Rhodium-catalyzed hydroborations of allylamine and allylimines

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Abstract: The in situ rhodium-catalyzed addition of catecholborane (HBcat, cat = 1,2-O2C6H4) and pinacolborane (HBpin, pin = 1,2-O2C2Me4) to allylamine, allylimine, 2- and 4-vinylpyridines, and a thienyl imine has been examined using multinuclear NMR spectroscopy. Although reactions of allylamine (H2NCH2CH=CH2) and HBcat gave complex product distributions arising from competing dehydrogenative borylation pathways, addition of HBpin to allylamine using a rhodium catalyst afforded only products arising from hydroboration (RN(Bpin)CH2CH2CH2Bpin, where R = H, Bpin) and hydrogenation (RN(Bpin)CH2CH2CH3). Hydroboration of allylimines (RHC=NCH2CH=CH2, R = Ar) with HBcat occurs initially at the more reactive imine functionality to give unsaturated borylamines (RCH2N(Bcat)CH2CH=CH2). Further reaction with HBcat gives varying amounts of hydroboration products RCH2N(Bcat)CH2CH2CH2Bcat and RCH2N(Bcat)CH2CH(Bcat)CH3 as well as the diboration product RCH2N(Bcat)CH2CH2CH(Bcat)2, depending on the choice of catalyst. Reactions with related unsaturated pyridine derivatives are complicated by extensive degradation, which can be avoided by coordination of the pyridine nitrogen to a Lewis acid. The first examples of metal-catalyzed hydroboration of imines using HBpin are also reported.

Key words: catalysis, hydroboration, boronate esters, dehydrogenative borylation, allylimines.

Introduction

The hydroboration of alkenes and alkynes, which constitutes the formal addition of a B-H bond across a carbon—carbon multiple bond, is an extremely important reaction in organic synthesis (1). Although simple boron hydride reagents such as borane (H3B·X, where X is a Lewis base) and 9-borabicyclo[3.3.1]nonane react readily with alkenes at room temperature, hydroborations with catecholborane (HBcat, cat = 1,2-O2C6H4) generally require elevated temperatures. The discovery that transition metals can be used to catalyze the addition of HBcat to organic substrates has become an important and well-established technique in organic synthesis (for an excellent review on hydroborations catalyzed by transition-metal complexes, see ref. 2) (3, 4). These reactions can have regio-, chemo-, or stereoselectivities, complementary, or more remarkably, opposite to those from products obtained via the uncatalyzed variant. Indeed, hydroborations of 5-hexene-2-one with HBcat proceed readily at room temperature to give exclusive formation of a borate product where the borane has added to the more reactive carbonyl double bond (4). However, when the reaction is carried out at 0°C in the pres-
ence of a catalytic amount of Wilkinson's catalyst (RhCl(PPh₃)₃), addition of the B—H bond occurs primarily at the less reactive alkene moiety to give an organoboronate ester product (Scheme 1).

Organoborinate esters (RB(OR)₂) and boronic acids (RB(OH)₂) belong to a remarkable class of compounds that have been used extensively in organic (5–9), organometallic (10, 11), and solid-phase synthesis (12, 13), as well as in macromolecular chemistry (14), molecular recognition (15), transporting molecules across biological membranes (16), redox switching (17), and as glucose sensors (18, 19). Interest in these compounds also arises from their unique biological activities (20). For instance, peptide boronic acids are among the most potent, known inhibitors of serine proteases (21). As a result, the synthesis of boron-containing amino acid derivatives has become an area of considerable interest (22, 23).

