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Consecutive reduction, radical-cyclization, and oxidative-dehydrogenation reaction of ortho-substituted diboryl compounds

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Abstract

An elegant synthetic route to a ladder-type di-borate compound 2a was reported based on the reduction, radical-cyclization, and oxidative-dehydrogenation reaction of 1. The existence of the biradical intermediate $[1^{\bullet\bullet}]^{2-}$ was supported by both EPR measurements and DFT calculations.

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Consecutive reduction, radical-cyclization, and oxidative-dehydrogenation reaction of ortho-substituted diboryl compound

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An elegant synthetic route to a ladder-type di-borate compound 2a was reported based on the reduction, radical-cyclization, and oxidative-dehydrogenation reaction of 1. The existence of biradical intermediate [1··]²⁻ was supported by both EPR measurements and DFT calculations.

Owing to their isoelectronic relationship to neutral methyl radicals, the chemistry of boron-containing radical anions has been intensively investigated.[1] These species possess unique chemical reactivity and are usually prepared by chemical[2] or electrochemical reduction[3] of the corresponding precursors. They not only are important for building new boron-containing molecular skeletons but also play essential roles in organic synthesis and functional materials.[1] Consequently, the study of the chemical reactivity of these radical species has become one of the most active research fields in boron-based chemistry. Continuous efforts have led to the emergence of some reactions involving boric radical species. For instance, Curran et al.[4] reported the reactivity of N-heterocyclic carbene borane radicals (**A**, Scheme 1) with various reaction substrates including methyl acrylate, O_2, Ph_2IPF_6, etc.. Braunschweig[5] and Nozaki[6] et al. demonstrated the reaction of borole radical anion (**B**, Scheme 1) and B-heterocyclic π-radical (**C**, Scheme 1) with benzoquinone (BQ) or benzoyl peroxide (BPO), respectively. Bourissou et al.[7] displayed a Gomberg-type dimerization process of P-coordinated boryl radical (**D**, Scheme 1) through single-crystal X-ray diffraction. Stephan et al.[8] described the reaction process of phenanthrenedione- and pyenedione-derived borocyclic radicals (**E**, Scheme 1), $C_nH_8O_2B(C_6F_5)_2\bullet$ (n =14 or 16) with a variety of nucleophiles.

Tamm and co-works[9] obtained bicyclic C-H activation products from the reaction of $NHC\text{-}BR_2\bullet$ (**F**, Scheme 1) with benzoquinone (BQ). Wang and co-works[10] exhibited intramolecular cyclization and hydrogen abstraction reaction of diradical **G** and **H** (Scheme 1), respectively. However, the application of boron-centered radicals in synthetic methods has been less explored compared to other radical species.[11]
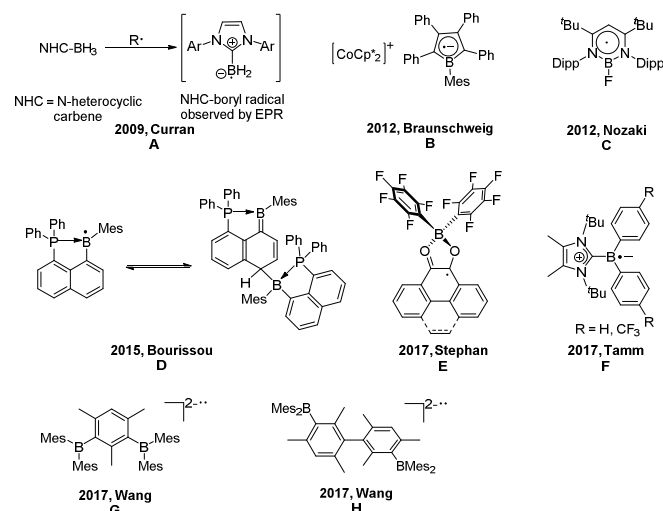
Scheme 1. Some reactions involving boric radical species **A–H**.

