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Reduction of *C,N*-chelated chloroborane: straightforward formation of the unprecedented 1*H*-2,1-benzazaborolyl potassium salt†

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Reduction of *C,N*-chelated chloroborane [2-(CH=N*t*Bu)C_6H_4]-BPhCl (1) with the potassium metal afforded (3,3′)-bis(1-Ph-2-*t*Bu-1*H*-2,1-benzazaborole) (2). Compound 2 is formed *via* C–C reductive coupling reaction. Subsequent reduction of 2 with two equivalents of the potassium metal produced orange crystals of 1Ph-2*t*Bu-1*H*-2,1-benzazaborolyl (Bab) potassium salt K(THF)(Bab) (3). Compound 3 is able to react with simple electrophiles (MeI or Me_3SiCl) resulting in the formation of substituted 1*H*-2,1-benzazaboroles.

The isoelectronic relationship between B–N and C=C moieties 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 has led to the development of a new generation of materials with desirable photophysical, electrochemical or biological activity.[1] A 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 pioneering studies were later on followed by the groups of Ashe, Fu and Fang.[3] Benzazaborolyl anions, in which the azaborolyl fragment is fused with an extra aromatic ring, are known only in the form 1*H*-1,2-benzazaborolyl isomer (Fig. 1A) and were used as indenyl analogues for the coordination of transition metals (Ti or Zr), and these results have been reported in the patent literature.[4] Nevertheless, the 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 the preparation of 1*H*-2,1-benzazaboroles *via* the nucleophilic addition of lithium reagents to the 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-2*t*Bu-1*H*-2,1-benzazaborolyl) as a 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**.

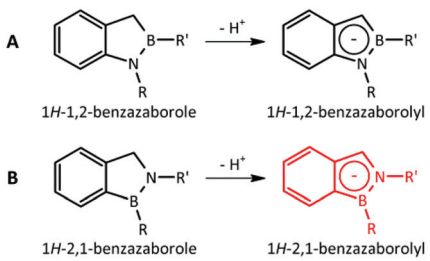

Fig. 1 Structures of the discussed BN analogues of indenyl anions.

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, presence of *RR*-**2**, *SS*-**2** and *meso*-**2** was expected in the reaction mixture (see details in the ESI†).

This fact was reflected by the observation of two sets of signals in the corresponding ^{1}H and ^{13}C NMR spectra of the reaction mixture (Fig. S1†). Nevertheless, *meso*-**2** and the racemate *rac*-*RR*/*SS*-**2** could be separated by fractional crystallization and independently characterized by ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy (see details in the ESI†). Especially, the presence of typical resonances for methine groups *CH*–N in ^{1}H and ^{13}C NMR spectra [δ(^{1}H) = 5.36 and 5.81 ppm for *meso*-**2**;[7a] 5.22 ppm for *rac*-*RR*/*SS*-**2**; δ(^{13}C) = 74.7 and 71.9 ppm for *meso*-**2**;[7a] 70.0 ppm for *rac*-*RR*/*SS*-**2**] together with the absence of any signal attributable to the imino *CH*=N group approved the structure of **2**. The ^{11}B NMR spectra revealed one singlet at

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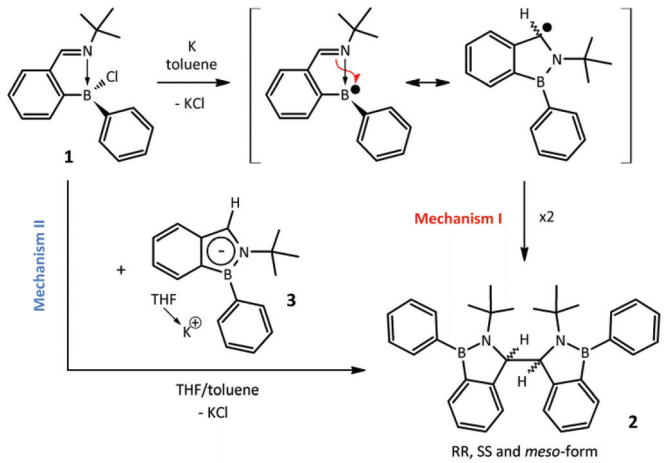


Scheme 1 Synthesis of compound **2** illustrating two possible mechanisms for its formation.

