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Communication

Beyond the Hawthorne Reaction: Li^+ Induced Thermal Dehydrocoupling of *closo*-10-vertex Carborane Anions

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ABSTRACT: In the 1970s Hawthorne reported an electrochemical dehydrocoupling reaction of the *closo*-carborane anion $[HCB_9H_9^{1-}]$ **1** to form the biscarborane $[C_2B_{18}H_{18}^{2-}]$ **2**. In this Communication we show that the said "Hawthorne Reaction" can be achieved thermally and that it tolerates C-butylation. The new compound $\mathbf{2}_{butyl}$ was fully characterized by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopies, high-resolution mass spectrometry, and single-crystal X-ray diffraction. One interesting caveat is that **2** or $\mathbf{2}_{butyl}$ only form thermally when they are salts of Li^+ and not NEt_4^+, Na^+, K^+, or Cs^+. This observation means that Li^+ in some way facilitates this process, introducing a new kind of Li^+ effect.

In 1967 Knöth reported the synthesis of the first *closo*-10-vertex $[HCB_9H_9^{1-}]$ carborane anion **1**.[1] This molecule, as well as its 12-vertex cousin $[HCB_{11}H_{11}^{1-}]$ and their neutral analogues and derivatives,[2−7] have found a variety of applications, including in medicine,[8−10] catalysis,[11−16] and electrolyte design[17−22] and as building blocks for a variety of molecular architectures.[23−26] The anionic carborane clusters and their isoelectronic all boron cousins are well-known for their unusual stability in both a chemical and electrochemical sense as well as their weak coordinative ability when halogenated. Chris Reed elegantly demonstrated this latter property by using such carborane and boron cluster anions to isolate a plethora of bottleable reactive carbo- and other main group cationic species of fundamental interest.[27−30] In 1973, Hawthorne reported[31] a new kind of reaction to form biscarboranes, namely, the electrochemical dehydrocoupling (E_{ox} = +1.95 V vs. SCE) of **1** to form the B−B linked dimer **2**, $[C_2B_{18}H_{18}^{2-}]$ (Figure 1). Reed invoked this sort of reaction to

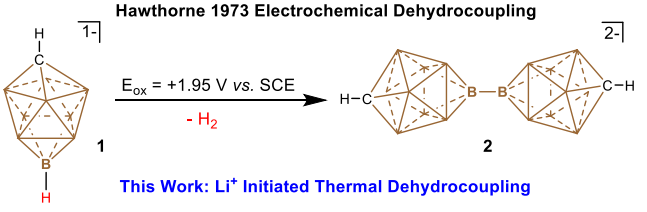

Figure 1. Hawthorne reaction: B−H dehydrocoupling of the $[HCB_9H_9^{1-}]$ anion. Unlabeled vertices = B−H.

explain the instability of trityl salts of $[HCB_{11}H_{11}^{1-}]$,[32] which we later showed was in fact not a dimerization reaction but rather an electrophilic arylation of the cage.[33] Herein we report that Hawthorne's electrochemical dehydrocoupling of **1** and a C-alkylated derivative $\mathbf{1}_{butyl}$ can occur thermally. Very interestingly, these reactions only occur with Li^+ salts, and not NEt_4^+, Na^+, K^+, or Cs^+ analogues. This observation indicates that somehow Li^+ facilitates this kind of reaction, thus introducing a new kind of Li^+ effect.

While exploring the thermal desolvation of Li^+ carborane salts for ligand design and battery applications, we noticed that the C-butylated derivative of **1**, $\mathbf{1}_{butyl}$, begins to decompose at 195 °C under high vacuum over a period of 5 days. This decomposition was surprisingly clean and primarily formed a single new compound that displays similar local C_{4v} symmetry compared to $\mathbf{1}_{butyl}$ (Figure 2). The ^{11}B NMR also indicated a

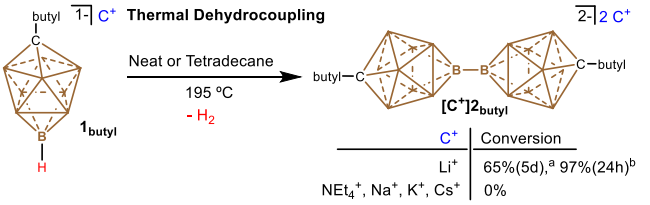

Figure 2. Thermal B−H dehydrocoupling. [a]Neat; [b]0.15 M tetradecane solution.

downfield shift in the boron atom antipodal to carbon by 13 ppm and the lack of B−H coupling indicates that a substitution reaction of some sort occurred (Figure S47).

