Volume 1 | Number 1 | Jan 2013 | Pages 1–100

ChemComm

Chemical Communications
www.rsc.org/chemcomm

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

www.rsc.org/chemcomm

Journal Name

ChemComm

ARTICLE TYPE

Application of a Nucleophilic Boryl Complex in Frustrated Lewis Pair: Activation of H-H, B-H and C=C bonds with $B(C_6F_5)_3$ and Boryl-borate Lithium

**Junhao Zheng‡,[a] Yuwen Wang‡,[a] Zhen Hua Li[a] and Huadong Wang*[a]**

The frustrated Lewis pair comprised of $B(C_6F_5)_3$ and a boryl-borate lithium salt Li[pinBB(Ph)pin] can efficiently activate dihydrogen, pinacolborane and ethylene at ambient
10 **temperature. Theoretical studies suggest that the nucleophilic sp^2 boryl moiety of Li[pinBB(Ph)pin] plays different roles in these reactions.**

The chemistry of frustrated Lewis pair (FLP) has emerged as an innovative strategy for small molecule activation.[1,2] Due to the
15 coexistence of unquenched Lewis acid and base centers in FLPs, they can activate H_2,[3] alkenes[4] and other substrates[2] in a synergistic manner. While original FLPs involve Group 13/15 as Lewis acid/base components, much attention was drawn to extend the scope of Lewis acids employed in FLP chemistry. For
20 example, Group 14 (C,[5] Si[6] and Sn[7]) electrophiles have been combined with Lewis bases to achieve FLP reactivity. Transition metal complexes based on Zr,[8] Hf,[9] Ru[10] or Au[11] were also employed as Lewis acids in FLPs. In an elegant example reported by Stephan, phosphonium salts were shown to function as the
25 Lewis acid partner for FLP chemistry.[12] On the other hand, besides Group 15 nucleophiles, the Lewis bases in FLP chemistry haven been limited with only Group 14 (carbene,[5a, 5b, 13] carbanion[14] and silyene[15]) and Group 16 (O[16] and S[17]) based Lewis bases.
30 Recently Hoveyda,[18] Fernández[19] and other groups[20] have reported that base-coordinated sp^3-sp^2 diboron compounds, such as $(NHC)B_2pin_2$ (NHC = 1,3-bis(cyclohexyl)imidazol-2-ylidene, pin = pinacolate) and $[(MeO)B_2pin_2]^-$, possess a nucleophilic sp^2-hybridized boryl moiety, which can interact with olefins or
35 alkynes to form C-B bonds. Inspired by their work, we speculated that if a sufficiently stable sp^3-sp^2 diboron compound can be synthesized, it might behave as a unique boron-based Lewis base for FLP chemistry. Furthermore, considering the wide application of boronate functionality in organic synthesis, such FLP system
40 could provide new methods for the synthesis of boronate derivatives. Herein we describe the preparation of a nucleophilic boryl-borate lithium and its application as a Lewis base in FLP chemistry.

