MINIREVIEW

Inorganic benzene valence isomers

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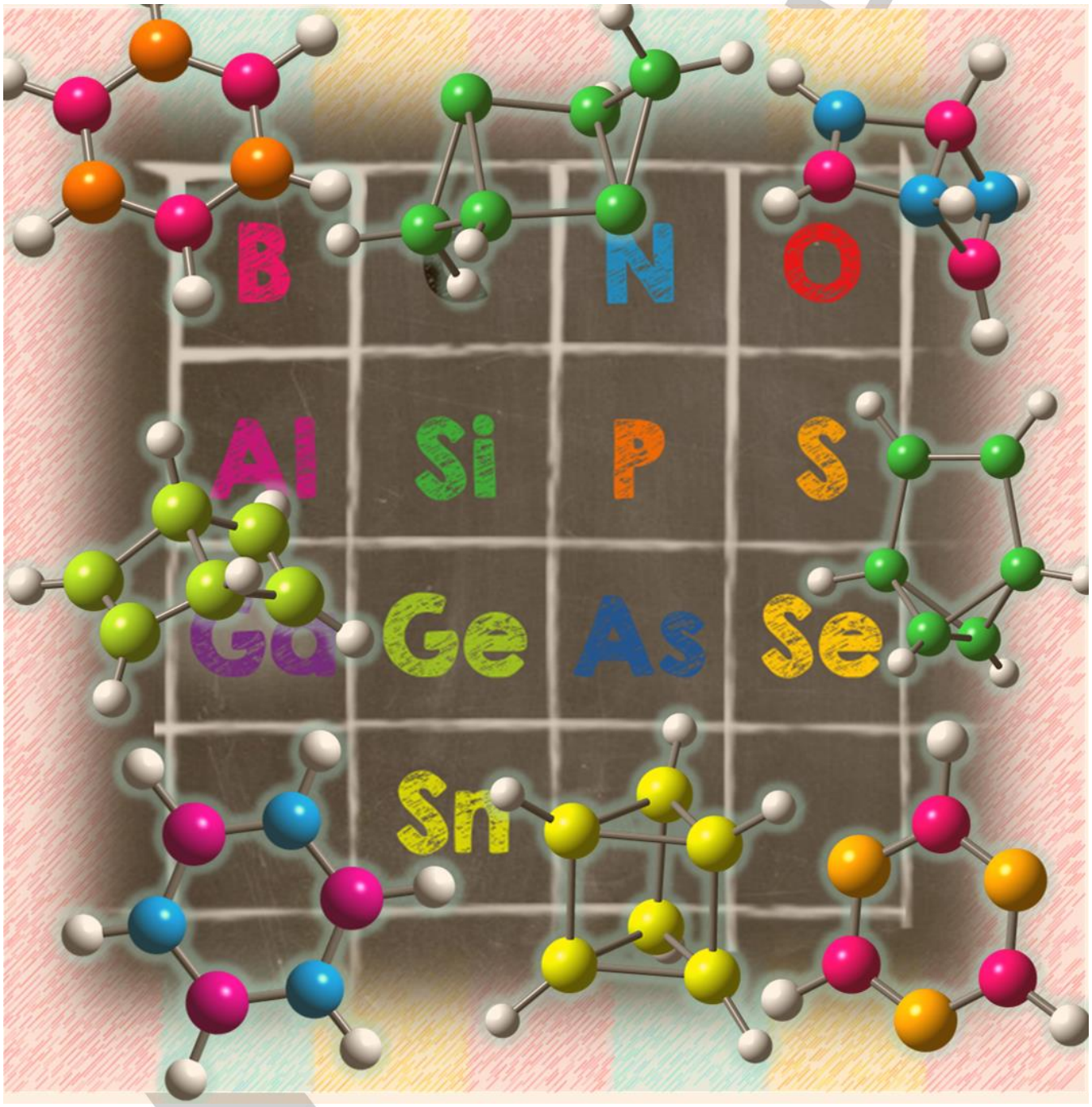

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Abstract: It has been computationally proposed that there are more than 200 possible isomeric structures for C_6H_6 molecule, among which benzene $(CH)_6$ represents the most thermodynamically stable molecule and its chemistry has been extensively developed. Three benzene valence isomers $(CR)_6$, namely, prismane, Dewar benzene, and benzvalene, have also been synthesized to date. Incorporation of heteroatoms in the skeletal frameworks allows access to inorganic analogues of benzene and its valence isomers, which have attracted considerable attention due to the peculiar structural and electronic features. Experimentally, more than 30 examples of inorganic benzene and its valence isomers have been developed and characterized so far. In this contribution, their synthesis and characterization, as well as their stability and chemical properties, are discussed.

1. Introduction

In 1825, Faraday discovered a molecule of C_6H_6, namely benzene,[1] and forty years later it was found by Kekulé that benzene nucleus is cyclic (Figure 1, **I**),[2] which represents the beginning of aromatic chemistry. Significantly, computational studies indicate that benzene **I** is just one of the more than 200 possible isomeric structures for C_6H_6 molecules,[3] and to date about 30 isomers of C_6H_6 have been experimentally synthesized or observed, among which three valence isomers $(CH)_6$: prismane, Dewar benzene, and benzvalene (Figure 1, **II** – **IV**), have been isolated and extensively studied.[2, 4],[5]

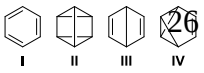


Figure 1. Historically proposed and synthesized valence isomers of benzene.

Interestingly, theoretical calculations revealed that the relative energies amongst the heavier analogues $(EH)_6$ (E = Si, Ge, Sn, Pb) are markedly different from those of the carbon systems (Table 1).[6] For example, while the benzene structure **I** is the most stable in the carbon system, for the case of the heavier group 14 element systems, the saturated prismane **II** is instead the most stable isomers.[6a, 6b]

On the other hand, inorganic benzene analogues involving other p-block elements such as borazine $(HBNH)_3$,[7] boroxines $(RBO)_3$ and phosphazenes $(R_2PN)_3$,[8] have also been developed to date and their aromatic nature has been under debate for a long time. The computational and experimental studies indicate that incorporation of heteroatoms into the skeletal framework of benzene (and its valence isomers) may lead to inorganic derivatives featuring peculiar structural and electronic properties. To date, more than 30 examples of inorganic benzene (valence) isomers have been experimentally synthesized and characterized.

This review summarizes the synthesis, structural and chemical properties of the reported non-carbon analogues of benzene and its isomers, starting from inorganic benzenes (type-**I**), and subsequently its isomers, such as Dewar benzene (type-**II**), prismane (type-**III**), and benzvalene (type-**IV**). Other isomeric forms (type-**V**), which have not been found in the carbon systems, will also be discussed in the last section. The systems containing p-block elements are focused on, and transition metal-containing systems are not described herein. For clarity, inorganic analogues of benzene, Dewar benzene, prismane, benzvalene and other isomeric forms are numbered as **I-E#**, **II-E#**, **III-E#**, **IV-E#** and **V-E#**, respectively (**E** and # represent the elements involved in and the compound number, respectively). In order to facilitate the reading, the substituents, which will often be involved, have been abbreviated as shown in Table 2. Additionally, the selected structural and spectroscopic data of inorganic benzenes and its valence isomers discussed in this review are summarized in Tables at the last part.

Table 1. Relative energies (kcal mol^{-1}) of $(EH)_6$.

E	I	II	III	IV
C[a]	0.0	127.6	88.1	84.5
Si[a]	0.0	–9.5	3.7	0.5
Ge[b]	0.0	–13.5	–1.8	–1.2
Sn[b]	0.0	–31.3	–6.5	–11.0
Pb[b]	0.0	–67.0	–10.6	-

[a] Calculated at the HF/6-31G level of theory.

[b] Calculated at the MP2/DZ+d//HF/DZ+d level of theory.

Table 2 List of abbreviations.

Me	methyl
iPr	isopropyl
tBu	tert-butyl
nBu	n-butyl
Cy	cyclohexyl
BTSM	bis(trimethylsilyl)methyl
TMS	trimethylsilyl
Ibt	isopropylbis(trimethylsilyl)silyl
Ph	phenyl
Mes	2,4,6-trimethylphenyl
Mes*	2,4,6-tri-tert-butylphenyl
Dip	2,6-diisopropylphenyl
Tip	2,4,6-triisopropylphenyl
triph	2,4,6-triphenylphenyl

Rei Kinjo obtained his Ph.D. from University of Tsukuba (Japan). From 2007 to 2011, he was a research fellow at University of California, Riverside. From 2011 to 2017, he has been an assistant professor at Nanyang Technological University (NTU) (Singapore), and since 2017 he is an associate professor at NTU. His research interest involves main group chemistry and catalysis.

