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Intramolecular B/N frustrated Lewis pairs and the hydrogenation of carbon dioxide†

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The FLP species 1-BR$_2$-2-NMe$_2$-C$_6$H$_4$ (R = 2,4,6-Me$_3$C$_6$H$_2$ **1**, 2,4,5-Me$_3$C$_6$H$_2$ **2**) reacts with H$_2$ in sequential hydrogen activation and protodeborylation reactions to give (1-BH$_2$-2-NMe$_2$-C$_6$H$_4$)$_2$ **3**. While **1** reacts with H$_2$/CO$_2$ to give formyl, acetal and methoxy-derivatives, **2** reacts with H$_2$/CO$_2$ to give C$_6$H$_4$(NMe$_2$)(B(2,4,5-Me$_3$C$_6$H$_2$)O)$_2$CH$_2$ **4**. The mechanism of CO$_2$ reduction is considered.

General concerns regarding global warming, climate changes, and the need for renewable fuels have prompted researchers from around the world to target methodologies to utilize CO$_2$ as a C1 source.[1] Transition metal catalysts have been uncovered that either hydrogenate,[2] hydrosilylate,[3] or hydroborate CO$_2$ to formic acid, methanol, methane, CO and methoxide derivatives.[4] An alternative strategy for the reduction of CO$_2$ which is gaining attention is based on non-metal catalysts. While strong Lewis bases can reduce CO$_2$ using either hydrosilanes or hydroboranes,[3b,5] our research groups have been exploring the utility of frustrated Lewis pairs (FLPs) for the capture and the reduction of CO$_2$. Since the original report by Stephan, Erker, and co-workers on the capture of CO$_2$ by FLPs,[6] a number of inter- or intramolecular FLP variants have been employed to sequester CO$_2$ and much of this chemistry has been recently reviewed.[7] Beyond capture, FLP mediated CO$_2$ reductions have been probed. The reaction of Al/P FLPs with CO$_2$ and ammonia-borane was shown to give methanol,[8] while an alternative reaction pathway affords CO.[9] In a related study, Piers and coworkers used Et$_3$SiH as a reductant to catalytically generate CH$_4$ and (Et$_3$Si)$_2$O.[10] While Stephan and coworkers have also reported the catalytic reduction of CO$_2$ using phosphine/CH$_2$I$_2$ and ZnBr$_2$ to give CO and phosphine oxide,[11] Fontaine and coworkers described one of the most efficient systems to date for the reduction of CO$_2$ using ambiphilic FLP Ph$_2$PC$_6$H$_4$B(O$_2$C$_6$H$_4$), generating methoxyboranes with TOF exceeding 900 h^{-1} at 70 °C.[12] In related work, Stephan and co-workers have also described the use of C$_3$H$_2$(NPR$_2$)$_2$BC$_8$H$_{14}$[13] and phosphines[14] to catalyze the hydroboration of CO$_2$ affording mixtures of HCO$_2$(B(C$_8$H$_{14}$)), H$_2$C(OB(C$_8$H$_{14}$))$_2$ and MeOB(C$_8$H$_{14}$).

Although hydroboration and hydrosilylation of CO$_2$ to methanol are academically interesting, only the hydrogenation of CO$_2$ could be industrially viable. Ashley and O'Hare[15] have reported the only metal-free system in which CO$_2$ is hydrogenated. Employing the FLP TMP/B(C$_6$F$_5$)$_3$ (TMP = tetramethylpiperidine), CH$_3$OH was generated after 6 days at 160 °C under CO$_2$ and H$_2$. While this precedent establishes the concept, the development of an efficient FLP catalyst requires attention to the entropic challenge associated with bringing all reagents together. In addition, since the transformation of CO$_2$ to methanol is a 6-electron process generating formic acid and formaldehyde as intermediates, thus involving three very distinct reduction steps, the Lewis acidity of the electrophilic boron center must be judiciously designed to facilitate hydride delivery. To address these issues, we are exploring intramolecular FLP systems which incorporate tri-aryl boron centers that are significantly less Lewis acidic than the ubiquitous B(C$_6$F$_5$)$_3$.[16] In this fashion, the proximity of the Lewis acid and base reduces the entropic barrier, while the reduced Lewis acidity at B is expected to promote hydride delivery. In this communication, we describe the reactivity of these B/N FLPs with H$_2$ and the subsequent hydrogenation of CO$_2$ at ambient temperature.

