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Perspective

Counterintuitive Chemistry: Carbene Stabilization of Zero-Oxidation State Main Group Species

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Cite This: J. Am. Chem. Soc. 2023, 145, 5592−5612

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ABSTRACT: Carbenes have evolved from transient laboratory curiosities to a robust, diverse, and surprisingly impactful ligand class. A variety of different carbenes have significantly contributed to the development of low-oxidation state main group chemistry. This Perspective focuses upon advances in the chemistry of carbene complexes containing main group element cores in the formal oxidation state of zero, including their diverse synthetic strategies, unusual bonding and structural motifs, and utility in transition metal coordination chemistry and activation of small molecules.

INTRODUCTION

Carbenes, neutral molecules possessing a divalent carbon atom with six valence electrons, have evolved from transient laboratory curiosities to a robust, diverse, and surprisingly impactful ligand class. The first stable carbene, λ^3-phosphino-carbene, was reported by Bertrand in 1988.[1,2] Although reports of N-heterocyclic carbene (NHC, Figure 1)-based transition metal complexes date back to the 1960s,[3] Arduengo reported the first stable N-heterocyclic carbene only three decades ago.[4] These seminal discoveries were prelude to a frenetic period of unprecedented advances in the development of carbene chemistry. Perhaps expectedly, the variety of stable carbenes has expanded dramatically. Notably, *nonclassical* carbenes, species containing one, or even no heteroatom in positions α to the carbene carbon center, are presently receiving increased attention.[5] Of particular note are cyclic (alkyl)(amino)-carbenes (CAACs, Figure 1),[6−8] first reported by Bertrand in 2005.[9] CAACs exhibit electronic properties that are quite distinct from classical N-heterocyclic carbenes. Notably, both computational and experimental data suggest that CAACs are not only stronger σ-donors but also more potent π-acceptors than NHCs.[7,10−13] Although carbenes continue to be extensively utilized throughout the whole of chemistry, their impact in organic synthesis, catalysis,[14] and the development of low-oxidation-state main group chemistry has been particularly significant.[6,7,15−19]

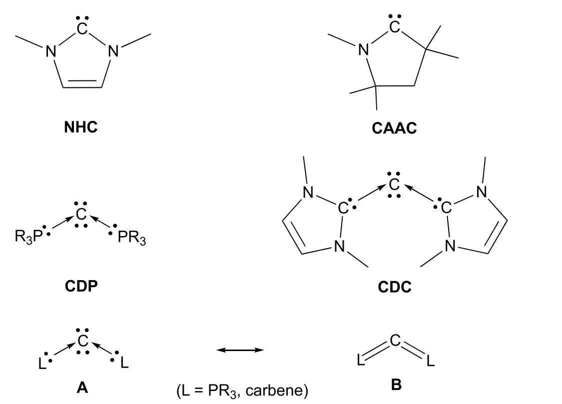


Figure 1. Representative divalent carbon(II) (**NHC** and **CAAC**) and divalent carbon(0) compounds (i.e., carbones) (**CDP** and **CDC**) and resonance structures of **CDP** and **CDC**: carbone (**A**) and allene (**B**).

As evidenced by such iconic molecules as $Ni(CO)_4$ and $(C_6H_6)_2Cr$, transition metals can readily adopt the formal oxidation state of zero. However, embracing the formal oxidation state of zero is a considerably less common endeavor for main group elements. The stabilization of molecules containing main group elements in the zero-oxidation state has become a popular research area over the past two decades,.[16,20−24] To this end, carbenes—both NHCs and CAACs—are particularly attractive, considering their strong electron-donating capabilities coupled with their tunable electronic and steric properties.

This Perspective will chronologically review seminal advances in the counterintuitive chemistry of carbene-stabilized zero-oxidation state main group species—logically proceeding from atomic moieties to more complicated allotropic entities.

CARBENE-STABILIZED $E_1(0)$ SPECIES

While diamond and graphite—the two most common carbon allotropes—possess remarkable industrial utility, the carbon(0) atom, the simplest building block of these stable carbon allotropes, is highly reactive. As a result, the study of complexes containing a carbon(0) core is intriguing. The first compounds

Published: March 6, 2023

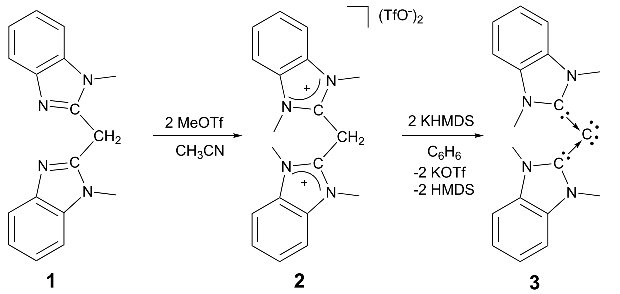
https://doi.org/10.1021/jacs.2c13574
J. Am. Chem. Soc. 2023, 145, 5592−5612

containing a carbon(0) core are traced to the carbodiphosphorane (CDP) (Figure 1), $(Ph_3P)_2C$, synthesized by Ramirez in 1961.[25] Decades later Frenking further clarified the "carbon(0) compound" essence of CDPs with theoretical and experimental data.[26] Theoretical evidence for the presence of a divalent carbon(0) core in $(NHC)_2C$ complexes (i.e., carbodicarbenes, CDCs, Figure 1) was also obtained.[27,28]

Consistent with the molecular orbitals of CDPs, the HOMO and HOMO−1 of CDCs correspond to the π-type and σ-type lone pair orbitals, respectively.[27] For CDPs and CDCs, while the σ-type lone pair orbital is localized at the central carbon atom, the π-type lone pair orbital largely resides at the central carbon possessing a measure of delocalization over the phosphine or carbene ligands. The bonding between the central C(0) atom and the ligands in CDPs and CDCs, therefore, can be best described as donor−acceptor interactions (resonance structure **A**, Figure 1). Singlet carbenes (such as NHCs and CAACs) have a lone pair of electrons and an empty p orbital on the carbene carbon atom (Figure 1). Consequently, the most remarkable distinction between carbones and carbenes is the unique double donor capability of the former.

Soon after the theoretical prediction by Frenking,[27] Bertrand synthesized the first carbodicarbene (**3**) from bis(*N*-methylbenzimidazol-2-yl)methane (**1**) (Scheme 1) in 2008.[29] X-ray structural analysis shows that the two N−C1−N planes in **3** are twisted by 69° (Figure 2). While the C1−C2 bond distance of **3** [1.343(2) Å] compares well to the theoretical value (1.355 Å),[30] the C2−C1−C2′ angle of **3** [134.8(2)°] is more acute than the calculated data (142.5°). This difference may be attributed to the intermolecular interactions in crystals and the shallow bending potential of carbon(0) compounds.[30]

Scheme 1. Synthesis of Carbodicarbene 3



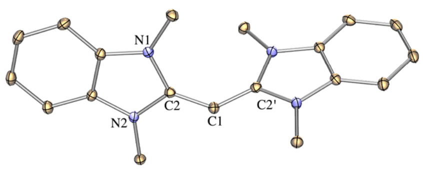
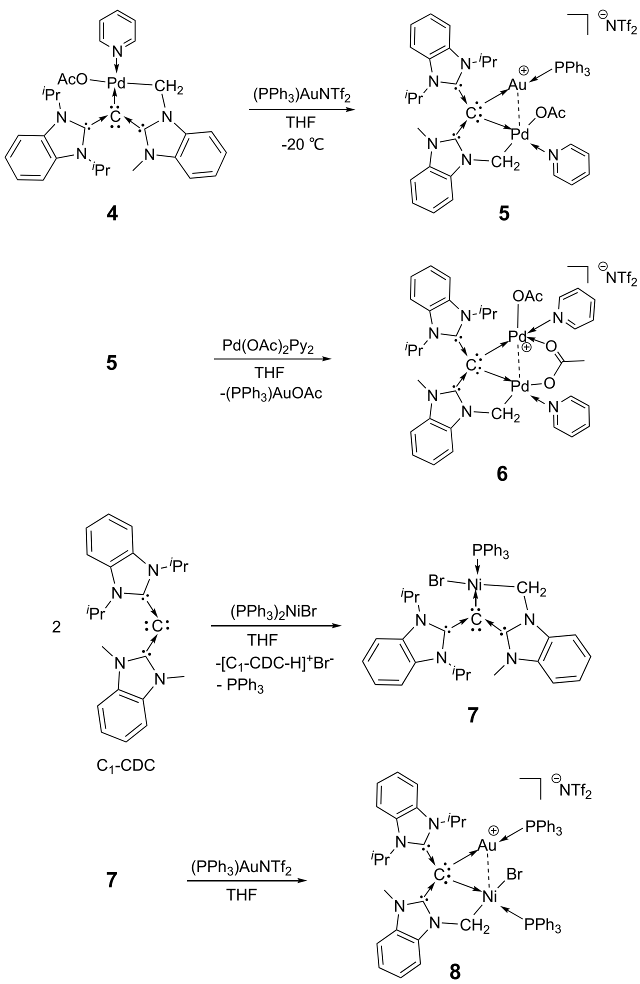


Figure 2. Molecular structure of **3**.

Tetraaminoallenes are powerful nucleophiles and bases. Computations support the $(R_2N)_2C \rightarrow C \leftarrow C(NR_2)_2$ bonding description, wherein the central carbon atom bears two lone pairs of electrons.[27] Both carbodicarbene **3**[29] and the tetraaminoallene $[(Me_2N)_2C]_2C$[31] were reported to form an η^1 complex with transition metal species, whereas reactions of "regular allenes" with transition metal species give η^2 complexes involving one of the two C═C π bonds.[32] While carbenes are widely recognized as single σ-donors, carbones, bearing two electron pairs at the central carbon(0) centers, may serve as double donors. Although dimetalations of the carbone centers of CDPs are well documented,[33] synthesis of CDC-based geminal-bimetallic complexes is still challenging. The dormancy of the π-type lone pair of the C(0) center of CDC may be ascribed to back-donation of electron density from the carbon(0) atom to the NHC moieties. Ong recently made a breakthrough in this field by suppressing the π-acidity of the flanked NHC moiety in CDC.[34]

Geminal-bimetallic CDC complexes **5**, **6**, and **8** were synthesized using the corresponding CDC-based mononuclear complexes (**4** and **7**) (Scheme 2).[34] Both X-ray structural analyses and theoretical studies of **5**, **6**, and **8** support that the carbone center of the cyclometalated CDC moiety provides two lone electron pairs to the two metal centers via two dative bonds.

Scheme 2. Synthesis of Gem-Double Dative Bimetallic CDC Complexes (5, 6, and 8)



The chelating binding of CDC, via C−H bond activation, has twisted the flanking NHC moiety in these geminal-bimetallics of CDC, thereby decreasing the π-conjugation within the allenic framework (Figure 3). The solid-state structural analysis also revealed the presence of noncovalent ligand−ligand interactions (Figure 3) [between acetate (L:) and CDC for **5** and **6** and between bromide (L:) and CDC for **8**]. Thus, Ong suggested that the electron density from the

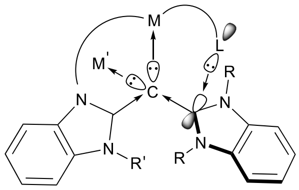
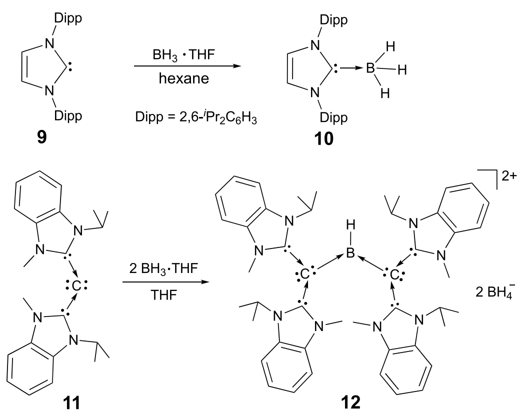


Figure 3. Activation of the second lone pair of CDC via chelating effect and ligand−ligand interaction.

external ligand (L:) (i.e., acetate or bromide) may be donated to the flanked NHC moiety of CDC and thus quench its π-acidity. As a result, the second dormant lone pair of the carbon(0) center may be activated via the cooperative effect between the chelating mode of CDC and ligand−ligand interactions. Recent observation of 1,2-addition of E−H bonds (E = B, C, Si) across the CDC central carbon atom and that of the flanking NHC unit in CDC, coupled with the results of X-ray structural analysis, indicates significant π-acidity of the C_{NHC} atom in CDC.[35] This finding is unexpected since NHCs are well-known as strong σ-donors, but weak π-acceptors. Thus, CDCs, bearing both an electron-rich carbone center and two π-acidic C_{NHC} centers, are expected to exhibit frustrated Lewis pairs (FLPs)-like reactivity.[35] Consequently, potential applications of such CDCs in catalysis and small molecule activation are promising.[36,37]

In addition to offering double-donor functionality, CDCs have also exhibited reactivity quite distinct from carbenes. While reaction of the bulky NHC^{Dipp} ligand (**9**) with BH_3·THF gives the 1:1 adduct (**10**),[38] reaction of CDC (**11**) with BH_3·THF gives an unusual three-coordinate dicationic hydrido boron complex (**12**) (Scheme 3).[39] Notably, computations

