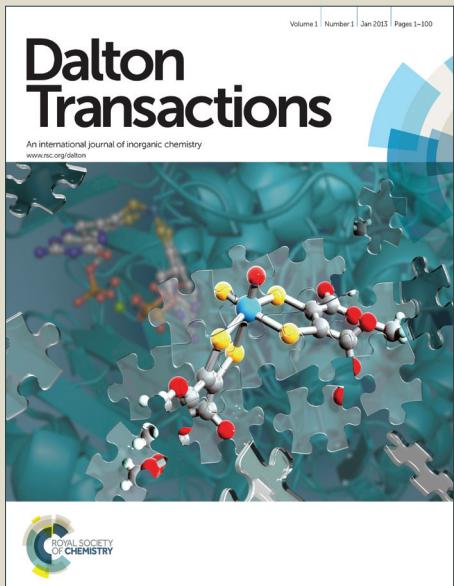


Dalton Transactions

Accepted Manuscript



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

COMMUNICATION

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Reduction of *C,N*-chelated Chloroborane: Straightforward Formation of Unprecedented 1*H*-2,1-benzazaborolyl Potassium Salt

Martin Hejda,^a Roman Jambor,^a Aleš Růžička,^a Antonín Lyčka^b and Libor Dostál^{a*}

Reduction of *C,N*-chelated chloroborane [2-(CH=NtBu)C₆H₄]BPhCl (1) with potassium metal afforded (3,3')-bis(1-Ph-2-tBu-1*H*-2,1-benzazaborole) (2). Compound 2 is formed via C-C reductive coupling reaction. Subsequent reduction of 2 with two equivalents of potassium metal produced orange crystals of 1Ph-2tBu-1*H*-2,1-benzazaborolyl (Bab) potassium salt K(THF)(Bab) (3). Compound 3 is able to react with simple electrophiles (MeI or Me₃SiCl) under formation of substituted 1*H*-2,1-benzazaboroles.

The isoelectronic relationship between B-N and C=C moiety has been appreciated and exploited for several decades. Thus, it is not surprising that substitution of one or more B-N fragments for C=C fragments in classical aromatic hydrocarbons led to the development of new generation of materials with desirable photophysical, electrochemical or biological activity.¹ Similar approach has been used by Schmid in the 1980s for the synthesis of 1,2-azaborolyl anions by deprotonation of 1,2-azaboroles, which were subsequently ligated to numerous transition metals as BN analogues of the cyclopentadienyl anion.² These pioneer works were later on followed by groups of Ashe, Fu and Fang.³ Benzazaborolyl anions, in which the azaborolyl fragment is fused with extra aromatic ring, are known only in the form 1*H*-1,2-benzazaborolyl isomer (Fig. 1A) and were used as indenyl analogues for coordination of transition metals (Ti or Zr) and these results were reported in patent literature.⁴ Nevertheless, molecular structure of none of these complexes has been reported. In addition, there is no report dealing with the second possible isomer 1*H*-2,1-benzazaborolyl, although several neutral 1*H*-2,1-benzazaboroles are known (Fig. 1B).⁵ We have recently discovered a facile synthetic strategy for preparation of 1*H*-2,1-benzazaboroles via the nucleophilic addition of lithium reagents to activated imine C=N double bond in *C,N*-chelated chloroboranes.⁶ As a part of our research in this field, we report herein the straightforward formation of potassium salt K(THF)(Bab) (3) (Bab = 1Ph-2tBu-1*H*-2,1-benzazaborolyl) as the representative of 1*H*-2,1-benzazaborolyl anions (Fig. 1B). Compound 3 was formed via non-conventional two step reduction of *C,N*-chelated chloroborane 1.

Reduction of 1 with potassium in toluene afforded compound 2 (Scheme 1) as a mixture of isomers as a result of the presence of two stereogenic centres in 2. Thus, existence of RR-2, SS-2 and *meso*-2 was expected in the reaction mixture (see details in ESI†).

