PAPER

Hydroboration of nitriles and imines by highly active zinc dihydride catalysts†

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Eco-friendly zinc dihydrides stabilized by N-heterocyclic carbenes were demonstrated to be highly efficient catalysts for the double hydroboration of nitriles with pinacolborane, exhibiting turnover frequencies up to 3000 h^{-1} at room temperature under solvent-free conditions. The reactions afforded corresponding diboronated amines with excellent yields and good functional group tolerance. A single Zn–H insertion product was isolated from a stoichiometric reaction of zinc dihydride with nitrile, and was proved to be an active species in this transformation. Kinetic studies were performed to give some insights into the catalytic reactions. In addition, zinc dihydride species also showed high activity for the hydroboration of imines to boronated amines.

Introduction

The development of efficient synthetic approaches for amines is of great significance because this class of compounds has a widespread application in the fine chemical, agrochemical, and pharmaceutical industries.[1,2] In this context, catalytic reduction of unsaturated compounds containing *e.g.* C≡N or C=N bonds with borane has recently emerged and attracted extensive attention, because it usually affords high reaction selectivity and employs mild reaction conditions.[3] Moreover, corresponding hydroboration products, *i.e.* borylamines, can be used for the synthesis of a variety of organic compounds.[4] The first example of nitrile dihydroboration was reported by Nikonov *et al.* using a molybdenum complex $(2,6\text{-}^{i}Pr_2\text{-}C_6H_3N)Mo(H)(Cl)(PMe_3)_3$ (**1a**, Fig. 1), achieving a turnover frequency (TOF) up to 1.7 h^{-1}.[5] Since then, many efforts have been made for the development of catalysts used for this transformation.[6] Over the last few years, it has been expanded to include a variety of metal complexes, including s-,[7] p-,[8] d-[9] and f-block[10] elements, and the representatives of effective complexes for the dihydroboration of nitriles are shown in Fig. 1. However, most of above complexes show low to mediate catalytic activity and some of them are unattractive due to their precious or combustible nature.

Considering the biocompatibility, environmental friendliness and abundance of zinc ion, it is attractive to use zinc-based catalysts for various organic transformations. Zinc-based complexes have been successfully used in the hydroboration of a series of unsaturated molecules, including ketones,[11] imines,[12] alkynes,[13] and N-heterocycles,[14] but are rarely seen to be used in the

hydroboration of organic nitriles. To the best of our knowledge, only one precedent was reported by Panda *et al.*[15] recently by disclosing that the imidazoline-2-iminato ligand-based zinc alkyl complexes were active toward hydroboration of nitriles under heating conditions (60 °C), achieving a maximum TOF of 50 h^{-1}. In our previous work, we synthesized two molecular zinc(II) dihydrides supported by phosphine-functionalized N-heterocyclic carbene ligands (Fig. 2), that were found to be efficient for hydroboration of thermodynamic stable and kinetic inert CO_2 under mild conditions.[16] Being inspired by this result, we herein investigated further of these complexes for the catalytic hydroboration of nitriles and imines. Gratifyingly, zinc dihydrides **2** exhibit remarkably high activity for hydroboration of a variety of nitriles and imines, producing boronated amines with a TOF of up to 3000 h^{-1} at room temperature in the absence of solvent. A plausible mechanism is also proposed based on the isolation of a catalytic intermediate and kinetic studies.

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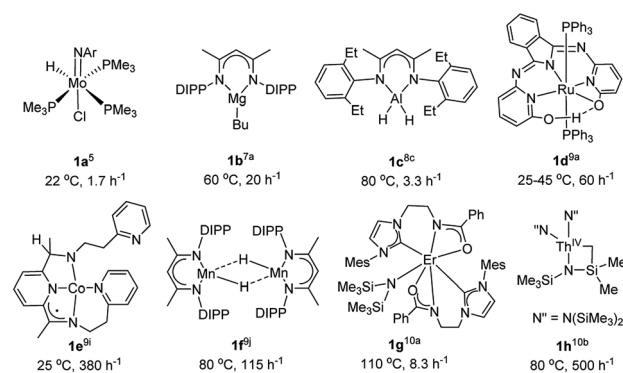
Fig. 1 Selected metal complexes effective for the hydroboration of nitriles (reaction temperature and maximum TOF obtained were also listed).

