ChemComm

FEATURE ARTICLE

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Cite this: *Chem. Commun.*, 2019, **55**, 1684

Teaching an old dog new tricks: new directions in fundamental and applied *closo*-carborane anion chemistry

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Received 5th December 2018,
Accepted 10th January 2019

DOI: 10.1039/c8cc09663e

rsc.li/chemcomm

This feature article covers new directions in the fundamental and applied chemistry of the *closo*-carborane anions $[HCB_{11}H_{11}]^-$ and $[HCB_9H_9]^-$, as well as some related chemistry with the dicarbolide ion $[H_2C_2B_9]^{2-}$. Specifically the manuscript will focus on summarizing the authors' as well as related novel contributions to the field. The application of such clusters as solution based electrolytes for Mg batteries and related materials for ionic liquids will be discussed. In addition, the preparation of heterocycles and radicals fused to carborane anions will be discussed as well as various novel chemical transformations. Furthermore, new developments in anionic carboranyl phosphines and N-heterocyclic carbenes in the context of catalysis will be summarized.

1. Introduction

Since the early 20th century the unusual chemical bonding and structural motifs of borohydride clusters have intrigued the scientific community. Between 1912 and 1936 Alfred Stock[1] successfully synthesized a handful of pyrophoric borohydrides[2] including diborane (B_2H_6), the notorious ''green dragon'' pentaborane (B_5H_9) and the relatively stable decaborane ($B_{10}H_{14}$).[3] Despite their synthesis the structure and bonding of these compounds was far from understood. In fact the structure of decaborane ($B_{10}H_{14}$) was highly debated[4] and finally in 1950 its structure elucidated by X-ray diffraction.[5] Surprisingly, these reactive borohydrides led to the formation of ''the most stable molecule known to science''[6] the dianionic dodecaborate, $[B_{12}H_{12}]^{2-}$, discovered by Hawthorne and Pitochelli.[7,8] In 1963 three reports were simultaneously released describing the synthesis of a neutral boron cluster **1** that incorporated two carbon atoms, this compound is called 1,2-dicarba-*closo*-dodecaborane or *o*-carborane (Fig. 1).[9–11] In 1967 Knoth at DuPont successfully synthesized the mono anionic cluster 1-carba-*closo*-dodecaborate **2** and 1-carba-*closo*-decaborate **3** (Fig. 1).[12] For simplicity, going forward we will refer to compounds **2** and **3** as 12-vertex and 10-vertex carborane anions, respectively. There are many other examples of borohydrides and boron containing clusters that exist and the reader is redirected to Hosmane and Grimes's comprehensive books,[6,13] and various review articles.[14–22] Carboranes **1–3** are considered 3-dimensionally aromatic and detailed analysis of the cluster chemical bonding in these molecules can be found elsewhere.[23–28] Our interest in molecules **2** and **3** stems from their properties, which we capitalize on to create unusual molecules, catalysts, and other materials of interest. Specifically, their attractive properties are: (1) their high electrochemical and chemical stability; (2) their inherent weak coordinative ability; (3) their large steric profile; and (4) the ability of these molecules to be functionalized easily and integrated into more complex systems. In this article we will cover our, and related, work utilizing carboranes **2** and **3** as solution based ionic conducting materials, as platforms for new reaction methodology to create carborane fused heterocycles, and ligand substituents for coordination chemistry and catalysis.

2. Solution based ionic conducting materials

Electrolytes for Mg-batteries

Salts of **2** and **3** as well as their derivatives are of great interest to our lab and multiple approaches to utilizing these compounds in electrochemical systems have been explored.[29–31] As recently as 2015, carboranes have caught the attention of energy storage research as reliable counter-anions that facilitate high performance ion conducting mediums and electrolyte solutions.[30–32] In parallel to our lab's independent work,[29,31] The Toyota Research Institute (TRI) utilized the 12-vertex *closo*-carborane anion **2** to facilitate the exotic multivalent ion chemistry of

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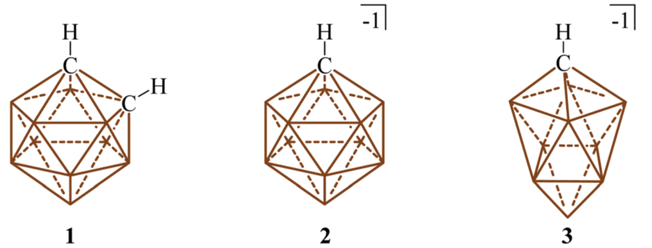


1 **2** **3**

Fig. 1 The structures of *o*-carborane **1**, the carba-*closo*-dodecaborate anion **2**, and the carb-*closo*-decaborate anion **3** (unlabelled vertex = B–H).

magnesium batteries.[30,31] While electrolytes employed for these magnesium systems typically employ corrosive, nucleophilic, or electrochemically unstable anions, the carborane displays none of these problems.[33,34] Indeed, the 12-vertex carborane anion **2** displays extreme redox stability, resulting in a large electrochemical stability window capable of hosting high voltage electrodes (Li–metal compatibility and oxidative stability to +5.7 V *vs.* Li).[12,17] Additionally, **2** and its derivatives are considered to be some of the most weakly coordinating anions known, which is important for cation mobility.

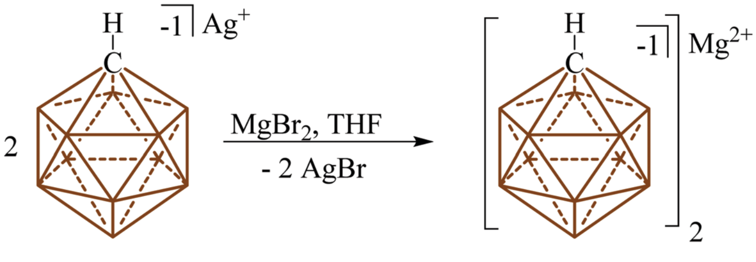
At the same time as TRI reported utilization of Mg salts of **2** to realize non-corrosive, and highly electrochemically stable electrolytes for Mg batteries we devised a novel and superior synthesis of **2[Mg]**.[31,35] In fact, TRI have since abandoned their approach and adopted our synthesis.[36] In TRI's publication, the electrochemical characterization of **2[Mg]** was achieved following synthesis of this material by salt metathesis between **2[Ag]** and $MgBr_2$ (Scheme 1).[30]

While this synthesis yields the corresponding **2[Mg]** product, it is not sufficiently pure for electrochemical testing. Thus, repeated recrystallization of the material is required in order to obtain a product of suitable purity. Furthermore, this synthesis results in a precipitation of 2 equivalents of precious AgBr byproduct for every 1 equivalent of electroactive **2[Mg]** material. As a result, this synthesis is not economically viable when considering industrial scale-up and suffers from a mixture of products. Our novel and patented approach[35] to Mg-based electrolytes is called cation reduction. Here we simply directly chemically reduce a $HNMe_3^+$ cation with Mg metal, resulting in a Mg salt with whatever counter anion is present, in this case carboranes **2** and **3**.[31] Reduction of the trimethylammonium cation results in 2 equivalents of NMe_3 gas and 1 equivalent of H_2 as easily removed gaseous byproducts (Scheme 2, top). The resulting **2[Mg]** product benefits directly from this method as few, if any, impurities remain resulting in pure **2[Mg]** in high yield. This synthetic route also offers a means for our lab to efficiently explore and develop a library of carboranyl magnesium salts that may have interesting electrochemical properties.

In the same publication, we published the synthesis and electrochemical characterization of **2[MgPh]**.[31] This monocationic Mg species was synthesized by comproportionation between **2[Mg]** and $MgPh_2$ (Scheme 3).

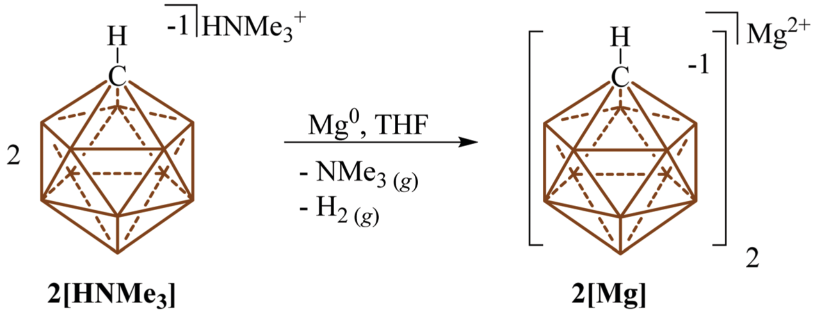
The resulting Mg species, **2[MgPh]**, is charge stabilized by a single carborane while a phenyl ligand remains coordinated to the metal center. The monopositive charge of this complex likely results in its favorable solubility properties compared to **2[Mg]**, which displays appreciable solubility only in higher glymes (>0.73 g mL^{-1}), and results in electrolyte solutions that utilize more ionically conductive lower glyme solvents. A magnesium electrolyte consisting of this material dissolved in DME solvent was prepared. Gratifyingly, we observed that this material has an ionic conductivity 4× greater than that of **2[Mg]** in tetraglyme solution of similar concentration; a direct result of developing a magnesium salt soluble in solvents of lower viscosity. By utilizing DME rather than tetraglyme, the electrochemical window in which the electrolyte can safely be reduced and oxidized changes significantly. In the case of **2[MgPh]** in DME, our group observed an unprecedented oxidative stability of +4.6 V *vs.* $Mg^{0/2+}$ which remains, multiple years later, the most oxidatively stable magnesium electrolyte to date.[37–39] This material is also intriguing in that, despite changing the coordination environment of the Mg center, XRD and XPS surface analysis confirms the deposition of pure magnesium deposits upon repeated cycling. In this way, our lab has demonstrated that ligands can be added to Mg cations to dramatically improve certain properties of these electrolytes.

