H_2 Activation

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Reversible Dihydrogen Activation by Reduced Aryl Boranes as Main-Group Ambiphiles

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Dedicated to Professor Gerhard Erker on the occasion of his 70th birthday

Abstract: *A new approach to main-group H_2 activation combining concepts of transition-metal and frustrated Lewis pair chemistry is reported. Ambiphilic, metal-like reactivity toward H_2 can be conferred to 9,10-dihydro-9,10-diboraanthracene (DBA) acceptors by the injection of two electrons. The resulting $[DBA]^{2-}$ ions cleave the H−H bond with the formation of hydridoborates under moderate conditions (T= 50–100°C; $p<1$ atm). Depending on the boron-bonded substituents R, the addition is either reversible (R = C≡CtBu) or irreversible (R = H). The reaction rate is strongly influenced by the nature and the coordination behavior of the countercation (Li^+ slower than K^+). Quantum-chemical calculations support the experimental observations and suggest a concerted, homolytic addition of H_2 across both boron atoms. As proven by the successful conversion of Me_3SiCl into Me_3SiH, the system $Li_2[DBA]/H_2$ appears generally relevant for the hydrogenation of element–halide bonds.*

Reversible activation of dihydrogen (H_2) is a common reaction of various transition-metal complexes, the most prominent example being the Wilkinson catalyst ($[Rh(PPh_3)_3Cl]$).[1] According to the generally accepted transition-state model, H_2 splitting results from the interaction between a vacant metal d orbital with the H_2 σ-MO augmented by back-bonding from a filled d orbital into the H_2 σ*-MO (Figure 1, middle; MO = molecular orbital). It was a change of paradigm when Stephan and co-workers disclosed that H_2 activation is not unique to transition metals, but is also possible with suitable combinations of main-group Lewis acids and bases.[2] For example, sterically demanding organoboranes and -phosphanes, incapable of stabilization through adduct formation (frustrated Lewis pairs, FLPs), retain their reactivity and can cooperatively act on an H_2 molecule to heterolytically cleave its covalent bond.[3] In such cases, the boron center provides the acceptor orbital, and the phosphorus lone pair takes the role of the filled metal d orbital to accomplish back donation. Moreover, optimal orbital interactions in the transition state demand a stereochemical arrangement of the two Lewis sites as shown in Figure 1, left.[3] Conceptually, a comparison of the modes of action of FLPs and transition-metal centers raises the question: Do we really need the Lewis base, or can we simplify the system to just a main-group acceptor and evoke ambiphilic, metal-like behavior toward H_2 by injecting two electrons?

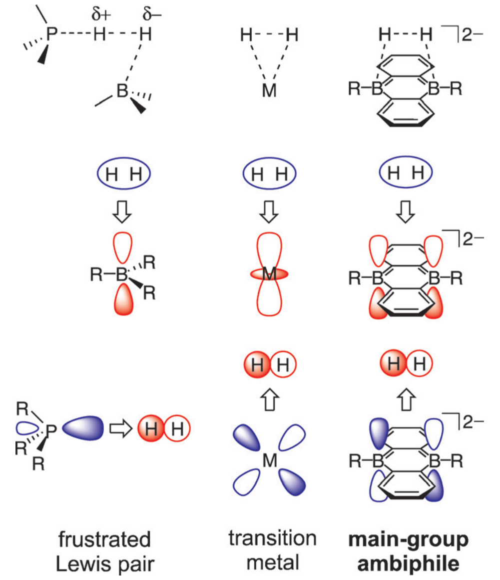

Figure 1. Transition-state orbital interactions relevant for H_2 activation: Heterolytic cleavage by FLPs (left) versus homolytic cleavage at a transition-metal center (middle) and at $[DBA]^{2-}$ (right). HOMOs and LUMOs are shown in blue and red, respectively.

