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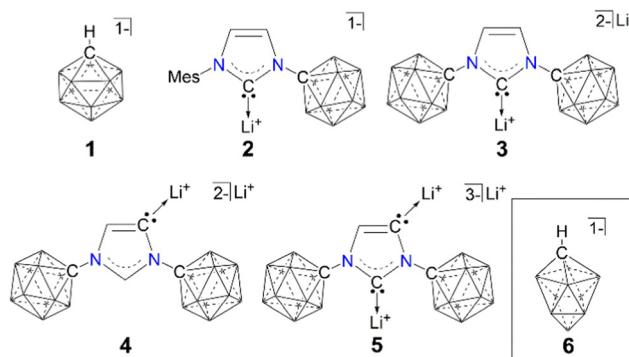
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**Discovered by Knöth in 1964, the 10-vertex *closو-carborane anion*  $[\text{HCB}_9\text{H}_9^{1-}]$  is a classical bicapped square antiprism that contains an unusual pentacoordinate carbon center. Compared to its larger icosahedral cousin  $[\text{HCB}_{11}\text{H}_{11}^{1-}]$ , few investigations have been made into its use as a weakly coordinating anion or as a ligand substituent. Here we show that it is possible to prepare both a dianionic N-heterocyclic carbene (NHC)  $\text{Li}^+$  adduct as well as a trianionic C-2, C-5 dilithio species featuring two 10-vertex carborane anion substituents. All compounds were characterized via multinuclear NMR spectroscopy, single crystal X-ray diffraction, and HRMS when possible.**

The icosahedral carborane anion  $[\text{HCB}_{11}\text{H}_{11}^{1-}]$  **1** and its derivatives are among an elite set of weakly coordinating anions that feature unmatched chemical robustness (Fig. 1).<sup>1</sup> Polyhalogenation of the B-H vertices of this cluster amplifies its robustness and also enhances the weak coordinative ability of the cluster as a whole. These properties have allowed for the isolation of a variety of super reactive cations<sup>1b</sup> as well as the design of main group catalysts capable of C-F<sup>2</sup> and C-H functionalization.<sup>3</sup> More recently, we have shown that such clusters can be utilized as substituents<sup>4</sup> for ligands<sup>5</sup> in catalyst design, which in some cases have led to superior catalysts<sup>5b,g</sup> compared to the systems containing ligands with pure hydrocarbon groups. In addition, we have shown that it is possible to prepare stable monoanionic **2**,<sup>5e</sup> dianionic normal **3**, dianionic abnormal **4**, and trianionic **5**<sup>5f,6</sup> N-heterocyclic carbene (NHC)<sup>7</sup>  $\text{Li}^+$  adducts. Thus, these species are actually carbenoids and not carbenes, since they are ligating their counter cations. Another interesting feature in these systems is that the polyanionic

carbenoids **3–5** can be selectively formed from a single anionic imidazolium precursor, which is not possible with hydrocarbon N-substituents. There has been growing interest in anionic NHC ligands, since they offer the possibility of preparing distinct coordination environments as well as allowing the formation of zwitterionic transition metal complexes with enhanced solubility in hydrocarbons compared to standard cationic catalysts. Tamm has elegantly demonstrated the advantages of such systems<sup>8</sup> and recently reviewed the topic.<sup>7c</sup>

Compared to the icosahedral carborane anion **1**, the smaller ten-vertex bicapped square antiprism  $[\text{HCB}_9\text{H}_9^{1-}]$  **6**, which was discovered by Knöth in 1967,<sup>9</sup> has been far less investigated. A survey of the literature indicates that this anion is compatible with strong acids/bases<sup>10</sup> and studies from our lab<sup>11</sup> have shown it is very stable towards redox chemistry. In addition, similar to **1**, **6** can undergo selective B-H halogenation to form more weakly coordinating derivatives.<sup>12</sup> We therefore became interested in the use of **6** as a less sterically demanding surrogate of **1** in ligand design. Recently we reported<sup>5c</sup> the first phosphine ligands containing this smaller cluster and showed that the  $[\text{-CB}_9\text{H}_9^{1-}]$  group is not only less sterically demanding



**Fig. 1** Representations of the 12-vertex carborane anion **1**, the unsymmetrical carboranyl N-heterocyclic carbenoid **2**, the symmetric carboranyl N-heterocyclic carbenoids **3**, **4**, **5**, and the 10-vertex *closо-carborane anion* **6**. Unlabelled vertices = B-H.