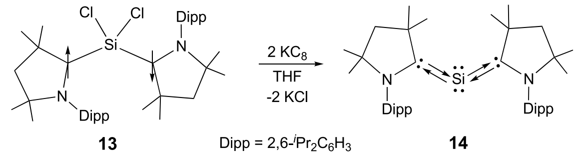
Scheme 3. Synthesis of 10 and 12



indicate that the C(0)-to-B electron donation involves two electron pairs of the CDC ligand (**11**). Synthesis of the dicationic borane complex via CDC coordination reveals the possible broad utility of CDCs in stabilizing highly charged main group species. The same CDC ligand (**11**) was subsequently employed in the synthesis of CDC-based di- and tricationic bismaalkenes, involving C(0)-to-Bi double dative bonds.[40] Redox noninnocent ligands have attracted increased attention in the field of catalysis. England recently reported the redox noninnocence of CDC ligands in highly oxidized chromium and cobalt complexes.[41]

Theoretical studies[42] suggest that the *bent* trisilaallene, reported by Kira et al. in 2003, may also be interpreted as a silylone (L_2Si, where L = a cyclic silylene ligand).[43] The first carbene-based silylone (**14**) was obtained by Roesky in 2013 via potassium graphite reduction of ^{Me}CAAC-complexed $SiCl_2$ (**13**) (Scheme 4).[44] **13** exists as both diamagnetic polymorph-

Scheme 4. Synthesis of CAAC-Based Silylone 14



II (major component) and paramagnetic polymorph-I with two unpaired electrons residing at the carbene carbon atoms (as shown in Scheme 4).[45]

14 exhibits an obviously bent C_2Si core (Figure 4). The C−Si−C angle of 117.44(8)° (av) of **14** is more acute than that of

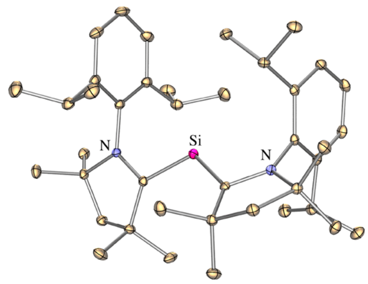


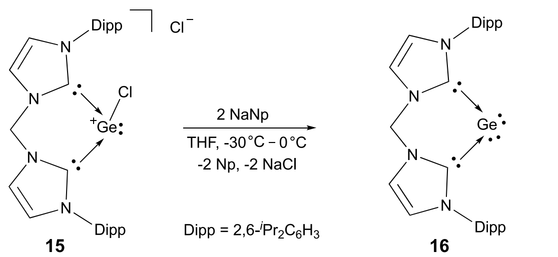
Figure 4. Molecular structure of **14**.

Kira's "trisilaallene" [136.49(6)°].[43] Although the Si−C bonds in **14** [1.8414(18) Å, av] are obviously longer than Si═C double bonds (1.702−1.775 Å),[46] the π-type lone pair orbital at the central silicon atom (HOMO) of **14** involves notable Si−C π bonding. While **14** is EPR-silent, computations show that **14**, with low electronic excitation energy, has a biradicaloid character.[44] Subsequently, the So laboratory synthesized a mixed carbene-based analog of **14**, in which the silicon atom is embraced by both ^{Me}CAAC and NHC^{iPr} [i.e.,:C{(^{i}Pr)NC(Me)}$_2$].[47] While being close to the reported Si═C double bonds (1.702−1.775 Å),[46] the Si−C_{CAAC} bond in this compound [1.792(4) Å] is clearly shorter than the Si−C_{NHC} bond [1.957(5) Å][47] and the Si−C_{CAAC} bonds in **14** [1.8414(18) Å, av].[44] Both experimental and theoretical data suggest that this (^{Me}CAAC)Si(NHC^{iPr}) species can be described as a bent silaallene with a perturbed electronic structure.

Soon after compound **14** was reported, a cyclic germylone (**16**) was synthesized by Driess via low-temperature sodium naphthalenide (NaNp) reduction of the bis-NHC-complexed $GeCl^+$ cation (**15**) (Scheme 5).[48] **15** was synthesized by reaction of the corresponding bis-NHC ligand with $GeCl_2$·dioxane.

X-ray structural analysis[48] (Figure 5) reveals that the six-membered C_3N_2Ge ring in **16** adopts a boat conformation with an acute C−Ge−C angle of 86.6(1)°. The Ge−C bonds in **16** [1.962(2) and 1.967(2) Å] are ca. 0.10 Å shorter than those for **15** [2.058(3) Å, av] and ca. 0.15 Å shorter than that in NHC^{Dipp}-$GeCl_2$ [2.110(4) Å].[49] While the HOMO−1 of **16** represents a σ-type lone pair orbital at the germanium atom, the HOMO of **16** corresponds to a π-type lone pair orbital of the germanium atom (with Ge−C π bonding interactions).[48]

Scheme 5. Synthesis of Cyclic Germylone 16



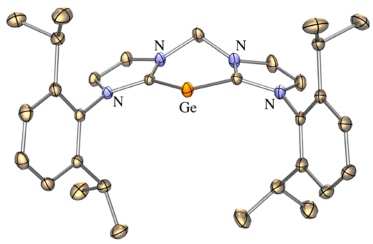
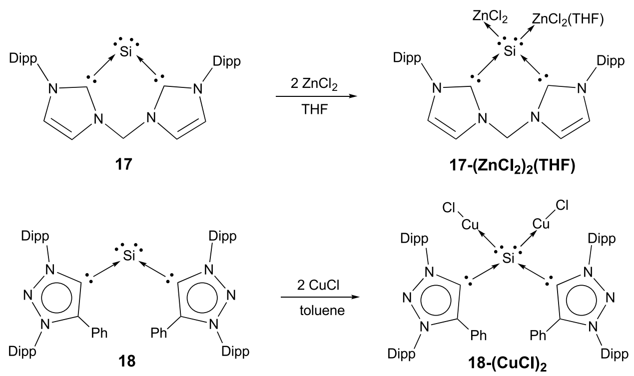


Figure 5. Molecular structure of **16**.

This π interaction is consistent with the relatively short Ge−C bonds in **16**. The large second proton affinities (PAs) of **14** (186.7 kcal mol^{-1})[44] and **16** (175.0 kcal mol^{-1})[48] suggest that these two molecules may be classified as divalent E(0) compounds (E = Si for **14**; Ge for **16**). Both the germanium analogue[50] of **14** and silicon analogue[51] of **16** were subsequently obtained. Notably, compound **17** (i.e., the silicon analogue of **16**)[51] and the recently reported mesoionic carbene-stabilized silylone (**18**)[52] demonstrate the capability of bonding to two metal centers (Scheme 6).[22,52] By

Scheme 6. Synthesis of 17-$(ZnCl_2)_2$(THF) and 18-$(CuCl)_2$ Binuclear Complexes (Dipp = 2,6-Diisopropylphenyl)

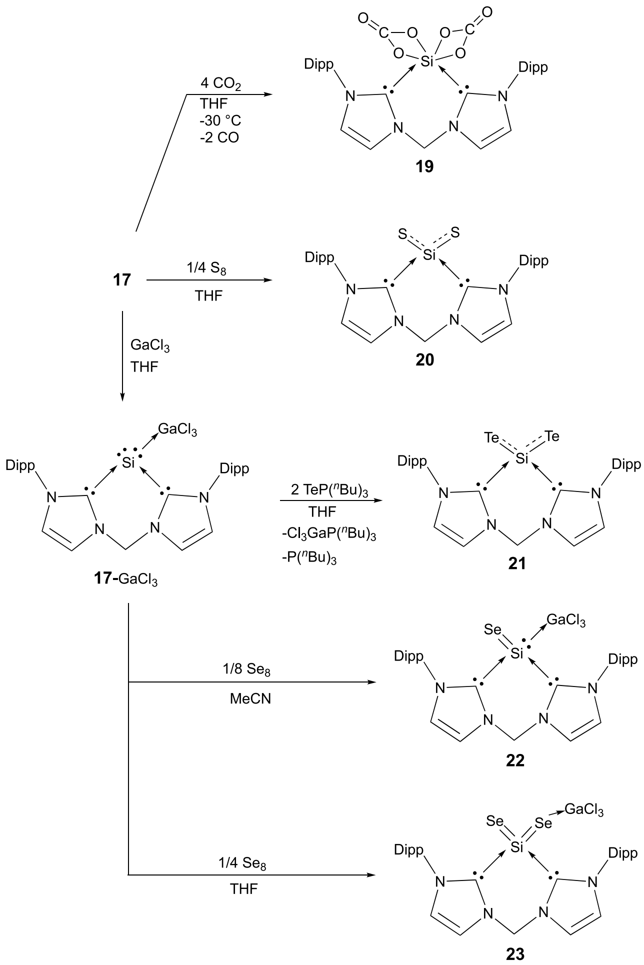


comparison to that of the CAAC-based silylone **14** (66.7 ppm in C_6D_6),[44] the ^{29}Si NMR resonances of **17** (−80.1 ppm in C_6D_6)[51] and **18** (−54.6 ppm, in the solid state)[52] are obviously higher-field shifted, indicating the presence of more electron-rich silicon cores in NHC and mesoionic carbene-based silylones. This should be ascribed to the weaker π-electron accepting capabilities of NHCs and mesoionic carbenes than CAACs.[19,53] As a result, the electron-rich silylone cores of **17** and **18** favor the formation of the corresponding binuclear complexes.

Imino-NHC[54] and diiminoNHC[55] ligands have also been utilized in accessing cyclic germylones. While NHC-stabilized acyclic germylones have not been reported, Jana synthesized $(L:)_2Ge(0)[Fe(CO)_4]_2$ complexes (L: = NHC ligands) using a "push−pull" stabilization strategy, wherein the germylone center serves as a double σ-donor (coordinating to two $Fe(CO)_4$ moieties).[56]

Considering their electron-rich E(0) (E = Si or Ge) centers, both silylones and germylones may be expected to demonstrate some utility in small molecule activation. To this end, reaction of **17** with CO_2 yielded the bis-NHC^{Dipp}-complexed silicon decarbonate (**19**) (Scheme 7).[57] Although

Scheme 7. Cyclic Silylone-Based Small Molecule Activation (Dipp = 2,6-Diisopropylphenyl)



the mechanism remains unclear, both L:SiO and L:SiO$_2$ (L: = bis-NHC^{Dipp}) have been proposed as possible intermediates in the synthesis of **19**. While bis-NHC^{Dipp}-stabilized monomeric silicon disulfide (**20**) was obtained from reaction of **17** with elemental sulfur,[58] the Lewis acid−base adduct **17**-$GaCl_3$ was employed as a precursor to access bis-NHC-stabilized monomeric $SiTe_2$ (**21**), "push−pull" stabilized SiSe (**22**), and $SiSe_2$ (**23**) (Scheme 7).[59] A series of "push−pull" stabilized GeE (E = Se or Te), GeE_2 (E = S or Se) species have been prepared by reaction of the germanium analogue of **17**-$GaCl_3$ with the corresponding elemental chalcogens.[60] Notably, attempts to obtain CAAC-stabilized silicon oxides via aerial (or N_2O) oxidation of CAAC-based Si(0) species were unsuccessful, resulting in both SiO_2 and N-aryl amide derivatives (CAAC═O).[61] In the aerial oxidation process, splitting of O_2 involves not only the electron-rich silicon(0)

https://doi.org/10.1021/jacs.2c13574
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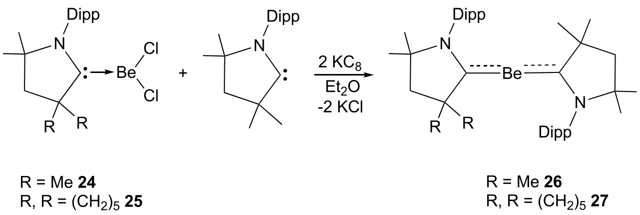
atom but also the electrophilic CAAC carbene centers. Thus, electrophilic carbene-stabilized Si(0) species may not be an ideal platform to access the corresponding silicon oxide complexes. Despite encouraging computational efforts,[62,63] carbene-stabilized stannylones and plumbylones have not been experimentally realized. The recent synthesis of bis(silylene)- or bis(germylene)-stabilized plumbylones may inspire synthetic chemists to finally prepare the corresponding *carbene* analogs.[64,65]

Dutton's computations concerning carbene-stabilization of monatomic Be(0) and diatomic Be_2(0) species[66] suggested that carbene-complexed beryllium(0) complexes are considerably more stable than the corresponding magnesium(0) analogues. Braunschweig reported the first carbene-stabilized beryllium(0) complexes, $(CAAC)_2Be(0)$ (**26** and **27**) in 2016, via the potassium graphite reduction of CAAC-$BeCl_2$ complexes (**24** and **25**), respectively (Scheme 8).[67]

Scheme 8. Synthesis of CAAC-Stabilized Be(0) Complexes (26 and 27) (Dipp = 2,6-Diisopropylphenyl)



The solid-state structure of **26** (Figure 6) shows that two coplanar C_4N rings are bridged by a linear $C_{carbene}$−Be−$C_{carbene}$ core, which, coupled with the short Be−$C_{carbene}$ bonds (1.662 Å (av) for **26**; vs 1.779 Å for **24**), suggest considerable Be−$C_{carbene}$ π bonding interactions.[67] The Be−$C_{carbene}$ bonding in **26** and **27** is best described as a combination of donor−acceptor interactions between ground state singlet carbene ligands and the central Be(0) atom (in a $1s^2 2s^0 2p^2$ electronic configuration). Consequently, a 3c-2e π bond is formed through the $C_{carbene}$−Be−$C_{carbene}$ core. The strong π-accepting capabilities of CAACs are critical in stabilizing the highly reactive single Be(0) atom. However, this serves to diminish the reactivity of the beryllium(0) centers in **26** and **27**. For example, while reacting with CO_2 and elemental selenium, giving zwitterionic ^{Me}CAAC:CO_2 and selenone, respectively, **26** was shown to be inert toward dihydrogen, boranes, borohydrides, and bulky alcohols.[67]

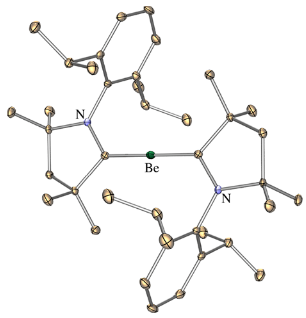


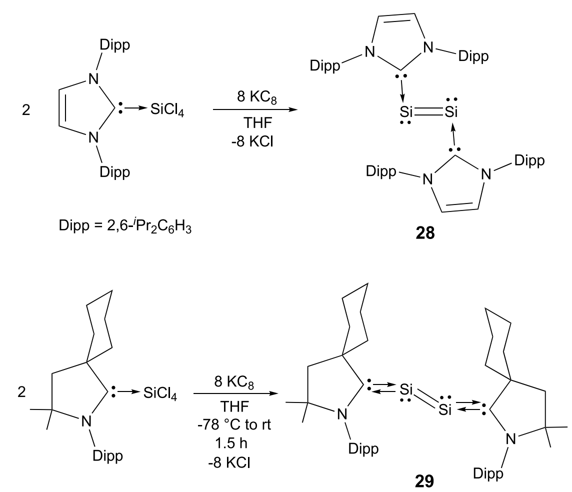
Figure 6. Molecular structure of **26**.

