

Research Progress on N-heterocyclic Carbene Boranes

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Abstract

N-heterocyclic carbene boranes (NHC-boranes) are a new kind of compounds which have characteristic structures, luxuriant chemical properties, and preparation with a simple method. They can be widely utilized in various organic synthetic chemical reactions. As practical synthetic reagents or intermediates, it has now attracted attention. In order to show that the status of NHC-boranes in organic synthesis cannot be ignored, this article reviews the structural characteristics, preparation methods and typical chemical reactions of NHC-boranes. We hope that this review can attract more attention, promote the development of synthetic organic chemistry, and apply them to a wider range of areas.

Keywords: NHC-boranes, Preparation, Reaction.

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INTRODUCTION

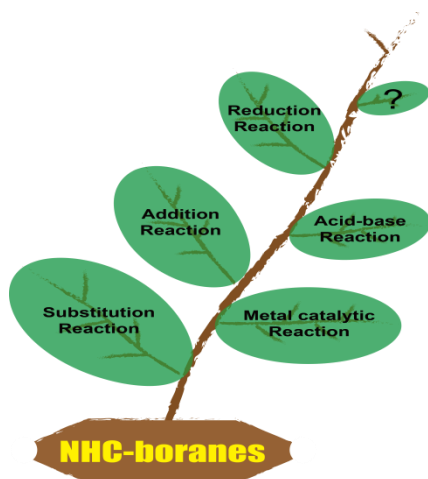
N-Heterocyclic carbenes (NHCs) are a class of compounds with σ -type lone pair of electrons¹. As a Lewis base, they can be stabilized by electron-deficient boranes to form a new type of complex called N-Heterocyclic Carbene Boranes (NHC-boranes or NHC-BH₃). These compounds are similar in form to the complexes of Lewis acid and Lewis base, but in fact they have higher stability (higher than R₃N•BH₃ and R₃P•BH₃). Their chemical reaction properties are also different from trivalent neutral boranes. They have their own unique chemical properties and can construct unusual new boron compounds and reaction intermediates.

In recent years, several hot spots in the development of boron chemistry have focused on the construction of boron-boron multiple bonds [2-4], boron multi-center bonds [5] and NHC-boranes chemistry [6, 7].

Compounds with stable NHC-boranes structure take boron atom and its substituent as the reaction center, and it is easy to obtain many very stable synthetic intermediates. NHC-boranes did not show the typical chemical characteristics of borane, but proved their own rich chemical properties. As a low-cost stable white solid, NHC-boranes are easy to prepare, separate and handle; have good solubility in organic solvents and can be used as reagents or catalysts and co-initiators. Therefore, the position in organic chemical synthesis are becoming more and more prominent.

Structure and preparation of NHC-boranes

Since Arduengo [8] reported stable N-heterocyclic carbene, the types of atoms or groups that form new compounds with these stable carbenes have gradually increased [9, 10]. The carbene carbon atom is hybridized in the form of sp², with a pair of electrons on the σ orbital, generally in the form of singlet with only six electrons around it, which is an electron-deficient system. Considering the electronic effect, the lone pair of electrons on the p-orbitals of the two N atoms on the carbene ring and the empty p-orbitals on the carbene carbon atoms can form a conjugation effect, which can reduce the electron deficiency of the carbene carbon atoms. Considering the inductive effect, two



nitrogen atoms with greater electronegativity are connected to the carbene carbon atom, and the lone pair of electrons on the carbene carbon atom can be stabilized due to the electron withdrawing effect of the nitrogen atom. In addition, if a C=C double bond participates in the conjugation, the stability of the system can also be increased. Therefore, the N-heterocyclic carbene formed by the imidazole ring is a relatively stable system. Figure 1 showed a typical structure of 1,3-dimethylimidazole-2-subunit (diMe-Imd; 1). Since this structure had a strong σ -donor and weak π -acceptor, it was considered to be a typical Lewis base. 2 is the simplest and typical NHC-boranes structure. They played an important role in transition metal chemistry [11, 12], ligands as catalysts [13, 14] and other reactions [15].

Few people pay attention to the coordination of N-heterocyclic carbene with main group elements. This may be because it is inferred from the formal charge and nature of the hydrogen atom that 2 may itself undergo a hydroboration reaction. However, the structural analysis of 2 shows that the B atom in 2 is a four-valent atom with eight electrons, which is a stable compound and does not undergo 1,2-transition to generate boron hydride compounds. Therefore, NHC-borane complexes have gradually gained attention in recent years [16, 17]. Figure-2 was a complex NHC-borane 3 structure first described by Robinson [18] in 2007. The name of this type of substance is usually composed of three parts: N-substituent abbreviations (such as dipp) are written in front, plus NHC ring abbreviations (such as Imd) and borane formula (such as BH_3), so 3 can also be written as dipp-Imd- BH_3 .

