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Electronic Supplemental Information for:

"Unlocking Metal Coordination of Diborylamides through Ring Constraints"

by W. Kice Brown, Kevin K. Klausmeyer, Brian M. Lindley

Department of Chemistry & Biochemistry, Baylor University, One Bear Place #97348, Waco, TX 76798
Email: brian_lindley@baylor.edu

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1. General Considerations.

All synthetic procedures were conducted in a N_2 glovebox. Dry and degassed solvent was obtained by dispensing solvent from a JC Meyer solvent purification system and storing over molecular sieves. Degassed C_6D_6 was dried by passing through a plug of neutral alumina and storing over molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to C_6D_6 (^1H δ 7.16, ^{13}C δ 128.06).

2. Synthetic Details

1,2-bis(trimethylsilyl)benzene**.** We used a procedure adapted from Kitamura and coworkers.[1] In a N_2 glovebox, a 2-neck, 1L rb flask was charged with LiCl (16.98 g, 0.400 mol), CuCl (4.95 g, 0.0500 mol), Mg powder (9.73 g, 0.400 mol) and a magnetic stirbar. The flask was equipped with a rubber septum and a reflux condenser topped with a 180° needle valve. 1,3-Dimethyl-2-imidazolidinone (300 mL), TMSCl (100 mL, 0.600 mol), and 1,2-dichlorobenzene (5.7 mL, 0.050 mol) were added to the flask, resulting in a pale yellow solution with suspended gray solids. The mixture was heated at 55 °C for 20 h, then cooled to RT and carefully poured into a beaker with 250 mL hexanes, 250 mL sat. $NaHCO_{3(aq)}$, and a large scoop of ice. After bubbling subsided, the mixture was filtered through Celite and the layers were separated. The aqueous layer was extracted with hexanes (3 × 150 mL) and the combined organics were dried over $MgSO_4$, filtered, and dried *in vacuo* to give a pale yellow or pink liquid. Aromatic impurities were removed by vacuum distillation (40 °C, 50 mtorr), then the remaining yellow liquid was passed through a plug of silica gel (hexanes eluent) to remove polar impurities. Removal of hexanes *in vacuo* provided the pure product as a colorless to pale yellow oil (7.34 g, 66.0%). ^1H NMR resonances matched literature values.

1,2-bis(dichloroboryl)benzene (**1**). We used a procedure adapted from Kaufmann and Wegner.[2,3] In a N_2 glovebox, a heavy-walled Schlenk tube with Teflon plug was charged with 1,2-bis(trimethylsilyl)benzene (3.775 g, 16.92 mmol) and 1,2-dichloroethane (30 mL). The Schlenk tube was cooled to 0 °C and a solution of BCl_3 (1.0 M in heptane, 44 mL, 44 mmol) was added through intramedic tubing under a stream of N_2 over the course of 5 min. The colorless solution was stirred at 0 °C for 2 h, then sealed and heated to 100 °C, at which temperature stirring was continued for 5 days. The yellow mixture was cooled to RT and volatiles were removed *in vacuo* to give a yellow oil with colorless solid. In a N_2 glovebox, 15 mL of pentane was added to the Schlenk tube and the mixture filtered into a 100 mL rb flask. The solids were washed with pentane (3 × 2 mL). The filtrate was pumped down to give a yellow oil with colorless solid. The crude product was purified by flask-to-flask vacuum distillation (60 °C, 50 mtorr) to give the product as a colorless liquid (3.525 g, 87.0 % yield). Though the purity of the material is typically ~90 %, the compound can be used in subsequent reactions. ^1H NMR (C_6D_6): δ 6.90 (m, 3.3 Hz, AA'XX', 2H, Ar CH), 7.39 (m, 3.3 Hz, AA'XX', 2H, Ar CH). ^{11}B NMR (C_6D_6): δ 56.8 (br s, $\nu_{1/2}$ = 105 Hz).

2. To a heavy-walled rb flask with a Teflon adapter in a N_2 glovebox was added mesityllithium (2.086 g, 15.73 mmol, 2.20 equiv.) and toluene (60 mL). A solution of 1,2-bis(dichloroboryl)benzene (1.712 g, 7.15 mmol) in toluene (5 mL) was added slowly and the

reaction vessel sealed with a Teflon plug. The resultant cloudy colorless mixture was heated at 40 °C for 16 h, then cooled to RT and brought back into the N_2 glovebox. The mixture was filtered through Celite and dried *in vacuo* to give a yellow solid. The solid was triturated with pentane (2 × 5 mL), then suspended in pentane and filtered to obtain the product as a white solid (1.596 g, 54.9 % yield). ^{1}H NMR (C_6D_6): δ 2.14 (s, 6H, Mes *p*-CH_3), 2.30 (s, 12H, Mes *o*-CH_3), 6.73 (s, 4H, Mes *m*-CH), 6.99 (m, 3.3 Hz, AA'XX', 2H, Ar CH), 7.64 (m, 3.3 Hz, AA'XX', 2H, Ar CH). ^{13}C NMR (C_6D_6): δ 21.25 (s, Mes *p*-CH_3), 23.53 (s, Mes *o*-CH_3), 128.82 (s, Ar C), 131.54 (s, Ar C), 136.60 (s, Ar C), 137.90 (br s, Ar C-B), 139.94 (s, Ar C), 140.94 (s, Ar C), 148.93 (br s, C-B). ^{11}B NMR (C_6D_6): δ 66.40 (br s, $\nu_{1/2}$ = 1120 Hz).

3. Under a nitrogen atmosphere, a solution of **2** (676 mg, 1.66 mmol) in toluene (10 mL) was added to a Schlenk tube. A solution of NH_3 (11.5 mL, 0.5 M in dioxane, 5.75 mmol, 3.5 equiv.) was added slowly to the Schlenk tube, resulting in a cloudy colorless solution. The Schlenk tube was sealed with a Teflon plug and the mixture was stirred at 20 °C for 2 h, then heated at 85 °C for 17 h. After cooling back to 20 °C, the volatiles were removed in vacuo to give a colorless oil, which was triturated once with pentane (10 mL). More pentane (10 mL) was added to the oily residue and the resultant mixture was filtered through Celite. The filtrate was pumped down to give the product as a flocculent white solid (463 mg, 79.5% yield). X-ray quality crystals were grown by slow evaporation of a pentane solution of **3** at −35 °C. ^{1}H NMR (C_6D_6): δ 2.25 (s, 6H, Mes *p*-CH_3), 2.29 (s, 12H, Mes *o*-CH_3), 5.26 (br s, 1H, NH), 6.86 (s, 4H, Mes *m*-CH), 7.12 (m, 3 Hz, AA'XX', 2H, Ar CH), 7.42 (m, 3 Hz, AA'XX', 2H, Ar CH). ^{13}C NMR (C_6D_6): δ 21.40 (s, Mes *p*-CH_3), 22.42 (s, Mes *o*-CH_3), 127.67 (s, Ar C), 131.63 (s, Ar C), 131.99 (s, Ar C), 135.51 (br s, Ar C-B), 137.99 (s, Ar C), 139.14 (s, Ar C), 148.34 (br s, Ar C-B). ^{11}B NMR (C_6D_6): δ 55.64 (br s, $\nu_{1/2}$ = 660 Hz).

4. In a N_2 glovebox, a 20 mL scintillation vial was charged with **3** (463 mg, 1.32 mmol) and 12 mL Et_2O. After cooling the solution to −35 °C, a solution of ^{n}BuLi (0.84 mL, 1.6 M in hexanes, 1.34 mmol) was added dropwise, resulting in a change from colorless to pale yellow. The solution was allowed to warm to 25 °C, at which temperature stirring continued for 1 h. The reaction mixture was pumped down in vacuo to give the crude product as a waxy solid. The solid was triturated with 10 mL of pentane, then suspended in 8 mL pentane, filtered and washed with pentane (2 × 2 mL) and dried *in vacuo* to give the product as a white solid (297 mg, 63.0 % yield). X-ray quality crystals were grown by slow evaporation of a pentane:Et_2O solution of **4** at −35 °C. ^{1}H NMR (C_6D_6): δ 2.08 (s, 12H, Mes *o*-CH_3), 2.24 (s, 6H, Mes *p*-CH_3), 6.69 (s, 4H, Mes *m*-CH), 7.08 (m, 3 Hz, AA'XX', 2H, Ar CH), 7.26 (m, 3 Hz, AA'XX', 2H, Ar CH). ^{13}C NMR (C_6D_6): δ 21.44 (s, Mes *p*-CH_3), 21.77 (s, Mes *o*-CH_3), 128.69 (s, Ar C), 129.71 (s, Ar C), 130.21 (s, Ar C), 136.28 (br s, Ar C-B), 138.30 (s, Ar C), 139.42 (s, Ar C), 153.17 (br s, Ar C-B). ^{11}B NMR (C_6D_6): δ 56.9 (br s, $\nu_{1/2}$ = 1400 Hz).

Fe(^{Mes}BNB)$_2$ (**5**) and {Fe(^{Mes}BNB)(μ-Mes)}$_2$ (**6**). In a N_2 glovebox, a 25 mL rb flask was charged with diborylamide **4** (109 mg, 0.306 mmol), $FeCl_2$ (19.2 mg, 0.153 mmol), and a stirbar. The flask was equipped with a 180 ° needle valve with Teflon plug and evacuated on the Schlenk line. The flask was cooled to −78 °C and degassed Et_2O (8 mL) was transferred *in vacuo* to the flask. The reaction mixture was stirred at −78 °C for 4 h, then slowly allowed to warm to room temperature and stirred for 16 h, resulting in a pale orange-pink solution. The solvent was removed *in vacuo* and

the resultant pink-tan solid was extracted with pentane (10 mL). The solvent was removed from the filtrate to give the mixture of products **5** and **6** as a yellow-orange solid (62.1 mg). X-ray quality, yellow crystals of **5** were grown by slow evaporation of a pentane solution of **5** and **6**. X-ray quality, red crystals of **6** were grown by slow evaporation of an Et_2O solution of **5** and **6**. Though fractional crystallization of the mixture could be employed to enrich the sample in either **5** or **6**, pure samples of **5** and **6** proved elusive, so elemental analysis was not successful.

5: ^{1}H NMR (C_6D_6): δ 68.38 (s, 4H, $\nu_{1/2}$ = 270 Hz), 39.50 (s, 8H, $\nu_{1/2}$ = 86 Hz), 4.11 (s, 12H, $\nu_{1/2}$ = 43 Hz), −29.69 (s, 4H, $\nu_{1/2}$ = 700 Hz), −36.09 (s, 12H, $\nu_{1/2}$ = 190 Hz).

6: ^{1}H NMR (C_6D_6): δ 14.68 (s, 6H), 14.47 (s, 4H), 14.23 ("t", 4H, 3.5 Hz), 11.13 ("t", 4H, 3.5 Hz), 2.85 (s, 8H), 2,69 (s, 24H), −0.44 (s, 12H), −14.69 (s, 12H).

3. NMR Spectra

1,2-bis(dichloroboryl)benzene (1)

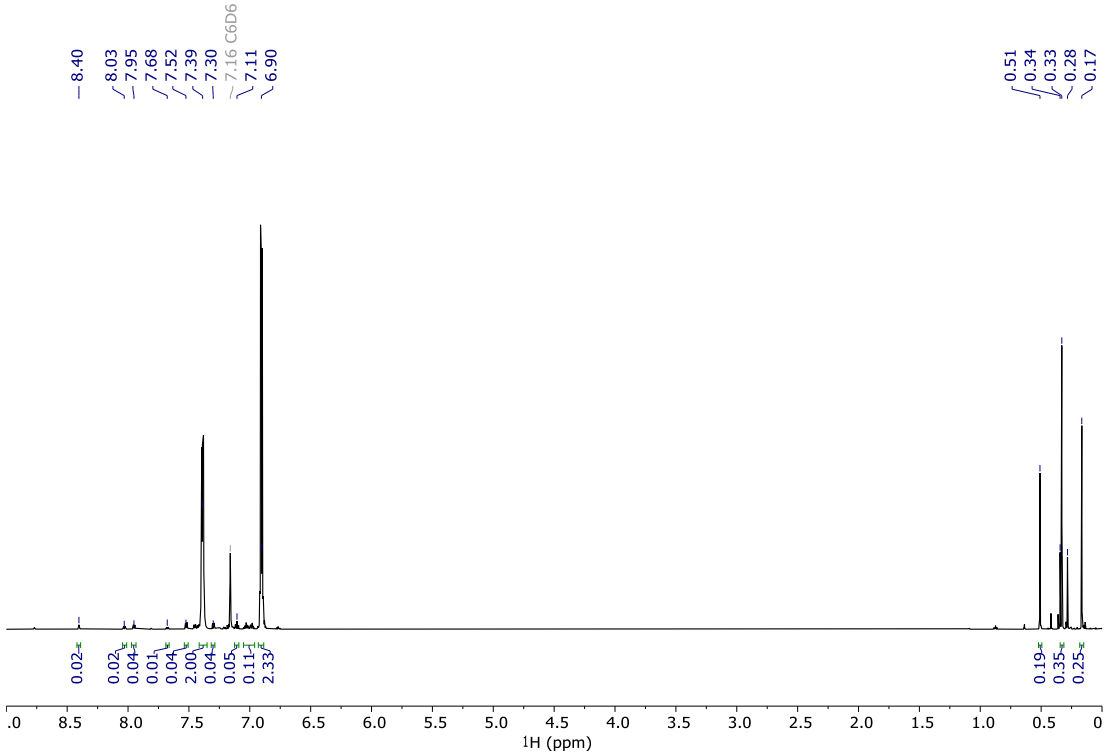


Figure S1. ^{1}H NMR spectrum of 1,2-bis(BCl_2)benzene (**1**) in C_6D_6.