CARBENE-STABILIZED E_2(0) SPECIES

Seminal advances in low-oxidation state silicon chemistry over the past four decades necessarily include West's 1981 synthesis of the first disilene,[68] $R_2Si{=}SiR_2$ (R = 2,4,6-$(CH_3)_3C_6H_2$), and Sekiguchi's 2004 report of the first disilyne,[69] R-Si≡Si-R (R = $Dis_2{}^iPrSi$, Dis = bis(trimethylsilyl)methyl). The formal oxidation states of the silicon atoms in the disilene and disilyne are +2 and +1, respectively. In subsequent years a question was asked with increasing frequency: Was it possible to push the boundaries even further and prepare a compound containing a disilicon core with both silicon atoms in the formal oxidation state of zero? Relatedly, the highly reactive diatomic Si_2(0) molecule has a triplet ground state ($X^3\Sigma_g^-$) and has been probed in the gas phase and in argon matrices.[70] The key role of elemental silicon in the semiconductor industry, coupled with its unique utility in organosilicon synthesis, only added to the allure of the elusive Si_2(0) species.

Carbene-stabilization of disilicon, Si_2(0), was experimentally realized by this laboratory in 2008 via the potassium graphite reduction of L:$SiCl_4$ (L: = NHC^{Dipp}) (**28**) (Scheme 9).[71]

Scheme 9. Synthesis of Carbene-Stabilized Disilicon (28 and 29)



Schreiner subsequently suggested that London dispersion forces critically contribute to the thermodynamic stability of **28**, as well as many other bulky carbene-stabilized reactive main-group species.[72] One-electron oxidation of **28** by $[Fe(C_5Me_5)_2]^+[B(Ar^F)_4]^-$ (Ar^F = C_6H_3-3,5-$(CF_3)_2$) results in $[\mathbf{28}]^{\bullet+}$ $[B(Ar^F)_4]^-$.[73] NHC^{Dipp}-stabilized $Si^I_2Cl_2$ and $Si^{II}Cl_2$ were also prepared by changing solvent and the reaction stoichiometry.[71,74] In 2014, Roesky synthesized the ^{Cy}CAAC-based disilicon (**29**) via potassium graphite reduction of ^{Cy}CAAC:$SiCl_4$ (Scheme 9).[75]

X-ray structural analysis[71] (Figure 7) shows that the Si═Si double bond distance in **28** (2.2294(11) Å) compares well to the experimental value (2.246 Å) of Si_2 (obtained from photoelectron spectroscopic studies).[76] The trans-bent geometry around the Si_2 core [C−Si−Si angle = 93.57(11)°], the single Si−C_{NHC} bond [1.9271(15) Å], and the perpendicularity of the Si═Si vector to the imidazole plane are consistent with the silicon atoms in **28** residing in the formal oxidation state of zero. In contrast, if the silicon atoms in **28** reside in the +2 oxidation state, the molecule would be expected to exhibit a linear C_{NHC}═Si═Si═C_{NHC} core with short C═Si double

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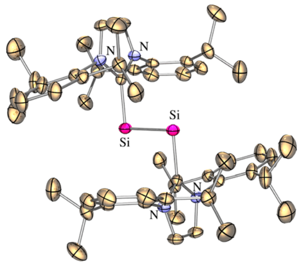


Figure 7. Molecular structure of **28**.

bonds.[20] Computations of the simplified model **28-Ph** (Figure 8) show that the HOMO and HOMO−1 correspond to the silicon−silicon π- and σ-bonds, respectively, while HOMO−2 represents one of the two lone electron pair orbitals of the $Si_2(0)$ core.[71]

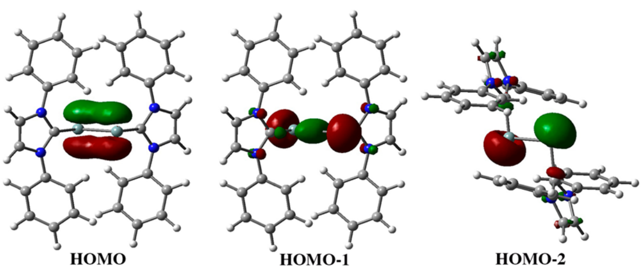
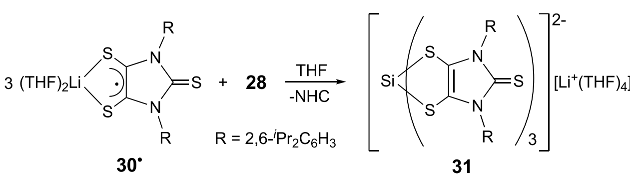


Figure 8. HOMO, HOMO−1, and HOMO−2 molecular orbitals of the simplified **28-Ph** model.

Due to the strong π-accepting capability of CAAC ligands, the lone electron pairs of silicon atoms in **29** back-donate significantly to each carbene carbon atom. Consequently, **29** exhibits shortened Si−C bonds [1.887(4) Å] and broadened C−Si−Si angles [from 101.22(13)° to 105.14(13)°] by comparison with those of **28** [d_{Si-C} = 1.9271(15) Å; C−Si−Si angle = 93.57(11)°].[75] Additionally, the ^{29}Si NMR resonance of **29** (249.1 ppm) is considerably shifted downfield as compared to that of **28** (224.5 ppm).

The coordinate bond essence of the Si−C_{NHC} bonds in **28** was further confirmed by the reaction of **28** with the lithium dithiolene radical **30•**.[77] This reaction resulted in the release of the N-heterocyclic carbenes from the silicon atoms and subsequent formation of the dianionic silicon(IV) tris(dithiolene) complex **31** (Scheme 10).[78] Due to the redox-active character of the dithiolene ligand, the silicon atom is oxidized from the oxidation state of zero (in **28**) to +4 (in **31**). **28** acts as a silicon-transfer agent in this transformation, which joins a group of single-E-species-transfer reactions (such as E = N,[79] P,[80,81] Si,[82] Al,[83] and Pb[65]).

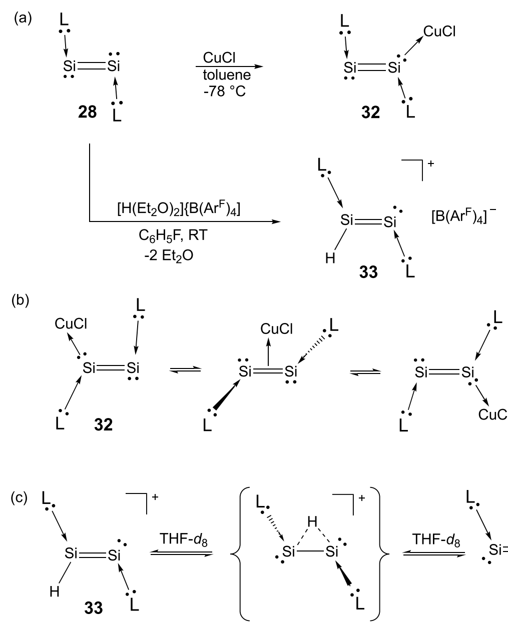
Scheme 10. Carbene-Stabilized $Si_2(0)$ (28) as a Silicon-Transfer Agent



In contrast to the silicon−silicon doubly bonded disilenes, carbene-stabilized disilicon(0) species contain one Si═Si double bond in addition to two silicon-based lone pairs. The Si═Si double bond and the silicon-based lone pairs may function as π- and σ-donors, respectively. Thus, carbene-stabilized $Si_2(0)$ species are expected to exhibit considerably different coordination behavior from disilenes.

Reaction of **28** with CuCl in toluene at −78 °C gave the 1:1 adduct (**32**) (Scheme 11a).[84] Perhaps due to steric repulsions,

Scheme 11. (a) Synthesis of 32 and 33, (b) σ−π Interconversion of 32 in Solution, (c) Topomerization of 33 in THF-d_8 Solution (L: = NHC^{Dipp}, Dipp = 2,6-Diisopropylphenyl)



attempts to isolate the 1:2 adduct [**28**:$(CuCl)_2$] repeatedly proved unsuccessful. X-ray structural analysis of **32** shows that one of the two silicon atoms is σ-bonded to one CuCl species. The Si−Cu bond distance in **32** [2.2081(9) Å] is marginally shorter than those in lithium bis(disilenyl)cuprate [2.2412(8) and 2.2458(8) Å].[85] Computations revealed that the Si−Cu single bond (WBI = 0.66) in **32** is highly polarized toward silicon (78%). Notably, the Si═Si double bond distance in **32** [2.2061(12) Å] is similar to that in **28** [2.2294(11) Å],[71] indicating that in the solid state the silicon−silicon π-bond in **32** is largely not involved in the coordination to CuCl. Indeed, the simplified **32-Me** model (NHC: = :C[N(Me)CH]$_2$) in π-bonding mode with CuCl has an elongated silicon−silicon bond (2.295 Å), which is similar to those for disilene-transition metal π complexes.[86] However, **32** only shows a singlet ^{29}Si NMR resonance in solution. In addition, the two carbenes are chemically equivalent in both ^{1}H and ^{13}C NMR spectra of **32**. These NMR spectroscopic data, coupled with the results from variable-temperature (VT) ^{1}H NMR experiments, reveal that, in solution, **32** may either exist as a π-complex isomer or rapidly equilibrate at room temperature via a π-complex intermediate (Scheme 11b).[84] Computations show that the π-complex of **32-Me** model (optimized in C_2 symmetry) is only 0.2 kcal/mol higher in energy than the corresponding σ-complex. The σ−π interconversion of **32** (Scheme 11b) is significant since σ−π rearrangements of organotransition-metal complexes are particularly important in catalytic processes.[87] Filippou synthesized **33** (the protonated product of **28**) by

https://doi.org/10.1021/jacs.2c13574
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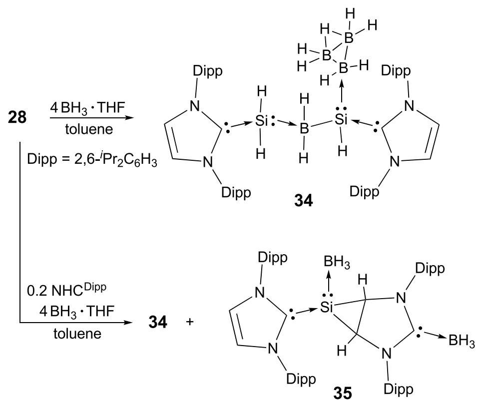
reaction of **28** with $[H(Et_2O)_2]\{B(Ar^F)_4]$ (Ar^F = C_6H_3-3,5-$(CF_3)_2$) (Scheme 11a).[88] The dynamic NMR studies in solution revealed the topomerization (degenerate isomerization) of the *σ*-bonded tautomers of **33**, proceeding via a *π*-bonded isomer intermediate (NHC^{Dipp}-based disilahydronium ion) (Scheme 11c). The same intramolecular topomerization phenomenon was also observed for the $[L:(I)Si = Si:L]^+$ cation (L: = NHC^{Dipp}).[89]

Carbene-stabilized disilicon(0), **28**, may serve as an effective platform to access unusual silylene complexes. For example, the 1:4 reaction of **28** with BH_3·THF in toluene resulted in the cleavage of the Si=Si double bond, giving **34** in 72% yield (Scheme 12).[90] The highly reactive SiH_2 species has been

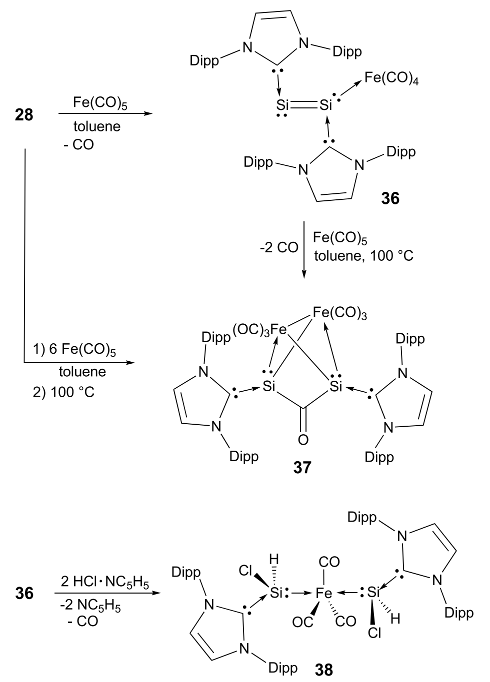
Scheme 12. Borane-Mediated Cleavage of 28



observed as an intermediate in the chemical vapor deposition of silicon film via SiH_4 pyrolysis.[91] **34** represents the first "push–pull"-stabilized parent silylene (SiH_2), wherein the SiH_2 unit accepts one pair of electrons from the NHC ligand, while donating one electron pair to the NHC:Si(H)(B_3H_7)BH_2 moiety. In the presence of a small amount of free NHC ligand (**28** to NHC = 5:1), the parallel reaction gives a mixture containing both **34** (30% yield) and **35** (28% yield) (Scheme 12).[90] Compound **35** is a "push–pull"-stabilized three-membered cyclosilylene, wherein the silylene center accepts an electron pair from the carbene ligand, while donating a pair of electrons to the BH_3 unit. The formation of **35** may involve cycloaddition of the silicon(0) atom of the NHC:Si(BH_3) intermediate to the C=C backbone of the NHC ligand.

