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Deboronation and Deprotonation of *ortho*-Carborane with N-Heterocyclic Carbenes

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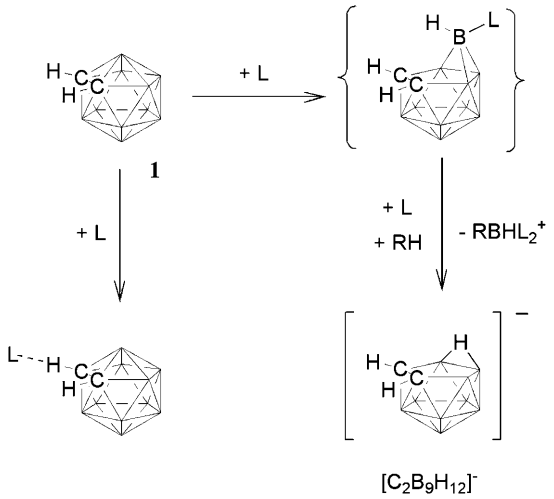
As *ortho*-carborane ($1,2\text{-}C_2B_{10}H_{12}$, **1**) contains acidic hydrogen atoms at the cage carbons, hydrogen-bond adducts have been isolated in the solid state with some bases (Scheme 1).[1,2] The carborane has long been known to be susceptible to strong Lewis bases such as alkoxides,[3] amines[4] and fluorides[5] to form salts of the anion *nido*-7,8-$C_2B_9H_{12}^-$. The initial step in the latter reactions is the attack of a base molecule on the most electropositive boron atom (bonded to both carbon atoms) of **1**.[6] The next step involves cleaving a boron atom from the cluster with a second base molecule combined with a proton from the base (e.g., primary or secondary amines)[7] or from the solvent (e.g., alcohols, water).[8] The process of removing a boron atom from the carborane cluster framework is described as 'deboronation' and does not necessarily result in complete detachment of a boron atom from a carborane molecule. N-Heterocyclic carbenes (NHCs) as neutral bases are stronger than amines and phosphines,[9] so reactions of *ortho*-carborane **1** with NHCs would be expected to give deboronated products as imidazolium salts of the anion *nido*-7,8-$C_2B_9H_{12}^-$.



Scheme 1. Typical reactions of *ortho*-carborane **1** with base L. Each unmarked cluster vertex represents BH.

The reaction of the NHC 1,3-dimethylimidazol-2-ylidene (**2**) with *ortho*-carborane (**1**) in a 3:1 ratio was carried out in dry THF (Scheme 2).[10] A carborane/base ratio of 1:2 or lower[3–8,11] is typically used for the deboronation of *ortho*-carborane. After two hours at ambient temperature, the solvents were removed in vacuo and isopropanol was added. The precipitate formed was filtered and recrystallised from dichloromethane. The ^{11}B NMR data of the product revealed similar peak patterns to neutral 10-L-7,8-$C_2B_9H_{11}$ derivatives,[12,13] but with an extra boron peak. The ^1H NMR spectrum showed expected peaks corresponding to two NHC groups and a peak at $\delta = -3.23$ ppm characteristic of a bridging B-H-B proton. Elemental analyses and an accurate mass cut-off of m/z 336.324 are in agreement with the formula corresponding to a 1:2 carborane–carbene adduct.[10] X-ray crystallography of the stable solid confirmed it to be the new 1:2 adduct **3** (Figure 1). Similarly from 1-ethyl-3-methylimidazol-2-ylidene (**4**) and *ortho*-carborane, a 1:2 carborane–carbene adduct **5** was obtained and its crystal structure was determined (Figure 1).[10] If a 1:1 carborane/carbene ratio is used instead of 1:3 in the preparation of **3** and **5**, half of the starting carborane is recovered in the work up for both reactions.

