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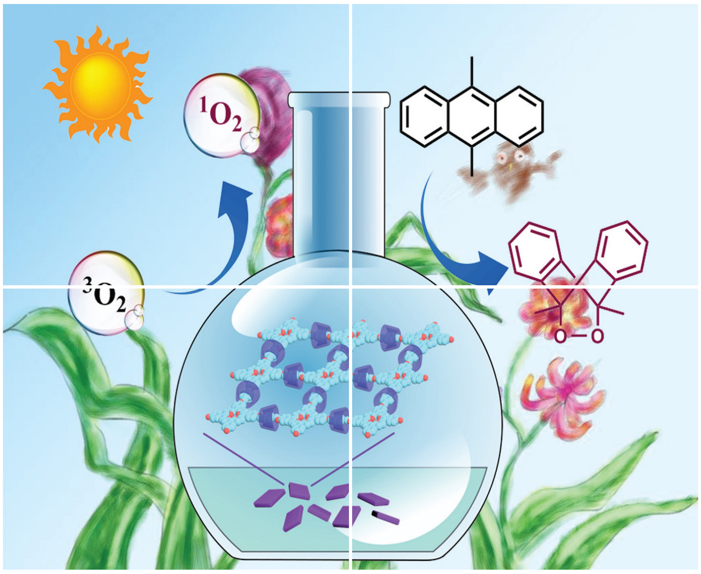

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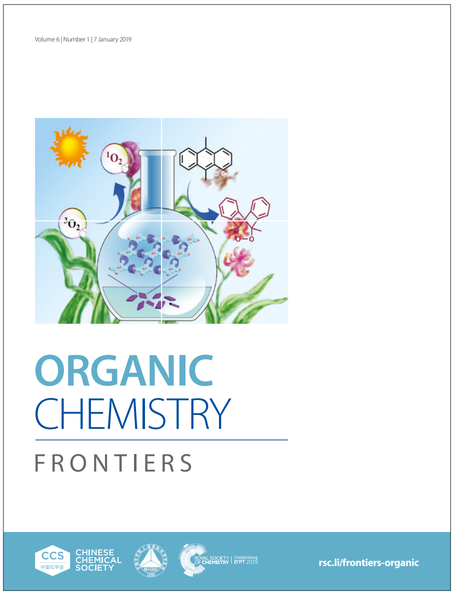
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REVIEW

# α-Borylcarbene Precursors: Design, Generation, and Synthetic Opportunities

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α-Boryl carbenes combine the high reactivity of carbenes with the synthetic versatility of organoboron compounds, enabling unique strategies for molecular construction. However, their practical use has long been limited by the intrinsic instability of α-boryl diazo intermediates and the difficulty of generating these carbenes in a controlled manner. In recent years, significant progress has been achieved through the development of well-designed precursors that balance stability with efficient carbene generation. This review summarizes recent advances in α-boryl carbene precursor design and reactivity. The discussion is organized according to precursor classes, including diazo compounds and sulfonyl hydrazones, alkynes, cyclopropenes, and haloalkanes. Key design principles that enable controlled carbene formation are highlighted together with representative synthetic transformations. These developments demonstrate how molecular design has transformed α-boryl carbene chemistry into a practical platform for organoboron synthesis.

## 1. Introduction

Carbenes are neutral divalent carbon species possessing six valence electrons. Owing to their intrinsic electron deficiency and unique electronic structures, they exist either as singlet carbenes with paired electrons in an $sp^2$ orbital or as triplet carbenes with unpaired electrons distributed in $sp^2$ and p orbitals. These electronic characteristics endow carbenes with remarkable reactivity, enabling a wide range of transformations such as C–H insertion,[1] cyclopropanation,[2] metathesis,[3] cyclization,[4] and rearrangement reactions.[5]In contrast, organoboron compounds, particularly boronates, are widely recognized as versatile synthetic handles. They serve as key intermediates in cross-coupling reactions for the construction of carbon–carbon and carbon–heteroatom bonds.[6] Moreover, boron functionalities can be converted into hydroxyl or amino groups through oxidation and amination processes.[7] Classical transformations such as the Matteson homologation further highlight the utility of boron in enabling 1,2-migration processes and carbon chain elongation.[8]

α-Boryl carbenes combine these two powerful motifs within a minimal carbon framework (Fig. 1A). By combining the exceptional reactivity of carbenes with the synthetic versatility of boronates, α-boryl carbenes represent highly attractive intermediates for carbon–carbon bond formation and molecular framework construction. However, their practical implementation poses several challenges (Fig. 1B). Highly reactive carbene species must be generated and controlled in a chemoselective manner without undesired reactions involving the boron moiety. Furthermore, careful precursor design is required to enable controlled carbene generation while preserving the boron functionality. From an electronic perspective, the carbene center may adopt either singlet or triplet character, which can introduce radical reactivity and raise concerns regarding stability and stereocontrol.

To address these challenges, significant efforts have been devoted to the development of stable and readily accessible precursors capable of generating α-boryl carbenes under controlled conditions (Fig. 1C). Starting from early diazo compounds, various precursor classes have been developed, including sulfonyl hydrazones, alkynes, cyclopropenes, and haloalkanes. It should be noted that, although boryl alkenes can in principle generate boryl-substituted metal carbenes under olefin metathesis conditions, the catalytically active metal alkylidene typically originates from more reactive olefins. Clear examples in which a boryl alkene first forms an α-boryl metal carbene have not been reported. Therefore, boryl alkenes are not treated as α-boryl carbene precursors in this review. In addition, the nature of the boron substituent plays a critical role in balancing stability and reactivity. Commonly employed boron groups include catechol boronates (Bcat), pinacol boronates (Bpin), trifluoroborate salts ($MBF_3$), and MIDA boronates (BMIDA)[9] (Fig. 1D).

Although numerous reviews have discussed organoboron chemistry, asymmetric metal-carbene insertions,[10] chiral diboryl compounds,[11] acylboron chemistry,[12] and heteroatom-substituted carbenes,[13] a comprehensive overview specifically focusing on α-boryl carbene precursors has not yet been reported. Therefore, this review aims to summarize the development of α-boryl carbene precursors and to classify them according to precursor type. The following chapters describe diazo compounds and sulfonyl hydrazones (Chapter 2), alkynes (Chapter 3), cyclopropenes (Chapter 4), and haloalkanes

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(Chapter 5), highlighting their carbene-generation modes, reactivity profiles, and synthetic applications.

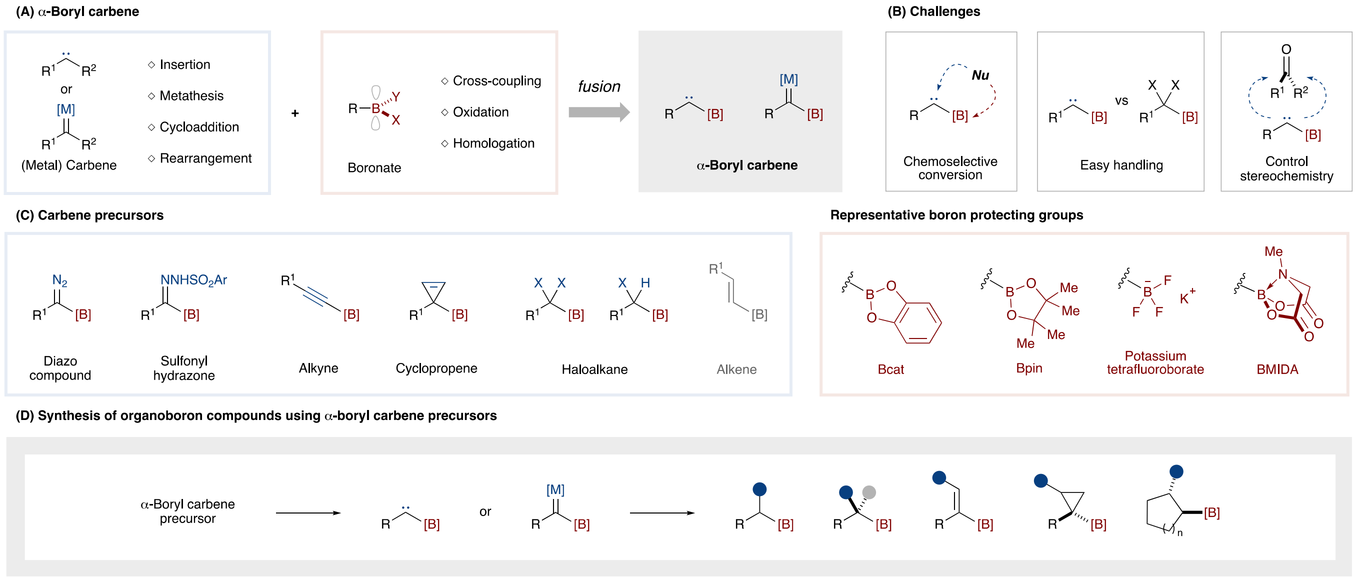

**Fig. 1** Design concept of α-boryl carbenes. (A) Fusion of carbene reactivity and boronate functionality. (B) Challenges in chemoselectivity and stability. (C) Representative precursor classes. (D) Synthetic application of α-boryl carbenes from distinguished precursors.

## 2. Diazo Compounds and Sulfonyl Hydrazones

### 2.1 Design, Synthesis, and Stability

α-Boryl diazo compounds represent atom-economical precursors to α-boryl carbenes, as extrusion of dinitrogen directly generates the desired reactive intermediate. In principle, this straightforward mode of carbene generation renders diazo compounds highly attractive. Indeed, numerous synthetic routes to α-boryl diazo compounds have been reported. However, despite their synthetic accessibility, practical applications of α-boryl diazo compounds remain surprisingly limited. This discrepancy arises primarily from their inherent instability. The origin of this instability is closely related to the electronic interplay between the diazo group and the adjacent boron substituent (Fig. 2A). The vacant p orbital of boron can stabilize the developing carbene center through π-acceptor interaction. Consequently, the resulting α-boryl carbene is comparatively stabilized relative to simple alkyl carbenes. While this stabilization is beneficial for controlling carbene reactivity, it simultaneously lowers the activation barrier for nitrogen extrusion. In other words, the α-boryl diazo compounds are predisposed to spontaneous loss of $N_2$, rendering them thermally and chemically unstable. Even when generated, the α-boryl carbene is not indefinitely persistent. Secondary decomposition pathways are frequently observed, including 1,2-migration of the adjacent boron substituent to the carbene center and polarization-induced cleavage of the C–B bond (Fig. 2B). Thus, although the carbene may be electronically stabilized, it remains highly reactive and prone to rapid transformation.

This behavior contrasts with that of conventional α-diazo carbonyl compounds, which benefit from conjugative stabilization, between the carbonyl group and the diazo functionality. The π-system of the carbonyl moiety provides additional resonance stabilization, allowing such diazo compounds to be handled under relatively mild conditions. In the absence of this stabilizing framework—and with the additional electronic influence of boron—α-boryl diazo compounds become significantly more susceptible to decomposition.

To address these intrinsic challenges, three main stabilization strategies have been developed (Fig. 2C). The first is to reduce the Lewis acidity of boron by introducing electron-donating substituents on the boron atom. The second is to install sterically bulky substituents on boron to suppress undesired reactivity toward nucleophiles. The third is to render boron tetracoordinate, thereby effectively attenuating its reactivity. Given these challenges, an important question arises: how have α-boryl diazo compounds been synthesized, and what structural designs have been developed to balance reactivity and stability? To answer this question, it is useful to trace the historical development of these compounds from the perspectives of both synthetic strategy and molecular design (Fig. 2D).

The earliest example of an α-boryl diazo compound was reported in 1974 by Schöllkopf and co-workers, who synthesized (benzodioxaborolyl)diazoacetate **A**.[14] **A** was prepared by borylation of a diazo anion. This represented the first example of a carbon center simultaneously bearing both a boron substituent and a diazo group. However, its stability was limited compared with that of simple α-diazo carbonyl compounds. Although it could be isolated, it decomposed in air with evolution of nitrogen. In solution under an inert atmosphere, it remained stable for several days at 0 °C, provided that oxygen and moisture were rigorously excluded. The catecholato framework, while capable of π-donation and

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partial electronic delocalization, likely increased polarization of the C–B bond and thereby contributed to its tendency toward decomposition.

