Facile Hydrogen Atom Transfer to Iron(III) Imido Radical Complexes Supported by a Dianionic Pentadentate Ligand

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Supporting Information

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Experimental Details.

General. Unless mentioned otherwise, all manipulations were performed under an inert gas (argon) in gloveboxes or using standard Schlenk techniques. NMR spectra were recorded on Bruker DRY400 and RDQ400 spectrometers. All ^{11}B chemical shifts are relative to $BF_3 \cdot OEt_2$. ^{1}H and ^{13}C chemical shifts were measured relative to the solvent peaks, but are reported relative to TMS. Me_3SnCl was purchased from VWR. All other chemicals obtained from Sigma Aldrich; BBr_3 was stored over copper wire. All anhydrous solvents were prepared by passing through Mbraun SP-800 solvent purification system and were stored over sodium, K/Na, or CaH_2.

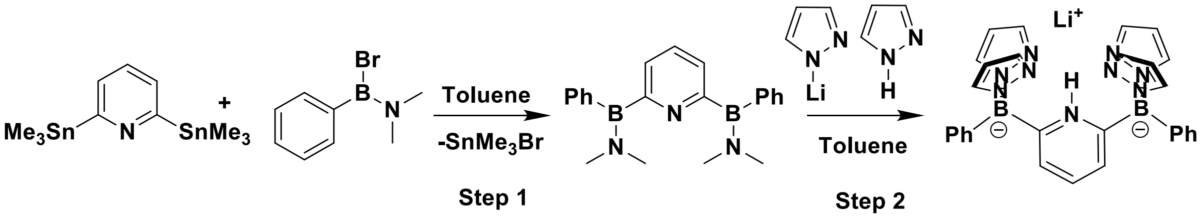
Syntheses.

Dibromo(phenyl)borane. This is a modification of a published procedure.[1] To a solution of trimethyl(phenyl)silane (17.2 mL, 0.10 mol) in 60 mL of pentane was added BBr_3 (10.5 mL, 0.11 mol). The resulting mixture was refluxed for 5 h in a thick-walled glass vessel. ***Caution: Ensure proper protective measures when heating a closed system.*** After that time, pentane was removed *in vacuo* to yield off-white/grey solid. Yield 24.0 g, 97 %. ^{1}H NMR (400 MHz, [D2]DCM) δ 8.25 (d, *J*(HH) = 7.1 Hz, 2H, {Ph}H^{ortho}), 7.77 – 7.65 (m, 1H, {Ph}H^{para}), 7.57 – 7.40 (m, 2H, {Ph}H^{meta}). ^{13}C{^{1}H} NMR (101 MHz, [D2]DCM) δ 138.27 (s, {Ph}C^{ortho}), 136.07 (s, {Ph}C^{para}), 128.84 (s, {Ph}C^{meta}), (ipso carbon was not observed). ^{11}B{^{1}H} NMR (128 MHz, [D2]DCM) δ 57.3(s).

Bromo(dimethylamino)phenylborane. This is a new preparative method for a known compound.[2] A 50 mL Schlenk flask containing $PhBBr_2$ (5.00 g, 20.2 mmol) in 5 mL of toluene was cooled to -78 ºC and N,N-dimethyltrimethylsilylamine (3.24 mL, 20.2 mmol) was added dropwise over the course of 3 minutes. The low temperature bath was removed and semi-frozen mixture was allowed to melt. The pale yellow solution that resulted was stirred for 1 h at room temperature and then toluene and Me_3SiBr were removed *in vacuo* (50 mTorr) over the course of ≈40 minutes. Removal of Me_3SiBr was verified by NMR spectroscopy. Yield: 3.72 g, 87% ^{1}H NMR (400 MHz, [D2]DCM) δ 7.54 – 7.46 (m, 2H, {Ph}H^{ortho}), 7.38 – 7.32 (m, 3H, {Ph}$H^{meta+para}$), 3.14 (s, 3H, CH_3), 2.92 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, D2[DCM]) δ 133.03 (s, {Ph}C^{ortho}), 129.45 (s, {Ph}C^{para}), 128.10 (s, {Ph}C^{meta}), 42.83 (s, CH_3), 41.45 (s, CH_3). ^{11}B{^{1}H} NMR (128 MHz, [D2]DCM) δ 37.11 (s).

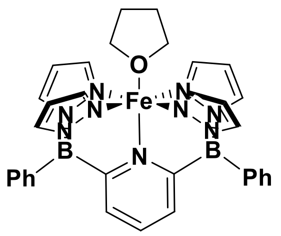
2,6-bis(trimethylstannyl)pyridine. This is a modification of a published procedure.[3] To a suspension of sodium (8.00 g, 348 mmol, ~5 mm^3 granules) in 150 mL of dry DME cooled to -40 °C was added a solution of Me_3SnCl (20 g, 101 mmol) in 15 mL of THF. The resulting mixture was stirred for 2 hours at -40 °C and then left stirring overnight at room temperature. The resulting grey suspension was transferred via cannula into another Schlenk flask to remove the excess sodium. The filtrate was cooled to -78 °C and a solution of 2,6-dibromopyridine (10.0 g, 42.2 mmol in 20 mL of THF) was slowly added during 10 min. The reaction was stirred for one hour at -78°C, warmed up to r.t., and stirred for an additional 1 h. After this time, solvents were removed *in vacuo* and the remaining solid was extracted with 3×50 of pentane, the extracts combined, and filtered through a short plug of basic Al_2O_3 (3 cm×2 cm). Pentane was removed *in vacuo* to obtain colorless oil of slightly impure 2,6-bis(trimethylstannyl)pyridine. The product was purified by distillation while collecting a fraction at 98-100 °C (79 mTorr). Yield: 12.7 g (68 %). ^{1}H NMR (400 MHz, D2[DCM]) δ 7.45 – 7.28 (m, 3H, Py), 0.35 (s, 18H, Sn satellite *J*(HSn) = 112 Hz, CH_3). ^{13}C{^{1}H} NMR (101 MHz, D2[DCM]) δ 174.62 (s), 131.69 (s, Sn satellite *J*(CSn) = 34.1 Hz), 130.56 (s, Sn satellite *J*(CSn) = 92.5 Hz), -9.31 (s, Sn satellite *J*(CSn) = 339.2 Hz, CH_3). ^{119}Sn NMR (149 MHz, D2[DCM]) δ -51.43 (s, 2Sn).

Synthesis of $[B_2Pz_4LiPyH]_2$ ligand.

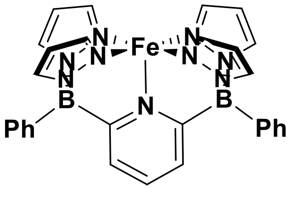


Step 1. A 50 mL Schlenk vessel containing a mixture of 2,6-bis(trimethylstannyl)pyridine (4.00 g, 9.90 mmol) and freshly-prepared bromo(dimethylamino)phenylborane (4.40 g, 20.72 mmol) in 30 mL of toluene was stirred at r.t. for 24 h to get a pale yellow oil, which eventually crystallized as a white semi-solid. After that time, all volatiles were removed *in vacuo* during 3 hour using a warm bath (45 ºC). The oil of 1,1'-(pyridine-2,6-diyl)bis(N,N-dimethyl-1-phenylboranamine) was found to be sensitive to coordinating solvents and water. The product was used without purification for the next step.

Step 2. A 50 mL Schlenk vessel containing an emulsion of 1,1'-(pyridine-2,6-diyl)bis(N,N-dimethyl-1-phenylboranamine) in 30 mL of dry toluene was mixed with freshly sublimed pyrazole (2.02 g, 29.70 mmol), lithium pyrazolate (734 mg, 9.90 mmol), and left to stir at 110 °C in an oil bath for 16 h. After that time the reaction mixture was cooled to r.t., diluted with 3 mL of pentane, and left in a freezer at -23 °C for 3 h. The final ligand was isolated by filtration, washed with 5 mL of ethyl acetate, and dried under vacuum for 16 h to obtain a white solid. Yield: 4.24 g (81 %) The ligand precursor is air and water stable. Single crystals of this compound suitable for X-ray diffraction were grown by slow diffusion of hexanes into THF solution of the ligand. ^{1}H NMR ([D8]THF) δ 7.76 – 7.60 (m, 1H, PyH^{4}), 7.44 (d, *J*(HH) = 1.5 Hz, 4H, 4×{Pz}H^{5}), 7.20 – 7.04 (m, 10H, 4×{Pz}H^{3} overlapped with 4×{Ph}H^{meta} and 2×{Ph}H^{para}), 6.99 – 6.92 (m, 4H, 4×{Ph}H^{ortho}), 6.90 (d, *J*(HH) = 7.7 Hz, 2H, {Py}H^{3,5}), 6.09 (t, *J*(HH) = 1.9 Hz, 4H, 4×{Pz}H^{4}), ^{13}C{^{1}H} NMR ([D8]THF) δ 140.64 (s, {Pz}C^{5}), 139.32 (s, {Py}C^{4}), 136.21 (s, {Pz}C^{3}), 134.82 (s, {Ph}C^{meta}), 128.88 (s, {Py}C^{3,5}), 127.88 (s, {Ph}C^{ortho}), 127.09 (s, {Ph}C^{para}), 103.73 (s, {Pz}C^{4}). ^{11}B NMR (128 MHz, [D8]THF) δ -1.32 (s, 2B). MS (ESI) *m/z* calcd for $C_{29}H_{27}B_{2}LiN_{9}$: 530.2736 [M+H]$^{+}$, 524.2654 [M-Li+2H]$^{+}$, 456.2279 [M-PzLi+H]$^{+}$; *m/z* found: 530.2730 (100 %, [M+H]$^{+}$), 524.2658 (100 %, [M-Li+2H]$^{+}$), 456.2287 (100 %, [M-PzLi+H]$^{+}$).

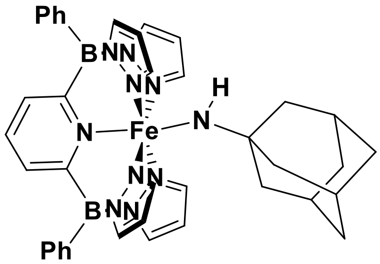


Synthesis of [FeB$_{2}$Pz$_{4}$Py]THF (1•THF). A solution of the ligand precursor **[B$_{2}$Pz$_{4}$LiPyH]$_{2}$** (529 mg, 1.00 mmol) in THF (3 mL) was treated with LiO*i*Pr (79.2 mg, 1.20 mmol) at room temperature and then left to stir for 20 min. After this time the solution of ligand was cannula-transferred into a suspension of FeBr$_{2}$ (216 mg, 1.00 mmol) in 5 mL of THF.The resulting brown solution was left to stir for 6 hour at r.t. and then 3 mL of pentane was added with vigorous stirring. The resulting mixture was filtered and a further 8 mL of pentane was added to filtrate. This mixture was left to crystallize at room temperature. A yellow crystalline solid was isolated by filtration, washed with pentane, and dried *in vacuo* for 2 h. Yield: 396 mg (61 %). The complex is paramagnetic and highly air sensitive. Crystals suitable for X-ray crystallography were obtained by slow diffusion of pentane into concentrated solution of the complex in THF. ^{1}H NMR ([D8]THF) δ 55.27 (br), 48.74 (b), 45.35 (b), 36.34 (b) 23.38 (b). Anal. Calcd for $C_{33}H_{33}B_{2}FeN_{9}O$: C, 61.06; H, 5.12; N, 19.42 Found: C, 59.68; H, 5.59; N, 19.52. ESI MS (ESI) for $C_{29}H_{25}B_{2}FeN_{9}$ *m/z* calcd: 577.1768 (100.0, [M-THF]$^{+}$); *m/z* found: 577.1761 (100%, [M-THF]$^{+}$). UV-Vis in benzene: λ_{max} 376 nm. Evans Method determination of magnetic moment: Sample mass 5 mg; Solvent [D6]Benzene; Standard=SiMe$_{4}$ (6%); μ_{eff}= 5.64 B. M.; s=2, n=4.

