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Efficient Co-catalyzed Double Hydroboration of Nitriles: Application to One-Pot Conversion of Nitriles to Aldimines

Kristina A. Gudun,[a] Ainur Slamova,[b] Davit Hayrapetyan,*[a] and Andrey Y. Khalimon*[a,c]

Abstract: *The commercially available and bench-stable Co(acac)$_2$/dpephos system is employed as a pre-catalyst for selective and efficient room temperature hydroboration of organic nitriles with HBPin to produce a series of N,N-diborylamines (RN(Bin)$_2$), which react in situ with aldehydes to give aldimines. Formation of aldimines from N,N-diborylamines does not require a dehydrating agent, is applicable to a wide range of N,N-diborylamine and aldehyde substrates and is highly chemoselective, being unaffected by various common functional groups, such as alkenes, alkynes, secondary amines, ketones, esters, amides, carboxylic acids, pyridines, nitriles, and nitro compounds. The overall transformation represents a synthetically valuable approach to aldimines from nitriles and can be performed in a sequential one-pot manner, tolerating ester, lactone, carboxamide and unactivated alkene functionalities.*

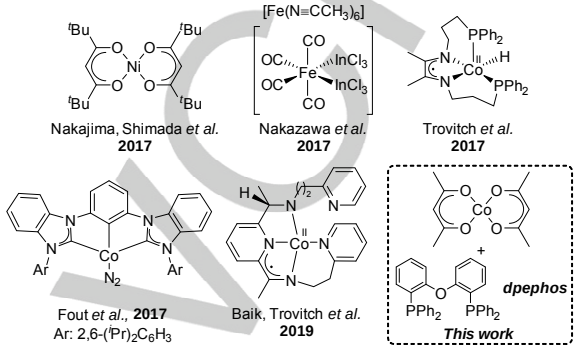

Figure 1. Base metal catalysts for double hydroboration of nitriles.

Amines and imines represent synthetically important classes of compounds, relevant to preparation of commodity and fine organic chemicals, synthesis of biologically active molecules and natural products, pharmaceuticals, agrochemicals, etc.[1] Conventional methods for preparation of amines, such as N-H alkylation reactions, stoichiometric reduction of imines, amides and nitriles as well as reductive amination of carbonyl compounds with metal hydride reagents often suffer from lack of control and functional group tolerance and lead to formation of large amounts of byproducts.[1,2] In contrast, catalytic reduction of readily available nitriles to amines by means of hydrogenation,[3] hydrosilylation[4] and hydroboration[4,5] reactions serves as an attractive alternative to conventional stoichiometric methods. Although direct hydrogenation of nitriles to amines represents the most atom-economical approach, the reactions usually require precious metal catalysts and harsh conditions[7] and often show poor selectivity, affording mixtures of aldimines and primary, secondary and tertiary amines.[6] Whereas a number of transition metal catalysts, including non-precious metal systems, have been developed for hydrosilylation of nitriles,[4] the examples of mild and selective hydroboration of nitriles are still scarce.[4,5,8] With regard to the reactions catalyzed by earth abundant metals (Fe, Co, Ni), only a handful of systems for selective double addition of hydroboranes (akin to HBPin or HBCat; Pin = pinacol, Cat = catechol) to nitriles have been reported,[4,5] many of which require elevated temperatures and/or the use of rather sophisticated ligands (Figure 1).[9]

Besides, catalytic hydroboration of nitriles results in formation of *N,N*-diborylamines, which are thought to possess labile B-N bonds and, therefore, can be used in the synthesis of a variety of *N*-containing organic molecules beyond simple protodeborylation.[5,8e,10-12] Although synthetic routes to *N,N*-diborylamines have been developed only recently[4,5,8] and their chemistry is rather underdeveloped, a few examples of applications of *N,N*-diborylamines in C-N bond forming reactions have been already demonstrated (Scheme 1).[5,8e,10] Thus, our previous studies revealed unprecedented reactivity of $PhCH_2N(BCat)_2$ with benzaldehyde to afford *N*-benzylidenebenzylamine (Scheme 1).[10,11] Very recently, Tobita *et al.* reported on application of *N,N*-diborylamines in Pd-catalyzed cross-coupling with aryl bromides.[8e] During the preparation of this manuscript, Baik and Trovitch *et. al.* have disclosed the ability of *N,N*-diborylamines to form secondary carboxamides upon treatment with aromatic carboxylic acids at 120 °C (Scheme 1).[5] Moreover, borylamines have been previously reported as useful precursors for generation of iminium ions in aminative C-C bond formation reactions,[12] whereas *N*-monoborylamines $RN(H)BR'_2$ have been recently used as reagents for preparation of aldimines.[13]

