

Intramolecular B/N Frustrated Lewis Pairs and the Hydrogenation of Carbon Dioxide

Marc-André Courtemanche,^a Alexander P. Pulis,^b Étienne Rochette,^a Marc-André Légaré,^a Douglas W.
Stephan,^{*b} Frédéric-Georges Fontaine^{*a}

^a Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec (Québec), Canada,
G1V 0A6

^b Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6,
Canada

Emails : frederic.fontaine@chm.ulaval.ca and dstephan@chem.utoronto.ca

This is the peer reviewed version of the following article: [Intramolecular B/N Frustrated Lewis Pairs and the Hydrogenation of Carbon Dioxide, Chem. Commun., 2015, 51, 9797--9800], which has been published in final form at [\[10.1039/c5cc03072b\]](https://doi.org/10.1039/c5cc03072b).

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x
www.rsc.org/

Intramolecular B/N Frustrated Lewis Pairs and the Hydrogenation of Carbon Dioxide

Marc-André Courtemanche,^a Alexander P. Pulis,^b Étienne Rochette,^a Marc-André Légaré,^a Douglas W. Stephan,^{* b,c} Frédéric-Georges Fontaine^{*a}

The FLP species 1-BR₂-2-NMe₂-C₆H₄ (R = 2,4,6-Me₃C₆H₂ **1**, 2,4,5-Me₃C₆H₂ **2**) react with H₂ in sequential hydrogen activation and protodeborylation reactions to give (1-BH₂-2-NMe₂-C₆H₄)₂ **3**. While **1** reacts with H₂/CO₂ to give formyl, acetal and methoxy-derivatives, **2** reacts with H₂/CO₂ to give (C₆H₄(NMe₂)(B(2,4,5-Me₃C₆H₂)O)₂CH₂ **4**. The mechanism of CO₂ reduction is considered.

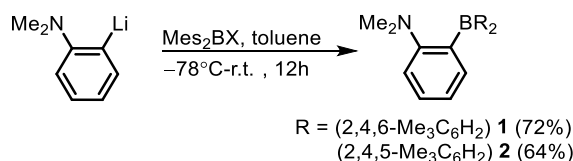
catalyze the hydroboration of CO₂ affording mixtures of HCO₂(B(C₆H₁₄)), H₂C(OB(C₆H₁₄))₂ and MeOB(C₆H₁₄).

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 CO₂ as a C1 source.¹ Transition metal catalysts have been uncovered that either hydrogenate², hydrosilylate³, or hydroborate CO₂ to formic acid, methanol, methane, CO and methoxide derivatives.⁴ An alternative strategy for the reduction of CO₂ which is gaining attention is based on non-metal catalysts. While strong Lewis bases can reduce CO₂ 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 CO₂. Since the original report by Stephan and co-workers on the capture of CO₂ by FLPs,⁶ a number of inter- or intramolecular FLP variants have been employed to sequester CO₂ and much of this chemistry has been recently reviewed.⁷ Beyond capture, FLP mediated CO₂ reductions have been probed. The reaction of Al/P FLPs with CO₂ 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 Et₃SiH as a reductant to catalytically generate CH₄ and (Et₃Si)₂O.¹⁰ While Stephan and coworkers have also reported the catalytic reduction of CO₂ using phosphine/CH₂I₂ and ZnBr₂ to give CO and phosphine oxide,¹¹ Fontaine and coworkers described one of the most efficient systems to date for the reduction of CO₂ using ambiphilic FLP Ph₂PC₆H₄B(O₂C₆H₄), 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 C₃H₂(NPR₂)₂BC₈H₁₄¹³ and phosphines¹⁴ to

Although hydroboration and hydrosilylation of CO₂ to methanol are academically interesting, only the hydrogenation of CO₂ could be industrially viable. Ashley and O'Hare¹⁵ have reported the only metal-free system in which CO₂ is hydrogenated. Employing the FLP TMP/B(C₆F₅)₃ (TMP = tetramethylpiperidine), CH₃OH was generated after 6 days at 160 °C under CO₂ and H₂. 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 CO₂ 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(C₆F₅)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 manuscript, we describe the reactivity of these B/N FLPs with H₂ and the subsequent hydrogenation of CO₂ at ambient temperature.

