Supporting Information for:

Tetrahedral Iron Featuring an Appended Lewis Acid: Distinct Pathways

for the Reduction of Hydroxylamine and Hydrazine

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Experimental Procedures	S4-S11
Figure S1 ¹ H NMR spectrum of ^{allyi} NN ^{tBu}	S12
Figure S2 ¹³ C NMR spectrum of ^{allyI} NN ^{tBu}	S12
Figure S3 ¹ H NMR spectrum of ^{butyl} NN ^{tBu}	S13
Figure S4 ¹³ C NMR spectrum of ^{butyl} NN ^{tBu}	S13
Figure S5 ¹ H NMR spectrum of (allyINN ^{tBu})FeBr ₂	S14
Figure S6 ¹ H NMR spectrum of (ally NN ^{tBu})FeCl ₂	S14
Figure S7 ¹ H NMR spectrum of (allyINN ^{tBu})ZnBr ₂	S15
Figure S8 ¹³ C NMR spectrum of (^{allyl} NN ^{tBu})ZnBr ₂	S15
Figure S9 ¹ H- ¹ H COSY spectrum of (^{allyl} NN ^{tBu})ZnBr ₂	S16
Figure S10 ¹ H NMR spectrum of (BBNNNtBu)FeBr ₂	S16
Figure S11 ¹ H NMR spectrum of (BBNNN ^{tBu})FeCl ₂	S17
Figure S12 ¹ H NMR spectrum of (BBNNNtBu)ZnBr ₂	S17
Figure S13 ¹³ C NMR spectrum of (BBNNN ^{tBU})ZnBr ₂	S18
Figure S14 ¹¹ B NMR spectrum of (BBNNNtBU)ZnBr ₂	S18
Figure S15 ¹ H- ¹ H COSY spectrum of (BBNNN ^{tBU})ZnBr ₂	S19
Figure S16 ¹ H NMR spectrum of (^{butyl} NN ^{tBu})FeBr ₂	S19
Figure S17 ¹ H NMR spectrum of (BBNNN ^{tBu})FeBr ₂ (N ₂ H ₄)	S20
Figure S18 ¹ H NMR spectrum of [(BBNNNtBu)FeBr ₂] ₂ (N ₂ H ₄)	S20
Figure S19 ¹ H NMR spectrum of (BBNNN ^{tBu})ZnBr ₂ (N ₂ H ₄)	S21
Figure S20 ¹³ C NMR spectrum of (BBNNN ^{tBU})ZnBr ₂ (N ₂ H ₄)	S21
Figure S21 ¹¹ B NMR spectrum of (BBNNN ^{tBU})ZnBr ₂ (N ₂ H ₄)	S22
Figure S22 ¹ H- ¹ H COSY spectrum of (BBNNN ^{tBu})ZnBr ₂ (N ₂ H ₄)	S22
Figure S23 ¹ H NMR spectrum of [(BBNNNtBu)ZnBr ₂] ₂ (N ₂ H ₄)	S23
Figure S24 ¹³ C NMR spectrum of [(^{BBN} NN ^{tBu})ZnBr ₂] ₂ (N ₂ H ₄)	S23
Figure S25 ¹¹ B NMR spectrum of [(BBNNNtBu)ZnBr ₂] ₂ (N ₂ H ₄)	S24
Figure S26 ¹ H- ¹ H COSY spectrum of [(BBNNN ^{tBu})ZnBr ₂] ₂ (N ₂ H ₄)	S24
Figure S27 ¹ H NMR spectrum of (BBNNN ^{tBu})FeBr(NH ₂)	S25
Figure S28 ¹ H NMR spectrum of (BBNNN ^{tBu})Fe(NH ₂)(NPh ₂)	S25
Figure S29 ¹ H NMR spectrum of (BBNNN ^{tBu})Fe(NH ₂)(Cbz)	S26
Figure S30 VT ¹ H NMR spectrum of mixture of (BBNNN ^{tBu})FeBr ₂ and 1,1-diphenylhydrazine	S26
Figure S31 VT ¹ H NMR spectrum of (BBNNN ^{tBu})FeBr ₂	S27
Figure S32 ¹ H NMR spectrum of (BBNNN ^{tBu})FeBr ₂ (NH ₃)	S27
Figure S33 ¹ H NMR spectra of titrating H ₂ O into (BBNNNtBu)FeBr ₂	S28
Figure S34 ¹ H NMR spectra of titrating NH ₃ into (BBNNN ^{tBu})FeBr ₂	S28
Figure S35 ¹ H NMR spectrum of (BBNNNtBu)ZnBr ₂ (NH ₂ OH) in CDCl ₃	S29
Figure S36 ¹ H NMR spectrum of (BBNNN ^{tBu})ZnBr ₂ (NH ₂ OH) in THF	S29
Figure S37 ¹³ C NMR spectrum of (BBNNNtBu)ZnBr ₂ (NH ₂ OH)	S30
Figure S38 ¹¹ B NMR spectrum of (BBNNN ^{tBu})ZnBr ₂ (NH ₂ OH)	S30
Figure S39 ¹ H- ¹ H COSY spectrum of (BBNNN ^{tBu})ZnBr ₂ (NH ₂ OH)	S31
Figure S40 ¹ H NMR spectrum of slow degradation of (BBNNNtBu)ZnBr ₂ (NH ₂ OH)	S31
Electronic absorption spectra Figures S41-S43	S32-S33
Infrared spectra Figures S44-S50	\$33-\$37
MALDI-TOF spectra Figures S51-S59	S38-S42
Figure S60 Electrochemical analysis of (allyiNNtBu)FeBr2	S42
Figure S61 Electrochemical analysis of (allyiNNtBu)FeCl ₂	S43
Figure S62 Electrochemical analysis of (BBNNNtBu)FeBr2	S43
Figure S63 Electrochemical analysis of (BBNNN ^{tBu})FeCl ₂	S44
Figure S64 Electrochemical analysis of (butyINNtBu)FeBr2	S44
Figure S65 Electrochemical analysis of (BBNNN ^{tBu})ZnBr ₂	S45
Figure S66 Electrochemical analysis of (BBNNNtBu)FeBr ₂ (N ₂ H ₄)	S45
Figure S67 Electrochemical analysis of [(BBNNNtBu)FeBr2]2(N2H4)	S46
Figure S68 Electrochemical analysis of (BBNNN(Bu)FeBr(NH2)	S46
Table S1 Electrochemical properties.	S47
Quantification of NH ₄ +	S47-S48
Table S2 Quantification of NH ₄ ⁺	S47

Crystallographic Details	S49-S84
Table S3 Experimental parameters for (allyINN ^{tBu})FeBr2	S49
Figure S69 Molecular structure of (allyINNtBu)FeBr2	S50
Table S4 Experimental parameters for (allyINN ^{tBu})FeCl ₂	S51
Figure S70 Molecular structure of (allyINN ^{tBu})FeCl ₂	S52
Table S5 Experimental parameters for (allyINN ^{tBu})ZnBr2	S53
Figure S71 Molecular structure of (allyINN ^{tBu})ZnBr ₂	S54
Table S6 Experimental parameters for (butylNNtBu)FeBr2	S55
Figure S72 Molecular structure of (butylNNfBu)FeBr2	S56
Table S7 Experimental parameters for (BBNNN/Bu)FeBr2	S57
Figure S73 Molecular structure of (BBBNNtBu)FeBr2	S58
Table S8 Experimental parameters for (BBNNN/Bu)FeCl2	S59
Figure S74 Molecular structure of (BBBNNtBu)FeCl2	S60
Table S9 Experimental parameters for (BBNNN/Bu)ZnBr2	S61
Figure S75 Molecular structure of (BBBNNtBu)ZnBr2	S62
Table S10 Experimental parameters for (BBNNNtBu)FeBr2(N2H4)	S63
Figure S76 Molecular structure of (BBNNNtBu)FeBr ₂ (N ₂ H ₄)	S64
Table S11 Experimental parameters for (BBNNNtBu)ZnBr2(N2H4)	S65
Figure S77 Molecular structure of (BBNNNtBu)ZnBr ₂ (N ₂ H ₄)	S66
Table S12 Experimental parameters for [(BBNNNtBu)FeBr2]2(N2H4)	S67
Figure S78 Molecular structure of [(BBNNNtBu)FeBr2]2(N2H4)	S68
Table S13 Experimental parameters for [(BBNNNtBu)ZnBr2]2(N2H4)	S69
Figure S79 Molecular structure of [(BBNNNtBu)ZnBr2]2(N2H4)	S71
Table S14 Experimental parameters for (BBNNNtBu)FeBr(NH2)	S72
Figure S80 Molecular structure of (BBNNNtBu)FeBr(NH2)	S73
Table S15 Experimental parameters for (BBNNNtBu)Fe(NH2)(Cbz)	S74
Figure S81 Molecular structure of (BBNNNtBu)Fe(NH ₂)(Cbz)	S75
Table S16 Experimental parameters for (BBNNN ^{tBu})Fe(NH ₂)(NPh ₂)	S76
Figure S82 Molecular structure of (BBNNNtBu)Fe(NH ₂)(NPh ₂)	S77
Table S17 Experimental parameters for (BBNNN ^{tBu})FeBr ₂ (NH ₃)	S78
Figure S83 Molecular structure of (BBNNNtBu)FeBr ₂ (NH ₃)	S79
Table S18 Experimental parameters for (BBNNNtBu)ZnBr2(NH2OH)	S80
Figure S84 Molecular structure of (BBNNNtBu)ZnBr ₂ (NH ₂ OH)	S81
Table S19 Experimental parameters for [(^{BBN} NN ^{tBu})ZnBr ₂](μ-NH ₂ O)[(^{BBN-NH2} NN ^{tBu})ZnBr ₂]	S82
Figure S85 Molecular structure of [(^{BBN} NN ^{tBu})ZnBr ₂](μ-NH ₂ O)[(^{BBN-NH2} NN ^{tBu})ZnBr ₂]	S83
Table S20 Experimental bond distances	S84
Table S21 Experimental bond distances	S84
Table S22 Experimental bond distances	S84
References	S85

General Considerations. All air- and moisture-sensitive manipulations were performed using standard Schlenk techniques or in an inert atmosphere drybox with an atmosphere of purified nitrogen. The drybox was equipped with a cold well designed for freezing samples in liquid nitrogen as well as a –35 °C freezer for cooling samples and crystallizations. Solvents were purified using a Glass Contour solvent purification system through percolation through a Cu catalyst, molecular sieves, and alumina. Solvents were then stored over sodium and/or sieves. Benzene- d_6 , THF- d_8 , toluene- d_8 , and chloroform-d were purchased from Cambridge Isotope Laboratories. Benzene- d_6 was dried with molecular sieves and sodium, and degassed by three freeze–pump–thaw cycles. Chloroform-d and toluene- d_8 were distilled from CaH₂. THF- d_8 was dried over molecular sieves.

Metal dihalides, NaH, allylbromide, iodobutane, 9-borabicyclo[3.3.1]nonane, anhydrous hydrazine, hydroxylamine (50% w/w in H₂O), and triethylammonium bromide were purchased from commercial vendors and used as received. $KC_{8,1}^{1}$ HNN^{tBu,2} 1,1-diphenylhydrazine,³ and 1-aminocarbazole^{4,3} were synthesized according to literature procedures.

NMR spectra were recorded on Varian Vnmrs 700 or Varian MR400 spectrometers. ¹H, ¹³C, and ¹¹B chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane and referenced internally to the residual solvent peak. ¹¹B spectra were referenced on a unified scale, where the single primary reference is the frequency of the residual solvent peak in the ¹H NMR spectrum. ¹¹B spectra are referenced vs. BF₃(OEt₂). Multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q). Infrared spectra were recorded using a Nicolet iS10 FT-IR spectrometer. Samples were diluted into dry KBr and recorded as pellets. Electronic absorption spectra were recorded at ambient temperature in sealed 1 cm quartz cuvettes with a Varian Cary-50 spectrophotometer.

of (^{allyl}NN^{tBu})FeBr₂, (^{BBN}NN^{tBu})Fe(NH₂)(Cbz), (^{BBN}NN^{tBu})Fe(NH₂)(NPh₂), Single crystals (^{BBN}NN^{tBu})ZnBr₂(NH₂OH), and [(^{BBN}NN^{tBu})ZnBr₂](NH₂O)[(^{BBN-NH2}NN^{tBu})ZnBr₂] suitable for X-ray diffraction were coated with poly(isobutylene) oil and quickly transferred to the goniometer head of a Bruker AXS D8 Quest diffractometer with kappa geometry, an I-µ-S microsource X-ray tube, laterally graded multilayer (Goebel) mirror for monochromatization, a Photon2 CMOS area detector and an Oxford Cryosystems low temperature device. Examination and data collection were performed with Cu Ka radiation ($\lambda = 1.54184$ Å). Single crystals of (^{allyl}NN^{tBu})FeCl₂, (^{allyl}NN^{tBu})ZnBr₂, (^{BBN}NN^{tBu})FeBr(NH₂), (^{BBN}NN^{tBu})FeBr₂(NH₃), (^{BBN}NN^{tBu})FeBr₂(N₂H₄), (^{BBN}NN^{tBu})FeCl₂, (^{BBN}NN^{tBu})ZnBr₂, (^{BBN}NN^{tBu})ZnBr₂(N₂H₄), (^{butyl}NN^{tBu})FeBr₂, [(^{BBN}NN^{tBu})FeBr₂]₂(N₂H₄), and [(^{BBN}NN^{tBu})ZnBr₂]₂(N₂H₄) suitable for X-ray diffraction were coated with poly(isobutylene) oil and quickly transferred to the goniometer head of a Bruker AXS D8 Quest diffractometer with a fixed chi angle, a sealed tube fine focus X-ray tube, single crystal curved graphite incident beam monochromator and a Photon100 CMOS area detector. Examination and data collection were performed with Mo K α radiation (λ = 0.71073 Å). A single crystal of (^{BBN}NN^{tBU})FeBr₂ suitable for X-ray diffraction was coated with poly(isobutylene) oil and guickly transferred to the goniometer head of a Bruker AXS APEXII Kappa CCD diffractometer with a sealed tube fine focus X-ray tube, single crystal graphite incident beam monochromator and an ApexII CCD area detector. Examination and data collection were performed with Mo K α radiation ($\lambda = 0.71073$ Å). For all instruments, data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX3.⁵ For all samples, the space groups were assigned and the structures were solved by direct methods using XPREP within the SHELXTL suite of programs⁶ and refined by full matrix least squares against F² with all reflections using Shelxl2017 or Shelxl2018⁷ using the graphical interface Shelxle.⁸ If not specified otherwise, H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms,

with carbon hydrogen bond distances of 0.95 Å for and aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH_2 , and CH_3 moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}(H)$ values were set to a multiple of $U_{eq}(C)$ with 1.5 for CH_3 , and 1.2 for CH_2 , and C-H units, respectively. Additional data collection and refinement details, including description of disorder (where present) can be found with the individual structure descriptions, below.

