Boryl Anions

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Lithiumboryl—A Synthon for a Nucleophilic Boryl Anion

*Holger Braunschweig**

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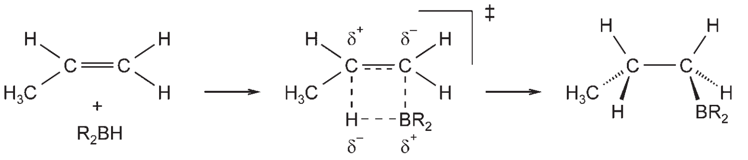
The functionalization of organic substrates by borylation, that is, the attachment of an R_2B group to a carbon atom or a heteroatom, is of fundamental importance for organic and organometallic synthesis. An early milestone in this area was marked by the work of H. C. Brown, who developed the hydroboration of alkenes.[1] The R_2B moiety can be replaced by a wide range of functional groups, thus rendering organoboranes extremely useful reagents for synthetic chemistry.[2–4] Moreover, hydroboration is characterized by a high anti-Markovnikov regioselectivity and a pronounced chemoselectivity, that is, the reaction occurs preferentially at C=O rather than C=C bonds with addition of the boron atom to the oxygen atom.[5–6]

The formation of anti-Markovnikov products requires the approach of a formal hydride to the most substituted carbon atom of the organic substrate, since the latter stabilizes the partial positive charge occurring during the transition state of this concerted reaction most effectively [Eq. (1)]. Hence, both aspects of selectivity associated with conventional (i.e. noncatalyzed) hydroboration provide conclusive proof for a $B^{\delta+}$–$H^{\delta-}$ polarization of the boron–hydrogen bond in boranes and the electrophilic character of the boron center. These findings are in agreement with the slightly higher electronegativity of hydrogen.

In addition to conventional hydroboration an ample range of metal-mediated protocols has been investigated over the past 15 years. In particular, transition-metal-catalyzed hydroboration[7–9] and diboration[10] have been developed into standard procedures for the synthesis of specific organoboranes. Detailed knowledge on boryl and bisboryl complexes,[11–15] which commonly occur as key intermediates in these homogeneous catalysis reactions, has enabled the development of "tailor-made" catalysts. Although transition metals are commonly less electronegative than boron, detailed DFT studies on boryl compexes have revealed that the metal–boron bond is polarized towards the metal (i.e. $M^{\delta-}$–$B^{\delta+}$).[16,17] Consequently, reactions of boryl complexes $[L_xMBR_2]$ as formal synthons for an R_2B^- ion represent extremely rare cases.[18,19] Likewise, the reversed chemoselectivity often observed for the transition-metal-catalyzed hydroboration of alkenones, that is, a distinct preference for the addition of B−H towards the C=C rather than the C=O bond, is supposed to be due to the activation of the C=C bond during the catalytic process and not to the transfer of a formal boryl anion.[20]



(1)

Besides their well-established role in organic synthesis, organoboranes have recently received much attention owing to their particular chemical and electronic properties. Over the past few years, various studies have impressively documented the potential that boron-containing compounds have, for example, as electronic materials, molecular sensors, or conjugated polymers.[21–23]

The increasing importance of boron-containing molecular systems raises the need for new and alternative synthetic approaches to this interesting class of compounds, because borylations commonly rely on reactants that provide a formal R_2B^+ moiety, and hence, are restricted to substrates that readily accept an intrinsically electrophilic boron center. Therefore, a complementary synthon providing a nucleophilic boryl group would be highly desirable. This long-standing goal in boron chemistry,[24] however, is not easily achieved. First of all, boranes most commonly react as strong Lewis acids so as to satisfy their inherent electron deficiency. Hence, attempts to simply deprotonate R_2BH species usually result in the addition of the base to the boron center. Indeed, all corresponding boron-based anions display boron centers with coordination numbers of four or higher, thus precluding any nucleophilicity of the boron center. Furthermore, attempts to obtain boryl anions by reduction of (diorganyl)haloboranes R_2BX (X = halogen) with alkaline metals are commonly hampered by the formation of highly reactive radical species, which lead to the formation of unwanted insertion or hydrogen-abstraction products.[25,26] Electronegative substituents at the bor-