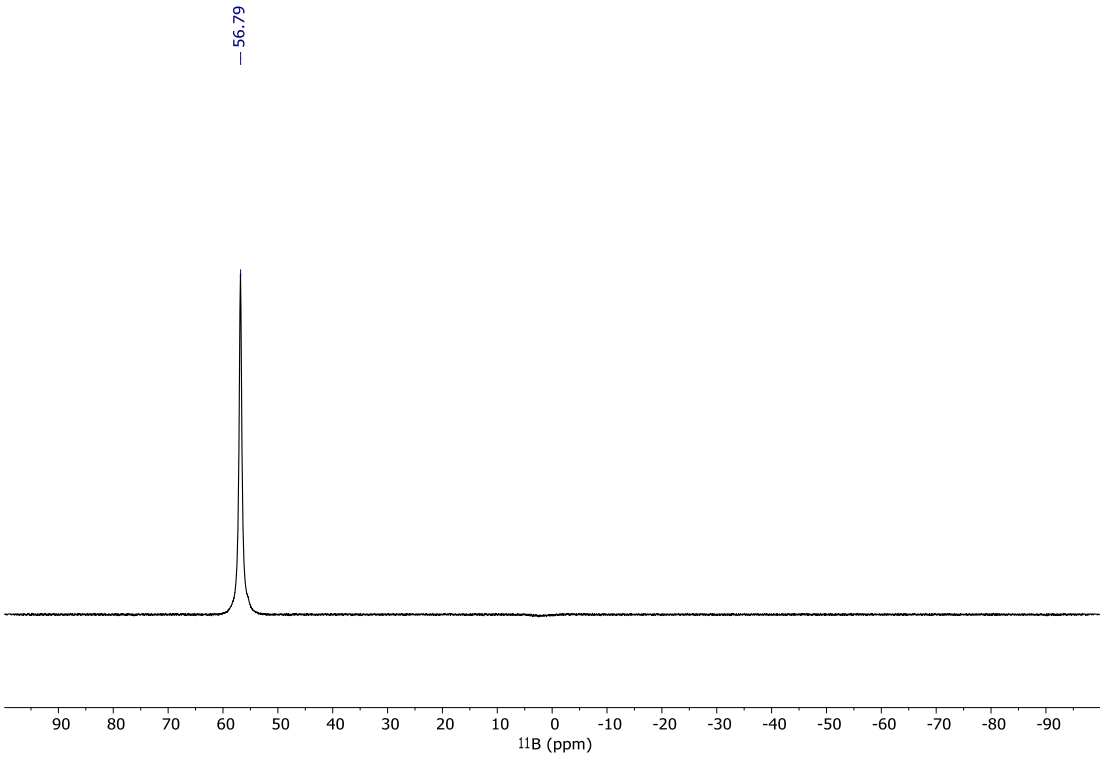


Figure S2. $^{11}B\{^{1}H\}$ NMR spectrum of 1,2-bis(BCl_2)benzene (**1**) in C_6D_6.

Compound **2**

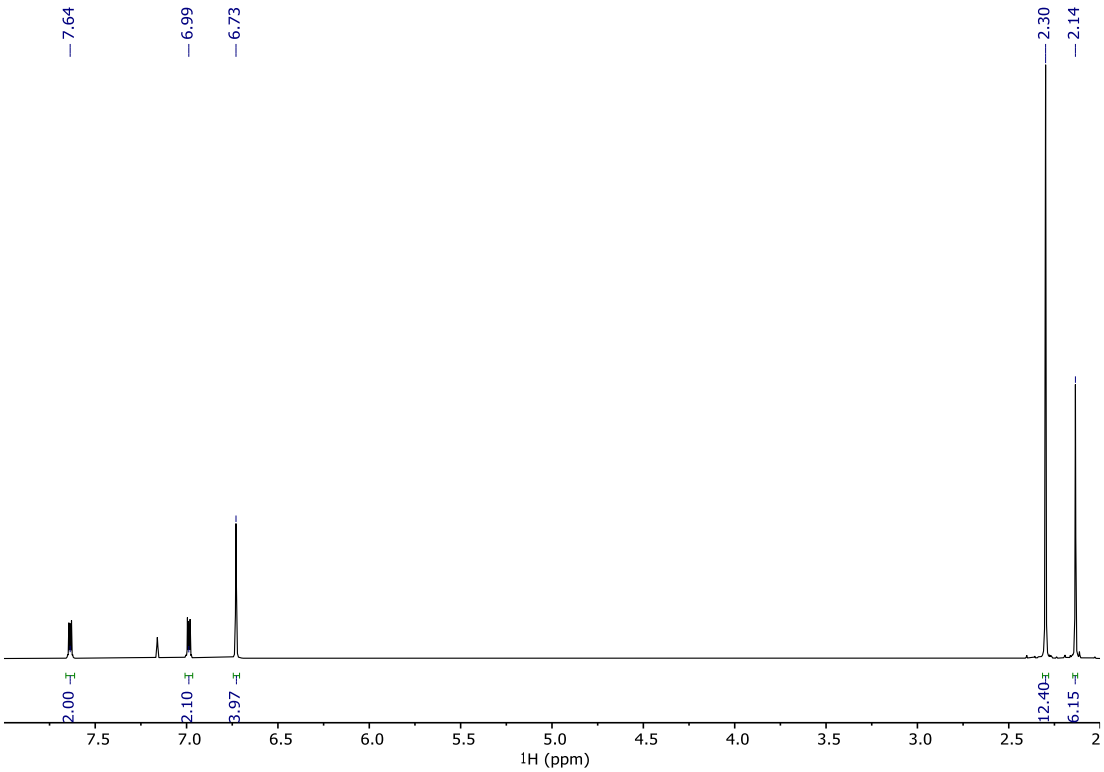


Figure S3. ^{1}H NMR spectrum of **2** in C_6D_6.

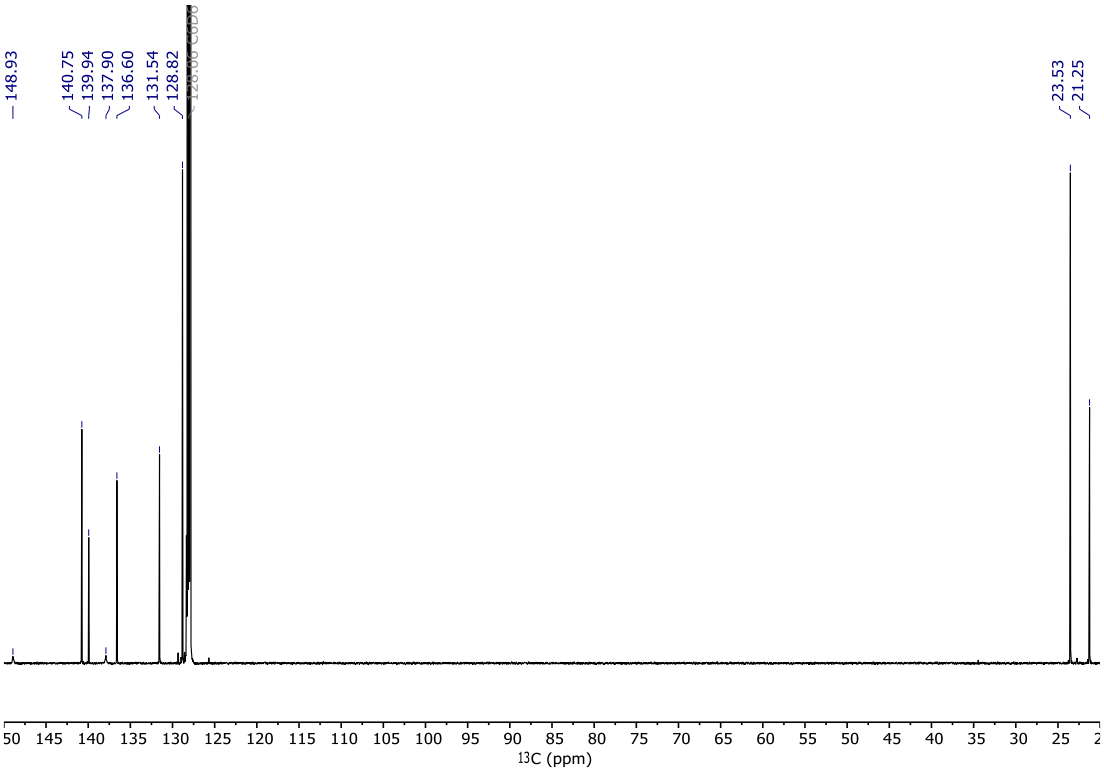


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

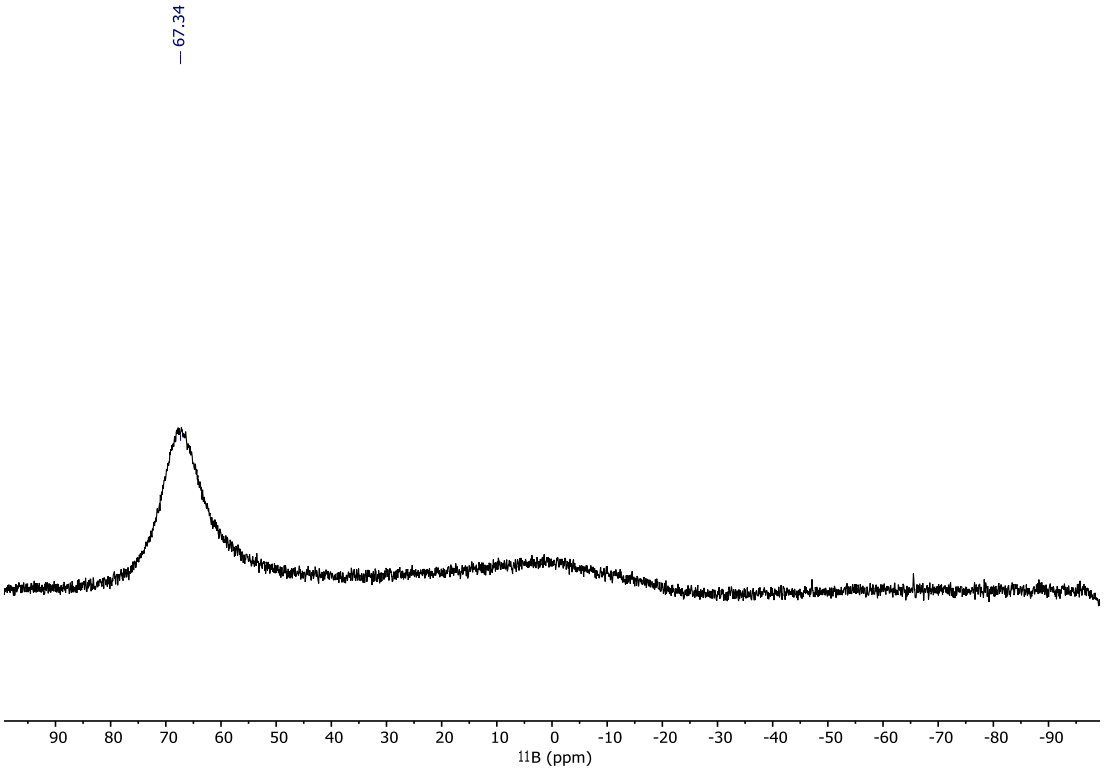


Figure S5. ^{11}B NMR spectrum of **2** in C_6D_6.