Synthesis of ^{allyl}NN^{tBu} ligand. Inside a glovebox, a 250 mL Schlenk flask was charged with sodium hydride (0.660 g, 27.551 mmol), 50 mL THF, a stir bar, and sealed with a glass stopper. The flask was removed from the glovebox and attached to a Schlenk line and cooled to -78 °C. Against a N₂ flow, the glass stopper was removed, ^HNN^{tBu} (3.950 g, 18.346 mmol) was added, then the flask resealed with a septum containing a gas outlet oil bubbler. The flask was allowed to slowly warm to room temperature over ca. 20 min resulting in gas evolution. Stirring was maintained at room temperature until gas evolution ceased. Via syringe, allylbromide (6.660 g, 55.046 mmol) was added while purging the system with a flow of N_2 . The solution was stirred for 18 hr at room temperature, then volatiles were removed in vacuo. The product was extracted into 50 mL CHCl₃, filtered over Celite, and dried to afford yellow oil. The material was purified by column chromatography on silica (R_f = 0.50; 2:1 hexane:ethyl acetate) to afford viscous yellow oil (3.555 g, 13.921 mmol, 76%) assigned as ^{allyl}NN^{tBu}. The oil solidifies upon storage at -35 °C for approx. 1 week. High-Res MS of $C_{16}H_{21}N_3$ + H: Calc. 256.1814; Found 256.1891. ¹H NMR (CDCl₃, 25 °C) δ = 1.40 (s, 9H, C(CH₃)₃), 2.59 (s, 3H, CH₃), 4.92 (m, 2H, CH₂), 5.01 (d, J = 17.5, 1H, C=CHH), 5.20 (d, J = 10.5, 1H, C=CHH), 6.06 (m, 1H, CH=CH₂), 6.68 (s, 1H, pyrazole-CH), 7.02 (d, J = 7.7, 1H, pyridine-CH), 7.55 (t, J = 7.7, 1H, ppyridine-CH), 7.72 (d, J = 7.7, 1H, pyridine-CH). ¹³C NMR (CDCl₃, 25 °C) $\delta = 24.80$ (CH₃), 30.33 (C(CH₃)₃), 31.52 (C(CH₃)₃), 53.70 (N-CH₂), 102.35 (pyrazole-CH), 116.95, 117.14, 121.76, 134.36 (C=CH₂), 136.67 (ppyridine-CH), 150.41, 152.15, 152.97, 158.03. Selected IR data (ATR, neat) υ = 2968, 1576, 1422, 1366, 1216, 913, 794, 729 cm⁻¹.

Synthesis of ^{butyl}NN^{tBu} ligand. Inside a glovebox, a 100 mL Schlenk flask was charged with sodium hydride (0.334 g, 13.934 mmol) and 50 mL THF. The flask was removed from the glovebox and attached to a Schlenk line and chilled to -78 °C. While stirring and against positive N₂ flow, ^HNN^{rBu} (2.000 g, 9.289 mmol) was added. The flask was resealed with a septum containing a gas outlet. The reaction was slowly warmed to room temperature and stirred until all gas evolution subsided. With stirring, 1-iodobutane (5.128 g, 27.868 mmol) was added via syringe. The light yellow solution was stirred 19 hours and volatiles were removed in vacuo. Orange solid dissolved in 50 mL chloroform and filtered through Celite and concentrated to a deep orange solid. The material was purified by column chromatography on silica (R_f = 0.57; 2:1 hexane:ethyl acetate), and dried to afford off-white powder (0.270 g, 0.995 mmol, 10%) assigned as ^{butyl}NN^{tBu}. High-Res MS of C₁₇H₂₅N₃ + H: Calc. 272.2121; Found 272.2221. ¹H NMR (C₆D₆, 25 °C) δ = 0.79 $(t, J = 7.4, 3H, CH_2CH_2CH_2CH_3), 1.12 (s, 9H, C(CH_3)_3), 1.20 (m, 2H, CH_2CH_2CH_2CH_3), 1.90 (m, 2H, 2H, 2H)$ CH₂CH₂CH₂CH₃), 2.47 (s, 3H, CH₃), 3.94 (t, J = 7.6, 2H, CH₂CH₂CH₂CH₂CH₃), 6.60 (d, J = 7.5, 1H, pyridine-CH), 7.15 (m, 2H, p-pyridine-CH and pyrazole-CH), 8.21 (d, J = 7.5, 1H, pyridine-CH). ¹³C NMR (C_6D_6 , 25 °C) δ = 13.70 (CH₂CH₂CH₂CH₃), 20.07 (CH₂CH₂CH₂CH₃), 24.39 (CH₃), 29.88 (C(CH₃)₃), 30.94 (C(CH₃)₃), 32.90 (CH₂CH₂CH₂CH₃), 50.88 (CH₂CH₂CH₂CH₃), 102.62 (pyrazole-CH), 116.36, 120.96, 136.05 (*p*-pyridine-CH), 150.51, 151.51, 153.03, 157.57. Selected IR data (KBr) υ = 2962, 1593, 1489, 1212, 1013, 799 cm⁻¹.

Synthesis of (^{allyI}NN^{tBu})FeCl₂. A 20 mL scintillation vial was charged with FeCl₂ (0.261 g, 2.056 mmol) and 10 mL DCM. While stirring, ^{allyI}NN^{tBu} (0.500 g, 1.958 mmol) in 7 mL DCM was added. After 19 hr, the cloudy yellow solution filtered through Celite and volatiles removed in vacuo. The resulting yellow solid was washed with 3 x 10 mL *n*-pentane and dried to afford yellow powder (0.692 g, 1.810 mmol, 93%) assigned as (^{allyI}NN^{tBu})FeCl₂. Single, X-ray quality crystals were obtained from slow diffusion of *n*-pentane into a THF solution at room temperature. ¹H NMR (C₆D₆, 25 °C) δ = -24.54 (1670, 3H & 2H, CH₃ & N-CH₂), -21.31 (1090, 1H), -16.72 (172, 1H), -4.46 (606, 1H), 0.38 (382, 1H), 1.22 (141, 9H, C(CH₃)₃), 36.53 (242, 1H, Ar-CH), 45.81 (231, 1H, Ar-CH), 49.89 (238, 1H, Ar-CH). Selected IR data (KBr) υ = 2977, 1611, 1481, 1264, 1035, 816 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max} , molar absorptivity): 302 nm, 30500 M⁻¹cm⁻¹. μ_{eff} = 5.53 +/- 0.07 μ_B (25 °C, THF).

Synthesis of (^{allyl}**NN**^{tBu}**)FeBr₂.** A 20 mL scintillation vial was charged with FeBr₂ (0.190 g, 0.881 mmol), a^{llyl}NN^{tBu} (0.219 g, 0.858 mmol), and 10 mL DCM. The reaction was stirred 16 hr, filtered over Celite, and dried. The resulting orange material was washed with 2 x 10 mL *n*-pentane and dried to afford orange powder (0.379 g, 0.805 mmol, 94%) assigned as (^{allyl}NN^{tBu})FeBr₂. Single, X-ray quality crystals were obtained by diffusing *n*-hexane into a THF solution of (^{allyl}NN^{tBu})FeBr₂ at room temperature. ¹H NMR (C₆D₆, 25 °C) δ = -25.18 (850, 1H x 2), -22.52 (750, 3H & 2H), -16.63 (111, 1H), -2.89 (292, 1H), 1.74 (43, 9H, C(CH₃)₃), 39.07 (154, 1H, Ar-CH), 49.51 (223, 1H, Ar-CH), 52.48 (223, 1H, Ar-CH). Selected IR data (KBr) υ = 2971, 1610, 1574, 1371, 1096, 797 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max} , molar absorptivity): 301 nm, 9200 M⁻¹cm⁻¹. μ_{eff} = 5.56 +/- 0.15 μ_{B} (25 °C, THF).

Synthesis of (^{allyl}**NN**^{tBu}**)ZnBr₂.** A 20 mL scintillation vial was charged with ZnBr₂ (0.290 g, 1.324 mmol) and 7 mL DCM. While stirring, ^{allyl}NN^{tBu} (0.322 g, 1.261 mmol) in 7 mL DCM was added. After 24 hours at room temperature, the cloudy white solution was filtered, and volatiles were removed in vacuo from the colorless solution. The resulting white solid was washed with 3 x 10 mL *n*-pentane and dried to afford white powder (0.610 g, 1.269 mmol, quantitative yield) assigned as (^{allyl}NN^{tBu})ZnBr₂. Single, X-ray quality crystals were obtained from slow diffusion of *n*-pentane into a THF solution at room temperature. ¹H NMR (CDCl₃, 25 °C) δ = 1.43 (s, 9H, C(CH₃)₃), 2.89 (s, 3H, CH₃), 5.08 (d, *J* = 5.7, 2H, N-CH₂), 5.44 (d, *J* = 17.1, 1H), 5.48 (d, *J* = 10.2, 1H), 6.17 (m, 1H, CH₂CHCH₂), 6.63 (s, 1H, pyrazole C-H), 7.34 (d, *J* = 7.8, 1H, pyridine C-H), 7.63 (d, *J* = 7.7, 1H, pyridine C-H), 7.91 (t, *J* = 7.8, 1H, p-pyridine C-H). ¹³C NMR (CDCl₃, 25 °C) δ = 24.27 (CH₃), 29.94 (C(CH₃)₃), 32.05 (C(CH₃)₃, 54.67 (N-CH₂), 101.98 (pyrazole C-H), 118.17, 122.15, 125.88, 130.47, 141.04 (*p*-pyridine C-H), 146.01, 146.11, 157.37, 159.39. Selected IR data (KBr) υ = 2970, 1611, 1437, 1264, 997, 797 cm⁻¹.

Synthesis of (^{butyl}**NN**^{*t*Bu}**)FeBr₂.** A 20 mL scintillation vial was charged with FeBr₂ (0.173 g, 0.801 mmol) and 7 mL DCM. While stirring, ^{butyl}NN^{*t*Bu} (0.207 g, 0.763 mmol) in 6 mL DCM was added. After 16 hours at room temperature, the brown suspension was filtered, and volatiles were removed from the orange solution. The resulting orange solid was washed with 5 mL Et₂O and 3 x 10 mL *n*-pentane and dried to afford yellow-orange powder (0.328 g, 0.683 mmol, 90%) assigned as (^{butyl}NN^{*t*Bu})FeBr₂. Single, X-ray quality crystals were obtained by diffusing *n*-hexane into a THF solution of (^{butyl}NN^{*t*Bu})FeBr₂ at room temperature. ¹H NMR (C₆D₆, 25 °C) δ = -26.80 (1220, 2 x 2H), -22.31 (1310, 3H, CH₃), -17.81 (86, 1H, Ar-CH), -9.11 (197, 2H), -4.30 (118, 3H), 2.24 (49, 9H, C(CH₃)₃), 39.16 (163, 1H, Ar-CH), 48.52 (161, 1H, Ar-CH), 52.65 (132, 1H, Ar-CH). Selected IR data (KBr) υ = 3131, 2972, 2872, 1608, 1471, 1395, 1094, 808 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max} , molar absorptivity): 305 nm, 10400 M⁻¹cm⁻¹. μ_{eff} = 5.60 +/- 0.18 μ_B (25 °C, THF).

Synthesis of (^{BBN}NN^{tBu})FeCl₂. A 20 mL scintillation vial was charged with (^{allyI}NN^{tBu})FeCl₂ (0.500 g, 1.308 mmol) and 15 mL THF. While stirring, 9-borabicyclo[3.3.1]nonane (0.240 g, 1.963 mmol) was added. After 19 hours at room temperature, the cloudy brown solution was filtered through Celite, volatiles were removed in vacuo from the yellow solution, and the resulting material was washed with 3 x 10 mL *n*-pentane and 1 x 10 mL diethyl ether and dried to afford yellow powder (0.641 g, 1.271 mmol, 97%) assigned as (^{BBN}NN^{tBu})FeCl₂. Single, X-ray quality crystals were obtained from slow diffusion of *n*-hexane into a THF solution at room temperature. MALDI-TOF of 2(C₂₄H₃₆N₃B₁Cl₂Fe₁) – Cl: Calc. 971.377; Found 972.446. ¹H NMR (C₆D₆, 25 °C) δ = -26.72 (1690, 3H, CH₃), -24.42 (2320, 2 x 2H), -17.80 (114, 1H), -8.94 (299, 2H), -0.97 (182, 2H), 1.05 (110, 4H, BBN-C*H*), 1.19 (94, 2H), 1.52 (52, 9H, C(CH₃)₃), 1.93 (79, 4H & 2H, BBN-C*H*), 36.41 (172, 1H, Ar-C*H*), 44.94 (172, 1H, Ar-C*H*), 50.46 (197, 1H, Ar-C*H*). Selected IR data (KBr) υ = 2894, 1609, 1480, 1447, 1266, 811 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max}, molar absorptivity): 305 nm, 14300 M⁻¹cm⁻¹. μ_{eff} = 5.43 +/- 0.26 μ_B (25 °C, THF).

