

Superbases

International Edition: DOI: 10.1002/anie.201605005
German Edition: DOI: 10.1002/ange.201605005

A Potassium Diboryllithate: Synthesis, Bonding Properties, and the Deprotonation of Benzene

Takuto Ohsato, Yuri Okuno, Shintaro Ishida, Takeaki Iwamoto, Ka-Ho Lee, Zhenyang Lin,* Makoto Yamashita,* and Kyoko Nozaki*

Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday

Abstract: A potassium diboryllithate (B_2LiK) was synthesized and structurally characterized. DFT calculations, including NPA and AIM analyses of B_2LiK , revealed ionic interactions between the two bridging boryl anions and Li^+ and K^+ . Upon standing in benzene, B_2LiK deprotonated the solvent to form a hydroborane and a phenylborane. On the basis of DFT calculations, a detailed reaction mechanism, involving deprotonation and hydride/phenyl exchange processes, is proposed. An NBO analysis of the transition state for the deprotonation of benzene suggests that the deprotonation should be induced by the coordination of benzene to the K^+ .

Even though benzene was discovered as early as 1825,^[1] its structure was proposed only almost half a century later, in 1872.^[2] Benzene is one of the most basic hydrocarbon molecules and many methods for its functionalization are described in organic chemistry textbooks. In contrast to the most popular functionalization method for benzene, that is, electrophilic substitution reactions, the deprotonation of benzene using very strong bases is less developed. The first deprotonation of benzene was achieved with ethylsodium in 1908.^[3] Although alkylolithiums do not deprotonate benzene in

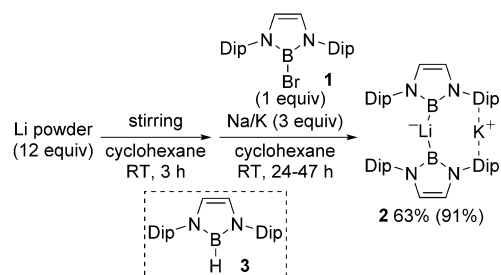
n-hexane or ether solvents,^[4] they may accomplish the deprotonation of benzene in the presence of potassium alkoxide (superbase)^[5] or chelating diamine ligands.^[6] The deprotonation of benzene with NH_2^- in the gas phase was also studied, and a free-energy change of $\Delta G = (392.9 \pm 0.4)$ kcal mol⁻¹ was estimated.^[7]

The basicity of anionic species depends on the main-group element carrying the negative charge. Anionic mononuclear hydrides of p-block elements possessing lower electronegativity exhibit a higher basicity in general, as theoretical calculations indicate. Accordingly, boron-centered anions may exhibit a higher basicity than carbon-centered anions.^[8] We recently reported the first isolation of a lithium salt of a boryl anion^[9] and demonstrated that the THF-solvated boryllithium is able to deprotonate toluene and dihydrogen.^[10] However, this THF-solvated boryllithium is stable toward benzene as confirmed by the fact that the reactions in benzene did not afford phenyllithium.^[10,11] Herein, we report the synthesis, structure, and bonding properties of a potassium diboryllithate,^[12] in which two boryl anions coordinate to a lithium cation to form an ate complex. Moreover, we report the deprotonating reactivity of this complex toward benzene, and propose a detailed mechanism for the deprotonation step based on DFT calculations.

The potassium diboryllithate **2** was obtained from the treatment of **1** with lithium powder (containing 1% Na) and Na/K (1:4) alloy in cyclohexane at room temperature (Scheme 1). For the reproducibility of this reaction, the initial stirring period of the lithium powder is critical. A reaction in $[D_{12}]$ cyclohexane enabled us to estimate the yield (91%) of **2** by NMR methods, and the only detectable side-product was the protonated hydroborane **3**. The boryl anion **2** could be isolated as a crystalline solid in 63% yield. Single crystals