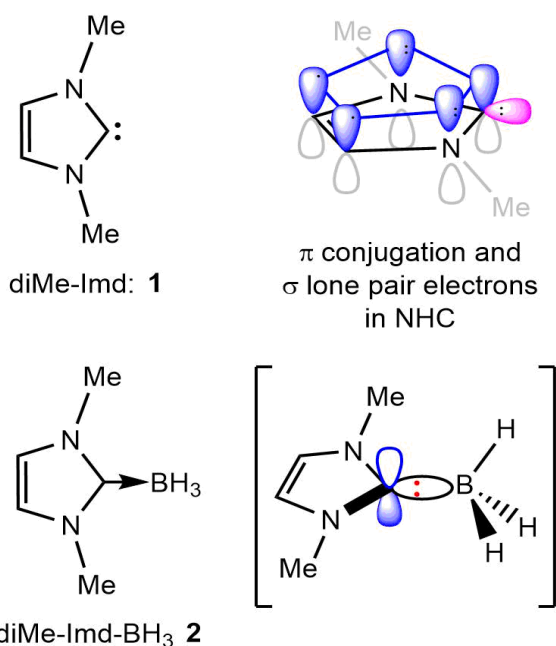


Fig-1: Structure and orbital diagram of NHC-boranes 1 and 2

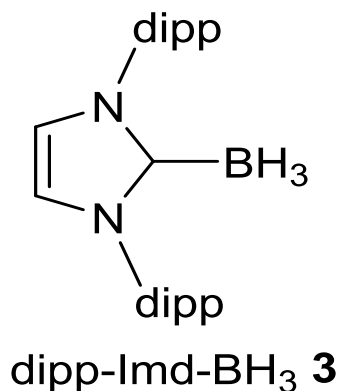


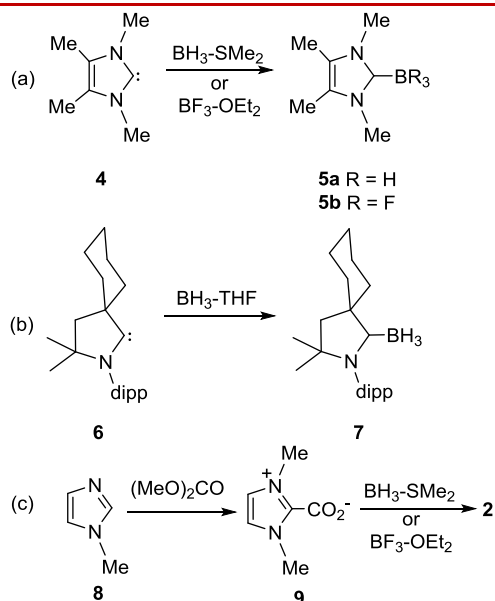
Fig-2: Structures of NHC-boranes 3

Ueng [19] used NHC-boranes for the radical chain reduction reaction of xanthate and related functional groups. In addition, based on the work of amine boranes [20] and phosphine boranes [21], DFT calculations showed that the B-H bond dissociation energy (BDE) of NHC-boranes 3 is $79 \sim 80 \text{ kcal}\cdot\text{mol}^{-1}$ [19, 22], which was significantly lower than the bond dissociation energy of the B-H bond in borane complexes of amines and phosphines²³, so it had strong chemical activity.

Preparation of NHC-boranes complex

In 1993, Kuhn [24] used 1,3,4,5-trimethylimidazole-2-subunit carbene 4 and $\text{BH}_3\text{-SMe}_2$ or $\text{BF}_3\text{-OEt}_2$ to form stable NHC-boranes, as shown in Scheme 1(a). In 2010, Bertrand group²⁵ used cyclic (alkyl)-(amino) carbenes (CAAC) 6 instead of imidazole carbenes to react with Lewis acid BH_3 to generate carbene borane 7, as shown in Scheme 1(b). In the same year, Bissinger [26] used carboxylic acid 9 to react with $\text{BH}_3\text{-SMe}_2$ using toluene as solvent and heated at 110°C to synthesize NHC-boranes 2 with a 64% yield, as shown in Scheme 1(c). In some preparation reactions, borohydride was used as a base to provide borane groups. Yamaguchi [27] made NHC- BEt_3 complex by reacting imidazole salt with LiBEt_3H . Tang [28] used 1:10 equivalent of LiBH_4 to produce 2 with a yield of 75%.