After salt metathesis with CsCl in water, the new compound was separated from the residual starting material and other minor impurities due to its poor water solubility. The new compound, which we tentatively assigned as $\mathbf{2}_{butyl}$, based both on NMR and high-resolution mass spectrometry (HRMS), was isolated in 65% conversion (45% isolated). Attempts to further the conversion with temperatures nearing 210 °C led to the

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destruction of $\mathbf{2}_{butyl}$ as well as the starting material (Figure S81). However, we noticed that the reaction occurs beyond the melting point of $\mathbf{1}_{butyl}$ and that $\mathbf{2}_{butyl}$ is a solid at these temperatures, so as $\mathbf{2}_{butyl}$ accumulates a solid mass forms that perhaps impedes mass transfer and blocks dimerization. Thus, we envisioned that the reaction might benefit from the addition of a high boiling point and relatively inert solvent, such as tetradecane. Indeed, the addition of *n*-tetradecane dramatically increases the rate and conversion of the reaction, achieving 97% conversion in just 24 h (Figure S63).

Hawthorne identified **2** solely by intuition and ^{11}B NMR,[31] but a crystal structure of such a dimer has never been reported. To unambiguously determined the 3-dimensional structure of $\mathbf{2}_{butyl}$, a single-crystal X-ray diffraction study of its trimethylammonium salt $[\mathbf{HNMe_3}^+]\mathbf{2}_{butyl}$ was conducted. Indeed, the solid-state structure of $[\mathbf{HNMe_3}^+]\mathbf{2}_{butyl}$ clearly shows the dimer held together by a B−B bond and the two counter cations in close contact with the square belt adjacent to the antipodal boron (Figure 3). Although there is currently some disagreement in the literature[34,35] as to what should be defined as a hydrogen bond, the positioning of the cations is not a random crystal packing effect. Rather, the calculated positions of the hydrogen atoms and their subsequent inferred distances are an excellent demonstration of charge inverted H···H dihydrogen bonding between the N−H bearing a δ^+ charge and two of the cluster B−H bonds that bear δ^- charges because of their hydridic nature. The fact that these hydrogen bonds occur at the square belt furthest from the more electronegative cage carbon is consistent with these positions being the most hydridic.[36]

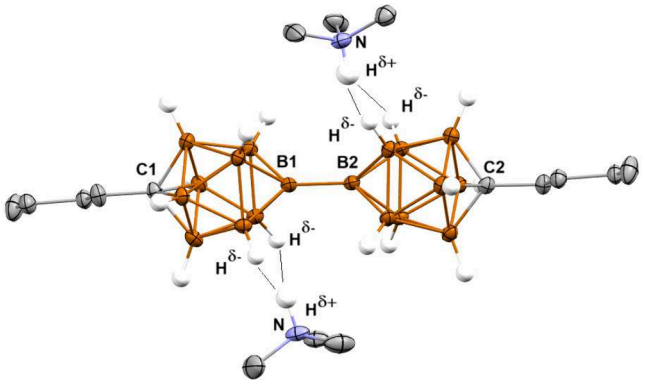

Figure 3. Solid-state structure of $[\mathbf{HNMe_3}^+]\mathbf{2}_{butyl}$. Color code: Gray = C, Brown = B, Blue = N, White = H. Selected distances: B1−B2 = 1.672 ± 0.003 Å; Average estimated distance of B−H to H−N dihydrogen bonds = 2.161 Å. Hydrogens attached to carbons omitted for clarity. Thermal ellipsoids drawn at the 50% probability level.