As the coordination of NHC to B_2pin_2 is very labile[20a] and
45 alkoxyl group can be susceptible to electrophilic attack due to the lone pair of electrons on O atom, we decided to choose organolithium as a base to react with B_2pin_2.[21] Treatment of
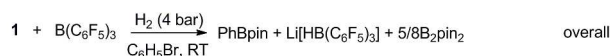
B_2pin_2 with phenyllithium in Et_2O at -78 °C led to the formation of phenyl-substituted boryl-borate salt **1** in 75% yield. Complex **1**
50 is poorly soluble in non-coordinating solvents, such as hexane, toluene and bromobenzene, but moderately soluble in THF. ^{1}H NMR spectrum suggests that each boryl-borate salt molecule contains 1/8 equivalent of B_2pin_2 molecule, which possibly coordinate to lithium cations through oxygen atoms on the
55 pinacolate moiety. Besides the signal at 1.19 ppm from B_2pin_2, the ^{1}H NMR spectrum of **1** in d_8-THF shows the presence of three methyl signals (1.13, 1.04 and 0.93 ppm) from pinacolate moiety with an integration ratio of 12:6:6. The 1.13 ppm signal is assigned to the sp^2 Bpin fragment, and the other two signals
60 correspond to two different methyl groups (face toward or against the organo-substituent) from the sp^3 Bpin. In the ^{11}B NMR spectrum, complex **1** features two singlet resonances (39.2 and 4.0 ppm) besides the signal for B_2pin_2 (30.5 ppm). The lower-field singlet is believed to correspond to the sp^2 Bpin moiety, and
65 the higher field singlet corresponds to the sp^3 Bpin moiety. Similar pattern was also observed for other sp^3-sp^2 diboron species.[19c, 19f, 20a]
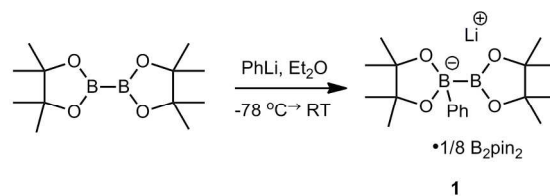
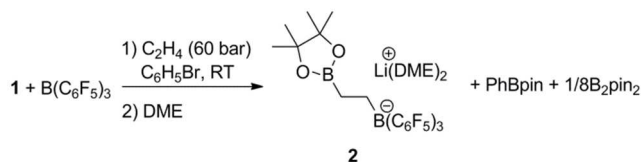**Scheme 1** Synthesis of boryl-borate lithium **1**

70 The degassed mixture of equal molar of $B(C_6F_5)_3$ and **1** in C_6D_5Br showed no noticeable change in the ^{1}H, ^{19}F and ^{11}B NMR spectra. Subsequent treatment of this mixture with H_2 (4 bar) at room temperature for 12 hours resulted in full conversion of $B(C_6F_5)_3$ to $Li[HB(C_6F_5)_3]$,[22] which was confirmed by the
75 characteristic ^{19}F NMR spectrum featuring signals at -136.6, -159.3 and -163.3 ppm in a 6 : 3 : 6 intensity ratio and a ^{11}B NMR doublet at -23.7 ppm ($^1J_{BH}$ = 78 Hz). After work-up, $Li[HB(C_6F_5)_3]$ can be isolated in 71% yield. Additionally, PhBpin can also be isolated in 73% yield after chromatography. This
80 reaction should also produce HBpin (Equation 1 in Scheme 2). However, no signal from HBpin was observed in the ^{11}B NMR spectrum of the reaction mixtures. Instead, substantial amount of

B$_2$pin$_2$ was detected in the reaction mixture. The molar ratio of B$_2$pin$_2$ to PhBpin is around 1:2 as determined by ^{1}H NMR spectrum. Suspecting that B$_2$pin$_2$ could be formed through activation of in situ generated HBpin by **1** and B(C$_6$F$_5$)$_3$, we performed the reaction between HBpin, **1** and B(C$_6$F$_5$)$_3$ in bromobenzene. Indeed, B$_2$pin$_2$, PhBpin and Li[HB(C$_6$F$_5$)$_3$] were observed as major products with isolated yields of 41%, 80% and 73%, respectively.[23] Activation of H-B bond by FLPs is known in the literature and has been applied in metal-free hydrogenation and hydroboration reactions.[24] Therefore, the equation for the overall reaction is as depicted in Scheme 2, in which both H atoms from H$_2$ eventually are reduced to hydride. When the mixture of **1** and B(C$_6$F$_5$)$_3$ was treated with D$_2$, formation of Li[DB(C$_6$F$_5$)$_3$] was observed, as evidenced by a singlet at -24.0 ppm in the ^{11}B NMR spectrum and a broad singlet at 2.80 ppm in the ^{2}H NMR spectrum.
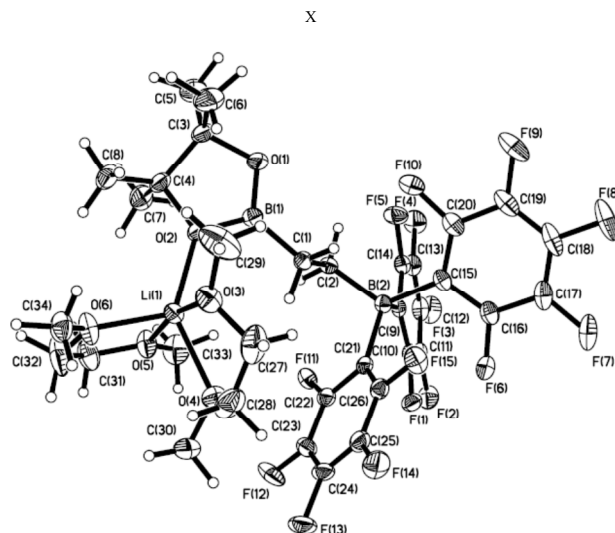
1 + B(C$_6$F$_5$)$_3$ $\xrightarrow[\text{C}_6\text{H}_5\text{Br, RT}]{\text{H}_2\text{ (4 bar)}}$ PhBpin + Li[HB(C$_6$F$_5$)$_3$] + [HBpin] + 1/8B$_2$pin$_2$ (1)