Numerous aryl boranes are redox active.[4] Among them, derivatives of 9,10-dihydro-9,10-diboraanthracene (DBA) stand out for their ability to accept two electrons in a reversible manner ($[DBA]^{2-}$).[5–7] Both boron atoms are also ideally prearranged within the rigid scaffold for cooperative action.[8] Notably, the HOMO and the LUMO of $[DBA]^{2-}$ have the same local symmetries at the boron atoms as the corresponding frontier orbitals involved in metal-mediated H_2 splitting (Figure 1, right).[6] As a related case, we have previously demonstrated that the derivative Li_2[**1**] reacts with terminal alkynes, such as HC≡CtBu, through C−H splitting to give an addition product of the type Li_2[**2**] (Scheme 1).[7] Herein, we show that $[DBA]^{2-}$ is actually capable of adding H_2 across the two boron atoms

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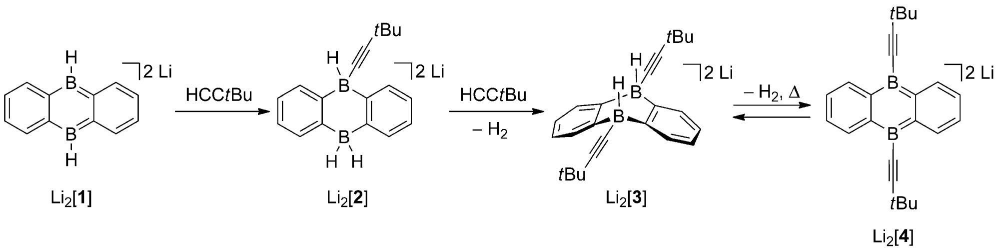


Scheme 1. The $[DBA]^{2-}$ derivative Li_2[**1**] reacts with HC≡C*t*Bu to form Li_2[**2**] or Li_2[**3**]. At elevated temperatures, a dynamic equilibrium exists between Li_2[**3**] and Li_2[**4**]/H_2.

under mild conditions. The ability to undergo this prototypical reaction renders our system unique among main-group ambiphiles (MGAs).[9]

We first revisited and optimized the reaction between Li_2[**1**] and HC≡C*t*Bu: An equimolar mixture of both compounds furnished the monoalkynyl derivative Li_2[**2**] together with Li_2[**3**] (Scheme 1). In contrast, selective formation of Li_2[**3**] was observed upon the treatment of Li_2[**1**] with excess HC≡C*t*Bu (4 equiv) at 50 °C for 3 days. Remarkably, the crude product gave rise to only one set of signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra, thus ruling out the presence of *syn*/*anti* isomers. In the majority of crystallographically characterized DBA derivatives with tetracoordinated boron atoms, the central B_2C_4 ring adopts a boat conformation in the solid state (the same is true for Li_2[**5**]; Figure 5 b; see below).[10] If this preferred conformation prevails also in solution, the sterically more demanding alkynyl substituents of Li_2[**3**] should occupy both equatorial positions, which would not only explain the observed NMR spectral features, but also place the two hydrogen substituents in the axial positions and thereby render them ideally preoriented for the concerted elimination of H_2. Given this background, we continued our investigations with the thermolysis of Li_2[**3**] in a closed system.

A solution of Li_2[**3**] in [D_8]THF in a vacuum-sealed NMR tube was heated to 100 °C over a period of several days, and the reaction progress was monitored by ^{1}H NMR spectroscopy at room temperature (see Figure S1 in the Supporting Information). We observed a successive decrease in the amount of Li_2[**3**] with the concomitant formation of H_2 ($\delta(^1H) = 4.55$ ppm[11]) and a new symmetrical $[DBA]^{2-}$ derivative, identified as Li_2[**4**] ($\delta(^{11}B) = 13.7$ ppm). After 8 days at 100 °C, a stationary state was reached (Li_2[**3**]/Li_2[**4**] ≈ 1:2). The relative proportion of Li_2[**3**] in the reaction mixture increased again (Li_2[**3**]/Li_2[**4**] ≈ 1:1) when the temperature was subsequently lowered to 50 °C, which corresponds to the conditions initially applied for the synthesis of Li_2[**3**]. X-ray crystallography on $[Li(thf)_2]_2$[**4**] revealed an essentially planar tricylic core structure ($\Sigma B^{CCC} = 360°$; Figure 5 a); no residual electron density attributable to BH hydrogen atoms was present in the electron-density map. Similar to the solid-state structure of Li_2[**1**],[6,7] two $[Li(thf)_2]^+$ cations are located above and below the centroid (COG) of the B_2C_4 ring ($Li^+\cdots$COG distance: 1.942(5) Å).

