Supporting Information to

Cation Effects on Dynamics of Ligand-Benzylated Formazanate Boron and Aluminium

Complexes

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Experimental Section

General Considerations. All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. The compounds **1**, $[^{Bn}1][Na]$, $[^{Bn}1][NBu_4]$, $[^{Bn}2][Na]$ and $[^{Bn}2][NBu_4]$ are prepared according to published procedures.¹⁻³ Potassium graphite (KC₈) and Rubidium graphite (RbC₈) were synthesized following the published procedures.⁴ THF and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka). The solvents (THF, hexane, THF-*d*₈) used in this study were additionally dried on Na/K alloy and subsequently vacuum transferred, degassed and stored under nitrogen. 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. UV-vis spectra were recorded in THF solution (~ 10⁻³ M) in a quartz cuvette that was sealed under N₂ atmosphere using an AVANTES AvaSpec-2048 spectrometer. Samples for elemental analyses were sent to Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany). However, despite our best efforts, no satisfactory analysis data could be obtained for these compounds, which is likely due to their highly airsensitive nature.

Synthesis of $[LBPh_2][K_2(THF)_2]$ ([1][K₂]). Compound 1 (100.0 mg, 0.21 mmol) was dissolved in a 4 mL THF in a vial inside the glove box. To the dark pink color THF solution of 1 was added 2.2 equivalents of KC₈ (62.5 mg, 0.46 mmol). The reaction mixture was stirred for overnight, during which it changed color to orange. Then the orange color solution was filtered through a plug of celite. After concentrating the filtrate under vacuum, a layer of hexane (3 mL) was added onto the THF solution (filtrate), and allowed the two layers to diffuse slowly by keeping the mixture at -30 °C. Even after keeping for 7 days, no crystals were obtained, but the product precipitated as orange powder. The precipitate was washed with pentane (3 x 2 mL) and dried to give compound [1][K₂] as a powder (72.0 mg, 0.10 mmol, 48 %). ¹H NMR (400 MHz, THF-*d*₈, 25 °C) δ 8.21 (d, *J* = 7.8 Hz, 2H, p-tol *o*-H), 7.52 (d, *J* = 7.1 Hz, 4H, BPh *o*-H), 6.91-6.96 (m, 10H, p-tol *m*-H, BPh *m*-H, NPh *o*-H), 6.85 (t, *J* =

7.0 Hz, 2H, BPh *p*-H), 6.49 (t, *J* = 7.7 Hz, 4H, NPh *m*-H), 5.82 (t, *J* = 6.9 Hz, 2H, NPh *p*-H), 3.55-3.59 (m, 7H, THF), 2.23 (s, 3H, p-tol CH₃), 1.71-1.75 (m, 7H, THF). ¹¹B NMR (128.0 MHz, *d*₈-THF, 25 °C) δ -1.69 (s). ¹³C NMR (100 MHz, THF-*d*₈, 25 °C) δ 157.75 (B-C(ipso) Ph), 153.21 (N-C(ipso) Ph), 147.97 (NCN), 142.22 (p-tol *C*(ipso)-NCN), 135.29 (BPh *o*-CH), 134.41 (p-tol C-CH₃), 127.78 (p-tol *m*-CH), 127.66 (NPh *o*-CH), 127.33 (BPh *m*-CH), 126.38 (p-tol *o*-CH), 124.24 (BPh *p*-CH), 115.34 (NPh *m*-CH), 110.16 (NPh *p*-CH), 68.27 (THF), 26.43 (THF), 21.31 (p-tol CH₃).