Compounds **3** and **5** are the first examples of 1:2 adducts from *ortho*-carborane and nucleophiles. A closely related

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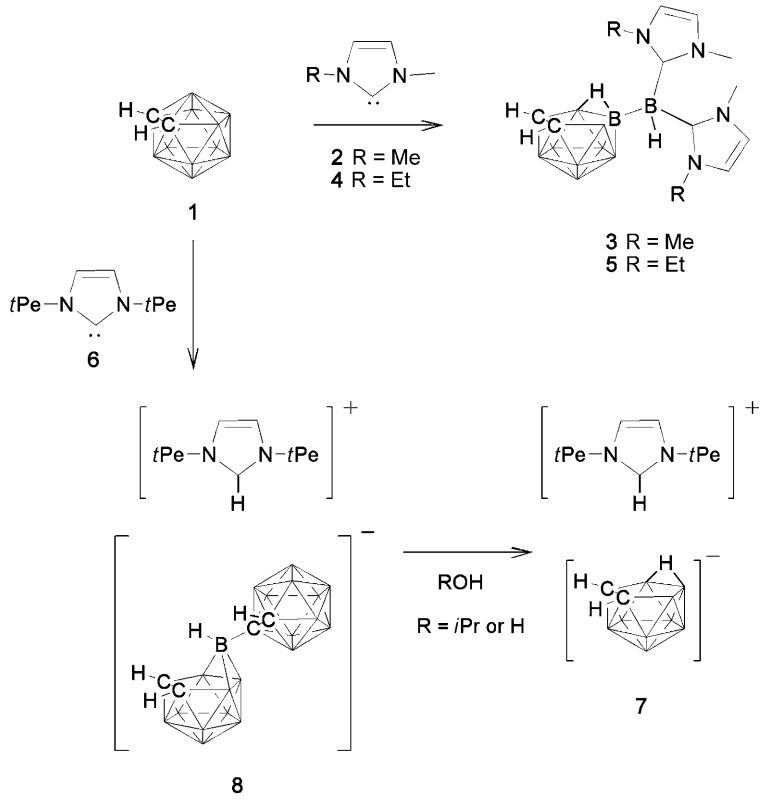


Scheme 2. Reactions of NHCs with *ortho*-carborane **1**.

1:2 adduct has been reported from the reaction of *C*-bromocarborane (1-Br-1,2-$C_2B_{10}H_{11}$) with neat pyridine.[14] It was suggested that the brominated 1:2 adduct is an intermediate to the formation of a pyridinium salt of a brominated 7-Br-7,8-$C_2B_9H_{11}^-$ anion by reacting with neat pyridine under more forcing conditions. However, the balanced equation for this reaction involving cleavage of the boron atom from the cluster requires an extra proton from an unidentified source.

The carbene adducts **3** and **5** are stable in air and in common solvents. No evidence for *nido*-7,8-$C_2B_9H_{12}^-$ ion formation was found in the presence of protic solvents, such as water and alcohols. In DMSO, a portion of adduct **5** slowly changes to what appears to be an equilibrium mixture of **5** and an 11-vertex carborane species as identified by NMR spectroscopy. The latter is tentatively identified as the 9-substituted analogue of **5**. Somewhat more complex NMR spectra were observed for **3** in DMSO, where a third species was seen. The boron NMR spectra viewed are remarkably like those of the thermal rearrangements of 10-R_2S-7,8-$C_2B_9H_{11}$ (R = alkyl group), where 9-R_2S-7,8-$C_2B_9H_{11}$ and $C_2B_9H_{11}$ are formed.[15]

The C_2B_9-cage cluster frameworks in the crystal structures of **3** and **5**[10] are similar to those in other 10-L-7,8-$C_2B_9H_{11}$ compounds[12,15] with bridging hydrogen atoms between B9 and B10 on the open face. There are few structural examples involving a boron atom attached to two carbene groups with B–C(carbene) bond lengths of 1.60–1.64 Å,[16] which are similar to the values of 1.634(2) and 1.614(2) Å determined for **5**.

When a more bulky NHC, 1,3-di-*tert*-pentylimidazol-2-ylidene (**6**), was used, after work up involving isopropanol, the imidazolium salt of *nido*-7,8-$C_2B_9H_{12}^-$ (**7**) and recovered *ortho*-carborane were isolated (Scheme 2). The recovery of the starting carborane was surprising, given that a three-fold excess of the base was used. The material obtained after the reaction under air- and moisture-free conditions was then examined by NMR spectroscopy and mass spectrometry.[10] The material, which was soluble in THF, was identified as the imidazolium salt of a new two-cage anion, [12-(1′-{1′,2′-$C_2B_{10}H_{11}$})-7,8-$C_2B_{10}H_{12}$]$^-$ (**8**) (Scheme 2, Figure 2). The boron NMR spectrum of the two-cage anion reveals a doublet at $\delta = +37$ ppm corresponding to the unique boron attached to the carbon of the second cage (Figure 3). The accurate mass cut-off of *m*/*z* 291.367 observed, is in agreement with the formula of the anion $[C_4B_{20}H_{23}]^-$. This anion is extremely air and moisture sensitive. Unlike the stable adducts **3** and **5**, the salt **8** is rapidly converted to the salt of the *nido*-7,8-$C_2B_9H_{12}^-$ ion **7** and *ortho*-carborane in a 1:1 ratio after exposure to traces of water.