Hydroborations of tertiary allylic amines (R₂NCH₂CH=CH₂, R = alkyl, aryl) with borane (H₃B·X, X = SMe₂, THF) are known to give initial formation of the expected anti-Markovnikov products, R₂NCH₂CH₂BH₂ (6, 24–26). Analogous reactions with primary and secondary amines, however, are complicated by direct interaction with the N—H bond to give a number of N-boryl products (27, 28). Protection of the N—H bond is usually required in these reactions to ensure chemoselective addition of the borane at the allyl group (29, 30). Unfortunately, deprotection methodologies frequently compromise the integrity of the B—C bond (31). We, therefore, decided to investigate the in situ reactions of allylamine. The mixture was allowed to stir for 1 h and then analyzed by multinuclear NMR spectroscopy. Attempts to control the selectivity of these reactions always gave minor amounts of 2, which precipitated out of solution after ca. 1 h. IR (Nujol): 3200, 2940, 2868, 2443, 1600, 1464, 1377, 1335, 1232, 1099, 1057, 1083, 815, 739, 700. H NMR (in d₆-acetone) ð 8.00 (br, cat), 7.09 (br ov m, cat), 6.48 (br ov m, cat), 6.05 (br ov m, 1H, CH=CH₂), 5.40 (br ov m, 2H, cat), 3.58 (br, 8H, cat), 1.68 11B NMR (in C₆D₆) ð 7.01 (d of d, J = 6, 3 Hz, 4H, cat), 6.73 (d of d, J = 6, 3 Hz, 4H, cat), 5.82 (ov d of d of t, J = 17, 10, 7 Hz, 1H, -CH=CH₂), 5.16 (d of d, J = 17, 2 Hz, 1H, -CH=CH₂), 4.94 (d of d, J = 10, 2 Hz, 1H, -CH=CH₂), 3.92 (d, J = 7 Hz, 2H, -CH₂CH=CH₂). 13C NMR ð 148.6, 136.3, 122.3, 115.1, 112.1, 46.3.

Addition of catecholborane (HBcat) to allylamine (1)

In a typical reaction, 2 equiv of HBcat in 0.5 mL of C₆D₆ were added dropwise to a 0.5 mL C₆D₆ solution of allylamine. The mixture was allowed to stir for 1 h and then analyzed by multinuclear NMR spectroscopy. Attempts to control the selectivity of these reactions always gave minor amounts of 2, which precipitated out of solution after ca. 1 h. IR (Nujol): 3200, 2940, 2868, 2443, 1600, 1464, 1377, 1335, 1232, 1099, 1057, 1083, 815, 739, 700. H NMR (in d₆-acetone) ð 8.00 (br, cat), 7.09 (br ov m, cat), 6.48 (br ov m, cat), 6.05 (br ov m, 1H, CH=CH₂), 5.40 (br ov m, 2H, CH=CH₂), 3.88 (br, 2H, -CH₂CH=CH₂), 11B NMR ð 7.01 (d of d, J = 6, 3 Hz, 4H, cat), 6.73 (d of d, J = 6, 3 Hz, 4H, cat), 5.82 (ov d of d of t, J = 17, 10, 7 Hz, 1H, -CH=CH₂), 5.16 (d of d, J = 17, 2 Hz, 1H, -CH=CH₂), 4.94 (d of d, J = 10, 2 Hz, 1H, -CH=CH₂), 3.92 (d, J = 7 Hz, 2H, -CH₂CH=CH₂). 13C NMR ð 148.6, 136.3, 122.3, 115.1, 112.1, 46.3.

Catalyzed hydroborations of allylamine (1) with HBcat

In a typical reaction, 5 equiv of HBcat in 0.5 mL of C₆D₆ were added to a 0.5 mL C₆D₆ solution of allylamine and 1 mol% RhCl(PPh₃)₃. The mixture was allowed to stir for 1 h and then analyzed by multinuclear NMR spectroscopy. 4: IR
Catalyzed hydroborations of allylamine (16a–16d) with HBcat

In a typical reaction, 3 equiv of catecholborane in 0.5 mL of C₆D₆ were added to a 0.5 mL C₆D₆ solution of allylamine 16c in the presence of 1 mol% RhCl(PPh₃)₂. The mixture was allowed to stir for 1 h and then analyzed by multinuclear NMR spectroscopy. 17c: 1H NMR (in C₆D₆) 7.01–6.65 (ov m, 11H, cat and Ar), 4.30 (s, 2H, -NCH₂Ar), 3.09 (t, J = 8 Hz, 2H, -NCH₂Ar), 2.24 (s, 2H, -CH₂CH₂CH₂, 0.99 (t, J = 8 Hz, 2H, -CH₂B). 11B NMR & 35 (br, Cbcat), 26 (br, Nbcat). 18c: 1H NMR & 7.01–6.65 (ov m, 11H, cat and Ar), 4.31 (s, 2H, -NCH₂Ar), 3.46 (2nd order d of d, J = 14, 8 Hz, 1H, -NCH(CH₃)), 3.31 (2nd order d of d, J = 14, 8 Hz, 1H, -NCH(CH₃)), 1.68 (ov t of q, J = 8 Hz, 2H, -CH(Bcat)(CH₃)), 1.07 (d, J = 8 Hz, 3H, -CH₃). 11B NMR & 35 (br, Cbcat), 26 (br, Nbcat). 19c: 1H NMR & 7.01–6.65 (ov m, 15H, cat and Ar), 4.30 (s, 2H, -NCH₂Ar), 3.25 (t, J = 8 Hz, 2H, -NCH₂Ar), 2.18 (ov d of t, J = 8 Hz, 2H, -CH₂CH₂CH₂), 1.63 (t, J = 8 Hz, 1H, -CH(Bcat)(CH₃)). 11B NMR & 35 (br, Cbcat), 26 (br, Nbcat). 20c: 1H NMR & 7.01–6.65 (ov m, 7H, cat and Ar), 4.30 (s, 2H, -NCH₂Ar), 3.00 (t, J = 8 Hz, 2H, -NCH₂Ar), 1.38 (ov t of q, J = 8 Hz, 2H, -CH₂CH₂CH₂), 0.71 (t, J = 8 Hz, 3H, -CH₃). 11B NMR & 26 (br, Nbcat).