Synthesis of (^{BBN}NN^{tBu})FeBr₂. A 20 mL scintillation vial was charged with (^{allyl}NN^{tBu})FeBr₂ (0.207 g, 0.439 mmol), 9-borabicyclo[3.3.1]nonane (0.086 g, 0.705 mmol), and 10 mL THF. The solution was stirred at room temperature for 16 hr, then volatiles were removed in vacuo from the yellow solution. The resulting solid was washed with 3 x 10 mL *n*-pentane to afford light yellow powder (0.227 g, 0.383 mmol, 87%) assigned as (^{BBN}NN^{tBu})FeBr₂. Single, X-ray quality crystals were obtained by diffusing *n*-pentane into a THF solution of (^{BBN}NN^{tBu})FeBr₂ at room temperature. MALDI-TOF of C₂₄H₃₆N₃B₁Br₂Fe₁: Calc. 591.072; Found 591.294. ¹H NMR (C₆D₆, 25 °C) δ = -27.12 (960, 2H), -25.35 (900, 2H), -22.47 (1100, 3H, CH₃), -17.95 (66, 1H, Ar-CH), -8.32 (193, 2H), -1.10 (97, 2H), 0.80 (50, 2H), 1.02 (52, 2H), 1.75 (44, 4H, BBN-CH), 2.22 (34, 9H, C(CH₃)₃), 3.29 (22, 4H, BBN-CH), 39.28 (116, 1H, Ar-CH), 48.65 (129, 1H, Ar-CH), 52.86 (101, 1H, Ar-CH). Selected IR data (KBr) υ = 3130, 1609, 1574, 1479, 1469, 1370, 1095, 807, 797 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max} , molar absorptivity): 306 nm, 6700 M⁻¹cm⁻¹. μ_{eff} = 5.57 +/- 0.11 μ_B (25 °C, THF).

Synthesis of (^{BBN}**NN**^{tBu}**)ZnBr**₂**.** A 20 mL scintillation vial was charged with (^{allyl}**NN**^{tBu}**)ZnBr**₂ (0.300 g, 0.624 mmol) and 15 mL THF. While stirring, 9-borabicyclo[3.3.1]nonane (0.114 g, 0.936 mmol) was added. After 19 hours at room temperature, volatiles were removed in vacuo from the colorless solution, and the resulting material was washed with 3 x 10 mL *n*-pentane and 1 x 10 mL diethyl ether and dried to afford white powder (0.314 g, 0.521 mmol, 83%) assigned as (^{BBN}NN^{tBu})ZnBr₂. Single, X-ray quality crystals were obtained from slow diffusion of *n*-pentane into a THF solution at room temperature. ¹H NMR (CDCl₃, 25 °C) δ = 1.23 (t, *J* = 8.1, 2H, B-CH₂), 1.47 (s, 9H, C(CH₃)₃), 1.52 (t, *J* = 8.1, 2H), 1.79 (m, 12H), 2.43 (m, 2H, CH₂CH₂CH₂), 2.91 (s, 3H, CH₃), 4.42 (t, *J* = 8.2, 2H, N-CH₂), 6.58 (s, 1H, pyrazole C-H), 7.34 (d, *J* = 7.7, 1H, pyridine C-H), 7.61 (d, *J* = 7.7, 1H, pyridine C-H), 7.90 (t, *J* = 7.7, 1H, p-pyridine C-H). ¹³C NMR (CDCl₃, 25 °C) δ = 23.44 (CH₃), 24.68, 26.84 (B-CH₂), 30.21 (C(CH₃)₃), 31.45 (CH₂CH₂CH₂), 32.38 (C(CH₃)₃), 33.45, 55.05 (N-CH₂), 101.84 (pyrazole C-H), 118.24 (pyridine C-H), 125.86 (pyridine C-H), 141.20 (p-pyridine C-H), 145.76, 146.76, 156.90, 159.68. ¹¹B NMR (CDCl₃, 25 °C) δ = 88.05. Selected IR data (KBr) υ = 3129, 2879, 1609, 1480, 1370, 1095, 809 cm⁻¹.

Synthesis of (^{BBN}NN^{tBu})FeBr₂(N₂H₄). A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})FeBr₂ (0.150 g, 0.253 mmol) and 8 mL THF. While stirring, hydrazine (0.0079 mL, 0.253 mmol) was added. After 1 hr, volatiles were removed in vacuo from the yellow solution, and the resulting material was washed with 3 x 5 mL *n*-pentane and dried to afford yellow powder (0.157 g, 0.251 mmol, 99%) assigned as (^{BBN}NN^{tBu})FeBr₂(N₂H₄). Single, X-ray quality crystals were obtained from slow diffusion of diethyl ether into a DCM solution at room temperature. MALDI-TOF of C₂₄H₄₀N₅B₁Br₂Fe₁ – N₂H₄: Calc. 591.072; Found 591.694. ¹H NMR (CDCl₃, 25 °C) δ = -37.59 (2190, 2H), -31.18 (1480, 2H), -28.06 (1270, 3H, CH₃), -16.56 (72, 1H, Ar-CH), -7.51 (179, 2H), -3.40 (137, 2H), 0.25 (328, unresolved BBN-CH), 0.45 (258, unresolved BBN-CH), 2.48 (45, 9H, C(CH₃)₃), 41.70 (138, 1H, Ar-CH), 53.34 (175, 1H, Ar-CH), 56.02 (130, 1H, Ar-CH). Selected IR data (KBr) υ = 3262, 2870, 1611, 1480, 1265, 1101, 799 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max}, molar absorptivity): 309 nm, 11900 M⁻¹cm⁻¹. μ_{eff} = 5.25 +/- 0.24 μ_B (25 °C, THF).

Synthesis of [(^{BBN}NN^{*t***Bu})FeBr₂]₂(N₂H₄).** A 20 mL scintillation vial was charged with (^{BBN}NN^{*t*Bu})FeBr₂ (0.200 g, 0.337 mmol) and 6 mL THF. While stirring, hydrazine (0.159 M stock solution in THF, 0.169 mmol) was added. After 15 minutes, volatiles were removed in vacuo from the pale yellow solution, and the resulting material was washed with 20 mL *n*-pentane and dried to afford yellow powder (0.202 g, 0.166 mmol, 98%) assigned as [(^{BBN}NN^{*t*Bu})FeBr₂]₂(N₂H₄). Single, X-ray quality crystals were obtained from slow diffusion of diethyl ether into a DCM solution at room temperature. MALDI-TOF of (C₂₄H₃₈N₄B₁Br₂Fe₁)/2 – ½N₂H₄: Calc. 591.072; Found 591.679. ¹H NMR (CDCl₃, 25 °C) δ = -30.71 (1450, 2H), -28.22 (1890, 2H), -25.56 (1950, 3H, CH₃), -16.88 (99, 1H, Ar-CH), -6.82 (269, 2H), -0.07 (200, 2H), 1.62 (262, unresolved BBN-CH), 2.07 (140, unresolved BBN-CH), 2.80 (48, 9H, C(CH₃)₃), 40.72 (168, 1H, Ar-CH), 52.07 (202, 1H, Ar-CH), 55.99 (156, 1H, Ar-CH). Selected IR data (KBr) υ = 3279, 3124, 2866, 1610, 1480, 1266, 1096, 800 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max}, molar absorptivity): 309 nm, 20900 M⁻¹cm⁻¹. μ_{eff} = 5.38 +/- 0.16 μ_B (25 °C, THF).

Synthesis of (^{BBN}NN^{tBu})FeBr₂(N₂H₄) from [(^{BBN}NN^{tBu})FeBr₂]₂(N₂H₄). A 20 mL scintillation vial was charged with [(^{BBN}NN^{tBu})FeBr₂]₂(N₂H₄) (0.012 g, 0.010 mmol) and 1.25 mL THF. While stirring, hydrazine (0.159 M stock solution in THF, 0.010 mmol) was added. After 20 minutes, the solution was transferred to an NMR tube and analyzed by ¹H NMR spectroscopy revealing quantitative conversion to (^{BBN}NN^{tBu})FeBr₂(N₂H₄).

Synthesis of (^{BBN}NN^{tBu})ZnBr₂(N₂H₄). A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})ZnBr₂ (0.206 g. 0.342 mmol) and 6 mL THF. While stirring, hydrazine (0.0107 mL, 0.341 mmol) was added and the solution stirred for 10 min. Volatiles were removed in vacuo and the resulting solid washed with 2 x 10 mL npentane and dried to afford white powder (0.191 g, 0.301 mmol, 88%) assigned as (^{BBN}NN^{rBu})ZnBr₂(N₂H₄). Single, X-ray quality crystals were obtained by diffusion *n*-pentane into a dilute dichloromethane solution of $(^{BBN}NN^{tBu})ZnBr_2(N_2H_4)$ at room temperature. MALDI-TOF of $C_{24}H_{40}N_5B_1Br_2Zn_1 - HBr$: Calc. 551.177; Found 550.815. ¹H NMR (CDCl₃, 25 °C) δ = 0.60 (t, J = 8.4, 2H, B-CH₂), 0.64 (s, 2H, B-CH), 1.47 (s, 9H, C(CH₃)₃), 1.52 (m, 2H, BBN-CH), 1.64 (m, 2 x 2H, BBN-CH), 1.69 (m, 2 x 2H, BBN-CH), 1.85 (m, 2H, BBN-CH), 2.03 (m, 2H, CH₂CH₂CH₂), 2.92 (s, 3H, CH₃), 4.39 (t, J = 8.4, 2H, N-CH₂), 4.55 (broad, 4H, N₂H₄), 6.54 (s, 1H, pyrazole-CH), 7.37 (d, J = 7.7, 1H, pyridine-CH), 7.62 (d, J = 7.7, 1H, pyridine-CH), 7.93 (t, J = 8.4, 1H, ppyridine-CH). ¹³C NMR (CDCl₃, 25 °C) δ = 14.58 (B-CH₂), 22.32 (B-CH), 24.57, 24.81 (BBN-CH₂), 27.47, 29.89 (C(CH₃)₃), 31.53 (BBN-CH₂), 32.15, 55.99 (N-CH₂), 101.27 (pyrazole-CH), 118.12 (*m*-pyridine-CH), 125.74 (*m*-pyridine-*C*H), 141.23 (*p*-pyridine-*C*H), 145.23 (pyrazole-*C*), 146.69 (pyrazole-*C*), 156.88 (pyridine-*C*), 159.51 (pyridine-*C*). ¹¹B NMR (CDCl₃, 25 °C) δ = 0.43 (*B*-N₂H₄). Selected IR data (KBr) υ = 3358 (N-H), 3309 (N-H), 3282 (N-H), 3258 (N-H), 3231 (N-H), 3169 (N-H), 3135, 3067, 1613, 1373, 1318, 1245, 1104, 800 cm⁻ 1

Synthesis of [(^{BBN}**NN**^{*tBu*}**)ZnBr**₂**]**₂**(N**₂**H**₄**).** A 20 mL scintillation vial was charged with (^{BBN}**NN**^{*tBu*}**)**2nBr₂ (0.174 g, 0.289 mmol) and 6 mL THF. While stirring, hydrazine (THF stock solution, 0.145 mmol) was added and the solution stirred for 10 min. Volatiles were removed in vacuo and the resulting solid washed with 10 mL *n*-pentane and dried to afford white powder (0.191 g, 0.301 mmol, 88%) assigned as [(^{BBN}**NN**^{*tBu*}**)**2nBr₂]₂(N₂H₄). Single, X-ray quality crystals were obtained by diffusion *n*-pentane into a dilute dichloromethane solution of [(^{BBN}**NN**^{*tBu*}**)**2nBr₂]₂(N₂H₄) at room temperature. MALDI-TOF of $2(C_{24}H_{40}N_5B_1Br_2Zn_1)/2 - HBr$: Calc. 551.177; Found 550.821. ¹H NMR (CDCl₃, 25 °C) δ = 0.97 (s, 4H, B-CH₂), 1.14 (s, 4H, B-CH), 1.42 (m, 4H, BBN-CH), 1.47 (s, 18H, C(CH₃)₃), 1.69 (m, 8H, BBN-CH), 1.75 (m, 8H, BBN-CH), 1.84 (m, 4H, BBN-CH), 2.22 (m, 4H, CH₂CH₂CH₂), 2.91 (s, 6H, CH₃), 4.42 (t, *J* = 8.4, 4H, N-CH₂), 4.88 (broad, 4H, N₂H₄), 6.54 (s, 2H, pyrazole-CH). ¹³C NMR (CDCl₃, 25 °C) δ = 18.63 (B-CH₂), 24.13, 24.52, 25.75, 27.14, 30.01 (C(CH₃)₃), 31.53 (BBN-CH₂), 32.29, 55.63 (N-CH₂), 101.48 (pyrazole-CH), 118.06 (*m*-pyridine-CH), 125.65 (*m*-pyridine-CH), 141.10 (*p*-pyridine-CH), 145.32 (pyrazole-C), 146.64 (pyrazole-C), 156.80 (pyridine-C), 159.49 (pyridine-C). ¹¹B NMR (CDCl₃, 25 °C) δ = -22.90 (*B*-N₂H₄). Selected IR data (KBr) υ = 3280 (N-H), 3212 (N-H), 3121 (N-H), 1611, 1575, 1371, 1244, 898, 800 cm⁻¹.

