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Recent developments in the synthesis and synthetic applications of borane–amines

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Borane–amine complexes occupy an increasingly important position in modern main-group chemistry. Their tunable electronic and steric properties offer a balance between the high reactivity of borane and enhanced stability provided by amine coordination, making them unique reagents for organic synthesis and materials chemistry. This feature article presents a review of the recent advances in the synthesis of borane–amines, as well as their diverse synthetic applications. The main synthetic strategies for the preparation of borane–amines, direct reaction with diborane or *in situ* generated borane, salt metathesis, and Lewis base exchange, are discussed in detail with emphasis on recent protocols and borane–ammonia preparation techniques. Applications of borane–amines in organic synthesis where they serve as selective and more easily handled alternatives to traditional borane reagents include reduction, reductive amination, and hydroboration reactions. Recent progress demonstrates that beyond their use as practical borane alternatives, borane–amines offer distinct mechanistic and synthetic utility in transfer hydrogenation, borylation, B–H insertion, as sources of amine–ligated boryl radicals, and as amine surrogates in amidation methodologies. This feature article aims to consolidate recent developments in well-known reactions and emerging methodologies, as well as underscore the growing role of borane–amines as adaptable tools in synthetic organic chemistry.

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1. Introduction

Borane (BH_3) is an electron-deficient,[1] highly reactive species which is rarely observed under ambient conditions; instead, it typically exists as the dimer (B_2H_6),[2] a pyrophoric gas with strong Lewis acidity.[3] While diborane's reactivity underpins its early applications in semiconductor doping,[4] polymerization catalysis,[5] and rocket propellants,[6] it also poses significant hazards in handling the material. A practical solution is the stabilization of BH_3 *via* Lewis base coordination, as is the case with borane–tetrahydrofuran (BTHF) and borane–dimethylsulfide

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(BMS). Borane–amines combine the synthetic utility of BH_3 with enhanced air and moisture stability, with the added benefit of tunable reactivity, depending on the coordinated amine.

While several reviews have addressed specific aspects of borane–amine chemistry,[7–13] to date, comprehensive summaries explicitly focusing on the methods of borane–amine synthesis and their broad range of synthetic applications remain limited. This feature article aims to fill that gap with the purpose of highlighting the distinct reactivity and promoting the versatility of borane–amines as synthetic reagents. We provide a systematic outline in the progress of borane–amine synthesis, including functionalized examples, as well as their applications in synthetic organic chemistry. In the section on borane–amine synthesis we detail the main synthetic strategies for their preparation, suggest the best contemporary routes for the synthesis of specific complexes, and provide characterization details on a wide range of previously prepared examples. Several syntheses of borane–amines and borane–ammonia have been recently reported,[14–18] circumventing prior difficult synthesis and high commercial cost, which should facilitate further development of this area.

The discussion on synthetic applications of borane–amines is organized by reaction type and focused on recent reports, highlighting our contributions to the field. The characteristic reactions of borane–amines are discussed, with emphasis on the aspects of those reactions which are uniquely possible with borane–amine chemistry. Due to space limitations, several aspects of borane–amine chemistry have not been described, including their conversion to related derivatives such as aminoboranes and aminoborohydrides, and their use as polarity reversal catalysts in hydrogen atom transfer reactions. The applications of borane–amines in materials chemistry, including hydrogen storage applications, are also not detailed in this review. Any omission of specific references within the discussed areas is inadvertent, and all efforts were made to include all recent, relevant references.

The title compounds of this review are referred to in literature as both borane–amines and alternately as amine–boranes, we have opted to use borane–amine throughout this review to maintain consistency with other borane complexes, such as borane–tetrahydrofuran and borane–dimethylsulfide.

2. Synthesis of borane–amines

The first true borane–amine, borane–trimethylamine, was synthesized in 1937 by Burg and Schlesinger.[19] This foundational discovery laid the groundwork for the broad utility of borane–amines in synthesis and materials chemistry. Since this first synthesis, numerous methods for generalized borane–amine synthesis have been developed, driven by growing interest in their synthetic and materials applications. These methods vary by the source of boron, type of amine, and reaction conditions. Three main strategies dominate borane–amine synthesis: reaction with diborane or *in situ* generated borane, salt metathesis, and Lewis base exchange.

2.1 Properties and stability of borane–amines

These complexes are formed by the donation of a nitrogen lone pair from an amine to the electron-deficient boron in borane (BH_3), resulting in a dative (coordinate) bond. This interaction alters boron's geometry from trigonal planar (sp^2) to tetrahedral (sp^3), producing, in the case of coordination with ammonia, a molecule similar in shape to ethane but electronically distinct.[20]

In borane–amines, bond lengths and angles shift upon complexation, reflecting this hybridization change, and produce a polarized B–N bond.[21] The intrinsic electronegativities of nitrogen and boron also result in slightly acidic N–H bonds and hydridic B–H bonds. This molecular and bond polarity promotes both dipole–dipole interactions and distinctive dihydrogen bonding (attraction between $H^{\delta+}$ on nitrogen and $H^{\delta-}$ on boron),[22] and account for the high melting point of borane–amines relative to nonpolar analogues.

The stability of borane–amines is influenced by electronic factors, such as the Lewis basicity of the amine (estimated *via* the pK_a of its conjugate acid), and steric hindrance, which can reduce bond strength due to poor orbital overlap.[23–25] Amines with conjugate acid pK_a values >5, aliphatic amines for examples, typically form stable complexes, whereas aryl and heteroaromatic amines (*e.g.*, aniline, pyridine) whose conjugate acid $pK_a \approx 5$, form less stable or only moderately stable adducts.[7] Amines whose conjugate acid pK_a is substantially <5 (*e.g.*, pyrrole, pyrimidines) tend not form adducts with borane or form only highly unstable adducts. Steric hinderance can offset strong Lewis basicity, as in borane–triisobutylamine, which is weakly bound despite a strongly donating nitrogen.

While predictive rules (like conjugate acid pK_a) and inference of complex stability using ^{11}B NMR chemical shift values[26] offer useful guidance, borane–amine stability ultimately depends on a combination of electronic, steric, and solvation effects. Successful synthesis and isolation remains the most reliable method for determining if a complex can be formed, with the absence of decomposition over long-term storage the best indicator of stability.

2.2 Reaction with diborane or *in situ* generated borane

The first synthesis of borane–trimethylamine is of obvious fundamental importance to the development of borane–amine chemistry. This synthesis was achieved *via* reaction of diborane with excess carbon monoxide to generate a borane–carbonyl intermediate (BH_3CO). Displacement of carbon monoxide by trimethylamine yielded the corresponding amine complex in what amounts to a Lewis base exchange reaction. However, this method was quickly superseded by direct reaction of diborane with trimethylamine and later pyridine.[27]

The numerous subsequent methods which were devised for the preparation of diborane can be divided into two categories, the reduction of boron trihalides or trialkylboranes using metal hydrides,[28–31] and the reaction of borohydride salts with Brønsted or Lewis acids.[32–39] Several of these routes of diborane generation have been used for the preparation of

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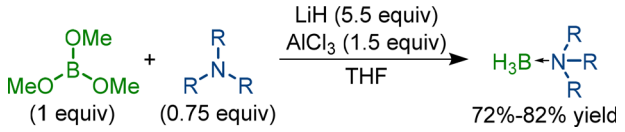


Scheme 1 One-pot synthesis of borane–trialkylamines from trimethyl borate. Adapted from ref. 42 with permission from the American Chemical Society,[42] Copyright 2012.

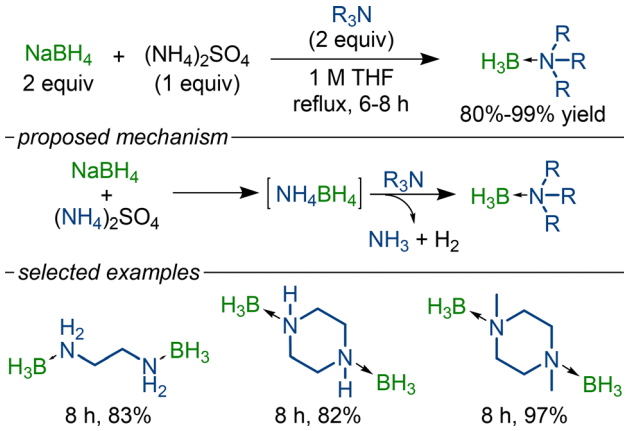
borane–amines. When performed in the presence of an amine, the *in situ* generated borane readily forms the corresponding borane–amine complex. Hydrogenolysis of trialkylboranes (R_3B),[29] sodium hydride reduction of boron trichloride,[31] reduction of boron trifluoride–diethyl etherate with sodium borohydride ($NaBH_4$),[38] and the reaction of $NaBH_4$ with iodine[39] have each been used for this purpose. Closely related methods are also the primary means of preparing the aluminum analog alane–amines.[40,41]

While methods utilizing *in situ* borane generation are used infrequently for the preparation of borane–amines, they are unique in that they start from boron precursors other than $NaBH_4$, as is the case for salt metathesis and Lewis base exchange protocols. Our reported synthesis of borane–trialkylamines employed trimethyl borate as a boron source (Scheme 1).[42] *In situ* borane generation was accomplished from trimethyl borate using lithium hydride and aluminum trichloride in tetrahydrofuran (THF). Capture of the produced borane by trialkyl and heteroaromatic amines provided the corresponding borane–amines in yields of 70% to 82%. There remains much untapped potential in such syntheses which circumvent the use of $NaBH_4$ and employ reductants which are less energy intensive to produce than NaH for the conversion of alternative boron sources to borane–amines.

2.3 Salt metathesis reactions

The second main strategy for borane–amine synthesis is the salt metathesis reaction which involves ion exchange between an ammonium salt and a metal borohydride, typically $NaBH_4$ or lithium borohydride ($LiBH_4$), followed by *in situ* dehydrogenation. This approach is more practical for routine laboratory application with the key advantage of using safer, more stable reagents, avoiding the handling of gaseous diborane. Initial reports using this strategy utilized $LiBH_4$ with di- and trimethylammonium chloride,[43] although subsequent systematic study would expand this scope significantly.[44] Following declassification and publication of Brown and Schlesinger's method for the production of $NaBH_4$,[45] salt metathesis protocols using $NaBH_4$ soon followed.[46] $NaBH_4$ is more convenient to handle than $LiBH_4$ which is flammable and moisture sensitive.

A primary disadvantage of the early salt metathesis protocols is the necessary use of the ammonium salt of the desired amine. This salt must either be prepared or purchased, although the selection of commercially available salts is limited. Based on earlier work in our group on the synthesis of borane–ammonia *via* salt metathesis[47] and borane–amines *via* transamination[48] (discussed in subsequent sections), we



Scheme 2 Synthesis of borane–amines *via* tandem nucleophilic attack-dehydrogenation of ammonium borohydride intermediate. Adapted from ref. 49 with permission from the American Chemical Society,[49] Copyright 2015.

have devised several procedures for the preparation of borane–amines *via* salt metathesis which utilize the free amine as starting material. The first of these protocols was initially proposed as a tandem amine–ammonium salt equilibration–metathesis sequence with ammonium sulfate and the added amine undergoing an equilibration, being driven to the formation of the new ammonium salt by liberation of ammonia from the reaction. However, it is now believed that ammonium borohydride formed *via* salt metathesis undergoes a tandem nucleophilic attack–dehydrogenation by the added amine (Scheme 2).[49] Using this methodology a variety of aliphatic and heteroaromatic amines were converted to the corresponding borane–amines in 80% to 99% yields under refluxing conditions.