[*] T. Ohsato, Prof. Dr. M. Yamashita
Department of Applied Chemistry
Faculty of Science and Engineering, Chuo University
1-13-27 Kasuga, Bunkyo-ku, 112-8551 Tokyo (Japan)
E-mail: makoto@oec.chem.chuo-u.ac.jp
Homepage: <http://www.chem.chuo-u.ac.jp/~element/index-e.html>
Dr. Y. Okuno, Prof. Dr. K. Nozaki
Department of Chemistry and Biotechnology
Graduate School of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, 113-8656 Tokyo (Japan)
E-mail: nozaki@chembio.t.u-tokyo.ac.jp
Homepage: <http://park.itc.u-tokyo.ac.jp/nozakilab/indexE.html>
Prof. Dr. S. Ishida, Prof. Dr. T. Iwamoto
Department of Chemistry, Graduate School of Science
Tohoku University, 980-8578 Sendai (Japan)
Homepage: http://www.ssoc.chem.tohoku.ac.jp/en_index.html
Dr. K.-H. Lee, Prof. Dr. Z. Lin
Department of Chemistry
The Hong Kong University of Science and Technology
Clear Water Bay, Kowloon (Hong Kong)
E-mail: chzlin@ust.hk
Homepage: <http://home.ust.hk/~chzlin/>

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/anie.201605005>.



Scheme 1. Synthesis of the potassium diboryllithate **2** (Dip = 2,6-*i*Pr₂C₆H₃). Yield as determined by ¹H NMR spectroscopy, in $[D_{12}]$ cyclohexane, is given within parentheses.

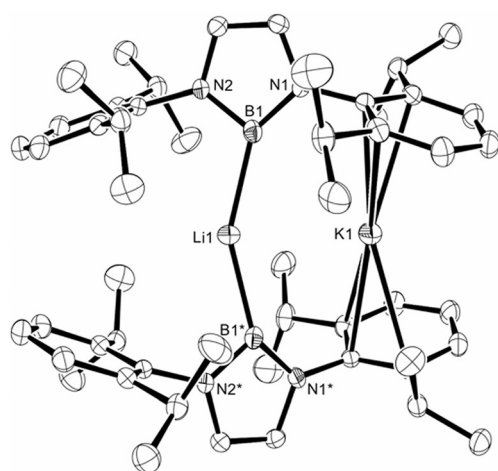
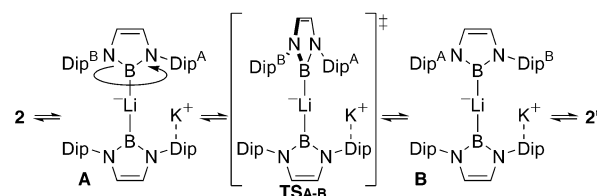


Figure 1. Molecular structure of **2** (thermal ellipsoids set at 50% probability, hydrogen atoms and co-crystallized 2,2,4,4-tetramethylpentane omitted for clarity).^[23] Selected bond distances (Å) and angles (°): B1–Li1 2.286(4), B1–N1 1.461(4), B1–N2 1.461(3), K1...C(Dip) 3.018(4), 3.129(3), 3.218(5), Li1...K1 (no interaction; see main text) 3.077(7), N1–B1–N2 100.1(2), N1–B1–Li1 141.7(2), N2–B1–Li1 116.3(2).

suitable for X-ray diffraction analysis were obtained by recrystallization of the crude reaction mixture from 2,2,4,4-tetramethylpentane. The crystal structure of **2** displayed two boryl anions coordinated to a lithium cation, thus forming a lithium ate complex, while the potassium cation was coordinated by two Dip rings in an η^3 -fashion (Figure 1). Both Li^+ and K^+ are located on the C_2 axis of the $C2/c$ space group and separated by an interatomic distance of 3.077(7) Å, which is far longer than the sum of the ionic radii of Li^+ and K^+ (2.11 Å).^[13] The observed B–Li distance [2.286(4) Å] is similar to those of previously reported boryllithium compounds,^[9b] thus indicating a similar type of ionic interaction between B and Li, even in the presence of a formal anionic charge on the Li center. The B–Li–B angle [153.2(3)°] deviates substantially from linearity, probably because of the repulsion between Li^+ and K^+ . For the crystal structures of similar $[\text{LiR}_2]^-$ dialkylolithate species, linear C–Li–C angles were reported.^[14] The observed B–N bond lengths [1.461(3) and 1.461(4) Å], as well as the N–B–N bond angle [100.1(2)°] are close to those of previously reported boryllithium compounds. It should be noted that **2** can be considered as a non-solvated boryl anion which is soluble in hydrocarbon solvents. The structural features of **2**, in which the central alkali metal cations are surrounded by lipophilic groups, is similar to the hexameric structure of commercially available *n*BuLi in both the solid and solution state.^[15]