Room temperature reaction of **28** with iron pentacarbonyl (in a 1:1 ratio) in toluene gives the tetracarbonyliron adduct, **36**, as a dark purple solid in 81% yield (Scheme 13).[92] X-ray structural analysis of **36** shows one silicon atom is *σ*-bonded to one $Fe(CO)_4$ moiety. In contrast to **32**,[84] which only shows one singlet ^{29}Si NMR resonance (226.7 ppm in C_6D_6), **36** exhibits two ^{29}Si NMR resonances (142.5 and 201.3 ppm in THF-d_8), indicating the presence of the asymmetrical structure of **36** not only in the solid state but also in solution. The lack of dynamic complexation behavior of **36** in solution may be due to the steric bulk of the $Fe(CO)_4$ fragment. Compound **37** can be prepared either through the 1:1 reaction of **36** with $Fe(CO)_5$ at 100 °C or by direct reaction of **28** with excess $Fe(CO)_5$ (Scheme 13).[92] The **28**-to-**37** conversion involves the insertions of both CO and $Fe_2(CO)_6$ into the two NHC^{Dipp}-stabilized silicon atoms. Furthermore, reaction of **36** with pyridine hydrochloride (HCl·NC_5H_5) gave a "push–pull"-stabilized parent monochlorosilylene [:Si(H)Cl] (**38**)

Scheme 13. Synthesis of 36–38 (Dipp = 2,6-Diisopropylphenyl)



(Scheme 13), in which two NHC^{Dipp}-complexed :Si(H)Cl silylene units donate electron pairs to an $Fe(CO)_3$ moiety.[93]

Unlike naturally occurring stable silica (SiO_2), which consists of a covalent Si–O–Si network, molecular SiO_2 and other small silicon oxides are highly reactive. Molecular SiO_2 has been detected in solid noble-gas matrices[94,95] and gas-phase reactions[96] and explored by photoelectron spectroscopy.[97] By allowing **28** to react with O_2 and N_2O, this laboratory obtained two novel molecules—NHC^{Dipp}-stabilized Si_2O_4 (**39**) and Si_2O_3 (**40**), respectively (Scheme 14).[98] X-ray structural analysis shows that the Si_2O_4 core of **39** adopts C_{2h} symmetry due to carbene coordination. While each silicon(IV) atom in **39** is capped by a terminal oxygen atom with a 1.5260(14) Å Si–$O_{terminal}$ bond (bearing modest double-bond character), these two silicon(IV) atoms are also bridged by two additional oxygen atoms with Si–O_{bridge} single bonds (1.675 Å, av). The Si–C_{NHC} bond distance in **39** [1.9259(17) Å] compares well to that in **28** [1.9271(15) Å].[71] Regarding the Si_2O_3 core of **40**, the two silicon(III) atoms are bridged by one oxygen atom while retaining a silicon–silicon single bond [2.2405(14) Å].[98] Further oxidation of **40** by CO_2 gives a carbene-stabilized silicon–carbon mixed oxide $(SiO_2)_2CO_2$ (**41**), which can also be directly prepared via CO_2 oxidation of **28** (Scheme 14).[99] By allowing **28** to react with elemental tellurium, So and coworkers synthesized not only the tellurium analogues of **39** and **40** but also NHC^{Dipp}-stabilized Si_2Te_2 and Si_2Te_2S clusters.[100] Notably, the NHC-stabilized Si_2Te_2 may exist in two isomeric forms [i.e., NHC(Te)Si=Si(Te)NHC and NHC(Te)Si(*μ*-Te)SiNHC]. The stability sequence of these NHC-complexed Si_2Te_n (n = 2, 3, and 4) clusters are Si_2Te_4 > Si_2Te_3 > (Te)Si(*μ*-Te)Si > (Te)Si=Si(Te).[100]

By utilizing CAAC-stabilized disilicon complexes (**29** and **42**)[75,101] (Scheme 14), Roesky synthesized CAAC-stabilized Si_2S_4 (**43**)[102] and Si_2Se_4 (**44** and **45**).[101] In contrast to **43**–**45**, which are stable for months under an inert atmosphere at room temperature, crystals of NHC^{Dipp}-stabilized Si_2O_4 (**39**)

https://doi.org/10.1021/jacs.2c13574
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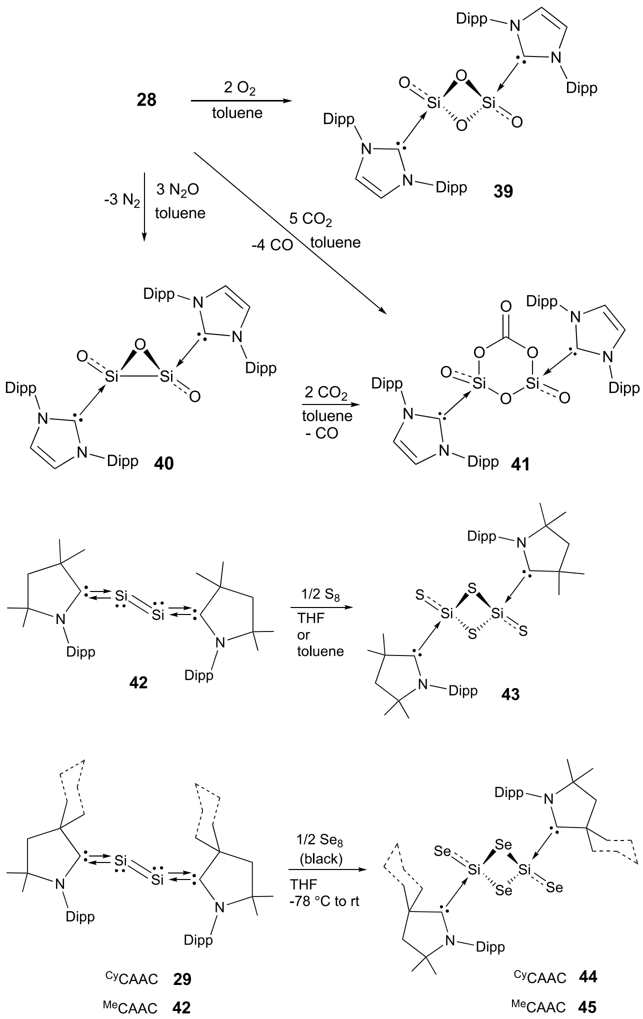
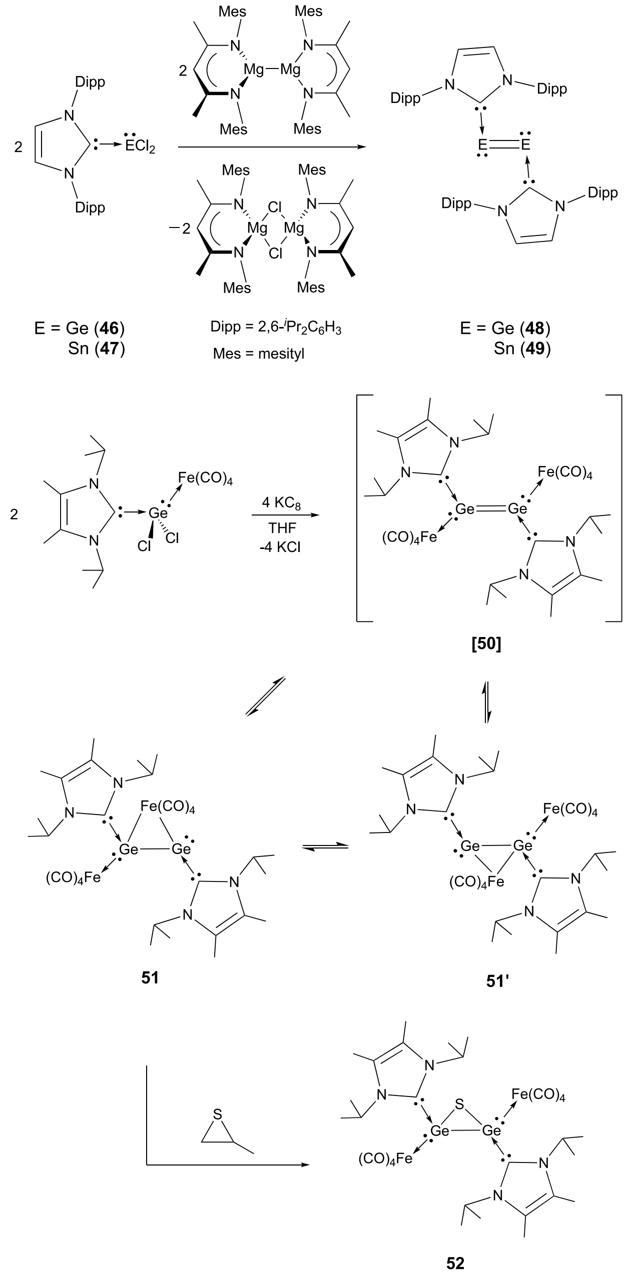
Scheme 14. Carbene-Stabilized-Disilicon-Mediated Small Molecule Activation (Dipp = 2,6-Diisopropylphenyl, Cy = Cyclohexyl)



Scheme 15. Synthesis of NHC-Stabilized $Ge_2(0)$ (48), $Sn_2(0)$ (49), and "Push–Pull"-Stabilized $Ge_2(0)$ (51)



and Si_2O_3 (**40**) slowly decompose, even under argon protection. Storage of **39** and **40** at low temperature (−40 °C) would obviously increase the stability of these two compounds. The high reactivity of **39** and **40** indicates that these compounds may be employed to transfer and integrate the "Si_2O_3" or "Si_2O_4" units into various inorganic and organometallic substrates. CAAC-stabilized silicon oxides, via oxidation of **29** and **42**, have not been reported. When exposed to air, **42** decomposed to ^{Me}CAAC═O and SiO_2.[61,101]

Employing RMg−MgR (R = β-diketiminate ligand) as a two-center, two-electron reducing agent to react with $NHC^{Dipp}ECl_2$ [E = Ge (**46**), Sn (**47**)], Jones and Stasch synthesized carbene-stabilized $Ge_2(0)$ (**48**) and $Sn_2(0)$ (**49**), respectively (Scheme 15).[49,103] Similar to carbene-stabilized $Si_2(0)$ (**28**),[71] both **48** and **49** adopt the trans-bent geometry around the E═E double bond [$d_{E═E}$ = 2.3490(8) Å, E = Ge (**48**); $d_{E═E}$ = 2.7225(5) Å, Sn (**49**)]. The carbene ^{13}C NMR resonances of NHC^{Dipp}-stabilized $Si_2(0)$ (**28**) (196.3 ppm), $Ge_2(0)$ (**48**) (203.3 ppm), and $Sn_2(0)$ (**49**) (210.3 ppm) are shifted downfield upon descending the group, thus indicating a weaker $E−C_{NHC}$ bonding interaction with increasing atomic mass of E.

