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C–C Bond Cleavage

Homolytic, Heterolytic, Mesolytic - As You Like It: Steering the Cleavage of a HC(sp^3)–C(sp^3)H Bond in Bis(1*H*-2,1-benzazaborole) Derivatives

Martin Hejda,[a] Antonín Lyčka,[b] Tomáš Mikysek,[c] Roman Jambor,[a] Aleš Růžička,[a] Jaromír Vinklárek,[a] Claudia Wilfer,[d] Alexander Hoffmann,[d] Sonja Herres-Pawlis,*[d] and Libor Dostál*[a]

Abstract: A set of (3,3′)-bis(1-Ph-2-R-1*H*-2,1-benzazaborole) compounds, in which R = *t*Bu **(Bab-*t*Bu)$_2$**, R = Dipp **(Bab-Dipp)$_2$** or R = *t*Bu and Dipp **(Bab-Dipp)(Bab-*t*Bu)**, was synthesized and fully characterized using ^{1}H, ^{11}B, ^{13}C, and ^{15}N NMR spectroscopy as well as single-crystal X-ray diffraction analysis. The central HC(sp^3)–C(sp^3)H bond with restricted rotation at the junction of both 1*H*-2,1-benzazaborole rings displayed an intriguing reactivity. It was demonstrated that this bond is easily mesolytically cleaved using alkali metals to form the respective aromatic 1Ph-2R-1*H*-2,1-benzazaborolyl anions **M$^+$(THF)$_n$(Bab-*t*Bu)$^-$** (M = Li, Na, K) and **K$^+$(THF)$_n$(Bab-Dipp)$^-$**. Furthermore, the central HC(sp^3)–C(sp^3)H bond of bis(1*H*-2,1-benzazaborole)s is also homolytically cleaved either by heating or photochemical means, giving corresponding 1Ph-2R-1*H*-2,1-benzazaborolyl radicals **(Bab-*t*Bu)$^\bullet$** and **(Bab-Dipp)$^\bullet$,** which rapidly self-terminate. Nevertheless, their formation was unambiguously established by NMR analysis of the reaction mixtures containing products of the self-termination of the radicals after heating or irradiation. **(Bab-Dipp)$^\bullet$** radical was also characterized using EPR spectroscopy. Importantly, it turned out that the essentially non-polarized HC(sp^3)–C(sp^3)H bond in **(Bab-*t*Bu)$_2$** is also cleaved heterolytically with 2 equiv of MeLi, giving the mixture of **Li$^+$(SOL)$_n$(Bab-*t*Bu)$^-$** (SOL = THF or Et_2O) and lithium methyl-substituted borate complex **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** in a diastereoselective fashion.

Introduction

The utilization of various types of monoanionic C,N- or N,C,N-chelating ligands, enabling the closure of a five-membered chelating ring (built up as (bis)*ortho*-functionalized aryls) is ubiquitous in the chemistry of main group elements.[1] These ligands contain a pendant amino donor group in most cases. Despite the fact that they facilitated the isolation of a plethora of interesting and unprecedented compounds, at least from the structural and fundamental point of view, they generally behave as spectator ligands.[1,2] Recently, a new approach appeared, based on the substitution of relatively chemically inert and redox-innocent amino moieties by corresponding imino donor groups.[3] It is obvious that this pendant HC=N group exhibits a pronounced tendency to undergo further chemical transformations upon coordination to the central element, a property typical for so-called actor ligands. For instance, they are prone to the attack of sufficiently strong nucleophiles (Scheme 1 A).[4] On a similar basis, the saturation of the HC=N moiety is quite easily achieved using various element hydrides that are subject to a spontaneous hydrogen shift as intermediates (Scheme 1 B).[5] In both cases, various types of five-membered heterocycles are formed that would hardly be accessible otherwise.[6,7] The reduction of these main group element (N,)C,N-chelates also led to the isolation of unprecedented derivatives in many cases.[8] A special class of these reactions constitutes those in which the particular ligand acts in a non-innocent fashion. These processes are then accompanied by C–C coupling reactions within the ligand backbone either directly at the carbon atom of the HC=N moiety (Scheme 1 C),[9a–e] or in the special case of the annulated central ring.[9f] It was also demonstrated that in few cases further reduction of these C–C coupled species resulted in the formation of unprecedented heterocyclic aromatic anions (Scheme 1 C, D).[9a,e,8d,e,f]

[a] *M. Hejda, Dr. R. Jambor, Prof. A. Růžička, Dr. J. Vinklárek, Dr. L. Dostál*
Department of General and Inorganic Chemistry
Faculty of Chemical Technology, University of Pardubice
Studentská 573, CZ-532 10, Pardubice (Czech Republic)
E-mail: libor.dostal@upce.cz

[b] *Prof. A. Lyčka*
Research Institute for Organic Syntheses
Rybitví 296, CZ-533 54, Pardubice (Czech Republic)

[c] *Dr. T. Mikysek*
Department of Analytical Chemistry, Faculty of Chemical Technology
University of Pardubice
Studentská 573, CZ-532 10, Pardubice (Czech Republic)

[d] *Dr. C. Wilfer, Dr. A. Hoffmann, Prof. S. Herres-Pawlis*
Institute for Inorganic Chemistry, RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: sonja.herresec-pawlis@ac.rwth-aachen.de

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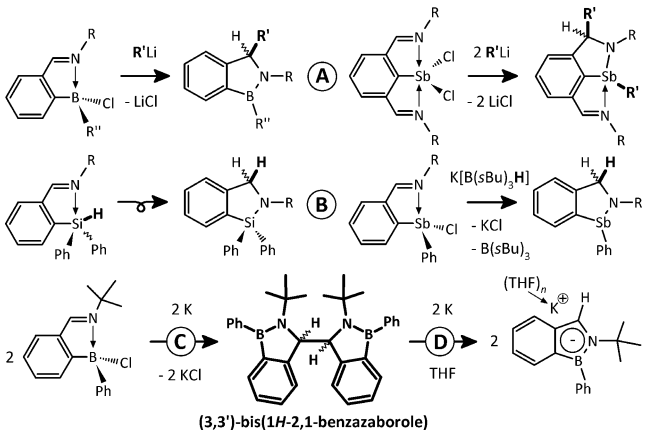


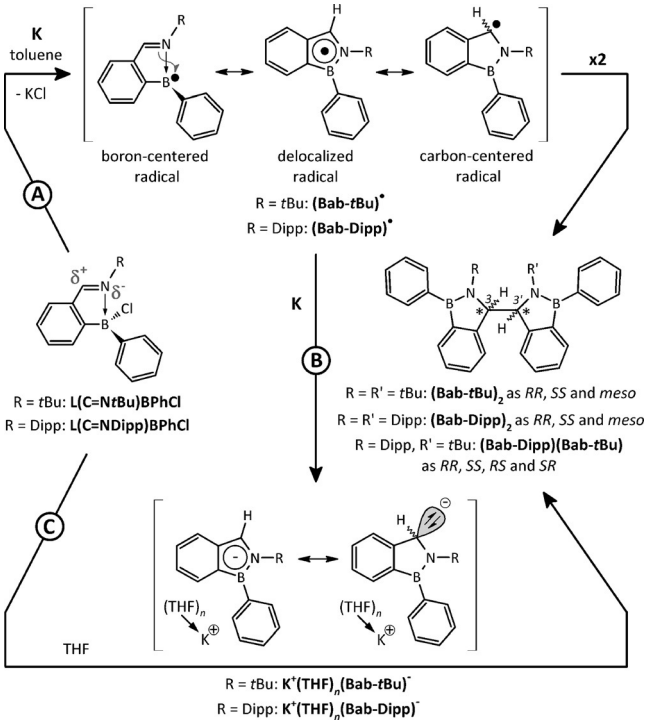
Scheme 1. Discussed transformations of C,N- or N,C,N-chelated compounds.