2a: R = 2,4,6-Me$_3$-C$_6$H$_2$
**2b**: R = 2,6-^{i}Pr$_2$-C$_6$H$_3$
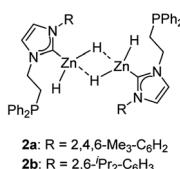
Fig. 2 Zinc dihydrides used in this study.

Results and discussion

We initiated our study by using complex **2a** (1 mol% based on Zn) for the reaction of benzonitrile with pinacolborane (HBpin) at room temperature in various solvents and the results are summarized in Table 1. The reactions gave low conversions of benzonitrile in the employed solvents (entries 1–3; 54% in C$_6$D$_6$, 29% in PhF, 26% in THF) in 2 h. It's noteworthy that in all of these cases, no intermediate species, *i.e.* PhCH=NBpin, was detected. Excitingly, a significant increase in activity was achieved when reaction was conducted in the absence of any solvent, which consumed all of the benzonitrile in a short time (8 min; entry 4), exclusively affording diboronated amine PhCH$_2$-N(Bpin)$_2$ (**5a**) with a TOF of 750 h^{-1}. To our knowledge, this represents the highest activity reported to date for the hydroboration of benzonitrile.[7c,10b] Complex **2b** was also applied in this reaction under similar conditions, which resulted in a lower conversion of benzonitrile (85%; entry 5) probably due to the sterically bulky NHC ligand employed for complex **2b**. To make a comparison, a tridentate monoanionic ligand-based zinc monohydride, *i.e.* **L^{NNP}**ZnH [**L^{NNP}** = CH$_3$C(2,6-^{i}Pr$_2$C$_6$H$_3$N)CHC(CH$_3$)(-NCH$_2$CH$_2$PPh$_2$)],[17] previously reported by our group, was also prepared and examined under neat conditions. However, it is almost ineffective toward the current reaction with 1 mol% loading in 2 h (entry 6). NHC ligand employed in **2a** alone was found inert for the reaction under the same conditions (entry 7).

Subsequently, reactions of a variety of nitriles with HBpin promoted by complex **2a** were examined under our typical

conditions (0.5 mol% catalyst loading, room temperature, in the absence of any solvent; Table 2). Reactions of *para*- or *ortho*-methyl-substituted benzonitriles with HBpin offered the corresponding diboronated amines **5b** and **5c** in 93% and 86% isolated yields, respectively. Additionally, benzonitriles containing polar functional groups are tolerated in the reaction. For example, methoxy, dimethylamino, halogen (F, Cl, and Br) substituted benzonitriles gave corresponding hydroboration products **5d–5h** in 5–40 min with high isolated yields. Notably, the reaction was significantly accelerated when using *para*-trifluoromethyl substituted benzonitrile, leading to a full conversion of substrate only in 2 min. As a result, it afforded compound **5i** with a TOF of 3000 h^{-1}, which is the maximum value reported to date in nitrile hydroboration.[7c,10b] For polycyclic 1-naphthonitrile, the quantitative conversion was observed in 40 min, producing **5j** in 90% isolated yield. Heterocyclic aromatic substrates comprised of a furan, thiophene or pyridine framework are applicable in current study to give anticipated dihydroboration products **5k–5m**. The selectivity in the reduction of the nitriles when containing other unsaturated functional groups was also investigated. In the case of 4-acetylbenzonitrile, hydroboration of both C=O and C≡N groups occurred at a comparable rate, and only **5n** was isolated. In contrast, methyl 4-cyanobenzoate underwent selective hydroboration reaction only at C≡N moiety even with excess amount of HBpin, affording compound **5o** and keeping ester