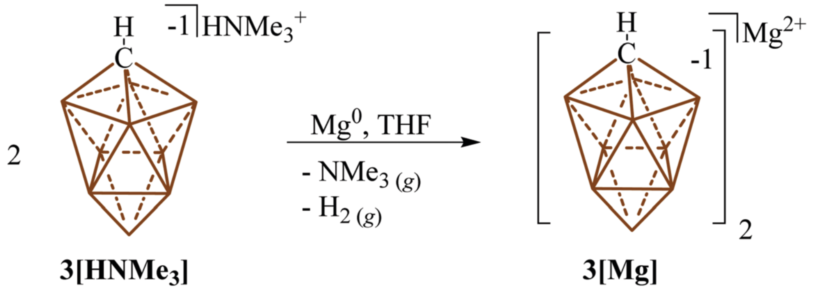
Following the publication of **2[Mg]**, our group sought to explore carborane anions of similar charge but different geometry as a means to further explore the utility of these materials in electrolyte solutions. While the performance of **2[Mg]** is truly remarkable, the realization of commercialized electrolytes using this material suffers from a multistep and thus synthesis of the base cluster **2**.[22] Our lab regularly works with the smaller carborane anion **3**, which benefits from a shorter synthesis that



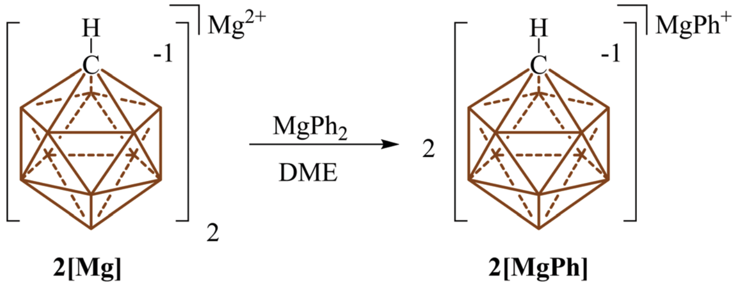
2[Ag] **2[Mg]**

Scheme 1 Salt metathesis of **2[Ag]** and $MgBr_2$ to achieve **2[Mg]**.





Scheme 2 Cation reduction of **2** and **3** using magnesium metal as an efficient means to obtain **2[Mg]** and **3[Mg]**.



Scheme 3 Comproportionation of **2[Mg]** and $MgPh_2$ to yield **2[MgPh]**.

does not involve the use of sodium metal or effervescence of HCN gas as the synthesis of **2** does.[12] For this reason, we synthesized **3[Mg]** and explored the electrochemical performance of this material in comparison to **2[Mg]**.[29] This material was synthesized *via* cation reduction, analogous to **2[Mg]** (Scheme 2, bottom).

As expected, **3[Mg]** displays similar solubility properties to **2[Mg]** in that it remains confined to higher glyme solvents such as triglyme or tetraglyme (>0.34 g mL^{-1}), and displays reversible electrochemical deposition and dissolution of magnesium metal from a platinum electrode.[29] When placed in a full cell consisting of a magnesium metal anode and Mo_6S_8 cathode, **3[Mg]** displays a comparatively unfavourable cycling stability and capacity to that of **2[Mg]**. Pairing **3[Mg]** with cathode materials other than Mo_6S_8 may result in greater performance, and thus remains an interesting alternative to **2[Mg]** due to the economic benefits of its synthesis. CV experiments conducted on **3[Mg]** hint at an interesting relationship between carborane cluster size and ionic conductivity. A 0.45 M solution of **3[Mg]** displays a similar ionic conductivity to a 0.75 M solution of **2[Mg]** in the same tetraglyme solvent. Both the ease of synthesis and smaller amount of active material required to make a magnesium electrolyte with similar properties makes **3[Mg]** an interesting material for magnesium battery technologies. Currently further development of this material as a more practical alternative to **2[Mg]** is hindered by its performance upon repeated cell cycling and available cathode materials, and perhaps functionalized derivatives of **3[Mg]** may result in improved electrochemical behaviour with Mo_6S_8 cathodes.

Ionic liquids

Utilization of carborane clusters as ionic liquids was first investigated by Chris Reed[40] in 2000, and more recently Zhu in 2017.[41] In his seminal report, Reed identified six compounds that displayed melting points below 100 °C (Fig. 2).[40] The advantages of utilizing a carborane cluster are three fold: its robust chemical nature as opposed to common components of ionic liquids (BF_4^-, PF_6^-, and TFSI), its relative ease of chemical modification (C–H and B–H functionalization), and lastly its electrochemical stability.

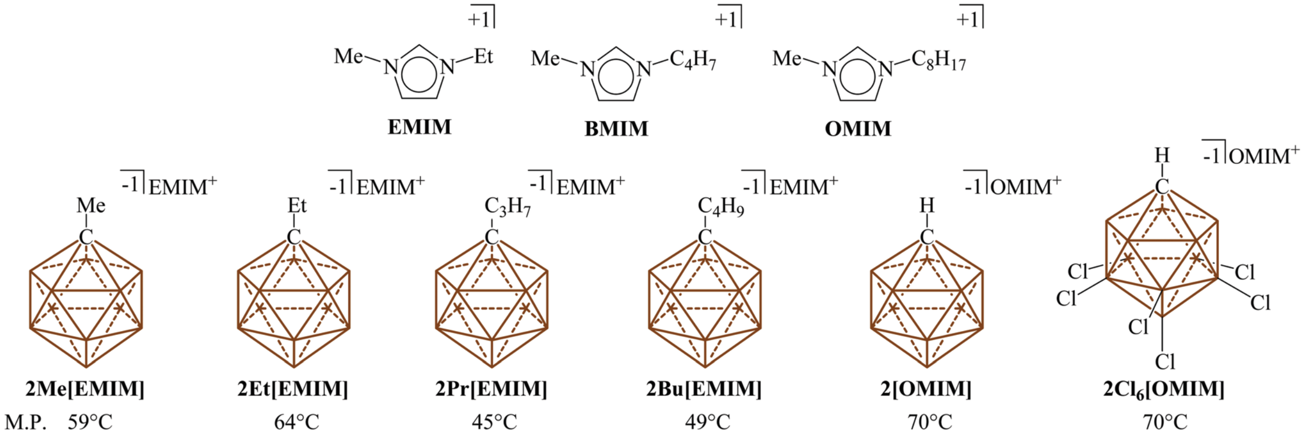
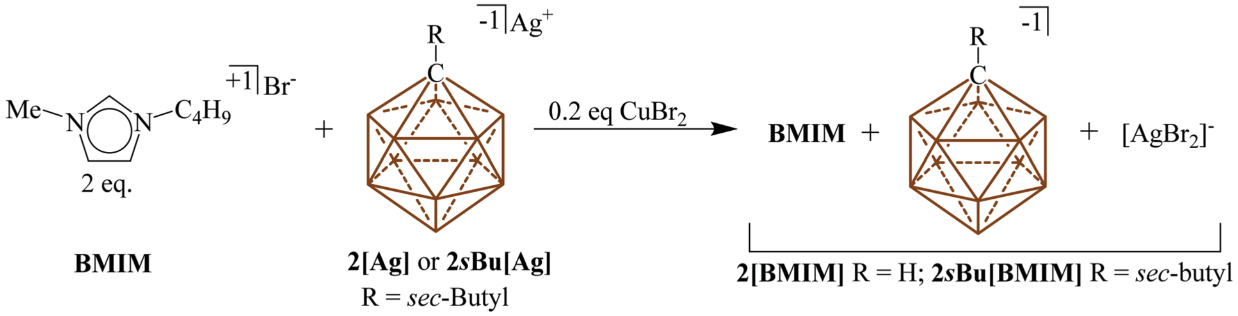


Fig. 2 Some early examples of carborane based ionic liquids.

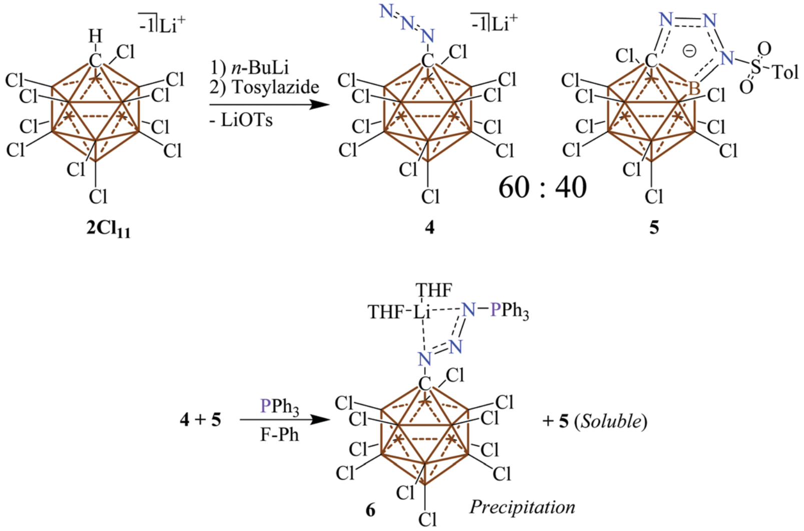
In collaboration with Boron Specialties LLC, and the Spokoyny group at UCLA we have been designing ionic liquid blends containing carborane anions for the reversible electrodeposition of metal thin films in high vacuum environments, such as space. One embodiment of this chemistry has been published and is being utilized to construct electrochemically adaptive and regenerative spacecraft components. Specifically, we developed a system to allow the reversible deposition of high quality Ag mirrors.[42] In contrast to a recent publication by TRI in which **2** was paired with a variety of cations to achieve ionic liquids for energy storage applications,[43] this approach focuses on chemical modification of the carborane anion to develop a boron cluster based ionic liquid with high silver content.[43] This ionic liquid was achieved by reacting [BMIM]Br with **2[Ag]** resulting in an ionic blend of $[\mathrm{BMIM}]^+$ **2**, and $[\mathrm{AgBr_2}]^-$ ions (Scheme 4).[42] This mixture was then sandwiched between two fluorine doped tin oxide (FTO) electrodes furnishing an IR transparent, two-electrode electrodeposition cell. Cyclic voltammetry revealed reversible silver electrodeposition even when performed under 98% humidity, a testament to the superior stability of the carborane anion. However, electrolyte **2[BMIM]** tends to gradually crystallize over time compromising the electrodeposition process. In an effort to prevent crystallization of the electrolyte, the carborane C–H was functionalized with a *sec*-butyl group. This electrolyte showed comparable deposition currents over time (24 hours) as well as no visible crystallization. The ionic liquid **2*s*Bu[BMIM]** performed admirably with an 8% decrease in total energy transmission (Ag dissolved/Ag deposited) with 3 second activation of −2.5 V (deposition) to maximum reflectance.

3. Platforms for new reaction methodology and carborane-fused heterocycles

Early on in our lab's investigations involving carboranyl compounds, we explored the N-functionalization of carborane anions, with the goal of developing access to various carboranyl amines for chemical building blocks for ligands and materials. Although some amine derivatives of **2** and **3** were known,[44–47] we sought a late stage amination reaction using Staudinger reduction conditions. We first investigated the possible synthesis of the still unreported amine $[\mathrm{H_2NCB_{11}Cl_{11}}]^-$. To achieve this we envisioned deprotonating **2Cl₁₁** with a strong base followed by reaction with tosyl azide to produce the corresponding amine. However, upon preparation of the azide precursor **4** a mixture of two products could be observed (Scheme 5, top). The serendipitous discovery of the cycloaddition product **5** through a B–Cl bond of **2Cl₁₁** resulted in further investigation by our lab, however proved an obstacle when isolating **4**. Only upon addition of $\mathrm{PPh_3}$ to the solution of mixed products were we able to isolate the resulting phosphazide **6** (Scheme 5, bottom). Compound **6**, unlike previous phosphazides derived from *o*-carborane, is air and light stable and is the first



Scheme 4 Formation of a boron cluster ionic liquid featuring a silver ion.



