Supporting Information to

# Stable, crystalline boron complexes with mono-, di- and trianionic formazanate ligands

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#### **Experimental Section**

#### **General Considerations.**

All manipulations were carried out under nitrogen or argon atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al<sub>2</sub>O<sub>3</sub> (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al<sub>2</sub>O<sub>3</sub> (Fluka). For synthesis of the very sensitive compounds 4, THF and hexane were additionally dried on Na/K alloy and subsequently vacuum transferred and stored under nitrogen. All solvents were degassed prior to use and stored under nitrogen.  $C_6D_6$  (Aldrich) and  $d_8$ -THF (Sigma-Aldrich) were vacuum transferred from Na/K alloy and stored under nitrogen. The compound { $[MesN_2]^+[BF_4]^-$ } and ligands PhNNC(p-tolyl)NNPh (**1a**)<sup>2</sup> & PhNNC(p-tolyl)NNMes (**1b**)<sup>3</sup> were synthesized according to published procedures. NMR spectra were recorded on Varian Mercury 400 or Inova 500 spectrometers. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); J is reported in Hz. Assignments of NMR resonances was aided by COSY, NOESY, HSQC and HMBC experiments using standard pulse sequences. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany). UV-Vis spectra were recorded in THF solution (~ 10<sup>-4</sup> M) using a Perkin Elmer Lambda 900 in a quartz cell that was sealed under N<sub>2</sub> atmosphere. EPR spectra were recorded on a Bruker EMXplus spectrometer at 300K in THF solution. Cyclic voltammetry (CV) was performed using a threeelectrode configuration comprising a Pt wire counter electrode, a Ag wire pseudo reference electrode and a Pt disk working electrode (CHI102, CH Instruments, diameter = 2 mm). The Pt working electrode was polished before each experiment using an alumina slurry (0.05 µm), rinsed (thrice) with distilled water and acetone. The electrodes were then dried in an oven at 75 °C for at least one hour to remove any residual traces of water. The CV data were referenced by measuring the redox potential of ferrocene, which was added as a THF solution at the end of the experiment. In all cases, there is no indication that addition of ferrocene influences the electrochemical behavior. All electrochemical measurements were performed at ambient temperatures in a nitrogen glovebox with the compounds dissolved in THF containing 0.1 M [ $^{n}Bu_{4}N$ ][PF<sub>6</sub>] as the supporting electrolyte. The electrochemical data were measured using an Autolab PGSTAT 100 computer-controlled potentiostat with Autolab NOVA software (v.1.11).

Synthesis of (PhNNC(*p*-tol)NNPh)BPh<sub>2</sub> (2a). 3-*p*-tolyl-1,5-diphenyl-formazan 1a (1.005 g, 3.2 mmol) and triphenyl borane (1.55 g, 6.4 mmol) were weighed out inside a glovebox, added into a 250 mL Schlenk flask and subsequently dissolved by addition of 110 mL of dry toluene. The mixture was heated to 125 °C under an inert atmosphere for 3 days. After this the solvent was evaporated. NMR analysis of the crude product ( $C_6D_6$ ) indicated full conversion of the formazan starting material and the presence of minor impurities. Purification was achieved by column chromatography (Al<sub>2</sub>O<sub>3</sub>; hexane:DCM = 7:3). The solvent was removed under reduced pressure and the solid product was recrystallized by cooling a hot hexane solution to -30 °C. After standing at -30 °C for 1 day, crystals had separated which were collected by filtration. Subsequent drying gave 2a as dark pink crystalline material (970 mg, 2.03 mmol, 63 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C)  $\delta$  8.02 (d, J = 8.1

