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Chemical Communications

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ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/D5CC03873A

Highlights

Diboron compounds as reductants in reactions of hydrogenation, hydrofunctionalization and deoxygenation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Reduction reactions are among the most commonly employed methods in organic synthesis, both in laboratory and industry. Typical reductants include hydrogen gas, as well as metal-, silicon-, and boron-based hydrides. Although hydrogen gas is considered the greenest reductant, its production currently depends heavily on fossil fuel–derived processes. Metal-, silicon-, and boron-hydrides are effective but often inconvenient to handle, and their preparation is energy-intensive. In recent decades, the use of diboron compounds as reductants has gained increasing attention. These compounds can generate hydrogen gas from protic solvents effectively for hydrogenation reactions and can also be used in situ for hydrofunctionalization and deoxygenation transformations. This review highlights various types of diboron compounds, elucidates their mechanisms in these transformations, and discusses representative examples from recent literature.

1. Introduction

Reduction reactions, typically characterized in organic chemistry by the addition of hydrogen atoms to, or the removal of oxygen atoms from, organic compounds—including hydrogenation and deoxygenation—are fundamental transformations in organic synthesis.[1] These reactions are indispensable to the production of food additives,[2] pharmaceutical agents,[3] agrochemicals,[4] and larger-scale chemical substances.[5]

Among the various reductants employed, molecular hydrogen (H_2) is the most commonly used one in hydrogenation reactions due to its low cost and environmentally benign nature (Figure 1a).[6] In these reactions, H_2 typically supplies both hydrogen atoms incorporated into the product. Currently, the industrial production of H_2 is heavily reliant on fossil fuel-derived processes, such as coal gasification, biomass gasification, and steam methane reforming, with less than 5% of global hydrogen being produced via water splitting, including photocatalytic and electrocatalytic methods, and it raises significant concerns regarding its sustainability and environmental impact.[7] In addition to H_2, certain organic hydrogen-donor compounds—such as ammonium formate[8] and hydrazine hydrate[9]—serve as effective reductants, functioning as sources of hydrogen in various reduction reactions (Figure 1b).

Furthermore, metal and metalloid hydrides, including sodium hydride (NaH), lithium aluminium hydride ($LiAlH_4$), tributyltin hydride (Bu_3SnH), diisobutylaluminium hydride (DIBAL-H), and trialkylsilane (R_3SiH), are also frequently employed as reductants (Figure 1c).[10] These reagents typically deliver a single hydrogen atom, with the complementary proton often sourced from water, methanol, or other protic solvents. However, the hydride ions in these compounds are nucleophilic and possess high reactivity, necessitating stringent handling conditions such as an inert atmosphere. Their synthesis is also energy-intensive and costly, factors that limit their practicality for large-scale industrial applications.

Boron, a metalloid element, forms a variety of compounds—such as borane (BH_3), sodium borohydride ($NaBH_4$), and 9-borabicyclo[3.3.1]nonane (9-BBN)—that are widely employed as reductants in organic synthesis.[11] First demonstrated by Schlesinger and Brown,[12] borohydride reagents exhibit remarkable reducing activity and chemoselectivity, contributing to their widespread use in both academic and industrial settings.[13] Despite their effectiveness, borohydrides share several limitations with metal hydrides. They are typically synthesized under harsh conditions and are often air-sensitive or volatile, necessitating careful handling and storage. These drawbacks diminish their attractiveness compared to molecular hydrogen (H_2), which remains the preferred reductant for large-scale industrial applications.

In the recent decade, researchers have discovered that another class of boron compounds—diboranes—exhibit notable reducing activity in a variety of reactions, often in conjunction with transition metal catalysts or even simple bases (Figure 1d).[14] Mechanistic investigations have revealed that diboron compounds can function as reductants, facilitating the in-situ generation of molecular hydrogen (H_2) or the formation of metal hydride species from protic solvents such as water and alcohols. This emerging strategy represents a significant expansion of the current toolkit for reduction reactions in organic synthesis, and holds the potential to reshape conventional paradigms in reductive transformations. To gain deeper insights into these processes and promote further advancements in the field, we herein provide a comprehensive

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summary of representative studies involving hydrogenation and deoxygenation reactions that utilize diboron compounds as reductants.

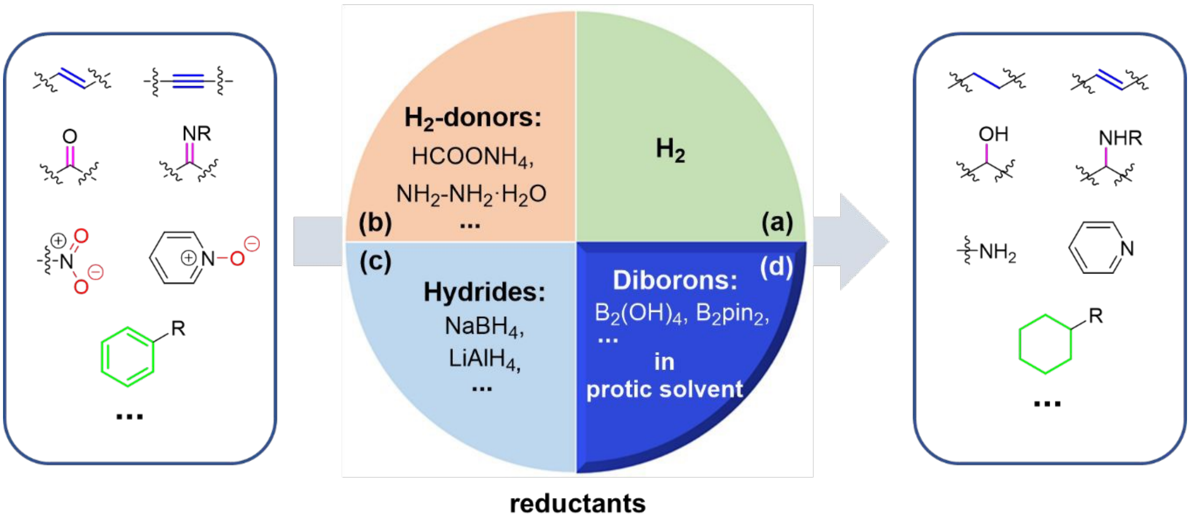

Fig. 1 Typical reductants used in reduction reactions.

2. The diboron compounds

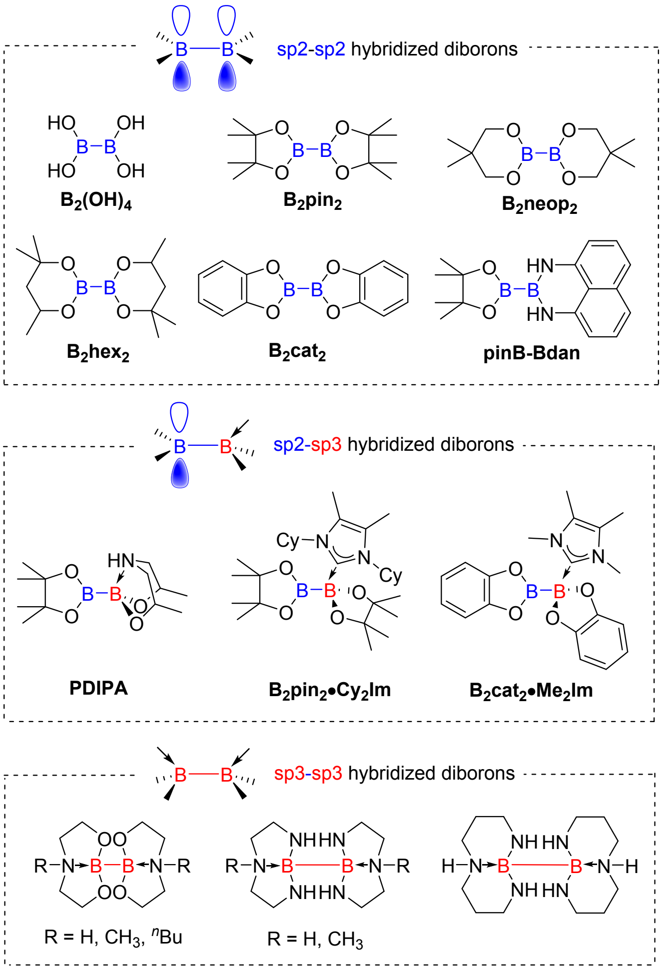

Fig. 2 Commonly used diboron compounds

The diboron compounds, or are called diboranes by others, have long been used as borylating reagents ubiquitously in organic synthesis.[15] They bear unique homoatomic boron-boron single bonds, in which the two boron atoms can be sp2-sp2, sp2-sp3, or sp3-sp3 hybridization depending on if there is a binding atom or not in the structure of the diborons. In the sp2-sp2 hybridized diborons, there are two vacant p orbitals in the two boron atoms, which make the diborons labile to be attacked by an anion or an atom bearing lonely pair of electrons. Therefore, these diborons have high affinity to water, alcohol, amines, carbenes, etc. Indeed, the sp2-hybridized boron atom can change into sp3-hybridized boron atom if one of the vacant p orbitals of the diborons accepts a pair of electrons from the binding atom, resulting in the formation of sp2-sp3 or sp3-sp3 hybridized diborons that are active anionic species in reactions.[16, 17]

In this review, we will focus on how these diboron compounds coordinate with protic solvents, such as water and alcohol, to act as reducing agent in the presence of a transition-metal or under transition-metal free conditions.

3. Transition-metal-catalysed reactions

3.1 Pd-catalysed reactions

Palladium has long been known to be able to facilitate the hydrogen-transfer process and catalyse the addition of H_2 to unsaturated double or triple bond.[18] In 2016, Stokes and co-workers reported the first Pd-catalysed transfer hydrogenation of alkenes and alkynes using H_2O as the hydrogen donor and tetrahydroxydiboron as the reductant (Scheme 1).[19] The reaction featured wide substrate scope, including various styrenes, terminal non-styrenyl alkenes, cyclic alkenes, acyclic internal alkenes, terminal and internal alkynes, which indicates the reaction has high tolerance to the electron property and