This work is focused on the closer inspection of the synthesis, structure, and reactivity of one of the above mentioned C–C bonded heterocyclic systems, that is, bis(1*H*-2,1-benzazaborole) derivatives. It is demonstrated how the non-polarized central HC(sp^3)–C(sp^3)H bond is with a surprising ease cleaved not only chemically (using strong reducing agents such as alkali metals) in a mesolytic fashion, but also thermally and photochemically in a homolytic fashion. Importantly, it was established that this bond is able to undergo, under certain reaction conditions, a heterolytical scission as well, which makes this central HC(sp^3)–C(sp^3)H bond quite extraordinary. Although the cleavage of C–C bonds has been extensively studied for a long time, it is still a challenging area. Homolytic cleavage of nonpolar C–C bonds is a fairly common mechanism, but isolation and/or characterization of unstable radical species formed during this these reactions are often difficult.[10a] Similarly, heterolytic cleavage of C–X bonds (where X is a heteroatom such as halogen, nitrogen, etc.) is the foundation for many organic reactions; however, similar cleavage of C–C bonds is still very rare.[10b] Maslak et al. described an extraordinary system in which both mechanisms (homolytic and heterolytic) of C–C bond cleavage are possible. He even introduced a third mechanism, the so-called mesolytic cleavage.[10c,d] Thus, this work describes another interesting example of a system (i.e., bis(1*H*-2,1-benzazaborole) where the C–C bond can be cleaved in all these three ways depending on the reaction conditions.

Results and Discussion

Syntheses and structures of (3,3′)-bis(1-Ph-2-R-1*H*-2,1-benzazaborole) compounds

The reduction of the *C,N*-chelated chloroborane **L(C=NDipp)BPhCl** [**L(C=NDipp)** = *o*-(CH=N-2,6-*i*Pr$_2$C$_6$H$_3$)C$_6$H$_4$] with potassium in toluene gave a mixture of (3,3′)-bis(1-Ph-2-Dip-1*H*-2,1-benzazaborole) compounds ***rac*-*RR*/*SS*-(Bab-Dipp)$_2$** and ***meso*-(Bab-Dipp)$_2$** (Scheme 2A and Figure S1 in the Supporting Information), similar to ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** and ***meso*-(Bab-*t*Bu)$_2$** reported recently.[9a] After separation, both compounds were independently characterized by ^{1}H, ^{13}C, ^{11}B, and ^{15}N NMR spectroscopy. Especially the signals of mutually coupled methine HC–N groups unambiguously confirmed the proposed structures (see details in Supporting Information; Table S1). Regarding the formation of ***rac*-*RR*/*SS*-(Bab-Dipp)$_2$** and ***meso*-(Bab-Dipp)$_2$**, the in situ formation of the potassium salt of **(Bab-Dipp)$^-$**, which further reacts with the respective *C,N*-chelated chloroborane, is not ruled out as we have previously discussed for *t*Bu-substituted analogues (Scheme 2B).[9a]



Scheme 2. Synthesis of coupled (3,3′)-bis(1*H*-2,1-benzazaborole) derivatives.

This approach (Scheme 2C) was applied for the preparation of unsymmetrically substituted derivatives ***rac*-*RR*/*SS*-(Bab-Dipp)(Bab-*t*Bu)** and ***rac*-*RS*/*SR*-(Bab-Dipp)(Bab-*t*Bu)**. Both products were again separated and characterized by ^{1}H, ^{11}B, ^{13}C, and ^{15}N NMR spectroscopy (Table S1). Molecular structures of new (3,3′)-bis(1*H*-2,1-benzazaborole)s were unambiguously confirmed using single-crystal X-ray diffraction analysis (Figure 1). All structures contain two mutually coupled 1*H*-2,1-benzazaborole rings. The central HC(sp^3)–C(sp^3)H bond lengths from 1.559(2) to 1.594(3) Å are longer in comparison to standard C(sp^3)–C(sp^3) (1.54 Å) bonds.[11] The B–N bond lengths within the 1*H*-2,1-benzazaborole rings [in the range of 1.405(3)–1.421(3) Å] reflect strong π(N)→π(B) interactions (cf. Σ_{rcov}(N–B) = 1.56 Å vs. Σ_{rcov}(N=B) = 1.38 Å[11]).

Importantly, all stereoisomers of the respective compounds form very stable conformers and some of them may even be regarded as atropisomers due to the greatly restricted rotation around the central HC(sp^3)–C(sp^3)H bond (Figure 2 and the Supporting Information for details).[12] This phenomenon was studied by variable-temperature (VT) ^{1}H NMR spectroscopy of ***meso*-(Bab-Dipp)$_2$** and ***meso*-(Bab-*t*Bu)$_2$**.[13] In the latter case,

