Received: 2 March 2020 | Revised: 1 April 2020 | Accepted: 7 April 2020

DOI: 10.1002/aoc.5765

FULL PAPER

Applied Organometallic Chemistry WILEY

Alkali Metal–Promoted Facile Synthesis of Secondary Amines from Imines and Carbodiimides

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Funding information
Science and Engineering Research Board, Grant/Award Number: EMR/2016/005150

Abstract

We present here an efficient method for the hydroboration of aldimines (-C=N-) with pinacolborane (HBpin) using an alkali metal catalyst, potassium benzyl. The reaction was accomplished with unprecedented catalytic efficiency under mild and solvent-free conditions to afford the high yield of the corresponding N-boryl amines up to 97%. Various functionalities on aldimines were incorporated for hydroboration. The corresponding boryl amines were subjected to further hydrolysis to yield the corresponding secondary amines with good yields up to 89%. This protocol for the reaction demonstrates an atom-economic and green method with diverse imines that bears excellent functional group tolerance. Chemoselective reduction of imines was also attained, with good yields of 74–89%. We also propose the most plausible mechanism involving the formation of metal hydride as the active pre-catalyst.

KEYWORDS

Aldimines and carbodiimides, alkali metal alkyl, Chemoselectivity, hydroboration

1 | INTRODUCTION

Primary and secondary amines and their derivatives are abundant in nature and are pre-eminent compounds in biology and chemistry.[1] They are extensively applied in dyes, polymers, natural products, drugs and textiles.[2,3] In organic chemistry, the hydrogenation of imines is significant, as the resultant products are amines and are widely used in pharmaceuticals and agrochemicals.[3] Conventional procedures for the hydrogenation process involve either the use of stoichiometric metal hydrides as reducing agents or hydrogen gas as the source of hydrogen and these techniques have been well exploited.[4] The utility of these methods is limited since they require a high-pressure H_2 set-up, as well as the use of greater quantities of reagents, with large inorganic wastes being formed as by-products and poor selectivity over other feasible functionalities.[5] However, very recent study displayed catalytic amount of $LiAlH_4$ was used for imine hydrogenation at convenient pressure and conditions.[6] Current trends show that catalytic hydroelementation of several unsaturated compounds is an advantageous method for effecting a wide range of syntheses in modern chemistry.[7]

Catalytic reactions such as hydroboration and hydrosilylation have become elementary processes, as they possess academic and industrial importance and are widely explored using several unsaturated substrates.[8] Organoboron compounds are crucial intermediates in an extensive range of organic transformations.[9] Hydroboration of various organic substrates has paved the way for the development of several useful precursors.[10] In this regard, catalytic hydroboration of imines is the most fundamental means for the synthesis of easily available secondary and tertiary amine precursors.[11] The synthesis of imines is readily achievable by the condensation of carbonyl compounds and primary amines.[4f,12] Therefore, the reduction of imines has widely

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exploited several transition-metal as well as the main group–metal catalysts.[3,4h,12h,13] In 1995, the Baker and Westcott research group first reported the use of gold(I) metal complexes supported by bidentate phosphine ligands in the hydroboration of imines.[14] Since then, catalytic hydroboration of imines has been explored to a large extent, prompted by the use of transition metals,[9f,15] rare-earth metals[16] and Lewis acid–base pairs[17] (Figure FS1 in ESI).

In recent years, hydroboration of imines has been studied using a few main-group metals as well (Figure FS2 in ESI). In 2013, Hill et al. identified an effective Mg (II) metal complex that catalyzed the hydroboration of imines, yielding the corresponding N-boryl amines in excellent quantities.[18] Recently, Sen et al. reported a Ca (II) compound as an active catalyst for the reduction of carbonyl compounds and imines. However, the yield of imines obtained was moderate and required high temperature and long reaction time.[19] In the same year, the same working group also developed a Si^{IV} hydride as an improved catalyst for the hydroboration of imines with good yields, although the reaction time required was still long.[20] Recently, Mulvey et al. reported a series of bimetallic aluminum complexes for the hydroboration of carbonyls, imines, and acetylenes (Figure FS2 in ESI).[21] Moderate to good yields were obtained in a short span of time. Very recently, a commercially available organometallic compound such as ^{n}BuLi was observed to undergo catalytic hydroboration of imines at room temperature with THF as the solvent.[22] Other than metal catalyst promoters, substantial efforts have been put into developing metal-free and solvent-free approaches by varying conditions for the hydroboration reaction of imines.[23]

Apart from other C = E (E = C, N, O) functional groups, the N=C=N framework in carbodiimide substrates is also useful, as the subsequent hydroboration does not yield by-products and the high reactivity of carbodiimides towards nucleophiles occasions biologically important guanidines.[24] Nonetheless, the hydroboration of carbodiimides is uncommon, as the reaction affords both mono and dihydroborated products. In recent years, a few metal catalysts such as Mg,[25] U or Th,[26] B,[27] and Al[28] have been known to be used in the mono-hydroboration of carbodiimides.

