Electronic Supporting Information

for

Iron(II) complexes featuring κ^3- and κ^2-bound PNP pincer ligands - The significance of sterics

Mathias Glatz, Bernhard Bichler, Berthold Stöger, Matthias Weil, Kurt Mereiter, Ernst Pittenauer, Günter Allmaier, Luis F. Veiros, and Karl Kirchner

Content:

Synthesis and Characterization of Ligands 1e and 1f

N,N'-Bis(*n*-propylphosphino)-2,6-diaminopyridine (PNP-*n*Pr) (1e). 1e was prepared analogously to **1d** with 2,6-diaminopyridine (1.1 g, 10.0 mmol) and *n*Pr$_2$PCl (3.0 g, 20 mmol) as starting materials. After removal of the solvent under reduced pressure **1e** was obtained as colorless oil. Yield: 3.37 g (98 %). Anal. Calcd. for $C_{17}H_{33}N_3P_2$ (341.41): C, 59.81; H, 9.74; N, 12.31. Found: C, 59.83; H, 9.61; N, 12.60. ^{1}H NMR (δ, $CDCl_3$, 20°C): 7.15 (t, J_{HH} = 7.0 Hz, 1H, py^4), 6.32 (d, J_{HH} = 7.8 Hz, 2H, py^{3,5}), 4.23 (d, J_{HP} = 8,5 Hz, 2H, NH), 1.49-1.46 (m, 16H, CH_2), 0.96 (m, 12H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20°C): 158.7 (d, J_{CP} = 18.3 Hz, py), 139.2 (d, J_{CP} = 10.7 Hz, py), 97.9 (d, J_{CP} = 18.0 Hz, py), 34.3 (d, J_{CP} = 11.1 Hz, *C*H$_2$), 18.1 (d, J_{CP} = 13.6 Hz, CH_2), 15.7 (d, J_{CP} = 11.8 Hz, *C*H$_3$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20°C): 26.2.

N,N'-Bis(*n*-butylphosphino)-2,6-diaminopyridine (PNP-*n*Bu) (1f). 1f was prepared analogously to **1d** with 2,6-diaminopyridine (450 mg, 4.4 mmol) and *n*Bu$_2$PCl (1.6 g, 8.8 mmol) as starting materials. After removal of the solvent under reduced pressure a colorless oil was obtained. Yield: 1.68 g (96 %). Anal. Calcd. for $C_{21}H_{41}N_3P_2$ (397.52): C, 63.45; H, 10.40; N, 10.57. Found: C, 64.23; H, 10.21; N, 10.71. ^{1}H NMR (δ, $CDCl_3$, 20°C): 7.18 (t, J_{HH} = 7.6 Hz, 1H, py^4), 6.29 (d, J_{HH} = 7.7 Hz, 2H, py^{3,5}), 4.14 (d, J_{HP} = 9.0 Hz, 2H, NH), 1.4-1.31 (m, 24H, CH_2), 0.80 (m, 12H, CH_3). ^{13}C{^{1}H} NMR (δ, $CDCl_3$, 20°C): 158.6 (d, J_{CP} = 18.4 Hz, py), 139.3 (d, J_{CP} = 14.3 Hz, py), 97.9 (d, J_{CP} = 18.1 Hz, py), 31.7 (d, J_{CP} = 11.2 Hz, *C*H$_2$), 26.8 (d, J_{CP} = 13.1 Hz, *C*H$_2$), 24.2 (d, J_{CP} = 11.6 Hz, *C*H$_2$), 18.8 (*C*H$_3$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$, 20°C): 27.0.

Synthesis and Characterization of Complexes 2fBPh$^{Me}_4$, 2gBF$_4$, 2hBF$_4$ 5dBF$_4$, 5eBF$_4$, and 5fBF$_4$.