The optimised geometry of the two-cage anion **8** has a 12-vertex 28 skeletal electron *nido* cluster linked to a 12-vertex 26 skeletal electron *closo* cluster through a C–B bond. This framework is similar to the crystal structure of a related anion with phenyl groups attached to C2′ and C7.[17] The rare *nido*-carborane cluster geometry in **8** is close to the experimental geometry observed for the 1:1 $HNP(NMe_2)_3$–carborane adduct.[6,10]

Computed gas-phase acidities of the compounds used in this study reveal that the carbene **6** is as basic as the more common NHC 1,3-dimesitylimidazol-2-ylidene (**9**).[10,18,19] Carbenes **2** and **4** are somewhat less basic than **6** and **9**. All carbenes are considerably more basic than the iminophosphorane $HNP(NMe_2)_3$. The latter base deboronates **1** easily[6] and it would be expected that the other carbenes would also deboronate **1**.

Table 1 shows the relative energies in kcal mol^{-1} of the sum of one carborane and two carbene molecules as 1:1 and 1:2 hydrogen-bond adducts (**A** and **B**, respectively) and 1:1 and 1:2 B–C adducts (**C** and **D**, respectively).[10] It is clear that the 1:2 adduct **D** from **1** and **2** is energetically favoura-

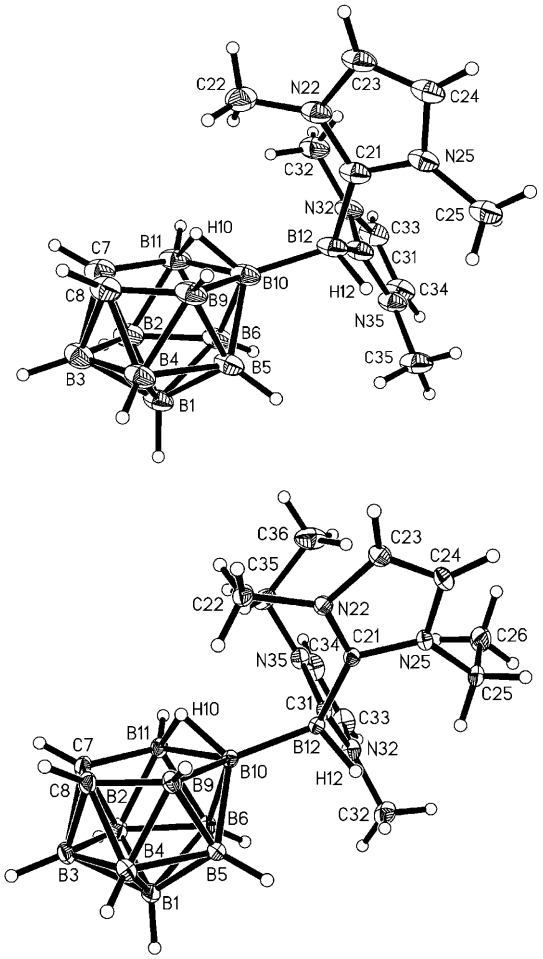


Figure 1. X-ray structures of **3** (top) and **5** (bottom) with 30% probability ellipsoids. Selected bond lengths [Å] for **5**: B10–B12 1.753(2), C7–C8 1.550(2), C8–B9 1.626(2), B9–B10 1.885(2), B10–B11 1.843(2), B12–C21 1.634(2), B12–C31 1.614(2).

