



ChemComm

Fusing 10-vertex closo-Carborane Anions with N-Heterocyclic Carbenes

Journal:	<i>ChemComm</i>
Manuscript ID	CC-COM-05-2022-002596.R2
Article Type:	Communication

SCHOLARONE™
Manuscripts

COMMUNICATION

Fusing 10-vertex *closo*-Carborane Anions with N-Heterocyclic Carbenes

Received 00th January 20xx,
Accepted 00th January 20xx

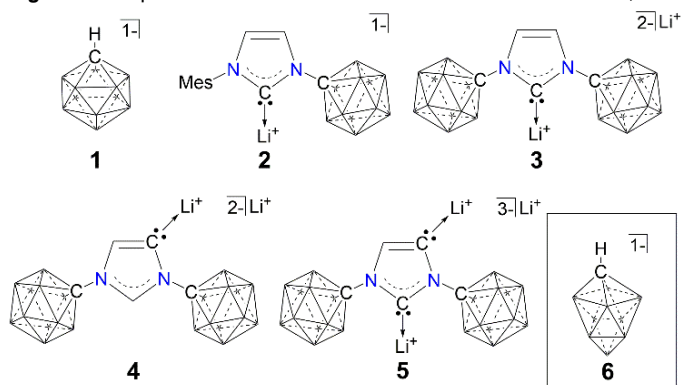
DOI: 10.1039/x0xx00000x

Varun Teja^a, Sarah E. McArthur^{*b}, Isaac Banda^a, Aaron Gregory^a, Scott G. McArthur^a, Steven P. Fisher^a, Vincent Lavallo^{*a}

Abstract: Discovered by Knöth in 1964, the 10-vertex *closo*-carborane anion [HCB₉H₉]⁻¹ is a classical bicapped square antiprism that contains an unusual pentacoordinate carbon center. Compared to its larger icosahedral cousin [HCB₁₁H₁₁]⁻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) 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 [HCB₁₁H₁₁]⁻¹ **1** and its derivatives are among an elite set of weakly coordinating anions that feature unmatched chemical robustness (Figure 1).^[1] 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^[1b] as well as the design of main group catalysts capable of C-F^[2] and C-H functionalization.^[3] More recently, we have shown that such clusters can be utilized as substituents^[4] for ligands^[5] in catalyst design, which in some cases have led to superior catalysts^[5b, 5g] compared to the systems containing ligands with pure hydrocarbon groups. In addition, we have shown that it is possible to prepare stable monoanionic **2**,^[5e] dianionic normal **3**, dianionic abnormal **4**, and trianionic **5**.^[5f, 6] N-Heterocyclic Carbene (NHC)^[7] 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^[8] and recently reviewed the topic.^[7c]

Figure 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 *closo*-carborane anion **6**. Unlabelled vertices = B-H.

Compared to the icosahedral carborane anion **1**, the smaller ten-vertex bicapped square antiprism [HCB₉H₉]⁻¹ **6**, which was discovered by Knöth in 1967,^[10] has been far less investigated. A survey of the literature indicates that this anion is compatible with strong acids/bases^[11] and studies from our lab^[12] 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.^[13] We therefore became interested in the use of **6** as a less sterically demanding surrogate of **1** in ligand design. Recently we reported^[5c] the first phosphine ligands containing this smaller cluster and showed that the [-CB₉H₉]⁻¹ group is not only less sterically demanding than **1**, but also a significantly stronger σ -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 *closo*-carborane amine [H₂NCB₁₁H₁₁]⁻¹ to access N-*closo*-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 *closo*-amine [H₂NCB₉H₉]⁻¹ **7** was first reported by Kennedy and coworkers in 1997,^[14] but similarly, condensation reactions with C=O multiple bonds have not been reported (Figure 2).