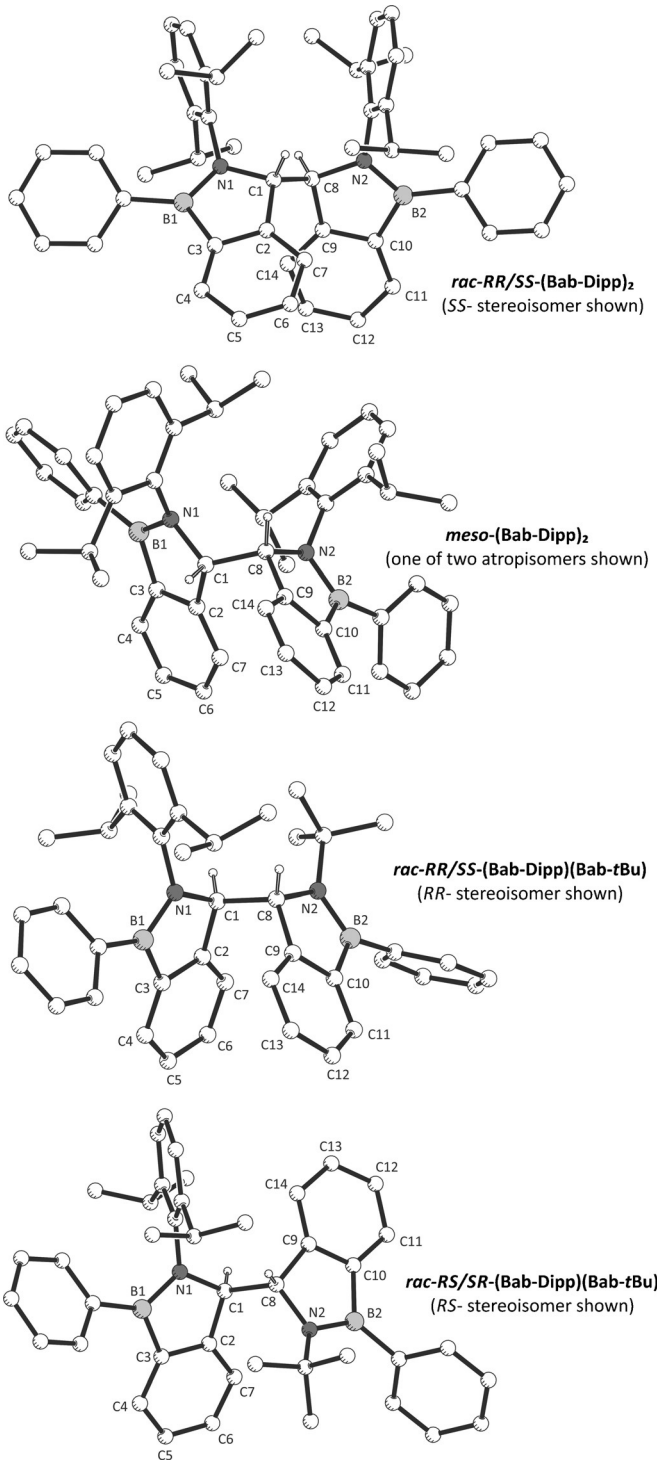


Figure 1. Molecular structures of C(sp^3)–C(sp^3) coupled bis(1*H*-2,1-benzazaborole) derivatives. Hydrogen atoms were omitted except for those of the methine carbons in HC(3)–C(3′)H.

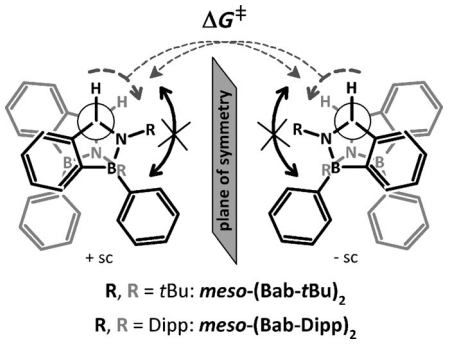


Figure 2. Newman projection of the greatly hindered rotation (highlighted by the black arrows) of enantiomeric pairs (+sc and -sc) for ***meso*-(Bab-*t*Bu)$_2$** and ***meso*-(Bab-Dipp)$_2$**. Dashed arrows represent the hypothetic situation, in which one enantiomer of *meso*- (e.g. +sc) turns into to the second enantiomer (-sc) merely by rotation around the central HC(sp^3)–C(sp^3)H bond and vice versa.

indeed the spectra between the slow- and fast-exchange limit could be obtained and mathematically processed (Figures S2 and S3).

A particular area of interest represents two singlets corresponding to the bridging C*H* groups at 5.33 and 5.79 ppm at 295 K, and their coalescence occurs at 361 K. Based on this observation, calculated parameters of the rotation around the HC(sp^3)–C(sp^3)H bond for ***meso*-(Bab-*t*Bu)$_2$** extracted from DNMR3 simulations (Figure S3, Supporting Information) are as follows: $k_r = k_c = 405\ s^{-1}$, $\Delta G^{\ddagger}_{361K} = 17.0\ kcal\,mol^{-1}$, $\Delta H^{\ddagger} = 13.6\ kcal\,mol^{-1}$, $\Delta S^{\ddagger} = -9.4\ cal\,K^{-1}\,mol^{-1}$. In contrast, no coalescence could be achieved in the case of ***meso*-(Bab-Dipp)$_2$** in the accessible temperature range (up to 373 K), but this is evidently a consequence of the presence of bulky Dipp groups.

These results, in combination with the fact that both ***meso*-(Bab-*t*Bu)$_2$** and ***meso*-(Bab-Dipp)$_2$** crystallize in the centrosymmetric space groups [as a racemate of two enantiomeric forms (+sc and −sc) of these stereoisomers], indicate that both mesoforms exist as racemates of two enantiomers [in the case of ***meso*-(Bab-Dipp)$_2$**, as a racemate of two enantiomeric atropisomers] as a consequence of a hindered rotation around the central HC(sp^3)–C(sp^3)H bond.[9a] To gain similar activation rotation barriers for all six bis(1*H*-2,1-benzazaborole) derivatives, plots of potential energy versus the torsion angle on the HC(sp^3)–C(sp^3)H bond junction were calculated. The according energy values were obtained by density functional theory calculations using the Gaussian 09 program suite.[14] From these calculations, it is evident that the value derived for ***meso*-(Bab-*t*Bu)$_2$** by ^{1}H VT-NMR (17.0 kcal mol^{-1}) is in very good agreement with the theoretical value (19.0 kcal mol^{-1}). All remaining bis(1*H*-2,1-benzazaborole) derivatives revealed higher values of activation rotation barriers (ranging from 20–35 kcal mol^{-1}; see Figures S6–S11 in the Supporting Information).

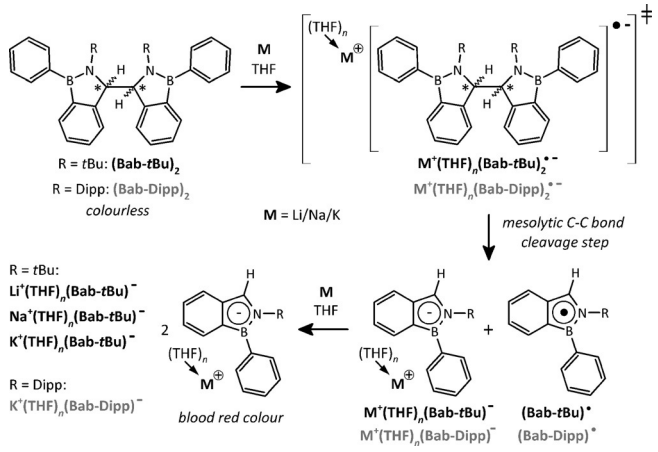
Regarding the photophysical properties, all bis(1*H*-2,1-benzazaborole) compounds showed two strong absorptions between approximately 240 and 270 nm in UV/Vis absorption spectra (Figure S14, Table S7). This is an important property of these compounds; see the further discussion for details.

Synthesis and characterization of 1*H*-2,1-benzazaborolyl anions

Both ***rac*-RR/SS-(Bab-*t*Bu)$_2$** and ***meso*-(Bab-*t*Bu)$_2$**[9a] are readily reduced in THF by two equivalents of an alkali metal leading to the cleavage of the central HC(sp^3)–C(sp^3)H bond and for-

