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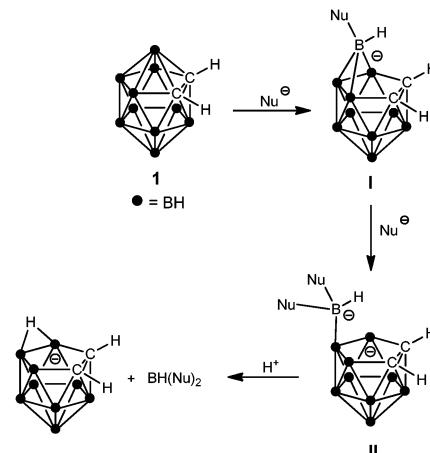
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An unprecedented deboronation reaction of icosahedral carboranes is described, in which a BH group of *o*-carborane is detached from the cage and incorporated into an unusual *nido*-carborane-anellated diazadiborepine ring system.

Icosahedral carboranes form an exciting and highly important class of inorganic cage compounds due to their numerous important applications, including energy storage, optoelectronics, nanomaterials, radiopharmaceuticals, medicine, and boron neutron capture therapy.^{1,2} Deboration, *i.e.* the removal of a vertex from a carborane cage under formation of an anionic *nido*-C₂B₉ cluster, is one of the most important and longest known reactions of icosahedral carboranes.^{3,4} Deboration of *closo*-carboranes is normally achieved by treatment with strong Lewis bases (neutral or anionic) such as fluorides,⁵ alkoxides,^{3b} amines,⁶ or N-heterocyclic carbenes.⁷ Deboration rates have been reported to decrease from *o*- to *p*-carborane.^{5b} According to the generally accepted mechanism (Scheme 1, illustrated for *o*-carborane (**1**)), deboration starts with nucleophilic attack at one of the most positive boron vertices, which is followed by attack of a second nucleophile at the same B atom.⁴

Protonation of the resulting negatively charged *nido*-cluster leads to elimination of BH(Nu)₂ which can undergo further reactions with nucleophiles.^{7,8} For example, in fluoride ion-initiated deboration reactions, the fluoroborate anion HOBF₄⁻ has been detected as monoborane by-product.⁹ On rare occasions, it has been possible to isolate type I (*e.g.* Nu = (Me₂N)₃PNH,^{8a,10} pyridine,^{8b} N-heterocyclic carbene⁷) intermediates, thereby backing the proposed mechanism experimentally. In all these



Scheme 1 Mechanism of the deboronation of *o*-carborane (**1**) with anionic nucleophiles (taken from ref. 4).

intermediates, the BH unit bearing the nucleophile(s) remains attached to the original vertex of the carborane cage.

Recently, carboranyl amidinates, a novel type of *o*-carborane-based chelating ligands, have been discovered in our lab.¹¹ Carboranyl amidinate anions combine the versatile characteristics of carboranes and the widely employed amidinate anions¹² into one system. The general synthetic route to lithium carboranyl amidinates involves *in situ*-preparation of monolithio-*o*-carborane, followed by treatment with a *N,N'*-diorganocarbodiimide, R-N=C=N-R (R = ¹Pr, cyclohexyl (Cy)) (Scheme 2). Quite unique and typical for the new carboranyl amidinates is the *C,N*-chelating coordination mode while retaining an NH-functionality.¹¹

Following our initial report, the chemistry of carboranyl amidinates has been rapidly extended to various main group element derivatives as well as early and late transition metal complexes, some of them showing promising catalytic activities.¹³ It was also demonstrated that the carboranyl amidinate system can be modified by introducing thiolate or selenolate functional groups or by designing novel *nido*-carboranyl amidinate ligands.¹⁴ Thus far, the synthetic protocol leading to carboranyl amidinates

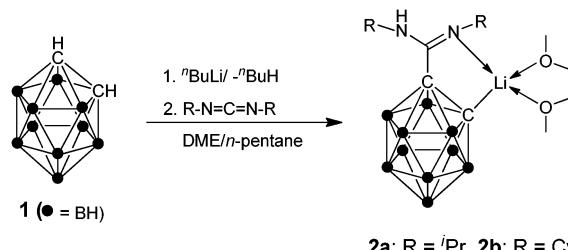
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† Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday.

‡ Electronic supplementary information (ESI) available: Detailed experimental and analytical data as well as full crystallographic data for **4a**, **4b**, and **5**. CCDC 1016818–1016820. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc06261b



Scheme 2 Synthesis of lithium-*o*-carboranyl amidinates from *o*-carborane (**1**).