Ladder-type boron-containing π-conjugated molecules[12] are promising materials for organic-based devices, including light-emitting diodes, field-effect transistors, and optically pumped solid-state lasers. To date, only a few synthetic pathways to such compounds have been developed, such as photochemical,[13] intramolecular cascade cyclization,[14] metal-boron exchange[15] and others.[16] They have become important synthetic strategies by which the incorporation of boron element into the structural frameworks of these ladder compounds was achieved. However, the exploration of new synthetic tactics is still desirable and challenging. In this paper, we presented a novel synthetic approach for the preparation of a ladder di-borate **2a** using consecutive reduction, radical-cyclization, and oxidative-dehydrogenation reaction.

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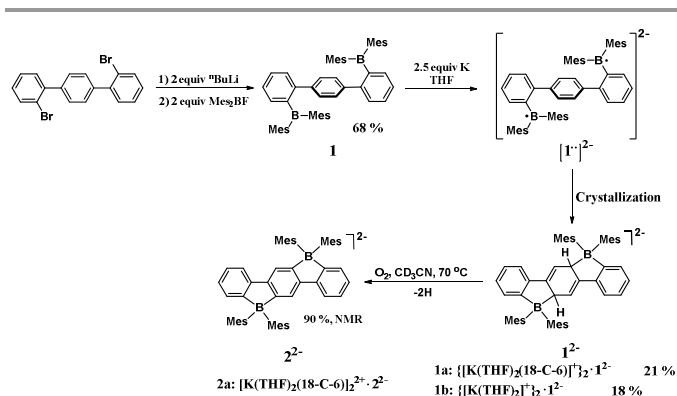
Scheme 2. Synthesis route of compound **1**, dianion **[1··]²⁻**, **1²⁻** and **2²⁻**.

The synthesis of precursor **1**, as well as the route to **2a**, is depicted in Scheme 2. First, 2,2''-dibromo-1,1':4',1''-terphenyl was synthesized according to literature method[17] through Suzuki-Miyaura coupling. Subsequently, treatment of this 2,2''-dibromophenyl product with ^{n}BuLi (molar ratio = 1:2) in THF at −78 °C afforded 2,2''-dilithio-1,1':4',1''-terphenyl, which could react with Mes₂BF to produce 2,2''-bis(dimesitylboranyl)-1,1':4',1''-terphenyl (**1**) in 68 % yield (Scheme 2). Compound **1** is stable towards moisture and air. ^{11}B NMR resonance of **1** appears at 72.6 ppm, which is slightly different from those reported diboryl substituted compounds (75.0[2k] and 74.8 ppm[10]) as the electron density is different at boron atoms possessing different substituted groups. The precursor **1** was further characterized by NMR and X-ray diffraction (Fig. S1). To study the redox properties of precursor **1**, cyclic voltammetry (Fig. S2) was recorded in THF with ^{n}Bu₄NPF₆ as the supporting electrolyte. Two distinct sets of irreversible reduction waves were observed at $E_{1/2}$ = −2.11 and E_{pc} = −2.37 V vs Fc/Fc⁺, indicating a significant structural change is associated with the electron-transfer step.[18]
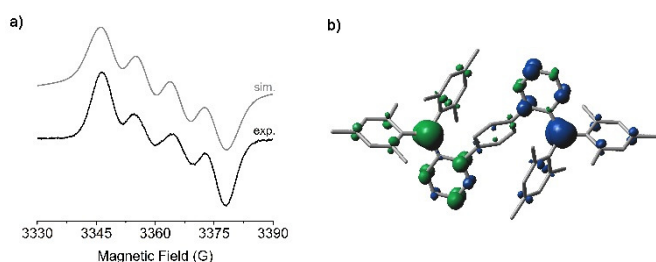
Fig.1 a) Experimental (black) and simulated (gray) EPR spectra of **[1··]²⁻** in THF solution (c = 1.4×10⁻³ mol/L) at room temperature; b) Spin density distribution of OS **[1··]²⁻** (isovalue = 0.005 au).