mation of corresponding alkali metal salts of 1Ph-2*t*Bu-1*H*-2,1-benzazaborolyl anions, that is, **M$^+$(THF)$_n$(Bab-*t*Bu)$^-$** (M = Li, Na, K,[9a] Scheme 3). Attempts to isolate C–C coupled radical anion **M$^+$(THF)$_n$(Bab-*t*Bu)$_2^{\cdot-}$** by reaction with one equivalent of an alkali metal led only to the mixture of the corresponding 1*H*-2,1-benzazaborolyl alkali salt and starting compounds, indicating that this species is probably only an elusive intermediate (see further discussion). All alkali metal salts were isolated as air- and moisture-sensitive solids that are almost insoluble in aromatic and aliphatic solvents, but readily soluble in THF (Scheme 3). They were characterized using ^{1}H, ^{11}B, ^{13}C, ^{15}N NMR, and in case of **Li$^+$(THF)$_n$(Bab-*t*Bu)$^-$**, also by ^{7}Li NMR spectroscopy showing closely related structures of all compounds in solution (Table S1, Supporting Information). The signals of the *CH*–N moiety in ^{1}H and ^{13}C NMR spectra are significantly low-field shifted [δ(^{1}H) in the range of 6.13–6.27 ppm and δ(^{13}C) of 95.4–96.6 ppm, Table S1] pointing to an aromatic character of these ring systems (see below for the molecular orbital description).[15] The ^{11}B NMR spectra revealed one signal in each case [δ(^{11}B) in the range 23.3–23.4 ppm, Table S1], which is slightly high-field shifted in comparison to closely related 1,2-azaborolyl lithium salts [δ(^{11}B) = 30–35 ppm].[16] The ^{7}Li NMR chemical shift (−1.4 ppm) of **Li$^+$(THF)$_n$(Bab-*t*Bu)$^-$** indicates the presence of a solvent-separated ion pair (SSIP) in solution.[17] All NMR data prove similarity of **M$^+$(THF)$_n$(Bab-*t*Bu)$^-$** in solution regardless of the alkali metal used. Therefore, only the potassium salt of the sterically more crowded system, that is, **K$^+$(THF)$_n$(Bab-Dipp)$^-$**, was synthesized for comparison. Again the ^{1}H, ^{11}B, ^{13}C, and ^{15}N NMR spectra proved the analogous structure of **K$^+$(THF)$_n$(Bab-Dipp)$^-$** (Table S1).

The molecular structure of **K$^+$(THF)$_n$(Bab-*t*Bu)$^-$** with a polymeric chain structure, has been described by us recently.[9a] Unfortunately, all of our numerous attempts to grow single crystals of any other analogue suitable for X-ray diffraction analysis failed. UV/Vis absorption spectra of **M$^+$(THF)$_n$(Bab-*t*Bu)$^-$** (where M = Li, Na, K[9a]) and **K$^+$(THF)$_n$(Bab-Dipp)$^-$** were acquired (Figure S13 and Table S2 in the Supporting Information). To gain further insight into the structure of 1*H*-2,1-benzazaborolyl anions, the structure of **(Bab-Dipp)$^-$** was used for time dependent (TD)-DFT calculations, considering that the influence of the counter cation is believed to be negligible. TD-DFT calculations for the **(Bab-Dipp)$^-$** anion show two intensive transitions at 410 and 451 nm, which correspond to the experimentally observed transitions at 394 and 504 nm (Figure S13, Table S2). These transitions are all related to excitations starting from the HOMO (Figure S13), which is the π-orbital of the aromatic benzazaborolyl ring. For the 410 nm feature, the excitation goes into the LUMO + 2, which lies more on the Dipp group. For the 451 nm feature, LUMO + 1 and LUMO serve as accepting orbitals, with the LUMO being Dipp group-based and the LUMO + 1 being totally delocalized.



Scheme 3. Plausible mechanism of formation of related **Bab$^-$** alkali metal salts during the reduction of symmetrically substituted bis(1*H*-2,1-benzazaborole) derivatives (based on cyclic voltammetry, see Figures 3 and S16).

To gain additional insight into the formation of 1*H*-2,1-benzazaborolyl anions by the reduction of bis(1*H*-2,1-benzazaborole) compounds, a CV (cyclic voltammogram) study on ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** (or ***meso*-(Bab-*t*Bu)$_2$**) was undertaken. Unfortunately, no signal was detected in the case of Dipp-substituted bis(1*H*-2,1-benzazaborole) variants, despite very high concentrations in the voltammetric cell (see details in the Supporting Information). These CVs revealed one irreversible and one quasi-reversible process in each case,[18a] (scan rates of 20–1000 mV s^{-1}) indicating that the reduction goes through two discrete one-electron transfers. This finding supports the mechanism shown in Scheme 3 that probably follows the so-called ECE[18b] electrochemical mechanism. In the first irreversible process of this proposed mechanism [at $E_p = -1.65$ V vs. saturated calomel electrode (SCE); all following potentials are also given vs. SCE], an elusive radical anion **(Bab-*t*Bu)$_2^{\cdot-}$** is formed that is immediately cleaved to give anion **(Bab-*t*Bu)$^-$** and radical **(Bab-*t*Bu)$^{\bullet}$**, the latter being reduced in a second quasi-reversible[18a] step to another equivalent of anion **(Bab-*t*Bu)$^-$** (at $E^{0F} = -1.93$ V, peak separation of 144 mV at 100 mV s^{-1}, Figure 3). It must be noted that this second quasi-reversible step is superimposed on to the exponentially growing background because the electrochemical window was cut-off by the sample itself (this is an intrinsic characteristic of the studied compound because the background measurement was allowed to reach more negative potential in pure THF, up to −2.6 V). CV curves were also acquired for parent chloroborane **L(C=N*t*Bu)BPhCl** [where **L(C=N*t*Bu)** = *o*-(CH = N*t*Bu)C$_6$H$_4$]. This measurement showed even three redox processes. The first irreversible process at $E_p = -1.44$ V in the cathodic direction was tentatively assigned to a one-electron reduction to the corresponding radical **(Bab-*t*Bu)$^{\bullet}$** with elimination of a chloride anion (Figure 3). The second quasi-reversible process (at $E^{0F} = -1.93$ V) corresponds to the reduction of the radical **(Bab-*t*Bu)$^{\bullet}$** to the anion **(Bab-*t*Bu)$^-$** [see the CV of the corresponding bis(1*H*-2,1-benzazaborole)]. The origin of the third irreversible process in the CV of **L(C=N*t*Bu)BPhCl** at $E_p = -2.54$ V (denoted by an asterisk in Figure 3) is still unclear and importantly, this redox process was not observed in the CVs of ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** or ***meso*-(Bab-*t*Bu)$_2$**, indicating that it is not important for the reduction of these bis(1*H*-2,1-benzazaborole) compounds. Importantly, a visible shoulder at $E_p = -1.65$ V is also found in the CV curve of **L(C=N*t*Bu)BPhCl**, that becomes even slightly more intense at lower scan rates. This finding could be rationalized by in situ

formation of ***rac-RR/SS*-(Bab-*t*Bu)$_2$** and/or ***meso*-(Bab-*t*Bu)$_2$** from electrochemically generated **(Bab-*t*Bu)$^\bullet$** radicals directly in the voltammetric cell (they are indeed prone to self-termination; see further discussion). that are then reduced as described before (Figure 3 and Figure S16 in the Supporting Information). Considering that the CV of **L(C=NDipp)BPhCl** is closely related to that of its *t*Bu analogue, showing again three processes (Figure S15), it seems reasonable to consider a similar reduction mechanism also in the case of Dipp-substituted derivatives. The first process occurring at $E_p = -1.46$ V in the cathodic direction corresponds to the formation of radical **(Bab-Dipp)$^\bullet$** (Figure S15), followed by further reduction at $E^{0F} = -1.80$ V (peak separation of 236 mV at 100 mV s^{-1}), leading to anion **(Bab-Dipp)$^-$** (the chemical meaning of the third redox process at exactly the same redox potential as in the *t*Bu-substituted derivative with $E_p = -2.54$ V is unclear). Notably, the comparison of values of redox potentials $E^{0F}_{(\text{Bab-}t\text{Bu})^\bullet/(\text{Bab}^-t\text{Bu})^-} = -1.93$ V with $E_{p\,\text{L(C=NDipp)BPhCl/(Bab—Dipp)}^\bullet} = -1.46$ V indicates that the former may be viewed as a stronger reducing agent. Consequently, preparation of unsymmetrically substituted bis(1*H*-2,1-benzazaborole) derivatives by the reaction of **K$^+$(THF)$_n$(Bab-*t*Bu)$^-$** and **L(C=NDipp)BPhCl** should probably be considered as a nucleophilic addition accompanied by an internal redox reaction, rather than a simple nucleophilic addition of a **(Bab-*t*Bu)$^-$** anion to the imino C=N bond of **L(C=NDipp)BPhCl** (Scheme 2). However, we have recently discovered that simple nucleophiles such as anilides and carbanions are able to react with this C=N bond in the structure of the chelating ligand merely through nucleophilic attack.[4a,b]

Conclusions regarding the mechanism of reduction of bis(1*H*-2,1-benzazaborole) compounds are also supported by theoretical data, which can be found in the Supporting Information (Tables S3–S5).