The experimental data acquired so far indicate that the conversion of Li_2[**3**] into Li_2[**4**] is a reversible thermolysis reaction. In a closed system from which H_2 can not escape, a dynamic equilibrium between Li_2[**3**] and Li_2[**4**]/H_2 exists: At 100 °C, the equilibrium is shifted to the side of Li_2[**4**], at 50 °C, both organoboron species are equally abundant, and at room temperature, the equilibrium is largely frozen in (see the Supporting Information). To further confirm this conclusion, we prepared an authentic sample of Li_2[**4**] through the reduction of **4** with lithium metal in [D_8]THF. The solution was transferred to an NMR tube, covered with a blanket of H_2 (< 1 atm), and flame-sealed. At this stage, exclusively Li_2[**4**] was detectable in the ^{1}H NMR spectrum (Figure 2). Upon heating to 100 °C, the signals belonging to Li_2[**4**] lost intensity, whereas resonances assignable to Li_2[**3**] gradually evolved. After 34 h, the ratio between Li_2[**4**] and Li_2[**3**] approached 1:1. The largest fraction of Li_2[**3**] was again generated after further heating of the sample at 50 °C. Since the amount of H_2 was significantly higher in the H_2-activation experiment as compared to the thermolysis reaction, the equilibrium was reached faster, and the equilibrating mixture contained a higher relative proportion of Li_2[**3**]. However, irrespective of the conditions applied, the conversion of Li_2[**4**] into Li_2[**3**] could never be driven to completion. This finding agrees with the assumption of a dynamic equilibrium between Li_2[**3**] and Li_2[**4**]/H_2.

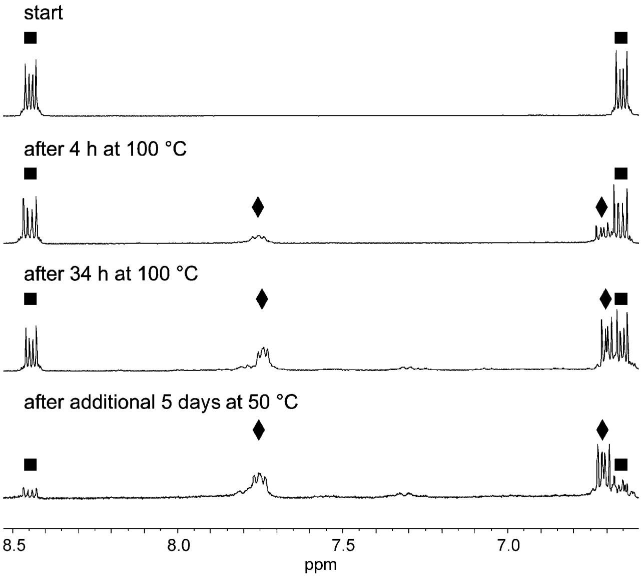
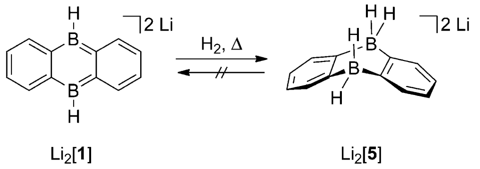


Figure 2. Changes in the ^{1}H NMR spectrum (500.2 MHz, [D_8]THF) of a solution of Li_2[**4**] under an H_2 atmosphere (< 1 atm) upon heat treatment. The spectra were recorded at room temperature in a flame-sealed NMR tube; ■ Li_2[**4**], ◆ Li_2[**3**].

We next attempted H_2 activation by the parent system Li_2[**1**]. In the presence of excess H_2 (< 1 atm) and at 100 °C, solutions of Li_2[**1**] in [D_8]THF afforded the hydrogen-addition



Scheme 2. Irreversible H_2 addition to Li_2[**1**] to afford Li_2[**5**].

product Li_2[**5**] in quantitative yield after 2 days (Scheme 2). Contrary to Li_2[**3**], vacuum-sealed solutions of Li_2[**5**] in THF showed no tendency to liberate H_2 at temperatures up to 100 °C. The chemical composition of Li_2[**5**] was confirmed by a comparison of its NMR data with those of a sample independently prepared from 9,10-dihydroxy-DBA and $LiAlH_4$.[12] According to X-ray crystal-structure analysis of $[Li(thf)_2][Li(thf)]$[**5**], the central B_2C_4 heterocycle of the dianionic moiety $[\mathbf{5}]^{2-}$ adopts a boat conformation with a dihedral angle C1B1C11//C2B2C12 of 56.2(3)° (Figure 5 b). All four BH hydrogen atoms were isotropically refined. As a blind test, we also heated solutions of Li_2[**1**] in THF in the absence of H_2 to 100 °C, but observed no formation of Li_2[**5**]. Moreover, the deuterium analogue Li_2[**1**-D_2] of Li_2[**1**] was prepared by two-electron reduction of 9,10-dideuterio-DBA with lithium metal. Subsequent H_2 activation in $[D_8]$THF afforded Li_2[**5**-D_2], which exhibited a signal for boron-bonded deuterium atoms at 2.29 ppm in the $^2H\{^{11}B\}$ NMR spectrum and a BH resonance, which integrated to 2 H (instead of 4 H), at the same chemical-shift value in the ^1H NMR spectrum (see the Supporting Information).