After NHC-boranes has been widely concerned in organic synthesis reactions, the types of its preparation have also increased significantly in recent years [25, 29-34]. In the past few years, various NHC-boranes have been successfully prepared by selecting different NHC rings and substituents. The various structures are shown in Figure-3.



Scheme 1: Typical reaction for preparing NHC-boranes

The reaction of NHC-boranes in organic synthesis

NHC-boranes take boron atom as the reactive center and has unique properties. They can be used as hydrogen donors to terminate free radical reactions [32], as reagents to participate in reduction reactions [19, 35], and occurred addition to unsaturated bonds [36-39], addition-elimination reactions [40-43] or substitution reaction [44, 45]. They also can be used as substrates for boronation reactions to build new boron-containing chemical bonds [46-48], and used as catalysts and polymerization co-initiators [33, 49-52] to participate in chemical reactions. These organic reactions provide new methods and ideas for the synthesis of boron-containing molecules and materials, the construction of boron-containing organic functional groups, and the development of boron chemistry.

They also provide valuable synthetic routes for the research of organic chemistry and expand the practicality of organic synthetic chemistry.

Acid-Base Reaction

NHC-boranes are weak bases similar to ammonia boranes and phosphine boranes. NHC-boranes 3 does not react with acetic acid at room temperature or when heated to about 100°C, so it appears to be a weaker base than borohydride. Therefore, NHC-boranes do not react with weak acids.

Solovyev [53] and Lindsay [30, 54] have reported that NHC-boranes only react with strong acids with $pK_a = 1 \sim 2$. Scheme 2 showed an example of acid-base reaction between 3 and a typical strong acid. Such reaction was very important for the preparation of active NHC-boranes reagent. Most of the acid-base reactions in Scheme 2(a) produced monosubstituted products, with the exception of trifluoromethanesulfonic acid. The reaction between 3

and 2 equivalents of trifluoromethanesulfonic acid was very rapid, and the disubstituted product 11 was formed. A new onium ion was discovered in the study of the acid/base reaction of substituted NHC-boranes. It is known that treating NHC-boranes with 1 equivalent of trifluoromethanesulfonic acid or HCl will give monotrifluoromethanesulfonate NHC-BH₂(OTf) or monochloride. The reaction with 2.5 equivalents of trifluoromethanesulfonic acid gives the ditrifluoromethane-sulfonate NHC-BH(OTf)₂. However, even at 5 equivalents, the trit trifluoromethanesulfonate NHC-B(OTf)₃ will not appear, but a substance containing a hydrogen bond structure is formed, as shown in Scheme 2(b) [55].

NHC-boranes reacted slowly with oxalic acid in acetonitrile at room temperature and rapidly forms NHC-borane oxalate at 80°C. For example, in acetonitrile solvent, heated 2 and oxalic acid at 80°C for 2h. After two consecutive acid-base reactions, a new unknown heterocyclic NHC-boryl oxalate was obtained. A stable white solid 13 was isolated in a yield of 59%, as shown in Scheme 3 [56].

