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Unprecedented Formation of Polycyclic Diazadiborepine Derivatives through Cage Deboronation of *m*-Carborane†

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An unprecedented deboronation reaction of icosahedral carboranes is described, in which a BH group of *m*-carborane is detached from the cage and incorporated into an unusual
10 ***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
15 neutron capture therapy.[1,2] Deboronation, *i.e.* the removal of a vertex from a carborane cage under formation of an anionic *nido*-C_2B_9 cluster, is one of the most important and longest known reactions of icosahedral carboranes.[3,4] Deboronation of *closo*-carboranes is normally achieved by treatment with strong Lewis
20 bases (neutral or anionic) such as fluorides,[5] alkoxides,[3b] amines,[6] or *N*-heterocyclic carbenes.[7] Deboronation 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**)), deboronation starts with nucleophilic attack at one
25 of the most positive boron vertices, which is followed by attack of a second nucleophile at the same B atom.[4]
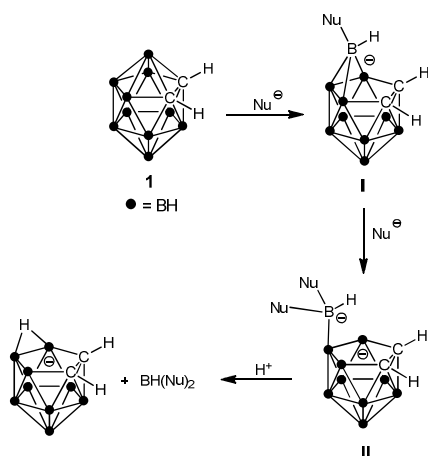

Scheme 1 Mechanism of the deboronation of *o*-carborane (**1**) with anionic nucleophiles (taken from Ref. 4).

30 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-initialized deboronation reactions, the fluoroborate anion $HOBHF_2^-$ has been

detected as monoborane by-product.[9] On rare occasions, it has
35 been possible to isolate type I (*e.g.* Nu = $(Me_2N)_3PNH$,[8a,10] pyridine,[8b] *N*-heterocyclic carbene[7]) intermediates, thereby backing the proposed mechanism experimentally. In all these intermediates, the BH unit bearing the nucleophile(s) remains attached to the original vertex of the carborane cage.
40 Recently, carboranylamidinates, a novel type of *o*-carborane-based chelating ligands, have been discovered in our lab.[11] Carboranylamidinate anions combine the versatile characteristics of carboranes and the widely employed amidinate anions[12] into one system. The general synthetic route to lithium
45 carboranylamidinates involves *in situ*-preparation of monolithio-*o*-carborane, followed by treatment with a *N,N'*-diorganocarbodiimide, R-N=C=N-R (R = *i*Pr, cyclohexyl (Cy)) (Scheme 2). Quite unique and typical for the new carboranylamidinates is the *C,N*-chelating coordination mode
50 while retaining an NH-functionality.[11]
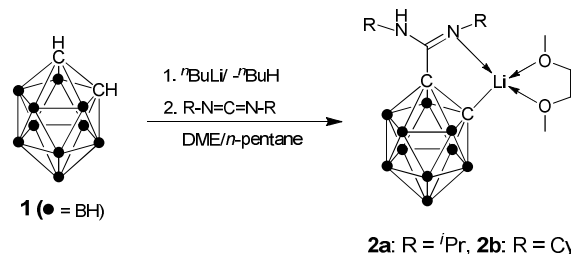
Scheme 2 Synthesis of lithium-*o*-carboranylamidinates from *o*-carborane (**1**).

Following our initial report, the chemistry of
55 carboranylamidinates 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 carboranylamidinate system can be modified by introducing thiolate or selenolate
60 functional groups or by designing novel *nido*-carboranylamidinate ligands.[14] Thus far, the synthetic protocol leading to carboranylamidinates (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
65 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-metalated in the usual manner[11] 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
5 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.
10 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 carboranylamidinates from *o*-
15 carborane (**1**) according to Scheme 2, *in situ*-prepared monolithio-*m*-carborane reacts with *2 equiv.* of *N,N'*-diiso-propylcarbodiimide. 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
20 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
25 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 with either THF (**4a**) or diethylether (**4b**)
30 after recrystallization from the respective solvent (Scheme 3).
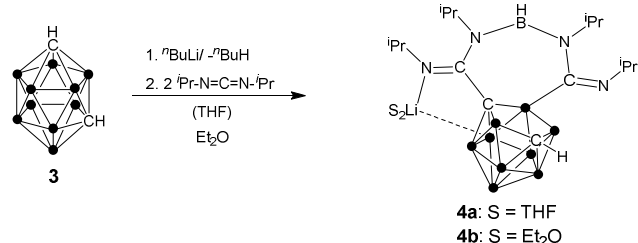
Scheme 3. Formation of the polycyclic diazadiborepines **4a** and **4b** from *m*-carborane.