More than a decade later, Paetzold and co-workers (1989) reported a second example of a boron-substituted diazo compound **B**.[15] This compound was obtained by thermal decomposition of a triazaboroline precursor. Although it was isolable and spectroscopically characterized, no particular emphasis was placed on its stability, and its structure differed significantly from the classical α-boryldiazomethane framework typically associated with carbene chemistry.

A major conceptual advance came in 1991, when Bertrand and co-workers reported two distinct types of boron-substituted diazo systems. Their initial study employed a phosphorane-derived system, demonstrating that boron could indeed be incorporated into a diazo framework, although the resulting compound **C** remained moisture-sensitive.[16] Later that same year, however, they reported the first genuinely distillable α-boranyldiazomethane **D**.[17] As described in their report, "Diazoborane **D** is thermally stable and was obtained in 54% yield as a yellow oil after distillation (bp 70–74 °C/$10^{-1}$ mmHg).", this statement clearly established that the compound possessed practical thermal stability. The key design principle underlying this breakthrough was the installation of strongly π-donating diisopropylamino substituents on boron. Introduction of the $B(N^iPr_2)_2$ unit significantly reduced the intrinsic Lewis acidity of boron, providing electronic stabilization of the adjacent carbon center while suppressing undesired self-decomposition pathways. In addition to electronic donation, steric protection from the bulky amino substituents further enhanced kinetic stability. This combination of electronic modulation and steric shielding marked the first successful strategy for achieving a practically stable α-boryl diazo compound.

In 1993, Bürger and co-workers reported a borylated diazoester **E** obtained from ethyl diazoacetate and (dimethylamino)bis(trifluoromethyl)borane. Remarkably, this compound was thermally stable, melted without decomposition (mp 84 °C), and was structurally characterized by X-ray diffraction.[18] The planar diazo–ester–boron fragment and the shortened C–C bond length indicated significant π-delocalization, suggesting a stabilization mode distinct from that of earlier aminoborane-based systems.

In 2001, Weber and co-workers reported 1,3,2-diazaborolyl(trimethylsilyl)diazomethane **F** as a thermally stable α-boranyldiazomethane.[19] This compound could be purified by vacuum distillation, and its solid-state structure was established by X-ray crystallography. Structural analysis indicated that significant B–C π-interaction was absent, suggesting that stabilization was mainly achieved through modulation of the electronic properties of the boron center itself.

In 2021, Hansmann and co-workers introduced a fundamentally different stabilization strategy for α-boryl diazo compounds. Whereas earlier studies had relied on strongly π-donating substituents to reduce the Lewis acidity of boron, compound **G** bears a strongly electron-withdrawing $B(C_6F_5)_3$ substituent.[20] The strong inductive effect and substantial steric bulk of the perfluoroaryl groups generate an α-boryl diazo compound that is both kinetically protected and electronically activated. In this design, the Lewis acidity of boron is retained while uncontrolled decomposition is suppressed. As a result, compound **G** can be isolated and handled under standard conditions, yet readily undergoes nitrogen extrusion by irradiating LED light (390 nm).

At approximately the same time, Erker and co-workers reported α-boryl diazo compound **H** in the context of internally stabilized boraalkene chemistry.[21] In this system, a diazo group was introduced at the carbon adjacent to a strongly Lewis acidic boron center embedded within a rigid framework. Although the resulting compound was isolable and structurally characterized, it was not developed as a general carbene precursor, nor was its broader synthetic utility explored.

With the recognition that α-boryl diazo compounds can participate in classical diazo chemistry, recent attention has increasingly turned to their use as carbene precursors under controlled catalytic conditions. In 2021, Liu and co-workers reported diazomethyl-1,2-azaborine **I**, a thermally stable α-boryl diazo compound embedded within an aromatic BN framework.[22] This compound combines high thermal stability with diverse reactivity, and its synthetic applications will be discussed in a later section (Scheme 1).

In 2022, Lee and co-workers reported the generation of diazo *o*-carboranes **J** via ADMP-mediated diazo transfer from B(4)-acylmethyl *o*-carboranes (ADMP = 2-azido-1,3-dimethylimidazolinium hexafluorophosphate).[23] The resulting α-boryl diazo compounds were isolable and fully characterized, including by X-ray crystallography. However, the focus of this work was not on intrinsic stability, but rather on the use of these diazo species as reactive intermediates in subsequent intramolecular pyrazole formation.

More recently, in 2024, Dong, Liu, Houk, and co-workers reported structurally related α-boryl diazo compound **K** embedded within a 1,2-azaborine framework.[24] Although this system resembles the 2021 diazomethyl-1,2-azaborine reported by Liu and co-workers, it was accessed through a distinct synthetic strategy and investigated by means of combined experimental and computational mechanistic studies. This work further refined the design principles governing the stability and reactivity of α-boryl diazo compounds. Its synthetic applications will also be discussed in a later section (Scheme 6).

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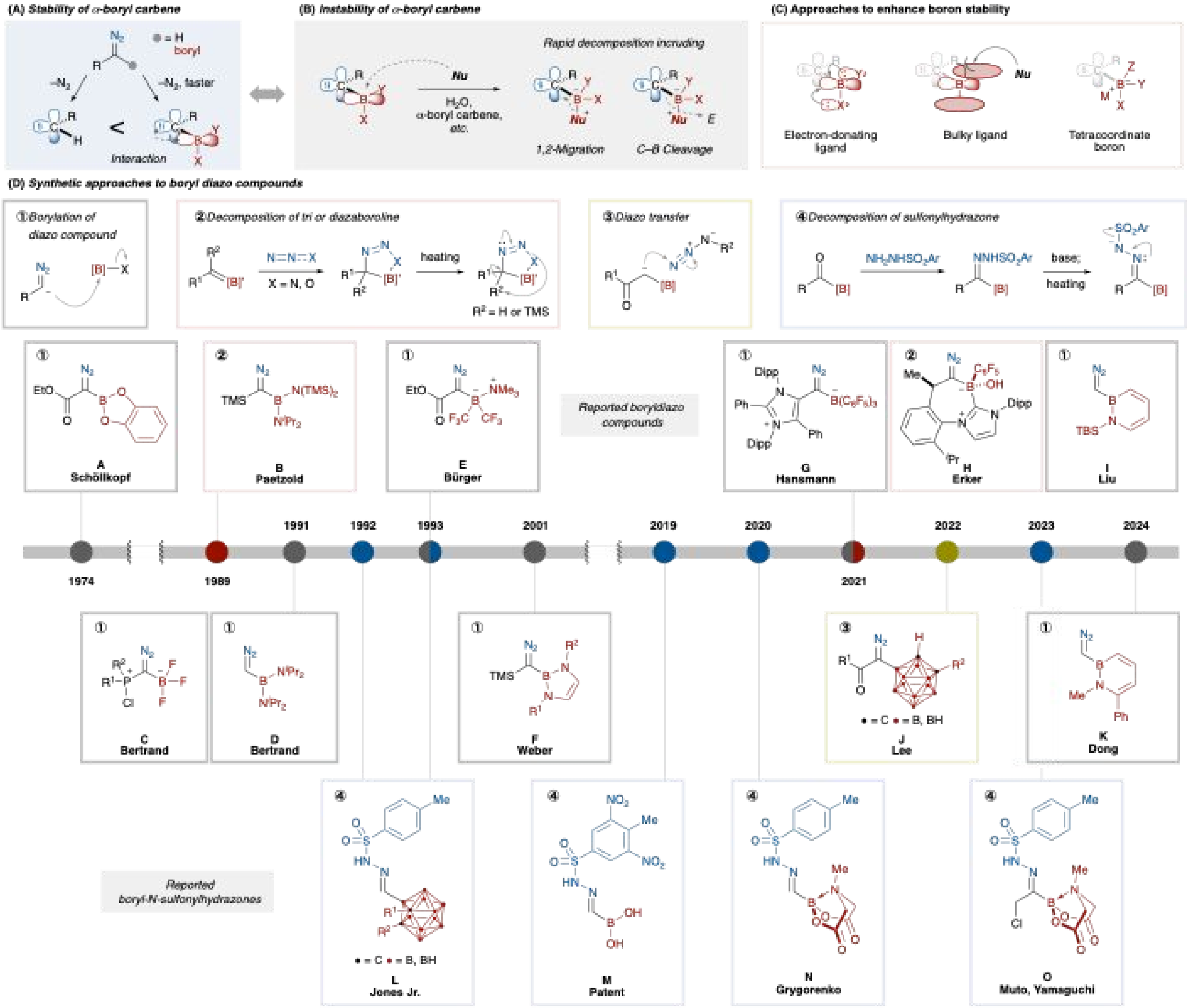

**Fig. 2** Electronic features, stabilization strategies, and historical development of α-boryl diazo compounds. (A) π-Acceptor interaction between the diazo group and the adjacent boron substituent. (B) Influence of boron stabilization on the barrier for dinitrogen extrusion. (C) General stabilization strategies for α-boryl diazo compounds. (D) Historical development of representative α-boryl diazo compounds and hydrazones.

As summarized above, until the work of Liu and co-workers in 2021, most α-boryl diazo compounds had primarily been regarded as conceptual precursors to boryl carbenes, while synthetically practical and broadly useful variants remained scarce. A key conceptual breakthrough came from the recognition that sulfonyl hydrazones can serve as stable, isolable precursors to diazo compounds. Upon treatment with base, these compounds generate diazo intermediates in situ. This "masked diazomethyl" strategy provided an effective design solution to the long-standing challenge of balancing stability and reactivity in α-boryl diazo systems.

The first example in which a sulfonyl hydrazone was used to generate a boryl carbene was reported by Jones and co-workers in 1992.[25] Starting from carboranyl lithium, they prepared *N*-tosylhydrazone-substituted carborane derivative **L** through a multistep sequence. Although this study is historically significant as an early experimental demonstration of a boron-substituted carbene precursor, the use of a carborane

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framework inherently limited synthetic modification at the boron center.

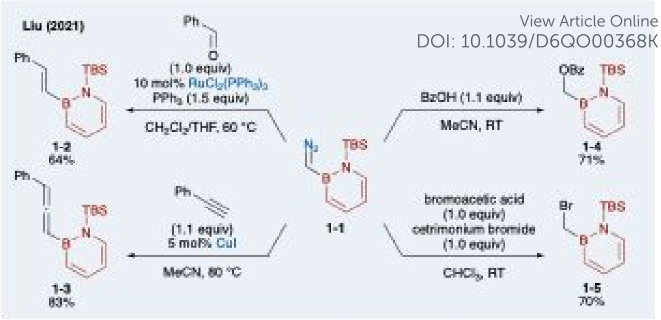
A major conceptual shift occurred with the development of boronate-based sulfonyl hydrazones bearing synthetically transformable boron substituents. Unlike carboranes, boronic esters such as MIDA boronates offer both bench stability and versatile downstream functionalization. However, such boryl sulfonyl hydrazones bearing transformable boron units were not reported until nearly three decades later. In 2019, a Chinese patent described boronic acid-derived sulfonyl hydrazone **M**, although it remains unclear whether these compounds were fully isolated and characterized.[26] The first peer-reviewed report appeared in 2020, when Grygorenko and co-workers disclosed formyl MIDA boronate chemistry in which *N*-tosylhydrazone-type boronate derivative **N** was prepared during the course of the synthetic study.[27] Subsequently, in 2023, Yamaguchi and Muto reported the synthesis of related derivative **O** by treating α-chloroacyl MIDA boronates with a *N*-tosylhydrazone reagent (CABT).[28] CABT derivatives are generally isolable, air-stable solids that can be stored under standard laboratory conditions, yet they undergo controlled base-induced diazo formation when required. This combination of kinetic stability and on-demand activation represents the central design principle underlying synthetically practical α-boryl diazo sulfonyl hydrazones.

Thus, among α-boryl diazo derivatives that balance stability and reactivity, compounds in which both the diazo functionality and the boron center are effectively masked have ultimately proven to be particularly suitable. In the following section, their synthetic applications are discussed.

### 2.2. α-Boryl Diazo Compounds and Sulfonyl Hydrazone: Synthetic Opportunities

In this section, the application of α-boryl diazo compounds and sulfonyl hydrazone derivatives as precursors to α-boryl carbenes is discussed. As described above, among structurally defined α-boryl diazo compounds, only the 1,2-azaborine system has been reported to undergo subsequent synthetic transformations.

