

Hydrogenations at Room Temperature and Atmospheric Pressure with Mesoionic Carbene-Stabilized Borenium Catalysts**

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Abstract: 1,2,3-Triazolylidene-based mesoionic carbene boranes have been synthesized in a convenient one-pot protocol from the corresponding 1,2,3-triazolium salts, base, and borane. Borenium ions are obtained by hydride abstraction and serve as catalysts in mild hydrogenation reactions of imines and unsaturated N-heterocycles at ambient pressure and temperature.

Homogeneous transition-metal-catalyzed hydrogenations have been a key tool in synthetic organic chemistry since their discovery more than half a century ago.^[1] Since that time, great strides have been made to improve upon the reaction in terms of chemo- and stereoselectivity as well as functional group tolerance.^[2] Significant mechanistic advances include the use of frustrated Lewis pairs (FLPs) as catalysts. In FLP-type hydrogenations, main-group elements conspire to split H₂ heterolytically by the cooperative action of bulky, strong Lewis acid/base pairs, and the resulting acids/borohydrides transfer H₂ to organic compounds, regenerating the FLP catalyst (Scheme 1).^[3]

In their most common incarnation, FLP reductions employ N-heterocycles or imines as the Lewis base components, with B(C₆F₅)₃ as the most commonly employed Lewis acid.^[4] Recent advances have widened the scope of this reaction to include enantioselective catalysts,^[5] however, preparing analogues of B(C₆F₅)₃ that still possess the neces-

sary high Lewis acidity to split H₂ heterolytically is a significant challenge and has delayed the development of new catalysts in this area.^[6]

An interesting alternative is the use of borenium ions, which have made sporadic appearances in the literature in other contexts.^[7] However, several groups have recently shown that these species possess interesting and novel properties as reagents in direct electrophilic aromatic borylations,^[8] the haloboration^[9] and carboration of alkynes,^[10] the enantioselective reduction of ketones,^[11] and even in catalytic reduction schemes.^[12] Imidazole-based N-heterocyclic carbene (NHC) borane adducts provide a particularly interesting platform for the generation of borenium ions by hydride abstraction.^[11] Building on this work, the Stephan group reported the use of NHC-stabilized borenium ions as catalysts for hydrogenation of imines and N-heterocycles at elevated pressures.^[12e]

1,2,3-Triazolylidenes, the mesoionic cousins of NHCs^[13] can be prepared using a Huisgen cycloaddition between azides and alkynes, greatly simplifying their synthesis. Because the carbenic carbon is flanked by only one heteroatom, triazolylidenes are electronically unique.^[13a] We previously demonstrated that borane adducts of simple triazole-derived mesoionic N-heterocyclic carbenes (MIC) have significantly greater hydricity compared to their NHC congeners,^[14] which are already known to be among the most reactive neutral hydride donors.^[15] The increased sigma donor capacity of the mesoionic carbene unit also provides greater stabilization to the electron-deficient borenium ion. Finally, the ability to easily access MICs with low steric hindrance is another important feature of these previously unreported MIC-based borenium ions.

Herein, we report the first examples of MIC-stabilized borenium ions, which have unprecedented reactivity in the hydrogenation of imines and N-heterocycles. These reactions can be carried out at room temperature and low pressures without rigorous scrubbing of H₂, representing a significant advantage over typical B(C₆F₅)₃-mediated reductions (Figure 1).

Scheme 1. Basic mechanism for reduction using FLP chemistry.

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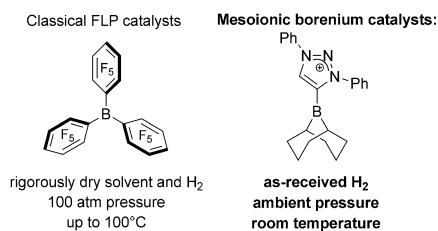
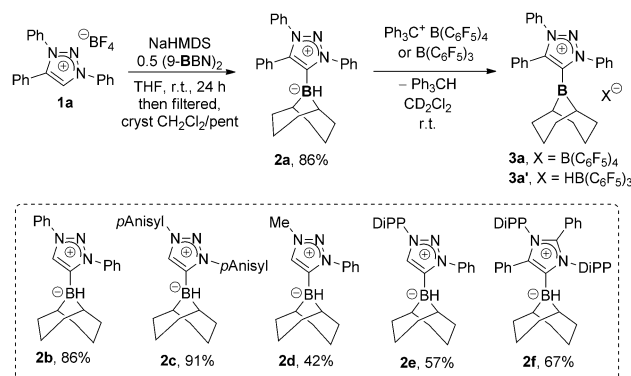


Figure 1. Classical versus borenium-based Lewis acids.

