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PERSPECTIVE

Carbene-stabilized main group diatomic allotropes

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While transition metals are well known for assuming the formal oxidation state of zero in various compounds main group elements have rarely engaged in this practice. Recent reports of N-heterocyclic carbene-stabilized main group diatomic allotropes (*i.e.*, Si_2, Ge_2, P_2, As_2) denote a breakthrough of zero-oxidation state main group chemistry. This Perspective addresses the synthesis and characterization of these highly reactive main group molecules, with a particular emphasis on the very recent progress in the reactivity study of carbene-stabilized Si_2 and P_2.

1. Introduction

Both Plato and Aristotle ultimately embraced the view put forth by Empedokles: the existence of four terrestrial elements—earth, air, fire, and water.[1] Out of convenience, "symbols" were subsequently assigned to these elements: cube for earth, octahedron for air, tetrahedron for fire, and icosahedron for water. Centuries later, it was the profound realization of a "periodic repetition of chemical properties" by Dmitri Mendeleev and Lothar Meyer that eventually facilitated the Periodic Table of Elements—arguably, the most important discovery in the history of mankind.[2] Although the synthetic prowess of the present day chemist in preparing amazing new molecules seems, at times, equal parts science and art, the elements themselves still hold a metaphysical, seemingly mystical, connection to mankind. To hold crystals of iodine, metallic chunks of aluminum, a flask of argon, or a vial of mercury in one's hands often fuels a distinctive—even "elemental"—response in individuals. The concept of allotropes, different structural modifications of the same element, only augments this attraction. The allotropy of main group elements such as carbon (diamond, graphite, fullerenes), oxygen (dioxygen and ozone), and phosphorus (white, red, and black phosphorus) is well established.[3] Nonetheless, allotropes of a given element usually possess distinctly different properties and find utility in disparate applications. Consider two allotropes of carbon: diamond, an extremely hard material, finds great industrial utility as an abrasive (not to mention its ubiquitous presence in the jewelry industry) while graphite, a considerably softer material, is frequently utilized as an industrial lubricant (applications of

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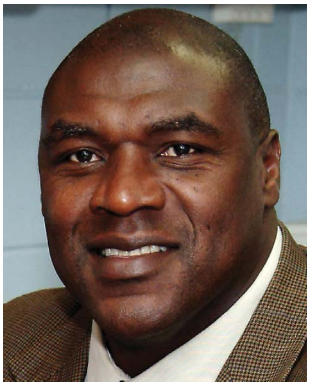


Gregory H. Robinson

Gregory H. Robinson gained his B.S. (1980) in Chemistry from Jacksonville State University. In addition to studying Chemistry he was also a standout in football earning All-American and Gulf South Conference Defensive Player of the Year honors in 1979. Robinson pursued graduate studies at The University of Alabama, studying under the guidance of Professor Jerry L. Atwood. After obtaining his Ph.D. (1984) Robinson joined the faculty of Clemson University and pursued a research program in main group chemistry. Robinson joined the faculty of The University of Georgia in 1995, where he is now Franklin Professor of Chemistry.

C_{60} are still being sorted out). Some allotropic forms, however, may only exist under extreme conditions.[4] For example, white phosphorus (P_4) is metastable[5] and has been extensively utilized as a reagent in the synthesis of organophosphorus compounds,[6,7] whereas diphosphorus (P_2) is highly reactive and only persistent at high temperatures.[4] Similar to diphosphorus, a number of main group diatomic allotropes are extremely reactive and their examination involves sophisticated instruments and elaborate techniques.[8] Is there a convenient means to stabilize highly reactive main group diatomic allotropes that will allow a systematic examination of their chemistry?

As organometallic chemistry has repeatedly demonstrated, the choice of ligand is critical. To synthetically approach a molecular compound containing a main group *elemental* core (in the formal oxidation state of zero), neutral donor ligands are a reasonable choice. Among the well-known neutral donor ligands such as amines, phosphines, and N-heterocyclic carbenes (NHCs), NHC ligands are particularly attractive due to their excellent σ-donating capacity. The chemistry of NHC ligands has rapidly developed since Arduengo's seminar 1991 discovery.[9] NHCs have subsequently had a profound impact on a number of research fields including organic catalysis, transition metal catalysis[10] and various aspects of main group chemistry.[11–15] Moreover, a number of novel NHC ligands with unique electronic and steric properties have been reported.[16,17]

To stabilize main group diatomic allotropes, the NHC ligands should not only be able to provide effective steric protection to the highly reactive *elemental* cores, but also be robust under particularly harsh reaction conditions (*i.e.*, alkali metal reduction). Among the diverse NHCs that are readily available, **I** (L: = :$C\{N(2,6\text{-}Pr^i{}_2C_6H_3)CH\}_2$) and **II** (L′: = :$C\{N(2,4,6\text{-}Me_3C_6H_2)CH\}_2$) (Fig. 1), are particularly attractive due to: (a) their sterically demanding N-substituents (2,6-diisopropylphenyl groups in **I** and mesityl groups in **II**) can confer significant kinetic stability on the main group *elemental* cores; (b) the aromatic imidazole ring of **I** and **II** results in significant stability under harsh reduction conditions, whereas ligands **III** and **IV** contain saturated, nonaromatic C_3N_2 rings, which would be more easily attacked.[15] Beginning in 2007 our laboratory successfully utilized NHC ligands in stabilizing a series of highly reactive main group molecules, including diatomic allotropes (Si_2,[18] P_2,[19] and As_2[20]).[15] Furthermore, recent studies from our laboratory suggest that carbene-stabilized diatomic allotropes may possess unusual reactivity. This Perspective will focus on the synthesis and characterization of a number of carbene-stabilized diatomic allotropes and their novel reactivity. In addition, notable discoveries in this field from other laboratories (NHC-stabilized Ge_2, P_2^+, and P_2^{2+}) will also be discussed.[21–23]

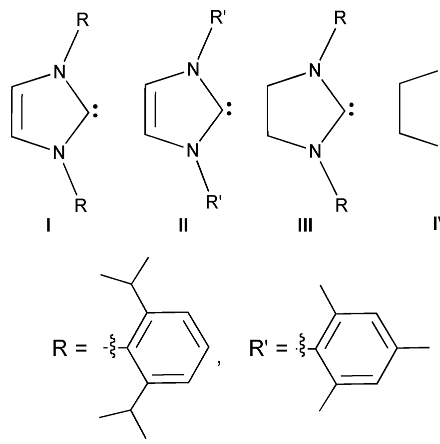


Fig. 1 Selection of NHC ligands.