We hypothesized that the dimerization reaction of $\mathbf{1}_{butyl}$ may occur because of the electronic perturbation of the system induced by alkylation compared to that of the parent compound **1**. Hence, we subjected **1** to the same experimental conditions as $\mathbf{1}_{butyl}$, and to our surprise we also observed the thermal dimerization to form Hawthorne's compound **2**, as confirmed by NMR and HRMS. At 195 °C, neat **1** only converts to ∼5% dimer in 5 days; however, increasing the temperature to 230 °C allows for a slight increase to ∼12% conversion in the same time period (Figure S46). Further increasing the temperature to 250 °C does not equate to a faster reaction, but rather gradual decomposition of **1** and **2** (Figure S80). The neat reaction of **1** to form **2** under vacuum may not work well since the compound initially melts but then resolidifies as all of the THF is removed from the Li^+ cation, which subsequently sublimes as the pure, THF-free Li^+ salt of **1** as is observed at 0.5 Torr and 230 °C (Figures S77−S79). However, when *n*-tetradecane is used as a solvent and the mixture is heated to 195 °C for 24 h, 92% conversion to **2** is observed (Figure S62).

Since we now know that this thermal dehydrocoupling is not enabled by C-alkylation of the cage, we next turned our attention to possible countercation effects. In Hawthorne's original report,[31] their electrochemical experiments were carried out with the tetraethylammonium salt of **1** and not alkali-metal cations. Thus, we prepared the NEt_4^+, Na^+, K^+, and Cs^+ salts of **1** and $\mathbf{1}_{butyl}$. To our surprise, none of these salts undergo thermal dehydrocoupling at temperatures of 195−275 °C, indicating the key role of Li^+ to initiate such reactions (Figures S64−S71). While we do not completely understand this Li^+ effect, it likely has to do with the more covalent bonding interactions and higher Lewis acidity of Li^+ especially as it becomes naked via desolvation. Indeed, it is well-known in organic chemistry that Li^+ can be a very potent Lewis acid, especially when generated in a weakly coordinating solvent.[37,38] Michl has reported a distinct Li^+ effect that operates via a σ bond metathesis pathway resulting in cage methyl for aryl exchange at a 12-vertex carborane anion surface.[39] Additionally, Michl has shown that somehow, certain 12-vertex carborane Li^+ salts are able to initiate controlled radical polymerizations of unfunctionalized olefins to create polyolefins with interesting microstructures.[40] This is a distinct Li^+ effect in that it allows B−H activation and must involve Li^+ coordination to the antipodal B−H bond. We suspect that this interaction facilitates homolytic cleavage of this bond and subsequent dimerization of the ensuing radicals. A σ bond pathway as proposed by Michl, vide supra, would require two bulky negatively charged cages to obtain intimate contact to achieve the requisite 4-centered transition state for concerted H_2 elimination. Thus, this mechanism can be ruled out for both steric and Coulombic reasons. To provide evidence that radicals are at play in this reaction, we performed the reaction under the optimized conditions with the addition of one equivalent of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (S-51). No dimerization is observed in the presence of TEMPO, and the starting material remains primarily intact aside from a few unidentified baseline bumps in the ^{11}B spectrum, which is consistent with the quenching of radical species. Additionally, when the reaction is performed neat in a J. Young tube, we observe a small resonance at 4.54 ppm in the ^{1}H NMR spectrum (S-52), which is consistent with the presence of H_2.

Recently, there has been growing fundamental interest in B−B linked biscarboranes.[41] In a practical sense, the observation of this phenomenon is important for those investigating the potential of carborane anions as next-generation battery materials,[12] as thermal stability is a key requirement for such devices. Additionally, one could imagine developing novel solid-state ion-conducting materials by designing the appropriate C−C-linked cages to initiate polymerizations to form molecular wires. We are currently pursuing this idea to access such novel functional ionic materials.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c04644.

Additional experimental details, materials, methods, and all spectroscopic data discussed herein (PDF)

Accession Codes

Deposition Number 2382874 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Author Contributions

V.L. lead the overall direction of the project and wrote the paper with S.P.. S.P. synthesized all molecules and collected spectroscopic data. P.H. and V.C. performed XRD analysis and provided the necessary data for the crystal structure.

Notes

The authors declare no competing financial interest.

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