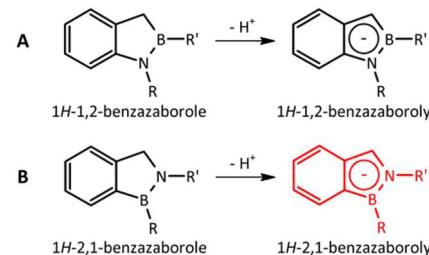
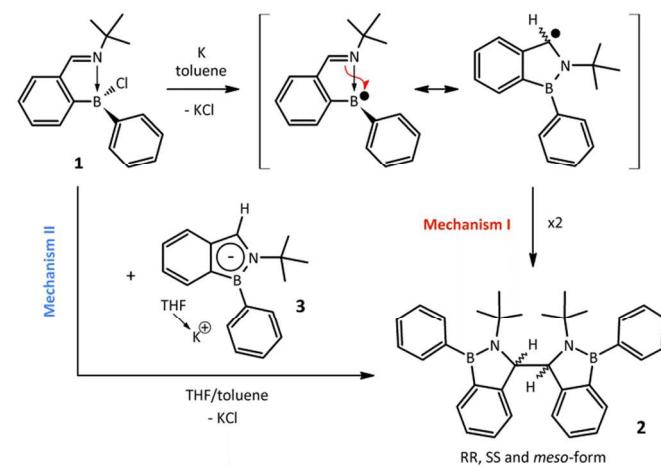


Fig. 1 Structures of discussed BN analogues of indenyl anions.



Scheme 1 Synthesis of compound 2 illustrating two possible mechanisms for its formation.

This fact was reflected by observation of two sets of signals in corresponding ¹H and ¹³C NMR spectra of reaction mixture (Fig. S1). Nevertheless, *meso*-2 and the racemate *rac*-RR/SS-2 could be separated by fractional crystallization and independently

characterized by ^1H , ^{11}B , ^{13}C and ^{15}N NMR spectroscopy (see details in ESI†). Especially, the presence of typical resonances for methine groups $\text{CH}-\text{N}$ in ^1H and ^{13}C NMR spectra [$\delta(^1\text{H}) = 5.36$ and 5.81 ppm for *meso*-**2**; 7^{a} 5.22 ppm for *rac*-RR/SS-**2**; $\delta(^{13}\text{C}) = 74.7$ and 71.9 ppm for *meso*-**2**; 7^{a} 70.0 ppm for *rac*-RR/SS-**2**] together with the absence of any signal attributable to the imino $\text{CH}=\text{N}$ group approved the structure of **2**. The ^{11}B NMR spectra revealed one singlet at 44.8 and 42.0 ppm for *meso*-**2**^{7b} and *rac*-RR/SS-**2**, respectively, thereby proving the presence of sp^2 hybridized boron atoms within the $1\text{H}-2,1$ -benzazaborole core.^{2b} Noteworthy, it turned out that heating of toluene solution of *meso*-**2** led to quantitative conversion to *rac*-RR/SS-**2** within 48 h (see details in ESI†).

Molecular structures of *rac*-RR/SS-**2** and *meso*-**2** were unambiguously determined using single-crystal X-ray diffraction analysis (Fig. 2). *rac*-RR/SS-**2** crystallizes in the centrosymmetric $P2_1/c$ space group. Based on molecular structures of *rac*-RR/SS-**2** and *meso*-**2**, all stereoisomers form stable atropisomers due to the restricted rotation around the $\text{C}(7)\text{-C}(24)$ bond, which is induced by favourable alignment of highly substituted $1\text{H}-2,1$ -benzazaborole moieties (see details in ESI†). This is the reason, why the *meso*-**2** also crystallizes in the centrosymmetric space group (*P*-1) as a racemate⁸, but now due to the molecular chirality caused by asymmetry at the $\text{C}(7)\text{-C}(24)$ bond (Figure S5). The $\text{C}(7)\text{-C}(24)$ bond lengths of $1.584(2)$ and $1.581(2)$ Å for *rac*-RR/SS-**2** and *meso*-**2**, respectively, indicate the presence of C-C single bond, which is a bit elongated in comparison to standard $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ (1.54 Å) bond. The B-N bond lengths within the benzazaborole rings [$1.409(2)$ - $1.415(2)$ Å] are apparently shorter than the sum of covalent radii for single bond $\Sigma_{\text{cov}}(\text{N},\text{B}) = 1.56$ Å⁹ and correspond to the value for the respective double bond (1.48 Å)⁹ reflecting strong $\pi(\text{N})\rightarrow\pi(\text{B})$ interaction. Consequently, the coordination geometry around both nitrogen and boron atoms remains essentially trigonal planar.