2. Carbene-stabilized disilicon

2.1 Synthesis and characterization of carbene-stabilized disilicon

Unlike its heavier group 14 congener lead, the most common oxidation state of silicon is +4, not +2. The utilization of sterically demanding ligands has proven to be an effective strategy for the stabilization of low-oxidation state silicon compounds for decades.[14,24–28] Most prominent among these are disilenes [$R_2Si{=}SiR_2$] and disilynes [$RSi{\equiv}SiR$], wherein the silicon oxidation states are +2 and +1, respectively (Fig. 2).[24,25,29,30] Elemental silicon is widely used both as a semiconductor in advanced electronics and for its unique role in organosilicon synthesis (*i.e.*, Müller–Rochow synthesis).[31] Thus, the synthesis of compounds containing silicon atoms in the formal oxidation state of zero, essentially *elemental* silicon, is particularly intriguing. Such species may not only act as model compounds to mimic the chemical transformations on the silicon surface,[32] but may also provide a critical nexus between silicon allotropes and low-oxidation state organosilicon compounds. Recently, through utilizing the "carbene-stabilization" strategy, we synthesized the first disilicon–carbene adduct L:Si=Si:L (**2** as shown in Fig. 3) and explored its unusual reactivity.[18,33]

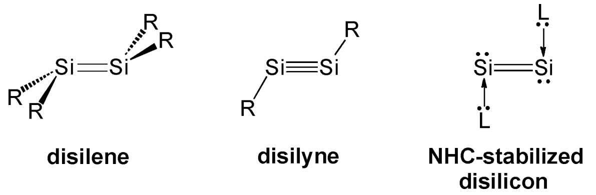


Fig. 2 Typical low oxidation state silicon compounds with silicon–silicon multiple bonds.

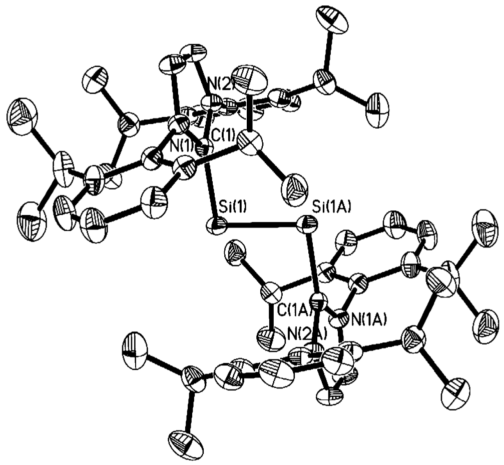
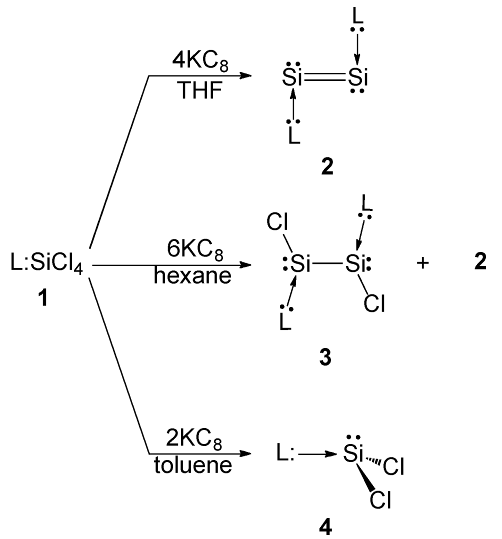


Fig. 3 Molecular structure of L:Si=Si:L **2**. Hydrogen atoms are omitted for clarity.

Our strategy to synthesize NHC-stabilized disilicon concerns the potassium graphite reduction of L:SiCl$_4$ (L: = NHC). Kuhn *et al.* reported the preparation of L′:SiCl$_4$ (L′: = :C[N(R)C(CH$_3$)]$_2$) in moderate yield in THF.[34] Our study shows that reaction of L: (**I**) with SiCl$_4$ in hexane afforded L:SiCl$_4$, **1**, in an almost quantitative yield. This strategy may be extended to other L:EX$_n$ (E = main group elements).[15]

Both the solvent and the stoichiometric ratio of the reactants have an effect on the formation of the products **2–4**. Carbene-stabilized disilicon, **2**, isolated as dark-red crystals, was synthesized in 23.2% yield by the potassium graphite (KC$_8$) reduction of **1** (**1** : KC$_8$ = 1 : 4) in THF. However, in hexane the 1 : 6 combination of **1** with KC$_8$ afforded carbene-stabilized bis-silylene L:(Cl)Si–Si(Cl):L, **3**, which was accompanied by **2** as a minor product.[18] Roesky *et al.* subsequently synthesized ligand **I**-stabilized dichlorosilylene L:SiCl$_2$, **4**, by combining **1** with KC$_8$ (**1** : KC$_8$ = 1 : 2) in toluene (Scheme 1).[35] Obviously, compounds **3** and **4** are the intermediates involved in the transformation from **1** to **2**. Furthermore, both **3** and **4** can be isolated as crystalline solids.