Compound **3**

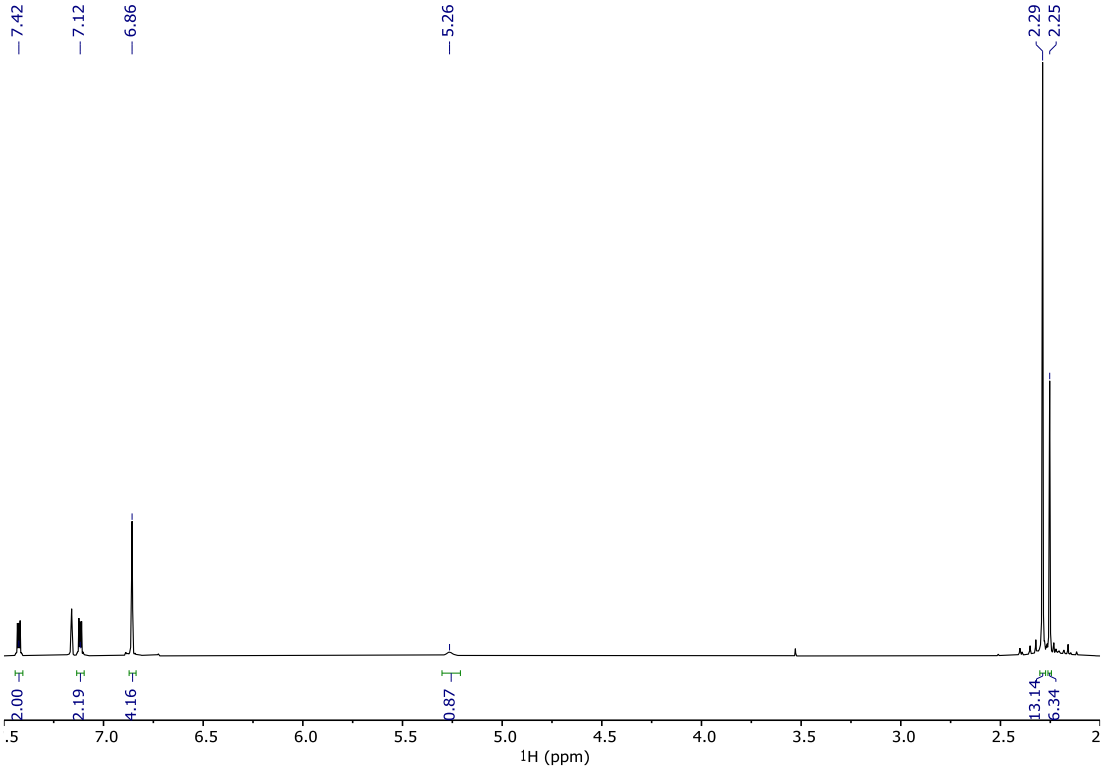


Figure S6. ^{1}H NMR spectrum of **3** in C_6D_6.

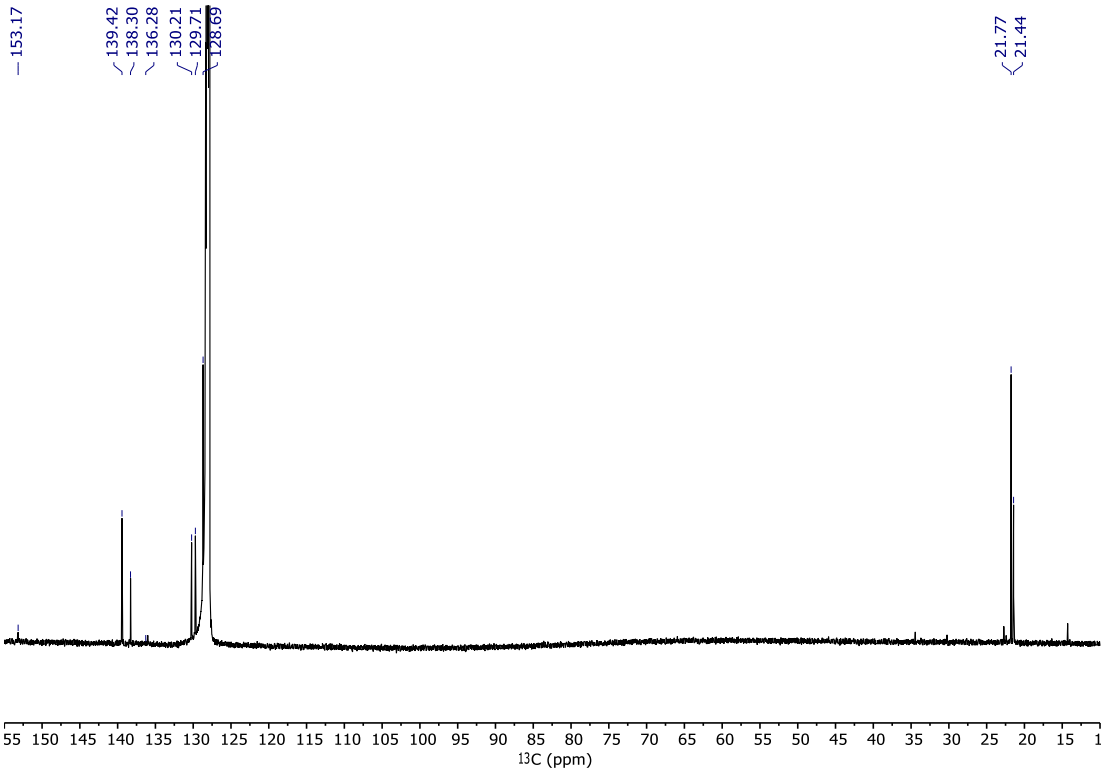


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

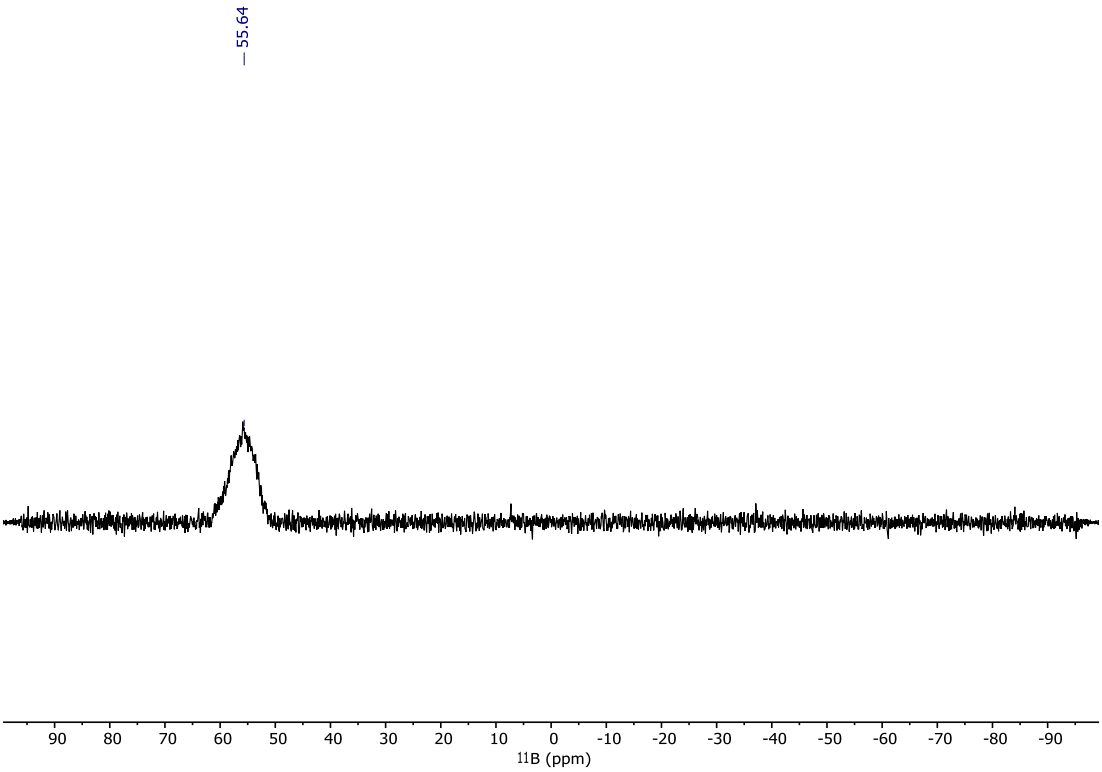


Figure S8. $^{11}B\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

Compound **4**

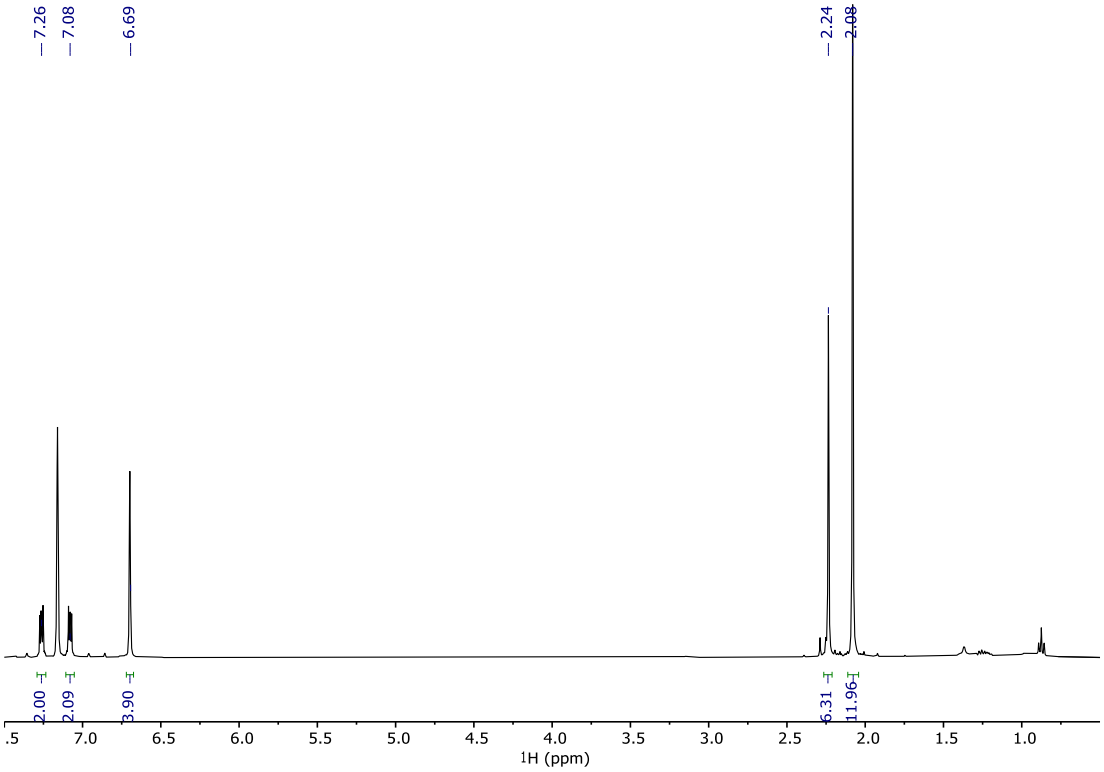


Figure S9. ^{1}H NMR spectrum of **4** in C_6D_6.