Synthesis of [LBPh₂][Rb₂(THF)₂] ([1][Rb₂]). Compound 1 (100.0 mg, 0.21 mmol) was dissolved in a 4 mL THF in a vial inside the glove box. To the dark pink color THF solution of 1 was added 2.2 equivalents of RbC_8 (83.5 mg, 0.46 mmol). The reaction mixture was stirred for overnight, during which it changed color to orange. Then the orange color solution was filtered through a plug of celite. After concentrating the filtrate under vacuum, a layer of hexane (3 mL) was added onto the THF solution (filtrate), and allowed the two layers to diffuse slowly by keeping the mixture at -30 °C. Even after keeping for 7 days, no crystalline materials were afforded, only the orange color precipitates were obtained. The precipitates were washed with pentane (3 x 2 mL) and dried to give compound [1][**Rb**₂] as a powder material (75.0 mg, 0.09 mmol, 43 %). ¹H NMR (400 MHz, THF-*d*₈, 25 °C) δ 8.28 (d, J = 8.0 Hz, 2H, p-tol o-H), 7.59 (d, J = 6.9 Hz, 4H, BPh o-H), 7.08 – 6.92 (m, 10H, p-tol m-H, BPh m-H, NPh *o*-H), 6.88 (t, J = 7.2 Hz, 2H, BPh *p*-H), 6.49 (t, J = 7.7 Hz, 4H, NPh *m*-H), 5.84 (t, J = 6.9 Hz, 2H, NPh *p*-H), 3.59-3.67 (m, 6H, THF), 2.28 (s, 3H, p-tol CH₃), 1.75-1.83 (m, 6H, THF). ¹¹B NMR (128.0 MHz, *d*₈-THF, 25 °C) δ -1.61 (s). ¹³C NMR (100 MHz, THF-d₈, 25 °C) δ 157.95 (B-C(ipso) Ph), 153.10 (N-C(ipso) Ph), 147.17 (NCN), 142.21 (p-tol C(ipso)-NCN), 135.71 (BPh o-CH), 134.27 (p-tol C-CH₃), 127.87 (p-tol m-CH), 127.63 (NPh *o*-CH), 127.34 (BPh *m*-CH), 126.23 (p-tol *o*-CH), 124.27 (BPh *p*-CH), 115.36 (NPh *m*-CH), 109.84 (NPh *p*-CH), 68.27 (THF), 26.43 (THF), 21.32 (p-tol CH₃).

Synthesis of $[B^nLBPh_2][K(THF)_1]$ ($[B^n1][K]$). Compound $[1][K_2]$ (50.0 mg, 0.07 mmol) was dissolved in 3 ml of THF in a vial inside the glove box. To this was added 1 equiv of benzyl bromide, which caused the color to change from orange to green. After stirring the mixture for 30 minutes, all the volatiles were removed under

reduced pressure and the crude product was washed with hexane (3 x 2ml). Subsequently, drying under vacuum gave compound [^{Bn}1][K] as an oily green material (33.0 mg, 0.05 mmol, 71 %). ¹H NMR (400 MHz, THF- d_8 , 25 °C) δ 7.82 (d, J = 7.8 Hz, 2H, p-tol *o*-H), 7.66 (bs, 2H, B(1)Ph *o*-H), 7.04-6.97 (overlapped, 9H, (benzyl)Ph *o*-H, N(1)Ph *o*-H, B(2)Ph *o*-H, p-tol *m*-H and B(1)Ph *p*-H), 6.83-6.82 (m, 3H, (benzyl)Ph (*m*+*p*)-H), 6.60 (overlapped, 3H, N(1)Ph *m*-H and B(2)Ph *p*-H), 6.48 (overlapped, 4H, N(2)Ph (*o*+*m*)-H), 6.16 (p, J = 3.9 Hz, 1H, N(2)Ph *p*-H), 6.11 (t, J = 7.0 Hz, 1H, N(1)Ph *p*-H), 3.62 (m, 3H, THF), 2.29 (s, 3H, p-tol CH₃), 1.77 (m, 3H, THF), at room temperature due to the broadening in the NMR spectrum the resonances of benzyl-CH₂ and B(1,2)Ph *m*-H could not be assigned correctly. ¹¹B NMR (128.3 MHz, THF- d_8 , 25 °C) δ 1.07 (s). ¹³C NMR (100 MHz, THF- d_8 , 25 °C) δ 158.27 (N(2)Ph *ipso*-C), 154.07 (N(1)Ph *ipso*-C), 143.56 (NCN), 141.30 ((benzyl)Ph ipso-C)), 137.53 (NCN-p-tol *ipso*-C), 137.06 (B(1,2)Ph *o*-CH), 135.76 (p-tol-CH₃ *ipso*-C), 129.86 ((benzyl)Ph *o*-CH), 128.89 (p-tol *m*-CH), 127.64 (p-tol *o*-CH), 127.44 ((benzyl)Ph *p*-CH), 126.96 (N(1) Ph *m*-CH), 126.35 (N(2) Ph *m*-CH), 125.80 ((benzyl)Ph *m*-CH), 123.40 ((N(2)Ph *o*-CH), 118.42 (N(1) Ph *o*-CH), 116.34 (N(2)Ph *p*-CH), 113.77 (N(1)Ph *p*-CH), 68.27 (THF), 58.57 (benzyl-CH₂), 26.43 (THF), 21.35 (p-tol CH₃), (B(1,2)Ph *ipso*-C) and (B(1,2)Ph (*m*+*p*)-CH) could not be assigned correctly.