Scheme 1 Synthesis of L:Si═Si:L **2**, L:(Cl)Si–Si(Cl):L **3**, L:SiCl$_2$ **4**.

It is interesting to compare the structural and spectroscopic characteristics of carbene-stabilized disilicon **2** with the disilenes. The Si═Si double bond distance of **2** (2.2294(11) Å) compares well to both the computed (2.249 Å, BHLYP)[36] and experimental (2.246 Å)[37] bond distances of Si$_2$. It is also comparable to the distances computed for OC:Si═Si:CO (2.310 Å, B3LYP) and reported disilene bond distances (from 2.14 to 2.29 Å).[38] The $\pi_{Si=Si}$–$\pi^*_{Si=Si}$ absorption (λ_{max} = 468 nm, in THF) of **2**, supportive of its Si═Si double bond character, is within the range of the reported UV absorption maxima (390–480 nm) of stable disilenes.[38] The ^{29}Si chemical shift (224.5 ppm) of **2** is considerably shifted downfield compared to ^{29}Si values reported for disilenes (50 – 155 ppm). The Si–C bond distance of **2** (1.9271(15) Å), similar to that (1.928(2) Å) in **1**, is somewhat longer than those in disilenes (*i.e.*, d_{Si-C} = 1.87 to 1.88 Å in R$_2$Si═SiR$_2$, R = mesityl group)[39,40] and thus corresponds to a Si–C single bond.

Besides the central Si═Si double bond with Wiberg bond index (WBI) of 1.73, the *trans*-bent geometry around the two-coordinate silicon atoms in **2** (C–Si–Si angles of 93.57(11)°) are also noteworthy. This *trans*-bent geometry around the Si$_2$ core is in accordance with a weak hybridization between the 3s and 3p orbitals of silicon atoms in **2**. This is also supported by NBO analysis. Both the Si–Si σ- and π-bonds have mainly p-character (with 82.2% and 99.6% p character, respectively), whereas the silicon lone-pair orbitals have predominantly s-character (with 72.8% s character). MOs of L:Si═Si:L (L: = :C{N(C$_6$H$_5$)CH}$_2$) model, **2-Ph**, are shown in Fig. 4. The planes of the imidazole rings of the NHC ligands in **2** are perpendicular to the Si═Si vector with the N(1)–C(1)–Si(1)–Si(1A) torsion angle of 91.01°. This structural feature, coupled with the Si–C$_{NHC}$ single bond and the *trans*-bent geometry around the Si$_2$ core, suggests that the silicon atoms in **2** are in the formal oxidation state of zero. By comparison, structure **2a**, corresponding to a molecule with the formula of L═Si═Si═L (where silicon atoms are in the +2 oxidation state), is shown in Fig. 5. In **2a**, the C$_3$N$_2$SiSiC$_3$N$_2$ core would be expected to be planar, containing short C═Si double bonds and a linear C–Si–Si–C axis.[41]

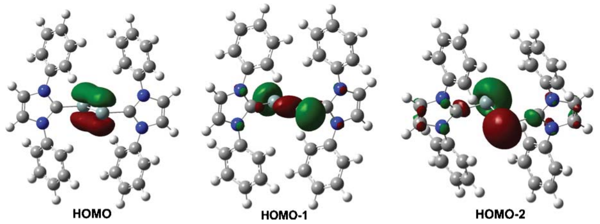
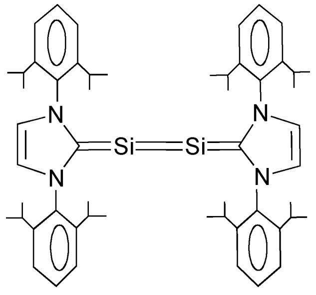


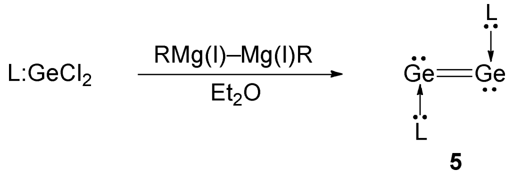
Fig. 4 Representation of the HOMO (Si–Si π-bonding orbital), HOMO–1 (Si–Si σ-bonding orbital), and HOMO–2 (lone pair orbital) of **2-Ph**.



2a

Fig. 5 Structure of L═Si═Si═L **2a**.

Carbene-stabilized digermanium L:Ge═Ge:L (L: = **I**), **5**, was prepared in 20% yield by Jones *et al.* using RMg(I)–Mg(I)R (R = [(MesNCMe)$_2$CH]) to reduce L:GeCl$_2$ (L: = **I**) (Scheme 2).[21] The steric bulk of the nacnac ligands in RMg(I)–Mg(I)R may have an effect on the formation of **5**. For example, only less than 5% yield of **5** was achieved when the more sterically demanding

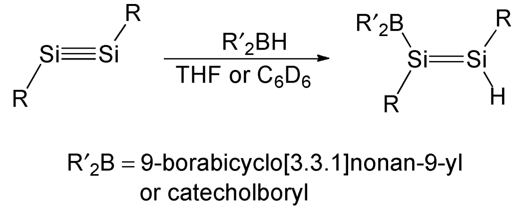


Scheme 2 Synthesis of L:Ge═Ge:L **5**.

R′Mg(I)–Mg(I)R′ (R′ = [(2,6-$Pr^i_2C_6H_3NCMe)_2CH$]) was employed to reduce L:$GeCl_2$ (L: = **I**).

