**Superbases**

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

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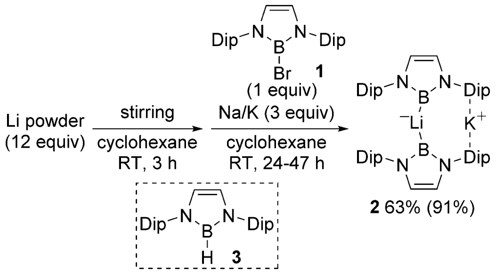
*Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday*

**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 alkyllithiums 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



**Scheme 1.** Synthesis of the potassium diboryllithate **2** (Dip = 2,6-$iPr_2C_6H_3$). Yield as determined by $^1H$ NMR spectroscopy, in [$D_{12}$]cyclohexane, is given within parentheses.

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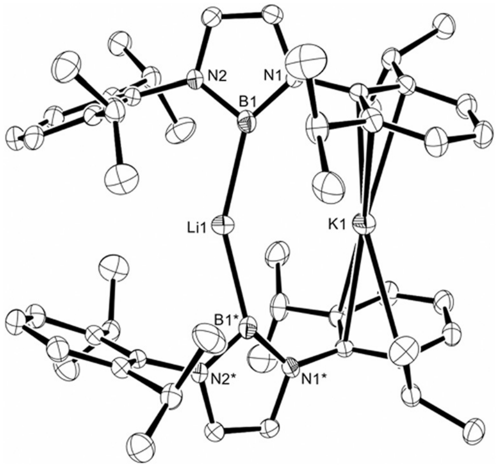
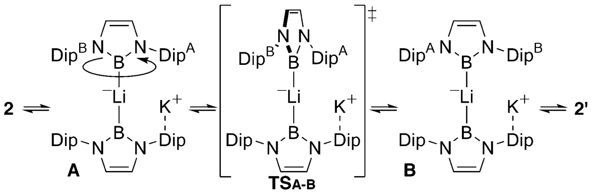


***Figure 1.*** Molecular structure of **2** (thermal ellipsoids set at 50% probability, hydrogen atoms and co-crystallized 2,2,4,4-tetramethylpentane omitted for clarity).[23] Selected bond distances (Å) and angles (°): B1-Li1 2.286(4), B1-N1 1.461(4), B1-N2 1.461(3), K1⋯C(Dip) 3.018(4), 3.129(3), 3.218(5), 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).



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

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 $\eta^3$-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 $[LiR_2]^-$ dialkyllithate 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 $[D_{12}]$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 $\mathbf{TS_{A\text{-}B}}$, and c) re-coordination of Dip to $K^+$. The $^{11}B$ NMR spectrum of **2** in $[D_{12}]$cyclohexane showed one broad singlet at $\delta_B = 43$ ppm, thus indicating an anionic character of the boron center. The $^7Li$ NMR spectrum of **2** in $[D_{12}]$cyclohexane exhibited a remarkably low-field shifted signal ($\delta_{Li} = 4.7$ ppm) relative to the signals of THF-solvated boryllithium species ($\delta_{Li} = 0.44$–$0.68$ ppm). A similar low-field signal was also observed in the solid-state CPMAS-$^7Li$ spectrum ($\delta_{Li} = 5.5$ 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 $\pi$ 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 [$\delta_{Li} = 6.7$ ppm, vs. $Li^+(OH_2)_4$], while an atoms-in-molecules (AIM)

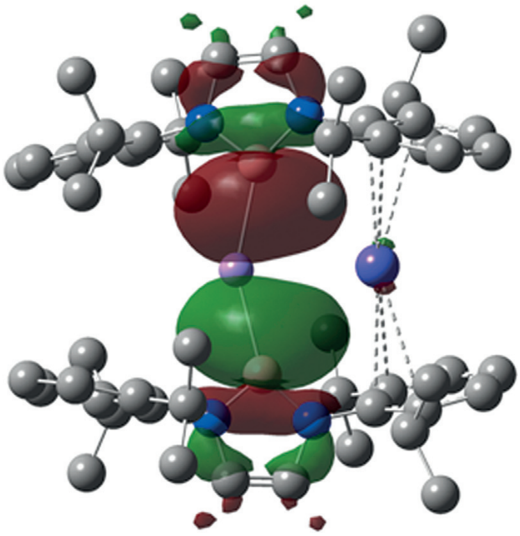


***Figure 2.*** HOMO of **2** (isovalue = 0.020) optimized at the B3LYP/6-31 + G(d) level of theory. Hydrogen atoms omitted for clarity.