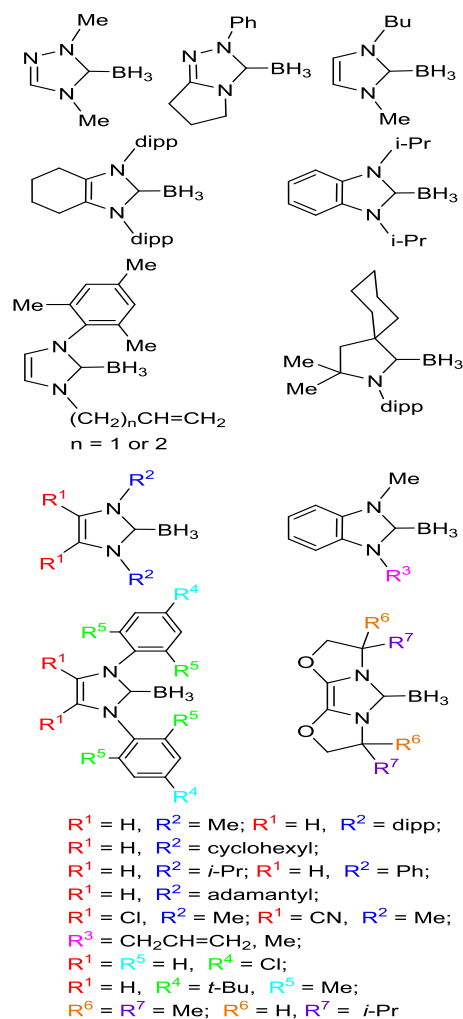
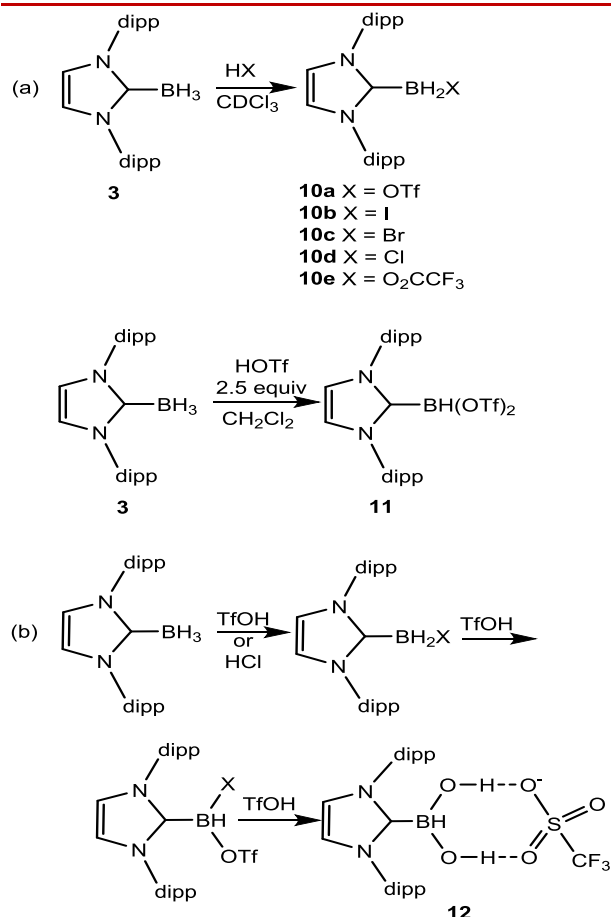
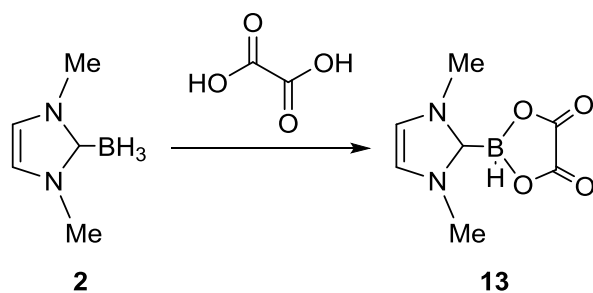


Fig-3: The species of the NHC-boranes



Scheme 2: NHC-boranes 3 representative acid-base reaction

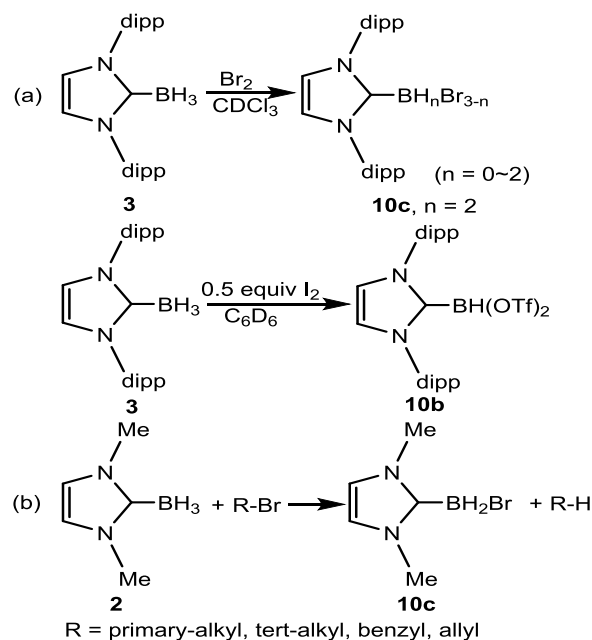


Scheme 3: NHC-boranes 2 reaction with oxalic acid

NHC-Boranes substitution reaction

NHC-Boranes can also react with a variety of halogenating reagents, such as N-bromosuccinimide (NBS), Niodosuccinimide (NIS), bromine and iodine, etc., as shown in Scheme 4 [53]. The resulting products were mono-, di- and tri-substituted. Among them, 3 iodination had higher selectivity. The reaction of 3 with only 0.5 equivalent of I₂ gave a higher yield of 10b. It was speculated that the electrophilic substitution produced 0.5 equivalents of 10b and HI. The generated 0.5 equivalent of HI was then reacted with the remaining part of 3 through an acid-base reaction and converted into the target product 10b. The substitution

reaction between 2 and R-Br generates bromide 10c [57].