Next, the chemical reduction of **1** was investigated in fresh distilled THF at room temperature. The solution immediately changed from colorless to dark-blue when 2.5 equivalent of potassium were added. The X-band EPR spectrum in THF solution at room temperature (Fig. 1a) shows a four-line signal (centered at g = 2.0039) that maintains for several days and no half-field signal or zero field splitting was observed, indicating the formation of a persistent biradical dianion[19] (**[1··]²⁻**). This EPR spectrum resembles that of radical anion **B**[5], therefore we

assume that **[1··]²⁻** could be considered a biradical bearing two nearly independent borol monoradicals with extremely weak couplings.[19] The simulation analysis successfully reproduced the spectrum. The hyperfine coupling constant ($a(^{11}$B) = 8.56 G) is within those of other triarylborane radical anions, such as [Ph₃B·]⁻ (7.84 G)[20a] and [Mes₃B·]⁻ (9.87 G).[20b] Reaction of **1** with excess potassium resulted identical EPR spectrum, therefore the possibility of a half-reduced species (**[1·]⁻**) could be excluded. To further understand the structure of **[1··]²⁻**, DFT calculations were carried out. The geometry was optimized at the UCAM-B3LYP/6-31G(d) level of theory. Both the open-shell singlet (OS) and triplet (T) states were investigated and they show nearly identical geometries (RMSD = 0.008 Å) with a narrow energy gap (ΔE_{T-OS} = 0.30 kcal/mol). The estimated electron exchange coupling constant (J = -1/2ΔE_{T-OS}) was small (-52 cm⁻¹), suggesting a rather weak interaction between the two radical centers. The spin density is mainly localized on the two boron atoms (65%) and the carbon atoms (27%) of the adjacent benzene moiety, with negligible distribution on the central benzene unit (Figs. 1b and S3), indicating rather small spin-spin couplings. The EPR spectrum together with the DFT calculations supports the biradical character of **[1··]²⁻**. Meanwhile, UV-Vis absorption spectrum (Fig. S4) of **[1··]²⁻** shows two broad absorption peaks at λ =1056 and 734 nm, which further verified the existence of **[1··]²⁻**.
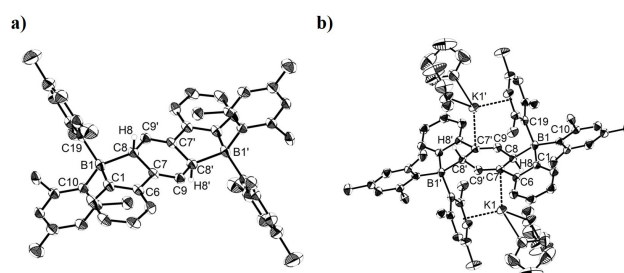
Fig.2 Thermal ellipsoid (50%) drawings of a) **1²⁻** (in **1a**), and b) **1b**. H atoms except H8 and H8' are omitted for clarity. Selected bond lengths (Å): in **1a**, B1–C1 1.662(5), B1–C8 1.710(5), B1–C10 1.681(5), B1–C19 1.655(5), C6–C7 1.477(4), C7–C8 1.510(5), C7–C9 1.329(4), C8–C9' 1.504(4), C1–C6 1.413(5), C1–C2 1.410(5); in **1b**, B1–C1 1.661(4), B1–C8 1.728(4), B1–C10 1.668(5), B1–C19 1.670(4), C6–C7 1.478(4), C8–C9 1.498(4), C7–C8 1.513(4), C7–C9' 1.339(4), C1–C6 1.411(4), C1–C2 1.401(4).

Recently Bourissou et al. reported[7] the dimerization reaction of P-coordinated boryl radical [Ph₂P-(naphthyl)BMes]•, encouraging us to explore if **[1··]²⁻** has similar property. Crystals of complexes **1a** and **1b** suitable for single-crystal X-ray diffraction were obtained at room temperature. Figs. 2a and 2b display their solid structures. A list of their important structure parameters, as well as those of **1**, is given in Table 1. According to X-ray diffraction, **1²⁻** adopts a cyclohexadiene bridged di-borate structure with a boron-carbon bond between B1 (B1') and C8 (C8'). The dihedral angle formed by the C1–C6 benzene ring (Ring_A) and the C7C8C9C7'C8'C9' ring (Ring_B) obviously decreases from **1** to **1²⁻** (49.2° in **1**, 18.4° in **1a**, 23.0° in **1b**; see Fig. S5). The lengths of B1–C8 (or B1'–C8') bonds (1.710(5) Å in **1a**, 1.728(4) Å in **1b**) are longer than those reported compounds (1.670(7) Å[7],