Catalyzed hydroborations of vinylpyridines-BF₃ with HBpin

In a typical reaction, 1.1 equiv of BF₃·OMe₂ were added to a 0.5 mL solution of the vinylpyridine in C₆D₆. The resulting solution was allowed to stir for 2 h whereupon 1 mol% of Rh(acac)(coe)(dpdp) (dpdp = 1,4-bis(diphenylphosphino)butane) solution was added to the mixture, followed by the addition of a 0.25 mL C₆D₆ solution of 1.2 equiv of HBpin. The mixture was allowed to stir for 1 h and then analyzed by multinuclear NMR spectroscopy. 22: 1H NMR (in C₆D₆) 8.55 (d, J = 5 Hz, 1H), 7.04–6.78 (ov m, 6H), 6.50 (app t, J = 5 Hz, 1H), 4.34 (q, J = 8 Hz, 1H, -CH(Bcat)-). 11B NMR & 34 (br, Cbcat), 1 (s, Nbcat). 13C NMR & 162.2, 148.5, 143.7, 142.5, 123.0, 122.4, 112.7, 23.8 (br, CBcat), 14.9, 24: 1H NMR & 8.28 (d, J = 5 Hz, 2H), 7.07 (d of d, J = 3, 1 Hz, 2H), 6.88 (d of d, J = 3, 1 Hz, 2H), 6.66 (d, J = 5 Hz, 2H), 2.39 (q, J = 8 Hz, 1H, -CH(Bcat)-), 1.14 (d, J = 8 Hz, 3H, -CH₃). 11B NMR & 34 (br, Cbcat), 1 (s, Nbcat). 13C NMR & 161.2, 148.8, 143.3, 125.5, 124.1, 113.2, 25.6 (br, CBcat), 15.0.

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Scheme 2.

\[
\begin{align*}
\text{NH}_2 & \quad \text{H}_2\text{Bcat} \\
1 & \quad \text{N(Bcat)H} \\
2 & \quad \text{H}_2\text{Bcat} \quad \text{N(Bcat)H} \\
3 & \quad \text{H}_2\text{Bcat} \quad \text{N(Bcat)H} \\
\text{H}_2\text{Bcat} & \quad \text{N(Bcat)H} \\
4 & \quad \text{H}_2\text{Bcat} \quad \text{N(Bcat)H} \\
\text{Hydroboration} & \quad \text{N(Bcat)H} \\
\text{Borylation} & \quad \text{Bcat} \\
\text{Hydroboration} & \quad \text{Bcat} \\
\text{Dehydrogenation} & \quad \text{Bcat} \\
\text{Borylation} & \quad \text{Bcat} \\
\text{Hydrogenation} & \quad \text{Bcat}
\end{align*}
\]

\( R = \text{H, Bcat} \)

\( {\Delta} 3.90 \) (br q, \( J = 8 \) Hz, 1H, \(-\text{CH(Bpin)-}\))

\( 3.07 \) (q, \( J = 8 \) Hz, 2H, \(-\text{CH}_2\text{CH}_3\)), 1.28 (d, \( J = 8 \) Hz, 3H, \(-\text{CH(Bpin)CH}_3\)), 1.00 (s, Bpin), 0.94 (t, \( J = 8 \) Hz, 3H, \(-\text{CH}_2\text{CH}_3\)).

\( ^{13} \text{C NMR} \Delta {\Delta} 33 \) (br, CBpin), 23, 21, 1 (s, NBF$_3$). Selected spectroscopic data for reactions with 23.