^a Department of Chemistry, University of California-Riverside, Riverside, CA 92521, USA. E-mail: vincent.lavallo@ucr.edu

^b Department of Chemistry, Butte College, Oroville, CA 95965, USA. E-mail: mcarthursa@butte.edu

Electronic Supplementary Information (ESI) available: Synthetic procedures, NMR and X-Ray data available. See DOI: 10.1039/x0xx00000x

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 SI, pages 2-3). With the 10-vertex amine in hand, we reacted two equivalents of the anionic amine **7**^[5] with glyoxal and observed the formation of the corresponding dianionic carboranyl diimine **8**, as indicated by the ¹H NMR spectroscopy. Subsequent ring closure with *para*-formaldehyde and cation exchange with trimethylammonium chloride afforded the desired anionic imidazolium salt **9** in 76% yield (Figure 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.

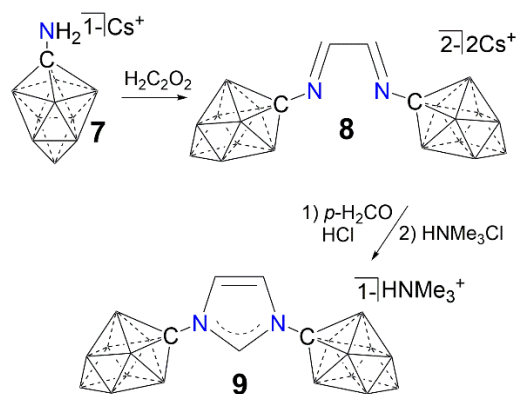


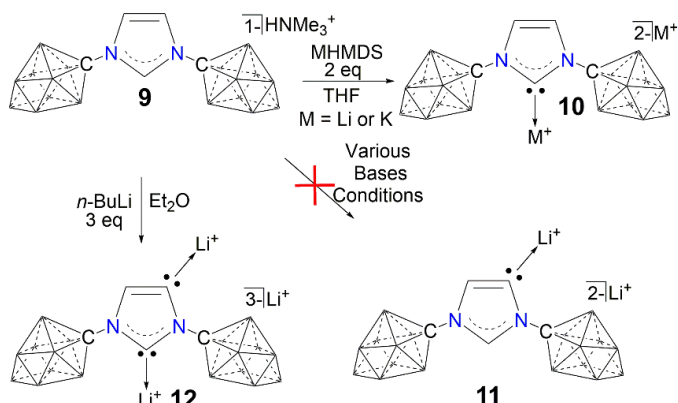
Figure 2. Synthesis of the anionic imidazolium salt **9**. Unlabelled vertices = B-H.

We next turned our attention to the possibility of preparing the corresponding normal C-2 deprotonated NHC Li Complex **10**[Li⁺] (Figure 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 ¹H 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**[Li⁺]. The ¹¹B NMR spectrum shows a set of 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 ¹³C NMR spectrum shows the appearance of a new resonance at 197.7 ppm, which is also consistent with the generation of the carbenoid **10**[Li⁺]. All attempts to grow single crystals of **10**[Li⁺] for X-ray diffraction studies were unsuccessful. However, utilizing KHMDS in lieu of LiHMDS afforded **10**[K⁺], which readily crystallized (Figure 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** (Figure 3), which is in stark contrast to the exquisite selectivity previously reported^[5] for formation of **3** and **4** (Figure 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 **12** was corroborated by ¹H NMR spectroscopy, which shows an upfield shift of the carbenoid backbone proton to 7.0 ppm. In addition, the ¹³C 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

Figure 3. Synthesis of carbenoids **10** and **12** and attempted selective preparation



of **11**. Unlabelled vertices = B-H.

the ¹¹B 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 (Figure 4). What we can say is that similar to its 12-vertex homolog, in the solid state **12** adopts a dimeric structure with terminal Li⁺ cations coordinated to the C-2 positions and two bridging Li⁺ cations gluing the dimer together via the C-5 positions

