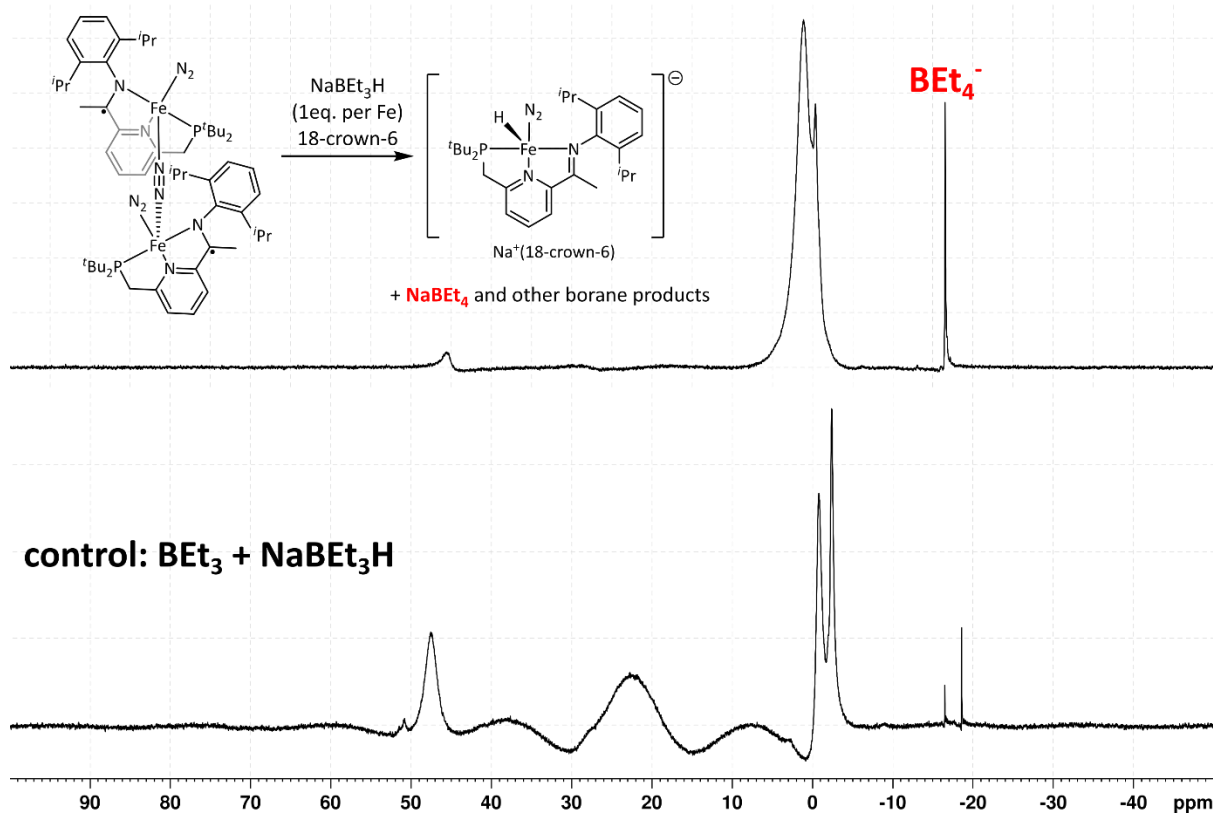


Figure S30. $^{11}\text{B}\{^1\text{H}\}$ NMR: reaction mixture of **6** (top) and control (bottom) (193 MHz, THF-d_8 , 295 K).

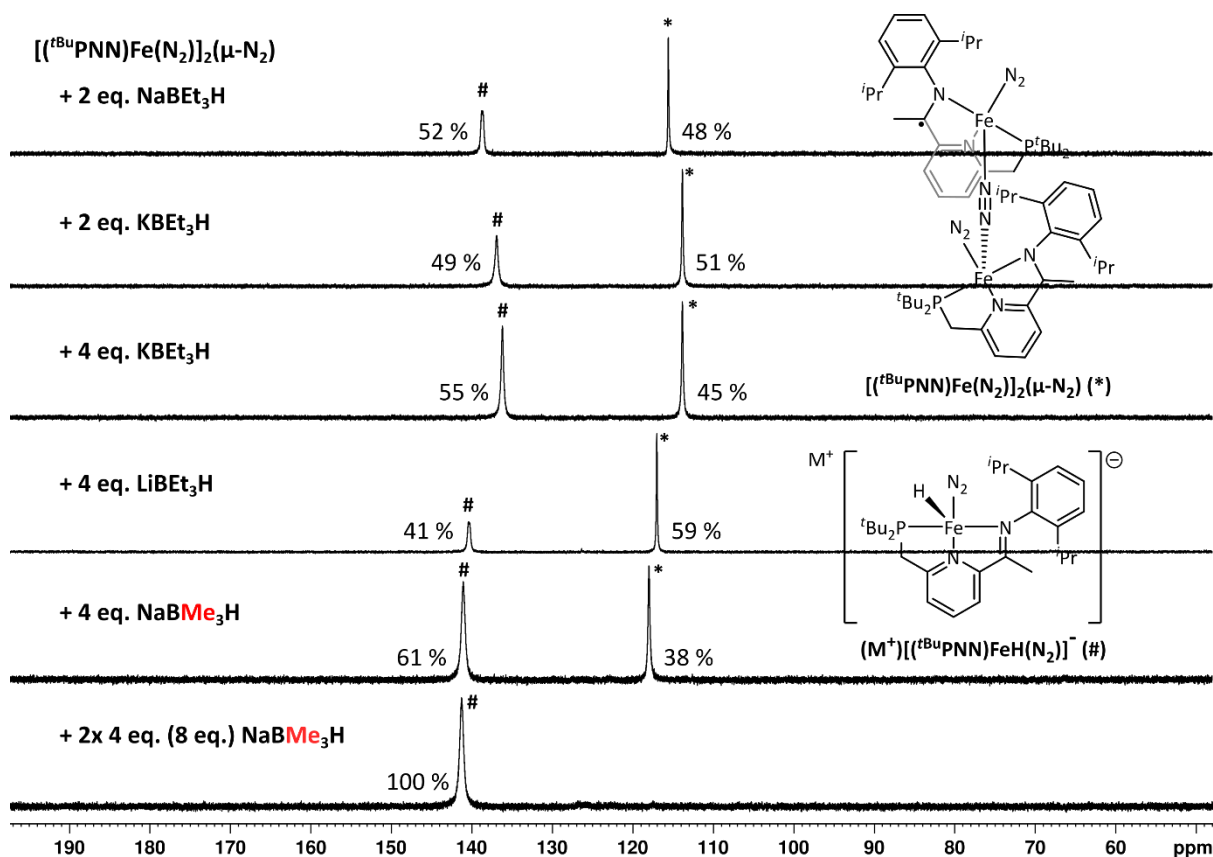


Figure S31. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction of **2** with various equivalents of different hydride sources (243 MHz, THF-H_8 or THF-d_8 , 295 K).

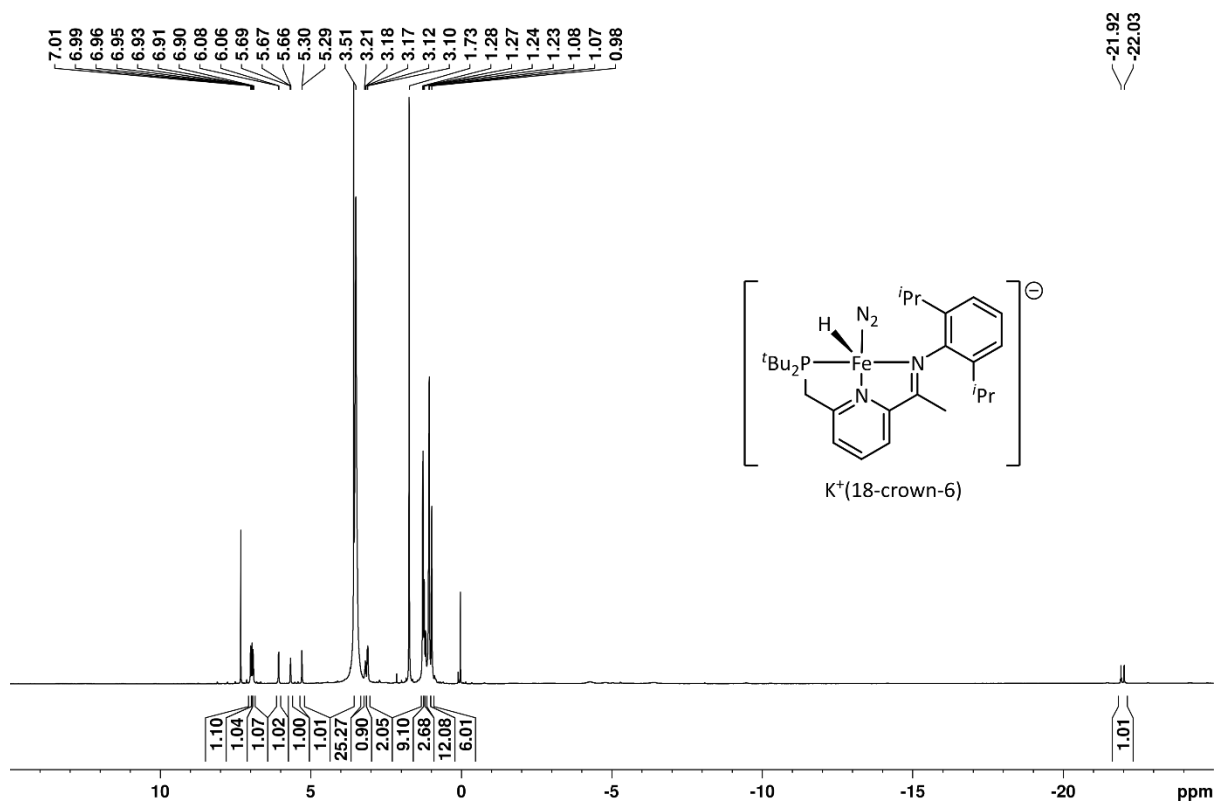


Figure S32. ¹H NMR spectrum of **6b** (600 MHz, THF-d₈, 295 K).