The fluorescence properties related to compounds 1-BR₂-2-NMe₂-C₆H₄ (R = 2,4,6-Me₃C₆H₂ (**1**), 2,4,5-Me₃C₆H₂ (**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-NMe₂-C₆H₄ with (2,4,6-Me₃C₆H₂)₂BF in toluene. In a similar fashion, the corresponding reaction with (2,4,5-Me₃C₆H₂)₂BCl yielded **2** in 64% yield, following crystallization from a saturated solution in cold hexanes (Scheme 1).

Scheme 1: Preparation of 1-2.

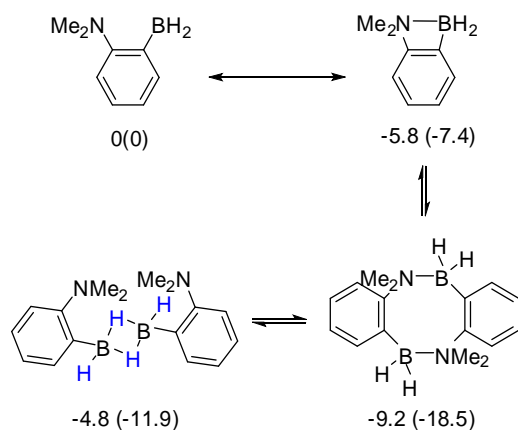


Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec (Québec), Canada, G1V 0A6
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada
Chemistry Department-Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

*Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

The reactivity of these bright green compounds with both H₂ and CO₂ was investigated. When a *benzene-d*₆ solution of **1** was exposed to either 1 atm of CO₂ or 4 atm of H₂, 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 H₂ 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 H₂. 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-BH₂-2-NMe₂-C₆H₄)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 H₂ 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 ¹¹B decoupling. The presence of the B-H bonds was further confirmed by the broad ¹¹B 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-BH₂-2-TMP-C₆H₄, which is also a dimer; however in this case, structural characterization confirmed that the steric congestion favors dimerization via the B-H bonds.¹⁹

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.



DFT calculations were also employed to shed light on the mechanism of this transformation (Scheme 3). The activation of H₂ 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 H₂ 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.

Scheme 3: DFT study of H₂ 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-Me₃C₆H₂, X'' refers to 2,4,5-Me₃C₆H₂.

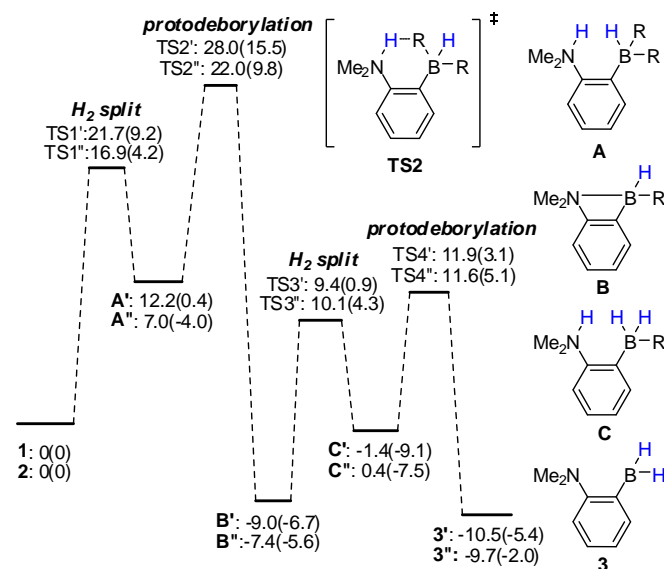
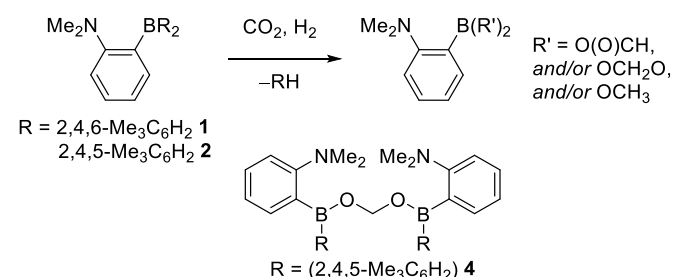