\( ^{1} \text{H NMR} \Delta 2.72 \) (d, \( J = 8 \) Hz, 2.30 (t, \( J = 8 \) Hz, \(-\text{CH}_2\text{CH}_3\)), 2.14 (q, \( J = 8 \) Hz, 1H, \(-\text{CH(Bpin)-}\)), 1.95 (q, \( J = 8 \) Hz, 2H, \(-\text{CH}_2\text{CH}_3\)), 1.17 (br s), 1.06 (d, \( J = 8 \) Hz, 3H, \(-\text{CH(Bpin)CH}_3\)), 0.98 (s, Bpin), 0.66 (t, \( J = 8 \) Hz, 3H, \(-\text{CH}_2\text{CH}_3\)).

\( ^{13} \text{C NMR} \Delta 33 \) (br, CBpin), 21, 1 (s, NBF$_3$).

### Catalyzed hydroborations of aldime 25 with pinacolborane (HBpin)

To a 0.5 mL \( \text{C}_6\text{D}_6 \) solution of 25 and 1 mol% RhCl\((\text{PPh}_3)_3 \) was added 1.2 equiv of HBpin in 0.5 mL of \( \text{C}_6\text{D}_6 \). The reaction was heated at reflux for 2 h and then analyzed by multinuclear NMR spectroscopy. 26:

\( ^{1} \text{H NMR} \) (in \( \text{C}_6\text{D}_6 \))\( \Delta 6.88–6.73 \) (ov m, 3H, Ar), 4.33 (s, 2H, \(-\text{NCH}_2\text{Ar}\)), 3.01 (t, \( J = 8 \) Hz, 2H, \(-\text{NCH}_2\text{Ar}\)), 1.42 (ov t of q, \( J = 8 \) Hz, 2H, \(-\text{CH}_2\text{CH}_2\text{CH}_3\)), 1.15 (s, 12H, pin), 0.78 (t, \( J = 8 \) Hz, 3H, \(-\text{CH}_3\)).

\( ^{13} \text{C NMR} \Delta 145.8, 126.4, 124.8, 124.1, 82.2, 46.8, 44.4, 24.5, 22.0, 11.1. \)

\( ^{11} \text{B NMR} \Delta 24 \) (br, NBpin).

### Results and discussion

As with reactions using borane, we have found that the in situ addition of HBcat to allylamine (1) resulted in the initial formation of a mixture of products. Although minor amounts of Lewis acid–base adducts HBcat-HNRC\(_2\text{CH}_2\text{CH} = \text{CH}_2\) (2, \( R = \text{H, Bcat} \)) are formed (40), a competing reaction gave N(Bcat)\(_2\text{CH}_2\text{CH} = \text{CH}_2\) (3) as the major boron-containing product in solution. No adduct formation is observed with 3, however, as coordination of two electron-withdrawing boryl groups has either significantly reduced the nucleophilic nature of the amine or increased the steric hindrance around the nitrogen atom. Although HBcat eventually adds to the activated alkyne group in these organoboryl species, reactions take several days. However, we have found that certain rhodium complexes can be used to catalyze this addition. Rhodium-catalyzed hydroborations are believed to arise via oxidative addition of the B—H bond of the boronate ester at the metal centre, followed by coordination and subsequent insertion of the alkene into the Rh—H or Rh—B bond (41). Reductive elimination affords the desired organoboronate ester product.

Addition of excess HBcat is required in all of these catalyzed reactions to ensure 100% conversion of the starting alkene. While hydroboration of intermediate 2 gave minor amounts of HBcat-HNRC\(_2\text{CH}_2\text{CH}_2\text{Bcat} \) (4, \( R = \text{H, Bcat} \)), reactions with 3 gave surprisingly complex product distributions, regardless of the catalyst system used to affect this transformation (Scheme 2). Although significant amounts of the hydroboration products 5 and 6 were formed in these reactions, products (such as 8) derived from a competing dehydrogenative borylation pathway were also observed (by NMR spectroscopy). We propose that these unique products originate from the transient alkenylboronate ester 7, which presumably results from insertion of the activated alkene into the Rh—B bond (3, 41). Subsequent β-hydride elimination would afford the alkenylboronate ester with concomitant formation of dihydrogen (2, 41). It is possible that “hydroboration product” 5 also arises from hydrogenation of alkenylboronate ester 7. Hydride elimination appears to be specific as products arising from abstraction of a methylene hydrogen α to the activated amine group are not observed. Alkenylboronate ester 7 can also add another equiv of HBcat to give 8. Interestingly, we have found that compound 8 can also be generated as the major product in analogous hydroborations of H\(_2\)NCH\(_2\)C=CH. As with most catalyzed hydroboration reactions, a small amount of hydrogenation product 9 is almost always observed.