The ^1H NMR spectra of **2** in $[\text{D}_{12}]$ cyclohexane showed two sets of doublets, which were assigned to the CH_3 groups on the Dip substituents. Considering that the rotation around the N–C(Dip) bond should be restricted by the steric hindrance arising from the isopropyl groups, this result indicates that on the NMR time scale, the coordination of the Dip rings to the potassium cation exchanges rapidly and includes all four Dip rings (Scheme 2). The exchange process would thus consist of a) linearization of the B–Li–B angle and dissociation of Dip from K^+ , b) rotation around the B–Li bond in **A** to exchange the Dip^{A} and Dip^{B} rings through $\text{TS}_{\text{A-B}}$, and c) re-coordination



Scheme 2. Possible dynamic exchange of the Dip rings coordinating to the K^+ cation.

of Dip to K^+ . The ^{11}B NMR spectrum of **2** in $[\text{D}_{12}]$ cyclohexane showed one broad singlet at $\delta_{\text{B}} = 43$ ppm, thus indicating an anionic character of the boron center. The ^7Li NMR spectrum of **2** in $[\text{D}_{12}]$ cyclohexane exhibited a remarkably low-field shifted signal ($\delta_{\text{Li}} = 4.7$ ppm) relative to the signals of THF-solvated boryllithium species ($\delta_{\text{Li}} = 0.44$ – 0.68 ppm). A similar low-field signal was also observed in the solid-state CPMAS- ^7Li spectrum ($\delta_{\text{Li}} = 5.5$ ppm), thus suggesting that the diboryllithate structure that was observed for **2** in the crystalline solid state was retained even in solution. The origin of the low-field shift of the ^7Li NMR resonance of **2** should be attributed to the deshielding by delocalized π electrons of the two N–B–N moieties in the diazaborole rings.

To clarify the bonding situation in **2**, DFT calculations were carried out at the B3LYP/6-31 + G(d) level of theory. An optimization of the crystal structure, which was used as the initial geometry, in the absence of any symmetrical restrictions, furnished a slightly unsymmetrical structure which is essentially similar to the experimentally determined crystal structure. The HOMO can be considered a combination of two lone pairs on each boron atom (Figure 2), in which each component is similar to that of the previously reported boryllithium.^[9b] A natural population analysis (NPA)^[16] exhibited positive charges for all electropositive elements in **2** (B: 0.1231, 0.1228; Li: 0.5163, and K: 0.6588). The calculation of the ^7Li NMR chemical shift by the GIAO method^[17] furnished a highly deshielded ^7Li nucleus [$\delta_{\text{Li}} = 6.7$ ppm, vs. $\text{Li}^+(\text{OH}_2)_4$], while an atoms-in-molecules (AIM)

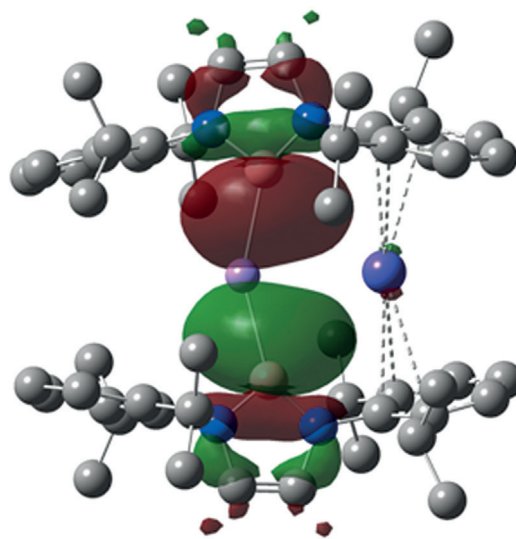


Figure 2. HOMO of **2** (isovalue = 0.020) optimized at the B3LYP/6-31 + G(d) level of theory. Hydrogen atoms omitted for clarity.