[Fe(κ^3-*P,N,P*-PNP-Et)(κ^2-*P,N*-PNP-Et)Br]BPh$^{Me}_4$ (2fBPh$^{Me}_4$**).** The synthesis of **2f**BPh$^{Me}_4$ was performed analogously to **2e**BPh$^{Me}_4$ with PNP-Et (**1d**) (200 mg, 0.70 mmol) and anhydrous $FeBr_2$ (151 mg, 0.35 mmol) as starting materials. Yield 232 mg (95%) of [Fe(κ^3-*P,N,P*-PNP-Et)(κ^2-*P,N*-PNP-Et)Br]Br. Anal. Calcd. for $C_{26}H_{50}Br_2FeN_6P_4$ (786.26): C, 39.72; H, 6.41; N, 10.69. Found: C, 39.10; H, 6.29; N, 10.05. The green precipitate was suspended in 8 mL of THF and NaBPh$^{Me}_4$ was added (139 mg, 0.35 mmol). Workup was done analogously to the procedure of **2c**. Crystals of **2f**BPh$^{Me}_4$ were grown from a solution of THF by slow diffusion of diethyl ether. Yield: 352 mg (93%). Anal. Calcd. for $C_{54}H_{78}BBrFeN_6P_4 \cdot C_{12}H_{24}O_3$ (1298.04): C, 61.07; H, 7.92; N, 6.47. Found: C, 60.85; H, 7.61; N, 6.51. ^{1}H NMR (δ, acetone-d$_6$, 20°C): 8.25 (s, 2H, NH), 7.98 (s, 1H, NH), 7.50 (t, J_{HP} = 8.0 Hz, 1H, py), 7.23 (m, 8H, Ph), 7.09 (t, J_{HP} = 7.8 Hz, 1H, py), 6.74 (m, 8H, Ph), 6.65 (d, J_{HP} = 8.0 Hz, 2H, py), 6.40 (dd, J_{HP} = 4.0 Hz, 1H, py), 6.09 (d, J_{HP} = 7.0 Hz, 1H, py), 4.81 (d, J_{HP} = 10.0 Hz, 1H, NH), 2.85 - 2.54 (m, 8H, C*H*$_2$), 2.51 - 2.34 (m, 4H, C*H*$_2$), 2.15 (s, 12H, C*H*$_3$), 2.07 - 2.00 (m, 18H, C*H*$_3$), 1.38 - 1.31 (m, C*H*$_2$), 1.10 - 0.85 (m, C*H*$_3$). ^{31}P{^{1}H} NMR (δ, acetone-d$_6$, 20°C): A_2B spin system, δ_A = 114.8 (2P), δ_B = 114.7 (1P), J_{PP} = 50 Hz (shifts and J_{PP} determined from simulation), 36.5 (1P).

[Fe(κ^3-*P,N,P*-PNP-*n*Pr)(κ^2-*P,N*-PNP-*n*Pr)Cl]BF$_4$ (2gBF$_4$**).** To a solution of PNP-*n*Pr (**1e**) (200 mg, 0.59 mmol) in acetone (7 mL) anhydrous $FeCl_2$ (37 mg, 0.29 mmol) and $NaBF_4$ (32 mg, 0.29 mmol) was added and the mixture was stirred for 3 h. The green suspension was then filtrated over Celite and the solution was evaporated to dryness. The remaining solid was washed with diethyl ether (5 mL) and *n*-hexane (10 mL). The remaining green powder is dried in vacuum. Yield: 240 mg (95 %). Anal. Calcd. for $C_{34}H_{66}BClF_4FeN_6P_4$ (860.93): C, 47.43; H, 7.73; N, 9.76. Found: C, 46.99; H, 7.53; N, 9.88. ^{1}H NMR (δ, acetone-d$_6$, 20°C): 8.18 (s, 2H, NH), 7.97 (d, J_{HP} = 6.1 Hz, 1H, NH), 7.49 (t, J_{HH} = 8.0 Hz, 1H, py), 7.06 (t, J_{HH} = 7.5 Hz, 1H, py^4), 6.64 (d, J_{HH} = 8.0 Hz, 2H, py), 6.31 (m, 1H, py), 6.07 (d, J_{HH} = 7.8 Hz, 1H, py), 4.86 (d, J_{HP} = 10.1 Hz, 1H, NH), 2.61-2.18 (m, 4H, CH_2), 1.89-1-53 (m, 4H, CH_2), 1.23-0.84 (m, 15H, CH_2, CH_3), 0.64 (t, J_{HP} = 6.8 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, acetone-d$_6$, 20°C): 165.5 (d, J_{CP} = 18 Hz, py), 164.3-163.8 (m, py), 140.0 (py), 138.1 (py), 99.4 (py), 97.9 (py), 97.4 (py), 37.5 (d, J_{CP} = 24.5 Hz, CH_2), 32.7 (d, J_{CP} = 11.0 Hz, CH_2), 31.2 (m, CH_2), 22.3 (m, CH_2), 18.5 (d, J_{CP} = 16.1 Hz, CH_2), 17.1 (CH_3) 16.7 (d, J_{CP} = 3.7 Hz, CH_3), 15.4-14.7 (m, CH_2, CH_3), 13.4 (CH_3). ^{31}P{^{1}H} NMR (δ, acetone-d$_6$, 20°C): A_2B spin-system, δ_A = 110.1 (2P), δ_B = 107.5 (1P), J_{PP} = 50 Hz (shifts and J_{PP} determined from simulation), 27.5 (1P).