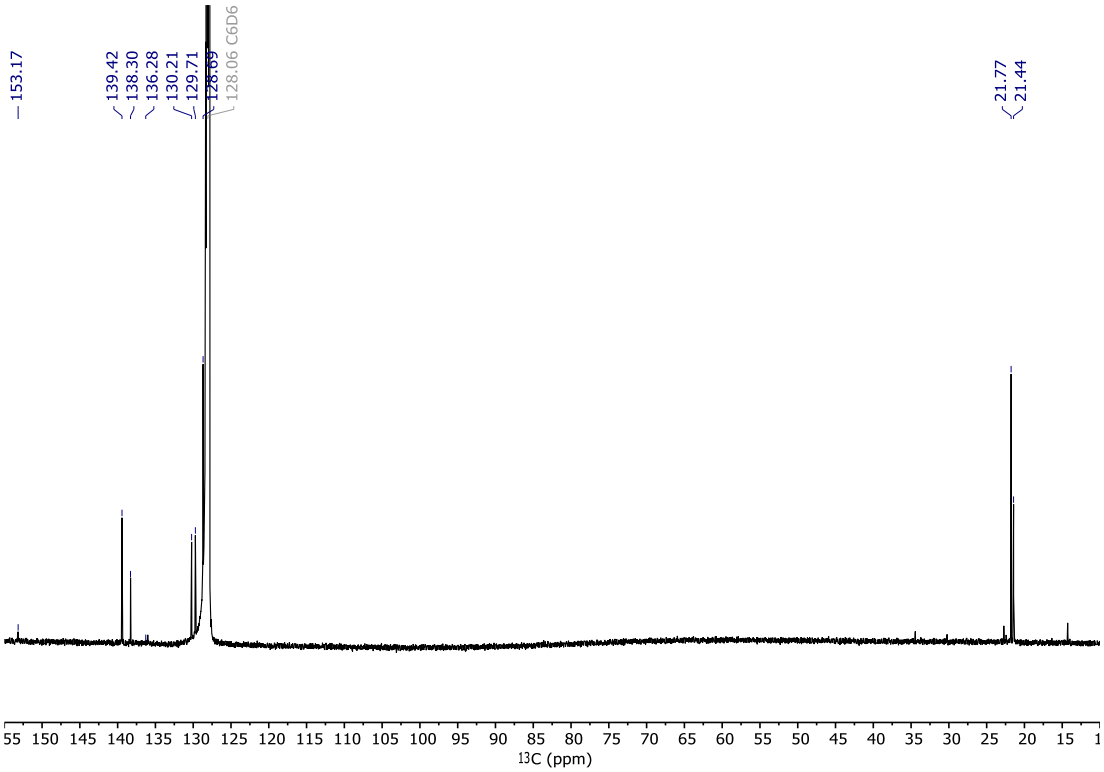


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

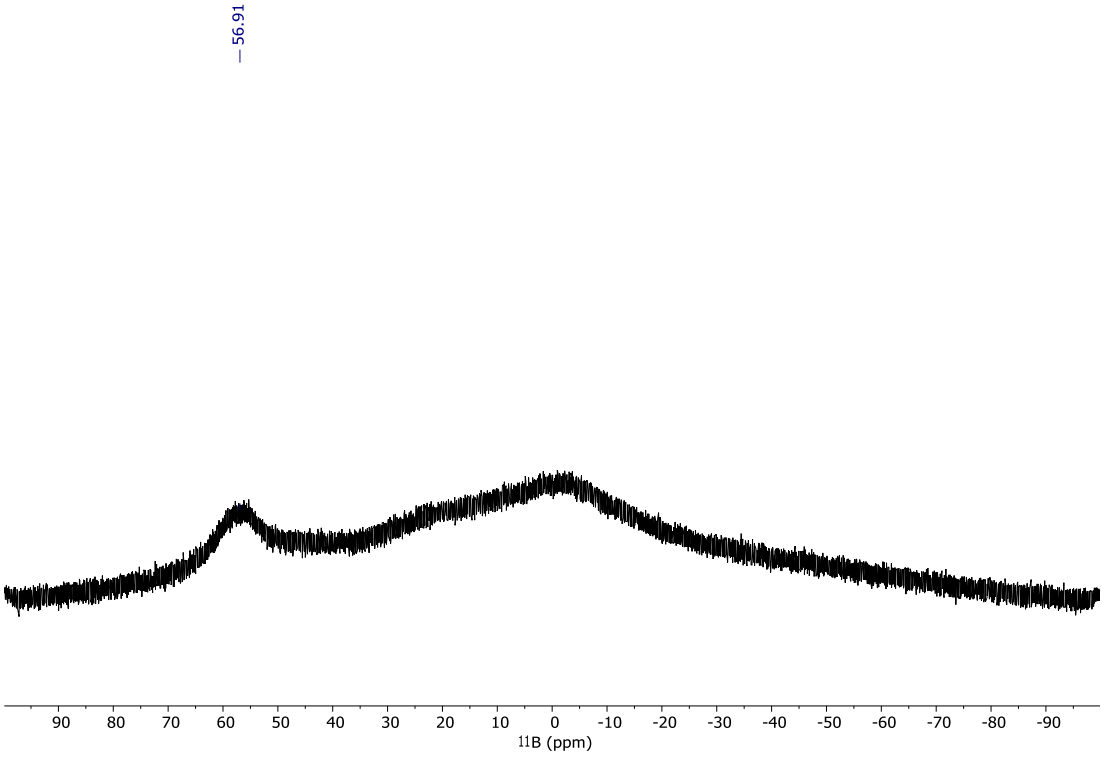


Figure S11. $^{11}B\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

Compound **5**

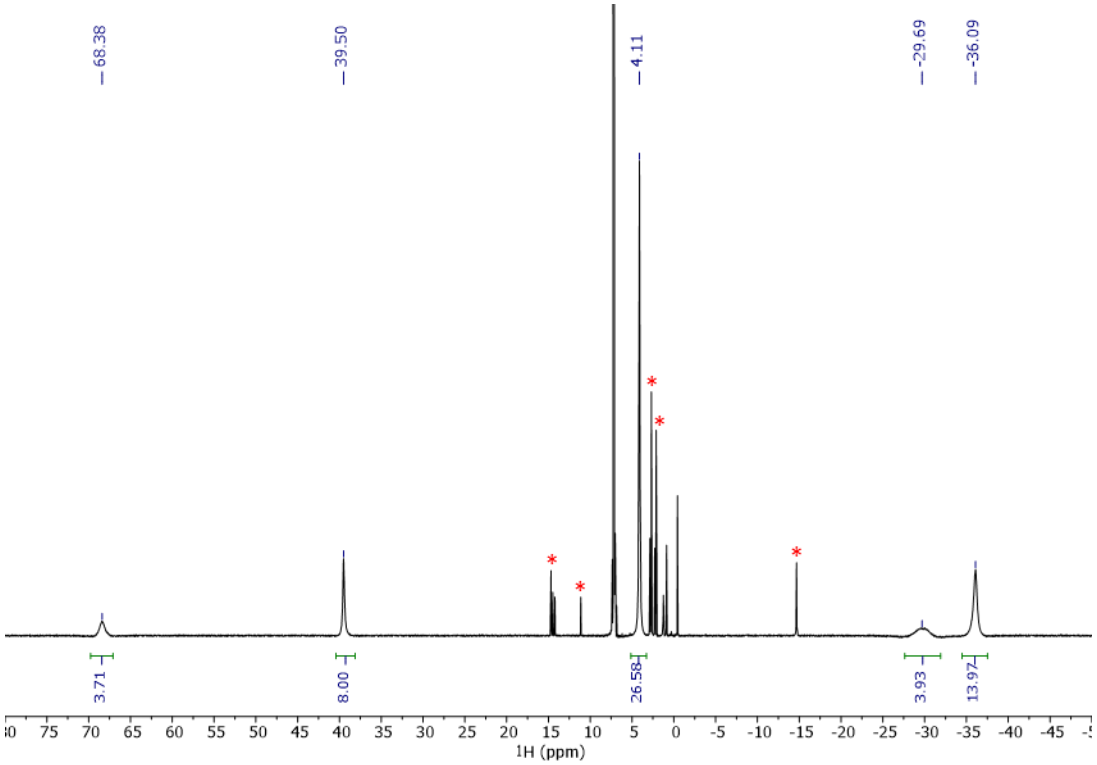


Figure S12. ^{1}H NMR spectrum of Fe(^{Mes}BNB)$_2$ (**5**) in C_6D_6. Note: * indicate resonances for **6**.

Compound **6**

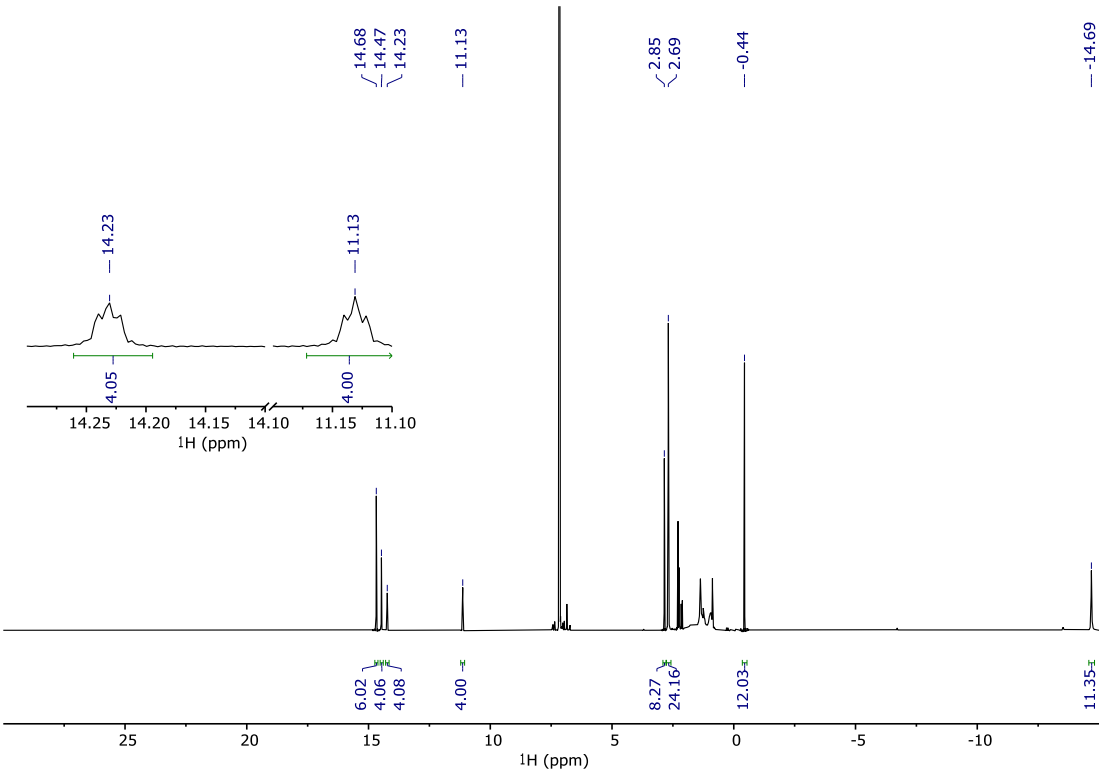
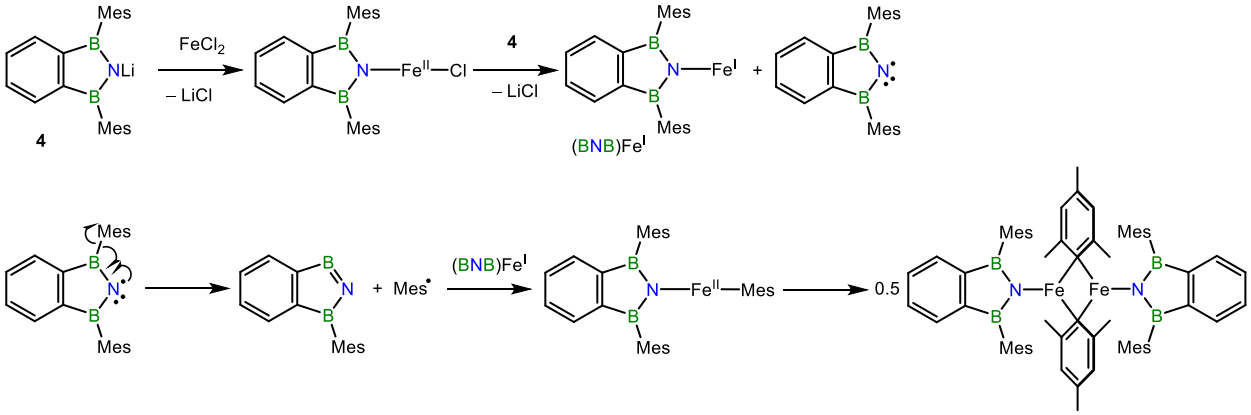


Figure S13. ^{1}H NMR spectrum of {Fe(^{Mes}BNB)(μ-Mes)}$_2$ (**6**) in C_6D_6.

4. Proposed Mechanism for formation of {(^{Mes}BNB)Fe(μ-Mes)}$_2$ (6)



Scheme S1. Proposed mechanism for the formation of the diiron complex **6**.

Other pathways, e.g. B-C(Mes) oxidative addition, cannot be ruled out. A thorough mechanistic investigation will be carried out in a future publication.

5. X-ray Crystallographic Data

Suitable crystals were selected under a microscope and mounted on a Bruker Apex II-CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Structures were solved and refined using SHELXTL and OLEX2.[4,5] Compounds **3** and **4** were isolated as colorless crystals. Compound **5** was isolated as yellow crystals and compound **6** was isolated as red crystals.

Compound 3.

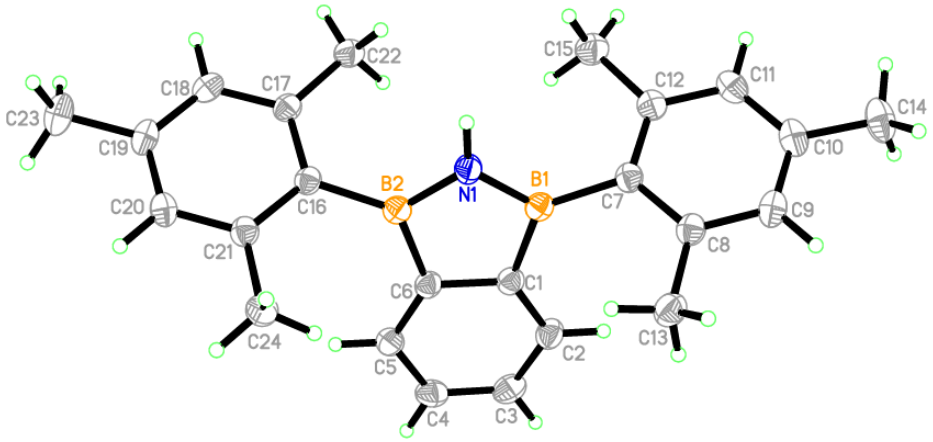


Table S1. Crystal data and structure refinement for **3**.