We have recently reported a diversity of Co(acac)$_2$/dpephos-catalyzed deoxygenative hydrosilylation of carboxamides, including rare examples of reduction of secondary and primary amides to the corresponding amines.[14] Although deoxygenative hydrosilylation of primary amides is generally thought to proceed *via* silane-assisted dehydration of the amides to nitriles, followed by their hydrosilylation to *N,N*-disilylamines,[15] Co(acac)$_2$ was found to be inactive in hydrosilylation of nitriles.[14] Believing that compared to hydrosilanes hydroboranes such as HBCat and

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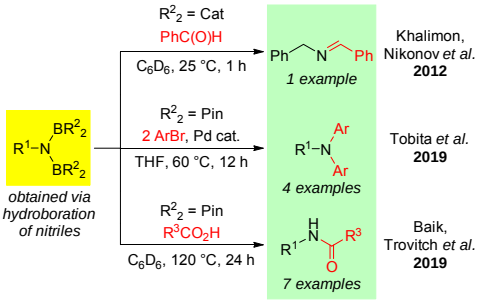
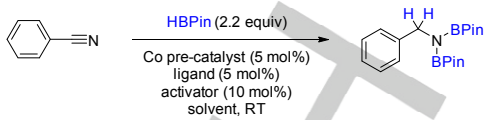


Scheme 1. Applications of *N,N*-diborylamines in the synthesis of *N*-containing organic compounds.

HBPin may exhibit superior reactivity patterns due to more hydridic nature of the B-H bond *vs.* the Si-H bond and the enhanced Lewis acidity of the boron centre *vs.* the silicon centre, we elected to study the hydroboration of nitriles. Herein, we describe an efficient and mild hydroboration of nitriles to *N,N*-diborylamines catalyzed by the bench-stable and commercially available $Co(acac)_2$/dpephos system. Moreover, the *N,N*-diborylamine products can *in situ* react with aldehydes under mild conditions, allowing for synthetically valuable selective one-pot conversion of nitriles R^1CN to aldimines $R^1CH_2N{=}C(H)R^2$ (Scheme 2).[16]

First, hydroboration of PhCN with HBPin (2.2 equiv.) was tested on NMR scale (0.27 M) using a series of bench-stable commercially available or easily prepared Co(II) pre-catalysts: $(dpephos)CoCl_2$,[17] $Co(OAc)_2$/dpephos and $Co(acac)_2$/dpephos (5 mol% of Co). The choice of dpephos ligand was determined by our previous success of its application in Co-catalyzed hydrosilylation reactions.[14] For $(dpephos)CoCl_2$ the hydroboration reactions were activated with 2 equiv. of $LiBHEt_3$ to generate the reactive Co(I)-H species,[18] whereas in the case of the Co(II) acetate and acetylacetonate pre-catalysts the reactions were initiated by HBPin.[19] The reactions were performed at room temperature and monitored by ^{1}H-NMR spectroscopy and the results of these trials are summarized in Table 1. Thus, no hydroboration of PhCN was observed for $(dpephos)CoCl_2$ in the absence $LiBHEt_3$ as an external activator (Table 1, entry 1). With 10 mol% of $LiBHEt_3$ added, $(dpephos)CoCl_2$-catalyzed (5 mol%) hydroboration of PhCN proceeded with 59% conversion to *N,N*-bis(pinacolboryl)benzylamine, $PhCH_2N(BPin)_2$ (Table 1, entry 2). In contrast, reactions with both $Co(OAc)_2$ and $Co(acac)_2$ did not require an external activator (Table 1, entries 3-6). However, without any ligand added, both $Co(OAc)_2$ and $Co(acac)_2$-catalyzed hydroboration reactions proved inefficient and resulted only in <3% and 15% conversion of PhCN to $PhCH_2N(BPin)_2$ in 20 hours at room temperature, respectively (Table 1, entries 3 and 5). Using dpephos, both $Co(OAc)_2$ and $Co(acac)_2$-catalyzed reactions (5 mol.% of Co) showed complete hydroboration of PhCN to $PhCH_2N(BPin)_2$ within 3 h at room temperature (Table 1, entries 4 and 6). Reducing the loading of $Co(acac)_2$ to 3 mol% resulted in more sluggish reaction and only 49% conversion of PhCN was observed in 3 h at room temperature (Table 1, entry 7). Considering the reduced cost of anhydrous $Co(acac)_2$ *vs.* $Co(OAc)_2$[20] all further studies were performed with $Co(acac)_2$ as a pre-catalyst.

