N-Heterocyclic Carbenes | Hot Paper

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Fusing N-Heterocyclic Carbenes with Carborane Anions**

*Ahmad El-Hellani and Vincent Lavallo**

Abstract: *Here we describe the fusion of two families of unusual carbon-containing molecules that readily disregard the tendency of carbon to form four chemical bonds, namely N-heterocyclic carbenes (NHCs) and carborane anions. Deprotonation of an anionic imidazolium salt with lithium diisopropylamide at room temperature leads to a mixture of lithium complexes of C-2 and C-5 dianionic NHC constitutional isomers as well as a trianionic (C-2, C-5) adduct. Judicious choice of the base and reaction conditions allows the selective formation of all three stable polyanionic carbenes. In solution, the so-called abnormal C-5 NHC lithium complex slowly isomerizes to the normal C-2 NHC, and the process can be proton-catalyzed by the addition of the anionic imidazolium salt. These results indicate that the combination of two unusual forms of carbon atoms can lead to unexpected chemical behavior, and that this strategy paves the way for the development of a broad new generation of NHC ligands for catalysis.*

In the last two decades there has been an explosion of research in stable carbene chemistry.[1] This is largely due to the fact that NHCs, such as the imidazolylidenes **1**, have found extraordinary utility as ligands for catalysts[1b,f,2] and the stabilization of reactive species,[3] as well as catalysts in their own right[4] (Figure 1). Typically, NHCs **1** are generated from imidazolium cations by deprotonation of the most acidic proton in the C-2 position of the aromatic ring with a strong Brønsted base. In 2001, Crabtree and co-workers[5] made a key discovery that it was possible for imidazolylidenes to adopt a C-5 coordination mode with transition metals. Evidence has since mounted that these "abnormal" NHCs[6] convey distinct and sometimes superior catalytic properties[6f,g] to the metals they bind, compared to the normal C-2 isomer. In 2009, Bertrand and co-workers reported that if the acidic proton in the C-2 position of the imidazolium salt precursor was substituted by a hydrocarbon fragment, deprotonation at C-2 could be blocked and abnormal C-5 imidazolylidenes **2** could be isolated as metal-free species (Figure 1).[7] In 2010, Robinson and co-workers reported[8a] that imidazolium salts could be deprotonated at both the C-2 and C-5 positions to afford anionic species **3** that can bind to two metal fragments (Figure 1).[8]

Another class of molecules that contain an unusual form of carbon, wherein the carbon atom forms 6 chemical bonds with neighboring elements, are icosahedral carboranes.[9] In contrast to carbenes, icosahedral carboranes are extraordinarily stable molecules and certain members of these families, such as the carba-*closo*-dodecaborate anion $HCB_{11}H_{11}^-$ **4**, reported by Knoth in 1967,[10] are well-known for their inert properties (Figure 1). The carborane anion **4** delocalizes its charge throughout the 12 cage atoms, rendering the cluster and its derivatives very weakly coordinating. The combination of weak coordinative ability and resistance to chemical decomposition explains why these molecules are widely used as counteranions for highly reactive cationic species.[9a,11] Here we report the fusion of carbenes with carborane anions to selectively produce stable lithium adducts of dianionic normal C-2 and abnormal C-5 imidazolylidene constitutional isomers, as well as a trianionic C-2/C-5 deprotonated species from a single precursor.

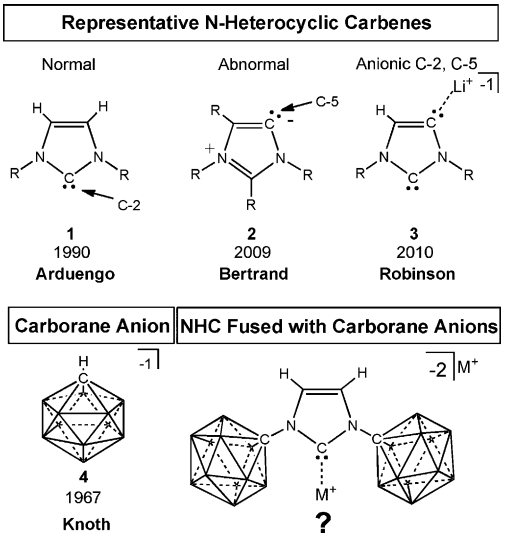

Figure 1. Different classes of NHCs and an icosahedral carborane anion. Generic representations of a normal (C-2; **1**), abnormal (C-5; **2**), and anionic dicarbene (C-2, C-5; **3**) (R = alkyl or aryl), and the carba-*closo*-dodecaborate anion **4** (chemical formula: $HCB_{11}H_{11}^-$, unlabeled vertices: B–H).