The synthesis of 1,3,4-triphenyl-triazolyldiene-5-(9-borabicyclo[3.3.1]nonane) (**2a**) was accomplished by in situ deprotonation of triazolium salt **1a** with NaHMDS in the presence of (9-BBN)₂ (9-BBN = 9-borabicyclo[3.3.1]nonane). This gives **2a** directly in high yield under noncryogenic conditions due to the increased stability of the free carbene derived from **1a** compared to related N-alkyl derivatives (Scheme 2).



Scheme 2. Synthesis of MIC-9-BBN adducts and representative borenium ions. Note: The synthesis of **2d** was carried out at -78°C , starting from the corresponding triazolium iodide **1d**. DiPP = 2,6-diisopropylphenyl.

In ^{11}B NMR spectra, the boron atom of **2a** appears as a doublet centered at -17.4 ppm with a coupling constant of $^1J_{\text{B,H}} = 71.2$ Hz, similar to reported values for IMes-9-BBN ($\delta_{\text{B}} = -16.6$ (d, $^1J_{\text{B,H}} = 59.6$ Hz); IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazolyldiene)^[11b] and IPr-9-BBN ($\delta_{\text{B}} = -16.64$ (d, $^1J_{\text{B,H}} = 80.0$ Hz); IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazolyldiene).^[12e] The borohydride signal appears as a broad resonance in the ^1H NMR spectrum centered at 2.09 ppm. Replacing NaHMDS with the more atom-economical NaH resulted in similarly efficient formation of **2b** in 78% yield. Interestingly, when isolated Na(9-BBN)H₂ was mixed with triazolylum **1b**, the expected carbene borane **2b** was not formed.

With these convenient synthetic methods in hand, a number of sterically and electronically diverse triazolylum-9-BBN adducts **2b–e** were synthesized and isolated. Related borohydride **2f** was also prepared featuring a so-called abnormal carbene.^[16] When asymmetrically substituted **1d** was exposed to an adapted protocol developed for our MIC-borohydride synthesis,^[14] **2d** was isolated with high selectivity for the 5-ylidene over the 4-ylidene ($>10:1$ by ^1H NMR spectroscopy), albeit in moderate yield.

Crystals suitable for single-crystal X-ray diffraction were obtained by layering a CH_2Cl_2 solution of the zwitterionic MIC-borohydrides (**2a** or **2d**) with pentanes at -24°C (Figure 2). Compound **2e** was isolated as a single regioisomer. The metrics about the boron atom range within expected values for related structures including the expected decreases in N-C_{carbene}-C bond angles (**2a**: $101.28(18)^{\circ}$, **2d**: $100.9(2)^{\circ}$) and characteristic C_{carbene}-B single-bond lengths (**2a**: $1.641(3)$ Å, **2d**: $1.616(4)$ Å), comparable (within experimen-

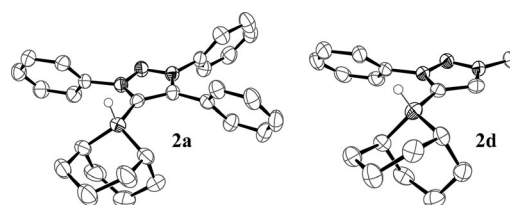


Figure 2. ORTEP-III representation of MIC-9-BBN **2a** and **2d**. Thermal ellipsoids are drawn at 50% probability and hydrogen atoms other than bound to boron are omitted for clarity. Select bond lengths [Å] and angles [$^{\circ}$]: **2a** C_{carbene}-B $1.641(3)$, $\angle$ C-C_{carbene}-N $101.28(18)$, $\Sigma \angle$ C_{carbene} $360.0(2)$; **2d** C_{carbene}-B $1.616(4)$, $\angle$ C-C_{carbene}-N $100.9(2)$, $\Sigma \angle$ C_{carbene} $360.0(2)$.