Currently, synthetic chemists are keen to promote alkali metal amides and alkyls among main-group metal catalysts due to their less toxicity and biocompatibility. Alkali metal alkyl reagents are still underdeveloped due to their high sensitivity and the difficulty in handling them. Thus, the use of alkali metal alkyls as pre-catalysts in the hydroboration of imines and carbodiimides has been scarce which influenced us to carry out a new methodology. Among alkali metal catalysts, we were curious about the efficacy of potassium benzyl as a non-toxic and economically viable pre-catalyst for the hydroboration of aldimines and carbodiimides.

Here, we report the facile synthesis of a library of secondary amines through the mono-hydroboration of a wide range of imines and several carbodiimides, promoted by potassium benzyl as an active catalyst at room temperature and under mild and solvent-free conditions.

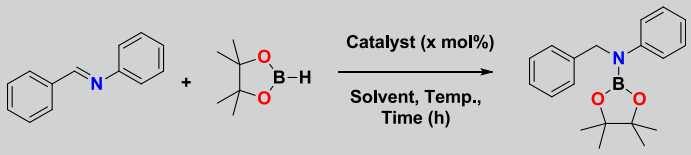
2 | RESULTS AND DISCUSSION

At the outset of our study, the efficiency of various alkali metal catalysts was tested for the hydroboration of aldimines. Initially, alkali metal hexamethyldisilazides [MN $(SiMe_3)_2$] (M = Li, Na, K) (5 mol%) were chosen as pre-catalysts for the hydroboration of N-benzylidene aniline and reacted with 1.1 equivalent of pinacolborane (HBpin) at room temperature and under neat condition for six hours, yielding moderate quantities of amines (Table 1, entries 1–3). Potassium amide [KN $(SiMe_3)_2$] was found to produce a better yield than other metal precursors. Hence, we chose a variety of K-metal catalysts and used them for the hydroboration of aldimines. Notably, KH, KOH, K^{t}OBu, and K_2CO_3 were unable to produce the desired product and only trace amounts of products were observed in each case even after 12 hours (Table 1, entries 4–7). But to our delight, when 5 mol% of potassium benzyl (KCH_2Ph) was used as the pre-catalyst for hydroboration at room temperature, an excellent yield of 97% was obtained within three hours of reaction time (Table 1, entry 8). When hydroboration was completed in the presence of solvents such as toluene and THF, a slightly lower yield was observed after three hours of reaction time (Table 1, entries 9–10).

With room temperature and neat condition being optimal reaction settings for the hydroboration of aldimines, we set out to examine the scope of substrates of various substituted aldimines and HBpin in the presence of 5 mol% of potassium benzyl as the pre-catalyst. The results of the catalytic hydroboration reactions are set out in Table 2.

After the benchmark reaction of unsubstituted N-benzylidene aniline as the substrate, promoted by potassium benzyl, which afforded a yield of 97% within three hours of reaction time (Table 2, entry 2a), we employed a range of imine substrates with electron-withdrawing and electron-donating functionalities as well as heterocyclic groups on aldimines for the corresponding mono-borylated product under optimal conditions (Table 2). Substituted aldimines such as N-benzylidene-2-fluoroaniline and N-benzylidene-4-bromoaniline were

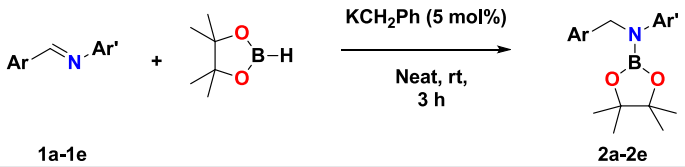
TABLE 1 Screening of alkali metal catalysts for hydroboration of N-benzylideneaniline and HBpin