For future applications of MGAs as hydrogenation catalysts, it would be desirable to further accelerate the H_2-activation reaction and to lower the required temperatures. For this goal to be achieved, a largely unhindered interaction of the H_2 molecule with the B_2C_4 ring has to be ensured. The solid-state structure of Li_2[**1**] shows two $[Li(thf)_2]^+$ ions coordinated to both sides of the heterocyclic core, thereby blocking access to the boron centers. A prominent resonance at −9.0 ppm in the room-temperature ^7Li NMR spectrum of Li_2[**1**] proves that the compound forms contact-ion pairs also in $[D_8]$THF solution (similar observations hold for Li_2[**4**]).[1] We therefore assumed that heating is (at least in part) required to break up ion pairing and create the necessary space for the incoming H_2 substrate. Cation dissociation can alternatively be promoted by an exchange of Li^+ for K^+, because K^+ tends to bind organic π-electron systems less tightly than Li^+.[13] K_2[**1**] was synthesized by the reduction of **1** with KC_8 (2 equiv). A comparison of the ^1H NMR spectra of K_2[**1**] and Li_2[**1**] revealed a close relationship between both species. Small but significant shifts of their NMR signals are probably due to the aimed-for differences in cation coordination. This assumption is supported by the observation that the addition of 12-crown-4 to a solution of Li_2[**1**] in $[D_8]$THF had a similar qualitative effect on the proton resonances of $[\mathbf{1}]^{2-}$ as the replacement of Li^+ with K^+ (see Figure S4).

To compare the reactivities of Li_2[**1**], Li_2[**1**]/12-crown-4, and K_2[**1**], equimolar solutions of the three salts in $[D_8]$THF were prepared in NMR tubes under an atmosphere of H_2 (< 1 atm) and flame-sealed. After heating at 50 °C for 24 h, the sample with Li_2[**1**] contained only 25 % of the dihydride adduct Li_2[**5**]. In contrast, Li_2[**5**] already constituted the major component (75 %) of the second sample. H_2 activation by K_2[**1**] was quantitative in less than 15 h (Figure 3; see also the Supporting Information).

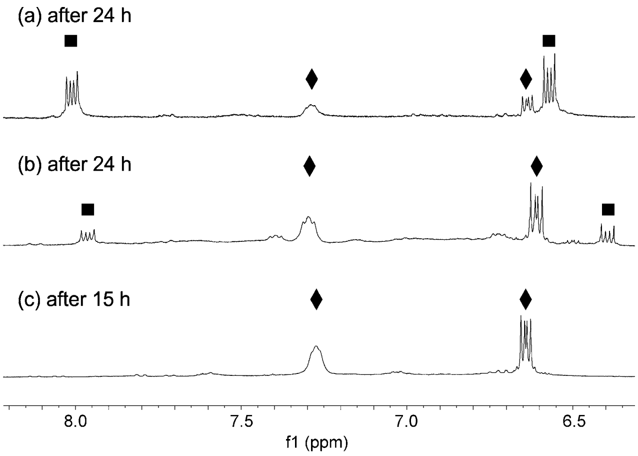


Figure 3. ^1H NMR spectra (300.0 MHz, $[D_8]$THF) showing the progress of H_2 activation (< 1 atm) at 50 °C by a) Li_2[**1**], b) Li_2[**1**]/12-crown-4, and c) K_2[**1**]. ■ M_2[**1**], ◆ M_2[**5**].