[Fe(κ^3-*P,N,P*-PNP-*n*Bu)(κ^2-*P,N*-PNP-*n*Bu)Cl]BF$_4$ (2hBF$_4$**).** This compound was prepared analogously to **2g**BF_4 using PNP-*n*Bu (**1f**) (200 mg, 0.50 mmol) in acetone (7 mL), anhydrous $FeCl_2$ (32 mg, 0.25 mmol) and $NaBF_4$ (28 mg, 0.25 mmol) as reactants. Yield: 235 mg (96 %). Anal. Calcd. for $C_{42}H_{82}BClF_4FeN_6P_4$ (973.15): C, 51.84; H, 8.49; N, 8.64. Found: C, 52.03; H, 8.23; N, 8.76. ^{1}H NMR (δ, acetone-d$_6$, 20°C): 8.42 (s, 2H, NH^{κ3}), 8.31 (d, J_{HP} = 5.3 Hz, 1H, NH^{κ2}), 7.47 (t, J_{HH} = 7.5 Hz, 1H, py^4), 7.04 (t, J_{HH} = 7.9 Hz, 2H, py^4), 6.63 (d, J_{HH} = 7.7 Hz, 1H, py^{3,5}), 6.29 (m, 1H, py^3), 6.09 (d, J_{HH} = 7.4 Hz, 1H, py^5), 4.85 (d, J_{HP} = 10.2 Hz, 1H, NH), 2.71-2.20 (m, 4H, CH_2), 1.87-1-14 (m, 20H, CH_2), 0.88 (m, 9H, CH_3), 0.65 (m, 3H, CH_3). ^{13}C{^{1}H} NMR (δ, acetone-d$_6$, 20°C): 165.7 (d, J_{CP} = 21 Hz, py), 165.3-164.3 (m, py), 139.8 (py), 138.0 (py), 99.2 (py), 97.8 (py), 97.3 (py), 39.6 (m, CH_2), 35.0 (m, CH_2), 30.2 (d, J_{HP} = 11.0 Hz, CH_2), 27.2 (d, J_{CP} = 15.5 Hz, CH_2), 25.6-25.2 (m, CH_2), 24.2-23.5 (m, CH_2, CH_3), 13.2 (d, J_{CP} = 17.5 Hz, CH_3), 12.9 (d, J_{CP} = 22.9 Hz, CH_3). ^{31}P{^{1}H} NMR (δ, acetone-d$_6$, 20°C): A_2B spin-system, δ_A = 110.3 (2P), δ_B = 107.6 (1P), J_{PP} = 50 Hz (shifts and J_{PP} determined from simulation), 28.0 (1P).

[Fe(κ^3-*P,N,P*-PNP-Et)$_2$](BF$_4$)$_2$ (5dBF$_4$**).** This complex was prepared in analogous fashion to **5c**BF_4 with **1d** (200 mg, 0.70 mmol), anhydrous $FeCl_2$ (44 mg, 0.35 mmol), and $AgBF_4$ (136 mg, 0.70 mmol) as starting materials. Yield: 265 mg (95%). Anal. Calcd. for $C_{26}H_{50}B_2F_8FeN_6P_4$ (800.08): C, 39.03; H,

6.30; N, 10.50. Found: C, 39.18; H, 6.17; N, 10.21. ^{1}H NMR (δ, acetone-d_6, 20°C): 7.86 (s, 4H, NH), 7.34 (m, 18H, py^4, Ph), 6.89 (m, 16H, Ph), 6.77 (m, 8H, Ph), 6.37 (d, J_{HP} = 7.8 Hz, 4H, py^{3,5}), 2.87 (m, 16H, CH_2), 1.03 (m, 24H, CH_3). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20°C): 163.3 (py), 141.7 (py), 100.6 (py), 25.6 (*C*H_2), 7.71 (*C*H_3). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20°C): 119.0. Crystals suitable for X-ray crystallography were grown with BPh_4^- as counterion (analogously prepared with $NaBPh_4$ as halide scavenger) from an acetone solution by slow diffusion of diethyl ether.