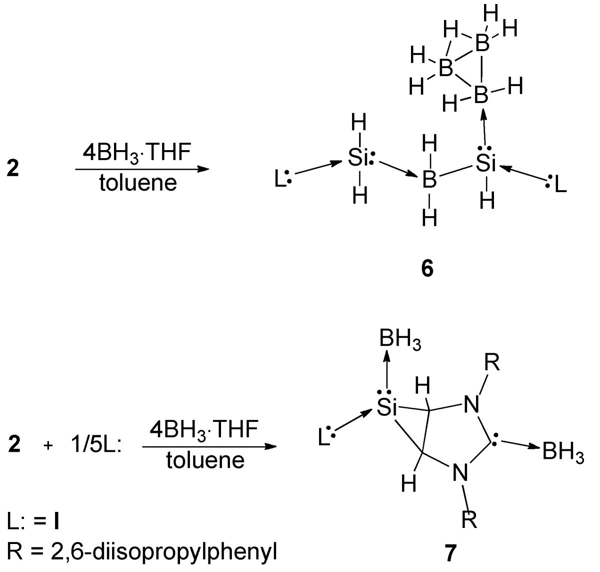
2.1 Reactivity of carbene-stabilized disilicon

Hydroboration is a very useful reaction for unsaturated hydrocarbons. However, the literature reveals a paucity of studies for their silicon counterparts. Hydroboration of disilenes has only been explored computationally.[42] Recently, utilizing reagents such as 9-BBN and catecholborane, Sekiguchi *et al.* achieved hydroboration of disilyne RSi≡SiR (R = $SiPr^i[CH(SiMe_3)_2]_2$),[43] rendering boryl-substituted disilenes (Scheme 3).[44,45] Mechanistic studies suggests that these reactions are initiated by the interaction of the HOMO of the disilyne with the LUMO of the borane.[45]



Scheme 3 Hydroboration of disilyne RSi≡SiR (R = $SiPr^i[CH(SiMe_3)_2]_2$).

Recently we investigated the reaction between **2** and BH_3·THF. Reaction of pure **2** with BH_3·THF (1 : 4) in toluene resulted in **6** (72% yield); which contains a parent silylene (:SiH_2) moiety. However, in the presence of carbene ligand **I** as an impurity in **2** (NHC ligand (**I**):**2** = 1 : 5), the corresponding BH_3·THF reaction led to the isolation of three-membered cyclosilylene **7**, together with **6** (30% yield for **6**; 28% yield for **7**) (Scheme 4).[33]



Scheme 4 Reaction of **2** with BH_3·THF.

The broad ^1H NMR singlet resonance at −0.29 ppm and the ^{11}B NMR multiplet at −30.0 ppm were assigned to the B_3H_7 ring in **6**. The triplet resonance of BH_2 was clearly observed at −50.4 ppm in the proton-coupled ^{11}B NMR. The ^1H NMR spectrum of **6** showed a SiH doublet at 2.90 ppm (J = 7.0 Hz) and a SiH_2 triplet at 3.13 ppm (J = 12.0 Hz). Both of the −35.0 ppm (^1J = 87 Hz) quartet resonance of the BH_3 at the C_{NHC} and the −47.0 ppm broad doublet resonance of BH_3 coordinating to the central silicon atom have been observed in the ^1H-coupled ^{11}B-NMR spectrum of **7**, which are close to the reported values.[46,47] The ^{29}Si resonance of the silicon atoms in **6** and **7** could not be observed due to the strong line-broadening caused by quadrupolar boron nuclei.[47]

The B(1)–Si(1) (1.980 Å, av) and B(1)–Si(2) (1.902 Å, av) bond distances are comparable to that of the B(2)–Si(1) bond (1.965(7) Å) (Fig. 6).[33] Computations suggest that the positive natural charges on the silicon atoms in **6** [*i.e.*, +0.95 for Si(1) and +0.90 for Si(2)] and the negative charges of the B(1) atom (−0.92) and the B_3H_7 ring (−1.03), are supportive of the dative character of the B(1)–Si(2) and B(2)–Si(1) bonds. The most intriguing structural feature of **6**, however, is the "push–pull" stabilized parent silylene unit (:SiH_2). The stabilization of parent heavy methylenes has recently attracted considerable attention.[48] Rivard *et al.* synthesized the "push–pull" stabilized GeH_2 and SnH_2 molecules, L:EH_2(R) [L: = **I**; E = Ge, R = BH_3 (**8**);[49] E = Ge, R = $W(CO)_5$ (**9**); E = Sn, R = $W(CO)_5$ (**10**)],[50] by reacting L:$GeCl_2$ or L:$GeCl_2[W(CO)_5]$ with $LiBH_4$ (Scheme 5). The L:$SiH(BH_2)(B_3H_7)$ fragment in **6** may be regarded as the counterpart of Lewis acidic R groups in **8–10**. The synthesis of the "push–pull" stabilized :EH_2 triad [E = Si (**6**), Ge (**8** and **9**), Sn (**10**)] again illustrates the promising future of carbene ligands in low oxidation state main group chemistry.

