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Alkoxide Activation of Aminoboranes towards Selective Amination**

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Dedicated to Professor Mukaiyama

Recent advances in the activation of B–B and B–Si interelement bonds have led to them increasingly being used to functionalize unsaturated compounds by boryl or silyl addition. Although it is well known that B–B and B–Si bonds can be activated in the presence of transition-metal complexes by oxidative addition or transmetallation pathways,[1] current metal-free approaches make intermolecular boryl[2] and silyl[3] transfer possible by the sole addition of catalytic amounts of donor reagents. Simple alkoxides ($^-$OMe, $^-$O*t*Bu) favor the formation of the Lewis acid-base adducts [$RO^- \rightarrow B(OR)_2$–$B(OR)_2$][4] and [$RO^- \rightarrow B(OR)_2$–$SiMe_2Ph$],[3c] which facilitate the release of a boryl or silyl moiety with enhanced nucleophilic character (Figure 1). In this context, we

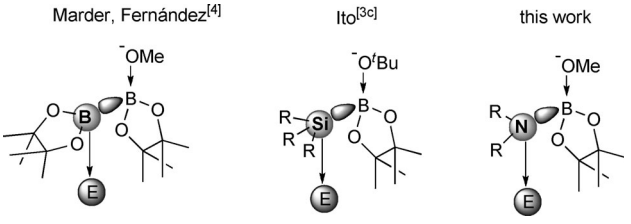
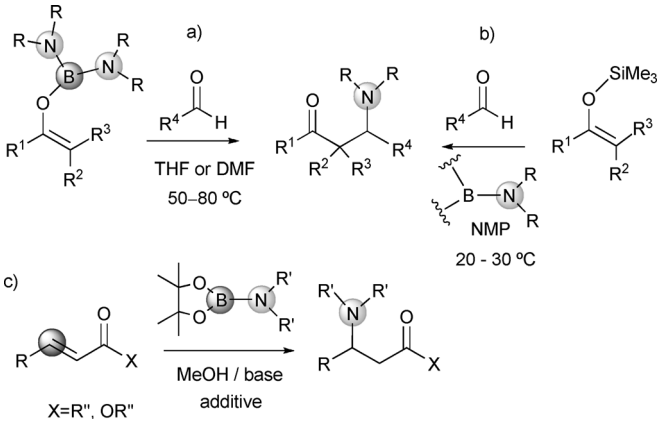


Figure 1. Illustrative pictures of the Lewis acid-base adducts [$MeO^- \rightarrow B(OR)_2$-$B(OR)_2$], [$tBuO^- \rightarrow B(OR)_2$–$SiMe_2Ph$], and [$RO^- \rightarrow B(OR)_2$–$N(R')_2$]. E = electrophilic reagent.

became intrigued with elucidating the possible Lewis acid–base interaction between aminoboranes, having the formula $(RO)_2B$-NR'_2, and alkoxides so that the nucleophilic character of the amine group towards organic electrophiles could be increased.

Aminoboranes have been previously synthesized from $B(NR_2)_3$[5] or borylnitrenes[6] and applied in organic synthesis to generate organoboron compounds.[7] Suginome and coworkers efficiently demonstrated the use of aminoborane derivatives in amination reactions[8] such as as Strecker-type aminative cyanation,[9] reductive amination,[10] and a Mannich-type reaction.[11] By using this latter methodology,



Scheme 1. a,b) Amination reactions that proceed through iminium ion formation. Refs. [10, 11] c) Amination reaction developed in this study. DMF = *N*,*N*-dimethylformamide, NMP = *N*-methylpyrrolidone, THF = tetrahydrofuran.

a series of β-amino ketones and esters were synthesized by reacting bis(dialkylamino)boron enolates with aldehydes (Scheme 1 a), or alternatively silyl ketene acetals with aldehydes and aminoboranes (Scheme 1 b). The function of the amino-substituted boron compounds was attributed to an iminium-ion generator from carbonyl compounds. Herein, we have developed a new method for preparing β-amino carbonyl compounds by the simple Lewis acid–base interaction of aminoboranes with alkoxydes, thus forming the adduct [$RO^- \rightarrow B(OR)_2$–$N(R')_2$] in situ, and enhancing the nucleophilic character of the amino group so that it can react selectively with α,β-unsaturated carbonyl compounds (Scheme 1 c).