[Fe(κ^3-*P,N,P*-PNP-*n*Pr)$_2$](BF$_4$)$_2$ (5eBF$_4$**).** This compound was prepared analogously to **5c**BF_4 using PNP-*n*Pr (200 mg, 0.59 mmol) in acetone (10 mL), anhydrous $FeCl_2$ (37 mg, 0.29 mmol) and $AgBF_4$ (114 mg, 0.59 mmol) as reactants. Yield: 254 mg (95 %). Anal. Calcd. for $C_{34}H_{66}B_2F_8FeN_6P_4$ (912.29): C, 44.76; H, 7.29; N, 9.20. Found: C, 44.56; H, 7.32; N, 9.50. ^{1}H NMR (δ, acetone-d_6, 20°C): 7.74 (s, 4H, NH), 7.34 (t, J_{HH} = 7.8 Hz, 2H, py^4), 6.36 (d, J_{HH} = 7.9 Hz, 4H, py^{3,5}), 2.65 (m, 8H, CH_2), 2.34 (m, 8H, CH_2), 0.98 (t, J_{HH} = 6.4 Hz, 24H, CH_3). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20°C): 162.5 (py), 140.7 (py), 99.5 (py), 27.5 (*C*H_2), 16.6 (*C*H_2), 14.9 (*C*H_3). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20°C): 114.2. Crystals suitable for X-ray crystallography were grown from a THF solution by slow diffusion of *n*-pentane.

[Fe(κ^3-*P,N,P*-PNP-*n*Bu)$_2$](BF$_4$)$_2$ (5fBF$_4$**).** This compound was prepared analogously to **5c**BF_4 using PNP-*n*Pr (200 mg, 0.50 mmol) in acetone (10 mL), anhydrous $FeCl_2$ (32 mg, 0.25 mmol) and $AgBF_4$ (98 mg, 0.50 mmol) as reactants. Yield: 211 mg (92 %). Anal. Calcd. for $C_{42}H_{82}B_2F_8FeN_6P_4$ (1024.50): C, 49.24; H, 8.07; N, 8.20. Found: C, 49.43; H, 8.12; N, 8.08. ^{1}H NMR (δ, acetone-d_6, 20°C): 7.69 (s, 4H, NH), 7.32 (s, 2H, py^4), 6.33 (s, 4H, py^{3,5}), 2.59 (m, 16H, CH_2), 1.33 (m, 32H, CH_2), 0.76 (m, 24H, CH_3). ^{13}C{^{1}H} NMR (δ, acetone-d_6, 20°C): 162.5 (py), 140.5 (py), 99.6 (py), 27.7 (*C*H_2), 25.1.6 (*C*H_2), 23.8 (*C*H_2), 13.0 (*C*H_3). ^{31}P{^{1}H} NMR (δ, acetone-d_6, 20°C): 115.0.

Table S1. Details for the crystal structure determinations of complexes **2e**, **2f, 3**, **5a**, **5b**, **5c**, **5d**, and **5e**. -- *Part 1*