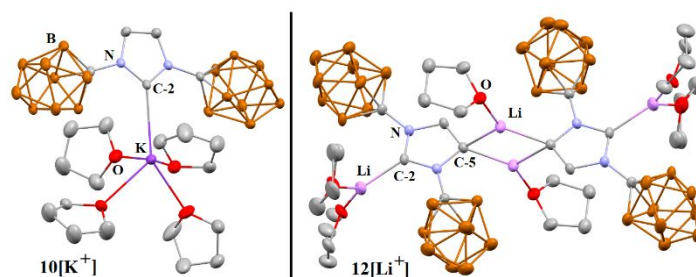


Figure 4. Solid-State structures of **10**[K⁺] and **12**[Li⁺]. Note, although the connectivity can be unambiguously determined via single crystal x-ray diffraction (thermal ellipsoids drawn at the 50% probability level), it is not of sufficient quality to have a meaningful discussion of bond lengths and angles. Additional THF solvated K⁺ for **10**[K⁺] and Li⁺ for **12**[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.

In conclusion, over 50 years after the Knöth's discovery of the [HCB₉H₉]¹⁻ anion and 30 years after Arduengo's seminal discovery of the first stable NHC,^[16] 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.¹⁶

We are grateful to the National Science Foundation of the USA for funding this work (Grant # CHE-200-3418). We thank Dr. Fook S. Tham for X-ray crystallography assistance.

Conflicts of interest

There are no conflicts of interest to declare.