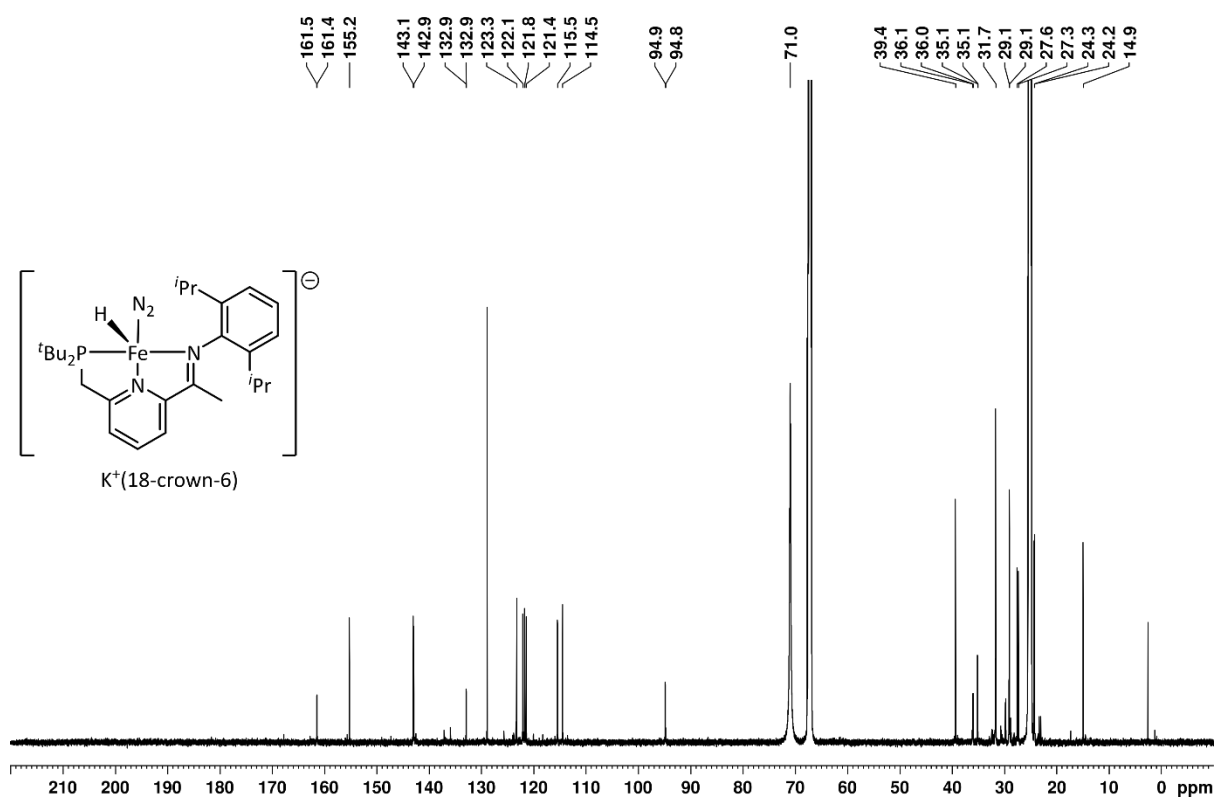


Figure S33. ¹³C{¹H} NMR spectrum of **6b** (151 MHz, THF-d₈, 295 K).

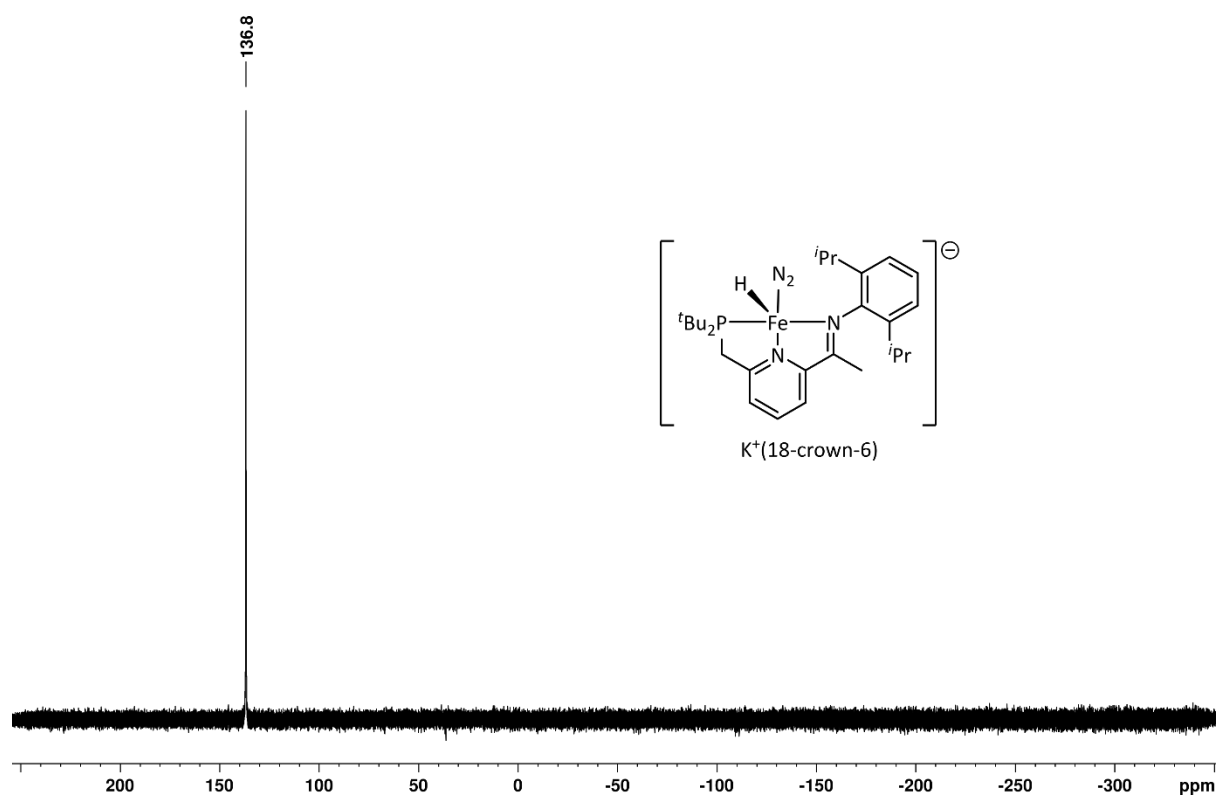


Figure S34. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6b** (243 MHz, THF- d_8 , 295 K).

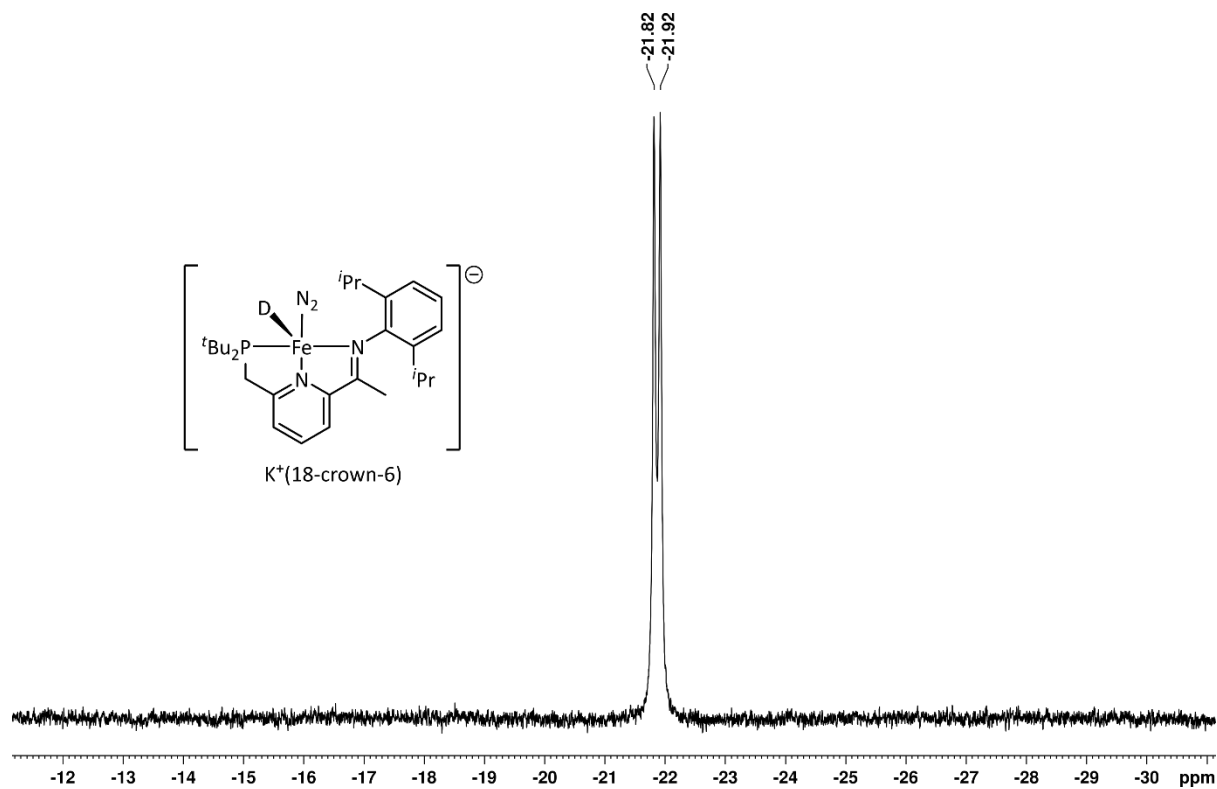
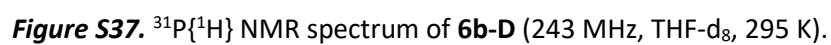
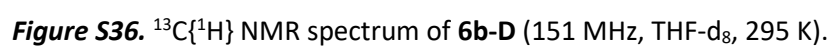
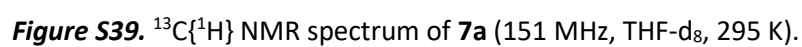
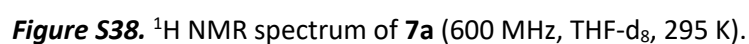
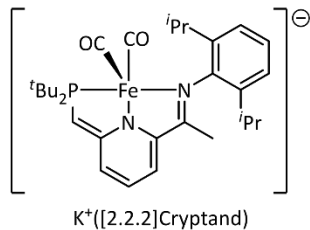


Figure S35. ^2H NMR spectrum of **6b-D** (92 MHz, THF- d_8 , 295 K).