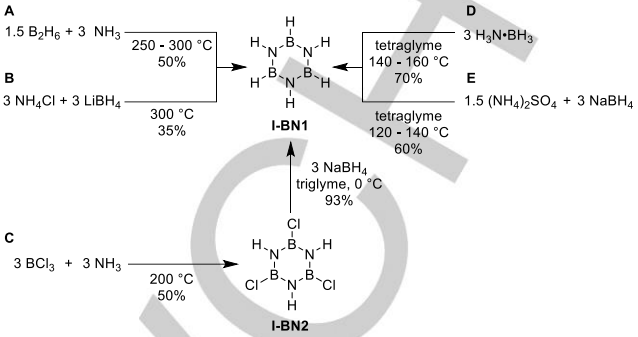
Kei Ota was born in 1994 in Toyonaka, Japan. She graduated from University of Tsukuba (Japan) in 2017. She is currently pursuing graduate studies in Nanyang Technological University, Singapore under the supervision of Prof. Rei Kinjo. Her research interest lies in the field of main group chemistry, the synthesis and examination of interesting molecules. Her favourite chemical is fluorobenzene, for it being a good solvent for recrystallization (as of 16 Apr. 2020).

2. Benzene I

Inorganic cyclic ring systems which are isoelectronic with benzene **I** have been known for many years. During the late 19th and early 20th centuries, borazine, boroxine and cyclophosphazene have come forward. A large number of studies have focused on fundamental interests such as their bonding modes and industrial applications e.g. material science. The heavier analogues of boroxine have been explored from the middle of the 20th century. In the 1980s and 90s, the Power group has dramatically developed this field by the synthesis of several "heavier" analogues of borazines. While inorganic benzenes have a six-membered six-π-electron system, the presence of aromaticity is still discussed.

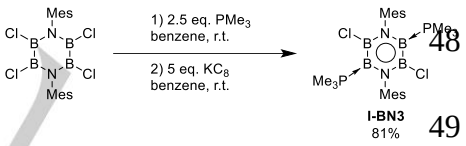
2.1. Group 13/15

In 1926, the parent compound of borazine $(HBNH)_3$ **I-BN1** was originally prepared by Stock and Pohland by pyrolysis of the mixture of borane (B_2H_6) and ammonia (NH_3) (Scheme 1, **A**).[9] Since that, further synthetic procedures have been developed. Schlesinger and co-workers discovered that the high temperature (300 °C) solid-state reaction of lithium borohydride ($LiBH_4$) with ammonium chloride (NH_4Cl) yields **I-BN1** (Scheme 1, **B**).[10] One of the laboratory syntheses of **I-BN1** involves the preparation of B-trichloroborazine **I-BN2** and its subsequent reduction by metal borohydrides (Scheme 1, **C**).[11] The group of Sneddon reported improvement of the laboratory preparation of **I-BN1** by the thermal dehydrogenation of ammonia—borane (H_3NBH_3) (Scheme 1, **D**) or reaction of sodium borohydride ($NaBH_4$) with ammonium sulfate ($(NH_4)_2SO_4$) in tetraglyme solution (Scheme 1, **E**).[12] The structure of borazine was investigated by electron diffraction in 1969.[13] **I-BN1** has a planar hexagonal structure with the equalized B–N bond length of 1.4355(21) Å, which is between B–N single and double bonds. The studies of the formation, functionalization, and application of borazine derivatives have been summarized in several review articles.[9, 14]



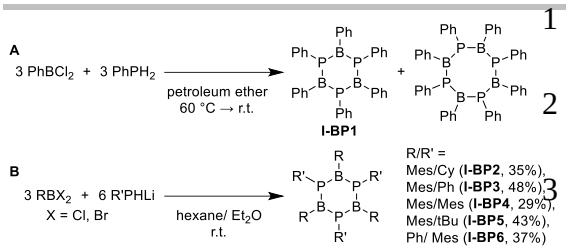
Scheme 1. Synthesis of borazine **I-BN1**.

In 2020, the Kinjo group reported a BN derivative **I-BN3** containing four boron and two nitrogen atoms.[15] Neutral B_4N_2 ring with the six π-electron system was prepared by the reduction of the tetrachloro-substituted precursor with potassium graphite (KC_8) in the presence of trimethyl phosphine (PMe_3) (Scheme 2). An X-ray diffraction study shows that **I-BN3** adopts C_2 symmetry and the B_4N_2 six-membered ring is completely planar. The B–B bond length (1.622(6) Å) and B–N bond lengths (1.432(5)–1.464(5) Å) are within the typical range of boron–boron and boron–nitrogen single and double bonds, respectively.



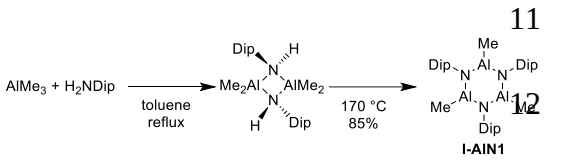
Scheme 2. Formation of **I-BN3** (Mes = 2,4,6-trimethylphenyl).

English reported the first stable boron–phosphorous analogue of borazine **I-BP1** in a mixture of compounds $(PhBPPh)_n$ (n = 3 or 4) (Scheme 3, **A**).[16] Later, the Power group succeeded the first isolation of $(MesBPCy)_3$ **I-BP2** during the synthesis of $MesB(PHCy)_2$ by the reaction of $MesBBr_2$ with two equivalents of $C_6H_{11}PHLi$ (Scheme 3, **B**).[17] A series of phosphaborazines **I-BP3**–**I-BP6** with variable substituents were also synthesized by the same methods.[18] The structural features of these phosphaborazines **I-BP2**–**I-BP6** were characterized by X-ray and NMR analysis. The solid-state structures of **I-BP2**–**I-BP6** show that the B_3P_3 array and the six *ipso*-carbon atoms of the substituents are coplanar. All the B–P distances in **I-BP2** and **I-BP3** are essentially equal and shortening about 1.84 Å length relative to the reported B–P single-bond.[19] These structural data suggest considerable delocalization of the phosphorus lone pairs over the six-membered ring system.



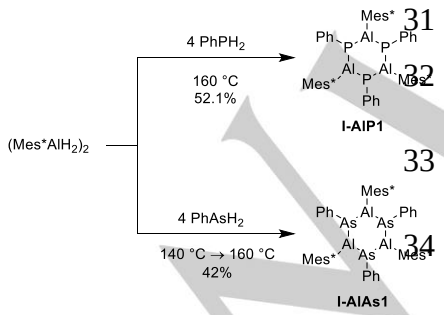
Scheme 3. Synthesis of phosphaborazines.

In 1988, the Power group developed an aluminum-nitrogen analogue of borazine $(MeAlNDip)_3$ **I-AlN1**, via a two-step alkane elimination reaction between $AlMe_3$ and $DipNH_2$ (Scheme 4).[20] The crystal structure of **I-AlN1** consists of the planar Al_3N_3 six-membered ring with an average Al–N bond length of 1.78 Å. The C atoms bonded to Al and N are coplanar with the central ring.



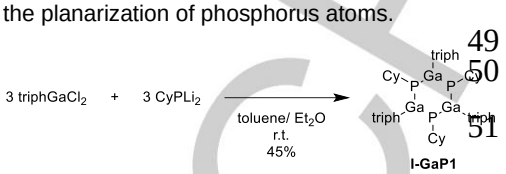
Scheme 4. Formation of the alumazene **I-AlN1**.