Identification code	BML006	
Empirical formula	C24 H27 B2 N	
Formula weight	351.08	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.5782(6) Å	α= 90°.
	b = 15.6055(10) Å	β= 95.448(2)°.
	c = 12.3273(7) Å	γ = 90°.
Volume	2025.8(2) $Å^3$	
Z	4	
Density (calculated)	1.151 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	752	
Crystal size	0.222 x 0.184 x 0.092 mm^3	
Theta range for data collection	2.610 to 25.696°.	
Index ranges	-12<=h<=12, -19<=k<=18, -15<=l<=15	
Reflections collected	29191	
Independent reflections	3821 [R(int) = 0.0387]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.957 and 0.949	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3821 / 0 / 254
Goodness-of-fit on F^2	1.151
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1348
R indices (all data)	R1 = 0.0536, wR2 = 0.1449
Extinction coefficient	n/a
Largest diff. peak and hole	0.279 and -0.275 e.$Å^{-3}$

Table S2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	564(1)	378(1)	1838(1)	25(1)
B(1)	1664(2)	-9(1)	1462(1)	23(1)
B(2)	839(2)	808(1)	2864(1)	22(1)
C(1)	2810(2)	227(1)	2326(1)	23(1)
C(2)	4088(2)	3(1)	2419(1)	28(1)
C(3)	4890(2)	301(1)	3299(2)	32(1)
C(4)	4424(2)	817(1)	4085(1)	30(1)
C(5)	3139(2)	1030(1)	4015(1)	26(1)
C(6)	2331(2)	738(1)	3140(1)	23(1)
C(7)	1752(1)	-600(1)	438(1)	23(1)
C(8)	2590(2)	-388(1)	-344(1)	25(1)
C(9)	2821(2)	-972(1)	-1155(1)	29(1)
C(10)	2234(2)	-1770(1)	-1231(1)	29(1)
C(11)	1354(2)	-1955(1)	-500(1)	28(1)
C(12)	1105(2)	-1391(1)	333(1)	25(1)
C(13)	3227(2)	480(1)	-333(2)	32(1)
C(14)	2573(2)	-2414(1)	-2070(2)	40(1)
C(15)	166(2)	-1656(1)	1120(2)	35(1)
C(16)	-127(1)	1178(1)	3628(1)	22(1)
C(17)	-1070(1)	649(1)	4017(1)	23(1)
C(18)	-1812(2)	958(1)	4807(1)	26(1)
C(19)	-1648(2)	1777(1)	5240(1)	28(1)
C(20)	-735(2)	2300(1)	4840(1)	27(1)

C(21)	3(2)	2021(1)	4034(1)	24(1)
C(22)	-1274(2)	-262(1)	3616(1)	28(1)
C(23)	-2451(2)	2091(1)	6109(2)	40(1)
C(24)	873(2)	2653(1)	3554(1)	29(1)

Table S3. Bond lengths [Å] and angles [°] for **3**.

N(1)-B(1)	1.426(2)
N(1)-B(2)	1.437(2)
B(1)-C(7)	1.573(2)
B(1)-C(1)	1.580(2)
B(2)-C(16)	1.564(2)
B(2)-C(6)	1.587(2)
C(1)-C(2)	1.391(2)
C(1)-C(6)	1.413(2)
C(2)-C(3)	1.392(2)
C(3)-C(4)	1.386(3)
C(4)-C(5)	1.394(2)
C(5)-C(6)	1.387(2)
C(7)-C(8)	1.410(2)
C(7)-C(12)	1.412(2)
C(8)-C(9)	1.391(2)
C(8)-C(13)	1.512(2)
C(9)-C(10)	1.391(3)
C(10)-C(11)	1.386(3)
C(10)-C(14)	1.509(2)
C(11)-C(12)	1.396(2)
C(12)-C(15)	1.511(2)
C(16)-C(21)	1.410(2)
C(16)-C(17)	1.413(2)
C(17)-C(18)	1.394(2)
C(17)-C(22)	1.513(2)
C(18)-C(19)	1.390(2)
C(19)-C(20)	1.390(2)
C(19)-C(23)	1.511(2)

C(20)-C(21)	1.391(2)
C(21)-C(24)	1.507(2)

B(1)-N(1)-B(2)	112.38(13)
N(1)-B(1)-C(7)	128.40(14)
N(1)-B(1)-C(1)	106.23(13)
C(7)-B(1)-C(1)	125.29(14)
N(1)-B(2)-C(16)	127.82(14)
N(1)-B(2)-C(6)	105.72(13)
C(16)-B(2)-C(6)	126.11(14)
C(2)-C(1)-C(6)	119.66(15)
C(2)-C(1)-B(1)	132.45(15)
C(6)-C(1)-B(1)	107.84(13)
C(1)-C(2)-C(3)	119.73(15)
C(4)-C(3)-C(2)	120.51(15)
C(3)-C(4)-C(5)	120.32(15)
C(6)-C(5)-C(4)	119.66(15)
C(5)-C(6)-C(1)	120.08(14)
C(5)-C(6)-B(2)	132.14(14)
C(1)-C(6)-B(2)	107.64(13)
C(8)-C(7)-C(12)	118.29(14)
C(8)-C(7)-B(1)	120.02(14)
C(12)-C(7)-B(1)	121.37(14)
C(9)-C(8)-C(7)	120.15(15)
C(9)-C(8)-C(13)	119.01(15)
C(7)-C(8)-C(13)	120.83(14)
C(8)-C(9)-C(10)	121.82(16)
C(11)-C(10)-C(9)	117.77(15)
C(11)-C(10)-C(14)	121.65(17)
C(9)-C(10)-C(14)	120.57(17)
C(10)-C(11)-C(12)	122.16(16)
C(11)-C(12)-C(7)	119.64(15)
C(11)-C(12)-C(15)	118.81(15)
C(7)-C(12)-C(15)	121.54(15)
C(21)-C(16)-C(17)	118.23(14)
C(21)-C(16)-B(2)	120.68(14)

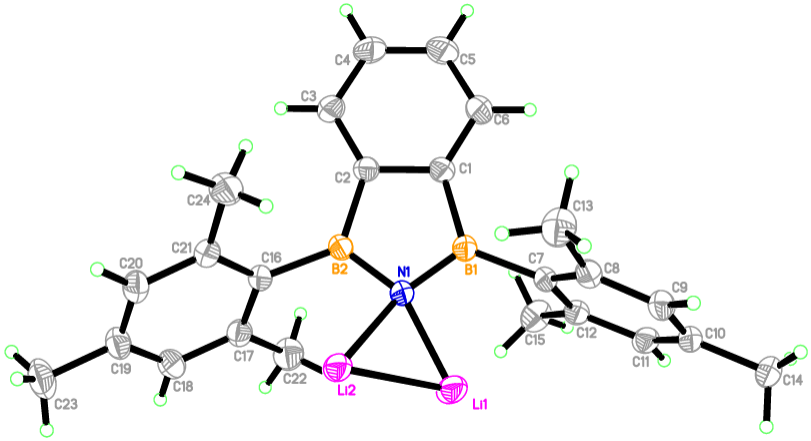
C(17)-C(16)-B(2)	120.79(14)
C(18)-C(17)-C(16)	119.87(14)
C(18)-C(17)-C(22)	118.70(14)
C(16)-C(17)-C(22)	121.41(14)
C(19)-C(18)-C(17)	121.86(15)
C(20)-C(19)-C(18)	118.01(15)
C(20)-C(19)-C(23)	121.16(16)
C(18)-C(19)-C(23)	120.82(16)
C(19)-C(20)-C(21)	121.74(15)
C(20)-C(21)-C(16)	120.21(15)
C(20)-C(21)-C(24)	118.74(14)
C(16)-C(21)-C(24)	120.92(14)

Table S4. Anisotropic displacement parameters ($Å^2x10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	22(1)	30(1)	24(1)	-4(1)	2(1)	2(1)
B(1)	23(1)	22(1)	23(1)	2(1)	4(1)	1(1)
B(2)	23(1)	19(1)	24(1)	2(1)	3(1)	0(1)
C(1)	23(1)	22(1)	24(1)	1(1)	4(1)	0(1)
C(2)	24(1)	31(1)	31(1)	-2(1)	5(1)	4(1)
C(3)	21(1)	39(1)	36(1)	4(1)	2(1)	2(1)
C(4)	26(1)	34(1)	29(1)	1(1)	-2(1)	-5(1)
C(5)	27(1)	26(1)	24(1)	-1(1)	4(1)	-2(1)
C(6)	24(1)	22(1)	23(1)	2(1)	6(1)	-1(1)
C(7)	22(1)	24(1)	23(1)	-1(1)	1(1)	4(1)
C(8)	24(1)	27(1)	25(1)	1(1)	2(1)	4(1)
C(9)	32(1)	33(1)	23(1)	1(1)	6(1)	8(1)
C(10)	34(1)	29(1)	23(1)	-2(1)	-3(1)	12(1)
C(11)	31(1)	22(1)	29(1)	-2(1)	-4(1)	4(1)
C(12)	25(1)	26(1)	25(1)	1(1)	-1(1)	3(1)
C(13)	33(1)	31(1)	33(1)	1(1)	10(1)	-1(1)
C(14)	50(1)	38(1)	31(1)	-8(1)	0(1)	16(1)
C(15)	35(1)	33(1)	39(1)	-1(1)	9(1)	-5(1)

C(16)	21(1)	24(1)	21(1)	0(1)	2(1)	2(1)
C(17)	20(1)	25(1)	24(1)	2(1)	1(1)	2(1)
C(18)	22(1)	30(1)	27(1)	5(1)	5(1)	1(1)
C(19)	27(1)	34(1)	24(1)	1(1)	6(1)	9(1)
C(20)	31(1)	24(1)	26(1)	-2(1)	4(1)	5(1)
C(21)	23(1)	24(1)	24(1)	0(1)	2(1)	3(1)
C(22)	26(1)	27(1)	32(1)	0(1)	5(1)	-3(1)
C(23)	42(1)	46(1)	34(1)	-1(1)	16(1)	10(1)
C(24)	31(1)	24(1)	34(1)	0(1)	6(1)	-1(1)

Compound 4.



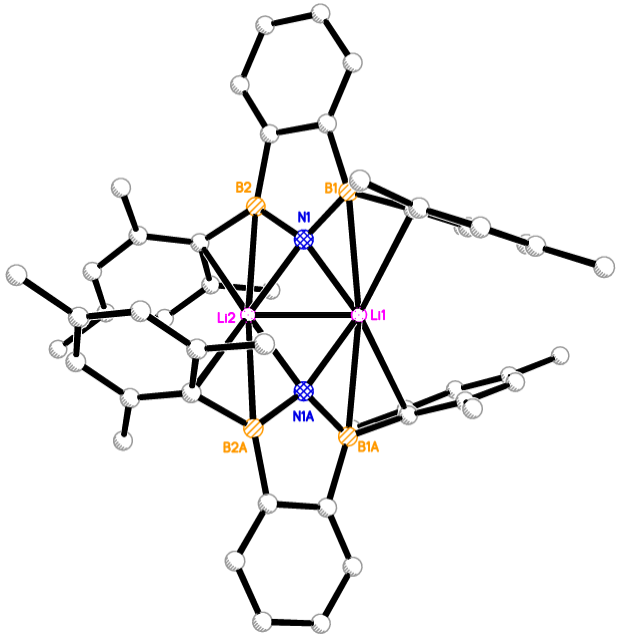


Table S5. Crystal data and structure refinement for **4**.