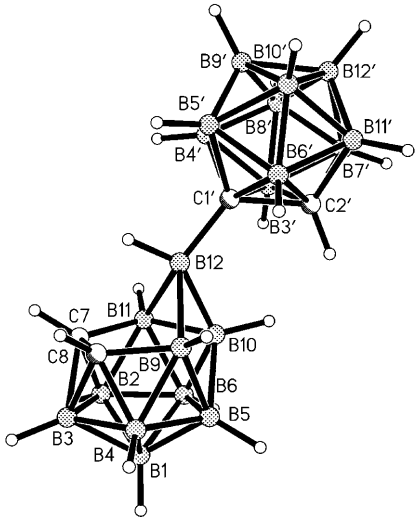


Figure 2. Optimised geometry of the anion in **8**. Selected bond lengths in [Å]: B10–B12 1.716, C7–C8 1.530, B9–B12 2.019, B11–B12 2.032, B12–C1′ 1.645, C1′–C2′ 1.651.

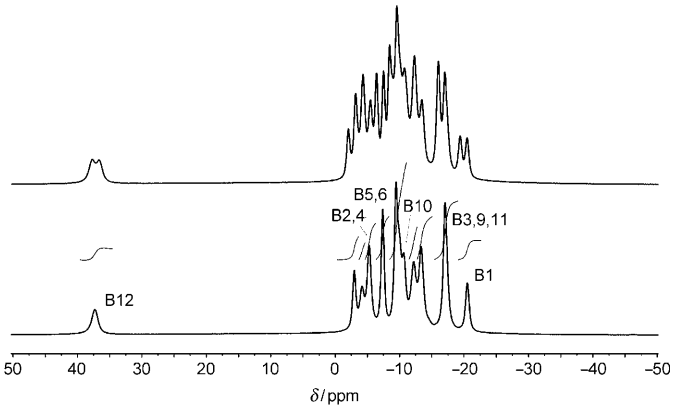
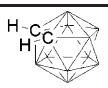
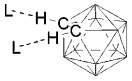
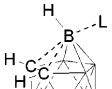
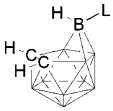
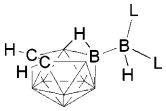


Figure 3. ^{11}B (top) and $^{11}B\{^1H\}$ (bottom) NMR spectra for **8**. Unlabelled peaks in the $\delta = -3$ to -14 ppm region correspond to the boron atoms B3′–B12′.[10]

Table 1. Comparison of computed relative energies [kcal mol^{-1}] for 1:2 carborane **1**–nucleophile L adducts.

			L		
			2	**6**	**10**
		+ 2L	0.0	0.0	0.0
A		+ L	−9.9	−6.9	−13.4
B			−20.1	−14.4	7.3
TS		+ L	12.0	23.1	2.1
C			−13.4	4.9	−29.7
D			−38.4	29.7	2.2

ble, whereas the 1:2 adduct **D** from **1** and **6** is not favourable. These computations are in accordance with our experimental observations.

The first stage of the deboronation process is the attack of one base molecule on the most electropositive boron atom to form the 1:1 carbene–carborane adduct **C** comparable to the structurally characterised $HNP(NMe_2)_3$–carborane adduct.[6] Table 1 lists the energies for geometries of the transition states **TS** for the formation of the 1:1 B–C adducts **C** from **1** and the carbene.[10,20] A large energy barrier of 23.1 kcal mol^{-1} for the formation of the 1:1 B–C adduct **C** from **1** and **6** is due to the bulky pentyl groups hindering the formation of the carbene C–B bond in the initial step of the

deboronation process. The pathway from a 1:1 adduct with the second carbene **2** to the 1:2 adduct **3** is less straightforward, since there is no obvious route from the cluster containing an *endo*-BHL group (**C**) and L to the cluster containing an *exo*-BHL_2 group (**D**).

The deprotonation process in the reaction of **1** with the bulky carbene **6** must take place as the geometry of the two-cage anion in **8** suggests formation of a carborane anion, $C_2B_{10}H_{11}^-$ **10**, as an intermediate. The anion **10** then attacks the electropositive boron of a second carborane molecule.[21] The two-cage formation from **1** and **10** is computationally favourable (Table 1). Two optimised geometries involving cluster C–H···C(carbene) interactions are found for **1** and **6**, where the hydrogen-bonded adduct **A** is more stable than the imidazolium salt of $C_2B_{10}H_{11}^-$ by 13.3 kcal mol^{-1}. These results indicate that the imidazolium salt of $C_2B_{10}H_{11}^-$ from **1** and **6** is likely to exist in solution, but rapidly reacts with a second molecule of **1**. The imidazolium salt (Figure 4) contains a significant imidazolium H···C(carborane) interaction with a distance of 3.29 Å.