Scheme 5 (top) Synthesis of azide **4** and cycloaddition side-product **5** and (bottom) subsequent reaction with PPh_3 to yield stable anionic phosphazide **6**.

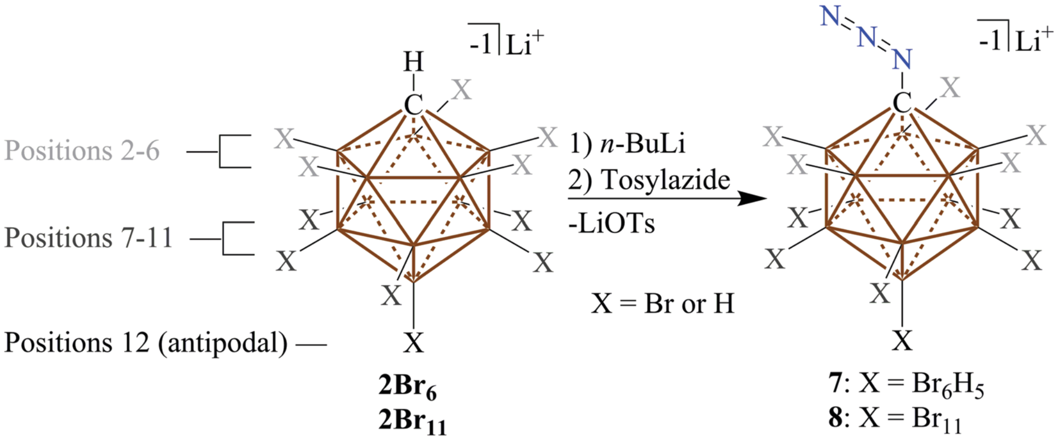
example of an anionic phosphine azide adduct.[48,49] Successful isolation of compound **6** opens up the possibility to prepare similar carborane based phosphazides that may function as interesting ligands in catalysis.

Having observed the unfavourable reactivity of the perchlorinated azide (**4**) and its cycloaddition to **5**[50] we decided to test the properties of the 12-vertex perbrominated **$2Br_{11}$** and the hexabrominated **$2Br_6$** (upper pentagonal belt (positions 2–6) = B–H while the lower pentagonal belt (positions 7–11) = B–Br also the boron opposite the carbon (position 12) = B–Br) anions. For clarity the boron positions have been explicitly labelled in Scheme 6. We hypothesized that **$2Br_{11}$** would not be susceptible to cycloaddition because the proposed pathway followed an associative substitution, thus the larger size of the Br atom should retard B–Br cleavage. As for **$2Br_6$** we proposed that having a belt of hydrogen atoms in place of a belt of halogen atoms should eliminate any cycloaddition reactions from occurring. Using the same reaction conditions as **4** we were able to isolate the hexabrominated azide (**7**) and perbrominated azide (**8**) in pure form (Scheme 6).[51] Azides **7** and **8** show the characteristic azide stretch at 2135 and 2119 cm^{-1} respectively and are not shock sensitive. Both compounds have good thermal stability and do not decompose until heated to 185 and 190 °C, respectively.

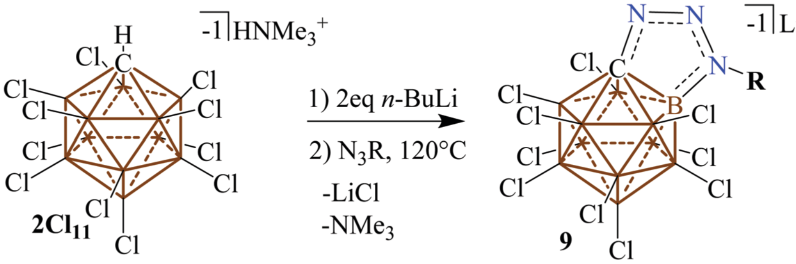
Due to their stability we were able to perform the first single crystal X-ray diffraction study on **7** and **8**. The high disorder associated with **7** led to inaccurate structural metrics, however the connectivity could be confirmed. The bond metrics for **8** were decent and allowed for analysis of the N–N–N bonds, and as expected the internal N–N bond (1.248(5) Å) is longer than the terminal N–N bond (1.129(5) Å). Currently we are exploring the reactivity of these compounds in click chemistry and their use as precursors to carboranyl imide ligands.

4. Anionic *closo*-carborane fused heterocycles

Our previous investigations towards synthesis of $[H_2NCB_{11}Cl_{11}^{-}]$ resulted in the serendipitous discovery of **5** which occurred



Scheme 6 Brominated anionic carborane azide.



R =	: % Yield
Ph	: 95%
$4\text{-}FC_6H_4$	: 94.5%
$4\text{-}MeOC_6H_4$	: 95%
$2\text{-}MeC_6H_4$	: 85%
Mesityl	: 84%
Adamantyl	: 15%

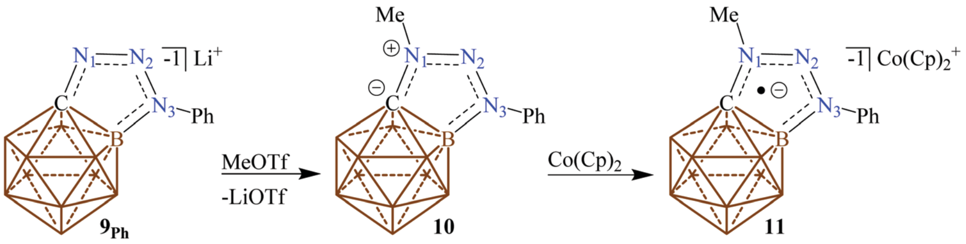
Scheme 7 Cycloaddition of various azides to yield carborane-fused heterocycles **9**.

through cycloaddition of the azide into a B–Cl bond of $\mathbf{2Cl_{11}}$. This compound is intriguing for multiple reasons. Compound $\mathbf{2Cl_{11}}$ has previously been reported as being completely unreactive through the B–Cl bonds that decorate its surface but intramolecular addition of the azide seems to dispel these observations.[52] Furthermore, prior to this investigation, it had remained unknown whether significant conjugation between 2-D and 3-D aromatic systems could exist.[53–56] Derivatives of this "carborane-fused heterocycle" may present a scheme for studying molecules that may illustrate such characteristics. If an azide is utilized that does not have a leaving group, carborane fused heterocycles **9** can be selectively formed with varying R groups (Scheme 7).[55]

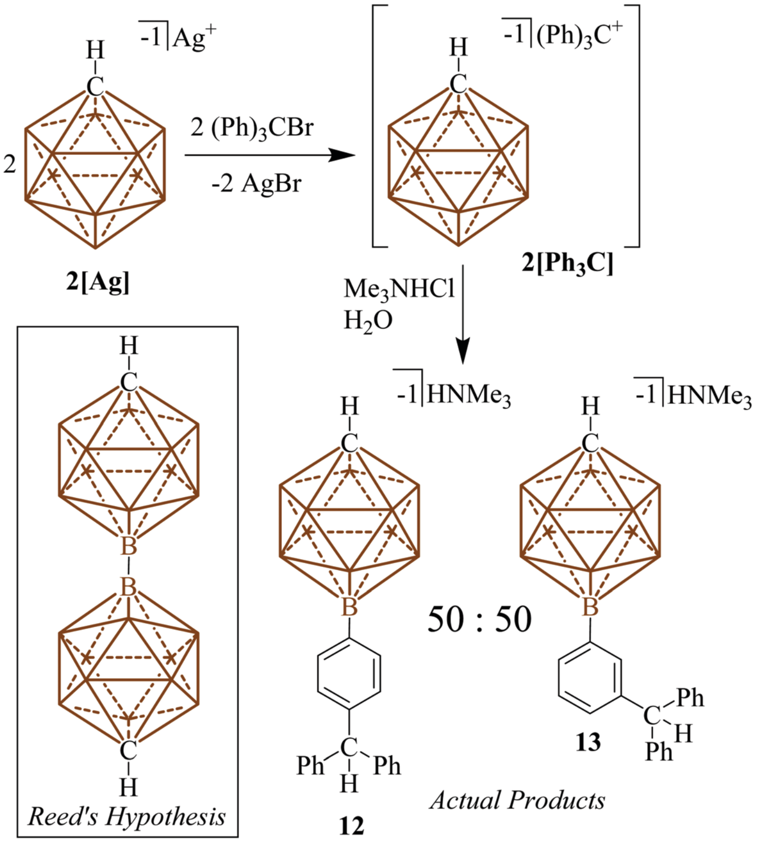
Whether or not a precedent for conjugation between these two aromatic systems exists, as was previously speculated, was of further interest. Indeed, computational investigations into potential aromatic character displayed by **9** proved fruitful, and visualization of the molecular orbitals (MO) reveals significant mixing of the π-type MOs between the carborane and outer heterocycle. Specifically, the HOMO of **9** has significant cluster orbital contributions while the LUMO resides almost entirely out of the 3D framework. The resulting HOMO–LUMO transition of this molecule corresponds to a strong absorption band in the UV region (λ_{max} = 313 nm) and is supportive of extended delocalization between the carborane, heterocycle, and pendant R group. Further computational investigations into the aromatic character of this molecule reveal negative nucleus independent chemical shift (NICS) values (5-membered heterocycle of $\mathbf{9_{Ph}}$: NICS(0) = −7.8, NICS(1) = −8.8, and $\mathrm{NICS(1)}_{zz}$ = −19.3 ppm; fused carborane of $\mathbf{9_{Ph}}$: NICS(0) = −27.8 ppm, $\mathbf{2Cl_{11}}$: NICS(0) = −30.8 ppm, and C_6H_6: $\mathrm{NICS(1)}_{zz}$ = −29.2 ppm) that suggest that both the carborane and fused heterocycle display significant aromatic character. Similar computational predictions have been undertaken in an attempt to determine the cycloaddition reaction pathway which is described in detail in the original publication.[50]

The intriguing aromatic characteristics of these carborane-fused heterocycles led us to investigate **9** through electrochemical means in order to develop a greater understanding of the properties of these molecules. A few examples of icosahedral boranes and functionalized carboranes subject to chemical and electrochemical oxidations have previously resulted in isolable radical species.[57–59] We reasoned that since **9** possesses some degree of *exo*-cluster delocalization independent of the carborane, these compounds may also display interesting redox properties as well. Cyclic voltammetry (CV) experiments of **9** indicated no observable oxidation processes and only irreversible reduction of the compound at large negative potentials. We associated this reductive stability with the unfavorable electrostatic repulsions associated with forming a radical dianion species, and reasoned a related zwitterionic derivative might enable a reversible reduction process. To achieve such a molecule, the N_1 nitrogen of $\mathbf{9_{Ph}}$ was alkylated using methyl triflate to generate the zwitterion **10** in high yield (Scheme 8).