Other formal valence analogues of the heavier borazine, Al_3P_3 **I-AlP1** and Al_3As_3 **I-AlAs1**, were prepared through dehydrogenation of $(Mes^*AlH_2)_2$ with the corresponding H_2EPh (E = P, As) under the heating conditions (Scheme 5).[21] The six-membered rings of **I-AlP1** and **I-AlAs1** arrange in a nonplanar boat conformation. The aluminum atoms have planar coordination whereas the phosphorus and arsenic atoms are pyramidally coordinated. The average Al–P and Al–As distances are 2.328(3) Å and 2.430(5) Å, respectively, and the average sums of the bond angles (Σ°) at the phosphorus and arsenic atoms are 329.1(3.0)° and 319.7(3.0)°, respectively. These features are consistent with the negligible delocalization of π-electrons over the central ring. The major reasons for the lack of delocalization in either **I-AlP1** or **I-AlAs1** could be the high inversion barriers of P or As atoms and the relatively large sizes of Al, P, or As atoms which hampers the efficient side-on p–p π-type overlap.



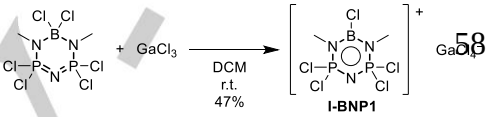
Scheme 5. Synthesis of **I- AlP1** and **I-AlAs1** from $(Mes^*AlH_2)_2$.

The Power group reported the construction of the six-membered ring exclusively composed of heavier main-group elements. In 1991, they successfully prepared the Ga_3P_3 ring compound, $[triphGaP(C_6H_{11})]_3$ **I-GaP1** (triph = 2,4,6-triphenylphenyl) by treatment of $triphGaCl_2$ with $Li_2P(C_6H_{11})$ (Scheme 6).[22] The Ga_3P_3 six-membered ring is not planar, but exhibits a twist-boat geometry with normal single Ga–P bond lengths (2.279(4)–2.338(5) Å). The P atoms adopt pyramidal geometry and the sum of the bond angles at the P centers are in the range from 315.7° to 331.1°. It may be envisaged that the energy gained by forming Ga–P π-bonds is insufficient to overcome the energy required for the planarization of phosphorus atoms.



Scheme 6. Formation of **I-GaP1**.

In 1994, the Manners group reported the synthesis of the first hybrid borazine phosphazene cation **I-BNP1** by the dechlorination of precursor (Scheme 7).[23] The B–N bond length is 1.429(10) Å and the average distance of P–N bond is 1.624(6) Å.

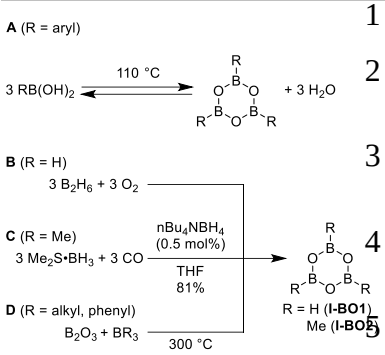


Scheme 7. Synthesis of **I-BNP1**.

2.2. Group 13/16

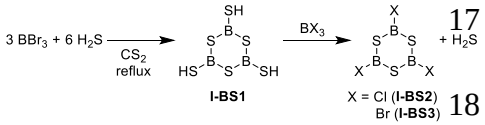
In 1936, Kinney and Pontz reported the first preparation of boroxines by heating the corresponding boric acids $RB(OH)_2$ (R = aryl) (Scheme 8, **A**).[24] Cyclic structure of boroxine was proposed based on its molecular weight. Considering the selective formation of the six-membered ring regardless of the nature of the organic substituents on the B atoms, the Snyder group hypothesized the presence of the resonance stabilization effect of the conjugated six π-electron system.[25]

The simple hydrides of boroxine $(HBO)_3$ **I-BO1** was synthesized by explosive oxidation of diborane (Scheme 8, **B**),[26] and its structure in the gas phase was determined by electron diffraction,[27] disclosing that the boron and oxygen atoms are arranged in a planar D_{3h} symmetry. The B–O bond lengths of 1.3758(21) Å are found to be identical. The general procedure for the formation of boroxine $(RBO)_3$ is dehydrogenation of boronic acid (Scheme 8, **A**). The dehydration and hydrolysis processes proceed reversibly.[28] Trimethylboroxin $(MeBO)_3$ **I-BO2** was prepared by the carbonylation of borane dimethylsulfide ($Me_2S{\bullet}BH_3$) in the presence of tetrabutylammonium borohydride (nBu_4NBH_4) (Scheme 8, **C**).[29] The reaction of triorganoboranes (BR_3) with boric oxide (B_2O_3) gives the corresponding boroxine (Scheme 8, **D**, R = alkyl, phenyl).[30] The detailed boroxine chemistry and their applications have been covered in several review articles.[8b, 8c]



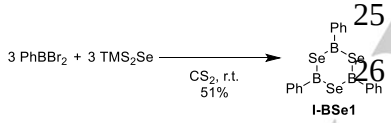
Scheme 8. Synthesis of boroxines.

In 1953, Wiberg and Sturm reported the series of borthiin (RBS)$_3$, the heavier analog of boroxine.[31] The reaction of BBr_3 and H_2S gave $[(HS)BS]_3$ **I-BS1** (Scheme 9). Subsequent treatment with boron trihalides afforded $(XBS)_3$ (X = Cl: **I-BS2**, Br: **I-BS3**). The structures of **I-BS1** and **I-BS3** were determined by the Schwarz group in the 1970s by X-ray diffraction analysis.[32] The B_3S_3 six-membered rings are nearly planar and the values of the cyclic B–S bond length are almost identical. The detailed discussion of the structural feature of other relevant boron-sulfur compounds is shown in the Krebs's review.[33]



Scheme 9. Synthesis and functionalization of borthiins **I-BS1--BS3**.

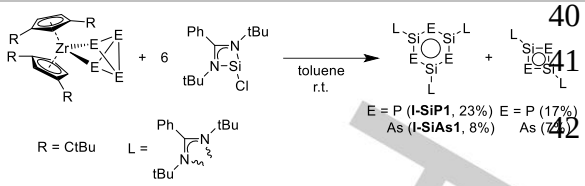
In 1971, Schmidt and Kiewert reported the first preparation of triphenylboroselenol $(PhBSe)_3$ **I-BSe1**.[34] The reaction of phenyl boron dibromide $PhBBr_2$ with hexamethyldisilselenan TMS_2Se afforded **I-BSe1** in moderate yield (Scheme 10). The B-Se bond length is 1.93 Å.[33]



Scheme 10. Formation of triphenylboroselenol **I-BSe1**.

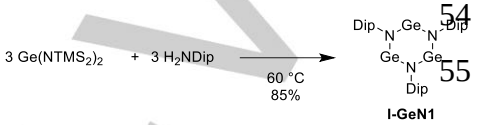
2.3. Group 14/15

Recently, the Scheer group reported the pure heavier borazine analogues, thus, pnictogen−silicon analogues of benzene.[35] The reactions of $[Cp''_2Zr(\eta^{1:1}E_4)]$ (E = P, As) with the monochlorosilylene $[(PhC(NtBu)_2)SiCl]$ resulted in the formation of triarsa- and triphospha-trisilabenzenes $[(PhC(NtBu)_2)Si E]_3$ (E = P (**I-SiP1**), As (**I-SiAs1**)) accompanied with the four-membered ring derivatives $[PhC(NtBu)_2SiE]_2$ (E = P, As) (Scheme 11). The solid-state structures of **I-SiP1** and **I-SiAs1** display the nearly planar six-membered Si_3P_3 and Si_3As_3 ring systems with Si–P and Si−As distances falling between the respective single and double bonds.



Scheme 11. Formation of heavier borazines **I-SiP1** and **I-SiAs1**.

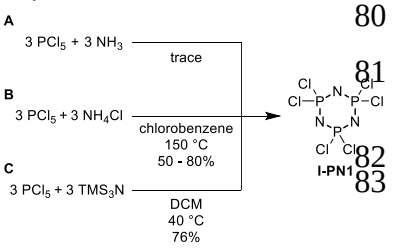
The Power group also achieved the preparation of the heavier group 14 element-containing borazine. The first "germanazene", $(GeNDip)_3$ **I-GeN1**, was synthesized through aggregation of $Ge(NTMS_2)_2$ with H_2NDip under the mild conditions in good yield (Scheme 12).[36] The solid-state structure of **I-GeN1** exhibits the essentially planar Ge_3N_3 array, including the three *ipso*-carbons of the Dip substituents. The Ge–N bonds are essentially equal, and the average distance is 1.859(2) Å. These data indicate that the p-orbitals on the N and Ge atoms have the correct orientation to induce some degree of delocalization over the ring.