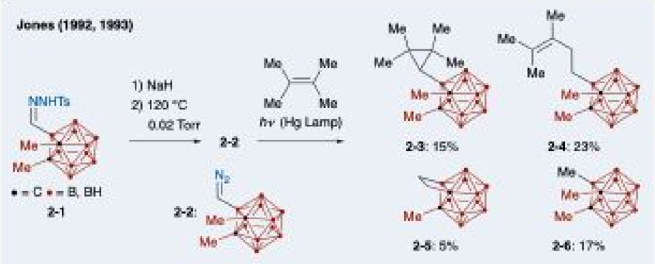
Liu and co-workers examined a range of reactions of the 1,2-azaborine-derived diazo compound **1-1** (Scheme 1).[22] For example, in the presence of a rhodium catalyst, reaction with benzaldehyde generated a boryl carbene intermediate, affording olefin **1-2**. Under similar catalytic conditions, treatment with phenylacetylene led to the formation of allene **1-3** in good yield. Furthermore, reaction with benzoic acid proceeded through O–H insertion to give benzoate **1-4**. Bromination could also be achieved by treatment with bromoacetic acid in the presence of the cationic surfactant cetrimonium bromide. These results demonstrate that within the 1,2-azaborine framework the boron center remains intact and does not directly participate in the reaction, while the carbene center undergoes characteristic carbene-type transformations.



**Scheme 1** Reactivity of 1,2-azaborine-derived α-boryl diazo compound.

In contrast, a broader range of transformations has been explored for sulfonyl hydrazone derivatives. In 1992–1993, Jones and co-workers prepared a *N*-tosylhydrazone-substituted carborane and investigated its subsequent reactivity, although only a limited number of examples were examined (Scheme 2).[25] Treatment of *N*-tosylhydrazone-substituted carborane **2-1** with sodium hydride generated the corresponding boryl diazo compound **2-2**. Upon heating under reduced pressure, compound **2-2** could be distilled and isolated in pure form and was described as a remarkably stable compound. Notably, this work represents an early example of the preparation and reaction of α-boryl diazo compound, predating the later studies by Liu and co-workers.

When compound **2-2** was subjected to photolysis in the presence of alkenes using a high-pressure mercury lamp, a boryl carbene intermediate was generated. This reactive species afforded cyclopropane **2-3**, alkene **2-4**, bora-cyclobutane **2-5**, and methylated carborane **2-6**. Although the reactions were not well controlled due to the inherently high reactivity of the carbene intermediate, the study demonstrated that such species can participate in a variety of carbon–carbon bond-forming reactions typical of carbene chemistry.



**Scheme 2** Generation and photochemical reactions of *N*-tosylhydrazone-substituted carborane.

In 2019, a Chinese patent disclosed the preparation of a boryl sulfonyl hydrazone **3-3** from formylboronic acid **3-1** and sulfonyl hydrazine **3-2** (Scheme 3).[26] Treatment of this intermediate with *n*-BuLi in the presence of an iron catalyst, followed by introduction of ethylene and acidic workup, furnished cyclopropyl boronic acid (**3-4**) in a high yield. Although the mechanism was not fully elucidated, the transformation is most plausibly explained by in situ generation of a boryl diazo species and subsequent formation of α-boryl carbene intermediate,

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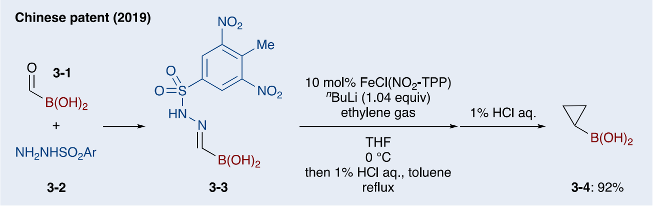
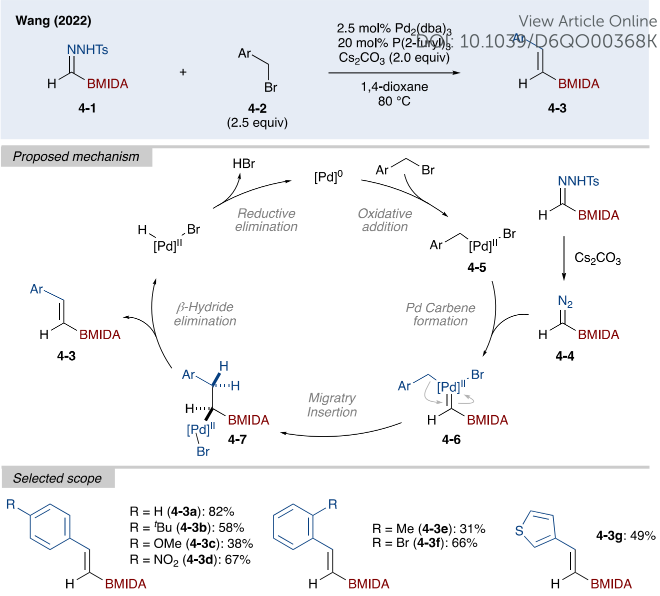
which undergoes cyclopropanation with ethylene prior to protonation during workup.



**Scheme 3** Cyclopropanation via base-induced in situ formation of an α-boryl diazo intermediate.

A more synthetically useful transformation was reported by Wang and co-workers, who applied the BMIDA-substituted *N*-tosylhydrazone **4-1**, originally prepared by Grygorenko and co-workers,[27] to the synthesis of alkenyl MIDA boronates (Scheme 4).[29] When compound **4-1** was treated with $Cs_2CO_3$ in the presence of a palladium catalyst and reacted with benzyl bromide **4-2**, the corresponding alkenyl MIDA boronate **4-3** was obtained. Mechanistically, $Cs_2CO_3$ promotes deprotonation of **4-1** followed by elimination of the tosyl group, generating an α-boryl diazo species **4-4** in situ. Oxidative addition of the benzylic bromide to Pd(0) forms a benzyl–Pd complex **4-5**, which reacts with the diazo intermediate **4-4** to generate a Pd–carbene species **4-6** after nitrogen extrusion. Subsequent migratory insertion of the benzyl group into the carbene center (intermediate **4-7**), followed by β-hydride elimination, furnishes the olefin product **4-3**. A variety of substituted benzylic bromides are tolerated. *Para*-unsubstituted (**4-3a**), alkyl-substituted (**4-3b**), methoxy-substituted (**4-3c**), and nitro-substituted (**4-3d**) substrates afford the corresponding alkenyl MIDA boronates in good yields. An *ortho*-methyl substituent leads to diminished yield (**4-3e**), whereas a bromo substituent remains intact under the reaction conditions (**4-3f**). Heteroaromatic substrates are also compatible, providing the corresponding alkenyl MIDA boronates (**4-3g**).

The authors had previously developed methods for converting *N*-tosylhydrazones into alkenes,[30] and by extending this strategy to α-boryl diazo *N*-tosylhydrazones they demonstrated a straightforward route to structurally unique organoboron compounds.

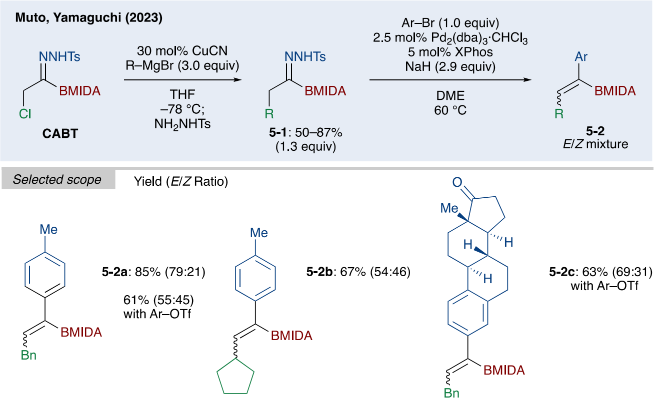


**Scheme 4** Pd-catalyzed coupling of BMIDA-substituted tosylhydrazone via in situ α-boryl carbene generation.

As described above, **CABT** contains three orthogonal reactive functional groups: a chloro substituent, a *N*-tosylhydrazone moiety, and a MIDA boronate. Consequently, it can function not only as a precursor to an α-boryl carbene but also as a versatile organic building block that enables sequential transformations at each of these functional sites (Scheme 5).[28]

For example, **CABT** can first undergo copper-catalyzed alkylation at the chloro position to give intermediate **5-1**. Subsequently, following the strategy reported by Barluenga and co-workers,[31] cross-coupling through in situ generation of the α-boryl diazo species furnishes alkenyl MIDA boronates **5-2**. Finally, the MIDA boronate unit can participate in further cross-coupling reactions, such as coupling with aryl iodides, to provide trisubstituted alkenes.

These transformations illustrate how the long-standing challenge of balancing stability and reactivity in α-boryl diazo compounds can be addressed through strategic molecular design. By combining controlled diazo generation with the synthetic flexibility of MIDA boronates, both stability and reactivity are successfully integrated into a practical synthetic platform.



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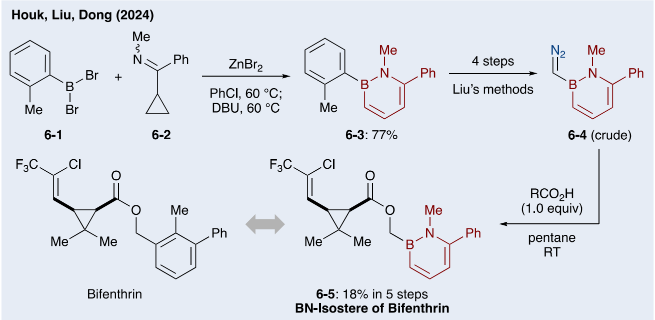
**Scheme 5** Sequential functionalization of CABT as a multifunctional α-boryl carbene precursor and building block.

Finally, the synthesis of a biologically relevant analogue of a pharmaceutical compound is highlighted. Houk, Liu, Dong, and co-workers developed a metal-free synthetic route to azaborines. In their study, cyclopropyl phenyl imine **6-2** was treated with (*o*-tolyl)BBr$_2$ (**6-1**) in the presence of ZnBr$_2$ as a Lewis acid additive under heating conditions, followed by treatment with DBU, affording azaborine **6-3** in 77% yield. Subsequently, following the strategy reported by Liu and co-workers, azaborine **6-3** was converted into α-diazo azaborine **6-4**. Reaction of this intermediate with a carboxylic acid proceeded via a O–H insertion process, enabling the synthesis of **6-5**, a biologically relevant analogue of the insecticide bifenthrin.



**Scheme 6** Synthesis of biologically relevant analogue of the insecticide bifenthrin.

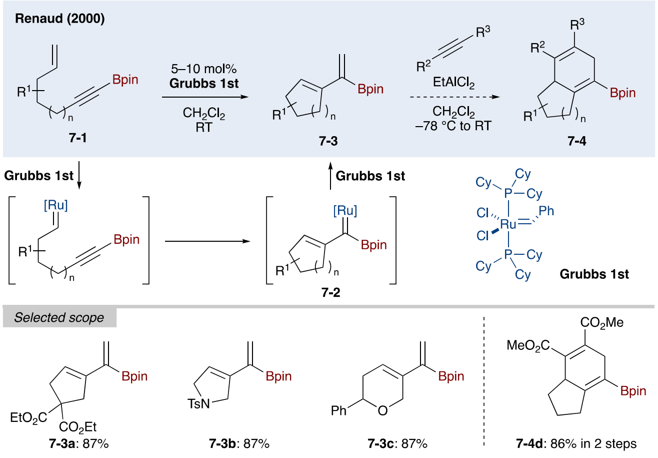
These studies demonstrate that sulfonyl hydrazone derivatives provide a practical solution to the intrinsic instability of α-boryl diazo compounds, enabling controlled generation of α-boryl carbenes and expanding their synthetic utility.