Synthesis of (^{BBN}NN^{tBu})FeBr(NH₂) from (^{BBN}NN^{tBu})FeBr₂(N₂H₄). A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})FeBr₂ (0.100 g, 0.169 mmol) and 10 mL THF. While stirring, hydrazine (THF stock solution, 0.165 mmol) was added to generate (^{BBN}NN^{tBu})FeBr₂(N₂H₄) in situ. The solution was frozen. Upon thawing, potassium graphite (0.045 g, 0.333 mmol) resulting in a rapid darkening of the solution. After 10 min, the solution was filtered over Celite and dried. The resulting solid was washed with 10 mL *n*-pentane, then dissolved in minimal THF and precipitated with excess *n*-pentane and dried. The solid was then extracted into 10 mL benzene/diethyl ether (1:2), filtered, and dried to afford yellow powder (0.027 g, 0.051 mmol, 30%) assigned as (^{BBN}NN^{tBu})FeBr(NH₂). Single, X-ray quality crystals were obtained by layering a concentrated toluene solution of (^{BBN}NN^{tBu})FeBr(NH₂) with hexamethyldisiloxane at room temperature. ¹H NMR (CDCl₃, 25 °C) δ = -33.56 (434, 1H), -22.85 (633, 3H, CH₃), 0.18 (44, 9H, C(CH₃)₃), 5.52 (62, 1H), 8.37 (72, 1H), 9.49 (159, 1H), 10.48 (82, 1H), 10.77 (104, 1H), 13.80 (188, 1H), 17.42 (189, 1H), 19.08 (178, 1H), 19.84 (294, 1H), 30.89 (342, 1H), 33.06 (90, 1H), 34.69 (155, 1H), 39.24 (542, 1H), 41.43 (900, 1H), 52.52 (484, 1H), 54.18 (100, 1H), 57.20 (125, 1H). Selected IR data (KBr) υ = 3328 (N-H), 3264 (N-H), 1609, 1370, 793 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max}, molar absorptivity): 296 nm, 12000 M⁻¹cm⁻¹. μ_{eff} = 4.96 +/- 0.11 μ_B (25 °C, THF).

Synthesis of (^{BBN}NN^{tBu})FeBr(NH₂) from [(^{BBN}NN^{tBu})FeBr₂]₂(N₂H₄). A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})FeBr₂ (0.100 g, 0.169 mmol) and 10 mL THF. While stirring, hydrazine (THF stock solution, 0.084 mmol) was added to generate [(^{BBN}NN^{tBu})FeBr₂]₂(N₂H₄) in situ. The solution was frozen. Upon thawing, potassium graphite (0.023 g, 0.170 mmol) resulting in a rapid darkening of the solution. After 10 min, the solution was filtered over Celite and dried. The resulting solid was washed with 10 mL *n*-pentane, then dissolved in minimal THF and precipitated with excess *n*-pentane and dried. The solid was then extracted into 10 mL benzene/diethyl ether (1:2), filtered, and dried to afford yellow powder (0.042 g, 0.079 mmol, 47%) assigned as (^{BBN}NN^{tBu})FeBr(NH₂).

Synthesis of (BBNNN^{tBu})Fe(NH₂)(NPh₂). A 20 mL scintillation vial was charged with (BBNNN^{tBu})FeBr₂ (0.130 g, 0.219 mmol) and 8 mL THF. While stirring, 1,1-diphenylhydrazine (0.040 g, 0.217 mmol) was added and the solution frozen. Upon thawing, potassium graphite (0.030 g, 0.222 mmol) was added resulting in a rapid darkening of the solution. After 10 min, the solution was filtered over Celite to afford an orange solution that was dried. The solid was redissolved in 8 mL C₆H₆, filtered, and concentrated to ~2 mL. n-Pentane (18 mL) was added to induce precipitation of a brown sludge. The orange solution was set aside. The brown sludge was redissolved in 2 mL C_6H_6 and addition of 18 mL *n*-pentane resulted in a tan precipitate and orange solution. The tan precipitate was discarded. The orange solution was combined with the other fraction of orange solution and dried. The material was then washed with 10 mL n-pentane to afford orange powder (0.110 g, 0.178 mmol, 81%) assigned as (BBNNN^{tBu})Fe(NH₂)(NPh₂). Single, X-ray quality crystals were obtained by layering a THF solution of (BBNNN^{tBu})Fe(NH₂)(NPh₂) with *n*-pentane at room temperature. MALDI-TOF of $C_{36}H_{48}N_5B_1Fe_1$: Calc. 617.335; Found 617.013. For $C_{36}H_{48}N_5B_1Fe_1 - NH_2$: Calc. 601.316; Found 601.992. ¹H NMR (C₆D₆, 25 °C) δ = -44.28 (89, 2H, *p*-NPh-C*H*), -31.22 (1800, 4H, NPh-CH), -17.97 (79, 1H), -15.32 (560, 1H), -9.07 (1000, 3H, CH₃), -0.35 (190, 1H), -0.15 (33, 1H), 1.67 (51, 9H, C(CH₃)₃), 2.48 (41, 1H), 2.88 (56, 1H), 3.03 (34, 1H), 4.16 (114, 1H), 6.75 (135, 1H), 10.01 (85, 1H), 11.15 (540, 1H), 11.15 (540, 1H), 11.68 (385, 1H), 23.66 (65, 1H), 30.42 (160, 1H), 35.38 (127, 4H, NPh-CH), 41.63 (304, 1H), 44.84 (182, 1H), 45.14 (150, 1H), 49.96 (514, 1H). Selected IR data (KBr) υ = 3320 (N-H), 3256 (N-H), 1582, 1480, 1205, 787, 750 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max} , molar absorptivity): 292 nm, 21800 M⁻¹cm⁻¹. μ_{eff} = 5.09 +/- 0.03 μ_B (25 °C, THF).

Synthesis of (^{BBN}NN^{rBu})Fe(NH₂)(Cbz). A 20 mL scintillation vial was charged with (^{BBN}NN^{rBu})FeBr₂ (0.126 g, 0.212 mmol) and 8 mL THF. While stirring, 1-aminocarbazole (0.039 g, 0.214 mmol) was added and the solution frozen. Upon thawing, potassium graphite (0.028 g, 0.207 mmol) was added resulting in a rapid darkening of the solution. After 10 min, the solution was filtered over Celite and dried. The material was extracted with 15 mL dichloromethane, filtered, and dried. The solid was washed with 2 x 10 mL diethyl ether to afford yellow powder (0.052 g, 0.084 mmol, 40%) assigned as (^{BBN}NN^{rBu})Fe(NH₂)(Cbz). Single, X-ray quality crystals were obtained by layering a THF solution of (^{BBN}NN^{rBu})Fe(NH₂)(Cbz) with hexamethyldisiloxane at room temperature. MALDI-TOF of C₃₆H₄₆N₅B₁Fe₁: Calc. 615.319; Found 614.907. For C₃₆H₄₆N₅B₁Fe₁ – NH₂: Calc. 599.301; Found 599.881. ¹H NMR (THF, 25 °C) δ = -30.68 (1800, 2H, Cbz-CH), -21.37 (560, 1H), -20.14 (65, 1H), -18.22 (43, 2H, Cbz-CH), -1.15 (110, 3H, CH₃), 2.71 (52, 1H), 6.54 (89, 1H), 8.76 (67, 1H), 9.25 (320, 1H), 9.86 (75, 1H), 12.35 (310, 1H), 16.57 (93, 2H, Cbz-CH), 24.72 (56, 1H), 29.19 (121, 1H), 35.76 (261, 1H), 38.36 (65, 2H, Cbz-CH), 48.80 (191, 1H), 48.80 (150, 1H), 55.29 (490, 1H). Selected IR data (KBr) υ = 3315 (N-H), 3253 (N-H), 1608, 1439, 1227, 799, 758, 724 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max}, molar absorptivity): 266 nm, 25000 M⁻¹cm⁻¹; 303 nm, 16200 M⁻¹cm⁻¹; 402 nm, 3600 M⁻¹cm⁻¹. μ_{eff} = 4.79 +/- 0.04 μ₈ (25 °C, THF).

Formation of (^{BBN}**NN**^{tBu}**)FeBr₂(NH₃) from NH₂OH.** A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})FeBr₂ (0.200 g, 0.337 mmol) and 10 mL THF. While stirring, hydroxylamine (50% w/w in H₂O; one equiv., 0.0112 mL, 0.337 mmol) was added. After 10 min, an aliquot was removed for ¹H NMR analysis revealing primarily (^{BBN}NN^{tBu})FeBr₂ as well as the formation of (^{BBN}NN^{tBu})FeBr₂(NH₃). The process of adding two equivalents of hydroxylamine and aliquot analysis was continued until decomposition occurred (see ¹H NMR spectra below).

Synthesis of (^{BBN}NN^{tBu})FeBr₂(NH₃) from protonation of (^{BBN}NN^{tBu})FeBr(NH₂). A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})FeBr(NH₂) (0.057 g, 0.108 mmol) and 6 mL THF. While stirring, triethylammonium bromide (0.020 g, 0.110 mmol) was added and the solution stirred for 3 hr. The solution was filtered, dried, and washed with 15 mL diethyl ether to afford yellow powder (0.032 g, 0.052 mmol, 49%) assigned as (^{BBN}NN^{tBu})FeBr₂(NH₃). Single, X-ray quality crystals were obtained by layering a dichloromethane solution of (^{BBN}NN^{tBu})FeBr₂(NH₃) with *n*-pentane at room temperature. MALDI-TOF of C₂₄H₃₉N₄B₁Br₂Fe₁ – NH₃: Calc. 591.072; Found 591.722. ¹H NMR (CDCl₃, 25 °C) δ = -34.91 (1100, 2H), -31.16 (990, 2H), -28.00 (1000, 3H, CH₃), -16.37 (43, 1H), -7.70 (118, 2H), -3.62 (43, 2H), -3.21 (40, 2H), -1.21 (32, 1H), -0.80 (27, 2H), -0.22 (39, 1H), 0.88 (25, 3H, NH₃), 1.44 (59, 2H x 2), 2.37 (21, 9H, C(CH₃)₃), 3.05 (158, 1H), 41.00 (91, 1H, Ar-CH), 52.95 (93, 1H, Ar-CH), 55.69 (74, 1H, Ar-CH). Selected IR data (KBr) υ = 3338 (N-H), 3306 (N-H), 3246 (N-H), 3204 (N-H), 1610, 1372, 1241, 792 cm⁻¹. UV-Vis (THF, ambient temperature; λ_{max}, molar absorptivity): 310 nm, 9100 M⁻¹cm⁻¹. μ_{eff} = 5.18 +/- 0.15 μ_B (25 °C, THF).

Synthesis of (BBNNN^{tBu})ZnBr₂(NH₂OH). A 20 mL scintillation vial was charged with (BBNNN^{tBu})ZnBr₂ (0.116 g, 0.193 mmol) and 8 mL THF. While stirring, hydroxylamine (50% w/w in H₂O; 0.0127 mL, 0.386 mmol) was added and the solution stirred for 20 min. Volatiles were removed in vacuo. The resulted solid was triturated with *n*-pentane to afford white powder assigned as (^{BBN}NN^{tBu})ZnBr₂(NH₂OH). Note, two equiv. NH₂OH were used to favor Lewis acid/base interaction in THF solution. Therefore, the material likely contains an extra equivalent of NH₂OH. Attempts to further purify the material through washing (diethyl ether) or rapid precipitation (THF/pentane) resulted in gradual reformation of (BBNNN^{tBu})ZnBr₂. Single, Xray quality crystals of the title compound were obtained by diffusing *n*-pentane into a dichloromethane solution at room temperature. In solution, (^{BBN}NN^{tBu})ZnBr₂(NH₂OH) is not indefinitely stable: slower crystal growth, by diffusing *n*-pentane into a dichloroethane solution at room temperature produced single crystals of [(^{BBN}NN^{tBu})ZnBr₂](µ-NH₂O)[(^{BBN-NH2}NN^{tBu})ZnBr₂] through formal H₂O loss. See ¹H NMR spectra and molecular structures below for more information. ¹H NMR (CDCl₃, 25 °C) δ = 0.56 (t, J = 9.1, 2H, B-CH₂), 0.65 (s, 2H, B-CH), 1.47 (s, 9H C(CH₃)₃), 1.50-1.60 (m, 4H, BBN-CH), 1.64 (s, 2H, BBN-CH), 1.67-1.80 (m, 6H, BBN-CH), 2.09 (m, 2H, CH₂CH₂CH₂), 2.92 (s, 3H, CH₃), 4.39 (t, J = 8.4, 2H, N-CH₂), 4.98 (s, 1H, OH), 6.55 (s, 1H, pyrazole-CH), 7.01 (s, 2H, NH₂), 7.36 (d, J = 7.7, 1H, pyridine-CH), 7.62 (d, J = 8.4, 1H, pyridine-CH), 7.92 (t, J = 7.7, 1H, p-pyridine-CH). Observable resonances in THF (25 °C) δ = 0.52 (t, J = 8.4, 2H, B-CH₂), 0.60 (s, 2H, B-CH), 2.82 (s, 3H, CH₃), 4.36 (t, J = 8.4, 2H, N-CH₂), 6.44 (t, J = 3.6, 1H, OH), 6.84 (s, 1H, pyrazole-CH), 7.38 (d, J = 3.2, 2H, NH₂), 7.42 (d, J = 8.0, 1H, pyridine-CH), 7.84 (d, J = 7.6, 1H, pyridine-CH), 7.98 (t, J = 8.0, 1H, *p*-pyridine-CH). ¹³C NMR (CDCl₃, 25 °C) δ = 14.08 (B-CH₂), 21.27, 24.43, 24.52, 25.03, 27.60, 29.93, 30.69, 31.84, 32.14, 55.82 (N-CH₂), 101.34 (pyrazole-CH), 118.11 (*m*-pyridine-CH), 125.73 (*m*-pyridine-CH), 141.21 (p-pyridine-CH), 145.27 (pyrazole-C), 146.65 (pyrazole-C), 156.87 (pyridine-C), 159.48 (pyridine-C). ¹¹B NMR (CDCl₃, 25 °C) δ = -2.94 (B-NH₂OH). Selected IR data (KBr) υ = 3405 (O-H), 3206 (N-H), 3136 (N-H), 1612, 1578, 1373, 1321, 904, 797 cm⁻¹.