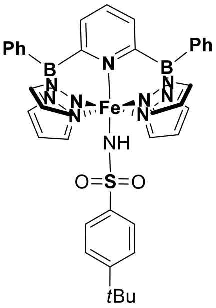


Synthesis of [FeB$_{2}$Pz$_{4}$Py] (1). A solid sample of **1•THF** (300 mg, 0.462 mmol) in a glass vessel equipped with a Kontes valve was placed in an oil bath at 25 ºC. The vessel was evacuated to 40 mTorr and the temperature in the oil bath was gradually increased to 150 ºC and kept at this temperature for 2 hours. During this time, the yellow solid slowly turned green. After this time, the vessel was sealed and immediately brought to the dry box and the solid stored at -35˚C. Yield: 226 mg, (85 %) Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane in saturated solution of **1** in benzene. Both pentane and benzene solvents were dried over K/Na alloy and freshly distilled before use. Anal. Calcd for $C_{29}H_{25}B_2FeN_9$: C, 60.36; H, 4.37; N, 21.85 Found: C, 59.86; H, 4.71; N, 20.86. MS (ESI) m/z calcd: 577.1768 (100%, M^+) m/z found: 577.1767 (100 %, M^+). FT-IR (Nujol, cm^{-1}): 2025.6 (Ph), 1909.2(Ph), 1976.0(Ph), 1725.51, 1572.9, 1554.4, 1498.6, 1461.3, 1399.3, 1287.7, 1188.5, 1163.7, 1095.5, 1064.5, 940.5, 890.9, 816.5, 754.5, 717.2, 636.6. UV-Vis in benzene: λ_{max} 378 nm. Evans Method determination of magnetic moment: Sample mass 5 mg; Solvent [D6]Benzene; Standard=$SiMe_4$ (6%); μ_{eff}= 5.33 B. M.; s=2, n=4.

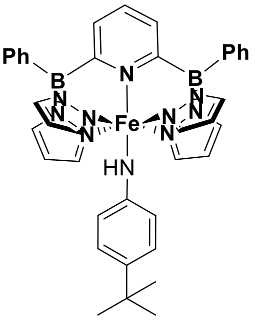
Synthesis of [FeB$_2$Pz$_4$Py](NHAd) (2•Ad). A suspension of **1·THF** (200 mg, 0.308 mmol) in 2 mL of benzene and solution of adamantyl azide (67.4 mg, 0.380 mmol in 2 mL of benzene) was mixed together in a tube equipped with a Teflon tap. The vessel was sealed and placed in an oil bath at 70 ºC for 48 hours. After this time, the reaction was cooled to room temperature and the product was crystallized by slow diffusion of n-pentane (4 mL) into a saturated solution of the complex in benzene. The complex was isolated as a blue crystalline solid by slow decantation of the solvent, washing crystals with pentane, and drying it *in vacuo* for 5 hours. Yield: 154 mg, (62 %) Anal. Calcd for $C_{39}H_{41}B_2FeN_{10}$+2/3 C_6H_6: 66.10; H, 6.06; N, 17.93 Found: C, 66.22; H, 6.21; N, 17.99. FT-IR (Nujol, cm^{-1}): 3261.8 (wn, NH). UV-Vis: λ_{max} 325, 373, 625 nm. Evans Method determination of magnetic moment: Sample mass 5 mg; Solvent [D6]Benzene; Standard=$O(SiMe_3)_2$ (3%); μ_{eff}= 2.05 B. M.; s=1/2, n=1.



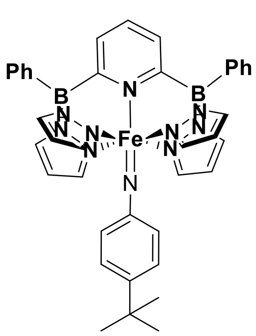
Synthesis of [FeB2Pz4Py](NHPhtBu) (2•SO2Ar). To a pressure tube containing suspension of **1•THF** (200 mg, 0.308 mmol) in 5 mL of toluene, a solution of 4-tert-butylbenzenesulfonyl azide (79.0 mg, 0.337 mmol in 1 mL of benzene) was slowly added. Vigorous evolution of nitrogen gas was observed. The dark red reaction mixture was stirred for 1 h and then treated with and 1,4-cyclohexadiene (27 mg, 0.337 mmol) in 1 mL of benzene. The resulting red solution was stirred for an additional 1 h at room temperature. Pentane (14 mL) was layered on top of the reaction solution crystalline material allowed to deposit for 24 hours at room temperature. The red crystalline material was separated by filtration and dried *in vacuo* to give 194 mg (80 %) of a



red solid. FT-IR (neat, cm^{-1}): 3071.26 (w, NH), Anal. Calcd for $C_{39}H_{39}B_2FeN_{10}O_2S$: 59.07; H, 4.96; N, 16.90 Found: C, 59.34; H, 4.98; N, 17.75.

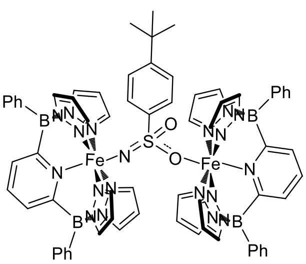


Synthesis of [FeB$_2$Pz$_4$Py](NHPhtBu) (2•Ar). To a pressure tube containing suspension of **1·THF** (200 mg, 0.308 mmol) in 6 mL of benzene a solution of 1-azido-4-tert-butylbenzene (60 mg, 0.339 mmol in solution of hexamethyldisiloxane) was added. Vigorous evolution of nitrogen gas was observed. The obtained dark brown reaction mixture was left to stir for 20 min and then 1 mL of 1,4-cyclohexadiene (27 mg, 0.337 mmol) in solution of benzene was added. The reaction was stirred for an additional 1 h during which time the reaction mixture turned green. The mixture was concentrated *in vacuo* to about 2 mL and pentane (6 mL) was layered on top of the obtained solution. The resulting mixture was left to crystallize at ambient temperature for 2 hours. After this time green crystalline material was separated by filtration and dried *in vacuo* to give 162 mg (74 %) of sea-green solid. Anal. Calcd for $C_{39}H_{39}B_2FeN_{10}$: 64.59; H, 5.42; N, 19.31 Found: C, 64.40; H, 5.47; N, 19.08. UV-Vis: λ_{max} 371, 863 nm. MS (APCI) m/z calcd for $C_{39}H_{39}B_2FeN_{10}$: 577.1768 (core), 725.2894 (M$^+$), m/z found: 577.1756 (100%, core), 725.2877 (100%, M$^+$). FT-IR (neat, cm^{-1}): 3301.7 (wn, NH). **2·Ar**-*d$_1$* was obtained in reaction of **3·Ar** complex with **D8[THF]**. FT-IR (neat, cm^{-1}): 3303.4 (wn, NH), 2450.8 (wn, ND). MS (APCI) m/z calcd for $C_{39}H_{38}DB_2FeN_{10}$: 577.1768 ([M-*t*BuPhNH]$^+$), 726.2972 (M$^+$), m/z found: 577.1716 (100%, [M-*t*BuPhNH]$^+$), 726.2889 (100%, M$^+$). Evans Method determination of magnetic moment: Sample mass 5 mg; Solvent [D6]Benzene; Standard=O(SiMe$_3$)$_2$ (3%); μ_{eff}= 1.82 B. M.; s=1/2, n=1.



Synthesis of [FeB$_2$Pz$_4$Py](NPhtBu) (3•Ar). To a pressure tube containing suspension of **1** (200 mg, 0.346 mmol) in 6 mL of bromobenzene a solution of 1-azido-4-tert-butylbenzene (62.0 mg, 0.354 mmol in solution of hexamethyldisiloxane) was added. Vigorous evolution of nitrogen gas was observed. The obtained dark brown reaction mixture was vigorously stirred for 10 min at room temperature. Hexamethyldisiloxane (5 mL) was added to give a dark brown suspension which was placed in a freezer at -35 ºC. After 30 min in a freezer the reaction mixture was filtered, washed with hexamethyldisiloxane (4 mL) and dried *in vacuo* for 1 h to give 166 mg (67 %) of a dark green solid. This product was found to be extremely moisture sensitive and unstable in THF, toluene, and methylene chloride. Anal. Calcd for $C_{39}H_{38}B_2FeN_{10}$: 64.65; H, 5.29; N, 19.33 Found: C, 64.21; H, 5.23; N, 18.97. UV-

Vis: λ_{max} 470, 725, 871 nm. MS (APCI) m/z calcd for $C_{39}H_{38}B_2FeN_{10}$: 577.1768 (core), 725.2972 ($[M+H]^+$), m/z found: 577.1693 (100%, core), 725.2808 (100%, $[M+H]^+$). Evans Method determination of magnetic moment: Sample mass 5 mg; Solvent [D6]Benzene; Standard=$O(SiMe_3)_2$ (6%); μ_{eff}= 2.87 B. M.; s=1, n=2.



Synthesis of $[FeB_2Pz_4Py]\mu^2(NSO_2PhtBu)$ (4). To a pressure tube containing suspension of **1** (200 mg, 0.347 mmol) in 5 mL of benzene a solution of 4-^{t}Bu-benzenesulfonyl azide (89.0 mg, 0.347 mmol in 0.2 mL of benzene) was slowly added. Vigorous evolution of nitrogen gas was observed during this time. The resulting dark brown reaction mixture was stirred for a further 30 min. Pentane (14 mL) was layered on top of the reaction mixture and left to crystallize at ambient temperature for one day. After this time, dark-brown crystalline material was separated by filtration and dried *in vacuo* for 2 h to give 151 mg (59 %) of a brown solid. Anal. Calcd for $C_{68}H_{63}B_4Fe_2N_{19}O_2S$: C, 59.82; H, 4.65; N, 19.49 Found: C, 59.95; H, 4.93; N, 17.76. Evans Method determination of magnetic moment: Sample mass 5 mg; Solvent [D6]Benzene; Standard=$O(SiMe_3)_2$ (3%); μ_{eff}= 7.18 B. M.; s=3/2 per iron center, n=3.

UV-Vis monitored reaction of toluene with 3•Ar complex. Using a UV-Vis cuvette co-joined with a round bottomed flask, equipped with Kontes valves, a solution of **3•Ar** complex (0.526 mL, C=0.656 mmol/L) in C_6D_6 was placed into the cuvette, while a solution of toluene in 1.58 mL of C_6D_6 was placed in the round bottomed flask. The apparatus was sealed and carefully, without mixing of the two reagents, was taken out of a glovebox. The reagents were rapidly mixed at room temperature (19°C) and shook for 30 seconds, then reaction mixture was transferred into UV-Vis cuvette (l = 2 mm) and the progress of the reaction was monitored for > 5 half lives by UV-Vis using 640 nm/min scan rate; only a quarter of the data presented in Figure S8 below. The experiment was repeated for various concentrations of toluene (Figure S9). All solvents used in this study were dried over Na/K alloy, distilled and stored over Na/K before use.

Determination of intermolecular primary kinetic isotope effect for hydrogen atom transfer reaction. A solution of **3•Ar** (20 mg, 0.0280) in [D8]THF ([D7H]THF=0.23 %)[4] was heated at 61 ºC for 6 hours. The resulting green solution of the **2•Ar** complex was analyzed by FT-IR spectroscopy using neat sample deposited on CsF pellet. The ratio of **2•Ar(NH)** vs. **2•Ar(ND)** was obtained by integrating the corresponding NH (3303.4, wn) and

ND **(**2450.8, wn) cm^{-1} stretches for theses complexes**.** The experiment was repeated 3 times. The estimated value for kinetic isotope effect was found to be k_H/k_D=567(16).

Reaction of [Fe]=NPhtBu complex with toluene and THF.

In a J-Young tube 20 mg of [Fe]=NPhtBu was dissolved in 700 mg of C_6D_6 and 20 mg of THF or Toluene was added. Reaction mixture was sealed with a Teflon cap and heated for 20 minutes at 60 °C until characteristic brown-green colour changed to blue-green. Resulting mixture was diluted with 0.500 mL of EtOH/H_2O solution (9:1) and heating continued for another 30 min. The obtained mixture was filtered through a short plug of Al_2O_3 to remove [Fe]O[Fe] dimer and obtained filtrate was analyzed by GC/MS. The analyzed mixture has the following content: a) Reaction with toluene: m/z 149.02 (97 %, *t*BuPhNH_2), 239.00 (2 % *t*BuPhNH_2+CH_2Ph) b) Reaction with THF: m/z 149.00 (94 %, *t*BuPhNH_2), 219.01 (4 % *t*BuPhNH_2+C_4H_7O). An additional peak of mass 147.00 (less than 1 %) was also observed in both experiments, but could not be reliably identified.

Mössbauer Spectroscopy. Solid-state samples for ^{57}Fe Mössbauer spectroscopy were prepared in an inert atmosphere glove box equipped with a liquid nitrogen fill port to enable sample freezing to 77 K within the glove box. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low temperature, zero-field ^{57}Fe Mössbauer measurements were performed using a See Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N_2 cryostat for measurements from 5 K to 140 K. Isomer shifts were determined relative to α-Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SeeCo). Errors of the fit analyses were the following: $\delta \pm 0.02$ mm/s and $\Delta E_Q \pm 3\%$. For multi-component fits the quantitation errors were ± 3% (e.g. 67 ± 3%).