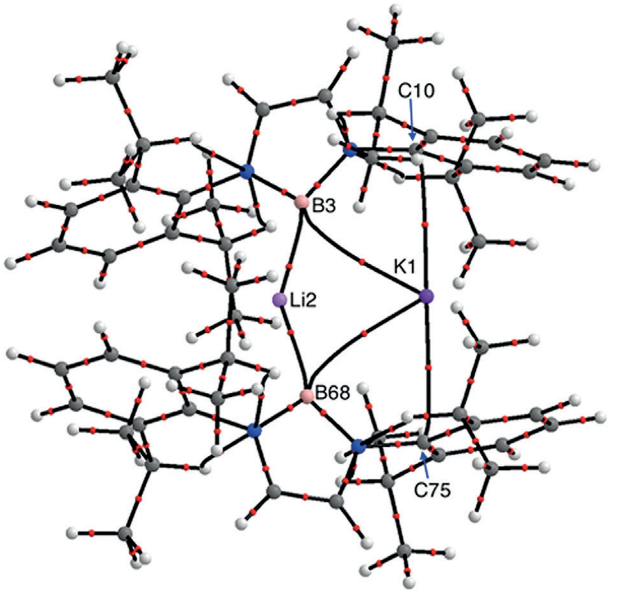
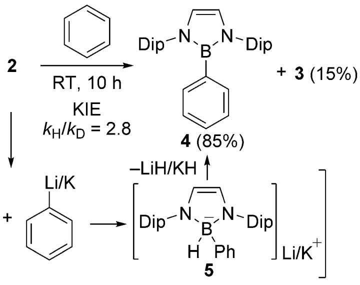


***Figure 3.*** AIM-generated molecular graph (red spheres: bond critical points, solid lines: bond paths, labeling based on the results of the DFT calculations); for selected bond critical points, properties such as $\rho(r)$ $(e/a_0^3)$, $\nabla^2\rho(r)$ $(e/a_0^5)$, and $\varepsilon$ are listed in 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 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 $C_6H_6$ or $C_6D_6$ (100 equiv each) in $[D_{12}]$cyclohexane were monitored by $^1$H 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 alkyllithiums, which do not deprotonate benzene in hydrocarbon solvents.[4]



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

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 $\mathbf{TS_{2-6}}$ (activation energy = 28.6 kcal mol$^{-1}$). $\mathbf{TS_{2-6}}$ can be generated by interaction between benzene and the Dip-dissociated K$^+$ (**A** or **B** in Scheme 2). In $\mathbf{TS_{2-6}}$, 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 tetracoordinate 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 $\mathbf{TS_{11-12}}$ 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