^tBu

Figure S1 ¹H NMR spectrum (CDCl₃, 25 °C) of ^{allyl}NN^{tBu}.



Figure S2 13 C NMR spectrum (CDCl₃, 25 $^{\circ}$ C) of allyl NN tBu .



^tBu

Figure S3 1 H NMR spectrum (C₆D₆, 25 $^{\circ}$ C) of $^{butyl}NN^{tBu}$.



Figure S4 13 C NMR spectrum (C₆D₆, 25 $^{\circ}$ C) of butyl NN tBu .



Figure S5 ¹H NMR spectrum (C₆D₆, 25 $^{\circ}$ C) of (^{allyl}NN^{tBu})FeBr₂.



Figure S6 ¹H NMR spectrum (C₆D₆, 25 °C) of (^{allyl}NN^{tBu})FeCl₂.



Figure S8 ^{13}C NMR spectrum (CDCl₃, 25 $^{\circ}C$) of ($^{allyl}NN^{tBu}$)ZnBr₂.



Figure S9 ¹H-¹H COSY spectrum (CDCl₃, 25 °C) of (^{allyI}NN^{tBu})ZnBr₂.



Figure S10 1H NMR spectrum (C₆D₆, 25 $^\circ\text{C}$) of ($^{BBN}\text{NN}^{tBu}\text{)FeBr}_2.$



Figure S11 ¹H NMR spectrum (C₆D₆, 25 °C) of (^{BBN}NN^{tBu})FeCl₂.



Figure S12 ^1H NMR spectrum (CDCl_3, 25 $^\circ\text{C}$) of ($^{BBN}\text{NN}^{tBu}\text{)ZnBr}_2.$



Figure S13 ¹³C NMR spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})ZnBr₂.



Figure S14 ^{11}B NMR spectrum (CDCl₃, 25 $^{\circ}C$) of ($^{BBN}NN^{tBu})ZnBr_{2}.$



Figure S15 ¹H⁻¹H COSY spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})ZnBr₂.



Figure S16 ¹H NMR spectrum (C₆D₆, 25 °C) of (^{butyl}NN^{tBu})FeBr₂.



Figure S17 1 H NMR spectrum (CDCl₃, 25 $^{\circ}$ C) of (^{BBN}NN^{tBu})FeBr₂(N₂H₄).



Figure S18 1 H NMR spectrum (CDCl₃, 25 $^{\circ}$ C) of [($^{BBN}NN^{tBu}$)FeBr₂]₂(N₂H₄).



Figure S19 ¹H NMR spectrum (CDCl₃, 25 °C) of ($^{BBN}NN^{tBu}$)ZnBr₂(N₂H₄).



Figure S20 ^{13}C NMR spectrum (CDCl₃, 25 $^{\circ}C$) of ($^{BBN}NN^{tBu})ZnBr_{2}(N_{2}H_{4}).$



Figure S21 ¹¹B NMR spectrum (CDCl₃, 25 $^{\circ}$ C) of (^{BBN}NN^{tBu})ZnBr₂(N₂H₄).



Figure S22 1 H- 1 H COSY spectrum (CDCl₃, 25 $^{\circ}$ C) of (^{BBN}NN^{tBu})ZnBr₂(N₂H₄).



Figure S23 ¹H NMR spectrum (CDCl₃, 25 °C) of [(^{BBN}NN^{tBu})ZnBr₂]₂(N₂H₄). Residual THF is present at 3.76 and 1.85 ppm.



Figure S24 ¹H NMR spectrum (CDCl₃, 25 °C) of [(^{BBN}NN^{tBu})ZnBr₂]₂(N₂H₄).



Figure S25 ¹¹B NMR spectrum (CDCl₃, 25 $^{\circ}$ C) of [(^{BBN}NN^{tBu})ZnBr₂]₂(N₂H₄).



Figure S26 $^{1}H^{-1}H$ COSY spectrum (CDCl₃, 25 $^{\circ}C$) of [(^{BBN}NN^{tBu})ZnBr₂]₂(N₂H₄).



Figure S27 ¹H NMR spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})FeBr(NH₂).



Figure S28 ¹H NMR spectrum (C₆D₆, 25 $^{\circ}$ C) of (^{BBN}NN^{tBu})Fe(NH₂)(NPh₂).



Figure S29 ¹H NMR spectrum (THF, 25 °C) of (^{BBN}NN^{tBu})Fe(NH₂)(Cbz).



Figure S30 Variable temperature ¹H NMR spectrum (THF) of a stoichiometric mixture of (^{BBN}NN^{tBu})FeBr₂ and 1,1-diphenylhydrazine. The region between 1-4 ppm is omitted for clarity.



Figure S31 Variable temperature ¹H NMR spectrum (THF) of (^{BBN}NN^{tBu})FeBr₂. The region between 1-4 ppm is omitted for clarity.



Figure S32 ¹H NMR spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})FeBr₂(NH₃).



Figure S33 ¹H NMR spectra (THF, 25 °C) of addition of increasing equivalents of H₂O to (^{BBN}NN^{tBu})FeBr₂. The region between 1-4 ppm is omitted for clarity.



Figure S34 ¹H NMR spectra (THF, 25 °C) of addition of increasing equivalents of NH₃ to (^{BBN}NN^{tBu})FeBr₂. The region between 1-4 ppm is omitted for clarity. The resonances appearing in the diamagnetic region correspond to uncoordinated ^{BBN}NN^{tBu} ligand.



Figure S35 ¹H NMR spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})ZnBr₂(NH₂OH). Residual THF is present at 3.76 and 1.85 ppm.





Figure S37 ¹³C NMR spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})ZnBr₂(NH₂OH).



Figure S38 ¹¹B NMR spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})ZnBr₂(NH₂OH).



Figure S39 ¹H-¹H COSY spectrum (CDCl₃, 25 °C) of (^{BBN}NN^{tBu})ZnBr₂(NH₂OH).



Figure S40 ¹H NMR spectrum (CDCl₃, 25 °C) of ($^{BBN}NN^{tBu}$)ZnBr₂(NH₂OH) after slow recrystallization by vapor diffusion (Et₂O/1,2-dichloroethane).



Figure S41 Electronic absorption spectra (THF, ambient temperature) of (^{BBN}NN^{tBu})FeCl₂ (black), (^{allyl}NN^{tBu})FeBr₂ (red), (^{BBN}NN^{tBu})FeBr₂ (blue), and (^{butyl}NN^{tBu})FeBr₂] (pink).



Figure S42 Electronic absorption spectra (THF, ambient temperature) of ($^{BBN}NN^{tBu}$)FeBr₂(NH₃) (black), ($^{BBN}NN^{tBu}$)FeBr₂(N₂H₄) (red), and [($^{BBN}NN^{tBu}$)FeBr₂]₂[N₂H₄] (blue).



Figure S43 Electronic absorption spectra (THF, ambient temperature) of (^{BBN}NN^{tBu})FeBr(NH₂) (black), (^{BBN}NN^{tBu})Fe(NH₂)(NPh₂) (red), and [(^{BBN}NN^{tBu})Fe(NH₂)(Cbz) (blue).



Figure S44 Infrared spectra (KBr, ambient temperature) of (^{allyl}NN^{tBu})FeBr₂ (purple, top), (^{butyl}NN^{tBu})FeBr₂ (red, middle), and (^{BBN}NN^{tBu})FeBr₂ (green, bottom).



Figure S45 Infrared spectra (KBr, ambient temperature) of (^{allyl}NN^{tBu})FeCl₂ (blue, top) and (^{BBN}NN^{tBu})FeCl₂ (red, bottom).



Figure S46 Infrared spectra (KBr, ambient temperature) of (^{allyl}NN^{tBu})ZnBr₂ (blue, top) and (^{BBN}NN^{tBu})ZnBr₂ (red, bottom).



Figure S47 Infrared spectra (KBr, ambient temperature) of $({}^{BBN}NN^{tBu})ZnBr_2(N_2H_4)$ (blue, top), $[({}^{BBN}NN^{tBu})ZnBr_2]_2[N_2H_4]$ (red, middle), and $({}^{BBN}NN^{tBu})ZnBr_2(NH_2OH)$ (green, bottom).



Figure S48 Infrared spectra (KBr, ambient temperature) of $({}^{BBN}NN^{tBu})FeBr_2(N_2H_4)$ (blue, top), $[({}^{BBN}NN^{tBu})FeBr_2]_2[N_2H_4]$ (red, middle), and $({}^{BBN}NN^{tBu})FeBr_2(NH_3)$ (green, bottom).



Figure S49 Infrared spectra (KBr, ambient temperature) of (^{BBN}NN^{tBu})FeBr(NH₂) (blue, top), (^{BBN}NN^{tBu})Fe(NH₂)(NPh₂) (red, middle), and (^{BBN}NN^{tBu})Fe(NH₂)(Cbz) (green, bottom).
Experimental setup for N₂O detection by infrared spectroscopy

The reactions were carried out analogous to the NH_4^+ quantification studies (entries 8-13) detailed below. The iron complex of interest (20 mol%) was dissolved in 5.000 mL THF with a stir bar in a 50 mL Schlenk tube containing a Teflon seal. The flask was frozen and hydroxylamine (0.005 mL, 50 wt% in H_2O , 5 equiv. with respect to Fe) was added and the flask resealed. The reaction flask was stirred at room temperature for 30 min. The reaction headspace was transferred to a previously evacuated gasphase IR cell containing glass stopcocks. The IR cell was sealed and a transmission IR spectrum obtained. The spectra were background corrected by correcting for the headspace of a reaction flask containing only THF solvent. Each reaction spectrum (below) displays diagnostic N_2O absorptions at 2236 and 2212 cm⁻¹.



Figure S50 Gas phase infrared spectra (ambient temperature) of headspace of reactions of (^{BBN}NN^{tBu})FeBr₂ (purple), (^{butyl}NN^{tBu})FeBr₂ (green), and FeBr₂ (red) with five equivalents of NH₂OH. The top spectrum (blue) is an authentic sample of N₂O from a THF solution for comparison.



Figure S51 MALDI-TOF spectrum of (^{BBN}NN^{tBu})Fe(NH₂)(Cbz) (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S52 MALDI-TOF spectrum of $(^{BBN}NN^{tBu})Fe(NH_2)(NPh_2)$ (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S53 MALDI-TOF spectrum of ($^{BBN}NN^{tBu}$)FeBr₂(NH₃) (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S54 MALDI-TOF spectrum of $(^{BBN}NN^{tBu})$ FeBr₂ (N_2H_4) (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S55 MALDI-TOF spectrum of (^{BBN}NN^{tBu})FeBr₂ (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S56 MALDI-TOF spectrum of $[(^{BBN}NN^{tBu})FeBr_2]_2(N_2H_4)$ (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S57 MALDI-TOF spectrum of (^{BBN}NN^{tBu})FeCl₂ (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S58 MALDI-TOF spectrum of $(^{BBN}NN^{tBu})ZnBr_2(N_2H_4)$ (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S59 MALDI-TOF spectrum of $[(^{BBN}NN^{tBu})ZnBr_2]_2(N_2H_4)$ (bottom, black) obtained in an anthracene matrix and the predicted isotopic pattern (top, red).



Figure S60 Electrochemical data for $(^{allyl}NN^{tBu})$ FeBr₂ (2.1 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Middle: full scan. Right: square wave voltammogram.



Figure S61 Electrochemical data for $(^{allyl}NN^{tBu})$ FeCl₂ (1.7 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Middle: full scan. Right: square wave voltammogram.



Figure S62 Electrochemical data for (^{BBN}NN^{tBu})FeBr₂ (1.7 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Top: full scan. Bottom: scan rate dependence of reductive wave, square wave voltammogram, and plot of $v^{1/2}$ vs current.



Figure S63 Electrochemical data for (^{BBN}NN^{tBu})FeCl₂ (1.3 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Top: full scan. Bottom: scan rate dependence of reductive wave, square wave voltammogram, and plot of $v^{1/2}$ vs current.



Figure S64 Electrochemical data for (^{butyl}NN^{tBu})FeBr₂ (1.4 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Top: full scan. Bottom: scan rate dependence of reductive wave, square wave voltammogram, and plot of $v^{1/2}$ vs current.



Figure S65 Electrochemical data for (^{BBN}NN^{tBu})ZnBr₂ (1.1 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Middle: full scan. Right: square wave voltammogram.



Figure S66 Electrochemical data for (^{BBN}NN^{tBu})FeBr₂(N₂H₄) (1.1 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Top: full scan. Bottom: scan rate dependence of reductive wave, square wave voltammogram, and plot of $v^{1/2}$ vs current.