## 3. Alkynes

In contrast to the long and systematic development of α-boryl diazo compounds and α-boryl sulfonyl hydrazones as carbene precursors, boryl alkynes represent a conceptually distinct entry point into α-boryl carbene chemistry. Rather than relying on preformed diazo functionality, this strategy exploits the intrinsic reactivity of alkynes and converts them into carbene equivalents under catalytic oxidative conditions. Before discussing this modern platform, it is worth briefly noting that α-boryl metal carbene intermediates can also arise in the context of olefin metathesis. In particular, developments in enyne metathesis have enabled the transient formation of α-boryl ruthenium carbene species.

An early example was reported in 2000 by Renaud and co-workers (Scheme 7).[32] When substrate **7-1** was treated with the first-generation Grubbs catalyst, a ruthenium carbene was generated, triggering intramolecular enyne metathesis to produce an α-boryl ruthenium carbene intermediate **7-2**. Subsequent metathesis with another olefin moiety is proposed to regenerate the catalyst and afford boryl alkene **7-3**. Using this strategy, five-membered carbocycles (**7-3a**), nitrogen-containing five-membered rings (**7-3b**), and six-membered rings (**7-3c**) were synthesized. Furthermore, the resulting boryl alkene could be transformed into cyclized product **7-4d** upon treatment with EtAlCl$_2$ and an alkyne.

Although the formation of an α-boryl ruthenium carbene was not explicitly described in the original report, such an intermediate is strongly implied by the established mechanism of enyne metathesis. Importantly, however, turnover of the metathesis catalyst requires reaction with a conventional olefin partner. Consequently, this system does not allow the unique reactivity of α-boryl metal carbenes to be exploited independently of the metathesis cycle.



**Scheme 7** Enyne metathesis involving α-boryl alkyne and the proposed formation of an α-boryl ruthenium carbene intermediate.

The emergence of this platform was enabled by two independent methodological advances. (Fig. 3). First, the development of alkynyl boron compounds, particularly alkynyl MIDA boronates,[33] provided access to boryl-substituted alkynes in which the boron functionality remains chemically intact during subsequent transformations. Second, the discovery of gold-catalyzed oxidative activation of alkynes using nucleophilic oxidants established a general route to α-oxo gold carbene intermediates.[34,35] Because both enabling technologies matured around 2010, the merger of these concepts to generate α-boryl carbene precursors from boryl alkynes became feasible only in the following decade.

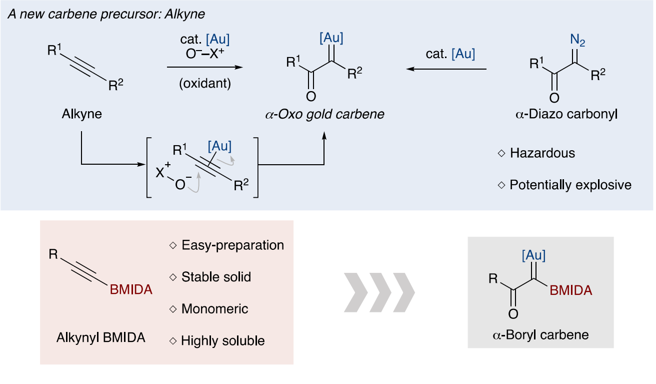


**Fig. 3** Conceptual advances enabling the generation of α-boryl carbenes from boryl alkynes.

This conceptual fusion was first realized in 2023 by Zhang and

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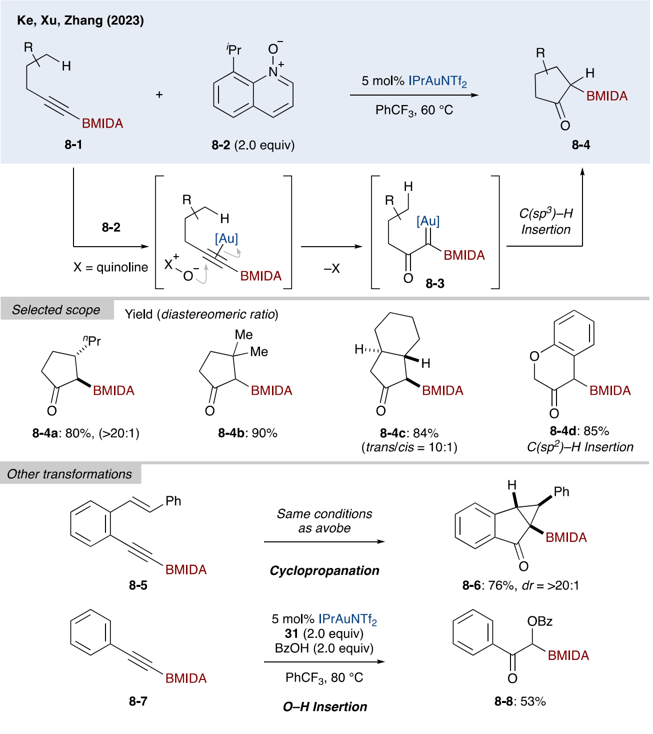
co-workers, marking the advent of boryl alkynes as a new class of α-boryl carbene precursors (Scheme 8).[36] They prepared BMIDA-substituted alkyne **8-1** and found that, in the presence of IPrAuNTf$_2$ (5.0 mol%) as the catalyst and 8-isopropylquinoline *N*-oxide (**8-2**) as the oxidant, the reaction afforded boryl ketone **8-4**. Mechanistically, coordination of the gold catalyst to the alkyne activates the π-system toward nucleophilic attack by the oxidant, generating an α-boryl gold carbene complex **8-3**. Subsequent intramolecular C(sp$^3$)–H insertion furnishes the desired products **8-4**. Both secondary (**8-4a**) and tertiary (**8-4b**) C–H bonds undergo efficient insertion to give the corresponding α-boryl ketones in good yields. Bicyclic frameworks (**8-4c**) can also be constructed under these conditions, and insertion into aryl C(sp$^2$)–H bonds proceeds to afford product **8-4d**.

In addition to C–H insertion, the α-boryl gold carbene intermediate participates in other carbene-type transformations. For example, when enyne **8-5** was employed, cyclopropanation occurred to give **8-6**. Furthermore, addition of external benzoic acid to alkyne **8-7** led to O–H insertion, furnishing product **8-8**.

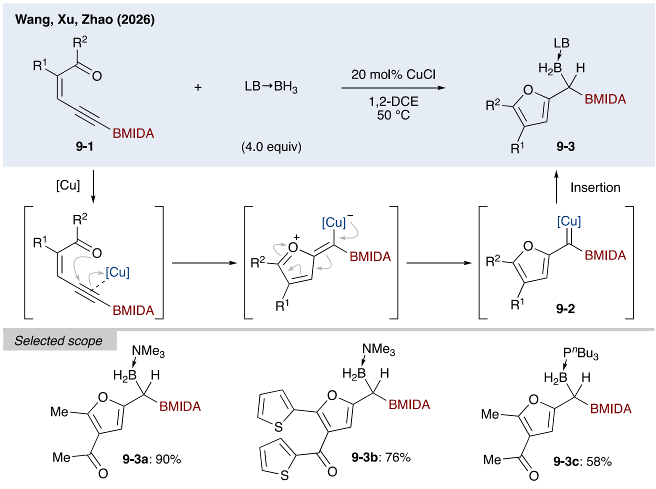
Although this work represents a straightforward extension of gold-catalyzed oxidative alkyne activation to boryl-substituted systems, it constitutes a seminal demonstration that boryl alkynes can serve as a new class of α-boryl carbene precursors.



**Scheme 8** Gold-catalyzed oxidation of boryl alkynes enabling α-boryl carbene reactivity.

Very recently, although representing a more specialized example, α-boryl alkynes have been used as precursors to α-boryl carbenes in further bond-forming reactions (Scheme 9).[37] In 2026, Zhao and co-workers employed a related catalytic system to promote a 5-*exo-dig* cyclization of alkyne **9-1**, followed by isomerization to a furan framework. Formation of the aromatic furan ring provided the driving force for the generation of a copper carbene intermediate **9-2**, which subsequently underwent insertion with an additional boron source.

While insertion of boron reagents into metal carbenes is well established,[38] this study represents the first example in which an α-boryl carbene was converted into a *gem*-diboryl compound through borane insertion. The reaction furnished *gem*-diboryl products bearing highly substituted furan frameworks (**9-3a**–**9-3c**) in good yields.



**Scheme 9** Copper-catalyzed boron insertion into α-boryl carbene derived from boryl alkyne.

Thus, the development of α-boryl alkynes as precursors to α-boryl carbenes has only just begun. Given their unique activation mode and compatibility with transition-metal catalysis, further transformations using a wider range of metal catalysts and reaction partners can be anticipated. Such advances are expected to enable the synthesis of structurally unique MIDA boronate derivatives and further expand the synthetic potential of α-boryl carbene chemistry.

## 4. Cyclopropenes

α-Boryl cyclopropenes represent a recently developed class of α-boryl carbene precursors, first reported by Zhu and co-workers in 2024.[39] The generation of metal carbenes from cyclopropenes is well established[40] and in the preceding year Zhu and co-workers had also reported silyl-substituted cyclopropenes as precursors to silyl carbenes. [41] Inspired by this concept, they extended the strategy to boryl-substituted systems.

α-Boryl cyclopropenes can be synthesized by two complementary approaches (Scheme 10). In one method, 1,1,2-tribromocyclopropane **10-1** is treated with two equivalents of *n*-BuLi to generate cyclopropenyllithium **10-2**. Alternatively, cyclopropane **10-3** itself can be deprotonated with one equivalent of *n*-BuLi to afford the same intermediate. Subsequent reaction of resulting **10-2** with *i*-PrOBpin enables the one-step synthesis of the corresponding α-boryl cyclopropane **10-4**.

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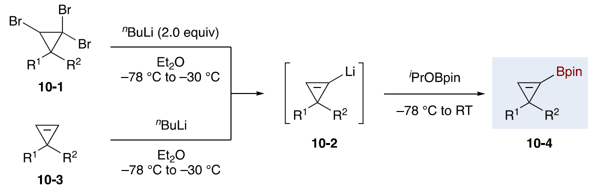
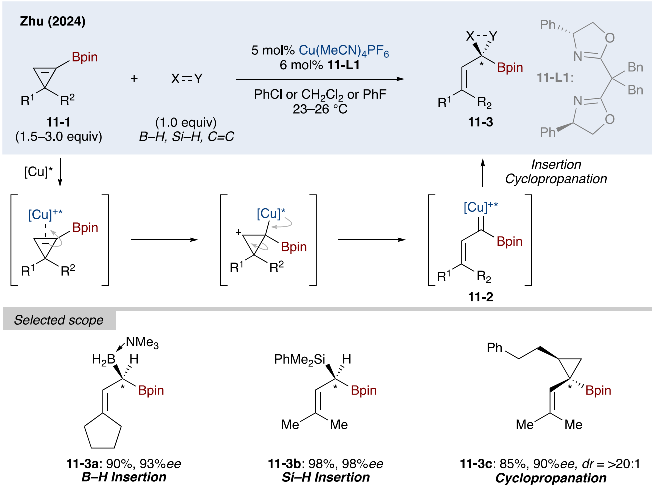


**Scheme 10** Synthesis of α-boryl cyclopropenes.

When synthesized α-boryl cyclopropene **11-1** is subjected to copper catalysis in the presence of chiral ligand **11-L1**, reactions with B–H, Si–H, or alkenes afford chiral boryl alkanes **11-3** (Scheme 11). Mechanistically, coordination of the α-boryl cyclopropene to a cationic copper species is followed by electrophilic cupration and ring opening of the cyclopropene framework, generating an α-boryl copper carbene intermediate **11-2**. This species subsequently undergoes carbene-type transformations depending on the reaction partner. For example, reaction with a borane leads to B–H insertion to give **11-3a**, whereas treatment with a silane such as $PhMe_2Si–H$ affords **11-3b** through Si–H insertion. In addition, reaction with an alkene proceeds through cyclopropanation to furnish **11-3c**. These reactions occur in high yields and with excellent enantioselectivity.