Compound	**2eBPh$^{Me}_4$**.3THF – [Fe(κ^3-*P,N,P*-PNP-Et)(κ^2-*P,N*-PNP-Et)Cl]BPh$^{Me}_4$.3THF	**2fBPh$^{Me}_4$**.3THF -- [Fe(κ^3-*P,N,P*-PNP-Et)(κ^2-*P,N*-PNP-Et)Br]BPh$^{Me}_4$.3THF	**3BF$_4$** -- [Fe(κ^3-*P,N,P*-PNP^{Me}-Ph)(κ^2-*P,N*-PN^{NHMe}-Ph)Cl]BF$_4$	**5aCl**.*solv* – [Fe(κ^3-*P,N,P*-PNP-Ph)$_2$](Cl)$_2$·solv
CCDC number	1005380	1005381	1005382	1005385
formula	$C_{66}H_{102}BClFeN_6\ O_{3.16}P_4$	$C_{66}H_{102}BBrFeN_6O_3P_4$	$C_{50}H_{49}BClF_4FeN_6P_3$	$C_{58}H_{50}Cl_2FeN_6P_4$ [b]
fw	1256.1	1298.0	1005.0	1081.67
cryst.size, mm	0.72 x 0.35 x 0.25	0.50 x 0.32 x 0.06	0.46 x 0.40 x 0.19	0.55 x 0.42 x 0.35
color, shape	green rod	green plate	green prism	red block
crystal system	triclinic	triclinic	monoclinic	tetragonal
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	I-42d (no. 122)
a, Å	12.725(2)	12.778(5)	14.5198(17)	15.1224(2)
b, Å	15.628(3)	15.546(6)	21.308(3)	15.1224(2)
c, Å	18.643(3)	18.790(7)	15.1462(18)	30.8856(6)
α, deg	75.440(6)	75.954(7)	90	90
β, deg	70.622(6)	70.741(7)	99.710(4)	90
γ, deg	86.483(6)	86.697(8)	90	90
V, Å^3	3384.0(11)	3417(2)	4618.9(10)	7063.1(2)
T, K	100	100	100	100
Z	2	2	4	4
ρ_{calc}, g cm^{-3}	1.233	1.2611	1.4448	1.017
μ, mm^{-1} (MoKα)	0.405	0.947	0.549	0.414
F(000)	1346.6	1380	2080	2240
absorption corrections	multi-scan, 0.76–0.91	multi-scan, 0.70–0.95	multi-scan, 0.77–0.90	multi-scan, 0.87–0.77
θ range, deg	1.70–30.17	2.03–28.34	1.67–32.61	2.39–30.00
no. of rflns measd	155879	27496	275623	31615
R_{int}	0.037	0.023	0.047	0.031
no. of rflns unique	19859	16613	16814	5139
no. of rflns $I>2\sigma(I)$	16152	12623	13277	4943
no. of params / restraints	772 / 0	755 / 0	599 / 0	162 / 0
R_1 ($I > 2\sigma(I)$) [a]	0.0459	0.0436 ($I > 3\sigma(I)$)	0.0319 ($I > 3\sigma(I)$)	0.0259
R_1 (all data)	0.0620	0.0599	0.0487	0.0278
wR_2 ($I > 2\sigma(I)$)	0.1112	0.1036 ($I > 3\sigma(I)$)	0.0868 ($I > 3\sigma(I)$)	0.0692
wR_2 (all data)	0.1236	0.1110	0.0976	0.0707
GooF	1.02	1.42	1.63	1.06
Diff.Four.peaks min/max, eÅ^{-3}	-1.19 / 1.56	-0.45 / 0.91	-0.29 / 0.42	-0.22 / 0.34

[a] $R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$, GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{½}$

[b] Disordered solvent (methanol, diethyl ether) squeezed, solvent amount unknown and therefore not given in chemical formula or derived quantities.

Table S1. Details for the crystal structure determinations of complexes **2e**, **2f, 3**, **5a**, **5b**, **5c**, **5d**, and **5e**. -- *Part 2*

Compound	**5bCF$_3$SO$_3$**·6.5THF [Fe(κ^3-*P,N,P*-PNP-bipol)$_2$](CF$_3$SO$_3$)$_2$·-6.5THF	**5cCF$_3$SO$_3$.**2(Me$_2$CO) -- [Fe(κ^3-*P,N,P*-PNP-Me)$_2$]-(CF$_3$SO$_3$)$_2$·(Me$_2$CO)$_2$	**5dBPh$_4$**·0.5Et$_2$O -- [Fe(κ^3-*P,N,P*-PNP-Et)$_2$]-(BPh$_4$)$_2$·0.5Et$_2$O	**5eBF$_4$**.2(Me$_2$CO) -- [Fe(κ^3-*P,N,P*-PNP-*n*Pr)$_2$](BF$_4$)$_2$·(Me$_2$CO)$_2$
CCDC number	1005384	1005387	1005386	1024076
formula	$C_{86}H_{94}F_6FeN_6O_{20.5}P_4S_2$	$C_{26}H_{46}F_6FeN_6O_8P_4S_2$	$C_{76}H_{95}B_2FeN_6O_{0.5}P_4$	$C_{40}H_{78}B_2F_8FeN_6O_2P_4$
fw	1897.52	928.54	1302.0	1028.5
cryst.size, mm	0.40 x 0.25 x 0.06	0.35 x 0.25 x 0.15	0.42 x 0.32 x 0.22	0.68 x 0.60 x 0.10
color, shape	red plate	red block	red block	red plate
crystal system	triclinic	monoclinic	triclinic	orthorhombic
space group	$P\bar{1}$ (no. 2)	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)	*C*cce (no. 68)
a, Å	13.4039(8)	13.6764(17)	13.3977(13)	15.1780(6)
b, Å	16.9467(9)	18.291(2)	14.1994(14)	21.4529(9)
c, Å	20.9385(13)	16.390(2)	21.6176(19)	16.2363(6)
α, deg	78.058(4)	90	93.677(3)	90
β, deg	80.833(4)	98.886(2)	105.861(3)	90
γ, deg	68.818(3)	90	117.314(3)	90
V, Å^3	5283.5(3)	4051.0(9)	3427.3(6)	5286.7(4)
T, K	100	100	100	100
Z	2	4	2	4
ρ_{calc}, g cm^{-3}	1.459	1.522	1.261	1.292
μ, mm^{-1} (MoKα)	0.386	0.712	0.362	0.473
F(000)	1976	1920	1386	2176
absorption corrections	multi-scan, 0.97–0.83	multi-scan, 0.79–0.90	multi-scan, 0.87–0.92	multi-scan, 0.73–0.95
θ range, deg	1.71–23.82	1.87–32.00	1.00–27.54	1.90–34.93
no. of rflns measd	41700	33718	134214	36808
R_{int}	0.049	0.026	0.036	0.038
no. of rflns unique	12816	6952	15798	5804
no. of rflns $I>2\sigma(I)$	10115	6060	12425	4420
no. of params / restraints	1141 / 358	261 / 2	836 / 0	150 / 1
R_1 ($I > 2\sigma(I)$) [a]	0.1130	0.0460	0.0328 ($I > 3\sigma(I)$)	0.0400 ($I > 3\sigma(I)$)
R_1 (all data)	0.1353	0.0525	0.0489	0.0588
wR_2 ($I > 2\sigma(I)$)	0.2895	0.1237	0.0870 ($I > 3\sigma(I)$)	0.1036 ($I > 3\sigma(I)$)
wR_2 (all data)	0.3093	0.1277	0.0939	0.1117
GooF	1.10	1.03	1.53	1.63
Diff.Four.peaks min/max, eÅ^{-3}	-1.38 / 3.22	-0.91 / 1.20	-0.34 / 0.37	-0.29 / 0.64