Hz, 2H, p-tolyl-o-H), 7.40 – 7.29 (m, 8H, (B-Ph & N-Ph) m-H), 7.09–7.02 (m, 6H, B-Ph o-H & p-H), 6.95 (d, J = 8.1 Hz, 2H, p-tolyl-m-H), 6.86 – 6.77 (m, 6H, N-Ph o-H & p-H), 2.02 (s, 3H, p-tolyl-CH<sub>3</sub>). <sup>11</sup>B NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ 1.74 (s ). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ 154.37 (N**C**N), 146.91 (N-C(ipso)-Ph), 143.80 (B-C(ipso)-Ph), 139.03 (p-tolyl CH<sub>3</sub>), 135.30 (B-Ph m-CH), 131.46 (p-tolyl-C(ipso)-NCN), 129.60 (p-tolyl m-CH), 128.44 (N-Ph o-CH), 127.94 (N-Ph p-CH), 127.61 (B-Ph o-CH), 127.33 (B-Ph p-CH), 126.78 (N-Ph m-CH), 125.60 (p-tolyl o-CH), 21.23 (p-tol CH<sub>3</sub>). Anal. Calcd for C<sub>32</sub>H<sub>27</sub>BN<sub>4</sub>: C, 80.34; H, 5.69; N, 11.71. Found: C, 80.05; H, 5.71; N, 11.59.

**Synthesis of [(PhNNC(***p***-tol)NNPh)BPh**<sub>2</sub>**][Cp**\*<sub>2</sub>**Co]**·(**2THF) (3a).** Compound **2a** (151 mg, 0.316 mmol) and decamethylcobaltocene (**Cp**\*<sub>2</sub>**Co)** (107 mg, 0.325 mmol) were mixed in 2ml dry THF in a vial and the reaction mixture was kept stirring for 12 h, during which time the mixture turned green. Filtration and addition of hexane (4 mL) precipitated a green crystalline material. The mixture was subsequently cooled to -30 °C to complete precipitation of the product. The intense green color crystals were washed with pentane (3 x 2 mL) and dried to give **3a** as green crystals (201 mg, 0.228 mmol, 72 %).

Based on the X-ray analysis, there are 2 THF solvate molecules present per boron fragment, one of which is somewhat disordered. Elemental analysis data for crystalline **3a** are in better agreement with the presence of 1 THF molecule, which suggests that the disordered THF may have only partial occupancy, or is partially removed upon drying the crystals. For comparison, we report here the calculated analysis data with 1 and 2 THF molecules present. The found analysis values are consistent with a THF/B ration of somewhere in between 1 and 2. With 1 THF,  $C_{56}H_{65}BCoN_4O$ : C, 76.44; H, 7.45; N, 6.37. With 2 THF,  $C_{60}H_{73}BCoN_4O_2$ : C, 75.70; H, 7.73; N, 5.89. Found: C, 76.51; H, 7.98; N, 5.88.

[(PhNNC(p-tol)NNPh)BPh<sub>2</sub>][Na<sub>2</sub>(THF)<sub>6</sub>]<sup>•</sup>THF (4a). To a solution of naphthalene (73.05 mg, 0.57 mmol) in 4 mL of THF was added sodium metal (19.55 mg, 0.85 mmol). After stirring for 12 h, the mixture was filtered and the green solution was added to a vial containing **2a** (134 mg, 0.28 mmol). The reaction mixture was stirred for 12 h, during which it changed color from dark pink to green and finally orange. A layer of hexane (3 mL) was added onto the THF solution, and after slow diffusion of the two layers the mixture was stored at -30 °C for 2 more days. The resulting orange crystals were washed with pentane (3 x 2 mL) and dried to give compound 4a as a highly air-sensitive solid (150 mg, 0.157 mmol, 56 %). <sup>1</sup>H NMR (400 MHz, THF- $d_8$ , 25°C)  $\delta$  8.17 (d, J = 7.9 Hz, 2H, p-tol o-H), 7.62 (d, J = 7.1 Hz, 4H, BPh o-H), 7.03 (d, J = 7.8 Hz, 2H, p-tol m-H), 6.95 (q, J = 7.4 Hz, 8H, BPh & NPh m-H), 6.84 (t, J = 7.1 Hz, 2H, BPh p-H), 6.55 (t, J = 7.7 Hz, 4H, NPh o-H), 5.85 (t, J = 6.9 Hz, 2H, NPh p-H), 3.62 (t, J = 6.4 Hz, 14H, THF), 2.30 (s, 3H, p-tol CH<sub>3</sub>), 1.82 – 1.70 (m, 14H, THF). <sup>11</sup>B NMR (128.3 MHz, d<sub>8</sub>-THF, 25 °C) δ -0.99 (s). <sup>13</sup>C NMR (125 MHz, THF-*d*<sub>8</sub>, 25°C) δ 153.07 (N-C(ipso) Ph), 152.71 (N*C*N), 142.94 (p-tol CCH<sub>3</sub>), 136.11 (B-C(ipso) Ph), 135.46 (p-tol C(ipso)-NCN), 135.08 (BPh o-CH), 128.16 (p-tol m-CH), 128.06 (NPh o-CH), 127.65 (p-tol o-CH) , 127.18 (BPh m-CH), 124.00 (BPh p-CH), 114.11 (NPh m-CH), 109.69 (NPh p-CH), 68.39 (THF), 26.56 (THF), 21.46 (p-tol CH<sub>3</sub>). According to X-ray analysis, the crystals contain 6 molecules of THF that are bound to Na<sup>+</sup> cations, and one THF solvate molecule. Drying of the crystals changed their lustrous appearance, indicating that (partial) loss of the THF solvate may be occurring. Due to its highly air-sensitive nature combined with the facile loss of solvent, all our elemental analysis measurements gave consistently low values, especially for C and H analyses.