We are interested in utilizing the carba-*closo*-dodecaborate anion **4** and its halogenated derivatives as alkyl and aryl surrogates for ligand and catalyst design.[12] We envisioned synthesizing a normal NHC that would be rendered dianionic, as a result of containing two negatively charged and weakly coordinating[13] N-carboranyl substituents (Figure 1). When generated with an alkali metal-containing base, such an NHC would inevitably form a complex with one of the two countercations. Although the prerequisite anionic carboranyl amine **5** was reported over 25 years ago, and is accessible in large quantities from decaborane ($B_{10}H_{14}$),[14] this unusual

[*] Dr. A. El-Hellani, Prof. V. Lavallo
Department of Chemistry, University of California Riverside
Riverside, CA 92521 (USA)
E-mail: vincent.lavallo@ucr.edu
Homepage: http://faculty.ucr.edu/~vincentl/index.html

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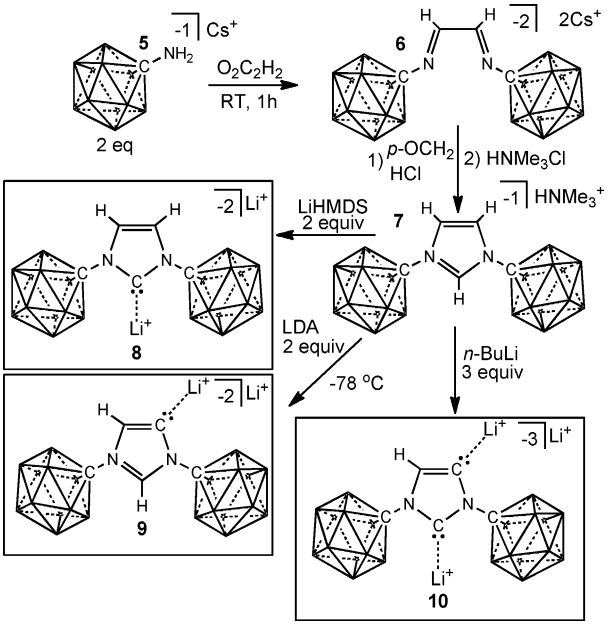

Figure 2. Synthesis of polyanionic normal (C-2; **8**), abnormal (C-5; **9**), and C-2/C-5 deprotonated species (**10**) (unlabeled carborane vertices: B–H).

anionic amine has never been reported to undergo condensation reactions with aldehydes or ketones (Figure 2). Gratifyingly, when amine **5** was treated with glyoxal ($O_2C_2H_2$) we observed a rapid double condensation reaction to afford the dianionic diimine **6** in 96% yield (Figure 2). Subsequent treatment of **6** with *para*-formaldehyde (*p*-OCH_2), activated with HCl, rapidly induces ring closure and formation of the anionic imidazolium salt **7** in 94% isolated yield (Figure 2). The ^{1}H NMR spectrum of **7** shows a characteristic triplet (C-$H_{C\text{-}2}$, 1H, $^4J_{H\text{-}H}$ = 1.74 Hz) and doublet (C-$H_{C\text{-}4,5}$, 2H, $^4J_{H\text{-}H}$ = 1.74 Hz) at 8.50 and 7.63 ppm, respectively, which correspond to the imidazolium ring protons. The ^{13}C NMR spectrum of **7** displays two C–H resonances for the symmetrical imidazolium ring (C-$H_{C\text{-}2}$ 134.6, C-$H_{C\text{-}4,5}$ 123.7 ppm) as well as a quaternary carborane carbon at 67.6 ppm. Initial attempts to deprotonate **7** with excess lithium diisopropylamide (LDA) at ambient temperature led to a puzzling mixture of three new compounds as indicated by ^{1}H NMR spectroscopy (ultimately determined to be **8**, **9**, and **10**) (Figure 2). Two of the three compounds feature a single singlet resonance in the ^{1}H NMR spectra at 6.91 and 6.13 ppm, respectively. We postulated that the low-field singlet at 6.91 ppm corresponded to the desired normal dianionic NHC **8**, and the higher-field resonance at 6.13 ppm might correspond to the C-2/C-5 deprotonated species **10**. Interestingly, the third compound displays two distinct doublet resonances that are coupled at 8.26 (C-$H_{C\text{-}2}$, 1H, $^4J_{H\text{-}H}$ = 1.5 Hz) and 6.31 ppm (C-$H_{C\text{-}4}$, 1H, $^4J_{H\text{-}H}$ = 1.5 Hz), which we tentatively assigned to the abnormal NHC **9**.