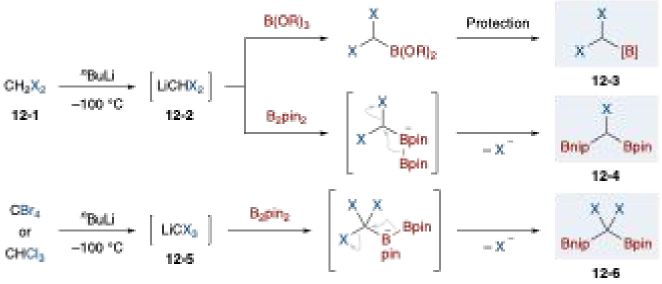
This strategy provides a unique approach to chiral organoboron compounds that were previously difficult to access while retaining versatile boron functionality for further transformations. As such, it expands the synthetic scope of both carbene chemistry and organoboron chemistry.



**Scheme 11** Cu-catalyzed enantioselective transformations of α-boryl cyclopropenes.

## 5. Haloalkanes

α-Boryl haloalkanes represent a relatively early class of precursors to α-boryl carbenes. Their synthesis is comparatively straightforward. For example, α-boryl halomethanes can be prepared from dihalomethanes (Scheme 12).[42] Treatment of a dihalomethane **12-1** with *n*-BuLi at –100 °C generates the corresponding dihalomethyllithium intermediate **12-2**. Subsequent reaction with a trialkoxyborane results in borylation, and after protection of the boron center in a stable form, the desired α-boryl halomethane **12-3** can be obtained. Alternatively, when $B_2pin_2$ is employed instead of a trialkoxyborane, borylation followed by B–B bond rearrangement and halogen elimination affords *gem*-diboryl monohalomethanes **12-4**.[43,44] A similar operation is feasible to synthesizing *gem*-diboryldihalomethane **12-6** by using a tetrabromomethane or chloroform as a starting material.[45] These compounds serve as versatile precursors for subsequent carbene generation.



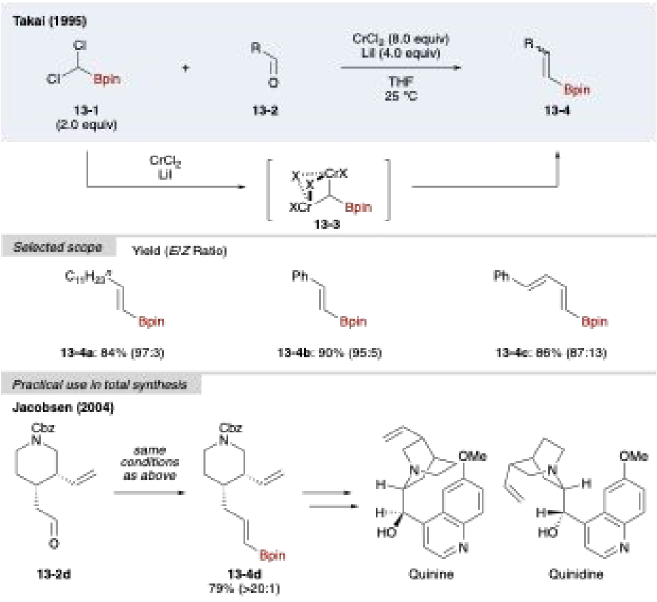
**Scheme 12** Preparation of α-boryl haloalkanes, *gem*-diboryl monohalomethanes, and *gem*-diboryl dihalomethanes.

These α-boryl dihaloalkanes and α-diboryl haloalkanes can generate α-boryl carbenes and *gem*-diboryl carbenes through several distinct activation pathways. In the following section, their synthetic applications will be discussed according to the mode of carbene generation.

### 5.1 Chromium carbene and zinc carbenoid

The application of α-boryl dichloroalkanes as precursors to α-boryl carbenes dates back to the 1995 report by Takai, Moriwake, and Utimoto.[46] At that time, they had developed *gem*-chromium reagents capable of converting carbonyl compounds into olefins, now known as the Takai–Utimoto olefination.[47] In this context, dichloromethyl boronate **13-1** was employed (Scheme 13).

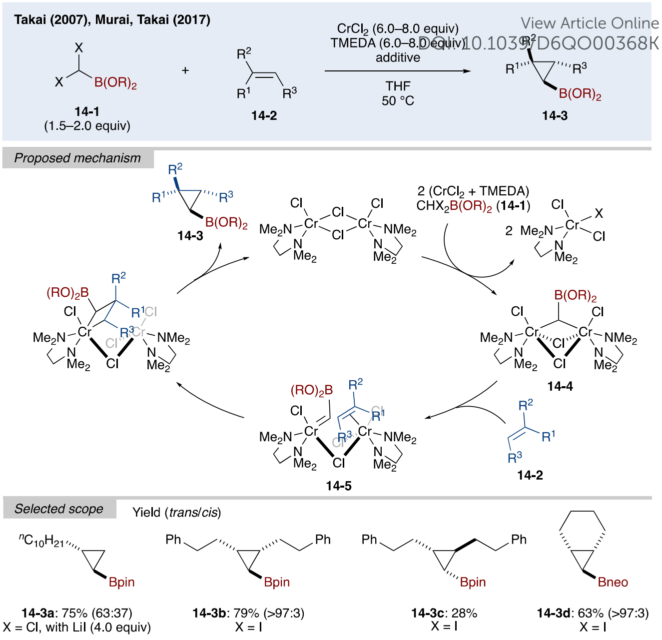
When **13-1** was treated with excess $CrCl_2$ in the presence of LiI and reacted with aldehydes **13-2**, alkenyl boronates **13-4** were obtained. Mechanistically, reaction of **13-1** with $CrCl_2$ and LiI generates a *gem*-dichromium species **13-3**. It is proposed that chloride ligands on chromium are replaced by iodide from LiI, and during this process a boryl chromium carbene intermediate **13-3** is formed. This species then reacts with the aldehyde to furnish the corresponding olefin. Saturated aldehydes (**13-4a**), aromatic aldehydes (**13-4b**), and even α,β-unsaturated aldehydes (**13-4c**) undergo the transformation to afford alkenyl boronates in good yields. Because the reagent can be readily prepared, this methodology found application in natural product synthesis. Indeed, in 2004, Jacobsen and co-workers employed this reaction in the total synthesis of quinine and quinidine.[48] Treatment of aldehyde **13-2d** under the Takai conditions furnished alkenyl boronate **13-4d** in good yield with high *E*/*Z* selectivity. The resulting alkenyl boronate was subsequently utilized to complete the synthesis of both natural products.



**Scheme 13** Takai–Utimoto olefination using dichloromethyl boronate as a precursor.

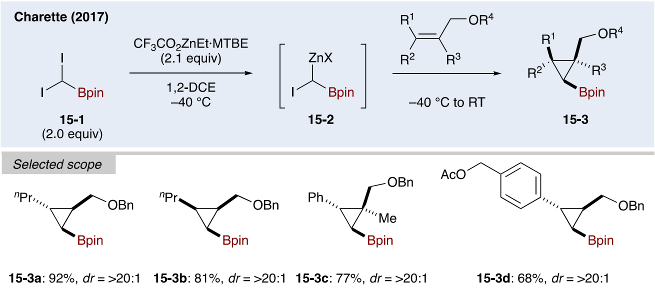
In 2007, Takai and co-workers reported the cyclopropanation of olefins via dihalocarbenes generated from dihalomethanes or dihalosilyl compounds. As an extension of this chemistry, they also described cyclopropanation using dichloroborylmethane (Scheme 14).[49] Similar to the previously developed systems, treatment of dichloroborylmethane **14-1** with LiI generated diiodoborylmethane in situ, which subsequently formed α-boryl chromium carbene species under the reaction conditions. This intermediate underwent cyclopropanation with alkenes **14-2** to afford boryl-substituted cyclopropanes **14-3**. However, only two examples were reported, and the diastereoselectivity was modest (e.g. **14-3a**, ca. 63:37). Mechanistic discussion at this stage remained largely qualitative, and the specific role of the boryl substituent in carbene generation and reactivity was not fully elucidated. Thus, this study primarily served as a proof-of-concept, demonstrating that boryl-substituted dihalomethanes could function as carbene precursors in chromium-mediated cyclopropanation.

A decade later, in 2017, Murai, Takai, and co-workers reported a substantially refined and mechanistically more detailed version of this transformation.[50] Through systematic optimization and broader substrate evaluation, improved reaction efficiency and stereocontrol were achieved across a wide range of alkenes. Importantly, mechanistic studies clarified the involvement of *gem*-dichromium intermediates **14-4** and discrete boryl chromium carbene species **14-5**, and the electronic influence of the boryl substituent was analyzed in terms of carbene stabilization and reactivity modulation. These studies transformed the earlier proof-of-concept into a well-defined and synthetically reliable platform, firmly establishing α-boryl dihaloalkanes as practical carbene precursors.



**Scheme 14** Chromium-mediated cyclopropanation of alkenes.

Shortly before the 2017 report by Murai, Takai, and co-workers, Charette and co-workers described the cyclopropanation of alkenes using the same diiodoborylmethane precursor (Scheme 15).[51] In their study, treatment of **15-1** with EtZnX (X = OCOCF$_3$) generated a boromethylzinc carbenoid **15-2**, which underwent Simmons–Smith-type cyclopropanation to afford boryl-substituted cyclopropanes **15-3** in high efficiency. The reaction proceeded in a stereospecific manner: *trans*-alkenes furnished the corresponding borylcyclopropane **15-3a**, whereas *cis*-alkenes afforded **15-3b** in good yields. Trisubstituted alkenes were also competent substrates (**15-3c**), and styrene derivatives underwent smooth cyclopropanation to give the desired products (**15-3d**). Although this system proceeds through a zinc carbenoid rather than a discrete metal–carbene complex, it represents an early example in which an α-boryl carbenoid engages in carbene-type cyclopropanation.



**Scheme 15** Simmons–Smith-type cyclopropanation of alkenes.

More recently, Wang and co-workers reported in 2025 a systematic study of cyclopropanation reactions of α-boryl dibromomethanes under a Cr(II)-based metalloradical catalysis (MRC) platform (Scheme 16).[52] In this work, α-boryl dibromomethanes such as BpinCHBr$_2$ (**16-1**) were employed as carbene precursors, and asymmetric radical cyclopropanation

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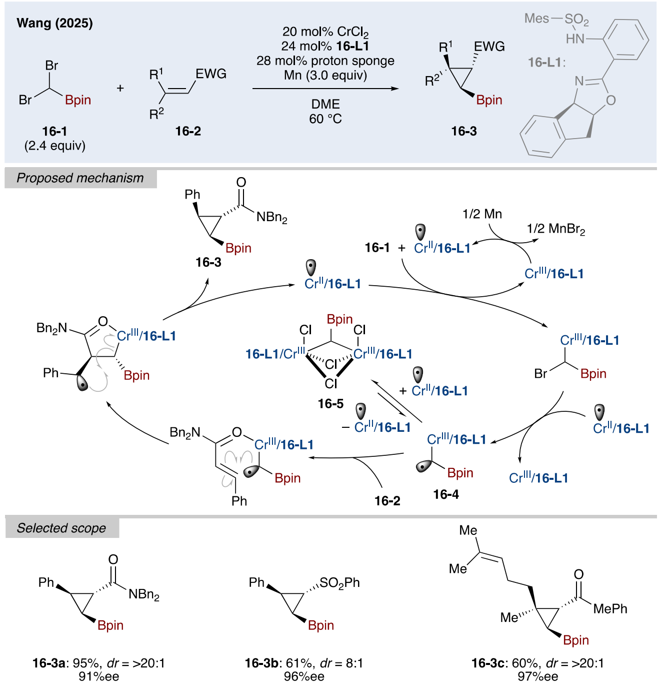
of α,β-unsaturated amides was achieved using a Cr(II)/chiral ligand **16-L1** system with Mn as the reductant. A notable feature of this transformation is the formation of products bearing three contiguous stereocenters with high diastereoselectivity and enantioselectivity (**16-3a**–**16-3c**).



**Scheme 16** Cr(II)-based metalloradical catalytic cyclopropanation of α,β-unsaturated amides.

Although Takai, Charette, and Wang all employed α-boryl dihaloalkanes as precursors to carbene-type reactivity, their studies differ fundamentally in mechanistic interpretation and activation mode. Takai's work was framed within a classical two-electron chromium–carbene model analogous to olefination chemistry. In contrast, Charette's approach relied on zinc carbenoid formation, demonstrating that α-boryl species can participate in stereospecific Simmons–Smith-type cyclopropanation without invoking discrete metal–carbene complexes. More recently, Wang's mechanistic studies suggested that activation under chromium conditions may proceed through a single-electron pathway involving radical intermediates prior to carbenoid formation.