Figure S67 Electrochemical data for $[(^{BBN}NN^{tBu})FeBr_2]_2(N_2H_4)$ (0.5 mM) recorded in THF with 0.2 M $[Bu_4N][PF_6]$. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Top: full scan. Bottom: scan rate dependence of reductive wave, square wave voltammogram, and plot of $v^{1/2}$ vs current.



Figure S68 Electrochemical data for (^{BBN}NN^{tBu})FeBr(NH₂) (1.3 mM) recorded in THF with 0.2 M [Bu₄N][PF₆]. Working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: silver wire. Top: full scan. Bottom: scan rate dependence of reductive wave, square wave voltammogram, and plot of $v^{1/2}$ vs current.

Table S1. Electrochemical properties assessed by square wave voltammetry (vs. Fc/Fc⁺).

	1-Cl	1-Br	(^{butyl} NN ^{tBu})FeBr ₂	2-Cl	2-Br	(^{BBN} NN ^{tBu})ZnBr ₂	4	3	5-Br
E _{reduction} (V)	-2.168	-2.053	-2.069	-2.133	-2.117	-2.384	-2.076	-2.053	-2.156

Table S2. Quantification of NH₄⁺.

				equivalents	of NH ₄ ⁺ detecte	ed
Entry	Reaction		Trial 1	Trial 2	Trial 3	Average
1	(^{BBN} NN ^{tBu})FeBr(NH ₂)	HCI quench →	0.855	0.878	0.880	0.871 +/- 0.011 (87.06 +/- 1.13%)
2	(^{BBN} NN ^{tBu})FeBr ₂ (N ₂ H ₄)	HCI quench	0			
3	[(^{BBN} NN ^{rBu})FeBr ₂] ₂ (N ₂ H ₄) + 2 KC ₈	HCl quench →	1.298	1.397	1.398	1.364 +/- 0.047 (68.21 +/- 2.34%)
4	[(^{BBN} NN ^{tBu})ZnBr ₂] ₂ (N ₂ H ₄) + 2 KC ₈	HCI quench	0	0	0	0 (0%)
5	(^{BBN} NN ^{tBu})FeBr ₂ (N ₂ H ₄) + 2 KC ₈	HCI quench →	1.493	1.430	1.561	1.495 +/- 0.053 (74.73 +/- 2.69%)
6	(^{BBN} NN ^{tBu})ZnBr ₂ (N ₂ H ₄) + 2 KC ₈	HCI quench →	0	0	0	0 (0%)
7	(^{butyl} NN ^{<i>t</i>Bu})FeBr ₂ + 5 N ₂ H ₄	HCI quench →	0			
8	(^{BBN} NN ^{tBu})FeBr ₂ + 1 NH ₂ OH	HCI quench →	0.261	0.275	0.209	0.248 +/- 0.028 (24.79 +/- 2.83%)
9	(^{BBN} NN ^{tBu})FeBr ₂ + 6 NH ₂ OH	HCI quench →	1.118 (0.1	98 equiv. NH ₄ †	່ produced per e	equiv. NH ₂ OH used)
10	(^{BBN} NN ^{tBu})FeBr ₂ + 18 NH ₂ OH	HCI quench ────	3.956 (0.2	20 equiv. NH ₄ †	່ produced per e	equiv. NH ₂ OH used)
11	(^{butyI} NN ^{/Bu})FeBr ₂ + 5 NH ₂ OH	HCl quench →	1.245 (0.24	49 equiv. NH ₄ †	⁺ produced per e	equiv. NH ₂ OH used)
12	FeBr ₂ + 1 NH ₂ OH	HCl quench →	0.417 (0.4	17 equiv. NH ₄ *	⁺ produced per e	equiv. NH ₂ OH used)
13	FeBr ₂ + 5 NH ₂ OH	HCl quench →	1.317 (0.2	63 equiv. NH ₄	⁺ produced per e	equiv. NH ₂ OH used)
14	FeBr ₂ + 20 NH ₂ OH	HCl quench →	4.558 (0.2	28 equiv. NH ₄ *	⁺ produced per e	equiv. NH ₂ OH used)

Details for Entry 1 and 2

All digestion studies are adapted from the procedure of Schrock *et al.*⁹ Both entries were performed analogously, therefore only Entry 1 will be described. The complex (^{BBN}NN^{tBu})FeBr(NH₂) (between 0.010 mmol and 0.014 mmol, sample mass varied for each run) was dissolved in 4 mL THF and stirred in a 20 mL scintillation vial. The sample was removed from the glovebox and HCl (4.0 M in dioxane, 40 equivalents) was added. The solution was stirred 30 min and volatiles were removed in vacuo. The

resulting solid was dissolved in 0.800 mL DMSO- d_6 and a known quantity of NaBAr^F₂₄ (DMSO stock solution) as an internal standard. Samples were then diluted by a factor of 10x and an ¹H NMR spectrum was obtained to quantify NH₄⁺.

Details for Entries 3-6

In a 20 mL scintillation vial, a known quantity of the complex of interest was dissolved in 6 mL of THF and frozen (sample mass varied for each sample between 0.020 mmol and 0.034 mmol). Upon thawing, the appropriate amount of potassium graphite (see equivalencies in table) was added. After stirring to room temperature for 5 min, the solution was filtered. The sample was removed from the glovebox and HCl (4.0 M in dioxane, 40 equivalents per metal center) was added. The solution was stirred 30 min and volatiles were removed in vacuo. The resulting solid was dissolved in 0.800 mL DMSO- d_6 and a known quantity of NaBAr^F₂₄ (DMSO stock solution) as an internal standard. Samples were then diluted by a factor of 10x and an ¹H NMR spectrum was obtained to quantify NH₄⁺.

Details for Entry 7

A 20 mL Schlenk flask was charged with (^{butyl}NN^{tBu})FeBr₂ (2.000 mL, 6.365 mM stock solution in THF, 0.013 mmol) and 2 mL THF and frozen. While frozen, hydrazine (5 equiv., 0.065 mmol, 0.400 mL, 0.159 M THF stock solution) was added on top of the frozen Fe-containing solution. The flask was sealed and allowed to thaw to room temperature and stirred for 30 min. The flask was removed from the glovebox and frozen. HCl (4.0 M in dioxane, 40 equivalents per equiv. N₂H₄, 0.640 mL) was added and the flask resealed. The flask was stirred 20 min at room temperature and volatiles were removed in vacuo. The solid was dissolved in 2.000 mL DMSO- d_6 and a known quantity of NaBAr^F₂₄ (DMSO stock solution) as an internal standard. Samples were then diluted by a factor of 10x and an ¹H NMR spectrum was obtained to quantify NH₄⁺.

Details for Entry 8

A 20 mL scintillation vial was charged with (^{BBN}NN^{tBu})FeBr₂ (0.090 g, 0.152 mmol, all three trials run with same quantity) and 5.000 mL THF. While stirring, hydroxylamine (1 equiv., 30.275 M in H₂O, 0.005 mL) was added. The reaction was stirred 45 min then removed from the glovebox. HCl (4.0 M in dioxane, 50 equivalents, 1.900 mL) was added. The solution was stirred 30 min and volatiles were removed in vacuo. The resulting solid was dissolved in 2.000 mL DMSO- d_6 and a known quantity of NaBAr^F₂₄ (DMSO stock solution) as an internal standard. Samples were then diluted by a factor of 10x and an ¹H NMR spectrum was obtained to quantify NH₄⁺.

Details for Entries 9-14

Single analysis was performed for each of these entries. A 20 mL Schlenk flask was charged with the iron complex of interest (quantity varied based on stoichiometry noted in table) and 5 mL THF and frozen. While frozen, hydroxylamine (30.275 M in H₂O, 0.005 mL in each reaction, 0.151 mmol) was added on top of the frozen Fe-containing solution and the flask resealed. The flask was warmed to room temperature and stirred 45 min then removed from the glovebox. The flask was again frozen and HCl (4.0 M in dioxane, 50 equivalents per NH₂OH equivalent, 1.900 mL) was added. The solution was stirred 30 min and volatiles were removed in vacuo. The resulting solid was dissolved in 2.000 mL DMSO- d_6 and a known quantity of NaBAr^F₂₄ (DMSO stock solution) as an internal standard. Samples were then diluted by a factor of 10x and an ¹H NMR spectrum was obtained to quantify NH₄⁺.

Complex: (allylNN^{tBu})FeBr₂

Local name: jk4179

CCDC: 1941365

Table S3 Experimental parameters for (allyl NN^{tBu})FeBr₂.

Crystal data			
Chemical formula	$C_{16}H_{21}Br_2FeN_3$		
<i>M</i> _r	471.03		
Crystal system, space group	Monoclinic, P21/c		
Temperature (K)	240		
a, b, c (Å)	9.965 (2), 11.407 (3), 16.929 (4)		
β(°)	93.044 (4)		
<i>V</i> (Å ³)	1921.6 (8)		
Ζ	4		
Radiation type	Μο Κα		
μ (mm ⁻¹)	4.94		
Crystal size (mm)	0.44 × 0.32 × 0.28		
Data collection			
Diffractometer	Bruker AXS APEXII Kappa CCD diffractometer		
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.426, 0.746		
No. of measured, independent and observed [I > 2s(I)] reflections	18297, 5525, 3667		
R _{int}	0.035		
(sin θ/λ) _{max} (Å ⁻¹)	0.704		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.080, 1.01		
No. of reflections	5525		
No. of parameters	203		
H-atom treatment	H-atom parameters constrained		
$\Delta \rho_{max}, \Delta \rho_{min}$ (e Å ⁻³)	0.72, -0.64		

Computer programs: Apex3 v2017.3-0 (Bruker, 2016), SAINT V8.38A (Bruker, 2016), SHELXS97

The crystal undergoes a destructive phase change upon cooling to around 200 K (triclinic distortion of the monoclinic cell). Crystals shatter into multiple fragments. Data were collected above the phase change temperature at 240 K.



Figure S69 Molecular structure of (^{allyl}NN^{tBu})FeBr₂ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to allyl fragment are omitted for clarity.

Complex: (^{allyl}NN^{tBu})FeCl₂

Local name: en17

CCDC: 1941363

Table S4 Experimental parameters for (^{allyl}NN^{tBu})FeCl₂.

Crystal data		
Chemical formula	C ₁₆ H ₂₁ Cl ₂ FeN ₃	
Mr	382.11	
Crystal system, space group	Monoclinic, P21/c	
Temperature (K)	150	
a, b, c (Å)	10.6209 (4), 11.3090 (4), 15.1998 (5)	
β(°)	98.3000 (16)	
<i>V</i> (Å ³)	1806.55 (11)	
Ζ	4	
Radiation type	Cu <i>K</i> α	
μ (mm ⁻¹)	9.40	
Crystal size (mm)	0.35 × 0.31 × 0.22	
Data collection		
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer	
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10	
T _{min} , T _{max}	0.383, 0.754	
No. of measured, independent and observed [/ > 2s(/)] reflections	16963, 3805, 3456	
R _{int}	0.053	
(sin θ/λ) _{max} (Å ⁻¹)	0.640	
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.137, 1.18	
No. of reflections	3805	
No. of parameters	204	
H-atom treatment	H-atom parameters constrained	
$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å ⁻³)	0.55, -0.61	

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97



Figure S70 Molecular structure of $(^{allyl}NN^{tBu})$ FeCl₂ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to allyl fragment are omitted for clarity.

Complex: (^{allyl}NN^{tBu})ZnBr₂

Local name: en129

CCDC: 1941364

Table S5 Experimental parameters for $(^{allyl}NN^{tBu})ZnBr_2$.

Crystal data	
Chemical formula	$C_{16}H_{21}Br_2N_3Zn\cdot C_6H_6$
<i>M</i> _r	558.66
Crystal system, space group	Orthorhombic, Pbca
Temperature (K)	150
a, b, c (Å)	16.0116 (4), 14.9760 (3), 20.0132 (5)
<i>V</i> (Å ³)	4798.96 (19)
Ζ	8
Radiation type	Cu Κα
μ (mm ⁻¹)	5.40
Crystal size (mm)	0.23 × 0.22 × 0.18
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T _{min} , T _{max}	0.555, 0.754
No. of measured, independent and observed [/ > 2s(/)] reflections	29510, 5163, 4597
R _{int}	0.048
(sin θ/λ) _{max} (Å ⁻¹)	0.640
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.083, 1.06
No. of reflections	5163
No. of parameters	257
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.44, -0.62

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97



Figure S71 Molecular structure of (^{allyl}NN^{tBu})ZnBr₂ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to allyl fragment are omitted for clarity.

Complex: (^{butyl}NN^{tBu})FeBr₂

Local name: en133

CCDC: 1941377

Table S6 Experimental parameters for (^{butyl}NN^{tBu})FeBr₂.

Crystal data			
Chemical formula	$C_{17}H_{25}Br_2FeN_3$		
Mr	487.07		
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>		
Temperature (K)	150		
a, b, c (Å)	12.9565 (6), 11.5700 (5), 14.3493 (6)		
β(°)	103.9302 (17)		
V (Å ³)	2087.79 (16)		
Ζ	4		
Radiation type	Cu <i>K</i> α		
μ (mm ⁻¹)	10.28		
Crystal size (mm)	0.23 × 0.20 × 0.11		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48 3- 10.		
T _{min} , T _{max}	0.465, 0.754		
No. of measured, independent and observed [<i>l</i> > 2s(<i>l</i>)] reflections	27075, 4473, 4163		
R _{int}	0.047		
(sin θ/λ) _{max} (Å ⁻¹)	0.641		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.089, 1.15		
No. of reflections	4473		
No. of parameters	214		
H-atom treatment	H-atom parameters constrained		
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.55, -0.46		

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97



Figure S72 Molecular structure of (^{butyl}NN^{tBu})FeBr₂ displayed with 50% probability ellipsoids. All hydrogen atoms are omitted for clarity.