The fluorescence properties related to compounds 1-BR$_2$-2-NMe$_2$-C$_6$H$_4$ (R = 2,4,6-Me$_3$C$_6$H$_2$ (**1**), 2,4,5-Me$_3$C$_6$H$_2$ (**2**)) have been previously studied, although in our hands the reported synthetic route proved problematic.[17] Nonetheless, **1** was prepared in 72% yield by the stoichiometric reaction of 1-Li-2-NMe$_2$-C$_6$H$_4$ with (2,4,6-Me$_3$C$_6$H$_2$)$_2$BF in toluene. In a similar fashion, the corresponding reaction with (2,4,5-Me$_3$C$_6$H$_2$)$_2$BCl yielded **2** in 64% yield, following crystallization from a saturated solution in cold hexanes (Scheme 1).

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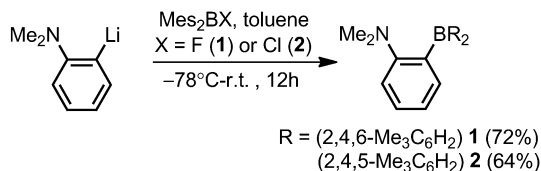
Scheme 1 Preparation of **1–2**.

The reactivity of these bright green compounds with both H_2 and CO_2 was investigated. When a benzene-d_6 solution of **1** was exposed to either 1 atm of CO_2 or 4 atm of H_2, no change was evidenced by ^1H NMR spectroscopy. However, heating for 24 h a solution of **1** at 80 °C under 1 atm of HD led to isotopic scrambling as evidenced by the observation of H_2 and HD by ^1H NMR spectroscopy. In addition, new signals at 6.72 and 2.16 ppm were observed and assigned to free mesitylene, suggesting that protodeborylation occurred after the activation of H_2. Indeed, protodeborylation reactions have been shown to occur before in related systems.[18] Monitoring of this protodeborylation with the use of cyclohexane as an internal standard, revealed that **1** releases both of its mesityl groups after 72 hours at 80 °C affording $(1-BH_2-2-NMe_2-C_6H_4)_2$ (**3**). The nature of the aryl group impacts the facility of protodeborylation as the species **2**, with one less methyl in *ortho* position than **1**, was converted to **3** after 72 hours at room temperature or after 6 hours at 80 °C. Compound **3** was prepared on a larger scale from **1** at 80 °C under 4 atm of H_2 for 48 hours and was ultimately isolated in 54% yield. The broad signal at 3.55 ppm in the ^1H NMR spectrum was attributed to B–H protons, which became sharper with ^{11}B decoupling. The presence of the B–H bonds was further confirmed by the broad ^{11}B NMR signal at 2.5 ppm. The HRMS data suggest that compound **3** is dimeric (m/z: 265 = [M–H]), which is further supported by the observation of inequivalent methyl groups on nitrogen (see ESI†). This view was further supported by computational studies, in which a number of isomeric forms of **3** were considered and where the dimeric form which adopts a "boat" shaped 8-membered ring was computed to be 9.2 kcal mol^{-1} more stable than the monomeric form (Scheme 2). It is noteworthy that Repo and coworkers have recently described $1-BH_2-2-TMP-C_6H_4$, which is also a dimer; however in this case, structural characterization confirmed that the steric congestion favors dimerization *via* the B–H bonds.[19]

DFT calculations were also employed to shed light on the mechanism of this transformation (Scheme 3). The activation of H_2 by **1** or **2** proceeds through TS1 to generate **A′** and **A″**, respectively, in a slightly endothermic process. Subsequent protodeborylation can occur through TS2, eliminating the B-bound aryl substituent to give the ambiphilic hydroboranes **B′** and **B″**, respectively.[20] Further activation of H_2 *via* TS3 to give **C′** and **C″**, prompts a second protodeborylation reaction pathway *via* TS4 affording the primary amino-borane product **3**. While the computed energies for these reactions of **1** and **2** follow the same trends, the reduced steric demands of **2** leads to significant lowering of the activation barriers.