Electron Paramagnetic Resonance Spectroscopy. All samples for EPR spectroscopy were prepared in an inert atmosphere glove box equipped with a liquid nitrogen fill port to enable sample freezing to 77 K within the glove box. EPR samples were prepared in 4 mM OD suprasil quartz EPR tubes from Wilmad Labglass. Samples for spin integration utilized high precision suprasil quartz tubes to allow for direct comparison of intensities between different samples. Iron samples were prepared in C_6D_6 at concentrations of 8 mM. X-band EPR spectra were recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity and an Oxford ESR-900 helium flow cryostat. The instrumental parameters employed for all samples were as follows: 1 mW power; time constant 41 ms; modulation amplitude 1 G; 9.38 GHz; modulation frequency 100 kHz. All spectra were recorded at 10 K. Spin integration was performed using an 8 mM $CuSO_4$ standard under non-saturating conditions. Identical instrumentation parameters were used for both the iron and standard samples.

Crystal Structure Determinations. Diffraction data for the ligand, **1, 1·THF, 3·Ar** and **4** were collected with Cu Kα radiation on a Bruker Smart diffractometer equipped with Apex II detector, fixed-CHI goniometer, and sealed-tube (Cu) source. Cell refinement and data reduction were done using SAINT[5]. An empirical absorption correction, based on the multiple measurements of equivalent reflections, was applied using the program SADABS.[6] The space group was confirmed by XPREP routine[7]. The structures were solved by direct-methods and refined by full-matrix least squares and difference Fourier techniques with SHELX-2013[8] as a part of LinXTL[9] tool box. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter, except those of the NH moiety, which were positioned from residual peaks in the difference Fourier map. All publication materials (cif files validation, listings of bonds and angles, and ORTEP drawings) were prepared using LinXTL, Mercury[10], and Platon[11] programs. Crystallographic data and selected metrical data are summarized in Tables S8-11.

Deposited crystallographic data: $[B_2Pz_4LiPyH]_2$ (CCDC: 1439938), **1** (CCDC: 1439242), **1•THF** (CCDC: 1439243), **2•Ad** (CCDC: 1439244), **2•Ar (CCDC:** 1439245), **4** (CCDC: 1439246) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. All the quantum-chemical calculations were conducted using the Gaussian09 program suite.[12] As functional we have used the Becke's 3-parameter hybrid one, combined with the non-local correlation functional provided by Perdew/Wang, denoted as B3PW91.[13,14] For Fe, the relativistic energy-consistent pseudopotential of the Stuttgart-Köln ECP library was used in combination with its adapted segmented basis.[15] For all other atoms, a standard 6-31G** basis set was used.[16] All stationary points have been identified as minima (number of imaginary frequencies Nimag=0) or transition states (Nimag=1). The BDE of the N-H bond in the amido complex **2•Ar** was computed using the formula 2.Ar -> 3.Ar + H•. Using the enthalpy computed after geometry optimization of the complexes **2•Ar** and **3•Ar** and the one obtained for H•, a value of 91.3 kcal/mol for the BDE was found. Together with the computed enthalpy of the H-abstraction from toluene, this leads to a BDE of roughly 89 kcal/mol for toluene, in agreement with the experimentally reported value.

The Mössbauer spectroscopic parameters were computed using the ORCA program[17] by performing single point calculations on the already optimized geometries, and using the same level of DFT theory. In particular for these calculations, the Ahlrichs-TZV basis set for Fe was employed (denoted as TZVPP), along with the Ahlrichs-VDZ basis set (denoted as SV(P)) for the remaining atoms.[18] In contrast to the quadrupole splitting value, that is generated directly from the calculation, to estimate the corresponding isomer shifts (δ) the linear regression formula has to be considered, $\delta = \alpha(\rho_0 - C) + \beta$, as it was derived from Neese group in a recent paper.[19] In particular, the ρ_0 refers to the electron density at the Fe nuclei, when α and β are fit parameters, and the C is a prefixed value. Since the B3PW91 is considered here as functional the corresponding values derived from the calibration were used, $\alpha = -0.366$, $\beta = 2.852$, $C = 111810$.

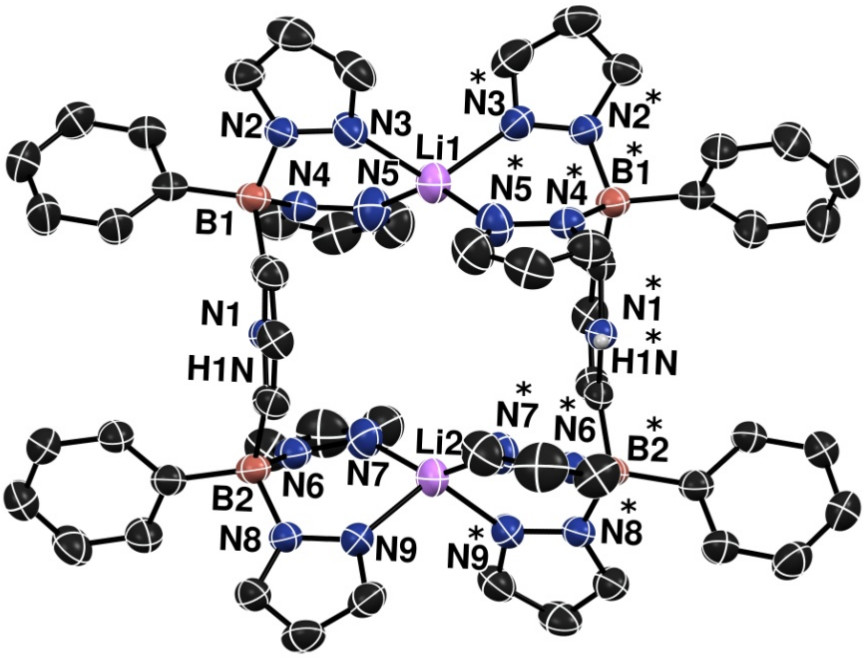


Figure S1. ORTEP diagrams for **B_2Pz_4Py**.Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. Selected metrical data given in Tables S9 and S10.

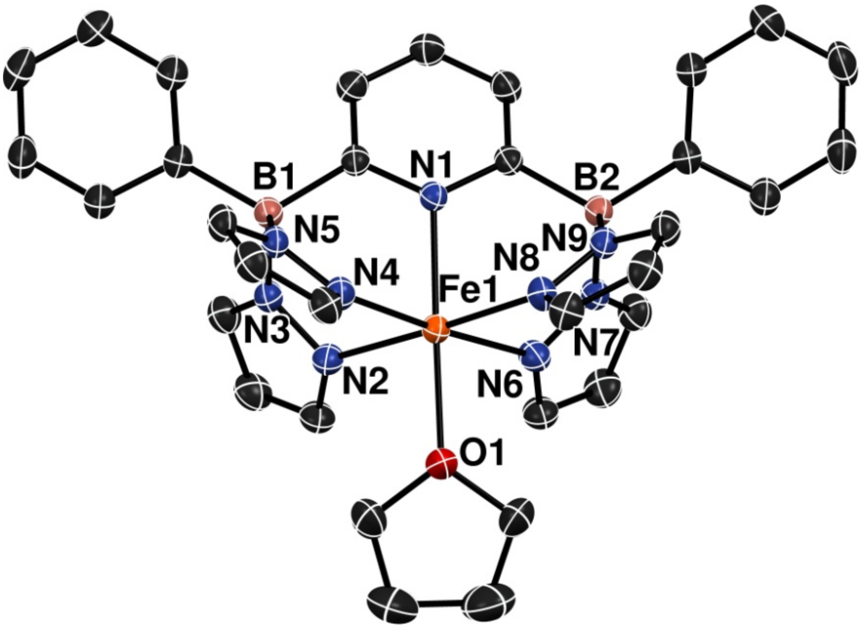


Figure S2. ORTEP diagrams for **1·THF.** Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. Selected metrical data given in Tables S9 and S10.

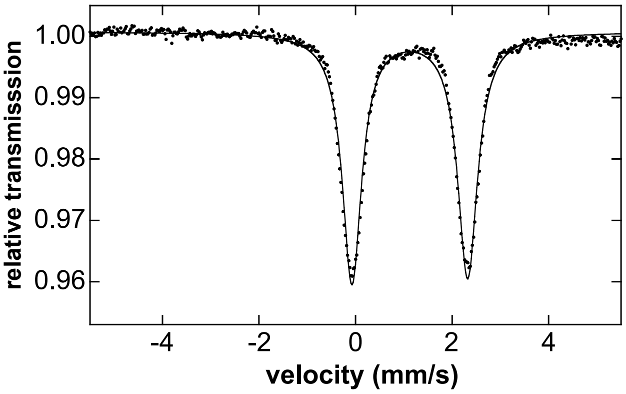


Figure S3. 80 K Mössbauer spectra of solid **1•THF**. The Mössbauer parameters of this complex are given in Table 1, main text.

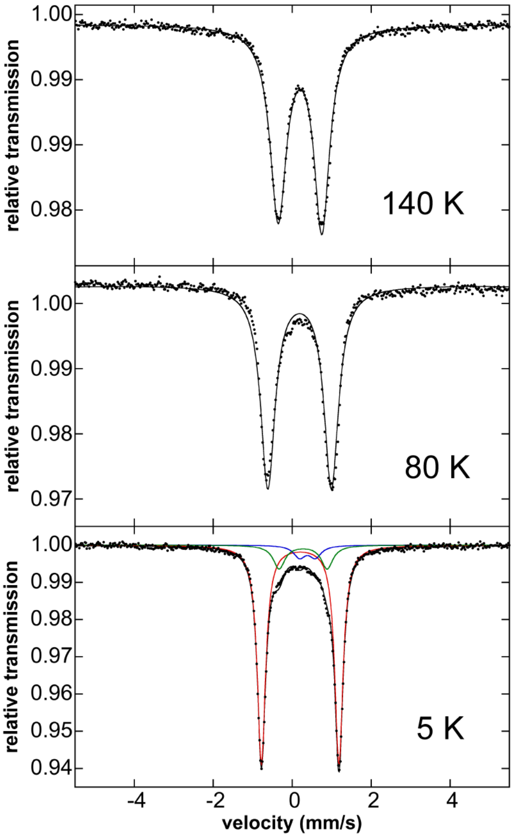


Figure S4. Variable temperature Mössbauer spectra of solid **3•Ar**. The Mössbauer parameters of the 5 K spectrum are given in the main text. At elevated temperatures, the Mössbauer spectra greatly broaden and the minor impurities are not unambiguous to observe due to the broad, featureless spectra. Simplified fits to a single species are shown for the 80 K and 140 K spectra to demonstrate the general changes observed (80 K: $\delta = 0.19$ mm/s, $\Delta E_Q =$ 1.61 mm/s; 140 K: $\delta = 0.20$ mm/s, $\Delta E_Q = 1.10$ mm/s). It is interesting to note that while no change in the isomer shift is observed with temperature (within the error of the fits, ± 0.02 mm/s for δ), the quadrupole splitting decreases with increasing temperature. The origin of this will be further investigated once samples lacking the minor species contributions can be obtained in the future.

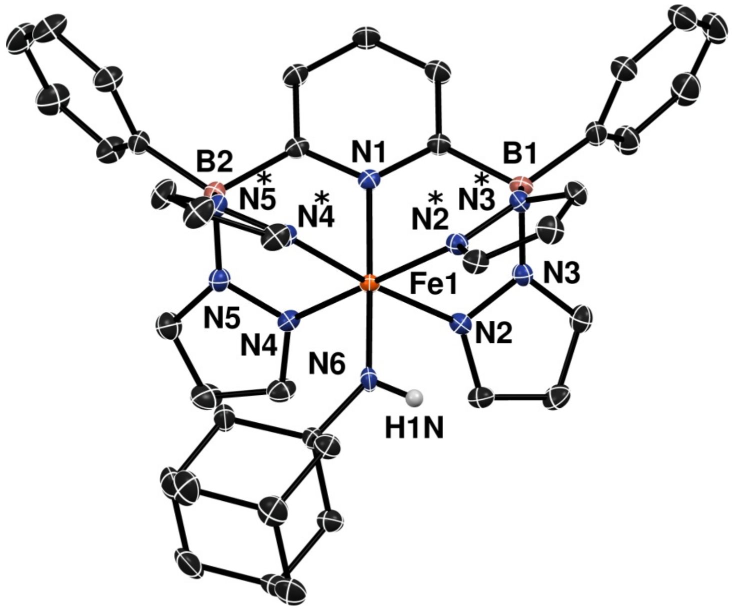


Figure S5. ORTEP diagrams for **2·Ad.** Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. Selected metrical data given in Tables S9 and S10.