Identification code	BML001	
Empirical formula	C48 H52 B4 Li2 N2	
Formula weight	714.03	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 16.3616(18) Å	α= 90°.
	b = 17.7703(19) Å	β= 118.958(4)°.
	c = 16.512(2) Å	γ = 90°.
Volume	4200.6(9) $Å^3$	
Z	4	
Density (calculated)	1.129 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	1520	
Crystal size	0.345 x 0.201 x 0.159 mm^3	
Theta range for data collection	2.292 to 28.340°.	
Index ranges	-21<=h<=21, -23<=k<=23, -22<=l<=22	
Reflections collected	120961	
Independent reflections	5226 [R(int) = 0.0447]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.967 and 0.957	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5226 / 0 / 260	
Goodness-of-fit on F^2	1.119	
Final R indices [I>2sigma(I)]	R1 = 0.0645, wR2 = 0.1721	
R indices (all data)	R1 = 0.0687, wR2 = 0.1752	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.372 and -0.264 $e.Å^{-3}$	

Table S6. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	6448(1)	2073(1)	4154(1)	26(1)
C(1)	4788(1)	2349(1)	3017(1)	25(1)
C(2)	5008(1)	1658(1)	2741(1)	23(1)
C(3)	4338(1)	1286(1)	1962(1)	29(1)
C(4)	3447(1)	1599(1)	1457(1)	38(1)
C(5)	3231(1)	2273(1)	1728(1)	42(1)
C(6)	3900(1)	2654(1)	2511(1)	35(1)
C(7)	5853(1)	3346(1)	4507(1)	23(1)
C(8)	5646(1)	3362(1)	5244(1)	27(1)
C(9)	5813(1)	4011(1)	5773(1)	29(1)
C(10)	6160(1)	4662(1)	5586(1)	28(1)
C(11)	6337(1)	4652(1)	4844(1)	28(1)
C(12)	6197(1)	4008(1)	4310(1)	24(1)
C(13)	5180(2)	2691(1)	5419(2)	40(1)
C(14)	6326(1)	5360(1)	6168(1)	38(1)
C(15)	6403(1)	4022(1)	3509(1)	35(1)
C(16)	6686(1)	789(1)	3509(1)	23(1)
C(17)	7481(1)	891(1)	3392(1)	27(1)
C(18)	8070(1)	287(1)	3506(1)	32(1)
C(19)	7894(1)	-430(1)	3727(1)	33(1)
C(20)	7105(1)	-533(1)	3825(1)	30(1)
C(21)	6502(1)	59(1)	3719(1)	26(1)
C(22)	7674(1)	1647(1)	3102(1)	38(1)
C(23)	8540(2)	-1074(1)	3851(2)	48(1)
C(24)	5662(1)	-87(1)	3847(1)	35(1)
B(1)	5707(1)	2602(1)	3921(1)	23(1)
B(2)	6067(1)	1489(1)	3469(1)	22(1)
Li(1)	7500	2729(2)	5000	37(1)
Li(2)	7500	1413(2)	5000	31(1)

Table S7. Bond lengths [Å] and angles [°] for **4**.

N(1)-B(1)	1.432(2)
N(1)-B(2)	1.436(2)
N(1)-Li(1)	1.987(3)
N(1)-Li(2)	1.990(3)
C(1)-C(6)	1.388(2)
C(1)-C(2)	1.416(2)
C(1)-B(1)	1.587(2)
C(2)-C(3)	1.389(2)
C(2)-B(2)	1.587(2)
C(3)-C(4)	1.397(2)
C(4)-C(5)	1.383(3)
C(5)-C(6)	1.400(3)
C(7)-C(12)	1.408(2)
C(7)-C(8)	1.412(2)
C(7)-B(1)	1.587(2)
C(8)-C(9)	1.391(2)
C(8)-C(13)	1.516(2)
C(9)-C(10)	1.388(2)
C(10)-C(11)	1.389(2)
C(10)-C(14)	1.511(2)
C(11)-C(12)	1.396(2)
C(12)-C(15)	1.514(2)
C(16)-C(21)	1.411(2)
C(16)-C(17)	1.417(2)
C(16)-B(2)	1.585(2)
C(17)-C(18)	1.393(2)
C(17)-C(22)	1.510(2)
C(18)-C(19)	1.394(2)
C(19)-C(20)	1.388(2)
C(19)-C(23)	1.504(2)
C(20)-C(21)	1.394(2)
C(21)-C(24)	1.511(2)
Li(1)-N(1)#1	1.987(3)
Li(1)-Li(2)	2.339(6)

Li(2)-N(1)#1	1.990(3)
B(1)-N(1)-B(2)	105.94(13)
B(1)-N(1)-Li(1)	97.82(13)
B(2)-N(1)-Li(1)	151.17(12)
B(1)-N(1)-Li(2)	155.14(12)
B(2)-N(1)-Li(2)	91.46(12)
Li(1)-N(1)-Li(2)	72.07(14)
C(6)-C(1)-C(2)	120.03(14)
C(6)-C(1)-B(1)	134.00(15)
C(2)-C(1)-B(1)	105.97(12)
C(3)-C(2)-C(1)	120.06(14)
C(3)-C(2)-B(2)	133.95(14)
C(1)-C(2)-B(2)	105.99(12)
C(2)-C(3)-C(4)	119.43(15)
C(5)-C(4)-C(3)	120.51(16)
C(4)-C(5)-C(6)	120.66(16)
C(1)-C(6)-C(5)	119.31(16)
C(12)-C(7)-C(8)	118.21(13)
C(12)-C(7)-B(1)	120.89(13)
C(8)-C(7)-B(1)	120.90(13)
C(9)-C(8)-C(7)	120.08(14)
C(9)-C(8)-C(13)	119.75(15)
C(7)-C(8)-C(13)	120.04(14)
C(10)-C(9)-C(8)	121.90(15)
C(9)-C(10)-C(11)	117.89(14)
C(9)-C(10)-C(14)	120.64(16)
C(11)-C(10)-C(14)	121.46(16)
C(10)-C(11)-C(12)	121.88(15)
C(11)-C(12)-C(7)	119.99(14)
C(11)-C(12)-C(15)	120.02(14)
C(7)-C(12)-C(15)	119.98(14)
C(21)-C(16)-C(17)	118.05(13)
C(21)-C(16)-B(2)	121.66(13)
C(17)-C(16)-B(2)	120.18(13)
C(18)-C(17)-C(16)	120.26(15)

C(18)-C(17)-C(22)	119.34(15)
C(16)-C(17)-C(22)	120.34(14)
C(17)-C(18)-C(19)	121.42(15)
C(20)-C(19)-C(18)	118.33(15)
C(20)-C(19)-C(23)	121.02(17)
C(18)-C(19)-C(23)	120.65(17)
C(19)-C(20)-C(21)	121.75(15)
C(20)-C(21)-C(16)	120.17(14)
C(20)-C(21)-C(24)	119.30(15)
C(16)-C(21)-C(24)	120.52(14)
N(1)-B(1)-C(7)	121.70(13)
N(1)-B(1)-C(1)	111.10(13)
C(7)-B(1)-C(1)	127.16(13)
N(1)-B(2)-C(16)	120.61(13)
N(1)-B(2)-C(2)	110.99(13)
C(16)-B(2)-C(2)	128.39(13)
N(1)#1-Li(1)-N(1)	108.1(2)
N(1)#1-Li(1)-Li(2)	54.04(10)
N(1)-Li(1)-Li(2)	54.04(10)
N(1)-Li(2)-N(1)#1	107.79(19)
N(1)-Li(2)-Li(1)	53.90(10)
N(1)#1-Li(2)-Li(1)	53.89(10)

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2,y,-z+1

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	22(1)	23(1)	27(1)	-4(1)	7(1)	3(1)
C(1)	22(1)	24(1)	25(1)	1(1)	9(1)	2(1)
C(2)	22(1)	24(1)	23(1)	0(1)	10(1)	0(1)
C(3)	28(1)	30(1)	27(1)	-5(1)	12(1)	-2(1)
C(4)	28(1)	42(1)	30(1)	-5(1)	3(1)	-3(1)
C(5)	24(1)	42(1)	42(1)	1(1)	2(1)	7(1)
C(6)	28(1)	30(1)	37(1)	0(1)	8(1)	7(1)
C(7)	21(1)	22(1)	24(1)	-2(1)	8(1)	4(1)
C(8)	26(1)	25(1)	30(1)	-1(1)	14(1)	2(1)
C(9)	28(1)	33(1)	28(1)	-5(1)	15(1)	2(1)
C(10)	23(1)	26(1)	28(1)	-6(1)	7(1)	4(1)
C(11)	26(1)	22(1)	30(1)	0(1)	9(1)	-1(1)
C(12)	23(1)	24(1)	23(1)	0(1)	8(1)	1(1)
C(13)	48(1)	34(1)	48(1)	-1(1)	32(1)	-6(1)
C(14)	35(1)	33(1)	37(1)	-13(1)	10(1)	3(1)
C(15)	44(1)	36(1)	29(1)	-1(1)	20(1)	-5(1)
C(16)	23(1)	22(1)	24(1)	-2(1)	11(1)	1(1)
C(17)	27(1)	25(1)	30(1)	-3(1)	15(1)	-1(1)
C(18)	29(1)	34(1)	39(1)	-4(1)	20(1)	2(1)
C(19)	33(1)	29(1)	36(1)	-4(1)	17(1)	7(1)
C(20)	35(1)	22(1)	33(1)	0(1)	16(1)	3(1)
C(21)	27(1)	24(1)	26(1)	-2(1)	13(1)	-1(1)
C(22)	40(1)	32(1)	50(1)	1(1)	29(1)	-5(1)
C(23)	48(1)	36(1)	67(1)	-1(1)	33(1)	14(1)
C(24)	32(1)	32(1)	44(1)	4(1)	22(1)	-2(1)
B(1)	24(1)	21(1)	24(1)	-1(1)	11(1)	1(1)
B(2)	22(1)	22(1)	24(1)	1(1)	12(1)	2(1)
Li(1)	32(2)	23(2)	37(2)	0	1(2)	0
Li(2)	28(2)	23(2)	32(2)	0	7(2)	0

Compound 5.

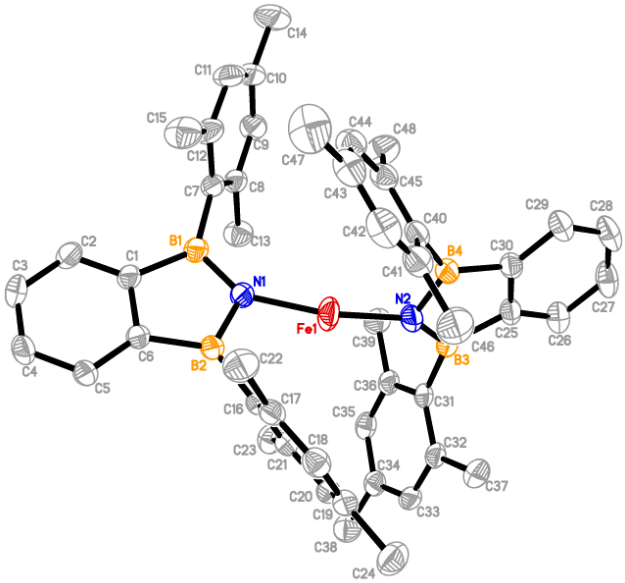


Table S9. Crystal data and structure refinement for **5**.

Identification code	BML025	
Empirical formula	C48 H52 B4 Fe N2	
Formula weight	756.00	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 19.0371(5) Å	α= 90°.
	b = 12.9687(3) Å	β= 90°.
	c = 34.8721(12) Å	γ = 90°.
Volume	8609.4(4) $Å^3$	
Z	8	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	0.385 mm^{-1}	
F(000)	3200	
Crystal size	0.267 x 0.181 x 0.166 mm^3	
Theta range for data collection	2.438 to 25.681°.	
Index ranges	-23<=h<=23, -15<=k<=15, -42<=l<=42	
Reflections collected	145474	
Independent reflections	8154 [R(int) = 0.0625]	

Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.888 and 0.855
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8154 / 0 / 508
Goodness-of-fit on F^2	1.088
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1183
R indices (all data)	R1 = 0.0561, wR2 = 0.1222
Extinction coefficient	n/a
Largest diff. peak and hole	0.268 and -0.471 e.$Å^{-3}$

Table S10. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	5095(1)	5112(1)	1289(1)	44(1)
N(1)	5028(1)	3824(1)	1032(1)	38(1)
B(1)	4589(1)	3146(2)	812(1)	31(1)
B(2)	5670(1)	3298(2)	1121(1)	30(1)
C(1)	5018(1)	2118(2)	731(1)	30(1)
C(2)	4872(1)	1234(2)	523(1)	35(1)
C(3)	5366(1)	441(2)	503(1)	38(1)
C(4)	6000(1)	524(2)	692(1)	38(1)
C(5)	6155(1)	1408(2)	904(1)	34(1)
C(6)	5672(1)	2204(2)	924(1)	29(1)
C(7)	3806(1)	3418(2)	705(1)	30(1)
C(8)	3636(1)	4188(2)	438(1)	31(1)
C(9)	2937(1)	4457(2)	378(1)	37(1)
C(10)	2394(1)	4001(2)	579(1)	40(1)
C(11)	2561(1)	3239(2)	842(1)	43(1)
C(12)	3254(1)	2936(2)	905(1)	38(1)
C(13)	4201(1)	4712(2)	208(1)	42(1)
C(14)	1640(1)	4326(3)	513(1)	63(1)
C(15)	3417(1)	2114(2)	1199(1)	52(1)
C(16)	6216(1)	3879(1)	1389(1)	27(1)

C(17)	6284(1)	3600(2)	1780(1)	31(1)
C(18)	6735(1)	4153(2)	2016(1)	34(1)
C(19)	7127(1)	4983(2)	1882(1)	33(1)
C(20)	7056(1)	5258(2)	1501(1)	31(1)
C(21)	6612(1)	4723(2)	1251(1)	28(1)
C(22)	5856(1)	2716(2)	1941(1)	47(1)
C(23)	6592(1)	5042(2)	835(1)	38(1)
C(24)	7624(1)	5557(2)	2144(1)	50(1)
N(2)	4992(1)	6523(1)	1416(1)	39(1)
B(3)	5205(1)	7531(2)	1290(1)	33(1)
B(4)	4430(1)	6620(2)	1686(1)	34(1)
C(25)	4717(1)	8354(2)	1498(1)	32(1)
C(26)	4677(1)	9418(2)	1478(1)	39(1)
C(27)	4154(1)	9936(2)	1682(1)	45(1)
C(28)	3675(1)	9395(2)	1900(1)	47(1)
C(29)	3714(1)	8321(2)	1927(1)	39(1)
C(30)	4235(1)	7800(2)	1729(1)	32(1)
C(31)	5823(1)	7711(1)	999(1)	30(1)
C(32)	6506(1)	7890(2)	1134(1)	31(1)
C(33)	7061(1)	7946(2)	877(1)	32(1)
C(34)	6961(1)	7834(2)	483(1)	33(1)
C(35)	6277(1)	7688(2)	351(1)	33(1)
C(36)	5713(1)	7625(1)	601(1)	32(1)
C(37)	6636(1)	8004(2)	1560(1)	42(1)
C(38)	7576(1)	7845(2)	209(1)	46(1)
C(39)	4980(1)	7452(2)	449(1)	44(1)
C(40)	4132(1)	5609(2)	1878(1)	34(1)
C(41)	4483(1)	5158(2)	2194(1)	42(1)
C(42)	4245(1)	4220(2)	2342(1)	48(1)
C(43)	3672(1)	3711(2)	2187(1)	46(1)
C(44)	3328(1)	4161(2)	1878(1)	40(1)
C(45)	3548(1)	5093(2)	1723(1)	34(1)
C(46)	5108(2)	5694(2)	2372(1)	61(1)
C(47)	3419(2)	2696(2)	2350(1)	69(1)
C(48)	3167(1)	5538(2)	1383(1)	49(1)

Table S11. Bond lengths [Å] and angles [°] for **5**.