The formation of these products is somewhat unusual as catalyzed hydroborations of simple alkenes, such as 1-octene, proceed smoothly to give predominant formation of the expected organoborane ester product (2, 41). In this study, replacement of the two N—H bonds with N-Bcat groups in 3 appears to be ineffective in deactivating the amine group and catalyzed reactions proceed to give complex product distributions. The formation of multiple boronated compounds has recently been an area of considerable interest (42–44).

Metal-catalyzed hydroborations of unsaturated C—C bonds using HBpin have been reported previously (45–47). In a further attempt to control selectivity we decided to examine hydroboration using HBpin (Scheme 3). Unlike reactions with HBcat, which is a stronger Lewis acid, no adduct formation was observed. Addition of excess HBpin gave the monoboryl amine HN(Bpin)CH\(_2\text{CH}_2\text{CH} = \text{CH}_2\) (10), where a second equiv of the boronate ester failed to add to the amine N—H bond even at elevated temperatures. Remarkably, we have found

\[ ^{3} \text{C. M. Crudden and A. Chen. Unpublished results.} \]
that a rhodium catalyst could be used to facilitate the addition of another equiv of HBpin to give N(Bpin)_2 CH_2 CH_2 =CH_2 (11). This observation provides the first example of a metal-catalyzed hydroboration of N—H bonds.

Compound 11 was observed in only minor amounts (<5% by 1H NMR spectroscopy) as a competing hydroboration reaction occurred at the alkene moiety to afford a mixture of HN(Bpin)CH_2 CH_2 CH_2 Bpin (12) and N(Bpin)_2 CH_2 CH_2 Bpin (13). Not surprisingly, significant amounts of hydrogenation products RN(Bpin)CH_2 CH_2 CH_3 (where R = H or Bpin, 14 and 15, respectively) were also observed in these reactions. The 1H NMR data for the propyl group in 13 is similar to that observed for 12, except that chemical shifts are moved to a lower field due to addition of another electron-withdrawing Bpin group. For instance, the middle CH_2 resonance in 12 is observed as an overlapping triplet of triplets at 1.60 ppm, yet for 13 this peak is found at 2.04 ppm. The 11B NMR of RN(Bpin)CH_2 CH_2 CH_3 (where R = H or Bpin) shows a peak at 25 ppm corresponding to the B—N bond and a resonance at 33 ppm for the new B—C bond. No appreciable intramolecular interactions are observed in these molecules as the boron atoms appear to be three-coordinate (40, 48). This result is consistent with previous NMR data on related NH_2 CH_2 CH_2 CH_2 B(OH)_2 ·HCl which shows a peak in the 11B NMR at 32.6 ppm (49). Interestingly, the analogous neutral compound (NH_2 CH_2 CH_2 CH_2 B(OH)_2) displays a resonance at 8 ppm suggesting intramolecular adduct formation between the nitrogen and the boron atom (50).

To avoid complications arising from addition of the boronate esters at the amine N—H bond, we decided to investigate hydroboration of allylimine derivatives 16a–d. Addition of 1 equiv of catecholborane to allylimines 16a–c proceeds cleanly to give the corresponding borylamines, where the electron-deficient boron group has added to the nitrogen atom of the imine double bond (51). A rhodium catalyst can once again be used to facilitate the addition of a second equiv of HBcat to the alkene moiety. While selectivity to 3-aminopropylboronate esters has been increased in these reactions, products arising from competing Markovnikov hydroboration, dehydrogenative borylation, and hydrogenation are still all observed to some extent (Table 1).