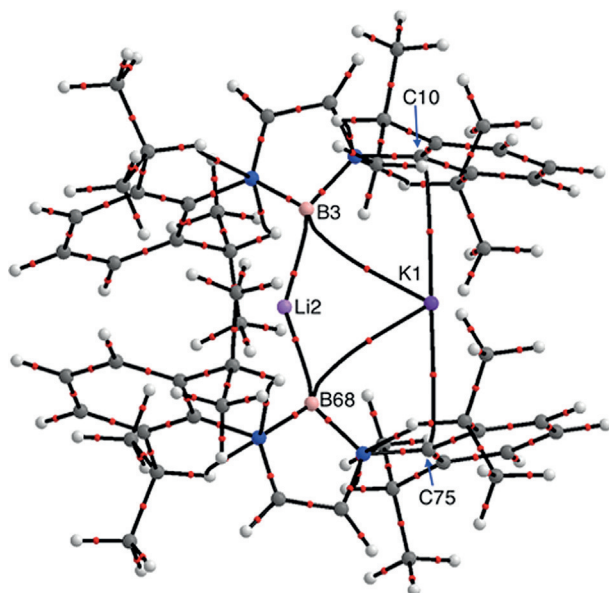
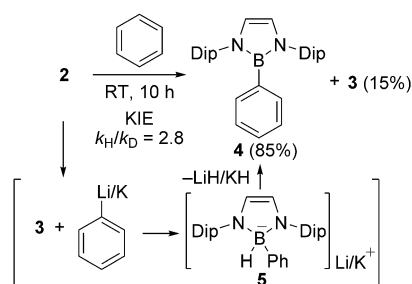


Figure 3. AIM-generated molecular graph (red spheres: bond critical points, solid lines: bond paths, labeling based on the results of the DFT calculations); for selected bond critical points, properties such as $\rho(r)$ (e/a_0^3), $\nabla^2\rho(r)$ (e/a_0^5), and ε are listed in the Supporting Information.

analysis^[18] revealed the absence of a bond path^[19] between Li2 and K1, and confirmed the absence of any interactions (Figure 3). Given the presence of bond paths for B3-Li2, B68-Li2, B3-K1, and B68-K1, the bonding situation in **2** can be interpreted in terms of two boryl anions that bridge Li⁺ and K⁺ from both sides, even though no direct interactions exist between Li⁺ and K⁺. Additional bond paths between the *ipso*-carbon atoms of the Dip rings and K⁺ support the presence of interactions between the π electrons and K⁺.

We also found that the present boryl anion **2** reacts with benzene at room temperature (Scheme 3). Leaving **2** to stand in benzene ($pK_a = 37$)^[20] at room temperature for 10 hours resulted in the complete consumption of **2** with the concomitant formation of the phenylborane **4** (85%), hydroborane **3** (15%), and a white precipitate. It is feasible to imagine that a simple deprotonation of benzene with **2** would liberate **3**. The formation of **4** may be explained by a deprotonation of benzene to give **3** and either phenyllithium or phenylpotassium, followed by a nucleophilic attack of the phenylmetal



Scheme 3. Reaction of **2** with benzene (yield determined by NMR spectroscopy and based on two diaminoborole units). KIE = kinetic isotope effect.

species toward the boron atom of **3** to form the (hydride)-(phenyl)borate species **5**. Subsequently, an elimination of a metal hydride (hydride/phenyl exchange) would afford **4**, as observed for the deprotonation of toluene ($pK_a = 35$)^[20] to give benzylborane in one of our previous reports.^[10] Reactions of **2** with either C₆H₆ or C₆D₆ (100 equiv each) in [D₁₂]cyclohexane were monitored by ¹H NMR spectroscopy and the consumption of **2** was observed to follow pseudo-first-order kinetics. A kinetic isotope effect (k_H/k_D) of 2.8 was determined, and is comparable to the reported value for the deprotonation of benzene with either ethylpotassium or *n*BuLi/*t*BuOK.^[5c,21] This result suggests that the deprotonation, rather than a hydride/phenyl exchange, should be the rate-determining step in this reaction. Accordingly, the basicity of **2** is higher than those of alkylolithiums, which do not deprotonate benzene in hydrocarbon solvents.^[4]