Table 1. Evaluation of conditions for CoX_2/dpephos-catalyzed hydroboration of PhCN with HBPin (X = Cl, OAc, acac).[a]



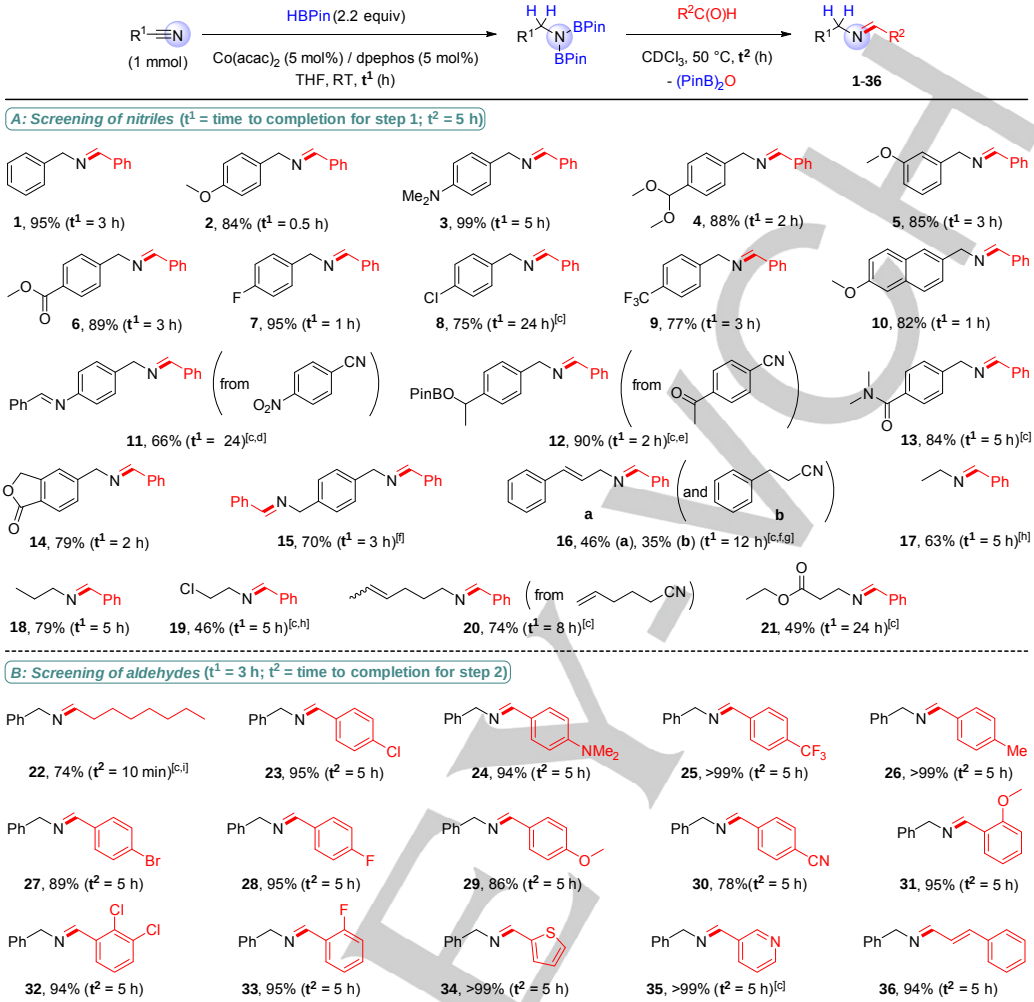
#	Pre-catalyst	Ligand	Activator	Solvent	Time [h] / Conv., %[b]
1	$(dpephos)CoCl_2$	—	—	C_6D_6[c]	20 / 0
2	$(dpephos)CoCl_2$	—	$LiBHEt_3$	C_6D_6	3 / 59
3	$Co(OAc)_2$	—	—	THF	20 / <3
4	$Co(OAc)_2$	dpephos	—	THF	3 / >99
5	$Co(acac)_2$	—	—	THF	20 / 15
6	$Co(acac)_2$	dpephos	—	THF	3 / >99
7[d]	$Co(acac)_2$	dpephos	—	THF	3 / 49

[a] 0.27 M. [b] NMR conv. [c] No reaction was also detected in THF. [d] 3 mol% of $Co(acac)_2$ and dpephos were used.