1.665(3) Å[9] and 1.645(3) Å[21]), but shorter than that reported (1.842(3) Å) by Yamaguchi.[22] The formation of these B1–C8 (or B1'–C8') bonds causes significant change of in the bonding condition of Ring$_B$, leading to increasing bond length alternation (BLA). Compared to parent **1**, the lengths of C7 (or C7')–C9 (or C9') (1.329(4) Å in **1a**, 1.339(4) Å in **1b**) are significantly shorter and typical of C=C double bonds (≈ 1.32 Å), while the lengths of C7–C8 (1.510(5) Å in **1a**, 1.513(4) Å in **1b**) and C8–C9' (or C9) (1.504(4) Å in **1a**, 1.498(4) Å in **1b**) are clearly longer, featuring C–C single bonds (≈ 1.51 Å). These structural changes illustrate the formation of 1,4-cyclohexadiene geometry, with the hybridization mode of C8 atom changing from sp^2 to sp^3, which is consistent with the loss of aromaticity of the central ring. In addition, the coordination of potassium cation causes slight differences in the structures of **1a** and **1b**, including variations in some characteristic bond lengths and angles.
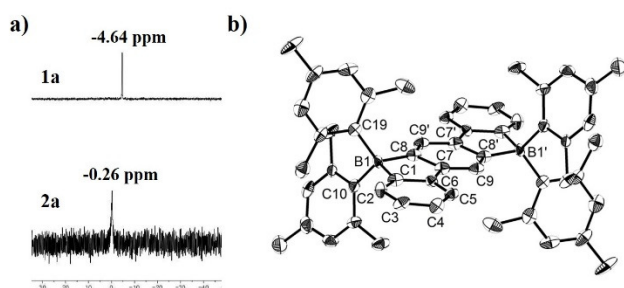
Fig.3 a) Comparison of the ^{11}B NMR spectra of **1a** (top) and **2a** (bottom); b) Thermal ellipsoid (50%) drawings of **2²⁻**, all H atoms have been omitted for clarity. Selected bond lengths (Å): B1–C1 1.678(8), B1–C8 1.635(8), B1–C10 1.657(8), B1–C19 1.661(8), C1–C2 1.405(7), C1–C6 1.406(7), C6–C7 1.467(7), C7–C8 1.422(8), C7–C9 1.403(7), C8–C9' 1.400(6).

In contrast to **[1¨]²⁻**, the THF solutions of **1a** and **1b** are colorless and EPR silent, but they give well resolved NMR spectra in CD$_3$CN. The ^{11}B NMR resonances of **1a** and **1b** appear both at δ = -4.64 ppm, close to those previously reported four-coordinated boron compounds.[9, 21] All ^{1}H and ^{13}C NMR chemical shifts were completely assigned. Compared to that of **1**, the ^{1}H NMR resonances of C8–*H* (or C8'–*H*) at δ = 2.98 ppm in **1a** and **1b** are both shifted upfield by δ = 3.7 ppm. While another set of characteristic signals of C9–*H* (or C9'–*H*) at δ ≈ 5.93 ppm in **1a** and **1b** both are shifted upfield by δ ≈ 1.05. These shifts indicate the change of hybridization mode of C8 atom from sp^2 to sp^3 and the formation of 1,4-cyclohexadiene structure in **1²⁻**, which finally result in the loss of aromaticity of the central Ring$_B$. Meanwhile, an equilibrium was usually observed between radical species and dimer.[7, 23] To prove whether the equilibrium between **1²⁻** and **[1¨]²⁻** exists, the variable-temperature NMR spectroscopy of **1a** was studied (Fig. S6). The signals of C8–*H* (or C8'–*H*) and C9–*H* (or C9'–*H*) have no variations from 20 °C to 70 °C in CD$_3$CN solution, indicating **1a** is stable. In other words, **1a** did not reverted to the biradical dianion **[1¨]²⁻** in this temperature scope. Therefore, this radical cyclization process is irreversible.

Table 1. Experimental and calculated bond lengths (Å) for **1**, **[1¨]²⁻**, **1²⁻** and **2²⁻**.