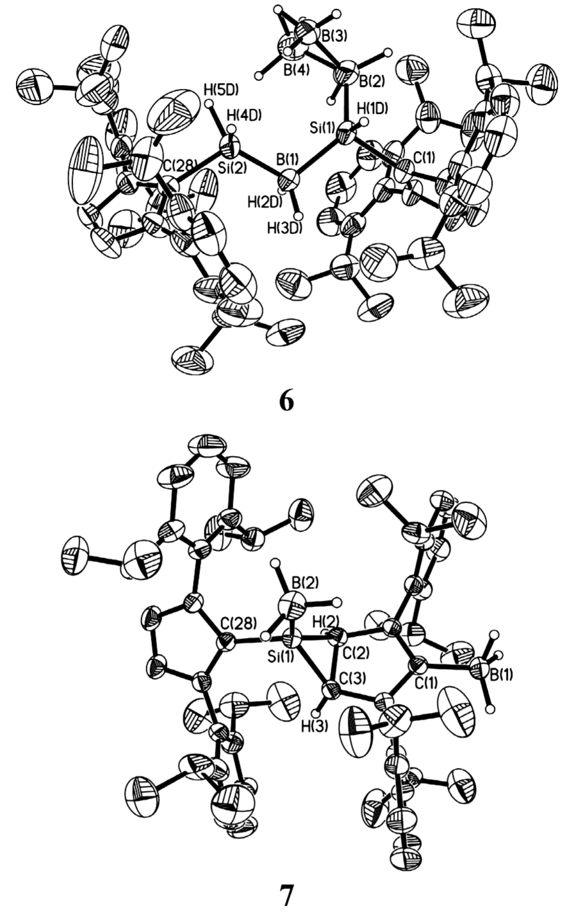
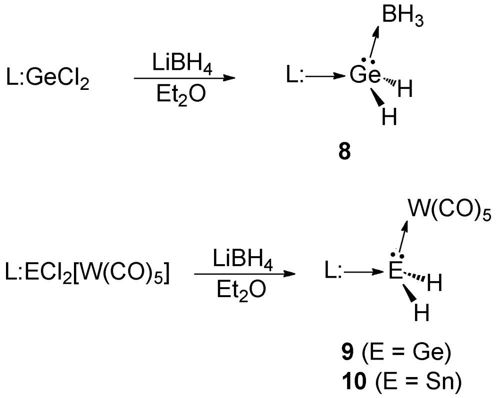


Fig. 6 Molecular structures of **6** and **7**. Some hydrogen atoms are omitted for clarity.



Scheme 5 Synthesis of "push–pull" stabilized :GeH_2 **8** and **9** and :SnH_2 **10**.

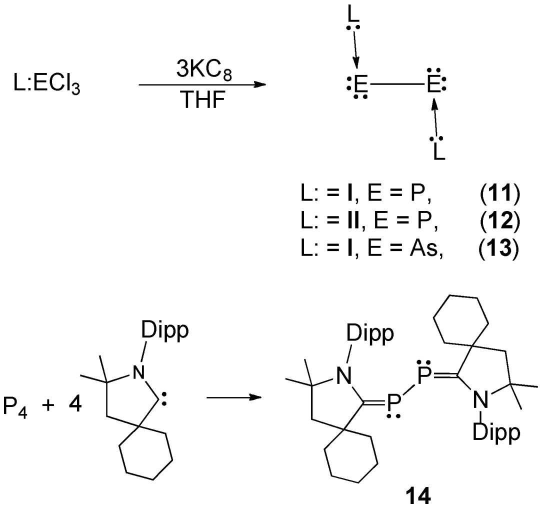
Compound **7** (Fig. 6) is also remarkable due to its three-membered silylene ring that is stabilized by donating its electron pair to a BH_3 while *simultaneously* accepting an electron pair from the carbene ligand.[33] While five and six-membered cyclosilylenes have been reported,[51,52] three-membered cyclic silylenes based on C_2H_4Si: have only been studied by matrix-isolation techniques.[53] Compound **7** is the first experimental realization of a three-membered cyclic silylene persistent at ambient temperature through this "push–pull" stabilization.

While the mechanistic details in the formation of **6** and **7** are obscure, our structural and computational examination suggests that the formation of **6** may involve multiple complexations of boranes to **2**, concomitant with cleavage of silicon–silicon bond, boron-to-silicon hydrogen transfer, and BH_2 insertion between two silicon(II) atoms. The formation of **7** may involve the cycloaddition of the highly reactive Si(0) atom of an L:Si(BH_3) intermediate to the C=C bond of an imidazole ring in a L:BH_3 fragment (L: = **I**). Notably, similar reactions of silicon(0) atoms with π-conjugated systems have been observed using matrix isolation techniques.[53–55] The presence of free NHC ligand in the reaction system appears to be required for the formation of **7**, where the NHC ligand acts as a "trapping agent" for the "push–pull" stabilized Si(0) atom.

3. Carbene-stabilized diphosphorus and diarsenic

3.1 Synthesis and characterization of carbene-stabilized diphosphorus and diarsenic

In contrast to the "allotropic void" of their lighter pnictogen congener, nitrogen, both phosphorus and arsenic possess an extensive allotropy. For example, diatomic allotropes P_2 and As_2 are highly reactive, association prone, and only persistent at high temperatures.[4] Is there a way to easily assess the synthetic potential of these fragments?[56] Cummins *et al.* produced P_2 by mild thermal extrusion from niobium diphosphaazide complexes or by photolysis of P_4, which was then captured by organic substrates.[7,57,58] Kinetic stabilization of P_2 and As_2 using sterically demanding NHC ligands denotes another strategy to explore the chemistry of these species. Indeed, a series of carbene–phosphorus allotropes adducts have been reported.[6,59,60] This laboratory recently reported the synthesis of NHC-stabilized P_2 (**11** and **12**)[19] and As_2 (**13**)[20] by potassium graphite reduction of the corresponding NHC-ECl_3 (E = P, As), respectively (Scheme 6). Although NHC-$SbCl_3$ has been synthesized and structurally characterized, the KC_8 reduction of it only resulted in decomposition products (elemental antimony and NHC ligand). The failure to prepare L:Sb–Sb:L, coupled with the decreasing yield (19.2%) of **13** with compared to that (56.6% yield)) of **11**, suggests that the "carbene-stabilization" strategy may be less effective with the heavier pnictogens. An (alkyl)(amino)carbene (CAAC)-stabilized P_2, **14**, was synthesized (12% yield) by Bertrand *et al.* through carbene-induced fragmentation of P_4 (Scheme 6) (Dipp = 2,6-diisopropylphenyl).[61]