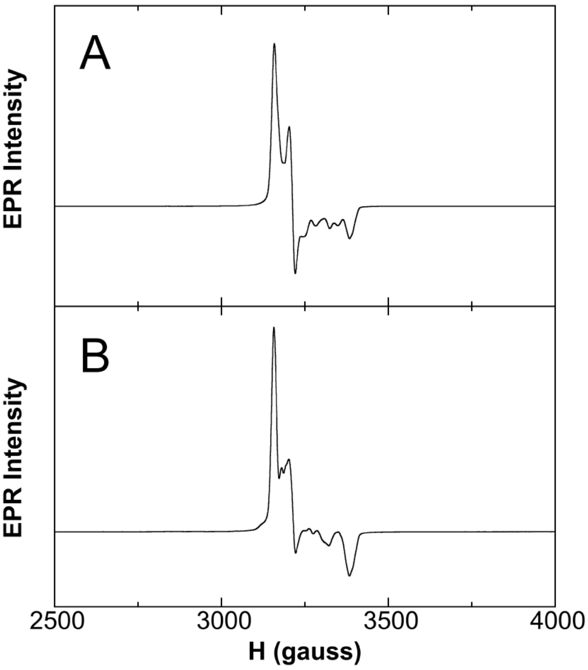


Figure S6. 10 K EPR spectra of samples of (A) **2•Ar** and (B) **3•Ar** in C_6D_6**.** Both samples exhibit signals consist with $S = 1/2$ species. Fine structure due to nitrogen hyperfine coupling is also observed but could not be adequately simulated. For the **3•Ar** sample, spin integration indicates that the EPR active $S = 1/2$ species accounts for ~ 35 % of all the iron in the sample, thus, indicating that this signal dervies from the impurity observed in Mossbauer spectroscopy (~ 33 % of all iron). Thus, **3•Ar** exhibits no EPR signal, consistent with its assignment as a $S = 1$ non-Kramers species.

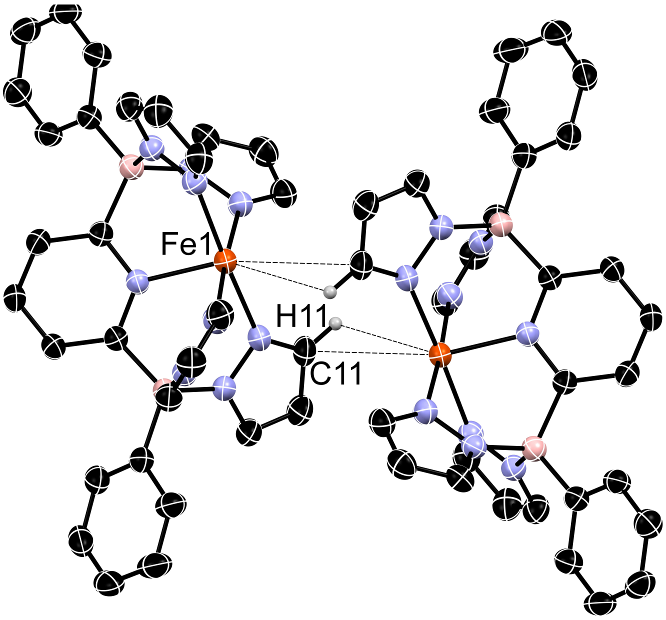


Figure S7. ORTEP diagrams for **1.** Thermal ellipsoids are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. Selected metrical data given in Tables S9 and S10.

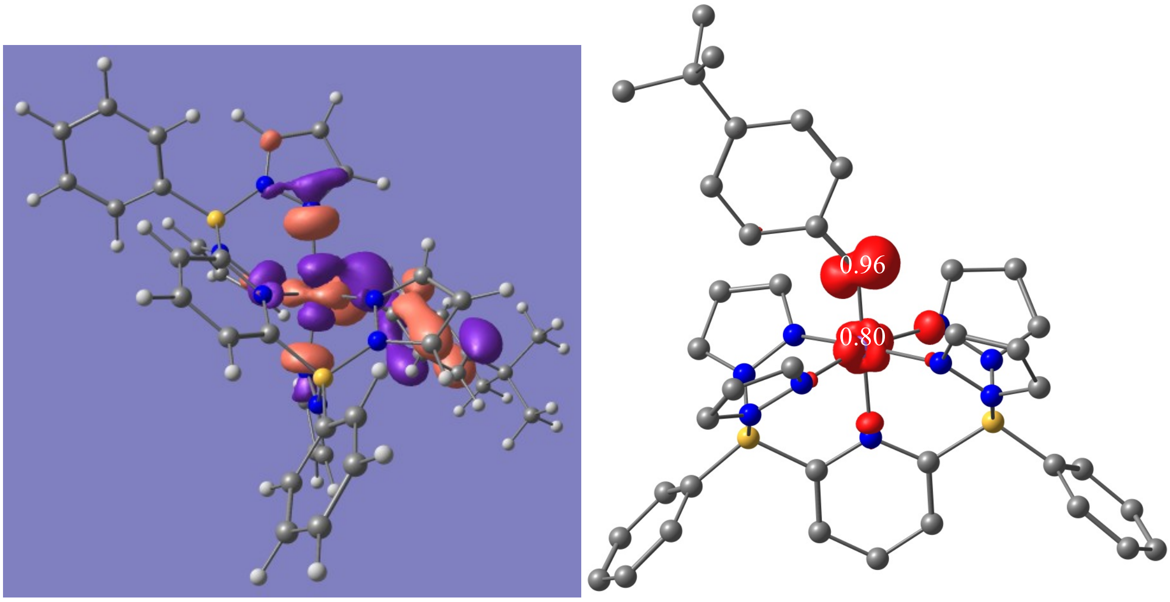


Figure S8. Left: Depiction of the metal-based SOMO in the imido radical **3•Ar**. Right: Calculated spin density population in **3•Ar** (α – β, S = 1).

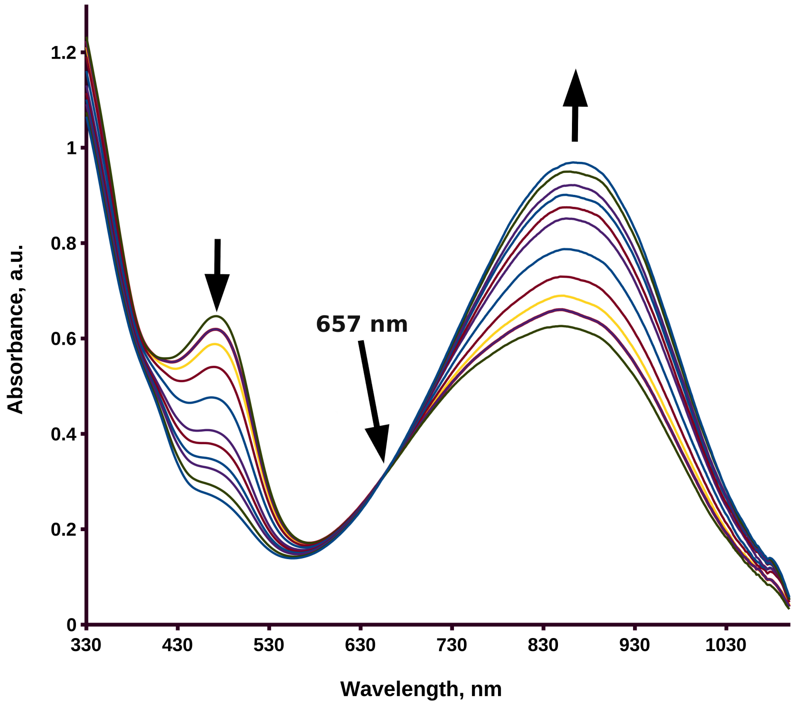


Figure S9. UV-Vis scanning kinetics of the reaction of **3•Ar** complex with toluene (0.165 mol/L)

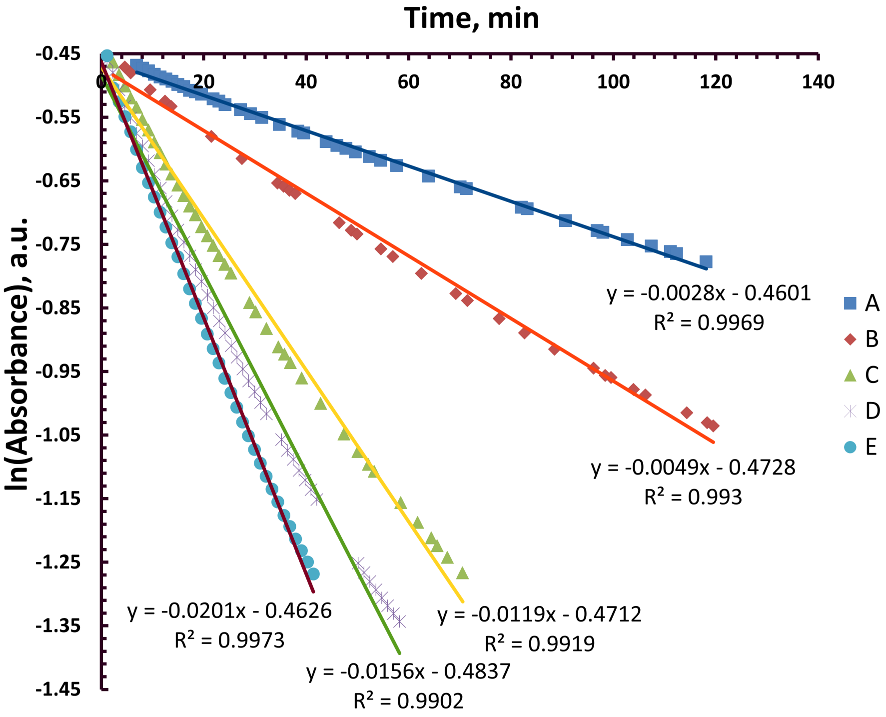


Figure S10. The reaction of **3•Ar** (C=0.656 mmol/L) complex with different concentrations of toluene (**A**=0.0152, **B**=0.0661, **C**=0.132 **D**=0.165, **E**=0.198 mol/L) in C_6D_6.

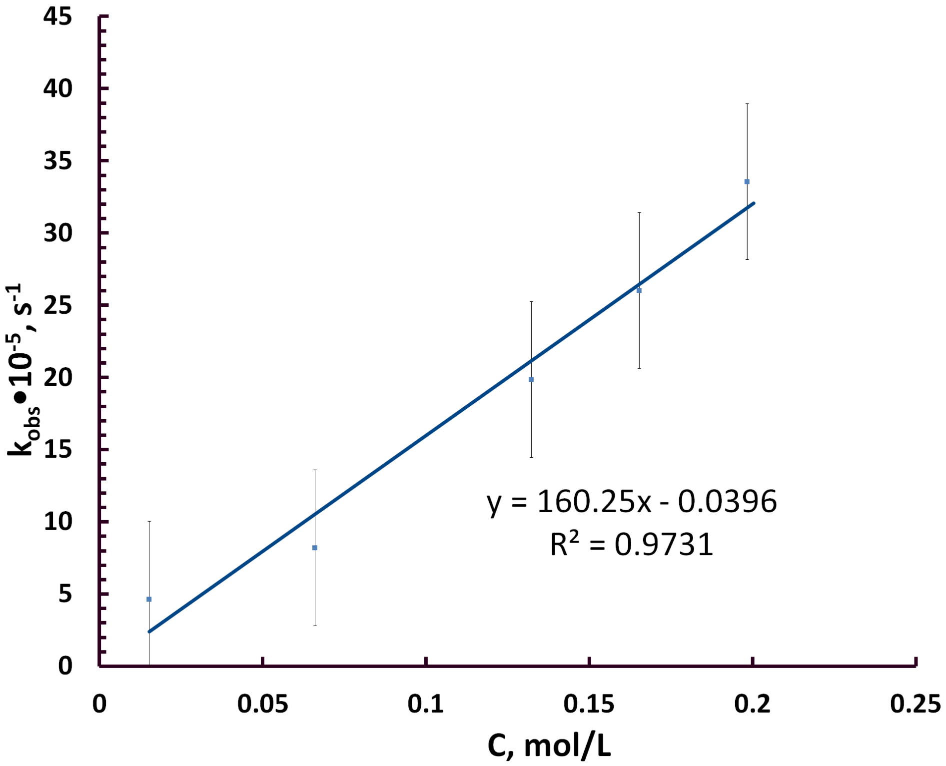


Figure S11. Values of the observed pseudo-first-order rate constant, $\mathbf{k_{obs}}$, plotted against toluene concentration.