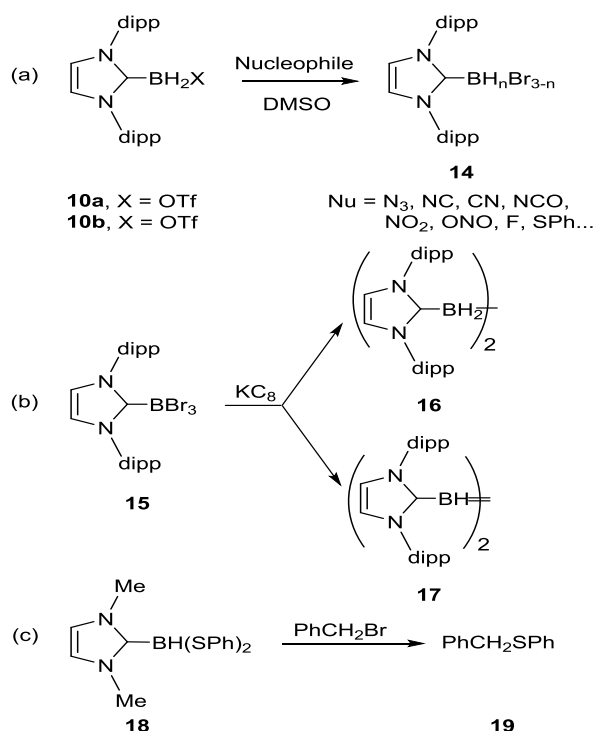


Scheme 4: NHC-boranes 3 and 2 electrophilic halogenation reaction

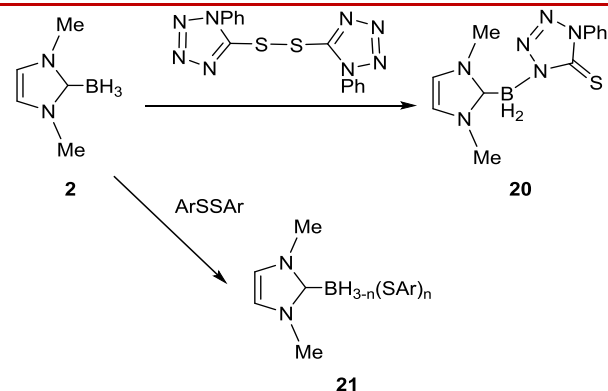
Substituted NHC-boranes can also react with nucleophiles to undergo further substitution to generate a variety of NHC-borane derivatives. Substituted NHC-boranes such as halogenated and sulfonate can undergo substitution reactions with nucleophiles to synthesize a variety of NHC boron-containing halides, cyanides and sulfur derivatives, as shown in Scheme 5(a). The boron compound 14 is isocyanide, isocyanate and nitro compounds. These rare new members have stable chromatography and have important research value in organic synthesis. Robinson [18] reported a neutral and stable NHC-boranes containing B=B, which attracted considerable attention. Pan [58] reacted the treated diMe-Imd-BBr₃ complex 15 with potassium graphite (KC₈) to obtain borane 16 and B=B product 17. Mixture 17 was a secondary product, but it was also stable, and can be separated from 16 with a separation yield of 12%, as shown in Scheme 5(b). The substituted NHC-boranes can also be used as a source of other types of neutral nucleophiles to prepare thioethers and thioesters. NHC-BH_{3-n}Y_n (Y is a potential nucleophile), such as NHC-BH(SPh)₂ 18 can also provide -SPh to prepare thioether 19, as shown in Scheme 5(c).

The reaction of NHC-boranes 2 and diaryl or diisooaryl disulfides resulted in diMe-Imd-BH₂SAr 20 and diMe-Imd-BH(SAr)₂ 21. One equivalent of disulfide protected from light was conducive to the formation of NHC-boron-based monosulfide 20, and 2 equivalents of disulfide illuminated by light was conducive to the formation of NHC-boron-based disulfide 21. Most of these substitution reactions were thought to proceed through free radical chains, in which

S-S bond breaking and substitution by NHC-boron was a key step, as shown in Scheme 6 [59].