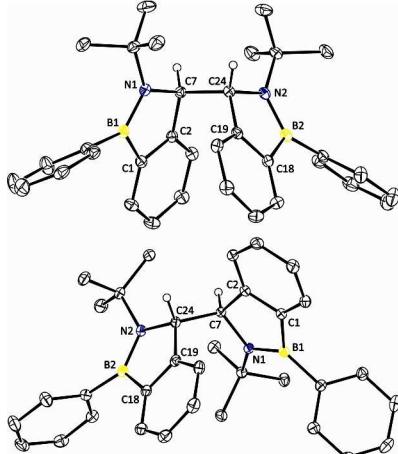
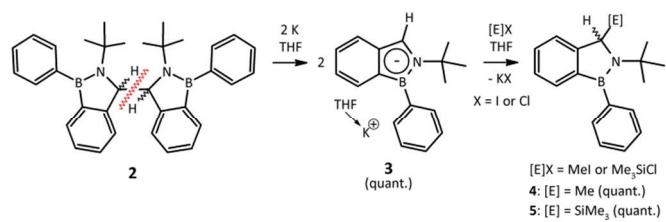


Fig. 2 Molecular structures of RR isomer of *rac*-RR/SS-**2** (top) and one of atropisomers of *meso*-**2** (bottom) (30% thermal ellipsoids; hydrogen atoms omitted except connecting CH groups). Selected bond lengths (Å), angles and torsion angles (°) of RR isomer of *rac*-RR/SS-**2** (values for atropisomer of *meso*-**2** are given in brackets): C(24)-C(7) 1.584(2) [1.581(2)], B(1)-N(1) 1.413(2) [1.409(2)], B(2)-N(2) 1.412(2) [1.415(2)], N(1)-C(7) 1.497(2) [1.4920(19)], N(2)-C(24) 1.495(2) [1.486(2)], N(1)-C(7)-C(24) 112.33(12) [118.59(12)], N(2)-C(24)-C(7) 112.44(12) [117.60(12)], N(1)-C(7)-C(24)-N(2) 179.32(12) [82.65(16)].



Scheme 2 Synthesis of compound **3** and its reactivity with selected electrophiles.

Treatment of **2**¹⁰ with potassium in THF at ambient temperature produced red solution from which dark orange crystals of **3** were obtained after work up (Scheme 2). Compound **3** was characterized by the help of ^1H , ^{11}B , ^{13}C and ^{15}N NMR spectroscopy (see details in ESI†). The signals due to the $\text{CH}-\text{N}$ moiety in ^1H and ^{13}C NMR spectra are significantly low-field shifted [$\delta(^1\text{H}) = 6.21$ and $\delta(^{13}\text{C}) = 96.4$ ppm] in comparison with **2** or related $1\text{H}-2,1$ -benzazaboroles⁶ pointing to an aromatic character of this ring system.^{1b} The ^{11}B NMR spectrum of **3** revealed one signal at 23.4 ppm, which is high-field shifted in comparison to related 1,2-azaborolyl transition metal complexes [$\delta(^{11}\text{B}) = 30$ - 35 ppm] thereby indicating higher electron density on the boron atom in **3** in comparison to these 1,2-azaborolyl metal complexes.^{1b,2b} The ^{15}N NMR spectrum of **3** revealed one signal at -209.4 ppm, that is slightly down-field shifted in comparison to the values observed for *meso*-**2** [$\delta(^{15}\text{N}) = -232.6$ and -233.3 ppm]^{7a} and for *rac*-RR/SS-**2** [$\delta(^{15}\text{N}) = -234.5$ ppm]. The molecular structure of **3** was unambiguously established by single-crystal X-ray diffraction analysis (Fig. 3). To the best of our knowledge, **3** represents the first example of structurally characterized $1\text{H}-2,1$ -benzazaborolyl anion (in the form of its potassium salt) as BN analogue of indenyl moiety. The potassium atom K(1) is coordinated by two benzazaborolyl anions and one THF molecule with the bond length K(1)-O(1) $2.668(2)$ Å that approaches $\Sigma_{\text{cov}}(\text{K},\text{O}) = 2.59$ Å.⁹ This bonding situation leads to formation of a chiral supramolecular structure of **3**, which crystallizes in space group $P2_1$. This supramolecular chirality is caused by rotation around a bisector defined by the centroid of the five-membered C_3BN ring of $1\text{H}-2,1$ -benzazaborolyl moiety and the potassium atom.

