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Observation of Room Temperature B−Cl Activation of the $HCB_{11}Cl_{11}^-$ Anion and Isolation of a Stable Anionic Carboranyl Phosphazide

Allen L. Chan, Javier Fajardo, Jr., James H. Wright, II, Matthew Asay, and Vincent Lavallo*

Department of Chemistry, University of California at Riverside (UCR), Riverside, California 92521, United States

Supporting Information

ABSTRACT: The perchlorinated carba-*closo*-dodecaborate anion is typically inert toward B−Cl functionalization. We present here the observation of two competing reactions that occur with this anion at ambient temperature. When this molecule is treated with *n*-BuLi and subsequently reacted with tosyl azide, a cycloaddition occurs and results in chloride substitution at a B−Cl vertex. The competing and dominant pathway is a substitution reaction to form the azide $N_3CB_{11}Cl_{11}^-$. This rare anionic carboranyl azide reacts with PPh_3 in FC_6H_5 to afford a stable anionic phosphazide. When dissolved in tetrahydrofuran, the phosphazide is in equilibrium with free PPh_3 and $N_3CB_{11}Cl_{11}^-$. Both the triazole and phosphazide are characterized by single-crystal X-ray diffraction, NMR and IR spectroscopy, and high-resolution mass spectrometry.

Perhalogenated carba-*closo*-dodecaborate clusters are exceptionally weakly coordinating anions that have allowed isolation of a variety of fundamentally important and exotic cationic species.[1] The property that distinguishes them from other "noncoordinating" counteranions, such as $B(C_6F_5)_4^-$ and SbF_6^-,[1a,2] is that they are exceptionally resistant to bond cleavage or oxidation by potent electrophilic cations. This combination of poor Lewis basicity and inertness renders these anions ideal for silylium catalysis and related processes.[1i,m,n] Aside from the anomalous reactivity of $HCB_{11}F_{11}^-$ toward the hydroxide ion,[1q] the other perhalogenated congeners of the carba-*closo*-dodecaborate cluster are also extremely unreactive toward cluster degradation or B−X bond cleavage by strong Brønsted or Lewis bases. However, the C−H bond of these clusters can be deprotonated with strong bases to generate dianionic species that can be carbon-functionalized with electrophiles.[1d] Recently, we reported the first example of a controlled reaction that allows for the nucleophilic substitution of a B−Cl bond of the $HCB_{11}Cl_{11}^-$ anion.[3a] Specifically, we disclosed a base-induced cycloaddition reaction between the $HCB_{11}Cl_{11}^-$ anion and simple organic azides that leads to carborane-fused triazoles with unusual aromatic character. Although very thermodynamically favorable, this reaction occurs at temperatures above 100 °C. More recently, we reported that one of these heterocycles can be rendered zwitterionic through alkylation and chemically reduced to form the first isolable triazole radical anion.[3b] Here we report the observation of two competing reactions that occur with the $HCB_{11}Cl_{11}^-$ anion at ambient temperature, namely, B−Cl activation/cycloaddition and electrophilic N_3 transfer. Further, we discuss the isolation of an unusual anionic lithium carboranyl phosphazide complex.

We are interested in functionalized perhalogenated carboranes for use as ligand building blocks for catalyst design.[4] An interesting molecule that we have been targeting is the anionic perchlorinated carba-*closo*-dodecaborate azide $N_3CB_{11}Cl_{11}^-$, which should be a versatile synthon. Carbon-functionalized azides of the carba-*closo*-dodecaborate anion are extremely rare. In fact, only a single report exists from Michl et al.,[5] in which a permethylated carborane azide is prepared by the trapping of a highly reactive naked C-vertex carborane cluster with N_3^-. We attempted to prepare the perchlorinated carborane azide $N_3CB_{11}Cl_{11}^-$ in a direct route, analogous to Blanch's synthesis of *o*-carborane azides,[6] via deprotonation of **1**, followed by quenching with tosyl azide (Figure 1). ^{11}B NMR spectroscopy monitoring of the reaction indicates the formation of two products in a ratio of approximately 60:40. The minor product displays seven resonances in the ^{11}B NMR, which indicates a disruption of the local C_{5v} symmetry in the cluster. Regardless of the reaction temperature, order of addition, or solvent, the ratio of the two compounds stays approximately the same. Analysis of the mixture by high-resolution mass spectrometry confirmed the formation of $N_3CB_{11}Cl_{11}^-$ and also revealed a molecular-ion peak