The resulting air-stable zwitterion was subjected to similar CV experiments where it was revealed that reversible reduction of this material was achievable at −0.87 V *vs.* $Fc^{0/+}$ followed by irreversible reduction processes beyond −2.5 V. Cobaltocene, which has a reduction potential of −1.33 V *vs.* $Fc^{0/+}$ seemed the ideal reducing agent to isolate the radical species, and successful isolation of **11** was achieved through charge stabilization with the corresponding cobaltocenium cation (Scheme 8).[60] This species is further stabilized by a combination of forces, which include its extended delocalization through the heterocycle π-system, and kinetic protection of the said radical by the chlorinated surface of the carborane. These efforts resulted in our group achieving the first example of an isolable triazole



Scheme 8 Synthesis of carborane-fused heterocycle zwitterion **10**, and subsequent reduction with cobaltocene to form radical **11**. B–Cl vertices unlabelled for clarity.



Scheme 9 The trityl salt conundrum; Reed's proposed product is in the box and to the right are the actual products.

"like" radical anion by utilization of a carborane-fused heterocycle. Furthermore, isolation of radicals through the use of zwitterionic carboranyl heterocycles can likely be applied to achieve species of similar stability. Our group remains interested in such radical species, which may find application in functional materials.

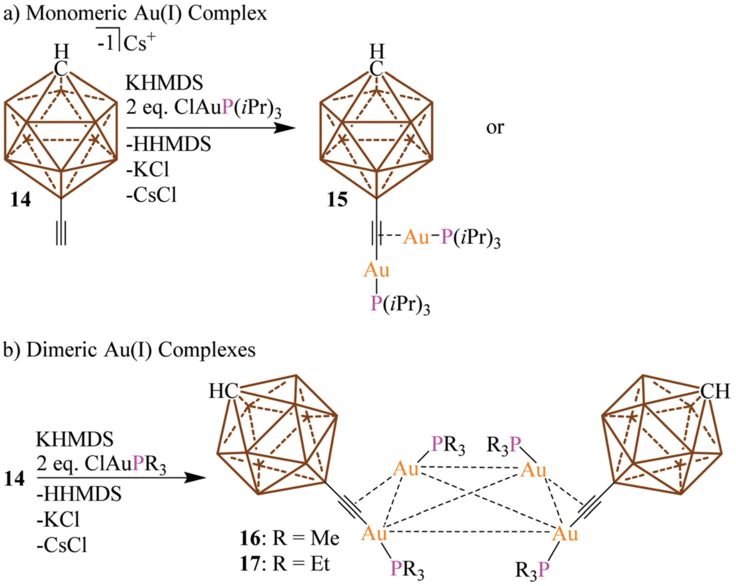
Electrophilic arylation of 2

We became interested in a reaction reported in 1994 by Chris Reed and coworkers. They reported that treatment of **2[Ag]** with trityl bromide led to complicated reactions. The authors did notice an unidentified boron containing compound which retained its local C_{5V} symmetry but the antipodal boron did not split into the expected doublet, as indicated by the ^{11}B NMR spectrum.[61] Upon inspection of the literature they found a report by Hawthorne where oxidation of the 10-vertex cluster, **3**, led to the formation of an antipodal–antipodal B–B dimer.[62] Based on Hawthorne's earlier work Reed and coworkers proposed a possible dimer **23** (Scheme 9, inset). Out of genuine curiosity we decided to see what would happen if **2[Li]** was reacted with tritylbromide in fluorobenzene. During this reaction we observed the precipitation of LiBr and formation of a C_{5V} symmetric compound in the ^{11}B NMR spectrum.[63] As Reed had predicted the reaction mixture was not a single product and the ^{1}H NMR spectrum displayed a complicated spectrum displaying a multitude of aromatic resonances. Upon close inspection we were able to pick out some new resonances which showed coupling patterns reminiscent of a *para* substituted benzene ring. We speculated that a transient species (**2[Ph3C]**) was generated, but rapidly undergoes an electrophilic aromatic substitution "like" reaction producing new arylated products. To investigate this hypothesis we grew crystals and found at least two distinct crystal morphologies. The first crystal structure displayed a B bound trityl compound which confirmed the existence of a *para* bound trityl product **12**. Upon inspection of the other set of crystals we were able to identify a *meta* arylated product **13** (Scheme 9). To confirm the results of Reed from 1994 we performed the same reaction and found the same two products (**12** and **13**).

5. *closo*-Carborane anions as ligand substituents for coordination chemistry and catalysis

Alkynes with carborane anions 2 and 3 as ligand substituents

Compared to ancillary ligands featuring pendant C_2B_{10} clusters, there were almost no investigations into the utility of *closo*-carborane anions **2** and **3** as ligand substituents until we began our research program in 2011. That being said it is important to point out the elegant work done by Maik Finze. The B-bound ethynyl ligand **14** has a unique coordination motif as it could



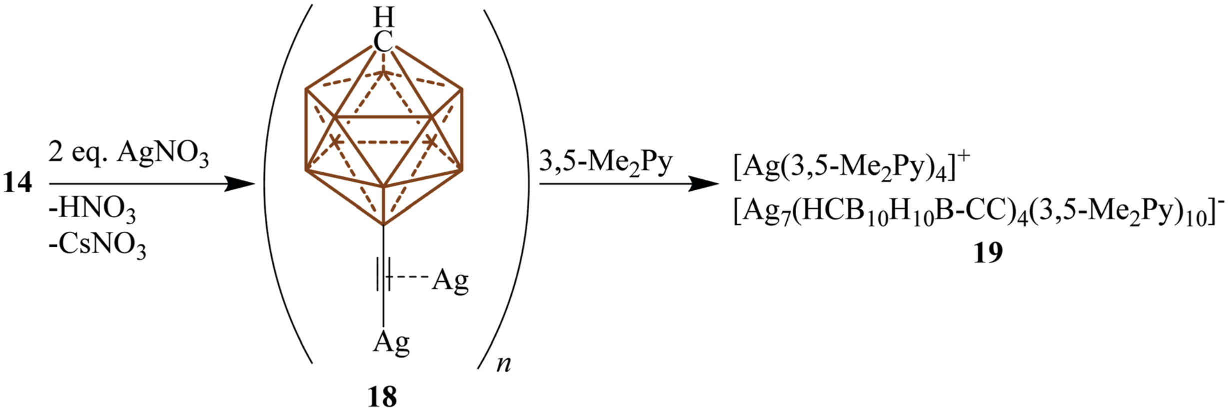
Scheme 10 Synthesis of Au(I) complexes **15–17** with the B-bound ethynyl ligand.

behave as a σ-type ligand, a π-type ligand, or both. In 2011 Finze *et al.*[64] demonstrated that it can act as both, here they reacted **14** with potassium bis(trimethylsilyl)amide (KHMDS) and two equivalents of $ClAuPR_3$ forming discrete Au(I) complexes. This type of reaction likely proceeds *via* deprotonation of the terminal alkyne forming the intermediate dianionic $[Cs]^+[K]^+[CC\text{-}\mathbf{2}]^{2-}$ which undergoes a salt metathesis to $[Cs]^+[R_3PAu\text{–}CC\text{-}\mathbf{2}]^-$ and KCl, which in turn undergoes another salt metathesis giving the complex ion pair $[R_3Au]^+[R_3PAu\text{–}CC\text{-}\mathbf{2}]^-$ and CsCl. The complex ion pair takes on either a monomeric or dimeric form depending on the given R group. If the R group is isopropyl the complex is monomeric giving **15** (Scheme 10a). However if the R group is methyl or ethyl a dimeric complex is formed, which gives complexes **16** and **17**, respectively (Scheme 10b).

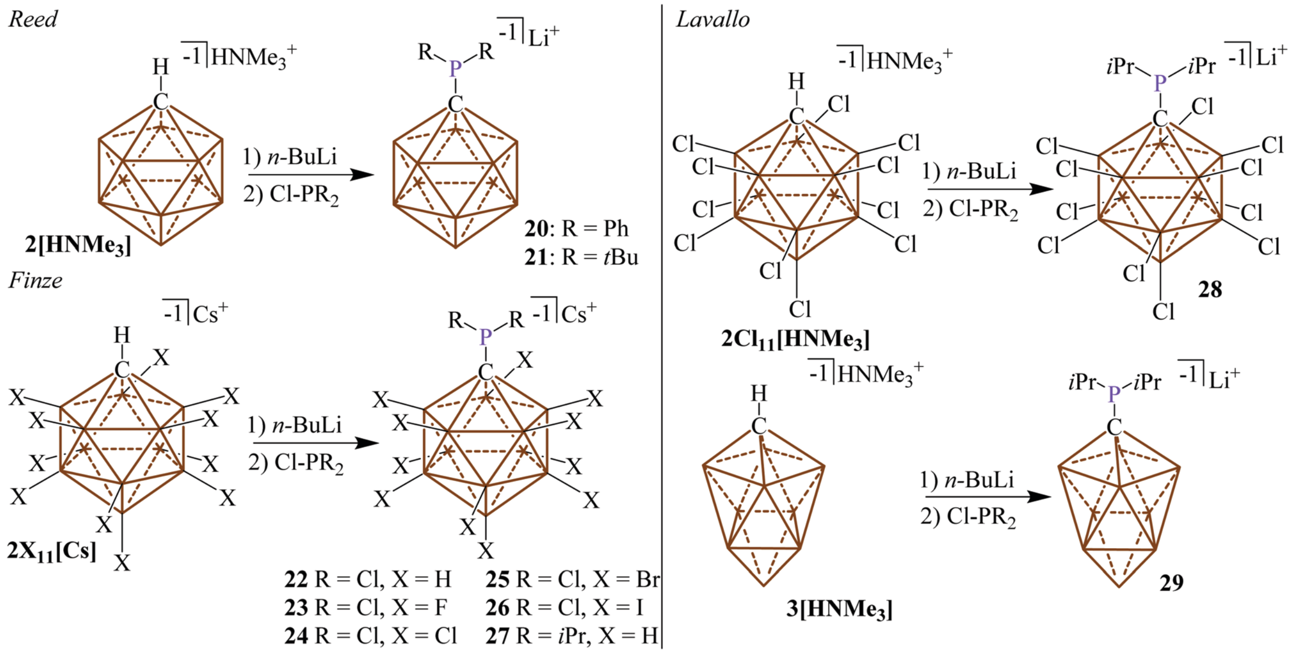
Along the same lines Finze *et al.*[65,66] created a multitude of Ag(I) self-assemblies with **14**. To create these self-assemblies the ligand **14** was reacted with two equivalents of $AgNO_3$ producing the polymeric Ag(I) complex **18** (Scheme 11). The exact structure of **18** was not determined but the Raman spectrum indicated that more than one Ag(I) was bound to the ethynyl motif. Compound **18** proved to be quite a fruitful precursor and a plethora of Ag(I) self-assemblies were created. This library of compounds was created by reacting **18** with different pyridine (Py) ligands. As it turns out, one of these compounds, **19**, displays exceptional phosphorescent properties.[66]