Scheme 12. Synthesis of the germanazene **I-GeN1**.

2.4. Group 15/15

In 1834, Liebig, Wöhler, and Rose reported the synthesis of hexachlorocyclotriphosphazene $(Cl_2PN)_3$ **I-PN1** which was gained by the reaction of ammonium chloride (NH_4Cl) or ammonia (NH_3) with phosphorus pentachloride (PCl_5) (Scheme 13, **A**).[37] The chemical formula was established based on the vapor density by Gladstone and Holmes in 1864.[38] Its cyclic structure was proposed in 1985 by Stokes,[39] and confirmed by using X-ray diffraction analysis by Bullen in 1971.[40] To date, **I-PN1** is commonly prepared by treatment of PCl_5 with NH_4Cl at 150 °C (Scheme 13, **B**) or the reaction of PCl_5 with tris(trimethylsilyl)amine at 40 °C (Scheme 13, **C**).[41] The geometry of cyclophosphazene ring $(R_2PN)_3$ mainly depends on the substituents. For example, **I-PN1** has the nearly planer P_3N_3 ring, while derivatives bearing the alkyl and alkoxy groups exhibit distorted structure. All the P–N bond lengths of **I-PN1** are equal (1.58 Å) and lies in between the P–N single and double bond lengths. A variety of cyclophosphazene derivatives have been reported so far, and the most convenient synthetic route is the direct functionalization of the commercially available halide derivatives, such as **I-PN1**. There are reviews summarizing the preparation, structure, reactivity and application of cyclophosphazenes.[8a, 41-42]



Scheme 13. Synthesis of hexachlorocyclotriphosphazene **I-PN1**.

2.5. Aromaticity of inorganic benzenes

One of the most important features on benzene and its derivatives is aromaticity, which can be evaluated by several aspects both experimentally and theoretically.

Although almost all of the isolated inorganic benzenes exhibit the planar geometry of the six-membered ring core, similar to that of benzene, the theoretical calculations point out the nonaromatic nature, or at least a weaker aromatic character, compared with that of benzene. In this section, we briefly summarize the geometric property, spectroscopic data, as well as, the nucleus independent chemical shifts (NICS) values of inorganic benzenes. The selected experimental data of inorganic benzenes are sumerized in Table 3.

2.5.1. Molecular geometry

The central C_6 core of benzene (C_6H_6) is a planar six-membered ring with almost identical C-C bond lengths of 1.391(7) – 1.397(7) Å, which are in between C-C single and C-C double bond lengths.[43]

Among inorganic benzenes, the six-membered ring of **I-AlP1**, **I-AlAs1**, and **I-GaP1** are non-planar, that of **I-PN1** is nearly planar, and those of other systems are planar. No bond-alternation is observed in all systems. Moreover, the E-E‘ bond lengths of **I-BN1**, **I-BP2**, **I-BP3**, **I-AlN1**, **I-BO1**, **I-BS1**, **I-BS3**, **I-BSe1**, **I-GeN1**, **I-PN1**, **I-SiP1**, **I-SiAs1**, **I-BN3**, and **I-BNP1** are in the range between the typical E-E‘ single and double bonds. By contrast, the E-E‘ bond lengths in **I-GaP1**, **I-AlP1**, **I-AlAs1** are consistent with the corresponding single bond.

2.5.2 Spectroscopy

The NMR spectroscopy may provide information regarding a ring current of π-conjugated cyclic molecules

The ^{11}B NMR chemical shifts of **I-BN1** (δ = 28.5 ppm), **I-BN3** (δ = 38.6 ppm, 20.8 ppm), and **I-BNP1** (δ = 31.7 ppm) are in the range of aromatic 1,2-azaborinine system (δ = 20 - 40 ppm, e.g. 1,2-dihydro-1,2-azaborinine: δ = 31.0 ppm).[44] The ^{31}P NMR resonance of **I-BNP1** (δ = 35.5 ppm) is shifted downfield compared to the corresponding precursor (δ = 28.2 ppm) (Scheme 7).[45] The ^{31}P NMR of phosphazene **I-PN1** (δ = 19.3 ppm) is somewhat upfield compared to **I-BNP1**. The ^{11}B NMR chemical shifts of phosphaborazines (**I-BP2** - **I-BP6**) appear around δ = 52 ppm, which are upfield-shifted with respect to that observed for the antiaromatic system (ThexylBPMes)$_2$ (Thexyl = *tert*-hexyl) (δ = 95.1 ppm).[17-18] On the other hand, the ^{11}B chemical shifts are downfield than that of (ThexylBPMes)$_2$ (δ = 70.7 ppm). These results support delocalization of electrons in the π-system indicating the considerable aromatic character of phosphaborazines. On the other hand, the upfield ^{31}P chemical shifts of **I-AlP1** (δ = –144.2 ppm) and **I-GaP1** (δ = –61 ppm) suggest the delocalization of electrons over the ring is not extensive.[21-22]

The ^{11}B NMR chemical shifts of **I-BS1** (δ = 56.6 ppm) and **I-BS3** (δ = 54.5 ppm) are similar to that of $B(SH)_2Br$ (δ = 60.6 ppm) and $B(SMe)_3$ (δ = 61.3 ppm), indicative of no explicit evidence for the ring current[46]

The ^{29}Si NMR signals of **I-SiP1** (δ = 70.6 ppm) and **I-SiAs1** (δ = 70.4 ppm) are shifted downfield compared to the corresponding dimer $[PhC(NtBu)_2SiE]_2$ (E = P: δ = 26.5 ppm E = As: δ = 3.1 ppm), whereas the ^{31}P chemical shift of **I-SiP1** (δ = –241.9 ppm) shows a highfield shift relative to $[PhC(NtBu)_2SiP]_2$ (δ = –164.9 ppm).[35]

In addition to the NMR spectroscopy, the π–π* electronic transition is one of the features seen in the aromatic ring, which can be experimentally observed in the UV/Vis absorption spectrum. The UV/Vis absorption spectrum for benzene (C_6H_6) displays a strong absorption band at 208 nm and a weak absorption band at around 255 nm.[47]

The reported λ_{max} values of inorganic benzenes are listed in Table 3. The Liu and Dixon group compared UV/Vis absorption spectrum of borazine **I-BN1**, benzene, and 1,2-hydro-1,2-azaborinine BNC_4.[47] In contrast to benzene and 1,2-azaborinine (λ = 205 nm, 269 nm (λ_{max})), the absorption spectrum of borazine shows only a very weak band at 203 nm and negligible absorbance at higher wavelengths. It is predicted that the electronic structure of **I-BN1** differs substantially from that of the reported aromatic system.

The UV/Vis absorption spectrum of cyclophosphazene **I-PN1** displays the characteristic π–π* transition at around 200 nm.[48] The UV/Vis spectrum (332 nm) of **I-SiP1** is in agreement with the calculated HOMO (π) - LUMO+12 (π*) gap of 5.39 eV.[49] **I-BN3** shows an absorption band with a maximum at a wavelength of 607 nm, which is consistent with calculated HOMO (π) - LUMO (π*) gap (2.45 eV).[15]

2.5.3. Theoretical calculation

The computation of nucleus independent chemical shifts (NICS) is one of the most commonly used theoretical strategies to quantify the aromaticity.[50] For NICS values, the gauge independent atomic orbital (GIAO) scheme is used by placing a ghostatom (Bq) at the geometric centre of the ring, and 1 Å above the plane of the ring. They are denoted as NICS(0), and NICS(1), respectively. Generally, the rings with the large negative NICS values are classified as aromatic, whereas positive and zero values are associated as a symptom of antiaromaticity or nonaromaticity, respectively.

The reported NICS values of inorganic benzenes (real or model molecule), and benzene are summarized in Table 4.[15, 35, 51] Model compounds (the substituents are replaced with H atoms) are named as **I-E'**(**E** represents the elements involved in). The NICS(0) and NICS(1) values of benzene are –8.2 and –10.4, respectively.[51b] In order to focus on the influence of π-electrons over the respective ring system, here we compare the NICS(1) values. On the whole, all of the reported NICS(1) values of inorganic benzenes are smaller than that of benzene.