$PhCH_2N(BPin)_2$, produced *in situ* by $Co(acac)_2$/dpephos-catalyzed hydroboration of benzonitrile with HBPin, was then subjected to the reaction with equimolar amount of benzaldehyde in THF showing 56% conversion of $PhCH_2N(BPin)_2$ to *N*-benzylidenebenzylamine in 4 days at room temperature. Increasing the reaction temperature up to 100 °C led to complete conversion of $PhCH_2N(BPin)_2$ within 5 hours. Interestingly, switching the solvent to non-Lewis basic $CDCl_3$ resulted in shorter reaction times and full conversion of $PhCH_2N(BPin)_2$ to *N*-benzylidenebenzylamine was observed in 24 h at room temperature, whereas at 50 °C the reaction was completed within 5 hours.

Having identified the optimal reaction conditions for hydroboration of nitriles (Table 1, entry 6) and further coupling of *N,N*-diborylamines with aldehydes ($CDCl_3$, 50 °C, 5 h) we then probed the reactivity of a variety of nitrile and aldehyde substrates in one-pot transformation of nitriles to aldimines (Scheme 2). The reactions were performed on 1 mmol scale (1.0 M) and *N,N*-diborylamines, produced *via* $Co(acac)_2$/dpephos-catalyzed hydroboration of nitriles with HBPin (Scheme 2, step1), were subjected to reactions with aldehydes without isolation (Scheme 2, step 2). Complete conversion of nitriles to *N,N*-diborylamines as well the identity of *N,N*-diborylamine products were confirmed by NMR spectroscopy.[21] The second step, coupling of *N,N*-diborylamines with aldehydes, required the solvent change from THF to $CDCl_3$, but no additional purification was performed at that point. The resulting aldimine products were purified by flash chromatography using silica gel neutralized with NEt_3.

First, a series of nitriles bearing different functionalities (Scheme 2, A) were subjected to $Co(acac)_2$/dpephos-catalyzed

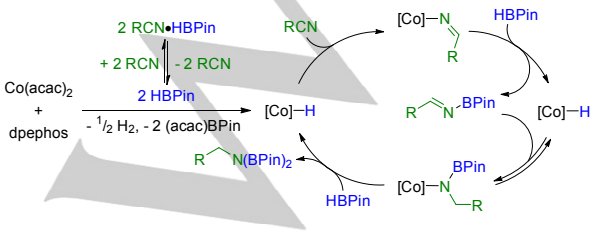


Scheme 2. Substrate scope for one-pot conversion of nitriles to aldimines. Unless mentioned otherwise, isolated yields (based on two steps) are reported. [a] 1.0 M. [b] ratio nitrile : aldehyde = 1 : 0.99. [c] Compounds are unstable under flash chromatography conditions (or could not be separated). NMR yields are reported. [d] 8 equiv. of HBPin were used in step 1. [e] 3.3 equiv. of HBPin were used in step 1. [f] 5 equiv. of HBPin were used in step 1. [g] Step 1 was performed at 50 °C, resulting a 22:78 mixture of 3-phenylpropionitrile and *N,N*-diborylcinnamylamine, respectively. [h] Step 1 was performed with 5 equiv. of HBPin at 50 °C. [i] Step 2 was performed at room temperature.

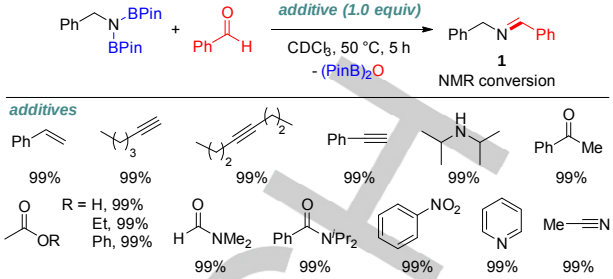
(5 mol%) hydroboration with HBPin, showing by NMR quantitative conversion to the corresponding *N,N*-diborylamines.[22] The subsequent addition of benzaldehyde produced the corresponding aldimines **1**-**21** in good to excellent yields (Scheme 2). With respect to nitriles, this methodology is readily applicable for both aliphatic and aromatic substrates featuring different electronic properties.[23] Benzonitriles with both ē-donating and ē-withdrawing groups are easily converted to the corresponding *N,N*-diborylamines, although, as expected, ē-rich benzonitriles exhibit somewhat enhanced reactivity due to increased basicity of the nitrogen centre (**2** and **10**; Scheme 2). More sluggish hydroboration reactions were observed for ē-poor nitriles, resulting in increased reaction times up to 24 hours at room temperature (**8**; Scheme 2). However, the next step, coupling of *N,N*-diborylamines with benzaldehyde did not seem to be affected much by the electronic properties of the initial nitrile. Acetonitrile and chloroacetonitrile were found to be exceptions from the above trend, showing rather long hydroboration reaction times and lower conversions (**17** and **19**; Scheme 2). This is likely a result of competing coordination of more than one molecule of CH_3CN and $ClCH_2CN$ to the cobalt centre due to relatively small size of these nitriles. Noteworthy, hydroboration of nitriles was found to be selective in the presence of ester, lactone, unactivated alkene and amide functionalities. Thus, methyl 4-cyanobenzoate, 4-cyano-*N,N*-dimethylbenzamide, 1-oxo-1,3-dihydroisobenzofuran-5-carbonitrile and ethyl 2-cyanoacetate were successfully converted to the corresponding aldimines **6**, **13**, **14**, and **21** (Scheme 2). Hydroboration of 5-hexenenitrile was accompanied by the alkene isomerization and formation of 4-hexenylamine