Table 2 Hydroboration of various organic nitriles with HBpin catalyzed by **2a**[a]

Table 1 Zinc hydride-catalyzed hydroboration of benzonitrile[a]
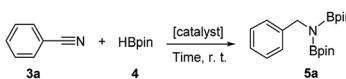
Entry	Catalyst	Loading (mol%)	Solvent	Time (min)	Conv.[b] (%)
1	**2a**	0.5	C$_6$D$_6$	120	54
2	**2a**	0.5	C$_6$H$_5$F	120	29
3	**2a**	0.5	THF	120	26
4	**2a**	0.5	Neat	8	99
5	**2b**	0.5	Neat	8	85
6	**L^{NNP}**ZnH	1	Neat	120	Trace
7	**NHC**	1	Neat	120	Trace

[a] Reaction conditions: nitrile (0.30 mmol), pinacolborane (0.63 mmol), room temperature. [b] Conversions were determined by ^{1}H NMR spectroscopy (integration of residual benzonitrile *vs.* diborylamine product).

[a] Reaction conditions: [**2a**] = 0.0015 mmol, [HBpin] = 0.63 mmol, [R-CN] = 0.30 mmol, room temperature. Conversions were determined by ^{1}H NMR spectroscopy (integration of residual **3** *vs.* **5**). Isolated yields were shown in the parentheses. [b] 3.1 eq. HBpin was used. [c] Reaction was conducted at 80 °C.

motif intact. Moreover, an intermolecular competition reaction between benzonitrile, styrene, and HBpin (1 : 1:2 molar ratio) was examined under above conditions. The hydroboration product **5a** was exclusively formed while the styrene remained intact, thus indicating a preference of nitrile reduction over the alkene in the reaction. Furthermore, the scope of the substrates was expanded to the more challenging aliphatic nitriles. As shown in Table 2, all three selected nitriles were also successfully converted to the target borylamines **5p–5r**, although the reactions required an elevated temperature (80 °C) and a prolonged reaction time (240 min) to achieve a complete conversion of nitriles.

Inspired by the excellent performance of complex **2a** in the hydroboration of C≡N bond, we next examined its application in the imine hydroboration, which provides an efficient method for the synthesis of secondary amines.[18] It was found that **2a** also showed high activity toward reduction of a variety of imines with HBpin under neat condition, affording hydroborated product **7** at room temperature (Table 3). Reaction of *N*-benzylideneaniline with 1.1 equiv. of HBpin gave **7a** in the presence of 0.5 mol% of zinc dihydride (**2a**), with complete consumption of imine in 15 min (TOF = 400 h^{-1}).[19] Subsequently, a wide range of *C*- and *N*-substituted imines were subjected to the reactions. For the imines bearing diverse substituents at *C*-phenyl ring, the expected hydroborated amines **7b–7h** could be obtained in excellent isolated yields (82–94%) from 10 to 40 min. Among them, substrates with electron-withdrawing groups (–Cl, –Br, –CF$_3$ or –NO$_2$) proceeded rapidly in comparison to those with electron-donating groups (–OMe or –NMe$_2$). Introduction of the substitute at *N*-phenyl of imine, either *p*-Cl or *p*-Me, slightly suppressed the rate of hydroboration reactions as in the cases of generation of **7i** and **7j**. Aliphatic *N*-substituted imines are also
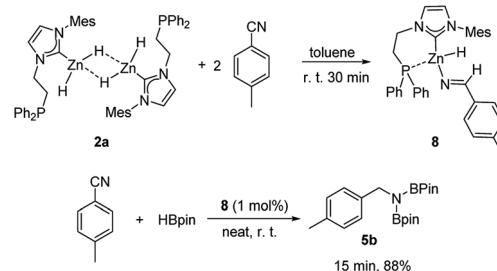
Scheme 1 Synthesis of complex **8** and its use in the hydroboration.

tolerated with current catalytic system and produced corresponding products **7k–7m**, albeit requiring an elevated temperature (80 °C) and a prolonged reaction time (6–16 h). Heterocyclic *C*-substituted imine was applied under the given conditions, providing boronated aniline **7n** in 40 min. When introducing an ester group to *C*-phenyl of imine, hydroboration reaction still occurred at C≡N moiety even with excess amount of HBpin, affording compound **7o** with 82% isolated yield.