Mechanistically, two scenarios for the H_2 activation appear plausible: i) On the basis of the nodal structures of the frontier orbitals of $[\mathbf{1}]^{2-}$ discussed above (see Figure 1 and the Supporting Information), a metal-like, concerted addition of H_2 to both boron atoms is conceivable; ii) on the basis of the mesomeric resonance structures of $[\mathbf{1}]^{2-}$ shown in Figure 4, an FLP-like, heterolytic addition of H_2 to one boron atom and to its electronegative *ipso* carbon neighbor could also take place,[14] followed by hydrogen-atom migration from the carbon atom to the second boron atom. For further insight, we performed quantum-chemical calculations on both pathways (Figure 4). Commencing with the bare dianion $[\mathbf{1}]^{2-}$, H_2 activation by concerted 9,10-addition

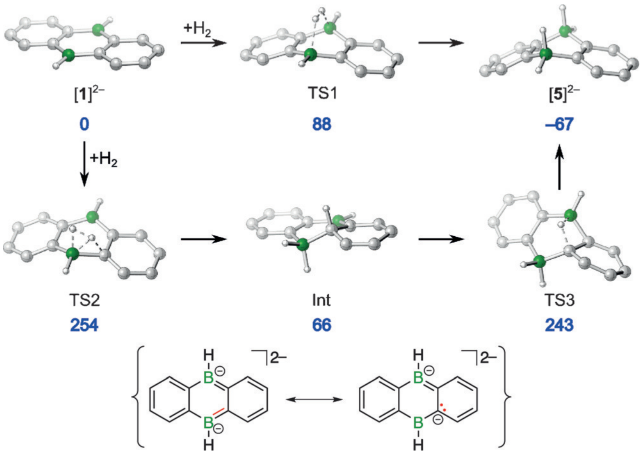


Figure 4. Reaction paths for the addition of H_2 to $[\mathbf{1}]^{2-}$ (ΔG^{298} in kJ mol^{-1}, B2GP-PLYP-D/CBS(T,Q)//SMD-PBE0D/6-31 + G(d,p) calculations). The barrier for the inversion of $[\mathbf{5}]^{2-}$ via a planar transition structure is $\Delta G^{\neq}_{inv} = 9$ kJ mol^{-1}.

requires passage of a moderate activation barrier ($\Delta G^{\neq} = 88\,\text{kJ}\,\text{mol}^{-1}$), and the formation of $[\mathbf{5}]^{2-}$ is exergonic by $\Delta_r G = -67\,\text{kJ}\,\text{mol}^{-1}$. Alternative 1,2-addition across the B–C bond (**TS2**) as well as subsequent [1,3]-H migration (**TS3**) are kinetically strongly disfavored and can safely be discarded in this case.[15] The presence of alkynyl substituents in $[\mathbf{4}]^{2-}$ hardly affects the computed activation barrier, but leads to a significantly less stable dihydride adduct (Table 1), consistent with the experimentally observed reversibility of the H_2 addition only for $[\mathbf{3}]^{2-}$. To assess the influence of coordinating counterions, we computed the H_2-activation paths for $[M(thf)_2]_2[\mathbf{1}]$ (M = Li, K; Figure 5c). In the optimized reactant structure $\mathbf{A}_{\mathbf{Li}}$, both $Li(thf)_2$ groups assume an η^6 coordination mode above and below the central B_2C_4 ring, in agreement with the published X-ray data for $[Li(thf)_2]_2[\mathbf{1}]$.[7] In the transition state $\mathbf{TS}_{\mathbf{Li}}$, one of the $Li(thf)_2$ groups slips into an η^2 coordination mode, thereby vacating space for the incoming H_2. As compared to the bare dianion, a moderately increased activation barrier results, and the transition state $\mathbf{TS}_{\mathbf{Li}}$ is directly connected to $\mathbf{B}_{\mathbf{Li}}$ (a slightly less stable minimum, more closely resembling the solid-state structure of $[Li(thf)_2][Li(thf)][\mathbf{5}]$, was also identified; see the Supporting Information). The same reaction path computed for M = K results in a lower activation barrier and higher product stability (Table 1), in line with the experimental observation of faster H_2 addition (see above). These differences are accompanied by a change in the metal coordination in $\mathbf{TS}_{\mathbf{K}}$ and a planarized central B_2C_4 ring in $\mathbf{B}_{\mathbf{K}}$.

Table 1: Activation barriers and product stabilities computed for the addition of H_2 to selected substrates (ΔG^{298} in $\text{kJ}\,\text{mol}^{-1}$, B2GP-PLYP-D/CBS(T,Q)//SMD-PBE0D/6-31+G(d,p) level of theory).