Notes and references

- For recent Reviews related to *closo*-carboranes and related molecules, see: a) C. Douvris, J. Michl, *Chem. Rev.* 2013, **113**, PR179; b) C. A. Reed, *Acc. Chem. Res.* 2009, **43**, 121; c) J. Zhang, Z. Xie, *Acc. Chem. Res.* 2014, **47**, 1623; d) A. R. Popescu, F. Teixidor, C. Viñas, *Coord. Chem. Rev.* 2014, **269**, 54; e) B. Ringstrand, P. Kaszynski, *Acc. Chem. Res.* 2013, **46**, 214; f) D. Olid, R. Núñez, C. Viñas, F. Teixidor, *Chem. Soc. Rev.* 2013, **42**, 3318; g) A. M. Spokoyny, *Pure Appl. Chem.* 2013, **85**, 903; h) M. Scholz, E. Hey-Hawkins, *Chem. Rev.* 2011, **111**, 7035; i) S. P. Fisher, A. W. Tomich, S. O. Lovera, J. Kleinsasser, J. Guo, M. Asay, H. M. Nelson, V. Lavallo, *Chem. Rev.*, 2019, **119**, **14**, 8262.
- a) O. Allemann, S. Duttwyler, P. Romanato, K. K. Baldrige, J. S. Siegel, *Science* 2011, **332**, 574; b) C. Douvris, C. M. Nagaraja, C.-H. Chen, B. M. Foxman, O. V. Ozerov, *J. Am. Chem. Soc.* 2010, **132**, 4946; c) S. Duttwyler, C. Douvris, N. L. P. Fackler, F. S. Tham, C. A. Reed, K. K. Baldrige, J. S. Siegel, *Angew. Chem. Int. Ed.* 2010, **49**, 7519; *Angew. Chem.* 2010, **122**, 7681; d) C. Douvris, O. V. Ozerov, *Science* 2008, **321**, 1188.
- B. Shao, A. L. Bagdasarian, S. Popov, H. M. Nelson, *Science* 2017, **355**, 1403; M. Khandelwal, R. J. Wehmschulte, *Angew. Chem. Int. Ed.* 2012, **51**, 7323.
- For the first example of a ligand featuring a pendant [CB₁₁H₁₁]¹⁻ cluster substituent, see: A. Himmelspach, M. Finze, S. Raub, *Angew. Chem. Int. Ed.* 2011, **50**.
- a) S. P. Fisher, A. El-Hellani, F. S. Tham, V. Lavallo, *Dalton Trans.* 2016, **45**, 9762; b) A. L. Chan, J. Estrada, C. E. Kefalidis, V. Lavallo, *Organometallics* 2016, **35**, 3257; c) J. Estrada, C. A. Lugo, S. G. McArthur, V. Lavallo, *Chem. Commun.* 2016, **52**, 1824; d) J. Estrada, D. H. Woen, F. S. Tham, G. M. Miyake, V. Lavallo, *Inorg. Chem.* 2015, **54**, 5142; e) M. J. Asay, S. P. Fisher, S. E. Lee, F. S. Tham, D. Borchart, V. Lavallo, *Chem. Commun.* 2015, **51**, 5359; f) A. El-Hellani, V. Lavallo, *Angew. Chem. Int. Ed.* 2014, **53**, 4489; g) V. Lavallo, J. H. Wright, F. S. Tham, S. Quinlivan, *Angew. Chem. Int. Ed.* 2013, **52**, 3172; h) A. El-Hellani, C. E. Kefalidis, F. S. Tham, L. Maron, V. Lavallo, *Organometallics* 2013, **32**, 6887.
- For the first example of a NHC featuring a related dicarbide-ion cluster substituent, see: J. Estrada, V. Lavallo, *Angew. Chem. Int. Ed.* 2017, **56**, 9906.
- For select reviews on NHCs, see: a) C. Xiang-Yu, L. Qiang, C. Pankaj, E. Dieter, *Angew. Chem. Int. Ed.* 2018, **57**, 3862; b) E. Peris, *Chem. Rev.* 2018, **118**, 9988; c) A. Nasr, A. Winkler, M. Tamm, *Coord. Chem. Rev.* 2016, **316**, 68; d) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* 2014, **510**, 485; e) M. C. Jahnke, F. E. Hahn, *Coord. Chem. Rev.* 2015, **293**, 95; f) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* 2013, **42**, 6723; g) A. Krüger, M. Albrecht, *Aust. J. Chem.* 2011, **64**, 1113; h) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* 2008, **47**, 3122.
- a) E. L. Kolychev, S. Kronig, K. Brandhorst, M. Freytag, P. G. Jones, M. Tamm, *J. Am. Chem. Soc.* 2013, **135**, 12448; b) S. Kronig, E. Theuergarten, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* 2012, **51**, 3240; *Angew. Chem.* 2012, **124**, 3294.
- For the only two examples of monoanionic NHCs that contain carbene lone pairs not coordinated to metals, see: a) K. E. Krahulic, H. M. Tuononen, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* 2009, **131**, 5858; b) V. César, N. Lugan, G. Lavigne, *J. Am. Chem. Soc.* 2008, **130**, 11286.
- W. H. Knoth, *J. Am. Chem. Soc.* 1967, **89**, 1274.
- R. J. Wiersema, M. F. Hawthorne, *Inorg. Chem.* 1973, **12**, 785.
- S. G. McArthur, R. Jay, L. Geng, J. Guo, V. Lavallo, *Chem. Commun.* 2017, **53**, 4453.
- C.-W. Tsang, Q. Yang, E. T.-P. Sze, T. C. W. Mak, D. T. W. Chan, Z. Xie, *Inorg. Chem.* 2000, **39**, 3582.
- T. Jelinek, B. Stibr, J. Plešek, M. Thornton-Pett, J. D. Kennedy, *J. Chem. Soc., Dalton Trans.* 1997, 4231.
- We found the previously reported preparation of **7**, ref 14, problematic, thus designed a superior and novel synthesis. For details and a discussion, see: pages S2-S9.
- S. P. Fisher, S. McArthur, V. Tej, S. Lee, A. Chan, I. Banda, A. Gregory, K. Berkely, C. Tsay, A. Rheingold, G. Guisado-Barrios, V. Lavallo, *J. Am. Chem. Soc.*, 2020, **142**, 251.