Following our above report on the amine/ammonium salt metathesis sequence we pursued alternatives to the use of ammonium salts. While the alkylammonium sulfate intermediate was readily formed at room temperature, leading to the desired borane–amine, borane–ammonia was also formed by a competing pathway. Elevated temperatures were required to transaminate borane–ammonia to the desired borane–amine. To avoid the formation of borane–ammonia as a side product we proposed the use of mild acids for *in situ*

formation of the requisite ammonium salt. It was found that carbonic acid, produced using a combination of sodium bicarbonate and water, would form the corresponding ammonium bicarbonate with the added amine. Following salt metathesis with $NaBH_4$ and dehydrogenation, the desired borane–amines were prepared with no side product formation.[15] This methodology was used to synthesize a wide range of borane–amines from primary, secondary, tertiary, and heteroaromatic amines (Scheme 3). It was additionally found that this protocol could be applied to amines bearing functional groups which would not be tolerated in methods using diborane, BTHF, or BMS, including alcohols, alkenes, alkynes, nitriles, and silyl ethers (Scheme 3). A validated report on the bicarbonate mediated synthesis of borane–amines has been detailed in Organic Syntheses.[50]

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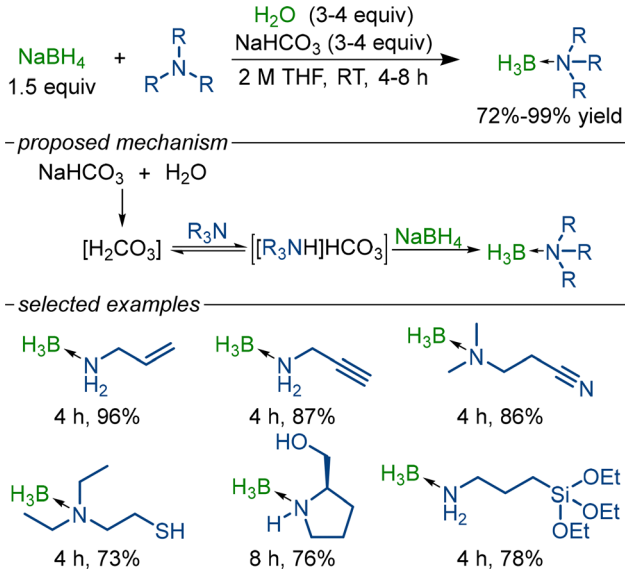
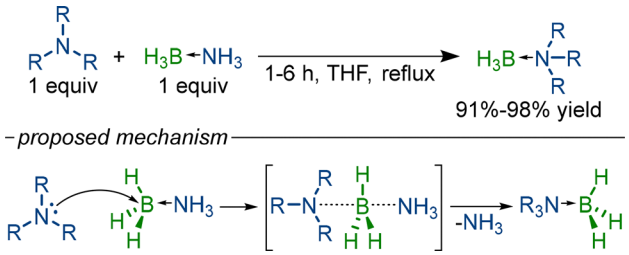


Scheme 3 Bicarbonate–mediated synthesis of borane–amines; access to substrates bearing borane-incompatible functionalities. Adapted from ref. 15 with permission from the Royal Society of Chemistry,[15] Copyright 2016.

The mild conditions and ability to produce functionalized borane–amines are clear advantages of the bicarbonate mediated protocol over other salt metathesis procedures. However, traditional salt metathesis between $NaBH_4$ and an ammonium salt is superior when the free amine would be gaseous under the reaction conditions (*i.e.* methylamine, ethylamine, *etc.*), particularly in the case of ammonia which will be discussed in an upcoming section.

2.4 Lewis base exchanges reactions

The third primary approach to borane–amine synthesis are the Lewis base exchange protocols. New borane–amine complexes are formed by displacing a weaker Lewis base from one borane complex (like BTHF or BMS) with a more Lewis basic amine. The first borane–amine synthesis utilized this strategy, displacing carbon monoxide from borane–carbonyl (BH_3CO) using trimethylamine.[19] This, however, required the use of diborane to generate the BH_3CO intermediate *via* reaction with carbon monoxide. Borane–trimethylamine was subsequently prepared *via* Lewis base exchange using borane–pyridine,[27] although this required separation of pyridine from the product. The advent of borane–tetrahydrofuran (BTHF) made the handling of borane more convenient,[51,52] and its use in the preparation of borane–amines was reported shortly after.[53] The sulfur complex of borane, borane–dimethyl sulfide (BMS), although discovered shortly after BTHF,[54] was not employed for the preparation of borane–amines *via* Lewis base exchange until many years later.[55] BMS has several advantages over BTHF, including increased stability[56] and the higher concentration[57] at which it can be prepared. BMS does, however, release malodorous dimethylsulfide, and both BMS and BTHF are moisture sensitive. The difficulties encountered when using BTHF or BMS for



Scheme 4 Nucleophilic displacement of ammonia from borane–ammonia for the preparation of borane–amines. Adapted from ref. 48 with permission from the Royal Society of Chemistry,[48] Copyright 2014.

the preparation of borane–amines *via* Lewis base exchange can be overcome by using borane–amines themselves for the reaction. The earlier report using borane–pyridine,[27] and later kinetic studies,[58] prompted us to investigate the possibility of using borane–ammonia for this purpose which would preclude the purification step due to liberation of gaseous ammonia.[48] It was found that near quantitative yields of borane–amines and borane–phosphines were achieved upon refluxing an equimolar mixture of borane–ammonia and the desired amine/phosphine in THF (Scheme 4). The reaction is proposed to occur *via* a nucleophilic substitution at boron (S_N2B), driven by liberation of ammonia, a mechanism which had earlier been proposed for the exchange of phosphines with borane–amines.[59]

Subsequent to our earlier report on the bicarbonate mediated salt metathesis procedure for borane–amine synthesis,[15] we undertook an in-depth examination of past reports mediated by carbon dioxide (CO_2).[60–62] These prior protocols had been applied only to the preparation of borane complexes with tertiary amines, had limited scope, and the mechanism of formation was not fully understood. It was our initial hypothesis that combining water and CO_2 would form carbonic acid, as had been proposed for the bicarbonate-mediated protocol. However, during our examination of the CO_2-mediated reaction it was found that water was not required for borane–amine formation (Scheme 5).[63] Detailed ^{11}B NMR study found that CO_2 was reduced by $NaBH_4$, forming a sodium monoformatoborohydride intermediate. The weakly bound formate ligand of this intermediate was then displaced by the added amine in a Lewis base exchange reaction. Further evidence of such a mechanism was provided by the activation of $NaBH_4$ using other carbonyl compounds (propanal, benzaldehyde, isobutyraldehyde, acetone, acetophenone). The resulting monoalkoxyborohydride intermediates reacted similarly with amines to provide the borane–amine complexes, however, this technique required separation of the resulting alcohols. CO_2 was determined to be the optimal activator providing borane–amines in 73% to 99% yields (Scheme 5). Quantitative to excellent yields were realized for tertiary or heteroaromatic amines, but formation of ammonium carbamate side-product with primary and secondary amines resulted in slightly decreased yields for those substrates.

The study of alternative $NaBH_4$ activators for borane–amine synthesis was later expanded to include carboxylic acids,[64,65]

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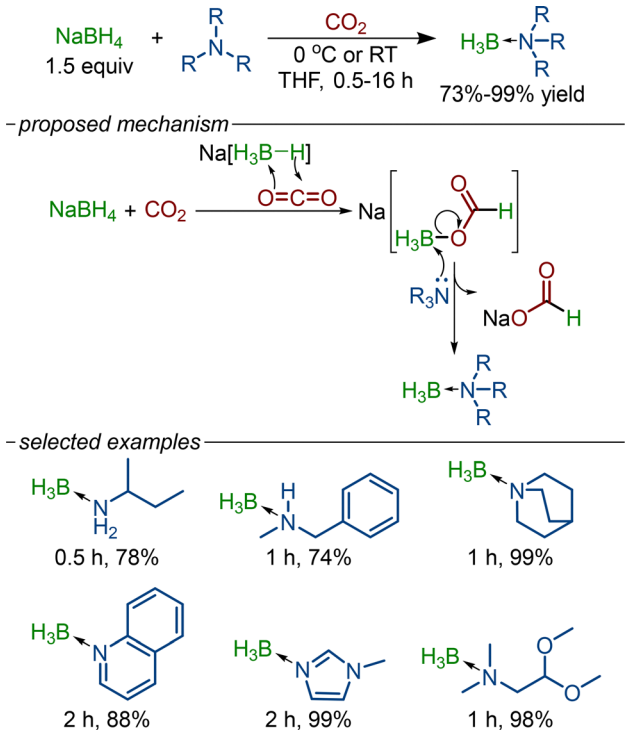
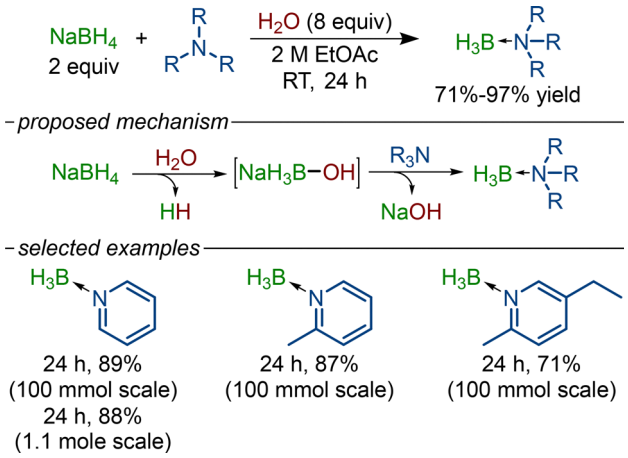


Scheme 5 Activation of sodium borohydride *via* carbon dioxide reduction for the synthesis of borane–amines. Adapted from ref. 63 with permission from the Royal Society of Chemistry,[63] Copyright 2021.

sulfonic acids, alcohols, and water. Replacement of the reaction solvent THF with a more environmentally benign alternative was also examined. These investigations revealed that water could play the role of activator when ethyl acetate (EtOAc) was used as the reaction solvent. No borane–amine was produced when water was used as an activator in THF, indicating a unique solvent dependency. These results led ultimately to the development of a greener approach to borane–amine synthesis.[17] Using a heterogeneous EtOAc/water solvent system, with water playing a dual role as solvent and activator of $NaBH_4$, primary, secondary, tertiary, and heteroaromatic amine complexes with borane could be prepared (Scheme 6), with a monohydroxy–borohydride intermediate proposed as the reactive species. This methodology was applied to the scaled-up preparation of several heteroaromatic borane–amines which are commonly used for reductive amination. Pyridine, 2-picoline, and 5-ethyl-2-methylpyridine were converted to the corresponding borane complexes in 71% to 89% yields at 100 mmol scale. Borane–pyridine was further scaled-up to 1.1 mole scale, where a yield of 88% was achieved. In general, the successful replacement of THF with EtOAc and utilization of environmentally benign activators of $NaBH_4$ are important steps in the development of greener protocols for the synthesis of borane–amines.