Anionic carboranyl phosphine ligands

The first synthesis of a carborane phosphine was in 1963 with the discovery of the *o*-carborane diphosphine by Alexander and Schroeder.[67] This was prepared by reacting the *o*-carborane **1** with two equivalents of *n*-Bu-Li followed by isolation of 1,2-dilithio-carborane, and sequential reaction with chlorodiphenylphosphine produced the bis(diphenylphosphino)-carborane. Phosphines based on **1** have profusely been investigated and a review has been written.[16] Phosphines based on the 12 and 10-vertex carborane anions, **2** and **3** respectively, have



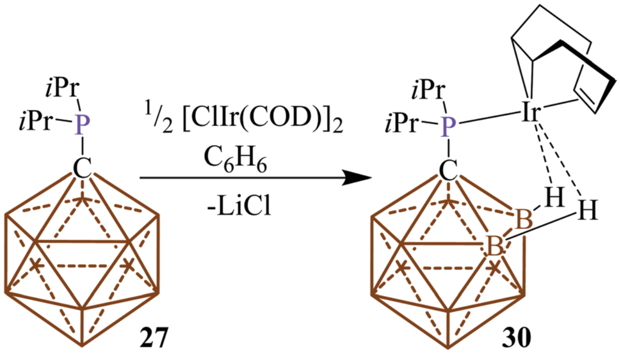
Scheme 11 Synthesis of a Ag(I) complex with a B-bound ethynyl ligand.



Scheme 12 Synthesis of carborane phosphines.

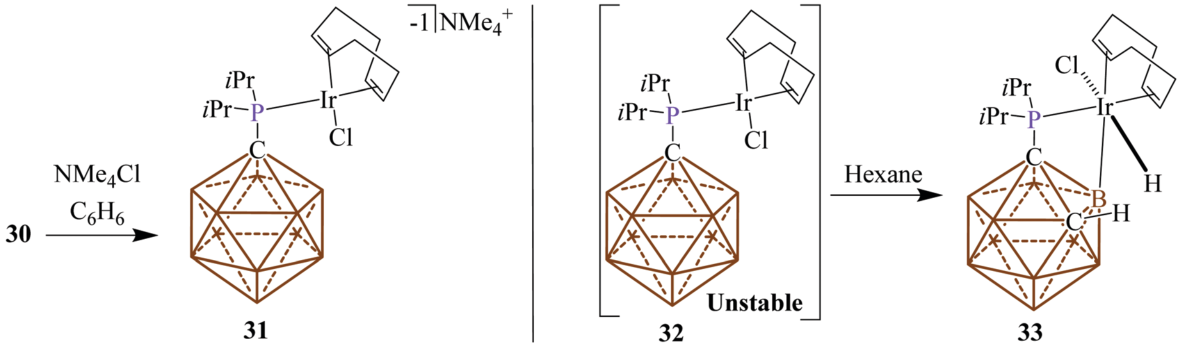
hardly been studied and it was not until 1993 when Chris Reed *et al.* reported the first phosphine with **2** as a substituent. This phosphine was created by the reaction of 2[$HNMe_3^+$] with *n*-BuLi followed by chlorodiphenylphosphine furnishing diphenylphopshine **20**[68] and later Reed and Nava utilized the same synthetic method to produce the *tert*-butyl phosphine **21**[69] (Scheme 12, top left). This method is fairly common and Finze *et al.* have used it to generate a variety of carboranyl phosphines including a family of dichlorophosphines, $[Cl_2P–CB_{11}X_{11}]^-$ (where X = H (**22**), F (**23**), Cl (**24**), Br (**25**), I (**26**)), as well as the diisopropylphosphine **27** (Scheme 12, bottom left).[70] At around the same time we reported the diisopropyl(perchlorinated-carboranyl)phosphine **28** followed by the smaller 10-vertex phosphine **29** (Scheme 12, right).[71–73]

While carborane anions **2** have long been known to be weakly coordinating when used as spectator counteranions, we were curious if the same behavior would be observed when clusters **2** were utilized as ligand substituents in close proximity to metal centers. To do this we reacted **28** and $[ClIr(COD)]_2$ (COD = 1,5-cyclooctadiene) in benzene driving the precipitation of LiCl and forming **30** (Scheme 13).[73] In the solid-state this complex displays two sigma interactions with the carborane B–Hs that are in the 2–6 positions, which is in contrast to what has been observed by Weller[74] for simple σ-complexes of untethered carborane anions **2** (in Weller's complex positions 7–11 closest to the boron antipodal to carbon interact with the metal). This of course is due to the geometric constraints caused by the dative phosphorous bond to the Ir^+ center. Similar to Weller's complex,[74] which shows a weak carborane *trans* influence to the corresponding olefinic COD bond, complex **30** displays the same behavior, even though it is intramolecularly tethered. This effect renders the carborane substituent in **30** negligibly σ-antibonding to the *trans* olefin, allowing for better d–π overlap for back bonding with the olefin π*, resulting in complete reduction of the olefin to a metallocyclopropane. The bonding in **30** was investigated computationally and it was found that along with the bridging B–H "agostic like" interactions with the Ir^+ center there is also a bonding interaction between the B–B sigma-bonding orbitals (two p orbitals with head on overlap) and the d_{z^2} orbital of the Ir^+.



Scheme 13 Synthesis of Ir complex **30**.

Knowing that the diisopropyl(carboranyl)phosphine **27** is a competent ligand we decided to test its stability *versus* the less stable *o*-carborane (**1**). In this context the term "less stable" is used to describe the many reactions where the *o*-carborane loses its structural integrity.[16] In particular, work by Hoel and Hawthorne demonstrated intramolecular B–H oxidative addition reactions at an Ir(I) center when utilizing a *o*-carborane phosphine.[75] We hypothesized that the more chemically robust anionic carboranyl phosphine **27** would resist cyclometalation. To test our hypothesis we set out to make a set of isoelectronic



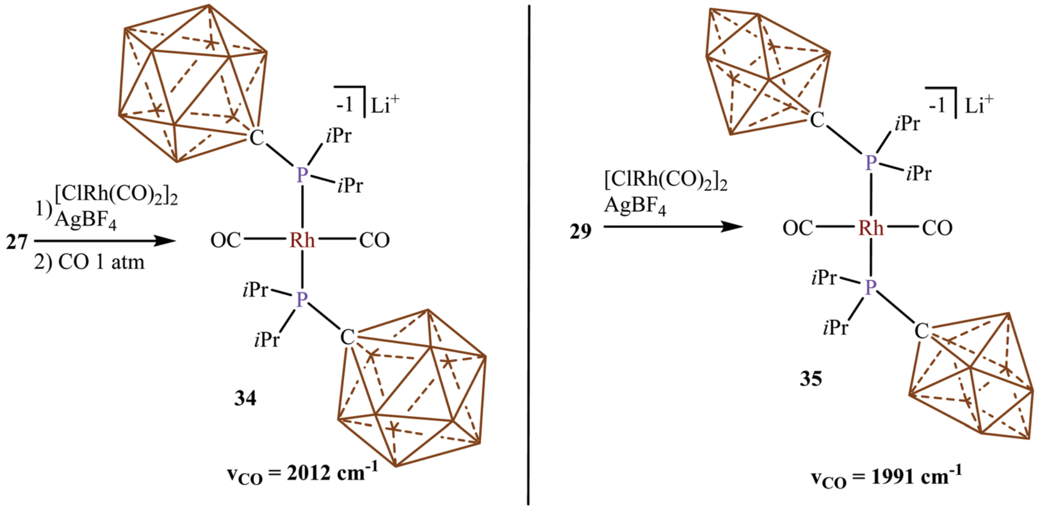
Scheme 14 Formation of Ir–Cl complexes **31–33**. Note: only the B-3 cyclometalated diasteromer of **33** is depicted.

compounds **31** and **32** (Scheme 14). Complex **31** was prepared by reacting **30** with $[NMe_4]Cl$ in benzene (Scheme 14, left).[76] Complex **32** was generated with the known diisopropyl *o*-carboranyl phosphine and $[ClIr(COD)]_2$, however it was not stable or observable by NMR even at low temperature. Instead it instantly B–H cyclometalated to form a 1 : 1 statistical distribution of the two possible diasteromers (two diasteromers arise because there are two possible boron atoms which could undergo B–H cyclometallation, these two boron atoms are those adjacent to both cluster carbon atoms), supporting our hypothesis.

