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Cite this: *Chem. Commun.*, 2022, **58**, 4060

Received 10th January 2022,
Accepted 3rd March 2022

DOI: 10.1039/d2cc00173j

rsc.li/chemcomm

Cesium carbonate mediated C–H functionalization of perhalogenated 12-vertex carborane anions†

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C–H functionalization of undecahalogenated carborane anions, [$HCB_{11}X_{11}^{-}$] (X = Cl, Br, I), is performed with Cs_2CO_3 in acetonitrile. We show that the requisite Cl, Br and I carborane dianions can all be efficiently accessed with Cs_2CO_3. The utilization of Cs_2CO_3 eliminates the complications associated with competing E2 elimination reactions providing an efficient, more functional group tolerant, and broader scope than previously reported. The ensuing functionalized cages provide potential synthons for constructing advanced materials and other molecular architectures for various applications.

Weakly-coordinating anions (WCAs) are highly useful tools that allow the full expression of their countercations reactivity profiles.[1] Their applications range from catalysis,[2–5] isolation of reactive intermediates,[6,7] and materials relevant to batteries and other devices.[2] Ideally, WCAs function as inert charge carriers that do not undergo undesirable side reactions. *Closo*-Carborane[8,9] anions[2,7,10–12] are a class of WCAs, which are carbon containing analogues of polyhedral boranes. The 12-vertex carborane anions [$RCB_{11}X_{11}^{1-}$], and derivatives of the isoelectronic [$B_{12}H_{12}^{2-}$] dianion, are the most stable,[7] and they display unmatched chemical, electrochemical,[2,11,13] and thermally stability. These anions can be readily modified at the B-vertices with electrophiles, such as halogens, which render them more weakly coordinating and robust.[10] Additionally, deprotonation of the parent 12-vertex carborane anion [$HCB_{11}H_{11}^{1-}$] carborane with very strong bases (*i.e.* *n*-BuLi or metal hydrides),[10] leads to the formation of the isolable[14,15] [$CB_{11}H_{11}^{2-}$] dianions that are nucleophilic but also very basic at carbon.[10] This basicity often leads to side reactions with the THF solvent, as well as elimination reactions, instead of clean nucleophilic substitution. As first demonstrated by Strauss,[16] perhalogenation of the carborane cage, specifically with fluorine, leads to dramatically enhanced acidity of the C–H vertex, enabling it to be deprotonated with relatively weak bases, such as hydroxide. However, the broad utility of this fluorinated anion is tempered by its facile cage degradation in aqueous hydroxide solution and its hazardous synthesis with F_2/HF. It should be noted that Viñas and Teixidor have been able to achieve some interesting functionalization reactions of halogenated *ortho*-and *nido* carboranes in aqueous media.[17–20]

A more accessible and base stable cluster is the [$HCB_{11}Cl_{11}^{1-}$] anion **$1Cl_{11}$** (Fig. 1).[21] Several years ago Ozerov and coworkers reported[17] that **$1Cl_{11}$** could be deprotonated with the strong base KO*t*-Bu and subsequently functionalized with simple alkyl electrophiles. This procedure is a 2-step/1-pot process utilizing *t*-butoxide (3.5 eq) in *t*-butanol solvent, with subsequent addition of an alkyl iodide (7 eq). Both the order of addition and excess base/electrophile are important to fully drive the reaction to completion, as both the base and alkyl iodide are consumed in undesirable E2 elimination reactions. This is perhaps the reason only terminal straight chain alkyl iodides were the sole substrates reported in this manuscript.

Here we report our findings on the C–H functionalization of [$HCB_{11}Cl_{11}^{1-}$] with the relatively weak base Cs_2CO_3. We show

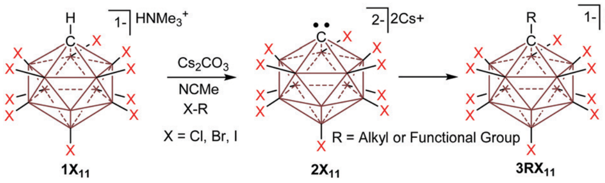

Fig. 1 Synthesis of C-functionalized [$RCB_{11}X_{11}^{1-}$] anions **$3RX_{11}$** with Cs_2CO_3.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d2cc00173j

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that it is possible to efficiently achieve C-alkylation of the cage with diverse alkyl groups containing functionality, which makes the ensuing compounds potential building blocks for advanced materials and other downstream applications. Importantly we also show that such reactions are also possible with $[HCB_{11}Br_{11}^{1-}]$ and $[HCB_{11}I_{11}^{1-}]$.