Fe(1)-N(2)	1.8936(18)
Fe(1)-N(1)	1.8981(18)
N(1)-B(2)	1.434(3)
N(1)-B(1)	1.436(3)
B(1)-C(7)	1.576(3)
B(1)-C(1)	1.589(3)
B(2)-C(6)	1.575(3)
B(2)-C(16)	1.589(3)
C(1)-C(2)	1.384(3)
C(1)-C(6)	1.420(3)
C(2)-C(3)	1.395(3)
C(3)-C(4)	1.381(3)
C(4)-C(5)	1.394(3)
C(5)-C(6)	1.385(3)
C(7)-C(8)	1.404(3)
C(7)-C(12)	1.408(3)
C(8)-C(9)	1.392(3)
C(8)-C(13)	1.505(3)
C(9)-C(10)	1.383(3)
C(10)-C(11)	1.384(3)
C(10)-C(14)	1.512(3)
C(11)-C(12)	1.393(3)
C(12)-C(15)	1.510(3)
C(16)-C(21)	1.413(3)
C(16)-C(17)	1.416(3)
C(17)-C(18)	1.389(3)
C(17)-C(22)	1.516(3)
C(18)-C(19)	1.390(3)
C(19)-C(20)	1.383(3)
C(19)-C(24)	1.510(3)
C(20)-C(21)	1.398(3)
C(21)-C(23)	1.511(3)
N(2)-B(4)	1.430(3)
N(2)-B(3)	1.438(3)

B(3)-C(31)	1.570(3)
B(3)-C(25)	1.590(3)
B(4)-C(40)	1.578(3)
B(4)-C(30)	1.583(3)
C(25)-C(26)	1.383(3)
C(25)-C(30)	1.417(3)
C(26)-C(27)	1.397(3)
C(27)-C(28)	1.379(4)
C(28)-C(29)	1.398(3)
C(29)-C(30)	1.384(3)
C(31)-C(32)	1.403(3)
C(31)-C(36)	1.408(3)
C(32)-C(33)	1.387(3)
C(32)-C(37)	1.515(3)
C(33)-C(34)	1.393(3)
C(34)-C(35)	1.394(3)
C(34)-C(38)	1.510(3)
C(35)-C(36)	1.385(3)
C(36)-C(39)	1.510(3)
C(40)-C(45)	1.406(3)
C(40)-C(41)	1.413(3)
C(41)-C(42)	1.397(4)
C(41)-C(46)	1.513(4)
C(42)-C(43)	1.384(4)
C(43)-C(44)	1.390(3)
C(43)-C(47)	1.513(4)
C(44)-C(45)	1.389(3)
C(45)-C(48)	1.507(3)

N(2)-Fe(1)-N(1)	162.49(9)
B(2)-N(1)-B(1)	108.63(17)
B(2)-N(1)-Fe(1)	105.11(14)
B(1)-N(1)-Fe(1)	146.06(14)
N(1)-B(1)-C(7)	122.66(18)
N(1)-B(1)-C(1)	108.05(17)
C(7)-B(1)-C(1)	129.18(18)

N(1)-B(2)-C(6)	109.68(18)
N(1)-B(2)-C(16)	117.30(18)
C(6)-B(2)-C(16)	133.02(18)
C(2)-C(1)-C(6)	119.28(18)
C(2)-C(1)-B(1)	133.25(18)
C(6)-C(1)-B(1)	107.47(17)
C(1)-C(2)-C(3)	120.17(19)
C(4)-C(3)-C(2)	120.4(2)
C(3)-C(4)-C(5)	120.21(19)
C(6)-C(5)-C(4)	119.94(19)
C(5)-C(6)-C(1)	119.95(18)
C(5)-C(6)-B(2)	134.01(18)
C(1)-C(6)-B(2)	106.03(16)
C(8)-C(7)-C(12)	118.14(18)
C(8)-C(7)-B(1)	122.29(18)
C(12)-C(7)-B(1)	119.37(18)
C(9)-C(8)-C(7)	119.95(19)
C(9)-C(8)-C(13)	119.33(19)
C(7)-C(8)-C(13)	120.70(18)
C(10)-C(9)-C(8)	122.1(2)
C(9)-C(10)-C(11)	117.95(19)
C(9)-C(10)-C(14)	120.7(2)
C(11)-C(10)-C(14)	121.3(2)
C(10)-C(11)-C(12)	121.7(2)
C(11)-C(12)-C(7)	120.2(2)
C(11)-C(12)-C(15)	120.1(2)
C(7)-C(12)-C(15)	119.7(2)
C(21)-C(16)-C(17)	118.45(18)
C(21)-C(16)-B(2)	121.05(18)
C(17)-C(16)-B(2)	120.38(18)
C(18)-C(17)-C(16)	119.74(19)
C(18)-C(17)-C(22)	120.2(2)
C(16)-C(17)-C(22)	120.07(19)
C(17)-C(18)-C(19)	122.1(2)
C(20)-C(19)-C(18)	118.04(19)
C(20)-C(19)-C(24)	120.9(2)

C(18)-C(19)-C(24)	121.0(2)
C(19)-C(20)-C(21)	122.06(19)
C(20)-C(21)-C(16)	119.62(19)
C(20)-C(21)-C(23)	118.64(18)
C(16)-C(21)-C(23)	121.69(18)
B(4)-N(2)-B(3)	109.43(18)
B(4)-N(2)-Fe(1)	108.47(15)
B(3)-N(2)-Fe(1)	141.05(16)
N(2)-B(3)-C(31)	122.96(18)
N(2)-B(3)-C(25)	107.77(19)
C(31)-B(3)-C(25)	129.28(19)
N(2)-B(4)-C(40)	118.40(19)
N(2)-B(4)-C(30)	108.86(19)
C(40)-B(4)-C(30)	132.74(19)
C(26)-C(25)-C(30)	119.9(2)
C(26)-C(25)-B(3)	132.7(2)
C(30)-C(25)-B(3)	107.37(18)
C(25)-C(26)-C(27)	119.5(2)
C(28)-C(27)-C(26)	120.5(2)
C(27)-C(28)-C(29)	120.6(2)
C(30)-C(29)-C(28)	119.4(2)
C(29)-C(30)-C(25)	120.0(2)
C(29)-C(30)-B(4)	133.5(2)
C(25)-C(30)-B(4)	106.49(17)
C(32)-C(31)-C(36)	118.80(19)
C(32)-C(31)-B(3)	120.14(19)
C(36)-C(31)-B(3)	120.91(18)
C(33)-C(32)-C(31)	119.88(19)
C(33)-C(32)-C(37)	120.34(19)
C(31)-C(32)-C(37)	119.77(19)
C(32)-C(33)-C(34)	121.83(19)
C(33)-C(34)-C(35)	117.79(19)
C(33)-C(34)-C(38)	121.2(2)
C(35)-C(34)-C(38)	121.0(2)
C(36)-C(35)-C(34)	121.7(2)
C(35)-C(36)-C(31)	119.94(19)

C(35)-C(36)-C(39)	120.3(2)
C(31)-C(36)-C(39)	119.74(19)
C(45)-C(40)-C(41)	118.5(2)
C(45)-C(40)-B(4)	121.08(19)
C(41)-C(40)-B(4)	120.3(2)
C(42)-C(41)-C(40)	119.6(2)
C(42)-C(41)-C(46)	120.3(2)
C(40)-C(41)-C(46)	120.1(2)
C(43)-C(42)-C(41)	121.8(2)
C(42)-C(43)-C(44)	118.2(2)
C(42)-C(43)-C(47)	121.3(2)
C(44)-C(43)-C(47)	120.4(3)
C(45)-C(44)-C(43)	121.6(2)
C(44)-C(45)-C(40)	120.2(2)
C(44)-C(45)-C(48)	119.7(2)
C(40)-C(45)-C(48)	120.1(2)

Table S12. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	55(1)	21(1)	54(1)	-8(1)	-6(1)	4(1)
N(1)	28(1)	26(1)	61(1)	-8(1)	-11(1)	6(1)
B(1)	30(1)	23(1)	41(1)	3(1)	-2(1)	-1(1)
B(2)	26(1)	23(1)	40(1)	0(1)	-1(1)	1(1)
C(1)	28(1)	23(1)	39(1)	2(1)	-3(1)	-1(1)
C(2)	35(1)	28(1)	42(1)	1(1)	-10(1)	-4(1)
C(3)	51(1)	22(1)	41(1)	-5(1)	-2(1)	-2(1)
C(4)	39(1)	24(1)	50(1)	0(1)	3(1)	8(1)
C(5)	28(1)	25(1)	47(1)	0(1)	-4(1)	4(1)
C(6)	26(1)	23(1)	39(1)	1(1)	-3(1)	1(1)
C(7)	25(1)	24(1)	41(1)	1(1)	-4(1)	-1(1)
C(8)	29(1)	25(1)	38(1)	1(1)	-3(1)	0(1)
C(9)	33(1)	35(1)	43(1)	4(1)	-8(1)	4(1)

C(10)	24(1)	42(1)	55(1)	-4(1)	-5(1)	2(1)
C(11)	27(1)	45(1)	58(2)	6(1)	4(1)	-10(1)
C(12)	34(1)	31(1)	49(1)	7(1)	-4(1)	-5(1)
C(13)	39(1)	38(1)	48(1)	9(1)	2(1)	-4(1)
C(14)	27(1)	73(2)	90(2)	-1(2)	-9(1)	6(1)
C(15)	48(1)	44(1)	66(2)	22(1)	2(1)	-6(1)
C(16)	21(1)	23(1)	37(1)	-4(1)	-1(1)	4(1)
C(17)	26(1)	32(1)	36(1)	0(1)	6(1)	2(1)
C(18)	36(1)	40(1)	28(1)	-2(1)	1(1)	6(1)
C(19)	29(1)	34(1)	37(1)	-9(1)	-3(1)	4(1)
C(20)	26(1)	24(1)	42(1)	-3(1)	2(1)	-1(1)
C(21)	24(1)	26(1)	34(1)	-3(1)	-1(1)	5(1)
C(22)	46(1)	45(1)	51(2)	7(1)	9(1)	-9(1)
C(23)	45(1)	30(1)	38(1)	2(1)	-3(1)	0(1)
C(24)	52(2)	47(1)	50(1)	-10(1)	-13(1)	-3(1)
N(2)	36(1)	26(1)	57(1)	-10(1)	11(1)	-1(1)
B(3)	32(1)	26(1)	40(1)	-8(1)	-4(1)	1(1)
B(4)	28(1)	34(1)	40(1)	-8(1)	-4(1)	4(1)
C(25)	35(1)	29(1)	32(1)	-6(1)	-4(1)	7(1)
C(26)	51(1)	32(1)	32(1)	-3(1)	-1(1)	7(1)
C(27)	67(2)	32(1)	35(1)	-4(1)	-5(1)	21(1)
C(28)	56(2)	48(1)	36(1)	-7(1)	1(1)	26(1)
C(29)	42(1)	41(1)	34(1)	-4(1)	1(1)	13(1)
C(30)	32(1)	34(1)	31(1)	-7(1)	-4(1)	6(1)
C(31)	31(1)	18(1)	40(1)	-6(1)	-1(1)	2(1)
C(32)	36(1)	21(1)	37(1)	-5(1)	-3(1)	0(1)
C(33)	30(1)	23(1)	45(1)	-2(1)	-4(1)	-2(1)
C(34)	38(1)	21(1)	40(1)	1(1)	2(1)	-1(1)
C(35)	44(1)	23(1)	33(1)	-1(1)	-4(1)	2(1)
C(36)	35(1)	20(1)	41(1)	-2(1)	-5(1)	2(1)
C(37)	43(1)	44(1)	40(1)	-10(1)	-5(1)	-5(1)
C(38)	49(1)	43(1)	47(1)	1(1)	9(1)	-9(1)
C(39)	38(1)	42(1)	51(1)	-5(1)	-11(1)	1(1)
C(40)	31(1)	34(1)	36(1)	-4(1)	2(1)	10(1)
C(41)	40(1)	48(1)	37(1)	-4(1)	-2(1)	10(1)
C(42)	58(2)	54(2)	34(1)	7(1)	-2(1)	18(1)

C(43)	55(2)	41(1)	42(1)	8(1)	12(1)	10(1)
C(44)	37(1)	37(1)	46(1)	4(1)	4(1)	2(1)
C(45)	31(1)	32(1)	40(1)	3(1)	0(1)	7(1)
C(46)	56(2)	72(2)	55(2)	-11(1)	-21(1)	9(1)
C(47)	96(2)	51(2)	60(2)	22(1)	11(2)	3(2)
C(48)	43(1)	40(1)	65(2)	12(1)	-18(1)	0(1)

Compound 6.