Synthesis of (PhNNC(p-tol)NNMes)BPh<sub>2</sub> (2b). 3-p-tolyl-1-mesityl-5-phenyl-formazan 1b (400 mg, 1.12 mmol) and triphenyl borane (406.8 mg, 1.68 mmol) were weighed out inside a glove box and added into a 250 mL Schlenk flask. After dissolution n 60 mL of dry toluene, the mixture was heated and stirred at 120 °C for 2 days. After this the solvent was evaporated. The crude product was purified by column chromatography (SiO<sub>2</sub>; hexane: DCM = 4:1) and the solvent was evaporated on the rotavap. The product was subsequently crystallized by cooling a hot hexane solution to room temperature and then to -30 °C overnight. The precipitate was collected by filtration to give 2b as intense pink crystalline product (430 mg, 0.826 mmol, 74 %). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25°C) δ 7.96 (d, J = 8.0 Hz, 2H, p-tol o-H), 7.53 – 7.48 (m, 2H, NPh m-H), 7.45 (s, 4H, BPh m-H), 7.07 - 6.99 (m, 6H, BPh (o + p)-H), 6.94 (d, J = 7.9 Hz, 2H, p-tol m-H), 6.88 (overlapped d, 2H, NPh o-H), 6.87 (overlapped m, 1H, NPh p-H), 6.40 (s, 2H, Mes m-H), 2.00 (s, 3H, p-tol CH<sub>3</sub>), 1.99 (s, 6H, Mes o-CH<sub>3</sub>), 1.89 (s, 3H, Mes p-CH<sub>3</sub>). <sup>11</sup>B NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ 2.27 (s). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C) δ 154.66 (NCN), 145.54 (N-C(ipso) Ph), 143.13 (N-C(ipso) Mes), 142.1 (B-C(ipso) Ph), 139.18 (p-tol CCH<sub>3</sub>), 138.30 (Mes-C(ipso) p-CH<sub>3</sub>), 136.40 (Mes-C(ipso) o-CH<sub>3</sub>), 136.02 (BPh m-CH), 131.19 (NCN-C-p-tol), 129.63 (Mes-CH), 129.59 (p-tol o-CH), 128.41 (NPh o-CH), 128.19 (NPh p-CH), 127.19 (NPh m-CH), 127.08 (BPh o-CH), 127.02 (BPh p-CH), 125.86 (p-tol m-CH), 21.22 (p-tol CH<sub>3</sub>), 20.77 (Mes p-CH<sub>3</sub>), 19.74 (Mes o-CH<sub>3</sub>). Despite repeated attempts, samples of **2b** consistently gave low analysis values for C content, while H and N analyses gave satisfactory agreement with calculated values. Anal. Calcd for C<sub>35</sub>H<sub>33</sub>BN<sub>4</sub>: C, 80.77; H, 6.39; N, 10.76. Found: C, 79.81; H, 6.39; N, 10.61.

