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Recent advances on carborane-based ligands in low-valent group 13 and group 14 elements chemistry

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ABSTRACT

Carboranes are a class of polyhedral boron-carbon molecular clusters, they can serve as versatile ligands in stabilizing low-valent main group element compounds, due to their exceptionally thermal and chemical stabilities, easy modifications at the cage carbon vertices, as well as large spherical steric effects. These carborane-based ligands provide interesting opportunities for the synthesis of low-valent main group element compounds with novel structure and reactivity, which indeed enrich the chemistry of low-valent element main group compounds. This review summarizes the recent advances in the chemistry of low-valent group 13 and group 14 element compounds supported by carborane-based ligands. Achievements and perspectives in this new and flourishing field are discussed in this review.

1. Introduction

Tremendous advances have been achieved in low-valent main group chemistry during the past three decades. Benefit from the appropriate design of ligands and synthetic strategies, a variety of low-valent main group element compounds, such as carbenes [1–5], silylenes [6–10], germylenes [6,7], borylenes [11], alanediyl [12], aluminyl anions [13], as well as boryl anions [14–17], which were long-considered as transient species have been synthesized and isolated in laboratory conditions. In this context, sterically and electronically demanding ligands are crucial, which affect not only the stability, but also the chemical and physical properties of such highly reactive species. Among them, *N*-heterocyclic ligand systems, such as β-diketiminato (“NacNac”) [18,19], ene-diamide [14,20,21], amidinate [22,23], amidophosphine [24], as well as monodentate ligand, *m*-terphenyl [12,25] are the most commonly utilized resulting from the facile modifiability of the ligand frameworks (Fig. 1).

Carboranes are a class of polyhedral boron-carbon molecular clusters, which have long been employed as versatile ligands for transition metals, leading to the formation of a new class of organometallic complexes with interesting structural features [26–33]. In contrast, carborane-based ligands were employed in main group chemistry only in recent years. On the other hand, carboranes can also be considered as an alternative ligand system for low-valent main group element compounds attributed to their exceptionally thermal and chemical stabilities, easy modifications at the cage carbon vertices, large spherical steric effects, as well as the *exo*-π-bonding interactions between low-valent main group elements and cage carbons [34–37]. This review summarizes recent achievements in the application of carborane-based ligands in low-valent group 13 and group 14 elements chemistry.

2. Application in low-valent group 13 elements chemistry

Borylenes (R-B:), the boron(I) derivatives analogous to carbenes, are extremely electron-deficient and reactive arising from their structural features, only one substituent, but two vacant orbitals. In fact, free borylenes have not been isolated thus far, nevertheless, a series of Lewis bases-stabilized borylenes were synthesized [38].

In 2015, Xie and coworkers investigated the application of *o*-carborane ligand in stabilization of borylenes by an iminocarborane **1** featuring an imino group attached to one cage carbon [39]. Treatment of **1** with *n*-BuLi in toluene, followed by the addition of BBr_3 resulted in the formation of iminocarboranyldibromoborane **2**. The desired iminocarboranylborylene **3** was prepared and isolated by reduction of **2** with potassium graphite in the presence of 1,3-diisopropyl-4,5-dimethylimidazole-2-ylidene in 57% yield (Scheme 1). Both X-ray analyses and density functional theory (DFT) calculations illustrate the presence of ligand-to-boron σ-donation and boron-to-ligand π-backdonation, which plays a crucial role for the stabilization of borylene **3**.

The presence of a lone pair of electrons at boron implies the potential of **3** to behave as a Lewis base, however, no

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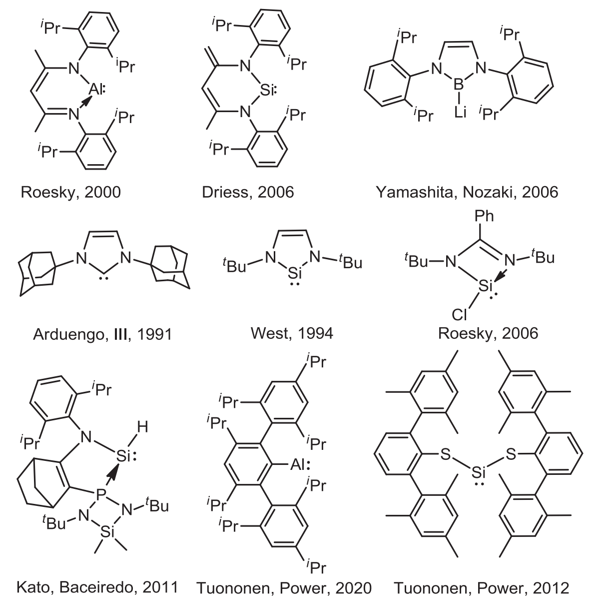
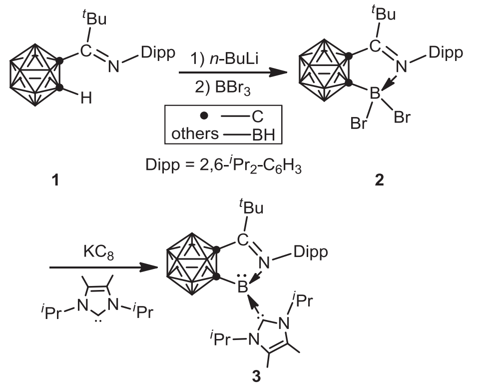
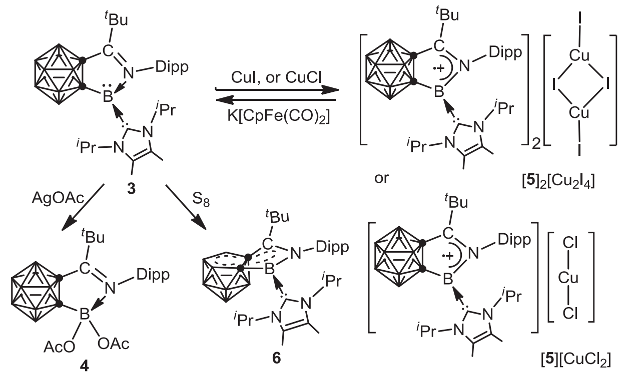