Complex: (BBNNN^{tBu})FeBr₂

Local name: jk4180

CCDC: 1941369

Table S7 Experimental parameters for (^{BBN}NN^{tBu})FeBr₂.

Crystal data		
Chemical formula	$C_{24}H_{36}BBr_2FeN_3$	
<i>M</i> _r	593.04	
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	
Temperature (K)	150	
a, b, c (Å)	15.581 (3), 11.673 (2), 16.580 (3)	
β(°)	90.635 (6)	
V (Å ³)	3015.4 (10)	
Ζ	4	
Radiation type	Μο Κα	
μ (mm ⁻¹)	3.16	
Crystal size (mm)	0.60 × 0.47 × 0.05	
Data collection		
Diffractometer	Bruker AXS APEXII Kappa CCD diffractometer	
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10	
T _{min} , T _{max}	0.101, 0.263	
No. of measured, independent and observed [/ > 2s(/)] reflections	24458, 7459, 5160	
R _{int}	0.084	
(sin θ/λ) _{max} (Å ⁻¹)	0.667	
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.059, 0.174, 1.03	
No. of reflections	7459	
No. of parameters	285	
H-atom treatment	H-atom parameters constrained	
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.94, -1.01	

Computer programs: Apex3 v2017.3-0 (Bruker, 2016), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev924 (Hübschle *et al.*, 2011).

The structure contains two solvent accessible voids of 548 Å³ combined. The content of the voids was ill defined. Attempts at refinement as disordered pentane required strong restraints and were altogether unsatisfactory. The structure factors were instead augmented via reverse Fourier transform methods using the SQUEEZE routine (P. van der Sluis & A.L. Spek (1990). Acta Cryst. A46, 194-201) as implemented in the program Platon. The resultant FAB file containing the structure factor contribution from the electron content of the void space was used in together with the original hkl file in the further refinement. (The FAB file with details of the Squeeze results is appended to this cif file). The Squeeze procedure corrected for 130 electrons within the solvent accessible voids.



Figure S73 Molecular structure of (^{BBN}NN^{tBu})FeBr₂ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity.

Complex: (BBNNN^{tBu})FeCl₂

Local name: en111

CCDC: 1941372

Table S8 Experimental parameters for (^{BBN}NN^{tBu})FeCl₂.

Crystal data			
Chemical formula	$2(C_{24}H_{36}BCl_2FeN_3)\cdot C_5H_{12}$		
<i>M</i> _r	1080.38		
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>		
Temperature (K)	150		
a, b, c (Å)	15.5954 (4), 11.5756 (3), 16.2879 (4)		
β(°)	91.1056 (12)		
V (Å ³)	2939.84 (13)		
Ζ	2		
Radiation type	Cu Κα		
μ (mm ⁻¹)	5.91		
Crystal size (mm)	0.23 × 0.20 × 0.12		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.370, 0.754		
No. of measured, independent and observed $[I > 2s(I)]$ reflections	24817, 6096, 5357		
R _{int}	0.040		
(sin θ/λ) _{max} (Å ⁻¹)	0.640		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.095, 1.09		
No. of reflections	6096		
No. of parameters	332		
No. of restraints	31		
H-atom treatment	H-atom parameters constrained		
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.44, -0.34		

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

A pentane molecule is disordered around an inversion center. C-C distances were restrained to target values of 1.55(2) and 1.50(2) Å and 1.3 distances to at least 2.50(2) Å. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar.



Figure S74 Molecular structure of (^{BBN}NN^{tBu})FeCl₂ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity.

Complex: (BBNNN^{tBu})ZnBr₂

Local name: en131

CCDC: 1941373

Table S9 Experimental parameters for ($^{BBN}NN^{\ell Bu})ZnBr_{2}.$

Crystal data			
Chemical formula	C _{26.50} H ₄₂ BBr ₂ N ₃ Zn		
Mr	638.63		
Crystal system, space group	Monoclinic, P21/c		
Temperature (K)	150		
a, b, c (Å)	15.5446 (4), 11.6473 (3), 16.4931 (4)		
β (°)	90.7931 (10)		
V (Å ³)	2985.83 (13)		
Ζ	4		
Radiation type	Cu <i>Κ</i> α		
μ (mm ⁻¹)	4.40		
Crystal size (mm)	0.29 × 0.22 × 0.04		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.494, 0.754		
No. of measured, independent and observed [/ > 2s(/)] reflections	31007, 6372, 5815		
R _{int}	0.043		
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.640		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.101, 1.13		
No. of reflections	6372		
No. of parameters	331		
No. of restraints	61		
H-atom treatment	H-atom parameters constrained		
$\Delta \rho_{max}, \Delta \rho_{min}$ (e Å ⁻³)	0.93, -0.56		

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

A pentane molecule is disordered around an inversion center. C-C bond distances were restrained to target values (1.55(2) and 1.47(2) Å) and bond angles to minimum values (1.3 distances to at least 2.50(2) Å). U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar.



Figure S75 Molecular structure of (^{BBN}NN^{tBu})ZnBr₂ displayed with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity.

Complex: (BBNNN^{tBu})FeBr₂(N₂H₄)

Local name: en151

CCDC: 1941378

Table S10 Experimental parameters for $(^{BBN}NN^{tBu})FeBr_2(N_2H_4)$.

Crystal data	
Chemical formula	$C_{24}H_{40}BBr_2FeN_5$
Mr	625.09
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	150
a, b, c (Å)	33.5193 (8), 12.4500 (3), 13.6964 (3)
β(°)	95.8345 (9)
V (Å ³)	5686.1 (2)
Ζ	8
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	7.70
Crystal size (mm)	0.44 × 0.05 × 0.04
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T _{min} , T _{max}	0.537, 0.754
No. of measured, independent and observed [/ > 2s(/)] reflections	37322, 6111, 5668
R _{int}	0.053
$(\sin \theta / \lambda)_{max} (Å^{-1})$	0.640
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.026, 0.069, 1.03
No. of reflections	6111
No. of parameters	308
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.56, -0.35

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

Terminal hydrazine H atom positions were refined, and N-H distances were restrained to 0.91(2) Å.



Figure S76 Molecular structure of (^{BBN}NN^{tBu})FeBr₂(N₂H₄) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. Complex: (^{BBN}NN^{tBu})ZnBr₂(N₂H₄)

Local name: jk4287

CCDC: 1941374

Table S11 Experimental parameters for $(^{BBN}NN^{tBu})ZnBr_2(N_2H_4)$.

Crystal data	
Chemical formula	$C_{24}H_{40}BBr_2N_5Zn$
Mr	634.61
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	150
a, b, c (Å)	33.5220 (13), 12.4233 (5), 13.6832 (7)
β (°)	95.838 (2)
V (Å ³)	5668.9 (4)
Ζ	8
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	4.65
Crystal size (mm)	0.44 × 0.04 × 0.02
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48 3-10.
T _{min} , T _{max}	0.489, 0.754
No. of measured, independent and observed [/ > 2s(/)] reflections	34319, 5264, 4801
R _{int}	0.051
$(\sin \theta / \lambda)_{max} (Å^{-1})$	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.035, 0.110, 1.13
No. of reflections	5264
No. of parameters	309
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.63, -0.80

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell Now, with the two components being related by a 180° rotation around the reciprocal a-axis. The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

12910 data (4106 unique) involve domain 1 only, mean I/sigma 29.8

12775 data (4089 unique) involve domain 2 only, mean I/sigma 11.3

8796 data (2903 unique) involve 2 domains, mean I/sigma 35.6

The exact twin matrix identified by the integration program was found to be:

0.99992 -0.00327 0.50349

-0.00043 -1.00000 -0.00079

0.00033 0.00083 -0.99992

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.177(1).

The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).



Figure S77 Molecular structure of (^{BBN}NN^{tBu})ZnBr₂(N₂H₄) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. Complex: [(^{BBN}NN^{tBu})FeBr₂]₂(N₂H₄)

Local name: en151

CCDC: 1941378

Table S12 Experimental parameters for $[(BBNNN^{tBu})FeBr_2]_2(N_2H_4)$.

Crystal data			
Chemical formula	C ₄₈ H ₇₆ B ₂ Br ₄ Fe ₂ N ₈ ·0.409(CH ₂ Cl ₂)		
Mr	1252.83		
Crystal system, space group	Triclinic, P1		
Temperature (K)	150		
a, b, c (Å)	14.0086 (4), 14.8635 (4), 15.9297 (4)		
α, β, γ (°)	70.8799 (10), 69.8088 (10), 65.8643 (9)		
V (Å ³)	2772.76 (13)		
Ζ	2		
Radiation type	Cu <i>K</i> α		
μ (mm ⁻¹)	8.24		
Crystal size (mm)	0.36 × 0.10 × 0.04		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.409, 0.754		
No. of measured, independent and observed [/ > 2s(/)] reflections	29079, 11053, 9165		
R _{int}	0.039		
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.640		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.045, 0.127, 1.12		
No. of reflections	11053		
No. of parameters	614		
No. of restraints	14		
H-atom treatment	H-atom parameters constrained		
Δρ _{max} , Δρ _{min} (e Å ^{.3})	0.86, -1.07		

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

A methylene chloride molecule is partially occupied and disordered around an inversion center. The two C-Cl distances were restrained to a target value of 1.74(2) Å, and U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions, the occupancy rates refined to two times 0.409(3).



Figure S78 Molecular structure of $[(^{BBN}NN^{tBu})FeBr_2]_2(N_2H_4)$ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moieties are displayed in wireframe for clarity.

Complex: [(^{BBN}NN^{tBu})ZnBr₂]₂(N₂H₄)

Local name: jk4288

CCDC: 1941379

Table S13 Experimental parameters for $[(^{BBN}NN^{tBu})ZnBr_2]_2(N_2H_4)$.

Crystal data	
Chemical formula	$C_{48}H_{76}B_2Br_4N_8Zn_2 \cdot 0.374(CH_2Cl_2)$
Mr	1268.96
Crystal system, space group	Triclinic, P1
Temperature (K)	150
a, b, c (Å)	14.0158 (5), 14.8791 (6), 15.8974 (6)
α, β, γ (°)	70.5598 (17), 69.5099 (18), 65.6987 (17)
V (Å ³)	2760.31 (19)
Z	2
Radiation type	Cu <i>Κ</i> α
μ (mm ⁻¹)	5.10
Crystal size (mm)	0.44 × 0.03 × 0.02
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan TWINABS 2012/1: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48 3-10.
T _{min} , T _{max}	0.508, 0.754
No. of measured, independent and observed [/ > 2s(/)] reflections	54688, 21498, 16450
R _{int}	0.093
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.626
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.059, 0.191, 1.06
No. of reflections	21498
No. of parameters	642
No. of restraints	66
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å ⁻³)	1.40, -1.40

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell Now, with the two components being related by a 180° rotation around the real axis (-1 0 1). The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

25979 data (9946 unique) involve domain 1 only, mean I/sigma 11.5

25959 data (9943 unique) involve domain 2 only, mean I/sigma 11.8

2816 data (1612 unique) involve 2 domains, mean I/sigma 15.7

The exact twin matrix identified by the integration program was found to be:

-0.27464 -0.00916 -0.76365

-0.00020 -0.99981 -0.00030

-1.21103 0.01618 0.27446

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.492(1).

The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

A partially occupied methylene chloride molecule is disordered around an inversion center over four positions (each two related to each other by inversion symmetry). All C-Cl distances were restrained to be similar to each other. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates refined to two times 0.179(12) and two times 0.195(12), for a total occupancy of the site of 74.8%. No other solvate molecules are resolved for the site.



Figure S79 Molecular structure of $[(^{BBN}NN^{tBu})ZnBr_2]_2(N_2H_4)$ displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moieties are displayed in wireframe for clarity. Complex: (BBNNN^{tBu})FeBr(NH₂)

Local name: jk4210

CCDC: 1941368

Table S14 Experimental parameters for (^{BBN}NN^{tBu})FeBr(NH₂).

Crystal data	
Chemical formula	C ₂₄ H ₃₈ BBrFeN ₄
<i>M</i> _r	529.15
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	150
a, b, c (Å)	21.6707 (4), 13.3677 (2), 18.9165 (3)
β(°)	107.2654 (8)
V (Å ³)	5232.95 (15)
Ζ	8
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	6.53
Crystal size (mm)	0.33 × 0.20 × 0.11
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T _{min} , T _{max}	0.541, 0.754
No. of measured, independent and observed [<i>I</i> > 2s(<i>I</i>)] reflections	18479, 5234, 4751
R _{int}	0.033
(sin θ/λ) _{max} (Å-1)	0.640
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.029, 0.073, 1.06
No. of reflections	5234
No. of parameters	285
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å ⁻³)	0.60, -0.55

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97


Figure S80 Molecular structure of (^{BBN}NN^{tBu})FeBr(NH₂) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. Complex: (^{BBN}NN^{tBu})Fe(NH₂)(CBz)

Local name: jk526

CCDC: 1941366

 Table S15 Experimental parameters for (^{BBN}NN^{tBu})Fe(NH₂)(CBz).