To gain more insights into the reaction mechanism, we conducted a stoichiometric reaction between the zinc dihydrides **2a** and two equimolar amounts of *p*-MePhCN in toluene. The reaction rapidly occurred and gave complex **8** in 93% isolated yield (Scheme 1) through the insertion of one Zn–H into the –C≡N moiety. It was fully characterized by multinuclear NMR spectroscopy and elemental analysis. Addition of an excessive amount of the nitrile did not lead to a further insertion reaction probably due to the steric hindrance. The ^{1}H NMR spectrum showed a sharp signal at δ 9.39 ppm which was identified as a characteristic imine N=C*H*-R, while the signal of remaining Zn–H was located at δ 4.81 ppm. This was further confirmed by a control experiment using deuterium labeling complex **2a-D** as a starting materiel (see the ESI for details†). Subsequently, complex **8** was directly employed as a catalyst for the reaction of *p*-MePhCN with pinacolborane under standard conditions. As expected, it efficiently provided the diboronated amine *p*-MePhCH$_2$N(Bpin)$_2$ (**5b**) in 88% isolated yield (Scheme

Table 3 Hydroboration of various imines with HBpin catalyzed by **2a**^{a}
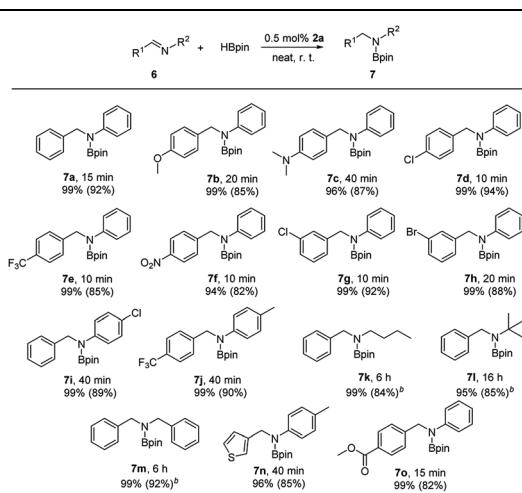
^{a} Reaction conditions: [**2a**] = 0.0015 mmol, [HBpin] = 0.33 mmol, [imine] = 0.30 mmol, room temperature. Conversions were determined by ^{1}H NMR spectroscopy (integration of residual **6** *vs.* **7**). Isolated yields were shown in the parentheses. ^{b} Reaction was conducted at 80 °C.


Fig. 3 Plots of ln[(*p*-MePhCN)$_t$/(*p*-MePhCN)$_0$] *versus* time for the hydroboration of *p*-MePhCN by catalyst **2a**. Reaction conditions: [*p*-MePhCN]$_0$ = 0.40 M, [HBpin]$_0$ = 0.84 M, [**2a**]$_0$ = 0.0146–0.0232 M.
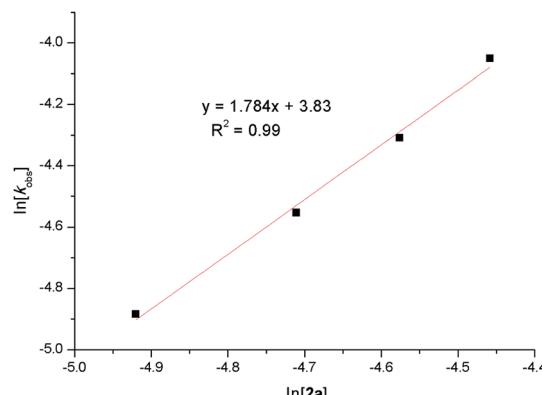
Fig. 4 Plots of $\ln k_{obs}$ *vs.* $\ln[2a]$ for the hydroboration of p-MePhCN by catalyst **2a**.