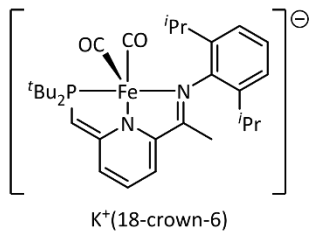


7.06
7.05
7.04
7.02
7.01
6.99

6.34
6.32
6.32
6.32
6.31
6.31
5.93
5.92
5.66
5.65

3.51
3.39
3.18
3.17
3.16
3.14
3.13
3.12
3.11

1.67
1.25
1.24
1.16
1.14
1.01
1.00



S41

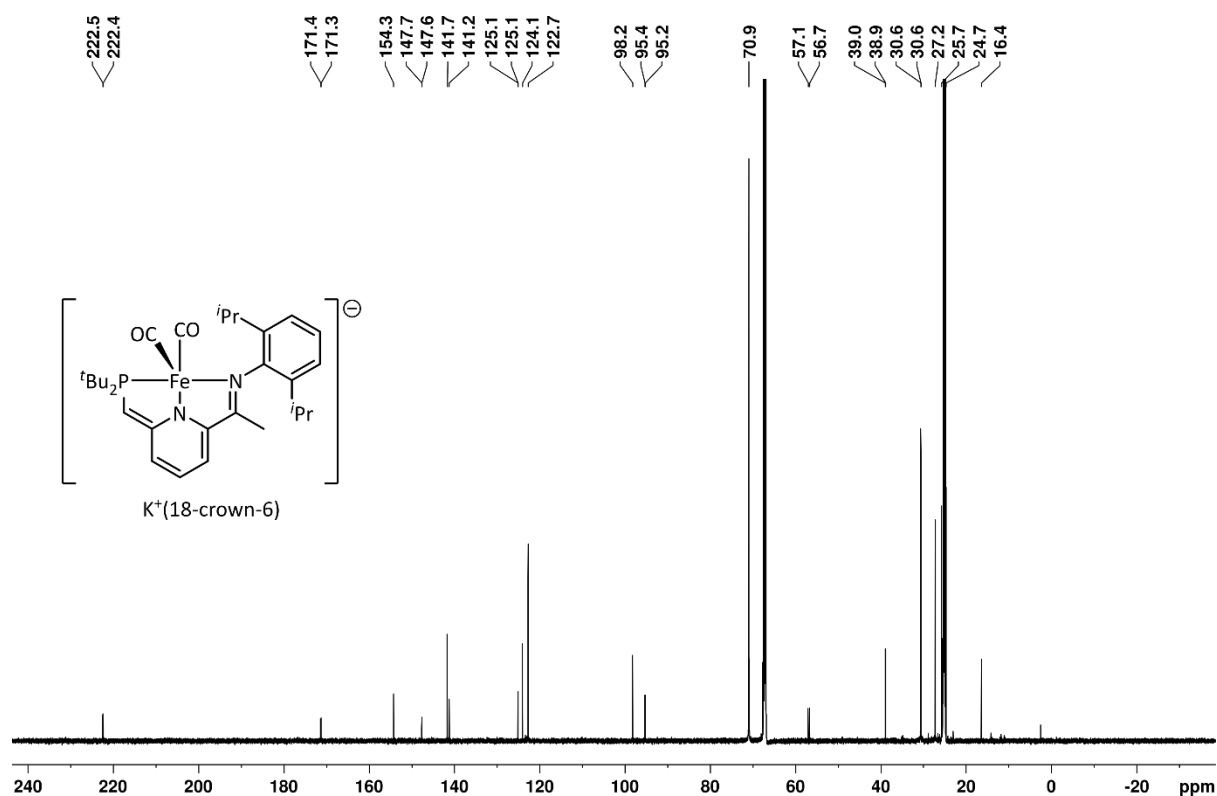


Figure S42. $^{13}C\{^1H\}$ NMR spectrum of **7b** (151 MHz, THF- d_8 , 295 K).

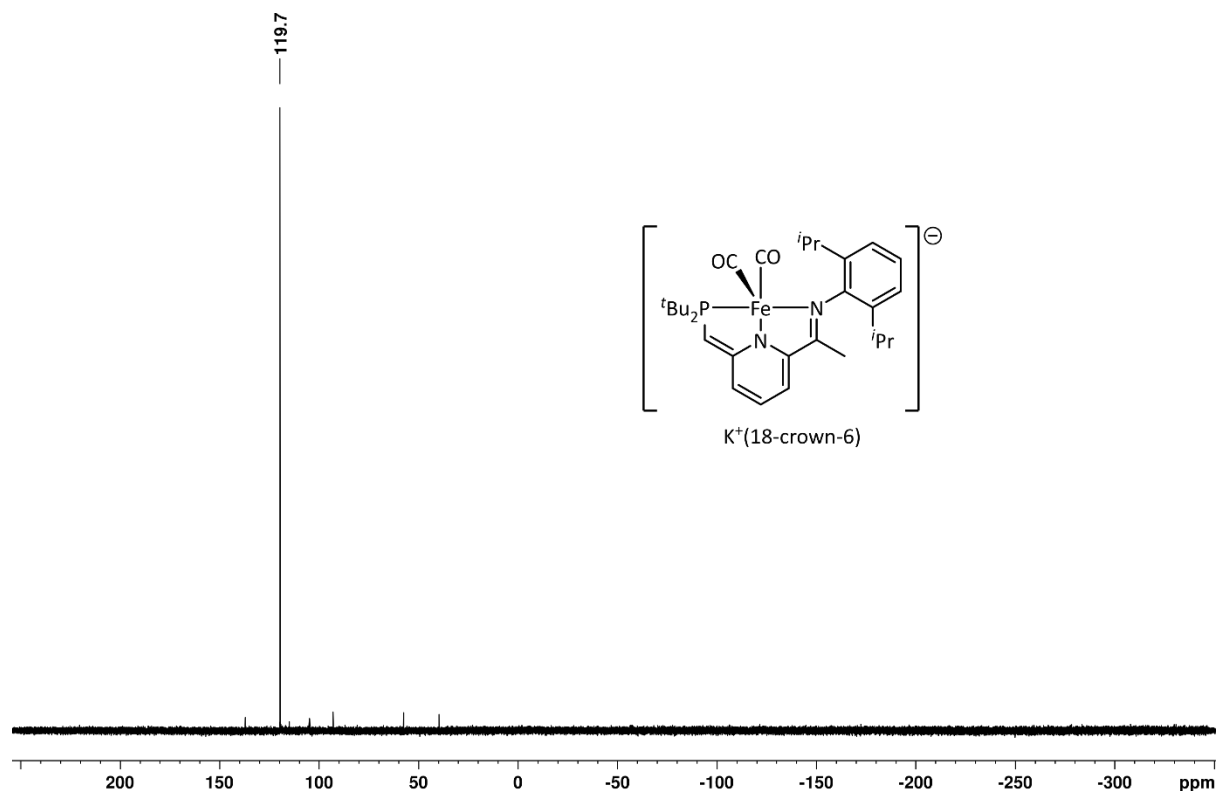


Figure S43. $^{31}P\{^1H\}$ NMR spectrum of **7b** (243 MHz, THF- d_8 , 295 K).

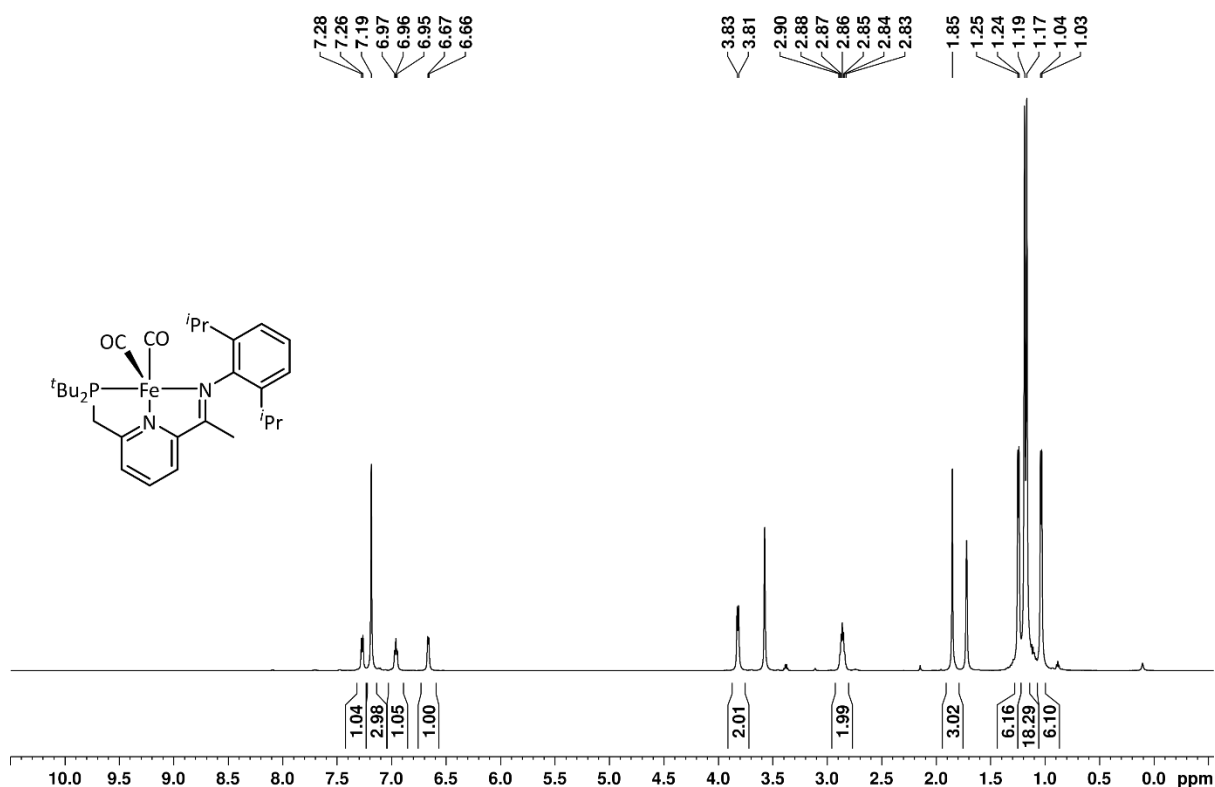


Figure S44. ¹H NMR spectrum of **8** (600 MHz, THF-d₈, 295 K).