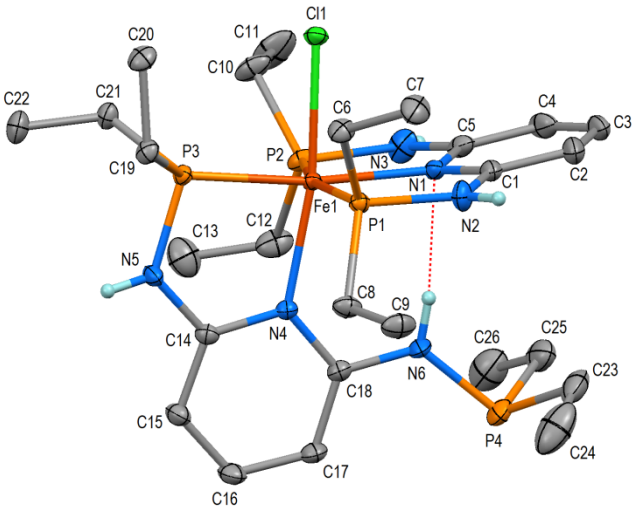

Figure S1. Structural view of complex **2e** in **2eBPh$^{Me}_4$**·3THF - [Fe(κ^3-*P,N,P*-PNP-Et)(κ^2-*P,N*-PNP-Et)Cl]BPh$^{Me}_4$·3THF **-** showing 50% thermal ellipsoids (H-atoms, solvents and BPh$^{Me}_4$$^-$ omitted for clarity). Selected bond lengths (Å) and bond angles (deg): Fe(1)-P(1) 2.2406(6), Fe(1)-P(2) 2.2461(7), Fe(1)-P(3) 2.1858(6), Fe(1)-N(1) 2.059(1), Fe(1)-N(4) 2.117(1), Fe(1)-Cl(1) 2.3504(6), P(1)-N(2) 1.706(2), P(2)-N(3) 1.711(2), P(3)-N(5) 1.687(1), P(4)-N(6) 1.722(2), N(2)-C(1) 1.362(2), N(3)-C(5) 1.355(3), N(5)-C(14) 1.375(2), N(6)-C(18) 1.383(2), P(1)-Fe(1)-P(2) 163.85(2), N(1)-Fe(1)-P(3) 171.59(4), Cl(1)-Fe(1)-N(4) 170.50(4). **2eBPh$^{Me}_4$**·3THF is isostructural with the corresponding Br complex **2fBPh$^{Me}_4$**·3THF. In **2eBPh$^{Me}_4$**·3THF about 15% of the phosphorus P4 is oxidized to the phosphinoxide.