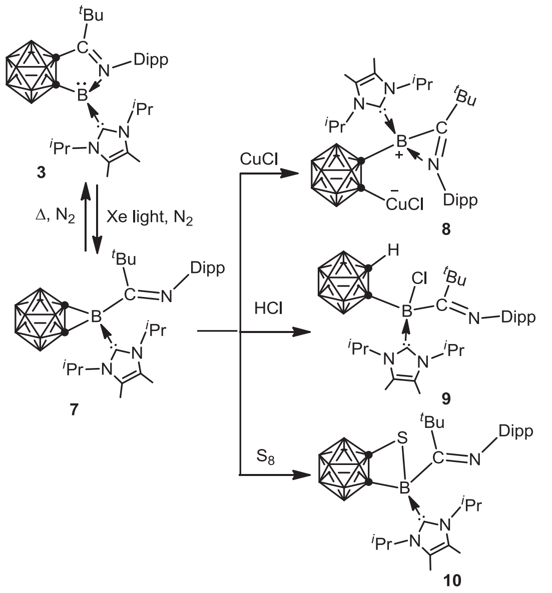
Fig. 1. Selected low-valent group 13 and group 14 element compounds supported by *N*-heterocyclic and *m*-terphenyl ligand systems.



Scheme 1. Synthesis of iminocarboranylborylene.



Scheme 2. Oxidation of **3**.



Scheme 3. Reversible photothermal isomerization between **3** and borirane **7**.

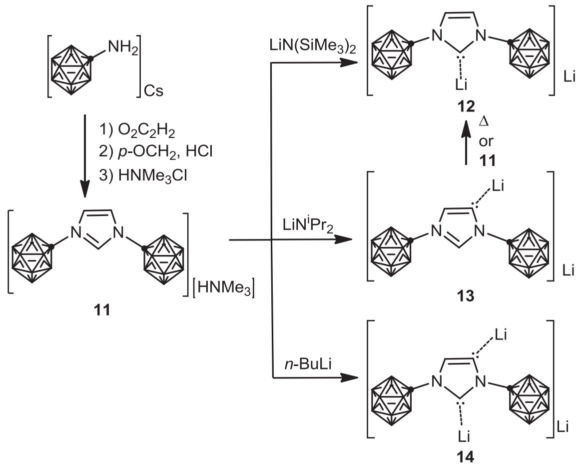
reactions of **3** were observed with various transition metals, such as $Ni(COD)_2$, $Pd(PPh_3)_4$, $Pd(dba)_2$ and $ZnMe_2$ (COD = 1,5-cyclooctadiene, dba = dibenzylideneacetone), probably because of the steric hindrance around boron. Nevertheless, the $2e^-$ oxidation reaction of **3** with 2 equiv. of AgOAc in THF proceeded smoothly at room temperature, which afforded the formation of the expected trivalent boron compound **4** and silver metal [39]. To probe the above reaction process, the oxidation of **3** was assessed electrochemically, and the cyclic voltammogram of **3** shows a reversible $1e^-$ oxidation at $E_{1/2} = -1.09$ V (*versus* Fc/Fc^+), which implied the oxidation reaction might involve a radical cation intermediate. Indeed, the corresponding azaborolyl radical cations $[\mathbf{5}]_2[Cu_2I_4]$ or $[\mathbf{5}][CuCl_2]$ were obtained as NMR-silent dark red crystals by treatment of **3** with CuI or CuCl in THF at room temperature [40], in addition, the radical cations could be fully converted back to **3** *via* the reaction with $K[CpFe(CO)_2]$ (Scheme 2). DFT calculations show that the electron is delocalized over the BNC moiety, and the spin density is mainly localized at carbon (~73%) and boron (~25%). On the other hand, an unexpected oxidative deboration reaction was observed when **3** reacts with elemental sulfur in THF, leading to the formation of an unprecedented carbene-stabilized dicarbollyl-fused azaborole **6**, rather than the compound with a "B=S" double bond [41–46]. Both X-ray analyses and DFT calculations clearly illustrate the existence of π-conjugation between the azaborole ring and dicarbollyl ring.

In 2017, the Xie group reported the reversible photothermal isomerization between **3** and borirane **7**, an obvious color change was observed from deep purple to pale yellow, which afforded the first example of carborane-fused borirane **7** (Scheme 3) [47]. DFT calculations show that **3** is thermodynamically more stable compared to borirane. It was noteworthy that, this reaction brought about a new avenue to approach carborane-main group elements three-membered ring. The B-C(cage) bond of **7** can be broken *via* the reaction with CuCl, HCl or elemental sulfur, resulting in the formation of ring-open and ring-expansion products **8**, **9** and **10**, respectively (Scheme 3).

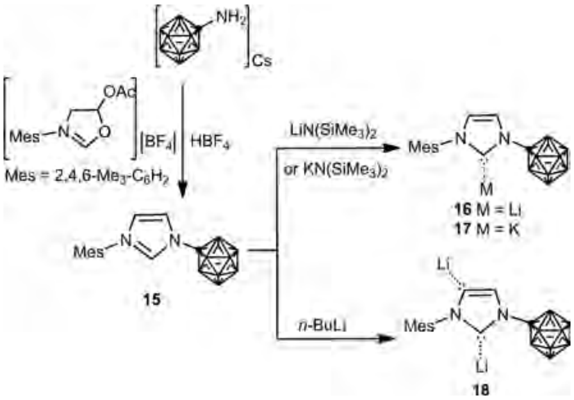
3. Application in low-valent group 14 elements chemistry

3.1. Application in carbene chemistry

In 2014, Lavallo and coworkers reported the isolation of a series of carborane anions-fused *N*-heterocyclic carbenes (NHCs) featuring two *N*-bound carborane anions *via* controllable selective deprotonation of an anionic imidazolium salt precursor **11**, including two dianionic and a trianionic NHC lithium adducts **12**, **13** and **14**, respectively (Scheme 4) [48]. It is noteworthy that, **13** can be completely converted to **12** after heating the solution of **13** at 50 °C for 24 h, moreover, this isomerization can also be proton-catalyzed



Scheme 4. Synthesis of carborane anions-fused *N*-heterocyclic carbenes.