While investigating the possibility of preparing functionalized carboranes with enhanced solubility in alkane solvents for silylium catalysis,[2] Nelson's team discovered that Cs_2CO_3 is sufficiently basic to generate and functionalize $[HCB_{11}Cl_{11}^{1-}]$ (Fig. 1). Given Lavallo's interest in functionalized clusters for ligand design and battery applications, we decided to develop this chemistry, but first probe the formation of the C-nucleophilic dianion $[CB_{11}Cl_{11}^{2-}]$ **$2Cl_{11}$** (Fig. 1).

As evidenced by ^{11}B-NMR spectroscopy reaction of $[HNMe_3^+][HCB_{11}Cl_{11}^{1-}]$ with two equivalents of Cs_2CO_3 (one eq is to destroy the $HNMe_3^+$ cation) in dry acetonitrile generates an equilibrium mixture (33 : 67) of the starting material and the dianion **$2Cl_{11}$**, respectively (Fig. 2). The equilibrium could be driven to essentially 100% dianion by increasing the amount of base to 4 equivalents. After confirming that a significant population of the dianion **$2Cl_{11}$** could be generated in solution with Cs_2CO_3 we were curious if related perhalogenated species **$1Br_{11}$** and **$1I_{11}$** could undergo similar reactions, even though they contained less electron withdrawing halides. Indeed, as indicated by ^{11}B-NMR we discovered that both **$1Br_{11}$** and **$1I_{11}$** have sufficiently acidic C–H vertices to undergo deprotonation with Cs_2CO_3. As one might expect because of electronegativity trends, under the same conditions (2 eq base), 50 : 50 and 75 : 25 equilibrium mixtures of **$1Br_{11}$/$2Br_{11}$** and **$1I_{11}$/$2I_{11}$** formed, respectively (Fig. 2). It should be noted we found that hexahalogenated species $[H_6CB_{11}X_6^{1-}]$ (X = Cl, Br, or I) are not suitable substrates under these reaction conditions, which highlights the importance of perhalogenation to achieve deprotonation with the weak base Cs_2CO_3.

The use of Cs_2CO_3 to generate the dianion was predicted to be adventitious for the functionalization of these cages, as E2 elimination can be avoided and other functional groups not compatible with K-O*t*Bu could be utilized. We subsequently began to explore different classes of electrophiles that may be utilized to functionalize the cages to produce derivatives **$3RX_{11}$** (Fig. 3). Under optimized reaction conditions **$1Cl_{11}$** with *n*-decyl iodide (1.1 eq), Cs_2CO_3 (5 eq), dissolved in acetonitrile in open air, the reaction proceeds to completion with a 96% isolated yield of **a** in 18 hours at room temperature (Fig. 3). Likewise, the bromo analogue **$1Br_{11}$** was also functionalized to afford **b** in identical yield under the same conditions (Fig. 3). However, while the iodo derivative could be similarly functionalized to produce **c** in comparable yield, it required the use of an inert atmosphere and dry acetonitrile for consistent results, likely due to adventitious water interfering with the formation of **$2I_{11}$**. We were also able to successfully react **$1Cl_{11}$** with more sterically hindered isopropyl iodide to afford **d** in 88% yield over 18 hours, at 85 °C (Fig. 3). However, the more sterically demanding **$1Br_{11}$** required 36 hours to completely form **e**,