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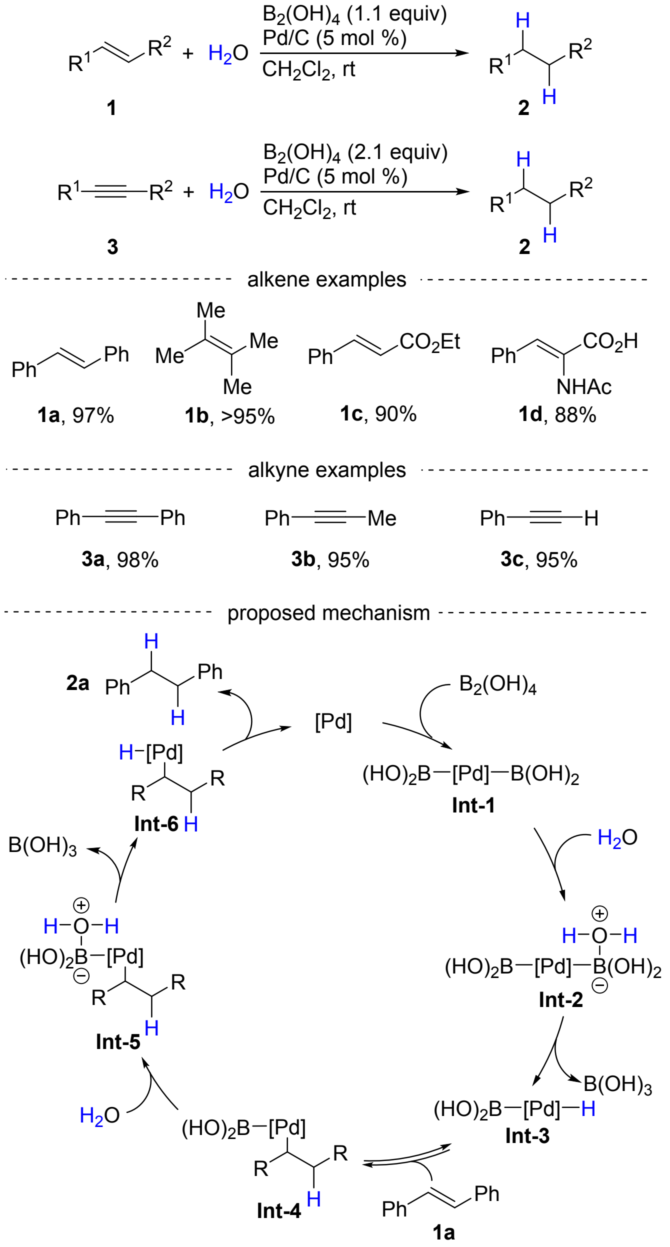
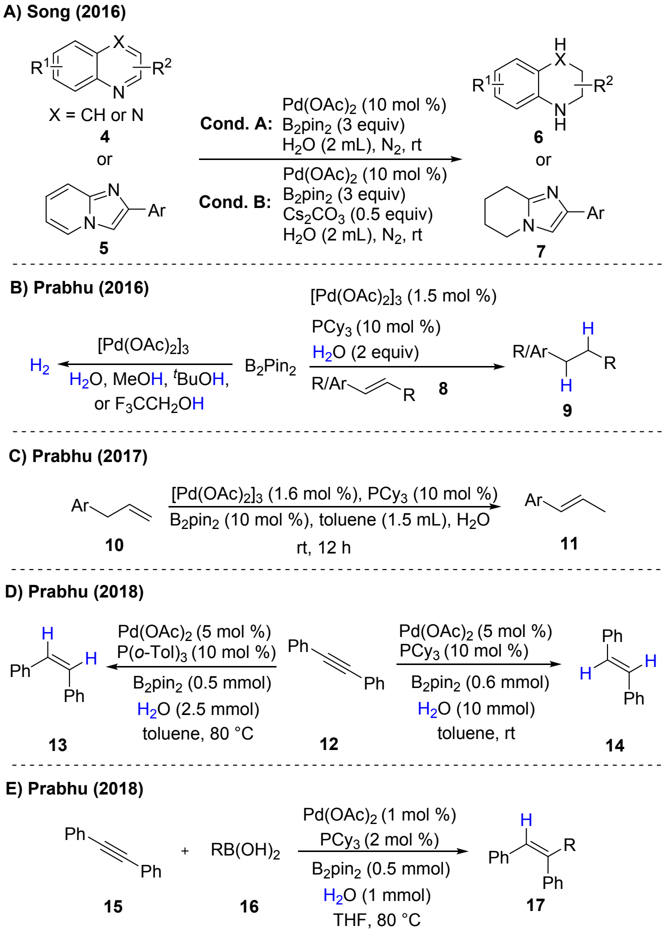


Scheme 1 Pd/C-catalyzed hydrogenation of alkenes and alkynes in the presence of $B_2(OH)_4/H_2O$.

functional groups of the substrates. Mechanistic studies insisted that the reaction initiates from the oxidative addition of the boron-boron bond of $B_2(OH)_4$ to palladium to generated intermediate **Int-1**, and the oxygen atom of H_2O binds to the boron atom forming **Int-2** which then generates the Pd-hydride **Int-3** by leaving one molecule of $B(OH)_3$. The Pd-hydride undergoes migratory insertion with the unsaturated alkenes forming intermediate **Int-4**, and the boron atom of **Int-4** would bind another molecule of H_2O forming **Int-5**. The **Int-5** then generates Intermediate **Int-6** which undergoes reductive elimination to afford the product **2a**.

Concurrently with Stokes' work, Song[20] and Prabhu[21] independently disclosed the Pd-catalysed transfer hydrogenation of N-heteroaromatic compounds and the Pd-catalysed transfer hydrogenation of alkenes using H_2O/B_2pin_2 respectively. Song and co-workers achieved the reductive dearomatization of quinolines, quinoxalines, and imidazo[1,2-a]pyridines bearing diverse substituents using $Pd(OAc)_2$ as the catalyst in the presence of B_2pin_2 and H_2O (Scheme 2A), and Prabhu and co-workers successfully reduced terminal alkenes into corresponding alkanes under the same conditions (Scheme 2B). In both of their works, a palladium-hydride intermediate formed from the interaction of [B-Pd-B] with H_2O was proposed. Notably, Prabhu and co-workers scrutinized the efficacy of the generation of H_2 catalysed by palladium in the presence of B_2pin_2 and protic solvents, and it was found that the amount of H_2 generated is dependent on the stoichiometry of both the diboron compound and water. Besides water, methanol, tert-butyl alcohol, and trifluoroethanol are also successful protic solvents that generate H_2 under the same conditions.



Scheme 2 Pd-catalysed transfer hydrogenation of N-heterocycles and alkenes using B_2pin_2/H_2O

Later on, Prabhu and co-workers expanded the strategy that the palladium-hydride can be generated in the presence of $Pd(OAc)_2/B_2pin_2/H_2O$ to more applications. In 2017, they developed a Pd-catalysed isomerization of olefins with B_2pin and H_2O, and the reaction is indicated to be initiated by the formation of [Pd-H], followed by migratory insertion into olefins and reductive β-H elimination (Scheme 2C).[22] In 2018, they achieved the reduction of alkynes catalysed by $Pd(OAc)_2$ in combination with B_2pin_2 and H_2O. The *Z/E* stereoselectivity is switchable while *Z*-alkenes were obtained when using P(o-Tol)$_3$

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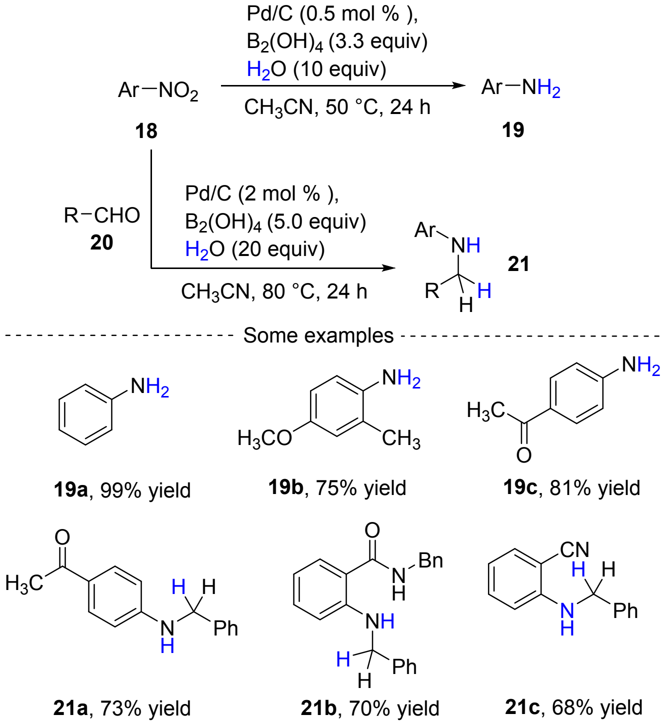
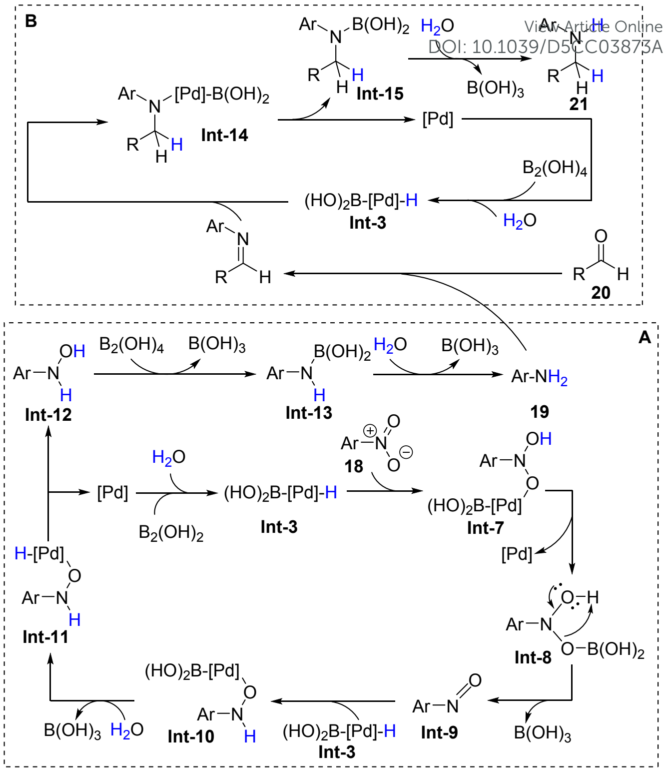


Scheme 3 Pd/C-catalysed reduction and reductive amination of nitroarenes with $B_2(OH)_4/H_2O$.



Scheme 4 Proposed mechanism for Pd/C-catalysed reduction and reductive amination of nitroarenes with $B_2(OH)_4/H_2O$.

as the ligand and *E*-alkenes were obtained when using PCy_3 as the ligand (Scheme 2D).[23] In the same year, they disclosed a Pd-catalysed hydroarylation of alkynes with arylboronic acids, and the newly added hydrogen in the product is believed to come from H_2O mediated by the diboron compound (Scheme 2E).[24]

In 2017, Zhou and co-workers reported a significant advancement in the field of palladium-catalyzed reactions, specifically the reduction and reductive amination of nitroarenes.[25] Their work utilized water as a hydrogen source and diboronic acid as a mediator, successfully producing a variety of aryl amines with diverse functional groups in good yields. The researchers employed detailed deuterium-labeling experiments to elucidate the mechanisms underlying these reactions (Scheme 4): (1) The reduction of nitroarenes proceeds through a series of well-defined steps. The process begins with the formation of a palladium-hydride intermediate **Int-3** from the Pd catalyst in the presence of $B_2(OH)_4/H_2O$ (refer to Scheme 1 for the detailed process), which then undergoes addition to the nitro group to form **Int-7**. Subsequently, the **Int-7** generates **Int-8** via reductive elimination accompanying the liberation of Pd catalyst. The **Int-8** then rearranges to generate nitrosoarene intermediate **Int-9** by losing one molecule of boronic acid. The **Int-9** is then attacked by another palladium-hydride **Int-3**, leading to the formation of **Int-10**, which then generates **Int-11** by leaving another molecule of $B(OH)_3$ with the assistance of H_2O. The **Int-11** then generates **Int-12** by reductive elimination accompanied by the regeneration of the Pd catalyst. The **Int-12**, in the presence of $B_2(OH)_4$, loses another boronic acid to form **Int-13**. Finally, hydrolysis of **Int-13** with water affords the product **19** (Scheme 4A). (2) In the reductive amination pathway, the product **19** from the reduction step reacts with an aldehyde **20** to form the imine. This imine then undergoes cross addition with the palladium-hydride **Int-3** intermediate to generate **Int-14**, and the **Int-14** subsequently undergoes reductive elimination, yielding **Int-15** with the regeneration of the Pd catalyst. The final step involves the hydrolysis of **Int-15** to afford the product **21** (Scheme 4B).

This catalytic reductive system is also suitable in asymmetric reactions. In 2017, the Zhu group developed an asymmetric palladium-catalyzed intramolecular Heck reduction of N-arylacrylamides in the presence of a chiral *P,N*-ligand (^{t}BuPHOX) to afford enantioenriched 3,3-disubstituted oxindoles in high yields and enantioselectivities (Scheme 5A).[26] The reaction features the use of $H_2O/B_2(OH)_4$ as the hydrogen source, and deuterated product was obtained in high efficiency when heavy water was used. The authors then proposed the mechanism: Firstly, chiral palladium complex was formed by mixing $PdCl_2(CH_3CN)_2$ with the chiral ligand and base, and it react with substrate **22** to form **Int-16** via the oxidative addition of the palladium complex to aryl triflate **22** followed by intramolecular carbopalladation. The **Int-16** then forms **Int-17** in the presence of H_2O via ligand exchange, and **Int-17** undergoes transmetalation with diboron compounds to generate **Int-18**. Subsequently, water interacts with the Lewis acidic boron atom of **Int-18** forming **Int-19** which undergoes 1,3-H migration via σ-bond metathesis to yield **Int-20**. Finally, **Int-20** yields the product **23** via reductive elimination and regenerate the palladium complex.