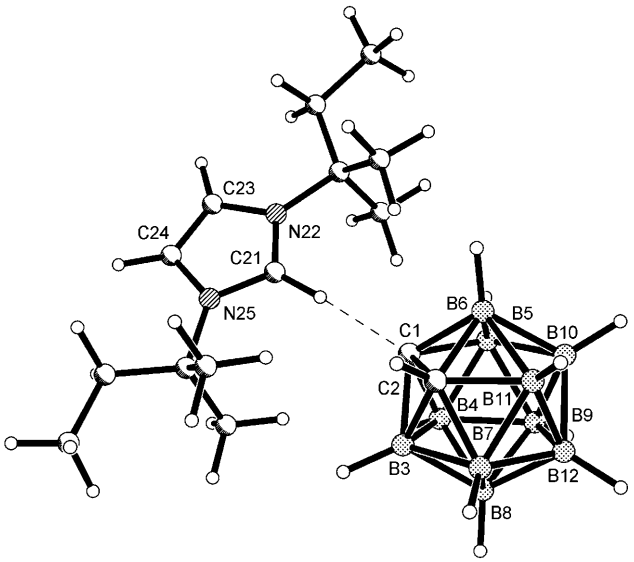


Figure 4. Optimised geometry of the 1,3-di-*tert*-pentylimidazolium salt of $[C_2B_{10}H_{11}]^-$. This salt is likely to react with a second molecule of *ortho*-carborane to form the salt **8**.

The bulky nature of the bases **6** and **10**, combined with the absence of a proton in the base and solvent (THF), inhibit formation of the *nido*-7,8-$C_2B_9H_{12}^-$ anion or a 1:2 adduct, which results in isolation of **8**. The possible formation of a 1:2 two-cage adduct from **8** and a less-bulky, non-protic nucleophile L′ will be investigated in the future to give insight into the pathway from the *endo*-BHL group in the 1:1 B–C adduct **C** and L′ to the *exo*-BHLL′ group in the 1:2 B–C adduct **D**.

The $[C_2B_{10}H_{11}]^-$ ion **10** has not been structurally determined as a weakly-coordinating (′discrete′) anion, but has been tentatively characterised as salts with organic cations.[22] The sodium salt $NaC_2B_{10}H_{11}$, which may contain the ′discrete′ anion **10**, is proposed to be formed from Na and 1,2-$C_2B_{10}H_{12}$ in liquid ammonia at −40 °C.[23] In electrochemical studies of **1**, anion **10** has been suggested to be formed on reduction.[24] This anion would not be expected to be isolated as a weakly-coordinating (′discrete′) anion since it contains a ′bare′ C vertex.[25] The acidic hydrogen atoms in *ortho*-carborane (**1**) are easily replaced with alkyllithium or alkylmagnesium chlorides to form *C*-lithiocarboranes or *C*-alkylmagnesiocarboranes but their crystal structures do not contain ′discrete′ $[C_2B_{10}H_{11}]^-$ anions.[26] NMR data for a lithiocarborane ($LiC_2B_{10}H_{11}$ in THF) are reported here for the first time despite many literature methods involving *C*-lithiocarboranes as precursors to a vast array of carborane derivatives. The observed data are in good agreement with NMR computations for $(thf)_3LiC_2B_{10}H_{11}$ but they are not in good agreement with computed values for the ′discrete′ anion $[C_2B_{10}H_{11}]^-$ (**10**). Salts of the ′discrete′ anion **10** reported previously are unlikely to be isolated.[22]

Many nucleophiles deboronate *ortho*-carborane to give salts of the 7,8-$C_2B_9H_{12}^-$ anion in high yields with the loss of a boron atom, but NHCs do not. Reactions of NHCs with *ortho*-carborane give previously unknown carborane compounds where all boron atoms are retained. Depending on the NHC used, either deboronation takes place to give a 1:2 carborane–carbene adduct or deprotonation occurs to give an imidazolium salt of a two-cage anion. These developments give insights into the deboronation process with *ortho*-carborane and the highly reactive $C_2B_{10}H_{11}^-$ anion. New 1:2 adducts are expected from many other NHCs and carborane derivatives. They are potential precursors to novel metallacarboranes, thus, opening up a new field of carborane–carbene chemistry.

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Keywords: cage compounds · carboranes · cluster compounds · N-heterocyclic carbenes

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