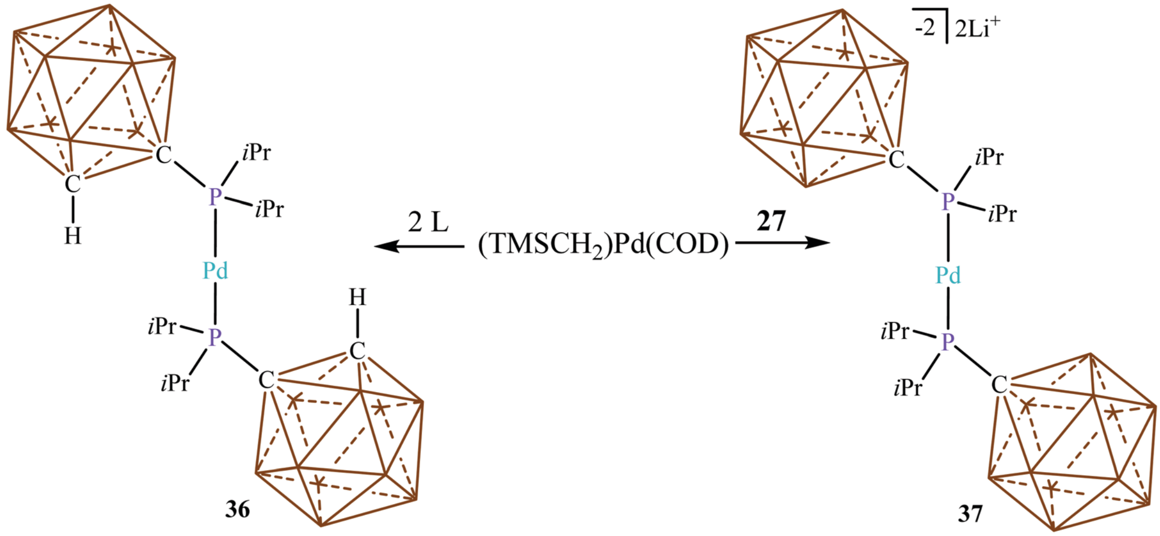
In a separate report we probed the inductive effects of the carboranyl substituents of **2** and **3** by the preparation of a series of locally isoelectronic $[Rh(CO)_2L_2]^+$ complexes. Thus, we prepared complexes **34** and **35** by reacting the corresponding anionic carboranyl phosphine and a mixture of $[RhCl(CO)_2]_2$ with $AgBF_4$ (Scheme 15).[71] Unlike complex **35**, which does not show any sign of CO dissociation, complex **34** readily loses a CO ligand and forms a B–H "agostic-like"[73] interaction in its place. Under 1 atmosphere of CO complex **34** can be regenerated and is stable if kept under CO pressure. This is likely due to the steric differences between the 10-vertex and 12-vertex carboranes and perhaps **35** might backbond stronger with the CO ligands. Indeed, measuring the ν_{co} of **34** and **35** gives values of 2012 cm^{-1} and 1997 cm^{-1}, respectively, thus confirming that the 10-vertex cluster is a better donor. When comparing these stretching frequencies to those of $[Rh(CO)_2(P(i\text{-}Pr)_3)_2]^+$ (ν_{co} = 2010 cm^{-1}) or $[Rh(CO)_2(P(Ph)_3)_2]^+$ (ν_{co} = 2047 cm^{-1}) one can conclude that the 12-vertex carborane anion **2** has similar donating properties to an isopropyl fragment while the 10-vertex carborane anion **3** is a much more potent electron donor than an isopropyl group. This is in stark contrast to the neutral *o*-carborane which is an electron withdrawing substituent when bound by the cluster carbon.[77] In addition, we analysed the steric profile of the phosphine ligands in complexes **34** and **35** and found their cone angles to be 171° and 168°, respectively.

Catalysis with carboranyl phosphine ligands

While there are various isolable neutral L_2Pd diphosphine complexes that are useful for Pd-catalysed cross-coupling chemistry, none of these molecules are anionic. Given the importance of salt additives in manipulating the performance of various cross-coupling chemistries, we became curious if we could prepare dianionic L_2Pd species, which might display interesting reactivity patterns. At the same time we wanted to prepare an isoelectronic neutral L_2Pd species supported by two *o*-carboranyl phosphines, which would be sterically similar but



Scheme 15 Synthesis of bisphosphine Rh dicarbonyl complexes.

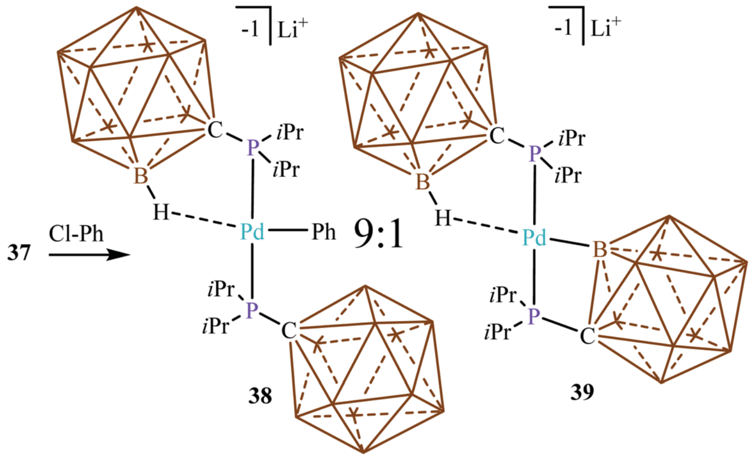


Scheme 16 Synthesis of isoelectronic neutral **36** and dianionic **37** L_2Pd complexes. L = 1-diisopropylphosphino-1,2-dicarba-*closo*-dodecaborane.

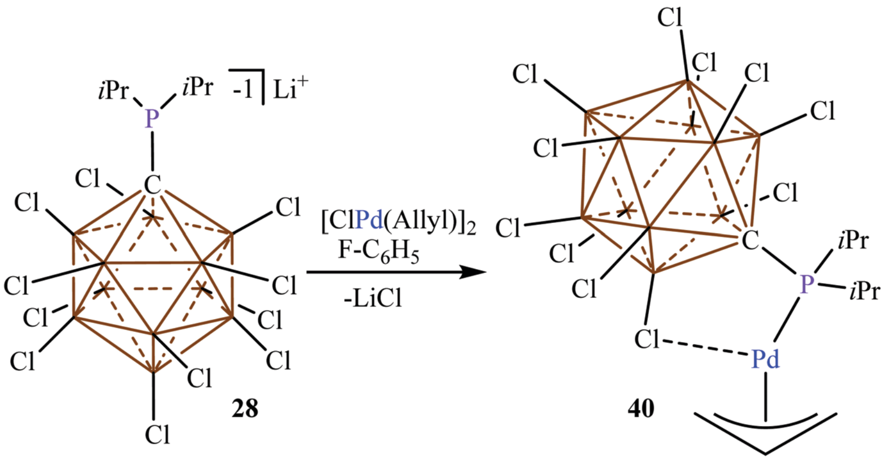
very electronically different. We prepared the systems **36** and **37** by reacting the corresponding neutral (L) and anionic carboranyl phosphines **27**, respectively, with 0.5 equivalents of $(TMSCH2)_2$-Pd(COD) (COD = 1,5-cyclooctadiene) in benzene (Scheme 16).[78] While complex **36** shows no reaction with Cl–benzene, compound **37** instantly undergoes oxidative addition at ambient temperature.

This reaction forms two distinct products in a 9 : 1 ratio, the major product being the bisphosphine Pd(II) aryl complex **38** and a minor product of B-cyclometallated Pd(II) complex **39** (Scheme 17). Rapid oxidative addition of chlorobenzene with **37** was not due to the alkali metal counter cation as there was no noticeable difference between Li^+, Na^+ and K^+. Furthermore, as the donor properties of ligand **27** are similar to diisopropyl phosphine and $L_2Pd(0)$ (L = diisopropyl phosphine) very slowly reacts with Cl–benzene at ambient temperature, the rapid oxidative addition of **37** cannot be explained by donor effects of the ligand. We hypothesized that perhaps one of the phosphines might readily dissociate because of electrostatic repulsion between the two charged carboranyl groups, thus allowing facile access to L–Pd–solvent species, which are known to be involved in Pd oxidative addition reactions. Indeed, the addition of excess ligand **27** to a solution with **37** and chlorobenzene results in an inverse first order dependence on oxidative addition, with respect to the added ligand, suggesting a dissociative pathway.

To better understand the relationship between **38** and **39** DFT calculations were performed. In the presence of Cl–benzene complex **37** undergoes a barrierless ligand exchange forming a L–Pd η^2 π-complexed chlorobenzene adduct, which subsequently undergoes a low barrier oxidative addition of the $Cl–C_{aryl}$ bond, which is in line with our empirical data. Reassociation of the displaced phosphine and simultaneous elimination of LiCl forms complex **38**. Side product **39** forms *via* a divergent pathway involving the σ-bond metathesis of an M–aryl bond and a B–H bond. Despite the minor decomposition of **38** to **39** the complex **37** is a competent precatalyst in the Kumada cross coupling of aryl chlorides.



Scheme 17 Reaction of an anionic carboranyl Pd(0) complex with chlorobenzene.



Scheme 18 Synthesis of allyl complex **40**.

In another study we investigated the utility of a perchlorinated carboranyl phosphine in olefin polymerization catalysis. Phosphine **28** reacts with 0.5 equivalents of $[ClPd(allyl)]_2$ in fluorobenzene to afford the zwitterionic compound **40** (Scheme 18).[79] Complex **40** is reminiscent of a Drent type single-component late-metal olefin polymerization catalyst, featuring a phosphine sulfonate ligand.[80] The similarity here is that both complexes contain a weakly coordinating anion in close proximity to the phosphine center. This is corroborated in the crystal structure of **40**, which displays a Pd–Cl bond of 2.401(7) Å, well within the range of typical Pd–Cl bonds of allyl complexes (bridging Pd–Cl bonds = 2.380–2.420 Å and terminal Pd–Cl bonds = 2.350–2.410 Å).[81–84] However, in solution there appears to be no rigid Pd–Cl bond and instead the cluster freely rotates, indictated by the retention of the local C_{5v} symmetry in the ^{11}B NMR spectrum (3 peaks in a 1 : 5 : 5 ratio).

Testing the reactivity of **40** we discovered that it rapidly isomerizes 1-hexene to 2-hexene (Fig. 3a). To avoid issues with isomerization we decided to react **40** with styrene. When heated to 50 °C we were able to obtain 75% yield of the head-to-tail dimer after 4 hours (Fig. 3b). When 0.1 mol% of **40** is reacted with norbornene at 80 °C for 24 hours a 75% yield of polynorbornene is found (Fig. 3c). The polymer was found to have an MW of 44 kDa and a polydispersity index of 1.71. What is unique about catalyst **40** is its ability to operate at temperatures above 70 °C where most Pd olefin polymerization catalysts rapidly decompose, this may be attributed to the stability of the perchlorinated carboranyl phosphine.