With this idea in mind, we first attempted to find the optimal reaction conditions for the amination of 4-hexen-3-one (**1**) with Bpin–NMe_2 (**2a**; pin = pinacol; Table 1). When the reaction was carried out in MeOH as the solvent at 70 °C, no amination product was observed (Table 1, entry 1). The sole addition of 5 mol % of NaO*t*Bu favored the formation of 5-dimethylamino-hexan-3-one (**3a**) as the only product, with a conversion of 28 % (Table 1, entry 2). This result is in agreement with the fact that the base reacts with MeOH to generate the alkoxide[4] which might interact with the aminoborane to form the Lewis acid-base adduct. The use of a phosphine as an additive (10 mol % of PCy_3) was beneficial and increased the formation of the desired product to 95 % (Table 1, entries 3–7). The role of the phosphine might involve an interaction with the α,β-unsaturated carbonyl substrate, thus resulting in the formation of a strongly basic zwitterionic phosphonium enolate species.[12] However, the

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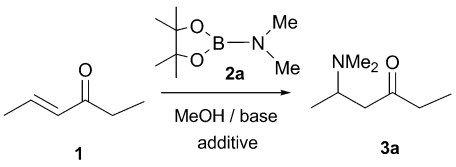
Table 1: Optimization of reaction conditions for the β-amination of 4-hexen-3-one with Bpin–NMe_2 (**2a**).[a]



Entry	Base (mol%)	Additive (mol%)	Solvent/ *T* [°C]	Conv. [%][b]
1	–	–	MeOH/70	–
2	NaO*t*Bu(5)	–	MeOH/70	28
3	NaO*t*Bu (5)	PPh_3(10)	MeOH/70	67
4	NaO*t*Bu(5)	PCy_3(10)	MeOH/70	90
5	NaO*t*Bu(10)	PCy_3(10)	MeOH/70	92 (88)
6	NaO*t*Bu(15)	PCy_3(10)	MeOH/70	95 (90)
7	NaO*t*Bu(15)	PCy_3(10)	*t*BuOH/70	93
8	–	PCy_3(10)	MeOH/70	7
9	NaO*t*Bu(5)	PCy_3(10)	MeOH/25	19
10	NaO*t*Bu(5)	PCy_3(10)	THF[c]/70	20
11	$CsCO_3$(15)	PCy_3(5)	MeOH/70	95

[a] Reaction conditions: **1** (0.25 mmol), Bpin–NMe_2 (0.275 mmol), base (5–15 mol%), PR_3 (5–10 mol%), MeOH (2 mL), 70°C, 17 h. [b] Conversion calculated by GC/MS from an average of two reactions. The yield of the isolated product is given in parentheses. [c] THF (2 mL) with 2 equiv of MeOH added to the reaction.

sole addition of phosphine, with no base, does not guarantee the β-amination reaction (Table 1, entry 8). A temperature of 70°C seems to be required for quantitative transformation of **1** into **3a** (Table 1, entries 4 and 9). It was also demonstrated that MeOH as the solvent had a greater positive influence than THF with 2 equivalents of MeOH as an additive (Table 1, entries 4 and 10). The nature of the base was also studied and under optimized reaction conditions Cs_2CO_3 was also efficient at promoting the amination of **1** (Table 1, entry 11). Overall, the reaction conditions shown in entry 6 of Table 1 were found to be optimal for the methodology to be extended to other α,β-unsaturated carbonyl compounds. The benefits of this methodology involve the direct and clean conjugate amination, because when we conducted the same reaction with $LiNMe_2$ instead of the aminoborane/base/MeOH system, the substrate **1** was transformed into a complex mixture of products, and product **3a** was not formed (see the Supporting Information for details).