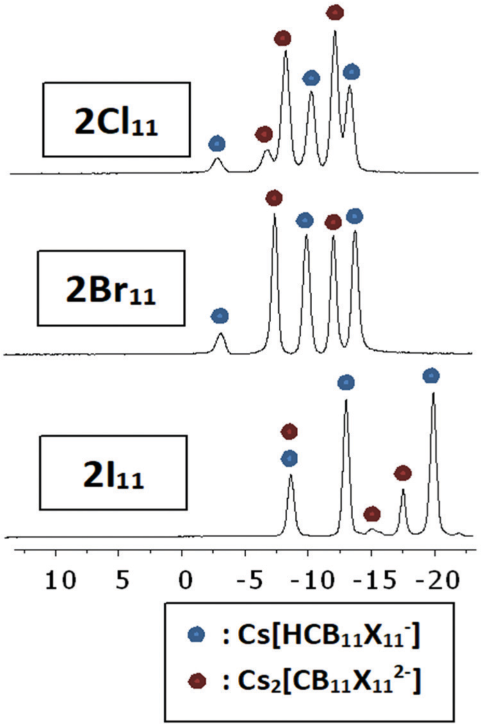

Fig. 2 $HNMe_3^+$ salts of **$1X_{11}$** reacted with 2 eq of Cs_2CO_3 yields equilibrium mixtures of **$1X_{11}$** and **$2X_{11}$**.

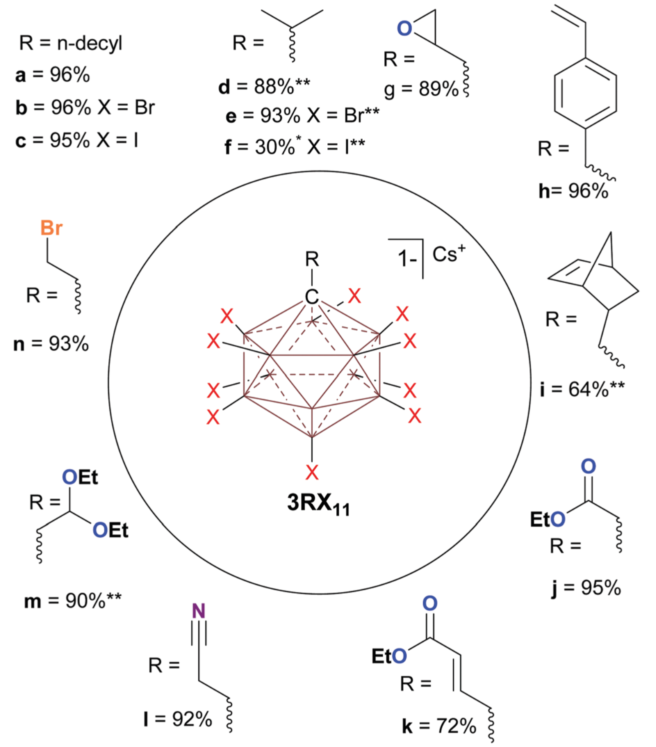

Fig. 3 Scope of cesium carbonate mediated C–H functionalization of $[HCB_{11}X_{11}^{1-}]$ cages **1**. Yields were calculated by weighing the purified salt products. * = conversion *via* NMR not isolated yield; reactions were performed at romm temperature unless indicated by ** (= 85 °C). Unlabeled vertices = B.

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and the analogous reaction with **$1I_{11}$** produced only 30% conversion to product **f** over one week.

After examining the scope of simple alkylations of compounds **$1X_{11}$**, we decided to further broaden the breadth of reactivity of **$1Cl_{11}$**. Utilizing the optimized procedure, we began investigating suitable substrates tolerant of the reaction conditions. Derivative **g**, featuring an epoxide moiety, was synthesized in 89% yield *via* nucleophilic addition to epichlorohydrin. Benzyl substituted cluster **h** was synthesized in 96% yield using vinylbenzyl chloride as the electrophile. The norbornene functionalized cage **i** was prepared in modest yield (64%) *via* reaction with the corresponding norbornyl tosylate, although the reaction required 5 days and heating to 85 °C. Ester derivative **j** was accessible in 95% yield *via* the reaction of **$1Cl_{11}$** with ethyl bromoacetate. Crotyl substituted species **k** was also isolated in moderate yield (72%) using technical grade 75% ethyl bromocrotonate as the electrophile. Compound **l**, featuring a pendant nitrile group, was prepared with bromopropionitrile in 92% yield. As demonstrated by the formation of compound **m**, a cluster functionalized with an acetal group could also be produced in 90% yield, but required heating to 85 °C. Lastly we utilized dibromoethane as an electrophile, affording compound **n** in 93% yield. Notably, no evidence for side elimination reactions were observed.