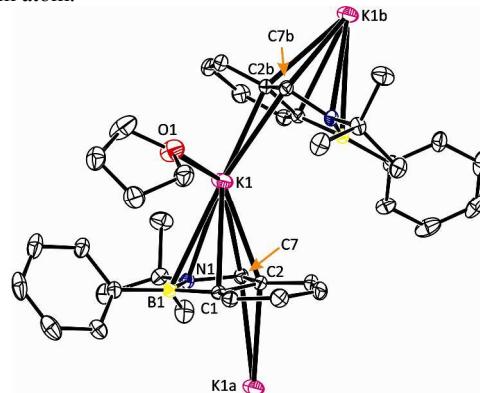


Fig. 3 View on the polymeric structure of **3** (30% thermal ellipsoids; hydrogen atoms omitted; symmetry operators: $a=1-x, -\frac{1}{2}+y, 1-z$ $b=1-x, \frac{1}{2}+y, 1-z$). Selected bond lengths (Å): K(1)-O(1) $2.668(2)$, K(1)-B(1) $3.192(2)$, K(1)-N(1) $3.1541(18)$, K(1)-C(1) $3.028(2)$, K(1)-C(2) $2.882(2)$, K(1)-C(7) $2.965(2)$, K(1)-B(1b) $3.479(2)$, K(1)-N(1b) $3.3388(17)$, K(1)-C(1b) $3.123(2)$, K(1)-C(2b) $2.838(2)$, K(1)-C(7b) $2.992(2)$, B(1)-N(1) $1.460(3)$, C(1)-B(1) $1.517(3)$, C(1)-C(2) $1.455(3)$, C(2)-C(7) $1.381(3)$, C(7)-N(1) $1.418(3)$.

One of C_3BN rings coordinates K(1) ion in approximately η^5 -fashion. The bond lengths describing this bonding interaction [K(1)-N(1) $3.1541(18)$, K(1)-C(1) $3.028(2)$, K(1)-C(2) $2.882(2)$, K(1)-C(7)

2.965(2) and K(1)-B(1) 3.192(2) Å] are similar to those observed for the only structurally characterized alkali metal analogue, i.e. lithium 1,2-azaborolyl reported by Schmid¹¹ considering different radii of both alkali metals. On the contrary, the interaction between the K(1) atom and the second C₃BN ring may be considered as η^2 -type mediated by C(2b) and C(7b) atoms [K(1)-C(2b) 2.838(2) and K(1)-C(7b) 2.992(2) Å]. The difference in coordination of both C₃BN rings is supported by distances between K(1) and centroids of respective C₃BN rings being 2.787 (η^5 ring) vs. 2.913 Å (η^2 ring). The B(1)-N(1) bond length [1.460(3) Å] is slightly shorter than the corresponding distance observed in the lithium 1,2-azaborolyl [1.503(6) Å], while other bond distances within the C₃BN ring are comparable with this lithium compound.¹¹