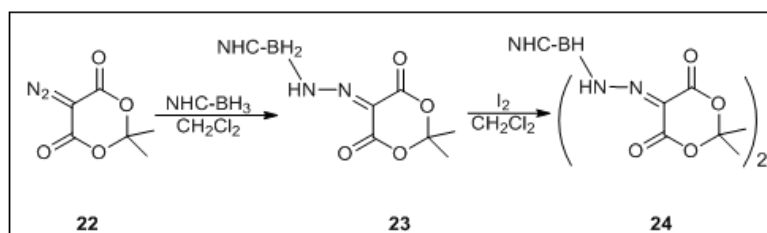


Scheme 5: Substituted NHC-boranes substitution reaction

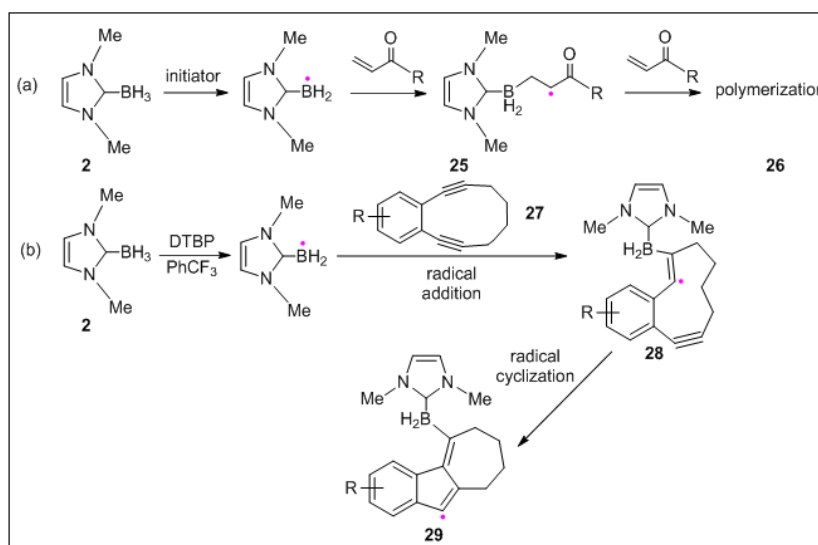


Scheme 6: NHC-boranes 2 and disulfide substitution reaction

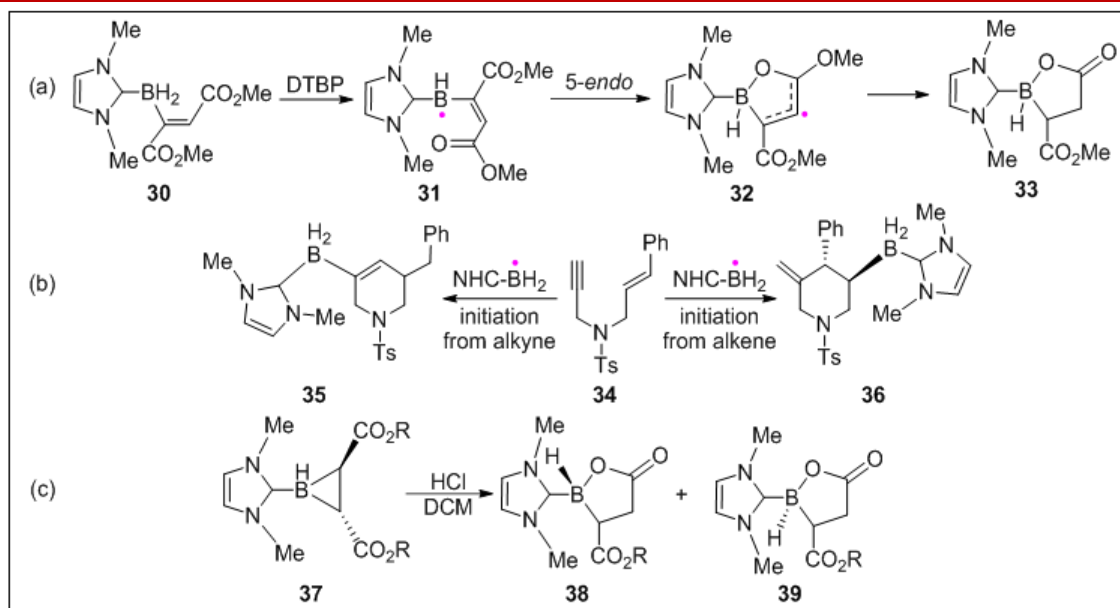
NHC-boranes reacted with 5-diazo-2,2-dimethyl-1,3-dioxane-4,6-dione 22 in dichloromethane at 40°C. The NHC-borohydrazone derivative 23 of 2,2-dimethyl-1,3-dioxane-4,6-dione was obtained. Dihydrazone 24 was generated when treated with I_2 at room temperature in dichloromethane. Both monohydrazone and dihydrazone were yellow solids that were stable to chromatography and storage, as shown in Scheme 7 [60].



