

Perspective

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Future prospects in boron chemistry: new boron compounds and Lewis acids for catalysis and materials science

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Abstract

Boron-containing compounds have a wide range of structures and rich and multifaceted reactivity patterns. As a result, these compounds are being increasingly used in organometallic, supramolecular, organic and inorganic chemistry, as well as in catalysis and materials science. This perspective describes recent ground-breaking studies and their implications for the future development of new catalysts and materials containing one or several trivalent boron atoms.

Keywords: Boron chemistry, organoboron compounds, boron Lewis acids, boron materials, boronic acid derivatives, organoboranes

Due to their structural diversity and rich reactivity, boron-containing compounds are being increasingly used as building blocks in organic^[1], organometallic, supramolecular and inorganic synthesis, as well as in catalysis^[2] and materials science^[3]. While trivalent organoboron species are textbook examples of Lewis acids and trivalent boron substituents are electron-withdrawing groups by nature, the nucleophilic reactivity of the C-B bond is readily increased by combining the trigonal boron atom with Lewis bases, anions or nucleophiles. Such activation of boronic acid derivatives is a widely used strategy in transition metal-catalysed (Suzuki-Miyaura cross-coupling reaction) and transition metal-free reactions^[4-6]. As recent reviews and perspectives have highlighted the chemistry of tetracoordinate anionic boron intermediates used for the



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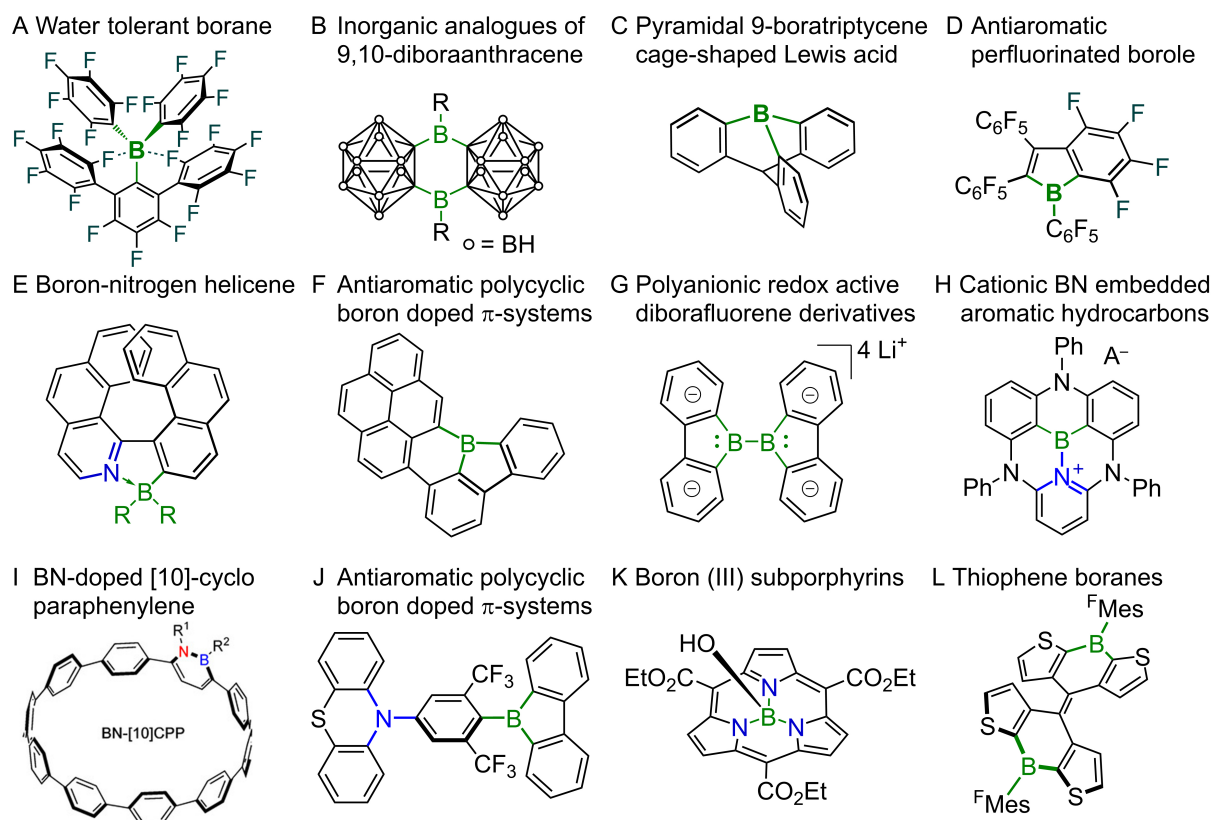


Figure 1. New boron-, diboron- and boron heteroatom-doped aromatic compounds.