Synthesis of [(PhNNC(*p*-tol)NNMes)BPh<sub>2</sub>][Cp\*<sub>2</sub>Co]<sup>-</sup>THF (3b). Compound 2b (50 mg, 0.096 mmol) and decamethylcobaltocene (31.64 mg, 0.096 mmol) were mixed in a vial and stirred with 1 mL of dry THF. After 12 h, the green reaction mixture was filtered and a layer of hexane was added on top of the THF solution. Slow interdiffusion of the layers resulted in the precipitation of green crystals. After removal of the supernatant, the crystals were washed with pentane (3 x 1 mL) and dried to give **7** as green crystalline material (62 mg, 0.073 mmol, 76 %). Anal. Calcd for  $C_{59}H_{71}BN_4CoO$ : C, 76.86; H, 7.76; N, 6.08. Found: C, 76.79; H, 7.81; N, 5.93.

Synthesis of [(PhNNC(p-tol)NNMes)BPh<sub>2</sub>]<sub>2</sub>[Na<sub>4</sub>(THF)<sub>7</sub>] (4b). A solution of NaC<sub>10</sub>H<sub>8</sub> was prepared as described for 4a (naphthalene: 24.6 mg, 0.192 mmol; Na: 6.6 mg, 0.288 mmol; in 1 mL of THF). This solution was added to compound 2b (50 mg, 0.096 mmol), which caused the color of the solution to change from pink to green and finally orange. After stirring for 12 h, hexane (2 mL) was added on top of the THF solution which, after standing for 2 days at room temperature, caused the precipitation of orange crystals. The crystals were washed with pentane (3 x 1 mL) and dried to give 4b as a highly air-sensitive solid (53 mg, 0.064 mmol, 67 %). <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, -30 °C)  $\delta$  7.70 (d, J = 7.3 Hz, 2H, p-tol o-H), 7.31 (br, 4H, B-Ph, m-H), 7.17 (d, J = 8.0 Hz, 1H, N-Ph o-H), 6.88 (d, J = 7.4 Hz, 2H, p-tol m-H), 6.77-6.72 (bd, J = 18.2 Hz, 7H, overlapped Ph m-H (1H) + B-Ph o/p-H (6H)), 6.29 (s, 2H, N-Mes m-H), 6.01 (t, J = 7.6 Hz, 1H, N-Ph m-H), 5.76 (d, J = 8.6 Hz, 1H, N-Ph o-H), 5.57 (t, J = 6.6 Hz, 1H, N-Ph p-H), 3.61 (m, THF), 2.21 (m, 3H, p-tol CH<sub>3</sub>), 1.99 (s, 3H, Mes p-CH<sub>3</sub>), 1.94 (s, 6H, Mes o-CH<sub>3</sub>), 1.78 (m, THF). <sup>11</sup>B NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C)  $\delta$  -0.97 (s). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, -30°C)  $\delta$ 156.32 (NCN), 152.55 (N-C(ipso)-Mes), 151.32 (N-C(ipso)-Ph), 144.08 (NCN-C(ipso)-p-tol), 136.35 (Mes-C(ipso)o-CH<sub>3</sub>), 136.20 (BPh m-CH), 134.29 (p-tol C(ipso)-p-CH<sub>3</sub>), 129.18 (NPh m-CH), 128.87 (Mes-CH), 127.93 (p-tol m-CH), 126.60 (Mes-C(ipso)-p-CH<sub>3</sub>), 126.56 (p-tol o-CH<sub>3</sub>), 126.41 (NPh m-CH), 125.53 (BPh o-CH), 123.12 (BPh p-CH), 117.59 (NPh o-CH), 109.06 (NPh o-CH), 106.15 (NPh p-CH), 68.29 (THF), 26.45 (THF), 21.38 (Mes o-CH<sub>3</sub>), 21.34 (p-tol CH<sub>3</sub>), 21.12 (Mes p-CH<sub>3</sub>).

According to X-ray analysis, the crystals contain 7 molecules of THF that are bound to 4 Na<sup>+</sup> cations, and disordered electron density that is likely due to the present of one (or more) solvent molecules (THF and/or hexane). Drying of the crystals changed their lustrous appearance, indicating that (partial) loss of the solvent molecules may be occurring. Due to this, and its high sensitivity, a satisfactory elemental analysis could not be obtained despite repeated attempts.

