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Synthesis of Unsymmetrical N-Carboranyl NHCs: Directing Effect of the Carborane Anion

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The syntheses of unsymmetrical N-Heterocyclic Carbenes (NHCs) that contain a single N-bound icosahedral carborane anion substituent are reported. Both anionic C-2 and doubly deprotonated dianionic C-2/C-5 NHC lithium complexes are isolated. The latter species is formed selectively, which reveals a surprising directing effect conveyed by icosahedral carborane anion substituents.

Ancillary ligands are typically constructed with combinations of ubiquitous alkyl and aryl substituents. An interesting alternative to classical alkyl and aryl ligand R-groups are the organomimetic[1] icosahedral carboranes,[2] which can be thought of as 3-dimensional analogues of benzene. The most common carboranes used in ligand design are derived from neutral icosahedral dicarbaborane clusters (C_2B_{10}).[2g] Due to its ready availability,[3] the *ortho*-carborane (*o*-carborane) isomer **1** (Fig 1, top left) is the most often implemented. While this cluster offers many distinct characteristics, such as a unique steric profile and the ability to form H-H hydrogen bonds,[2g] it exhibits reactivity that is perhaps undesirable for catalysis, such as facile B-H cyclometalation[4] and B-vertex extrusion reactions[5] to afford *nido*-carboranes. The latter reaction has been developed by Teixidor and Viñas to produce novel anionic phosphines and other ligands, featuring *nido*-cluster substituents.[2b, 6] Compared to icosahedral dicarbaboranes **1**, the isoelectronic anionic carba-*closo*-dodecaborate clusters **2** (CB_{11}^-)[2c] (Fig 1, right) do not undergo vertex extrusion reactions and are more resistant to cyclometalation.[7] Furthermore, clusters **2** are among the weakest coordinating and inert counter anions known and have been applied to the preparation of elusive reactive cations, super acids,[8] and superior systems for silylium catalysis.[9] We recently reported the first utilization of cluster **2** as a ligand substituent for a transition metal-based catalyst.[10] Our initial report disclosed the synthesis of a phosphine bearing a perchlorinated carborane anion substituent, which when complexed to Au(I) forms the most active catalyst ever
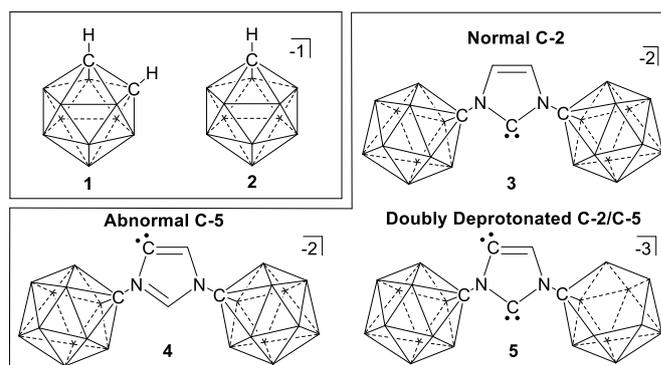
Fig. 1 Representations of *o*-carborane **1** ($H_2C_2B_{10}H_{10}$) and the isoelectronic carba-*closo*-dodecaborate anion **2** ($HCB_{11}H_{11}^-$) (top left). Representations of the dianionic normal C-2 **3**, abnormal C-5 **4**, and trianionic C-2/C-5 **5** N-carboranyl NHCs. Unlabeled vertices = B-H.

reported for alkyne hydroamination reactions. Encouraged by these results, we have begun to develop the synthetic methodology[7, 11] to access a wide range of ligand architectures, which contain covalently linked icosahedral carborane anions, for applications in catalysis.

Recently we disclosed the synthesis of polyanionic N-heterocyclic carbenes (NHCs) **3-5**,[12] featuring two N-bound carborane anions.[13] Through judicious choice of bases the selective deprotonation of an anionic imidazolium salt is achieved to afford normal (C-2) NHC **3** (via LiHMDS), abnormal[14] (C-5) NHC **4** (via LDA, -78 °C), or the doubly deprotonated[15] (C-2/C-5) NHC **5** (via *n*-BuLi) from a single precursor. Such selectivity of NHC formation has not been achieved in deprotonation reactions of imidazolium salts that contain N-hydrocarbon groups. We became curious to see if it was possible to prepare unsymmetrical NHCs, featuring both carborane and hydrocarbon substituents, and investigate if the same selectivity for NHC formation could be achieved. Here we report the synthesis of an imidazolium zwitterion, featuring mixed carborane and hydrocarbon N-substituents, and its deprotonation to form various anionic NHCs.