2.5 Synthesis of borane–ammonia

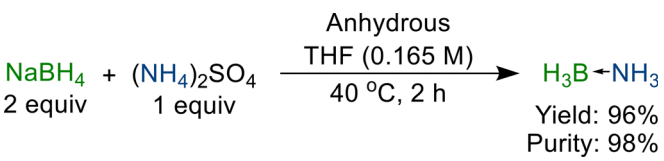
Given the status of borane–ammonia as the prototypical example of a borane–amine, and its importance in organic synthesis



Scheme 6 Water-mediated synthesis of borane–amines in ethyl acetate as a green alternative to tetrahydrofuran. Adapted from ref. 17 with permission from the American Chemical Society,[17] Copyright 2023.

and materials chemistry, it seems appropriate to discuss its synthesis specifically. Aside from its importance, specialized methods are often required to prepare borane–ammonia. Many of the reactions typically used to prepare borane–amines give unwanted byproducts when applied to the preparation of borane–ammonia. Reaction of ammonia with diborane, for example, yields the ionic $[(NH_3)_2BH_2][BH_4]$ diammoniate of diborane (DADB) *via* asymmetrical cleavage of diborane.[66] Other borane Lewis base adducts such as BTHF,[67] BMS,[68] and borane–OMe_2,[69] react with ammonia to give mixtures of borane–ammonia and the diammoniate. While pure borane–ammonia can be obtained from these procedures by recrystallization,[70] synthetic approaches utilizing salt metathesis are more convenient. Early salt metathesis protocols for preparing borane–ammonia reacted $LiBH_4$ with either ammonium chloride or ammonium sulfate to give isolated yields of 45% after purification.[71] Later replacement of $LiBH_4$ with the more easily handled and cost effective $NaBH_4$ gave dramatically improved yields of 80% when reacted with ammonium carbonate.[72]

Continuing the search for an efficient and economical synthesis of borane–ammonia, our group undertook a systematic study of the salt metathesis reaction.[47] A thorough examination of various ammonium salts and reaction solvents determined that reaction of ammonium sulfate with $NaBH_4$ in anhydrous THF at 40 °C for 2 hours would provide a 96% yield of borane–ammonia with a purity of 98% (Scheme 7). However, the low solubility of $NaBH_4$ in THF necessitated a



Scheme 7 Synthesis of borane–ammonia *via* salt metathesis in tetrahydrofuran. Adapted from ref. 47 with permission from the American Chemical Society,[47] Copyright 2007.

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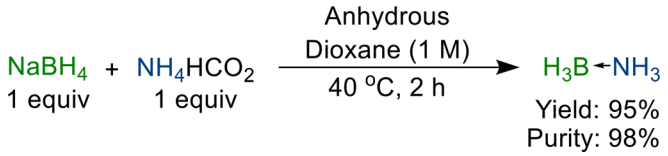
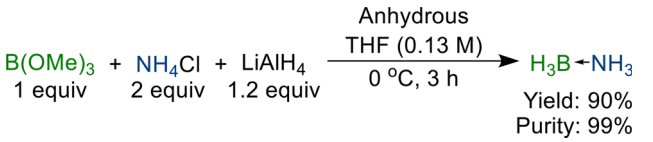


Scheme 8 Synthesis of borane–ammonia *via* salt metathesis at increased concentration in dioxane. Adapted from ref. 47 with permission from the American Chemical Society,[47] Copyright 2007.

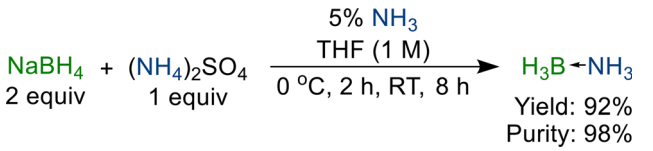


Scheme 9 *In situ* reduction of trimethyl borate for the synthesis of borane–ammonia. Adapted from ref. 42 with permission from the American Chemical Society,[42] Copyright 2012.

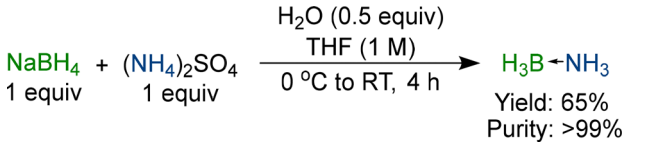
dilute 0.165 M reaction concentration. As part of the same study, we proposed an alternative method which reacted ammonium formate with $NaBH_4$ in dioxane, allowing for an increased concentration of 1 M, while providing borane–ammonia in similar yield and purity (Scheme 8).

A separate investigation of alternative boron sources by our group, described earlier for the synthesis of borane–amines, found that trimethyl borate when reacted with lithium aluminum hydride and ammonium chloride would produce borane–ammonia in 0.13 M THF (Scheme 9).[42] This process provided a 90% yield of 99% pure borane–ammonia, however, the handling of lithium aluminum hydride and necessity of very carefully controlled addition are hinderances to large-scale preparations.

Nearly quantitative yields of borane–ammonia were achieved *via* a two-step synthesis wherein ammonium borohydride was prepared by the salt metathesis reaction of ammonium chloride and $NaBH_4$ in liquid ammonia.[73] Dehydrogenative decomposition of the ammonium borohydride in THF subsequently provided borane–ammonia. The higher solubility of $NaBH_4$ in liquid ammonia as solvent[45] prompted our group to investigate the use of ammonia as an additive to improve solubility. It was found that reaction concentration of up to 2 M in THF could be attained by using 5% ammonia. The borane–ammonia prepared by the salt metathesis of $NaBH_4$ and ammonium sulfate using this solvent system was produced in 92% yield and 98% purity (Scheme 10).[14] This protocol was demonstrated in up to 10 mole scale with the same yield and purity. It was later found



Scheme 10 Ammonia-mediated synthesis of borane–ammonia. Adapted from ref. 14 with permission from the Royal Society of Chemistry,[14] Copyright 2014.



Scheme 11 Water-mediated synthesis of borane–ammonia. Adapted from ref. 16 with permission from Elsevier,[16] Copyright 2017.

that while ammonia was initially added to increase the reagent solubility, the added ammonia was incorporated into the borane–ammonia product.[74] This finding was uncovered during our investigations on the earlier described tandem nucleophilic attack–dehydrogenation protocol for borane–amine synthesis.[49]

Many of the methodologies described for the synthesis of borane–ammonia have limitations preventing their large-scale utilization. Low reaction concentration, anhydrous solvents, low reaction temperature, and the use of liquid ammonia are several factors making safe and convenient implementation difficult. Seeking a more energy efficient, non-toxic replacement for ammonia, our group later discovered that using water as an activator in borane–ammonia synthesis addresses the limitations described above. The salt metathesis reaction between $NaBH_4$ and ammonium sulfate in 1 M THF under ambient conditions using 0.5 molar equivalents of water was found to produce borane–ammonia of exceptional (>99%) purity (Scheme 11).[16] The lowered yield of 65% is attributed to the reaction of water with the intermediate ammonium borohydride, although this loss was deemed acceptable for laboratory scale reactions in light of the simplicity of the protocol and the high purity of the product. A validated step-by-step protocol for the water-mediated synthesis of borane–ammonia has been detailed in Organic Syntheses.[18]

2.6 Synthetic approaches to borane–amines

Owing to the diversity of protocols for borane–amine synthesis, and the variety of potential amine substrates, some guidelines for selecting an appropriate methodology to prepare specific borane–amines may be helpful. Not all methods work equally for all amines, and the optimal preparative method can depend on the structure of the amine, the physical state of the amine, availability of ammonium salt, and the presence of functional groups. Generally, amines which are gases under standard conditions (ammonia, methylamine, trimethylamine, *etc.*) are most simply converted to their borane complexes using salt metathesis between $NaBH_4$ and the corresponding ammonium salt. Weakly basic amines (anilines, polyamines, *etc.*) can sometimes be prepared using salt metathesis protocols, depending on the stability of the resulting borane–amine, however, Lewis base exchange with BMS is the generally preferred, although direct reaction with diborane may be required in the cases of especially weakly basic amines. Most amines which are liquid or solid under standard conditions and are at least moderately basic (conjugate acid $pK_a > 5$), can be prepared from the free amine and $NaBH_4$ either by metathesis with *in situ* generated ammonium salt[15,49] or Lewis base exchange with a derivatized

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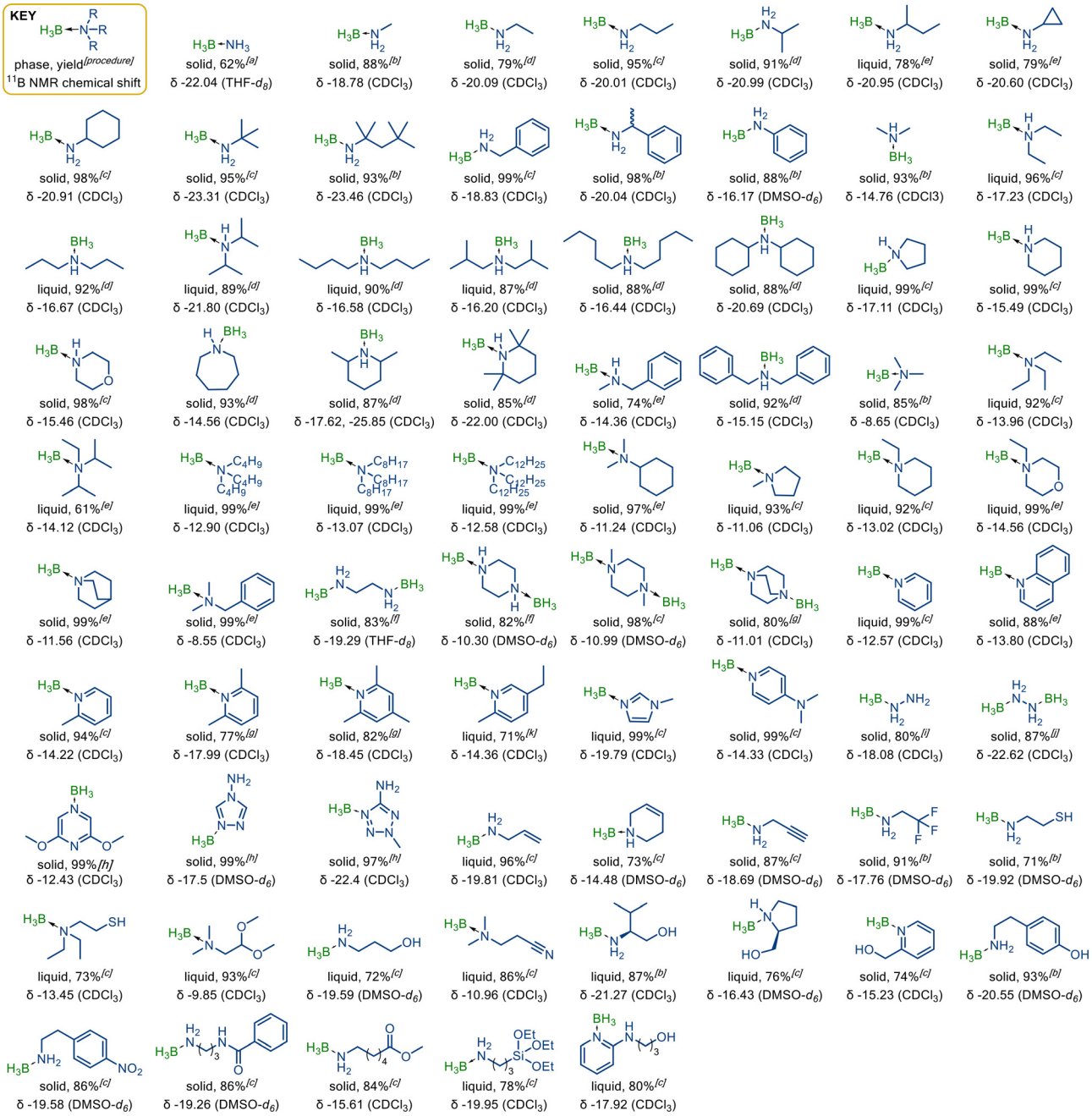

Fig. 1 Borane–amines prepared by various routes are shown with their physical state, % yield, ^{11}B NMR chemical shift value, and the procedure used for their preparation. Procedures: [a]ref. 18, [b]ref. 93, [c]ref. 15, [d]ref. 94, [e]ref. 63, [f]ref. 49, [g]ref. 42, [h]ref. 95, [i]ref. 96, [j]ref. 97, [k]ref. 17.

borohydride.[17,63] Our group has prepared a wide range of borane–amines in the development of dedicated borane–amine synthesis protocols and synthetic methodologies utilizing borane–amines. Fig. 1 displays those borane–amines which we have recently prepared, along with the reference containing the procedure for their preparation, the yield obtained, and the ^{11}B NMR chemical shift value observed for each example. The method used to prepare each borane–amine is by no means the only viable route but highlights one practical preparation. Our group has recently published independently verified step-by-step procedures for the preparation of borane–ammonia[18] and borane–amines,[50] which can be followed to obtain the majority of the borane–amines shown in Fig. 1. It is our hope that by making borane–amine synthesis protocols easily accessible, and highlighting their structural diversity, their unique chemistry can continue to be explored and expanded.