### X-ray crystallography

Suitable crystals of compounds 2a, 3a, 3b, 4a and 4b were mounted on top of a cryoloop and transferred into the cold (100 K) nitrogen stream of a Bruker D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX2<sup>4</sup>. Data collection was carried out at 100 K using Mo radiation (0.71073 Å). The final unit cell was obtained from the xyz centroids of 9867 (2a), 9792 (3a), 9798 (3b), 9668 (4a) or 9823 (4b) reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS)<sup>4</sup>. The structures were solved by direct methods using SHELXS, and refinement of the structure was performed using SHLELXL<sup>5</sup>. For **3a**, refinement indicated the presence of two THF solvate molecules, of which one was somewhat disordered and/or partially occupied. Removal of its contribution using the PLATON/SQUEEZE routine<sup>6</sup> allowed convergence of the refinement. Refinement of **4b** was frustrated by a disorder problem: several THF molecules bound to the Na cations showed high anisotropic displacement parameters. The THF-carbon atoms that were most affected by this disorder were split in two components for which site-occupancy factors were refined. In addition, large residual peaks were observed in the difference Fourier map, which is likely due to disordered solvate molecules. The contribution from this region was removed using the PLATON/SQUEEZE routine<sup>6</sup>. In the final stages of refinement, some atoms showed unrealistic displacement parameters, and one atom (C94A) refined to non-positive definite values. Ultimately, SIMU and DELU instructions were applied. The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Crystal data and details on data collection and refinement are presented in Table S1.



Figure S1. Molecular structure of **2a** (left) and **3a** (right) showing 50% probability ellipsoids, hydrogen atoms and THF solvate molecule (for 3a) omitted for clarity.

	2a	3a	3b	4a	{4b}2
chem formula	C32 H27 B N4	C56 H65 B Co N4 O	C59 H71 B Co N4 O	C60 H83 B N4 Na2 O7	C98 H122 B2 N8 Na4 O7
Mr	478.38	879.86	921.93	1029.09	1637.61
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	triclinic
color, habit	red, block	green, platelet	green, platelet	orange, block	orange, block
size (mm)	0.32 x 0.18 x 0.08	0.22 x 0.21 x 0.04	0.30 x 0.20 x 0.07	0.39 x 0.21 x 0.19	0.47 x 0.40 x 0.33
space group	<i>P</i> 2 <sub>1</sub> /c	P21/c	<i>C</i> 2/c	<i>P</i> -1	<i>P</i> -1
a (Å)	9.5375(3)	13.3417(6)	42.008(4)	11.0324(4)	13.2345(9)
b (Å)	15.5183(5)	14.8614(7)	11.3469(10)	12.8217(5)	19.0244(14)
c (Å)	17.4792(6)	25.5659(12)	21.4239(18)	20.6913(8)	22.8548(15)
α (°)				78.4851(12)	88.975(2)
β (°)	99.2996(12)	92.1498(16)	101.719(3)	84.7390(17)	78.902(2)
γ (°)				79.0342(14)	81.576(2)
V (ų)	2553.02(14)	5065.5(4)	9999.2(15)	2811.20(19)	5585.5(7)
Z	4	4	8	2	2
$ ho_{calc}$ , g.cm <sup>-3</sup>	1.245	1.154	1.225	1.216	0.974
Radiation [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ(Mo K <sub>α</sub> ), mm <sup>-1</sup>	0.074	0.380	0.388	0.092	0.074
F(000)	1008	1876	3944	1108	1752
temp (K)	100(2)	100(2)	100(2)	100(2)	100(2)
$\theta$ range (°)	2.879 - 27.148	2.855 - 25.027	2.834 - 27.195	2.712 - 26.372	2.877 - 24.814
data collected (h,k,l)	-12:12; -15:19; - 22:22	-15:15; -17:17; - 30:30	-53:53; -14:14; - 27:27	-13:13; -16:16; - 25:25	-15:15; -22:22; - 26:26
no. of rflns collected	31641	74035	108255	104408	86821
no. of indpndt reflns	5633	8925	11087	11468	19067
observed reflns $F_o \ge 2.0 \sigma (F_o)$	4698	6889	9613	9320	13763
R(F) (%)	3.75	6.19	6.56	7.21	6.98
wR(F <sup>2</sup> ) (%)	9.67	13.57	13.04	15.41	19.95
GooF	1.036	1.103	1.187	1.146	1.061
weighting a,b	0.0416, 1.0584	0.0281, 15.1406	0.0230, 47.2807	0.0373, 4.8816	0.0869, 7.4986
params refined	335	579	612	678	1120
min, max resid dens	-0.212, 0.305	-0.380, 0.544	-0.807, 0.637	-0.487, 0.559	-0.487, 0.559