The hydrogenation of CO_2 with **1** and **2** was investigated and in general was found to produce several boron bound formates,
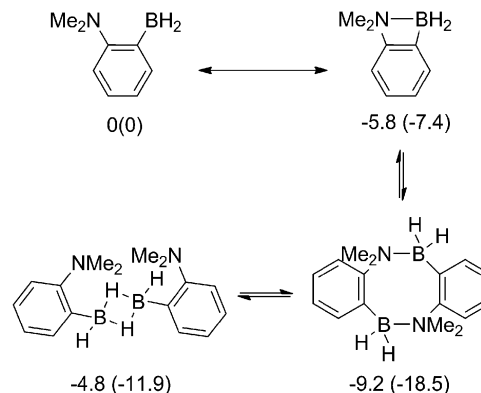
Scheme 2 DFT study of isomers **3**. Level of theory (ωB97XD/6-31++G**, solvent = benzene, SMD). ΔG (ΔH) are reported in kcal mol^{-1}.
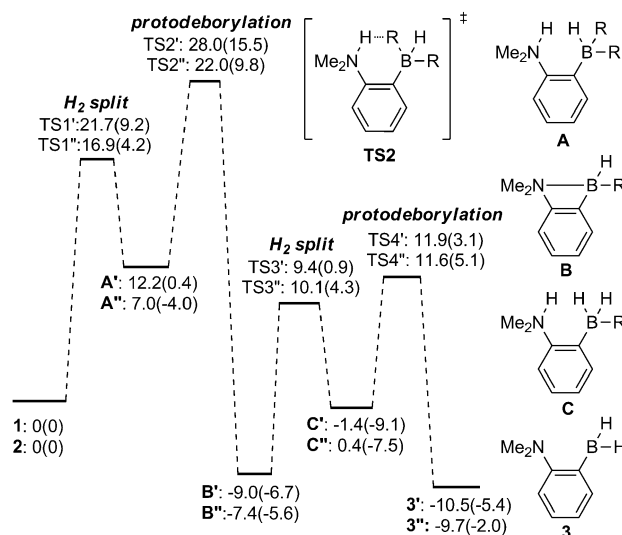
Scheme 3 DFT study of H_2 activation and protodeborylation at the (ωB97XD/6-31++G**, solvent = benzene, SMD) level of theory. ΔG (ΔH) are reported in kcal mol^{-1}, **X′** refers to R = 2,4,6-Me$_3$C$_6$H$_2$, **X″** refers to 2,4,5-Me$_3$C$_6$H$_2$.

acetals and methoxides (Table 1). Heating a benzene-d_6 solution of **1** to 80 °C for 24 hours under 4 atm of H_2 and 1 atm of $^{13}CO_2$, resulted in the appearance of doublets arising from the coupling with the ^{13}C atom for the formate (HCOO at *ca.* 8.5 ppm (J_{CH} ~ 210 Hz)) and acetal derivatives in ^1H NMR spectrum (*ca.* 5.2 ppm (J_{CH} ~ 165 Hz)). It was found that CO_2 was transformed into 0.89 equivalents of boron bound formates relative to the amount of **1** at the start of the reaction, and 0.31 equivalents of boron bound acetals. Repeating the experiment with a reduced CO_2 pressure (0.5 atm) led to similar conversions to formates and acetals, but in addition 0.1 equivalent boron bound methoxides were formed (*ca.* 3.5 ppm, J_{CH} ~ 140 Hz). Further reduction of the CO_2 pressure to 0.1 atm resulted in the formation of methoxides and traces of $^{13}CH_4$. An experiment under 1 atm of CO_2 and 4 atm H_2 in bromobenzene-d_5 yielded 0.75, 0.21 and 0.07 equivalents of formate, acetal and methoxide species respectively after only 24 hours at 130 °C. In contrast, **3** did not react in the presence of H_2 and CO_2, even after prolonged heating at 80 °C. This lack of

Table 1 Hydrogenation of carbon dioxide by **1** and **2**

R = 2,4,6-Me$_3$C$_6$H$_2$ **1**
2,4,5-Me$_3$C$_6$H$_2$ **2**

R = (2,4,5-Me$_3$C$_6$H$_2$) **4**
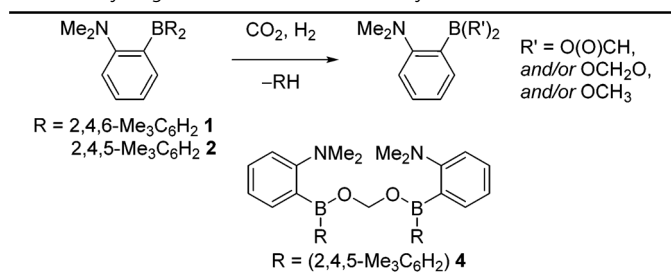
| | FLP | CO$_2$ (atm) | T (h) | T (°C) | Equivalents^a of | | | H$_2$ consumed |
					HCOO	OCH$_2$O	CH$_3$O	
1	**1**^{b}	1	216	80	0.89	0.31	0	1.5
2	**1**^{b}	0.5	216	80	0.84	0.34	0.1	1.8
3	**1**^{b}	0.1	216	80	0	0	0.08	0.25
4	**1**^{b,c}	1	24	130	0.75	0.21	0.07	1.4
5	**2**^{d,e}	1	72	23	0	0.37	0	0.74
6	**2**	1	3	80	0.21	0.30	0	0.81