To shed light on the mechanism for the deprotonation of benzene with **2** to furnish **3** and **4**, the entire mechanism was examined theoretically using DFT calculations, involving geometry optimizations of all intermediates and transition states (TSs), as well as considering the solvent effect (CPCM) of benzene. Based on these calculations, the energy profile of the most feasible reaction pathway is summarized in Figure 4, including schematic structures of all intermediates and TSs. Initially, **2** should deprotonate benzene to afford **3** and the (boryl)(phenyl)lithate **6** via TS₂₋₆ (activation energy = 28.6 kcal mol⁻¹). TS₂₋₆ can be generated by interaction between benzene and the Dip-dissociated K⁺ (**A** or **B** in Scheme 2). In TS₂₋₆, K⁺ should promote the deprotonation by acting as a Lewis acid, which would weaken the C–H bond in benzene by π coordination. The activation energy for the corresponding TS without π coordination to K⁺ was calculated to be 3.0 kcal mol⁻¹ higher (for details, see the Supporting Information). The interaction between **3** and **6** would thus afford **7** via two very low-energy TSs (<10 kcal mol⁻¹; for details, see the Supporting Information). Subsequently, **7** should undergo a nucleophilic migration of the phenyl anion moiety to the hydrogen-bonded boron atom to furnish the (hydrido)(phenyl)borate intermediate **8** (activation energy = 18.1 kcal mol⁻¹). Dissociation of the hydride from the tetra-coordinate borate center in **8** would generate **9**, which could dissociate into **4** and the potassium (boryl)(hydrido)lithate **10**. Subsequent complexation of **10** with another equivalent of benzene would result in the formation of the intermediate **11**, which should undergo deprotonation by the remaining boryl anion to furnish intermediate **12**. It should be noted that the activation energy for TS₁₁₋₁₂ from **10** (22.7 kcal mol⁻¹) is smaller than that of the deprotonation by **2**. Dissociation of **3** from **12** and subsequent re-complexation of **3** with the potassium (hydrido)(phenyl)lithate **13** should afford **14**. The following two-step hydride/phenyl exchange via the intermediate **15** should result in the formation of **16**, which could liberate **4** and the potassium dihydridolithate **17**. Considering the results of our calculations, **3** should be completely transformed into **4** given that all reactions after the first deprotonation step exhibit relatively low activation energy barriers. However, experimentally, the reaction between **2** and benzene affords **3** in 15% yield and **4** in 85% yield. At present, we assume that potassium (hydrido)(phenyl)lithate