Thus, while the substrate class remains constant, the underlying activation modes span two-electron metal–carbene chemistry, classical carbenoid reactivity, and radical–carbenoid pathways. These distinctions highlight the remarkable mechanistic diversity of α-boryl haloalkane chemistry and illustrate the increasing sophistication with which their reactivity is understood.

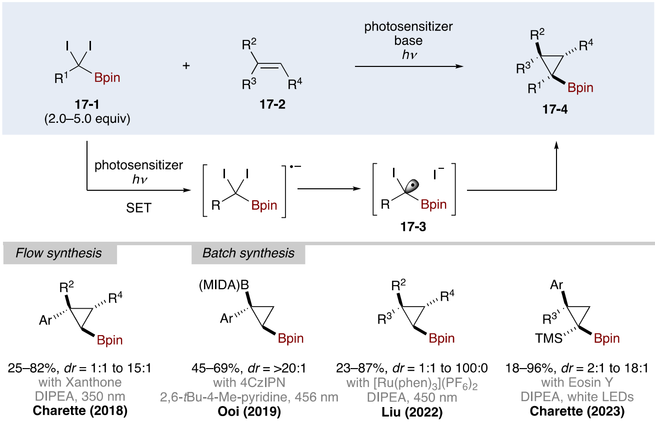
### 5.2. Radical carbenoid

Although the transformations described above involve metal carbenes or classical carbenoid intermediates, Charette and co-workers reported in 2018 a conceptually related radical carbenoid pathway (Scheme 17).[53] The cyclopropanation of olefins using diiodomethane under mercury-lamp UV irradiation has long been known,[54] and the advent of LED technology combined with photoredox catalysis enabled more practical photoirradiation. Shortly before this report, cyclopropanation of olefins using diiodomethane through LED-driven photoredox catalysis had also been disclosed.[55] Charette's contribution was to extend this strategy to diiodomethyl boronates.

In their system, xanthone was employed as an organic photosensitizer, and irradiation at 350 nm induced single-electron transfer to generate a radical anion species. Subsequent homolytic C–I bond cleavage produced an iodomethyl boronate radical, which can be regarded as a radical carbenoid equivalent. This species engages in cyclopropanation of styrenes under UV irradiation. DIPEA serves as a sacrificial reductant, regenerating ground-state xanthone from its radical cation and sustaining the photoredox cycle.

Although carbene or metal carbenoid systems often suffered from limited generality and modest yields with styrenes, this study demonstrated that borocyclopropanation could be achieved more efficiently under continuous-flow UV conditions. Subsequent developments further refined this radical manifold: in 2019, Ooi and co-workers reported a related transformation using 4CzIPN as a photoredox catalyst under blue LEDs (456 nm) irradiation,[56] in 2022, Liu and co-workers utilized trisubstituted alkenes in this transformation with a ruthenium-based photoredox catalyst,[57] and in 2023 Charette again disclosed a similar conversion under white light in the presence of eosin Y.[58]

Taken together, these studies illustrate that carbene-type cyclopropanation can be achieved even in the absence of a discrete metal carbene intermediate, representing the radical extreme of α-boryl carbene chemistry.



**Scheme 17** Photochemical radical carbenoid cyclopropanation of styrenes.

In 2023, Hu, Marder, and co-workers reported a visible-light-induced borylcyclopropanation of alkenes using a (diborylmethyl)iodide reagent, $CHI(Bpin)_2$ (**18-1**) (Scheme 18).[43] In this system, *fac*-$Ir(ppy)_3$ serves as the photocatalyst under blue LEDs irradiation, and CsF plays a crucial role in activating the diborylmethyl iodide precursor **18-1**. Mechanistic studies, including radical trapping experiments and Stern–Volmer analysis, support a pathway involving single-electron transfer from the excited photocatalyst to a fluoride-activated species derived from $CHI(Bpin)_2$, leading to generation of an α-

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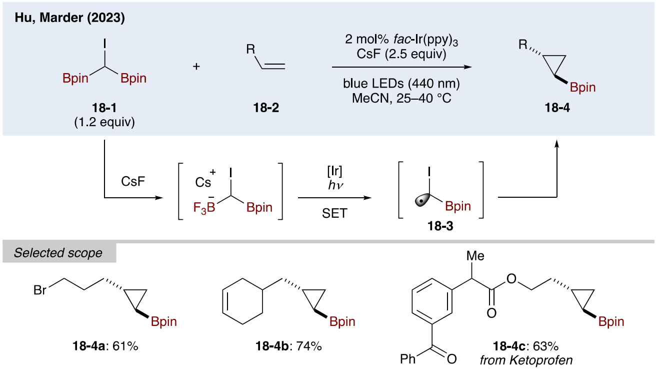
iodoboryl carbon-centered radical **18-3**. Subsequent radical addition to the alkene **18-2**, followed by single-electron reduction and intramolecular 3-*exo-tet* cyclization, furnishes the borylcyclopropane products (**18-4a**–**18-4c)**.

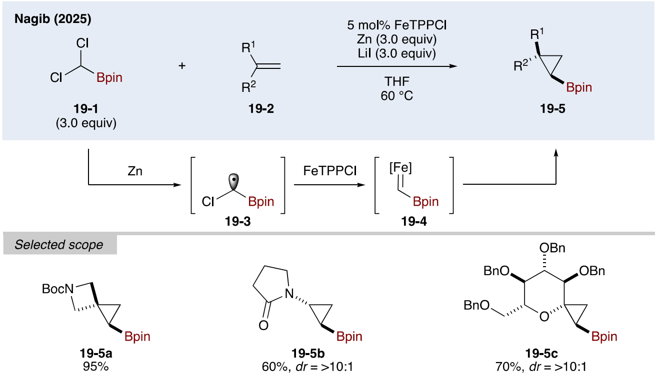
Notably, this transformation does not proceed through a discrete α-boryl metal carbene. Instead, the key reactive intermediate is best described as a radical carbenoid equivalent, generated under purely photochemical conditions. The reaction thus represents a fully developed radical manifold for α-boryl C1 transfer, distinct from classical two-electron carbenoid chemistry and from metalloradical carbene systems.



**Scheme 18** Visible-light-induced radical borylcyclopropanation of alkenes.

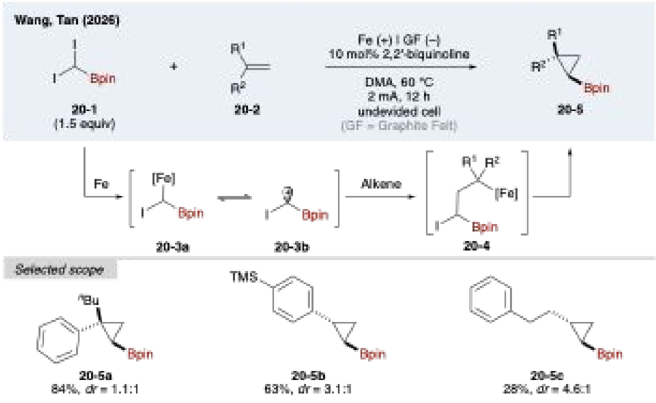
Nagib and co-workers in 2025 reported an intriguing methodology for generating Fe-carbene species from 1,1-dichloroalkanes, which was practically applied to cyclopropanation with alkenes.[59] In this study, the authors demonstrated that FeTPPCl (TPP: tetraphenylporphyrin) catalyst, together with Zn and LiI, promotes the cyclopropanation of an alkene **19-2** with dichloroborylmethane **19-1** via borylated Fe-carbene intermediate **19-4**. The reaction is proposed to proceed through single-electron reduction of **19-1** by Zn to generate chloroboryl carbon-centered radical **19-3**, which is subsequently captured by the iron catalyst to form **19-4**. The resulting **19-4** then reacts with alkene **19-2** to give borylcyclopropane **19-5**.

This reaction exhibits broad functional group tolerance, as demonstrated by the synthesis of nitrogen-containing spirocyclic compound **19-5a**, lactam-substituted cyclopropane **19-5b**, and sugar-derived product **19-5c**, all obtained with generally good diastereoselectivities.



**Scheme 19** Fe-carbene formation through the generation of radical carbenoid.

Relating to Nagib's report, Wang, Tan, and co-workers reported an electrochemical cyclopropanation of alkenes **20-2** with diiodoborylmethane **20-1** via the generation of α-iodoboryl carbon-centered radical **20-3**.[60] Under electrochemical conditions using an iron anode and a graphite felt (GF) cathode in the presence of a catalytic amount of 2,2'-biquinoline, the reaction of diiodoborylmethane **20-1** with alkenes **20-2** afforded borylcyclopropanes **20-5**. Mechanistic studies, including a series of control experiments and electrochemical investigations, indicated that iron species released from the anode play a key role. Low-valent iron species generated at the anode reduce **20-1** to form iodoborylmethyl–iron species **20-3a**, which is in equilibrium with iodoborylmethyl radical **20-3b**. Either species can react with the alkene to furnish borylcyclopropane **20-5** through the formation of Fe–alkyl intermediate **20-4**. This reaction enables the cyclopropanation of aryl alkenes and alkyl alkenes to yield the corresponding borylcyclopropanes (**20-5a**–**20-5c**), albeit with generally poor to moderate diastereoselectivities.



**Scheme 20** Electrochemical-driven radical borylcyclopropanation of alkenes.

Taken together with earlier developments, the evolution of α-boryl carbenoid chemistry can be viewed as a progression from classical metal carbenoids, to metal-bound α-boryl carbenes, to metalloradical intermediates, and ultimately to metal-free photochemical radical carbenoid pathways. This trajectory highlights the mechanistic diversification and increasing maturity of the field, expanding the conceptual boundaries of what constitutes α-boryl carbene reactivity.

### 5.3. Lithium carbenoid

Beyond metal carbenes and radical carbenoid manifolds, lithium carbenoids derived from α-halo *gem*-diborylmethanes have recently emerged as a distinct and highly controllable platform for C1 transfer chemistry. Although these intermediates are sometimes described as "boron ylides," their reactivity is more accurately interpreted as that of lithium-stabilized carbenoid species, in which the boryl substituents play a dual role in stabilizing the adjacent carbanion and directing cyclization.

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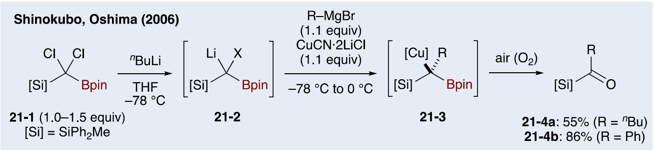
An earlier example relevant to this chemistry was reported in 2006 by Oshima, Shinokubo, and co-workers (Scheme 21).[61] In this study, a boryl-silyl substituted lithium carbanion **21-2** was generated via halogen–lithium exchange of boryldichloromethylsilane **21-1**, which was subsequently converted into a *gem*-borylsilylalkylcopper species **21-3** through transmetallation with CuCN·2LiCl and Grignard reagents. The resulting organocopper intermediate **21-3** underwent aerobic oxidation to give acylsilanes **21-4a** and **21-4b** efficiently. Mechanistically, this transformation proceeds through a stepwise sequence involving lithium carbanion formation, copper ate-complex generation, and subsequent migration processes rather than through a discrete metal carbene intermediate. Importantly, the authors demonstrated that the boryl substituent significantly alters the reactivity of the carbanion, enabling efficient formation of *gem*-borylsilylalkylcopper intermediates.

Although this system cannot be classified as a lithium carbenoid in the modern sense, it represents an early example in which boron-stabilized carbanions were exploited to generate carbene-type reactivity equivalents. In this context, it can be regarded as a conceptual precursor to later lithium carbenoid strategies involving α-boryl carbanions.



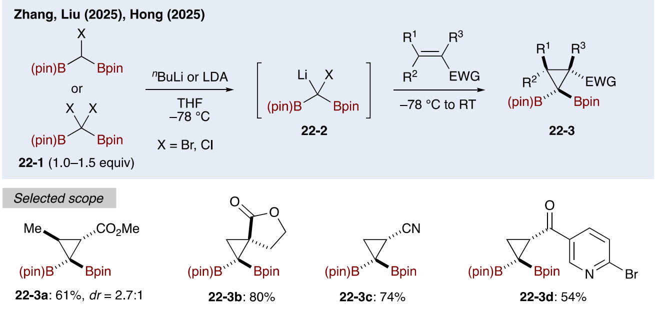
**Scheme 21** Early example of boron-stabilized carbanion chemistry leading to *gem*-borylsilylalkylcopper intermediates.