HBpin + **1** + B(C$_6$F$_5$)$_3$ $\xrightarrow[\text{C}_6\text{H}_5\text{Br, RT}]{}$ PhBpin + Li[HB(C$_6$F$_5$)$_3$] + 9/8B$_2$pin$_2$ (2)

1 + B(C$_6$F$_5$)$_3$ $\xrightarrow[\text{C}_6\text{H}_5\text{Br, RT}]{\text{H}_2\text{ (4 bar)}}$ PhBpin + Li[HB(C$_6$F$_5$)$_3$] + 5/8B$_2$pin$_2$ overall

Scheme 2 Reaction of H$_2$ with **1** and B(C$_6$F$_5$)$_3$.

The reactivity of **1** and B(C$_6$F$_5$)$_3$ against ethylene was also explored. After treating the mixture of **1** and B(C$_6$F$_5$)$_3$ with ethylene (60 bar) at room temperature for 12 h, (2-borylethyl)borate lithium salt **2** can be isolated in 64% yield after recrystalization from DME. The ^{19}F NMR spectra of **2** consists three peaks at -133.0, -165.0 and -167.4 ppm, indicating the existence of a tetra-coordinated B(C$_6$F$_5$)$_3$ moiety. The ^{11}B NMR spectra of **2** shows the presence of two singlet signals at 35.0 and -12.4 ppm, with the former assigned to Bpin and the latter to B(C$_6$F$_5$)$_3$ moiety. Two broad triplets at 1.12 and 0.21 ppm in ^{1}H NMR spectra of **2** were observed, which were assigned to the ethylene fragment. The structure of **2** was further corroborated by a single-crystal diffraction study (Figure 1). It is noteworthy that the direct diboration of alkenes with two different boryl groups has not been reported so far. [25]

1 + B(C$_6$F$_5$)$_3$ $\xrightarrow[\text{2) DME}]{\begin{array}{c}\text{1) C}_2\text{H}_4\text{ (60 bar)}\\ \text{C}_6\text{H}_5\text{Br, RT}\end{array}}$ [structure of **2**: O~B bonded to CH$_2$CH$_2$B(C$_6$F$_5$)$_3$$^{\ominus}$ with Li(DME)$_2$$^{\oplus}$] + PhBpin + 1/8B$_2pin_2$

2

Scheme 3 Reaction of C$_2$H$_4$ with **1** and B(C$_6$F$_5$)$_3$

Fig.1 ORTEP of the molecular structure of **2** (ellipsoids set at the 30% probability)