Spectroscopic evidence has demonstrated the formation of the Lewis acid-base adduct [$RO^- \rightarrow$Bpin–NMe_2].[13] The original ^{11}B NMR spectra of the aminoborane **2a**, in THF, shows a clear signal at $\delta = 22.55$ ppm which corresponds to a sp^2 Bpin moiety bonded to an amino group (Figure 2). After the addition of 1 equivalent of NaO*t*Bu, the signal completely shifted to higher fields ($\delta = 5.88$ ppm), even at room temperature. No further changes were observed even in the presence of 2 equivalents of MeOH at 60°C. The new signal might correspond to the sp^3 Bpin moiety of the adduct [*t*$BuO^- \rightarrow$ Bpin–NMe_2]. However, when 1 equivalent of NaOMe was added to the aminoborane **2a**, the signal at $\delta = 22.55$ ppm did not change significantly, and only one small signal appeared at $\delta = 8.74$ ppm. The equilibrium towards the free aminoborane

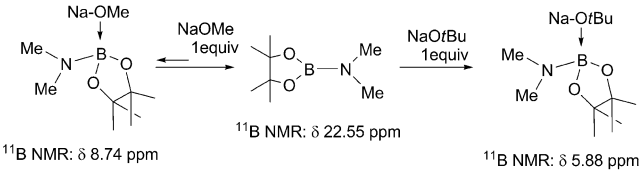
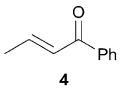
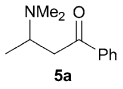
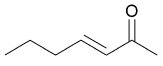
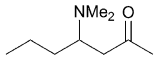
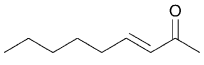
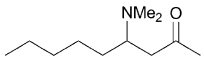
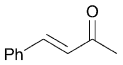
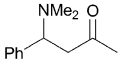
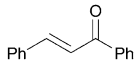
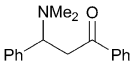
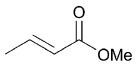
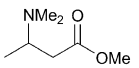
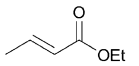
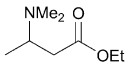
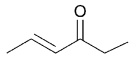
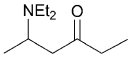
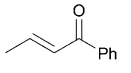
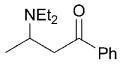
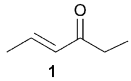
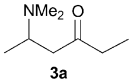


Figure 2. In situ ^{11}B NMR spectra of the suggested [$MeO^- \rightarrow$Bpin–NMe_2] and [*t*$BuO^- \rightarrow$Bpin–NMe_2] adducts.

was established when heating at 60°C and the small signal disappeared to show the original sp^2 Bpin signal. However, when 2 equivalents of MeOH were added, a total shift was observed towards the single signal at $\delta = 8.74$ ppm, at both room temperature and 60°C.

The scope of substrates for the preparation of β-dimethylamino carbonyl compounds was next examined. As shown in Table 2, the substrate *trans*-1-phenyl-2-buten-1-one (**4**) was

Table 2: β-Amination of α,β-unsaturated substrates with Bpin–NMe_2 (**2a**) and Bpin–NEt_2 (**2b**).[a]

Entry	Substrate	Reducing agent	Product	Conv. [%][b]
1	 **4**	Bpin–NMe_2	 **5a**	93 (84)
2	 **6**	Bpin–NMe_2	 **7**	75 (68)
3	 **8**	Bpin–NMe_2	 **9**	70 (65)
4	 **10**	Bpin–NMe_2	 **11**	20
5	 **12**	Bpin–NMe_2	 **13**	25
6	 **14**	Bpin–NMe_2	 **15**	43 (37)
7	 **16**	Bpin–NMe_2	 **17**	63 (58)
8	 **1**	Bpin–NEt_2	 **3b**	48 (27)
9	 **4**	Bpin–NEt_2	 **5b**	45 (32)
10	 **1**	Bpin–NMe_2/ $HNEt_2$	 **3a**	73[c]

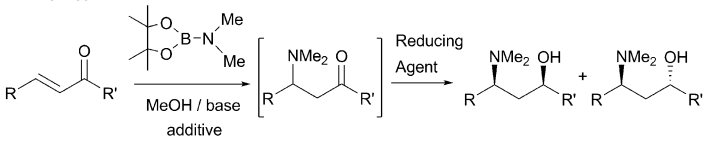
[a] Reaction conditions: substrate (0.25 mmol), Bpin–NR_2 R = Me,Et (0.27 mmol), NaO*t*Bu (15 mol%), PCy_3 (10 mol%), MeOH (2 mL), 70°C, 17 h. [b] Conversion calculated by GC/MS from an average of two reactions. The yield of the isolated product is given in parentheses. [c] 23% of product **3b** was also formed.