Donor−acceptor-stabilized $Ge_2(0)$ species (**51**) was synthesized by Scheschkewitz via potassium-graphite reduction of $NHC{:}Ge(Cl)_2[Fe(CO)_4]$ (NHC = :C{(^{i}Pr)NC(Me)}$_2$) in THF (Scheme 15).[104] X-ray structural analysis of **51** shows that while one $Fe(CO)_4$ moiety is terminally bonded to a germanium atom with a Ge−Fe σ-bond [2.4112(3) Å], the other $Fe(CO)_4$ unit acts as a bridge between the two germanium atoms [bridging Ge−Fe bond distances = 2.6292(3) Å, av]. Consequently, the Ge−Ge bond in **51** [2.4442(2) Å] is slightly longer (ca. 0.1 Å) than that in NHC^{Dipp}-stabilized $Ge_2(0)$ (**48**) [2.3490(8) Å].[49] Computations support that **51** has a metallacyclopropane-type bonding motif, according to the Dewar−Chatt−Duncanson model. Both the NMR spectral data and theoretical calculations of **51** imply a possible degenerate equilibrium between **51** and **51′** through an isomeric species with two terminal $Fe(CO)_4$ units

https://doi.org/10.1021/jacs.2c13574
J. Am. Chem. Soc. 2023, 145, 5592−5612

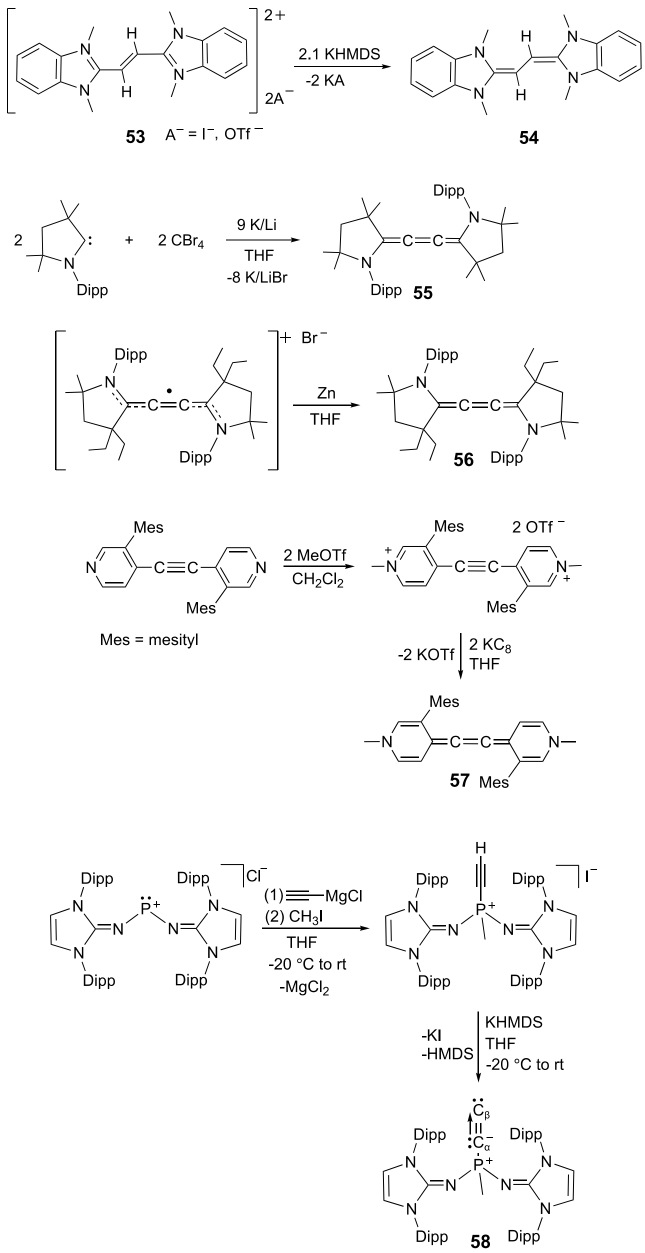
[50] (Scheme 15).[104] Indeed, [50] is only slightly higher in free energy (by only 7.4 kcal mol^{-1}) than **51**. The interaction between the digermanium unit and the bridging $Fe(CO)_4$ fragment is weak and should thus involve certain π-complex character. Room temperature reaction of **51** with propylene sulfide (in toluene) gives a digermathiirane (**52**) containing a Ge_2S three-membered ring (Scheme 15).[104]

In contrast to the NHC-stabilized heavier $E_2(0)$ (E = Si, Ge, and Sn) congeners, wherein the $E_2(0)$ cores exhibit trans-bent geometries [C_{NHC}−E−E angle = 93.57(11)°, E = Si (**28**);[71] 89.87(8)°, E = Ge (**48**);[49] 91.82(8)°, E = Sn (**49**)],[103] the NHC-based dicarbon derivative was predicted in 2012 by Dutton and Wilson to exist as a linear cumulene.[105] An experimental attempt to obtain the NHC-based dicarbon, through deprotonation of a doubly protonated precursor **53**, proved unsuccessful, affording only the reduced product **54** (Scheme 16).[106] CAAC-based cumulenes **55** and **56** were independently synthesized by the laboratories of Roesky and Bertrand, respectively (Scheme 16).[107,108] In addition, Kinjo reported a 4-pyridylidene-based cumulene (**57**) (Scheme 16).[109] The bonding analysis, using charge and energy decomposition methods, revealed that $(CAAC^{Me})_2C_2$ and $(DAC^{Me})_2C_2$ (DAC = diamidocarbene) possess genuine cumulene C_4 cores due to the electron-sharing bonding between quintet L_2 (L = $CAAC^{Me}$ and DAC^{Me}) and quintet C_2 fragments.[110] However, the bonding in $(NHC^{Me})_2C_2$ and $(SNHC^{Me})_2C_2$ (SNHC = saturated NHC) appears to have been based on a combination of dative and electron-sharing interactions between doublet L_2^+ (L = NHC^{Me} and $SNHC^{Me}$) and doublet C_2^- moieties.[110] In contrast to the linear "cumulene" cores of **55**−**57**, a monoligated L:C_2 complex (**58**) [L: = $(NHC^{Dipp}{=}N)_2(Me)P$] was recently synthesized by Ong, using a sterically demanding phosphine ligand (Scheme 16).[111] Notably, these phosphine-stabilized dicarbon complexes have been utilized as supporting ligands in transition-metal catalysis.[112]

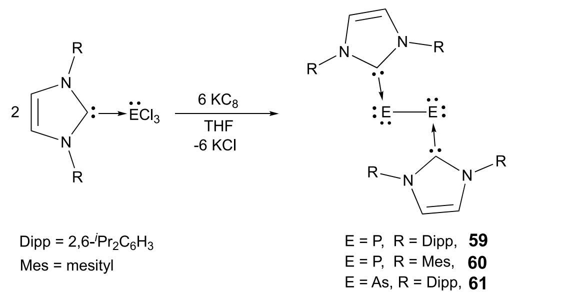
Following our discovery of carbene-stabilized disilicon (**28**), we extended the carbene-stabilization strategy to the group 15 elements. The potassium graphite reduction of NHC^R:ECl_3 in THF gives the corresponding carbene-stabilized $E_2(0)$ species (E = P, R = Dipp, **59**; E = P, R = Mes, **60**; E = As, R = Dipp, **61**) (Scheme 17).[113,114] Alternatively, **59** may also be accessed by using Na(OCP) as a phosphorus-transfer agent.[115]

The dominant structural feature of **59** and **60** is the phosphorus−phosphorus single bond [d_{P-P} = 2.2052(10) Å, **59**; d_{P-P} = 2.1897(11) Å, **60**] (Figure 9).[113] As a result, the steric demands of the carbenes may significantly affect the conformations of these complexes. While the P_2 core in **59** exhibits a trans-bent geometry with the C−P−P−C torsion angle of 180.0°, the corresponding P_2 core in **60** adopts a gauche conformation (the C−P−P−C torsion angle = 134.1°). The P−C_{NHC} bond distances of **59** [1.7504(17) Å] and **60** [1.754(3) Å] are between P═C double bond distances of the nonconjugated phosphaalkenes[116] (1.65−1.67 Å) and typical P−C single bond distances (such as that of NHC^{Dipp}:PCl_3 [1.871(11) Å]).[117] The WBI of **59** (1.40) suggests modest double bond character of the P−C_{NHC} (due to the back-donation of the electron pair of the phosphorus atom to the p orbital of the carbene carbon atom). However, the high-field ^{31}P NMR resonances for **59** (−52.4 ppm) and **60** (−73.6 ppm) support the presence of electron-rich bis(phosphinidene) cores in these two complexes. Isostructural to **59**, carbene-stabilized diarsenic, **61**, containing a singly bonded $As_2(0)$ core [d_{As-As} = 2.442(1) Å], may be described as a carbene-complexed diarsinidene.[114]

Scheme 16. Synthesis of Cumulenes (55−57) and Monoligated C_2 Complex (58) (Dipp = 2,6-Diisopropylphenyl)



Scheme 17. Synthesis of NHC-Stabilized $P_2(0)$ (59 and 60) and $As_2(0)$ (61)



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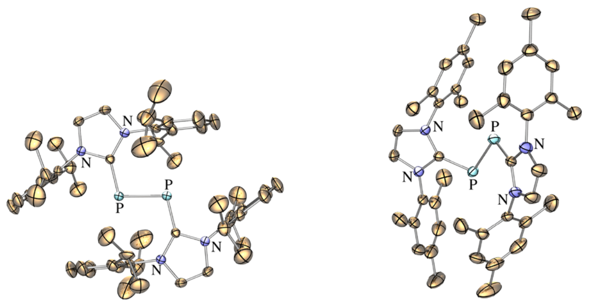
J. Am. Chem. Soc. 2023, 145, 5592−5612

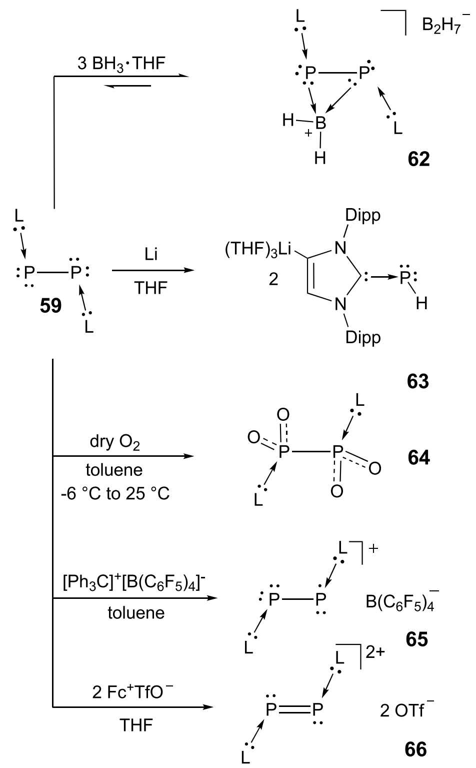


59 60

Figure 9. Molecular structures of **59** and **60**.

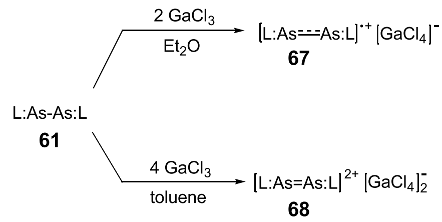
Reaction of **59** with excess $BH_3 \cdot THF$ gave the boronium complex **62** in 85% yield (Scheme 18), wherein the carbene-stabilized $P_2(0)$ core serves as a bidentate ligand to bind to a BH_2^+ cation.[118] The ^1H NMR spectroscopy suggests an equilibrium between **59** and **62**, which favors the formation of **62**. Addition of excess of $BH_3 \cdot THF$ was shown to significantly diminish the dissociation of **62**. While reduction of **59** with lithium metal in THF gave the C_4-lithiated NHC-stabilized parent phosphinidene (PH) (**63**),[117] oxidation of **59** with dioxygen in toluene results in NHC-stabilized P_2O_4 (**64**) (Scheme 18).[119] In contrast to the highly reactive carbene-stabilized Si_2O_4 (**39**) and Si_2O_3 (**40**),[98] complex **64** is air-stable. The splitting of triplet O_2 by the singlet $P_2(0)$ core of **59** may have involved single-electron transfer processes.[120] The P_2O_4 core in **64** exists as a PO_2 dimer containing a P–P single bond [2.310(2) Å]. Notably, free P_2O_4 energetically favors an oxo-bridged and nonplanar O_2POPO isomer[121,122] (with C_s symmetry) rather than the symmetric $O_2P–PO_2$ dimer observed in **64**. Bertrand reported that while $[Ph_3C]^+[B(C_6F_5)_4]^-$-mediated one-electron oxidation of **59** provided the NHC-stabilized $P_2^{\bullet+}$ radical cation (**65**), ferrocenium triflate mediated two-electron oxidation of **59** gave the NHC-stabilized P_2^{2+} dication (**66**) (Scheme 18).[123]

Scheme 18. Synthesis of 62–66 (L: = NHC^{Dipp}; Dipp = 2,6-Diisopropylphenyl)



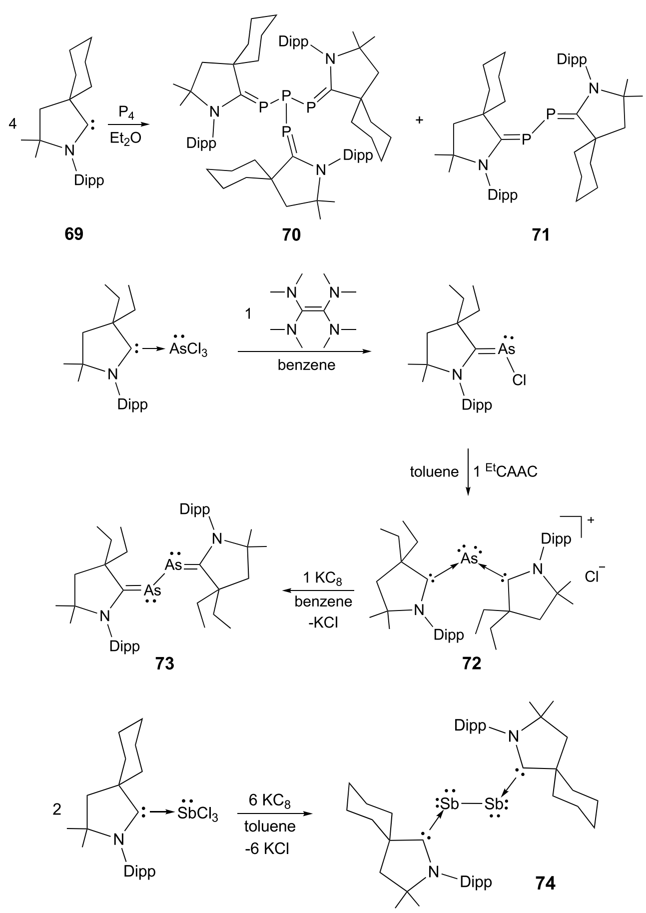
This laboratory subsequently discovered that the Lewis acid $GaCl_3$ may be employed as an oxidant to convert NHC-stabilized $As_2(0)$ (**61**) into either the corresponding monocationic diarsenic radical (**67**) or the dicationic diarsene (**68**) (Scheme 19).[124]

Scheme 19. Synthesis of 67 and 68 (L: = NHC^{Dipp}; Dipp = 2,6-Diisopropylphenyl)