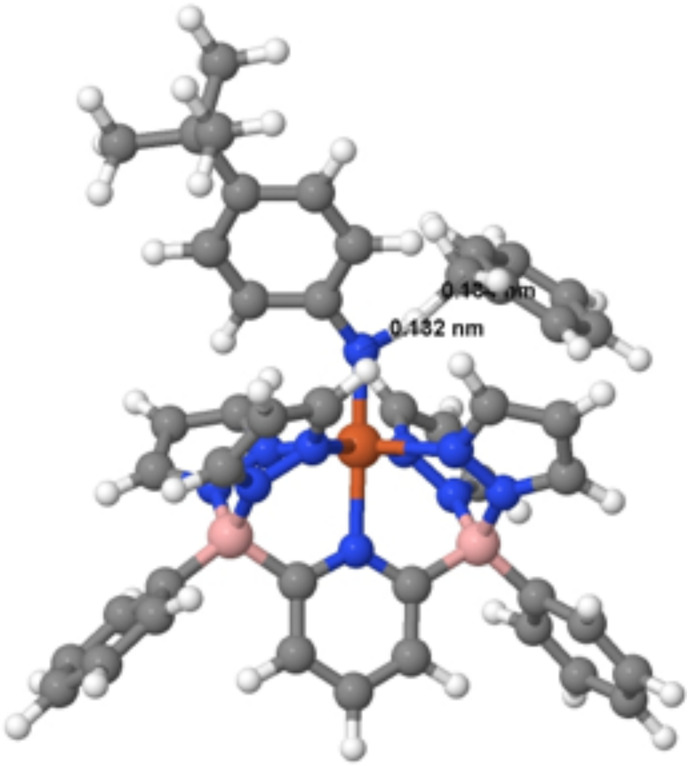


Figure S12. Computed transition state for the Hydrogen Atom Transfer reaction from toluene to **3•Ar**. Coordinates and calculated energy are given in Table S6.

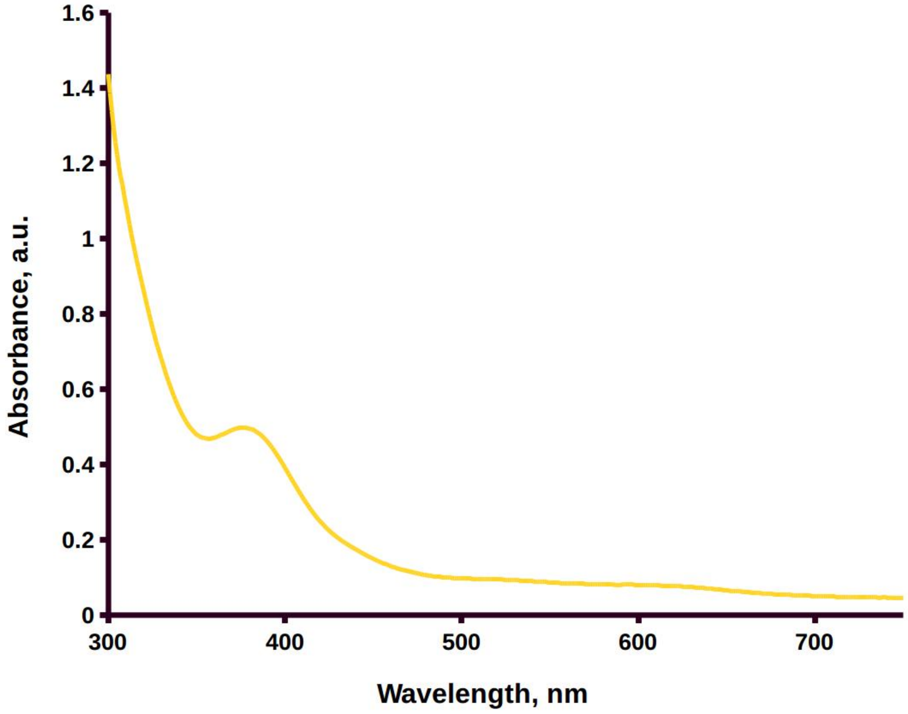


Figure S13. UV-Vis spectrum of **1•THF.**

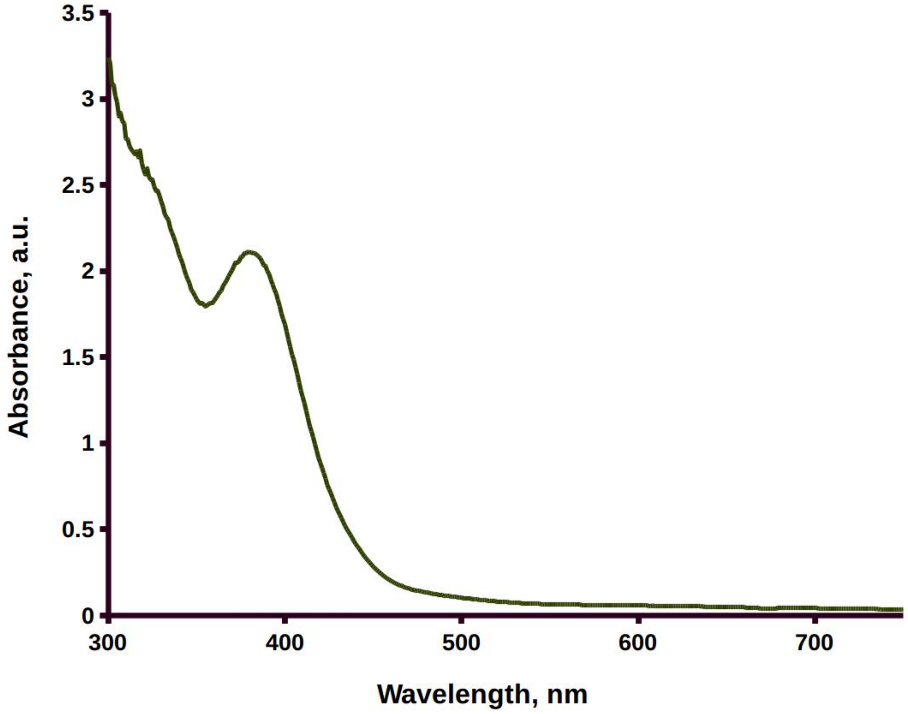


Figure S14. UV-Vis spectrum of **1.**

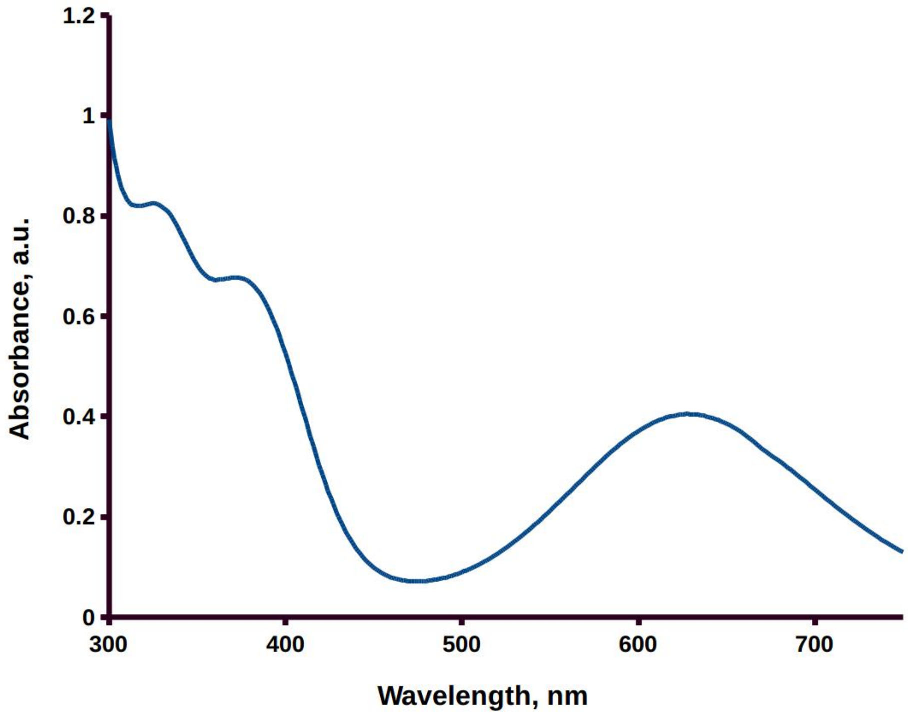


Figure S15. UV-Vis spectrum of **2•Ad.**

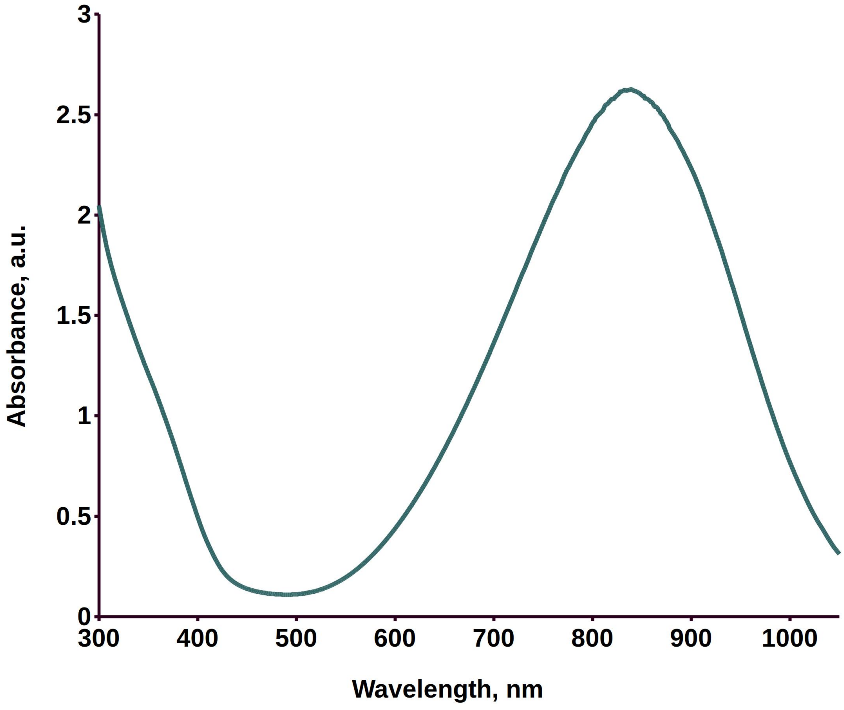


Figure S16. UV-Vis spectrum of **2•Ar.**

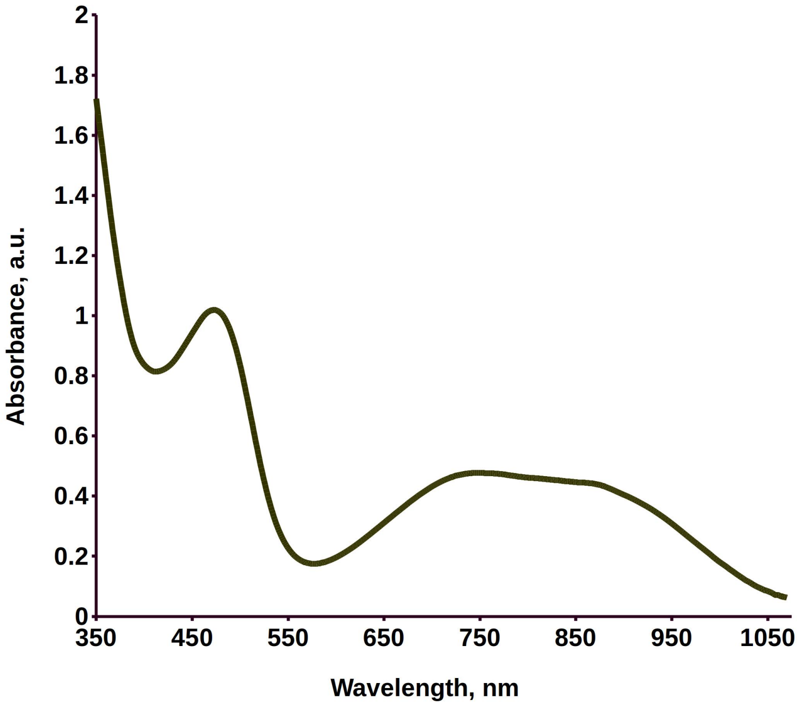


Figure S17. UV-Vis spectrum of **3•Ar.**

Table S1. Cartesian coordinates for compound **1•THF** in low spin and high spin states.