1), suggesting that complex **8** behaved as an active intermediate in the hydroboration of nitriles. Attempt to isolate other intermediate species by a stoichiometric reaction of complex **8** with pinacolborane failed because of the immediate generation of the corresponding diboronated amine **5b**.

Kinetic studies of the catalytic reactions were also performed in the presence of catalyst **2a** and monitored by ^{1}H NMR spectra (see the ESI for details†). Initial reactions were carried out using incremental catalyst starting concentrations in conjunction with a 1 : 2.1 molar ratio of p-MePhCN to HBpin. As shown in Fig. 3, plots of $\ln[(p\text{-MePhCN})_t/(p\text{-MePhCN})_0]$ *versus* time for all trials exhibited good straight lines, displaying a first-order kinetic behavior. As a result, pseudo-second order kinetic behavior on catalyst **2a** was obtained (Fig. 4) which is distinct with that in the zinc alkyl-catalyzed hydroboration of nitrile.[15] When large excess of p-MePhCN (5 equivalents) was used, a first-order dependence on HBpin was observed (ESI, Fig. S115†). A kinetic isotope effect (KIE, k_H/k_D) of 2.0 was obtained when replacement of HBpin by DBpin as the reductant in the reaction (ESI, Fig. S118†). In addition, a competitive deuterium labeling experiment using p-MePhCN, HBpin, and DBpin in a 1 : 2.1 : 2.1 molar ratio under our typical conditions was also

conducted and showed a KIE value of 3.1 (ESI, Fig. S119†). The experimental evidence herein implied that the B–H bond breaking processes might be the rate-determining step.[7a,10b]

Based on our observations and previous literature reports,[7a,8c,15] a plausible mechanistic framework for zinc dihydrides-catalyzed nitrile hydroboration is depicted in Scheme 2. The reaction of zinc dihydride **2** with nitrile gave single insertion product **8**, which then reacted with one molecule of HBpin to possibly give a zinc mixed hydride/amino **9**. Finally, complex **9** underwent a σ-bond metathesis reaction with another molecule of HBpin to afford final product **5** with the regeneration of catalyst **2**.

Conclusions

In summary, the double hydroboration of nitriles to the corresponding diboronated amines have been achieved with broad substrate scope by using a molecular zinc dihydride based on NHC ligand at room temperature under solvent-free conditions. Complex **2a** showed extremely high activity for this transformation, affording TOFs of up to 3000 h^{-1}. In addition, complex **2a** was also effective for the hydroboration of imines to boronated amines. The stoichiometric reaction of **2a** with a nitrile led to the isolation of a single Zn–H insertion product **8**, which was proved to be an active intermediate in the catalysis. Kinetic studies revealed a pseudo second-order dependence on the catalyst concentration. Further mechanistic studies and application to other catalytic reactions of this molecular zinc dihydride are underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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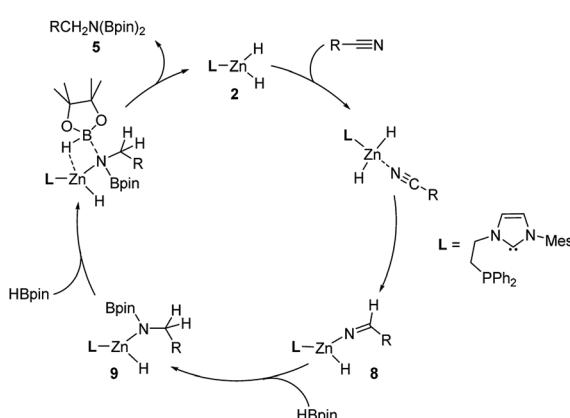
Scheme 2 The proposed mechanism of hydroboration of nitriles catalyzed by **2**.

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