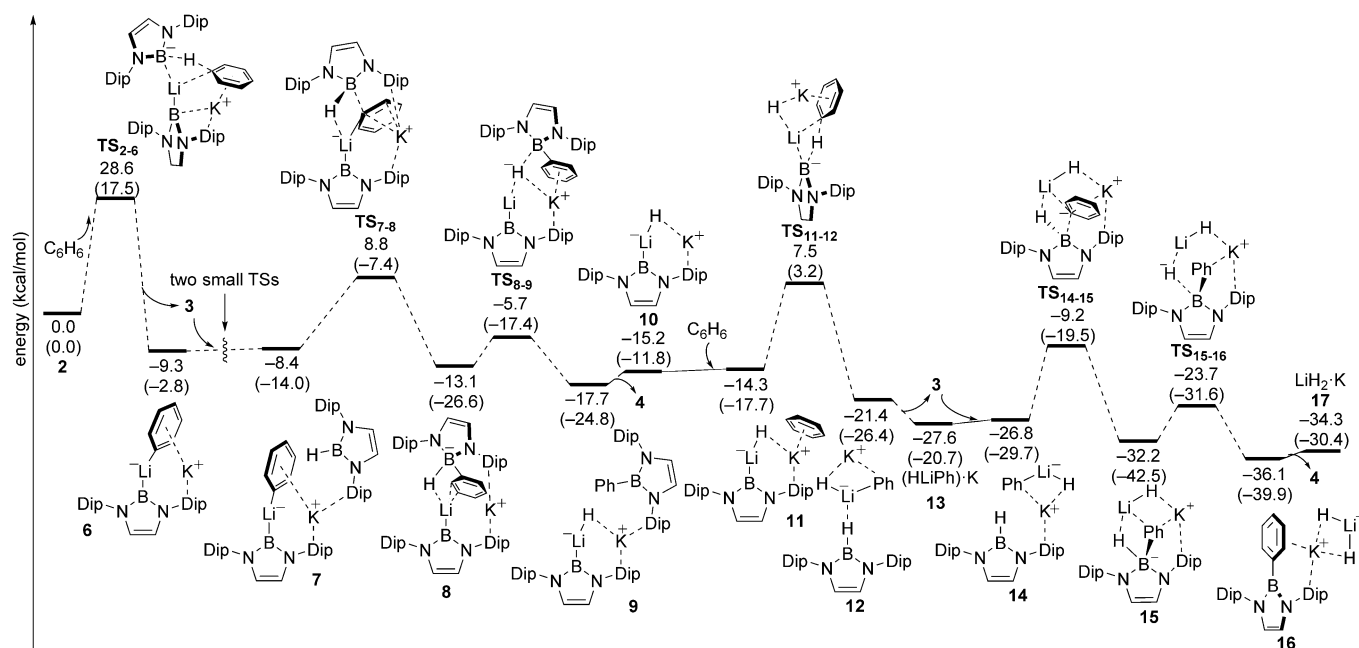


Figure 4. Energy profiles of the DFT-based mechanism for the deprotonation of benzene by **2**, including schematic structures of intermediates and transition states, calculated at the B3LYP-D3/6-311 + G(d,p)/CPCM(Benzene)//B3LYP/6-31G(d) level of theory. Relative Gibbs free energies and electronic energies (within parentheses) are given in kcal mol⁻¹.

13 precipitates from solution and that the resulting low concentration of **13** in the solution prevents the completion of the reaction between **3** and **13**, and would be consistent with the experimental observations.

To analyze the characteristic orbital interaction in the first transition state (**TS**₂₋₆) for the rate-determining deprotonation step, a natural bond orbital (NBO) analysis was carried out. The obtained natural bond orbitals (NBOs) 243, 242, and 228 are shown in Figure 5 together with the optimized structures (for other related NBOs, see the Supporting Information). In **TS**₂₋₆, the B-H-C angle at the reaction center is almost linear (169.3°), and thus similar to the C-H-C angle (176.08°) in the TS for the deprotonation of benzene with *n*BuLi/(*R,R*)-TMCDA.^[6d] The shape of NBO 243 shows the donor–acceptor interaction from the anionic boron center to the σ*_{C-H} orbital of the reacting benzene moiety, in which the boryl anion is still interacting with Li⁺ and K⁺. For these two types of interaction, second-order perturbation energies (*E*₂) of 196.5 and 36.3 kcal mol⁻¹ were calculated, respectively. In NBO 242, the bridging donor–acceptor interaction from the boryl anion to Li⁺ and K⁺ in **TS**₂₋₆ was assigned an *E*₂ value of 91.5 kcal mol⁻¹, which was confirmed by the AIM analysis for **2**. The third type of important donor–acceptor interaction in **TS**₂₋₆ was found in NBO 228: a π-coordination from an *ipso-ortho* C–C bond of the deprotonated benzene to Li⁺ and K⁺. Similarly, two additional π-coordination interactions from four other carbon atoms in the benzene ring to K⁺ were observed in NBOs 223 and 225 (see the Supporting Information). The sum of these interactions is *E*₂ = 90.9 kcal mol⁻¹. Although a contribution from the carbanionic character in the reaction center to coordinate to Li⁺ and K⁺ was also found in NBO 220 (see the Supporting Information), these interactions (*E*₂ = 9.5 kcal mol⁻¹) are relatively weak. Thus,

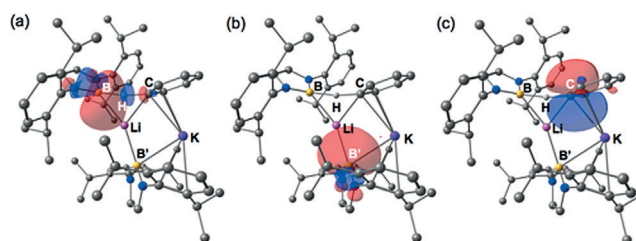


Figure 5. Natural bond orbitals: a) 243, b) 242, and c) 228 on the optimized transition state **TS**₂₋₆ for the deprotonation of benzene by **2**, showing donor–acceptor interactions (isovalue = 0.02). Hydrogen atoms except for those being deprotonated are omitted for clarity. H white, C gray, N blue, B yellow, K deep purple, Li light purple. For other natural bond orbitals mentioned in the main text, see the Supporting Information.

the deprotonation of benzene by **2** via transition state **TS**₂₋₆ is best described by two characteristics: 1) a potassium-assisted increase of the acidity of a C–H proton in benzene, and 2) a nucleophilic migration of the boryl anion from the diboryllithate structure to the acidic C–H proton through interaction with the C–H σ* orbital. This dual-mode activation could also be compared with the reaction mode of frustrated Lewis pairs (FLPs) toward small molecules.^[22]