One of the most elegant and versatile methods to synthesize unsymmetrically substituted imidazolium salts has been reported by Fürstner and co-workers[16] and involves the heterocyclic interconversion of oxazolinium salts, via reaction with amines. These oxazolinium salts are readily tunable at N and available in three steps from commercial starting materials. By analogy, we envisioned reacting the mesityl substituted oxazolinium cation **6** with anionic carboranyl amine **7**, followed by treatment with acid, would produce the zwitterionic imidazolium species **8** (Fig. 2, top).
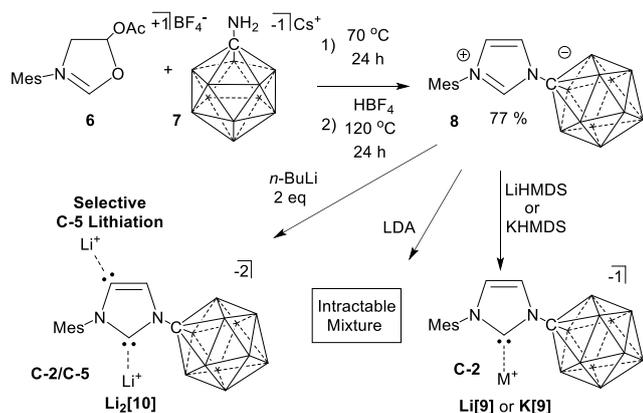
Fig. 2 Synthesis of zwitterionic imidazolium **8** and its reaction with different bases to form anionic **Li[9]**, **K[9]** and dianionic **Li₂[10]** NHCs. The second lithiation of **8** with *n*-BuLi occurs with perfect selectivity at the C-5 position to form **Li₂[10]**. M = Li or K, unsubstituted vertices = B-H.

Indeed, this reaction sequence is effective; affording the imidazolium species **8** in 77% yield based on the carboranyl amine. The zwitterion is soluble in benzene as well as most other common solvents, with the exception of alkanes and H_2O. The ^1H NMR spectrum of **8** shows three distinct doublets of doublets for the imidazolium ring protons (8.8 ppm, $^4J_{H-H}$ = 2.0, 1.8 Hz, (C-2); 7.7 ppm, $^3J_{H-H}$ = 2.0 Hz, $^4J_{H-H}$ = 1.8 Hz, (C-4); 7.3 ppm, $^4J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 2.0 Hz, (C-5)). Assignment of the imidazolium backbone protons was determined by NOESY NMR experiments that show coupling between the resonance at 7.7 ppm and the B-H pentagonal belt adjacent to the carborane carbon. In addition, through-space coupling is observed between the signal at 7.3 ppm and the *ortho*-mesityl methyl protons. The ^{13}C NMR spectrum of **8** displays three resonances (142.0 (C-2), 124.7 (C-4), 124.8 (C-5) ppm) for the imidazolium carbons.

Deprotonation of the zwitterionic imidazolium species **8** with LiHMDS dissolved in THF, results in rapid precipitation of a white powder **Li[9]**. Analysis of the material by ^1H NMR shows the disappearance of the low field C-2 proton at 8.8 ppm and the appearance of two doublets (7.4 ppm and 6.8 ppm; d, $^3J_{H-H}$ = 1.5 Hz), which is consistent with the formation of the normal C-2 NHC. The ^{13}C NMR spectrum of **Li[9]** displays a broad resonance at 199.9 ppm for the carbene center, which is in the expected range for aryl substituted imidazolylidenes and very close to the lithium complex of NHC **3** (**Li[3]**) (195.0 ppm). Interestingly, deprotonating **8** with KHMDS in lieu of LiHMDS, results in the formation of **K[9]**, which is very soluble in THF and benzene. The ^1H NMR spectrum of **K[9]** is nearly identical to **Li[9]**, however the ^{13}C NMR spectrum reveals a downfield shifted carbene resonance (211.1 ppm). The difference in chemical shift compared to **Li[9]** is likely due to the formation of an NHC Li^+ complex in solution, whereas the K^+ salt **K[9]** exists as a solvent separated ion pair. The ^7Li NMR of **Li[9]** shows a broad