To obtain some insight of the mechanism of these FLP reactions, DFT(M06-2X) calculations were carried out.[26,27] IRC calculation indicates that B(C$_6$F$_5$)$_3$ and **1** form a loosely associated complex **1**/B(C$_6$F$_5$)$_3$ which is 7.9 kcal mol^{-1} more stable than free **1** and B(C$_6$F$_5$)$_3$ in free energy. Activation of H$_2$ by complex **1**/B(C$_6$F$_5$)$_3$ occurs in a stepwise manner (Figure 2). In the first step, H$_2$ is cleaved by **1**/B(C$_6$F$_5$)$_3$, in which the oxygen atom in sp^3 Bpin moiety of **1** functions as the Lewis base site, affording the intermediate **IM$_{H2}$1** and Li[HB(C$_6$F$_5$)$_3$]. In the second step, the nucleophilic sp^2 Bpin moiety of **IM$_{H2}$1** attacks the proton to yield HBpin and PhBpin, which is the rate-determining step and requires 27.4 kcal mol^{-1} in free energy barrier.
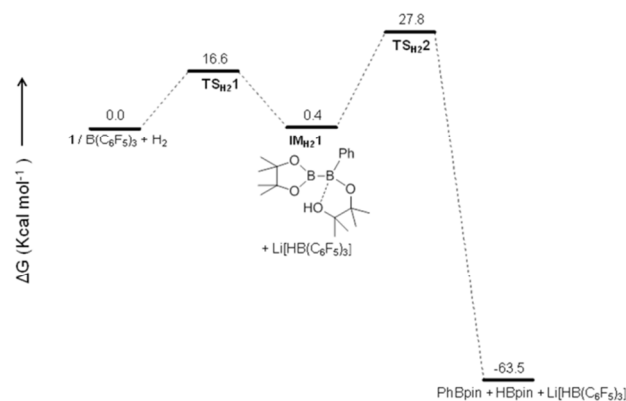
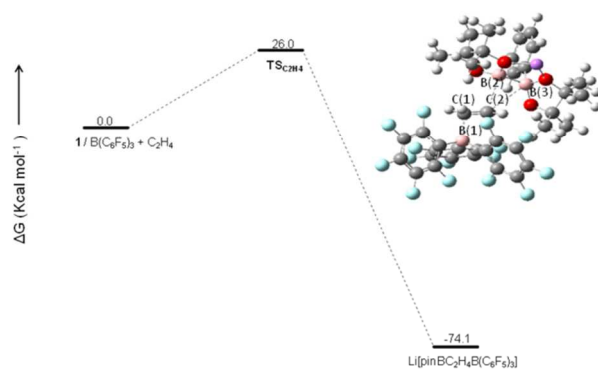**Fig.2** The Gibbs free energy profile at 298 K for the reaction between **1**/B(C$_6$F$_5$)$_3$ and H$_2$.

For HBpin activation, a similar stepwise reaction pathway was found (Figure 3). However, unlike the activation of H$_2$, when the oxygen atom in sp^3 Bpin moiety of **1** coordinates to the boron atom of HBpin, the H-B bond of HBpin is significantly activated. The hydride can transfer barrierlessly to B(C$_6$F$_5$)$_3$, affording the intermediate **IM$_{HB}$1** and Li[HB(C$_6$F$_5$)$_3$]. The nucleophilic sp^2 Bpin moiety of **IM$_{HB}$1** can then attack the electrophilic sp^2 Bpin

moiety to afford B_2pin_2 and PhBpin. This process requires 26.0 kcal mol^{-1} in free energy barrier.
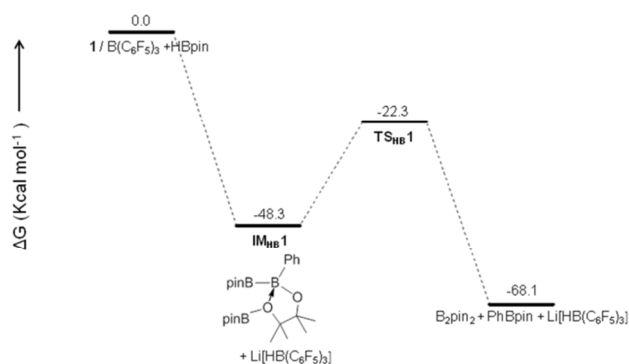

Fig. 3. The Gibbs free energy profile at 298 K for the reaction between $1/B(C_6F_5)_3$ and HBpin.