This study includes the preparation of a new boryl anion (**2**) with a potassium diboryllithate structure. We revealed the structural and spectroscopic properties of **2**, and delivered a theoretical analysis for its molecular orbital and bonding situation, as well as for its reactivity toward benzene to form **3** and **4**. A detailed reaction mechanism was developed based on DFT calculations. Additionally, the NBO analysis provided information on the interaction between benzene and K⁺. This interaction promotes the deprotonation of benzene

by the boryl anion. The fundamental properties of this boryl anion as a base and the participation of the K^+ cation to enhance the reactivity of C–H bonds in benzene should expand the current frontiers of acid/base chemistry.

Acknowledgments

This research was supported by Grants-in-Aid for Scientific Research on Innovative Areas [“Stimuli-responsive Chemical Species for Creation of Functional Molecules” (No. 2408), JSPS KAKENHI Grant Numbers JP24109012 (M.Y.) and JP24109004 (T.I.)]; “Precise Formation of a Catalyst Having a Specified Field for Use in Extremely Difficult Substrate Conversion Reactions”, 15H05796 (K.N.)] from MEXT and JSPS, Grants-in-Aid for Scientific Research (B) [26288019 (M.Y.)] from MEXT, HKUST603313 (Z.L.) and CUHK7/CRF/12G (Z.L.) from the Research Grants Council of Hong Kong, CREST (14529307, M.Y.) from JST, and research grants from The Science Research Promotion Fund (M.Y.) and The Asahi Glass Foundation (M.Y.). We thank Prof. Tamejiro Hiyama (Chuo University) for providing access to an X-ray diffractometer. Parts of the theoretical calculations were carried out using resources at the Research Center for Computational Science, Okazaki, Japan.

Keywords: benzene · boron · computational chemistry · structure determination · superbases

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11426–11430
Angew. Chem. **2016**, *128*, 11598–11602