All three species were persistent in solution, and thus we sought a strategy to selectively produce **8**, **9** and **10**. We rationalized that the observed competitive deprotonation reactions might be explained, in part, by kinetic factors resulting from the sterically demanding anionic carborane substituents and the size of the employed base (LDA). Hence, we attempted the deprotonation with (LiHMDS), a base with a less sterically congested environment at the amide center, due to the relatively longer N–Si bonds. Indeed, at room temperature or at −78 °C the deprotonation reaction occurs solely at the C-2 position to cleanly afford the normal dianonic NHC **8** in excellent yield (95%). The ^{13}C NMR spectrum of **8** shows a symmetrical imidazolium ring with a distinct low-field quaternary carbene resonance (196.9 ppm) as well as a signal for the equivalent hypercoordinate carborane carbons (81.4 ppm). ^{7}Li NMR spectroscopy shows a resonance that is upfield (−0.52 ppm) from a LiCl standard (0.1M/THF), which suggests the carbene complexes the alkali metal cation.

Indeed, a single-crystal X-ray diffraction study of **8** reveals that in the solid-state this NHC forms a complex with one of the two lithium countercations of the pendant carborane anions (Figure 3). All five atoms of the central heterocyclic

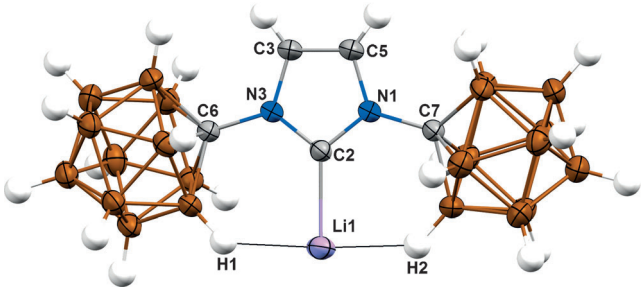

Figure 3. Solid-state structure of the normal dianionic NHC **8**.[20] For clarity, two tetrahydrofuran (THF) molecules coordinated to Li1 are omitted, as well as the second Li^+ countercation (×4 THF). Color code: C gray, B brown, H white, N blue, Li pink.

ring are coplanar (sum of internal pentagon angles = 540°) and both N1 and N3 are planar (sum of C-N-C angles = 360°). Relative to the monoanionic imidazolium precursor **7** (see Supporting Information for crystallographic data), the nitrogen–carbene bond lengths of **8** (N1–C2 1.3657(14), N3–C2 1.3645(15) Å) are elongated with respect to the imidazolium anion **7** (N1–C2/N3–C2 1.331(2) Å)), which is in line with standard NHCs and their Li complexes.[1f,8,13] The carborane–nitrogen bond lengths (N1–C7 1.4521(15), N3–C6 1.4514(14) Å) and carbon–boron distances in the cluster (average C–B distance 1.719(3) Å) are nearly identical to the precursor **7** (N1–C7/N3–C6 1.455(3), average C–B distance 1.716(3) Å), indicating no *exo*-π conjugation with the carbene ring or disruption of the three-dimensionally aromatic carborane core of **8**.[9a,15] The carbene–lithium bond length of 2.110(2) Å is in the range reported for standard NHC lithium complexes.[1f,8,13] Interestingly, two close B–H contacts with the lithium cation (H1–Li1 2.01, H2–Li1 2.19 Å) suggest the possibility of agostic-like bonding between the carborane anions and the alkali metal center.[12b,16]