For ethylene activation, we discovered that this reaction undergoes a one-step pathway (Figure 4). Only one transition state TS_{C2H4} is required, and the free energy barrier is 26.0 kcal mol^{-1} at 298K, in agreement with our experiment observation that such reaction takes place at ambient temperature. In the transition state TS_{C2H4}, the C-C bond length of C_2H_4 is elongated to 1.38 Å (compared to 1.33 Å for free C_2H_4). Meanwhile, one carbon atom of ethylene molecule closely interact with the boron atom of $B(C_6F_5)_3$ with B-C distance of 1.83 Å. The other carbon atom of ethylene molecule bears contact with both boron atoms of **1** with B-C distances of 2.53 Å for the sp^2 boron atom and 2.95 Å for the sp^3 boron atom. Natural Bond Orbital analysis reveals that the bond orders for C(1)-B(1), C(2)-B(2) and C(2)-B(3) are 0.57, 0.13 and 0.07, respectively, thus indicating that the formation of two new C-B bonds is asynchronous. The bond formation of C(1)-B(1) takes place before the C(2)-B(2) bond generation. Furthermore, the analysis of molecular orbitals of TS_{C2H4} shows that the π-bonding orbital of C_2H_4 interacts strongly with the empty p orbital of the boron atom of $B(C_6F_5)_3$ (Figure 5a). At the same time, electron density also transfers from the occupied σ-bonding orbital of B-B bond of **1** to the C_2H_4 π*-antibonding orbital (Figure 5b). The tendency of nucleophilic bory moiety of **1** to interact with soft electrophilies might contribute to the fact that it is the boron atom, instead of oxygen atom, functions as the Lewis base center during the activation of C_2H_4.

Fig.4 The Gibbs free energy profile at 298 K for the reaction between $1/B(C_6F_5)_3$ and C_2H_4.
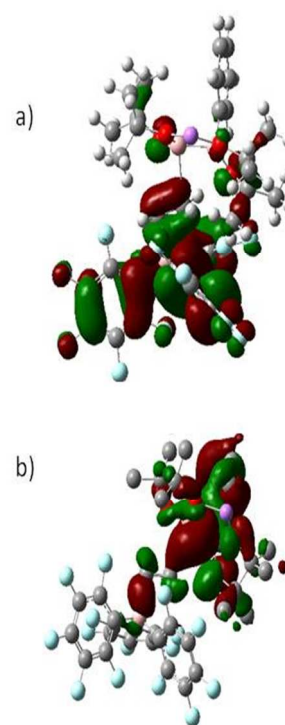
Fig.5 a) HOMO-3 of TS_{C2H4} b) HOMO of TS_{C2H4}

In summary, we have discovered that the frustrated Lewis pair comprised of boryl-borate lithium **1** and $B(C_6F_5)_3$ can efficiently activate H_2, HBpin and C_2H_4. Mechanism studies reveal that the nucleophilic boryl moiety of **1** plays different roles in these reactions. For the activation of H_2 and HBpin, the nucleophilic boryl moiety is not directly involved in the cleavage of H-H or H-B bond, and functions as a nucleophile in the following rearrangement step. By contrast, when applied in the activation of ethylene, nucleophilic boryl moiety of **1** serves as a Lewis base site in the process of breaking the π bond, while the boron atom of $B(C_6F_5)_3$ serves as a Lewis acid center. Such boron-based FLP does not only expand the scope of FLP chemistry, but also suggests a possible metal-free way for unsymmetrical diboration of unsaturated substrates. Investigation in this direction is currently underway.

Notes and references

[a] Shanghai Key Laboratory of Molecular Catalysis and Innovative Material, Department of Chemistry, Fudan University, Handan Rd. 220, Shanghai, 200433, China. Fax: 86 21 65641740; Tel: 86 021 65643345; E-mail: huadongwang@fudan.edu.cn
† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ These authors contributed equally to this work

1   G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science.* 2006, *314*, 1124.

2   a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* 2010, *49*, 46; b) D. W. Stephan, G. Erker, *Chem. Sci.*, 2014, *5*, 2625.