- [1] M. Faraday, *Philos. Trans. R. Soc. London* **1825**, *115*, 440–466.
[2] A. Kekulé, *Justus Liebig's Ann. Chem.* **1872**, *162*, 77–124.
[3] a) P. Schorigin, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 2711–2717; b) P. Schorigin, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 2723–2728.
[4] Reference [19] in Chapter 1 “Organoalkali Chemistry”: M. Schlosser, in *Organometallics in Synthesis Third Manual*, Wiley, Hoboken, **2013**.
[5] a) L. Lochmann, D. Lím, *J. Organomet. Chem.* **1971**, *28*, 153–158; b) L. Lochmann, *Collect. Czech. Chem. Commun.* **1987**, *52*, 2710–2716; c) M. Schlosser, H. C. Jung, S. Takagishi, *Tetrahedron* **1990**, *46*, 5633–5648.
[6] a) A. W. Langer, *Trans. N. Y. Acad. Sci.* **1965**, *27*, 741–747; b) M. D. Rausch, D. J. Ciappenelli, *J. Organomet. Chem.* **1967**, *10*, 127–136; c) C. Strohmman, V. H. Gessner, *J. Am. Chem. Soc.* **2007**, *129*, 8952–8953; d) C. Strohmman, V. H. Gessner, *J. Am. Chem. Soc.* **2008**, *130*, 11719–11725.
[7] G. E. Davico, V. M. Bierbaum, C. H. Depuy, G. B. Ellison, R. R. Squires, *J. Am. Chem. Soc.* **1995**, *117*, 2590–2599.
[8] K. E. Laidig, A. Streitwieser, *J. Comput. Chem.* **1996**, *17*, 1771–1781.
[9] a) Y. Segawa, M. Yamashita, K. Nozaki, *Science* **2006**, *314*, 113–115; b) Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.* **2008**, *130*, 16069–16079; c) M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *Chem. Lett.* **2008**, *37*, 802–803.
[10] N. Dettenrieder, Y. Aramaki, B. M. Wolf, C. Maichle-Mössmer, X. Zhao, M. Yamashita, K. Nozaki, R. Anwander, *Angew. Chem. Int. Ed.* **2014**, *53*, 6259–6262; *Angew. Chem.* **2014**, *126*, 6373–6377.
[11] a) A. V. Protchenko, L. M. A. Saleh, D. Vidovic, D. Dange, C. Jones, P. Mountford, S. Aldridge, *Chem. Commun.* **2010**, *46*, 8546–8548; b) A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500–6503; c) A. V. Protchenko, D. Dange, A. D. Schwarz, C. Y. Tang, N. Phillips, P. Mountford, C. Jones, S. Aldridge, *Chem. Commun.* **2014**, *50*, 3841–3844; d) B. Wang, M. Nishiura, J. Cheng, Z. Hou, *Dalton Trans.* **2014**, *43*, 14215–14218.
[12] The term lithate is the name for ate complex (coordination compound with an anionic charge on the metal center) of lithium. See: N. G. Connelly, T. Damhus, R. M. Hartshorn, A. T. Hutton, *Nomenclature of Inorganic Chemistry: IUPAC Recommendations 2005*, Royal Society of Chemistry, London, **2005**.
[13] J. Emsley, *The Elements*, 3rd ed., Oxford University Press, New York, **1998**.
[14] a) C. Eaborn, P. B. Hitchcock, J. D. Smith, A. C. Sullivan, *J. Chem. Soc. Chem. Commun.* **1983**, 827–828; b) A. G. Avent, C. Eaborn, P. B. Hitchcock, G. A. Lawless, P. D. Lickiss, M. Mallien, J. D. Smith, A. D. Webb, B. Wrackmeyer, *J. Chem. Soc. Dalton Trans.* **1993**, 3259–3264; c) T. Viehhaus, A. Walz, M. Niemeyer, W. Schwarz, J. Weidlein, *Z. Anorg. Allg. Chem.* **2000**, *626*, 2040–2042; d) M. S. Hill, P. B. Hitchcock, *Organometallics* **2002**, *21*, 220–225; e) S. S. Al-Juaid, A. G. Avent, C. Eaborn, S. M. El-Hamruni, S. A. Hawkes, M. S. Hill, M. Hopman, P. B. Hitchcock, J. D. Smith, *J. Organomet. Chem.* **2001**, *631*, 76–86.
[15] a) D. Margerison, J. P. Newport, *Trans. Faraday Soc.* **1963**, *59*, 2058–2063; b) I. Craubner, *Z. Phys. Chem. (Muenchen Ger.)* **1966**, *51*, 225; c) “The Structures of Organolithium Compound”: T. L. Brown, in *Adv. Organomet. Chem. Vol. 3* (Eds.: F. G. A. Stone, W. Robert), Academic Press, San Diego, **1966**, pp. 365–395; d) H. L. Lewis, T. L. Brown, *J. Am. Chem. Soc.* **1970**, *92*, 4664–4670; e) T. Kottke, D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 580–582; *Angew. Chem.* **1993**, *105*, 619–621.
[16] J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.
[17] a) R. Mcweeny, *Phys. Rev.* **1962**, *126*, 1028–1034; b) R. Ditchfield, *Mol. Phys.* **1974**, *27*, 789–807; c) K. Wolinski, J. F. Hinton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260; d) J. R. Cheeseman, G. W. Trucks, T. A. Keith, M. J. Frisch, *J. Chem. Phys.* **1996**, *104*, 5497–5509.
[18] a) R. F. W. Bader, *Atoms In Molecules—A Quantum Theory*, Oxford University Press, New York, **1990**; b) T. A. Keith, (version 14.04.17) ed., TK Gristmill Software, Overland Park KS, USA, **2014**.
[19] R. F. W. Bader, *J. Phys. Chem. A* **1998**, *102*, 7314–7323.
[20] Carbon Acids, D. J. Cram, in *Fundamentals of Carbanion Chemistry*, Academic Press, San Diego, **1965**.
[21] a) D. Bryce-Smith, E. E. Turner, *J. Chem. Soc.* **1953**, 861–867; b) D. Bryce-Smith, V. Gold, D. P. N. Satchell, *J. Chem. Soc.* **1954**, 2743–2747.
[22] a) D. W. Stephan, *Org. Biomol. Chem.* **2008**, *6*, 1535–1539; b) D. W. Stephan, *Dalton Trans.* **2009**, 3129–3136; c) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; d) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740–5746; e) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625–2641; f) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541; g) S. A. Weicker, D. W. Stephan, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1003–1016.
[23] CCDC 865529 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: May 22, 2016

Revised: July 19, 2016

Published online: August 17, 2016