In the field of gold chemistry, we have developed two hydroamination catalysis systems. Typical pre-Au catalysts require an acid or Ag^+ initiator to generate the active Au^+

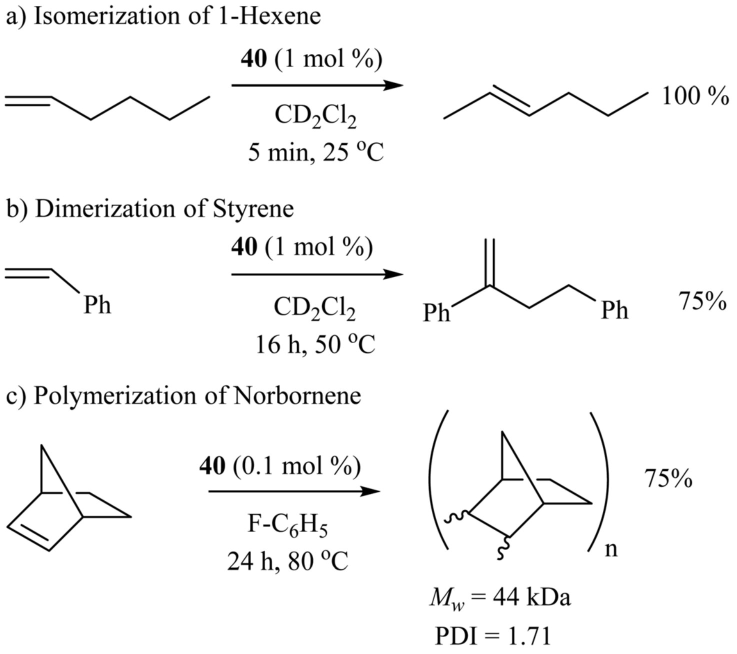
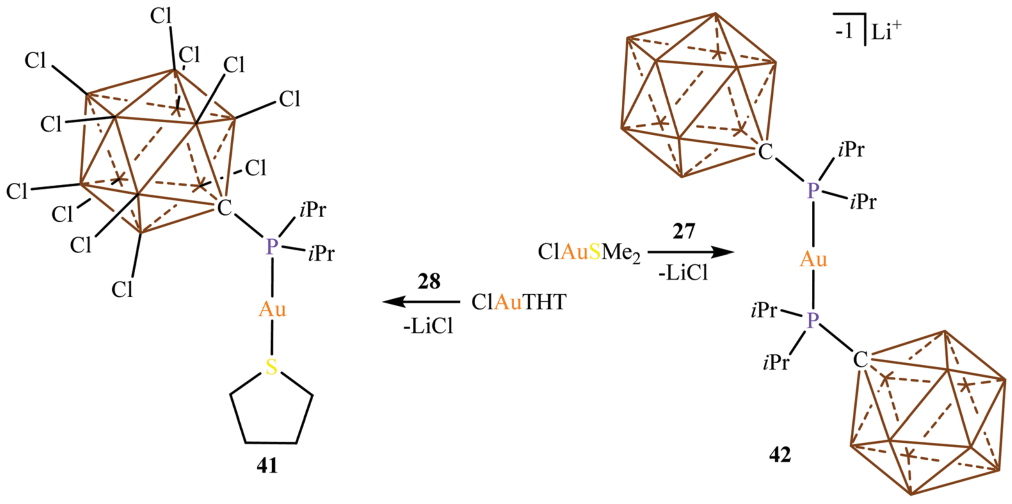


Fig. 3 Substrate scope for Pd catalyst **40**.



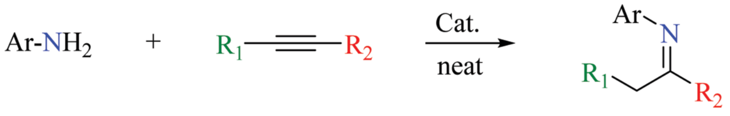
Scheme 19 Synthesis of Au(I) complexes **41** and **42**.

catalyst.[85–87] The reaction of the anionic perchlorinated phosphine **28** and Cl–Au–THT (THT = tetrahydrothiophene) in F–Ph produces the monophosphine ligated zwitterionic complex **41** (Scheme 19).[73] Compound **41** is a single component system that does not require an added initiator. In contrast when the lithium hydridocarboranyl phosphine **27** reacts with Cl–Au–SMe$_2$ it undergoes substitution of both the dimethylsuflide and chloride giving an anionic biscarboranylphopshine complex **42**, which contains a lithium counter cation.[88]

Although complex **42** contains two phosphine ligands we thought that it might readily dissociate a single phosphine ligand for electrostatic reasons similar to the Pd(0) complex[78] **37**, *vide supra*. The catalytic results for the hydroamination reactions of **41** and **42** are depicted in Table 1 and show that all complexes are competent catalysts for the hydroamination reaction. However, for all entries catalyst **41** is dramatically more active than anionic system **42**. In fact, the zwitterionic catalyst **41** to date displays the highest activity reported for the hydroamination of alkynes with any metal, for certain substrates (Table 1, entries 2, 3, 7–9, 13–15).

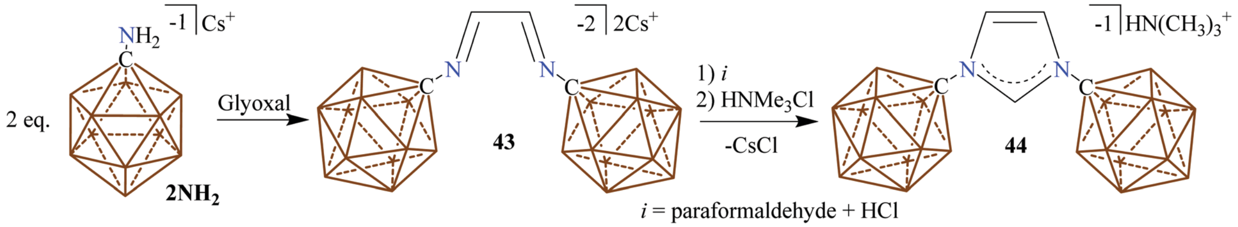
While investigating the reactivity differences between **41** and **42** we found that electrostatic repulsions of the two anion phosphine ligands in **42** was not strong enough to facilitate facile ligand dissociation without external heating. In contrast to the Pd(0) complex **37**, the reluctance of the ligand to dissociate in complex **42** is likely due to the reduced coulombic repulsion between the two clusters given that Au(I) is formally positively charged. We also noticed the formation of Au nanoparticles as

Table 1 Substrate scope for the hydroamination catalyst **41** and **42**



Entry	Cat.	Ar	R$_1$	R$_2$	Mol%	h	°C	% yield[a]	T.O.N.
1	**41**	Ph	H	Ph	0.004	16	50	88	22 000
2	**41**	Mes	H	Ph	0.001	24	50	67	67 000
3	**41**	Dipp	H	Ph	0.001	24	50	85	85 000
4	**42**	Ph	H	Ph	0.1	24	80	77(74)[b]	770
5	**42**	Mes	H	Ph	0.1	24	80	71	710
6	**42**	Dipp	H	Ph	1.0	24	80	80(74)[b]	80
7	**41**	Ph	H	4-FC$_6$H$_4$	0.001	24	50	54	54 000
8	**41**	Mes	H	4-FC$_6$H$_4$	0.001	24	50	75(60)[b]	75 000
9	**41**	Dipp	H	4-FC$_6$H$_4$	0.001	24	50	92	92 000
10	**42**	Ph	H	4-FC$_6$H$_4$	1.0	24	80	90(86)[b]	90
11	**42**	Mes	H	4-FC$_6$H$_4$	1.0	24	80	90	90
12	**42**	Dipp	H	4-FC$_6$H$_4$	1.0	24	80	87(83)[b]	87
13	**41**	Ph	H	4-MeOC$_6$H$_4$	0.001	24	50	90	90 000
14	**41**	Mes	H	4-MeOC$_6$H$_4$	0.001	24	50	94(93)[b]	94 000
15	**41**	Dipp	H	4-MeOC$_6$H$_4$	0.001	24	50	>95(88)[b]	>95 000
16	**42**	Ph	H	4-MeOC$_6$H$_4$	0.1	24	80	92	920
17	**42**	Mes	H	4-MeOC$_6$H$_4$	0.1	24	80	95(92)[b]	950
18	**42**	Dipp	H	4-MeOC$_6$H$_4$	0.1	24	80	78	780

[a] Yields determined by NMR. [b] Isolated yields.



Scheme 20 Synthesis of dianionic bis(carboranyl)imidazolium salt **44**.

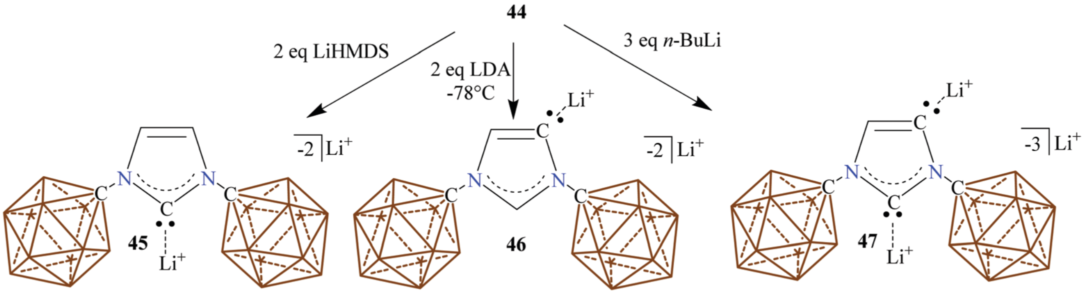
well as metallic plating on the walls of the reaction vessels containing **42**; no decomposition was noted after catalytic reactions with **41.** This is likely due to the decreased chemical stability of the hydrido cluster bound to phosphine **27** compared to the perchlorinated moiety in phosphine **28.** Phosphine ligand **28** is also more electron deficient compared to hydrido phosphine **27**; thus, the Au center is able to act as a stronger π-acid towards alkynes.

Anionic carboranyl NHC ligands

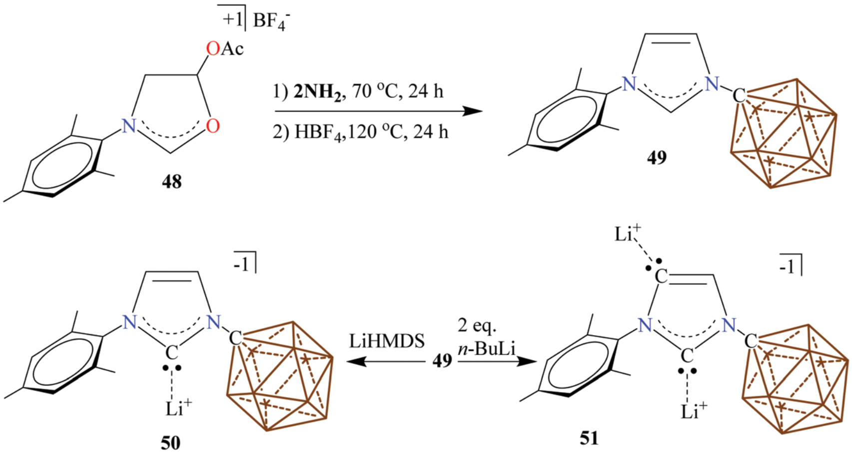
In 2014 we reported the first NHCs featuring carborane anions directly bound to the NHC nitrogen atoms. The synthesis was achieved *via* condensation of the amine **$2NH_2$** with glyoxal to form the dianionic diimine **43**, which subsequently was treated with paraformaldehyde to induce ring closure to afford the monoanionic imidazolium salt **44** (Scheme 20).[89]

Compound **44** is the first example of an imidazolium salt capable of producing three distinct NHCs from a single precursor. Deprotonation of **44** with lithium bis(trimethylsilyl)amide (LiHMDS) in THF produced the dianionic C-2 deprotonated NHC **45** (Scheme 21). Using lithium diisopropylamide (LDA) at −78 °C in THF selectively produced the C-5 deprotonated NHC **46.** Thirdly, deprotonation with *n*-BuLi gives the C-2/C-5 deprotonated NHC **47.** All three NHCS were fully characterized by multinuclear NMR spectroscopy and **45** and **47** were structurally confirmed by single crystal X-ray diffraction. NHC **46** was confirmed *via* multinuclear NMR as well as deuterium labeling experiments.