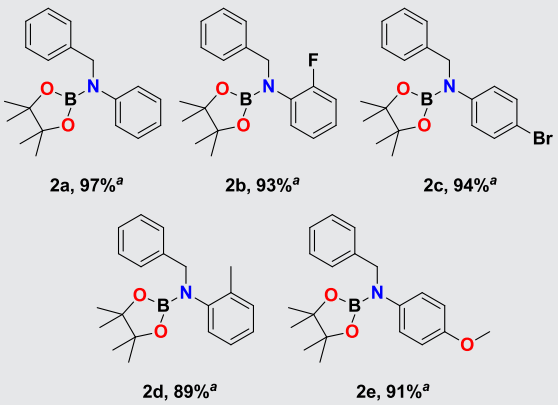


Entry	Alkali metal salts	Cat. loading (mol%)	Sol.	Temp. (°C)	Time (hr)	Yield (%)
1	LiN $(SiMe_3)_2$	5	Neat	r.t.	3	65 [a]
2	NaN $(SiMe_3)_2$	5	Neat	r.t.	3	70 [a]
3	KN $(SiMe_3)_2$	5	Neat	r.t.	3	79 [a]
4	KH	5	Neat	r.t.	12	<10 [b]
5	KOH	5	Neat	r.t.	12	11 [b]
6	KO^tBu	5	Neat	r.t.	12	14 [b]
7	K_2CO_3	5	Neat	r.t.	12	13 [b]
8	KCH_2Ph	5	Neat	r.t.	3	97 [a]
9	KCH_2Ph	5	Tol	r.t.	3	91 [b]
10	KCH_2Ph	5	THF	r.t.	3	68 [b]

Reaction conditions: All catalytic reactions were carried out in the presence of 5 mol% of catalyst loading followed by the addition of HBpin (1.1 eq.) and imine substrates (1 eq.). [a]Isolated yield. [b]Yield has been calculated in presence of 10 mol% hexamethylbenzene as internal standard.

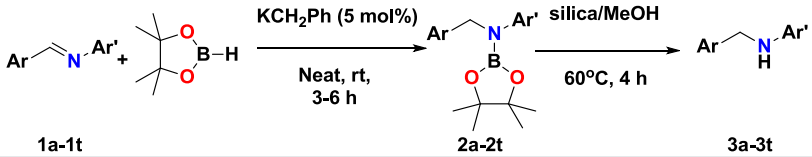
TABLE 2 The substrate scope of alkali metal–catalysed substituted aldimines with HBpin for hydroboration

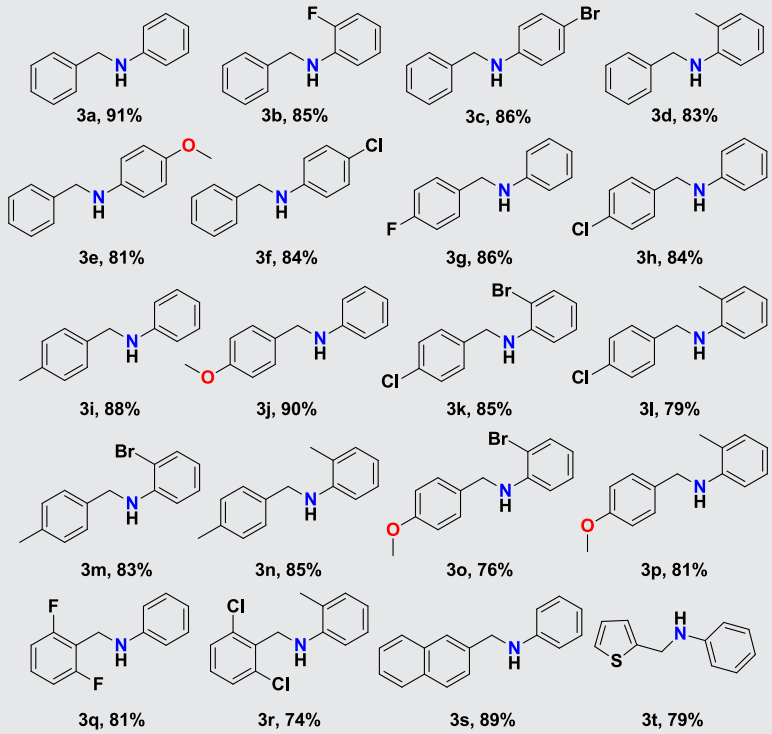




Reaction conditions: All the catalytic reactions were carried out in the presence of KCH_2Ph (5 mol%) followed by the addition of HBpin (1.1 eq.) and imine substrates (1 eq.). [a]Isolated yield.