Synthesis of $[^{Bn}LBPh_2][Rb(THF)_1]$ ($[^{Bn}1][Rb]$). Compound $[1][Rb_2]$ (45.0 mg, 0.06 mmol) was dissolved in 3 ml of THF in a vial inside the glove box. To this was added 1 equiv of benzyl bromide, which caused the color to change from orange to green. After stirring the mixture for 30 minutes, all the volatiles were removed under reduced pressure and the crude product was washed with hexane (3 x 2ml). Subsequently, drying under vacuum gave compound $[^{Bn}1][Rb]$ as an oily green material (26.0 mg, 0.04 mmol, 67 %). ¹H NMR (400 MHz, THF- d_8 , 25 °C) δ 7.84 (d, J = 7.8 Hz, 2H, p-tol *o*-H), 7.06-7.03 (overlapped, 6H, N(1)Ph *o*-H, B(2)Ph *o*-H and p-tol *m*-H), 6.98-6.96 (overlapped, 3H, (benzyl)Ph *o*-H and B(1)Ph *p*-H), 6.83-6.81 (m, 3H, (benzyl)Ph (*m*+*p*)-H), 6.65 (overlapped, 3H, N(1)Ph *m*-H and B(2)Ph *p*-H), 6.48 (overlapped, 4H, N(2)Ph (*o*+*m*)-H), 6.15 (t, J = 6.8 Hz, 2H, N(1,2)Ph *p*-H), 3.67-3.58 (m, 6H, THF), 2.30 (s, 3H, p-tol CH₃), 1.81-1.76 (m, 6H, THF), (at room temperature due to the broadening in the NMR spectrum the resonances of benzyl-CH2, B(1,2)Ph *m*-H and B(1)Ph *o*-H could

not be assigned correctly). ¹¹B NMR (128.3 MHz, THF-*d*₈, 25 °C) δ -0.70 (s). ¹³C NMR (100 MHz, THF-*d*₈, 25 °C) δ 157.82 (N(2)Ph *ipso*-C), 153.92 (N(1)Ph *ipso*-C), 144.43 (NCN), 140.87 ((benzyl)Ph ipso-C)), 137.22 (NCN-p-tol *ipso*-C), 136.98 (B(1,2)Ph *o*-CH), 136.19 (p-tol-CH₃ *ipso*-C), 130.03 ((benzyl)Ph *o*-CH), 128.99 (p-tol *m*-CH), 127.73 (p-tol *o*-CH), 127.47 ((benzyl)Ph *p*-CH), 127.39 (N(1) Ph *m*-CH), 126.53 (N(2) Ph *m*-CH), 125.97 ((benzyl)Ph *m*-CH), 122.78 ((N(2)Ph *o*-CH), 118.19 (N(1) Ph *o*-CH), 116.15 (N(2)Ph *p*-CH), 113.81 (N(1)Ph *p*-CH), 68.27 (THF), 58.63 (benzyl-CH₂), 26.43 (THF), 21.35 (p-tol CH₃), (B(1,2)Ph *ipso*-C) and (B(1,2)Ph *(m+p)*-CH) could not be assigned correctly.

UV/vis Spectroscopy



Figure S1. Absorbance spectra of compounds [1][K₂], [1][Rb₂], [^{Bn}1][K] and [^{Bn}1][Rb] in THF

NMR Spectra



Figure S2. ¹H-NMR (top), ¹³C-NMR (middle) and ¹¹B-NMR spectra of compound [1][K_2] in THF- d_8 at 25 °C.