In 2024, Fang, Zhang, and Liu reported the stereoselective cyclopropanation of electron-deficient olefins using halogenated *gem*-diborylmethanes **22-1** as precursors of so-called "boron ylides" (Scheme 22).[62] Treatment of diborodibromomethane with *n*-BuLi at low temperature generated lithium species **22-2** that engages olefins in cyclopropanation, affording *gem*-diborylcyclopropanes (**22-3a**–**22-3c**) in good to excellent yields with high diastereoselectivity. Mechanistic studies support deprotonation or lithium–halogen exchange to form an α-halo lithium carbenoid equivalent **22-2**, followed by nucleophilic addition to activated olefins and intramolecular ring closure. Importantly, control experiments demonstrated that replacement of the boryl groups with alkyl substituents suppressed cyclization, underscoring the essential stabilizing and stereodirecting role of the boron substituents. Furthermore, the retained diboryl units enabled extensive downstream functionalizations, including stereospecific C–B transformations, highlighting the synthetic versatility of this platform.

Subsequently, in 2025, Hong and co-workers reported a closely related strategy employing lithiated chlorodiborylmethane for the synthesis of *gem*-diborylcyclopropyl ketones.[63] In this study, chlorodiborylmethane was deprotonated with LDA at low temperature to generate the corresponding halodiborylmethyl lithium species **22-2**, which undergoes conjugate addition to α,β-unsaturated ketones, followed by intramolecular ring closure to furnish *gem*-diborylcyclopropyl ketone **22-3d** in a good to excellent yield.

Compared with the earlier "boron ylide" system, Hong's work significantly broadened substrate scope to include α,β-unsaturated ketones, delivering *gem*-diborylcyclopropyl ketones with high functional group tolerance and scalability. The reaction was demonstrated on gram scale, and the resulting cyclopropyl ketones underwent diverse downstream transformations, highlighting their synthetic utility.

Taken together, these studies established lithium carbenoids of *gem*-diborylmethanes as a mechanistically distinct branch of α-boryl C1 chemistry. In contrast to metal carbenes or radical pathways, these systems operate through polar two-electron processes, yet achieve high levels of stereocontrol and functional group compatibility. The emergence of this lithium carbenoid strategy further expands the mechanistic landscape of α-boryl carbenoid chemistry and illustrates its growing mechanistic maturity.



**Scheme 22** Cyclopropanation using lithium carbenoids.

In 2025, Maseras, Fernández and co-workers reported the stereoselective synthesis of tetrasubstituted epoxides using α-halo B–Si ylides **23-2** derived from boryl-substituted precursors **23-1** (Scheme 23).[64] Reaction with ketones proceeds through nucleophilic addition of the carbenoid **23-2** to the carbonyl group followed by intramolecular ring closure to afford highly substituted epoxides **23-3a** and **23-3b** with excellent stereocontrol. Shortly thereafter, the same concept was extended to imines, enabling the stereofacial assembly of multiply-functionalized chiral aziridines.[65] In this case, the lithium carbenoid **23-2** reacts with imines to form aziridines **23-3c** and **23-3d** through an analogous addition–cyclization sequence.

These studies demonstrate that α-boryl lithium carbenoids can function as versatile carbene equivalents, enabling classical carbene-type transformations such as epoxidation and aziridination while incorporating synthetically valuable boron substituents.

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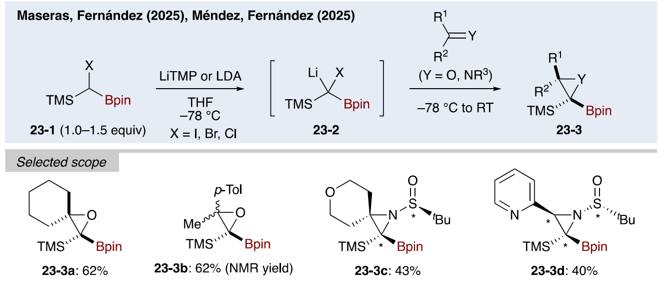
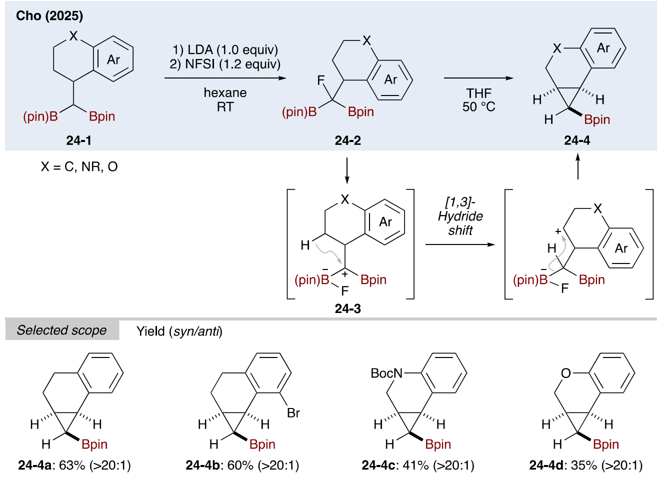


**Scheme 23** Epoxidation and aziridination using α-halo B–Si ylides as lithium carbenoid equivalents.

### 5.4. Others and summary of haloalkanes

The examples discussed in this chapter illustrate that the formation of reactive α-boryl anionic or radical species through metalation or single-electron transfer events can drive unique reactions. In contrast, Cho and co-workers uncovered a distinctive mode of reactivity in which the generation of an α-boryl cationic species from a *gem*-diborylfluoromethyl group plays a key role in an unusual [1,3]-hydride shift reaction (Scheme 24).[66] They demonstrated this unique reactivity by the synthesis of borylcyclopropane **24-4** via a sequential process consisting of lithiation and fluorination of **24-1** to construct **24-2**, followed by heating at 50 °C. Upon heating, intermediate **24-2** undergoes a [1,2]-fluoride migration to generate an α-boryl carbocation **24-3**. This highly electrophilic species then triggers the unusual [1,3]-hydride shift to give a carbocation, which subsequently undergoes F–Bpin elimination to furnish cyclopropane **24-4**. This reaction protocol synthesized three-membered-ring-fused tetralines **24-4a** and **24-4b**, and tetrahydroquinoline **24-4c**, and benzopyrane **24-4d** with a remarkable diastereoselectivity. Although this reactivity differs significantly from that of α-borylcarbene and boron-ylide species, this example highlights the unique ambiphilic character of *gem*-diborylfluoromethyl group.

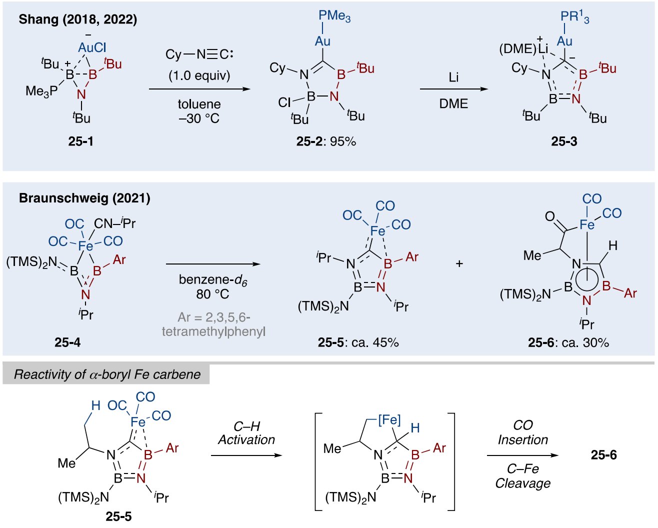


**Scheme 24** [1,3]-Hydride shift reaction of *gem*-diborylfluoromethyl compound.

*N*-Heterocyclic carbenes have been used as a promising supporting ligand in organometallic chemistry.[67] Recently, some efforts have been devoted to altering the predominantly nucleophilic carbene into electrophilic by incorporating a boron atom adjustment to the carbene center. In this context, before describing a representative achievement (*vide infra*) in reversing the electronic property of carbene by using an organohalide as a precursor, it would be valuable to introduce earlier example.

Shang and co-workers reported the unique reaction between borylgold(I)borane complex **25-1** with isocyanide to afford 1,3,2,4-diazadiborol-5-ylidene–gold(I) complex **25-2** (Scheme 25).[68,69] Using the π-accepting nature of boron, unique two-electron reduction of **25-2** with Li(0) proceeded to give anionic complex **25-3**. Although their distinct application to catalysis have yet been uncovered, it was concluded that the ligand on complex **25-2** behaves as Fischer-type carbene. The boryl group next the carbene center attributes to a low-lying LUMO of the ligand. In contrast, on the anionic complex **25-3**, its 6π-dianionic ligand likely behaves as Schrock-type carbene.

Related to Shang's work, the Braunschweig group reported the synthesis of iron–1,3,2,4-diazadiborol-5-ylidene complex **25-5** from **25-4**.[70] In this synthesis, together with **25-5**, $\eta^5$-1,3,2,4-diazadiborolyl ligand coordinated iron complex **25-6** was also generated. The group explained that the possible mechanism on the generation of **25-6** from **25-5**. Because the iron-bound carbon would be sufficiently basic to deprotonate a C–H bonds on the pendant alkyl group, an iron-alkyl complex could be generated. Upon CO insertion and Fe–C bond cleavage, complex **25-6** would be given.



**Scheme 25** Synthesis of metal–1,3,2,4-diazadiborol-5-ylidene complexes.

The above examples provided compelling evidence that a boron atom adjacent to the carbene center could invert the electronic character of an NHC-type carbene. A notable example in this area has very recently been presented by Kusumoto, Nozaki, and co-workers through the synthesis of a diborylcarbene (DBC) equivalent, K/F-diborylcarbenoid **26-1** (Scheme 26). [71,72] Through studies on the reactivity of **26-1**, they demonstrated that the presence of two boryl substituents at the carbene center leads to a fundamentally different electronic structure, resulting in a highly electrophilic carbene. Upon halide

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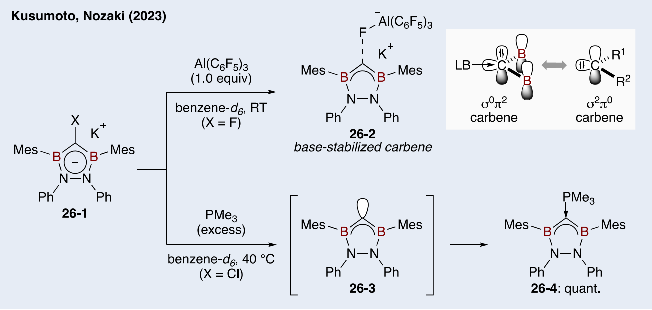
abstraction from **26-1**, they provided evidence for the formation of DBC **26-3** through trapping experiments. For instance, by treating **26-1** with Al($C_6F_5$)$_3$, they observed a base-stabilized DBC species **26-2**. Furthermore, dehalogenation of **26-1** (X = Cl, K/Cl-diborylcarbenoid) with an excess of PMe$_3$ at 40 °C afforded DBC–PMe$_3$ adduct **26-4** quantitatively. These experimental results combined with theoretical calculations indicated that this carbene **26-3** exhibits an unusual reversed electronic structure, featuring a filled pπ orbital and a vacant in-plane σ orbital at the carbene center, making DBC highly electrophilic. As this species has only recently been identified, its synthetic applications remain to be explored. This study illustrates how multiple π-accepting boryl substituents can dramatically alter the electronic character of a carbene center.



**Scheme 26** Experimental evidence of highly electrophilic diborylcarbenes.

As discussed in the preceding sections, α-boryl haloalkanes can generate carbene-type reactivity through a variety of mechanistic pathways (Fig. 4). These include classical two-electron metal–carbene formation, zinc or lithium carbenoid intermediates, metalloradical processes, and purely photochemical radical manifolds. Despite sharing a common substrate class, these activation modes differ fundamentally in their electronic structure and reaction mechanisms.