TABLE 3 Synthesis of secondary amines from substituted aldimines





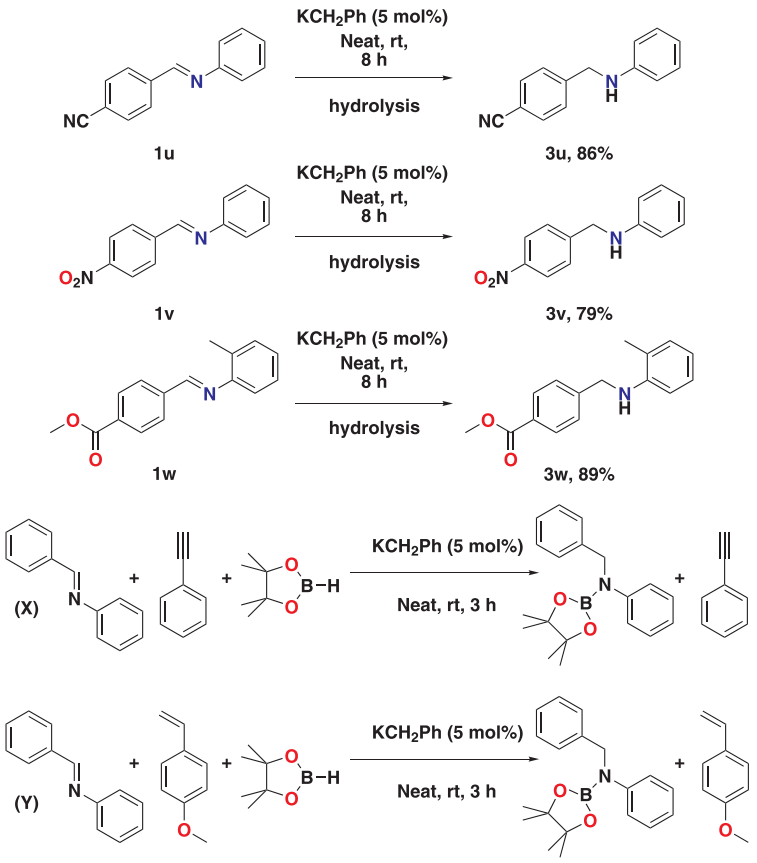
Reaction conditions: KCH_2Ph (5 mol%), HBpin (1.1 eq.) and imine substrates (1 eq.). The hydroborated products were hydrolysed with silica gel in methanol at 60 °C for 4 h. [a] Isolated yield.

subjected to hydroboration reaction to produce the desired products in excellent yields of 93% and 94% respectively (Table 2, entries 2b, 2c). Substrates with electron-donating groups such as N-benzylidene-2-methylaniline and N-benzylidene-4-methoxyaniline underwent smooth hydroboration with HBpin to provide yields of 89% and 91% respectively (Table 2, entries 2d, 2e).

From the interesting results, we were keen to obtain secondary amines as the final products from N-borylated amines through the hydrolysis of corresponding boronate amines using silica gel in methanol for four hours at 60 °C.[15b] The corresponding secondary amines were isolated in good yields after column chromatography and the results are set out in Table 3.

Initially, boryl amines 2a–2f with substitutions on N-phenyl rings and with both electron-withdrawing and electron-donating functionalities were subjected to hydrolysis. The desired substituted secondary amines were isolated through column chromatography with an excellent yield of up to 91% (Table 3, entries 3a–3f). Thereafter, the efficacy of the catalyst was examined by altering various substitutions on both C- and N-phenyl rings. The electron-withdrawing as well electron-donating substituents on the C-phenyl ring of the aldimines, such as N-(4-fluorobenzylidene)aniline, N-(4-chlorobenzylidene)aniline, N-(4-methylbenzylidene) aniline and N-(4-methoxybenzylidene)aniline afforded the corresponding secondary amines with an excellent yield of up to 90% (Table 3, entries 3g–3j). Further, slightly lower yields of 85% and 79% (respectively) were observed when substrates such as 2-bromo-N-(4-chlorobenzylidene)aniline and N-