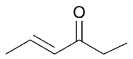
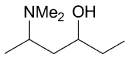
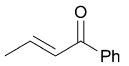
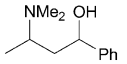
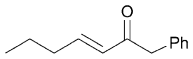
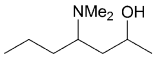
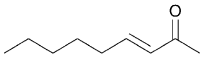
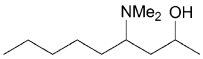
quantitatively converted into the corresponding β-dimethylamino ketone **5a** (Table 2, entry 1). However the aliphatic ketones 3-hepten-2-one (**6**) and 3-nonen-2-one (**8**) were only moderately transformed into the β-amino ketones **7** and **9**, respectively, as a consequence of the bulkier alkyl C_β substituents (Table 2, entries 2 and 3). The less efficient β-amination was observed for the chalcones **10** and **12** (Table 2, entries 4 and 5). It seems that the steric and electronic properties of the phenyl substituent on C_β diminished the nucleophilic attack of the activated aminoborane. Next, we turned our attention to explore the β-amination of the α,β-unsaturated esters methylcrotonate (**14**) and ethylcrotonate (**16**). In both cases the conversion towards the desired product was only moderate (Table 2, entries 6–7).

We also extended the organocatalytic addition of the diethylamino moiety when the aminoborane involved in the reaction was the analogue Bpin–NEt_2 (**2b**). When **2b** was activated with MeOH and base, the diethylamino moiety became nucleophilic enough to β-aminate substrates **1** and **4**, and isolate the corresponding β-diethylamino ketones in moderate yields (Table 2, entries 8 and 9). This reactivity seems to be related to the less accentuated nucleophilic character of the NEt_2 moiety in [$RO^- \rightarrow$Bpin–NEt_2] versus [$RO^- \rightarrow$Bpin–NMe_2]. To make the reaction system more suitable, we followed the elegant design by Suginome and co-workers,[8] thus taking advantage of the amino group exchange on aminoboranes with external amines. When we performed the optimized reaction on **1** (Table 2, entry 10), with 1 equivalent of [$RO^- \rightarrow$ Bpin–NMe_2] and 1 equivalent of NEt_2, the product formed was **3a** (73%) together with **3b** (27%). These preliminary experiments demonstrate the possible in situ iminium ion generation,[8] to be extended to bulkiers amines.

To highlight the role of the phosphine in this reaction, as we recently pointed out,[2b] chiral phosphines can assist the asymmetric organocatalytic β-boration of α,β-unsaturated carbonyl compounds. In this study, we explored this possibility and we conducted a parallel (β-boration with B_2pin_2) and β-amination (with Bpin–NMe_2) of the model substrate **1** in the presence of a Josiphos-type ligand. Scheme 2 shows that, under optimized reaction conditions, the asymmetric induction on the organocatalytic β-amination is lower than the corresponding organocatalytic β-boration, probably as a result of the less hindered NMe_2 versus Bpin nucleophilic counterpart.

Table 3: Synthesis of β-amino alcohols through β-dimethylamination with Bpin–NMe_2 (**2a**)/reduction.[a]



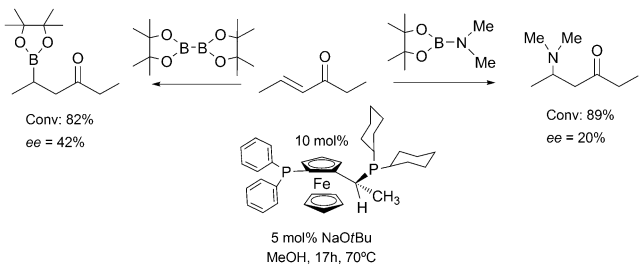
Entry	Substrate	Reducing agent	Product	Conv. [%][b]	*syn*/*anti*[c]
1	 **1**	$NaBH_4$	 **18**	90 (85)	93:7
2	 **4**	DIBALH	 **19**	95 (88)	85:15
3	 **6**	$NaBH_4$	 **20**	75 (62)	72:28
4	 **8**	$NaBH_4$	 **21**	69 (58)	62:38

[a] Reaction conditions: substrate (0.25 mmol), Bpin-NMe_2 (0.27 mmol), NaO*t*Bu (15 mol%), PCy_3(10 mol%), MeOH (2 mL), 70°C, 17 h. Reducing reagent was added at −78°C for 2 h. [b] Conversion calculated by GC/MS from an average of two reactions. The yield of the isolated *syn* isomer is given in parentheses. [c] The d.r. value was calculated from ^{1}H NMR spectroscopy. DIBALH = diisobutylaluminum hydride.