Thermal HC(sp^3)–C(sp^3)H bond cleavage in bis(1*H*-2,1-benzazaborole) compounds

In this work (vide supra), we have shown that all bis(1*H*-2,1-benzazaborole) derivatives suffer from a (partially) restricted rotation around the central C–C bond. We have also recently demonstrated that heating of a toluene solution of ***meso*-(Bab-*t*Bu)$_2$** at 130 °C led to quantitative conversion to the thermodynamically more stable ***rac-RR/SS*-(Bab-*t*Bu)$_2$** within 48 h.[9a] These findings led us to study this phenomenon in more detail. The heating of ***meso*-(Bab-Dipp)$_2$** to 140 °C in solution resulted in the formation of ***rac-RR/SS*-(Bab-Dipp)$_2$** (see the Supporting Information).[19] Initially, this finding has been ascribed to the inversion at stereogenic carbon centers, but the heating of a solution of ***rac-RS/SR*-(Bab-Dipp)(Bab-*t*Bu)** provided, besides the expected ***rac-RR/SS*-(Bab-Dipp)(Bab-*t*Bu),** the symmetrically substituted systems ***rac-RR/SS*-(Bab-*t*Bu)$_2$** and ***rac-RR/SS*-(Bab-Dipp)$_2$** (Scheme 4). This proves that the conversion between particular diastereoisomers must proceed by a homolytic cleavage of the central C(sp^3)–C(sp^3) bond with concomitant recombination to more stable diastereoisomers. This fact is further corroborated by the heating of a 1:1 stoichiometric mixture of ***meso*-(Bab-*t*Bu)$_2$** and ***meso*-(Bab-Dipp)$_2$** again providing a mixture of both symmetric and non-symmetric bis(1*H*-2,1-benzazaborole) compounds (Table S7, Figure S17).

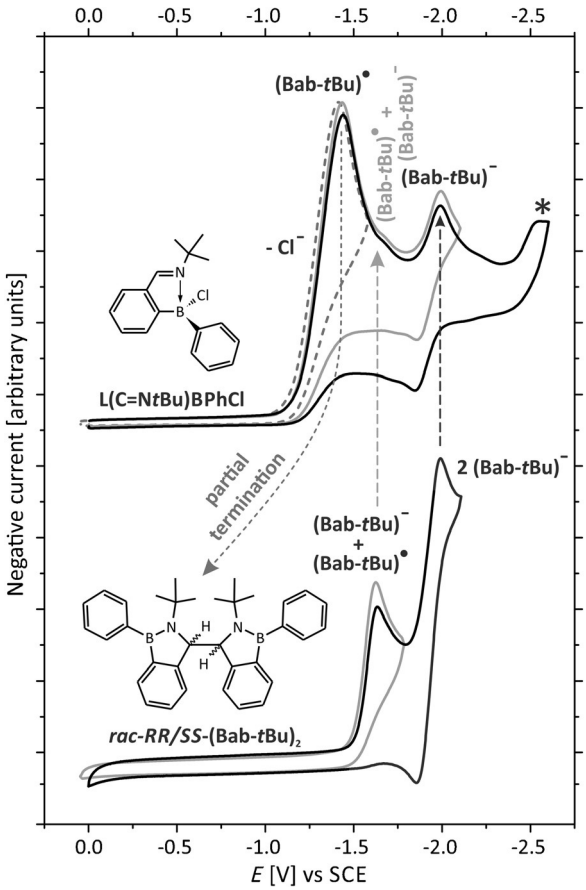
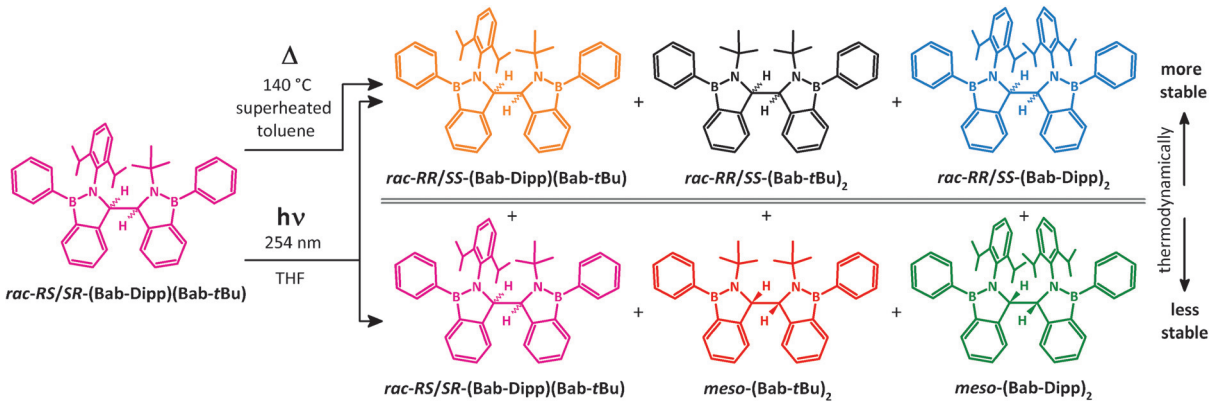


Figure 3. Cyclic voltammograms of parent **L(C=N*t*Bu)BPhCl** (top) and subsidiary ***rac-RR/SS*-(Bab-*t*Bu)$_2$** (bottom) in THF on a GC working electrode vs. SCE, 0.1 M nBu$_4$N$^+$PF6$^-$ as electrolyte. Scan rate 100 mV s^{-1}. * denotes an unknown redox process.

It is important to note, that final products ***rac-RR/SS*-(Bab-Dipp)(Bab-*t*Bu)**, ***rac-RR/SS*-(Bab-*t*Bu)$_2$**, and ***rac-RR/SS*-(Bab-Dipp)$_2$** are stable, even when heated up to 160 °C, thereby confirming that *RR/SS*- stereoisomers are thermodynamically the most stable. These findings are also supported by density functional energy calculations, which showed an energetic stabilization of these compounds in comparison with ***rac-RS/SR*-(Bab-Dipp)(Bab-*t*Bu)**, ***meso*-(Bab-*t*Bu)$_2$**, and ***meso*-(Bab-Dipp)$_2$** (Table S9 in the Supporting Information). It is obvious that the cleavage of the central HC(sp^3)–C(sp^3)H bonds during the conversion between respective stereoisomers should produce corresponding radicals **(Bab-Dipp)$^\bullet$** or **(Bab-*t*Bu)$^\bullet$**, but all of our attempts to identify them using EPR spectroscopy in the temperature range 140–180 °C, (both in a decaline solution as well as a molten neat sample) failed.[20] This fact is most probably a result of the low rate of C–C bond cleavage at the given temperature (full conversion requires at least 48 h at 140 °C in toluene solutions) and/or fast recombination of the respective short-lived radicals under these conditions, resulting in their low steady-state concentration.