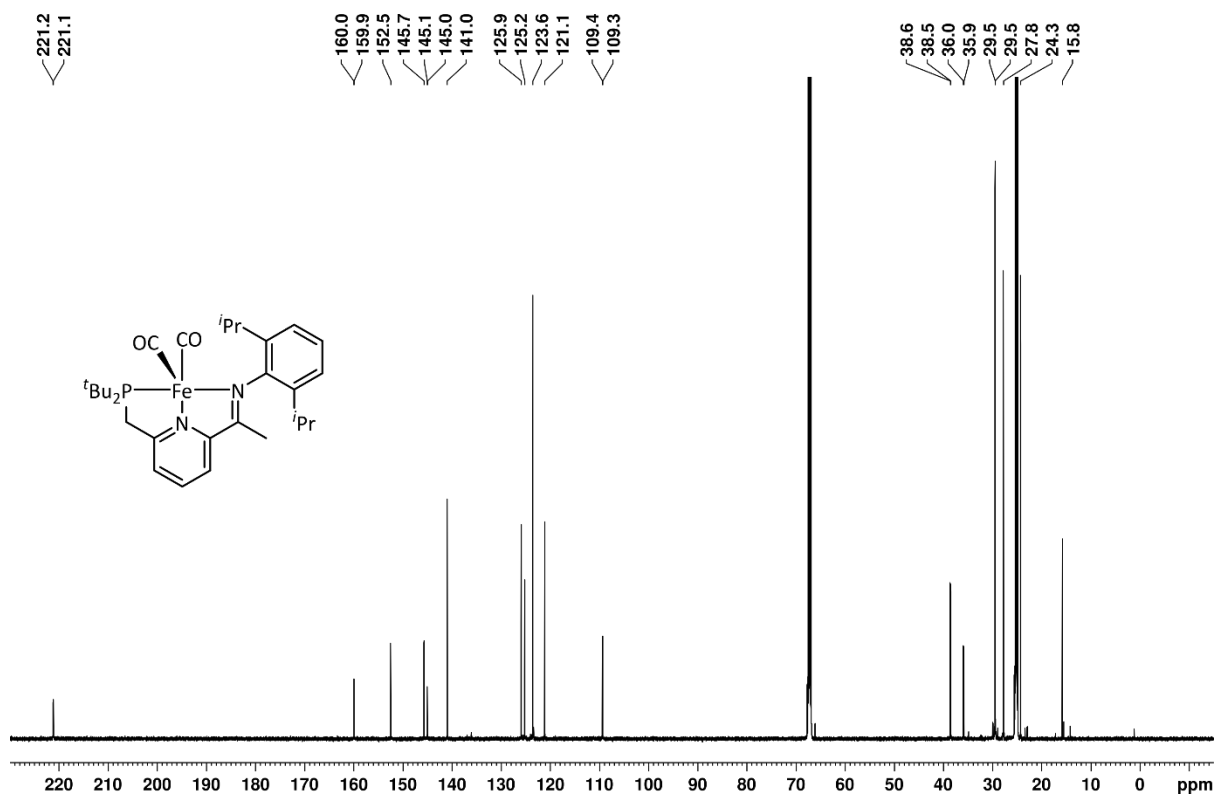


Figure S45. ¹³C{¹H} NMR spectrum of **8** (151 MHz, THF-d₈, 295 K).

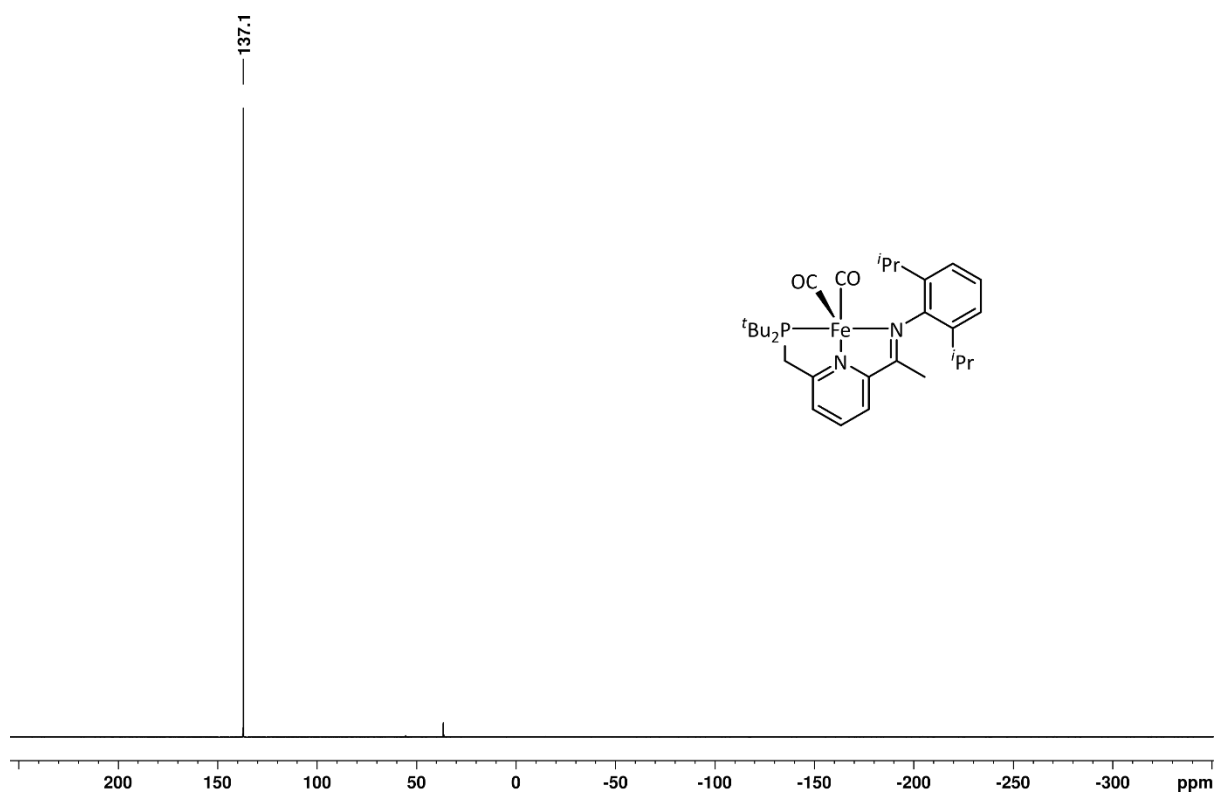
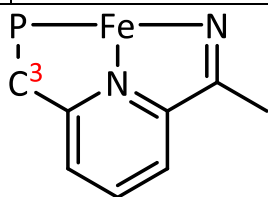


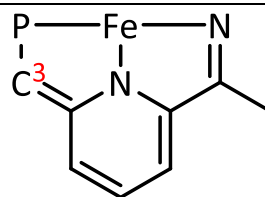
Figure S46. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8** (243 MHz, THF- d_8 , 295 K).

Table S5. Characteristic ^{13}C NMR chemical shifts and coupling constants of the dearomatized vs aromatic pyridine fragments of the complexes **2–8**.

Compound	Pyridine aromaticity	^{13}C δ [ppm] C3 (C–P)	$^1J_{\text{P-C}}$ [Hz]
2	aromatic	34.8	14.4
3b	<u>dearomatized</u>	54.6	49.4
6a	aromatic	36.2	16.5
6b	aromatic	36.1	16.6
6b-D	aromatic	36.3	15.3
7a	<u>dearomatized</u>	56.8	49.3
7b	<u>dearomatized</u>	56.9	49.0
8	aromatic	35.9	18.0



aromatic



dearomatized

IR Spectra

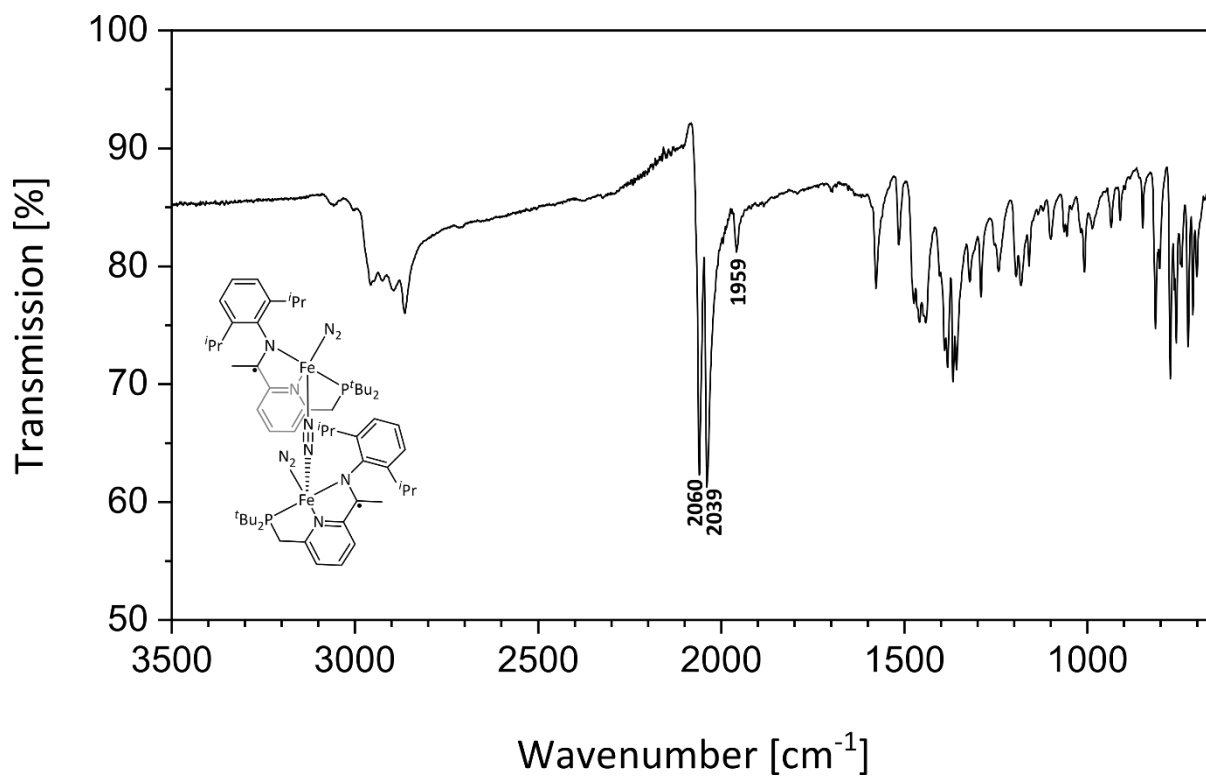


Figure S47. ATR-IR spectrum of **2**.