1.THF (Low Spin) 79 scf done: -2018.510553				**1.THF (High Spin)** 79 scf done: -2018.526858			
B	9.089966	10.959142	13.374093	B	9.094770	10.991085	13.331589
B	9.059859	6.121307	11.738152	B	9.075089	6.126438	11.679541
C	9.709797	9.462232	13.510550	C	9.697161	9.474710	13.495061
C	10.589519	9.118036	14.541511	C	10.470074	9.105669	14.603199
H	10.913886	9.885505	15.234695	H	10.750461	9.854694	15.335579
C	11.003885	7.804093	14.702534	C	10.839065	7.778620	14.782106
H	11.655657	7.522268	15.526230	H	11.413497	7.479619	15.656333
C	10.569171	6.858823	13.784953	C	10.460643	6.837072	13.833564
H	10.877255	5.823623	13.875796	H	10.731327	5.794566	13.959239
C	9.692671	7.219140	12.756792	C	9.689257	7.224487	12.730924
C	5.615099	6.742057	12.731685	C	5.608745	6.551710	12.792042
H	4.806072	7.452648	12.775515	H	4.758126	7.214348	12.868636
C	5.630135	5.408825	13.147464	C	5.767767	5.257086	13.291108
H	4.834289	4.846145	13.611876	H	5.062891	4.664771	13.855176
C	6.907361	4.972511	12.834860	C	7.049676	4.901530	12.898824
H	7.381458	4.017908	12.998958	H	7.609570	3.997054	13.079280
C	9.397778	6.198671	9.122887	C	9.557169	6.167310	9.088645
H	9.936114	5.264479	9.103916	H	10.154449	5.270971	9.136937
C	9.028157	7.051025	8.097655	C	9.219825	6.962936	8.006181
H	9.221985	6.938299	7.041591	H	9.509024	6.828056	6.974717
C	8.354444	8.091559	8.743348	C	8.427815	7.972090	8.559371
H	7.894525	8.965657	8.311692	H	7.949251	8.811278	8.073941
C	9.838949	4.704578	11.591153	C	9.879268	4.717552	11.569307
C	11.242485	4.636111	11.667791	C	11.275782	4.653467	11.722905
H	11.808216	5.533881	11.901876	H	11.823378	5.551285	11.997177
C	11.945954	3.455223	11.429960	C	11.994535	3.475788	11.514299
H	13.030669	3.449506	11.505131	H	13.073705	3.471767	11.647335
C	11.263165	2.289678	11.088831	C	11.334042	2.310988	11.129704
H	11.805861	1.365514	10.907767	H	11.888716	1.389894	10.970427
C	9.876588	2.331715	10.960615	C	9.954851	2.347915	10.932937
H	9.329076	1.439966	10.664800	H	9.426547	1.455077	10.606938
C	9.186715	3.520956	11.197173	C	9.250043	3.533402	11.140224
H	8.111594	3.526795	11.039118	H	8.181857	3.538509	10.937446
C	6.959792	11.209104	14.970820	C	7.072495	11.238441	15.047124
H	7.447529	11.862292	15.676772	H	7.638854	11.839462	15.741394
C	5.681985	10.674027	14.973967	C	5.785513	10.729789	15.141848
H	4.898990	10.835419	15.699577	H	5.082209	10.862407	15.950312
C	5.645998	9.873748	13.829935	C	5.619426	10.009040	13.957417
H	4.830446	9.282459	13.447353	H	4.763708	9.444584	13.614322
C	9.403017	12.500160	11.255765	C	9.580620	12.535094	11.251443
H	9.953225	13.247946	11.804375	H	10.184747	13.211742	11.834277
C	9.003177	12.460984	9.931864	C	9.236749	12.567358	9.910005
H	9.180194	13.200333	9.165339	H	9.527113	13.301700	9.173666
C	8.324940	11.244519	9.814693	C	8.436595	11.435343	9.736634
H	7.841191	10.824740	8.947452	H	7.951402	11.069300	8.842490
C	9.888784	12.163948	14.113014	C	9.916175	12.165554	14.099756
C	11.294559	12.161126	14.181184	C	11.314628	12.107031	14.239869
H	11.845031	11.303513	13.803685	H	11.847723	11.223639	13.898250
C	12.018550	13.235868	14.697344	C	12.053023	13.156971	14.786656
H	13.104205	13.187171	14.732879	H	13.132779	13.066817	14.878017
C	11.354785	14.371028	15.157722	C	11.411113	14.319465	15.207923
H	11.913588	15.209272	15.565715	H	11.980964	15.138417	15.639238

C	9.965746	14.425250	15.066575	C	10.030439	14.425486	15.051014
H	9.432202	15.314977	15.392471	H	9.516169	15.335790	15.350022
C	9.254991	13.344868	14.543021	C	9.305674	13.370136	14.497306
H	8.177734	13.444990	14.441545	H	8.236646	13.503007	14.350140
C	5.091608	8.330134	9.683729	C	4.816747	8.357624	9.573535
H	5.368482	7.315470	9.967649	H	5.120180	7.357430	9.884378
H	5.444089	8.523109	8.660981	H	5.097725	8.503991	8.520967
C	3.602100	8.660660	9.829873	C	3.333522	8.685307	9.804769
H	3.073514	8.547711	8.879591	H	2.760125	8.597033	8.878101
H	3.127890	7.989367	10.551093	H	2.889923	7.997889	10.530030
C	3.593381	10.120831	10.347153	C	3.348932	10.133703	10.354185
H	3.108633	10.184385	11.325294	H	2.984521	10.160706	11.384888
H	3.064643	10.801696	9.674765	H	2.726474	10.814733	9.767715
C	5.078503	10.484176	10.453708	C	4.827622	10.530192	10.299833
H	5.432171	10.988607	9.544157	H	5.074253	11.024655	9.348949
H	5.343212	11.090303	11.319250	H	5.166506	11.157324	11.124984
Fe	7.582420	8.870303	11.610087	Fe	7.469504	8.906629	11.500446
N	9.229020	8.495942	12.682562	N	9.299164	8.519397	12.617657
N	6.799763	7.092644	12.215722	N	6.712606	6.949671	12.148429
N	7.578050	5.986981	12.252882	N	7.589494	5.920388	12.198483
N	8.324079	7.884721	10.064396	N	8.301128	7.798365	9.877635
N	8.960951	6.717844	10.291026	N	8.995047	6.685545	10.203709
N	6.819118	9.911403	13.185534	N	6.723602	10.075423	13.204185
N	7.610768	10.762530	13.877840	N	7.608601	10.852363	13.871105
N	8.321498	10.593018	10.982962	N	8.311201	10.769426	10.887647
N	8.979158	11.371576	11.865451	N	9.014596	11.447484	11.821138
O	5.749617	9.225472	10.588352	O	5.537079	9.290909	10.385511

Table S2. Cartesian coordinates for compound **1** in low spin and high spin states.

1 (Low Spin) 66 scf done: -1786.114855				**1 (High Spin)** 66 scf done: -1786.137856			
B	0.311369	4.691458	15.661610	B	0.275676	4.700703	15.586327
B	5.084497	4.850328	13.833771	B	5.064093	4.845553	13.761657
C	1.888766	4.951136	15.976246	C	1.862874	4.959302	15.924368
C	2.375330	5.139764	17.273125	C	2.351978	5.055874	17.232390
H	1.674982	5.161015	18.099988	H	1.660981	5.037364	18.067748
C	3.738866	5.257632	17.502802	C	3.721451	5.133758	17.456966
H	4.123721	5.368917	18.513674	H	4.108251	5.181870	18.472562
C	4.600857	5.232989	16.415699	C	4.593466	5.139595	16.374617
H	5.670679	5.329840	16.560136	H	5.664670	5.187379	16.535408
C	4.105742	5.037553	15.122976	C	4.090936	5.036453	15.072259
C	-0.339359	2.097884	15.888464	C	-0.290641	2.134814	16.042833
H	-0.914822	2.216449	16.792662	H	-0.797948	2.336834	16.973299
C	-0.060455	0.963493	15.143301	C	-0.016136	0.929067	15.413919
H	-0.399353	-0.045569	15.322437	H	-0.285789	-0.062898	15.743641
C	0.762686	1.425289	14.114979	C	0.684198	1.297637	14.264929
H	1.194188	0.867721	13.298908	H	1.087578	0.671589	13.481611
C	-1.179524	6.209429	14.091345	C	-1.195664	6.324676	14.115980
H	-1.848623	6.493646	14.888008	H	-1.783822	6.638226	14.963593
C	-1.200932	6.513872	12.741497	C	-1.286366	6.681735	12.780507
H	-1.919385	7.120947	12.211932	H	-1.986078	7.368622	12.328846
C	-0.078751	5.862491	12.223362	C	-0.270524	5.950887	12.161491
H	0.272025	5.832805	11.203920	H	0.015219	5.923103	11.119184
C	-0.753517	5.155359	16.793467	C	-0.775678	5.160163	16.735942
C	-0.523883	6.308609	17.566989	C	-0.524975	6.279924	17.549479
H	0.411409	6.850148	17.454042	H	0.422155	6.804951	17.458381

C	-1.468484	6.805120	18.465136	C	-1.463684	6.762849	18.461828
H	-1.244342	7.697367	19.044616	H	-1.225378	7.630061	19.072847
C	-2.697689	6.166564	18.612823	C	-2.704442	6.141681	18.584559
H	-3.435413	6.545675	19.315153	H	-3.437291	6.510415	19.297494
C	-2.977270	5.049528	17.828800	C	-3.001292	5.054027	17.765475
H	-3.943841	4.557456	17.905491	H	-3.975499	4.575017	17.826892
C	-2.024802	4.566853	16.930878	C	-2.055516	4.585330	16.853804
H	-2.301124	3.727653	16.298665	H	-2.336970	3.764435	16.199089
C	3.899414	1.504579	13.014095	C	4.060445	1.391193	13.035099
H	3.064871	0.892355	12.713048	H	3.270909	0.724266	12.719002
C	5.219790	1.117591	13.247885	C	5.364608	1.087429	13.428456
H	5.644815	0.127555	13.181887	H	5.834621	0.117845	13.495243
C	5.861587	2.296253	13.591998	C	5.925954	2.322580	13.716795
H	6.883318	2.475763	13.886157	H	6.911445	2.574408	14.076330
C	3.044452	5.888126	10.991308	C	3.135741	6.007863	10.839503
H	2.114210	5.792483	10.453229	H	2.232112	5.936368	10.250241
C	4.193877	6.595194	10.628612	C	4.270764	6.791971	10.626736
H	4.352967	7.195057	9.745430	H	4.461512	7.487669	9.823640
C	5.082122	6.356657	11.662796	C	5.105739	6.475009	11.686026
H	6.094655	6.695384	11.815179	H	6.092269	6.836080	11.928995
C	6.602079	5.403249	13.980801	C	6.583367	5.394215	13.930625
C	6.863990	6.580213	14.706931	C	6.860772	6.535053	14.705344
H	6.050734	7.074716	15.231500	H	6.056254	7.011987	15.258892
C	8.133037	7.156055	14.762555	C	8.135975	7.096932	14.773656
H	8.288299	8.064030	15.340133	H	8.305166	7.977848	15.388090
C	9.195872	6.575059	14.074209	C	9.187274	6.535941	14.051983
H	10.188381	7.015716	14.118556	H	10.183903	6.966241	14.105622
C	8.962842	5.434668	13.308878	C	8.939135	5.428065	13.243861
H	9.772676	4.985712	12.738894	H	9.741557	4.994635	12.651782
C	7.686767	4.872736	13.257752	C	7.657968	4.880250	13.180337
H	7.534341	4.016109	12.607178	H	7.490106	4.045010	12.505201
Fe	2.157181	4.061083	13.273592	Fe	2.102711	3.990902	13.128803
N	2.771844	4.839764	14.948034	N	2.750445	4.918746	14.898914
N	0.977313	2.741753	14.235840	N	0.826264	2.627217	14.205561
N	0.265513	3.154168	15.310877	N	0.201701	3.141203	15.293550
N	0.575270	5.216084	13.195662	N	0.386232	5.211575	13.059878
N	-0.108557	5.425230	14.338679	N	-0.185625	5.439669	14.265077
N	3.748989	2.820658	13.211910	N	3.847392	2.711355	13.086183
N	4.971599	3.305995	13.534848	N	5.009662	3.283868	13.484848
N	3.226697	5.274094	12.166461	N	3.276921	5.274941	11.947830
N	4.481302	5.556625	12.569554	N	4.492669	5.560806	12.469339

Table S3. Cartesian coordinates for compound **3•Ar** in low spin and high spin states.