3. Applications of borane–amines

Since their discovery, borane–amines have become versatile tools in organic synthesis and materials chemistry. Their enhanced

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stability compared to other borane reagents allows them to function effectively under conditions where BTHF or BMS are impractical. In practice the stability of borane–amines must be balanced with their reactivity. The interactions which make them easier to handle, can attenuate reactivity, necessitating adjustment of reaction conditions, the use of additional reagents for activation, or careful selection of specific adducts. Borane–amines have been widely applied in organic and materials chemistry. They are employed in reactions characteristic of other borane reagents, such as reduction, and hydroboration, as well as reactions which are unique to borane–amines, including reductive amination, borylation, and amidation. Materials chemistry applications of borane–amines include application as reductants for nanoparticle synthesis,[75–77] hypergolic rocket propellants and energetic materials,[78–80] precursors for the synthesis of BN materials,[81–83] precursors for chemical vapor deposition,[84,85] and hydrogen storage media.[86–88] The materials chemistry applications of borane–amines, including hydrogen storage applications, though important, will not be a subject of this review; only organic transformations are discussed.

3.1 Reduction

Borane–amines are able to reduce a variety of functional groups, though their reactivity is generally milder than that of other borane reagents (BMS, BTHF, diborane) or borohydrides. Borane complexes with tertiary amines (*e.g.*, pyridine–borane, *N*,*N*-dimethylethylamine) were the first examples prepared and examined as reductants. However, they were limited to reducing only reactive carbonyl compounds (*e.g.*, aldehydes, acid chlorides, aryl ketones) at elevated temperatures.[89] However, improved methods using Lewis acid activation,[90] protic solvents,[91] and boranes with weakly bound bulky[92] and/or arylamines[98] expanded their scope to include more resistant substrates like carboxylic acids, amides, lactams, imines, oximes, and indoles. Selective and asymmetric reductions were made possible using chiral borane–amines.[99,100] Prior reviews adequately summarize this earlier literature on reductions using borane–amines.[7,8]

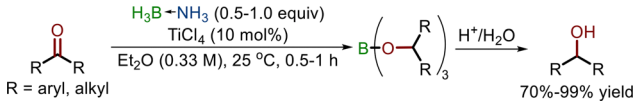
Recent advances in reductions using borane–amines have mostly utilized borane complexes with secondary or primary amines or ammonia. This is due to the greater reducing power of these reagents over their tertiary amine counterparts. In general, the reducing power of borane–amines decreases with increased alkyl group substitution on the amine. This is likely due to the confluence of inductive effects, ability to participate in transfer hydrogenation, and the greater quantity of available hydrogen, particularly on borane–ammonia.[101,102] Application of borane–amines to various functional group reductions are described individually in the following sections.

3.1.1 Aldehydes and ketones. The reduction of aldehydes and ketones to the corresponding alcohols is a fundamental transformation in organic chemistry. As such, borane–amines have been explored for this purpose for several decades.[89,103–111] In contrast with many earlier carbonyl reduction methodologies, borane–ammonia is now typically the reductant of choice. Recent approaches have emphasized the development of more environmentally friendly protocols, the use of transition metal catalysts, and conversion to more reactive borane–amine derivatives.

The use of protic solvent systems,[105] including water,[112] has been demonstrated to increase the efficacy of carbonyl reductions using borane–amines. However, this approach is seen to be most effective for aldehyde reduction, with ketone reduction remaining sluggish (>24 h for some examples). Prior reports on the use of superstoichiometric Lewis acids (BF_3,[90] $TiCl_4$) to promote the diastereoselective reduction of 1,3-diketones,[109] β-hydroxy ketones,[110] β-alkoxy ketones, and β-keto esters[108] using borane–pyridine and other borane–amines, prompted our investigation into the use of catalytic $TiCl_4$ promoted ketones reduction.[113] It was revealed that 10 mol% $TiCl_4$ promoted a highly facile reduction of diaryl, dialkyl, and aralkyl ketones in under 1 h using borane–ammonia as the reductant, even for previously slow reductions of diarylketones (Scheme 12). Reduction of substituted cyclic alkanones displayed diastereoselectivities in line with other hydride reducing agents, and chemoselective reductions in the presence of carboxylic acids and esters showed highly selective, but not specific, reduction of the ketone carbonyl.

The mechanism by which carbonyls are reduced by borane–ammonia has been a matter of some debate.[114–117] The observed formation of borate ester intermediates suggests hydroboration of the carbonyl. However, theoretical investigations point toward a slightly more complex mechanism where an initial transfer of hydrogen from the N and B of borane–ammonia to the O and C of the carbonyl, respectively, is followed by alcoholysis of the BH_2NH_2 byproduct.[118] This transfer hydrogenation and alcoholysis sequence would then provide the same initial borate intermediate one would expect if hydroboration were the predominant mechanism.

Mechanistic uncertainties aside, it was discovered through the course of our investigation that multiple alternative reduction products were accessible using the $TiCl_4$ and borane–ammonia reagent system. Simple adjustment of their relative stoichiometry enabled direct isolation of the benzylic halides[119] or completely deoxygenated alkanes from the corresponding aromatic aldehydes and ketones. Further stoichiometric modifications enabled conversion of the benzylic alcohols or halides to deoxygenated alkanes, as well as conversion of benzylic alcohols to the corresponding halides using $TiCl_4$ alone (Scheme 13).[120] Apart from the initial carbonyl reduction to the alcohol, the subsequent reactions were proposed to proceed by the formation of a carbocation intermediate. This was supported by the observed formation of rearrangement products for certain substrates, as well as the



Scheme 12 $TiCl_4$ catalyzed reduction of ketones using borane–ammonia. Adapted from ref. 113 with permission from the American Chemical Society,[113] Copyright 2022.

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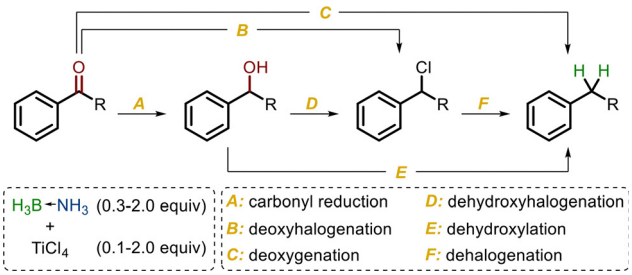
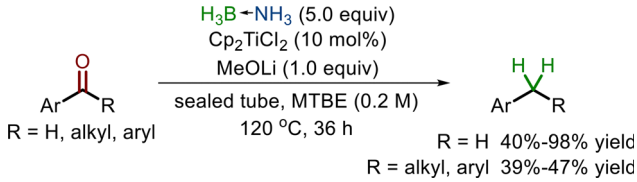


Scheme 13 Stoichiometry dependent reactions of ketones and reduction intermediates. Adapted from ref. 120 with permission from the American Chemical Society,[120] Copyright 2024.

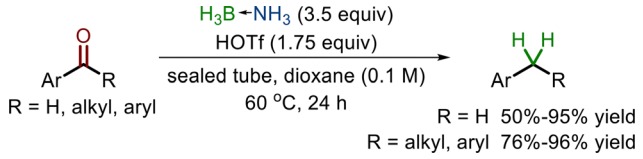
benzylic selectivity, strong solvent effects, and the influence on reactivity of electron–withdrawing and –donating groups, all of which are factors effecting carbocation stability. The carbocations formed by this methodology were later used by our group as electrophiles in Friedel–Crafts alkylation/benzylation reactions.[121]

In addition to the work of our group and others on the reductive deoxygenation of ketones using $TiCl_4$,[122] several other recent procedures have been reported for the "exhaustive" reduction of aromatic aldehydes and ketones. Using bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) as a catalyst, various oxygen containing functional groups, including aldehydes and ketones, were reduced to the corresponding alkanes by borane–ammonia.[123] Performed at 120 °C in a sealed tube, the protocol, much like $TiCl_4$ promoted carbonyl deoxygenation, was applicable to aryl aldehyde and ketones, with aldehydes providing better yields of the corresponding alkanes than did the examined ketone substrates (Scheme 14). Another exhaustive reduction of aryl aldehydes and ketones was developed using a composite with borenium-like properties prepared from borane–ammonia and triflic acid (Scheme 15).[124] Both Ti-catalyzed and borenium composite exhaustive reductions were additionally applied to other oxo-chemicals including carboxylic acids, esters, epoxides, and alcohols. Other recent aldehyde and ketone reductions utilizing borane–ammonia, including stereoselective, organocatalyst promoted, frustrated Lewis pair (FLP) promoted, and biocatalyzed reactions are described in a recent review on reductions using borane–ammonia.[11]

3.1.2 Carboxylic acids and esters. Relative to aldehyde and ketone reduction, the reduction of carboxylic acids or esters to the corresponding alcohols is difficult due to the low



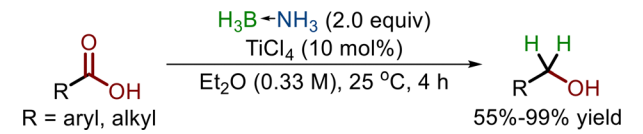
Scheme 14 Titanium catalyzed exhaustive reduction of ketones and aldehydes. Adapted from ref. 123 with permission from Wiley-VCH Verlag GmbH & Co. KGaA,[123] Copyright 2022.



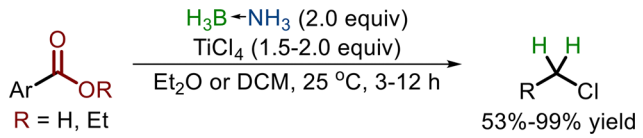
Scheme 15 Borenium composite based exhaustive reduction of ketones and aldehydes. Adapted from ref. 124 with permission from the American Chemical Society,[124] Copyright 2025.

electrophilicity and high oxidation state of the carbonyl carbon. Accordingly, stronger reducing agents such as lithium aluminum hydride ($LiAlH_4$),[125] alane (AlH_3),[126] diisobutylaluminum hydride (DIBAL-H),[127] and borane reagents (BTHF and BMS)[128,129] are frequently used. Several borane–amines including borane–pyridine,[89] borane–triethylamine,[130] and the weakly bound complexes borane-*N*,*N*-diethylaniline[131] and borane-*N*-ethyl-*N*-isopropylaniline[98] have previously been examined for carboxylic acid reduction. These methods, however, required elevated temperatures, were limited in scope, gave poor product yields, and were very slow or ineffective for the reduction of esters. Following our report of $TiCl_4$ catalyzed ketone reduction using borane–ammonia, we extended the methodology to the reduction of carboxylic acids.[132] Both aromatic and aliphatic carboxylic acids were reduced to the corresponding alcohols using 2 equiv of borane–ammonia and 10 mol% $TiCl_4$ (Scheme 16). The presence of free amines decreased the efficacy of the reaction, but *N*-Boc or *N*-Fmoc protected amines were well tolerated. As part of our work, described earlier, on the deoxyhalogenation of aryl aldehydes and ketones to the corresponding benzyl chlorides, we examined carboxylic acids as potential substrates. It was found that by increasing the quantity of borane–ammonia and extending the reaction time, both carboxylic acids and esters could be converted to the corresponding benzylic chlorides (Scheme 17).[119]

Further extension of our $TiCl_4$ catalyzed methodology to the reduction of esters revealed an unexpected transformation. When using $TiCl_4$ (200 mol%) as a stoichiometric catalyst for the reduction of esters by borane–ammonia (2.0–2.5 equiv.), the



Scheme 16 $TiCl_4$ catalyzed reduction of carboxylic acids using borane–ammonia. Adapted from ref. 132 with permission from the American Chemical Society,[132] Copyright 2022.