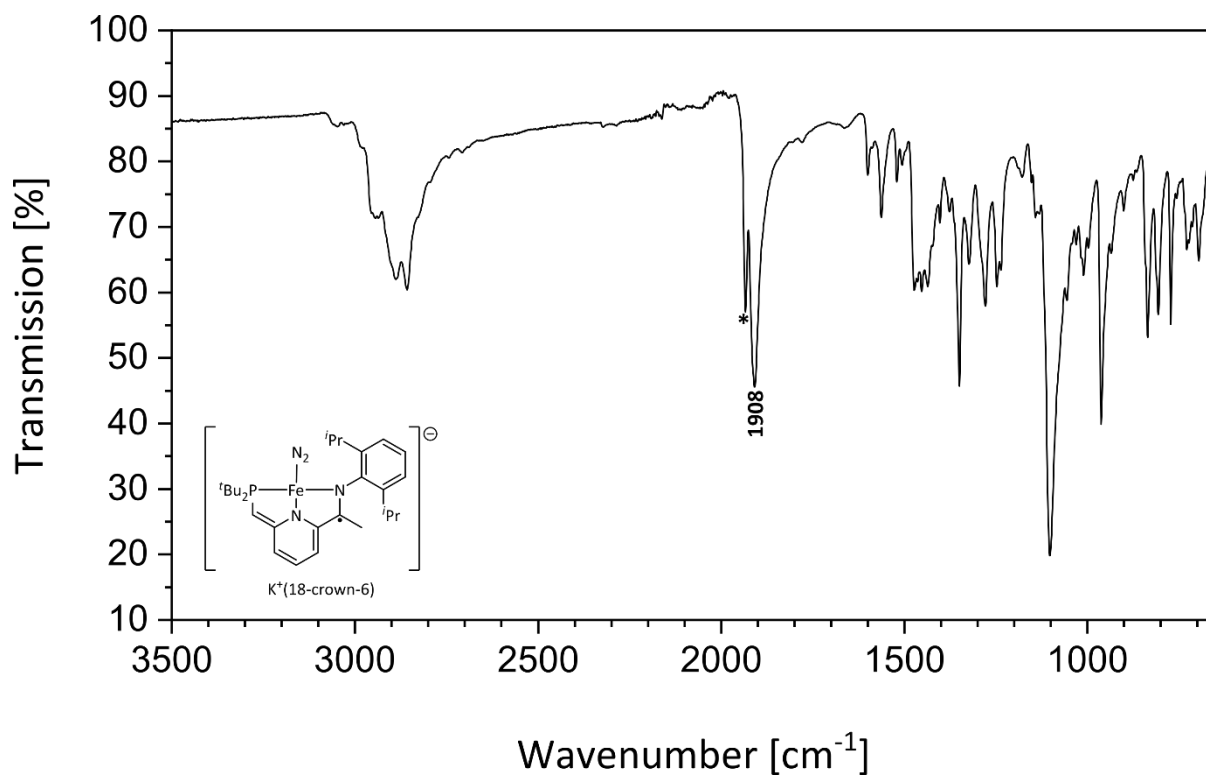


Figure S48. ATR-IR spectrum of **3b**. Due to the thermal instability of **3b** no clean spectrum could be obtained (disproportionation product marked with an asterisk).

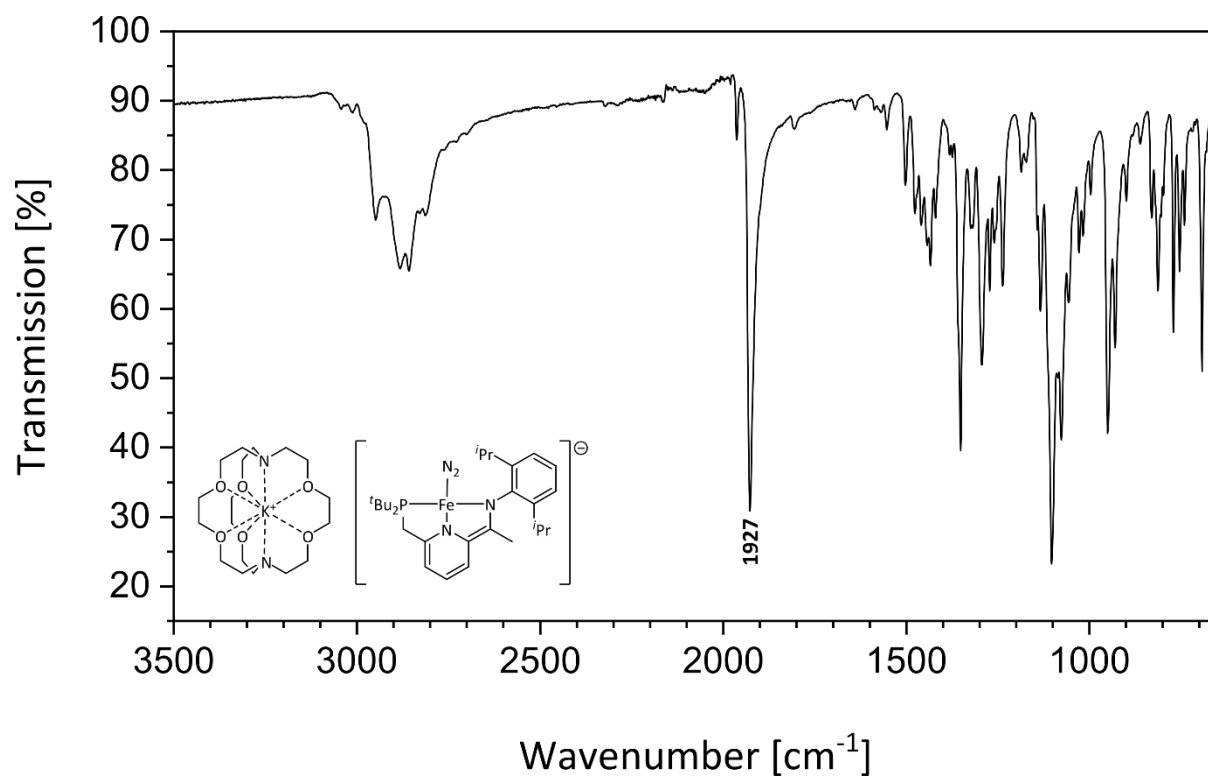


Figure S49. ATR-IR spectrum of **4a**.

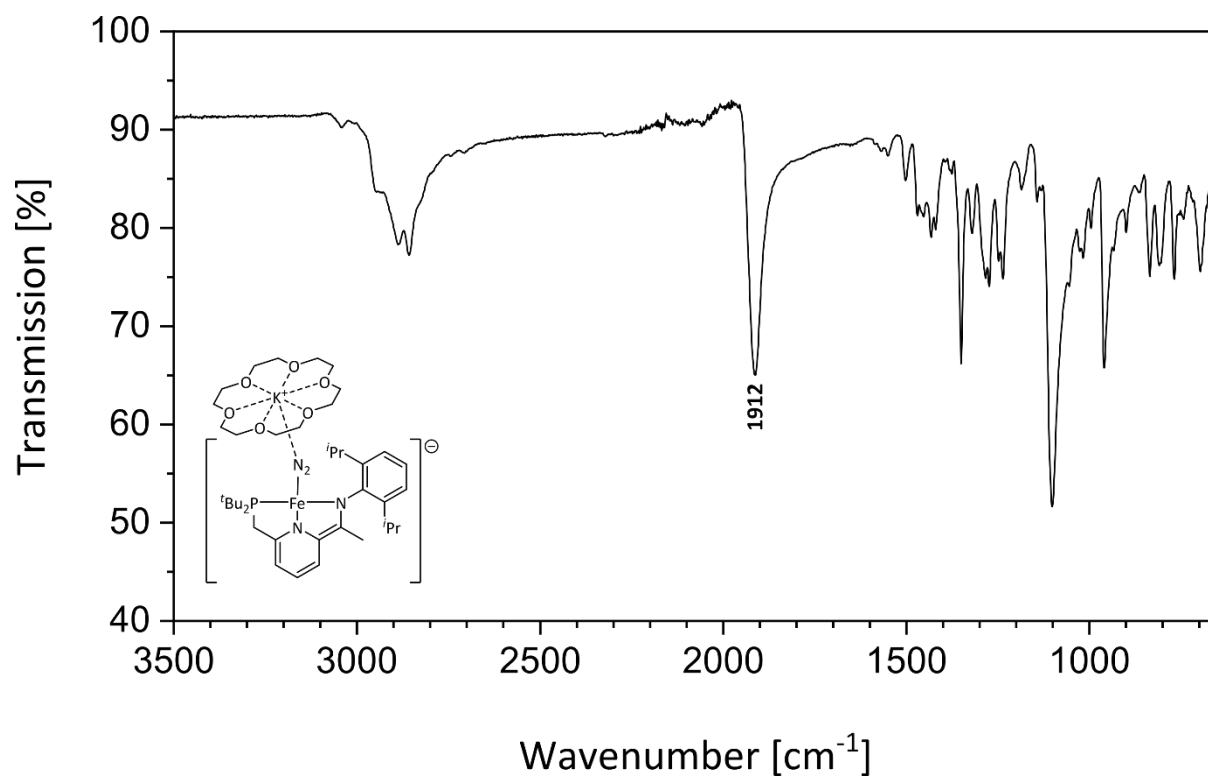


Figure S50. ATR-IR spectrum of **4b**.

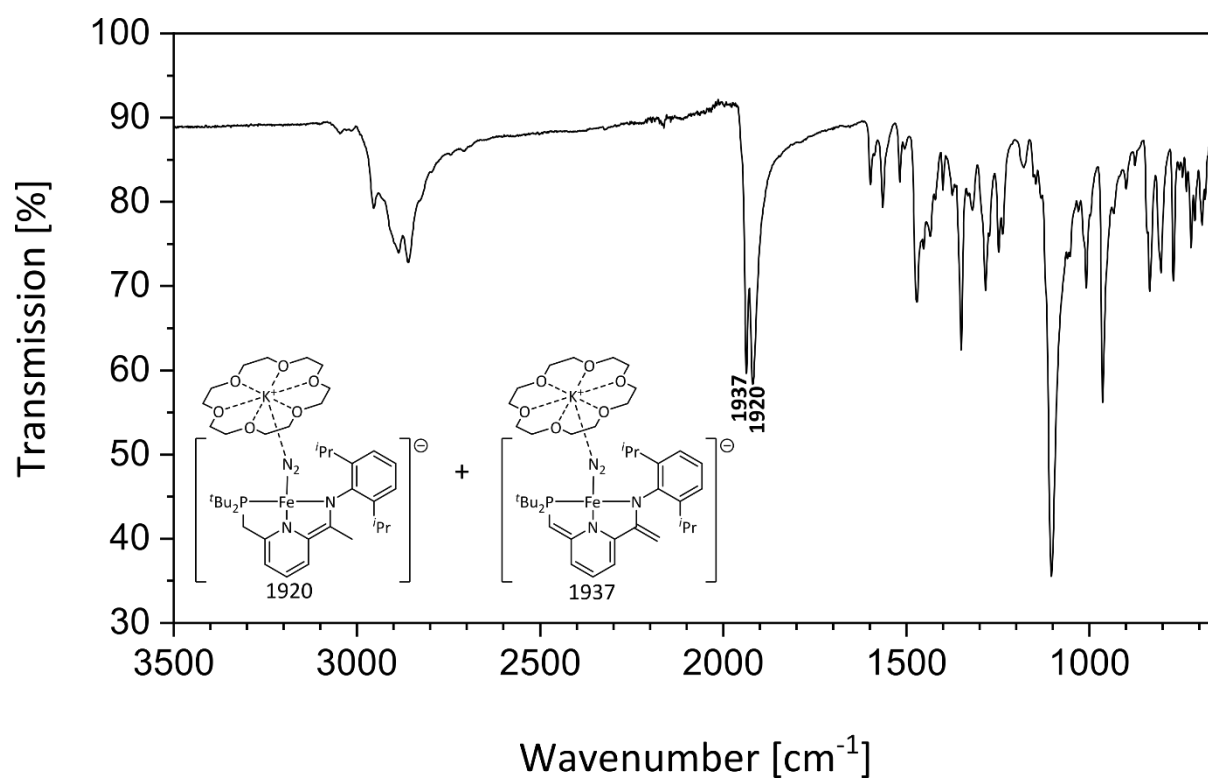


Figure S51. ATR-IR spectrum of the disproportionation products **4b** and **5b**.