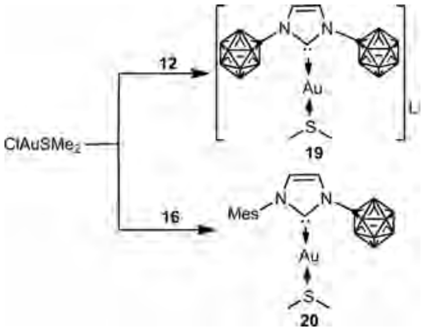
Scheme 5. Synthesis of unsymmetrical carborane anion-fused NHCs.

by **11**. This study demonstrates that introduction of carboranes into NHC readily results in the change of chemical behavior, which undoubtedly broaden the NHC family.

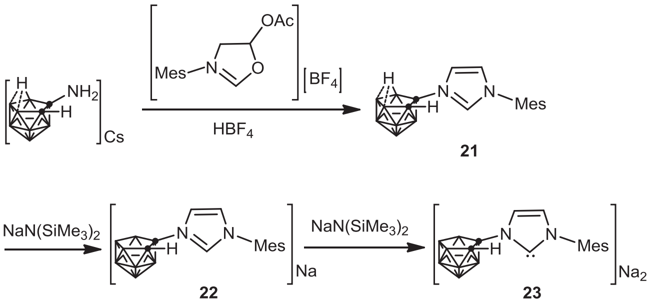
As an extension of this study, the Lavallo group subsequently reported the synthesis of unsymmetrical NHCs **16**, **17** and **18** featuring one carborane *N*-substituent and one hydrocarbon *N*-substituent by controllable deprotonation of unsymmetrical zwitterionic imidazolium species **15** with bases, which was prepared by treatment of mesityl substituted oxazolinium cation with carborane anion amine, followed by reaction with acid (Scheme 5) [49]. Interestingly, an obvious directing effect induced by the carborane anion substituent was observed in the reaction of **15** with *n*-BuLi, which leads to the selective formation of dianionic C-2/C-5 NHC lithium adduct **18**.

To investigate the ability of **12** and **16** to behave as viable ligands for transition metals, reactions of **12** and **16** with $ClAuSMe_2$ in a 1:1 ratio were performed in fluorobenzene, which indeed afforded the expected zwitterionic and anionic gold carbene complexes **19** and **20**, respectively (Scheme 6) [50].

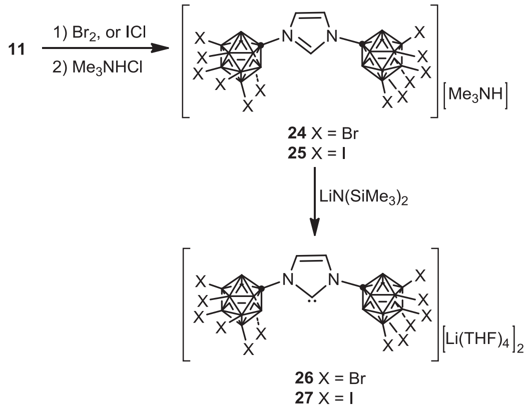
In a related report [51], Lavallo and coworkers illustrated the suitability of the *nido*-carborane as an *N*-substituent for NHCs by isolation of an *N*-dicarbollide NHC **23** *via* step deprotonation of the precursor mono-*nido*-carboranyl imidazolium zwitterion **21**, which was prepared *via* the reaction of anionic *nido*-amine with mesityl substituted oxazolinium cation, followed by treatment with HBF_4 (Scheme 7). Recently, Xiao and coworkers reported the synthesis of *nido*-carborane anion fused imidazolium zwitterions by reacting of the amino *o*-carboranes with triethyl orthoformate and $HBF_4{\cdot}Et_2O$ [52].



Scheme 6. Synthesis of carborane anion-fused NHC Au(I) complexes.



Scheme 7. Synthesis of *N*-dicarbollide NHC dianion.

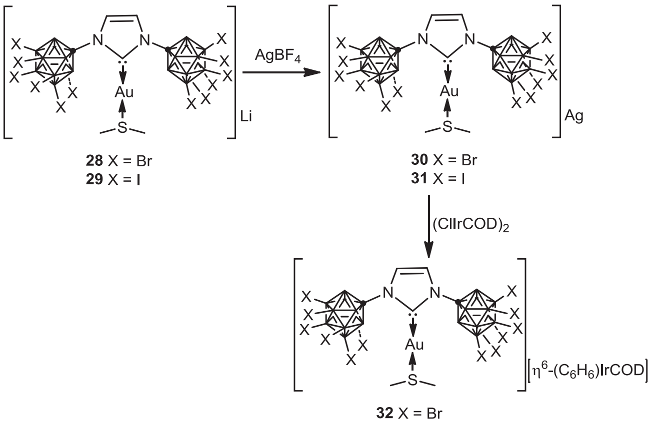


Scheme 8. Synthesis of polyhalogenated carboranyl NHCs.

In 2020, the Lavallo group reported the synthesis of polyhalogenated carboranyl NHCs **26** and **27**, by deprotonation of the corresponding polyhalogenated imidazolium anions, which were obtained by treatment of **11** with Br_2 or ICl *via* selectively bromination or iodination (Scheme 8) [53]. As an exploration of the implementation of carboranyl NHCs, the Au(I) carbene complexes were found to behave as weakly coordinating anions (WCAs) and catalysts (Scheme 9).

In 2016, Willans and coworkers reported the synthesis of a series of *o*-carboranyl imidazolium salts **33**, **34**, **35** and imidazolium *nido*-carborane zwitterion **36** by treatment of *N*-^{t}butyl or *N*-methylimidazole with bromoethylcarborane in toluene (Fig. 2) [54,55], which showed unique and versatile coordination modes to give a series of *o*-carboranyl carbene rhodium, iridium and ruthenium complexes (Fig. 3).