Bertrand reported that ^{Cy}CAAC (**69**) can mediate fragmentation of white phosphorus (P_4), giving both $(L:P)_3P$ (**70**) and L:P–P:L (**71**) (L: = **69**) (Scheme 20).[125] The P–C bond distance of **71** [1.719(7) Å] is ca. 0.03 Å shorter than that (ca. 1.75 Å) of NHC-stabilized $P_2(0)$ (**59** and **60**).[113] In

Scheme 20. Synthesis of CAAC-Based $P_2(0)$ (71), $As_2(0)$ (73), and $Sb_2(0)$ (74) (Dipp = 2,6-Diisopropylphenyl)



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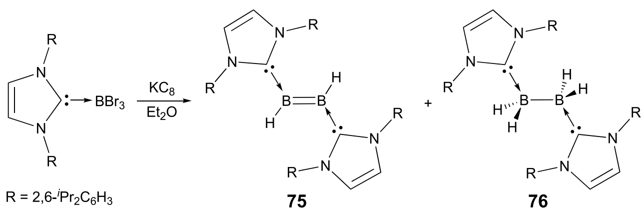
J. Am. Chem. Soc. 2023, 145, 5592–5612

contrast to the high-field ^{31}P NMR resonances of **59** (−52.4 ppm) and **60** (−73.6 ppm), compound **71** shows a low-field ^{31}P NMR resonance of 54.2 ppm. These structural and spectroscopic data strongly support the 2,3-diphosphabutadiene essence of **71**. While **59** can be converted to **65** and **66** via one-electron and two-electron oxidation, respectively (Scheme 18), CAAC-stabilized diphosphorus (**71**) can only be converted to the analogue of **65** via $[Ph_3C]^+[B(C_6F_5)_4]^-$-mediated one-electron oxidation.[123] The ^{Et}CAAC-stabilized diarsenic (**73**) was synthesized by Hudnall via potassium graphite reduction of the $[(^{Et}CAAC)_2As]^+Cl^-$ precursor (**72**) (Scheme 20).[126] The As−C bond distance of **73** [1.837(5) Å] is ca. 0.04 Å shorter than that of **61** [1.881(2) Å].[114] The E═C (E = P, As) double bond character (in **71** and **73**) should be attributed to the increased π-acidic character of the CAAC ligand compared to the NHC. By allowing one equivalent of ^{Cy}CAAC:$SbCl_3$ to react with 3 equiv of potassium graphite, Bertrand obtained ^{Cy}CAAC-stabilized $Sb_2(0)$ (**74**) (Scheme 20).[127] Compound **74** contains a singly bonded $Sb_2(0)$ core [d_{Sb-Sb} = 2.8125(10) Å], which adopts an anticlinal twisted-bent geometry [C−Sb−Sb-C torsion angle = 122.6(4)°]. The Sb−C bond distances in **74** [2.084(11)−2.088(10) Å] are longer than the theoretical value for the parent stiba-alkene (2.01 Å).[128] The WBI value of the Sb−C bond in **74** (1.23) is less than that of the As−C bond in **61** (1.34) and that of the P−C bond in **59** (1.40), indicating the decreased multiple bond character of the E−$C_{carbene}$ bonds, descending group 15. Notably, among carbene-stabilized main group $E_2(0)$ species, **74** contains the heaviest diatomic allotrope core reported.

This laboratory has long been fascinated by the multiple bond chemistry of the group 13 elements.[129,130] Although our initial goal was to prepare a molecule containing a boron−boron triple bond, the potassium graphite reduction of NHC^{Dipp}-complexed BBr_3 afforded a NHC^{Dipp}-stabilized neutral diborene (**75**) (orange-red crystals) and a diborane (**76**) (colorless crystals) (Scheme 21).[38] The stoichiometric

Scheme 21. Synthesis of NHC-Stabilized Neutral Diborene (75) and Diborane (76)



ratio of NHC^{Dipp}:BBr_3 to KC_8 has been observed to affect the yield of **75**. A higher yield (12%) of **75** was obtained with a 1:5.4 molar ratio of NHC^{Dipp}:BBr_3 to KC_8.

In contrast to the four-coordinate tetrahedral boron atoms of **76** (involving a boron−boron single bond of 1.828(4) Å), X-ray data[38] (Figure 10a) revealed the most salient structural feature of **75**[38]—the three-coordinate trigonal planar boron atoms constituting a boron−boron double bond—the first neutral diborene. The boron−boron double bond distance in **75** [1.560(18) Å, av] is shorter than those distances reported for diboron dianions $[Mes_2BB(Mes)Ph]^{2-}$ [1.636(11) Å][131] and $[\{Ph(Me_2N)BB(NMe_2)Ph\}]^{2-}$ (1.627 Å, av).[132] While the HOMO of the simplified **75-H** model corresponds to a B−B π-bonding orbital, the HOMO−1 involves mixed B−B and B−H σ-bonding character (Figure 10b).[38]

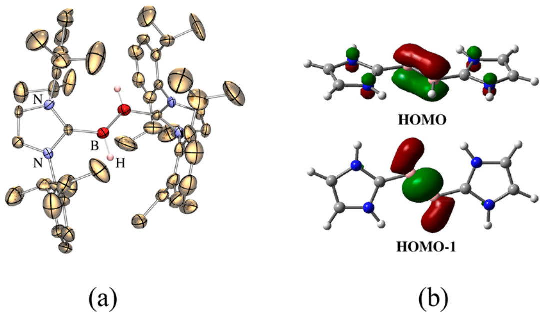
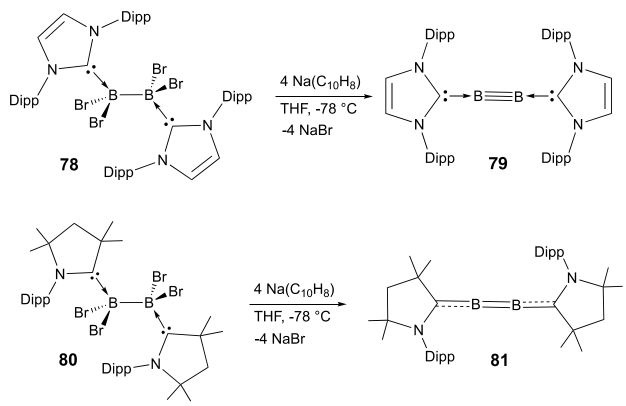


Figure 10. Molecular structure of **75** (a); the HOMO and HOMO−1 orbitals of the simplified **75-H** model (b).

The presence of hydrides (B−H) in **75** and **76** was presumed to be due to hydrogen abstraction from ethereal solvent in the presence of alkali metals.[133] Decreasing the steric bulk of the carbene ligand may aid the boron−boron bond formation and thus diminish the chance of hydrogen abstraction from the reaction media. Subsequently, this laboratory conducted potassium graphite reduction of less bulky NHC^{Mes}-complexed BBr_3. However, this reaction afforded three polymorphs of the neutral diborane L:B(H)═B(H):L (L: = NHC^{Mes}) (**77**) with planar, twisted, and trans-bent structures.[134] In 2012, the Braunschweig laboratory made a remarkable breakthrough in this field. Following the synthesis of **78** by reacting tetrabromodiborane(4) with 2 equiv of NHC^{Dipp},[135] they conducted sodium naphthalenide mediated reduction of **78** in THF at −78 °C. This resulted in the NHC^{Dipp}-stabilized $B_2(0)$ (**79**), containing the long-sought boron−boron triple bond (Scheme 22).[135]

Scheme 22. Synthesis of Carbene-Based Diboryne (79) and Diboracumulene (81) (Dipp = 2,6-Diisopropylphenyl)



In the solid state (Figure 11),[135] **79** contains an essentially linear C−B≡B−C core (the C−B−B−C torsion angle = −161.83°). Each boron atom is two-coordinate with a C−B−B angle of ca. 173.0°. The boron−boron triple bond distance of 1.449(3) Å matches well with the experimental values (1.453 to 1.468 Å) of OCBBCO.[136] It is interesting to compare the structural and spectroscopic data of **79** with the NHC^{Dipp}-complexed diborene (**75**) and diborane (**76**).[38] The B≡B triple bond in **79** [1.449(3) Å] is ca. 0.11 Å shorter than the B═B double bond in **75** [1.560(18) Å, av] and ca. 0.38 Å shorter than the B−B single bond in **76** [1.828(4) Å]. The B−C_{NHC} bond distances shorten in sequence: **76** [1.577(2) Å] > **75** [1.538(15) Å, av] > **79** [1.491(3) Å, av], indicating

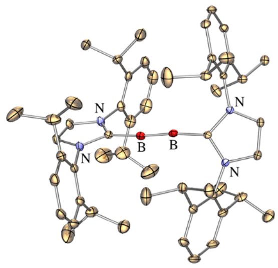


Figure 11. Molecular structure of **79**.

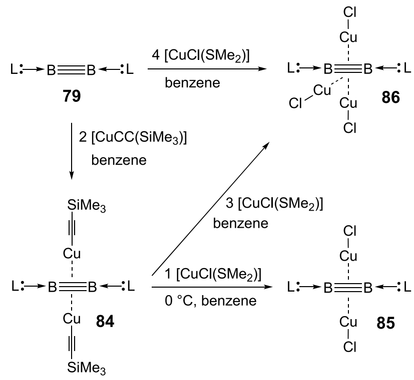
increased delocalization of the π-electrons of boron over the B−C$_{NHC}$ fragments. With the decrease of the coordination number of boron, the ^{11}B NMR resonances are shifted downfield in sequence: **76** (−31.6 ppm), **75** (25.3 ppm), **79** (39.0 ppm). The Raman[137] and NMR[138] spectroscopic studies provide further evidence for the *triple bond* character of the B_2(0) core in **79**.

Braunschweig also prepared the CAAC-complexed diboron **81** via sodium naphthalenide reduction of **80**, the CAAC-based analogue of **78** (Scheme 22).[139] The electronic properties of the carbene ligands have a remarkable effect on the bonding pattern of the C_2B_2 cores in these carbene-stabilized B_2 complexes. CAACs have been reported to be stronger σ-donors and π-acceptors than NHCs.[7] Hence, the boron−boron bond in **81** [1.489(2) Å] is somewhat longer than that in **79** [1.449(3) Å],[135] yet still shorter than the reported B=B double bonds (1.56−1.71 Å).[140,141] Concomitantly, the B−C bonds in **81** [1.458(2) Å, av] are shorter than those in **79** [1.491(3) Å, av]. Each boron atom in **79** bears an NPA charge of −0.13, indicating the electron-rich of the B_2(0) core in **79**. However, each boron atom in **81** has an NPA charge of +0.08. The 80.0 ppm ^{11}B NMR resonance of **81** is shifted significantly downfield compared to that of **79** (39.0 ppm). Thus, it may be appropriate to describe **81** as a diboracumulene. The π-acidity of the saturated NHC (i.e., SNHC) ligands is stronger than that of unsaturated NHCs but weaker than that of CAACs. As a result, the C_2B_2 cores in SNHC^{Dipp} or SNHC^{Dep}-stabilized diborons (**82**[142] and **83**[143]) exhibit an intermediate bonding pattern in-between that of **79** and that of **81**.

Considering the well developed chemistry of transition metal alkyne complexes, particularly their pivotal role in catalytic reactions, it is logical to investigate the coordination chemistry of the lightest triple bond (i.e., the B≡B bond) in **79**. The first transition metal π-complexes involving boron−boron triple bonds were synthesized by Braunschweig via reactions of **79** with copper(I) species (Scheme 23).[144] Reaction of **79** with 2 equiv of [CuCC(SiMe$_3$)] gave **84**, wherein the B_2(0) core of **79** is π-bonded to two [CuCC(SiMe$_3$)] units. Further reaction of **84** with 1 equiv (at 0 °C) or 3 equiv (at room temperature) of [CuCl(SMe$_2$)] produced diboryne-π-complexed $[CuCl]_2$ (**85**) or $[CuCl]_3$ (**86**), respectively. The trinuclear complex **86** was also directly prepared by reacting **79** with 4 equiv of [CuCl(SMe$_2$)] (Scheme 23).