Scheme 17 Deoxyhalogenation of aromatic carboxylic acids and esters. Adapted from ref. 119 with permission from the American Chemical Society,[119] Copyright 2023.

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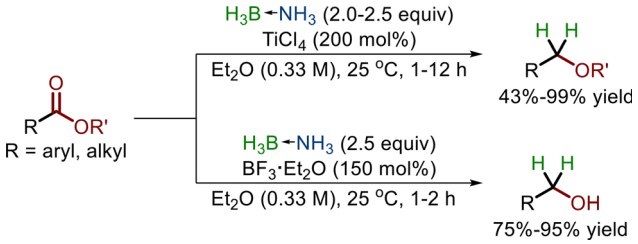
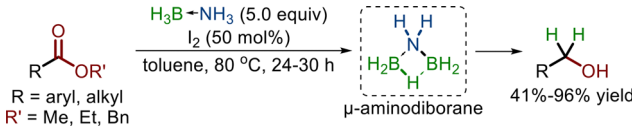


Scheme 18 Catalyst and stoichiometry dependent reduction of esters. Adapted from ref. 133 with permission from the American Chemical Society,[133] Copyright 2023.

corresponding ethers were obtained from both aromatic and aliphatic carboxylic esters (Scheme 18).[133] While good to excellent yields were obtained for most examples, deoxygenation of diesters, lactones, and nitrogen containing substrates resulted in reduced yields. Interestingly, replacing $TiCl_4$ with boron trifluoride diethyl etherate ($BF_3{\cdot}Et_2O$) (150 mol%) allowed for the isolation of the corresponding alcohols from a similar set of ester substrates (Scheme 18).

While our procedure for converting esters to ethers using borane–ammonia remains unique, several other methodologies have been developed for the preparation of the corresponding alcohols. An uncatalyzed ester reduction using borane–ammonia (8 equiv) is reported in THF at 120 °C (sealed tube) after 20 h.[134] Co-catalysts $BF_3{\cdot}Et_2O$ and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) promote the reduction in dichloroethane (DCE) at 55 °C after 24 h using borane–ammonia (2.5 equiv.).[135] *In situ* formation of μ-aminodiborane using borane–ammonia and iodine (50 mol%) has been reported for the reduction of esters, as well as carbonates and anhydrides, to the corresponding alcohols (Scheme 19).[136] Increasing the quantity of iodine present in the reaction additionally allowed for the isolation of the corresponding benzyl or alkyl iodides. A recent borane–ammonia catalyzed reduction of esters and lactones to the corresponding alcohols also invoked μ-aminodiborane as the catalytically active species.[137]

The reduction of carboxylic acids and esters to the corresponding fully reduced alkanes has been accomplished using the Ti-catalyzed[123] and borenium composite[124] exhaustive reductions described earlier in Section 3.1.1 on ketones reduction. Exhaustive reduction of carboxylic acids and esters has also been reported using borane–ammonia (3.5 equiv.) with $BF_3{\cdot}Et_2O$ (20 mol%) and (3-fluorophenyl)boronic acid (8 mol%) as co-catalysts.[138] This methodology was also shown to reduce carbamates to the corresponding *N*-methyl derivatives.

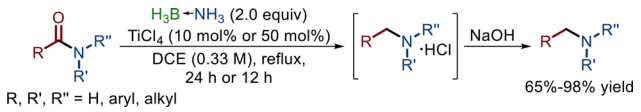


Scheme 19 Reduction of esters to alcohols using μ-aminodiborane. Adapted from ref. 136 with permission from the Royal Society of Chemistry,[136] Copyright 2023.

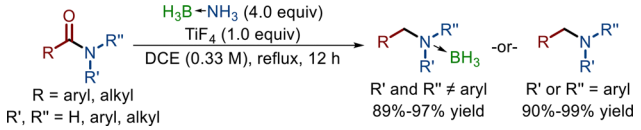
3.1.3 Amides and nitriles. Unlike the reduction of carboxylic acids and esters, which provide the corresponding alcohol products, substituted or primary amines are typically produced upon the reduction of amides and nitriles, respectively. While the obtained products may differ, many of the same methods of reduction have been applied to the nitrogen containing carboxylic acid derivatives including the use of $LiAlH_4$,[125,139] borane reagents (BTHF and BMS),[140–143] and activated borohydride systems.[144–147] Some of the earliest examples of borane–amines used for the reduction of amides and nitriles were the weakly bound complexes with arylamines[98,131] or bulky trialkylamines.[148] While these complexes were shown to be effective for the rapid reduction of tertiary amides, the reduction of secondary amides, and especially primary amides and nitriles were exceedingly slow.

Extending our work on the $TiCl_4$ catalyzed reductions of ketones, carboxylic acids, and esters using borane–ammonia, we reported the successful application of this system to the reduction of amides.[149] Using borane–ammonia (2 equiv.) in refluxing DCE, the reduction of amides to the corresponding amies was facilitated by $TiCl_4$ (10 mol%) in 24 h, or more rapidly (12 h) using 50 mol% $TiCl_4$ (Scheme 20). Another very similar protocol using borane–ammonia (1.5 equiv.) and $TiCl_4$ (10 mol%) in toluene was reported almost simultaneously.[150] Our group also utilized the related TiF_4 (1 equiv.) for amide reduction using borane–ammonia (4 equiv.) in refluxing DCE for 12 h.[151] This protocol yielded the corresponding borane–amine adduct, or the free amine in cases of anilide reduction (Scheme 21). We further extended this protocol for the reductive amination of carboxylic acids *via* a one-pot, tandem amidation/reduction sequence. Counterpart reactions for the reduction of amides have additionally been reported using the $BF_3{\cdot}Et_2O$ and $B(C_6F_5)_3$ co-catalyzed[152] and μ-aminodiborane mediated[153] reactions which occur under similar conditions to the corresponding ester reductions described earlier. An uncatalyzed amide reduction using borane–ammonia (2 equiv.) in diethyl ether at 120 °C (sealed tube) has also been recently reported.[154]

A differing approach has been taken regarding nitrile reduction. While borane–ammonia has been utilized as the reductant in high temperature (120 °C), uncatalyzed nitrile



Scheme 20 $TiCl_4$ catalyzed reduction of amides to amines. Adapted from ref. 149, used under CC BY 4.0.[149]



Scheme 21 TiF_4 mediated reduction of amides to amines or borane complexes. Adapted from ref. 151 with permission from the Royal Society of Chemistry,[151] Copyright 2024.

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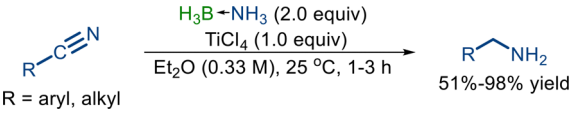
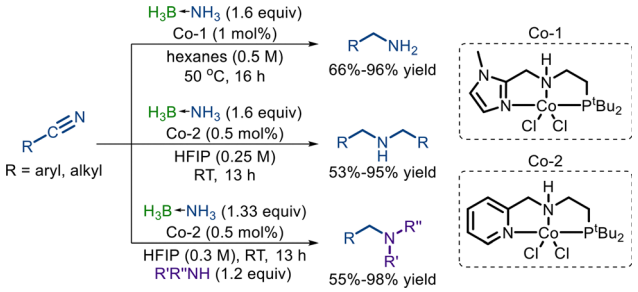


Scheme 22 $TiCl_4$ mediated reduction of nitriles to amines. Adapted from ref. 156, used under CC BY 4.0.[156]

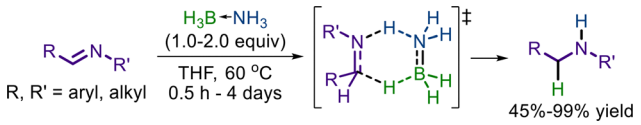


Scheme 23 Selective synthesis of primary and substituted amines using NNP pincer cobalt catalyst. Adapted from ref. 167 with permission from Wiley-VCH Verlag GmbH & Co. KGaA,[167] Copyright 2016.

reduction[155] and our group's extension of the $TiCl_4$ mediated methodology (Scheme 22),[156] many strategies use borane–ammonia as a hydrogen source for the reduction of nitriles *via* transfer hydrogenation. Many protocols have been reported utilizing metal nanoparticles[157–162] or transition metal catalysts[163–166] to reduce nitriles to primary amines or substituted amines *via* condensation of the primary imine intermediate. These protocols employ various borane–amines as the hydrogen source, although borane–ammonia is most commonly used. A representative procedure using NNP pincer cobalt catalysts reported by Zhou, Liu, *et al.* in 2016 is shown in Scheme 23.[167] This protocol was demonstrated for the selective synthesis of primary and symmetrical secondary amines, as well as unsymmetrical secondary and tertiary amines incorporating external added amine. The specific NNP pincer cobalt catalyst and solvent were shown to play a critical role in the observed selectivity.

3.1.4 Imines and reductive amination. As the nitrogen containing analogs of aldehydes and ketones, aldimines and ketimines respectively, the reduction of imines produces the corresponding amines. The reduction of imines, and the related iminium salts and enamines, occurs under conditions like those used for aldehydes and ketones. Many of the same approaches for imine reduction using borane–amines have been applied, including the use of acidic solvents[168,169] or activators[170] and transfer hydrogenation processes. An early example of isolated imine reduction *via* transfer hydrogenation was reported in 2010 by Berke *et al.*[171] The concerted double hydrogen transfer from borane–ammonia to the polarized imine bond occurred at 60 °C in THF, and provided the corresponding amines in 0.5 h to 4 days, dependent on substrate (Scheme 24).

While isolated imines have been reduced using a variety of techniques, a generally more convenient approach is the *in situ*



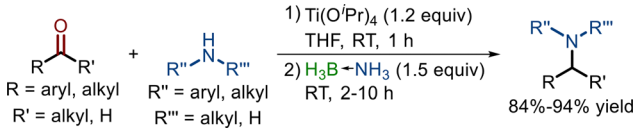
Scheme 24 Concerted double hydrogen transfers to imines using borane–ammonia. Adapted from ref. 171 with permission from Wiley-VCH Verlag GmbH & Co. KGaA,[171] Copyright 2010.

formation of an imine directly from an amine and an aldehyde or ketone followed by reduction, known as reductive amination. Borane–amines have been examined for many years as reagents for reductive amination. Using borane–amines to replace or supplement the widely used sodium cyanoborohydride ($NaBH_3CN$)[172] and sodium triacetoxyborohydride ($NaBH(OAc)_3$)[173] is motivated by the potential toxicity and substrate limitations, respectively, of these reagents. Many borane–amines have been investigated including the borane complexes with pyridine,[174–177] 2-picoline,[178,179] 5-ethyl-2-methylpyridine,[180] triethylamine,[181] benzylamine,[182] and 1,2,3-triazoles.[183] Several reviews describe the older literature on reductive amination using these compounds.[9,184]

A primary concern with the use of borane–amines for reductive amination is the release of the amine coordinated to borane which must be separated from the desired amine product. To address this issue, our group introduced borane–ammonia as a reductant for direct reductive amination.[185] Using titanium isopropoxide ($Ti(O^iPr)_4$) as a promotor, the *in situ* formation of imines in THF from a variety of aldehydes and ketones with an added amine was followed by reduction using borane–ammonia (Scheme 25). This protocol furnished the product amine in 2 h to 10 h with yields between 84% to 94% and was extended to the synthesis of primary amines using ammonium chloride as the ammonia source.

