

Supporting Information

Metal-free hydrogen activation and hydrogenation of imines by 1,8-Bis(dipentafluorophenylboryl)naphthalene

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Materials and Methods

All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N₂ by employing standard procedures and were degassed by freeze-thaw cycles prior to use. All organic reagents were purchased from Aldrich and used without further purification. 25 mL steel autoclave was used for the catalytic reaction.

¹H NMR, ¹⁹F NMR and ¹¹B{¹H} NMR data were recorded on a Varian Gemini-200 spectrometer. Chemical shift are expressed in parts per million (ppm) referenced to deuterated solvent used. ¹⁹F NMR and ¹¹B{¹H} NMR were referenced to CFCl₃ and BF₃·OEt₂, respectively. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Microanalyses were carried out at the Anorganisch-Chemisches Institute of the University of Zürich.

Crystallographic data were collected at 183(2) K on an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single wavelength Enhance X-ray source with MoK α radiation, $\lambda = 0.71073$ Å).^[1] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction^[2] and data reduction were performed with the Oxford program suite *CrysAlisPro*.^[3] The structures were solved with direct methods (*SHELXS-97*) and were refined by full-matrix least-squares methods on F^2 (*SHELXL-97*).^[4] All programs used during the crystal structure determination processes are included in the *WINGX* software.^[5] The program *PLATON*^[6] was used to check the result of the X-ray analyses.

The crystal structure of **1** contains one molecule per asymmetric unit. All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H distances of 0.95 Å and their isotropic displacement parameters constrained to 1.2 times the value of U_{eq} of the carbon atom it binds to. No classic hydrogen bonds found.

The asymmetric unit of **2** consists of six crystallographically independent species: two 2,2,4,4-tetramethylpiperidinium, two 1,8-bis(dipentafluorophenylhydroboryl)-naphthalene and two solvent molecules of benzene. The hydrogen atoms on B1, B3, N1 and N2 were located and either freely refined (on B1 and B3) or softly restrained (on N1 and N2). One solvent molecule of benzene is positionally disordered in a ratio 0.47:0.53. All other hydrogen positions were calculated after each cycle of refinement using a riding model with C—H distances of 0.93 - 0.97 Å and their isotropic displacement parameters constrained to 1.2 or 1.5 times the value of U_{eq} of the atom it binds to. No classical hydrogen bonds found. Despite a selected crystal with a suitable size (0.24 x 0.14 x 0.12 mm³) the ratio observed / unique reflections was quite low and may be responsible of the relatively high R_{int} observed.

The crystal structure of **3** consists of two crystallographically independent molecules of bis(dipentafluorophenylboryl)-naphthalene-dibenzophenoneimine and solvent molecules of chloroform and hexane. Restraints were used to correct the geometry of the hexane molecule (with *DFIX* and *DANG*) and the thermal parameters of the hexane molecule and one of the two chloroform molecules (with *EADP*). Both molecules of chloroform are positionally disordered (0.50:0.50 and 0.34:0.66). All hydrogen positions were calculated after each cycle of refinement using a riding model with C—H distances of 0.93 Å and N—H distances of 0.86 Å and their isotropic displacement parameters constrained to 1.2 times the value of U_{eq} of the atom it binds to. No classic hydrogen bonds found.

There is one relatively "strong" residual peak ($Q1 = 2.45 \text{ e}^- \cdot \text{Å}^{-3}$) located at 1.2 Å from C126 of the solvent molecule of hexane. The solvent molecule of hexane lies on a special position (center of inversion) which led to refine only one half of the molecule. One can not exclude the fact that the molecule is disordered or partially disordered about the crystallographic inversion center or that the molecule does not fully occupy the site but among the possible refinements the chosen one was the most satisfactory. F23 exhibits a cigar-shaped ellipsoid like its near carbon or fluorine neighbours. It seems that the whole corresponding C₆F₅ ligand could be very slightly disordered over two positions, but it is not sufficiently significant to be refined in a different way. The splitting of the sole F23 would

be meaningless.

Crystallographic data for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 724802 (1), CCDC 731638 (2), 724803 (3).

Crystal data for **1**: space group $P\bar{1}$, $a = 10.5171(4)$, $b = 11.9691(4)$, $c = 14.0547(5)$ Å, $\alpha = 69.240(3)$, $\beta = 84.669(3)$, $\gamma = 66.772(4)^\circ$, $V = 1517.98(11)$ Å³, $Z = 2$, $\mu = 0.189$ mm⁻¹, 17221 reflections collected, 6206 independent ($R_{\text{int}} = 0.0386$), $R_I = 0.0448$, $wR_2 = 0.0770$ (for 3517 observed reflections with $I \geq 2\sigma(I)$ and 505 refined parameters). CCDC 724802.