tal error for **2a**) to the values found in **2g** ($1.640(3)$ Å, $1.645(3)$ Å).^[12e]

Reaction of **2a** with an equimolar amount of $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ resulted in complete disappearance of the doublet at -17.4 ppm and the appearance of a new broad resonance at 82.0 ppm in the ^{11}B NMR spectrum, consistent with the formation of borenium salt **3a**. Similar ^{11}B NMR chemical shifts have been found for NHC-9-BBN borenium salts IMes-9-BBN $^+\text{OTf}^-$ ($\delta_{\text{B}} = 81.4$ ppm),^[11a] and **3g** ($\delta_{\text{B}} = 83.8$ ppm).^[12e] Hydride abstraction by the tritylium cation proceeds smoothly and rapidly, independent of the steric crowding about the boron center.

We next set out to investigate the activity of these borenium ions in the catalytic hydrogenation of aldimine **4a** and ketimine **4b** (Figure 3, Table 1). A convenient in situ protocol was developed, in which borenium ions were generated by hydride abstraction using $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ prior to addition of the substrate and exposure to H_2 .

For a direct comparison, two NHC-stabilized borenium ions, **3g** and **3h**, were included. As shown in Figure 3, MIC-

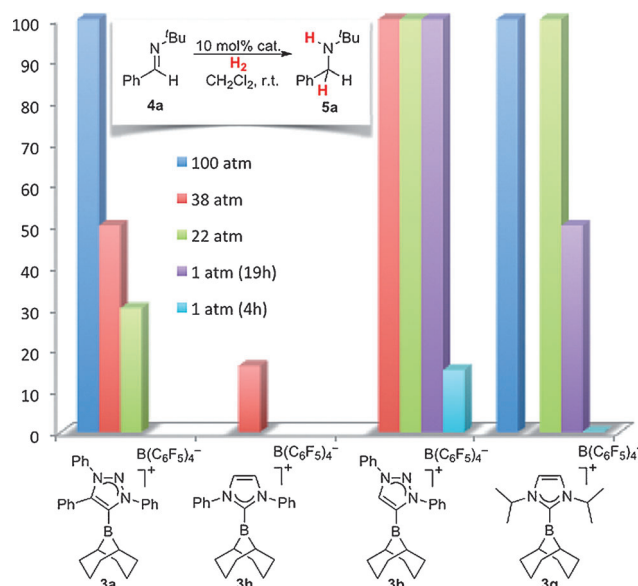
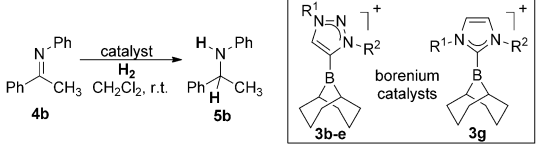


Figure 3. Catalyst development. Reaction conditions: 0.25 mmol imine in 0.25 mL CH_2Cl_2 in a vial inserted into a Parr bomb, 700 rpm stir rate, 4 h reaction time except for 1 atm runs which were left for 4 or 19 h as indicated.

Table 1: Hydrogenation of **4b** with MIC- and NHC-based borenium ions.



Entry ^[a]	Catalyst	R ¹ /R ²	Loading [%]	t [h]	Conversion [%] ^[b]
1	3b	Ph/Ph	10	19	100 (87)
2	3b	Ph/Ph	5	23	100
3	3b	Ph/Ph	2.5	24	40
4	3g	<i>i</i> Pr/ <i>i</i> Pr	5	23	37
5	3c	anisyl/anisyl	5	17.5	100
6	3c	anisyl/anisyl	2.5	24	0
7	3e	DiPP/Ph	5	17.5	33
8	3d	Me/Ph	5	6.5	40
9	B(C₆F₅)₃	—	5	17.5	0

[a] 0.25 mmol imine in 0.25 mL CH₂Cl₂ in a Schlenk tube, 1 atm H₂, 1200 rpm stir rate. [b] Conversion estimated by ¹H NMR spectroscopy, yield of isolated products in brackets.

borenium **3a** reduced imine **4a** quantitatively in less than 4 h at 100 atm hydrogen pressure. Decreasing the pressure to 38 atm and then 22 atm under otherwise identical conditions, gave conversions of 50 % and 30 %. Isosteric NHC-derivative **3h** gave only 16 % conversion under 38 atm of hydrogen illustrating the importance of the electronic effect of the MIC group and the higher inherent reactivity of MIC-stabilized borenium ions in this reaction.