There have been several important developments since our group's initial use of borane–ammonia in direct reductive amination protocols. We reported a procedure replacing $Ti(O^iPr)_4$ with the more environmentally benign trimethyl borate ($B(OMe)_3$) as a promoter of imine formation.[186] Using borane–ammonia as the reductant, the reaction was conducted at RT under neat conditions. Reductive aminations without the use of a promotor for imine formation have been reported under neat conditions using borane–triethylamine at 60 °C,[187] as well as borane–dimethylamine at 70 °C.[188] Beller *et al.* reported a promoter-free reductive amination performed at RT using borane–ammonia in trifluoroethanol (TFE).[189]

The introduction of electron-withdrawing groups to borohydrides produces milder reducing agents, such as $NaBH_3CN$ and



Scheme 25 Titanium isopropoxide mediated reductive amination using borane–ammonia. Adapted from ref. 185 with permission from Elsevier,[185] Copyright 2010.

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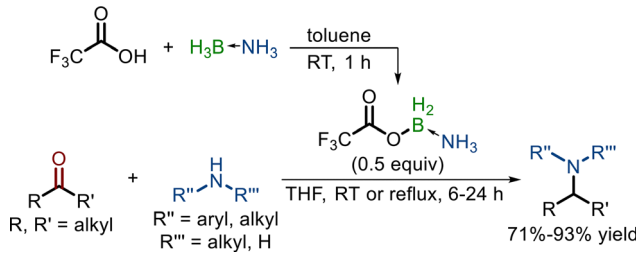
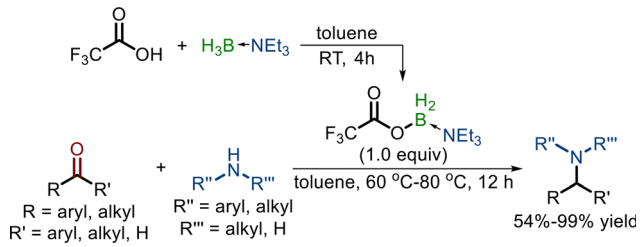


Scheme 26 Reductive amination of dialkyl ketones using TFAB–ammonia. Adapted from ref. 190 with permission from the Royal Society of Chemistry,[190] Copyright 2022.

$NaBH(OAc)_3$ for reductive amination. Our group recently applied this strategy to borane–amines, reporting the use of monotrifluoroacetoxyborane–amines (TFAB–amines) for reductive amination.[190] Prepared *via* the reaction of trifluoroacetic acid (TFA) with various borane–amines, reducing agents of varying strength, dependent on the coordinated amine, are obtained. TFAB–ammonia, prepared from borane–ammonia, was used for the reductive amination of aliphatic ketones with aliphatic and aromatic amines (Scheme 26). We utilized the milder TFAB–triethylamine, from borane–triethylamine, for the reductive amination of aldehydes and aromatic ketones due to the competing carbonyl reduction observed when using TFAB–ammonia (Scheme 27). This reductive amination strategy was successful even with difficult secondary and deactivated aromatic amine substrates. We subsequently extended the application of TFAB–amines to the one-pot preparation of lactams *via* a tandem reductive amination cycloamidation process.[191] The lactams in this protocol could be formed using keto acids with added amine or from amino acids with an added carbonyl compound. Previously, only the route using keto acids with an added amine had been examined using borane–ammonia as the reductant.[192]

During our work on reductive amination, it was noted that TFAB–amines with primary or secondary amines or ammonia reacted with aldehydes to yield a mixture of amine products. This was the result of successive reductive aminations incorporating the amine of the TFAB–amine reagent. A similar reaction was later reported by Mukherjee *et al.* for the synthesis of *N*,*N*-dimethyl amines from aldehydes and ketones using borane–dimethylamine.[193]

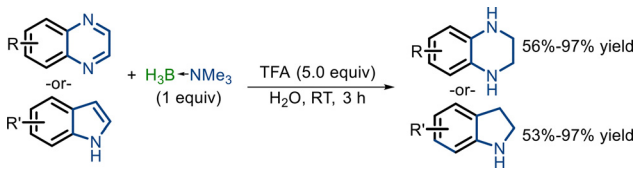


Scheme 27 Reductive amination of aryl ketones using TFAB–triethylamine. Adapted from ref. 191 with permission from the American Chemical Society,[191] Copyright 2023.

3.2 Transfer hydrogenation

The functional group reductions described in the preceding section could alternatively be accomplished using a strong hydride reducing agent such as $LiAlH_4$. The presence of a polar bond in the discussed substrates makes the electron deficient position open to hydride attack. Borane–amines are, however, not limited to reduction *via* hydride transfer or hydroboration mechanisms. The presence of hydrogen on both boron and nitrogen of borane–amines permits functional group transformation *via* transfer hydrogenation operating through three proposed mechanisms: double hydrogen transfer (from N–H and B–H), hydroboration/solvolysis, and dehydrogenation of the borane–amine followed by hydrogenation. In the prior section double hydrogen transfer was invoked as a mechanism to explain aldehyde, ketone, and imine reductions, and borane–amine dehydrogenation followed by substrate hydrogenation is the likely mechanism for the metal nanoparticle catalyzed nitrile reductions. Transfer hydrogenation processes utilizing borane–amines can additionally be applied to the reduction of nonpolar unsaturated bonds. This makes available many reactions which are inaccessible or slow using reagents like $LiAlH_4$ including the reduction/hydrogenation of alkenes, alkynes, azo arenes, nitro groups, benzene derivatives, and heteroarenes. These transformations and detailed mechanistic considerations are thoroughly described in a recent review on the topic of borane–amines for transfer hydrogenation.[12]

The plethora of reports, even in the short time since the prior review, reflect the burgeoning nature of transfer hydrogenation. While various borane–amines have been examined as the hydrogen source for these reactions, borane–ammonia remains dominant. Alkenes,[194–199] alkynes,[200–203] azo arenes,[204–208] nitro groups,[209–214] and aromatics[215–225] all persist as popular substrates for examination using transition metal complexes,[226–234] nanoparticles,[235–237] and other nanostructured materials[238–241] as catalysts. A recent development in metal-free transfer hydrogenation uses borane–trimethylamine with TFA in H_2O at RT to affect the hydrogenation of quinoxalines and indoles (Scheme 28).[242] This green protocol incorporates hydrogen into the product from both TFA and borane–trimethylamine, producing a byproduct related to the TFAB–amines utilized in our reductive amination protocols. While good to excellent yields were obtained for most products, isoquinoline, as well as imidazole, thiazole, and oxazole derivative were incompatible. Further recent developments in main group catalyzed and refined asymmetric protocols have been



Scheme 28 Transfer hydrogenation of heteroarenes using TFA and borane–trimethylamine. Adapted from ref. 242 with permission from Wiley-VCH Verlag GmbH & Co. KGaA,[242] Copyright 2022.

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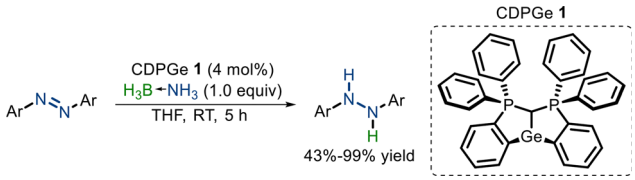
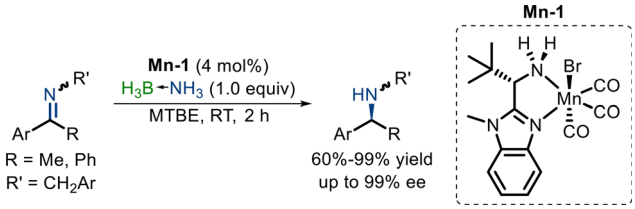


Scheme 29 Main group Ge catalyzed transfer hydrogenation of azo arenes. Adapted from ref. 243 with permission from the American Chemical Society,[243] Copyright 2025.



Scheme 30 Mn catalyzed asymmetric transfer hydrogenation of aryl and diaryl imines. Adapted from ref. 244 with permission from the American Chemical Society,[244] Copyright 2025.

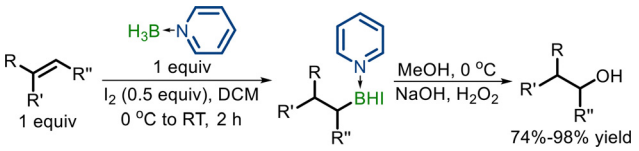
made using Ge and Mn based catalysts respectively. Using a C,C,C pincer-type carbodiphosphorane ligand with Ge, azo arenes, imines and heteroarenes were hydrogenated using borane–ammonia as the hydrogen source (Scheme 29).[243] Borane–ammonia was also used in the Mn catalyzed asymmetric reduction of imines, which notably opened the substrate scope to diaryl imines (Scheme 30).[244]

3.3 Hydroboration

Hydroboration is the addition of the B–H bond to alkenes and alkynes. This produces organoboranes which can undergo a number of useful transformations.[245–251] Since its discovery[252] a wide variety of reagents have been introduced for hydroboration.[253] Borane–amines also serve as hydroboration reagents for alkenes and alkynes, sharing the same anti-Markovnikov selectivity as traditional borane reagents. However, as with reduction, their increased stability attenuates their reactivity with alkenes and alkynes. In the past, several approaches have been taken to overcome this decreased reactivity including increased reaction temperatures,[29,254,255] activation using Lewis acids,[256] and the use of borane complexes with weakly coordinating arylamines (BACH reagents),[257–259] bulky amines,[148,260–262] or silylamines.[263,264]

3.3.1 Alkenes

The utilization of harsh reaction conditions, Lewis acid activators, or weakly coordinated borane–amine complexes to achieve the hydroboration of alkenes using borane–amines have been superseded by several modern techniques. Room temperature hydroboration using borane–pyridine, reported by Vedejs *et al.*, utilized iodine (I_2) for the *in situ* generation of an iodoborane–pyridine (BH_2I–pyridine) complex with borenium ion-like properties (Scheme 31).[265] Other activators (Br_2, TfOH, $HNTf_2$) were shown to result in decreased yield or selectivity. The

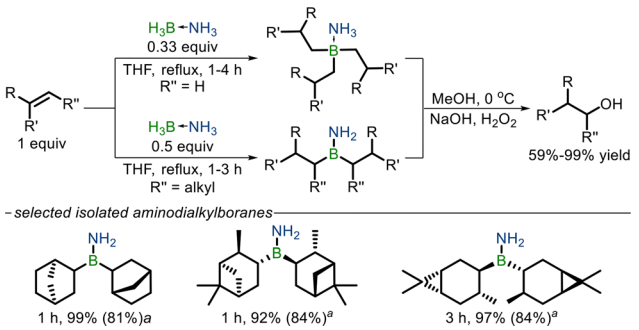


Scheme 31 Room temperature hydroboration of alkenes using borane–pyridine and iodine. Adapted from ref. 265 with permission from the American Chemical Society,[265] Copyright 2005.