In 2017, Zeitler and coworkers reported a novel carboranyl-fused triazolium **43** through the reaction of carboranyl hydrazinium salt with lactim ether (Scheme 10) [56], which showed excellent catalytic activity in a wide range of C-C bond-forming reactions.



Scheme 9. Synthesis of silver and iridium salts.

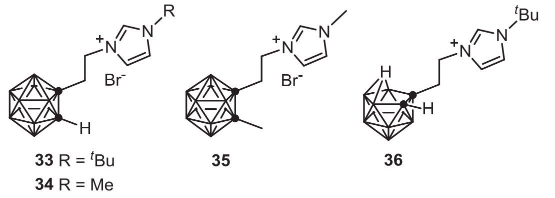


Fig. 2. Examples of *o*-carboranyl imidazolium salts and imidazolium *nido*-carborane zwitterion.

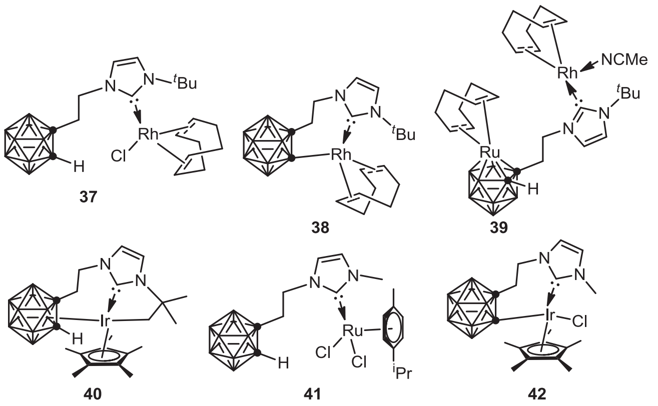
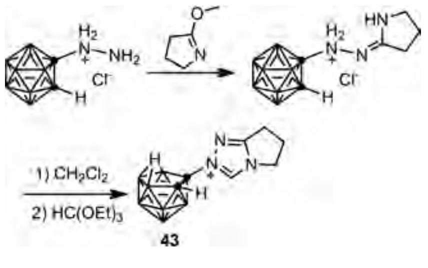


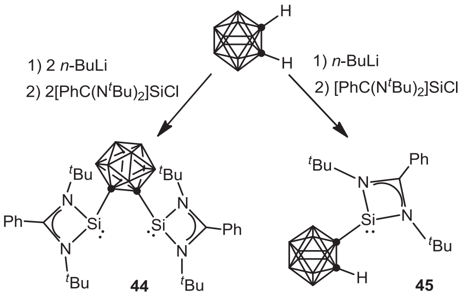
Fig. 3. Examples of *o*-carboranyl carbene transition metal complexes.



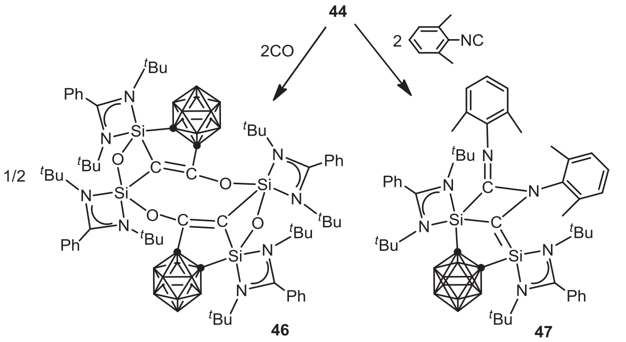
Scheme 10. Synthesis of carboranyl-fused triazolium.

3.2. Application in silylene chemistry

In 2016, Driess and coworkers demonstrated the isolation of *o*-carborane-substituted bis(silylene) **44** by treatment of *o*-carboranyl lithium salt with *N,N*'-di-*tert*-butyl(phenylamidinato)chlorosilylene [57,58] in a 1:2 ratio [59] (Scheme 11). Similarly, in 2018, the Xie group reported the synthesis of a carborane-fused silylene **45** *via* the metathesis reaction of *o*-carboranyl lithium salt with *N,N*'-di-*tert*-butyl(phenylamidinato)chlorosilylene in a 1:1 ratio (Scheme 11) [60].



Scheme 11. Synthesis of *o*-carborane-substituted silylenes.



Scheme 12. Reaction of **44** with carbon monoxide and 2,6-dimethylphenyl isocyanide.

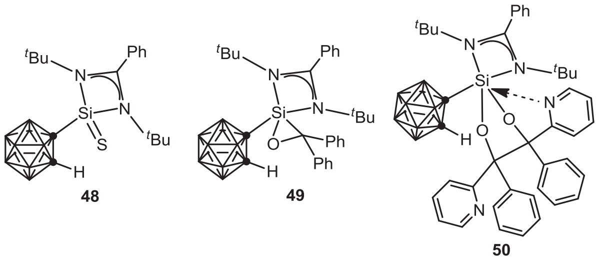


Fig. 4. Examples of carborane-fused silanethione and silaoxirane.

The Driess group investigated the reactivity of *o*-carborane-substituted bis(silylene) **44** toward carbon monoxide and 2,6-dimethylphenyl isocyanide [61], whereby selective CO and isocyanide activation proceeded affording the head-to-head of CO and head-to-tail of isocyanide homocoupling products **46** and **47**, respectively (Scheme 12).

Compound **45** reacts with elemental sulfur and benzophenone resulting in the formation of the corresponding carborane-fused silanethione **48** and silaoxirane **49**, respectively. On the other hand, treatment of **45** with 2-benzoylpyridine afforded the 2-benzoylpyridine homocoupling product **50** with a SiC_2O_2 five-membered ring (Fig. 4) [60].

The Driess group investigated the *o*-carborane-substituted bis(silylene) **44** as a viable ligand for transition metals, which is confirmed by the formation of silylene nickel complexes **51** and **52**, respectively (Fig. 5) [59].