derivative (**20**; Scheme 2); however, no products of hydroboration of C=C bond were detected by NMR. A similar chemoselective hydroboration of benzonitrile was observed in the presence of equimolar amounts of ethylacetate, DMF and PhC(O)N^{i}Pr$_2$.[22] In contrast, addition of HBPin to 4-nitrobenzonitrile and 4-acetylbenzonitrile was found to be non-selective and yielded 4-*N*-borylamino- and 4-(1-boryloxyethyl)diborylamine derivatives, which were converted to the corresponding aldimines **11** and **12** (Scheme 2). Interestingly, hydroboration of cinnamonitrile with 2.5 equiv. of HBPin in 5 h at room temperature selectively afforded the product of the C=C bond reduction, 3-phenylpropionitrile (**16b**; 52% conv. by ^{1}H-NMR).[22] In contrast, the NMR scale (0.27 M) reaction with 5 equiv. of HBPin at 50 °C in 12 h resulted in reverse selectivity and gave a mixture of *N,N*-diborylcinnamylamine and 3-phenylpropionitrile (**16b**) (>99% NMR conv.; 78:22 ratio by ^{1}H-NMR, respectively).[22] Repeating this reaction with 1 mmol of cinnamonitrile, followed by the treatment with benzaldehyde resulted in isolation of a 46:35 mixture of an aldimine **16a** and 3-phenylpropionitrile (**16b**), respectively (Scheme 2).

On the basis of literature precedents on Co-catalyzed hydroboration reactions[18a,19a] and our previous studies on Co(acac)$_2$-catalyzed hydrosilylation of amides,[14] we propose that hydroboration of nitriles is triggered by the formation of a (dpephos)Co(I)-H species (Scheme 3). This is followed by the migratory insertion of a nitrile into the Co-H bond and the subsequent reaction with HBPin to generate the *N*-borylimine RCH=N(BPin). The latter species can undergo insertion into the Co-H bond to yield a *N*-borylamide and finally the *N,N*-diborylamine products. Indeed, monitoring the hydroboration of CH_3CN with 1 equiv. of HBPin by ^{1}H-NMR revealed initial formation of a mixture of CH_3CH=N(BPin) and EtN(BPin)$_2$, suggesting initial elimination of *N*-borylimine. Our kinetic studies of hydroboration of 4-(trifluoromethyl)benzonitrile with 0.5-15 equiv. of HBPin revealed sigmoidal dependence for the product formation with an induction period being highly dependent on the HBPin concentration.[22] Since very fast reaction of Co(acac)$_2$ with HBPin was observed under stoichiometric conditions, the observed hydroboration induction period suggests that the pre-catalyst activation step is affected by the reversible formation of a nitrile-borane adduct and higher hydroboration rates were found for large HBPin concentrations.[24] Kinetic studies also revealed the initial hydroboration rates being proportional to HBPin concentration with a saturation behaviour at large concentrations of HBPin.[22] The empirical rate law derived for the reactions sequence shown in Scheme 3 qualitatively agrees with these observations (see Schemes S1 and S2 in the Supporting Information). Consideration of alternative pathways,



Scheme 3. Proposed mechanism for hydroboration of nitriles.