Scheme 4. Irradiation at ambient temperature leads to a mixture of all six isomers, whereas heating leads to the three thermodynamically more stable isomers.

Photo-induced HC(sp^3)–C(sp^3)H bond cleavage in bis(1*H*-2,1-benzazaborole) compounds

As mentioned above, all isolated bis(1*H*-2,1-benzazaborole) derivatives showed strong absorption between about 240–270 nm in the UV/Vis absorption spectra (Figure S14 in the Supporting Information). Consequently, all six enantiomeric pairs of bis(1*H*-2,1-benzazaborole) variants were independently irradiated at 254 nm for 2, 4, and 24 h in degassed THF and the samples were subsequently analyzed using ^{1}H and ^{13}C NMR spectroscopy. It turned out that the particular isomer converts into a mixture of expected products of the cleavage of the central HC(sp^3)–C(sp^3)H bond with concomitant recombination in all cases (Table S7). Thus, for the case of irradiation of ***rac-RS/SR*-(Bab-Dipp)(Bab-*t*Bu)**, even all six possible products were detected in the resulting mixture by ^{1}H and ^{13}C NMR spectroscopy (Scheme 4 and Figure 4). This finding unambiguously confirmed that the central HC(sp^3)–C(sp^3)H bond may be cleaved not only by heating, but also by photochemical means.[21] Considering that a homolytic cleavage of the target bond is expected, the radicals **(Bab-Dipp)$^\bullet$** or **(Bab-*t*Bu)$^\bullet$** should be formed as elusive intermediates. Indeed, an irradiation of ***rac-RR/SS*-(Bab-Dipp)$_2$** or ***meso*-(Bab-Dipp)$_2$** resulted in the observation of an EPR signal with noticeable splitting at $g = 2.002$, probably corresponding to the radical **(Bab-Dipp)$^\bullet$** (Figure 5).[22] Importantly, the analyzed solutions containing the radical **(Bab-Dipp)$^\bullet$** became EPR silent upon time indicating recombination of present radicals, but repeated irradiation of the same samples again led to the observation of the same EPR signal (Figure 5). Finally evaporation of these samples and their analysis using ^{1}H and ^{13}C NMR spectroscopy proved the presence of expected compounds, that is, ***rac-RR/SS*-(Bab-Dipp)$_2$** and ***meso*-(Bab-Dipp)$_2$**, thereby ruling out formation of any side-product and/or decomposition of the samples. The identification of the radical **(Bab-Dipp)$^\bullet$** contrasts with the failure in attempts to identify its counterpart **(Bab-*t*Bu)$^\bullet$** by EPR spectroscopy using an analogous procedure.[23,24] Nevertheless, indirect evidence for the formation of **(Bab-*t*Bu)$^\bullet$** in these processes was obtained by irradiation of a stoichiometric 1:1 mixture of ***rac-RR/SS*-(Bab-*t*Bu)$_2$** and ***rac-RR/SS*-(Bab-Dipp)$_2$** that provided the mixture of all six possible bis(1*H*-2,1-benzazaborole) derivatives (Table S7, Figure S20).

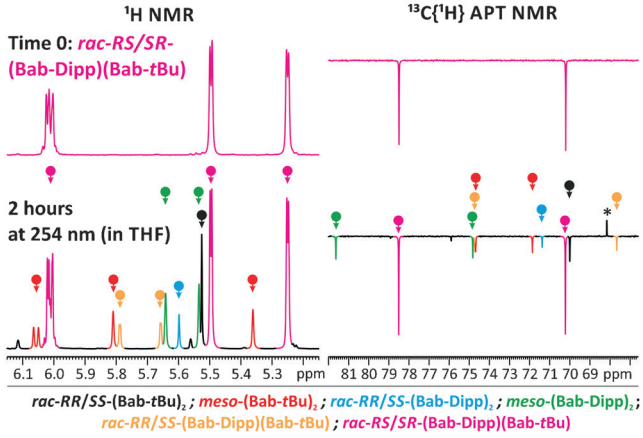


Figure 4. Stacked plot of ^{1}H NMR and ^{13}C{^{1}H} APT NMR spectra in the methine (*CH*–N) group region before and after irradiation of ***rac-RS/SR*-(Bab-Dipp)(Bab-*t*Bu)** at 254 nm, measured in C_6D_6 after evaporation of the reaction mixture. * denotes the residual THF signal.

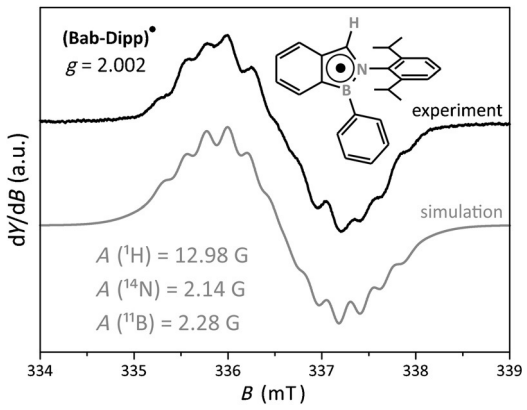


Figure 5. Room-temperature X-band (9.42711 GHz) continuous wave (CW) experimental and simulated EPR spectra of a solution of unstable **(Bab-Dipp)$^\bullet$** generated in a THF solution of ***rac-RR/SS*-(Bab-Dipp)$_2$** or ***meso*-(Bab-Dipp)$_2$** by irradiation at 254 nm. Interacting nuclei are colored in grey.

The room-temperature[25] EPR spectrum of the **(Bab-Dipp)•** radical agrees well with the simulated spectrum, in which hyperfine splitting corresponds to one hydrogen atom of the methine C(3)-carbon (12.98 G, I = $^1/_2$ for ^{1}H), one nitrogen atom (2.14 G, I = 1 for ^{14}N), and one boron atom (2.28 G, I = $^3/_2$ for ^{11}B). This finding is in excellent agreement with the theoretically obtained SOMO for the radical **(Bab-Dipp)•** (Figure 6, for calculated Mulliken spin densities, see Tables S10 and S11, Supporting Information), which is mainly localized at the boron atom and HC–N moiety. Although a number of radical species containing boron atoms within a heterocycle are known,[28] probably a most relevant congener of **(Bab-Dipp)•** is Nozaki's persistent *N,N*-stabilized neutral boron radical. In this case, however, the spin density localized at the boron atom seems to be considerably lower.[29] Furthermore the theoretical study also showed close similarity of both SOMOs of **(Bab-Dipp)•** and **(Bab-*t*Bu)•** (Figure 6).