Early studies primarily focused on chromium-mediated carbene chemistry (Takai, Wang) and Simmons–Smith-type carbenoid reactions (Charette), establishing the feasibility of using α-boryl haloalkanes as carbene precursors. Subsequent developments significantly expanded this landscape. Radical and photochemical strategies (Charette, Ooi, Liu, and Hu/Marder) as well as iron-based strategies (Nagib and Wang/Tan) revealed that carbene-type reactivity can also emerge through single-electron processes, while lithium carbenoid chemistry (Shinokubo/Oshima, Zhang/Liu, Hong, Maseras/Fernández) introduced highly controllable polar pathways that enable efficient cyclopropanation and related transformations. More recent example by Cho highlights the distinctive reaction mode, the generation of α-boryl cationic species, which enables the [1,3]-hydride shift. Finally, the development of K/F-diborylcarbenoid provided evidence that it can generate DBC, which behaves as an electrophilic carbene.

Taken together, these studies demonstrate that α-boryl haloalkanes constitute one of the most versatile platforms for generating α-boryl C1 units. The coexistence of multiple activation paradigms—two-electron and radical—provides exceptional flexibility in reaction design. Continued exploration of new catalytic systems, activation modes, and reaction partners is therefore expected to further expand the synthetic potential of α-boryl carbene chemistry.

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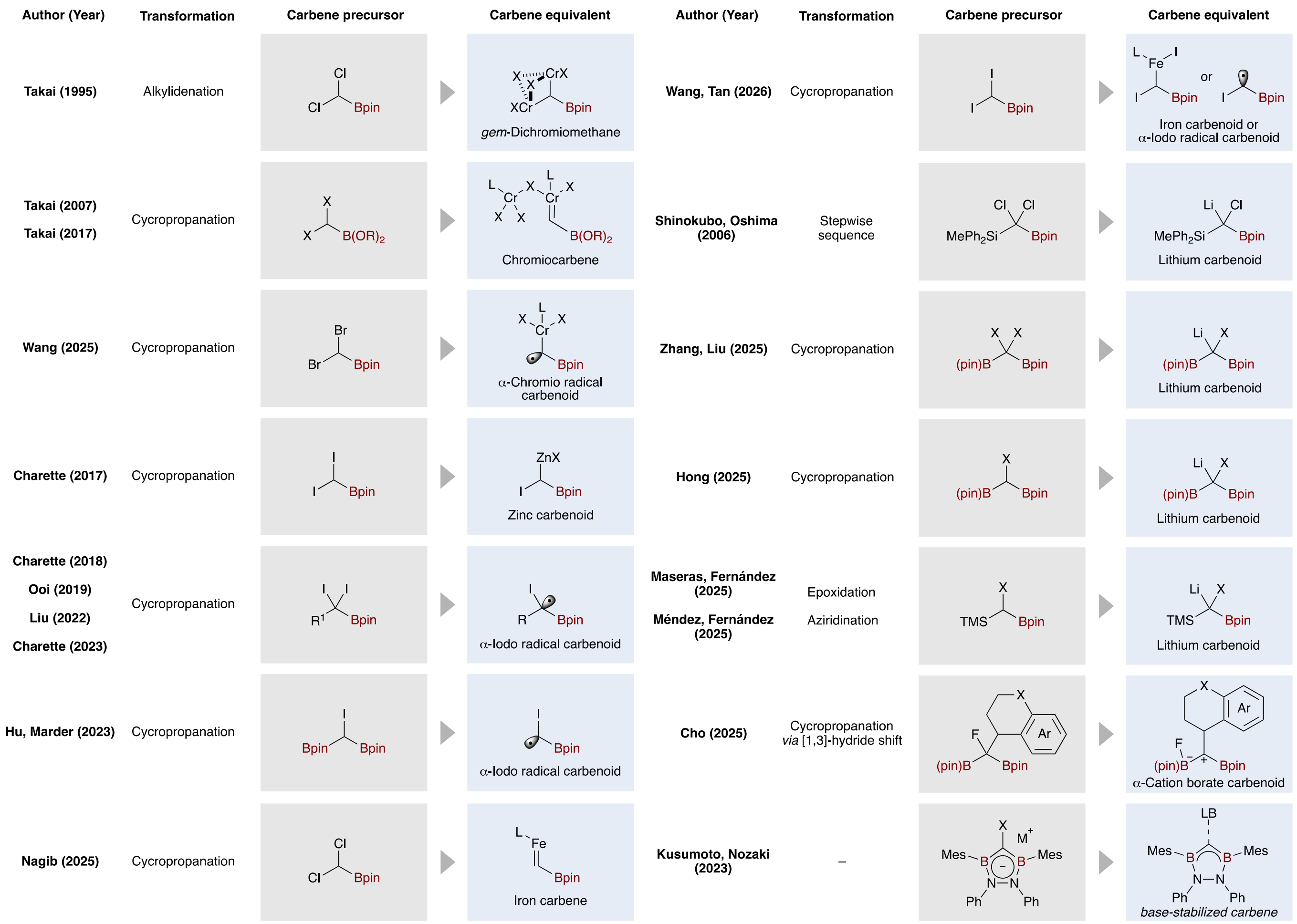

**Fig. 4** α-Boryl haloalkanes and the generation of the corresponding α-boryl carbenoids.

## Conclusions

α-Boryl carbenes represent a distinctive class of reactive intermediates that combine the high reactivity of carbenes with the versatile synthetic utility of organoboron compounds. Over the past decades, significant progress has been achieved in the development of precursors capable of generating α-boryl carbene species under controlled conditions. Early studies relied primarily on diazo compounds and sulfonyl hydrazones, whereas more recent strategies have introduced conceptually distinct platforms such as oxidative activation of boryl alkynes, ring opening of α-boryl cyclopropenes, and activation of α-boryl haloalkanes to form carbenoid species.

These advances reveal the mechanistic diversity through which α-boryl carbene reactivity can be accessed. Depending on the precursor and activation mode, α-boryl carbene chemistry now encompasses classical metal–carbene intermediates, metal carbenoids, metalloradical pathways, and metal-free radical processes. This diversity has enabled a range of transformations, including C–H insertion, cyclopropanation, rearrangement, and heteroatom insertion reactions, while preserving the synthetically valuable boron functionality.

For practical use, Figure 5 summarizes five classes of precursors, comparing their stability, atom-economy, and the requirement for a transition metal-catalyst (Fig. 5). Diazo compounds are indeed preferable precursors in terms of atom economy. However, their excessively high reactivity necessitates the use of a robust protecting group on the boryl

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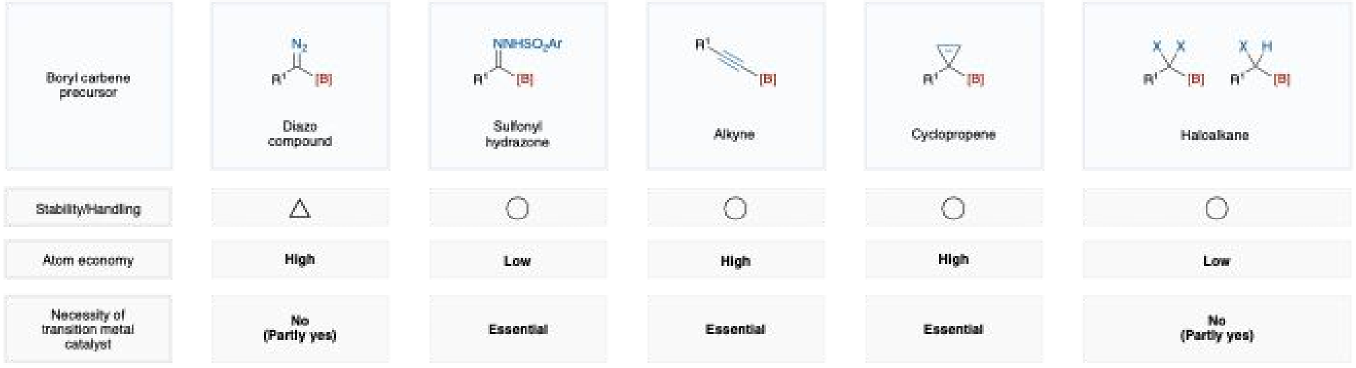
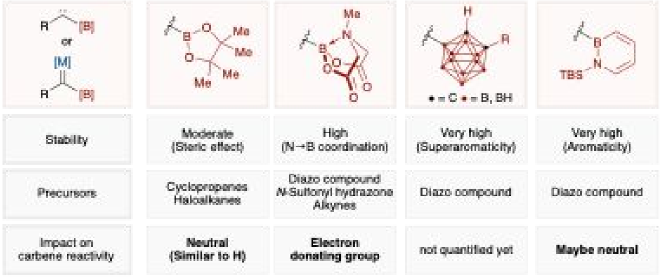
moiety, such as 1,2-azaborine and carborane. *N*-Sulfonylhydrazones, an alternative to diazo compounds, exhibit greater stability, which allows the use of BMIDA. However, their poor atom economy and the reliance on particular transition metal-catalyzed reactions remain issues to be addressed. Although the scope of reactions is still limited, borylalkyne as well as borylcyclopropenes are a stable precursor and can generate α-boryl-metal-carbene with a good atom-economy. Finally, haloalkanes, which are highly stable precursors with moderate atom economy, have typically been used with strongly basic organometallic reagents, resulting in only moderate functional group tolerance. However, recent advances have uncovered radical-based methodologies, improving functional group tolerance.



| Boryl carbene precursor | Diazo compound | Sulfonyl hydrazone | Alkyne | Cyclopropene | Haloalkane |
|---|---|---|---|---|---|
| Stability/Handling | △ | ○ | ○ | ○ | ○ |
| Atom economy | High | Low | High | High | Low |
| Necessity of transition metal catalyst | No<br>(Partly yes) | Essential | Essential | Essential | No<br>(Partly yes) |

**Fig. 5** Five classes of α-boryl carbene precursors.

The choice of the protecting group on the boryl moiety is important (Fig. 6). Bpin, which is the most familiar group to chemists, provides moderate stabilization. Therefore, it can only be used in relatively stable precursors such as cyclopropenes and haloalkanes. The generated metal carbenes likely behave as neutral carbene.[59] BMIDA, which is "masked boronate" formed via coordination of the Lewis basic nitrogen atom, exhibits higher stability, allowing the isolation and use of α-boryl diazo compounds as well as *N*-sulfonylhydrazones as precursors. The MIDA group has been reported to function as an electron-donating group, increasing the electron density of the corresponding carbene.[36] Finally, carboranes and 1,2-azaborines exhibit exceptionally high stability due to their (super)aromaticity, and are often used as protecting groups for α-boryl diazo compounds. Regarding reactivity, quantitative studies have not yet extensively conducted, but 1,2-azaborine group is suggested to provide an electronically neutral carbene species based on its N=N infrared frequency.[22]



| | | | | |
|---|---|---|---|---|
| Stability | Moderate<br>(Steric effect) | High<br>(N→B coordination) | Very high<br>(Superaromaticity) | Very high<br>(Aromaticity) |
| Precursors | Cyclopropenes<br>Haloalkanes | Diazo compound<br>N-Sulfonyl hydrazone<br>Alkynes | Diazo compound | Diazo compound |
| Impact on carbene reactivity | **Neutral<br>(Similar to H)** | **Electron donating group** | not quantified yet | **Maybe neutral** |

**Fig. 6** Protecting group on boryl moiety in α-boryl carbene chemistry.

Despite these developments, α-boryl carbene chemistry remains at a relatively early stage. Compared with classical carbene chemistry, general and synthetically practical methods are still limited, and many mechanistic aspects remain to be clarified. Particularly, although intermolecular C–H insertion and three-component reactions are well established in general transition metal carbene chemistry, reactions involving transition metal-α-boryl carbene species remain largely limited to the synthesis of boryl alkenes. Moreover, enantioselective reactions remain scarce, and there is little doubt that the development and application of asymmetric catalysts will further advance and mature this field. Future advances in catalyst design, precursor development, and mechanistic understanding are expected to expand the scope of α-boryl carbene reactions and further establish their utility in molecular construction and functional group editing.

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## Conflicts of interest

There are no conflicts to declare.

## Data availability

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

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