To further assess the effect of sterics on the reaction, compound **3b** with only one flanking phenyl group was examined and found to be the most active of all compounds tested (Figure 3). Complete reduction of the aldimine was observed in all cases, although longer reaction times were required at low pressures. Previously reported NHC-borenium **3g** had a reactivity similar to that of MIC-borenium **3b**, but at low conversion the MIC-borane was superior (pale blue bar, Figure 3). Having developed conditions under which metal-free hydrogenations can be affected in regular glassware under mild conditions, we turned to the more challenging ketimine **4b**.

To our delight, using 10 mol % **3b** under atmospheric pressure at 25 °C, the reduction of **4b** proceeded to full conversion in 19 h giving **5b** in 87 % yield (Table 1, entry 1). Lowering the catalyst loading to 5 mol % gave full conversion in less than 24 h, but at 2.5 mol % the conversion was diminished (entry 3). Comparison with NHC-based borenium ion **3g** (entry 4) illustrated the advantage of the MIC-stabilized borenium ion **3b**, because only 37 % conversion was obtained compared with 100 %.

Whereas the *p*-anisyl-derived borenium **3c** gave full conversion at 5 % loading in 17.5 h, it was clearly inferior to **3b** at 2.5 % loading (entries 3 versus 6). Remote steric effects also impacted reactivity such that **3e**, in which the distal N-substituent is a diisopropyl phenyl group, showed decreased reactivity (entry 7). Consistent with this, unsymmetrical MIC-borenium ion **3d**, with a methyl group at the distal position, has the highest activity observed yet, giving the same yield as diphenyl derivative **3b** in one fourth of the time, albeit at

higher catalyst loading (entry 8). Finally, under standard conditions, B(C₆F₅)₃ gave no reaction.

In terms of substrate scope, the reaction is sensitive to catalyst inhibition by imines and product amines lacking steric bulk. Thus, although *N*-Ph ketimines are effective substrates, the corresponding *N*-Bn compounds provide only trace product. However, the benzhydryl protecting group was a useful alternative, giving 26 % yield at 1 atm, and 90 % at 5 atm pressure.^[17] To assess functional group compatibility, the hydrogenation of **4b** was run concurrently with 1 equiv of fenchone and showed 82 % product by NMR spectroscopy and no reduction of fenchone, indicating that the ketone is not a competitive substrate. However, less hindered methoxycarbonyl substituents do inhibit the reduction of imine functionalities.^[17]

Next we investigated the ability of MIC-borenium-based catalysts to reduce N-heterocycles **6a–k** (Figure 4). Remark-

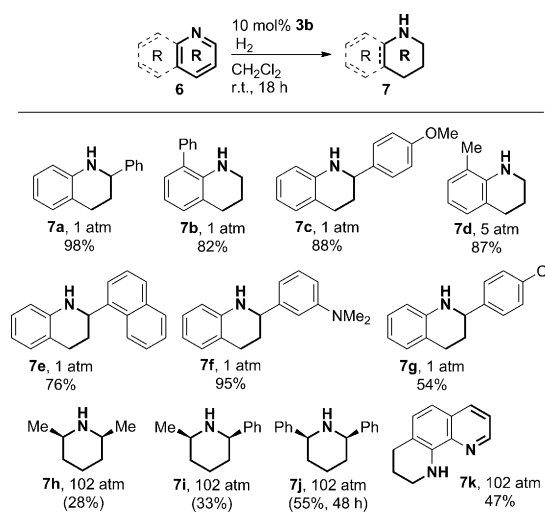


Figure 4. Mild hydrogenation of N-heterocycles catalyzed by **3b**. Reactions at 1 atm: **6** (0.25 mmol) in CH₂Cl₂ in a Schlenk tube (0.5–1 mL), 1200 rpm stir rate. Reactions at 5 or 102 atm: as above, but performed in an autoclave, 700 rpm stir rate. Yields of isolated products after purification by column chromatography; yields in parentheses were determined by ¹H NMR spectroscopy against an internal standard.