SCHEME 1 Chemoselective hydroboration of aldimines



(4-chlorobenzylidene)-2-methylaniline were used (Table 3, entries 3k–3 l). When imines with 4-methyl and 4-methoxy functionalities on the C-phenyl ring along with 2-bromo and 2-methyl groups on N-phenyl rings were subjected to hydroboration followed by hydrolysis, no significant change in the yield was observed (Table 3, entries 3m–3p). Additionally, aldimines bearing disubstituted functionalities on the C-phenyl moiety, such as N-(2,6-difluorobenzylidene)aniline and N-(2,-6-dichlorobenzylidene)-2-methylaniline, resulted in the formation of corresponding secondary amine products with a yield of up to 81% (Table 3, entries 3q–3r).

Notably, bulky substituents such as the naphthyl group also provided the desired N-(naphthalen-2-ylmethyl)aniline in excellent yield – 89% – (Table 3, entry 3s), while a heterocyclic substituted imine such thiophene-2-carboxaldehyde afforded a slightly lower yield of 79% upon hydroboration (Table 3, entries 3t). Further, the substrate scope was examined on aldimine having aliphatic substitution. When similar catalytic hydroboration was carried out on N-benzylidenebutan-1-amine, the corresponding N-benzylbutan-1-amine along with the aldimine was observed. However, separation and isolation of the product were complex and the limitation in aliphatic substituted aldimines is probably due to the reduced basicity of the aldimine. Henceforth we explored the reaction protocol on various aromatic substituted aldimines.

Furthermore, the scope of the reaction was examined for the chemoselective hydroboration of imines (Scheme 1). When aldimines such as 4-((phenylimino) methyl)benzonitrile, N-(4-nitrobenzylidene)-aniline and methyl 4-((o-tolylimino)methyl)benzoate were subjected to hydroboration at room temperature for eight hours followed by hydrolysis, we observed chemoselective reduction at the C=N group, without any effect on the nitrile, nitro and ester functionalities and the reaction achieved an excellent yield of up to 89% (Scheme 1, entries 3u – 3w). The molecular structure of compound **3u** was confirmed by single-crystalX-ray diffraction analysis (Figure FS3 in ESI).

Additionally, intermolecular chemoselectivity of imine versus alkyne and alkene were investigated respectively (Scheme 1, entries X-Y). In presence of 5 mol% KCH_2Ph, competitive experiments of the stoichiometric reaction of N-benzylideneaniline, phenylacetylene, 1.3 eq. pinacolborane and N-benzylideneaniline, *p*-methoxystyrene, 1.3 eq. pinacolborane in neat condition was conducted respectively. ^{1}H and $^{11}B\{^{1}H\}$ NMR indicated the formation of the preferred N-borylated product from the imine and no characteristic product peak from alkyne or alkene were observed. Thus, KCH_2Ph was concluded

to be an excellent catalyst for the selective hydroboration of imine over alkyne or alkene.

The previous report from Xue and coworkers displayed that good to excellent yields of the desired secondary amines were acquired by the n-BuLi catalyzed hydroboration of imines which required 6 mol% of catalyst loading in presence of THF as solvent.[22] On the other hand, Rit and coworkers displayed the solvent-free and catalyst-free approach for the hydroboration of imines but required an elevated reaction time of 6–24 h.[23c] Herein, we have carried out potassium benzyl catalyzed hydroboration of imines and carbodiimides to achieve a library of secondary amines with a broad range of substrate scope. Notably, the yield of the products and reaction conditions although comparable to the mentioned methodologies, the catalyst KCH_2Ph plays an advantageous role. The synthetic procedure of the catalyst is smooth and easily dissolves in the reaction mixture of imine and pinacolborane which facilitates the reaction within short span of time. Contrarily, *n*-BuLi handling requires much attention due to its moisture sensitive and pyrophoric property. Hence, as a congener we opted for easily available KCH_2Ph that proved to be an active pre-catalyst.