Crystal data for **2**: space group $P2_1/c$, $a = 28.2693(9)$, $b = 16.9611(5)$, $c = 18.6599(9)$ Å, $\beta = 96.118(3)^\circ$, $V = 8896.1(6)$ Å³, $Z = 8$, $\mu = 0.148$ mm⁻¹, 74894 reflections collected, 15793 independent ($R_{\text{int}} = 0.1511$), $R_I = 0.0679$, $wR_2 = 0.1414$ (for 6368 observed reflections with $I \geq 2\sigma(I)$ and 1288 refined parameters). CCDC 731638.

Crystal data for **3**: space group $P2_1/n$, $a = 19.6245(2)$, $b = 24.8943(3)$, $c = 22.7758(3)$ Å, $\beta = 98.977(1)^\circ$, $V = 10990.6(2)$ Å³, $Z = 2$, $\mu = 0.243$ mm⁻¹, 113766 reflections collected, 20853 independent ($R_{\text{int}} = 0.0395$), $R_I = 0.0696$, $wR_2 = 0.1941$ (for 13444 observed reflections with $I \geq 2\sigma(I)$ and 1599 refined parameters). CCDC 724803.

Preparation of compound **1**^[7]

In a 100mL flask, under N₂, (0.52g, 1.36 mmol) diiodonaphthalene^[8] was dissolved in 30 mL dry toluene. The solution was cooled to -78°C with stirring, 1.7mL (2.7mmol) of a solution of n-butyl lithium (1.6M in hexane) was added dropwise with a syringe. The solution became dark brown, and allowed to stir for 2h at -78°C. Then a solution of chlorodi(pentafluorophenyl)borane^[9] (1.03g, 2.7mmol) in 10mL toluene was added slowly through a cannula. The solution became orange in color, and was allowed to warm temperature. After 20h of stirring at room temperature, removed some precipitation through filtration and the solvent was removed *in vacuo* to half volume and hexane was added to promote precipitation. The mixture was filtered, washed with hexane and dried *in vacuo*. The product was collected as yellow solid. Yield: 25 %. Crystals were obtained from toluene solution at -35 °C. **Anal. Calcd** for C₃₄H₆B₂F₂₀: C, 50.04; H, 0.74. Found: C,

49.97; H, 0.80. $^1\text{H NMR}$ (toluene- d_8 , 200 MHz, 293 K): δ = 7.61 (d, 2H, $^3J_{\text{HH}} = 8\text{Hz}$, Ar-*H*), 7.41 (d, 2H, $^3J_{\text{HH}} = 8\text{Hz}$, Ar-*H*), 7.10 (t, 2H, $^3J_{\text{HH}} = 8\text{Hz}$, Ar-*H*). $^{19}\text{F NMR}$ (toluene- d_8 , 188 MHz, 293 K): δ = -127.43 (d, 8F, $^3J_{\text{FF}} = 21\text{Hz}$, *o*- C_6F_5), -145.87 (t, 4F, $^3J_{\text{FF}} = 21\text{Hz}$, *p*- C_6F_5), -161.83 (t, 8F, $^3J_{\text{FF}} = 19\text{Hz}$, *m*- C_6F_5). $^{13}\text{C NMR}$ (toluene- d_8 , 50MHz, 293 K): δ = 112.87 (B-C), 133.74 (C-3,6), 136.90(C-4,5), 137.94 (dm, $^1J_{\text{C-F}} = 250\text{Hz}$, *m*- C_6F_5), 139.36 (C-10), 141.30 (C-2,7), 144.71 (C-9), 144.88 (dm, $^1J_{\text{C-F}} = 252\text{Hz}$, *p*- C_6F_5), 147.16(C-1,8), 149.03 (dm, $^1J_{\text{C-F}} = 252\text{Hz}$, *o*- C_6F_5).