Figure 1 displays the molecular structure of the THF-adduct **4a**. The molecular structure of **4b** differs only in the coordinated
35 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
40 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
45 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
50 and analytical methods (see ESI).
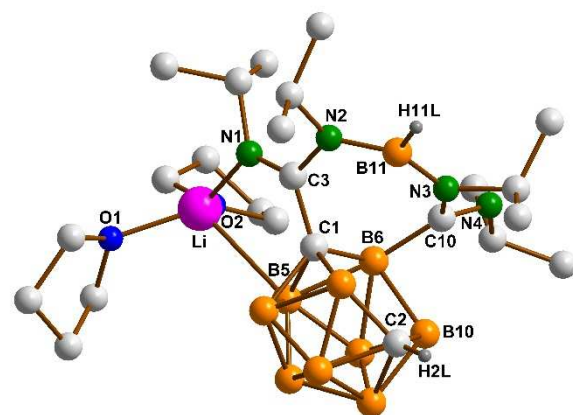
Figure 1. Molecular structure of **4a**. Selected bond lengths [Å] and angles [°]: N1-C3 1.2891(19), N1-Li 1.999(3), N2-C3 1.4106(19), N2-B11 1.437(2), N3-B11 1.418(2), N3-C10 1.427(2), N4-C10 1.2773(19), C1-C3 1.491(2), C10-B6 1.673(2), B5-Li 2.710(3); N1-C3-N2 126.41(14), N1-
55 C3-C1 120.42(14), N2-C3-C1 113.02(12), N3-B11-N2 130.11(15).

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).
60 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.
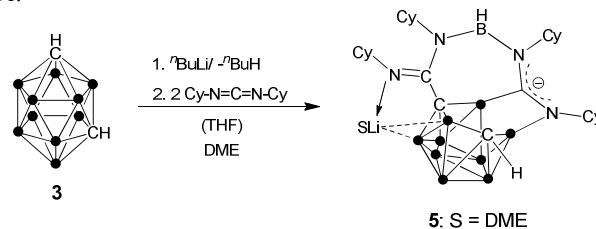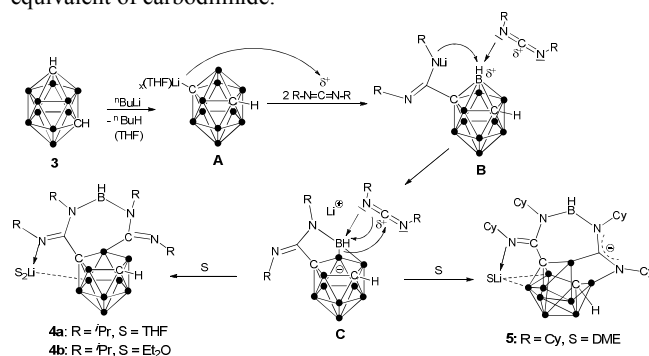

Scheme 4. Formation of the polycyclic diazadiborepine **5** from *m*-
65 carborane.

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** (^{1}H, ^{7}Li, ^{11}B, ^{13}C) showed far-reaching similarity
70 with those of **4a** and **4b** (apart from the different substituents). For example, in the ^{1}H 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
75 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
80 (*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
85 structural differences are a consequence of the different steric demand of the substituents (isopropyl *vs.* cyclohexyl) remains speculative at this stage.
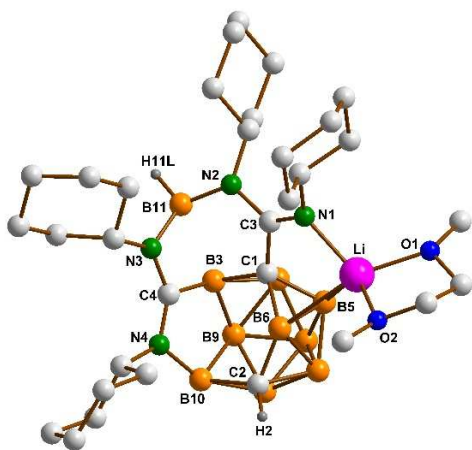
Figure 2. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: B3-C4 1.5438(18), B5-Li1 2.663(3), B6-Li1 2.637(3), B10-N4 1.5440(17), B11-N2 1.4756(17), B11-N3 1.5438(17), Li1-N1 2.011(2), N1-C3 1.2894(16), N2-C3 1.4063(15), N4-C4 1.3178(16), C4-N3 1.3400(16), C1-C3 1.4989(16); C4-B3-C1 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).

Based on the established knowledge about carboranylamidinate formation[11] and deboronation reactions[4] 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 carboranylamidinate **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.

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

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