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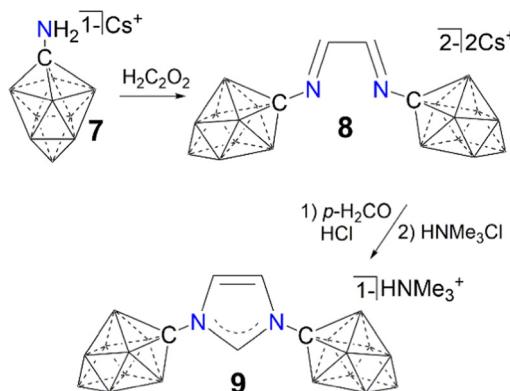


Fig. 2 Synthesis of the anionic imidazolium salt **9**. Unlabelled vertices = B–H.

than **1**, but also a significantly stronger  $\sigma$ -inductive donor. Subsequently, we became curious if it were possible to prepare N-carboranyl NHCs, featuring **6** as a ligand substituent. Here we report the isolation of the first 10-vertex N-carboranyl carbenoids.

Previously we utilized simple condensation chemistry with the known 12-vertex *closو*-carborane amine  $[\text{H}_2\text{NCB}_{11}\text{H}_{11}]^{1-}$  to access N-*closو*-carboranyl imidazolium NHC precursors. Surprisingly, this amine has been known for over 40 years but no investigator, until us, has attempted the condensation chemistry with ketones or aldehydes. The analogous 10-vertex *closو*-amine  $[\text{H}_2\text{NCB}_9\text{H}_9]^{1-}$  **7** was first reported by Kennedy and coworkers in 1997,<sup>13</sup> but similarly, condensation reactions with C=O multiple bonds have not been reported (Fig. 2). Given our experience with the 12-vertex amine, we predicted an analogous approach could be utilized to build an appropriate NHC precursor. However, we found that the reported synthesis of the requisite amine was not reliable, hence we developed an optimized synthesis (see ESI,† pages S2 and S3). With the 10-vertex amine in hand, we reacted two equivalents of the anionic amine **7**<sup>14</sup> with glyoxal and observed the formation of the corresponding dianionic carboranyl diimine **8**, as indicated by the  $^1\text{H}$  NMR spectroscopy. Subsequent ring closure with *para*-formaldehyde and cation exchange with trimethylammonium chloride afforded the desired anionic imidazolium salt **9** in 76% yield (Fig. 2). Cation exchange for trimethylammonium is advantageous, *vide infra*, since in subsequent imidazolium anion deprotonations one can choose the counter cation the ensuing NHCs will have, depending on the nature of the base employed.

We next turned our attention to the possibility of preparing the corresponding normal C-2 deprotonated NHC Li Complex **10** $[\text{Li}^+]$  (Fig. 3). Imidazolium anion **9** was thus reacted with two equivalents of lithium hexamethyl disilazide (LiHMDS) and the reaction was monitored by multinuclear NMR spectroscopy. The  $^1\text{H}$  NMR spectrum shows the disappearance of the characteristic triplet/doublet pattern (10.26; 8.45 ppm, respectively) of the imidazolium ring and the formation of a new upfield singlet resonance at 7.75 ppm, which is consistent with the formation of **10** $[\text{Li}^+]$ . The  $^{11}\text{B}$  NMR spectrum shows a set of

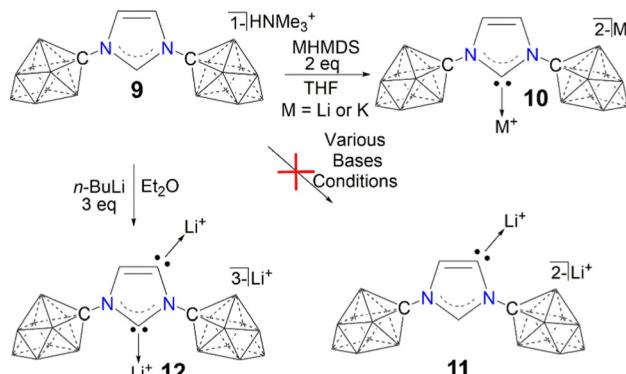


Fig. 3 Synthesis of carbenoids **10** and **12** and attempted selective preparation of **11**. Unlabelled vertices = B–H.