In 2021, Zhou group achieved the asymmetric Pd-catalysed hydrogenation of 1,3-diketones and indoles using hexafluoroisopropanol (HFIP) as the hydrogen source mediated by $B_2(OH)_4$.[27] By employing $Pd(OCOCF_3)_2$/(*S*)-SynPhos as the precatalyst, the desymmetric hydrogenation of various cyclic 1,3-diketones was performed, providing a series of chiral β-hydroxy ketones in excellent yields and enantioselectivities. In addition, the asymmetric diaromatic hydrogenation of indoles

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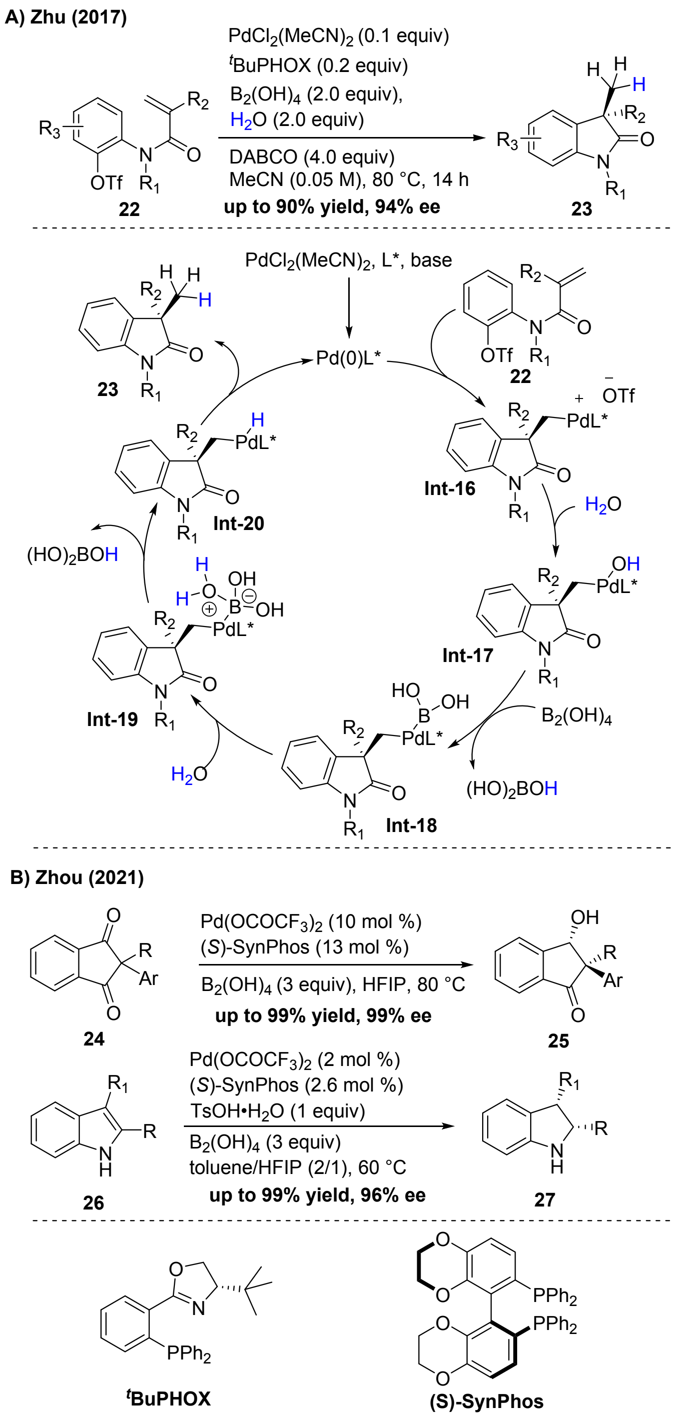
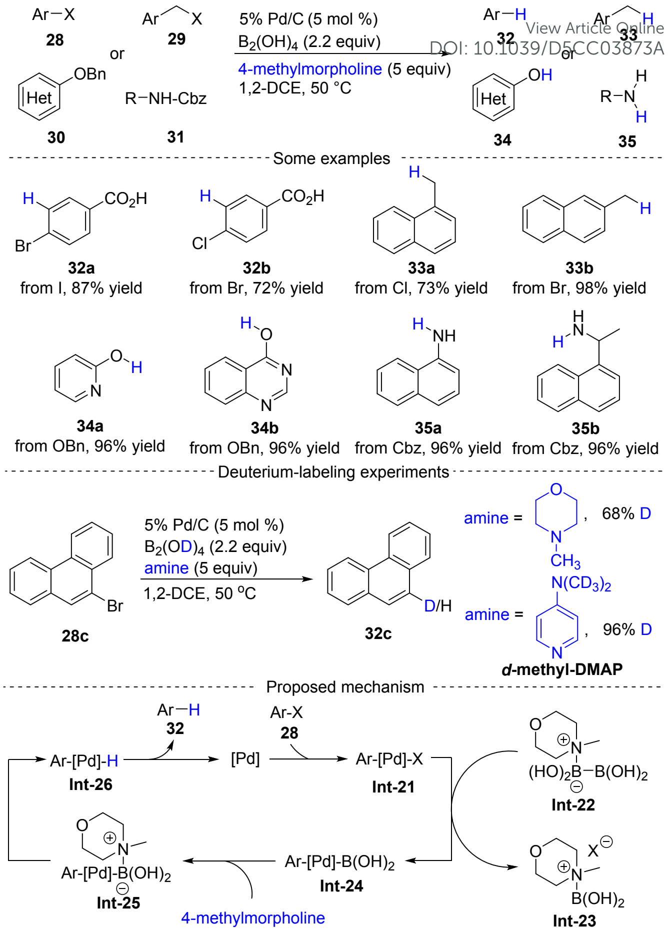


Scheme 5 Asymmetric Pd-catalysed reductions using water/diboron compounds.

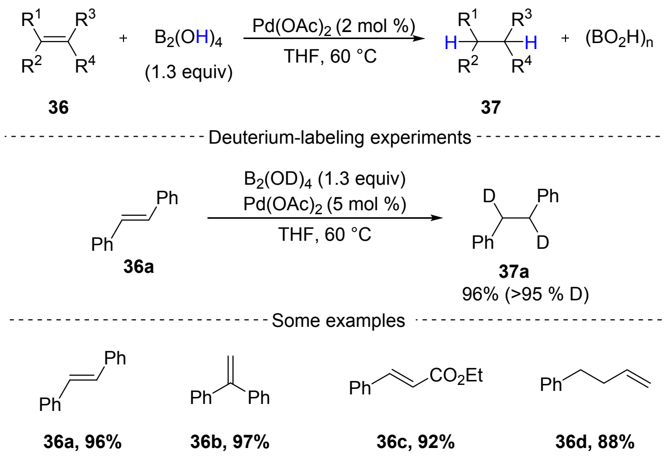


Scheme 6 Pd-catalysed reduction using amine/diboron compound.

were also achieved by slightly modifying the conditions. Mechanic studies and DFT calculation indicate that the crucial chiral palladium-hydride was formed from the proton of HFIP activated by $B_2(OH)_4$.

Besides protic solvents, such as water and alcohol, are used as hydrogen donors, amines (secondary and tertiary) have also been examined as hydrogen source in combination with diboron compounds by Lakshman group.[28] In the presence of Pd/C, $B_2(OH)_4$, and 4-methylmorpoline, aryl halides (iodides, bromides, and chlorides), benylic halides or ethers, alkenes, alkynes, aldehydes, azides, and N-Cbz protected amines are effectively reduced. Aryl halides bearing different halogen atoms undergo selective dehalogenation: iodides over bromides and chlorides, and bromides over chlorides. Surprisingly, it was found that H_2O are ineffective in the dehalogenation reactions, and tertiary amines (4-methylmorpholine, 1-mehylpyrrolidine, ^{i}Pr$_2$NEt) exhibits superior performance over secondary amine (pyrrolidine, PhNHMe). The authors carried out deuterium-labeling experiments to probe the mechanism. It was found that only 68% of D was incorporated in the product when $B_2(OD)_4$/4-methylmorpholine was used, and 96% of D was incorporated in the product when *d*-methyl-DMAP was used. Based on the results, the authors proposed a plausible mechanism. The reaction is initiated by the oxidative addition of palladium with the arylhalide **28** forming **Int-21**, and **Int-21** reacts with **Int-22** that is formed from the interaction of $B_2(OH)_4$ with 4-methylmorpholine to generate **Int-24** by losing one molecule of **Int-23**. Subsequently, **Int-24** coordinates with 4-methylmorpholine to form **Int-25**, from which **Int-26** is then generated. Finally, the reduction was completed when **Int-26** undergoes reductive elimination to yield product **32**, accompanied by regeneration of the Pd catalyst. However, it is still unclear how the hydrogen atom from the amine or/and the diboron compound attached to the Pd center.

In addition, Pd-catalysed transfer hydrogenation using $B_2(OH)_4$ as the reductant in the absence of a protic solvent has also been reported. In 2024, the Reyes group achieved a $Pd(OAc)_2$-catalyzed transfer hydrogenation of alkenes **36** using

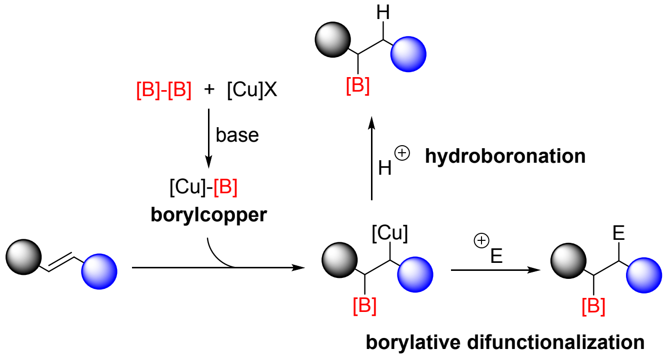


Scheme 7 Pd-catalysed reduction using $B_2(OH)_4$ without a polar protic additive.

$B_2(OH)_4$ without any protic additive, and corresponding alkanes **37** were obtained in good yields (Scheme 7).[29] The deuterium-labeling experiment exhibited that trans-stilbene almost quantitatively incorporated deuterium from $B_2(OD)_4$, which implied that the $B_2(OH)_4$ is the sole hydrogen donor.

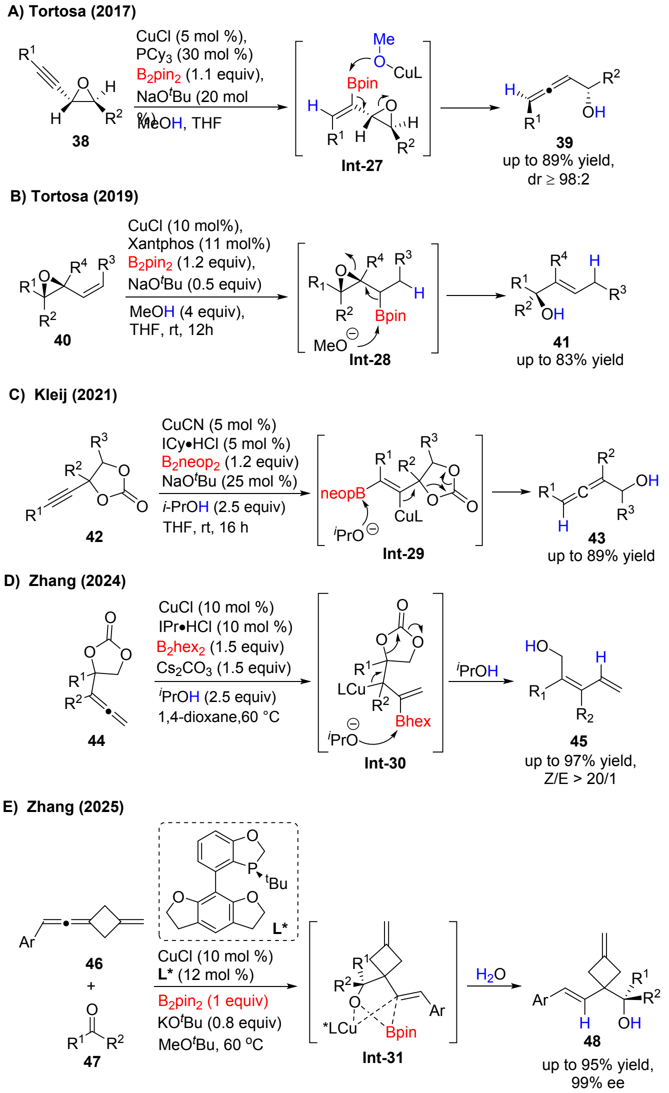
3.2 Cu-catalysed reactions

The diboron compound is known to be able to react with a copper salt to form borylcopper species Cu-[B] in the presence of a base at the beginning of the 21st century seminal reports were made by Miyaura and Hosomi,[30] and this borylcopper intermediate can undergo addition to a variety of unsaturated compounds, including α,β-unsaturated enones, alkenes, alkynes, allenes, enynes and etc., and the resulting organocopper intermediate is then hydrolyzed or trapped by electrophiles to either furnish hydroboration or borylative difunctionalization products.[31] These reactions have been intensively studied and reviewed during the past two decades.[32] So that, we will focus on the copper-catalyzed hydrogenation and deoxygenation reactions mediated by diboron compounds in this review.