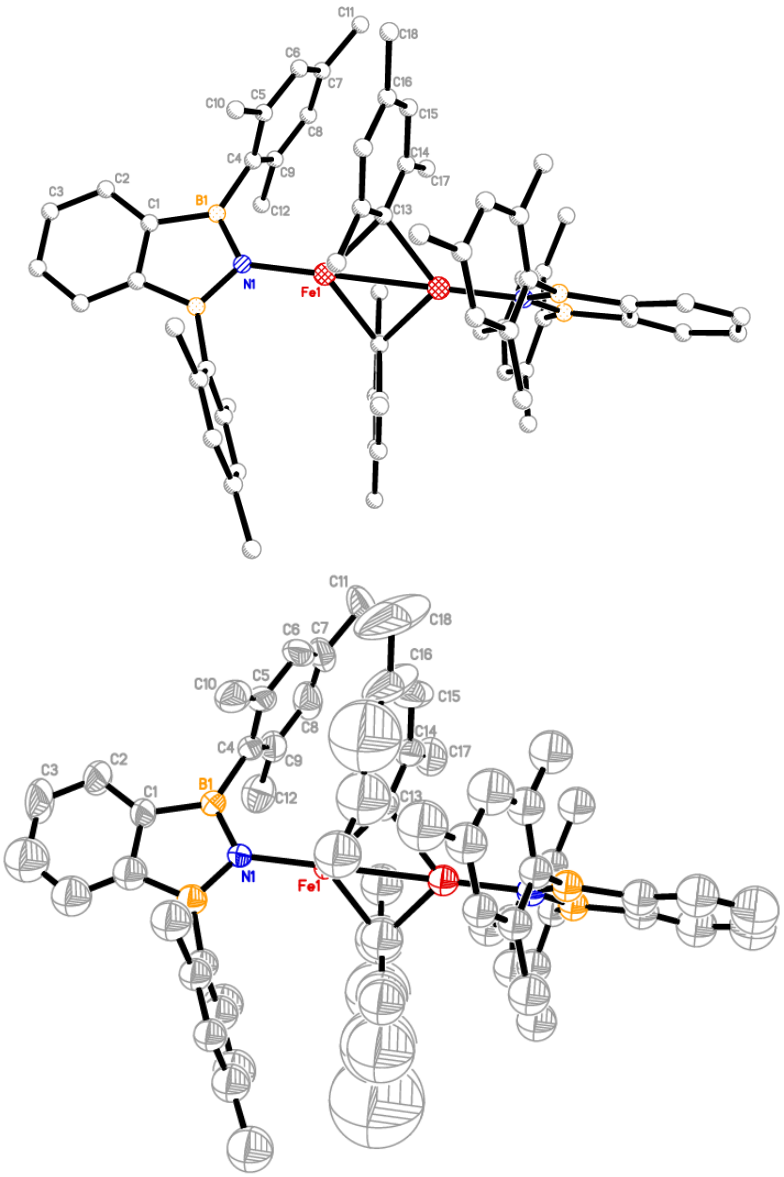


Table S13. Crystal data and structure refinement for **6**.

Identification code	BML27b	
Empirical formula	C66 H74 B4 Fe2 N2	
Formula weight	1050.21	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	F d d d	
Unit cell dimensions	a = 12.0221(12) Å	α= 90°.
	b = 30.358(3) Å	β= 90°.
	c = 32.270(3) Å	γ = 90°.
Volume	11777.6(18) $Å^3$	
Z	8	
Density (calculated)	1.185 Mg/m^3	
Absorption coefficient	0.533 mm^{-1}	
F(000)	4448	
Crystal size	0.282 x 0.095 x 0.092 mm^3	
Theta range for data collection	2.684 to 26.385°.	
Index ranges	-15<=h<=15, -37<=k<=37, -40<=l<=40	
Reflections collected	91965	
Independent reflections	3014 [R(int) = 0.0499]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.881 and 0.798	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3014 / 0 / 174	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1119	
R indices (all data)	R1 = 0.0464, wR2 = 0.1158	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.389 and -0.238 $e.Å^{-3}$	

Table S14. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	11250	1682(1)	1250	34(1)
N(1)	11250	2319(1)	1250	34(1)
B(1)	10504(2)	2598(1)	1021(1)	38(1)
C(1)	10808(2)	3096(1)	1103(1)	51(1)
C(2)	10390(3)	3492(1)	953(1)	72(1)
C(3)	10835(3)	3888(1)	1099(1)	98(1)
C(4)	9532(2)	2413(1)	745(1)	40(1)
C(5)	9723(2)	2308(1)	328(1)	48(1)
C(6)	8876(2)	2115(1)	95(1)	63(1)
C(7)	7845(2)	2030(1)	262(1)	68(1)
C(8)	7642(2)	2154(1)	666(1)	67(1)
C(9)	8467(2)	2346(1)	912(1)	52(1)
C(10)	10839(2)	2405(1)	135(1)	62(1)
C(11)	6959(3)	1803(1)	2(1)	101(1)
C(12)	8214(3)	2482(1)	1352(1)	72(1)
C(13)	11250	1250	735(1)	50(1)
C(14)	10262(3)	1163(1)	507(1)	74(1)
C(15)	10294(5)	1161(1)	72(1)	119(2)
C(16)	11250	1250	-145(2)	150(4)
C(17)	9178(3)	1082(1)	719(1)	96(1)
C(18)	11250	1250	-612(2)	239(7)

Table S15. Bond lengths [Å] and angles [°] for **6**.

Fe(1)-N(1)	1.934(2)
Fe(1)-C(13)	2.117(2)
Fe(1)-C(13)#1	2.117(2)
Fe(1)-Fe(1)#2	2.6227(7)
N(1)-B(1)	1.438(2)
N(1)-B(1)#1	1.438(2)
B(1)-C(4)	1.571(3)
B(1)-C(1)	1.580(3)
C(1)-C(2)	1.390(3)
C(1)-C(1)#1	1.426(4)
C(2)-C(3)	1.396(4)
C(3)-C(3)#1	1.395(7)
C(4)-C(5)	1.403(3)
C(4)-C(9)	1.404(3)
C(5)-C(6)	1.394(3)
C(5)-C(10)	1.508(4)
C(6)-C(7)	1.375(4)
C(7)-C(8)	1.379(4)
C(7)-C(11)	1.521(3)
C(8)-C(9)	1.398(3)
C(9)-C(12)	1.509(4)
C(13)-C(14)#2	1.422(3)
C(13)-C(14)	1.422(3)
C(13)-Fe(1)#2	2.117(2)
C(14)-C(15)	1.405(4)
C(14)-C(17)	1.492(5)
C(15)-C(16)	1.373(6)
C(16)-C(15)#2	1.373(6)
C(16)-C(18)	1.506(7)

N(1)-Fe(1)-C(13)	128.27(5)
N(1)-Fe(1)-C(13)#1	128.27(5)
C(13)-Fe(1)-C(13)#1	103.46(10)
N(1)-Fe(1)-Fe(1)#2	180.0

C(13)-Fe(1)-Fe(1)#2	51.73(5)
C(13)#1-Fe(1)-Fe(1)#2	51.73(5)
B(1)-N(1)-B(1)#1	108.0(2)
B(1)-N(1)-Fe(1)	126.02(11)
B(1)#1-N(1)-Fe(1)	126.02(11)
N(1)-B(1)-C(4)	123.06(17)
N(1)-B(1)-C(1)	109.45(17)
C(4)-B(1)-C(1)	127.48(17)
C(2)-C(1)-C(1)#1	120.08(15)
C(2)-C(1)-B(1)	133.4(2)
C(1)#1-C(1)-B(1)	106.51(11)
C(1)-C(2)-C(3)	119.2(3)
C(3)#1-C(3)-C(2)	120.67(17)
C(5)-C(4)-C(9)	118.98(19)
C(5)-C(4)-B(1)	120.16(19)
C(9)-C(4)-B(1)	120.86(19)
C(6)-C(5)-C(4)	119.6(2)
C(6)-C(5)-C(10)	120.6(2)
C(4)-C(5)-C(10)	119.8(2)
C(7)-C(6)-C(5)	121.7(2)
C(6)-C(7)-C(8)	118.6(2)
C(6)-C(7)-C(11)	120.1(3)
C(8)-C(7)-C(11)	121.3(3)
C(7)-C(8)-C(9)	121.7(3)
C(8)-C(9)-C(4)	119.3(2)
C(8)-C(9)-C(12)	120.4(2)
C(4)-C(9)-C(12)	120.3(2)
C(14)#2-C(13)-C(14)	117.6(3)
C(14)#2-C(13)-Fe(1)	106.96(13)
C(14)-C(13)-Fe(1)	121.42(13)
C(14)#2-C(13)-Fe(1)#2	121.42(13)
C(14)-C(13)-Fe(1)#2	106.96(13)
Fe(1)-C(13)-Fe(1)#2	76.55(10)
C(15)-C(14)-C(13)	119.7(4)
C(15)-C(14)-C(17)	118.8(4)
C(13)-C(14)-C(17)	121.5(2)

C(16)-C(15)-C(14)	122.1(5)
C(15)-C(16)-C(15)#2	118.7(5)
C(15)-C(16)-C(18)	120.7(2)
C(15)#2-C(16)-C(18)	120.7(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+9/4,y,-z+1/4 #2 -x+9/4,-y+1/4,z

Table S16. Anisotropic displacement parameters ($Å^2x10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	45(1)	24(1)	32(1)	0	-2(1)	0
N(1)	40(1)	28(1)	34(1)	0	-12(1)	0
B(1)	44(1)	31(1)	38(1)	2(1)	-8(1)	1(1)
C(1)	59(1)	31(1)	65(1)	2(1)	-24(1)	1(1)
C(2)	82(2)	37(1)	98(2)	12(1)	-38(2)	4(1)
C(3)	104(3)	30(1)	158(4)	10(2)	-47(2)	6(1)
C(4)	46(1)	31(1)	43(1)	2(1)	-17(1)	3(1)
C(5)	61(1)	37(1)	46(1)	-1(1)	-21(1)	11(1)
C(6)	88(2)	43(1)	57(1)	-10(1)	-36(1)	17(1)
C(7)	67(2)	36(1)	101(2)	-7(1)	-47(2)	6(1)
C(8)	47(1)	48(1)	105(2)	1(1)	-19(1)	-3(1)
C(9)	47(1)	42(1)	67(2)	4(1)	-12(1)	-2(1)
C(10)	82(2)	57(1)	46(1)	-1(1)	-1(1)	13(1)
C(11)	96(2)	49(2)	158(3)	-24(2)	-81(2)	6(2)
C(12)	72(2)	69(2)	75(2)	6(1)	14(2)	-2(1)
C(13)	89(2)	27(1)	34(1)	0	0	6(1)
C(14)	132(3)	34(1)	55(1)	-7(1)	-41(2)	21(1)
C(15)	234(6)	61(2)	62(2)	-24(2)	-71(3)	64(3)
C(16)	319(12)	92(4)	39(2)	0	0	106(6)
C(17)	96(3)	58(2)	134(3)	10(2)	-63(2)	-7(2)
C(18)	510(20)	174(8)	38(3)	0	0	179(10)

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