Supporting Information to

Structure and Bonding in Reduced Boron and Aluminium Complexes with Formazanate

Ligands

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UV-Vis Spectroscopy



Figure S1. UV-vis spectra of [^{Bn}1][Na],¹ [^{Bn}1][NBu₄], [^{Bn}2][Na] and [^{Bn}2][NBu₄] at room temperature in THF



Figure S2. ¹H NMR spectra of compound 2^{2-} at various temperatures in THF- $d_{8.}$



Figure S3. ¹H-NMR (top), ¹³C-NMR (middle) and ¹¹B-NMR (bottom) at 25 °C of [^{Bn}1][NBu₄] in THF-d₈.



Figure S4. ¹H-NMR (top) and ¹³C-NMR (bottom) at 25 °C of [^{Bn}2][Na] in THF-d₈.



Figure S5. ¹H-NMR (top) and ¹³C-NMR (bottom) at 25 °C of [^{Bn}2][NBu₄] in THF-d₈.

Estimation of Upper Limit of the Barrier for N-C(Ph) Bond Rotation in 1²⁻

The ¹H NMR spectra of 1^{2} do not show decoalescence down to 213 K. Even though the frequency difference between the exchanging ¹H resonances in 1^{2} could thus not be measured experimentally, an upper limit for the activation free energy can be estimated as follows:

The coalescence temperature found for 2^{2-} is ca. 283 K with a frequency difference at slow exchange of ca. 290 Hz; from this the exchange rate and activation free energy at the coalescence temperature can be determined as k = 644 s⁻¹ and $\Delta G^{\ddagger}_{283} = 54$ kJ/mol. Assuming that the frequency difference is similar in 1^{-2} , this means that in this compound the exchange rate at 213 K is substantially larger than 644 s⁻¹, meaning that the activation free energy at 213 K ($\Delta G^{\ddagger}_{213}$) is < 40 kJ/mol.

X-ray Crystallography

| | [^{Bn} 1][NBu ₄] | [^{Bn} 2][Na] |
|--|---|--|
| chem formula | $\frac{C_{55} H_{70} B N_{5}}{C_{55} H_{70} B N_{5}}$ | C_{51} H ₅₀ Al N ₄ Na O ₂ |
| M _r | 811 97 | 824 98 |
| cryst syst | Monoclinic | Monoclinic |
| color, habit | green, hexagonal | vellow, block |
| size (mm) | 0.21 x 0.19 x 0.06 | 0.36 x 0.33 x 0.33 |
| space group | $P2_1/c$ | $P2_1/n$ |
| $\frac{1}{a(\text{Å})}$ | 11.0674(3) | 14.8381(8) |
| b (Å) | 16.7937(4) | 16.7498(10) |
| c (Å) | 27.9584(6) | 18.1161(19) |
| α (°) | 90 | 90 |
| β(°) | 90.985(1) | 96.559(4) |
| γ (°) | 90 | 90 |
| V (Å ³) | 5195.7(2) | 4473.0(6) |
| Z | 4 | 4 |
| $\rho_{calc}, g.cm^{-3}$ | 1.038 | 1.225 |
| Radiation [Å] | 1.54178 | 0.71073 |
| μ (Mo K _{α}), mm ⁻¹ | | 0.102 |
| μ (Cu K _{α}), mm ⁻¹ | 0.454 | |
| F (000) | 1760 | 1760 |
| temp (K) | 100(2) | 100(2) |
| θ range (°) | 3.07 - 75.01 | 2.958 - 29.686 |
| Data collected (h,k,l) | -13:11; -20:19; -33:32; | -20:20; -23:23; -25:25; |
| no. of rflns collected | 51829 | 181202 |
| no. of indpndt reflns | 9493 | 12588 |
| observed reflns $F_o \ge 2.0 \sigma$ (F_o) | 8215 | 10500 |
| R(F) (%) | 4.96 | 3.98 |
| wR(F ²) (%) | 15.67 | 10.61 |
| GooF | 1.038 | 1.017 |
| weighting a,b | 0.0918, 2.0831 | 0.0471, 2.3119 |
| params refined | 555 | 598 |
| min, max resid dens | -0.343, 0.300 | -0.276, 0.367 |

Table S1. Crystallographic data for $[Bn1][NBu_4]$ and [Bn2][Na]

Determination of Exchange Kinetics in Compound 2²⁻

¹H NMR data for compound 2^{2} were collected in the temperature range 233 - 303 K. The Varian NMR data files were converted to the gNMR¹ 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 modelled; 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 S7.

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 11.2,² and activation parameters are determined using standard procedures from the slope and intercept.



Figure S6. Eyring plot for the calculation of activation parameters for rotation around the N-C(Ph) bond in compound 2^{2-} .



Figure S7. Comparison of experimental and simulated ¹H-NMR spectra of 2^{2-} (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.