3   a) D. W. Stephan, *Org. Biomol. Chem.* 2012, *10*, 5740; b) J. Paradies, *Angew. Chem. Int. Ed.* 2014, *53*, 3552; c) L. Hounjet, D.W. Stephan, *Org. Process Res. Dev.* 2014, *18*, 385.

4   a) J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem. Int. Ed.,* 2007, *46*, 4968; b) C. Mömming, S. Frömel, G. Kehr, R. Fröhlich, S. Grimme and G. Erker, *J. Am. Chem. Soc.,* 2009, *131*, 12280; c) T. Voss, C. Chen, G. Kehr, E. Nauha and G. Erker, D. W. Stephan, *Chem. Eur. J.,* 2010, *16*, 3005; d) A. Stirling, A. Hamza, T. A. Rokob and I. Papai, *Chem. Commun.,* 2008, 3148. e) Y. Guo and S. Li, *Eur. J. Inorg. Chem.,* 2008, 2501.

5   Examples see: a) B. Inés, S. Holle, R. Goddard and M. Alcarazo, *Angew. Chem. Int. Ed.,* 2010, *49*, 8389 –8391; b) J. W. Runyon, O. Steinhof, H. V. R. Dias, J. C. Calabrese, W. J. Marshall and A. J. Arduengo, *Aust. J. Chem.,* 2011, *64*, 1165; c) M. P. Boone and D. W. Stephan, *J. Am. Chem. Soc.,* 2013, *135*, 8508; d) M. P. Boone and D. W. Stephan, *Chem. Eur. J.,* 2014, *20*, 3333; e) E. R. Clark, M. J. Ingleson, *Angew. Chem. Int. Ed.,* DOI: 10.1002/anie.201406122.

6   A. Schäfer, M. Reißmann, A. Schäfer, W. Saak, D. Haase and T. Müller, *Angew. Chem. Int. Ed.,* 2011, *50*, 12636.

7   S. Freitag, J. Henning, H. Schubert and L. Wesemann *Angew. Chem. Int. Ed.,* 2013, *52*, 5640.

8   Examples see: a) A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.,* 2011, *133*, 8826; b) A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.,* 2011, *133*, 18463; c) R. C. Neu, E. Otten, A. Lough and D. W. Stephan, *Chem. Sci.,* 2011, *2*, 170; d) X. Xu, G. Kehr, C. G. Daniliuc and G. Erker *Angew. Chem. Int. Ed.,* 2013, *52*, 13629.

9   M. J. Sgro and D. W. Stephan, *Chem. Commun.,* 2013, *49*, 2610.

10 M. J. Sgro and D. W. Stephan, *Angew. Chem. Int. Ed.,* 2012, *51*, 11343.

11 G. Lu, P. Zhang, D. Sun, L. Wang, K. Zhou, Z. Wang and G. Guo, *Chem. Sci.*, 2013, *5*, 1082.

12 L. J. Hounjet, C. B. Caputo and D. W. Stephan, *Angew. Chem. Int. Ed.,* 2012, *51*, 4714.

13 Examples see: a) P. A. Chase and D. W. Stephan, *Angew. Chem. Int. Ed.,* 2008, *47*, 7433; b) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem. Int. Ed.,* 2008, *47*,7428; c) M. Alcarazo, C. Gomez, S. Holle and R. Goddard, *Angew. Chem. Int. Ed.,* 2010, *49*, 5788.

14 H. Li, A. J. A. Aquino, D. B. Cordes, F. Hung-Low, W. L. Hase and C. Krempner, *J. Am. Chem. Soc.,* 2013, *135*, 16066.

15 A. Schäfer, M. Reißmann, A. Schäfer, M. Schmidtmann and T. Müller, *Chem. Eur.J.,* 2014, *20*, 9381.

16 a) D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.,* 1996, *118*, 9440; b) M. Lindquist, N. Sarnela, V. Summerin, K. Chernichenko and M. Leskeläm T. Repo, *Dalton Trans.,* 2012, *41*, 4310; c) L. J. Hounjet, C. Bannwarth, C. N. Garon, C. B. Caputo, S. Grimme and D. W. Stephan, *Angew. Chem. Int. Ed.,* 2013, *52*, 7492; d) D. J. Scoot, M. J. Fuchter, A. E. Ashley, *Angew. Chem. Int. Ed.,* 2014, *53*, 10218.