(Scheme 2) has always been limited to the use of *o*-carborane (**1**) as starting material. This led us to the question of whether a similar chemistry could be developed around *m*-carborane (**3**). Here we report about the highly surprising and unexpected outcome of initial experiments in that direction.

m-Carborane (**3**) was mono-metallated in the usual manner¹¹ using 1 equiv. of *n*-butyllithium followed by treatment of the intermediate lithio-*m*-carborane with 1 equiv. of *N,N'*-diisopropylcarbodiimide. Crystallization from either THF or diethyl ether afforded large, colorless single crystals in estimated yields around 30–40%. However, under these conditions, fairly large amounts of unreacted *m*-carborane could be detected in the reaction mixtures. Initially, analytical and spectroscopic data did not allow unambiguous elucidation of the isolated products. Fortunately, in both cases well-formed single crystals were readily available. X-ray diffraction studies revealed the presence of the unexpected products **4a** and **4b** as illustrated in Scheme 3. Accordingly, the outcome of these reactions can be described as follows: Unlike the formation of carboranyl amidinates from *o*-carborane (**1**) according to Scheme 2, *in situ*-prepared monolithio-*m*-carborane reacts with 2 equiv. of *N,N'*-diisopropylcarbodiimide. This accounts for the presence of unreacted *m*-carborane in the original 1:1 reaction mixture. Instead of a simple addition of the carborane anion to the central carbodiimide carbon alone, subsequent deboronation occurs and a BH unit is detached from the carborane cage. The following step is unprecedented in the chemistry of icosahedral carboranes, in that the BH unit is not eliminated as a monoborane by-product but retained in a newly formed seven-membered diazadiborepine ring system which is assembled in the periphery of the resulting *nido*-carborane cage through coupling of two carbodiimides. The result is the formation of an unusual *nido*-carborane-anellated diazadiborepine ring system which is isolated in the form of its lithium salt solvated

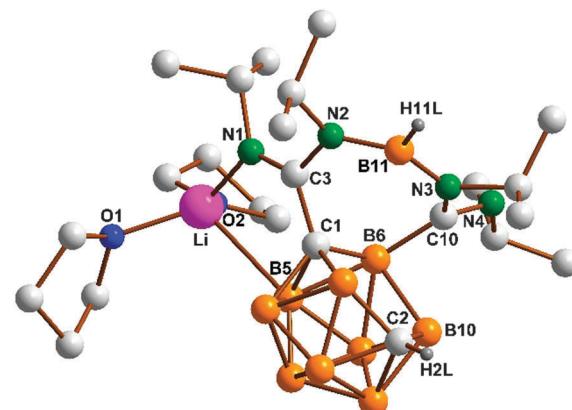
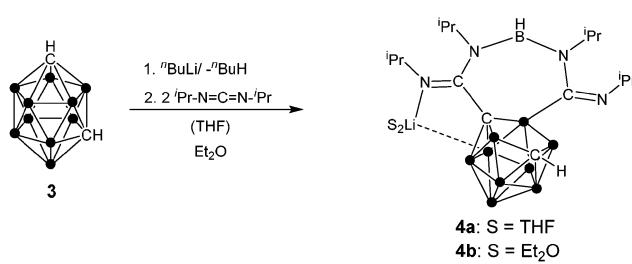
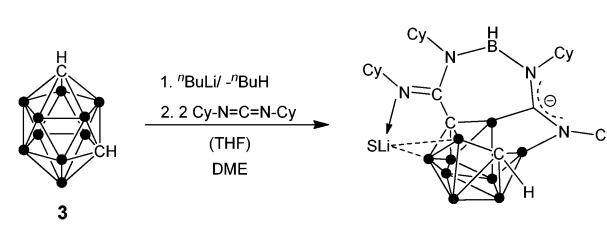


Fig. 1 Molecular structure of **4a**. Selected bond lengths [Å] and angles [°]: N1–C3 1.2891(19), N1–Li 1.999(3), N2–C3 1.4106(19), N2–B11 1.437(2), N3–B11 1.418(2), N3–C10 1.427(2), N4–C10 1.2773(19), C1–C3 1.491(2), C10–B6 1.673(2), B5–Li 2.710(3), N1–C3–N2 126.41(14), N1–C3–C1 120.42(14), N2–C3–C1 113.02(12), N3–B11–N2 130.11(15).

with either THF (**4a**) or diethylether (**4b**) after recrystallization from the respective solvent (Scheme 3).

Fig. 1 displays the molecular structure of the THF-adduct **4a**. The molecular structure of **4b** differs only in the coordinated solvent at Li (see ESI[‡] for full structural details of both **4a** and **4b**). The newly formed seven-membered diazadiborepine ring (C1–C3–N2–B11–C10–B6) is anellated to a B–C bond of the *nido*-carborane cage. With C3–N1 1.2891(19) Å and C10–N4 1.2773(19) Å the two exocyclic C=N bonds clearly have double bond character, whereas the bonds within the ring are single bonds (C3–N2 1.4106(19), C10–N3 1.427(2) Å). Lithium interacts with B5 (2.710(3) Å) and N1 (1.999(3) Å), thereby forming a five-membered C_2BNLi chelate ring. Two THF ligands complete the distorted tetrahedral coordination geometry around Li. After the crystal structures of **4a** and **4b** had been unequivocally established, it was shown that by using the proper 1:2 stoichiometry, the reaction reproducibly provided **4a** and **4b** in moderate (**4b**: 51%) to good (**4a**: 67%) isolated yields. Moreover, the compounds were thoroughly characterized by spectroscopic and analytical methods (see ESI[‡]).