		B1–C8	C7–C8	C7–C9	C8–C9'	BLA[d]
1	X-ray	3.282[a]	1.398(3)	1.395(3)	1.382(4)	0.005
	Calc.	3.321[a]	1.396	1.396	1.387	0.004
[1¨]²⁻	OS	3.375[a]	1.396	1.401	1.387	0.009
	T	3.382[a]	1.396	1.400	1.387	0.009
1a	X-ray	1.710(5)	1.510(5)	1.329(4)	1.504(4)	0.178
1b	X-ray	1.728(4)	1.513(4)	1.339(4)[b]	1.498(4)[c]	0.166
1²⁻	Calc.	1.716	1.507	1.340	1.500	0.164
2a	X-ray	1.635(8)	1.422(8)	1.403(7)	1.400(6)	0.008
2²⁻	Calc.	1.655	1.412	1.398	1.394	0.005

[a] The distance between B1 and C8. [b] The bond length of C7-C9'. [c] The bond length of C8-C9. [d] BLA = │[d(C7–C8) + d(C8–C9')]/2 – d(C7–C9)│.

The dehydrogenation of 1,4-cyclohexadiene with various oxidants or methods have been intensively studied.[24] Previous results show the dehydrogenation process could be accelerated using CD$_3$CN as the solvent.[24b] In order to investigate the dehydrogenation reaction of **1a**, we tried to oxidize it with trace amount of O$_2$ in heated CD$_3$CN solution, which is akin to those pioneered by Jacobson[24b], and obtained the product **2a**. In the ^{11}B NMR spectrum, the peak at δ = -0.26 was identified as the boron signal of **2a**, which is shifted downfield by δ = 4.38 ppm compared with **1a** (Fig. 3a). The original signals of H8 (or H8') and H9 (or H9') disappeared in **1a** and was replaced by the new peak of H9 (or H9') at δ = 6.93 ppm in **2a**, indicating H8 and H8' atoms have left and aromatization of the 1,4-cyclohexadiene unit has occurred (Fig. S7). This dehydrogenation process of **1a** was also verified by the changes of characteristic signals of H8 (or H8') and H9 (or H9', Fig. S8).

Crystals suitable for X-ray crystallographic studies were obtained from a THF solution at room temperature. The solid-state structure of **2a** revealed some interesting features (Fig. 3b). Unlike **1** and **1²⁻**, the five-membered ring fused borate skeleton in **2²⁻** is nearly planar, which can be reflected from the dihedral angles C5–C6–C1–B1, C5–C6–C7–C9, B1–C8–C7–C9, C1–C6–C7–C8, equal to 178.1°, 2.66°, 175.86°, 5.59°, respectively. The bond length of B1 (B1')–C8 (C8') (1.635(8) Å) in **2²⁻** is considerably shorter than that in **1²⁻** due to the formation of above plane. Notably, the central Ring$_B$ moiety has a small BLA: the C7–C8 and C8–C9' bond lengths are 1.422(8) and 1.400(6) Å, respectively, while C7–C9 bond length is 1.403(7) Å. This small BLA illustrates the aromatization of 1,4-cyclohexadiene, which is consistent with the Nucleus–Independent Chemical Shifts (NICS) calculations. The NICS values for Ring$_B$ are indicative of medium aromaticity (NICS(0) = -4.3, NICS(1) = -7.3, and NICS(1)$_{zz}$ = -19.7), while the flanking C1–C6 benzene rings are more aromatic (NICS(0) = -5.8, NICS(1) = -8.4, and NICS(1)$_{zz}$ = -22.8).

In conclusion, we have described a new synthetic approach to prepare the ladder di-borate **2a**, using successive reduction, radical-cyclization, and oxidative-dehydrogenation of **1**. A biradical dianion **[1¨]²⁻** is suggested to be involved in the intramolecular cyclization reaction which leads to the formation of B1–C8 (B1'–C8') bond. We find heating the CD$_3$CN

solution of **1a** will facilitate the dehydrogenation reaction, resulting in the aromatization of 1,4-cyclohexadiene moiety and the formation of **2a**. Further studies on the fluorescence properties of these anionic species, as well as syntheses using other central bridging units, are under way.

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