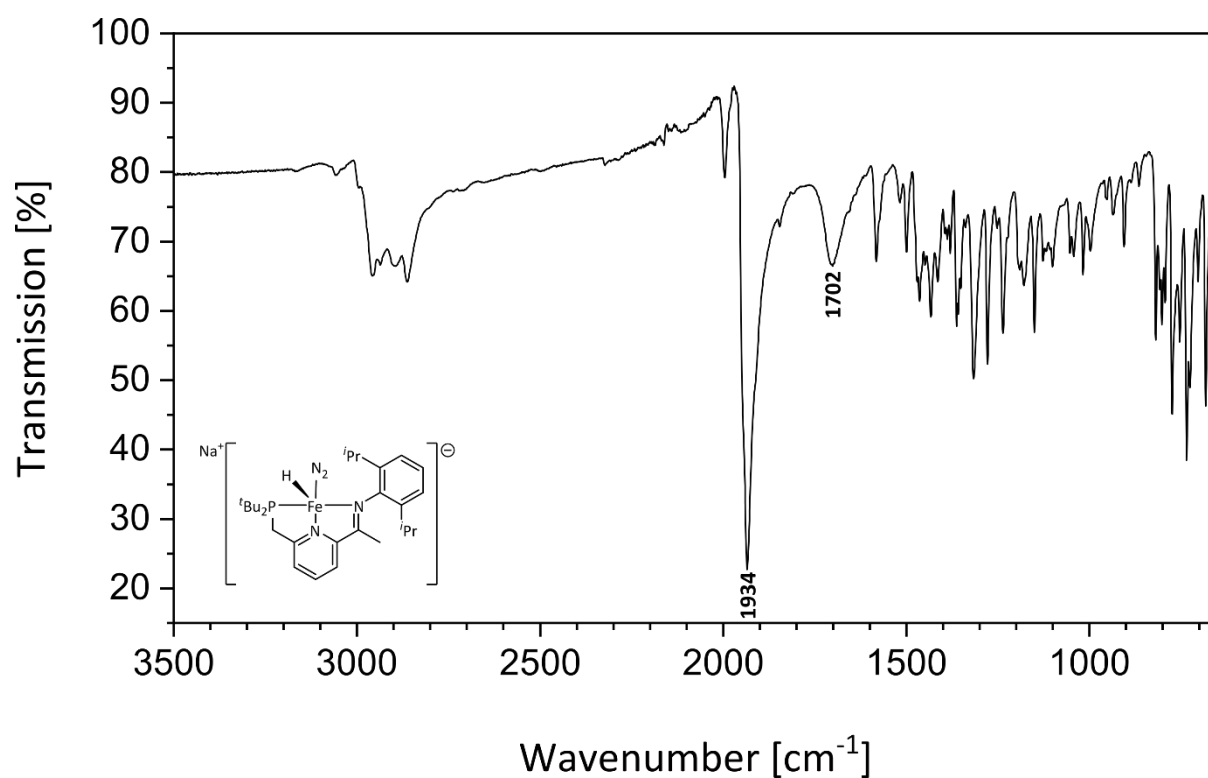


Figure S52. ATR-IR spectrum of **6a**.

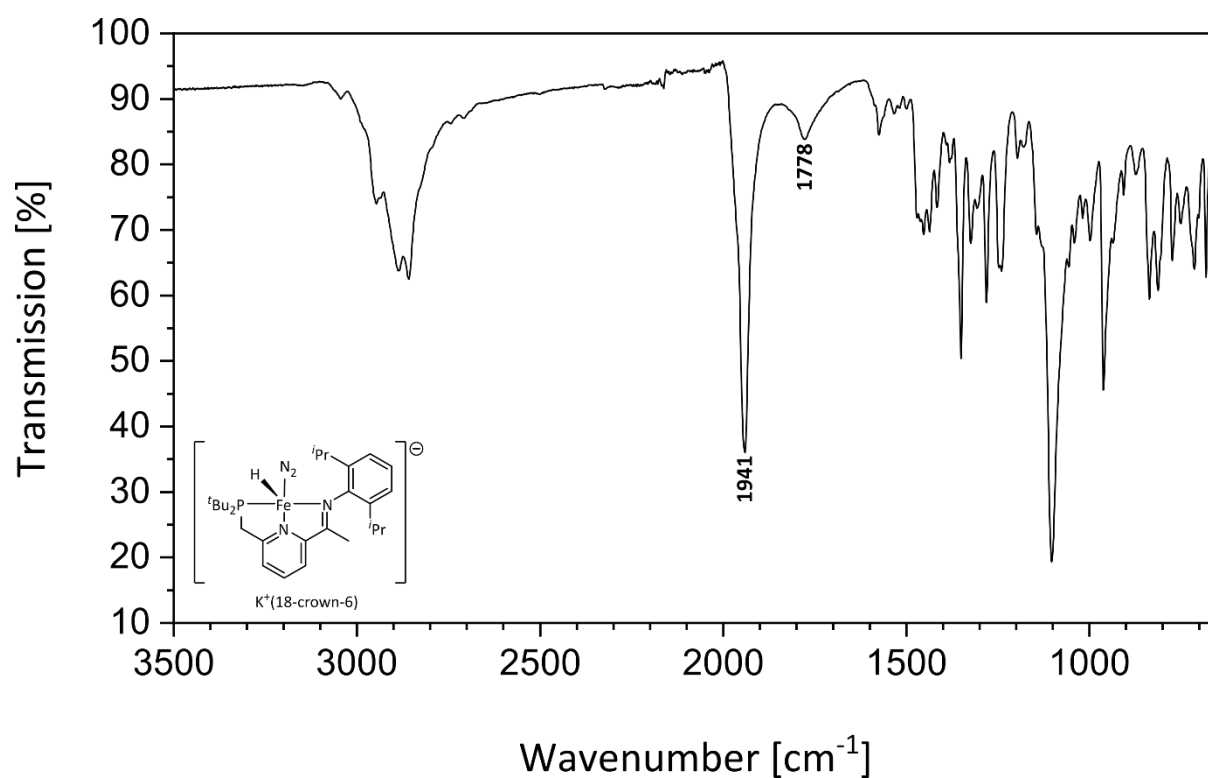


Figure S53. ATR-IR spectrum of **6b**.

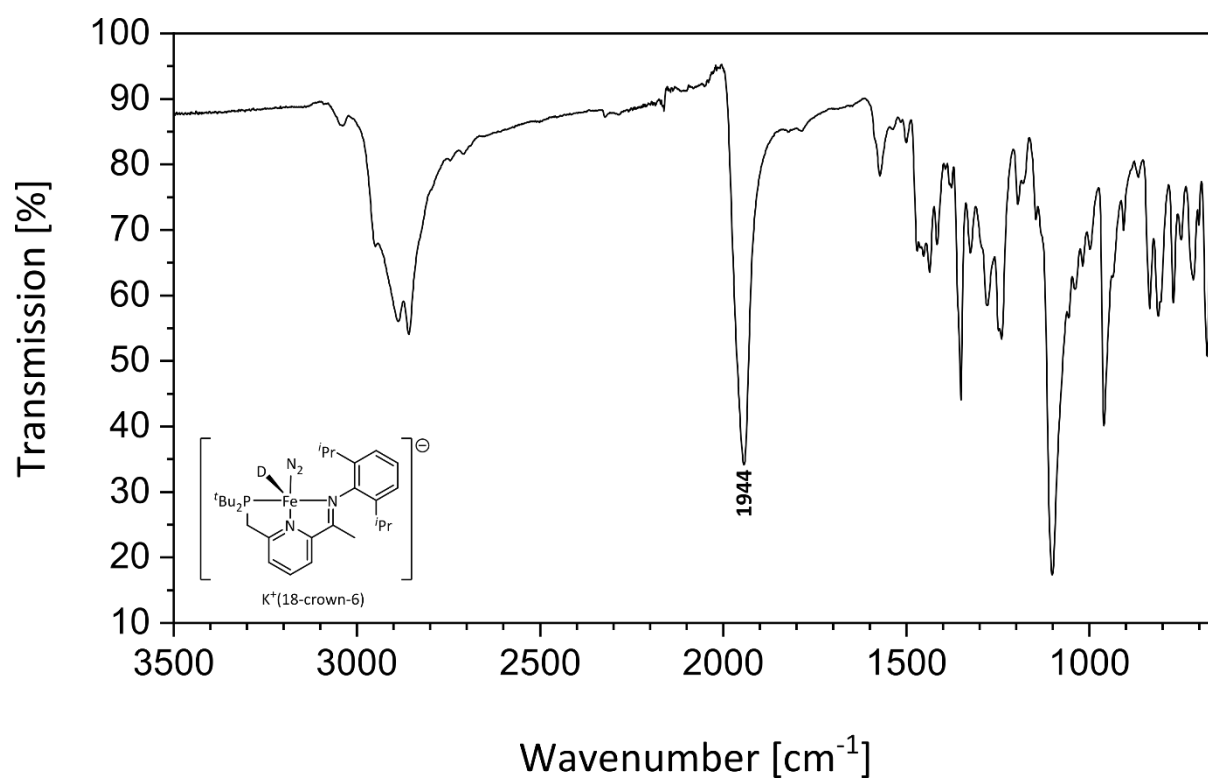


Figure S54. ATR-IR spectrum of **6b-D**.