BH_2I–pyridine complex selectively produced the monoadducts utilizing a single hydride and was applied to a series of O and N functionalized terminal and internal alkenes to provide the corresponding alcohols following oxidation. Alternate to oxidation, the monoadduct intermediates were converted to alkyltrifluoroborate salts upon reaction with KHF_2. The same intermediates were subsequently shown to be useful in the formation of pinacol boronate esters.[266] Formation of BH_2I–pyridine complexes was additionally applied to the intramolecular hydroboration of borane complexes with homoallylic and bis-homoallylic amines.[267,268]

Several transition metal catalyzed alkene hydroborations have been examined. Both $[Rh(xantphos)]^+$ and $[Rh(PR_3)_2]^+$ fragments were applied as catalysts for the hydroboration of *tert*-butylethene using borane–trimethylamine, with proposed B–H activation at the Rh(I) metal center.[269,270] When applying the $[Rh(PR_3)_2]^+$ fragment to the reaction of *tert*-butylethene with borane–dimethylamine a tandem hydroboration/ dehydrogenation process yields the corresponding aminodialkylborane. Both Rh catalysts, however, were applied only to a single substrate.

Recent work in our group demonstrated the effective use of borane–ammonia for non-dissociative hydroboration of both terminal and internal alkenes (Scheme 32).[271] The intermediate generated is dependent on the substitution of the alkene. Terminal alkenes provide corresponding trialkylborane–ammonia complexes, while internal alkenes give aminodialkylboranes, with both intermediates producing alcohols upon oxidation (Scheme 32). Our demonstration that ammonia is retained in the intermediate products is opposed to previously suggested hydroboration mechanisms utilizing BTHF, which are proposed to undergo an initial dissociation of borane prior



Scheme 32 Non-dissociative hydroboration of alkenes using borane–ammonia. [a]Isolated yield of corresponding alcohol following oxidation. Adapted from ref. 271 with permission from the Royal Society of Chemistry,[271] Copyright 2016.

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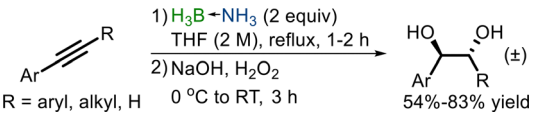
to hydroboration.[272–276] The trialkylborane–ammonia complexes generated by the hydroboration of terminal alkenes by borane–ammonia are unable to be isolated due to their instability. However, the aminodialkylboranes from internal alkenes can be separated *via* filtration or distillation, and similar compounds where the boron component is 9-BBN have shown synthetic utility as amine transfer reagents.[277,278]

3.3.2 Alkynes. The analogous hydroboration of alkynes differs from its alkene counterpart in several important respects. Addition of a single B–H bond to an alkyne produces alkenylboranes, while multiple B–H additions yield geminal or vicinal dihydroboration products. The increased number of potential hydroboration products leads to a wider range of possible oxidation products. Oxidation of alkenylboranes from terminal or internal alkynes produce aldehydes and ketones, respectively.[279] The geminal or vicinal diboro intermediates from the dihydroboration of terminal or internal alkynes give the primary alcohol or the vicinal diol following oxidation, respectively.[280,281]

While many of the traditional reagents used for the hydroboration of alkenes have also been deployed for alkynes,[282] boranes–amines remain relatively unexplored. The weakly coordinated borane–amine complex *N*,*N*-diethylaniline–borane has been used as a catalyst for terminal alkyne hydroboration and transborylation to form alkenyl catecholboranes.[283,284] Room temperature hydroboration enabled *via* the *in situ* generated BH_2I–pyridine complex, described in the section on alkene hydroboration, was additionally applied to alkynes.[265] Using the BH_2I–pyridine complex internal alkynes gave a mixture of ketone regioisomers following oxidation, terminal alkynes were not examined. Extension of the $[Rh(xantphos)]^+$ fragment catalyzed alkene hydroboration methodology, also described in the section on alkene hydroboration,[270] to alkynes has also been demonstrated.[285] The lone example, diphenylacetylene, was hydroborated using borane–trimethylamine to yield the corresponding vinylborane–amine complex. Vinylborane–amine complexes were also prepared *via* Zr and Mg co-catalyzed reaction of borane–diisopropylamine with terminal alkynes.[286] While yielding what are in essence hydroboration products, the overall reaction proceeds *via* hydrozirconation followed by bond metathesis with the *in situ* formed diisopropylaminoborane. In addition to these methodologies, cyano derivatives of borane–amines have been shown to be effective in forming 5 and 6 membered B–N heterocycles *via* Au-catalyzed intramolecular alkyne hydroboration.[287–289]

Following our utilization of borane–ammonia as an effective reagent for alkene hydroboration,[271] we extended this approach to alkynes.[290] Aromatic alkynes underwent a 1,2-dihydroboration by borane–ammonia, forming proposed intermediate polymeric alkylborane–ammonia complexes. Upon oxidation of the hydroboration intermediate a racemic mixture of the vicinal diols was obtained in 54% to 83% yield (Scheme 33).



Scheme 33 Alkyne hydroboration using borane–ammonia for the synthesis of vicinal diols. Adapted from ref. 290 with permission from Elsevier,[290] Copyright 2018.

3.4 Borylation

In the broadest definition, borylation refers to the introduction of a B atom to a molecule by the formation of a C–B bond. Borylation in its modern sense applies more specifically to the formation of organoboranes *via* functionalization of C–H and C–X bonds. This definition differentiates borylation, which is much more recent development, from hydroboration[252] and the even older methods of C–B bond formation using organometallic reagents and an electrophilic boron source.[291–293] Initial reports of both C–X[294] and C–H[295] borylation utilized Pd to catalyze the cross-coupling with bis(pinacolato)diboron (B_2pin_2) or pinacolborane (HBpin). In the years since those reports a broad range of variant methodologies have been developed. These methods have expanded borylation to an array of substrates (alkanes, alkenes, arenes, alkynes) using other transition metal and non-transition metal catalysts, incorporating boron from many source materials, including borane–amines. Among the methodologies utilizing borane–amines as the boron source borylation is most frequently accomplished using a transition metal or non-transition metal catalyst, and conversion of a borane–amine to a more reactive derivative (aminoborane, aminoborohydride, ligated boryl radical, or a complex with borenium ion-like properties). In light of the vast number of relevant borylation methodologies utilizing borane–amines, select examples will be described highlighting the various applicable substrate types and technical approaches.

Extension of the earlier described C–B bond formation using organometallic reagents and an electrophilic boron (typically borate ester) source was reported by Singaram *et al.* Investigating the reactions of various organolithium, organozinc, and Grignard reagents with diisopropylaminoborane ($(^iPr)_2N–BH_2$) derived from borane–diisopropylamine, it was found that *p*-tolylmagnesium bromide undergoes nucleophilic addition to the B of diisopropylaminoborane within 30 min.[296] This method was applied to various alkyl and aryl Grignard reagents which form the corresponding boronic acids upon aqueous quench. The ability to form the Grignard reagent *in situ* directly from the organohalide and Mg metal was also demonstrated for selected substrates.

This latter aspect was subsequently expanded significantly by Pucheault and co-workers who utilized the Barbier condition to prepare borinic acids and boronate ester adducts using diisopropylaminoborane.[297] Observation of the autocatalytic dehydrogenation of borane–diisopropylamine to diisopropylaminoborane in the presence of magnesium and the organohalide, where the borane–amine could now be used directly, led to improved procedures for borinic acid,[298] boronic acid,[299] and alkynylborane[300] synthesis.

A proposed intermediate of the Mg catalyzed borylation strategies described above is the magnesium aminoborohydride

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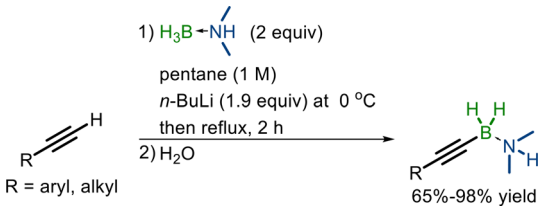
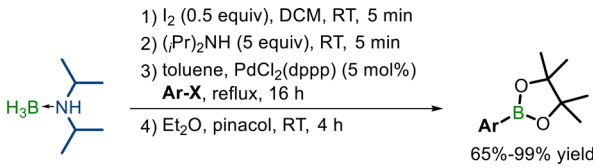


Scheme 34 Lithium aminoborohydrides in the dehydrogenative borylation of terminal alkynes. Adapted from ref. 301, used under CC BY 4.0.[301]

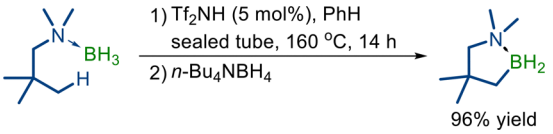
formed from borane–diisopropylamine following deprotonation by the Grignard reagent. By employing the related lithium dimethylaminoborohydride, formed from *n*-BuLi and borane–dimethylamine, as a stoichiometric reagent, our group devised a methodology for the dehydroborylation of terminal alkynes, creating alkynylborane–amine products (Scheme 34).[301] *In situ* formation of terminal alkyne *via* the Corey–Fuchs reaction allowed the scope of this reaction to be further expanded to include aldehydes as substrates to yield borylated terminal alkynes.

In addition to the Grignard based borylation strategies, diisopropylaminoborane has been utilized in several Pd catalyzed C–X arene borylation protocols. The diisopropylaminoborane, or other aminoboranes, used in these protocols is either prepared in advance *via* the thermal dehydrogenation of the corresponding borane–amine,[302,303] Pd nanoparticle catalyzed dehydrogenation,[304] or by sequential formation of a borylammonium salt and deprotonation.[305] Our group has reported a variant Pd catalyzed C–X arene borylation protocol, implementing a related borylammonium salt/deprotonation strategy, while taking inspiration from Vedejs's use of I_2 as an activator.[94] Aminoboranes were formed *via* tandem iodination/dehydroiodination, first forming the iodoborane–amine, then deprotonating with added amine. *In situ* aminoborane formation allowed for a simplified one-pot C–X arene borylation protocol (Scheme 35).