Apart from transition metal chemistry, *o*-carborane-substituted bis(silylene) **44** can also be utilized in main group chemistry. In 2017, Xie, Lin and coworkers reported the first example of bis(silylene)-stabilized bromoborylene **53** by reduction of bis(silylene)-BBr_3 adduct with potassium graphite in THF at room temperature [62]. Bromoborylene **53** reacts with CuCl at room temperature resulting in the formation of the expected borylene-

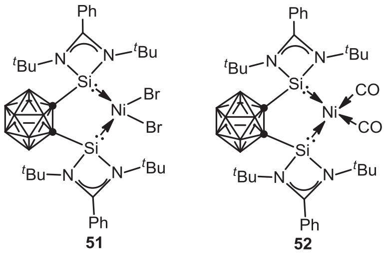
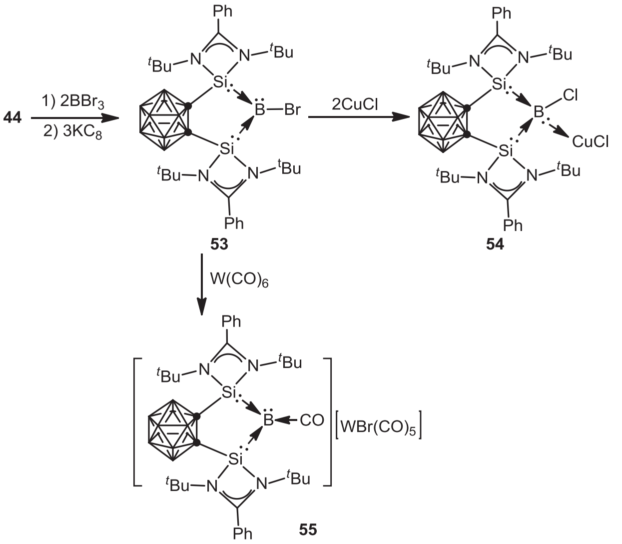
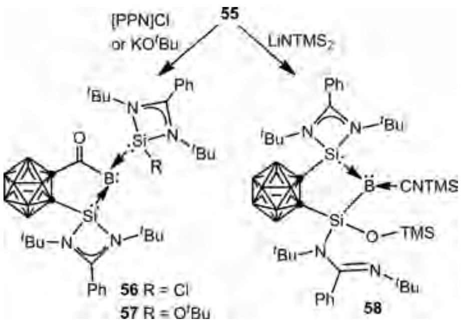


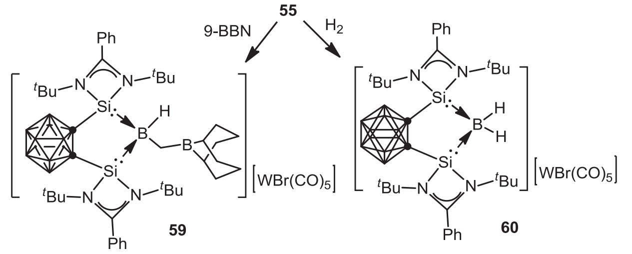
Fig. 5. Examples of *o*-carborane-substituted bis(silylene) nickel complexes.



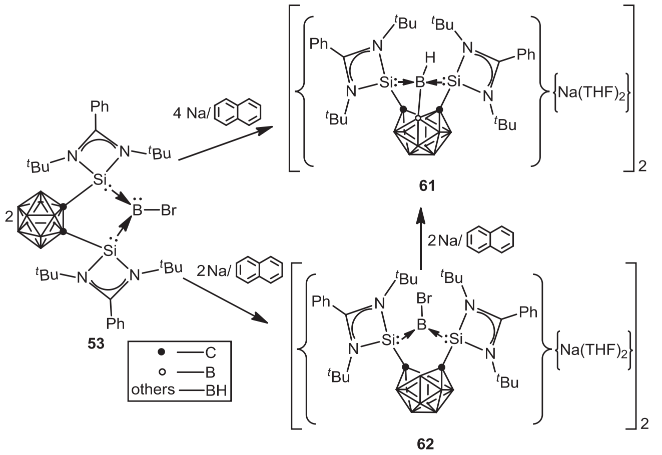
Scheme 13. Synthesis and reactivity of bis(silylene)-stabilized bromoborylene.



Scheme 14. Reaction of **55** with nucleophiles.



Scheme 15. Reaction of **55** with 9-BBN and dihydrogen.



Scheme 16. Reduction of bromoborylene.

copper complex **54**. In sharp contrast, treatment of **53** with W(CO)$_6$ in THF at 80 °C afforded an unprecedented bis(silylene)-CO-stabilized borylene cation **55** (Scheme 13).

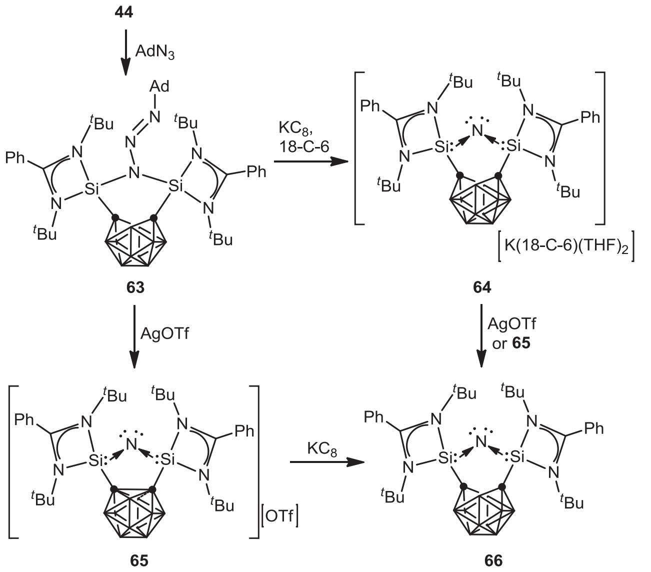
As an extension of this study, Xie, Lin and coworkers investigated the reactivity of **55** toward [PPN]Cl (PPN = Ph$_3$P=N=PPh$_3$), KO^{t}Bu, as well as LiN(SiMe$_3$)$_2$, whereby migration and complete cleavage of CO proceeded affording a series of novel silylene-stabilized carbonyl, silyl borylenes, **56**, **57** and **58** respectively (Scheme 14) [63]. On the other hand, treatment of **55** with 9-borabicyclo[3.3.1]nonane (9-BBN) gave a cationic borane **59** *via* CO reduction. It is noteworthy that, the borylene cation **55** can cleave dihydrogen to form the corresponding boronium species **60** (Scheme 15) [62].