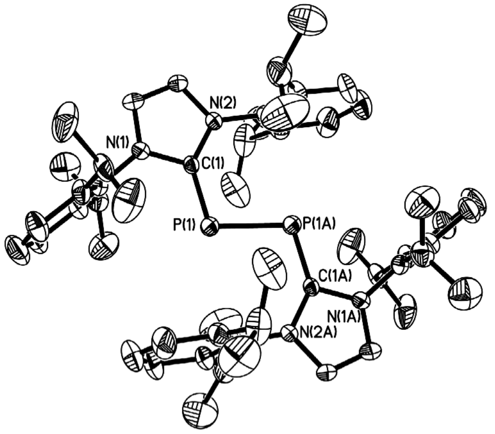


Scheme 6 Synthesis of carbene-stabilized P_2 **11**, **12**, and **14** and As_2 **13**.

The X-ray structural analyses of **11** and **12** show that the steric effect of NHC ligands in **11** and **12** significantly influence the resulting conformations (Fig. 7).[19] For instance, **11** (C_i symmetry) adopts a *trans*-bent geometry with the C(1)–P(1)–P(1A)–C(1A) torsion angle of 180.0°, whereas **12** is of a *gauche* conformation (the C(1)–P(1)–P(2)–C(22) torsion angle is 134.1°). Moreover, the C_2 minimum (C–P–P–C torsion angle = 98.6°). of the simplified L:P–P:L (where L: is :C($NHCH)_2$) model, **11-H**, further confirm this point.

Considering the higher electrophilicity of the CAAC ligands than NHCs,[61–64] it is interesting to compare the structures and bonding of their P_2 complexes. The P–P single bond distances in **11** (2.2052(10) Å) and in **12** (2.1897(11) Å) compare well to that of **14** (2.184(3) Å). The C(1)–P(1)–P(1A) bond angles of **11** and **12** (102.6–103.2°) are close to that of **14** (105.1°). Notably, the P–C bond distances (1.75 Å) in **11** and **12**, are between the P=C double bond distances (1.65–1.67 Å) of the nonconjugated phosphaalkenes[65] and the normal P–C single bond distance (*i.e.*, the P–C_{Ph} bond distance (1.839(5) Å) in L′:P(Ph) (L′: = **II**)),[66] however, is about 0.03 Å longer than that (1.719(7) Å) in CAAC-stabilized P_2 (**14**).[61] MO study shows that in **11** and **12** one lone pair orbital of each P atom back-donates electrons to the empty p orbital of C_{NHC}. The P–C Wiberg bond index (WBI) of 1.397, however, indicates that this interaction is not well developed due to the aromaticity of the imidazole ring.

Scheme 7 illustrates two canonical forms (*i.e.*, **A** (bis-phosphinidene) and **B** (bis-phosphaalkene) that may be utilized to interpret the bonding in **11**, **12**, and **14**. Considering the high-field ^{31}P chemical shifts of **11** (−52.4 ppm) and **12** (−73.6 ppm), and the relatively long P–C bond distances (about 1.75 Å), compounds



11

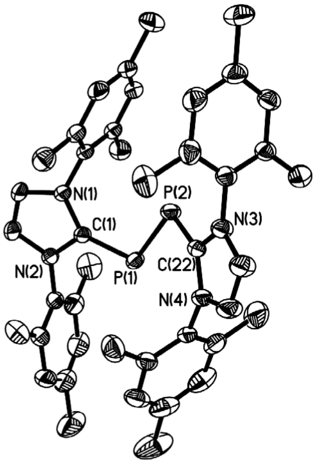


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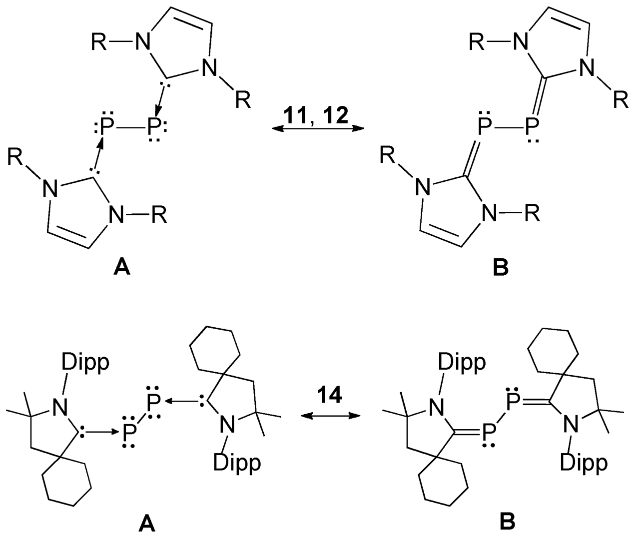
Fig. 7 Molecular structures of NHC-stabilized P_2 **11** and **12**. Hydrogen atoms are omitted for clarity.



Scheme 7 Canonical forms of carbene-stabilized P_2 molecules.