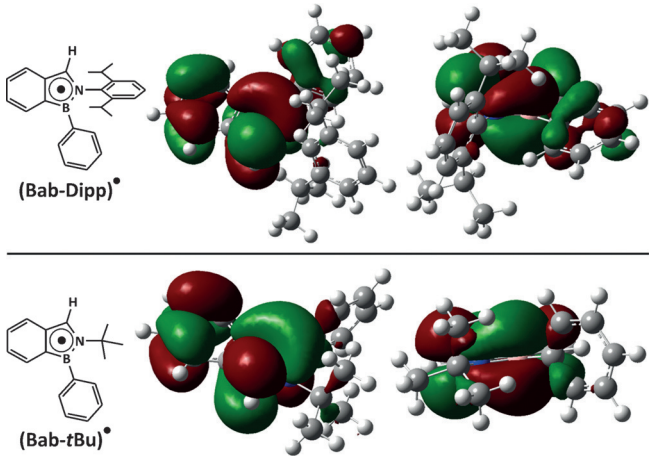


Figure 6. Calculated SOMOs of respective radicals, at M06-2X/def2-SVP level.[26,27]

Heterolytic HC(sp^3)–C(sp^3)H bond cleavage in bis(1*H*-2,1-benzazaborole) derivatives

It was demonstrated above that the central HC(sp^3)–C(sp^3)H bond in bis(1*H*-2,1-benzazaborole) derivatives is quite easily cleaved mesolytically and homolytically (thermally and photochemically). More surprisingly, it turned out that the same non-polarized HC(sp^3)–C(sp^3)H bond can be cleaved in a heterolytic fashion using MeLi. The reaction between either ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** or ***meso*-(Bab-*t*Bu)$_2$** (see the Supporting Information) in THF with one molar equivalent of MeLi in Et_2O lead to the formation of a familiar intensively red-colored solution, indicative of the formation of the 1*H*-2,1-benzazaborolyl lithium salt **Li$^+$(SOL)$_n$(Bab-*t*Bu)$^-$** (SOL = THF or diethylether). However, starting materials ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** with the methylborate **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** were isolated surprisingly as by-products instead of the expected 1-Ph-2-*t*Bu-3-Me-1*H*-2,1-benzazaborole (Scheme 5B and Figure 7B).[4b] Nevertheless, use of two molar equivalents of MeLi led to the formation of a 1:1 mixture of **Li$^+$(SOL)$_n$(Bab-*t*Bu)$^-$** and the methylborate **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** (Scheme 5C, Figure 7C). The progress of the reaction could be easily monitored by ^{11}B NMR spectroscopy as well (Figure S26).

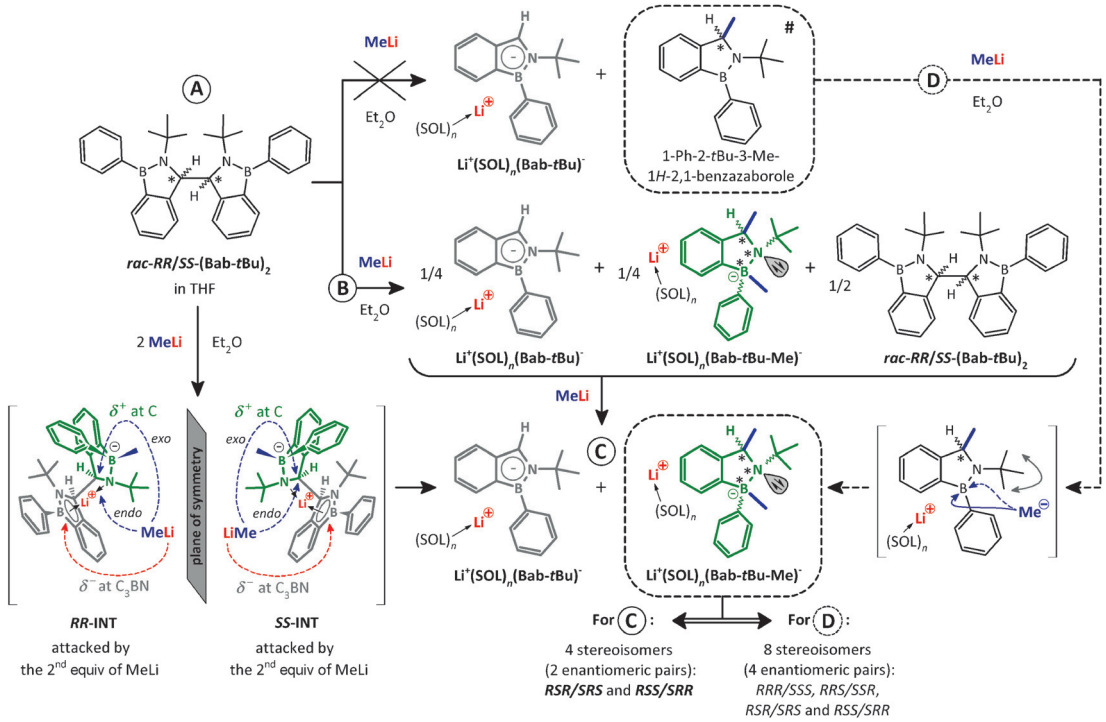
The **Li$^+$(SOL)$_n$(Bab-*t*Bu)$^-$** was characterized by a coincidence of experimental data with those obtained for this compound above (see Supporting Information). The methylborate **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** in the form of two enantiomeric pairs (1*R*,2*S*,3*S*/1*S*,2*R*,3*R* and 1*R*,2*S*,3*R*/1*S*,2*R*,3*S*; further abbreviated only as ***RSS*/*SRR*** and ***RSR*/*SRS***) was characterized by ^{1}H, ^{1}H-^{1}H NOESY, ^{11}B, ^{13}C, and ^{15}N NMR spectra (Figure 7B, C and the Supporting Information). The ^{1}H and ^{13}C NMR spectra showed typical signals for the *CH*(*CH*$_3$)N groups and the ^{11}B NMR spectra revealed signals typical for a borate-type boron atom (−3.6 and −4.3 ppm). Additional proof stems from ^{15}N NMR chemical shifts being high-field shifted by approximately 85 ppm in comparison with starting ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** (δ ^{15}N NMR = −234.5 ppm).

As two molar equivalents of MeLi are necessary for clean conversion, it is highly probable that the first equivalent of MeLi does not attack the central HC(sp^3)–C(sp^3)H bond, but adds to one of the B–N bonds in an antarafacial fashion in the starting ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$**, forming a highly reactive intermediate **INT** (Scheme 5). In this intermediate **INT**, the lithium cation seems to be able to approach and interact with the π-system of the five-membered C_3BN ring of the second 1*H*-2,1-benzazaborole ring (the grey one in the Scheme 5). Furthermore, in the structure of **INT**, the absolute configurations of *N*-*t*Bu and *B*–Ph groups, which are connected to newly formed nitrogen and boron stereogenic centers, are exactly the same as in the final products ***RSS*/*SRR*-** and ***RSR*/*SRS*-Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$**. Finally, the **INT** must be significantly more labile towards the attack of the second molecule of MeLi [the cleavage step of the HC(sp^3)–C(sp^3)H] from two possible directions (*endo* and *exo* attack), thus inevitably giving final products ***RSS*/*SRR*-** and ***RSR*/*SRS*-Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** and 1*H*-2,1-benzazaborole lithium salt **Li$^+$(SOL)$_n$(Bab-*t*Bu)$^-$** (Scheme 5).