Conditions: 0.014 mmol **1** or **2**, 0.4 mL C$_6$D$_6$, 4 atm H$_2$. Yields were determined by NMR integration with respect to an internal standard (cyclohexane). ^{a} Equivalents of the indicated hydrogenation moiety relative to the amount of starting aminoborane. ^{b} A white precipitate crashed out of the solution so 0.1 mL of CD$_3$CN was added before taking the spectra. ^{c} Reaction was carried out in bromobenzene-d_5. ^{d} Reaction was carried out under 1 atm of H$_2$. ^{e} Compound **4** was exclusively formed.

reactivity is consistent with its dimeric nature that provides a stabilization of 13.4 kcal mol^{-1}.

Interestingly, the analogous reactions of **2** gave a single acetal species after 72 hours at room temperature in the presence of 1 atm H$_2$ and 1 atm CO$_2$ as evidenced by ^{1}H NMR spectroscopy. On the other hand, higher temperature gave some additional formate species. When carried out on a larger scale, product **4** was isolated in 60% yield. The NMR data and the crystallographic structure (Fig. 1) supported the formulation of **4** as C$_6$H$_4$(NMe$_2$)-(B(2,4,5-Me$_3$C$_6$H$_2$)O)$_2$CH$_2$. Based on these observations, the first protodeborylation step is believed to be required prior to CO$_2$ reduction while complete protodeborylation inhibits the reduction processes due to dimerization of **3**.

The initial steps in reaction of **1** and **2** with H$_2$/CO$_2$ were probed using DFT computations. The reactions of the products of H$_2$ activation **A**–**C** (Scheme 3) with CO$_2$ were considered. The barriers to reduce CO$_2$ with **A** and **B** were computed to range between 27.2 and 34.7 kcal mol^{-1} whereas the transition state with **C**
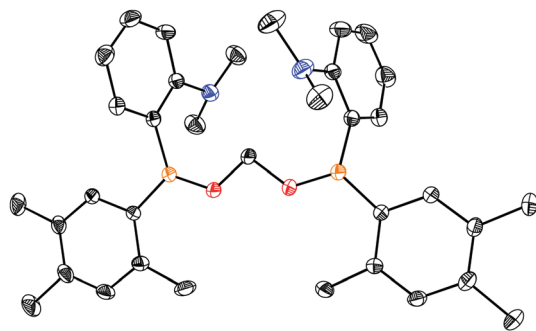

Fig. 1 ORTEP depiction of **4**, 50% thermal ellipsoids are shown, N: blue, C: black, O: red, B: orange. H-atoms are omitted for clarity.
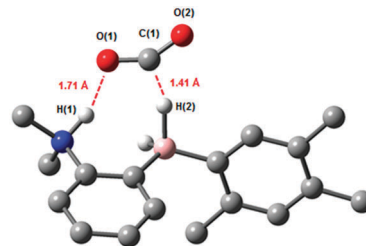

Fig. 2 Geometry of TS for reaction of **C** with CO$_2$ as calculated by ωB97XD/6-31++G** level of theory; (solvent = benzene, SMD).

was found to be only 24.4 kcal mol^{-1} for R = 2,4,6-Me$_3$C$_6$H$_2$ and 22.1 kcal mol^{-1} for R = 2,4,5-Me$_3$C$_6$H$_2$. The transition state of interest (Fig. 2) illustrates a concerted interaction of the proton on N with one of the O of CO$_2$ with the simultaneous interaction of the boron-bound hydride with the C atom, thus directing the hydride delivery to the carbon atom. This TS is reminiscent of that proposed for the bifunctional Noyori-type catalysts for metal-based ketone reduction and a similar transition state was proposed by Musgrave, Zhang and Zimmerman[21] for CO$_2$ reduction using ammonia borane as a model reductant.[22] Subsequent reductions of formic acid are thought to proceed either *via* similar hydride delivery to formate or by simple hydroboration, generating acetal derivatives. It is also interesting that the minor variation in the steric demands of the substituent on **B** provide a mixture of reduction products in the case of reactions of **1** yet allow the isolation of **4** at room temperature in the reaction of **2**.