ably, 2- and 8-arylated quinoline derivatives were hydrogenated at near ambient pressure and room temperature with catalyst **3b**, giving the corresponding isolated 1,2,3,4-tetrahydroquinolines **7a–g** in good to excellent yields. Although unfunctionalized quinoline or 3-arylated quinoline derivatives failed to undergo reduction even at 100 atm of H₂, 8-methyl quinoline (**6d**) reacted quantitatively at only 5 atm of H₂. The lack of reactivity with less hindered systems is likely due to strong coordination to the borenium-catalyst impeding H₂ activation.

At elevated H₂ pressure (102 atm), even 2,6-disubstituted pyridine derivatives were reactive giving products **7h–j** as single diastereomers. Despite the higher pressure, this system is still mild compared to the most effective FLP-type systems reported to date (100 °C, 50 atm H₂, 20 h, 10 mol % B-((CH₂)₂C₆F₅)(C₆F₅)₂).^[18] 9,10-Phenanthroline was also reac-

tive giving tetrahydro-9,10-phenanthroline **7k** in 47% yield with no evidence of overreduction. At extended reaction times, however, reduction of the second heterocycle was observed.

Stoichiometric reactions were conducted to better understand the high reactivity of **3b**. A modified Gutmann–Beckett study on carbene-borenium ions **3a**, **3b**, **3g**, and **3h** showed that all had similar inherent Lewis acidity as $B(C_6F_5)_3$ (**3b**, AN = 78.9; **3g**, AN = 78.4; $B(C_6F_5)_3$, AN = 79.8; AN = acceptor number).^[6,17,19] However, reacting MIC-borohydride **2a** with $B(C_6F_5)_3$ led to clean, quantitative hydride transfer to $B(C_6F_5)_3$, thereby producing **3a'** and demonstrating the greater hydride affinity of $B(C_6F_5)_3$. This observation qualitatively explains the observed high activity of MIC-based borenium ions in hydrogenation catalysis, because these species have high Lewis acidity as required for H_2 activation, and are still potent hydride donors.

Upon mixing MIC-borenium ion **3a** with imine **4b** under catalytic or stoichiometric conditions in the presence of atmospheric H_2 , only the borenium ion could be detected, indicating that hydrogen activation is most likely the turn-over-limiting step, followed by fast reduction of the resulting iminium ion by **2a**, consistent with the high hydride transfer ability of **2a**. When less hindered borenium ion **3b** was employed, only boronium ion **8b** was observed. Thus in this case, either equilibration to the free borenium or hydrogen activation would be the slow step. Interestingly, the reduction product **5b** displays minimal interaction with **3b** as demonstrated by ^{11}B NMR spectroscopy.^[17] These data support the mechanism shown in Scheme 3, in which imine **4b** and

more active. Steric effects on the MIC have a significant effect on reactivity, even in distal positions.