resonance at 2.3 ppm, which also supports the formation of a NHC Li^+ adduct in solution. Our hypothesis is in line with previous studies[14e, 17] that have shown that alkali metal free NHCs are formed when K bases are implemented in lieu of Li reagents.

The solid-state structure of **Li[9]** was unambiguously determined by a single crystal X-ray diffraction study, and shows the NHC and three THF molecules coordinated to the Li^+ (Fig. 3). Both N1 and N3 are planar (sum of C-N-C angles = 360°), indicating they are both sp^2 hybridized. The nitrogen carbene bond lengths of **Li[9]** (N1-C2 = 1.3671(17), N3-C2 = 1.3799(17) Å) are in the range reported for standard NHC Li adducts,[17] and comparable to **Li[3]**.[12] The carborane-N bond length (N3-C1 = 1.4597(16) Å) and carbon boron distances in the cluster (average C-B distance 1.7724(19) Å) are close to that reported for **Li[3]**, and suggest no exo-π-conjugation[18] between the carborane substituent and the carbene ring. The carbene/lithium bond length of **Li[9]** (C2-Li1= 2.214(3) Å) is in the range reported for standard NHC lithium complexes.[17]
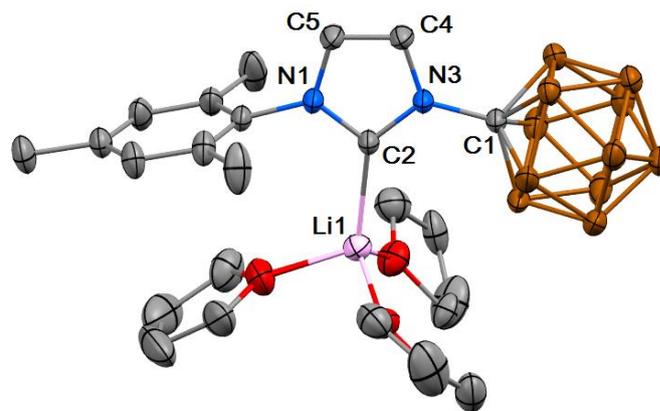
Fig. 3 Solid state structure of **Li[9]**. Hydrogens are omitted for clarity. Color code: C = grey, B = brown, N = blue, Li = pink, O = red.

We next explored the possibility of forming an abnormal NHC, analogous to **4**, by reaction of **8** with LDA. All of our attempts to selectively deprotonate the backbone of imidazolium **8** with LDA led to intractable mixtures of **Li[9]** and multiple unidentified compounds (Fig. 2). These results suggest that it is necessary to have two N-carboranyl substituents attached to the imidazolium ring in order to achieve selective backbone deprotonation.

Subsequently, we turned our attention to double deprotonation reactions with *n*-BuLi. In contrast to symmetrical N,N-carboranyl imidazolium salts[12] **8** contains distinct protons at the C-4 and C-5 positions adjacent to the mesityl and carborane anion substituents, respectively. Therefore, we were not only curious if we could isolate a doubly deprotonated species, but would selectivity be observed for C-4 or C-5 lithiation? Treatment of a solution of **8** dissolved in ether with 2 equivalents of *n*-BuLi results in the formation of a precipitate (Fig. 2). After stirring the mixture for two hours the precipitate was collected and analysed by NMR spectroscopy, which reveals clean formation of a single isomer of the doubly deprotonated dianionic species **Li₂[10]**. Counterintuitively and in contrast to monoanionic **Li[9]**, dianionic **Li₂[10]** is very soluble in THF. The ^1H NMR spectrum displays a single resonance for the imidazolium ring at 6.6 ppm, which through NOESY NMR analysis we assign to the C-4 proton adjacent to the carborane anion. This data indicates that lithiation of the imidazolium backbone occurs solely at the C-5 position of the ring. We speculate that this directing effect results from a combination of steric and electrostatic effects induced by the

carborane anion substituent. The ^{13}C NMR of **Li$_2$[10]** shows an unsymmetrical imidazolium ring with two low field quaternary resonances at 193.0 and 166.8 ppm that correspond to the C-2 and C-5 deprotonated carbon centers, respectively. The ^{7}Li NMR spectrum of **Li$_2$[10]** displays two resonances (3.5, 2.3 ppm), which suggests that both the C-2 and C-5 carbons are coordinated to Li$^+$ ions.