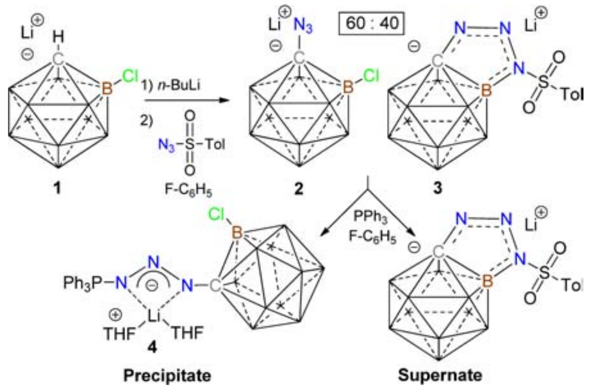

Figure 1. Scheme showing that when **1** is deprotonated and treated with tosyl azide, N_3 transfer is observed to afford $N_3CB_{11}Cl_{11}^-$ (**2**) along with the unexpected formation of heterocycle **3**. Treatment of the mixture with PPh_3 induces precipitation of the anionic phosphazide **4** (unlabeled vertices are B−Cl).

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for the heterocycle **3** (Figure 1). IR spectroscopy also confirms the formation of the azide **2** (absorbance at 2143 cm^{-1})

The ionic compounds **2** and **3** have very similar solubility, and all attempts to separate these two species were unsuccessful. However, crystallization of the crude reaction mixture led to a crystal of **3**, which was suitable for a single-crystal X-ray diffraction study (Figure 2). In the solid state, **3** shows no interaction with any lithium countercations in the lattice (closest contact 4.117 Å). Similar to the analogous phenyl-substituted heterocycle that was recently reported,[3a] all five atoms of the heterocyclic portion of **3** are coplanar (sum of internal pentagon angles = 540°) and the nitrogen-bearing tosyl group (N3) is sp^2-hybridized (sum of angles = 360°). The N1−N2 [1.267(3) Å] and N2−N3 [1.382(2) Å] bond lengths are asymmetric but still significantly shorter than standard N−N single bonds (1.450 Å).[7]

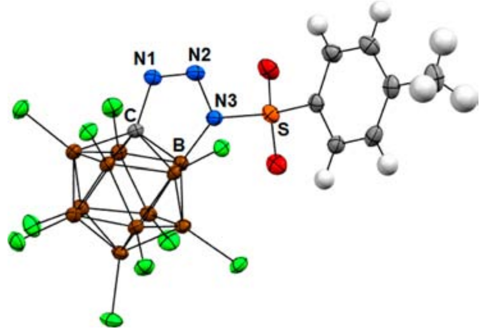

Figure 2. Solid-state structure of the heterocycle **3**. Color code: C, gray; H, white; N, blue; Cl, green; B, brown; O, red; S, orange.

The C−B portion of the pentagon is contracted [C1−B1 = 1.679(3) Å] with respect to the other C−B bonds in the cluster (average C−B bond lengths = 1.733 Å), which is close to the phenyl-substituted derivative and a characteristic of exocluster delocalization.[3a]

In the hopes of altering the solubility of the azide **2**, we sought to derivatize it via a Staudinger reaction to form an iminophosphorane. Typically, N$_2$ is readily extruded from azides upon contact with a phosphine. However, when the phosphine or azide reaction partner is sterically demanding, the intermediate phosphazide[8] adducts can be isolable species. Kennedy[9] recently reported the preparation of neutral phosphazides from *o*-carborane azides, which are stable in the absence of light and heat.

Thus, the reaction mixture was treated with a solution of triphenylphosphine in fluorobenzene, but no visible sign of N$_2$ elimination was observed. Over 24 h, large colorless crystals formed in the flask and were isolated. A single-crystal X-ray diffraction study confirmed that N$_2$ had been retained and revealed the unexpected formation of the anionic lithium phosphazide complex **4**, which exists in the s-trans configuration (Figure 3). In the solid state, two tetrahydrofuran (THF) molecules are bound to the lithium cation, and **4** acts as a bidentate ligand, coordinating via the terminal nitrogen atoms (N1 and N3) of the N$_3$ unit. Both the N1−N2 [1.284(2) Å] and N2−N3 [1.338(2) Å] distances are short, which suggests π delocalization between the three atoms. Interestingly, even though the carborane anion is acting as a ligand substituent to the N1 atom of the phosphazide core, no intramolecular contacts with the chlorine atoms are observed. Solid-state CPMAS ^{31}P NMR spectroscopy shows a single phosphorus resonance at +38 ppm, attributed to the static structure of **4**. A small shoulder resonance of the main signal might be attributed to a population of the less favorable s-cis isomer.