Subsequent to their work on room temperature hydroboration using the BH_2I–pyridine complex, Vedejs *et al.* discovered that related complexes could undergo nitrogen-directed C–H borylation. Initially reported for aromatic C–H borylation, the borenium ion-like complex was formed upon the treatment of borane-*N*,*N*-dimethylbenzylamine with trityl tetrakis(pentafluorophenyl)borate (TrTPFPB).[306] Dehydrogenation of the intermediate, removing a hydride from boron and an aromatic hydrogen *ortho* to the benzylic substitution, and quenching the reaction with Bu_4NBH_4 produced the corresponding benzazaborolidine. This methodology was later extended to



Scheme 35 One-pot aminoborane synthesis and Pd catalyzed arene borylation. Adapted from ref. 94, used under CC-BY-NC-ND 4.0.[94]



Scheme 36 Triflic acid catalyzed intramolecular C–H borylation. Adapted from ref. 307 with permission from the American Chemical Society,[307] Copyright 2011.

nitrogen-directed aliphatic C–H borylation of hindered borane–amines using bistriflimide (Tf_2NH) (Scheme 36),[307] as well as catalytic variants.[308]

A very recent addition to the collection of borylation strategies is the use of tertiary amine–boryl radicals, also referred to as amine–ligated boryl radicals.[309] The increased nucleophilicity and B–H bond strength of amine–ligated boryl radicals, relative to the more extensively investigated N-heterocyclic carbene (NHC)–boryl radicals,[310] permits unique Minisci-type[311] radical borylation. This strategy was initially introduced by Leonori *et al.* for the radical C–H borylation of azine heterocycles where the *ortho* position is selectively borylated,[312] offering complementary reactivity to current transition metal catalyzed *meta* borylation protocols. Using 1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) as the photocatalyst to initiate a single electron transfer reduction of ammonium persulfate $(NH_4)_2S_2O_8$ produces a sulfate radical anion. Hydrogen atom transfer from borane–trimethylamine to the sulfate radical anion generates the amine–ligated boryl radical which borylates the protonated azine substrate. Since this first report several variants have been described including the use of photoactive electron-donor–acceptor (EDA) complexes,[313] cobalt mediated dehydrogenative alkene borylation,[314] and a photoelectrocatalytic strategy for arene and heteroarene C–H borylation.[315] Trimethylamine carboxyborane has also been introduced as an effective precursor for generating amine ligated boryl radicals.[316–318]

3.5 B–H Insertion

Another important and recent development in the synthesis of organoboranes is the B–H insertion reaction. Typically performed using tertiary or heteroaromatic borane–amines, new C–B and C–H bonds are formed when a carbene species inserts into the electron rich B–H of the borane–amine complex. Early work on B–H insertion using dichlorocarbene showed a mixture of multiple insertion products.[319] A critical advancement in the area of B–H insertion was the development of a catalytic, enantioselective procedure using copper catalyst and chiral bisoxazoline ligands using the elimination of a diazo group to generate the carbene, report by Zhu, Zhou, *et al* (Scheme 37).[320] Demonstrated for both borane–amine and borane–phosphine adducts, this work paved the way for the many subsequent diverse and versatile ligand controlled catalytic asymmetric B–H insertion reactions. A recent review on metalloid–hydrogen bond insertion reactions thoroughly presents much of the recent literature on B–H insertion reactions,[13] and as such, only a broad overview highlighting important developments is described here.

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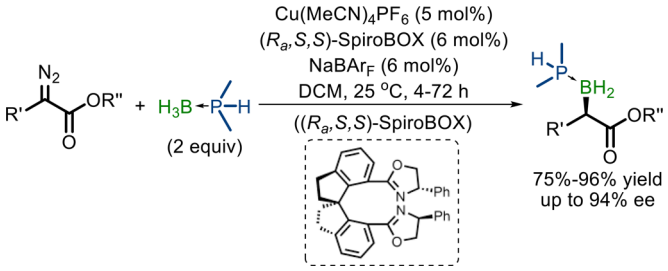
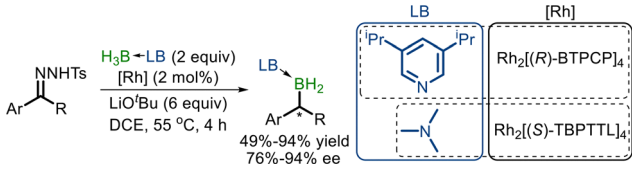


Scheme 37 Cu catalyzed B–H insertion using carbenes generated *via* diazo elimination. Adapted from ref. 320 with permission from the American Chemical Society,[320] Copyright 2013.



Scheme 38 B–H insertion using unstabilized diazo group generated *in situ* from *N*-tosylhydrazones. Adapted from ref. 336 with permission from the American Chemical Society,[336] Copyright 2018.

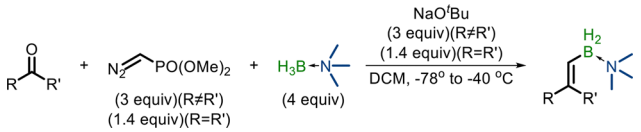
Since the initial report of catalytic, enantioselective B–H insertion into borane–amines, several subsequent procedures have utilized copper catalysts with chiral bisoxazoline ligands[321–325] and other copper catalyzed systems.[326–330] Introduction of diene ligands,[331–334] dirhodium catalysts,[335–339] and the Ru(II)–Pheox catalyst[340] to B–H insertion chemistry were correspondingly important developments. A dirhodium catalyst was additionally applied to B–H insertion of carbenes generated from diazo species prepared *in situ* from *N*-tosylhydrazones (Scheme 38).[336] All diazo substrates used up to that point had contained electron-withdrawing group for stabilization, limiting synthetic utility. Other stabilized diazo precursors have since been introduced for B–H insertion.[338,339,341]

While diazo groups have been the most frequently investigated carbene source, a variety of other carbene precursors have been examined including alkynes,[324,335,342] ynamides,[327,329] cyclopropenes,[322,325,328,343] sulfoxonium ylides,[344,345] and iodonium ylides,[346] as well as alkenyl triflates[347] for alkylidene carbene insertion.

Another recent, intriguing application of alkylidene carbene B–H insertion is their use in the preparation of trisubstituted *Z*-boryl alkenes.[348] Alkylidene carbenes were generated *via* an *in situ* Wittig reaction between a dialkyl ketone and diazomethyl phosphate or trimethylsilyldiazomethane. Tandem carbene insertion into the B–H bond of borane–trimethylamine yielded the thermodynamically unstable trisubstituted *Z*-boryl alkenes (Scheme 39). This work offers an important counterpart to the well-established chemistry of *E*-alkene synthesis using the Wittig reaction.

3.6 Amidation

Amide bond formation is critical in biology and biochemistry and is one of the most important organic functional group

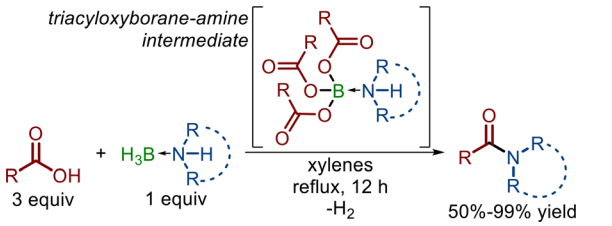


Scheme 39 Wittig reaction generated carbene and tandem B–H insertion for the preparation of trisubstituted *Z*-boryl alkenes. Adapted from ref. 348, used under CC BY-NC 4.0.[348]

transformations in many industries. Commensurate with its importance, numerous approaches to amide formation have been devised.[349–351] Traditionally a carboxylic acid is converted to an activated acid chloride or anhydride derivative.[352] The use of coupling reagents[353] or conversion to metal carboxylates are more recent advancements.[354–357] Catalytic approaches for amidation have focused on transition metal based catalysts,[358–360] silicon,[361,362] and boron.

While boron based catalysts for amidation have focused on boronate esters[363] and boronic acids,[364] boric acid[365–367] and BTHF[368] have also been employed for this purpose. Mechanistically, these boron-based methodologies are reported to undergo B–O bond exchange to form activated acyloxyborane derivatives. An early report by Trapani *et al.* using borane–trimethylamine as a catalyst for amidation, while not reported, is presumed to form a similar activated intermediate.[369] This work was later extended to the synthesis of esters.[370]

Based on this report, our group planned a direct amidation of carboxylic acids using borane–amine complexes containing nontertiary amines. Our hypothesis was that borane–amines could activate carboxylic acids and deliver the coordinated amine to form the corresponding amide.[93] We demonstrated that triacyloxyborane–amine complexes are generated by the reaction of carboxylic acids and borane–amines, which was confirmed by isolation and structural determination using X-ray crystallography. The coordinated amine is then delivered to the carbonyl carbon, forming the corresponding amide (Scheme 40). This process was applied to the synthesis of a wide range of amides, including those incorporating gaseous amines. We subsequently extended this process to utilize borane–ammonia as a catalyst (1–10%) for the amidation reaction.[371] Additional amine added to the reaction would initially transaminate borane–ammonia, forming a new borane–amine species. This borane–amine would then proceed through the triacyloxyborane–amine intermediate before



Scheme 40 Amidation using borane–amines as dual catalyst and amine surrogate. Adapted from ref. 93 with permission from the American Chemical Society,[93] Copyright 2020.

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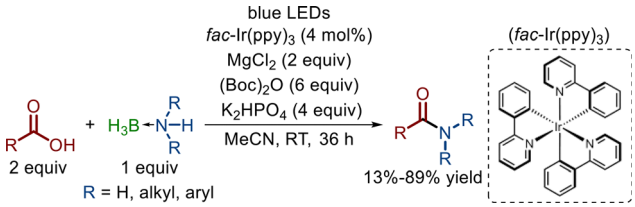


Scheme 41 Photocatalytic carboxylic acid amidation using borane–amines. Adapted from ref. 375 with permission from the Royal Society of Chemistry,[375] Copyright 2021.

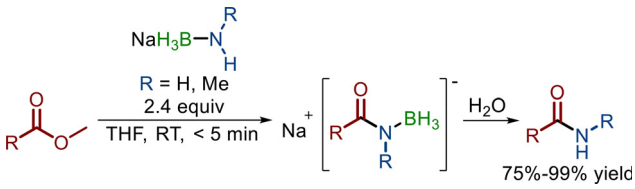
producing the corresponding amide. Subsequent work by our group and Zhang, Li, *et al.* found that borane complexes with pyridine and pyridine derivatives were also suitable catalysts for the formation of amides[372,373] as well as thioesters.[374]

A photocatalytic amidation protocol developed by Chen *et al.* utilizes tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] to catalyst the amidation of carboxylic acids with borane–amines, mediated by visible light (Scheme 41).[375] This methodology was applied primarily to the preparation of primary amides from borane–ammonia, but was also shown to be compatible with other borane complexes of alkyl and aryl amines. It was proposed that Ir(ppy)$_3$, excited by visible light, performed a single electron transfer to the mixed anhydride formed from the carboxylic acid and (Boc)$_2$O in the presence of a base and Lewis acid. Fragmentation to an acyl radical, which reacts with borane–ammonia and a *tert*-butoxy radical, generates the final intermediate, a borane–amide complex.

Chen *et al.* proposed a similar borane–amide complex as the intermediate in their ester amidation protocol utilizing borane–amine derivative, sodium amidoboranes. This approach was demonstrated to rapidly produce primary and *N*-methyl amides from either (NaNH$_2$BH$_3$) or its methyl substituted analog (NaMeNHBH$_3$) and the corresponding esters at room temperature (Scheme 42).[376] Subsequent work preparing sodium amidoborane *in situ* from borane–ammonia and sodium bis(trimethylsilyl)amide (NaHMDS) was also applied to the preparation of primary amide from esters.[377]

4. Summary and outlook

The chemistry of borane–amines continues to evolve from a niche area into a broad platform for synthetic transformations. Their synthesis from hazardous and reactive early protocols has developed into safe modern methodologies, transforming the accessibility of these complexes. Salt metathesis and Lewis base exchange dominate today's approaches to their synthesis, offering broad scope and practical versatility for preparing both simple and complex borane–amines. The ability of borane–amines to act as reducing agents, hydrogen donors, and boron-transfer reagents makes them essential tools in synthetic organic chemistry. Recent innovations in novel reactivity modes, including amine–ligated boryl radicals, borenium-type intermediates, and B–H insertion reactions extend their potential far beyond conventional hydride transfer chemistry. Continued mechanistic insights and the integration of catalytic, photochemical, and electrochemical activation strategies are expected to further expand their synthetic scope. Borane–amines represent a uniquely adaptable class of reagents balancing stability and reactivity, making them indispensable tools in advancing the frontiers of boron chemistry.



Scheme 42 Rapid, room temperature amidation of esters by sodium amidoboranes. Adapted from ref. 375, used under CC BY 4.0.[375]

Conflicts of interest

The authors declare no competing financial interest.

Data availability

No primary research results, software or code have been included, and no new data were generated or analysed as part of this review.

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