Scheme 4. Robustness test for the reaction of RCH$_2$N(BPin)$_2$ with benzaldehyde (0.27 M).

such as the initial reaction of the cobalt hydride with borane, followed by a reaction with nitrile, afforded reaction laws incompatible with our experimental findings.[22]

We then examined the scope of aldehyde substrates in the formation of aldimines from PhCH$_2$N(BPin)$_2$ (Scheme 2), which was generated *in situ via* hydroboration of PhCN. With respect to aldehydes, the reaction is widely applicable to aliphatic and aromatic substrates bearing both ē-withdrawing and ē-donating functionalities (**22**-**36**). To further demonstrate the general applicability of this approach we performed the robustness test for the reaction of PhCH$_2$N(BPin)$_2$ (generated *in situ via* hydroboration of PhCN) with PhC(O)H in the presence of equimolar amounts of additives bearing common functional groups, such as alkenes, alkynes, secondary amines, ketones, esters, amides, carboxylic acids, pyridines, nitriles and nitro compounds (Scheme 4). The reactions were analysed by NMR spectroscopy, showing excellent chemoselectivity towards aldimines with complete NMR recovery of the competing substrates. Unsurprisingly, in the presence of benzoic acid PhCH$_2$N(BPin)$_2$ was partially converted to PhCH$_2$N(H)(BPin)[13] and PhCO$_2$BPin (62% by ^{1}H-NMR). A similar hydrolysis but to a lot smaller extent was observed in other experiments when chloroform and additives were not dried additionally and presumably contained small amounts of residual water. However, this does not seem to affect the reaction with PhC(O)H since primary aminoboranes have been recently shown to couple with aldehydes to give aldimines.[13] Repeating the reactions under water free conditions had no influence on either the selectivity or the yield of *N*-benzylidenebenzylamine, suggesting that coupling of PhCH$_2$N(BPin)$_2$ with PhC(O)H does not necessarily proceed *via* formation of PhCH$_2$N(H)(BPin).[13] Moreover, cobalt species does not seem to participate in the aldimine formation as suggested by a control experiment between isolated PhCH$_2$N(BPin)$_2$[22] and benzaldehyde. The overall proposed pathway for the synthesis of aldimines from *N,N*-diborylamines is depicted in Scheme S3 in the Supporting Information and is similar to the mechanism previously reported for the reactions of aldehydes with primary aminoboranes.[13]

In summary, we have demonstrated efficient and mild hydroboration of a diversity of organic nitriles with HBPin using bench-stable and commercially available Co(acac)$_2$/dpephos system. The hydroboration reactions were shown to be chemoselective in the presence of ester, lactone, carboxamide and unactivated alkene functionalities. The produced *N,N*-

diborylamines were shown to react with a diversity of aldehydes to give the corresponding aldimines. The latter transformation was found to be highly selective tolerating various common functional groups, such as alkenes, alkynes, secondary amines, esters, amides, carboxylic acids, pyridines, nitriles, nitro compounds and even ketones. Combining the efficient generation of *N,N*-diborylamines from nitriles with their reactivity with aldehydes, for the first time we demonstrated selective and synthetically valuable one-pot conversion of nitriles to aldimines. General applicability of this method was demonstrated with a diverse scope of substrates as well as with chemoselectivity screening for the coupling of *N,N*-diborylamines with aldehydes. We are currently further investigating the reactivity of *N,N*-diborylamines as reagents for construction of other *N*-containing organic molecules.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cobalt • hydroboration • nitriles • aminoboranes • imines

[1] a) R. C. Larock, *Comprehensive Organic Transformations: A Guide to Functional Group Preparation*, Wiley-VCH, New York,**1989**; b) S. A. Lawrence, *Amines: Synthesis, Properties and Applications*, 1st Ed., Cambridge University Press, Cambridge, **2004**; c) K. Eller, E. Henkes, R. Rossbacher, H. Höke, *Amines, Aliphatic.* In *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, **2005**; d) A. Ricci, *Amino Group Chemistry. From Synthesis to Life Sciences* (Ed.: A. Ricci), Wiley-VCH, Weinheim, **2008**; e) M. Smith, *Organic Synthesis*, 4th Ed., Academic Press, London, **2017**.

[2] J. Seyden-Penne, *Reductions by the Alumino- and Borohydrides in Organic Synthesis*, 2nd Ed., Wiley, New York, **1997**.

[3] a) L. A. Oro, D. Carmona, J. M. Fraile, *Hydrogenation reactions.* In *Metal-catalysis in Industrial Organic Processes*, RSC Publishing, Cambridge, **2006**, pp. 79-113; b) J. G. d. Vries, *The handbook of homogeneous hydrogenation*, Wiley-VCH, Weinheim, **2007**.

