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Review

Boron-containing radical species

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ABSTRACT

Radicals are ubiquitously involved in numerous chemical and biological processes. They exhibit unique chemical bonding and physical properties applicable to functional materials. With respect to carbon and nitrogen, boron is commonly viewed as a lone-pair electrons acceptor and less often considered as a spin-carrier associated with radicals. In recent years, however, boron-containing radicals have attracted more and more interest on account of their potential applications such as chemical sensors, reagents in organic synthesis, initiators for polymerization and components of extended magnetic systems. This review presents the synthesis, characterization, and reactivity of persistent and stable boron-containing radicals in conjunction with theoretical calculations.

Contents

Abbreviations: Ar^f, 3,5-di(trifluoromethyl)phenyl; BLA, bond length alternation; cAAC, cyclic (alkyl)(amino)carbene; Cp, η^5-cyclopentadienyl; Cp^*, η^5-pentamethylcyclopentadienyl; CS, closed-shell singlet; CV, cyclic voltammetry; DFT, density functional theory; Dipp, 2,6-diisopropylphenyl; DME, dimethoxyethane; EPR, electron paramagnetic resonance; Fc, ferrocene; hfcc, hyperfine coupling constant; HOMO, highest occupied molecular orbital; HOTf, trifluoromethanesulfonic acid; LUMO, lowest unoccupied molecular orbital; Mes, 2,4,6-trimethylphenyl; NHC, N-heterocyclic carbene; Np, naphthalene; OS, open-shell singlet; SOMO, singly occupied molecular orbital; SCE, saturated calomel electrode; SQUID, superconducting quantum interference device; SHE, standard hydrogen electrode; Trip, 2,4,6-triisopropylphenyl; zfs, zero field splitting.

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Nomenclature

Symbols

a	Hyperfine splitting
g	Electron gyromagnetic ratio
G	Gauss
I	Nuclear spin quantum number

1. Introduction

Radicals, species embodying unpaired electron(s), play significant roles in numerous chemical and biological processes due to their unique chemical bonding and physical properties (optical, electrical, magnetic, etc.), as well as promising applications as functional materials [1–7]. The molecular oxygen (O_2) is one of the simplest well-known radicals which exist under ambient conditions. Most of main group radicals, however, are frequently transient as the unpaired electrons make them highly reactive [8–12]. The strategies to stabilize main group radicals mainly involve delocalization of the unpaired electron (thermodynamic stabilization) as well as the use of bulky groups to prevent its oligomerization (kinetic stabilization), which has indeed allowed for the generation, observation, and in some cases, isolation of radicals. Depending on the thermal stability, those radicals may be classified as either 'persistent' or 'stable' [8–10], and both terms can be applied to the long-lived radicals. The description 'persistent' refers to radicals that have relatively long lifetimes to be characterized by standard spectroscopic means and conventional chemical techniques, whereas the designation 'stable' is confined to radicals that can be isolated and stored without decomposition under an inert atmosphere for long periods, implying the solid-state structures can be determined by X-ray crystallography.

With respect to carbon and nitrogen, boron is commonly viewed as a lone-*pair* electrons acceptor center and less often considered as a spin-carrier associated with radicals. In fact, boron is a very interesting element for studying the spin density distribution in their paramagnetic species by electron paramagnetic resonance (EPR) spectroscopy, because both stable isotopes ^{11}B (80.2%, $I = 3/2$) and ^{10}B (19.8%, $I = 3$) possess nuclear spins and reasonable nuclear magnetic moments ($\mu(^{10}B)/\mu(^{11}B) = 0.335$) [13]. From the application point of view, boron-containing radicals have attracted more and more interest for potential applications as chemical sensors, reagents in organic synthesis, initiators for polymerization and components of extended magnetic systems [14,15].

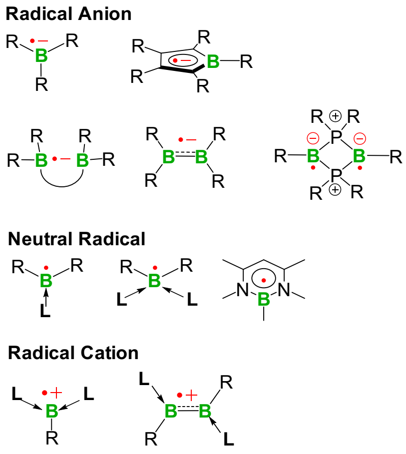


Fig. 1. General classes of boron-containing radicals.

This review focuses on the synthesis, characterization, and reactivity of persistent and stable boron-containing radicals in conjunction with theoretical calculations. Where appropriate, attention is drawn to potential use or known applications of the corresponding boron-containing radicals. The rapidly developing and increasingly important fields of polyhedral boron cage radicals [8,10,14] and boron-spiro-biphenalenyl radicals [6] have been covered comprehensively in several reviews and thus are beyond the scope of this review.

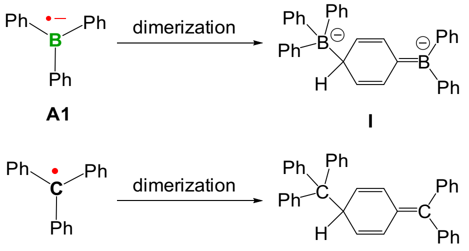
For clarity, anionic (**A**), neutral (**N**), and cationic (**C**) boron-containing radicals are numbered as **AX**, **NX**, and **CX**, respectively (**X** = number). Accordingly, the corresponding precursors are numbered as **PAX**, **PNX**, and **PCX**, respectively (Fig. 1).

2. Anionic boron radicals

2.1. Radical anions derived from triarylborane or trialkylborane

Given the isoelectronic relationship of triarylborane radical anions $Ar_3B^{\cdot-}$ and the neutral triarylmethyl radicals ($Ar_3C\bullet$), the early study of boron radicals originated from the attempts to prepare the triarylborane radical anions almost one century ago. In 1924, the Krause group reported that triphenylborane could be reduced by sodium in Et_2O to give an orange-yellow species having the chemical composition of $NaBPh_3$ [16]. Two years later, all of the alkali metal salts with the chemical formula of $MBPh_3$ (M = Li–Cs) were synthesized in comparable conditions by the same group [17]. Stimulated by these early work, the reduction of several other BR_3 species (R = *p*-tolyl, cyclohexyl, benzyl) was also investigated [18,19]. In 1953, the Chu group found that the sodium salt of $Ph_3B^{\cdot-}$ is diamagnetic in Et_2O or THF, presumably due to the association of ion pairs into clusters by the electrostatic attraction [20]. The ^1H and ^{11}B NMR studies reported by the Eisch group indicated that, as in the case of $Ph_3C\bullet$ [21], a head-to-tail dimer **I** is formed [22] (Scheme 1). In 1970, the Leffler group reported that the $Ph_3B^{\cdot-}$ **A1** could be formed in 1,2-dimethoxyethane (DME) [23]. The EPR spectrum of **A1** measured in DME at room temperature showed the hyperfine couplings with boron ($a(^{11}B) = 7.84$ G) and phenyl hydrogens ($a(p\text{-}^1H) = 2.73$ G, $a(o\text{-}^1H) = 1.99$ G, $a(m\text{-}^1H) = 0.67$ G).

Based on the familiar strategies in organic radical chemistry, the steric effect of the substituents and spin delocalization through π conjugation play key roles in stabilizing the radicals. It is not surprising, therefore, that the use of bulky aryl substituents such as mesityl (2,4,6-trimethylphenyl, Mes) [24–26], β-methylnaphthyl



Scheme 1. Dimerization of **A1** and $Ph_3C\bullet$.