three resonances (31.4; -12.8; -22.2 ppm) in 1:4:4 ratio, indicating that the new species retains the local  $C_{4v}$  symmetry of the cluster. Analysis of the  $^{13}\text{C}$  NMR spectrum shows the appearance of a new resonance at 197.7 ppm, which is also consistent with the generation of the carbenoid **10** $[\text{Li}^+]$ . All attempts to grow single crystals of **10** $[\text{Li}^+]$  for X-ray diffraction studies were unsuccessful. However, utilizing KHMDS in lieu of LiHMDS afforded **10** $[\text{K}^+]$ , which readily crystallized (Fig. 4). Although the structure is too disordered to have a meaningful discussion of bond lengths and angles, the connectivity of the square pyramidal structure is unambiguous.

We next sought to investigate if these small 10-vertex carborane anions would allow for the selective formation of the abnormal C-5 deprotonated NHC Li $^+$  adduct **11**. Regardless of the conditions or bases employed we did not observe any evidence for the formation of **11** (Fig. 3), which is in stark contrast to the exquisite selectivity previously reported<sup>5f</sup> for formation of **3** and **4** (Fig. 1). Therefore, the selectivity induced by the bulkier anionic icosahedral carborane substituents is likely a steric effect and not related to the charge of such anions. While we were unable to prepare **11**, the trianionic doubly deprotonated species **12** was readily accessible by reacting **9** with three equivalents of *n*-BuLi. The formation of

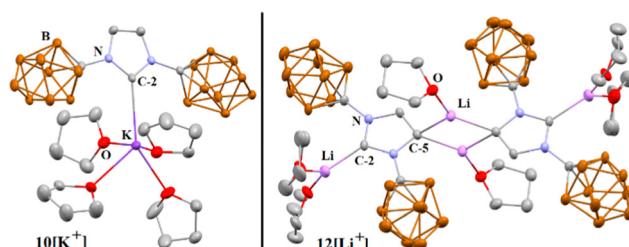


Fig. 4 Solid-State structures of **10** $[\text{K}^+]$  and **12** $[\text{Li}^+]$ . Note, although the connectivity can be unambiguously determined via single crystal X-ray diffraction (thermal ellipsoids drawn at the 50% probability level), it is not of sufficient quality to have a meaningful discussion of bond lengths and angles. Additional THF solvated K $^+$  for **10** $[\text{K}^+]$  and Li $^+$  for **12** $[\text{Li}^+]$  omitted for clarity. These cations are not coordinated to the NHCs but in the voids in the lattice. Color code: Brown = B, red = O, purple = K, pink = Li, grey = C, blue = N, hydrogens and solvents of crystallization omitted for clarity.

**12** was corroborated by  $^1\text{H}$  NMR spectroscopy, which shows an upfield shift of the carbenoid backbone proton to 7.0 ppm. In addition, the  $^{13}\text{C}$  spectrum shows two distinct downfield carbon resonances at 197.6 and 169.3 ppm, which is consistent with C-2 and C-5 imidazolium deprotonation, respectively. In the  $^{11}\text{B}$  NMR spectrum the two sets of resonances for the inequivalent carborane clusters are superimposed by coincidence. The carbenoid structure of **12** was unambiguously determined by a single crystal X-ray diffraction study, but the data is not of sufficient quality to discuss structural parameters (Fig. 4). What we can say is that similar to its 12-vertex homolog, in the solid state **12** adopts a dimeric structure with terminal  $\text{Li}^+$  cations coordinated to the C-2 positions and two bridging  $\text{Li}^+$  cations gluing the dimer together *via* the C-5 positions.

In conclusion, over 50 years after the Knöth's discovery of the  $[\text{HCB}_9\text{H}_9]^{1-}$  anion and 30 years after Arduengo's seminal discovery of the first stable NHC,<sup>15</sup> we show that these two families of molecules can be fused to form unusual charged carbenoids. We are currently investigating the possibility of utilizing these ligands in catalysis as well as for the formation of functional weakly coordinating anions.<sup>15</sup>

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## Conflicts of interest

There are no conflicts of interest to declare.

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