Table 1: Hydrogenation of carbon dioxide by **1** and **2**



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 C₆D₆, 4 atm H₂. 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 CD₃CN was added before taking the spectra. c. Reaction was carried out in *bromobenzene-d*₅. d. Reaction was carried out under 1 atm of H₂. Compound **4** was exclusively formed.

The hydrogenation of CO₂ with **1** and **2** was investigated and in general was found to produce several boron bound formates, acetals and methoxides (Table 1). Heating a benzene-*d*₆ solution of **1** to 80 °C for 24 hours under 4 atm of H₂ and 1 atm of ¹³CO₂, resulted in the appearance of doublets arising from the coupling with the ¹³C 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 CO₂ 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 CO₂ 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, $J_{CH} \sim 140$ Hz). Further reduction of the CO₂ pressure to 0.1 atm resulted in the formation of methoxides and traces of ¹³CH₄. An experiment under 1 atm of CO₂ and 4 atm H₂ 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 H₂ and CO₂, even after prolonged heating at 80°C. This lack of reactivity is consistent with its dimeric nature that provides a stabilization of 13.4 kcal.mol⁻¹.

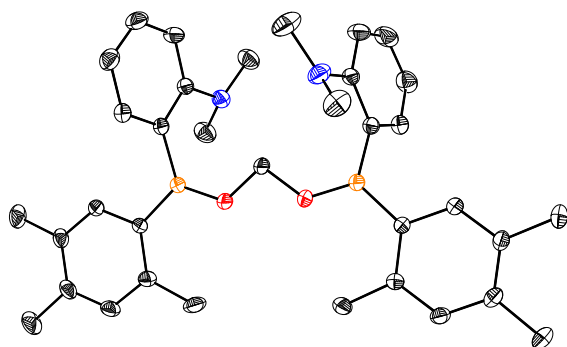


Figure 1: ORTEP depiction of **4**, 50% thermal ellipsoids are shown, N: blue, C: carbon, O: red, B: orange. H-atoms are omitted for clarity.

Interestingly, the analogous reactions of **2** gave a single acetal species after 72 hours at room temperature in the presence of 1 atm H₂ and 1 atm CO₂ as evidenced by ¹H 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 (Figure 1) supported the formulation of **4** as (C₆H₄(NMe₂))(B(2,4,5-Me₃C₆H₂)O)₂CH₂. Based on these observations, the first protodeborylation step is believed to be required prior to CO₂ reduction while complete protodeborylation inhibits the reduction processes due to dimerization of **3**.

The initial steps in reaction of **1** and **2** with H₂/CO₂ were probed using DFT computations. The reactions of the products of H₂ activation **A-C** (Scheme 3) with CO₂ were considered. The barriers to reduce CO₂ with **A** and **B** were computed to range between 27.2 and 34.7 kcal.mol⁻¹ whereas the transition state with **C** was found to be only 24.4 kcal.mol⁻¹ for R = 2,4,6-Me₃C₆H₂ and 22.1 kcal.mol⁻¹ for R = 2,4,5-Me₃C₆H₂. The transition state of interest (Figure 2) illustrates a concerted interaction of the proton on N with one of the O of CO₂ 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 Zimmerman²¹ for CO₂ 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**.

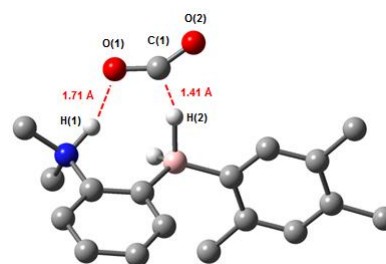


Figure 2: Geometry of TS for reaction of **C** with CO₂ as calculated by ωB97XD/6-31++G** level of theory; (solvent = benzene, SMD).