Scheme 7: Substitution reaction of NHC-boranes and diazodione



Scheme 8: NHC-boranes 2 addition reaction



Scheme 9: The addition reaction of substituted NHC-boranes

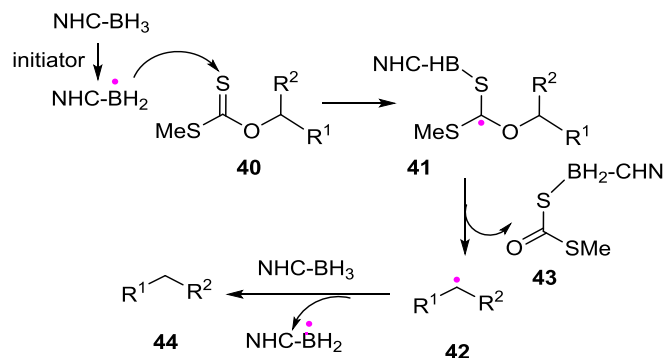
NHC-boranes addition reaction

NHC-boranes can also react with some unsaturated substances. For example, the free radical initiator initiated NHC-boranes 2 to generate NHC-boron radicals, and then reacted with ketene or cycloalkynes to generate carbon radical intermediates 25 or 28. Then, the addition reaction of free radicals continued to generate polymer 26 or cyclic compound 29, as shown in Scheme 8 [61].

NHC-boranes 30 containing ester substituents was initiated by DTBP to generate the NHC-borane intermediate 31. 31 Boron radicals underwent intramolecular 5-endo addition reaction to generate five-membered boron heterocyclic ring 32. Then 32 removed the alkyl radicals to generate the five-membered ring lactone 33 [62, 63]. NHC-boranes and 1,6-enyne substance 34 were added at different positions to generate six-membered azaheterocyclic ring 35 and six-membered azaheterocyclic ring 36⁶⁴,

such as Scheme 9(a), (b). Wen [65] studied the ring-opening addition of NHC-boranes 37 with ester substituents in the presence of HCl to generate stable γ-NHC-boron-γ-lactone 38 and 39, with a separation yield ranging from 40% to 73%, as shown in Scheme 9(c).

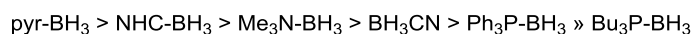
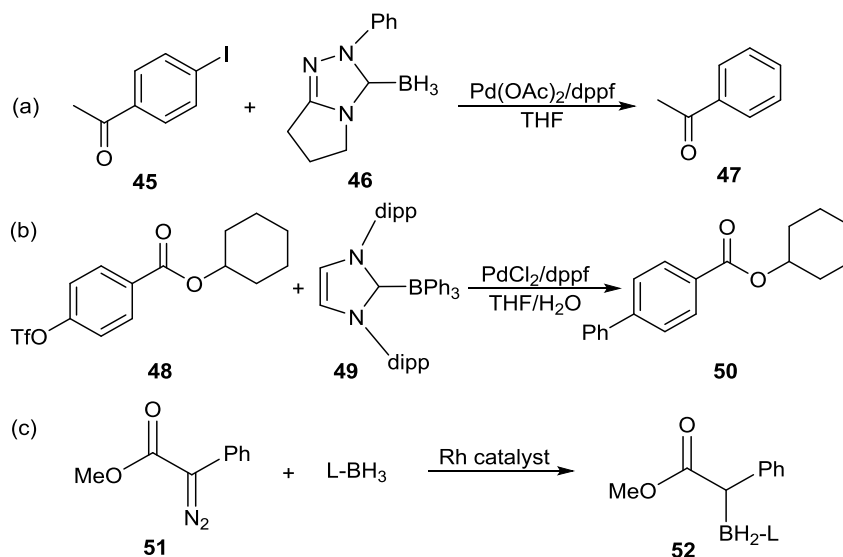
NHC-BH₂· was a new type of boron-centered radical. A large number of experiments had obtained the Barton-McCombie chain reaction mechanism [32], as shown in Scheme 10. For example, when various xanthogenates 40 reacted with NHC-boranes, they were first initiated by AIBN at 80°C or triethylborane at room temperature to generate NHC-BH₂· free radical. NHC-BH₂· free radical was then added to the C=S double bond in the xanthate to generate a carbon radical intermediate 41. C-O bond in 41 was broken, generating 42 free radical and NHC-substituted borane 43. NHC-boranes can continue to supply 42 hydrogen to generate 44 hydrogen migration reduction products.



Scheme 10: NHC-boranes free radical Barton-McCombie mechanism

Metal catalytic reaction

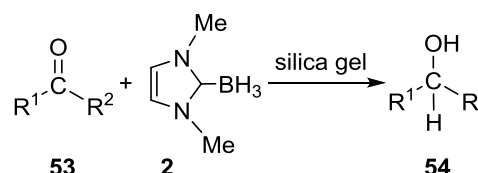
Aryl halides, alkenyl halides and triflate cannot be directly reduced by NHC-boranes, but these reductions can be promoted by various palladium catalysts. For example, 4-iodoacetophenone **45** and NHC-borane **46** added palladium acetate and 1,1'-bis(diphenylphosphine) ferrocene to tetrahydrofuran, and heated to obtain acetophenone **47**. The product detected by GC was unique³³, as shown in Scheme 11(a), (b). Therefore, aryl iodide and aryl triflate can be reduced by NHC-boranes when catalyzed by palladium.