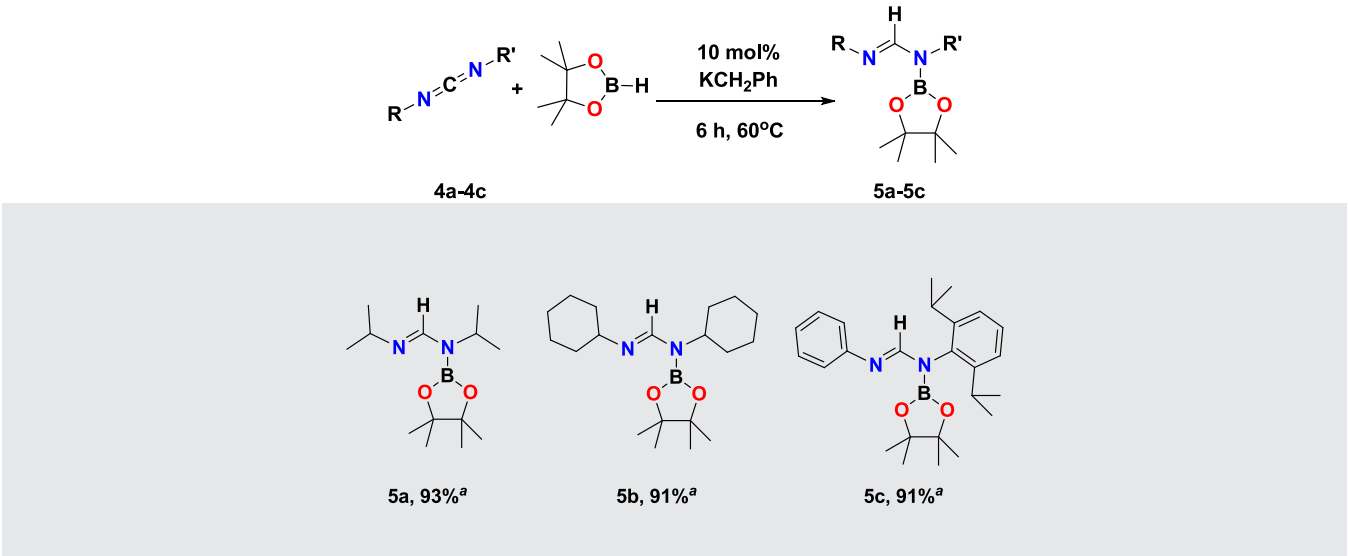
Further, from the response of the pre-catalyst, the efficacy of the alkali metal catalysts was extended to the hydroboration of carbodiimides. Catalytic hydroboration on diisopropylcarbodiimide was primarily examined with 1.1 equivalent HBpin in presence of 5 mol% of KCH_2Ph as the pre-catalyst. A very good yield (86%) was obtained. Increasing the catalyst loading up to 10 mol% produced the desired monoboryl formimidamide in excellent yield (93%) within six hours of reaction time under solvent-free condition (Table 4, entry 5a).

The compounds were analyzed by observing the singlet resonance signal at $\delta_H = 7.8$ ppm, which corresponds to the CH=N peak in the ^1H NMR spectra. The monohydroboration of dicyclohexylcarbodiimide (DCC) under similar reaction conditions afforded the desired product in a nearly quantitative yield (Table 4, entry 5b). Additionally, the reaction protocol also examined for unsymmetrically substituted carbodiimides to evaluate the steric impact of the addition of the HBpin unit. Though the substrate scope was limited, the reaction progressed smoothly to undergo hydroboration on (2,6-diisopropylphenyl)phenylcarbodiimide and we achieved N,N-{Bpin}-diisopropylphenyl-N-phenylformamidine as the sole product with an excellent yield of 91% (Table 4, entry 5c). This observation was confirmed by the appearance of a single singlet resonance for the N-CH=N moiety in ^1H NMR, as previously reported by Eisen and coworkers.[26]