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*H*-2,1-benzazaborole core.[2b] It is noteworthy that it turned out that heating of a toluene solution of *meso*-**2** led to quantitative conversion to *rac-RR*/*SS*-**2** within 48 h (see details in the ESI†).

Molecular structures of *rac-RR*/*SS*-**2** and *meso*-**2** were unambiguously determined by 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 C(7)–C(24) bond, which is induced by favourable alignment of highly substituted 1*H*-2,1-benzazaborole moieties (see details in the ESI†). This is the reason why the *meso*-**2** also crystallizes in the centrosymmetric space group ($P\bar{1}$) as a racemate,[8] but now due to the molecular chirality caused by asymmetry at the C(7)–C(24) bond (Fig. S5†). The C(7)–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 the C–C single bond, which is a bit elongated in comparison with the standard $C(sp^3)$–$C(sp^3)$ (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 the single bond Σ_{cov}(N,B) = 1.56 Å[9] and correspond to the value for the respective double bond (1.48 Å)[9] reflecting the strong π(N) → π(B) interaction. Consequently, the coordination geometry around both nitrogen and boron atoms remains essentially trigonal planar.

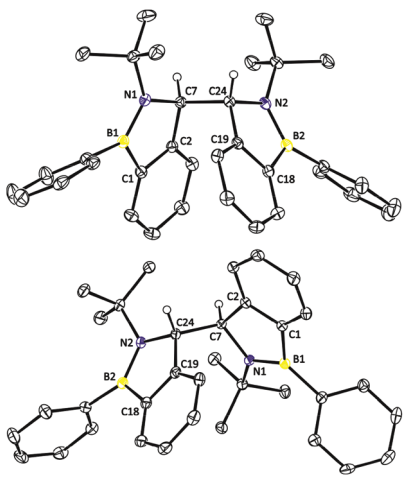
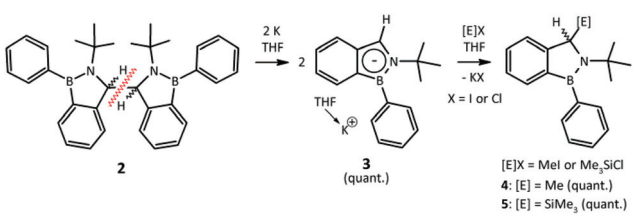


Fig. 2 Molecular structures of *RR* isomer of *rac-RR*/*SS*-**2** (top) and one of the atropisomers of *meso*-**2** (bottom) (30% thermal ellipsoids; hydrogen atoms omitted except those connecting CH groups). Selected bond lengths (Å), angles and torsion angles (°) of *RR* isomer of *rac-RR*/*SS*-**2** (values for the 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)].

Treatment of **2**[10] with potassium in THF at ambient temperature produced a red solution from which dark orange crystals of **3** were obtained after workup (Scheme 2). Compound **3** was characterized with the help of ^{1}H, ^{11}B, ^{13}C and ^{15}N NMR spectroscopy (see details in the ESI†). The signals due to the *CH*–N moiety in ^{1}H and ^{13}C NMR spectra are significantly low-field shifted [$\delta(^1H)$ = 6.21 and $\delta(^{13}C)$ = 96.4 ppm] in comparison with **2** or related 1*H*-2,1-benzazaboroles[6] pointing to the 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 with related 1,2-azaborolyl transition metal complexes [$\delta(^{11}B)$ = 30–35 ppm], thereby indicating higher electron density on the boron atom in **3** in comparison with these 1,2-azaborolyl metal complexes.[1b,2b] The ^{15}N NMR spectrum of **3** revealed one signal at −209.4 ppm, which is slightly down-field shifted in comparison with the values observed for *meso*-**2** [$\delta(^{15}N)$ = −232.6 and −233.3 ppm][7a] and for *rac-RR*/*SS*-**2** [$\delta(^{15}N)$ = −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 a structurally characterized 1*H*-2,1-benzazaborolyl anion (in the form of its potassium salt) as the BN analogue of the 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) of 2.668(2) Å that approaches Σ_{cov}(K,O) = 2.59 Å.[9] This bonding situation leads to the 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