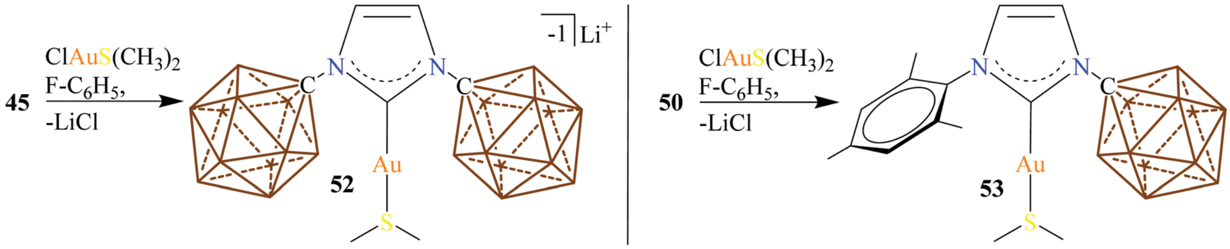
Subsequently we reported the synthesis of unsymmetrical anionic NHCs. The imidazolium zwitterion precursor was prepared with oxazolinium **48** and **$2NH_2$** furnishing the zwitterionic imidazolium **49** (Scheme 22).[90] Unlike the symmetrical



Scheme 21 Synthesis of three discrete NHC lithium adducts **45–47**.



Scheme 22 Synthesis of unsymmetrical imidazolium zwitterion **49** and subsequent deprotonation to form NHC lithium adducts **50** and **51**.



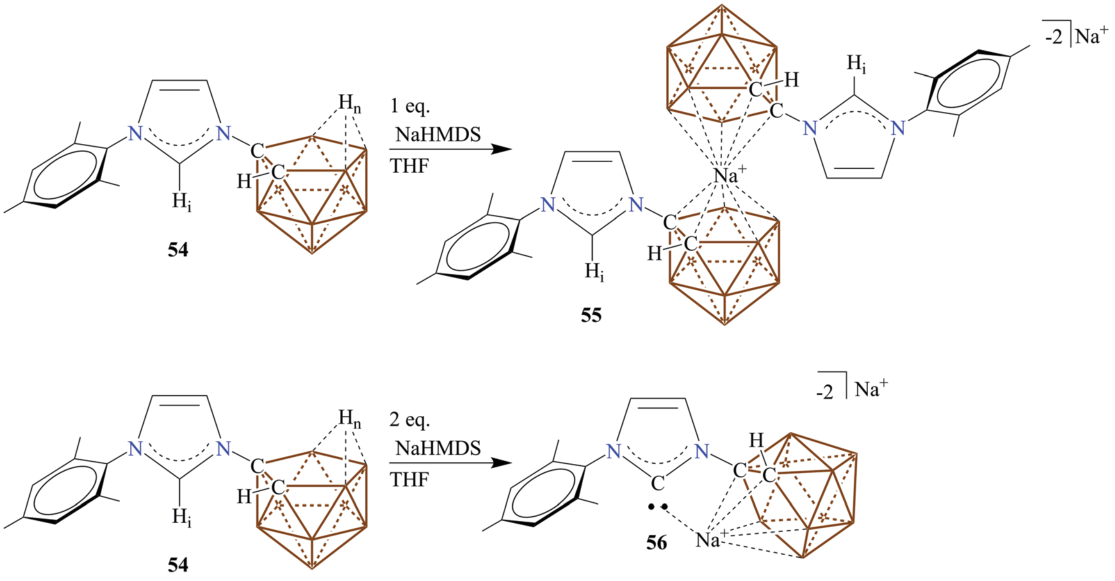
Scheme 23 Synthesis of Au(I) complexes bearing anionic carboranyl NHCs **52** and **53**.

imidazolium **44**, the deprotonation of compound **49** led only to the C-2 **50** and C-2/C-5 **51** deprotonated NHC Li adducts, demonstrating that two carborane substituents are necessary to form the C-5 isomer. Interestingly, since the double deprotonation occurs on an unsymmetrical precursor the base could react at either the C-5 or C-4 positions or create a mixture of compounds. However, the C-5 isomer is the only product obtained, likely due to steric reasons and the electrostatic repulsion that would occur between the cage and a C-4 deprotonated position.

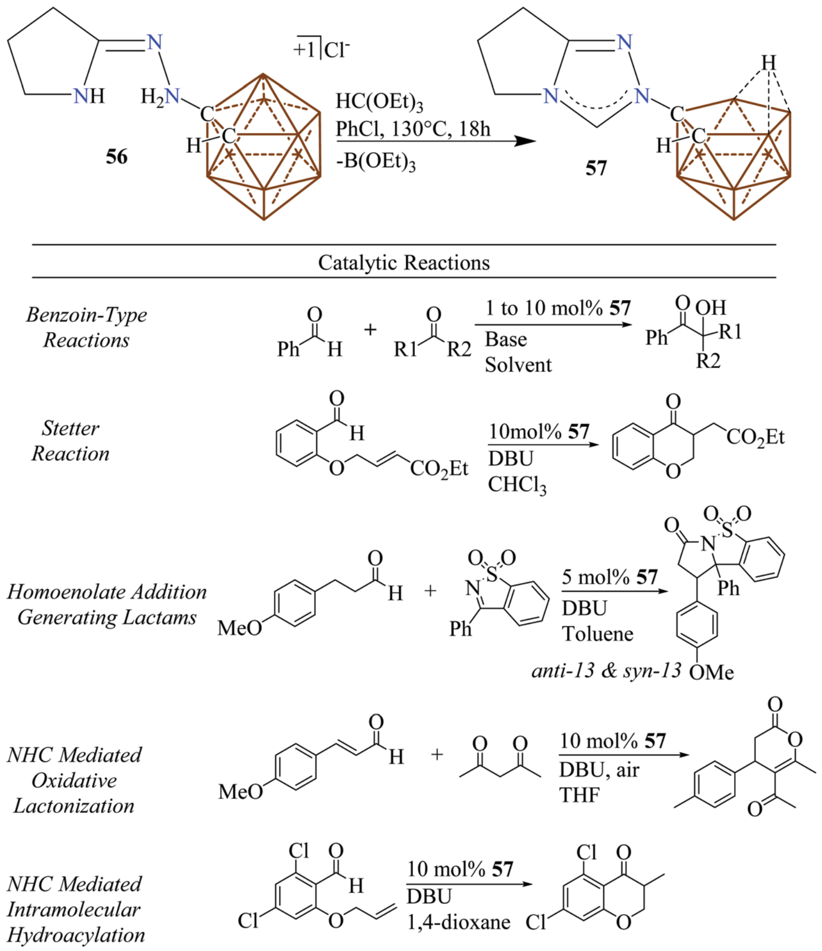
To determine if NHCs **45** and **50** were viable ligands for transition metals we prepared two Au(I) compounds.[91] In this report **45** and **50** were reacted with Cl–Au–SMe$_2$ in fluorobenzene, driving the precipitation of LiCl, and furnishing complexes **52** and **53,** respectively (Scheme 23). In the solid-state the anionic Au(I) complex **52** displays a nearly linear C–Au–S angle of 179.9° while the zwitterionic complex **53** has a respective angle of 171.7°. This deviation away from linearity is likely caused by the bulky steric profile of the carborane. The cluster substituent is canted away from the Au(I) center and the mesityl ring pulled close to the metal center, allowing for a cation–π interaction. To elucidate the steric difference between a hydrido substituted icosahedral carborane and an adamantyl group we performed percent buried volume (% V_{bur}) calculations and found the carborane to be larger by 3.7%.[92]

In a related report, we demonstrated that the classic dicarbollide ion can also act as a viable ligand substituent for NHCs.[93] The precursor zwitterionic nido-imidazolium salt **54** was produced in an analogous fashion to **49**, but starting from the corresponding anionic nido-amine. This zwitterionic imidazolium contains two acidic protons; one on the nido cluster H$_n$ (pK_a = 13.5, DMSO)[94] and the imidazolium proton H$_i$ (pK_a 16–24, DMSO).[95] Indeed, one equivalent of sodium bis(trimethylsilyl)amide (NaHMDS) removes proton H$_n$ and the sodium cation sits in the open face of the nido cluster giving the anionic bisdicarbolide complex **55.** With a second equivalent of NaHMDS, proton H$_i$ is deprotonated furnishing the dianionic NHC **56** (Scheme 24). In **56** the NHC portion of the molecule chelates the Na$^+$ center along with the η^5-coordinated dicarbollide wing tip.

In a report from another group a triazolium zwitterion appended with a nido cluster was reported as a pre-organocatalyst.[96] This compound was created by the cyclization of **57** with triethyl orthoformate giving **58** (Scheme 25, top). Although the pre-catalyst in the presence of a base was capable of oxidative lactonization, ketamine annulation, Stetter reactions and benzoin-type condensations, its activity was only moderate (Scheme 25, bottom). However, in this report it is unclear what is doing the catalysis as one could imagine multiple centers on the heterocycle being



Scheme 24 Synthesis of dicarbollide fused NHC **56**.



Scheme 25 A zwitterionic triazolium appended with a nido-cluster and its use in organocatalysis.

operative during the catalytic process (the N lone pair, dicarbollide ion, or NHC-if it forms in the reaction).

6. Conclusions

It is clear from the manuscript above that there is a diverse array of novel directions that one can take with carborane anion scaffolds. With the ever growing need for smaller, safer, and more energy dense batteries the *closo*-carborane anions **2** and **3** will likely find new applications beyond those already demonstrated for Mg-ion cells. Their electrochemical stability and tunability makes them amenable for other multivalent ion chemistries as well as Li batteries. The B–X substitution chemistry we have reported to form heterocycles that are precursors to unusual radicals, perhaps could be extended to different 1,3-dipoles other than azides. In addition, the electrophilic arylation chemistry outlined will probably be possible with other *closo*-carborane anions as well as borohydride clusters. The novel ligands formed by using these clusters as ligand substituents create such unique chemical environments that novel catalytic reactions and/or approaches will surely be discovered beyond that discussed in this manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

The authors would like to thank the Air Force Research Laboratory for funding through the SSTR program (Topic AF 16-AT20) and the NSF for support (DMR-1508537).

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