C-C and C-B bond formation^[7-9] of boryl anions, borylenes and diboron species^[10,11], and of the photochemical and photoinduced reactions with boron reagents^[12-14], they are not covered here. This perspective focuses on recent developments regarding new types of trivalent boron compounds and their applications for the design of boron-doped aromatic materials, of boron Lewis superacids and of new boron-based catalysts targeting the activation of small molecules and the C-H borylation reactions.

Trivalent boron compounds are prototypical Lewis acids with a very wide range of Lewis acidities^[15]. Triarylboranes are widely used as activators, catalysts and co-catalysts in a plethora of reactions^[16-18]. The recent development of polyfluorinated triphenyldiphenyl boranes tolerant to air and water [Figure 1A]^[19] will undoubtedly open new opportunities for improving well-established boron-mediated catalytic processes^[20]. Powerful boron Lewis acids and superacids with ever increasing Lewis acidity are also gaining increasing interest from the perspective of the recent intense development of new types of inorganic analogues, including diboraanthracene featuring carborane substituents [Figure 1B]^[21], pyramidal yet trivalent boron Lewis acids embedded in cage-shaped triptycene cores [Figure 1C]^[22-24] and antiaromatic perfluorinated boroles [Figure 1D]^[25]. These unprecedented boron compounds with new structures and reactivities will enable the observation of new coordination modes at boron, in the isolation of long sought after reaction intermediates and new classes of boron-mediated reactions in the near future.

Helical boron-containing materials [Figure 1E]^[26], π -conjugated boron compounds embedded in polyaromatic antiaromatic architectures [Figure 1F]^[27], redox-active tetraanionic diborafluorenes [Figure 1G]^[28], boron-nitrogen embedded polycyclic aromatic hydrocarbons [Figure 1H]^[29], BN-doped cycloparaphenylenes [Figure 1I]^[30], highly emissive donor-acceptor arylamino-9-borafluorene [Figure 1J]^[31],

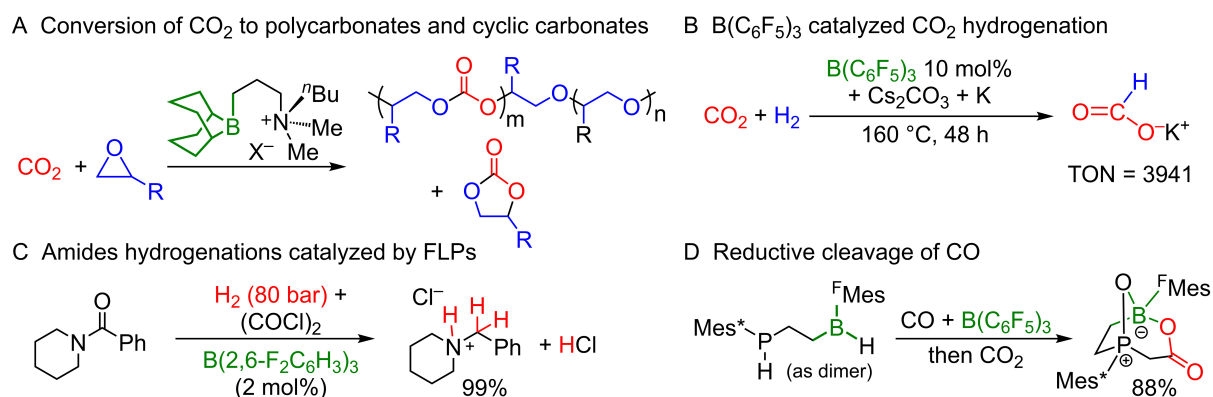


Figure 2. Boron mediated activation, hydrogenation or functionalization of small molecules.