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

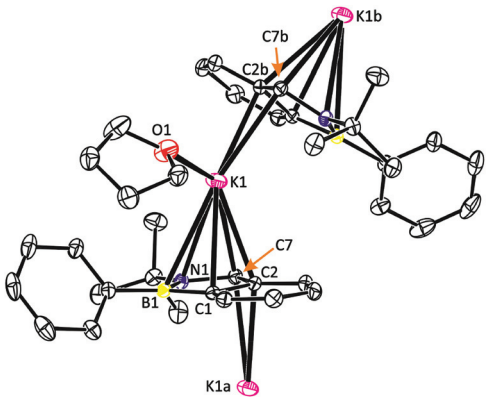


Fig. 3 View of the polymeric structure of **3** (30% thermal ellipsoids; hydrogen atoms omitted; symmetry operators: *a* = 1 − *x*, −1/2 + *y*, 1 − *z* *b* = 1 − *x*, 1/2 + *y*, 1 − *z*). Selected bond lengths (Å): K(1)–O(1) 2.668(2), K(1)–B(1) 3.192(2), K(1)–N(1) 3.1541(18), K(1)–C(1) 3.028(2), K(1)–C(2) 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).

of the five-membered C_3BN ring of the 1*H*-2,1-benzazaborolyl moiety and the potassium atom.

One of the C_3BN rings coordinates to the K(1) ion in an 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 Schmid[11] considering different radii of both alkali metals. In contrast, the interaction between the K(1) atom and the second C_3BN 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 C_3BN rings is supported by distances between K(1) and centroids of the respective C_3BN 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 C_3BN ring are comparable to this lithium compound.[11]

The mechanism of formation of **2** is also of particular interest. Compound **2** may be formed by fast[12] recombination of two carbon centred radicals, formed by reduction of **1** with potassium (Mechanism I in Scheme 1). It is worth 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 Mechanism I (Scheme 1). Despite these facts, the second mechanism (Mechanism II in Scheme 1) came into mind. The appearance of intensive red colour at 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 of *in situ* formation of the potassium salt **3**. Compound **3** can then smoothly react with the present chloroborane **1** resulting in the formation of **2**. To support this presumption, the reaction of isolated **3** with one molar equivalent of **1** was performed and, indeed, it provided a mixture of *rac-RR*/*SS*-**2** and *meso*-**2** in nearly quantitative yield as judged by NMR spectroscopy. This 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 these two mechanisms (I or II) at the moment, but it seems probable that **2** is formed by both of them simultaneously. It is noteworthy that analogous C–C coupling reactions have been recently observed for α-iminopyridyl substituted Ge, Al, Ga, and Zn complexes and lanthanide (Yb, Sm) derivatives of redox active ligands.[15] Compound **3** also readily reacts with simple electrophiles such as MeI or Me_3SiCl; in this case formation of substituted 1*H*-2,1-benzazaboroles **4** and **5** (Scheme 2) was observed. Compounds **4** and **5** were characterized by elemental analysis and ^1H, ^{11}B, ^{13}C, ^{15}N and ^{29}Si NMR spectroscopy (see details in the ESI†).

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

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7 (*a*) Due to the atropisomerism observed in *meso*-2 two signals for CH–N groups were observed in the corresponding ^{1}H, ^{13}C and ^{15}N NMR spectra (see details in the ESI†); (*b*) Two signals should be also observed in the ^{11}B 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 the 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.

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