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Figure S3. ¹H-NMR (top), ¹³C-NMR (middle) and ¹¹B-NMR (bottom) of [1][Rb₂] in THF- d_8 at 25 °C.







Figure S4. ¹H-NMR (top) and ¹¹B-NMR (bottom) of $[^{Bn}1][K]$ in THF- d_8 at 25 °C. Asterisks indicate residual hexane.





Figure S5. ¹H-NMR (top) and ¹¹B-NMR (bottom) of [$^{Bn}1$][Rb] in THF- d_8 at 25 °C. Asterisks indicate residual hexane.

Determination of Activation Parameters for the Dynamic Processes in Compounds [^{Bn}1][Na], [^{Bn}1][K], [^{Bn}1][Rb], [^{Bn}1][NBu₄], [^{Bn}2][Na] and [^{Bn}2][NBu₄]

¹H NMR spectra of compound [^{Bn}1][Na] were collected at 500 MHz NMR spectrometer in the temperature range -5 – 75 °C (Figure 6.9). The gCVT tool which was included in the gNMR⁵ installation had been used to convert the Varian NMR data files to the gNMR file format. The chemical shifts of the peaks of interest (i.e., the benzyl-CH₂ as well as BPh₂ moiety) were taken from the experimental spectrum and exchange between pairs (i.e., the two diasterotopic benzyl-CH₂ as well as the *ortho*-H from each B-Ph group) were modelled; the signal for the *p*tol-methyl-H was included without exchange. The peak of *p*-tol-methyl-H 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 S16.

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 11.2,⁶ and activation parameters are determined using standard procedures from the slope and intercept.

Following the above mentioned same methodology, the activation parameters for the dynamical processes in compounds [^{Bn}1][K], [^{Bn}1][Rb], [^{Bn}1][NBu₄], [^{Bn}2][Na] and [^{Bn}2][NBu₄] were determined.



Figure S6. Eyring plot for the calculation of activation parameters for the dynamical processes in [^{Bn}1][Na] and [^{Bn}2][Na].



Figure S7. Eyring plot for the calculation of activation parameters for nitrogen inversion in [^{Bn}1][NBu₄] and [^{Bn}2][NBu₄].



 $[^{Bn}1][NBu_4]$ ΔH[≠] = 66.7 (1.6) kJ/mol ΔS[≠] = -4.2 (5.0) J/mol/K

 $[^{Bn}1][K]$ $\Delta H^{\neq} = 68.4 (2.3) \text{ kJ/mol}$

 $\Delta S^{\neq} = 59.3 (7.3) \text{ J/mol/K}$

[^{Bn}1][**R**b]

 $\Delta H^{\neq} = 72.7 (5.5) \text{ kJ/mol}$ $\Delta S^{\neq} = 42.3 (18.0) \text{ J/mol/K}$ Figure S8. Eyring plot for the calculation of activation parameters for dynamic processes in [^{Bn}1][NBu₄], [^{Bn}1][Na], [^{Bn}1][K] and [^{Bn}1][Rb].



[^{Bn}1]⁻







7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 Figure S11. ¹H NMR of compound [^{Bn}1][K] in THF-*d*₈ at various temperatures.











igure S14. ¹H NMR of compound [$^{Bn}2$][Na] in THF- d_8 at various temperatures.

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Figure S15. Comparison of experimental and simulated ¹H-NMR spectra of [^{Bn}1][NBu₄] (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.



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Figure S16. Comparison of experimental and simulated ¹H-NMR spectra of [^{Bn}1][Na] (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.



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Figure S17. Comparison of experimental and simulated ¹H-NMR spectra of [^{Bn}1][K] (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.



Figure S18. Comparison of experimental and simulated ¹H-NMR spectra of [^{Bn}1][**Rb**] (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.



Figure S19. Comparison of experimental and simulated ¹H-NMR spectra of [^{Bn}2][NBu₄] (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.



318 K: estimated rate constant $k = 16 \pm 3 s^{-1}$







Figure S20. Comparison of experimental and simulated ¹H-NMR spectra of [^{Bn}2][Na] (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.

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