11 and **12** may best be described as carbene-(bis-phosphinidene) adducts (**A**). Alternatively, the low-field ^{31}P chemical shift (54.2 ppm) of **14** is similar to those of the diphosphabutadienes (34 to 54 ppm),[67] which, coupled with the short P–C bond distance (1.719(7) Å) in **14**, suggests that **14** possesses a 2,3-diphosphabutadiene structure (**B**). Indeed, these experimental observations are consistent with the higher electrophilicity of CAAC ligands than NHCs.[61–64]

Regarding the fact that the DFT-optimized structure of the simplified model L:As–As:L (L: = :C(NHCH)$_2$), **13-H**, favors a *gauche* conformation with C_2 symmetry (the C–As–As–C torsion angle = 93.9°), the *trans*-bent conformation (the torsion angle of C(1)–As(1)–As(1A)–C(1A) = 180°) of **13** may also attribute to the steric repulsion of the NHC ligands.[20] The central As–As bond distance of 2.442(1) Å is almost the same as that (2.44 Å) in gaseous As_4.[68] Compound **13** is not only isostructural to the carbene-stabilized P_2, **11**, but it also exhibits a bonding similarity to carbene–arsinidene adducts (Fig. 8).[66] Thus, compound **13** may be described as a carbene–(bis-arsinidene) adduct. It is noteworthy that the free bis-dipnictinidene species, featuring four lone pairs of electrons and an unsaturated valence shell, may act as an electrophile (*i.e.*, electron acceptor, as those in **11**, **12**, and **14**) or a nucleophile (*i.e.*, electron donor, as that in a P_2-transition metal carbonyl complex).[69]

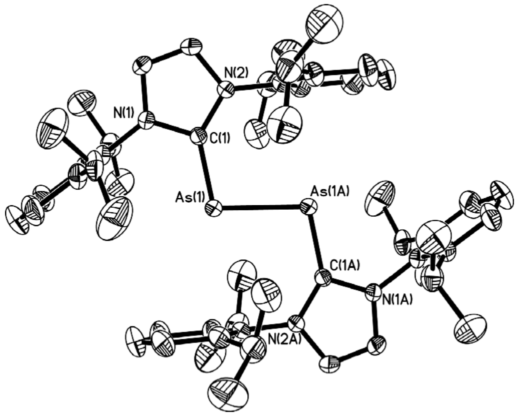
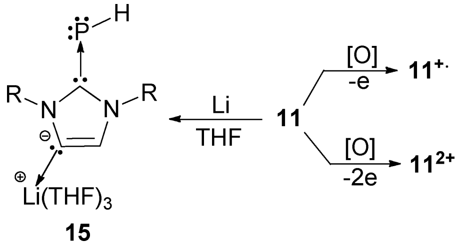


Fig. 8 Molecular structure of NHC-stabilized As_2 complex **13**. Hydrogen atoms are omitted for clarity.

3.2 Reactivity of carbene-stabilized diphosphorus

Our recent reduction of **11** with lithium metal led to the isolation of lithiated-NHC parent phosphinidene complex, L:P–H (L: = :C{[N(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$CHCLi(THF)$_3$}), **15**, as yellow crystals (Scheme 8).[70] The formation of **15** involves the lithium-mediated C–H activation of the imidazole ring and the cleavage of the central P–P bond of **11**.



Scheme 8 Redox reactions of NHC-stabilized P_2 **11**.

The P–C bond distance (1.763(2) Å) in **15** (Fig. 9) is similar to that computed for [CH(CH$_3$)N]$_2$CP–H (1.770 Å)[71] and marginally longer than the experimental value of [(CH$_3$)$_2$N]$_2$C=P–H (1.740(1) Å).[72] The presence of the P–H fragment in **15** is unambiguously confirmed by the doublet resonances both at 1.86 ppm (^1J(PH) = 167 Hz) in the ^{1}H NMR spectrum and at −143.0 ppm (^1J = 171 Hz) in the ^{1}H-coupled-^{31}P NMR spectrum. The pronounced high-field ^{31}P chemical shift of **15** is consistent with the carbene-parent phosphinidene bonding description. Given the −3 oxidation state of P in PH$_3$,[73] the formal oxidation state of P in **15** may be assigned as −1.

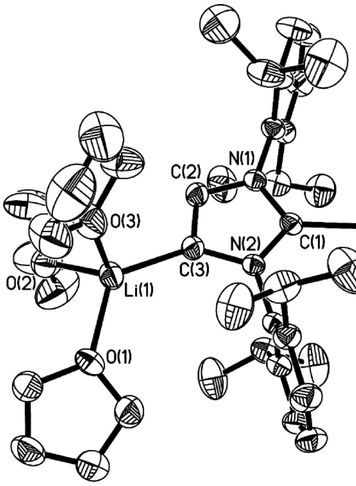
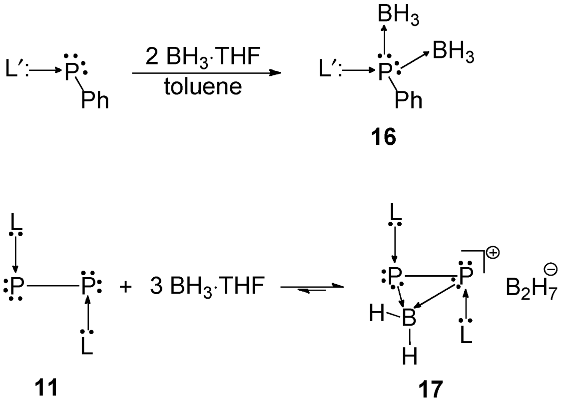


Fig. 9 Molecular structure of **15**. Hydrogen atoms are omitted for clarity.

Bertrand *et al.* recently reported the controlled oxidation of **11**, which may be singly oxidized to the radical cation **11**$^{+\cdot}$ by Ph$_3$C$^+$B(C$_6$F$_5$)$_4^-$ or doubly oxidized to NHC-stabilized P$_2^{2+}$ dication (**11**$^{2+}$) by ferrocenium triflate (Scheme 8).[22] Interestingly, X-ray structural analysis shows that with the evolution of **11** to **11**$^+$, and then to **11**$^{2+}$, the central single P–P bond distance of **11** (2.2052(10) Å) shortens to 2.0907(10) Å, and then to 2.0826(12) Å. The latter is close to that of a P=P double bond (about 2.02 Å).[74] Thus, **11**$^{2+}$ may be regarded as a dicationic diphosphene.