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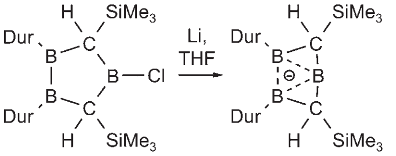
[*] Prof. Dr. H. Braunschweig
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail:
h.braunschweig@mail.uni-wuerzburg.de

on center, in particular amino groups, are believed to stabilize putative boryl anions much more effectively than alkyl groups;[27–29] however, reduction of $(R_2N)_2BX$, especially in the case of $R = Me$, leads to formation of diboranes(4) since small R groups fail to stabilize the $(R_2N)_2B^-$ ion.[30,31]

It is noteworthy that Berndt and co-workers have reported the fully characterized anionic species **1** [Eq. (2)]. This compound, which represents the first carbene analogue of boron, is best described as a bis-homoaromatic system, displaying strong BBB three-centered, two-electron bonds, thus accounting for a coordination number of four for all boron atoms.[32,33]



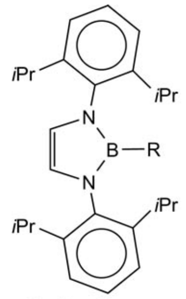
(2)

1; Dur = 2,3,5,6-$C_6Me_4H_4H$

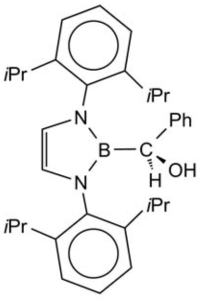
Yamashita, Nozaki, and co-workers have now solved the problem of synthesizing a stable, three-coordinate boryl anion by reduction of the 2-bromo-1,3,2-diazaborole[34] **2** [Eq. (3)].[35]

Suitable single crystals of **3** were obtained from DME solutions, and X-ray spectroscopy revealed the presence of a dimer with Li–B bond lengths of 2.291(6) Å, which are only slightly greater than the sum of the corresponding covalent radii. The elusive boryl anion was made accessible by utilizing the typical N-heterocyclic carbene (NHC) backbone in connection with sterically demanding aryl groups, thereby effectively protecting the reactive site. The NHC framework is well-known from many carbene-type species, not only of carbon[36] but also of silicon,[37] germanium,[38] and gallium,[39] and was, on the basis of various calculations, predicted to stabilize the isoelectronic boryl anion as well.[29,30]

The most notable result of Yamashita's studies is the conclusive proof of the nucleophilic character of the boron center in **3**, which was demonstrated by reactions with representative electrophiles, namely MeOTf, BuCl, and PhCHO. In all cases, a B–C bond with a positively polarized carbon atom was formed, resulting in the final products **4a–c** in average to good yields.

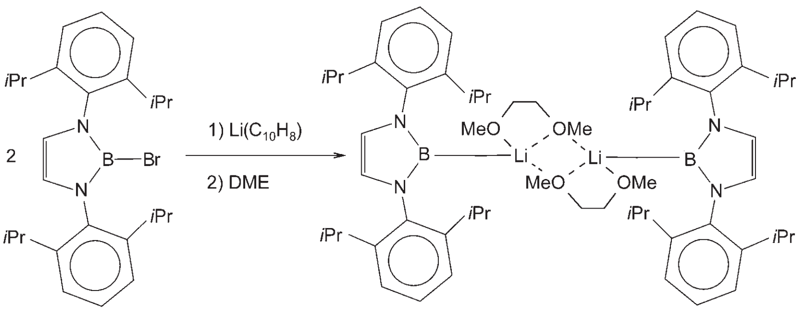


4a, R = Me
4b, R = Bu



4c

The realization of the first boryl anion represents a major achievement in main-group-element chemistry and will have a significant impact on the important area of organoboron chemistry. Future work, both experimental and theoretical, might be directed toward the elucidation of the electronic structure of this novel class of compounds. Earlier theoretical investigations on noncyclic lithioboranes R_2BLi concluded that the negative charge is delocalized over the substituents R (with the exception of the parent species H_2BLi), but nevertheless predicted their interesting potential as nucleophiles.[28] Given the importance of the isoelectronic NHCs in homogeneous catalysis on the one hand,[40] and the electronic properties of boryl ligands, in particular with respect to their distinct *trans* influence on the other hand,[41,42] one might also assume a significant development in the area of metal boryl complexes.



(3)

2

3

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