To selectively form the abnormal NHC **9**, we rationalized that carrying out the deprotonation reaction at low temperature with LDA might kinetically favor the attack of the bulky base at the less sterically hindered C-5 position. As predicted, carrying out the reaction at −78 °C solely affords the

abnormal NHC that can be isolated as an off-white solid in 98% yield. The ^{13}C NMR spectra of **9** shows an unsymmetrical imidazolium ring with a distinct quaternary carbene carbon resonance at 174.7 ppm, as well as two signals (82.0 and 76.4 ppm) for the inequivalent hexacoordinate carborane carbons. The carbene carbon of **9** is significantly shielded (+27.2 ppm) compared to Bertrand's neutral abnormal carbene (201.9 ppm), and might be explained by inductive effects from the carborane anions as well as interactions with Li^+ in solution.[7a] Analysis of the ^{7}Li NMR spectrum of **9** shows a resonance that is nearly identical (−0.51 ppm) to the normal NHC Li^+ adduct **8** (−0.52 ppm), which suggests the carbene is associated with the alkali metal cation in solution. Although we are unable to obtain crystals suitable for a single-crystal X-ray diffraction study, the identity of **9** was confirmed by experimentation. Addition of D_2O to a pure solution of **9** forms **7** with (83%) deuterium incorporation at the C-5 position. Although **9** is perfectly stable in the solid-state, when a solution of **9** is sealed in an NMR tube under an inert atmosphere and monitored by ^{1}H NMR spectroscopy, it partially ($t_{1/2}$ = 2 weeks) isomerizes[17] to the normal NHC Li^+ adduct **8** (Figure 4, top). If a solution of **9** is heated to 50 °C,

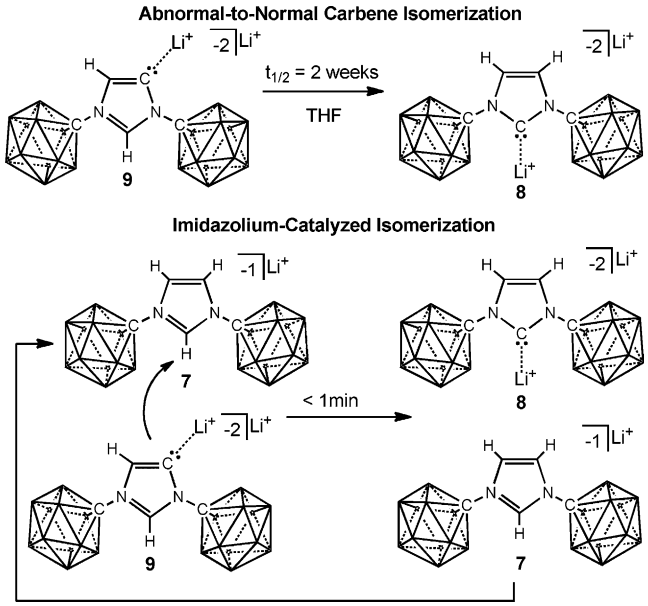

Figure 4. The abnormal NHC Li^+ adduct **9** slowly isomerizes to the normal NHC Li^+ complex **8** (top). The process can be proton-catalyzed by the anionic imidazolium precursor **7**, via the proposed reaction pathway (bottom).

complete isomerization of **9** to **8** is observed after 24 h. While we will not speculate on the mechanism of the thermal isomerization, the process can be proton-catalyzed by the anionic imidazolium salt **7**. Treating a ^{1}H NMR sample of pure **9** (30 mg) with a trace (< 1 mg) of **7**, containing Cs^+ instead of the acidic trimethylammonium countercation, results in instant (< 1 min) isomerization of **9** to **8**. A plausible pathway involves deprotonation of **7** at the C-2 position by **9** to form the normal NHC **8** and regenerate **7** (Figure 4, bottom).

In order to probe the possibility that the observed formation of the abnormal carbene was solely due to steric effects[18] provided by the carborane anions, we turned our attention to a similar cationic imidazolium salt, bearing alkyl groups. Having two adamantyl substituents that each have a similar Van der Waals Volume (V_{vdW} = 136 Å^3) to the carba-*closo*-dodecaborate anions of **7** (V_{vdW} = 141–148 Å^3),[9f] *N*,*N*-bisadamantylimidazolium chloride (the precursor to Arduengo's original stable NHC)[1h] was an ideal model for comparison. All attempts to generate the abnormal constitutional isomer of Arduengo's carbene by deprotonation with LDA, even with an excess of base to prevent potential proton catalyzed isomerization, resulted in the formation of the normal C-2 NHC.