Analysis of Reaction Kinetics of [Bn1][NBu4] + TEMPO, [Bn2][Na] + TEMPO and [Bn2][NBu4] + TEMPO

A solution of [Bn2][Na] in THF-d₈ was prepared in a J. Young's NMR tube and a few crystals of bibenzyl were added as internal standard. Subsequently, 20 equiv of TEMPO were added to efficiently trap the benzyl radical generated upon thermolysis. The tube was taken out from the glovebox and inserted into the probe of the NMR spectrometer, which was heated to the desired reaction temperature. The NMR probe was tuned and shimmed before insertion of the sample using another NMR tube with the same amount of THF- d_8 at that temperature. After the sample was inserted, an acquisition array was started that was set up to collect spectra at regular time intervals throughout the course of the reaction (see Figure S8 for example of a few traces of the reaction of [^{Bn}2][Na] with TEMPO (20 equiv)). Integration of the TEMPO-Bn resonance (δ 4.82 ppm in the ¹H NMR spectrum) relative to the internal standard bibenzyl allowed analysis of the rate constant at each temperature by non-linear curve fitting (a+b(1-Exp[-kt])) in Mathematica 11.2.² To investigate the effects of counter cation, the kinetics of benzyl transfer to TEMPO from [Bn1][NBu4] and [Bn2][NBu4] were measured using this procedure. For the kinetics of benzyl transfer to TEMPO from [Bn1][NBu4] and [Bn2][NBu4], the residual proton resonances from THF-*d*₈ (at 1.73 ppm for [^{Bn}1][NBu₄] and at 3.58 ppm for [^{Bn}2][NBu₄], respectively) were used as an internal standard due to the overlapping nature of the bibenzyl resonance (at 2.9 ppm) with the one of the proton resonances from NBu₄⁺ (see Figure S9 and Figure S10 for example of a few traces of the reaction of [^{Bn}2][NBu₄] and [^{Bn}1][NBu₄] with TEMPO (20 equiv), respectively).



Figure S8. Selected ¹H-NMR spectra from the 85 °C kinetics array for the reaction of [Bn2][Na] with TEMPO (20 equiv) in THF- d_8 .



Figure S9. Selected ¹H-NMR spectra from the 85 °C kinetics array for the reaction of [$^{Bn}2$][NBu₄] with TEMPO (20 equiv) in THF- d_8 .



Figure S10. Selected ¹H-NMR spectra from the 85 °C kinetics array for the reaction of [$^{Bn}1$][NBu₄] with TEMPO (20 equiv) in THF- d_8 .



Figure S11. Kinetic traces for the reaction of [Bn2][Na] with TEMPO (20 equiv) in THF- d_8 .



Figure S12. Eyring analysis for [^{Bn}2][Na]; $\Delta H^{\ddagger} = 107 \pm 4 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^{\ddagger} = 17 \pm 11 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$



Figure S13. Kinetic traces for the reaction of [Bn2][Na] (Blue) and $[Bn2][NBu_4]$ (Yellow) with TEMPO (20 equiv) in THF- d_8 at 75 °C (left) and at 85 °C (right).



Figure S14. Kinetic traces for the reaction of $[^{Bn}1][Na]$ (Blue)³ and $[^{Bn}1][NBu_4]$ (Yellow) with TEMPO (20 equiv) in THF-*d*₈ at 65 °C (left) and at 85 °C (right).

Computational Studies



Figure S15. HOMOs of 2^{2-}_{calc} (left) and the transition state for N-Ph rotation of 2^{2-}_{calc} ($2^{2-}_{calc-ts}$, right).

| Compounds | 12- | 1 ²⁻ calc | [^{Bn} 1][NBu ₄] | Bn1- _{calc} | | 22- | 2 ²⁻ calc | [^{Bn} 2][Na] | ^{Bn} 2 ⁻ calc |
|-----------|----------|----------------------|---------------------------------------|----------------------|---------|----------|----------------------|------------------------|-----------------------------------|
| B1-N1 | 1.578(3) | 1.590 | 1.575(2) | 1.585 | Al1-N1 | 1.871(2) | 1.896 | 1.866(9) | 1.902 |
| B1-N4 | 1.583(3) | 1.590 | 1.584(2) | 1.602 | Al1-N4 | 1.873(2) | 1.897 | 1.914(1) | 1.946 |
| B1-C21 | 1.637(4) | 1.651 | 1.635(2) | 1.645 | Al1-C21 | 2.011(2) | 2.03 | 1.991(1) | 2.009 |
| B1-C27 | 1.626(3) | 1.645 | 1.624(3) | 1.644 | Al1-C27 | 2.008(2) | 2.03 | 1.989(1) | 2.015 |
| N1-N2 | 1.428(3) | 1.402 | 1.428(2) | 1.426 | N1-N2 | 1.432(2) | 1.406 | 1.446(1) | 1.441 |
| N3-N4 | 1.433(3) | 1.402 | 1.393(2) | 1.356 | N3-N4 | 1.432(2) | 1.406 | 1.402(1) | 1.364 |
| N2-C7 | 1.325(3) | 1.328 | 1.396(2) | 1.413 | N2-C7 | 1.332(2) | 1.333 | 1.437(1) | 1.443 |
| C7-N3 | 1.326(3) | 1.327 | 1.289(2) | 1.293 | C7-N3 | 1.328(2) | 1.333 | 1.292(1) | 1.293 |
| N1-C1 | 1.379(3) | 1.372 | 1.414(2) | 1.412 | N1-C1 | 1.375(2) | 1.370 | 1.387(1) | 1.386 |
| N4-C15 | 1.384(3) | 1.372 | 1.392(2) | 1.404 | N4-C15 | 1.371(3) | 1.370 | 1.399(1) | 1.403 |
| N2-C33 | | | 1.468(2) | 1.472 | N2-C33 | | | 1.486(1) | 1.493 |