As a result of di- and trimetalations, both B≡B and B−C bond distances increase in sequence: **79** [d_{B-B} = 1.449(3) Å; d_{B-C} = 1.491(3) Å, av] < **84** [d_{B-B} = 1.478(2) Å; d_{B-C} = 1.534(2) Å, av] and **85** [d_{B-B} = 1.486(5) Å; d_{B-C} = 1.546(4) Å, av] < **86** [d_{B-B} = 1.526(4) Å; d_{B-C} = 1.562(3) Å]. In addition, these diboryne-π-complexed Cu$_n$ (n = 2, 3) species display intense (for **86**) or weak (for **84** and **85**)

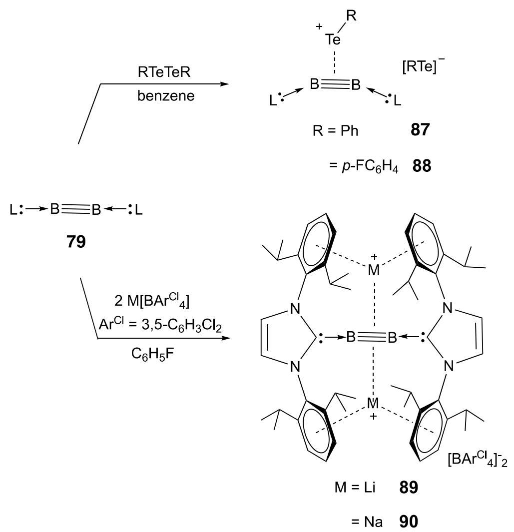
Scheme 23. Synthesis of 84−86 (L: = NHC^{Dipp}; Dipp = 2,6-Diisopropylphenyl)



phosphorescence in the red to near-IR region from their triplet excited states with quantum yields of up to 58%. DFT computations show that complexes **84−86** exhibit enhanced metal d orbital contributions to HOMO and HOMO−1. This leads to S_1 and T_1 with remarkable MLCT character and enables strong spin−orbit coupling for highly efficient intersystem-crossing $S_1 \to T_n$ and phosphorescence $T_1 \to S_0$ transitions.[144]

Diboryne **79** also formed π-complexes with main group cations. When **79** was combined with diaryltellurides, diboryne-π-complexed RTe$^+$ cations (**87** and **88**) were obtained via nucleophilic attack by **79** on one of the two tellurium atoms of diaryltellurides (Scheme 24).[145,146] The B−B bonds of **87** [1.490(6) Å] and **88** [1.494(10) Å] are somewhat longer than that of **79** [1.449(3) Å], but still obviously shorter than those for diborene complexes [such as $d_{B=B}$ = 1.560(18) Å (av) for **75**].[38] The elongation of the bound boron−boron bonds in **87** and **88** is limited. For example, the boron−boron bond in **87** is merely 2.8% longer than the free B≡B bond in **79**. The B−B−C angles in **87** and **88** (ca. 163−165°) are slightly bent from linearity. These structural features support assignment of **87** and **88** as *π-complexes*.[146] When **79** was combined with M[B(3,5-

Scheme 24. Synthesis of 87−90 (L: = NHC^{Dipp}; Dipp = 2,6-Diisopropylphenyl)



https://doi.org/10.1021/jacs.2c13574
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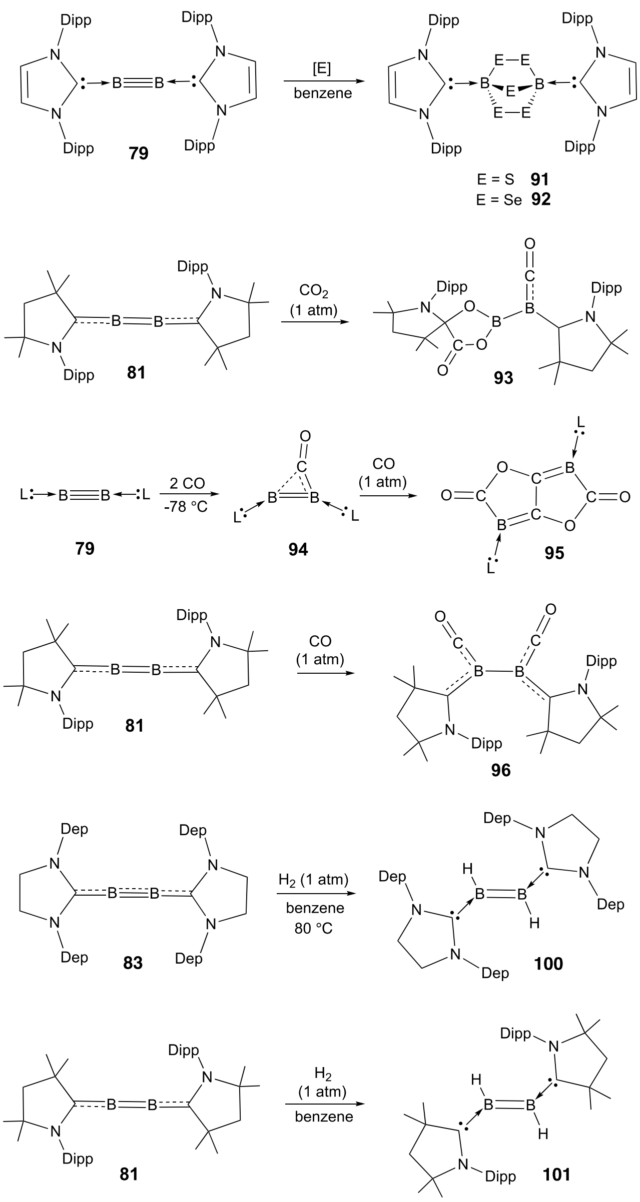
$C_6H_3Cl_2)_4]$ (M = Li, Na), complexes **89** and **90** were formed, respectively (Scheme 24).[147] In these complexes, the lithium or sodium cations are π-encapsulated by the diboryne unit, a rare feature for neutral molecules. In contrast to the cases of **84**−**88**, the B−B bond distances in **89** [1.452(6) Å] and **90** [1.459(4) Å] compare well to that of **79** [1.449(3) Å], indicating little covalent interaction between alkali metal cations and the B≡B triple bond. Notably, encapsulation of alkali metal cations by neutral NHC-stabilized $Si_2(0)$ (**28**) has also been observed.[88]

With a series of carbene-stabilized diboron complexes available, Braunschweig further investigated their capacity to activate small molecules. Room temperature reaction of **79** with excess elemental sulfur and selenium resulted in isostructural **91** and **92**, respectively, via reductive insertion of elemental chalcogens into the boron−boron triple bond (Scheme 25).[148] Both **91** and **92** contain a [2.2.1]-bicyclic system, wherein the two boron atoms are bridged by five chalcogen atoms. These reactions involved a six-electron reduction, supporting the B≡B triple bond character of **79**. While reactions of NHC-based diborynes with CO_2 provided intractable mixtures, the CO_2-mediated oxidation of diboracumulene (**81**), involving an initial [2 + 2] cycloaddition, resulted in **93** (Scheme 25).[149] The X-ray structural analysis of **93** demonstrated that **81** can fix two CO_2 molecules. One CO_2 molecule is cleaved to form a boron-bound terminal CO. Both the released oxygen atom and the other CO_2 molecule insert into a B−C_{CAAC} bond, giving a spiro five-membered C_2O_2B ring. In the contrast, the Si−C_{NHC} bonds remain intact in the CO_2-mediated oxidation of NHC-stabilized $Si_2(0)$ (**28**).[99] The low-temperature reaction of **79** with CO (in a 1:2 molar ratio) resulted in the isolation of a stable intermediate **94** [containing an unsymmetrically bridging CO between two doubly bonded boron atoms ($d_{B=B}$ = 1.549(3) Å)]. **94** was then quantitatively converted to the NHC^{Dipp}-stabilized bis(boralactone) (**95**) by reaction with excess CO at room temperature (Scheme 25).[150] However, the reaction of **81** with CO gave a stable bis(boraketene) (**96**) (Scheme 25),[142] which could not be converted to the CAAC-based bis(boralactone) even at 150 °C and under 50 bar of CO. When the SNHC^{Dipp}-stabilized diboron (**82**) was combined with CO, the corresponding carbene-stabilized bis(boraketene) (**97**) and bis(boralactone) (**98**) were obtained.[142] While **79**, **82**, and NHC^{Dep}-based $B_2(0)$ (**99**)[137] cannot undergo hydrogenation, both **83** and **81** may react with H_2 at 1 atm, giving SNHC^{Dep}- and CAAC-stabilized parent diborenes (**100** and **101**), respectively (Scheme 25).[143] These results suggest that the electronic and steric properties of the associated carbene ligands play a critical role in carbene-diboron-mediated activation of small molecules. A recent study indicated that the reactivity of carbene-stabilized diboron complexes may be enhanced by desymmetrization (i.e., formation of a zerovalent sp−sp^2 diboron complex via NHC coordination).[151]

In addition to the parent diborene (HB═BH),[143] carbene-stabilized diboron complexes have also been utilized in the synthesis of a variety of diborene derivatives (including the electron-poor cyano-substituted diborene,[152] *trans*-1-(2-propenyloxy)-2-hydrodiborene,[153] and diboryldiborenes[154]). Notably, SNHC^{Dipp,Mes}-stabilized diboron complex (**102**) has been shown to undergo stepwise hydroboration reactions with catecholborane to give hydro(boryl)-diborene (**103**) and 2,3-dihydrotetraborane (**104**) (Scheme 26).[155] MeOTf-mediated hydride (H^-) abstraction from **104** affords a unique planar

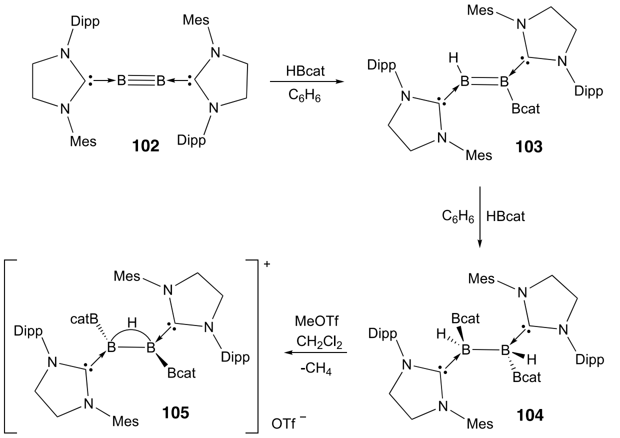
Scheme 25. Activation of Small Molecules by Carbene-Diboron Complexes (L: = NHC^{Dipp}; Dipp = 2,6-Diisopropylphenyl, Dep = 2,6-Diethylphenyl)



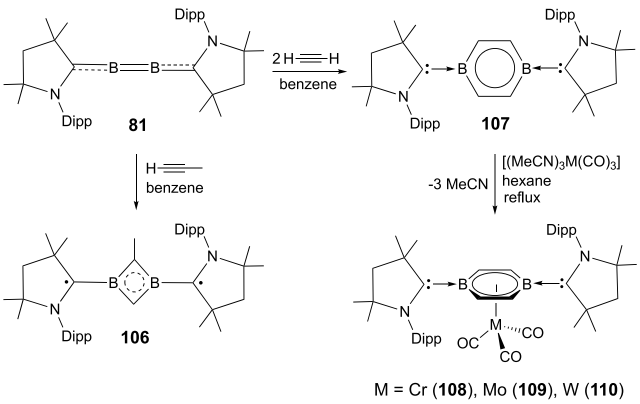
tetraborane cation (**105**), wherein a hydrogen atom serves as a bridge between the two boron atoms (Scheme 26). Both the solid-state structural data and DFT computations support its "protonated diborene" structural feature.

Braunschweig also utilized diboracumulene (**81**) in the synthesis of boron-containing aromatic heterocycles. While reacting with propyne to produce a CAAC-based 1,3-diborete (**106**), which exists as a triplet biradical with the unpaired electrons residing at the CAAC ligands, **81** may also react with acetylene to give a neutral CAAC-based 1,4-diborabenzene (**107**) via [2 + 2 + 2]-cycloaddition of two acetylene molecules to the B_2 core in **81** (Scheme 27).[156] **107** was further utilized as a 6π-aromatic analogue of benzene to prepare a series of half-sandwich complexes of transition metals (**108**−**110**) (Scheme 27).[157] Remarkably, unlike that of arene complexes of transition metals, the redox processes of these 1,4-

Scheme 26. Synthesis of 103−105 (Dipp = 2,6-Diisopropylphenyl, Mes = Mesityl, cat = Catechol)



Scheme 27. Synthesis of 106−110 ((Dipp = 2,6-Diisopropylphenyl)



diborabenzene-transition metal complexes are largely ligand-based.

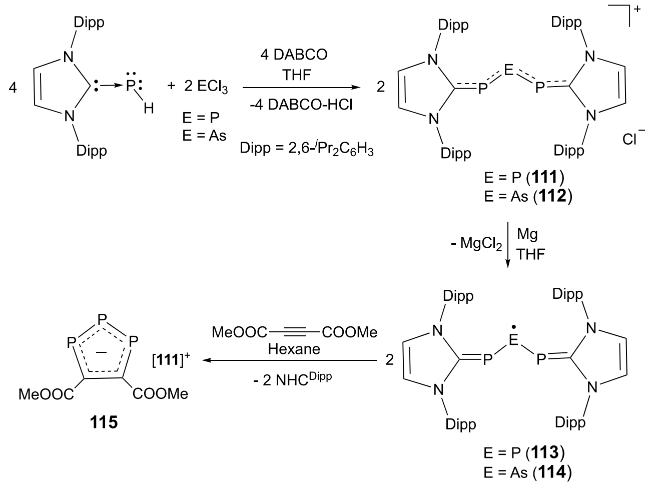
■ CARBENE-STABILIZED $E_N(0)$ (N = 3, 4, 8, 12) SPECIES

Carbene-stabilized triatomic molecules are rare. Grützmacher synthesized NHC-based P_3^+ (**111**) and P_2As^+ (**112**) cations in 2014 by allowing the NHC-stabilized parent phosphinidene (PH) to react with PCl_3 and $AsCl_3$, respectively, in the presence of DABCO (1,4-diazabicyclo[2.2.2]octane) (Scheme 28).[158] Subsequent magnesium reduction of **111** and **112** gave NHC-stabilized $P_3^\bullet$ (**113**) and $P_2As^\bullet$ (**114**) radicals, respectively (Scheme 28).[158]

The Mulliken spin densities [experimental (theoretical)] are largely located on the central P atom of **113** [64.4% (65.6%)] and the As atom of **114** [80.4% (67.3%)]. The P−C bonds of **113** [1.766(2) Å, av] compare well to that of NHC^{Dipp}-stabilized $P_2(0)$ (**59**)[113] [1.7504(17) Å]. In addition, the P−P bond distances of **113** [2.144(1) Å, av] are comparable to those of **111** [2.094(1) Å, av] and that of **59** [2.2052(10) Å]. When being combined with the activated alkyne MeOOC≡COOMe, **113** may serve as a "P_3" transfer agent to give **115** (Scheme 28).[158] This conversion involves cycloaddition between the alkyne unit and the P_3 species, along with subsequent single electron transfer.