While previous reports have described conceptually important metal-free catalytic hydrosilylation or hydroboration of CO$_2$, the present report is a rare example of direct FLP hydrogenation of CO$_2$ as only the earlier report by O'Hare and Ashley[15] described the use of H$_2$ in the metal-free reduction of CO$_2$. Nonetheless, the present intramolecular FLPs effect this reduction under much milder conditions (ambient temperature).

The reactions of the present N/B intramolecular FLPs with H$_2$ demonstrate a rare case where weakly Lewis acidic boron centres participate in H$_2$ activation. Such systems offer increased facility for hydride delivery and thus provide an avenue to CO$_2$ reduction. Moreover, the reaction with CO$_2$ is facilitated by the concurrent interaction of NH and BH fragments with CO$_2$ affording formate, acetal and methoxy-derivatives. While the present systems are generated by protodeborylation, the reactivity suggests that judicious substituent selection could provide an avenue to the design of intramolecular FLPs catalysts for H$_2$/CO$_2$ chemistry. Efforts towards such metal-free catalysts for CO$_2$ hydrogenation are the subject of current work in our laboratories.

Notes and references

1 (a) M. Aresta, *Carbon Dioxide as Chemical Feedstock*, Wiley-VCH, Weinheim, 2010; (b) A. Correa and R. Martin, *Angew. Chem., Int. Ed.*, 2009, **48**, 6201–6204; (c) C. Federsel, A. Boddien, R. Jackstell, R. Jennerjahn, P. J. Dyson, R. Scopelliti, G. Laurenczy and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 9777–9780; (d) D. M. Dalton and T. Rovis, *Nat. Chem.*, 2010, **2**, 710–711.

2 (a) T. J. Schmeier, G. E. Dobereiner, R. H. Crabtree and N. Hazari, *J. Am. Chem. Soc.*, 2011, **133**, 9274–9277; (b) R. Langer, Y. Diskin-Posner, G. Leitus, L. J. W. Shimon, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2011, **50**, 9948–9952; (c) C. A. Huff and M. S. Sanford, *J. Am. Chem. Soc.*, 2011, **133**, 18122–18125; (d) S. Wesselbaum, T. V. Stein, J. Klankermayer and W. Leitner, *Angew. Chem., Int. Ed.*, 2012, **51**, 7499–7502.

3 (a) K. Motokura, D. Kashiwame, A. Miyaji and T. Baba, *Org. Lett.*, 2012, **14**, 2642–2645; (b) F. Huang, G. Lu, L. Zhao, H. Li and Z. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 12388–12396; (c) T. Matsuo and H. Kawaguchi, *J. Am. Chem. Soc.*, 2006, **128**, 12362–12363; (d) S. Park, D. Bézier and M. Brookhart, *J. Am. Chem. Soc.*, 2012, **134**, 11404–11407; (e) M. Khandelwal and R. Wehmschulte, *Angew. Chem., Int. Ed.*, 2012, **51**, 7323–7326; (f) S. J. Mitton and L. Turculet, *Chem. – Eur. J.*, 2012, **18**, 15258–15262.

4 (a) S. Chakraborty, J. Zhang, J. A. Krause and H. R. Guan, *J. Am. Chem. Soc.*, 2010, **132**, 8872–8873; (b) F. Huang, C. Zhang, J. Jiang, Z. Wang and H. Guan, *Inorg. Chem.*, 2011, **50**, 3816–3825; (c) S. Chakraborty, J. Zhang, Y. J. Patel, J. A. Krause and H. Guan, *Inorg. Chem.*, 2013, **52**, 37–47; (d) S. Bontemps, L. Vendier and S. Sabo-Etienne, *Angew. Chem., Int. Ed.*, 2012, **51**, 1671–1674; (e) M. J. Sgro and D. W. Stephan, *Angew. Chem., Int. Ed. Engl.*, 2012, **51**, 11343–11345; (f) R. Shintani and K. Nozaki, *Organometallics*, 2013, **32**, 2459–2462.