3 | MOST PLAUSIBLE MECHANISM

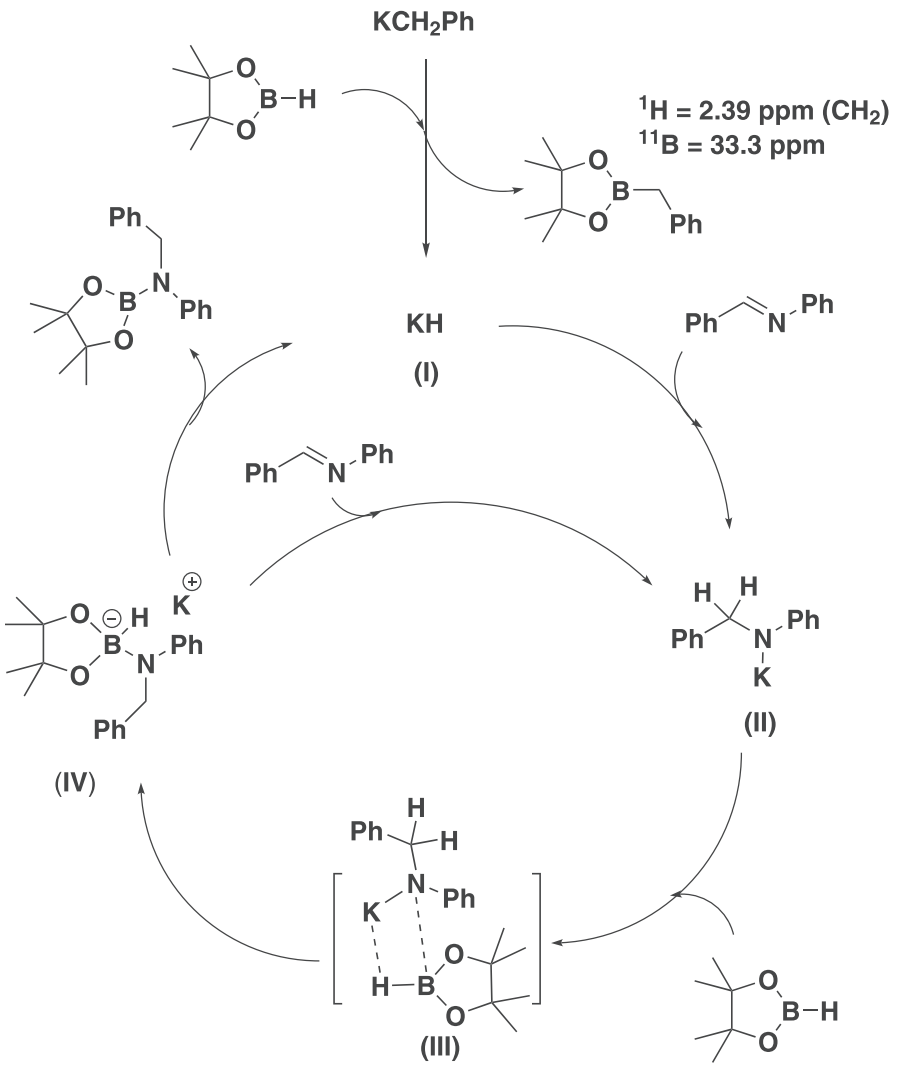
Initially, we subjected the stoichiometric reaction between the catalyst KCH_2Ph and one equivalent of HBpin in C_6D_6 for 6 h at room temperature. The

TABLE 4 Alkali metal promoted mono-hydroboration and hydrolysis of carbodiimides



Reaction condition: KCH_2Ph (10 mol%), HBpin (1.1 eq.) and carbodiimide substrates (1 eq.). [a] Isolated yield.

SCHEME 2 A most plausible mechanism for KCH_2Ph–catalyzed hydroboration of imines



formation of the $PhCH_2Bpin$ was observed and confirmed by ^1H NMR along with $^{11}B\{^1H\}$ NMR singlet at $\delta_B = 33.3$ ppm (Figure FS 72–73 in ESI).[29] In accordance with the observation and previous report by Hill et al. we have postulated the most plausible mechanism for the hydroboration of imines and carbodiimides mediated by the potassium benzyl complex in Scheme 2.[18,30]

The first step involves the formation of potassium hydride as the active pre-catalyst (**I**) by the reaction of KCH_2Ph and HBpin by the elimination of $PhCH_2Bpin$. The potassium hydride generated in situ further reacts with one molecule of imine substrate generating a metal imide bond (**II**). Additional incoming of one molecule of HBpin molecule undergoes the formation of a four-membered cyclic transition state (**III**) to result in a more stable intermediate (**IV**). Hydride migration occurs on **IV** to afford the desired mono-borylated amine product with the generation of active pre-catalyst**I**, which is involved in the next catalytic cycle.

4 | CONCLUSIONS

In summary, we have described here the use of a non-toxic potassium benzyl compound, KCH_2Ph, which could be smoothly synthesized as a competent pre-catalyst for the facile synthesis of a series of secondary amines. This protocol provides a green approach for the catalytic hydroboration of aldimines and carbodiimides with HBpin. The aldimines undergo hydroboration reactions at room temperature and solvent-free conditions within short reaction times to give near-quantitative yields up to 97%. Several substitutions and functional group variations have been implied to achieve a library of aldimines. The respected boryl amines were further hydrolyzed to achieve the substituted secondary amines with good yields of 74–91%. This protocol is highly efficient and gives atom-economical access to organoboron compounds, leading to the formation of secondary amines through hydrolysis. The key features

include high catalytic efficiency, wide substrate range with good functional group tolerance and excellent chemoselectivity.