Preparation of compound 2

Complex **1** (0.041 g, 0.05 mmol) and 2,2,6,6-tetramethylpiperidine (0.141g, 0.1mmol) were added to a 50 mL Schlenk and dissolved in toluene (5 mL) giving a yellow solution. The solution was filled with H_2 (1500 mbar) and allowed the solution to stir at 80°C for 24 h. There was no precipitation formed during this process. The reaction was then concentrated to half volume and hexane was added to promote precipitation. The product was washed by hexane after filtration and dried *in vacuo*. Yield: 23 %. Crystals were obtained from a mixture of benzene / hexane at 25°C . Anal.Calcd. for $\text{C}_{43}\text{H}_{27}\text{B}_2\text{F}_{20}\text{N}$: C, 53.84; H, 2.84; N, 1.46. Found: C, 53.69; H, 2.77; N, 1.39. $^1\text{H NMR}$ (benzene- d_6 , 200MHz): δ = 7.82 (d, 2H, $^3J_{\text{HH}} = 8\text{Hz}$, Ar-*H*), 7.51 (d, 2H, $^3J_{\text{HH}} = 8\text{Hz}$, Ar-*H*), 7.30 (t, 2H, $^3J_{\text{HH}} = 8\text{Hz}$, Ar-*H*), 2.89 (br, 1H, BHB), 2.11 (s, 2H, NH), 0.66 (m, 2H, CH_2), 0.48 (m, 4H, CH_2), 0.22 (s, 12H, CH_3). $^{19}\text{F NMR}$ (benzene- d_6 , 188MHz, 293K): δ = -129.82 (d, 8F, $^3J_{\text{FF}} = 24\text{ Hz}$, *o*- C_6F_5), -159.61 (t, 4F, $^3J_{\text{FF}} = 26\text{ Hz}$, *p*- C_6F_5), -166.28 (t, 8F, *m*- C_6F_5). The solubility of **2** was too low to permit weak (C_6F_5) resonances to be observed in the ^{13}C NMR spectrum.

Preparation of compound 3

Complex **1** (0.0082 g, 0.01 mmol) and benzophenone imine (0.0018 g, 0.01 mmol or 0.0036 g, 0.02 mmol) were dissolved in benzene (0.5 mL) giving a yellow solution. The yellow precipitate formed after 5 min at rt. The product was washed by hexane after

filtration and dried *in vacuo*. Yield: 65%. Crystals were obtained from a mixture of chloroform/hexane at 25 °C. Anal. Calcd. for C₆₀H₂₈B₂F₂₀N₂: C, 61.15; H, 2.39; N, 2.38. Found: C, 61.06; H, 2.31; N, 2.17. ¹H NMR (benzene-d₆, 200 MHz, 293K): δ = 10.67 (br, 2H, NH), 7.75 (d, 4H, ³J_{HH} = 8Hz, Ar-H), 7.23-6.98 (m, 14H, Ar-H), 6.52 (t, 2H, ³J_{HH} = 8Hz, Ar-H), 6.33 (t, 4H, ³J_{HH} = 8Hz, Ar-H) 6.17 (d, 2H, ³J_{HH} = 8Hz, Ar-H). ¹¹B {¹H} NMR (benzene-d₆, 64 MHz, 293 K): δ = -10.38 (s). ¹⁹F NMR (benzene-d₆, 188 MHz, 293 K): δ = -127.49 (d, 2F, ³J_{FF} = 23Hz, *ortho*-C₆F₅), -130.11 (d, 2F, ³J_{FF} = 26Hz, *ortho*-C₆F₅), -136.97 (br, 2F, *ortho*-C₆F₅), -140.60 (d, 2F, ³J_{FF} = 24 Hz, *ortho*-C₆F₅), -157.78 (t, 2F, ³J_{FF} = 19 Hz, *para*-C₆F₅), -160.14 (t, 1F, ³J_{FF} = 24 Hz, *para*-C₆F₅), -163.39 (br, 1F, *para*-C₆F₅), -165.46 (m, 8F, *meta*-C₆F₅). The solubility of **3** was too low to permit weak (C₆F₅) resonances to be observed in the ¹³C NMR spectrum.

Catalytic hydrogenation of imines using Complex **1** or B(C₆F₅)₃

1. 5 or 15 bar H₂

A [D]-benzene solution of imines (0.05 mmol) and complex **1** (0.0041g, 0.005mmol) or B(C₆F₅)₃ (0.0026g, 0.005mmol) was added to a 25 mL steel autoclave, and filled with (15 or 5) bar H₂. ¹H NMR spectra were taken after 1 h of the reaction at 120 °C.