Borazine **I-BN1** shows a less negative NICS(1) value (–2.7) compared with that of benzene. The substantial difference of

electronegativity between boron and nitrogen atoms in **I-BN1** makes the B–N bonds highly polar, which results in less cyclic delocalization of π-electrons. The boron-rich system **I-BN3** indicates a moderate NICS(1) value (–4.59), which is probably due to the less polarized nature of the B_4N_2 ring system of **I-BN3** in comparison to **I-BN1** .[15] Interestingly, **I-BN3** can be viewed as a benzene dication isostere supported by two Lewis bases , which system was proposed by Hoffmann et al.[52]

I-BP' is substantially aromatic according to the NICS(1) value (–6.9).[51a] On the other hand, **I-AlN'** shows a small NICS(1) value (–0.6), indicating a weak aromatic character.

Other heavier borazine analogues show moderate NICS(1) values (**I-AlP'** (–3.2), **I-AlAs'** (–3.9), **I-GaP'** (–3.8)), suggesting that they are more aromatic than borazine, but less aromatic than benzene.

The parent B_3E_3 systems (E = O, S, Se) exhibit very low or moderate NICS(1) values (**I-BO1** (–1.9), **I-BS'** (–3.1), **I-BSe'** (–2.7)), indicating no or weak aromaticity.[53]

Among phosphazenes, Cl-substituted **I-PN1** shows a moderate NICS(1) value (–3.1), while H-substituted phosphazene **I-PN'** shows very little NICS(1) value (0).[51b]

The NICS(1) values of **I-SiP1** (–2.8) and **I-SiAs1** (–3.4) are lower than that of benzene, indicating weak aromatic character of the central units.

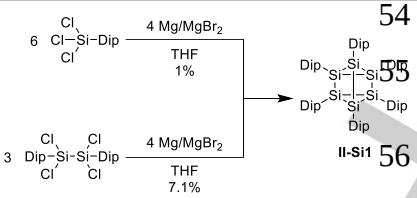
It is noteworthy that the theoretical evaluation of the aromaticity of inorganic benzene analogues has been a major area of current research and a matter of debate.[51b, 53-54]

3. Prismane II

The chemistry of carbon-free prismane E_6R_6 has been known for the heavier group 14 elements. In 1989, the group of Sekiguchi and Sakurai isolated the first hexagermaprismane **II-Ge1,** with kinetic stabilization provided by the sterically hindered bis(trimethylsilyl)methyl groups (BTSM). Consequently, the same group reported the first hexasilaprismane **II-SI1** and another hexagermaprismane **II-Ge2**. In 2008, hexastannaprismane **II-Sn1** bearing tri-tert-butylsilyl groups was isolated by Wiberg. After that, several examples bearing different substituents have also been prepared, and their synthetic methods have widely been studied so far.[55]

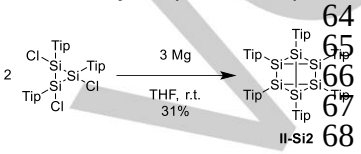
3.1. Hexasilaprismane II

Three groups have accomplished to synthesize of hexasilaprismane. The first hexasilaprismane Si_6Dip_6 **II-Si1** bearing bulkier 2,6-diisopropylphenyl (Dip) substituents was prepared by the reductive (Wurtz) coupling reactions (Scheme 14).[56] While the reaction of (2,6-diisopropylphenyl)trichlorosilane $DipSiCl_3$ with $Mg/MgBr_2$ gave **II-Si1** in very low yield (1%), the reaction of 1,2-bis(2,6-diisopropylphenyl)-1,1,2,2-tetrachlorodisilane ($DipSiCl_2SiCl_2Dip$) with $Mg/MgBr_2$ afforded **II-Si1** in a slightly better yield (7.1%).



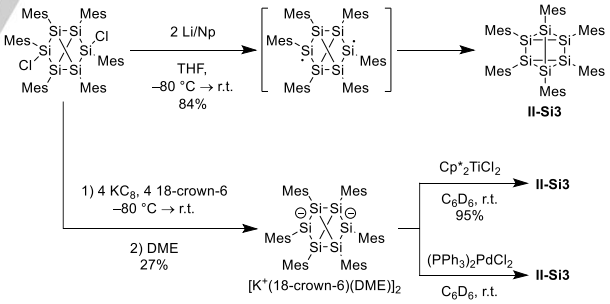
Scheme 14. Synthesis of hexasilaprismane with Dip **II-Si1**.

Recently, the Scheschkewitz group discovered a different synthetic route accessing to (2,4,6-triisopropylphenyl)hexasilaprismane Si_6Tip_6 **II-Si2**. A trichloricyclotrisilane derivative was employed as the starting material, and its reductive coupling with magnesium afforded **II-Si2** in 31% yield (Scheme 15).[57]



Scheme 15. Synthesis of hexasilaprismane with Tip **II-Si2**.

In 2018, the Cui group reported the less bulky 2,4,6-trimethylphenyl-substituted hexasilaprismane Si_6Mes_6 **II-Si3** (Mes = 2,4,6-trimethylphenyl), which could be obtained in excellent yield by several methods (Scheme 16).[58] First, treatment of the dichloro precursor with two equivalents of lithium naphthalenide (Li/Np) resulted in the formation of **II-Si3** in 84% yield. A transient diradical species is proposed to generate as the initial intermediate in the reaction. It has been shown that **II-Si3** could also be formed by the reactions of the tricyclic isomer of dianionic hexasilabenzene with $Cp^*_2TiCl_2$ ($Cp^* = C_5Me_5$) or $(PPh_3)_2PdCl_2$ in excellent yield.



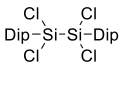
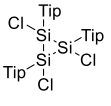
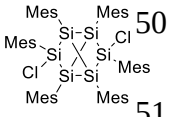
Scheme 16. Formation of hexasilaprismane with Mes **II-Si3**.

The Sekiguchi group has pointed out that of importance for the selectivity is the proper choice of both starting materials with a suitable substituent and reducing agent.[56] The latter was confirmed by two results: (1) the reaction of **II-Si1** with lithium naphthalenide (Li/Np) does not give prismane,[59] and (2) the use of two equivalents of KC_8 instead of Li/Np in the reaction with **II-Si2** facilitates the formation of **II-Si2** in less than 20% yield.

Moreover, the Scheschkewitz group proposed that the selectivity of the reduction coupling of precursors could be improved by the employment of larger n in Si_n precursors. Indeed, the yields were

improved by the employment of Si (1%) <Si_2 (7.1%) < Si_3 (31%) <Si_6 (84%) (Table 5).

Table 5. Summary of the precursor and yield of the formation of hexasilaprismanes.

Precursor				
Product	**II-Si1**	**II-Si1**	**II-Si2**	**II-Si3**
Yield (%)	1	7.1	31	84

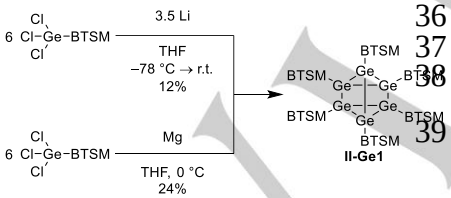
Both **II-Si1** and **II-Si2** are thermally and air-stable in the solid-state. **II-Si1** does not show any decomposition over a couple of months in the air. On the other hand, the mesityl-substituted **II-Si3** is sensitive to air, indicating that the stability depends on the steric influence of the substituents.

The structural parameters of isolated and calculated prismanes containing group 14 elements are summarized in Table 6. The calculations of C_6R_6 prismanes predict that the C–C bond lengths of the three-membered rings (*a*) are shorter than those of the four-membered rings (*b*).[60] Experimentally determined metric features of carbon-based prismanes (C_6H_6[61] and C_6Me_6[62]) are in accordance with the theoretical prediction.

The structurally characterized hexasilaprismanes show that all Si−Si bond lengths are consistent with a Si−Si single bond, but they are somewhat longer than those calculated for the parent derivative (Si_6H_6). The skeletal Si−Si bond lengths of the three-membered rings (*a*) and the four-membered rings (*b*) are nearly identical (Table 6). The Si-Si bond lengths in **II-Si1** and **II-Si2** are similar, but slightly longer than those in **II-Si3**, probably due to the steric effect of the substituents.