5 | GENERAL EXPERIMENTAL PROCEDURES

All manipulations involving air- and moisture-sensitive compounds were carried out under argon, using the standard Schlenk technique or argon-filled M. Braun glove box. Hydrocarbon solvents (*n*-hexane, toluene, benzene) were distilled under a nitrogen atmosphere from $LiAlH_4$ and stored inside the glove box. THF was dried and deoxygenated by distillation over sodium benzophenone under argon and then distilled and dried over CaH_2 prior to being stored in the glove box. ^1H NMR (400 MHz), $^{11}B\{^1H\}$ (128 MHz) and $^{13}C\{^1H\}$ (100 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. All the starting materials for the synthesis of imines were purchased from Sigma Aldrich India and used without further purification. HBpin was purchased from Sigma Aldrich India and distilled prior to use. The ligand N-(2, 6-diisopropyl)iminoacenaphthenone was prepared in accordance with methods reported in the literature.[31] The imines and carbodiimides were prepared according to procedures reported in the literature.[15b,16b,32] The metal precursors $Li(NSiMe_3)_2$, $Na(NSiMe_3)_2$, $K(NSiMe_3)_2$, KH, KOH, K^tOBu, and K_2CO_3 were purchased from Sigma Aldrich and TCI India Pvt. Ltd and used as received. Potassium benzyl was prepared according to the literature.[33] NMR solvent ($CDCl_3$) was purchased from Merck.

5.1 | Catalytic procedure for hydroboration of imines (2a–2e)

All catalytic reactions were performed using the following standard protocol. In the glove box, the preferred catalyst KCH_2Ph (3 mg, 0.02 mmol, 5 mol%) and HBpin (65 mg, 0.506 mmol) were added to a Schlenk tube, followed by the addition of imines (0.460 mmol). The reaction mixtures were stirred under the inert condition at room temperature for three hr. Toluene was then added, and the reaction mixture was filtered through a short plug of Celite and evaporated under reduced pressure to obtain a semi-solid residue. The mono-boryl amines are moisture- and air-sensitive, and hence experimental procedures were conducted and NMR samples were prepared inside the glove box. The products were characterized by ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and details are given in the Supporting Information.

5.2 | Catalytic procedure for hydroboration of Carbodiimides (5a–5c)

All catalytic reactions were performed using the following standard protocol. In the glove box, the preferred catalyst KCH_2Ph (5 mg, 0.038 mmol, 10 mol%) and HBpin (50 mg, 0.422 mmol) were added to a Schlenk tube, followed by the addition of carbodiimides (0.384 mmol). The reaction mixtures were stirred under the inert condition at 60 °C for six hr. Toluene was then added, and the reaction mixture was filtered through a short plug of Celite and evaporated under reduced pressure to obtain a semi-solid residue. The resultant formimidamides are moisture- and air-sensitive, and hence experimental procedures were conducted and NMR samples were prepared inside the glove box. The products were characterized by ^1H, $^{11}B\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy and results are given in the Supporting Information.

5.3 | General procedure for hydrolysis (3a–3w)

The resultant borylated amines were further treated with silica gel (150 mg, 100–200 mesh) in methanol at 60 °C for four hours. The completion of hydrolysis was monitored by TLC. The reaction mixture was then filtered and evaporated. The residue obtained was further purified by column chromatography over silica gel (100–200 mesh) with hexane/ethyl acetate (5:0.5–5:1). The products were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and details are given in the Supporting Information.

ACKNOWLEDGEMENTS

This work was financially supported by the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), India, under project no. (EMR/2016/005150). I.B. and S.S. thank the Ministry of Human Resource and Development (MHRD), Government of India, and CSIR respectively for their Ph.D. fellowships. Instrumental support was provided by the Indian Institute of Technology Hyderabad.

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How to cite this article: Panda TK, Banerjee I, Sagar S. Alkali Metal–Promoted Facile Synthesis of Secondary Amines from Imines and Carbodiimides. *Appl Organomet Chem*. 2020;e5765. https://doi.org/10.1002/aoc.5765