The mechanism of formation of **2** is of particular interest as well. Compound **2** may be formed by fast¹² recombination of two carbon centred radicals, formed by reduction of **1** with potassium (Mechanism I in Scheme 1). It is worth of noting, that analogous C-C reductive coupling has been recently reported by Nozaki *et al.* during reduction of base-stabilized difluoroboranes.¹³ Furthermore, the same working group clearly showed that even their stable *N*-coordinated heterocyclic boron radical may be described by several resonance structures, but the carbon centred radical has the major contribution to the structure.¹⁴ All these facts support the Mechanism I (Scheme 1). Despite these facts, the second mechanism (Mechanism II in Scheme 1) came into mind. The appearance of intensive red colour on the interface between the potassium mirror and the reaction mixture in the Schlenk tube during preparation of **2** (Fig. S2), which disappeared during the reaction, may be indicative for *in situ* formation of the potassium salt **3**. Compound **3** can then smoothly react with the present chloroborane **1** under formation of **2**. To support this presumption, the reaction of isolated **3** with one molar equivalent of **1** was performed and, indeed, it provided mixture of *rac*-RR/SS-**2** and *meso*-**2** in nearly quantitative yield as judged by NMR spectroscopy. It means that **3** may serve as a competing reagent to potassium metal during the formation of **2** (Scheme 1). In the light of these facts, we are not able to distinguish between both these mechanisms (I or II) at the moment, but it seems to be probable that **2** is formed by both of them simultaneously. Noteworthy, analogous C-C coupling reactions have been recently observed for α -iminopyridyl substituted Ge, Al, Ga, Zn complexes and lanthanide (Yb, Sm) derivatives of redox active ligands.¹⁵ Compound **3** also readily reacts with simple electrophiles such as MeI or Me₃SiCl, in this case a formation of substituted 1*H*-2,1-benzazaboroles **4** and **5** (Scheme 2) was observed. Compounds **4** and **5** were characterized by elemental analysis; ¹H, ¹¹B, ¹³C, ¹⁵N and ²⁹Si NMR spectroscopy (see details in ESI†).

In summary, compound **3**, potassium salt of the first structurally characterized BN analogue of the indenyl anion, has been prepared by unusual two step reduction of starting chloroborane **1** involving both C-C bond coupling and subsequent C-C bond cleavage reactions. This approach seems be applicable for preparation of related main group element aromatic systems. Furthermore, **3** is able to react not only with simple electrophiles leading to quantitative formation benzazaboroles **4** and **5**, but it also converts with chloroborane **1** to C-C coupled compound **2**, thereby opening a new strategy for preparation of such C-C bridged heterocyclic systems. Finally, compound **3** represents a promising starting material for preparation of indenyl-like metal complexes. All these possibilities are now studied in our labs.

The Grant Agency of the Czech Republic (project no. P207/12/0223) is acknowledged for financial support.

Notes and references

^a Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, CZ - 532 10, Pardubice, Czech Republic Fax: +420466037068; Tel: +420466037163; E-mail: libor.dostal@upce.cz.

^b Research Institute for Organic Syntheses, Rybitví 296, CZ-533 54, Pardubice, Czech Republic.

† Electronic Supplementary Information (ESI) available: Full synthetic, spectroscopic and crystallographic details for reported compounds. See DOI: 10.1039/c000000x/