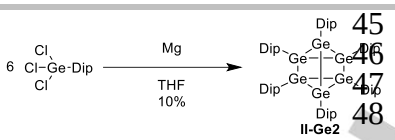
3.2. Hexagermaprismane

The Sekiguchi and Sakurai group reported that the reduction of bis(trimethylsily)methyltrichlorogermane with Li in THF led to the formation of the hexagermaprismane $Ge_6(BTSM)_6$ **II-Ge1** in 12% yield (Scheme 17).[63] The employment of Mg instead of Li improved the yield up to 24%.



Scheme 17. Synthesis of hexagermaprismane with BTSM **II-Ge1**.

In 1993, the same group reported another hexagermaprismane, Ge_6Dip_6 **II-Ge2** (10%) by reductive coupling of the trichlorogermane precursor with Mg in THF (Scheme 18).[56]

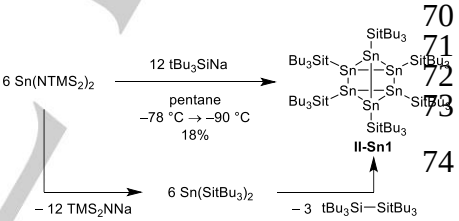


Scheme 18. Formation of hexagermaprismane with Dip **II-Ge2**.

Both **II-Ge1** and **II-Ge2** are stable toward atmospheric oxygen and moisture. All the Ge-Ge bond distances (2.465 - 2.584 Å) are slightly longer than the sum of the single-bond covalent radii of two Ge atoms (2.42 Å). Notably, in both **II-Ge1** and **II-Ge2**, the Ge-Ge bond lengths in the three-membered ring (*a*) are longer than those in the four-membered ring (*b*) (Table 6). This relationship is in marked contrast to theoretical results,[60b] and the reported carbon- and silicon-based prismanes. All the Ge-Ge bonds of **II-Ge1** are slightly longer than those of **II-Ge2**, probably due to the steric hindrance of bulky BTSM groups.

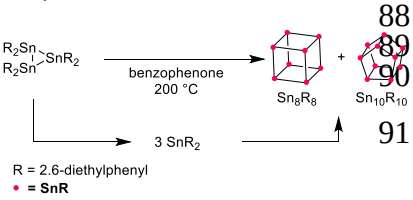
3.3. Hexastannaprismane

In 1999, the Wiberg group reported the isolation of a hexastannaprismane $Sn_6(SitBu_3)_6$ **II-Sn1** which was prepared by the reaction of $Sn[N(TMS)_2]_2$ with tBu_3SiNa (Scheme 19).[64] In contrast to the analogous silicon (**II-Si1** and **II-Si2**) and germanium systems, the crystals of **II-Sn1** can be stored only at room temperature in the absence of air, water, and solvents.



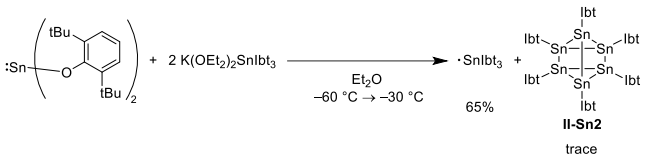
Scheme 19. Formation of hexastannaprismane with tri-tert-butylsilyl groups **II-Sn1**.

The proposed mechanism for the formation of **II-Sn1** involves an initial substitution of the amide groups by silyl groups to yield the stannylene $Sn(SitBu_3)_2$. Subsequent oligomerization of the stannylene with the concomitant elimination of the dimer of the silyl radicals may give **II-Sn1**. It has been disclosed that the skeletal property depends on the substituents. Thus, employing 2,6-diethylphenyl groups leads to the formation of the less strained Sn_nR_n (n = 8, 10) prismanes (Scheme 20).[65] This result indicates that the sterically more demanding super-silyl group (-$SitBu_3$) is indeed required for the formation of the more strained Sn_6 prismane **II-Sn1**.



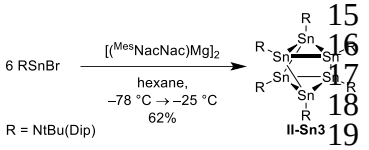
Scheme 20. Formation of perstanna[n]prismanes with 2,6-diethylphenyl groups.

A few years later, the Klinkhammer and Hinderberger group discovered that hexastannaprismane Sn_6Ibt_6 **II-Sn2** (Ibt = isopropylbis(trimethylsilyl)silyl) was formed as a side-product during the formation of a radical $SnIbt_3$ (Scheme 21).[66] **II-Sn2** was found in small amounts as small black crystals and could be analyzed by X-ray diffraction.



Scheme 21. Synthesis of hexastannaprismane with tris(trimethylsilyl)silyl group **II-Sn2.**

In 2019, Jones and coworkers reported the isolation of a twisted hexastannaprismane. The reduction of the amido-tin(II) bromide precursor with the magnesium(I) dimer [(^{Mes}NacNac)Mg]$_2$ (^{Mes}NacNac = [(MesNCMe)$_2$CH]$^-$) gave rise to the Sn_6(NtBuDip)$_6$ **II-Sn3** (Scheme 22).[67]



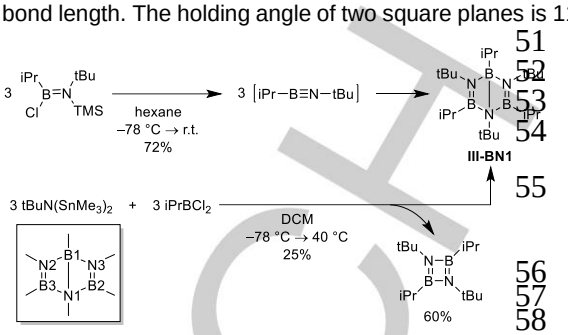
Scheme 22. Formation of hexastannaprismane with amido-group **II-Sn3.**

All Sn-Sn distances (2.811 - 2.941 Å) in **II-Sn1** and **II-Sn2** are slightly longer than the sum of the single-bond covalent radii of two Sn atoms (2.80 Å).[68] The Sn-Sn bonds in **II-Sn1** are longer compared with those in **II-Sn2**, due to the bulky substituents (Table 6). Analogous to the germanium system, hexastannaprismanes also have the long Sn-Sn bond in the three-membered ring (*a*) compared with those in the four-membered ring (*b*). Note that the structure of **II-Sn3** possesses a distorted trigonal anti-prism structure, and all of these bonds are quite long compared with those in **II-Sn1** and **II-Sn2**.

4. Dewar benzene III

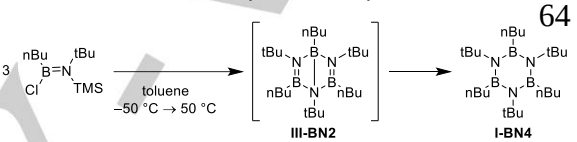
4.1. Group 13/15

Dewar type isomers of borazine (RBNR')$_3$ have been explored in the early 1980s. The general synthetic method of Dewar borazine is oligomerization of iminoboranes. The Paetzold group published a pioneering example of Dewar borazine in 1984.[69] Thermal isomerization of iminoboranes with tert-butyl and isopropyl group provided the corresponding Dewar borazine **III-BN1** in 72% yield (Scheme 23). The authors mentioned that the formation of **III-BN1** is initiated by the dimerization of iminoborane, followed by [4+2] cycloaddition with another iminoborane. In 1986, the Nöth and Storch group also isolated **III-BN1** by the reaction of tert-butyl bis(trimethylstannyl)amine tBuN(SnMe$_3$)$_2$ with dichloroisopropylborane (iPrBCl$_2$).[70] The central bond distance between the two tetracoordinate bridgehead atoms (B1 and N1) is 1.752(5) Å, which is an extra-long single bond. The two B-N double bonds between the tricoordinate atoms (B2-N3 and B3-N2) are 1.364(6) Å and 1.384(6) Å, respectively. The other four B-N bonds (1.548(5) Å – 1.564(5) Å) are in the typical B-N single bond length. The holding angle of two square planes is 114.6(3)°.