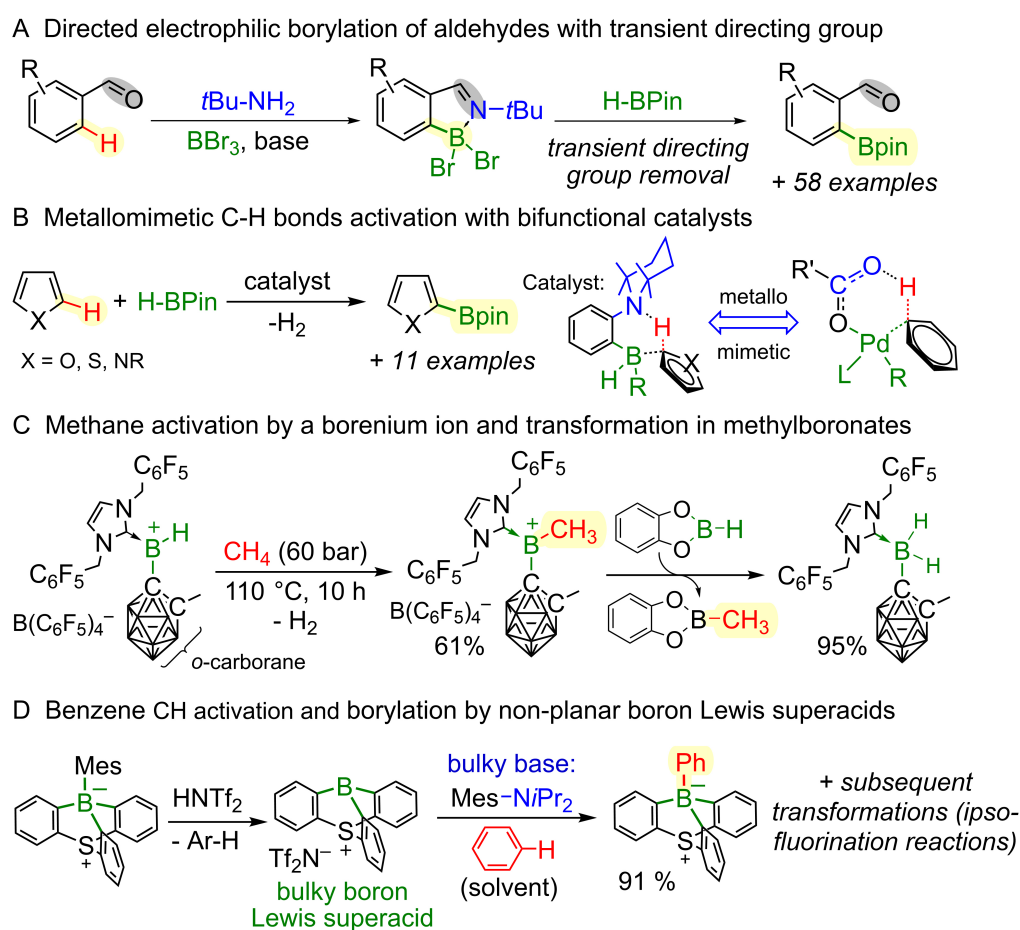


Figure 3. Recent seminal advances on C-H activation and borylation reactions foreshadowing future catalytic applications.

bora subporphyrins [Figure 1K]^[32] and thiophene-based polycyclic aromatic tricoordinate boron semiconductor [Figure 1L]^[33] are all receiving increasing recognition for their outstanding optical, photophysical, electrochemical and photoresponsive properties.

Trivalent organoboron compounds are of increasing importance for capturing and reacting with small molecules^[34,35]. The boron-mediated conversion of carbon dioxide to cyclic carbonates^[36] and copolymers [Figure 2A]^[37] and to formate [Figure 2B]^[38,39] with bifunctional borylated catalysts is a rapidly evolving area of chemical catalysis oriented towards green chemistry. New highly efficient frustrated Lewis pairs have been successfully employed for the highly challenging catalytic hydrogenation of amides to amines [Figure 2C]^[40,41] and for the reductive cleavage of carbon monoxide [Figure 2D]^[42].

The development of unprecedented transition metal-free borylation methodologies with transient protecting/directing groups [Figure 3A]^[43] and the catalytic activation of C-H bonds with bifunctional boron catalysts [Figure 3B]^[44] has achieved momentous interest among synthetic chemists and are challenging transition-metal complexes traditionally used for the functionalization of heterocycles^[45]. Frustrated Lewis pairs catalysts, often based on strong and bulky boron Lewis acids^[46], are increasingly used for transition metal-free C-H bond activations and borylations processes^[47,48]. The metallomimetic chemistry of boron compounds and the completely new area of metallomimetic catalysis are both rapidly evolving fields^[49,50].

Very recently, *N*-heterocyclic carbene-stabilized *o*-carboranyl-substituted borenium ions were used for the very first transition metal-free C-H bond activation and borylation of methane and longer alkanes [Figure 3C]^[51], and frustrated Lewis pairs constituted by weakly coordinating anion and pyramidal boron Lewis superacids were used for the C-H bond activation and borylation of unactivated arenes and for their subsequent conversion to fluoroaromatics [Figure 3D]^[52]. Thus, highly electron-deficient boron Lewis acids will likely be employed in the near future for the catalytic borylation, silylation and functionalization of hydrocarbons and for their subsequent functionalization.

Thus, the applications of boron reagents in C-H functionalization and borylation are likely to also be increasingly used in chemistry in light of these seminal advances and are predicted to be ever growing due to the major interest in borylated building blocks in the academic community and chemical industry^[53,54]. Thus, boron-based derivatives are important hybrid metal/non-metal compounds with high structural diversity and broad and rich applications in all fields of chemistry. Boron derivatives are anticipated to have a bright future and a profound impact on the future progress in chemical catalysis and materials science.

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Authors' contributions

The author contributed solely to the article.

Availability of data and materials

Not applicable.

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Conflicts of interest

The author declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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