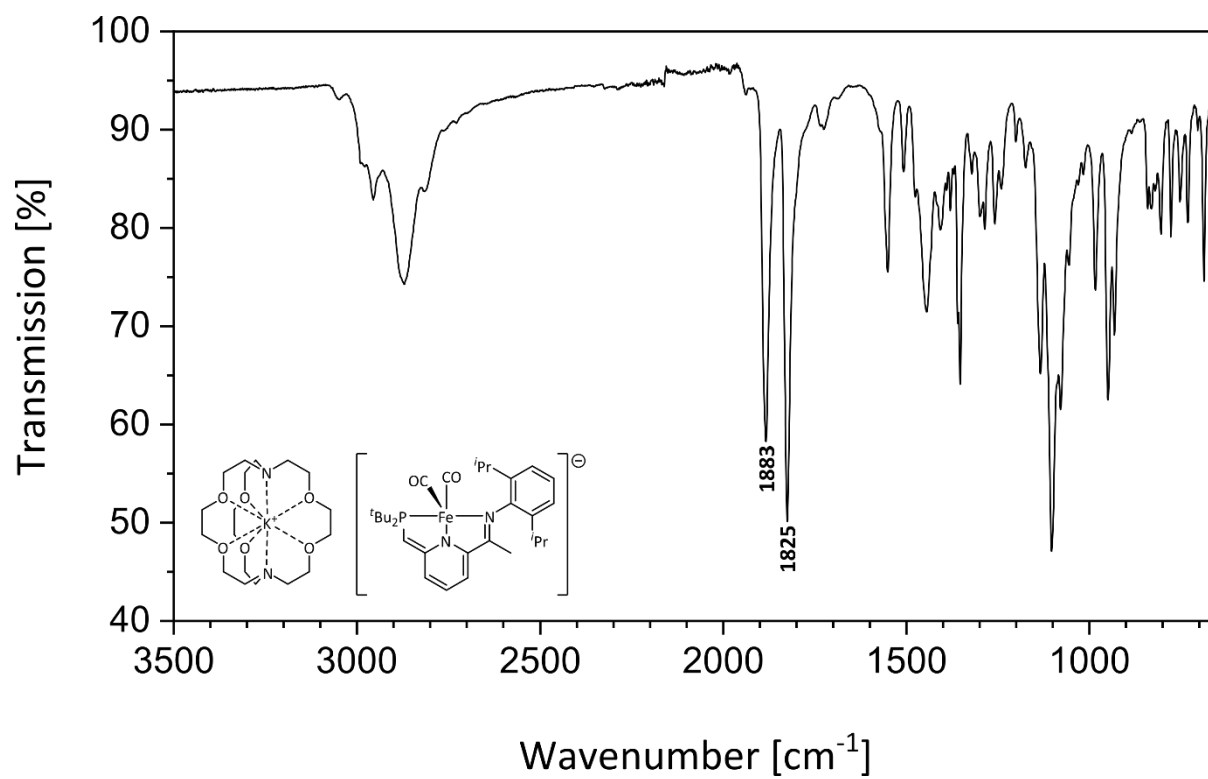


Figure S55. ATR-IR spectrum of **7a**.

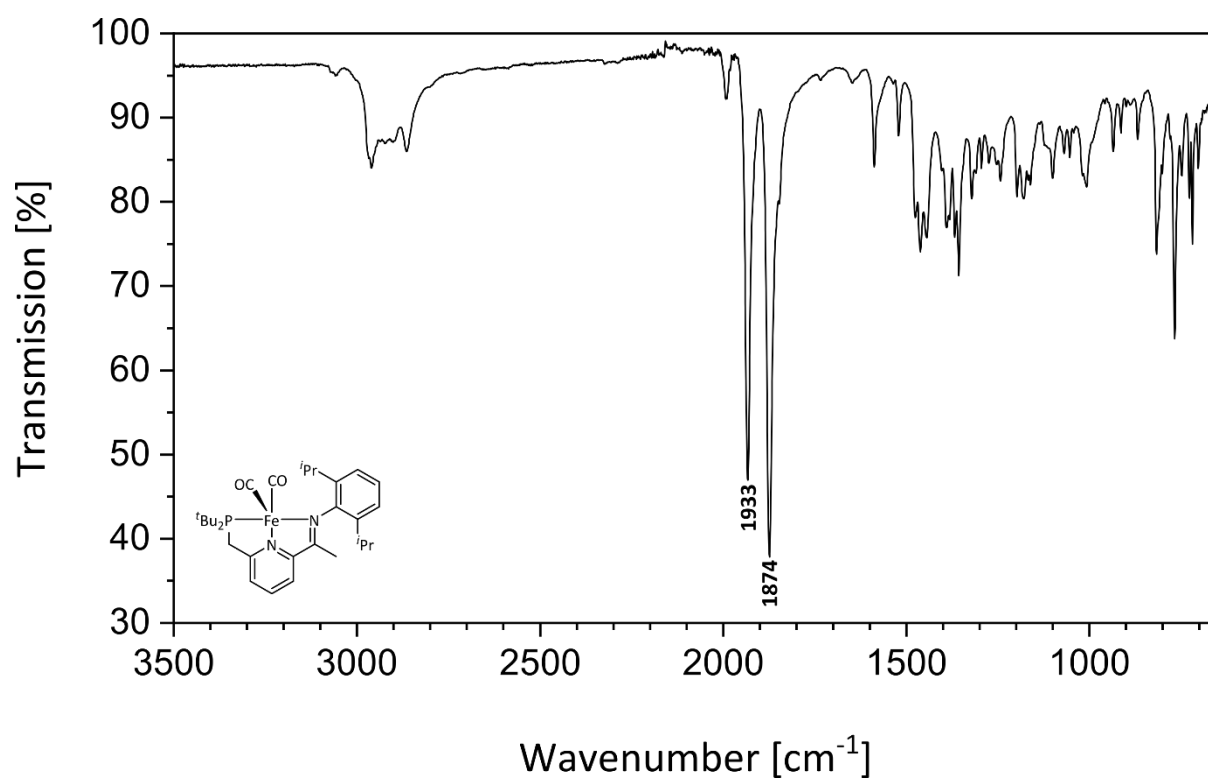


Figure S56. ATR-IR spectrum of **8**.

Computational Details

All density functional theory (DFT) calculations were performed using the ORCA quantum chemical program package (Version 4.2.1).²⁰ Geometry optimizations of the complexes **2** and **8** were performed using the corresponding crystal structures, without any truncation of their structures, as starting geometries. For the reduced or deprotonated complexes **3a**, **4a**, **5a** and **7a**, the K⁺([2.2.2]Cryptand) unit was truncated. For the hydride **6a** the Na⁺ ion was truncated in all calculations. Geometry optimizations of all complexes except **2** were undertaken by employing the hybrid-GGA (GGA = generalized gradient approximation) density functional B3LYP^{21,22} in conjunction with Ahlrichs triple- ζ def2-TZVP basis set²³ and the appropriate auxiliary basis set (def2/J)²⁴. For **2** a basis set combination was used: def2-TZVP(-f) on Fe, N and P atoms and def2-SVP on all other atoms. To speed up the overall calculations, the RIJCOSX²⁵ approximation was applied for the expensive integral calculations. Noncovalent interactions were accounted for by using atom-pairwise dispersion corrections with Becke-Johnson damping (D3BJ).²⁶ Solvent effects were accounted for using the Conductor-like Polarizable Continuum Model (C-PCM)²⁷ with the dielectric constant of THF. Subsequent numerical frequency calculations were undertaken for the optimized geometries to confirm they correspond to stationary points featuring no imaginary frequencies greater than 50 cm⁻¹. Molecular orbitals were visualised with Avogadro (Version 1.2.0) and plotted with an isosurface value of 0.05.

Sample keyword line for geometry optimizations:

```
! UKS B3LYP D3BJ RIJCOSX def2-TZVP CPCM(THF) def2/J Pal16 TightSCF Grid4 FinalGrid5 GridX4 Opt
xyzFile UCO Keepdens

%scf
  MaxIter 5000
end
%geom
  EnforceStrictConvergence True
end
%plots
  dim1 150 dim2 150 dim3 150
  Format cube
```

²⁰ a) Neese, F. The ORCA program system. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2012**, 2, 73-78. (b) Neese, F. Software update: the ORCA program system, version 4.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2017**, 8, e1327. Doi: 10.1002/wcms.1327

²¹ Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behaviour. *Phys. Rev. A* **1988**, 38, 3098-3100.

²² Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, 37, 785-789.

²³ Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy *Phys. Chem. Chem. Phys.* **2005**, 7, 3297-3305.

²⁴ Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn *Phys. Chem. Chem. Phys.* **2006**, 8, 1057-1065.

²⁵ Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient approximate and parallel Hartree-Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree-Fock exchange *Chem. Phys.* **2009**, 356, 98-109.

²⁶ a) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory *J. Comput. Chem.* **2011**, 32, 1456-1465. b) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu *J. Chem. Phys.* **2010**, 132, 154104.

²⁷ Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model *J. Phys. Chem. A* **1998**, 102, 1995-2001.

```

SpinDens("filename.cube");
end

*xyz charge multiplicity
xyz coordinates from x-ray structure
*

Sample keyword line for frequency calculations:
! UKS B3LYP D3BJ RIJCOSX def2-TZVP CPCM(THF) def2/J Pal16 TightSCF Grid4 FinalGrid5 GridX4
NumFreq MOread

% moinp "name_of_gbw_file.gbw"
%maxcore 2800
%scf
  MaxIter 5000
end

```

Broken-Symmetry Calculations

The broken symmetry (BS) formalism²⁸ was employed in unrestricted calculations to check for antiferromagnetic coupling of two spins. BS calculations were performed for all complexes using the B3LYP functional and the same basis set (def2-TZVP or def2-SVP//def2-TZVP for **2**) as mentioned earlier. In each case, multiple fragments were defined: PNN, Fe, CO/N₂ and H⁺. Because several BS solutions of the spin-unrestricted Kohn – Sham equations may be obtained, the general notation BS(*m*,*n*) was used, where *m* (*n*) denotes the number of spin-up (spin-down) electrons at the iron centre (*m*) or the PNN ligand (*n*). For the dimeric complex **2** the notation BS(*n*₁, *m*₁, *m*₂, *n*₂) was used, where the indices stand for the iron-PNN subunits, which are connected through a bridging N₂ ligand. The spin multiplicity for the broken symmetry calculations were chosen according to the high spin state – e.g. triplet for BS(1,1), quintet for BS(2,2), etc.