2. 1500 mbar H₂

In a 25 mL Young Schlenk, a [D]-benzene solution of PhCH=N*t*Bu (0.05 mmol) and complex **1** (0.0041 g, 0.005 mmol) or B(C₆F₅)₃ (0.0026 g, 0.005 mmol) were added. After freezing the solution, the N₂ atmosphere was exchanged with 1500 mbar of H₂. The solution was heated at 80 °C. Monitor the reaction mixture by ¹H NMR.

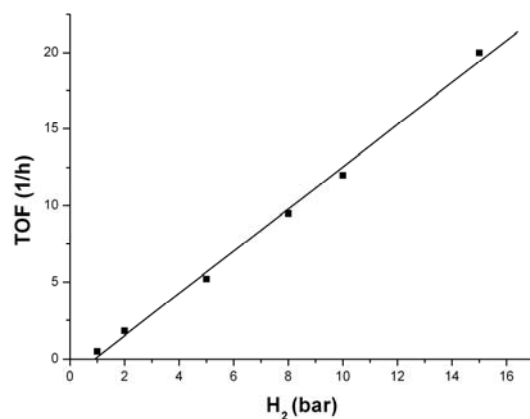
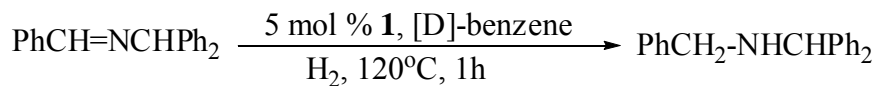
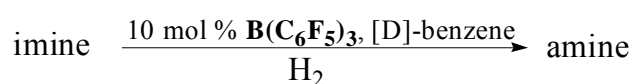


Figure S1. Catalytic hydrogenation of PhCH=NCHPh₂ with **1** at 120 °C for 1 h under variation of the H₂ pressure.

Table S1

Catalytic hydrogenation of imines with B(C₆F₅)₃ and H₂.



Entry	Substrate	t (h)	T (°C)	H ₂ (bar)	Product	Yield (%)
1	PhCH=N <i>t</i> Bu	1	80	1.5	PhCH ₂ NH <i>t</i> Bu	> 99
2	PhCH=N <i>t</i> Bu ^{a)}	12	80	1.5	PhCH ₂ NH <i>t</i> Bu	> 99
3	<i>p</i> -ClC ₆ H ₄ CH=NC ₆ H ₄ Cl- <i>p</i>	1	120	5	<i>p</i> -ClC ₆ H ₄ CH ₂ NHC ₆ H ₄ Cl- <i>p</i>	> 99
4	<i>p</i> -ClC ₆ H ₄ CH=NC ₆ H ₄ Cl- <i>p</i> ^{a)}	1	120	5	<i>p</i> -ClC ₆ H ₄ CH ₂ NHC ₆ H ₄ Cl- <i>p</i>	34

a) *cat.* compound **1**

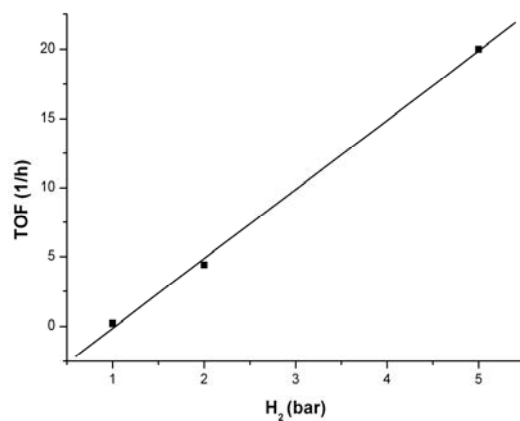
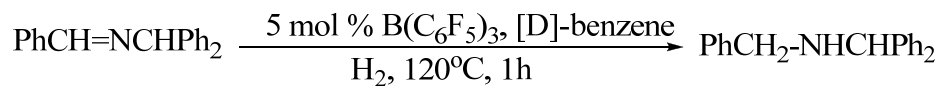


Figure S2. Catalytic hydrogenation of PhCH=NCHPh₂ with B(C₆F₅)₃ at 120 °C for 1 h under variation of the H₂ pressure.