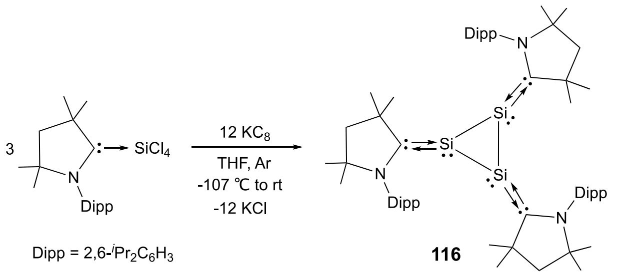
After obtaining a series of CAAC-stabilized monatomic[44,61] and diatomic silicon(0) species,[75,101] Roesky synthesized a

Scheme 28. Synthesis of 111−115



^{Me}CAAC-stabilized triatomic silicon(0) complex (**116**) in 2016, via potassium graphite reduction of ^{Me}CAAC:$SiCl_4$ at extremely low temperature (Scheme 29).[159] It was noted that

Scheme 29. Synthesis of CAAC-Stabilized $Si_3(0)$ Ring (116)



116 is acquired exclusively when the reduction of ^{Me}CAAC:-$SiCl_4$ proceeds slowly under an argon atmosphere. Otherwise, the reaction would give a mixture of both **116** and ^{Me}CAAC-stabilized $Si_2(0)$.[101] Further investigation of the possible conversion between CAAC-stabilized $Si_2(0)$ and $Si_3(0)$ species may provide insight for accessing larger silicon clusters.

X-ray structural analysis[159] (Figure 12) shows that **116** contains a three-membered silicon ring, with three silicon−

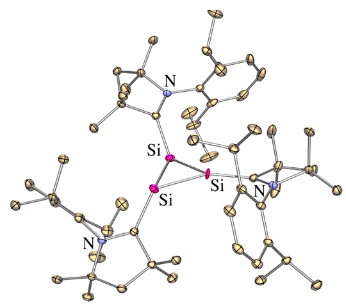


Figure 12. Molecular structure of **116**.

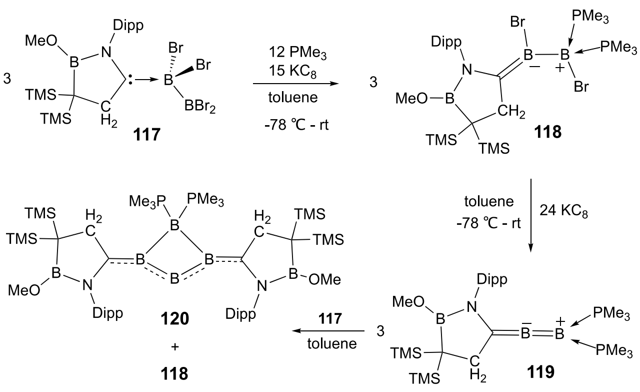
silicon single bonds (2.389 Å, av). Each three-coordinate silicon atom, bearing an electron pair, adopts the trigonal pyramidal geometry. The ^{29}Si NMR resonance of **116** (+7.20 ppm) is upfield-shifted compared to that of CAAC-stabilized mono silicon(0) atom (**14**) (+66.71 ppm)[44] and diatomic

https://doi.org/10.1021/jacs.2c13574
J. Am. Chem. Soc. 2023, 145, 5592−5612

silicon (**29**) (+254.60 ppm).[75] The shortened (ca. 0.08 Å) Si−C_{CAAC} bonds and elongated (ca. 0.08 Å) N−C_{CAAC} bonds of **116** (compared to those of the CAAC:$SiCl_4$ precursor) reveal significant π back-donation from each silicon(0) atom to the carbene carbon atom.[159] This π back-donation plays a key role in stabilizing the Si_3(0) core. Notably, the ligand-exchange reaction $(CAAC)_3Si_3 + 3NHC^{Ph} \rightarrow (NHC^{Ph})_3Si_3 + 3CAAC$ is endergonic (ΔG = 20.9 kcal mol^{-1}). At present, the NHC-based Si_3(0) complex remains elusive.

Kinjo recently synthesized a zwitterionic boraalkenyl boronium (**118**) by the reaction of 1,2-azaborole-derived CAAC-complexed B_2Br_4 (**117**) with 4 equiv of PMe_3 and subsequently with 5 equiv of potassium-graphite (Scheme 30).

Scheme 30. Synthesis of 118−120 (Dipp = 2,6-Diisopropylphenyl)



Further reduction of **118** by potassium-graphite (8 equiv) gave (CAAC and phosphine)-based neutral allenic diborene (**119**) (Scheme 30).[160] Reaction of **119** with **117** (in a 3:1 ratio) yielded a (CAAC and phosphine)-stabilized tetraatomic boron(0) species (**120**) (Scheme 30).[161]

The solid-state structure of compound **120** reveals a distinctive planar four-membered boron ring (Figure 13).[161]

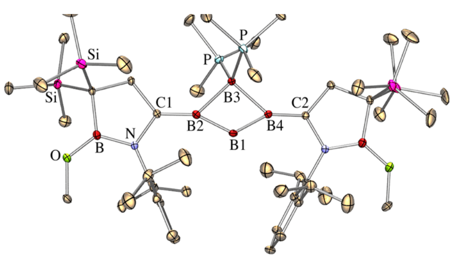
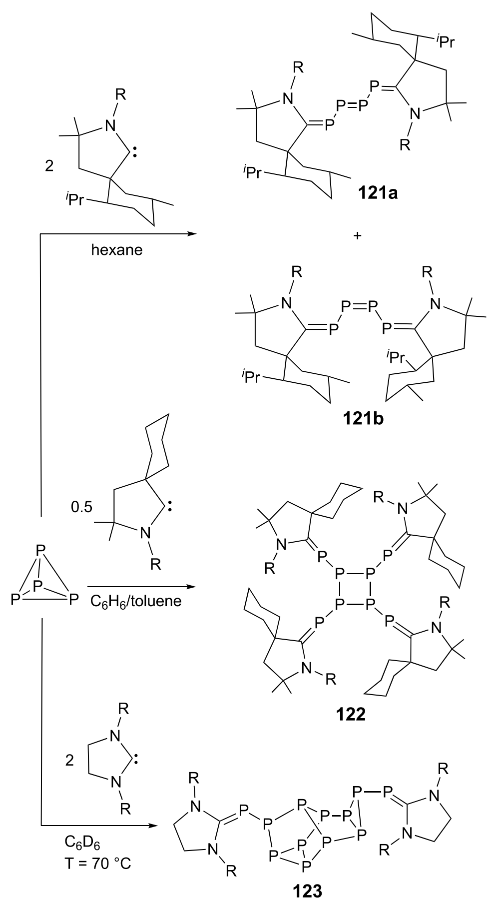


Figure 13. Molecular structure of **120**.

The bridging B1 atom is two-coordinate (bonding only to B2 and B4), whereas the bridging B3 atom is four-coordinate (bonding to B2 and B4, in addition to two PMe_3 ligands). The three-coordinate B2 and B4 atoms bond to the carbene carbon atoms. While the 1.564(3) Å B1−B2 and 1.554(3) Å B1−B4 bonds are double bonds with an identical WBI value of 1.31, the B2−B3 [1.833(3) Å] and B3−B4 [1.849(3) Å] bonds are single bonds with WBI values of 0.69 and 0.68, respectively. The 1.42 WBI values for both B2−C1 [1.456(3) Å] and B4−C2 [1.454(3) Å] bonds reveal the partially multiple bond nature of the boron−carbon bonds in **120**. Computations, coupled with X-ray structural data, indicate that the partial delocalization of electrons in **120** occurs not only in the σ-framework of the B_4 ring but also in the conjugated π-system over the C1−B2−B1−B4−C2 fragment.

Carbene-mediated activation of white phosphorus (P_4) has been confirmed to be an effective method to access various carbene-stabilized P_n clusters.[125,162−165] Bertrand has suggested that the electronic and steric properties of carbenes, as well the reaction stoichiometry, may impact the formation of carbene-complexed P_n clusters. While the 4:1 reaction of ^{Cy}CAAC (**69**) with P_4 in Et_2O gave both the ^{Cy}CAAC-stabilized pyramidal P_4 cluster (**70**) and P_2 (**71**) (Scheme 20),[125] the corresponding 1:2 reaction of **69** with P_4 in benzene/toluene mixed solvent afforded the ^{Cy}CAAC-stabilized P_8 cluster (**122**) (Scheme 31).[163] Interestingly, CAAC-

Scheme 31. Synthesis of 121−123 (R = 2,6-Diisopropylphenyl)



stabilized isomeric P_4 chains [**121a** (*E* isomer, major product) and **121b** (*Z* isomer)] were obtained by employing a more sterically demanding CAAC ligand (Scheme 31).[162] Dimerization of the P_4 core as shown in **121b** via [2 + 2] cycloaddition would give the P_8 cluster as observed in **122**. Notably, carbonyl-modified electrophilic carbenes have also been employed to stabilize the P_8 cluster by the Bertrand and Hudnall laboratories.[163,165] NHCs and CAACs have often demonstrated distinct reactivities. Indeed, the 2:1 reaction of $SNHC^{Dipp}$ with P_4 gave a carbene-P_{12} complex (**123**), which presently represents the largest elemental cluster stabilized by carbenes (Scheme 31).[164] Both (*E*)-tetraphosphatriene and triphosphirene species have been proposed as remarkable intermediates in the formation of **123**.

https://doi.org/10.1021/jacs.2c13574
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X-ray structural analysis (Figure 14) shows that the P_8 core in **122** consists of a central butterfly P_4 ring and four terminal P atoms. Each terminal phosphorus atom is bridged between one P atom of the P_4 ring and a ^{Cy}CAAC ligand.[163] The polycyclic structure of the P_{12} core in **123** (Figure 14) involves one six-membered ring, three five-membered rings, and two three-membered rings.[164] All of the P−P bonds in **122** (between 2.198 and 2.257 Å) and **123** (between 2.176 and 2.233 Å) are single bonds. The P−C_{CAAC} bonds in **122** (1.737 Å) are marginally shorter than those for **123** (1.756 and 1.777 Å) due to the stronger electrophilicity of CAACs (than NHCs). Formation of diverse carbene-stabilized P_n clusters (n = 2, 3, 4, 8, and 12) are unusual, which may be due to the unique catenation capability of phosphorus. Notably, carbene stabilization of (large-sized) *elemental* clusters of p-block metals are challenging, which may be ascribed to the relatively weak $C_{carbene}$−E bonds (E = p-block metals).

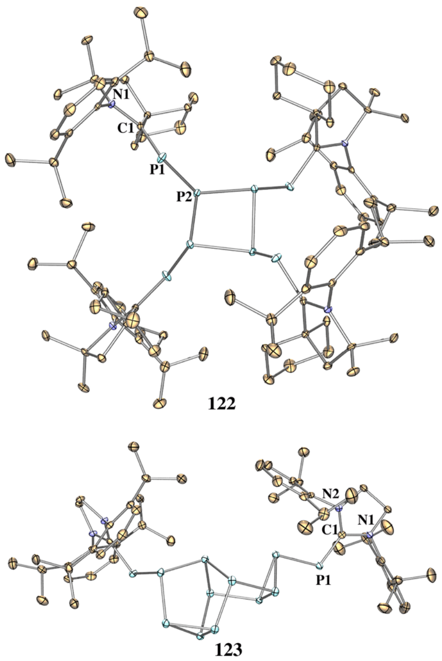

Figure 14. Molecular structures of **122** and **123**.

■ SUMMARY AND PERSPECTIVE

The chemistry of carbene-stabilized zero-oxidation state main group species is fascinating. Owing to the distinct electronic and steric properties of N-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino)carbenes (CAACs), the $E_n(0)$ cores stabilized by these two types of carbene ligands usually exhibit not only different structural and bonding motifs but also contrasting reactivities. The highly electron-rich $E_n(0)$ cores grant these carbene-stabilized zerovalent main group complexes unusual utilities in coordination chemistry and small molecule activations. For instance, in contrast to the carbene and silylene ligands, which may involve one dative bond with the Lewis acidic species, carbene-complexed E(0) cores (E = C and Si) have exhibited the unique capabilities of binding to two metal centers. The carbene-stabilized $E_2(0)$ species (E = Si and Ge) bearing a E═E double bond and two E-based lone pairs have shown different bonding modes toward Lewis acidic species from alkenes. In addition, the carbene-stabilized E(0) (E = Si and Ge) and $E_2(0)$ (E = B, Si, and P) species have been employed to activate a series of small molecules such as gaseous molecules (O_2, H_2, CO, CO_2, N_2O) and elemental chalcogens (sulfur, selenium, and tellurium).

Despite its rapid development, there remain many fascinating challenges in this field. For example, while CDC or silylone-based bimetallics have been obtained, such complexes remain rare. This is largely due to the second latent lone pair of the E(0) centers in these complexes. The design and synthesis of new E(0)-containing carbene complexes that possess two potent E(0)-based donating sites would substantially extend their applications in transition metal coordination chemistry and catalysis. Moreover, stabilization of the highly reactive $E_2(0)$ cores usually require sterically demanding carbene ligands. However, the steric bulk of the carbene ligands limits the access of many transition metal species. Tuning the steric properties of carbene ligands may enhance the utility of carbene-stabilized $E_2(0)$ species in transition metal coordination chemistry. Given the seminal discoveries detailed herein, many more wonders in this ascendent field await the imaginative chemist.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Science Foundation for support: CHE-1855641 and CHE-2153978 to G.H.R. and Y.W.

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