Scheme 8 Cu-Catalyzed hydroboration and borylative difunctionalization using diboron compounds.

With the boom of copper-catalyzed boron chemistry, researchers found that the boryl group that added to the carbon atom can undergo deboronation or just be hydrolyzed, especially when there is a functional group (such as the -OH group). In 2017, the Tortosa group reported a copper-catalyzed hydrogenation of propargylic epoxides in the presence of B_2pin_2 and MeOH, and various α-allenols were obtained in moderate to good yields with typically excellent diastereoselectivities (Scheme 9A).[33] Based on careful mechanic studies, the authors proposed a plausible mechanism. The reaction begins with the formation of a borylcopper species (shown in Scheme 8), and the borylcopper intermediate undergoes cross addition to the carbon-carbon triple bond of compound **38**, resulting in the formation of boron-substituted alkenylcopper intermediate which is protonated by MeOH to generate **Int-28** and copper methoxide. The copper methoxide facilitates the deboronation of **Int-28**, followed by rearrangement to generate copper allenoxide. Finally, protonation of the copper allenoxide yields the allenol **39**. Later on, they also applied this method to 1,4-rduction of vinyl epoxides **40** to prepare allylic alcohols **41** in good yields and *Z*/*E* selectivity (Scheme 9B).[34] The reaction undergoes a similar pathway to their first work to generate the final product via **Int-29**. It is worth to mention that there are both carbon-carbon double bond and triple bond in the substrates, for example R^3 is an alkynyl group, the addition of borylcopper to the double bond goes over to the triple bond, yielding γ-propargyl substituted allylic alcohols. The stereoselectivity of the reaction is independent of the ratios of *E*/*Z* isomers in the starting material When only *E*-allylic alcohol was found even utilizing *E*/*Z* mixtures of **40** as the substrates. The Kleij group further expanded this catalytic method to the



Scheme 9 Cu-catalysed hydrogenation mediated by the borylcopper species.

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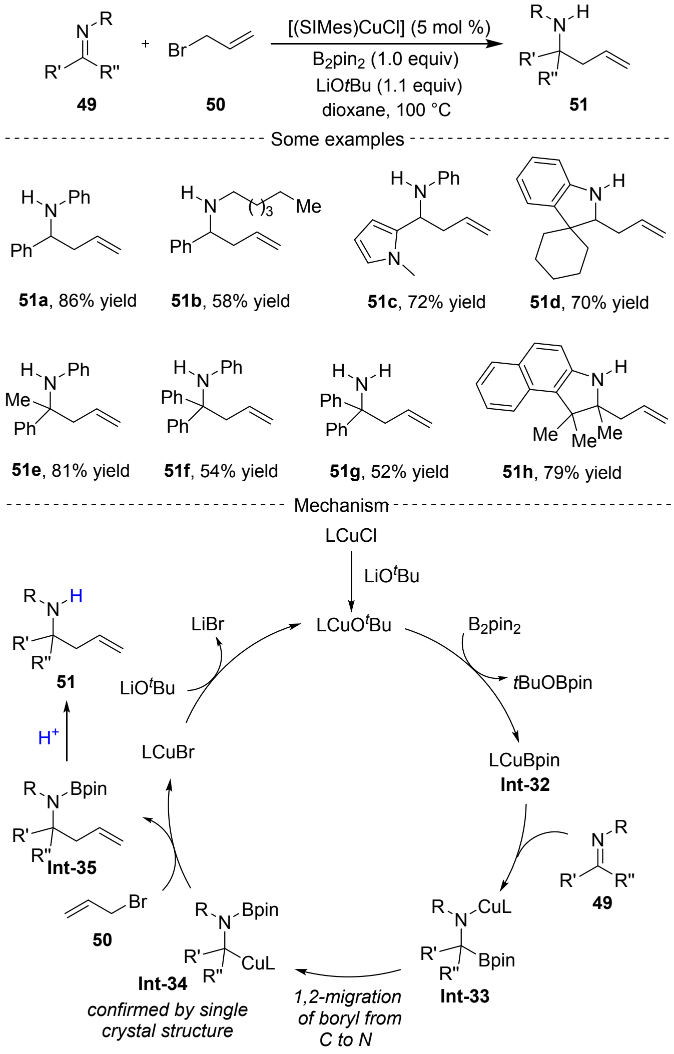
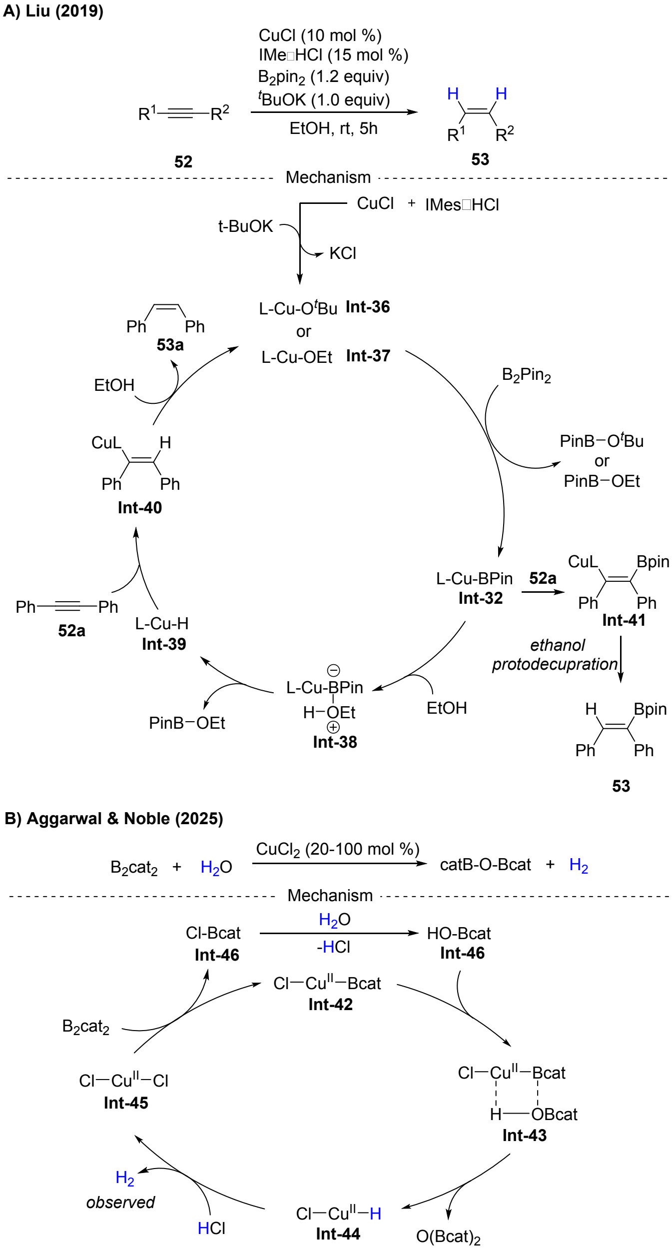
reduction of alknyl cyclic carbonates **42** in the presence of B_2neop_2 and ^iPrOH, and allenols **43** bearing diverse substituents were obtained in moderate to good yields (Scheme 9C).[35] Mechanism studies indicate a similar pathway: the borylcopper adds to the carbon-carbon triple bond yielding boron-substituted alkenylcopper species **Int-29**, followed by β-oxygen elimination, intramolecular transmetalation, and protonation to yield the final product.

Intrigued by the works above, our group achieved the reduction of allenyl cyclic carbonates **44** in the presence of B_2hex_2 and ^iPrOH. Under standard conditions, a variety of (*Z*)-penta-2,4-dien-1-ols **45** were obtained in typically moderate to good yields (Scheme 9D).[36] Based on the control experiments of mechanism studies, we believe the reaction proceed via the formation of **Int-30** through the addition of borycopper to the allenyl motif, and **Int-30** undergoes β-oxygen elimination and copper catalyzed protodeboronation to afford the final product. Very recently, our group try to prepare boron-substituted homoallylic alcohols through the asymmetric copper-catalysed reaction of internal allenes bearing a methylidene motif **46** with ketones **47** using B_2pin_2 in the presence of a chiral ligand **L***. Surprisingly, the deboronated homoallylic alcohol **48** was obtained (Scheme 9E).[37] Under optimal conditions, internal allenes and ketones bearing diverse substituents and different electronic properties were transformed into the corresponding chiral homoallylic alcohols in good yields and excellent enantioselectivities. We then investigated the mechanism by carrying out careful control experiments. The results indicate that the reaction indeed proceeds as we expected to generate **Int-31** which would form the boron-substituted homoallylic alcohols if it is then protonated. However, **Int-31** is unstable and labile to undergo rapid bora-Brook rearrangement and the resulting intermediate is pronated by trace amount of water in the solvent to yield the deboronated product. Besides, the possibility of a copper-catalyzed protodeboronation of **int-31** cannot be excluded.[38]

In 2019, Hou and Zhang a copper-catalyzed synthesis of homoallylic amines **51** by the reaction of imines **49**, allylbromides **50**, and B_2pin_2 via 1,2-bora-Brook rearrangement.[39] A variety of aldimines and ketimines were subjected to the standard conditions, and corresponding homoallylic amines were obtained in good yields (Scheme 10).



Scheme 10 Copper-catalyzed synthesis of homoallylic amines via bora-Brook rearrangement.



Scheme 11 Copper-catalyzed reduction reactions via copper-hydride specieces.