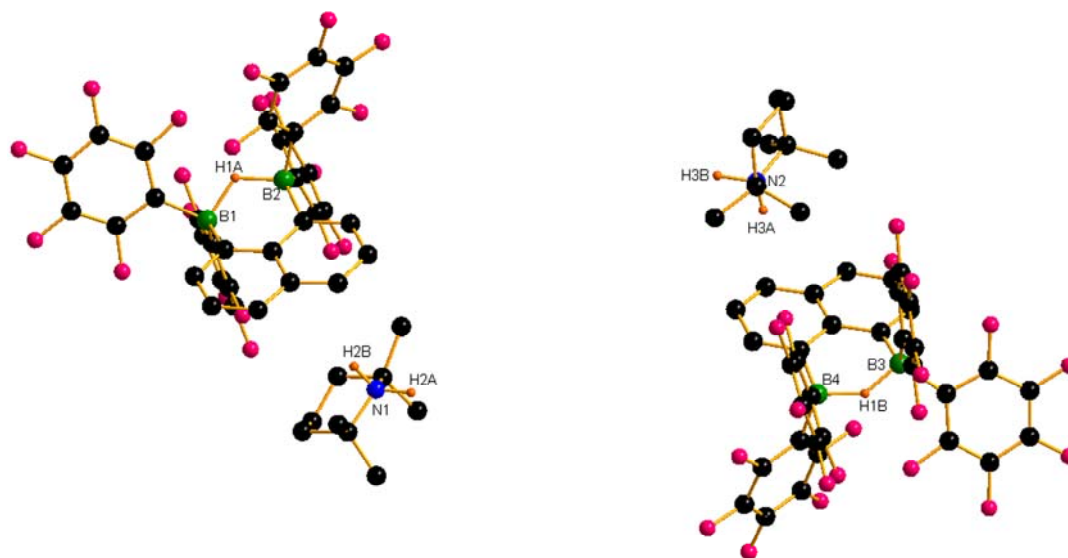


Figure S3. A view of the molecular structure of compound **2**. Hydrogen atoms except H_N and H_B are omitted for clarity. C: black, B: green, N: blue, F: pink, H: orange. B1-H1A-B2 121(3)°, B3-H1B-B4 143(3)°. B1-H1A 1.45(5) Å, B2-H1A 1.41(5) Å, B3-H1B 1.31(5) Å, B4-H1B 1.36(5) Å, N1-H2A 0.88(3) Å, N1-H2B 0.88(4) Å, N2-H3A 0.88(3) Å, N2-H3B 0.88(4) Å. B1...B2 2.491(8) Å, B3...B4 2.534(8) Å.

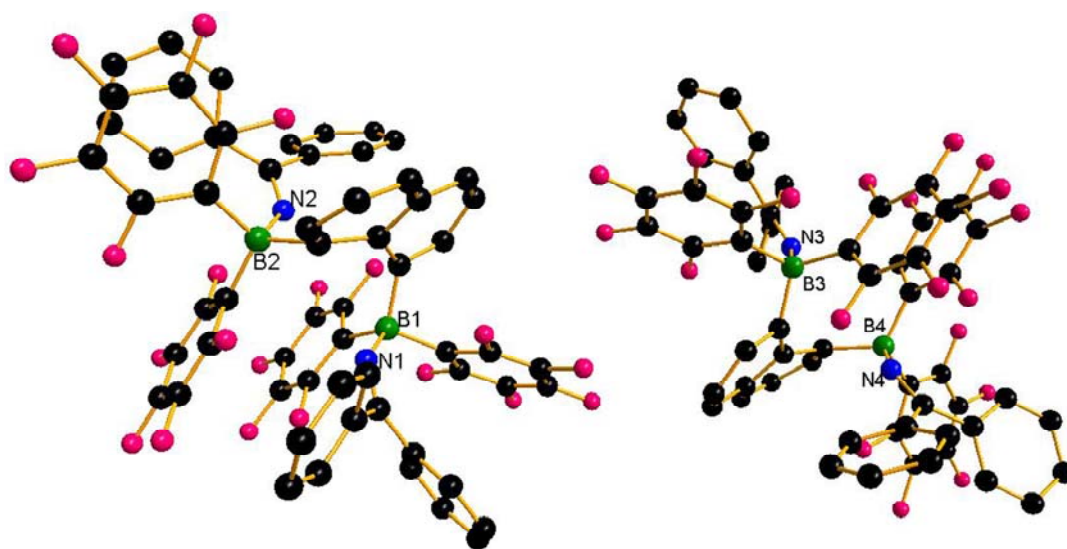


Figure S4. A view of the molecular structure of compound **3**. Hydrogen atoms are omitted for clarity. C: black, B: green, N: blue, F: pink. B1-N1 1.598(4), B2-N2 1.601(4), B3-N3 1.601(4), B4-N4 1.601(4), B1...B2 3.851(5), B3...B4 3.870(5) Å.

References

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