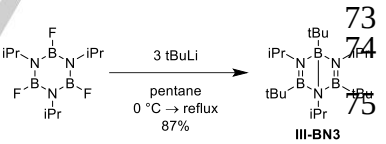
Scheme 23. Formation of **III-BN1.**

In 1984, the Paetzold group also reported the thermal isomerization of iminonborane with the n-butyl group on B atoms, which generated borazine **I-BN4** thorough a Dewar borazine **III-BN2** as an intermediate (Scheme 24).[71]



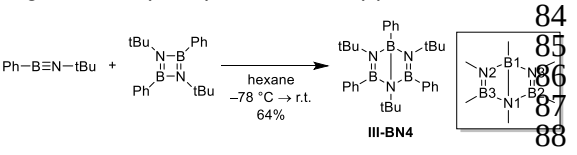
Scheme 24. Formation of **III-BN2** as the intermediate**.**

In 1985, the Eleter group reported the formation of a Dewar borazine **III-BN3** from borazine.[72] The substitution reaction of borazine (FBNiPr)$_3$ with tBuLi, afforded the tBu-substituted Dewar borazine **III-BN3** (Scheme 25). Employment of the bulky substituent results in the formation of Dewar borazine, which is thermally more favorable than the corresponding borazine.



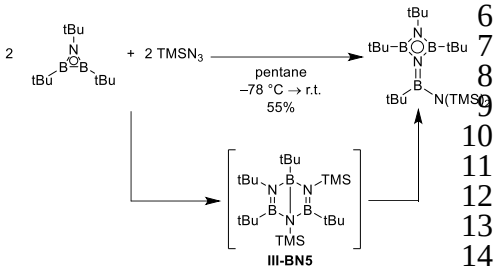
Scheme 25. Synthesis of **III-BN3.**

In 1991, the Paetzold group reported the second example of a structurally characterized Dewar borazine **III-BN4** by the reaction of an iminoborane (tBuNBPh) and its dimer (tBuNBPh)$_2$ (Scheme 26).[73] The structural parameter of **III-BN4** is similar to those of **II-BN1**. **III-BN4** has the long central B1-N1 bond (174.1(4) Å) as well as two B-N double bonds (1.370(4) – 1.376(4) Å). The holding angle of two square planes is 117.0(2)°.



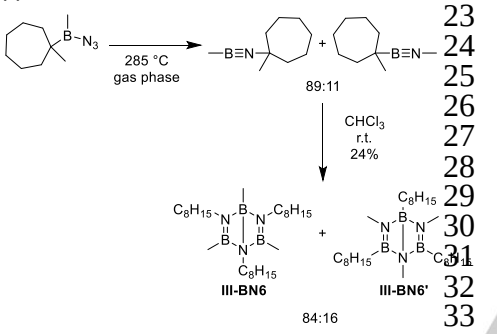
Scheme 26. Synthesis of **III-BN4.**

In 1995, the Paetzold group reported the Dewar borazine **III-BN5** as an intermediate in the reaction of tri-tert-butyl azadiboriridine ($tBuN(BtBu)_2$) with trimethylslylazide ($TMSN_3$) (Scheme 27).[74] **III-BN5** undergoes 1,3-sigmatropic silyl migration to furnish its isomer.



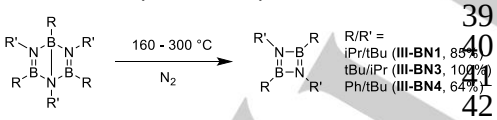
Scheme 27. Formation of **III-BN5** as an intermediate**.**

In 2004, the same group published the mixture of Dewar borazines **III-BN6/III-BN6'** derived from a mixture of methyl(1-methylcycloheptyl)iminoboranes, which were generated by the gas-phase thermolysis of the corresponding azidoborane (Scheme 28).[75] The structure of the Dewar borazines **III-BN6/III-BN6'** is proposed only by the ^{11}B NMR signal observed at δ = 30.8 ppm.



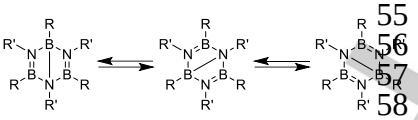
Scheme 28. Formation of a mixture of **III-BN6/III-BN6'.**

The thermal conversion of Dewar borazines has also been investigated and revealed that the conversion of **III-BN1**, **III-BN3** and **III-BN4** into the corresponding dimer $(RBNR')_2$ proceeded at 160 - 300 °C (Scheme 29).[69, 72-73]



Scheme 29. Thermal conversion of**III-BN1**, **III-BN3**, and **III-BN4**.

The reported ^{11}B NMR chemical shifts of Dewar borazines at room temperature appear around δ = 30 ppm, which are not in line with the value expected from the structure (Table 7). Low temperature ^{11}B NMR measurements of **III-BN3** or **III-BN6/III-BN6'** revealed that two peaks correspond to the expected Dewar borazine structure (δ = 35.9 ppm and 13.1 ppm or δ = 22.6 ppm and 31.2 ppm, respectively).[72, 75] Paetzold and co-workers suggested a fluxional process between the three possible equivalent structures of Dewar borazine in a $CDCl_3$ solution at room temperature (Scheme 30), with the corresponding borazine as the transition state.



Scheme 30. A fluxional rearrangement of Dewar borazine in a solution.

The Paetzold group performed the mechanistic study on the formation of Dewar borazines from iminoborane.[76] They discovered the size of the substituents on both boron and nitrogen atoms provides a great impact on the selectivity of the resulting cyclic structure. As shown in Figure 2, the oligomerization of iminoboranes may yield mainly five different types of products $(BN)_n$. With sterically less hindered ligands (e.g. R, R' = Me), the trimerization of iminoboranes occurs to give rise to borazines, whereas with the sterically demanding substituents (e.g. R = iPr, R' = tBu) the formation of Dewar borazines is more favorable. Employment of the more bulky substituents on both B and N atoms (e.g. R, R' = tBu) leads to the formation of dimers.

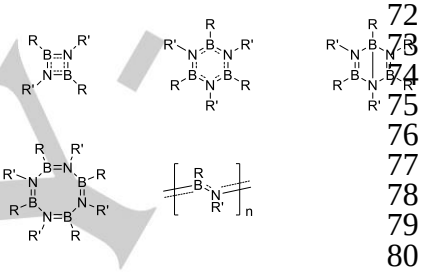
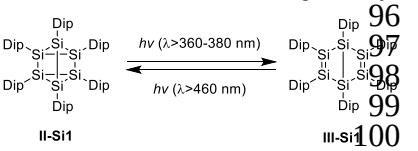


Figure 2. Products by oligomerization of iminoboranes (RBNR').

4.2. Group 14

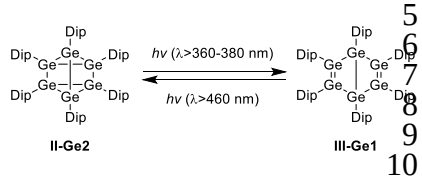
It has been reported that hexasila- and hexagerma-Dewar benzenes can be synthesized by photoisomerization of the corresponding prismanes. The group of Sekiguchi and Sakurai reported the generation of hexasila-Dewar benzene **III-Si1** upon irradiation of **II-Si1** with a light of 360-380 nm wavelength in solution (3-Methylpyridine or 2-MeTHF) at –50 ˚C or in a glass matrix at –196 ˚C (Scheme 31).[55a, 56, 77] The UV-vis spectrum of **III-Si1** shows absorption bands at 335 nm, 455 nm, and 500 nm. Excitation of the bands with wavelengths longer than 460 nm resulted in the immediate regeneration of **II-Si1**, which was confirmed by the original absorption at 241 nm. **III-Si1** is thermally stable at –150 ˚C, however, it gradually reverts to the **II-Si1**.



Scheme 31. Formation of hexasila Dewar benzene **III-Si1**.

The same group reported that upon irradiation of UV light to hexagermaprismane **II-Ge2** at low temperature new absorption bands appeared at 342 nm, 446 nm, and 560 nm corresponding to hexagerma-Dewar benzene **III-Ge1** (Scheme 32).[55a, 56, 77]

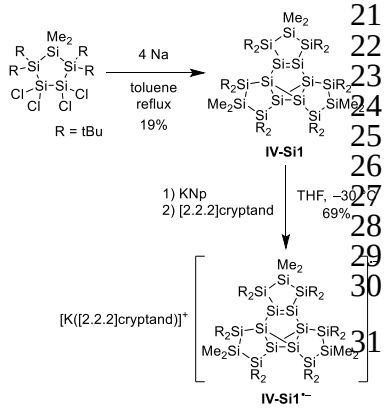
Excitation of these bands with λ > 460 nm light led to the regeneration of the original absorption due to **II-Ge2**. Hexagerma Dewar benzene **III-Ge1** is gradually reverted to the prismane **II-Ge1** above –160 ˚C.