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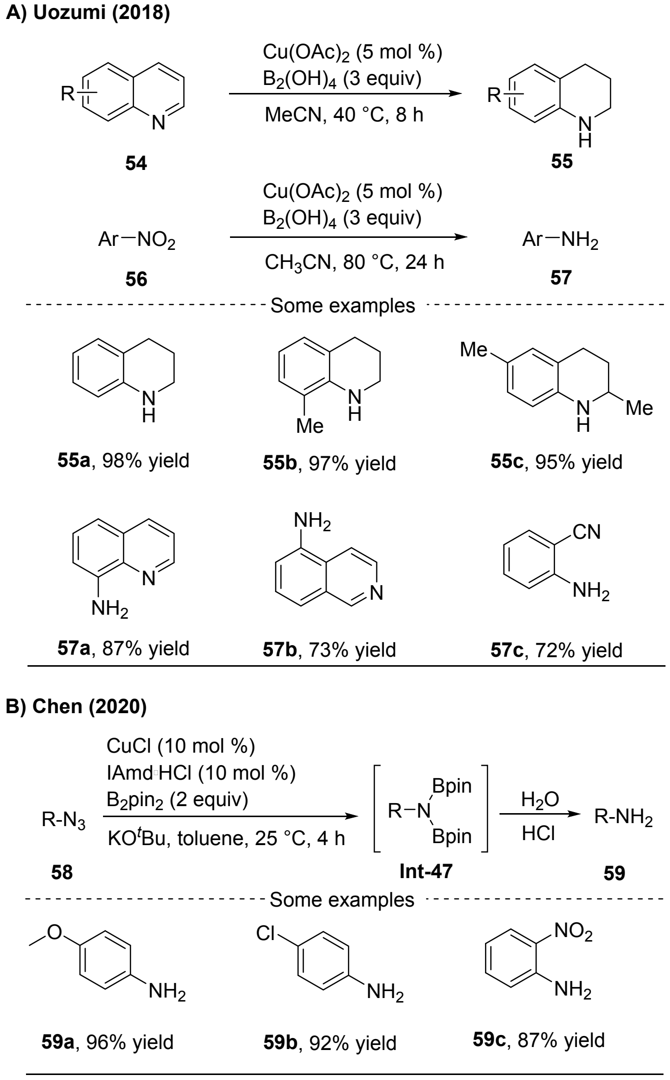
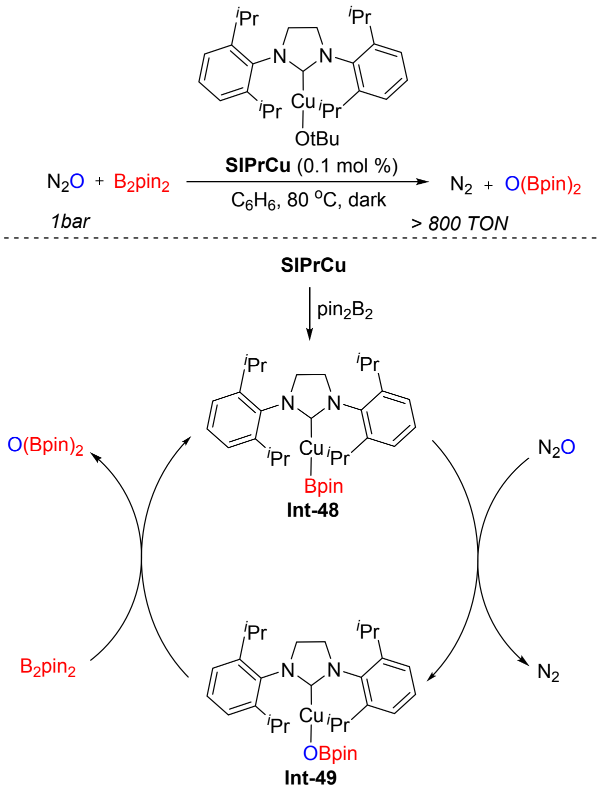
Besides allylic bromides, other allylic electrophiles such as allylic chlorides, carbonates, and phosphonates are all suitable reaction partners with the imines. Mechanic studies indicate that the borylcopper species **Int-32** is formed from mixing the copper catalyst, B_2pin_2, and LiO^tBu, and it undergoes nucleophilic addition to the imine **49** generating **Int-33**. Subsequently, the **Int-33** will transform to an α-borylaminoalkyl copper species **Int-34** via 1,2-bora-Brook rearrangement which is driven by the formation of a strong B-N bond. Finally, **Int-34** proceeds the nucleophilic substitution with allylic bromides **50** to afford **Int-35**, and **Int-35** is then protonated to yield the final product.

As mentioned before, the palladium-hydride is the key intermediate in Palladium-catalysed hydrogenation reactions using diboron compounds as reductants. Can the copper catalyst also form the copper-hydride intermediate in the presence of diborons and water? Liu and co-workers answer this question by reporting a copper-catalysed hydrogenation of alkynes using B_2pin_2 and KO^tBu in EtOH to afford corresponding alkenes (Scheme 11A).[40] The authors proposed a plausible mechanism based on the results of control experiments. The reaction is initiated by the formation of the typical borylcopper species **Int -32**. In traditional reactions, this borylcopper species will add to the triple-triple bond of alkyne **52a** to generate **Int-41**, and **Int-41** is then pronated to form product **53** of a hydroboronation process. In this reaction, however, ethyl alcohol interacts with the borylcopper species to for **Int-38** that is then form the copper hydride **Int-39** via σ-bond metathesis, accompanied by releasing pinB-OEt. Subsequently, copper-hydride **Int-39** undergoes cross addition to the alkyne **52a** to form alkenylcopper **Int-40** that is then protonated by EtOH to yield the final product **53a**. Very recently, Aggarwal and Noble group confirmed the generation of H_2 by treating B_2Cat_2 with $CuCl_2$ and water (Scheme 11B).[41] They probed the transformations of the starting material carefully via ^1H and ^{11}B NMR techniques and proposed the mechanism. The reaction begins with the formation of borylcopper species **Int-42** and **Int-46**, and **Int-42** interacts with **Int-46** that is generated by reaction of **Int-46** with H_2O, affording **Int-43**. Subsequently, **Int-43** yields copper hydride **Int-44** which is then react with HCl to form H_2 and regenerate $CuCl_2$.

Uozumi and Chen achieved the synthesis of amines via copper-catalysed reduction of quinolines, nitroaromatics and azides mediated by diboron compounds rescpectively in 2018 and 2020. Uozumi and co-workers employed $Cu(OAc)_2$ as the catalyst, a variety of quinolines **54** and nitroaromatics **56** were reduced to amines **55** and **57** in good yields in the presence of excess $B_2(OH)_4$ in acetonitrile at 40 °C (Scheme 12A).[42] Chen and co-workers subjected azides to the typical condition of borylative difunctionalization of unsaturated compounds, and the azides **58** bearing diverse substituents were reduced to corresponding amines **59** catalysed by CuCl/IAmd·HCl in the presence of B_2pin_2 and KO^tBu (Scheme 12B).[43] The reaction is thought to proceed via the hydrolysis of a diborylamine species **Int-**



Scheme 12 Copper-catalysed synthesis of amines via reduction of quinolines, nitroaromatics and azides mediated by diboron compounds.

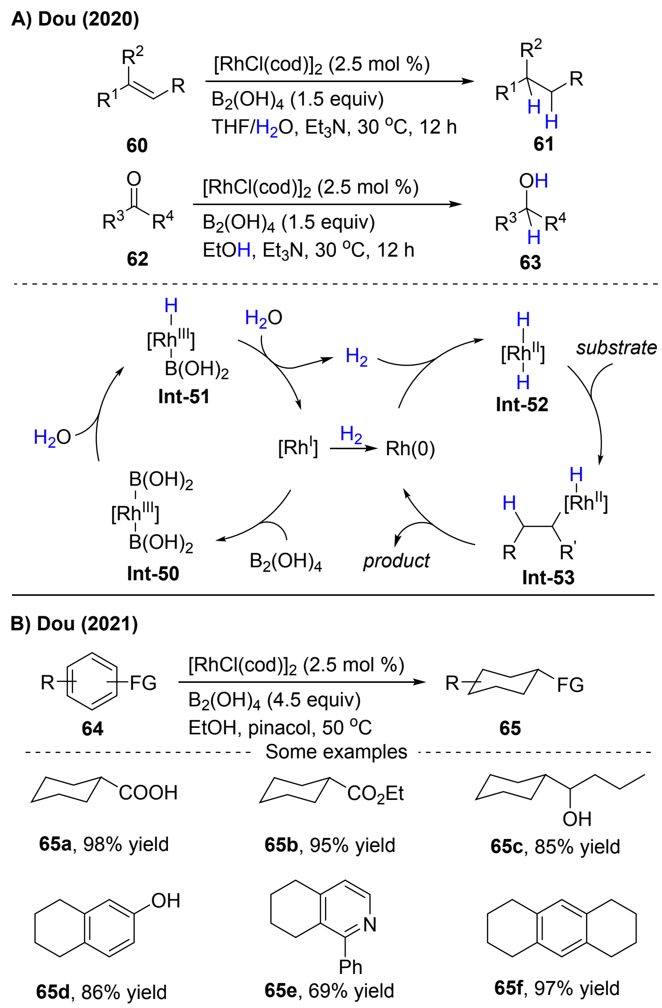


Scheme 13 Copper-catalysed deoxygenation of N_2O using B_2pin_2 as the reductants.

47 that is formed by reaction of the borylcopper and azide followed by further transmetalation with B_2pin_2.

Besides the hydrogenation reactions, copper-catalysed deoxygenation reaction has also been achieved recently. In 2024, Chaplin and co-workers reported the copper-catalysed reduction of nitrous oxide using B_2pin_2 as the reductant (Scheme 13).[44] By using a NHC-coordianted copper catalyst **SIPrCu**, the nitrous oxide is reduced into nitrogen gas with high catalytic turnover numbers at 80 ^oC in the dark under 1 bar atmosphere of N_2O (Scheme 13). The reaction is believed to be initiated by the active borylcopper species **Int-48** that is formed from the reaction of **SIPrCu** with B_2pin_2, and **Int-48** undergoes abstract the oxygen from N_2O to release N_2 accompanied by generating **Int-49**. Finally, **Int-49** reacts with B_2pin_2 to form the byproduct $O(Bpin)_2$ and regenerate the active borylcopper species **Int-48**.

As illustrated above, the borylcopper species is the key intermediate for the copper-catalyzed reaction using diboron compounds as reductants, and it either reacts with protic solvents to form the copper-hydride species which undergoes hydrometallation to completed the reduction, or undergoes addition reactions to the compounds to be reduced to form borylated intermediates followed by hydrolysis, or just undergoes deoxygenation reaction with the compounds.



Scheme 14 Rhodium-catalysed hydrogenation reactions using diboron compounds and protic solvents.

3.3 Rh-catalysed reactions

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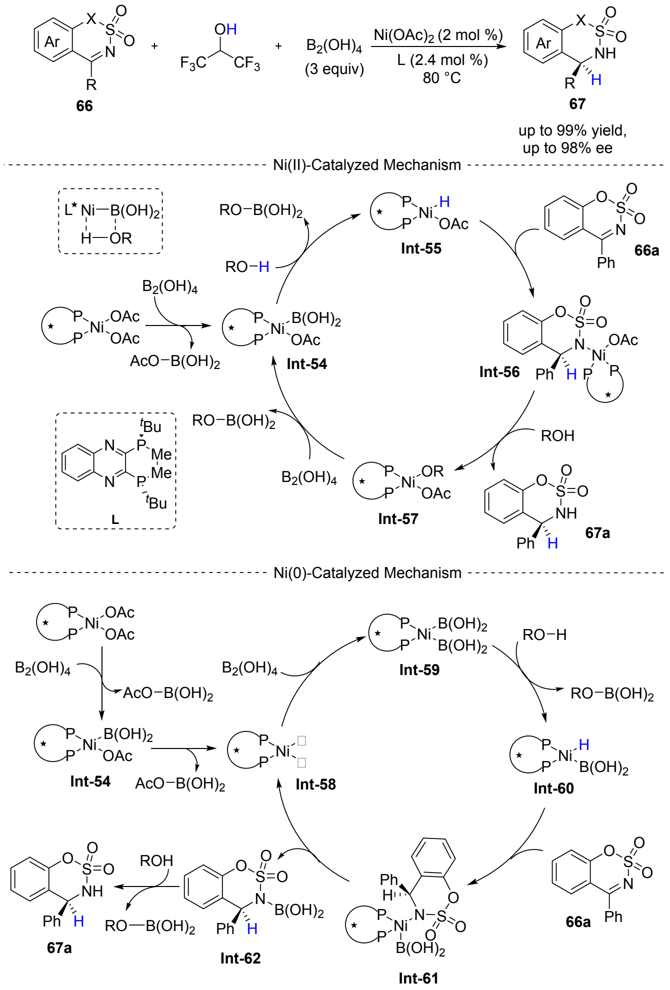
Rhodium is well-known for its role in catalytic hydrogenation of unsaturated compounds.[45] In 2020, Dou and co-workers disclosed a Rh-catalyzed hydrogenation of alkenes, aldehydes and ketones in the presence of water and diborons (Scheme 14A)[46]. By using a catalytic amount of $[RhCl(cod)]_2$, alkenes, aldehydes and ketones bearing diverse substituents were reduced into corresponding alkanes and alcohols. The reaction is proposed to proceed via two catalytic cycles. The first catalytic cycle begins with the formation of rhodium(III)-hydride **Int-51**. The reaction **Int-51** with water to release H_2 and $[Rh^I]$ complex. The $[Rh^I]$ complex undergoes oxidative addition with the diboron compound to form **Int-50** and it then reacts with water to reproduce the rhodium-hydride **Int-51**. The second catalytic cycle is initiated by the formation of Rh(0) complex via the reduction of $[Rh^I]$ complex by H_2. The Rh(0) complex reacts with H_2 to generated rhodium(II)-dihydride **Int-52**, subsequently, it undergoes migratory insertion to the substrate generating **Int-53**. Finally, reductive elimination of **Int-53** forms the product with the regeneration of Rh(0) complex. It is worth to mention that the formation of rhodium-hydride by treating $[RhCl(cod)]_2$ with HBpin is confirmed by Zhao and coworkers.[47] Later on, the Dou group employ this catalytic strategy to the hydrogenation of functionalized arenes (Scheme 14B).[48] Various functionalized benzenes, naphthalenes, anthracene, quinoline and isoquinolines were reduced to corresponding products in good yields using $B_2(OH)_4$ and ethanol. The authors carried out mechanistic experiments and confirmed that hydrogen gas are formed when mix the Rh-catalyst with $B_2(OH)_4$ and EtOH, and it is believed that the aromatic ring is reduced by H_2 under the catalysis of rhodium.