3.Ar (Low Spin) 90 scf done: -2229.5556793				**3.Ar (High Spin)** 90 scf done: -2229. 534326			
C	7.001476	3.357401	18.067760	C	6.995357	3.049252	18.625588
C	8.323145	3.203124	18.527600	C	8.330784	2.941734	19.058384
C	9.280325	2.871551	17.550353	C	9.262653	2.541134	18.082849
C	8.937259	2.651229	16.216209	C	8.883158	2.206600	16.782697
C	7.612070	2.771229	15.803765	C	7.545317	2.279400	16.401743
C	6.645539	3.140627	16.736674	C	6.602473	2.717714	17.328989
B	8.741998	3.582485	20.041251	B	8.787912	3.455013	20.524967
C	9.082246	5.173280	20.177552	C	9.102423	5.067301	20.494909
N	9.456130	5.670853	21.384722	N	9.478662	5.736828	21.615785
C	9.744109	6.988035	21.555057	C	9.760738	7.065614	21.615455
C	9.656293	7.856974	20.464650	C	9.648269	7.775868	20.415220

C	9.277571	7.382472	19.217641	C	9.262314	7.133133	19.249607
C	8.991806	6.032660	19.080149	C	8.993255	5.773632	19.293001
Fe	9.572636	4.439221	22.967359	Fe	9.602240	4.717974	23.343362
N	11.278919	5.307542	23.516734	N	11.357232	5.757753	23.802488
C	12.310461	4.804379	24.203198	C	12.383453	5.384911	24.572869
C	13.142593	5.834502	24.644007	C	13.176694	6.489872	24.887537
C	12.530183	6.991591	24.189736	C	12.538340	7.554587	24.269660
N	11.418471	6.654020	23.505464	N	11.457924	7.089687	23.608702
B	10.187332	7.519278	23.028957	B	10.227221	7.847708	22.981591
C	10.499318	9.101695	23.013644	C	10.567854	9.397537	22.659476
C	9.475737	10.063782	23.095969	C	9.580657	10.399703	22.687573
C	9.727341	11.430145	22.971066	C	9.846760	11.716450	22.310800
C	11.024015	11.886178	22.743790	C	11.119126	12.076773	21.872717
C	12.054556	10.957322	22.615470	C	12.109062	11.099378	21.793478
C	11.789564	9.593652	22.741156	C	11.829865	9.786467	22.172310
N	9.659684	3.328353	24.273688	N	9.693871	3.811300	24.828937
C	9.709771	2.426844	25.231443	C	9.700521	2.639128	25.470193
N	7.828642	3.618011	22.382085	N	7.856200	3.731610	22.844805
C	6.849724	3.077784	23.114998	C	6.890007	3.250527	23.634975
C	5.992840	2.336026	22.300543	C	6.079326	2.369203	22.919450
C	6.531870	2.460251	21.029506	C	6.639494	2.341709	21.650526
N	7.625844	3.244722	21.098232	N	7.693035	3.182292	21.621851
N	10.488895	3.096820	21.780495	N	10.681799	3.223480	22.157718
N	9.990001	2.779708	20.564407	N	10.063506	2.714610	21.069196
C	10.586033	1.656875	20.116317	C	10.656025	1.554223	20.714697
C	11.515768	1.241328	21.056857	C	11.715498	1.316595	21.576730
C	11.409604	2.177134	22.086862	C	11.682612	2.394219	22.466477
N	8.688792	5.808369	24.106536	N	8.576952	6.454026	24.254437
N	9.060232	7.109723	24.056820	N	9.103925	7.683262	24.065282
C	8.551591	7.756525	25.125484	C	8.683989	8.511974	25.045309
C	7.809599	6.860812	25.878736	C	7.829670	7.810741	25.881660
C	7.936676	5.648229	25.200686	C	7.806914	6.520769	25.342832
H	9.888147	8.904712	20.610557	H	9.869315	8.835803	20.411016
H	9.205971	8.054438	18.365905	H	9.174580	7.684734	18.316606
H	8.693204	5.622847	18.123252	H	8.695095	5.244367	18.396749
H	10.303169	1.224643	19.169604	H	10.286915	0.974958	19.882702
H	12.171582	0.385511	21.006580	H	12.404976	0.485827	21.560102
H	11.920068	2.203895	23.037230	H	12.319847	2.603069	23.312980
H	10.330396	2.810124	17.823756	H	10.320731	2.515847	18.328585
H	9.711015	2.392741	15.497492	H	9.638547	1.897879	16.064175
H	7.338991	2.595066	14.766764	H	7.244523	2.017219	15.390877
H	12.382203	3.742558	24.385179	H	12.483662	4.354093	24.879640
H	14.058626	5.748773	25.208458	H	14.077306	6.516604	25.482378
H	12.806960	8.026827	24.312994	H	12.772740	8.607752	24.270490
H	8.445443	9.743559	23.226350	H	8.567527	10.145886	22.988231
H	8.905234	12.137860	23.043950	H	9.054091	12.459559	22.352835
H	11.226149	12.949983	22.652030	H	11.331947	13.101793	21.580793
H	6.216295	2.037429	20.088791	H	6.363163	1.774907	20.775219
H	5.110215	1.788757	22.594824	H	5.216241	1.824203	23.270823
H	6.822590	3.212183	24.185439	H	6.842240	3.543957	24.672679
H	6.226783	3.685804	18.755677	H	6.239282	3.429787	19.307338
H	5.610807	3.268845	16.428486	H	5.558103	2.812541	17.041778
H	7.567139	4.671298	25.473185	H	7.285928	5.641806	25.693857
H	7.258492	7.056808	26.785883	H	7.306333	8.181824	26.750247
H	8.755555	8.803445	25.284674	H	9.023897	9.535156	25.089224
H	12.610479	8.896266	22.593257	H	12.613676	9.041377	22.060956
H	13.068102	11.292230	22.409065	H	13.100290	11.355765	21.427367
C	10.091786	2.797017	26.561569	C	9.861841	2.628917	26.889271

C	10.137177	1.844462	27.566941	C	9.873090	1.441598	27.593796
C	9.820617	0.493216	27.365609	C	9.713723	0.191955	26.960007
C	9.451861	0.139979	26.062390	C	9.543891	0.202614	25.566185
C	9.394069	1.050414	25.017526	C	9.540091	1.377636	24.829714
H	10.341034	3.834665	26.759063	H	9.981586	3.581173	27.397407
H	10.436045	2.189613	28.555611	H	10.005264	1.483650	28.672020
C	9.885728	-0.492946	28.518724	C	9.727121	-1.094105	27.791258
H	9.194040	-0.889505	25.828421	H	9.411786	-0.731879	25.030875
H	9.104028	0.739860	24.019183	H	9.404744	1.351238	23.754796
C	9.504468	-1.901956	28.077426	C	9.542445	-2.349106	26.927237
C	11.309847	-0.536841	29.082380	C	11.075456	-1.213037	28.530215
C	8.918040	-0.060120	29.625103	C	8.582429	-1.048321	28.823685
H	9.558965	-2.580627	28.933933	H	9.561982	-3.240295	27.563188
H	8.483296	-1.930103	27.686180	H	8.583315	-2.342983	26.398563
H	10.185038	-2.274237	27.306274	H	10.342264	-2.455608	26.186636
H	8.964557	-0.759860	30.465660	H	8.580735	-1.960918	29.430881
H	9.168711	0.937781	29.995397	H	8.679569	-0.197068	29.504593
H	7.891801	-0.035169	29.247088	H	7.610128	-0.968604	28.326461
H	11.364911	-1.237314	29.921914	H	11.096594	-2.124233	29.139082
H	12.015598	-0.858824	28.311061	H	11.908019	-1.258790	27.820451
H	11.620029	0.449653	29.437644	H	11.251800	-0.363738	29.197310

Table S4. Cartesian coordinates for compound **3•Ar** in the intermediate S = 1 spin state.

3.Ar (Intermediate Spin) 90 scf done: -2229.574994			
C	7.079645	2.856659	18.772183
C	8.413843	2.823720	19.220802
C	9.369174	2.421634	18.268082
C	9.015153	2.008385	16.983719
C	7.678492	2.001442	16.592322
C	6.711528	2.445346	17.491187
B	8.847795	3.426537	20.659194
C	9.107486	5.039987	20.550770
N	9.475158	5.743767	21.651410
C	9.707205	7.079866	21.615699
C	9.540058	7.760055	20.403236 -
C	9.157449	7.077592	19.258984
C	8.947660	5.707998	19.334185 -
Fe	9.662375	4.713867	23.425712
N	11.343759	5.829812	23.832536
C	12.379494	5.497713	24.606451
C	13.172586	6.619016	24.860700
C	12.524266	7.650146	24.200843
N	11.435565	7.151729	23.576712
B	10.189915	7.891765	22.954780
C	10.518128	9.434660	22.588672
C	9.529638	10.435229	22.624860
C	9.779197	11.742962	22.207218
C	11.035300	12.095307	21.718640
C	12.025019	11.118290	21.630949
C	11.762077	9.814443	22.050446
N	9.782744	3.884100	24.900498
C	9.740253	2.656126	25.457873
N	7.955699	3.827221	22.969286
C	6.936784	3.492249	23.768423
C	6.075881	2.620142	23.102498
C	6.654328	2.451244	21.853621

N	7.774474	3.198804	21.787544
N	10.722689	3.336818	22.326532
N	10.143087	2.757964	21.251906
C	10.825635	1.641020	20.926655
C	11.897650	1.504135	21.795732
C	11.784969	2.595410	22.658363
N	8.614591	6.509066	24.317711
N	9.100052	7.744261	24.070557
C	8.718873	8.590621	25.053874
C	7.933974	7.891789	25.955559
C	7.911358	6.587567	25.447912
H	9.718499	8.827739	20.371348
H	9.028314	7.606030	18.317313
H	8.656099	5.145611	18.455619
H	10.508459	1.018652	20.104851
H	12.648200	0.728147	21.799821
H	12.403652	2.872785	23.497179
H	10.426151	2.460809	18.515955
H	9.789632	1.701998	16.284823
H	7.397149	1.676951	15.594076
H	12.478889	4.487069	24.973292
H	14.078308	6.675723	25.445575
H	12.754319	8.702780	24.147930
H	8.527986	10.186472	22.965597
H	8.986134	12.485226	22.257368
H	11.235343	13.113338	21.394835
H	6.346645	1.846055	21.015947
H	5.167395	2.171481	23.474607
H	6.893395	3.868448	24.777784
H	6.302291	3.246669	19.423174
H	5.666583	2.484223	17.193373
H	7.440643	5.706744	25.860388
H	7.454178	8.271618	26.845385
H	9.036780	9.621808	25.053762
H	12.544198	9.068459	21.932075
H	13.002986	11.367776	21.226280
C	10.046848	2.537733	26.842424
C	9.992103	1.314137	27.483290 -
C	9.649803	0.131305	26.800239
C	9.357831	0.245746	25.432087
C	9.392011	1.464319	24.770269
H	10.315607	3.440217	27.383591
H	10.226864	1.274377	28.543927
C	9.609211	-1.201257	27.553258
H	9.092536	-0.636803	24.859567
H	9.159949	1.515556	23.712341
C	9.226477	-2.375641	26.642072
C	10.999373	-1.491287	28.154931
C	8.570123	-1.112465	28.689451
H	9.213087	-3.303415	27.223429
H	8.230270	-2.246005	26.206002
H	9.944389	-2.508994	25.825806
H	8.531468	-2.057143	29.243896
H	8.812691	-0.318008	29.401659
H	7.570512	-0.910659	28.290839
H	10.985620	-2.440471	28.702731
H	11.759185	-1.562355	27.369793
H	11.312725	-0.709463	28.853313

Table S5. Cartesian coordinates for the transition state of Hydrogen Atom Transfer from toluene to **3•Ar**.