5 (a) O. Jacquet, X. Frogneux, C. Das Neves Gomes and T. Cantat, *Chem. Sci.*, 2013, **4**, 2127–2131; (b) O. Jacquet, C. D. Gomes, M. Ephritikhine and T. Cantat, *J. Am. Chem. Soc.*, 2012, **134**, 2934–2937; (c) C. D. N. Gomes, O. Jacquet, C. Villiers, P. Thuery, M. Ephritikhine and T. Cantat, *Angew. Chem., Int. Ed.*, 2012, **51**, 187–190; (d) M.-A. Courtemanche, M.-A. Légaré, É. Rochette and F.-G. Fontaine, *Chem. Commun.*, 2015, **51**, 6858–6861; (e) S. N. Riduan, Y. G. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2009, **48**, 3322–3325; (f) M.-A. Légaré, M.-A. Courtemanche and F.-G. Fontaine, *Chem. Commun.*, 2014, **50**, 11362–11365.

6 C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2009, **48**, 6643–6646.

7 (a) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, DOI: 10.1002/anie.201409800; (b) D. W. Stephan, *Acc. Chem. Res.*, 2015, **48**, 306–316; (c) F.-G. Fontaine, M.-A. Courtemanche and M.-A. Légaré, *Chem. – Eur. J.*, 2014, **20**, 2990–2996; (d) A. E. Ashley and D. O'Hare, *Top. Curr. Chem.*, 2013, **334**, 191–217.

8 G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796–1797.

9 (a) G. Ménard and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2011, **50**, 8396–8399; (b) G. Ménard, T. M. Gilbert, J. A. Hatnean, A. Kraft, I. Krossing and D. W. Stephan, *Organometallics*, 2013, **32**, 4416–4422.

10 A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660–10661.

11 R. Dobrovetsky and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2013, **52**, 2516–2519.

12 (a) M. A. Courtemanche, M. A. Légaré, L. Maron and F. G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326–9329; (b) M.-A. Courtemanche, M.-A. Légaré, L. Maron and F.-G. Fontaine, *J. Am. Chem. Soc.*, 2014, **136**, 10708–10717; (c) M.-A. Courtemanche, J. Larouche, M.-A. Légaré, W. Bi, L. Maron and F.-G. Fontaine, *Organometallics*, 2013, **32**, 6804–6811; (d) R. Declercq, G. Bouhadir, D. Bourissou, M.-A. Légaré, M.-A. Courtemanche, K. S. Nahi, N. Bouchard, F.-G. Fontaine and L. Maron, *ACS Catal.*, 2015, **5**, 2513–2520.

13 T. Wang and D. W. Stephan, *Chem. – Eur. J.*, 2014, **20**, 3036–3039.

14 T. Wang and D. W. Stephan, *Chem. Commun.*, 2014, **50**, 7007–7010.

15 A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem., Int. Ed.*, 2009, **48**, 9839–9843.

16 The highly Lewis acidic analogues of **1** and **2** where R = C_6F_5 have been reported to activate H_2, see: (a) K. Chernichenko, M. Nieger, M. Leskelä and T. Repo, *Dalton Trans.*, 2012, **41**, 9029–9032; (b) K. Chernichenko, A. Madarász, I. Pápai, M. Nieger, M. Leskelä and T. Repo, *Nat. Chem.*, 2013, **5**, 718–723.

17 K. Albrecht, V. Kaiser, R. Boese, J. Adams and D. E. Kaufmann, *J. Chem. Soc., Perkin Trans.*, 2000, **2**, 2153–2157.

18 (a) S. Moebs-Sanchez, N. Saffon, G. Bouhadir, L. Maron and D. Bourissou, *Dalton Trans.*, 2010, **39**, 4417–4420; (b) Z. M. Heiden, M. Schedler and D. W. Stephan, *Inorg. Chem.*, 2011, **50**, 1470–1479; (c) M. Devillard, R. Brousses, K. Miqueu, G. Bouhadir and D. Bourissou, *Angew. Chem., Int. Ed.*, 2015, **127**, 5814–5818.

19 K. Chernichenko, B. Kótai, I. Pápai, V. Zhivonitko, M. Nieger, M. Leskelä and T. Repo, *Angew. Chem., Int. Ed.*, 2015, **54**, 1749–1753.

20 B could not be isolated as the second H_2 activation/protodeborylation events are faster than the first. Nonetheless, B was intercepted by reacting **1** with H_2 and benzaldehyde to give a borinic ester.

21 P. Zimmerman, Z. Zhang and C. Musgrave, *Inorg. Chem.*, 2010, **49**, 8724–8728.

22 R. Noyori, *Angew. Chem., Int. Ed.*, 2002, **41**, 2008–2022.