Finally, the identity of the methylborate **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** was also independently corroborated by its preparation from 1-Ph-2-*t*Bu-3-Me-1*H*-2,1-benzazaborole using MeLi.[4b] This reaction quantitatively gave the methylborate **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$**, but in this case as a mixture of all four possible enantiomeric pairs (Scheme 5D, Figure 7D, and page S55 in the Supporting Information). This contrasts with the observation of only two of such enantiomeric pairs in the reaction of ***rac*-*RR*/*SS*-(Bab-*t*Bu)$_2$** with two equivalents of MeLi (Scheme 5C, Figure 7C, and page S58). This fact further confirms that the 1-Ph-2-*t*Bu-3-Me-1*H*-2,1-benzazaborole is not formed during the addition of MeLi to bis(1*H*-2,1-benzazaborole) variants, thereby supporting the proposed mechanism going through the intermediate **INT**.

Conclusions

This contribution describes an intriguing and, to the best of our knowledge, unprecedented reactivity of a non-polar HC(sp^3)–C(sp^3)H bond at the junction between two five-membered C_3BN azaborole rings in (3,3′)-bis(1-Ph-2-R-1*H*-2,1-benzazaborole) compounds **(Bab-R)$_2$** (R = *t*Bu or Dipp). Such reactivi-



Scheme 5. Reaction between ***rac-RR/SS*-(Bab-*t*Bu)$_2$** or 1-Ph-2-*t*Bu-3-Me-1*H*-2,1-benzazaborole with MeLi, forming four enantiomeric pairs of the methylborate **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$**. The enantiomeric pair with configuration *RSS/SRR* is the most favorable due to steric reasons (D). Sterically induced formation of only two enantiomeric pairs during heterolytic HC(sp^3)–C(sp^3)H bond cleavage (C). For the full proposed mechanism, see page S65 in the Supporting Information. SOL = THF or Et$_2$O. The # denotes a compound recently prepared by us.[4b]

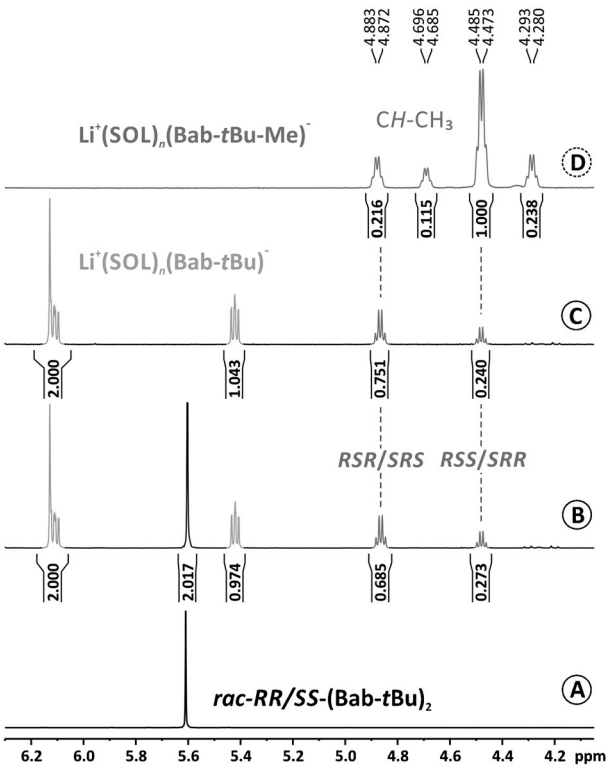


Figure 7. Stacked plot of ^{1}H NMR spectra ([D$_8$]THF at 294 K) in the region of 4.0–6.3 ppm of ***rac-RR/SS*-(Bab-*t*Bu)$_2$** (A), products after addition of MeLi (B,1 equiv; C, 2 equiv), and for comparison, the ^{1}H NMR spectrum of the methylborates **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** in all four possible enantiomeric pairs (D).

ty is far from the conventional behavior of "classical" HC(sp^3)–C(sp^3)H bonds. The target bond is smoothly cleaved chemically (in a mesolytic fashion) giving 1*H*-2,1-benzazaborolyl anions **M$^+$(THF)$_n$(Bab-*t*Bu)$^-$**, but is also cleaved by heating or irradiation giving thus short-lived 1*H*-2,1-benzazaborolyl radicals **(Bab-R)$^\bullet$**. The existence of these radicals has been confirmed by EPR spectroscopy [for **(Bab-R)$^\bullet$**, where R = Dipp] and/or using NMR analysis of the self-trapping products. Furthermore, **(Bab-*t*Bu)$_2$** shows intriguing reactivity with MeLi. This reaction sequence (with two equivalents of MeLi) yielding the 1*H*-2,1-benzazaborolyl lithium salt **Li$^+$(SOL)$_n$(Bab-*t*Bu)$^-$**, along with the corresponding methyl-substituted borate complexes **Li$^+$(SOL)$_n$(Bab-*t*Bu-Me)$^-$** (a derivative of the benzazaborole core), may be regarded as proof for heterolytical scission of the central HC(sp^3)–C(sp^3)H bond. We are convinced that the reactivity and chemical transformation described in this work are of general significant interest and will be applicable to a number of related C–C bonded heterocyclic systems. This fact may pave the way to compounds bearing interest from both theoretical and chemical point of views, representing otherwise hardly accessible species.

Acknowledgements

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Keywords: atropisomerism · boron · C–C bond cleavage · heterocycles · hindered rotation · radicals

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[20] We tried to trap them at 140 °C in toluene with benzoyl peroxide or diphenyldisulphide, however only a complicated mixture of products was detected by ^{1}H NMR spectroscopy.

[21] Irradiation in the solid state was also performed (1 hour at 254 nm), however only starting compounds were isolated, as judged by ^{1}H NMR.

[22] The set-up for the EPR measurement combined with irradiation enabled only irradiation outside the EPR spectrometer, thus not allowing for in situ irradiation (see details in the Supporting Information).

[23] Irradiation of THF solutions of ***rac*-*RR*/*SS*-(Bab-Dipp)(Bab-*t*Bu)** or ***rac*-*RS*/*SR*-(Bab-Dipp)(Bab-*t*Bu)** for the sake of possibly observing EPR signals of both respective **(Bab-Dipp)$^\bullet$** and **(Bab-*t*Bu)$^\bullet$** radicals was done.

However, no signals were detected despite the fact that after evaporation of the reaction mixtures and dissolving in C_6D_6, the NMR measurement proved the formation of a mixture of all six possible bis(Bab) compounds (Table S6 in the Supporting Information). This can only be rationalized by existence of the respective **(Bab-Dipp)•** and **(Bab-*t*Bu)•** radicals that immediately terminate to products.

[24] We tried to trap these radicals formed during the irradiation of any of isomers in THF at 254 nm with TEMPO, benzoyl peroxide, diphenyldisulphide, diphenyldiselenide, hexaphenylditin, 2,3-dimethyl-1,3-butadiene or decacarbonyl dimanganese(0). However, only a mixture of a variety of products was detected by ^{1}H NMR spectroscopy.

[25] For the purpose of obtaining EPR signals of **(Bab-Dipp)•** with higher resolution, the EPR measurement at lower temperature was performed. Whereas at room temperature, we were able to observe a relatively strong signal for this radical, after slight cooling (even at 5 °C), the initially relatively strong signal began to fade. When the temperature went down even further, the signal immediately disappeared and remained EPR silent after subsequent heating back to the room temperature. Observation of radicals in this sample required repeated irradiation. This led us to the conclusion that the rate of radical termination rapidly increases as the temperature decreases.

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