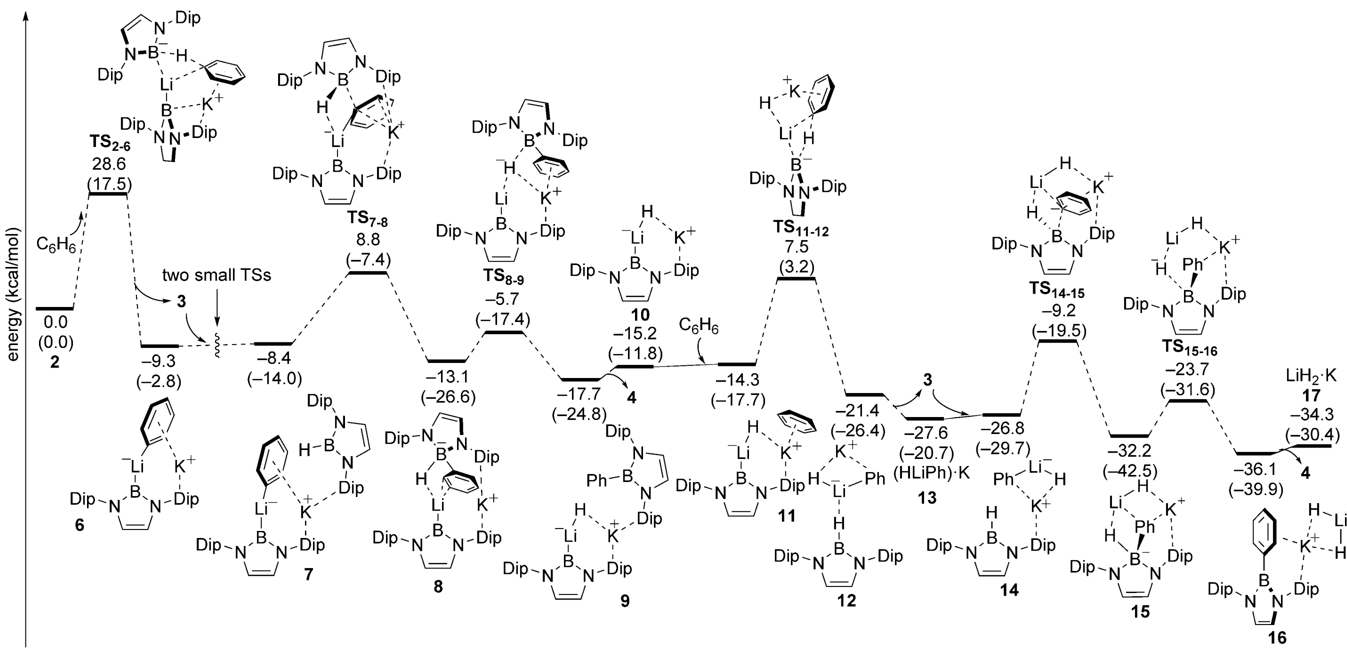


*Figure 4.* Energy profiles of the DFT-based mechanism for the deprotonation of benzene by **2**, including schematic structures of intermediates and transition states, calculated at the B3LYP-D3/6-311+G(d,p)/CPCM(Benzene)//B3LYP/6-31G(d) level of theory. Relative Gibbs free energies and electronic energies (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 ($\mathbf{TS_{2\text{-}6}}$) 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 $\mathbf{TS_{2\text{-}6}}$, 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 $\sigma^*_{\text{C-H}}$ 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 $\mathbf{TS_{2\text{-}6}}$ 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 $\mathbf{TS_{2\text{-}6}}$ 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 Interaction). 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, the deprotonation of benzene by **2** via transition state $\mathbf{TS_{2\text{-}6}}$ 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]

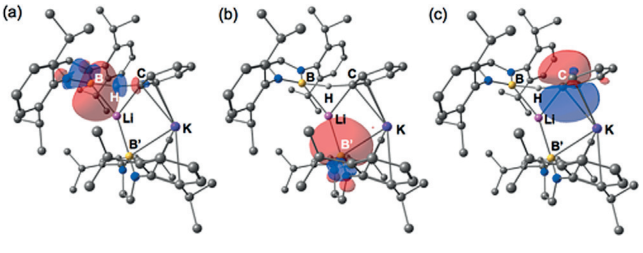


*Figure 5.* Natural bond orbitals: a) 243, b) 242, and c) 228 on the optimized transition state $\mathbf{TS_{2\text{-}6}}$ for the deprotonation of benzene by **2**, showing donor–acceptor interactions (isovalue = 0.02). Hydrogen atoms except for those being deprotonated are omitted for clarity. H white, 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.

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.

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[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.

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