[4] M. Itazaki, H. Nakazawa, *Molecules* **2018**, *23*, 2769 and references therein.

[5] C. Ghosh, S. Kim, M. R. Mena, J.-H. Kim, R. Pal, C. L. Rock, T. L. Groy, M.-H. Baik, R. J. Trovitch, *J. Am. Chem. Soc.* **2019**, *141*, 15327-15337.

[6] a) S. Gomez, J. A. Peters, T. Maschmeyer, *Adv. Synth. Catal.* **2002**, *344*, 10-37-1057; b) D. Srimani, M. Feller, Y. Ben-David, D. Milstein, *Chem. Commun.* **2012**, *48*, 11853-11855; c) J.-H. Choi, M. H. G. Prechtl, *ChemCatChem* **2015**, *7*, 1023-1028; d) S. Chakraborty, D. Milstein, *ACS Catal.* **2017**, *7*, 3968-3972; e) S. Chakraborty, G. Leitus, D. Milstein, *Angew. Chem. Int. Ed.* **2017**, *56*, 2074-2078; *Angew. Chem.* **2017**, *129*, 2106-2110; f) H. Dai, H. Guan, *ACS Catal.* **2018**, *8*, 9125-9130.

[7] a) S. Lange, S. Elangovan, C. Cordes, A. Spannenberg, H. Jiao, H. Junge, S. Bachmann, M. Scalone, C. Topf, K. Junge, M. Beller, *Catal. Sci. Technol.* **2016**, *6*, 4768-4772; b) A. Mukherjee, D. Srimani, S. Chakraborty, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2015**, *137*, 8888-8891; c) S. Chakraborty, G. Leitus, D. Milstein, *Chem. Commun.* **2016**, *52*, 1812-1815; d) C. Bornschein, S. Werkmeister, B. Wendt, H. Jiao, E. Alnerico, W. Baumann, H. Junge, K. Junge, M. Beller, *Nat. Commun* **2014**, *5*, 4111; e) S. Elangovan, C. Topf, S. Fischer, H. Jiao, A. Spannenberg, W. Baumann, R. Ludwig, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2016**, *138*, 8809-8814; f) K. Tokmic, B. J. Jackson, A. Salazar, T. J. Woods, A. R. Fout, *J. Am. Chem. Soc.* **2017**, *139*, 13554-13561; g) R. Adam, C. B. Bheeter, J. R. Cabrero-Antonio, K. Junge, R. Jackstell, M. Beller, *ChemSusChem* **2017**, *10*, 842-846.

[8] a) J. Li, M. Luo, X. Seng, H. Hua, W. Yao, S. A. Pullarkat, L. Xu, M. Ma, *Org. Chem. Front.* **2018**, *5*, 3538-3547; b) A. Bismuti, M. J. Cowley, S. P. Thomas, *ACS Catal.* **2018**, *8*, 2001-2005; c) Z. Huang, S. Wang, X. Zhu, Q. Yuan, Y. Wei, S. Zhou, X. Mu, *Inorg. Chem.* **2018**, *57*, 15069-15078; d) A. Harinath, J. Bhattacharjee, T. K. Panda, *Adv. Synth. Catal.* **2019**, *361*, 850-857; e) T. Kitano, T. Komuro, H. Tobita, *Organometallics* **2019**, *38*, 1417-1420.

[9] a) M. Ito, M. Itazaki, H. Nakazawa, *Inorg. Chem.* **2017**, *56*, 13709–13714; b) A. D. Ibrahim, S. W. Entsminger, A. R. Fout, *ACS Catal.* **2017**, *7*, 3730–3734. c) H. Ben-Daat, C. L. Rock, M. Flores, T. L. Groy, A. C. Bowman, R. J. Trovitch, *Chem. Commun.* **2017**, *53*, 7333-7336; d) G. Nakamura, Y. Nakajima, K. Matsumoto, V. Srinivas, S. Shimada, S. *Catal. Sci. Technol.* **2017**, *7*, 3196–3199.

[10] a) A. Y. Khalimon, P. Farha, L. G. Kuzmina, G. I. Nikonov, *Chem. Commun.* **2012**, *48*, 455-457; b) A. Y. Khalimon, P. M. Farha, G. I. Nikonov, *Dalton Trans.* **2015**, *44*, 18945-18956.