The above communication illustrates a facile method to access dianionic carboranes **$2X_{11}$** derived from $[HCB_{11}X_{11}{}^{1-}]$ **$1X_{11}$**. When the formation of these species is conducted in the presence of suitable electrophiles, efficient C–H functionalization of the cage is achieved. This novel methodology allows access to various hitherto unknown functionalized carborane building blocks that will likely be useful for catalyst and electrochemical materials design. We currently are investigating the utilization of these products to form single ion conducting polymers for electrochemical cells.

All authors contributed equally to the manuscript.

V. L. and J. G. gratefully thank the National Science Foundation (DMR-2004497) for supporting this investigation. H. M. N. thanks the N. I. H.-NIGMS for funding (R35-GM128936).

Conflicts of interest

There are no conflicts to declare.

Notes and references

1 I. M. Riddlestone, A. Kraft, J. Schaefer and I. Krossing, *Angew. Chem., Int. Ed.*, 2018, **57**, 13982–14024.
2 S. P. Fisher, A. W. Tomich, S. O. Lovera, J. F. Kleinsasser, J. Guo, M. J. Asay, H. M. Nelson and V. Lavallo, *Chem. Rev.*, 2019, **119**, 8262–8290.
3 A. M. Spokoyny, *Pure Appl. Chem.*, 2013, **85**, 903–919.
4 S. Popov, B. Shao, A. L. Bagdasarian, T. R. Benton, L. Zou, Z. Yang, K. N. Houk and H. M. Nelson, *Science*, 2018, **361**, 381–387.
5 B. Shao, A. L. Bagdasarian, S. Popov and H. M. Nelson, *Science*, 2017, **355**, 1403–1407.
6 T. A. Engesser, M. R. Lichtenthaler, M. Schleep and I. Krossing, *Chem. Soc. Rev.*, 2016, **45**, 789–899.
7 C. A. Reed, *Acc. Chem. Res.*, 2010, **43**, 121–128.
8 A. R. Popescu, F. Teixidor and C. Viñas, *Coord. Chem. Rev.*, 2014, **269**, 54–84.
9 B. J. Eleazer and D. V. Peryshkov, *Comments Inorg. Chem.*, 2018, **38**, 79–109.
10 C. Douvris and J. Michl, *Chem. Rev.*, 2013, **113**, PR179–PR233.
11 S. P. Fisher, A. Tomich, J. Guo and V. Lavallo, *Chem. Commun.*, 2019, **55**, 1684–1701.
12 S. Duttwyler, *Pure Appl. Chem.*, 2018, **90**, 733–744.
13 R. T. Boeré, C. Bolli, M. Finze, A. Himmelspach, C. Knapp and T. L. Roemmele, *Chem. – Eur. J.*, 2013, **19**, 1784–1795.
14 For the first example of the isolation of $[Li_2CB_{11}H_{11}{}^{2-}]$ see the SI for; A. El-Hellani, C. E. Kefalidis, F. S. Tham, L. Maron and V. Lavallo, *Organometallics*, 2013, **32**, 6887–6890.
15 For the first crystal structure of $[Li_2CB_{11}H_{11}{}^{2-}]$ see; R. Dontha, T.-C. Zhu, Y. Shen, M. Wörle, X. Hong and S. Duttwyler, *Angew. Chem., Int. Ed.*, 2019, **58**, 19007–19013.
16 S. V. Ivanov, J. J. Rockwell, O. G. Polyakov, C. M. Gaudinski, O. P. Anderson, K. A. Solntsev and S. H. Strauss, *J. Am. Chem. Soc.*, 1998, **120**, 4224–4225.
17 A. V. Puga, F. Teixidor, R. Sillanpaa, R. Kivekas, M. Arca, G. Barbera and C. Viñas, *Chem. – Eur. J.*, 2009, **15**, 9755–9763.
18 F. Teixidor, G. Barbera, C. Viñas, R. Sillanpaa and R. Kivekas, *Inorg. Chem.*, 2006, **45**, 3496–3498.
19 F. Teixidor, G. Barbera, R. Kivekäs, R. Sillanpää and C. Viñas, *Dalton Trans.*, 2007, 1668–1670.
20 G. Barbera, A. Vaca, F. Teixidor, R. Sillanpaa, R. Kivekas and C. Viñas, *Inorg. Chem.*, 2008, **47**, 7309–7316.
21 R. Ramírez-Contreras and O. V. Ozerov, *Dalton Trans.*, 2012, **41**, 7842–7844.

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