Table S1. Crystallographic data for **2a**, **3a**, **3b**, **4a** and  $\{4b\}_2$ 





Figure S2. EPR of 3a (top) and 3b (bottom) (experimental data taken in THF at 300 K and Simulated by using Easy Spin)<sup>7,8</sup>

# **UV-Vis spectra**





Figure S3. UV-VIS spectra of 2a, 3a and 4a (top) and 2b, 3b and 4b (bottom) in THF solution.

# NMR spectra



Figure S4. <sup>1</sup>H-NMR (Top), <sup>13</sup>C-NMR (Middle) and <sup>11</sup>B-NMR (Bottom) of **2a** in C<sub>6</sub>D<sub>6</sub> at 25°C



Figure S5. <sup>1</sup>H-NMR (Top), <sup>13</sup>C-NMR (Middle) and <sup>11</sup>B-NMR (Bottom) of 4a in d8-THF at 25°C





Figure S6. <sup>1</sup>H –NMR (Top), <sup>13</sup>C-NMR (Middle) and <sup>11</sup>B-NMR (Bottom) of **2b** in  $C_6D_6$  at 25°C

10 0 f1 (ppm)







Figure S7. <sup>1</sup>H-NMR (at -30°C) (Top),<sup>13</sup>C-NMR (at -30°C) (Middle) and <sup>11</sup>B-NMR (at 25°C) (Bottom) of **2a** in d8-THF.



Figure S8. <sup>1</sup>H NMR of compound 4b at various temperatures in THF-d<sub>8</sub>

#### Determination of exchange kinetics in compound 4b

<sup>1</sup>H NMR data for compound **4b** were collected in the temperature range 243 – 338 K. The Varian NMR data files were converted to the gNMR<sup>9</sup> file format using the gCVT tool included in the gNMR installation. The chemical shifts of the peaks of interest (those of the N-Ph group) were taken from the experimental spectrum and exchange between pairs (the two *ortho*-H and *meta*-H) was modeled; the signal for the *para*-H was included without exchange. The latter peak was used to estimate the linewidth in the absence of chemical exchange (due to relaxation, inhomogeneity of the magnetic field etc.). Additional line broadening due to chemical exchange was then included, and the agreement between experimental and simulated spectrum was inspected visually. Due to the presence of additional peaks in the region of interest, attempts to perform least-squares fitting of the line shapes were unsuccessful. An estimate of the error in the exchange rate constants was made visually by running simulations with different rate constants and evaluating in which range a satisfactory fit was still obtained. A comparison between experimental spectra and those with 'best' fit parameters are shown in Figure S8.

The rate constants thus obtained were used for constructing an Eyring plot of Ln(k/T) vs. 1/T. The estimated errors were taken into account by giving each data point a weight that was proportional to  $1/(\sigma(k)^2)$ . Fitting was performed using Wolfram Mathematica 10,<sup>10</sup> and activation parameters are determined using standard procedures from the slope and intercept.



**Figure S9.** (a) Eyring plot for the calculation of activation parameters for rotation around the N-C(Ph) bond in compound **4b.** 



**Figure S10.** Comparison of experimental and simulated <sup>1</sup>H-NMR spectra of **4b** (for each temperature, **top:** experimental spectrum, **bottom:** simulated). Rate constants used for the simulation are shown for each spectrum, including an estimate of the error.

# **Computational studies**

Calculations were performed with the Gaussian09 program<sup>11</sup> using density functional theory (DFT) in the gas phase. Geometries were fully optimised starting from the X-ray structures using the B3LYP exchangecorrelation functional with the 6-311+G(d,p) basis set. Optimizations were performed without (symmetry) constraints, and the resulting structures were confirmed to be minima on the potential energy surface by frequency calculations (number of imaginary frequencies = 0). The stationary point found for  $2a_{calc}$  closely resembles the structure determined by X-ray crystallography. For the singly reduced compounds 3a and 3b, geometry optimizations were performed on the isolated anions  $[L1BPh_2]^{-}$  ( $3a_{calc}$ ) and  $[L2BPh_2]^{-}$  ( $3b_{calc}$ ) and the converged optimized geometries were in good agreement with the structures determined by X-ray crystallography. For the doubly reduced compounds 4, geometry optimizations were performed on the isolated (monomeric) dianions  $[L1BPh_2]^{2-}$  ( $4a_{calc}$ ) and  $[L2BPh_2]^{2-}$  ( $4b_{calc}$ ).