[11] Prior to this research this single reaction was the only example of preparation of aldimines from *N,N*-diborylamines under mild conditions. The reaction of $PhCH_2N(BPin)_2$ with PhC(O)H was also reported but required harsh conditions (KHMDS 5 mol%, 18 h, 150 °C): J. B. Geri, N. K. Szymczak, *J. Am. Chem. Soc.*, **2015**, *137*, 12808-12814.

[12] M. Suginome, L. Uehlin, M. Murakami, *J. Am. Chem. Soc.* **2004**, *126*, 13196–13197.

[13] G. P. Junor, E. A. Romero, X. Chen, R. Jazzar, G. Bertrand, *Angew. Chem. Int. Ed.* **2019**, *58*, 2875-2878; *Angew. Chem.* **2019**, *131*, 2901-2904.

[14] A. Nurseiit, J. Janabel, K. A. Gudun, A. Kassymbek, M. Segizbaev, T. M. Seilkhanov, A. Y. Khalimon, *ChemCatChem* **2019**, *11*, 790-798.

[15] A. Y. Khalimon, K. A. Gudun, D. Hayrapetyan, *Catalysts* **2019**, *9*, 490.

[16] For conversion of nitriles to aldimines *via* cross-hydrogenative coupling of nitriles and amines, see references [6b-f].

[17] F. Yang, Q. Zhou, Y. Zhang, G. Zeng, G. Li, Z. Shi, B. Wang, S. Feng, *Chem. Commun.* **2013**, *49*, 5289–5291.

[18] For examples of Co-catalyzed hydroboration reactions activated by $MBHEt_3$ (M = Na, Li), see: a) L. Zhang, Z. Zuo, X. Wan, Z.. Huang, *J. Am. Chem. Soc.* **2014**, *136*, 15501-15504; b) L. Zhang, Z. Huang, *J. Am. Chem. Soc.* **2015**, *137*, 15600-15603; c) S. W. Reilly, C. E. Webster, T. K. Hollis, H. U. Valle, *Dalton Trans.* **2016**, *45*, 2823-2828.

[19] For examples of hydroboration reactions involving activation of acetylacetonate cobalt pre-catalysts with HBPin, see: a) S. Yu, C. Wu, S. Ge, *J. Am. Chem. Soc.* **2017**, *139*, 6526-6529; b) S. R. Tamang, D. Bedi, S. Shafiei-Haghighi, C. R. Smith, C. Crawford, M. Findlater, *Org. Lett.* **2018**, *20*, 6695-6700.

[20] The prices of anhydrous $Co(acac)_2$ and $Co(OAc)_2$ can be found under https://www.sigmaaldrich.com/united-states.html.

[21] For NMR data for *N,N*-bis(pinacolboryl)amines, see: a) A. Kaithal, B. Chatterjee, C. Gunanathan, *J. Org. Chem.* **2016**, *81*, 11153-11161; b) C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Kohn, D. J. Liptrot, M. F. Mahon, *Chem. Sci.* **2016**, *7*, 628-641; c) Y. Ding, X. Ma, Y. Liu, W. Liu, Z. Yang, H. W. Roesky, *Organometallics* **2019**, *38*, 3092-3097; d) W. Liu, Y. Ding, D. Jin, Q. Shen, B. Yan, X. Ma, Z. Yang, *Green Chem.* **2019**, *21*, 3812-3815; e) S. Saha, M. S. Eisen, *ACS Catal.* **2019**, *9*, 5947-5956; and references [5], [8c-e] and [9a,c].

[22] See the Supporting Information for details.

[23] Generally lower yields of aliphatic *vs.* aromatic aldimines can be attributed to the well-known relative instability of aliphatic aldimines.

[24] With 15 equiv. of HBPin hydroboration of 4-(trifluoromethyl)benzonitrile was completed within 40 min at room temperature.

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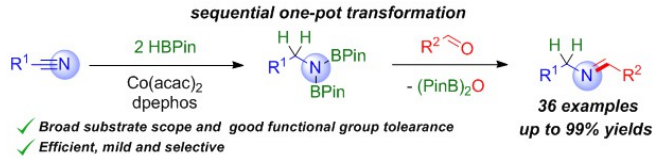

Simple and effective: $Co(acac)_2$/dperphos system is employed as a pre-catalyst for efficient hydroboration of nitriles with HBPin to produce of *N*,*N*-diborylamines, which selectively react *in situ* with aldehydes to give aldimines. The overall transformation represents a synthetically valuable approach to aldimines from nitriles and can be performed in a sequential one-pot manner, tolerating ester, lactone, carboxamide and unactivated alkene functionalities.

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