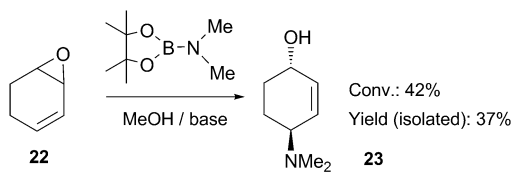
The in situ reduction of the β-dimethylamino ketones **3a**, **5a**, **7**, and **9**, led to the corresponding β-dimethyl amino alcohol with a favored *syn*/anti diastereomeric ratio depending on the reducing agent involved. Table 3 shows the high d.r. value of the *syn* β-dimethyl amino alcohols **18** and **19** when $NaBH_4$/MeOH or DIBALH respectively, was used as the reducing agent (Table 3, entries 1 and 2).

Alternatively, a complete diastereoselection was achieved on the direct amination ring-opening, through an S_N2' reaction between the adduct [$RO^- \rightarrow$Bpin–NMe_2] and the cyclic vinyl epoxide 3,4-epoxy-1-cyclohexene (**22**; Scheme 3). Therefore, 1,4-cyclohexenyl dimethylamino alcohol (**23**) was exclusively formed . When **23** was isolated and compared with the reported NMR data for this polyfunctionalized compound,[14] it was characterized as the *trans* isomer.

We then went on to explore the β-amination of the electron-deficient α,β-acethylenic carbonyl substrates in an attempt to find a direct methodology which exclusively forms



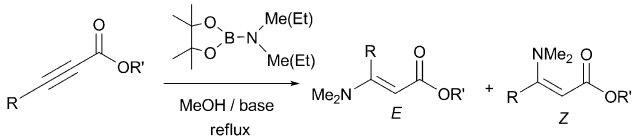
Scheme 2. Asymmetric β-amination reactions assisted by a Josiphos-type ligand. Comparison with the corresponding β-boration reaction.

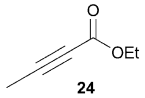
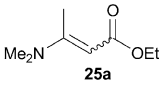
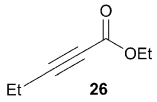
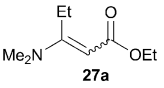
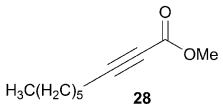
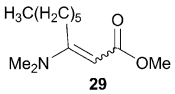
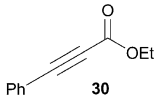
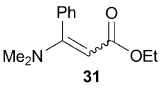
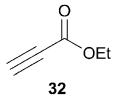
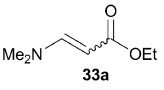
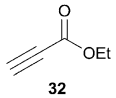
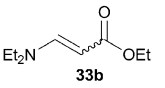
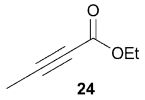
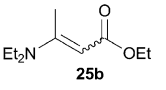
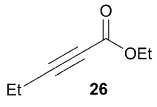
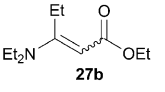


Scheme 3. Diastereoselective amination ring opening of 3,4-epoxy-1-cyclohexene (**22**) with [$RO^- \rightarrow$Bpin–NMe_2].