While previous reports have described conceptually important metal-free catalytic hydrosilylation or hydroboration of CO₂, the present report is a rare example of direct FLP hydrogenation of CO₂ as only the earlier report by O'Hare and Ashley¹⁵ described the use of H₂ in the metal-free reduction of CO₂. Nonetheless, the present intramolecular FLPs effect this reduction under much milder conditions (ambient temperature).

Conclusions

The reactions of the present N/B intramolecular FLPs with H₂ demonstrate a rare case where weakly Lewis acidic boron centres participate in H₂ activation. Such systems offer increased facility for hydride delivery and thus provide an avenue to CO₂ reduction. Moreover, the reaction with CO₂ is facilitated by the concurrent interaction of NH and BH fragments with CO₂ 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 H₂/CO₂ chemistry. Efforts towards such metal-free catalysts for CO₂ hydrogenation are the subject of current work in our laboratories.

Acknowledgements

This work was supported by the National Sciences and Engineering Research Council of Canada (NSERC, Canada) and the Centre de Catalyse et Chimie Verte (Quebec). M.-A. C., E. R. and M.-A. L. would like to thank NSERC and FQRNT for scholarships. DWS is grateful for the award of a Canada Research Chair. We acknowledge W. Bi for the resolution of the

crystal structure. The authors wish to acknowledge the Canadian Foundation for Innovation, project number 19119, and the Ontario Research Fund for funding of the Centre for Spectroscopic Investigation of Complex Organic Molecules and Polymers.

Notes and references

‡ Crystallographic data have been deposited in the CCDC; CDCC #: 1059372. Spectral and computational data have been deposited in the supplementary data.

- (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.
- (a) T. J. Schmeier, G. E. Dobreiner, R. H. Crabtree and N. Hazari, *J. Am. Chem. Soc.*, 2011, **133**, 9274-9277; (b) R. Langer, Y. Diskin-Posner, G. Leitun, 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.
- (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.
- (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.
- (a) O. Jacquet, X. Frogneux, C. Das Neves Gomes and T. Cantat, *Chem. Science*, 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.
- C. M. Mömring, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2009, **48**, 6643-6646.
- (a) D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, accepted; (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, *Topics Curr. Chem.*, 2013, **334**, 191-217.
- G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796-1797.
- (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. Crossing and D. W. Stephan, *Organometallics*, 2013, **32**, 4416-4422.
- A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660-10661.
- R. Dobrovetsky and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2013, **52**, 2516-2519.
- (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.
- T. Wang and D. W. Stephan, *Chem. Eur. J.*, 2014, **20**, 3036-3039.
- T. Wang and D. W. Stephan, *Chem. Commun.*, 2014, **50**, 7007-7010.
- A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem. Int. Ed.*, 2009, **48**, 9839-9843.
- The highly Lewis acidic analogues of **1** and **2** where R = C₆F₅ have been reported to activate H₂, 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, *Nature Chem.*, 2013, **5**, 718-723.
- K. Albrecht, V. Kaiser, R. Boese, J. Adams and D. E. Kaufmann, *J. Chem. Soc. Perkin Trans.*, 2000, **2**, 2153-2157.
- (a) S. Moebis-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, **54**, 5814-5818.
- K. Chernichenko, B. Kótai, I. Pápai, V. Zhivonitko, M. Nieger, M. Leskelä and T. Repo, *Angew. Chem. Int. Ed.*, 2015, **54**, 1749-1753.
- B could not be isolated as the second H₂ activation /protodeborylation events are faster than the first. Nonetheless, B was intercepted by reacting **1** with H₂ and benzaldehyde to give a borinic ester.
- P. Zimmerman, Z. Zhang and C. Musgrave, *Inorg. Chem.*, 2010, **49**, 8724-8728.
- R. Noyori, *Angew. Chem. Int. Ed.*, 2002, **41**, 2008-2022.