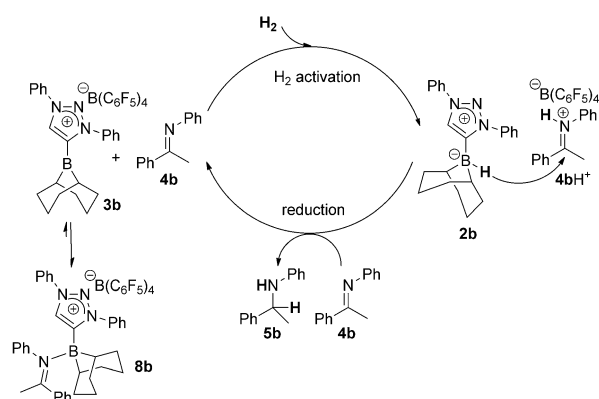
Experimental Section

In a glove box, a vial was charged with **2b** (8.5 mg, 25 μ mol) and $Ph_3C^+B(C_6F_5)_4^-$ (22.4 mg, 24 μ mol). After adding a stir bar, CH_2Cl_2 (0.1 mL) was added via syringe and the resulting homogenous mixture was stirred for 2–3 min until the solution turned colorless. A second vial was charged with *N*-(1-phenylethylidene)aniline (**4b**, 49.4 mg, 0.26 mmol), dissolved in CH_2Cl_2 (0.05 mL) and added to the catalyst solution. The contents of the vial were transferred to a Schlenk tube equipped with a teflon-stoppered side-arm, both vials rinsed with CH_2Cl_2 (0.1 mL), the tube sealed, and removed from the glove box. The flask was attached to a Schlenk line with a mercury bubbler, and the reaction mixture degassed by three freeze–pump–thaw cycles, backfilled with H_2 (supplier: Praxair, 5.0), and sealed. The combination of a mercury bubbler and back filling with H_2 after FPT likely leads to pressures slightly greater than 1 atm. The reaction was stirred (1200 rpm) at room temperature for 18 h. The reaction mixture was subjected to flash column chromatography giving product **5b**. Yield: 44 mg (0.22 mmol, 87%).^[17]

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Scheme 3. Proposed mechanism for **3b**-catalyzed hydrogenation of imines.

borenium **3b** heterolytically cleave H_2 to give the zwitterionic MIC-borohydride **2b** and iminium ion **4bH**⁺. After hydride delivery from **2b** to **4bH**⁺, **3b** is reformed and **5b** produced.

In conclusion, previously unknown MIC-boranes and borenium ions were synthesized based on a 1,2,3-triazolyli-dene motif. These novel borenium salts have been shown to catalyze the hydrogenation of aldimines, ketimines, and *N*-heterocycles under very mild conditions by an FLP-type mechanism. When the MIC-based systems were isosteric with the corresponding NHC-derived borenium ions, they were

- [1] R. Crabtree, *Acc. Chem. Res.* **1979**, *12*, 331–337.
- [2] J. G. de Vries, C. J. Elsevier, *The Handbook of Homogeneous Hydrogenation*, Wiley-VCH, Weinheim, **2007**.
- [3] a) G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126; b) “Frustrated Lewis Pairs I: Uncovering and Understanding”: *Topics in Current Chemistry*, Vol. 332 (Eds.: G. Erker, D. W. Stephan), Springer, Berlin, **2013**.
- [4] a) P. A. Chase, T. Jurca, D. W. Stephan, *Chem. Commun.* **2008**, 1701–1703; b) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050–8053; *Angew. Chem.* **2007**, *119*, 8196–8199.
- [5] a) G. Ghattas, D. Chen, F. Pan, J. Klankermayer, *Dalton Trans.* **2012**, *41*, 9026–9028; b) D. Chen, Y. Wang, J. Klankermayer, *Angew. Chem. Int. Ed.* **2010**, *49*, 9475–9478; *Angew. Chem.* **2010**, *122*, 9665–9668; c) D. Chen, J. Klankermayer, *Chem. Commun.* **2008**, 2130–2131; d) Y. Liu, H. Du, *J. Am. Chem. Soc.* **2013**, *135*, 6810–6813; e) V. Sumerin, K. Chernichenko, M. Nieger, M. Leskelä, B. Rieger, T. Repo, *Adv. Synth. Catal.* **2011**, *353*, 2093–2110; f) Z. M. Heiden, D. W. Stephan, *Chem. Commun.* **2011**, *47*, 5729–5731.
- [6] M. Mewald, R. Fröhlich, M. Oestreich, *Chem. Eur. J.* **2011**, *17*, 9406–9414.
- [7] Borenium chemistry: a) P. Kölle, H. Nöth, *Chem. Rev.* **1985**, *85*, 399–418; b) W. E. Piers, S. C. Bourke, K. D. Conroy, *Angew. Chem. Int. Ed.* **2005**, *44*, 5016–5036; *Angew. Chem.* **2005**, *117*, 5142–5163; c) T. S. De Vries, A. Prokofjevs, E. Vedejs, *Chem. Rev.* **2012**, *112*, 4246–4282; Oxazaborolidine catalysis: d) E. J. Corey, *Angew. Chem. Int. Ed.* **2009**, *48*, 2100–2117; *Angew. Chem.* **2009**, *121*, 2134–2151.
- [8] a) V. Bagutski, A. Del Grosso, J. A. Carrillo, I. A. Cade, M. D. Helm, J. R. Lawson, P. J. Singleton, S. A. Solomon, T. Marcelli, M. J. Ingleson, *J. Am. Chem. Soc.* **2013**, *135*, 474–487; b) A. Del Grosso, P. J. Singleton, C. A. Muryn, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2011**, *50*, 2102–2106; *Angew. Chem.* **2011**, *123*, 2150–2154.