the *E* isomer of the corresponding β-enamino ester. Although β-enamino derivatives are of considerable interest, both as bioactive leads and versatile building blocks,[15] they have mainly been synthesized by the direct condensation of 1,3-dicarbonyl compounds with ammonia and primary amines.[16] In these protocols, the *Z* isomer of the β-enamino ester was the main product formed. However, when we conducted the β-amination of ethyl-2-butynoate (**24**) and ethyl-2-pentynoate (**26**) with Bpin–NMe_2, the *E* isomer of the β-enamino ester was preferentially formed (Table 4, entry 1–3), probably as a consequence of the bulky properties of the [$RO^- \rightarrow$Bpin–NMe_2] adduct. For those substrates which had bulkier substituents on C_β, the *E*-β-enamino ester was exclusively formed (Table 4, entries 4 and 5). The total β-amination of the terminal α,β-acethylenic ester **32**, by adding Bpin-NMe_2 or Bpin-NEt_2, was carried out in shorter reaction times (1 h and 3 h, respectively; Table 4, entries 6 and 7). Finally, *E*-β-enamino esters were selectively formed from the reaction of Bpin–NEt_2 with ethyl-2-butynoate (**24**) and ethyl-2-pentynoate (**26**; Table 4, entries 8 and 9). Interestingly, test experiments based on direct reactivity of dimethylamine or diethylamine with the model substrate **24** did not lead to the formation of either the *E*- or *Z*-β-enamino ester. The implication of the aminoborane methodology opens a a new pathway towards direct synthesis of *E*-β-enamino ester through conjugate addition.

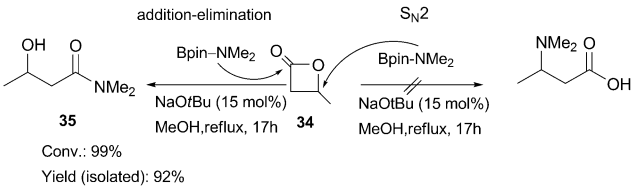
Table 4: β-Amination of the electron-deficient α,β-acethylenic carbonyl substrates with Bpin–NMe_2 (**2a**) and Bpin–NEt_2 (**2b**).[a]



Entry	Substrate	Product	Conv. [%][b]	*E*/*Z*[c]
1[d]	 **24**	 **25a**	75	85:15
2			81 (68)	84:16
3	 **26**	 **27a**	80 (74)	88:12
4	 **28**	 **29**	75 (63)	99:1
5	 **30**	 **31**	93 (85)	99:1
6[e]	 **32**	 **33a**	99 (93)	99:1
7[f]	 **32**	 **33b**	99 (93)	99:1
8	 **24**	 **25b**	70 (62)	99:1
9	 **26**	 **27b**	67 (60)	99:1

[a] Reaction conditions: substrate (0.25 mmol), Bpin-NR_2 (1.5 equiv), NaO*t*Bu (25 mol%), MeOH (2 mL), reflux, 17 h. [b] Conversion calculated by GC/MS from an average of two reactions. The yield of the isolated product is given in parentheses. [c] *Z*/*E* ratio calculated from ^{1}H NMR spectroscopy. [d] NaO*t*Bu (15 mol%). [e] 1 h. [f] 3 h.

To complete this survey of amination through aminoboranes, we became interested in reacting Bpin–NMe_2 with β-lactones to elucidate the nucleophilic character of the amino moiety in the adduct [$RO^- \rightarrow$Bpin–NMe_2]. As it has been described,[17] hard nucleophiles express a strong preference for addition to the lactone carbonyl group, thus providing ring opening by an addition-elimination pathway.[18] Alternatively, soft nucleophiles achieve better electronic matching with the electrophilic C_β, thereby promoting S_N2 displacement of the carboxylate residue (Scheme 4).[19] When we reacted Bpin–NMe_2 with β-butyrolactone (**34**) in MeOH/base media, the only product observed was the β-hydroxy N-dimethyl amide, thus evidencing the hard nucleophilic character of the amino moiety. This type of compound has also been recently prepared from the copper-[20a] or nickel-catalyzed[20b] β-boration of α,β-unsaturated amides with B_2pin_2 with a subsequent oxidation pathway. We were delighted to see the complementary organocatalytic fomation of the desired product in a one-step reaction.



Scheme 4. Hypothetical reactivity of activated aminoboranes with β-butyrolactone.

In conclusion, the simple Lewis acid–base interaction of aminoboranes with alkoxides, which forms the adduct [$RO^- \rightarrow B(OR)_2$–$N(R')_2$] in situ, seems to be the platform to enhance the nucleophilic attack of amino moieties towards electron-deficient olefins such as α,β-unsaturated carbonyl compounds and cyclic vinyl epoxides. Following a simple one-pot reaction, the 1,3-dialkylamino alcohols and 1,4-dialkylamino alcohols can be isolated in moderate to high yield. Extension of this methodology to more sterically demanding aminoboranes is currently under study.

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