The electron-rich P$_2$ core may also grant **11** the ability to react with a variety of electrophiles. We recently investigated the reaction of **11** with excess BH$_3$·THF.[75] The formation of L′:P(BH$_3$)$_2$Ph (L′: = **II**) (**16**) by reacting carbene–phosphinidene adduct L′:PPh with BH$_3$·THF in toluene (Scheme 9) has been reported.[76] This reaction, however, did not give the **16**-like product L:(BH$_3$)$_2$P–P(BH$_3$)$_2$:L, but rendered a **11**-complexed dihydroboronium salt [L:P(μ-BH$_2$)P:L]$^+$·B$_2$H$_7^-$ (**17**) in a 85% yield (Scheme 9).

The formation of **17** supports the bisphosphinidene bonding descrption of **11**.[19] In **17**, the L:P–P:L fragment utilizes two lone electron pairs (one from each phosphorus atom) to chelate one BH$_2^+$ cation. The fact that the remaining two lone pairs remain intact, even in the presence of excess BH$_3$·THF, may be ascribed to the steric bulk of the carbene ligands (**I**). Indeed, in less bulky **16** the phosphinidene center coordinates to two BH$_3$ units.[76] Although P$_2$ has been reported to function as four-, six-, and eight-electron donor ligands in transition metal carbonyl complexes,[4] **17** is the first example of P$_2$ serving as a four-electron donor to chelate a main group cation. The chelation of other main group cations using **11** as a bidentate ligand should be feasible and expected.



Scheme 9 Reaction of NHC-stabilized phosphinidene L′:P-Ph and bisphosphinidene **11** with BH$_3$·THF.

It is interesting that when **17** is dissolved in THF, it partially dissociates into neutral **11** and three BH$_3$·THF moieties (Scheme 9). The 4.5 : 1 molar ratio of **17** to **11** in the equilibrium mixture indicates that the equilibrium lies to the right side of the reaction forming **17**. The dissociation of **17** is greatly diminished by the presence of excess of BH$_3$·THF in THF. Analogously, a six-membered cyclic bisphosphine–boronium salt has been reported to exist as an equilibrium mixture with a bisphosphine–diborane adduct.[77] The mechanistic studies of the formation of such cyclic boronium cations have also been reported.[78] The plausible scenario of the formation of **17** is that the coordination of **11** to BH$_3$ results in the nucleophilic substitution at the boron center with the H$^-$ anion as a leaving group, which is then captured by two BH$_3$ units to form a B$_2$H$_7^-$ anion.

The cation of **17** contains a three-membered P$_2$B ring (Fig. 10). The P–B bonds of **17** (1.972(4) and 1.982(4) Å) are about 0.07 Å longer than those (1.910 ± 0.003 Å) of a cyclic bisphosphine–boronium salt.[78] The electronic effect of BH$_2^+$ cation on the P$_2$ core in **17** is illustrated by the dramatic upfield-shift of the ^{31}P{^{1}H} singlet resonance of **17** (−185.9 ppm) with compared to that for **11** (−53.3 ppm).[19] It is also interesting to investigate the structural change of the L:P–P:L fragment due to the coordination to the BH$_2^+$ cation.

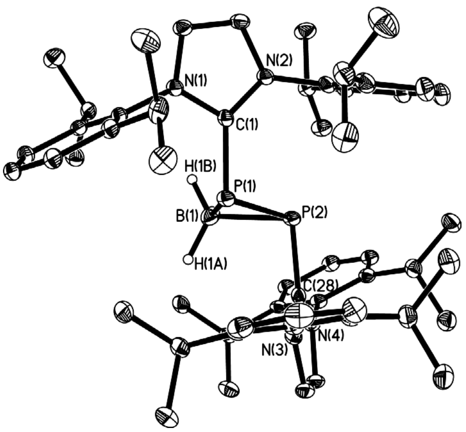


Fig. 10 Molecular structure of **17** cation. Hydrogen atoms on carbon are omitted for clarity.

The structural parameters of **17** are similar to those of **11**. The P–P single bond distance in **17** (2.1993(11) Å) is close to that of **11** (2.2052(10) Å). Moreover, the C–P–P–C torsion angle in **17** (174.9°) approaches that (180°) observed for **11**. However, the P–C bond distances of both **11** and **17** differ considerably. The 1.83 Å P–C distance of **17** corresponds to typical single P–C bonds (0.996 WBI),[76] while the 0.08 Å shorter P–C bond distance (1.7504(17) Å) of **11** suggests modest multiple bond character (1.397 WBI). The latter arises from p-π back donation of the lone pair of phosphorus into the empty p orbital of C_{NHC}.[19] However, in **17** such p-π back donation is replaced by the P-to-B donor–acceptor interactions.

4. Conclusions

Due to their excellent σ-donating ability and steric bulk, N-heterocyclic carbenes have been utilized in the stabilization of a series of highly reactive main group diatomic allotropes (Si_2, Ge_2, P_2, As_2). These molecules, with an electron-rich E_2 core, may provide unique access to a number of novel low-oxidation state main group species. The recent syntheses of "push–pull" stabilized parent silylene ($:SiH_2$), **6**, three-membered cyclic silylene, **7**, lithiated NHC-stabilized parent phosphinidene (PH), **15**, NHC-stabilized P_2^{+} (**11**$^{+}\cdot$) and P_2^{2+} (**11**$^{2+}$), and three-membered cyclic boronium salt, **17**, definitely prove this point. Tuning the electronic and steric properties of the carbene ligand, coupled with the appropriate reducing agent and solvent, the stabilization of other highly reactive main group diatomic allotropes should be possible.

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