3.4 Reactions catalysed by other transition-metals

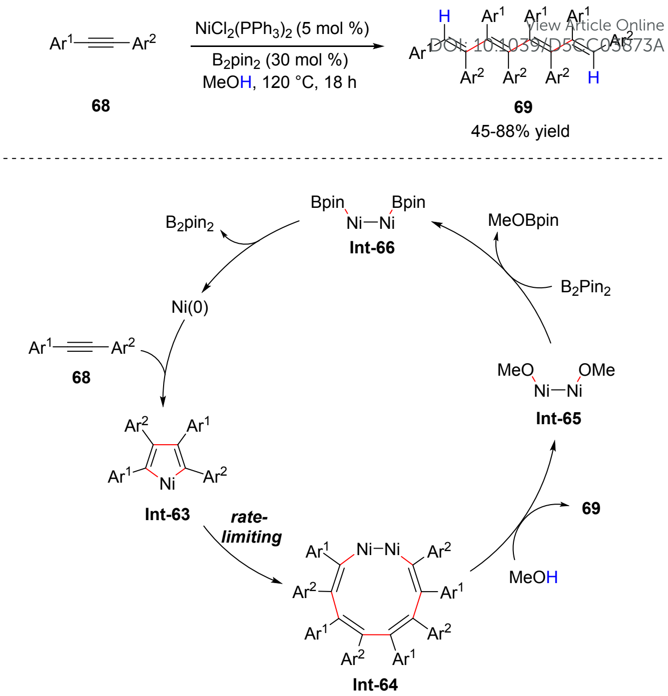
In 2023, the Zhou group reported an asymmetric transfer hydrogenation of N-sulfonyl imines 66 using $B_2(OH)_4$ as reductants in the presence of hexafluoroisopropanol catalyzed by nickel, and a variety of chiral cyclic sulfamidates **67** with good enantioselectivity (Scheme 15).[49] Considering that both Ni (II) and Ni (0) precursors can promote this asymmetric transfer hydrogenation, there are two possible mechanisms. One mechanism begins with the metal transfer between the Ni (II) catalyst and $B_2(OH)_4$ provides the Ni−B intermediate **Int-54**. Subsequently, alcohols coordinates to the boron atom of **Int-54**, and the hydrogen is transferred from alcohols to nickel via σ-bond metathesis, resulting in chiral nickel hydride active **Int-55**, which is inserted into **66a** by enantiomer migration to form **Int-56**. Finally, the protolysis of Int-56 yields the desired chiral sulfamidate product **67a** and **Int-57**, and **Int-57** will undergo transmetalation with $B_2(OH)_4$ to form **Int-54** and complete the catalytic cycle. The other possible mechanism begins with the formation of Ni (0) species **Int-58**, which is produced by the transmetalation and reductive elimination of the Ni (II) catalyst with $B_2(OH)_4$. The oxidative addition of the B-B bond in $B_2(OH)_4$ with the **Int-58** yields the Ni-B intermediate **Int-59**, and the boron atom of the **Int-59** can coordinate with the oxygen atom of the alcohols to provide the Ni-H species **Int-60**, which is inserted into **66a** by enantiomer migration to form **Int-61**. Finally, **Int-61** undergoes reductive elimination to regenerate Ni (0) species **Int-58** and **Int-62**, which can be protonated by alcohols to release the desired product **67a**. In addition, the **Int-61** can directly release the product **67a** and Ni (II) species via the protolysis with alcohol, and the Ni (II) species can regenerate



Scheme 15 Ni-catalyzed asymmetric transfer hydrogenation of cyclic N-sulfonyl imines.

Ni (0) species via reductive elimination and complete the catalytic cycle.

Nickel has been used as the catalyst in reductive coupling reactions of alkynes using B_2pin_2 as the reductant as early as in 2015 by Huang and coworkes (Scheme 16).[50] Under catalysis of 5 mol % $NiCl_2(PPh_3)_2$, internal aryl alkynes bearing diverse substituents proceed the tetramerization efficiently to afford alkenes with large π-conjugation system in the presence of in substoichiometric amount of B_2pin_2 in methanol. The authors carried out concrete and detailed experiments to interrogate the mechanism, and the results indicate that the reaction is initiated by the formation of Ni(0) in situ. The Ni(0) species undergoes oxidative cycloaddition with the alkyne **68** to furnish a five-membered nickelacyle **Int-63**, and **Int-63** will undergo dimerization to generate a dinuclear Ni-Ni intermediate **Int-64**. Kinetic studies reveal that the formation of **Int-64** is the rate-limiting step of the catalytic cycle. Finally, protonation of **Int-64** affords the product **69** and liberates dinuclear Ni-Ni intermediate **Int-65**. Reaction of **Int-65** with 2 equivalent of B2pin2 yields **Int-66**, followed by reductive elimination to regenerate the Ni(0) catalyst.



Scheme 16 Ni-catalyzed reductive coupling of alkynes using diboron compound as the reductant.

In 2017, the Song group reported a Ru-catalysed reductive amination of aldehydes with anilines in the presence of $B_2(OH)_4$ in water (Scheme 17A).[51] Catalysed by 3 mol % of $[RuCl_2(p\text{-}cymene)]_2$, aldehydes **70** react with anilines **71** to afford amines **72** as the products in good yields using $B_2(OH)_4$ as the reductant in water. Replacing H_2O with D_2O, a variety of deuterated amine were obtained with high deuterium incorporation (>90%). The reaction is believed to begin with the formation of **Int-67** from the reaction of the Ru catalyst and water with anilines binding to the Ru center as a ligand. Subsequently, **Int-67** reacts with $B_2(OH)_4$ generating **Int-68** by releasing the boronic acid, and **Int-68** reacts with water to generate the ruthenium-hydride **Int-69**. The final product was generated when the imines **73** that are formed by the reaction of aldehydes with anilines undergo transfer hydrogenation with **Int-69** via an outer-sphere mechanism.

As one of the most abundant metal in the earth's crust, iron is a fascinating catalyst in catalytic reduction reactions.[52] In 2019, Liu and co-workers disclosed an iron-catalyzed hydrodiborylation reaction of alkyl esters (Scheme 17B).[53] Catalyzed by 10 mol % of $FeBr_2$, alkyl esters **74** bearing different substituents were transformed into corresponding diborylalkanes **75** in moderate to high yields using excess B_2pin_2 as both the reactant and the borylation reagents, and using ethyl alcohol as the hydrogen donor in toluene at 100 ^{o}C. Based on the observation during the experiment, the authors proposed that esters are initially reduced into corresponding aldehydes **76** by the iron-hydride species **Int-70**. The iron-hydride **Int-70** is formed by the reaction of boryliron species **Int-71** with ethyl alcohol, and this pathway is very similar to that for the formation of former palladium-hydride, copper-hydride, ruthenium-hydride, etc. Finally, aldehydes **76** undergo gem-diborylation with B_2pin_2 to yield the products **75**.

Besides homogeneous catalysis, Astruc and Liu et al studied the performance of heterogeneous transition-metal catalyst in hydrogen evolution in the presence of $B_2(OH)_4$ and H_2O (Scheme 18).[54] The authors prepared several graphene quantum dot (GQD)-stabilized transition-metal nanoparticles to

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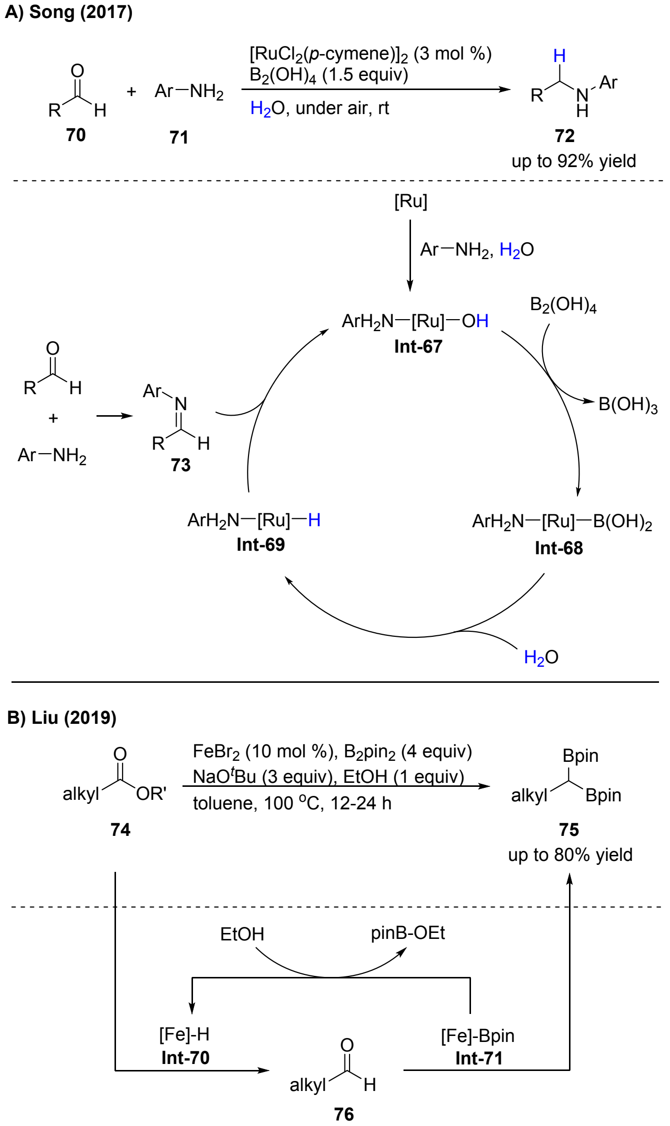
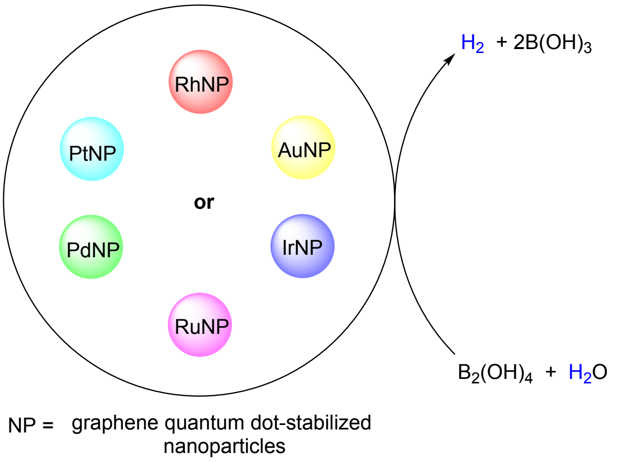
examine their catalytic activity towards the H_2 evolution from $B_2(OH)_4$ and H_2O. The results indicate the following catalytic activity: PtNP > RhNP > AuNP > PdNP > IrNP > RuNP. Mechanic studies support double water O−H bond cleavage on the NP surface via the formation of metal-dihydrides.



Scheme 17 Ru- and Fe-catalysed reduction using diboron compounds as reductants.