TS For C-H activation of Toluene 105 scf done: -2501.010295			
N	11.739155	7.087552	23.354955
N	11.549024	5.784913	23.659532
C	12.638758	5.368845	24.311024
C	13.555524	6.413600	24.446088
C	12.932461	7.491929	23.836897
Fe	9.737917	4.925287	23.463675
N	7.878131	4.216452	23.143061
N	7.581224	3.504416	22.034245
C	6.370771	2.929158	22.177020
C	5.841572	3.307184	23.400797
C	6.828393	4.115397	23.966332
B	8.649685	3.437658	20.886155
C	8.094616	2.756275	19.524587
C	6.774007	2.966356	19.083853
C	6.309033	2.492338	17.857586
C	7.164228	1.800112	17.003305
C	8.493194	1.623842	17.381296
C	8.944074	2.103828	18.611270
B	10.556217	7.877148	22.680863
C	10.031136	7.001532	21.411723
N	9.622355	5.724968	21.608461
C	9.148120	4.963633	20.591030
C	9.092384	5.498303	19.300888
C	9.514616	6.797227	19.061407
C	9.982021	7.550915	20.126797
N	9.898622	4.140158	25.124831
C	9.926644	2.839500	25.585679
C	8.954375	1.886535	25.210303
C	8.996635	0.580086	25.681953
C	9.993144	0.130787	26.556310
C	10.972942	1.069746	26.916368
C	10.952704	2.373685	26.446065
C	10.052911	-1.297913	27.106487
C	11.373339	-1.963196	26.668767
N	9.022900	6.631079	24.227090
N	9.443855	7.840126	23.787379
C	8.896425	8.807534	24.552714
C	8.075679	8.219584	25.498229
C	8.206069	6.851500	25.260974
N	10.477901	3.267287	22.586423
N	9.840935	2.674338	21.550793
C	10.384071	1.462825	21.320820
C	11.432182	1.270665	22.204038
C	11.445581	2.431328	22.977081
C	10.962684	9.369808	22.199452
C	10.004940	10.394438	22.074067
C	10.316844	11.649943	21.551914
C	11.608101	11.923837	21.107079
C	12.565705	10.914207	21.159394
C	12.240309	9.663697	21.685054
C	9.990731	-1.257828	28.646876

C	8.889792	-2.162952	26.602480
H	10.312331	8.571436	19.976893
H	9.476120	7.217171	18.059012
H	8.715704	4.883870	18.492707
H	9.984503	0.813431	20.559101
H	12.079964	0.411397	22.286780
H	12.079440	2.670068	23.813465
H	9.999518	1.992678	18.841027
H	9.188108	1.120796	16.713090
H	6.807005	1.425232	16.047699
H	12.700380	4.359119	24.682120
H	14.527157	6.390774	24.916335
H	13.254833	8.515156	23.726313
H	8.973440	10.203389	22.355691
H	9.543000	12.410711	21.482727
H	11.856982	12.901327	20.702899
H	5.969833	2.287964	21.408593
H	4.886552	3.032275	23.822126
H	6.841234	4.585811	24.933933
H	6.089243	3.547675	19.694430
H	5.277927	2.676142	17.565607
H	7.800653	6.025277	25.820354
H	7.511601	8.706120	26.278072
H	9.147357	9.844141	24.397289
H	13.000944	8.888274	21.658433
H	13.568565	11.093148	20.779713
H	11.753680	3.045550	26.734173
H	11.785720	0.775447	27.576500
H	8.217193	-0.099137	25.352410
H	8.162674	2.178379	24.534232
H	8.971194	-3.171788	27.020859
H	7.919437	-1.756633	26.906771
H	8.895313	-2.256815	25.511353
H	10.032554	-2.273305	29.058072
H	10.825281	-0.692380	29.073087
H	9.061868	-0.789666	28.988715
H	11.430534	-2.989077	27.051358
H	11.448245	-2.001934	25.577032
H	12.246081	-1.420039	27.044651
H	10.317723	4.922742	26.103778
C	10.800549	5.363398	27.279686
C	10.355105	6.674314	27.756117
H	10.480452	4.532535	27.910148
H	11.869371	5.323148	27.062076
C	9.242459	6.794055	28.611280
C	8.855520	8.029568	29.117600
C	9.568616	9.181936	28.778724
C	10.670689	9.083389	27.926543
C	11.058187	7.847609	27.420479
H	8.694618	5.897877	28.893322
H	8.002876	8.095791	29.788610
H	9.272039	10.147213	29.180544
H	11.233545	9.974958	27.661629
H	11.921446	7.774495	26.763340

Table S6. Cartesian coordinates for compound **2•Ar** in the low spin state.

2.Ar 91 scf done: -2230.237628			
C	9.435240	1.589703	24.846769
C	9.818671	2.736929	25.573010
C	10.086377	2.550328	26.952234
C	9.978649	1.306900	27.551319
C	9.599049	0.162448	26.828770
C	9.333269	0.348466	25.466555
N	9.940917	3.986284	25.014487
Fe	9.727379	4.810984	23.362248
N	8.827059	6.351605	24.300886
N	9.156826	7.633142	24.024063
C	8.630796	8.444853	24.963980
C	7.911983	7.676788	25.864967
C	8.074523	6.368197	25.407190
B	10.229726	7.890859	22.904170
C	10.472149	9.457697	22.584587
C	9.421615	10.394085	22.611350
C	9.598839	11.724095	22.229463
C	10.842052	12.165470	21.782122
C	11.890465	11.252449	21.694039
C	11.699737	9.925477	22.079165
C	9.493550	-1.194428	27.532696
C	8.447198	-1.109357	28.661628
N	9.519282	5.764844	21.620131
C	9.131008	5.056460	20.529939
C	8.976968	5.713605	19.306081
C	9.219211	7.075874	19.207190
C	9.615866	7.767114	20.342248
C	9.765480	7.096785	21.559692
B	8.852311	3.453363	20.666878
N	10.141720	2.794002	21.271486
N	10.663928	3.342221	22.392234
C	11.691276	2.573161	22.767266
C	11.841002	1.501143	21.887111
C	10.824255	1.672411	20.962298
C	8.411765	2.833522	19.238023
C	7.074777	2.852420	18.797752
C	6.702052	2.426382	17.522713
C	7.666776	1.980972	16.622236
C	9.005808	2.000624	17.005390
C	9.364489	2.429037	18.283392
N	7.791858	3.249328	21.805791
N	8.016149	3.859172	22.991943
C	7.037311	3.483190	23.821494
C	6.163226	2.608599	23.175215
C	6.691184	2.476054	21.901493
N	11.422078	5.839407	23.715540
C	12.510819	5.494658	24.413000
C	13.308021	6.614613	24.655168
C	12.615479	7.659694	24.066748
N	11.496242	7.170948	23.494262
C	9.071871	-2.315158	26.572402
C	10.861680	-1.570038	28.136378
H	9.813976	8.831141	20.299873
H	9.100576	7.592023	18.257448
H	8.666251	5.143906	18.438827

H	10.537070	1.066299	20.117917
H	12.572372	0.708311	21.925813
H	12.245004	2.796283	23.663612
H	10.422617	2.477921	18.525193
H	9.778101	1.692115	16.304969
H	7.381689	1.644780	15.628916
H	12.653080	4.475432	24.734568
H	14.247480	6.659349	25.184972
H	12.835520	8.714807	24.033920
H	8.425348	10.077310	22.908495
H	8.758810	12.413095	22.272684
H	10.986011	13.201238	21.486389
H	6.365163	1.875182	21.067676
H	5.284163	2.130122	23.579356
H	7.027782	3.820392	24.844280
H	6.298621	3.240847	19.451206
H	5.654983	2.454064	17.231025
H	7.715571	5.446927	25.837434
H	7.357747	8.014861	26.727428
H	8.816057	9.506872	24.941020
H	12.527336	9.232764	21.951235
H	12.858945	11.569182	21.314740
H	10.385124	3.409900	27.550789
H	10.197848	1.227297	28.613529
H	9.035144	-0.495238	24.852363
H	9.217789	1.674709	23.789427
H	9.012296	-3.264811	27.114961
H	8.087468	-2.124733	26.131661
H	9.792334	-2.444995	25.757750
H	8.364913	-2.070391	29.183128
H	8.712293	-0.349620	29.403567
H	7.460850	-0.853604	28.260655
H	10.802708	-2.536514	28.650824
H	11.625566	-1.645486	27.355394
H	11.202062	-0.826687	28.863937
H	10.230950	4.659346	25.718644

Table S7. Crystal Data Collection and Refinement Parameters for Compounds **B_2Pz_4Py, 1·THF, and 1.**

	B_2Pz_4Py	**1·THF**	**1**
chemical formula	$C_{58}H_{52}B_4Li_2N_{18}$	$C_{33}H_{33}B_2FeN_9O$, C_4H_8O	$C_{29}H_{25}B_2FeN_9$
crystal colour	Colourless	Yellow	Green
***Fw*; *F*(000)**	1058.29; 2208	721.26; 756	577.05; 1192
***T* (K)**	173(2)	173(2)	173(2)
wavelength (Å)	1.54178	1.54178	1.54178
space group	C2/c	P-1	P21/c
***a* (Å)**	18.1814(16)	8.6690(4)	14.0554(2)
***b* (Å)**	21.881(3)	12.5893(6)	8.4226(1)
***c* (Å)**	16.8907(14)	17.1783(7)	26.8488(3)
α (deg)	90	88.370(2)	90
β (deg)	102.199(6)	78.459(2)	121.048(1)
γ (deg)	90	73.105(3)	90
Z	4	2	4
V (Å^3)	6567.8(11)	1756.7(1)	2723.08(6)
ρ_{calcd} (g·cm^{-3})	1.070	1.364	1.408
μ (mm^{-1})	0.520	3.825	4.739
θ range (deg); completeness	3.204 − 67.124; 0.976	2.626 − 66.879; 0.955	3.670 − 66.996; 0.974
collected reflections; R_σ	19213; 0.0410	22929; 0.0349	17556; 0.0284
unique reflections; R_{int}	19213; 0.0370	22929; 0.0420	17556; 0.0373
R1^a; wR2^b [$I > 2\sigma(I)$]	0.0513; 0.1341	0.0370; 0.0960	0.0315; 0.0814
R1; wR2 [all data]	0.0722; 0.1453	0.0415; 0.0988	0.0356; 0.0844
GOF	0.967	1.057	1.029
largest diff peak and hole	0.580 and -0.197	0.284 and -0.317	0.184 and -0.337

Table S8. Crystal Data Collection and Refinement Parameters for Complexes **2·Ad**, **2·Ar**, and **4**.

	2·Ad	**2·Ar**	**4**
chemical formula	$C_{39}H_{41}B_2FeN_{10}$, C_6H_6	$C_{39}H_{39}B_2FeN_{10}$	$C_{68}H_{63}B_4Fe_2N_{19}O_2S$, C_6H_6
crystal colour	Blue	Sea green	Brown
***Fw*; *F*(000)**	805.39; 1692	725.27; 1516	1443.48; 1500
***T* (K)**	173(2)	173(2)	173(2)
wavelength (Å)	1.54178	1.54178	1.54178
space group	Pnma	Pnma	P-1
***a* (Å)**	16.6523(3)	25.518(4)	13.566(1)
***b* (Å)**	10.1363(2)	9.974(1)	16.623(1)
***c* (Å)**	29.6556(6)	13.879 (2)	19.612(2)
α (deg)	90	90	68.407(3)
β (deg)	90	90	83.226(3)
γ (deg)	90	90	68.207(3)
Z	4	4	2
***V* ($Å^3$)**	5005.7(2)	3532.5(8)	3817.4(6)
ρ_{calcd} ($g \cdot cm^{-3}$)	1.069	1.364	1.256
μ (mm^{-1})	2.708	3.776	3.758
θ range (deg); completeness	2.980 – 67.476; 0.996	3.464 – 67.483; 0.986	2.423 – 72.913; 0.965
collected reflections; R_σ	29896; 0.0248	14679; 0.0429	54443; 0.0928
unique reflections; R_{int}	29896; 0.0362	14679; 0.0502	54443; 0.0939
R1[a]; wR2[b] [I > 2σ(I)]	0.0424; 0.1143	0.0482; 0.1218	0.0769; 0.1918
R1; wR2 [all data]	0.0451; 0.1160	0.0686; 0.1329	0.1121; 0.2093
GOF	1.047	1.028	0.963
largest diff peak and hole	0.383 and -0.471	0.329 and -0.441	1.564 and -0.551

Table S9. Selected Bond Distances (Å) and Angles (deg) for Complexes **1·THF, 1, 2·Ad,** and **2·Ar.**

	1·THF	**1**	**2·Ad**	**2·Ar**
Fe1-N1	2.185(2)	2.098(1)	2.007(2)	1.994(3)
Fe1-N2	2.152(2)	2.159(2)	2.002(1)	1.982(2)
Fe1-N4	2.119(2)	2.101(2)	1.991(1)	2.002(3)
Fe1-X1	2.215(1)	-	1.854(2)	1.869(3)
Fe1-N1-X	178.43(6)	-	179.31(8)	178.34(2)
Fe1-N1-N2	89.74(6)	91.41(6)	90.69(6)	89.24(1)
Fe1-N1-N4	87.95(6)	89.96(6)	86.16(5)	89.33(1)

Table S10. Selected Bond Distances (Å) and Angles (deg) for Complex **4.**

Fe1-N1	2.144(4)	Fe2-O2	1.913(3)
Fe1-N2	2.082(4)	Fe2-N12	2.096(3)
Fe1-N4	2.119(4)	Fe2-N16	2.097(4)
Fe1-N6	2.125(4)	Fe2-N14	2.102(4)
Fe1-N10	1.909(4)	Fe2-N11	2.112(4)
Fe1-N8	2.157(4)	Fe2-N18	2.119(4)
S1-N10	1.504(4)	O2-Fe2-N12	98.0(1)
S1-O1	1.460(3)	O2-Fe2-N16	98.5(1)
S1-O2	1.512(3)	N12-Fe2-N16	94.0(1)
N10-Fe1-N2	96.2(2)	O2-Fe2-N14	90.2(1)
N10-Fe1-N6	94.7(2)	N12-Fe2-N14	84.9(1)
N2-Fe1-N4	85.6(2)	N16-Fe2-N14	171.3(2)
N4-Fe1-N6	167.6(2)	O2-Fe2-N11	173.1(1)
N10-Fe1-N1	176.9(2)	N12-Fe2-N11	87.3(1)

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