To explore the chemical exchange process of **4b** due to the rotation of N-Ph substituent around the N-C(Ph) bond we scanned the dihedral angle between the two adjacent N atoms in the ligand and the *ipso-* and *ortho*-carbons of the Ph group in steps of 10 degree (all other degrees of freedom were optimized). Starting from the highest energy points along the scan coordinate, the transition states were optimized and confirmed by frequency analysis (number of imaginary frequencies for  $4a_{calc-ts}$  and  $4b_{calc-ts}$  =1).

GaussView 5.0.9<sup>12</sup> was used to visualize the computed structures and molecular orbitals.

Bonds	Bond length:	S				
	2a	2a <sub>calc</sub>	3a	3a <sub>calc</sub>	4a	4a <sub>calc</sub>
N1-N2	1.306(1)	1.298	1.371(4)	1.352	1.428(3)	1.402
N2-C7	1.344(1)	1.343	1.345(5)	1.334	1.325(3)	1.328
C7-N3	1.347(1)	1.343	1.338(5)	1.334	1.326(3)	1.327
N3-N4	1.309(1)	1.298	1.370(4)	1.352	1.433(3)	1.402
N1-B1	1.599(2)	1.610	1.569(5)	1.594	1.578(3)	1.590
N4-B1	1.595(1)	1.609	1.567(5)	1.594	1.583(3)	1.590
N1-C1	1.434(2)	1.430	1.400(4)	1.404	1.379(3)	1.372
N4-C15	1.433(1)	1.430	1.403(4)	1.404	1.384(3)	1.372
B1-C21	1.618(2)	1.624	1.635(6)	1.640	1.637(4)	1.651
B1-C27	1.604(2)	1.616	1.613(5)	1.633	1.626(3)	1.645

**Table S2.** Comparison of selected bond lengths values (Å) between X-ray measured and DFT calculated for **2a**,**3a** & **4a** 

Table S3. Comparison of selected bond lengths values (Å) between X-ray measured and DFT calculated for 2b, 3b & (4b)<sub>2</sub>

Bonds	Bond lengths			Bonds	Bond lengths	
	2b <sub>calc</sub>	3b	3b <sub>calc</sub>		(4b) <sub>2</sub>	4b <sub>calc</sub>
N1-N2	1.301	1.36(3)	1.356	N1-N2/N5-N6	1.431(3)/1.428(3)	1.402
N2-C7	1.342	1.332(3)	1.334	N2-C7/N6-C42	1.319(4)/1.319(3)	1.330
C7-N3	1.347	1.342(3)	1.341	C7-N3/C42-N7	1.337(4)/1.337(4)	1.330
N3-N4	1.298	1.354(3)	1.354	N3-N4/N7-N8	1.469(3)/1.470(3)	1.417
N1-B1	1.615	1.589(4)	1.600	N1-B1/N5-B2	1.569(4)/1.577(4)	1.608
N4-B1	1.606	1.587(3)	1.586	N4-B1/N8-B2	1.583(4)/1.580(4)	1.568
N1-C1	1.431	1.407(3)	1.400	N1-C1/N5-C36	1.378(4)/1.376(3)	1.368
N4-C15	1.449	1.428(3)	1.431	N4-C15/N8-C50	1.436(4)/1.429(4)	1.400
B1-C24	1.631	1.639(4)	1.648	B1-C24/B2-C59	1.637(4)/1.632(4)	1.643
B1-C30	1.617	1.618(4)	1.633	B1-C30/B2-C65	1.645(4)/1.636(4)	1.656



Figure S11. HOMOs of  $4b_{calc}$  (left) and the transition state for N-Ph rotation of  $4b_{calc}$  ( $4b_{calc-ts}$ , right)

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