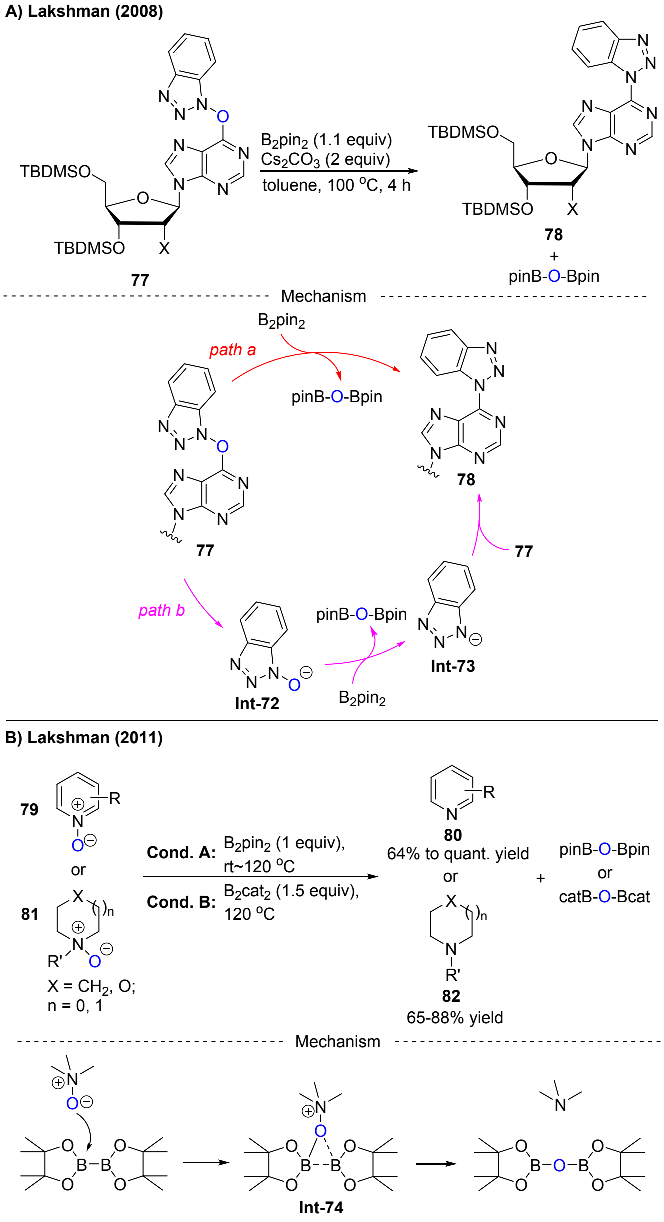


Scheme 18 Graphene quantum dot-stabilized transition-metal nano particles for H_2 evolution using $B_2(OH)_4/H_2O$.

As described before, several transition-metals have been applied in catalytic reductions in combination of diboron compounds and protic solvents, and it is almost for sure that some other metals in the periodic table that are suitable for the catalysis are to be uncovered. Such catalytic systems are highly efficient for reduction of various unsaturated structures, including polar/non-polar double/triple bonds, hetero-/non-heteroaromatics, as well as for deoxygenation reactions. What's more, transition-metal-catalyzed asymmetric versions of reactions can be achieved in the presence of chiral ligand. For concerns with metal-contamination, developing heterogenous metal catalysts might be a good solution.

4. Transition-metal-free reactions

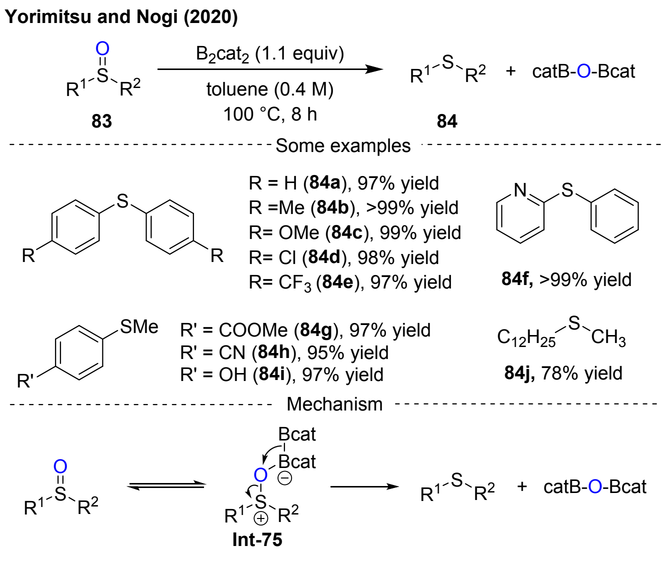
4.1 Deoxygenation



Scheme 19 Deoxygenation under metal-free conditions using diboron compounds as reductants.

The deoxygenation reaction using diboron compounds as reductants has been reported as early as in 2008 by Lakshman and co-workers.[55] They found that O^6-(benzotriazol-1-yl)inosine derivatives **77** were able to undergo deoxygenation reactions being treated with B_2pin_2 in the presence of Cs_2CO_3 in toluene at 100 °C, to yield C-6 (benzotriazol-1-yl)purine nucleoside derivatives **78** and generate pinB-O-Bpin as the byproduct (Scheme 19A). After carried out a series of mechanistic experiments, the authors proposed two possible pathways for the reaction. The path a is a synergistic process, wherein the substrate **77** interact with B_2pin_2 in the presence of Cs_2CO_3 to yield the products in a single step. The path b is a multistep process in which a low amount of benzotriazolate **Int-72** might be formed initially, and it then undergoes oxygen transfer to B_2pin_2 to generate **Int-73** that will cause nucleophilic substitution with **77** to yield the product. Later on, they expanded the application of this method to the deoxygenation of pyridine-N-oxides or amine-*N*-oxides (Scheme 19B).[56] In the absence of bases, a variety of pyridine-N-oxides **79** and amine-*N*-oxides **81** with diverse functional groups were reduced to corresponding pyridines **80** and amines **82** in good yields using B_2pin_2 or B_2cat_2 as the reductant in a proper solvent, at a proper temperature. Mechanistic studies indicate that the *N*-oxides will attack one boron atom of the diboron compound to form **Int-74** bearing a N-O-B bond. Subsequently, **Int-74** liberates the amine by releasing pinB-O-Bpin.

The deoxygenation of sulfoxides using diboron compounds as reductants was achieved by Yorimitsu and Nogi et al in 2020 (Scheme 20).[57] In the presence of 1.1 equivalent of B_2cat_2, various sulfoxides, including aryl-aryl, aryl-alkyl, alkyl-alkyl sulfoxides, were reduced to corresponding sulfides in good to excellent yields. The reaction features tolerance of broad spectrum of functional groups, such as halides, alkynes, carbonyls, nitriles, etc. The authors proposed that the reaction is initiated by the attack of sulfoxides to the boron center of the diboron compound, yielding Int-66 that will afford the sulfides accompanied by the release of catB-O-Bcat via 1,2-migration of the terminal boryl group to the oxygen.



Scheme 20 Deoxygenation of sulfoxides using B_2cat_2 as the reductant under metal-free conditions.

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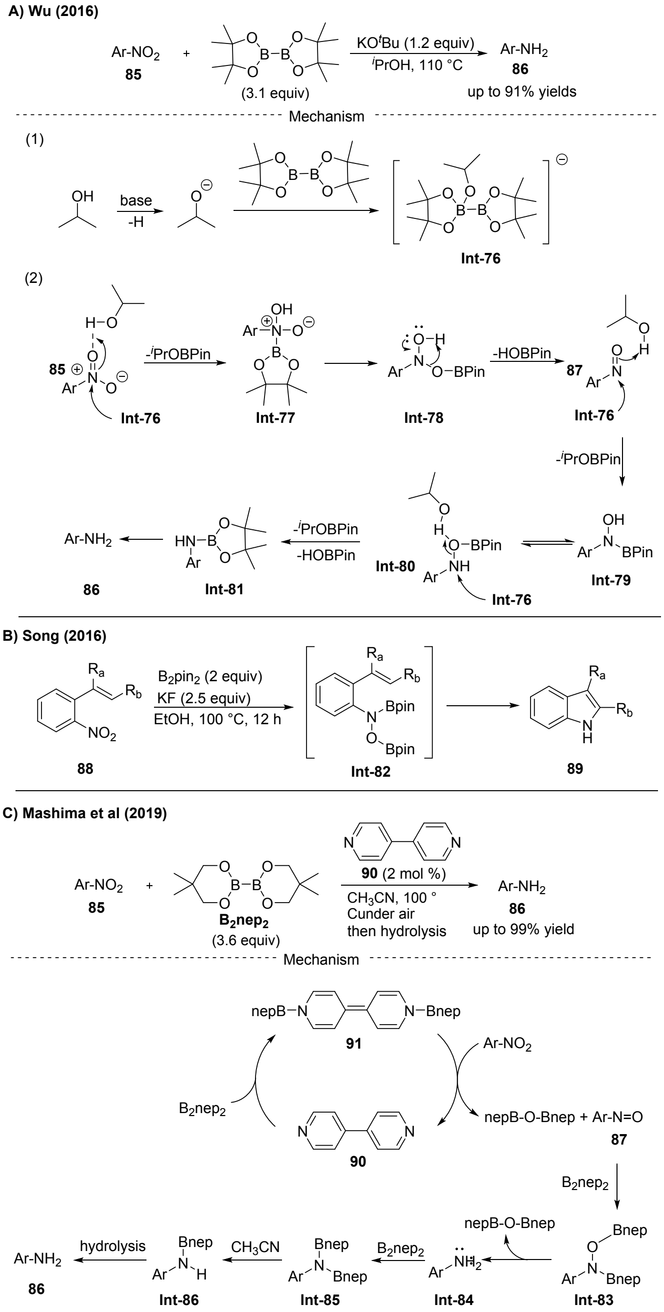
4.2 Reduction of nitro group



Scheme 21 Reduction of nitro compound using B_2pin_2/isopropanol.

Despite the previous work that the nitro group can be reduced by diboron compound with protic solvents in the presence of palladium catalyst,[25] many works about the reduction of nitro group under transition-metal-free conditions were also disclosed. In 2016, the Wu group achieved the reduction of aromatic nitro compound using B_2pin_2 as the reductants in isopropanol at 110 °C, and the corresponding anilines obtained in good to excellent yields (Scheme 21A).[58] The reaction has good tolerance to substituents diversity, and functional groups of halides, aldehydes, carboxylic acids, esters, alkynes, as well as nitriles, can be kept during the reduction. After carrying out a series of control experiments in