Reactions with 16c were carried out with 3 equiv of HBcat to ensure complete conversion of the allyl group. Although RhCl(PPh_3)_3 (entry 1) gave 71% of the anti-Markovnikov product 17c, use of [RhCl(coe)_2]_2/4PPh_3 (coe = cis-cyclooctene, entry 7) as a catalyst precursor gave 88% of this desired product (using 1H NMR spectroscopy). Significant amounts (23%) of the hydroboration product 18c were observed in reactions using [RhCl(coe)_2]_2 as a catalyst precursor (entry 6). This product arises from a Markovnikov addition of the borane to the allyl moiety. Remarkably, the diboronated ester 19c was a major product (38%) in reactions using Rh(acac)(coe)/dppe (dppe = 1,2-bis(diphenylphosphino) methane) (entry 10). Catalyst precursors of this type are known to generate the active zwitterionic catalyst Rh(dppe)(η^6-catBcat) (52, 53). It is interesting to note that no significant change in product distributions is observed when reactions were conducted using an excess of HBcat (entry 12) or when hydroborations were carried out in CDCl_3 (entry 11). Although only minor differences in product distributions were observed when 16a was used as the substrate (cf. entries 1 and 13), reactions with 16b gave significant amounts of hydrogenation product 20b (entry 14). Hydrogenation products are also observed in other reactions where extensive borane and (or) catalyst decomposition occurs (entries 6 and 8; 29).

Hydroborations of the pyridine derivative 16d gave rise to a number of different boron-containing products, also arising from the degradation of HBcat (2). Since no degradation was observed with the thiophene imine 16c using HBcat, it is plausible that the harder nitrogen atom in the pyridine ring is responsible for this unwanted degradation pathway. To test this hypothesis, we decided to investigate the analogous hydroborations with 2- and 4-vinylpyridine (21 and 23, respectively). Catalyzed hydroborations of styrene proceed.
smoothly to give selective formation of either the Markovnikov or anti-Markovnikov product, depending upon the metal catalyst employed (2). Not surprisingly, we have found that catalyzed reactions of the vinylpyridines with HBcat gave a mixture of hydroboration products, along with a significant amount of ethylpyridine. Although a number of metal complexes were examined as catalysts for this reaction, all gave mixtures of products. Oxidation of the resulting hydroborated mixtures with NaOH–H2O2 gave 4-ethylpyridine as the only isolable organic product (54). Similar results are also seen in reactions with HBpin. Coordination of a strong Lewis acid, such as BF3 (55–57), to the vinylpyridines effectively eliminated these degradation pathways and the Markovnikov hydroboration products (22 and 24, respectively) could be obtained in high yields (>95% by NMR). (Scheme 4) and HBcat. Reactions with HBpin gave a mixture of hydroboration products along with a significant amount of hydrogenation. Unfortunately, attempts to protect the nitrogen group with BF3 in the hydroboration of allylamines 1 and 16d led to polymerization of the activated alkene moiety.

We then decided to examine the rhodium-catalyzed hydroboration of allylimine 16c using HBpin. Although no reaction was observed at room temperature, complex product distributions arising from addition at the allyl group and the imine functionality were observed when reactions were carried out at elevated temperatures (60°C). Reduction of the imine was observed by disappearance of the aldimine hydrogen at 7.89 ppm with concomitant appearance of a benzylic hydrogen at 4.36 ppm. A peak at 24 ppm in the 11B NMR spectrum arises from the newly formed N—Bpin bond. This result is somewhat surprising as previous attempts to hydroborate imines using HBpin proved unsuccessful (58). To confirm that the imine was being reduced in these reactions, we decided to investigate hydroborations with saturated aldime 25 (Scheme 5). Indeed, these reactions proceeded...
to give selective formation of the desired N-boryl product \textit{26} and represent the first examples of a metal-catalyzed hydroboration of an imine using HBpin (45–47).\textsuperscript{3} Although the synthesis of chiral amines is of utmost importance in organic and medicinal chemistry, the enantioselective reduction of simple ketimine derivatives is often a synthetically challenging problem (59). As a result, future work in this area will focus on the asymmetric reduction of related ketimines using HBpin.

**Conclusion**

We have found that the in situ addition of HBcat to allylamine using a number of rhodium catalysts gave products derived from competing hydroboration and dehydrogenative borylation pathways.\textsuperscript{4} The use of HBpin effectively eliminated the dehydrogenative borylation reaction and a novel rhodium-catalyzed hydroboration of N—H bonds was observed to give \( \text{N(Bpin)}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Bpin} \) along with various amounts of hydrogenation product. Hydroboration of allylmines with HBcat occurs initially at the more reactive imine functionality to give unsaturated borylamines. Further reaction gives the corresponding anti-Markovnikov and Markovnikov hydroboration products. Reactions with related unsaturated pyridine derivatives are complicated by extensive degradation, which can be avoided by coordination of the pyridine nitrogen to a Lewis acid. We have also shown that catalyzed hydroborations of aldmines can be accomplished using HBpin. Further work will examine other catalyst systems to fine-tune product selectivities in these reactions.

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\textsuperscript{4} Supplementary material (NMR data) may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).