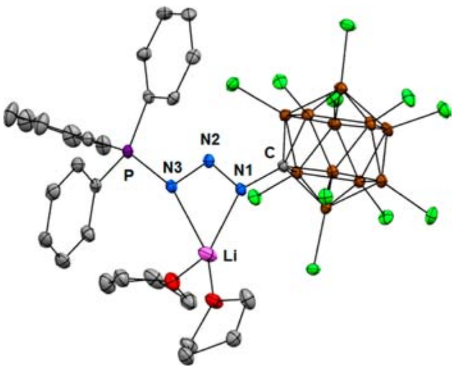

Figure 3. Solid-state structure of phosphazide **4**. Color code: C, gray; H, white; N, blue; Cl, green; B, brown; O, red; P, purple; Li, pink.

Phosphazide **4** is completely insoluble in nonpolar solvents (e.g., hexane, C$_6$H$_6$, FC$_6$H$_5$) but readily dissolves in THF and CH$_2$Cl$_2$. The ^{31}P NMR spectrum of **4** in THF shows a resonance at +21 ppm. The difference in chemical shift between the solution and solid-state spectra (17 ppm) of **4** might be explained by solvation effects. Interestingly, a signal at −5 ppm corresponding to free PPh$_3$ is always present in the THF solution of **4** at ambient temperature. Repeated washing of **4** with copious amounts of FC$_6$H$_5$, a solvent in which PPh$_3$ is readily soluble, does not remove the resonance that corresponds to free phosphine. It was postulated that in a THF solution an equilibrium exists,[10] where the PPh$_3$ moiety dissociates from **4** to reform the azide **2**. Variable-temperature NMR experiments support the presence of an equilibrium between PPh$_3$, **2**, and **4** in a THF solution and allow for determination of the equilibrium constant at a given temperature (see the Supporting Information). At +60 °C, only PPh$_3$ can be detected in the ^{31}P NMR spectrum, which is supportive of complete dissociation of the complex at elevated temperatures. Cooling the sample to −35 °C shifts the equilibrium completely to complex **4**, which is evidenced by the presence of only a single resonance in the ^{31}P NMR spectrum (+22 ppm). In contrast, ^{31}P NMR analysis of **4** dissolved in CD$_2$Cl$_2$ shows only a single resonance at +33 ppm corresponding to **4**, which is close to the solid-state NMR value (+38 ppm) and suggests the absence of equilibrium in this solvent. IR analysis of the phosphazide **4** in the solid state and in a CH$_2$Cl$_2$ solution shows no absorption band for the azide **2** and confirms that complex **4** does not dissociate in this solvent. In contrast, when **4** is dissolved in THF and analyzed by IR, the absorbance for the azide **2** is apparent. The differences in the stability of complex **4** in THF and CH$_2$Cl$_2$ can be explained by the stronger coordinative abilities of THF, which likely reversibly sequesters the lithium cation and disrupts the complex.

Unlike neutral phosphazides derived from *o*-carborane, complex **4** is not light- or air-sensitive. Furthermore, it shows no sign of N$_2$ loss upon heating for 24 h at 150 °C in FC$_6$H$_5$ (at this temperature **4** is soluble). In order to probe whether the stability of the phosphazide was related to its complexation with the lithium ion, we conducted an in situ cation metathesis reaction. When **4** is stirred with N(butyl)$_4$Br in FC$_6$H$_5$, it dissolves at ambient temperature, indicating that cation metathesis had occurred. Subsequent heating of the solution at 80 °C for 48 h shows by ^{31}P NMR partial decomposition of the phosphazide to unidentified phosphorus-containing species. The lithium cation likely brings enhanced stability to the phosphazide by preventing formation of the four-membered P−N−N−N ring transition state necessary for N_2 extrusion.

This paper describes a surprising reaction where a B−Cl bond of one of the least reactive anions is cleaved and substituted at room temperature. Similar reactions under mild conditions with 1,3-dipoles other than tosyl azide might be possible. The competing reaction to form the anionic azide **2** demonstrates that such perhalogenated azides are stable entities and accessible in a direct manner. Isolation of the phosphazide **4** is the first example of an anionic phosphine azide adduct and opens up the possibility of preparing other charged carborane-containing phosphazide derivatives. The preparation of such species is actively under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectroscopic data, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data for compounds **3** and **4** can also be found at the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif under CCDC 940701 and 940702, respectively.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vincent.lavallo@ucr.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

Notes

The authors declare no competing financial interest.

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