Scheme 11: NHC-boranes metal catalyzed reaction

Reduction reaction

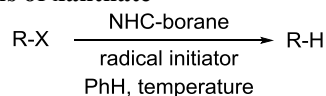
From another point of view, the aforementioned substitution reaction and metal-catalyzed reaction also show the performance of NHC-boranes to donate hydrogen to reduce halogenated compounds. Under silica gel conditions, aldehydes and ketones were selectively reduced to primary and secondary alcohols by NHC-boranes **2**, and the yield was high. This reaction process was worthy of attention, because all materials were stable, easy to handle, and the method was gentle, did not require quenching, and the reaction and separation processes were very convenient, as shown in Scheme 12 [52].



Scheme 12: Silica-catalyzed NHC-boranes 2 reduction of aldehydes and ketones

NHC-boranes can assist in the reduction of R-X to R-H with a radical chain reaction as a mechanism, and the reaction with xanthate was particularly typical. Scheme 1-13 listed a series of NHC-boranes reduction reactions of xanthate [37, 42, 67].

Scheme 13: A series of NHC-boranes reduction reactions of xanthate



X =	R =	NHC-borane	radical initiator (equiv.)	temperature	Yield (%)	ref.
OC(=S)SMe		3	AIBN (2.0)	80°C	65	37
		44	AIBN (0.5)	80°C	70	37
		3	AIBN (2.0)	80°C	64	37
		44	AIBN (0.5)	80°C	63	37
		44	AIBN (0.2)	80°C	67	37
		44	AIBN (0.5)	80°C	BnO-CH2-CH=CH-Et 57	37
		44	AIBN (0.5)	80°C	BnO-CH2-cyclopentyl 67	37
I		44	AIBN (0.5)	80°C	61	37
		2	Et3B (1.0)	r.t.	77	67
		3	Et3B (1.0)	r.t.	35	67
Br		2	AIBN (1.0)	80°C	63	67
		2	Et3B (1.0)	r.t.	79	67
		2	DTBP (1.0)	60°C	73	67

CONCLUSIONS AND PERSPECTIVE

Before 2008, NHC-boranes may be considered a rare compound. Due to the increasing attention in recent years, the research has progressed rapidly. The formation of NHC-boranes strengthened the borane family. Because the properties of NHC-boranes are very different from amine borane and phosphine borane, it greatly enriches the applications of borane in organic chemistry. Most of NHC-boranes are easy to synthesize and characterize, and many structures are stable in air and water which can be purified by simple chromatography. The production of new NHC-boron free radical active intermediates (boron free radicals, cationic free radicals and anionic free radicals) make NHC-boranes promising to become important organic synthesis reagents, catalysts and co-initiators. NHC-boranes will have more vitality and comprehensive potential in organic synthesis.

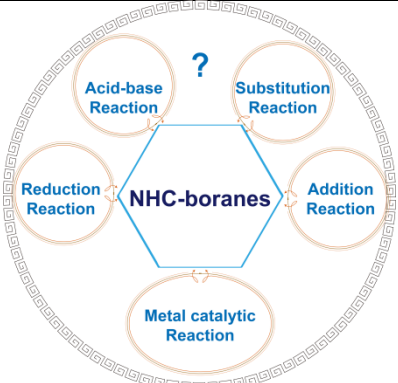
This work was supported by National University Student Innovation and Entrepreneurship Project (No.201810223016) of China.

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Graphical Abstract	
Textual Information	
A brief abstract (required)	N-heterocyclic carbene boranes (NHC-boranes) are a new kind of compounds which have characteristic structures, luxuriant chemical properties, and preparation with a simple method. They can be widely utilized in various organic synthetic chemical reactions. As practical synthetic reagents or intermediates, it has now attracted attention. In order to show that the status of NHC-boranes in organic synthesis cannot be ignored, this article reviews the structural characteristics, preparation methods and typical chemical reactions of NHC-boranes. We hope that this review can attract more attention, promote the development of synthetic organic chemistry, and apply them to a wider range of areas.
Title(required)	Research Progress on N-heterocyclic Carbene Boranes
Authors' Names(required)	Xue Wang, ¹ Yu-jie Yang, ¹ Yan-di Song, ¹ Shuang Zhao ¹ and Hong-jie Qu ^{*1}
Graphical Information	
	

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