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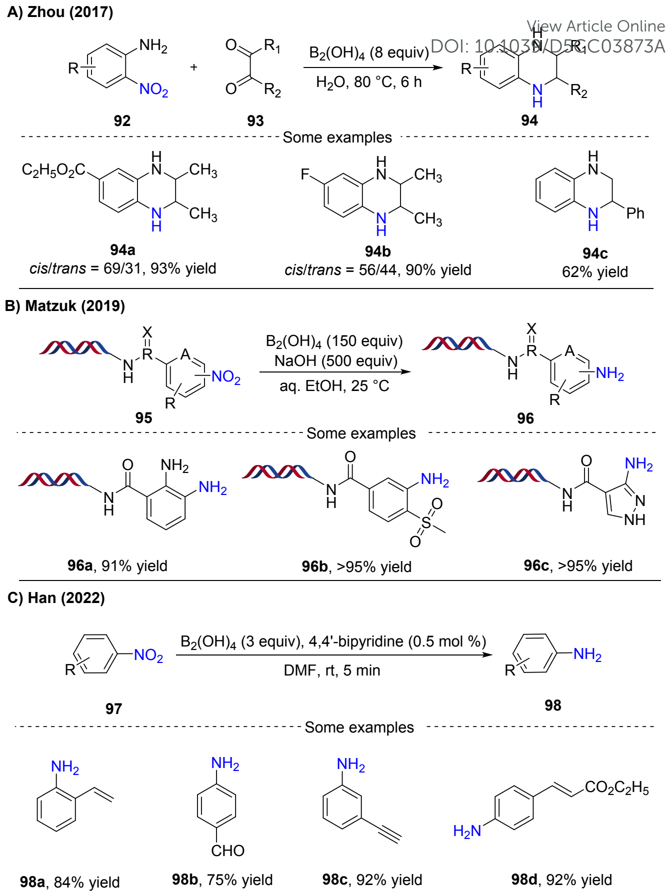
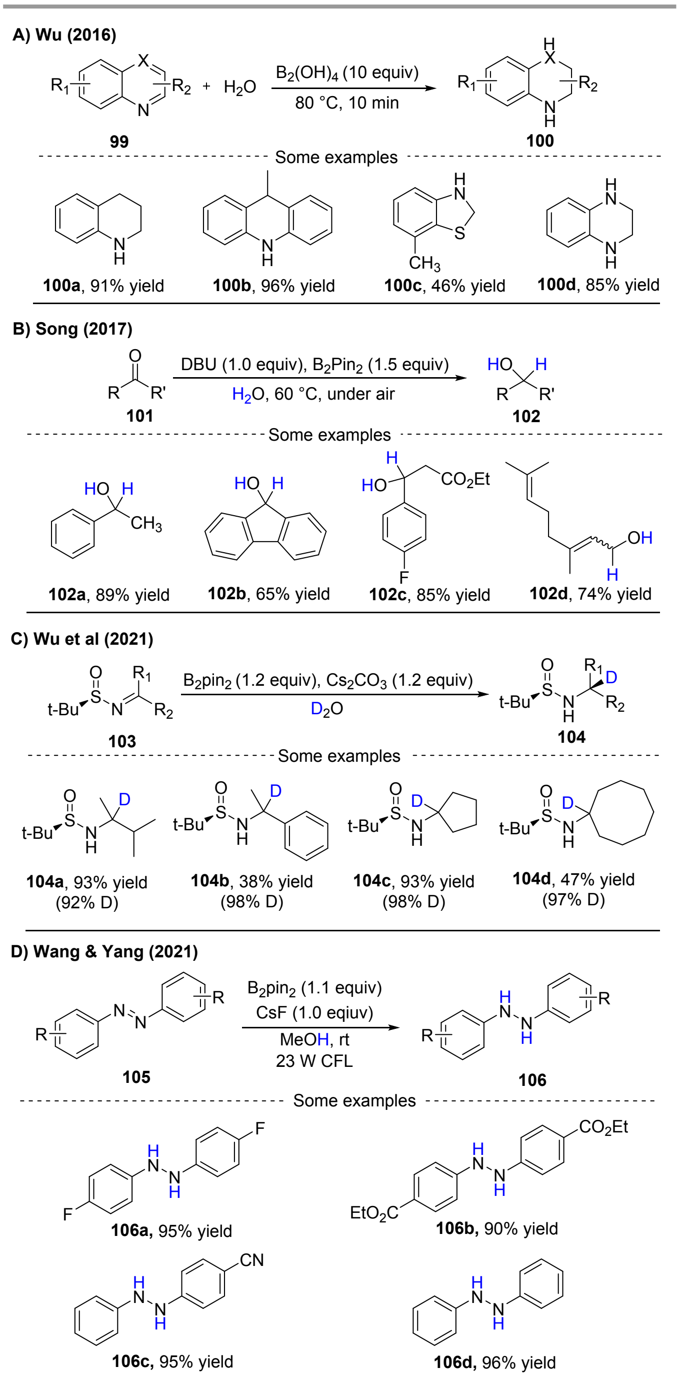
combination of ^{11}B NMR and GC-MS, the author proposed that the reaction is initiated by the formation of **Int-76** when B_2pin_2 is dissolved in isopropanol. Subsequently, the nucleophilic **Int-76** attack the nitro group of substrates **85** to form **Int-77** by releasing ^{i}PrOBpin, and **Int-77** forms the nitroso compound **87** by elimination of HOBpin. The nitroso compound **87** is further attacked by **Int-76** to afford **Int-79** that can convert to **Int-80** via 1,2-migration in an equilibrium. Finally, the **Int-80** is attacked by **Int-76** to form **Int-81** with the liberation of ^{i}PrOBpin and HOBpin, and protonation of **Int-81** affords the final product **86**. Almost at the same time, the Song group developed a very similar method to synthesize indoles via reductive cyclization of *o*-nitrostyrenes, and the adduct **Int-82** formed from the nitroso compound and B_2pin_2 is believed to be the key intermediate (Scheme 21B).[59]

A similar method has also been reported by Mashima and coworkers in 2019.[60] The authors employed excess B_2nep_2 in combination of 2 mol % of 4,4'-bipyridine to reduce a series of aromatic nitro compounds into corresponding aninlines in good yields. A plausible mechanism was then proposed based on the results of control experiments (Scheme 21C). Initially, the diboron compound B_2nep_2 interacts with the 4,4'-bipyridine **90** generating intermediate **91**, and it behaves as the reductant to reduce the nitro compound **85** into the nitroso compound **87**. Subsequently, B_2nep_2 undergoes nucleophilic addition to the nitroso compound **87** to yield **Int-83** that will generate the nitrene intermediate **Int-84**, and the reaction of **Int-84** with B_2nep_2 affording **Int-85**. Finally, the protonation of **Int-85** by CH_3CN yields **Int-86** that is then hydrolyzed to generated the final product **86**. It is worth to mention that super electron donors with good reductive ability were verified by Jiao et al when they mixed diboron compounds with pyridines in the presence of a base, which further verified the mechanism.[61]



Scheme 22 More examples for reduction of nitro group.

The two methods for reduction of nitro group were then expanded to more substrates. Zhou et al achieved the synthesis of tetrahydroquinoxalines **94** by the reaction of 2-amino(nitro)anilines **92** with 1, 2-dicarbonyl compounds **93** using $B_2(OH)_4$ as reductants in H_2O (Scheme 22A) in 2017.[62] Simmons and coworkers reported the reduction of DNA-compatible nitro compounds **95** using $B_2(OH)_4$ as reductants in the presence of NaOH in ethanol in 2019 (Scheme 22B).[63] Han and coworkers reported the reduction of nitro aromatics **97** using $B_2(OH)_4$ in the presence of catalytic amount of 4,4'-bipyridine in DMF (Scheme 22C).[64] The reaction proceeded efficiently for a variety of substrates at room temperature, while the similar method used by Mashima et al required much higher temperature.



Scheme 23 Reduction of ketones/aldehydes/azobenzenes/ aromatic heterocycles.

4.3 Reduction of ketones/aldehydes/azobenzenes/aromatic heterocycles

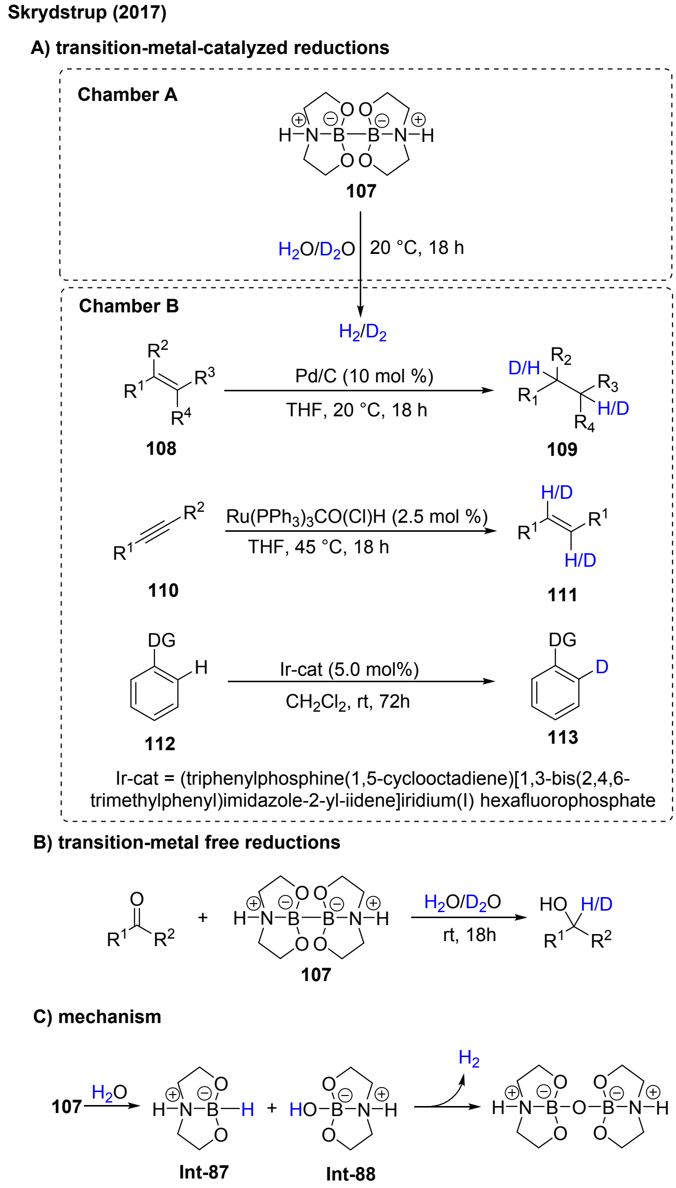
In 2016, Wu and coworkers accomplished the hydro-dearomatization of heterocycles **99** using excess $B_2(OH)_4$ as reductants in water (Scheme 23A).[65] Mechanistic studies indicate that the reaction is initiated by a 1,2-hydroboronation of the heterocycle via six-membered transition state formed from the substrate, diboronic acid and water. In 2017, Song group disclosed the reduction of ketones and aldehydes **101** using B_2pin_2 as the reductant in the presence of DBU in water, and the reaction featured high chemoelectivity and good tolerance to the functional group of the substrates (Scheme 23B).[66] Mechanistic studies suggested dual roles of the diboron compound as both the activator of water and the Lewis acid for activating the carbonyl group. Promoted by the prevalence of deuterated compound in drug discovery, Wu et al reported the deuteride reduction of N-tert-butanesulfinyl ketimines **103** using B_2pin_2 in the presence of Cs_2CO_3 in D_2O in 2021, and the products were obtained in good yields with high incorporation of deuterium (Scheme 23C).[67] In the same year, Wang and Yang et al developed a visible-ligand-driven reduction of azobenzenes **105** using B_2pin_2 in methanol, and corresponding hydrazobenzenes **106** were obtained in high yields (Scheme 23D).[68] Preliminary mechanistic studies indicate that the reaction proceeds via a radical pathway.

5. Reduction using sp3-sp3 hybridized diboron compounds

While most of works have been focusing on sp2-sp2 hybridized diboron compounds, Nielsen, Skrydstrup and co-workers became interested in sp3-sp3 hybridized diboron compunds participated reduction reactions in combination of water. They synthesized a series of sp3-sp3 hybridized diboron compounds (Fig. 2), and examined their performance in both the transition-metal-catalyzed reductions and transition-metal free reductions (Scheme 24).[17] For the transition-metal-catalyzed reductions, the reactions were carried out in two separate chambers connected with a tube which allows gas transfer. Chamber A was loaded with the diboron **107** and water, and Chamber B was loaded with the substrates along with corresponding catalysts and solvents. A series of alkenes **108**, alkynes **110** and substituted benzenes **112** installed with a directing group successfully undergo hydrogenation, semi-hydrogenation and hydrogen–deuterium exchange reactions respectively. For the transition-metal free reactions, a variety of ketones were subjected to the diboron in water to afford corresponding alcohols in good yields. The successfulness of these reactions relied on the generation of the boronhydride **Int-87**, and it either reacts with **Int-88** to release the hydrogen gas in the transition-metal-catalyzed reactions, or just reacts with the ketones to afford the alcohols.

6. Summary and outlook

The research on the diboron compounds as reductants in the presence of protic solvents has flourished in recent years, offering a novel and effective tool for extracting hydrogen atoms from easily accessible protic solvents (such as water and alcohol) as an alternative to traditional methods like



Scheme 24 Reductions using sp3-sp3 hybridized diborons as reductants.

electrocatalytic or photocatalytic water splitting, and it directly incorporating the hydrogen into target molecules for reduction. This novel reductive system has several advantages: (1) It generates hydrogen from protic solvents more effectively than conventional electrocatalytic or photocatalytic water-splitting approaches; (2) The reaction typically operates under milder and more practical conditions compared to systems relying on molecular hydrogen or hydrides; (3) When combined with transition metals, enantioselective reductions are readily achievable, enhancing synthetic utility. (4) Given the high value of deuterated compounds, this method offers a significantly more convenient and cost-effective approach for their preparation via reductive deuteration compared to conventional techniques. The primary limitation of this approach lies in its stoichiometry: one molecule of diboron compound yields only one molecule of H_2, making it less viable for large-scale chemical production but ideally suited for high-value compounds like deuterated and chiral molecules. However, this drawback could be addressed if the oxidized products of diboranes could be recycled to regenerate the diboranes. Due to the growing attention to this research area, we can expect significant advancements in the near future.

Conflicts of interest

There are no conflicts to declare.

Data availability

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

Acknowledgements

Support from the National Natural Science Foundation of China (No. 22071265) is gratefully acknowledged.

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View Article Online
DOI: 10.1039/D5CC03873A

Data availability

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