In 2018, Xie and coworkers investigated the reduction of bromoborylene **53** by 2 equiv. of sodium naphthalenide in THF, which leads to the formation of an unexpected diborane derivative **61** with a B-B(cage) single bond [64]. To probe the mechanism, reaction of **53** with 1 equiv. of sodium naphthalenide in THF was carried out, which affords a bis(silylene)-stabilized boron-centered radical cation **62** (Scheme 16). Further one electron reduction of **62** with sodium naphthalenide can also give **61**. Based on the experimental and DFT calculations, insertion of *in situ* generated borylene into B(cage)-H bond resulting in the formation B-B single bond was proposed, which paves a new way for the synthesis of diborane derivatives featuring an electron-precise B-B single bond.

In 2020, Driess and coworkers reported the isolation of a remarkable bis(silylium) N$^{\text{I}}$ complex **63** featuring an open-cage dianionic *nido*-carborane through the reaction of *o*-carborane-substituted bis(silylene) **44** with adamantly azide [65]. One-electron reduction of **63** with potassium graphite leads to the formation of the remarkable bis(silylene)-stabilized N$^{\text{I}}$ complex **64** with the liberation of N$_2$ and adamantine, and the regeneration of silylenes. On the other hand, one-electron oxidation of **63** with AgOTf affords the cationic bis(silylene) N$^{\text{I}}$ complex **65**, which reacts with potassium graphite to form the neutral N$^{\text{I}}$ radical complex **66** (Scheme 17). In addition, **66** can be also achieved by treatment of **64** with AgOTf or **65**.

In 2020, the Driess group reported an *o*-carborane-substituted bis(silylene)-stabilized silylone **68** by treatment of dianionic *nido*-carboranyl bis(silylene) **67** with NHC-SiCl$_2$ [66] (NHC = {[HCN(2,6-^{i}Pr$_2$C$_6$H$_3$)]$_2$C:}) in THF [67]. It was noteworthy that, the dianionic *nido*-carboranyl bis(silylene) **67** behaved as a 2e$^-$ reductant in the above reaction. Additionally, one electron reduction of **68** results in the isolation of an unexpected bis(silylene)-stabilized [Si$_2$]$^{2+}$ complex **69** with a Si-Si bond *via* the homocoupling of an elusive bis(silylene)-stabilized Si$^{\text{I}}$ radical cation generated from the intramolecular one electron transfer from the Si^{0} atom to the carborane cage (Scheme 18).

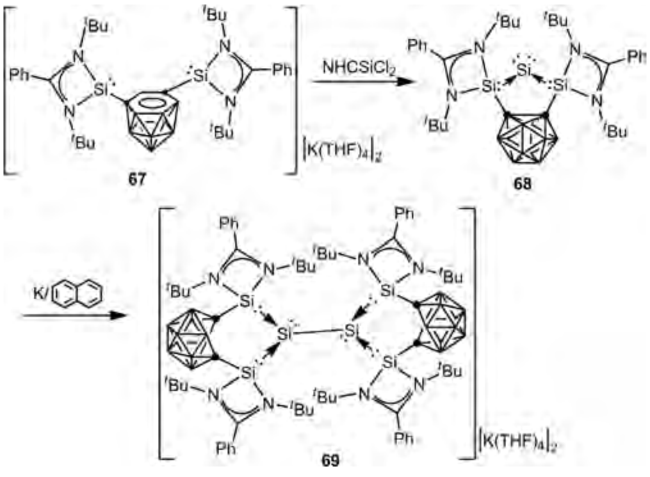
Very recently, Driess and coworkers reported the implementation of *o*-carborane-substituted silylene in low-valent germanium chemistry [68]. Treatment of *o*-carboranyl phosphine-silylene **70** with GeCl$_2$·dioxane afforded the novel Ge$_2$ and Ge$_4$ complexes **72** and **73**, respectively. Additionally, the Ge$_2$ complex **72** can be also



Scheme 17. Synthesis of bis(silylene)-stabilized N^I radical complex.

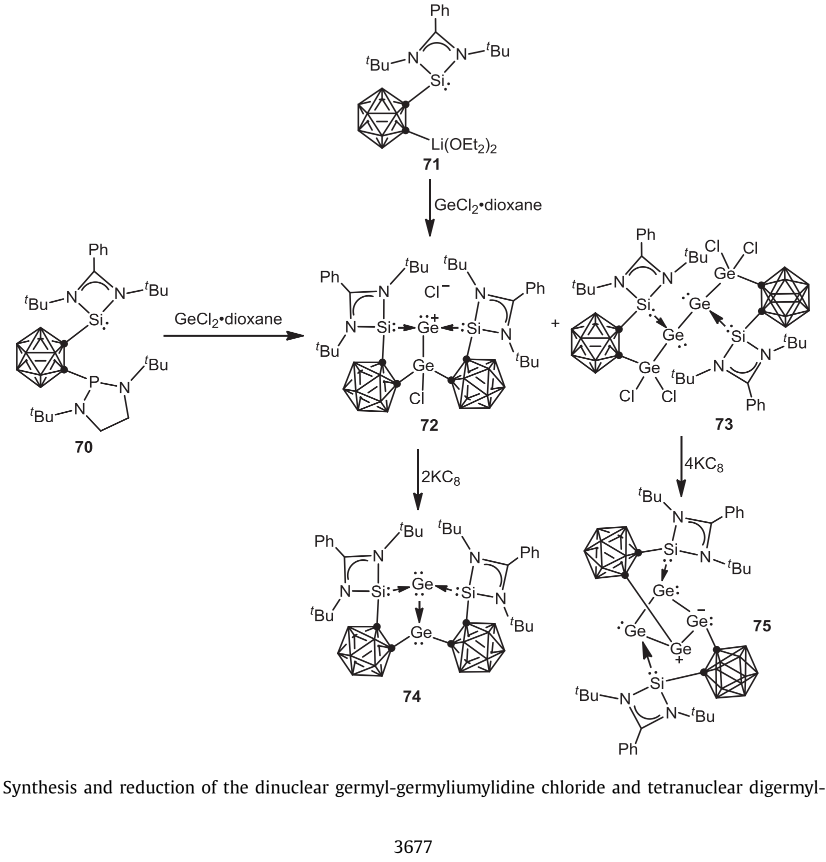
prepared *via* the reaction of *o*-carboranyl silylene lithium complex **71** with $GeCl_2$·dioxane in good yield. Further reduction of complexes **72** or **73** with potassium graphite yielded the novel Ge_2 complex **74** featuring a localized dative Ge(0)→Ge(II) bond or Ge_4 complex **75** bearing a four-membered Ge_4 ring with significant σ-electron delocalization over the Ge_4 moiety (Scheme 19).