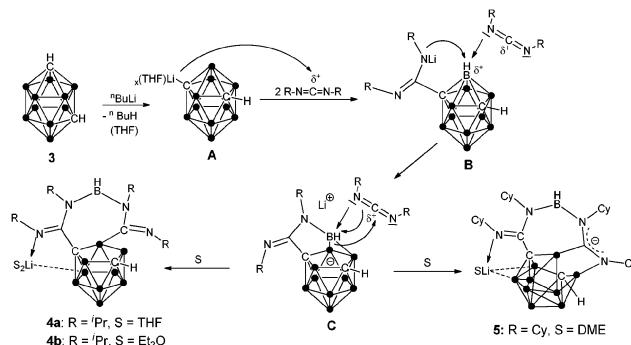
In a subsequent experiment it was shown that the analogous reaction with *N,N'*-dicyclohexylcarbodiimide proceeds in the same manner (Scheme 4). In this case, X-ray quality single crystals could be obtained from DME (=1,2-dimethoxyethane). Full spectroscopic characterization of the DME adduct **5** already indicated a similar outcome of this reaction as with *i*Pr–N=C=N–*i*Pr.

Scheme 3 Formation of the polycyclic diazadiborepines **4a** and **4b** from *m*-carborane.Scheme 4 Formation of the polycyclic diazadiborepine **5** from *m*-carborane.

Once again, deboronation and carbodiimide coupling under formation of a diazadiborepine had occurred, underlining the fact that this novel reaction is quite general in nature. The NMR spectra of **5** (^1H , ^7Li , ^{11}B , ^{13}C) showed far-reaching similarity with those of **4a** and **4b** (apart from the different substituents). For example, in the ^1H NMR spectrum of **5**, the BH unit in the seven-membered ring gives rise to a broad singlet at δ 4.03 ppm. However, a single-crystal X-ray diffraction study of **5** revealed interesting structural differences (Fig. 2 and ESI[‡]). One of these differences is that Li interacts with two cage boron atoms (Li–B5 2.663(3), Li–B6 2.637(3) Å). Moreover, the electron distribution within one of the amidinate moieties (N3–C4–N4) differs significantly from that in **4a** and **4b**. Whereas the diazadiborepine ring in **4a** and **4b** comprises two exocyclic C≡N double bonds (*vide supra*), there is a bond between N4 and B10 in **5** which leads to a seven-membered open face of the *nido*-carborane cluster. As a consequence, bond delocalization in the amidinate unit is observed which results in equilibrated C–N distances (C4–N3 1.3400(16) and C4–N4 1.3178(16) Å). Whether or not these structural differences are a consequence of the different steric demand of the substituents (isopropyl *vs.* cyclohexyl) remains speculative at this stage.

Based on the established knowledge about carboranyl-amidinate formation¹¹ and deboronation reactions⁴ it appears reasonable to propose the mechanism illustrated in Scheme 5 for the formation of the novel diazadiborepines **4** and **5**. Monolithiation of *m*-carborane (**3**) with 1 equiv. of *n*-butyllithium affords intermediate **A** which will add to the carbodiimide carbon to afford carboranyl amidinate **B**. B–N bond formation could then activate the BH unit in the hydridoborate intermediate **C** for deboronation and diazadiborepine formation initialized by the second equivalent of carbodiimide.

In summarizing the results reported here, we have discovered an unprecedented deboronation reaction of icosahedral carboranes



Scheme 5 Proposed mechanism for the formation of the polycyclic diazadiborepines **4a**, **4b**, and **5** from *m*-carborane.

in which a BH group is detached from the cage and incorporated into a *nido*-carborane-anellated diazadiborepine ring. The reactions illustrated in Schemes 3 and 4 clearly open up a new field of carborane chemistry. Future work will show if and how the readily accessible lithium salts **4** and **5** can be employed as starting materials for novel carborane-based polycycles incorporating other main group or transition metals.

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Notes and references

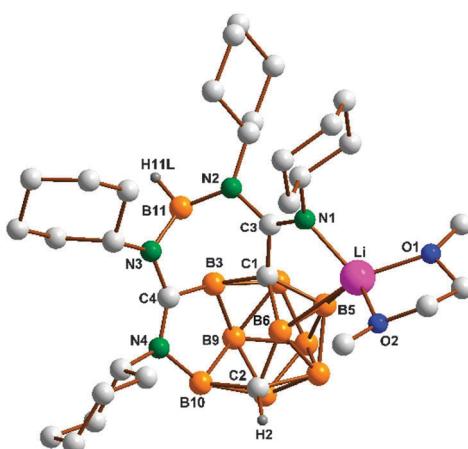


Fig. 2 Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: B3–C4 1.5438(18), B5–Li1 2.663(3), B6–Li1 2.637(3), B10–N4 1.5440(17), B11–N2 1.4756(17), B11–N3 1.5438(17), Li1–N1 2.011(2), N1–C3 1.2894(16), N2–C3 1.4063(15), N4–C4 1.3178(16), C4–N3 1.3400(16), C1–C3 1.4989(16); C4–B3–C1 104.68(10), N2–B11–N3 118.36(11), N4–C4–N3 137.04(12), C4–N3–B11 106.11(10), C3–N2–B11 118.46(10).

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