17 Examples see: a) C. A. Tanur and D. W. Stephan, *Organometallics*, 2011, *30*, 3652; b) C. Eller, G. Kehr, C. G. Daniliuc, R. Fröhlich and G. Erker, *Organometallics*, 2013, *32*, 384; c) C. Eller, K. Bussmann, G. Kehr, B. Wibbeling, C. G. Daniliuc and G. Erker, *Chem. Commun.,* 2014, *50*, 1980.

18 a) Y. Lee, H. Jiang and A. H. Hoveyda, *J. Am. Chem. Soc.,* 2009, *131*, 18234; b) H. Wu, S. Radomkit, J. M. O'Brien and A. H. Hoveyda, *J. Am. Chem. Soc.,* 2012, *134*, 8277.

19 a) A. Bonet, H. Gulyás and E. Fernández, *Angew. Chem. Int. Ed.,* 2010, *49*, 5130; b) A. Bnot, C. Pubill-Ulldemolins, C. Bo, H. Gulyás and E. Fernández, *Angew. Chem. Int. Ed.,* 2011, *50*, 7158; c) C. Pubill-Ulldemolins, A. Bnot, C. Bo, H. Gulyás and E. Fernández, *Chem. Eur. J.,* 2012, *18*, 1121; d) J. Cid, J. J. Carbó and E. Fernández, *Chem. Eur. J.,* 2012, *18*, 12794; e) J. Cid, J. Carbó and E. Fernández, *Chem. Eur. J.,* 2014, *20*, 3616.

20 a) C. Kleeberg, A. G. Crawford, A. S. Batsanov, P. Hodgkinson, D. C. Apperley, M. S. Cheung, Z. Lin and T. B. Marder, *J. Org. Chem.,* 2012, *77*, 785; b) Y. Nagashima, K. Hirano, R. Takita and M. Uchiyama, *J. Am. Chem. Soc.,* 2014, *136*, 8532; c) T. P. Blaisdell, T. C. Caya, L. Zhang, A. Sanz-Marco and J. P. Morken, *J. Am. Chem. Soc.,* 2014, *136*, 9264; d) H. Asakawa, K.-H. Lee, Z. Lin and M. Yamashita, *Nat. Commun.*, 2014, *5*, 4275.

21 The reaction of alkyllithium with B_2pins has been reported, but the adduct was not isolated, see: K. Takahashi, T. Ishiyama and N. Miyaura, *Chem. Lett.,* 2000, 982.

22 Complex **1** alone does not react with H_2 under simialr conditions.

23 Formation of B_2pin$_3$ (20 mol% compared to PhBpin as indicated by ^{1}H NMR spectrum) was observed, which could be a possible redistributive decomposition product of HBpin.

24 a) M. A. Dureen, A. Lough, T. M. Gilbert and D. W. Stephan, *Chem. Commun.,* 2008, 4303; b) C. J. Lata, C. M. Crudden *J. Am. Chem. Soc.,* 2010, *132*, 131; c) J. M. Farrell, J. Hatnean and D. W. Stephan, *J. Am. Chem. Soc.,* 2012, *134*, 15728; d) P. Eisenberger, A. M. Bailey and C. M. Crudden, *J. Am. Chem. Soc.,* 2012, *134*, 17384.

25 J. Takya and N. Iwasawa, *ACS Cat.,* 2012, *2*, 1993.

26 a) Y. Zhao and D. G. Truhlar, *J. Chem. Phys.,* 2006, *125*, 194101; b) Y. Zhao and D. G. Truhlar, *J. Chem. Phys. Chem. A,* 2006, *110*, 5121.

27 To simplify the calculation, the 1/8 B_2pin$_2$ molecule was omitted in the reaction process.

Chemical Communications Accepted Manuscript