We next turned our attention to isolating the trianionic doubly deprotonated C-2/C-5 species **10**, which can be cleanly formed (98% yield) by the treatment of **7** with three equivalents of *n*BuLi. The ^{13}C NMR of **10** shows an unsymmetrical imidazolium ring with two low-field quaternary resonances at 195.6 and 169.5 ppm that correspond to the C-2 and C-5 carbon centers, respectively, as well as signals (89.1, 83.0 ppm) for the inequivalent hypercoordinate carborane carbons. Interestingly, two overlapping resonances appear in the ^{7}Li NMR spectrum of **10** (−0.18, −0.21 ppm), which suggests that both the C-2 and C-5 centers of the molecule are complexed to alkali metal cations. Indeed, a single-crystal X-ray diffraction study shows that in the solid-state **10** is dimeric with the C-2 center bound to a single lithium cation, and the C-5 center bridging two other lithium cations (Figure 5). The

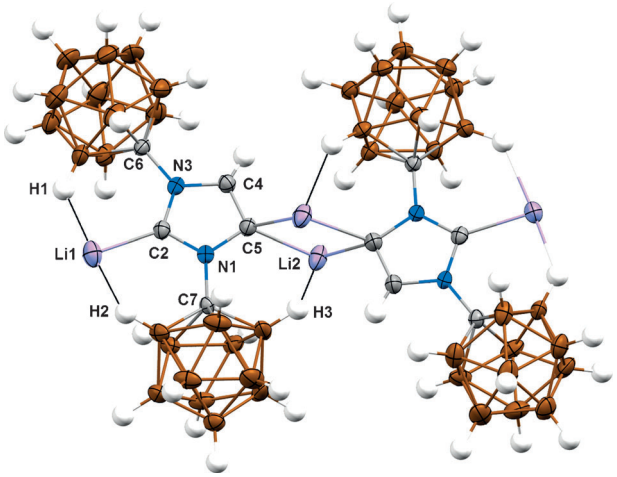

Figure 5. Solid-state structure of the dimeric trianionic species **10**.[20] For clarity, six molecules of coordinated THF have been omitted from the lithium countercations shown above, as well as two additional Li^+ countercations (×4 THF). Color code: C gray, B brown, H white, N blue, Li pink.

central heterocyclic ring bond lengths of **10** (N1–C2 1.364(3), N3–C2 1.353(3), N1–C5 1.429(3), C5–C4 1.363(3), C4–N3 1.402(3) Å) are similar (N1–C2 1.375(3), N3–C2 1.361(3), N1–C5 1.442(4), C5–C4 1.356(4), C4–N3 1.399(4) Å) to those reported by Robinson[8a] for an *N*-aryl substituted monoanionic C2/C-5 deprotonated species. The carborane nitrogen

bond lengths of (N1–C7 1.448(3), N3–C6 1.446(3) Å) and carborane–boron distances in the cluster (average C–B distances for carboranes 1.724(3), 1.712(3) Å) are nearly identical to imidazolium anion **7** and the normal C-2 dianionic carbene lithium adduct **8**, indicating no disruption of the icosahedral carborane cluster. The C-2 carbon–Li1 bond of 2.103(4) is slightly shorter than the C-5–Li2 bond (2.157(5) Å), which can be attributed to the 3-center-2-electron nature of the latter interaction.[19] Several close B–H contacts with the lithium cations (H1–Li1 2.05, H2–Li1 2.16, H3–Li2 2.14 Å) suggest the occurrence of multiple agostic-like interactions.

We have demonstrated that it is possible to prepare unusual families of multiply charged carbene lithium complexes that are fused to carborane anions. The results indicate that the carba-*closo*-dodecaborate anion is not simply a substitute for alkyl and aryl groups, but leads to superior control of carbene formation and the unique ability to allow the isolation of lithium complexes of two NHC constitutional isomers as well as a trianionic C-2/C-5 deprotonated species from a single precursor. Since the carba-*closo*-dodecaborate anion can be readily functionalized with a variety of substituents,[9a] this strategy paves the way for the development of a broad new generation of polyanionic N-heterocyclic carbenes with distinct steric and electronic profiles.

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[20] CCDC 973664 (**7**), 973666 (**8**), and 973665 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.