- 1 For reviews see: (a) M. J. D. Bosdet and W. E. Piers, *Can. J. Chem.*, 2008, **86**, 8 and references cited therein; (b) A. J. Ashe III, *Comprehensive Heterocyclic Chem. III*, 2008, vol. 4, chapter 4.17, 1190 and references cited therein.
- 2 For example see: (a) G. Schmid, *Comments Inorg. Chem.*, 1985, **4**, 17 and references cited therein; (b) G. Schmidt, *Comprehensive Heterocyclic Chem. II*, 1996, vol. 3, chapter 3.17, 739; (c) G. Schmid and M. Schütz, *J. Organomet. Chem.*, 1995, **492**, 185; (d) G. Schmid, O. Boltsch and R. Boese, *Organometallics*, 1987, **6**, 435.
- 3 For example see: (a) A. J. Ashe III, *Organometallics*, 2009, **28**, 4236; (b) S. Y. Liu, M. M. C. Lo and G. C. Fu, *Tetrahedron*, 2006, **62**, 11343; (c) S. Y. Liu, M. M. C. Lo and G. C. Fu, *Angew. Chem., Int. Ed.*, 2002, **41**, 174; (d) H. Yang, X. Fang, J. W. Kampf and A. J. Ashe III, *Polyhedron*, 2005, **24**, 1280; (e) X. Fang and J. Assoud, *Organometallics*, 2008, **27**, 2408.
- 4 (a) S. Nagy, R. Krishnamatti and B. P. Etherton, U.S. Patent 6,228,959, 2001; *Chem. Abstr.*, 1997, **126**, 19432j; (b) Q. Wang, P. Zoricak and X. Gao, Can. Patent Appl. 2,225,014, 1999; *Chem. Abstr.*, 1999, **142**, 219701.
- 5 For example see: (a) V. Lee *et al.*, U.S. Patent 7,465,836, 2008; (b) V. Lee *et al.*, U.S. Patent 8,106,031, 2012; (c) A. M. Genaev, S. M. Nagy, G. E. Salnikov and V. G. Shubin, *Chem. Commun.*, 2000, 1587; (d) T. S. De Vries, A. Prokofjevs, J. N. Harvey and E. Vedejs, *J. Am. Chem. Soc.* 2009, **131**, 14679; (e) A. Rydzewska, K. Slepokura, T. Lis, P. Kafarski and P. Mlynarz, *Tetrahedron Lett.*, 2009, **50**, 132.
- 6 M. Hejda, A. Lyčka, R. Jambor, A. Růžička and L. Dostál, *Dalton Trans.*, 2013, **42**, 6417.
- 7 (a) Due to the atropisomerism observed in *meso*-**2** two signals for CH-N groups were observed in corresponding ¹H, ¹³C and ¹⁵N NMR spectra (see details in ESI†). (b) Two signals should be also observed in ¹¹B NMR spectrum, but they are overlapped due to the similar chemical shifts and broadening of these signals.
- 8 As a racemate of two atropisomers see ESI† for a detailed discussion.
- 9 (a) P. Pyykkö and M. Atsumi, *Chem. Eur. J.* 2009, **15**, 186; (b) P. Pyykkö and M. Atsumi, *Chem. Eur. J.* 2009, **15**, 12770; (c) P. Pyykkö, S. Riedel and M. Patzschke *Chem. Eur. J.* 2005, **11**, 3511.
- 10 Regardless, if *meso*-**2** or *rac*-RR/SS-**2** or even mixture of both was used.
- 11 G. Schmid, D. Zaika, J. Lehr, N. Augart and R. Boese, *Chem. Ber.*, 1988, **121**, 1873.
- 12 All our attempts to characterize the radical intermediate by EPR spectroscopy failed.
- 13 M. Yamashita, Y. Aramaki and K. Nozaki, *New J. Chem.*, 2010, **34**, 1774.

14 Y. Aramaki, H. Omiya, M. Yamashita, K. Nakabayashi, S. Ohkoshi and K. Nozaki, *J. Am. Chem. Soc.*, 2012, **134**, 19989.

15 (a) Y. Li, K. C. Mondal, P. Stollberg, H. Zhu, H. W. Roesky, R. Herbst-Imer, D. Stalke and H. Fiegl, *Chem. Commun.*, 2014, doi:10.1039/C4CC00251B; (b) R. J. Baker, C. Jones, M. Kloth and D. P. Mills, *New. J. Chem.*, 2004, **28**, 207; (c) I. L. Fedushkin, S. Dechert and H. Schumann, *Angew. Chem. Int. Ed.*, 2001, **40**, 561; (d) M. Westerhausen, T. Bollwein, N. Makropoulos, T. M. Rotter, T. Harbereder, M. Suter and H. Nöth, *Eur. J. Inorg. Chem.*, 2001, 851. (e) R. J. Baker and C. Jones, *Chem. Commun.*, 2003, 390.

The BN analogue of the indenyl anion has been prepared by unusual two step reduction of *C,N*-chelated chloroborane.