Crystal data	
Chemical formula	C ₄₀ H ₅₄ BFeN ₅ O
Mr	687.54
Crystal system, space group	Monoclinic, P21/c
Temperature (K)	150
a, b, c (Å)	11.0311 (5), 14.6748 (6), 22.6949 (10)
β(°)	98.0876 (19)
V (Å ³)	3637.3 (3)
Ζ	4
Radiation type	Μο Κα
μ (mm ⁻¹)	0.45
Crystal size (mm)	0.45 × 0.09 × 0.07
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan <i>SADABS</i> 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T _{min} , T _{max}	0.687, 0.746
No. of measured, independent and observed [/ > 2s(/)] reflections	44978, 10246, 7654
R _{int}	0.050
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.715
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.041, 0.113, 1.03
No. of reflections	10246
No. of parameters	437
H-atom treatment	H-atom parameters constrained
$\Delta \rho_{max}, \Delta \rho_{min}$ (e Å ⁻³)	0.49, -0.40

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), SAINT V8.38A (Bruker, 2016), SHELXS97

(Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).



Figure S81 Molecular structure (^{BBN}NN^{tBu})Fe(NH₂)(CBz) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. Complex: (^{BBN}NN^{tBu})Fe(NH₂)(NPh₂)

Local name: jk519

CCDC: 1941367

Table S16 Experimental parameters for $(^{BBN}NN^{tBu})Fe(NH_2)(NPh_2)$.

Crystal data	
Chemical formula	$C_{36}H_{48}BFeN_5$
Mr	617.45
Crystal system, space group	Orthorhombic, Pna21
Temperature (K)	150
a, b, c (Å)	13.7625 (7), 16.9042 (8), 13.8498 (7)
V (Å ³)	3222.1 (3)
Z	4
Radiation type	Μο Κα
μ (mm ⁻¹)	0.50
Crystal size (mm)	0.46 × 0.43 × 0.39
Data collection	
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10
T _{min} , T _{max}	0.717, 0.747
No. of measured, independent and observed [/ > 2s(/)] reflections	211438, 12380, 11177
R _{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.772
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.031, 0.081, 1.06
No. of reflections	12380
No. of parameters	392
No. of restraints	1
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.60, -0.30
Absolute structure	Flack x determined using 5032 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.008 (2)

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), *SAINT* V8.38A (Bruker, 2016), *SHELXS97* (Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev937 (Hübschle *et al.*, 2011).



Figure S82 Molecular structure (^{BBN}NN^{tBu})Fe(NH₂)(NPh₂) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. Complex: (^{BBN}NN^{tBu})FeBr₂(NH₃)

Local name: jk4206

CCDC: 1941370

Table S17 Experimental parameters for $(^{BBN}NN^{tBu})FeBr_2(NH_3)$.

Crystal data			
Chemical formula	C ₂₄ H ₃₉ BBr ₂ FeN ₄		
Mr	610.07		
Crystal system, space group	Monoclinic, P21/n		
Temperature (K)	150		
a, b, c (Å)	10.7634 (4), 12.2556 (5), 21.1268 (8)		
β(°)	103.7575 (12)		
V (Å ³)	2706.92 (18)		
Z	4		
Radiation type	Cu <i>K</i> α		
μ (mm ⁻¹)	8.06		
Crystal size (mm)	0.22 × 0.22 × 0.20		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.560, 0.754		
No. of measured, independent and observed [/ > 2s(/)] reflections	18937, 5568, 5257		
R _{int}	0.034		
$(\sin \theta / \lambda)_{max} (Å^{-1})$	0.640		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.033, 0.096, 1.14		
No. of reflections	5568		
No. of parameters	298		
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		
$\Delta \rho_{max}, \Delta \rho_{min}$ (e Å ⁻³)	0.61, -0.69		

Computer programs: Apex3 v2017.3-0 (Bruker, 2017), SAINT V8.38A (Bruker, 2016), SHELXS97

(Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev937 (Hübschle *et al.*, 2011).

Refinement details: The high-quality SC-XRD data for **6** (R1 = 3.3%) allow unambiguous assignment of NH₃ vs OH₂. With NH₃, the difference density around the N atoms is featureless, indicating a good match between model and experimental electron density. Switching N for O leads to an increase of R value from 3.3% to 3.51%, and a substantial negative difference electron density located at the "O" atom (four out of the largest five difference density peaks, all negative are located within the van der Waals sphere of "O"). Omission of H atoms in a similar way leads to an increase of R value (to 3.49%), and the three largest positive difference density peaks are located in the positions expected for a tetrahedral NH₃ fragment. Their values are nearly equal and in the typical range for a single electron at hydrogen shared covalently with another atom: 0.71, 0.68 and 0.67.



Figure S83 Molecular structure of (^{BBN}NN^{tBu})FeBr₂(NH₃) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. Complex: (^{BBN}NN^{tBu})ZnBr₂(NH₂OH)

Local name: jk5101_2

CCDC: 1941375

 Table S18 Experimental parameters for (BBN NN^{tBu})ZnBr₂(NH₂OH).

Crystal data			
Chemical formula	$C_{24}H_{39}BBr_2N_4OZn$		
Mr	635.59		
Crystal system, space group	Monoclinic, <i>C</i> 2/ <i>c</i>		
Temperature (K)	150		
a, b, c (Å)	33.438 (3), 12.3550 (8), 13.6531 (10)		
β (°)	95.908 (3)		
V (Å ³)	5610.5 (7)		
Ζ	8		
Radiation type	Μο Κα		
μ (mm ⁻¹)	3.75		
Crystal size (mm)	0.22 × 0.15 × 0.04		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.482, 0.746		
No. of measured, independent and observed [<i>I</i> > 2s(<i>I</i>)] reflections	40403, 6257, 4832		
R _{int}	0.065		
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.669		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.043, 0.112, 1.04		
No. of reflections	6257		
No. of parameters	305		
H-atom treatment	H-atom parameters constrained		
	$w = 1/[s^2(F_o^2) + (0.057P)^2 + 12.3301P]$ where $P = (F_o^2 + 2F_c^2)/3$		
$\Delta \rho_{max}, \Delta \rho_{min}$ (e Å ⁻³)	0.72, -0.90		

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), SAINT V8.38A (Bruker, 2016), SHELXS97

(Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).

Refinement details:

The assignment of N vs O and O vs N is unambiguously supported by the SC-XRD data. With NH₂OH, difference density around the N atoms is featureless, indicating a good match between model and experimental electron density. Substituting N4 for an oxygen leads to a slight increase of R value from 4.32% to 4.47%, and a substantial negative difference electron density located at the "O" atom (with three negative difference density peaks between -0.7 and -0.6 located within the van der Waals sphere of "O"). Substituting O1 for a nitrogen leads to a slight increase of R value from 4.32% to 4.39%, and a substantial, now positive, difference electron density located at the "N" atom (the largest Q peak not nearby the metal or halogen is now located within the van der Waals sphere of "N"). The two N-bound H atoms are resolved in difference maps, with peaks 0.64 and 0.60 high. The position of the O bound H atom is slightly more ambiguous. Due to its rotating nature it is not resolved in difference density maps. Due to charge density considerations, and the unambiguous nature of this atom as oxygen (see above), assignment of one H atom to O1 is required. No negative electron density is located at or around O1 when refined as an OH group with rotating H (HFIX 147). Refinement is stable and the H atom is pointing towards the two Br atoms, as expected from H-bonding considerations, confirming the assignment as OH as correct.



Figure S84 Molecular structure of (^{BBN}NN^{tBu})ZnBr₂(NH₂OH) displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moiety is displayed in wireframe for clarity. $Complex: [({}^{BBN}NN^{tBu})ZnBr_2](\mu-NH_2O)[({}^{BBN-NH2}NN^{tBu})ZnBr_2]$

Local name: jk5101

CCDC: 1941376

 $\label{eq:constraint} \textbf{Table S19} \ \text{Experimental parameters for } [({}^{\text{BBN}}\text{NN}{}^{\text{tBu}}\text{)}\text{ZnBr}_2](\mu\text{-}\text{NH}_2\text{O})[({}^{\text{BBN-}\text{NH}2}\text{NN}{}^{\text{tBu}}\text{)}\text{ZnBr}_2].$

Crystal data			
Chemical formula	$C_{48}H_{76}B_2Br_4N_8OZn_2\cdot 3(C_2H_4Cl_2)$		
Mr	1550.13		
Crystal system, space group	Monoclinic, P2 ₁ /n		
Temperature (K)	150		
a, b, c (Å)	12.6626 (10), 25.463 (3), 21.457 (3)		
β (°)	102.524 (4)		
V (Å ³)	6753.6 (13)		
Z	4		
Radiation type	Μο Κα		
μ (mm ⁻¹)	3.36		
Crystal size (mm)	0.42 × 0.05 × 0.03		
Data collection			
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer		
Absorption correction	Multi-scan SADABS 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10		
T _{min} , T _{max}	0.586, 0.746		
No. of measured, independent and observed [/ > 2s(/)] reflections	71747, 15991, 9963		
R _{int}	0.098		
(sin θ/λ) _{max} (Å ⁻¹)	0.669		
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.065, 0.186, 1.03		
No. of reflections	15991		
No. of parameters	851		
No. of restraints	526		
H-atom treatment	H-atom parameters constrained		
	$w = 1/[s^2(F_o^2) + (0.0851P)^2 + 15.1843P]$ where $P = (F_o^2 + 2F_c^2)/3$		
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.14, -1.00		

Computer programs: Apex3 v2018.1-0 (Bruker, 2018), SAINT V8.38A (Bruker, 2016), SHELXS97

(Sheldrick, 2008), *SHELXL2018*/3 (Sheldrick, 2015, 2018), SHELXLE Rev946 (Hübschle *et al.*, 2011).

Refinement details:

Three 1,2-dichloroethane molecules were refined as disordered. Two over two positions, one over three positions. All disordered moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy rates refined to 0.751(6) and 0.249(6) for the molecule involving Cl1 and Cl2; to 0.485(3), 0.339(3) and 0.177(3) for the molecule involving Cl3 and Cl4; and to 0.552(13) and 0.448(13) for the molecule involving Cl5 and Cl6.



Figure S85 Molecular structure of [(^{BBN}NN^{tBu})ZnBr₂](µ-NH₂O)[(^{BBN-NH2}NN^{tBu})ZnBr₂] displayed with 50% probability ellipsoids. Hydrogen atoms not attached to heteroatoms are omitted for clarity. The 9-BBN moieties are displayed in wireframe for clarity.

Bond	(^{allyi} NN ^{tBu})FeCl ₂ (1-Cl)	(^{allyi} NN ^{tBu})FeBr ₂ (1-Br)	(^{butyl} NN ^{tBu})FeBr ₂	(BBNNNtBu)FeCl2 (2-Cl)	(BBNNNtBu)FeBr2 (2-Br)
Fe-N _{pyridine}	2.142(2)	2.142(2)	2.120(2)	2.1230(14)	2.125(3)
Fe-N _{pyrazole}	2.083(2)	2.072(2)	2.074(2)	2.0759(15)	2.068(3)
Fe-X1	2.2397(7)	2.3698(7)	2.3743(5)	2.2320(5)	2.3913(8)
Fe-X ₂	2.2404(7)	2.3820(6)	2.3700(5)	2.2404(5)	2.3730(7)
τ4	0.853	0.881	0.868	0.851	0.847
ΣB_{α}	n/a	n/a	n/a	359.63(18)	359.70(4)

 Table S21 Experimental bond distances for ZnBr₂ complexes.

Bond	(^{allyi} NN ^{tBu})ZnBr ₂	(^{BBN} NN ^{tBu})ZnBr ₂	(^{BBN} NN ^{tBu})ZnBr ₂ (N ₂ H ₄)	[(^{BBN} NN ^{tBu})ZnBr ₂] ₂ (N ₂ H ₄)	(^{BBN} NN ^{tBu})ZnBr ₂ (NH ₂ OH) (7)
Zn-N _{pyridine}	2.0808(19)	2.0758(19)	2.074(3)	2.083(4)/2.075(4)	2.065(3)
Zn-N _{pyrazole}	2.0481(19)	2.055(2)	2.042(3)	2.069(4)/2.061(4)	2.028(3)
Zn-X1	2.3427(4)	2.3500(4)	2.3769(6)	2.3253(9)/2.3101(9)	2.3775(5)
Zn-X ₂	2.3466(4)	2.3323(4)	2.3420(5)	2.3604(8)/2.3635(8)	2.3437(6)
τ ₄	0.897	0.865	0.901	0.893/0.884	0.907
B-N	n/a	n/a	1.651(5)	1.688(7)/1.676(7)	1.633(5)
N-N/O	n/a	n/a	1.450(4)	1.459(6)	1.430(4)
ΣB_{α}	n/a	359.70(3)	322.0(3)	320.3(5)/320.3(4)	320.3(3)

 Table S22 Experimental bond distances for Fe complexes.

Bond	3	4	5-Br	5-NPh₂	5-Cbz	6
Fe-N _{pyridine}	2.131(3)/2.120(3)	2.1195(15)	2.1462(17)	2.1496(12)	2.1564(13)	2.128(2)
Fe-N _{pyrazole}	2.086(3)/2.077(3)	2.0627(14)	2.0770(16)	2.0786(14)	2.0746(13)	2.063(2)
Fe-X ₁	2.3927(7)/2.3944(7)	2.3794(3)	2.3963(4) (X=Br)	1.9856(15) (X=NPh ₂)	1.9915(13) (X=cbz)	2.4049(5)
Fe-X ₂	2.3618(7)/2.3475(7)	2.4075(3)	2.0187(17) (X=NH ₂)	2.0533(14) (X=NH ₂)	2.0351(14) (X=NH ₂)	2.3782(5)
τ4	0.881/0.864	0.897	0.845	0.789	0.822	0.871
B-N	1.688(5)/1.685(5)	1.646(2)	1.628(3)	1.631(2)	1.636(2)	1.661(4)
N-N	1.464(4)	1.453(2)	n/a	n/a	n/a	n/a
ΣB_{α}	320.00(3)/319.20(3)	321.79(14)	324.28(16)	325.51(14)	324.61(14)	319.3(2)

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