In 2017, Xie and coworkers reported the isolation of a carbene-stabilized cyclic amino(carboranyl) silylene **77** by treatment of cyclic amino(carboranyl) chlorosilane **76** with *N*-heterocyclic carbene [69]. While the reaction of **77** with borane leads to the formation of a Lewis acid-base adduct **78**, the reactions of **77** with unsaturated molecules, such as diphenylacetylene and benzophenone afford cycloaddition products **79** and **80**, respectively (Scheme 20).

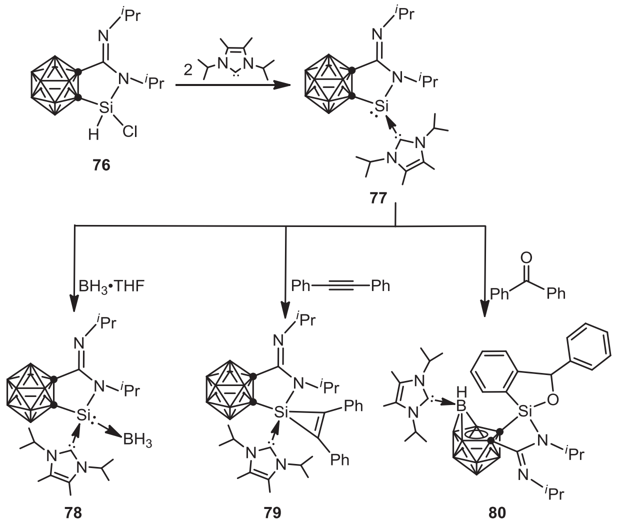


Scheme 18. Synthesis of bis(silylene)-stabilized silylone and $[Si_2]^{2+}$ complex.

Very recently, Driess and coworkers investigated the influence of the redox non-innocent carborane on the reactivity of an *o*-carborane-substituted bis(silylene) stabilized germylone **81** towards reductants and oxidants [70]. In this context, one electron oxidation of **81** with $[Cp_2Fe][B\{C_6H_3(CF_3)_2\}_4]$ affords the Ge^I-Ge^I homocoupling product, bis(silylene)-stabilized diatomic Ge_2 complex **82**, while one electron reduction of **81** with potassium naphthalenide also results in the formation of the unexpected bis(silylene)-stabilized diatomic Ge_2 complex **83** *via* one electron oxidation of Ge^0 to Ge^I and two electron reduction of the carborane cage. Moreover, a neutral Ge_2 complex **85** with a triplet diradical ground state was prepared by treatment of germylene-stabilized $GeCl_2$ **84** with potassium naphthalenide (Scheme 21).



Scheme 19. Synthesis and reduction of the dinuclear germyl-germyliumylidine chloride and tetranuclear digermyl-digermylene.



Scheme 20. Synthesis and reactivity of carbene-stabilized cyclic amino(carboranyl) silylene.

3.3. Application in germylene and stannylene chemistry

In 2017, Xie and coworkers reported the synthesis of two iminocarboranyl germylenes **86** and **87** through the reactions of iminocarborane lithium salt with $GeCl_2$·dioxane in a 1:1 ratio or 2:1 ratio [71]. Chlorogermylene **86** reacts with trimethylamine *N*-oxide or elemental sulfur in THF at room temperature to give the μ-oxo or μ-S dimer **88** and **89** featuring a four-membered Ge_2O_2 or Ge_2S_2 ring, respectively (Scheme 22). In addition, treatment of **86** with K[CpFe(CO)$_2$] in toluene at room temperature afforded an iron-germylene complex **90**.