A single crystal X-ray diffraction study confirms the identity of **Li$_2$[10]** (Fig. 4). In contrast to the related trianionic N,N-dicarboranyl species **Li$_2$[5]**,[12] which is a Li$^+$-bridged dimer in the solid-state, **Li$_2$[10]** is monomeric. The central heterocyclic ring bond lengths of **Li$_2$[10]** (N1-C2 = 1.363(2), N3-C2 = 1.364(2), N1-C5 = 1.426(2), N3-C4 = 1.407(2), C4-C5 = 1.369(3), Å) are similar to those reported for the trianionic species **5** (Fig. 1),[12] as well as monoanionic hydrocarbon derivatives reported by Robinson.[15a] The
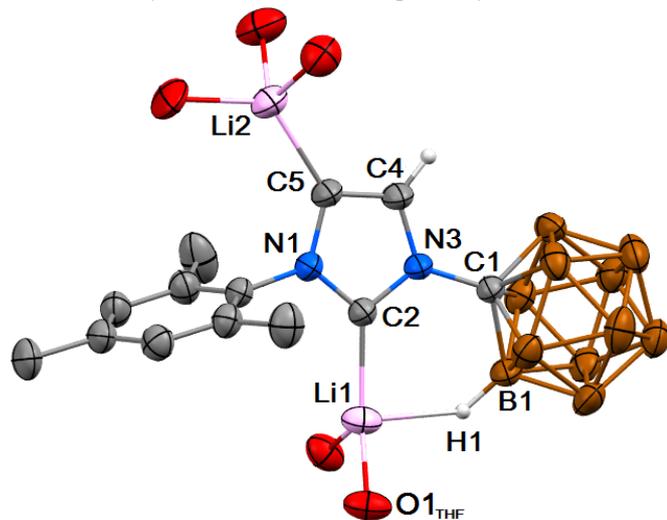
Fig. 4 Solid state structure of **Li$_2$[10]**. Carbon rings of THF molecules and most hydrogen atoms (except H1, and C4-H) are omitted for clarity. Color code: C = grey, B = brown, N = blue, Li = pink, O = red.

carborane nitrogen bond length of (N3-C1 = 1.446(2) Å) and carbon boron distances in the cluster (average C-B distances for carboranes 1.716(1) Å), are only slightly different compared to the normal C-2 dianionic carbene lithium adduct **Li[9]**. A single close B-H contact with the lithium cation bound to C2 (H1-Li1 = 2.14 Å) suggests the occurrence of an agostic-like[19] interaction. The C2-Li1 bond length of 2.079(4) Å is shorter than the C5-Li2 distance (2.133(4) Å), which is perhaps a result of the B-H-Li bonding interaction that draws the C-2 carbene center closer to the alkali metal cation.

Conclusions

This communication describes the facile synthesis of zwitterionic imidazolium species **8**, featuring N-hydrocarbon and N-carboranyl groups. Deprotonation of this zwitterion with alkali hexamethyl disilazide bases cleanly affords the normal C-2 NHC complexes **Li[9]** or **K[9]**. Attempted deprotonation of the zwitterion **8** with LDA to selectively form an abnormal NHC, leads to an intractable mixture. This result indicates that in order to achieve selective imidazolium backbone deprotonation two anionic N-carboranyl groups are required. Double deprotonation reactions of **8** with *n*-BuLi result in the selective formation of C-2/C-5 lithiated species **Li$_2$[10]**, revealing an unprecedented directing effect of the anionic icosahedral carborane substituent. We are currently investigating the implementation of these novel NHCs in catalysis.

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