 Table S2. Selected bond lengths (Å) for 1^{2-} , ⁸ 1^{2-} calc, ⁸ $[^{Bn}1][NBu_4]$, ^{Bn} 1^{-} calc, 2^{2-} , 2^{2-} calc, $[^{Bn}2][Na]$ and ^{Bn} 2^{-} calc.

| Compounds | [^{Bn} 1][NBu ₄], | ^{Bn} 1 ⁻ calc | | [^{Bn} 2][Na] | ^{Bn} 2- _{calc} |
|------------|--|-----------------------------------|-------------|------------------------|----------------------------------|
| N1-B1-N4 | 105.78(1) | 104.58 | N1-Al1-N4 | 95.24(4) | 95.02 |
| C21-B1-C27 | 115.82(1) | 112.73 | C21-Al1-C27 | 112.46(5) | 112.33 |
| C21-B1-N1 | 109.5(1) | 111.07 | C21-Al1-N1 | 109.15(4) | 113.2 |
| C21-B1-N4 | 110.28(1) | 108.93 | C21-Al1-N4 | 111.73(4) | 110.16 |
| C27-B1-N1 | 105.45(1) | 108.8 | C27-Al1-N1 | 114.96(4) | 112.92 |
| C27-B1-N4 | 109.44(1) | 110.43 | C27-Al1-N4 | 112.14(4) | 112.04 |
| N2-C7-N3 | 127.57(1) | 125.17 | N2-C7-N3 | 126.80(9) | 125.12 |
| B1-N1-N2 | 113.06(1) | 114.43 | Al1-N1-N2 | 119.07(6) | 114.84 |
| B1-N1-C1 | 124.31(1) | 124.8 | Al1-N1-C1 | 127.89(7) | 129.65 |
| C1-N1-N2 | 110.44(1) | 111.82 | C1-N1-N2 | 112.55(8) | 114.23 |
| N1-N2-C7 | 115.41(1) | 114.88 | N1-N2-C7 | 112.27(8) | 111.09 |
| N1-N2-C33 | 113.94(1) | 114.11 | N1-N2-C33 | 110.33(8) | 111.74 |
| C7-N2-C33 | 118.79(1) | 116.19 | C7-N2-C33 | 112.13(8) | 113.33 |
| N3-N4-B1 | 118.8(1) | 120.96 | N3-N4-Al1 | 117.27(7) | 120.34 |
| B1-N4-C15 | 127.75(1) | 126.84 | Al1-N4-C15 | 125.47(7) | 124.24 |
| N3-N4-C15 | 110.99(1) | 112.19 | N3-N4-C15 | 111.72(8) | 112.44 |

Table S3. Selected bond angles (°) for [^{Bn}1][NBu₄], ^{Bn}1⁻_{calc}, [^{Bn}2][Na] and ^{Bn}2⁻_{calc}.

Table S4. Wiberg bond indices for the selected bonds in 1²-calc, 1²-calc-ts, 2²-calc, 2²-calc-ts

| | 1 ² - _{calc} | 1 ² - _{calc-ts} | 2 ²⁻ calc | 2 ²⁻ calc-ts |
|-------------------------------------|----------------------------------|-------------------------------------|----------------------|-------------------------|
| Bonds | Wiberg Bond Index | | | |
| N-C(Ph) | 1.2196/1.2196 | 1.2262/1.0049 | 1.2412/1.2415 | 1.2605/1.0365 |
| <i>p</i> -tol-C-C(CH ₃) | 1.0319 | 1.0324 | 1.0156 | 1.0156 |

References

- 1 Budzelaar, P. H. M.; gNMR v. 5.0.6 (2006).
- 2 Wolfram Research, Inc., Mathematica, Version 11.2, Champaign, IL (2017).
- 3 R. Mondol and E. Otten, *Inorg. Chem.*, 2018, **57**, 9720–9727.