Input file example for the broken symmetry calculations, here: BS(2,2):

```

! UKS B3LYP D3BJ RIJCOSX def2-TZVP def2/J CPCM(THF) Pal16 TightSCF Grid4 FinalGrid5 GridX4 Opt
xyzFile UCO Keepdens

%scf
  MaxIter 5000
  Brokensym 2,2
end
%geom
  ReducePrint false
  EnforceStrictConvergence True
end
%plots
  dim1 150 dim2 150 dim3 150
  Format cube
  SpinDens("filename.cube");

```

²⁸ a) Ginsberg, A. P. Magnetic exchange in transition metal complexes. 12. Calculation of cluster exchange coupling constants with X.alpha.-scattered wave method *J. Am. Chem. Soc.* **1980**, *102*, 111-117. b) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J.-M. Orbital interactions, electron delocalization and spin coupling in iron-sulfur clusters *Coord. Chem. Rev.* **1995**, *144*, 199-244.

end
 *xyz charge multiplicity
 xyz coordinates from x-ray structure
 *

Computational Summary

In the case of the diamagnetic **2–3** and **6–8** four possible ground states were considered: a restricted singlet ground state (RKS) – corresponding to a Fe(0) centre stabilised by a neutral ligand – and two unrestricted singlet states (UKS singlet and BS(1,1)), the latter corresponding to a Fe(I) center stabilised by an anionic ligand radical with multiple possibilities for spin pairing. For **2**, an additional third unrestricted approach was investigated, namely the BS(2,2). For **2, 3, 6** and **7** the unrestricted triplet state was also investigated to see if there are any low lying triplet states accessible. Compound **4** was, because of possible redox-non-innocence of the ligand, modeled as unrestricted doublet, as well as BS(1,2) and BS(2,1). For **5**, because of the double deprotonation and hence a dianionic ligand (with no intact imine bond), the only spin state investigated was an unrestricted doublet.

Table S6. Optimization results of **2** for various spin states. B3LYP, SVP//TZVP(-f). L = ligand.

Compound 2	Converged to	S _{ab} (UCO)	ΔG (kcal/mol)
RKS	–	–	12.4
UKS (singlet)	BS(1,1,1,1) L ^{up} -Fe ^{down} -Fe ^{down} -L ^{up}	0.53/0.48	0.4
BS(1,1)	BS(1,1,1,1) L ^{up} -Fe ^{down} -Fe ^{up} -L ^{down}	0.52/0.49	0.0
BS(2,2)	BS(1,1,1,1) L ^{down} -Fe ^{up} -Fe ^{up} -L ^{down}	0.53/0.48	–
UKS (triplet)	L ^{down} -Fe ^{up} -Fe ^{up} -L ^{up}	0.51/0/0	3.7

Table S7. Optimization results of **3** for various spin states. B3LYP, TZVP, CPCM(THF). L = ligand.

Compound 3	Converged to	S _{ab} (UCO)	ΔG (kcal/mol)
RKS	–	–	17.6
UKS (singlet)	BS(1,1)	0.07	–
BS(1,1)	BS(1,1)	0.06	0.0
UKS (triplet)	triplet: Fe ^{up} -L ^{up}	0/0	-0.1

Table S8. Optimization results of **4** for various spin states. B3LYP, TZVP, CPCM(THF). L = ligand.

Compound 4	Converged to	S _{ab} (UCO)	ΔG (kcal/mol)
UKS (doublet)	doublet: Fe ^{up}	0.97/0	0.0
BS(2,1)	doublet: Fe ^{up}	0.97/0	–
BS(1,2)	doublet: Fe ^{up}	0.97/0	–

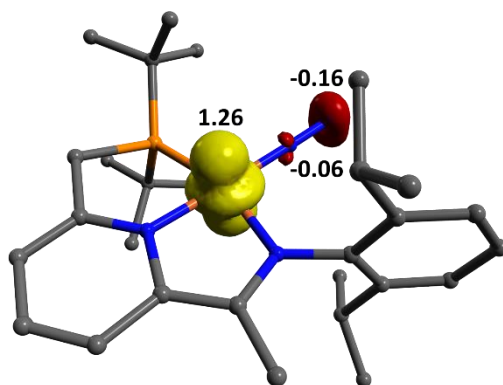


Figure S57. Spin density plot of **4** (UKS doublet, Löwdin population analysis, isovalue 0.01).

Table S9. Optimization results of **5**. B3LYP, TZVP, CPCM(THF). L = ligand.

Compound 5	Converged to	S_{ab} (UCO)	ΔG (kcal/mol)
UKS (doublet)	doublet: Fe ^{up}	0.98/0	0.0

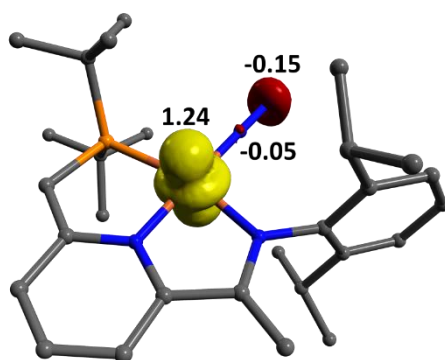


Figure S58. Spin density plot of **5** (UKS doublet, Löwdin population analysis, isovalue 0.01).

Table S10. Optimization results of **6** for various spin states. B3LYP, TZVP, CPCM(THF). L = ligand.

Compound 6	Converged to	S_{ab} (UCO)	ΔG (kcal/mol)
RKS	—	—	1.3
UKS (singlet)	RKS	1.0/1.0	0.9
BS(1,1)	RKS	1.0/1.0	0.0
UKS (triplet)	triplet: Fe ^{up} -L ^{up}	0/0	9.2

Table S11. Optimization results of **7** for various spin states. B3LYP, TZVP, CPCM(THF). L = ligand.

Compound 7	Converged to	S_{ab} (UCO)	ΔG (kcal/mol)
RKS	—	—	1.1
UKS (singlet)	RKS	1.00	1.0
BS(1,1)	BS(1,1)	0.82	0.0

Because of the small energy difference between the RKS and BS(1,1) state, the electronic structure of **7** is best described as a resonance between these forms (see **8**).

Table S12. Optimization results of **8** for various spin states. B3LYP, TZVP. L = ligand.

Compound 8	Converged to	S _{ab} (UCO)	ΔG (kcal/mol)
RKS	–	–	1.5
UKS (singlet)	RKS	1.00	1.5
BS(1,1)	BS(1,1)	0.78	0.0

Because the RKS and BS(1,1) state are very similar in energy, the best description of **8** would be a resonance between the iron(0) form with a neutral ligand and a low-spin Fe(I) with an antiferromagnetically coupled ligand radical. A more detailed investigation and discussion with additional spectroscopic methods was published by Milstein and coworkers.¹

Computational investigation of the HAT from the deprotonated complex **3**

Two approaches for modelling the HAT were computationally investigated: 1) Assuming that **3** reacts to give **5** and a hydrogen atom (H*, asterisk stands for the radical) to estimate the bond dissociation free energy (BDFE) and 2) Reacting **3** with TEMPO* to give **5** along with TEMPOH. Level of theory: as before (B3LYP, def2-TZVP, CPCM(THF)).

1): **BDFE** = G(compound **5**) + G(H*) – G(compound **3**) = **48.7 (kcal/mol)**

2): **ΔG** = [G(compound **5**) + G(TEMPOH)] - [G(compound **3**) + G(TEMPO*)] = **-8.1 (kcal/mol)**

G = Gibbs Free Energy; BDFE = Bond Dissociation Free Energy

Table S13. Gibbs Free Energies for the calculation of the BDFE of **3** and HAT with TEMPO*.

Compound	G (Eh)
3 (UKS; BS1,1)	-2915.66600117
5 (UKS doublet)	-2915.08169573
H* (UKS doublet)	-0.50672454
TEMPOH (RKS)	-484.01756370
TEMPO* (UKS doublet)	-483.42033866

Comparison between experimental structure and computational model

Table S14. Comparison between the experimental Xray structure and computational model.

		N¹–C¹⁵	C¹⁵–C¹	C¹–N²	N²–C⁵	C⁵–C⁶	C⁶–P
2	Xray	1.347(3) 1.352(3)	1.403(3) 1.408(4)	1.385(3) 1.392(3)	1.366(3) 1.367(3)	1.488(3) 1.499(3)	1.847(3) 1.850(2)
	comp.	1.344	1.417	1.388	1.351	1.505	1.850
4a	Xray	1.394(4)	1.367(4)	1.426(4)	1.370(4)	1.510(5)	1.837(3)
4b	Xray	1.3859(10)	1.3797(11)	1.4205(10)	1.3693(11)	1.5016(13)	1.8368(9)
4	comp.	1.385	1.373	1.432	1.360	1.507	1.851
5	Xray ^b	1.3791(15)	1.4398(16)	1.3823(14)	1.3816(15)	1.421(2)	1.7790(15)
	comp.	1.360	1.491	1.351	1.390	1.389	1.762
6	Xray	1.380(2)	1.380(3)	1.425(2)	1.380(2)	1.507(2)	1.8463(18)
	comp.	1.384	1.378	1.414	1.357	1.506	1.852
7	Xray ^b	1.345(3)	1.415(4)	1.372(3)	1.392(3)	1.393(14)	1.738(6)
	comp. ^c	1.332	1.421	1.364	1.394	1.392	1.755
8	Xray ^b	1.3423(18)	1.408(2)	1.3804(18)	1.3713(18)	1.494(2)	1.8482(15)
	comp. ^d	1.340	1.408	1.378	1.360	1.501	1.855

		Fe–N¹	Fe–N²	Fe–P	Fe–N³ Fe–C³
2	Xray	1.9273(19) 1.921(2)	1.920(2) 1.912(2)	2.2443(7) 2.2507(7)	1.804(2) 1.808(2)
	comp.	1.970	1.958	2.265	1.828
4a	Xray	1.926(3)	1.913(3)	2.1856(10)	1.753(3)
4b	Xray	1.9061(7)	1.9057(7)	2.1833(2)	1.7462(8)
4	comp.	1.941	1.936	2.208	1.763
5	Xray	1.9320(10)	1.9340(10)	2.2308(3)	1.7579(12)
	comp.	1.959	1.967	2.255	1.761
6	Xray	1.9126(14)	1.9087(14)	2.1938(5)	1.7501(16)
	comp.	1.903	1.933	2.195	1.769
7	Xray	1.922(2)	1.969(2)	2.268(7)	1.708(3) 1.746(4)
	comp.	1.939	1.952	2.275	1.754 1.735
8	Xray	1.9273(12)	1.9232(11)	2.2355(4)	1.7581(15) 1.7712(15)
	comp.	1.915	1.939	2.233	1.778 1.755