	$[\mathbf{1}]^{2-}$	$[\mathbf{4}]^{2-}$	$[Li(thf)_2]_2[\mathbf{1}]$	$[K(thf)_2]_2[\mathbf{1}]$	anthracene[15]
reactants	0	0	0	0	0
transition state	88	92	112	101	191
product	−67	−33	−28	−63	−33

To conclude, MGAs, such as $M_2[\mathbf{1}]$, must be conceptually distinguished from FLPs, such as R_3B/PR'_3: In the latter, the H_2 molecule undergoes heterolytic cleavage with a proton ending up at the Lewis base and a hydride ion at the Lewis acid. $M_2[\mathbf{1}]$ salts, however, generate two hydride ions from one H_2 molecule. $Li_2[\mathbf{4}]$ apparently adopts an intermediate position, because, similar to certain B/P FLPs, H_2 can be released again from the addition product $Li_2[\mathbf{3}]$. Given this overall background, $M_2[\mathbf{1}]$ salts are ideally suited for such reduction reactions, during which a hydride ion substitutes an appropriate leaving group. We are particularly interested in the economic conversion of chlorosilanes into hydrosilanes owing to their widespread application potential.[16] As a proof-of-principle experiment, $Li_2[\mathbf{5}]$ in $[D_8]$THF was treated with Me_3SiCl (2 equiv). In addition to quantitatively affording Me_3SiH, the reaction left the DBA skeleton (largely) intact. This result opens the perspective of converting element halides into element hydrides by use of a reducing agent and H_2 in the presence of suitably chosen 9,10-dihydro-9,10-diboraanthracenes as redox catalysts.

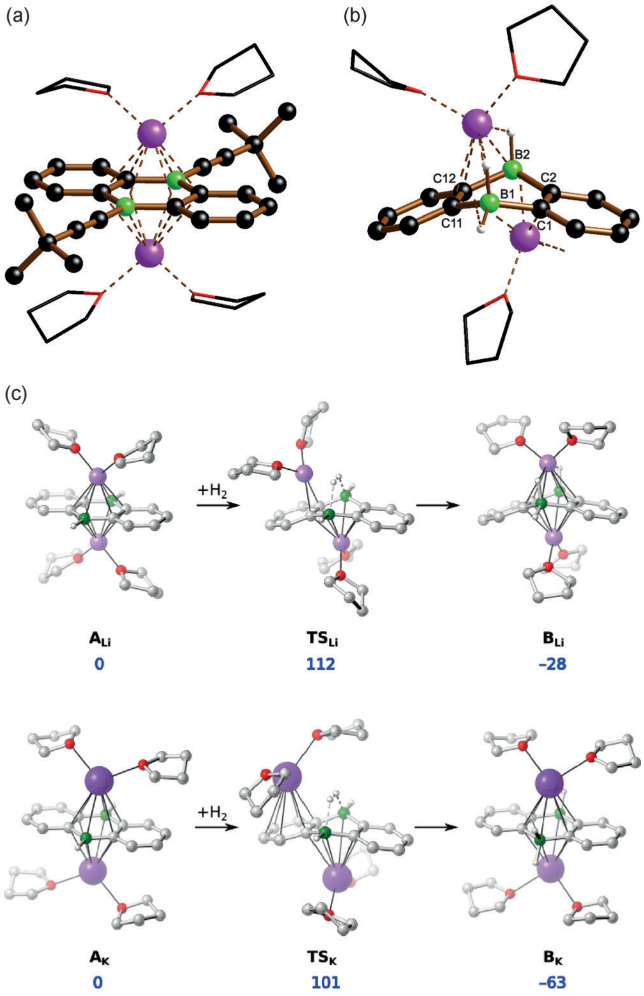


Figure 5. a, b) Solid-state structures of $[Li(thf)_2]_2[\mathbf{4}]$ (a) and $[Li(thf)_2][Li(thf)][\mathbf{5}]$ (b); H atoms bonded to carbon atoms are omitted for clarity. $[Li(thf)_2][Li(thf)][\mathbf{5}]$ forms coordination polymers in the crystal lattice. c) Reaction paths for the addition of H_2 to $[M(thf)_2]_2[\mathbf{1}]$ (M = Li, K; ΔG^{298} in $\text{kJ}\,\text{mol}^{-1}$, B2GP-PLYP-D/CBS(T,Q)//SMD-PBE0D/6-31+G-(d,p) calculations).

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