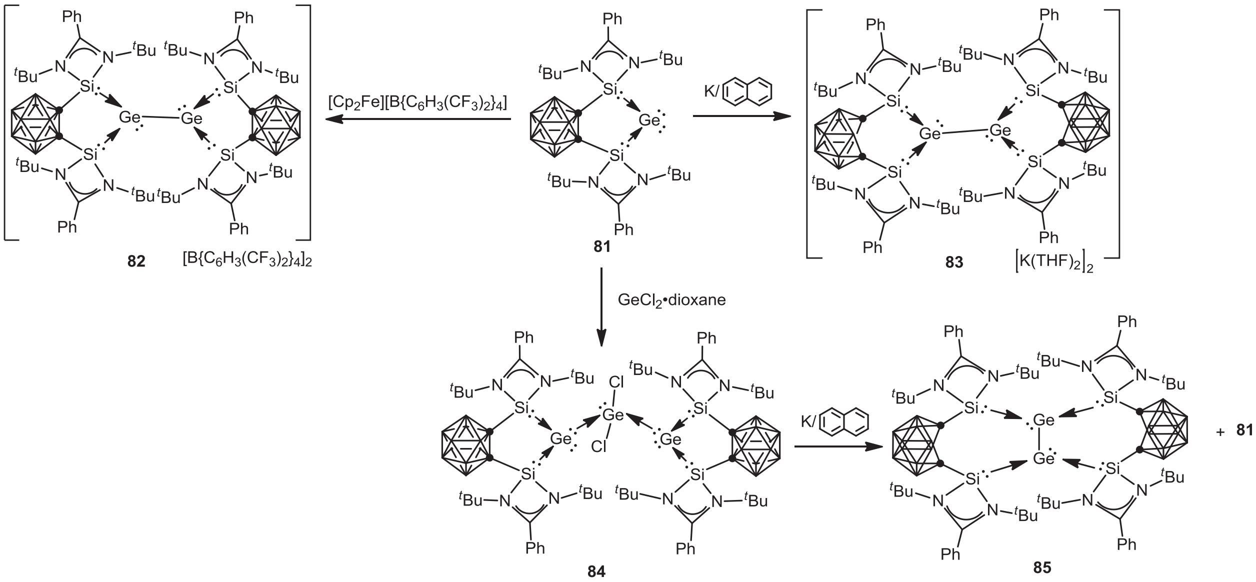
In 2010, the Edelmann group reported that *N,N*'-dialkylcarbodiimides reacts with *o*-carboranyl lithium complexes to form the lithium carboranylamidinate **91**, which underwent metathesis reaction with anhydrous $SnCl_2$ in THF in a 2:1 ratio to afford the *o*-carboranyl stannylene **92** [72]. In a similar manner, the chlorogermylene **93** was prepared by treatment of *in situ* formed **91** with $GeCl_2$·dioxane in a 1:1 ratio (Scheme 23) [73].

4. Conclusions and perspectives

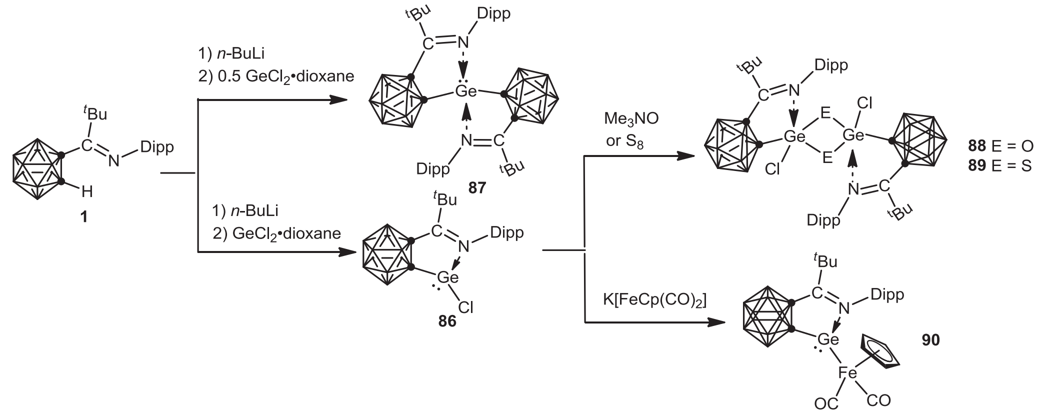
Employment of carborane-based ligands allowed the synthesis of a series of low-valent group 13 and group 14 element compounds with novel structure and reactivity *via* different synthetic routes, which indeed enriched the chemistry of low-valent main group element compounds. To date, a variety of carborane-based ligands supported borylenes, carbenes, silylenes, germylenes and stannylenes have been successfully synthesized whereby varied types of new chemical transformations are observed. These achievements indicate that both the carboranyl and ancillary ligands are critical for the stabilization of reactive low-valent main group element compounds. Notwithstanding, in comparison to the large amount of carboranyl transition metal complexes, the utilization of carborane-based ligands in low-valent main group chemistry is still in its early stage. On the other hand, the types of carborane-based ligands suitable for the stabilization of low-valent main group element compounds are scarce, which undoubtedly restrict the application of carborane-based ligands in the field of low-valent main group element chemistry. Furthermore, the reported carborane-based ligands are all cage carbon fused, the synthesis of cage boron involved ligands has still remained challenging.

The reported results show that the redox non-innocent character of carboranes can be served as reductants or oxidatants under different reaction conditions, which enables the adjustability of the electronic structure of low-valent main group element centers. Moreover, this unique electronic structure can enhance the ability of such carborane-based ligands supported low-valent main group element compounds to participate in the reactions involved multiple electrons transfer processes, such as catalysis and N_2 activation. It is quite possible that carborane-based ligands supported low-valent main group element compounds can achieve the abovementioned challenging tasks.

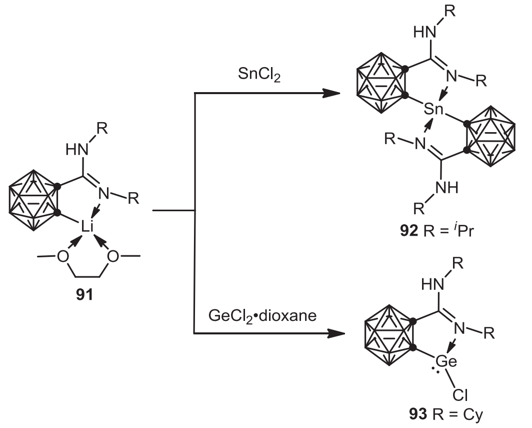
Additionally, the unique feature of carborane implies the structural diversity of carborane-based ligands, since both cage boron and cage carbon vertices can be fused in the ligand frameworks, which enable the flexibility in ligand design. In fact, design and synthesis of new types of carborane-based ligands are crucial for the development of this new and flourishing field. In addition, the fine design of carborane-based ligands may allow the development of low-valent main group element compounds that partic-



Scheme 21. Synthesis of the novel Ge_2 complexes.



Scheme 22. Synthesis and reactivity of iminocarboranyl germylenes.



Scheme 23. Synthesis of *o*-carboranyl stannylene and chlorogermylene.

ipate in those chemical transformations which were long dominant by transition metals, such as small molecule activation, catalysis.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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