- [9] a) J. R. Lawson, E. R. Clark, I. A. Cade, S. A. Solomon, M. J. Ingleson, *Angew. Chem. Int. Ed.* **2013**, 52, 7518–7522; *Angew. Chem.* **2013**, 125, 7666–7670; b) T. Stahl, K. M  ther, Y. Ohki, K. Tatsumi, M. Oestreich, *J. Am. Chem. Soc.* **2013**, 135, 10978–10981.
- [10] I. A. Cade, M. J. Ingleson, *Chem. Eur. J.* **2014**, 20, 12874.
- [11] a) D. McArthur, C. P. Butts, D. M. Lindsay, *Chem. Commun.* **2011**, 47, 6650–6652; b) D. M. Lindsay, D. McArthur, *Chem. Commun.* **2010**, 46, 2474–2476.
- [12] a) A. Prokofjevs, A. Boussonniere, L. F. Li, H. Bonin, E. Lacote, D. P. Curran, E. Vedejs, *J. Am. Chem. Soc.* **2012**, 134, 12281–12288; b) P. Eisenberger, A. M. Bailey, C. M. Crudden, *J. Am. Chem. Soc.* **2012**, 134, 17384–17387; c) S. E. Denmark, Y. Ueki, *Organometallics* **2013**, 32, 6631–6634; d) J. Chen, R. A. Lalancette, F. J  kle, *Chem. Commun.* **2013**, 49, 4893–4895; e) J. M. Farrell, J. A. Hatnean, D. W. Stephan, *J. Am. Chem. Soc.* **2012**, 134, 15728–15731.
- [13] a) P. Mathew, A. Neels, M. Albrecht, *J. Am. Chem. Soc.* **2008**, 130, 13534–13535; b) K. F. Donnelly, A. Petronilho, M. Albrecht, *Chem. Commun.* **2013**, 49, 1145–1159.
- [14] L. B. de Oliveira Freitas, P. Eisenberger, C. M. Crudden, *Organometallics* **2013**, 32, 6635–6638.
- [15] Nucleophilicity parameters for Lewis base borane adducts including NHC-BH₃ have been measured, and the rate dependence on increased Lewis basicity of the donor and decreased steric shielding of boron for hydride delivery demonstrated: a) M. Horn, L. H. Schappele, G. Lang-Wittkowski, H. Mayr, A. R. Ofial, *Chem. Eur. J.* **2013**, 19, 249–263; b) M. Horn, H. Mayr, E. Lacote, E. Merling, J. Deaner, S. Wells, T. McFadden, D. P. Curran, *Org. Lett.* **2012**, 14, 82–85.
- [16] a) E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2009**, 326, 556–559; b) S. Gr  ndemann, A. Kovacevic, M. Albrecht, J. W. Faller Robert, H. Crabtree, *Chem. Commun.* **2001**, 2274–2275.
- [17] See the Supporting Information for details.
- [18] Y. Liu, H. Du, *J. Am. Chem. Soc.* **2013**, 135, 12968–12971.
- [19] a) M. A. Beckett, D. S. Brassington, S. J. Coles, M. B. Hursthouse, *Inorg. Chem. Commun.* **2000**, 3, 530–533; b) M. A. Beckett, G. C. Strickland, J. R. Holland, K. Sukumar Varma, *Polymer* **1996**, 37, 4629–4631; c) V. Gutmann, *Coord. Chem. Rev.* **1976**, 18, 225–255; d) G. C. Welch, L. Cabrera, P. A. Chase, E. Hollink, J. D. Masuda, P. Wei, D. W. Stephan, *Dalton Trans.* **2007**, 3407–3414.