Scheme 32. Preparation of hexagerma Dewar benzene **III-Ge1**.

5. Benzvalene IV

It was not until recently that reports on noncarbon analogues of benzvalene had surfaced. In 2013, Kyushin and co-workers reported the reduction of a tetrachlorinated cyclopentasilane with sodium metal which gave rise to hexasilabenzvalene **IV-Si1** in 19% yield (Scheme 33).[78] X-ray crystallographic analysis of **IV-Si1** revealed that the hexasilabenzvalene skeleton involves a Si=Si double bond and bicyclo[1.1.0]tetrasilane moieties.

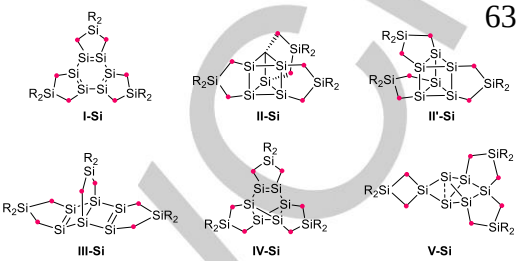


Scheme 33. Synthesis of hexasilabenzvalene **IV-Si1.**

Structural parameters of **IV-Si1** are listed in Table 8; Si=Si bond distance, bent angles (defined as the angle between the (R_2Si) plane and the Si=Si axis), and twist angle, (the angle between two (R_2Si) planes). The Si3−Si4 bond length (2.212(2) Å) is much shorter than the other Si−Si bonds (2.319(2) - 2.368(2) Å), and it lies within the range of reported of tetrasilyldisilenes, indicating the double-bond character. The Si3 and Si4 atoms show somewhat pyramidal geometries (ΣSi3 = 349.5° and ΣSi4 = 352.2°). The Si3=Si4 moiety is in large trans-bent fashion with the bent angles of 42.5° for Si3 and 36.5° for Si4, respectively, and a large twist angle of 16.2°. These unique features are due to the linkage of the hexasilabenzvalene moiety and the cyclopentasilane rings, as well as, the introduction of bulky tert-butyl groups on the cyclopentasilane rings (*vide infra*).

It has been computationally confirmed that the structure of **IV-Si1** is stabilized by the cyclopentasilane rings bearing the linkage structure and bulky substituents. Table 9 shows the relative energies obtained from the theoretical calculations for both modeled (**a**,**b**,**d**) and real molecules (**c**) of Si_6 valence isomers **I-Si** - **IV-Si** and the global minimum structure **V-Si**. (1) In modeled molecules, benzene **I-Si**, prismane **II'-Si**, and **V-Si** are more stable than benzvalene **IV-Si**. Note that, the relative energy differences of **IV** and **V-Si** in the linkage model (**a**, **b**) are small compared to that in Si_6H_6 (**d**). (2) Furthermore, the introduction of the tert-butyl groups (**c**) renders **IV-Si1** as the most stable isomer, which is due to the steric impact of tert-butyl groups.

Table 9. Relative energies (kcal mol^{-1}) of cyclopentasilane fused Si_6 Isomers I-Si−V-Si calculated at the B3LYP/6-31G(d) level of theory.



• = SiR_2; R = R' = H (**a**); R = R' = Me (**b**); R = tBu, R' = Me (**c**)

compd.	I-Si	II-Si	II'-Si	III-Si	IV-Si	V-Si
a	–2.0	6.6	–1.2	13.4	0.0	–8.3
b	–6.3	5.3	–3.5	9.9	0.0	–10.4
c	12.2	3.0	19.0	7.4	0.0	29.2
d	–1.8	–7.5	-	4.1	0.0	–37.2

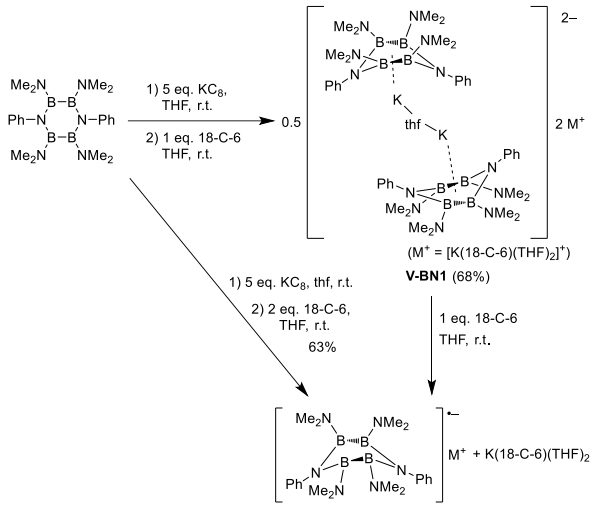
The authors demonstrated that reduction of **IV-Si1** generated the corresponding radical anion **IV-Si1**$^{\bullet-}$ in 69% yield (Scheme 33).[79] X-ray crystallographic analysis of **IV-Si1**$^{\bullet-}$ revealed that the hexasilabenzvalene skeleton retains even after the reduction.

6. Others V

6.1. Group 13/15

In 2018, the Kinjo group presented a diazatetraborabenzene analogue, which can be considered as a hypothetical zwitterionic valence isomer of benzene.[80] Dianionic B_4N_2 ring **V-BN1** was synthesized by the reduction of a substituted diazatetraborinane with potassium graphite (KC_8), and then stabilizing the potassium counterions with one equivalent of crown ether (18-C-6) (Scheme 34).

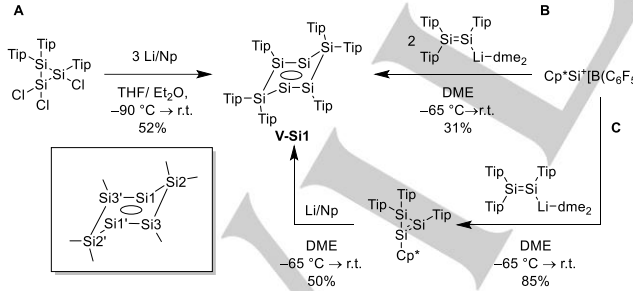
The B_4N_2 six-membered ring exhibits a distorted boat geometry whereby both N atoms are bent toward the coordinating potassium atom. The B−B bond distances (1.673(9) and 1.700(9) Å) are shorter than those in the neutral precursor. The structural parameters and theoretical calculation confirm the delocalization of the two electrons over the four B atoms, which results in the σ-bonding interaction between two odd-electron B−B π-orbitals. Simple treatment of **V-BN1** with another one equivalent of 18-C-6 leads to the formation of a paramagnetic potassium-doped radical ion pair that exhibits a thermally populated triplet character.



Scheme 34. Formation of B_4N_2 isomer **V-BN1**.

6.2. Group 14

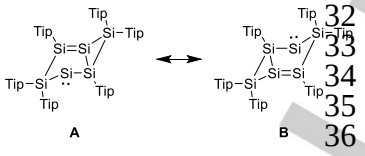
In 2010, the group of Rzepa and Scheschkewitz reported a tricyclic aromatic isomer of hexasilabenzene.[81] Reduction of a trichlorocyclotrisilane precursor with three equivalents of lithium naphthalenide (Li/Np) led to the hexasilabenzene isomer Si_6Tip_6 **V-Si1** in 52% yield (Scheme 35, **A**). In 2012, the same group reported the alternative synthetic pathway to **V-Si1** by employing Cp^*Si^+ as a stoichiometric source of silicon.[82] Reaction of the Cp^*Si^+ salt with two equivalents of the lithium disilenide ($Tip_2Si{=}SiTipLi(dms)_2$) afforded a mixture of **V-Si1** and tetrasilabutadiene Si_4Tip_6 as the main products (Scheme 35, **B**). Meanwhile the reaction of Cp^*Si^+ salt with one equivalent of $Tip_2Si{=}SiTipLi(dms)_2$ gave a cyclotrisilene ($Tip_3Si_3Cp^*$), reduction of which with one equivalent of Li/Np afforded **V-Si1** in 50% yield (Scheme 35, **C**). Surprisingly, **V-Si1** is stable to air for hours in the solid-state and for minutes even in a solution without detectable changes.



Scheme 35. Synthetic route of **V-Si1**.

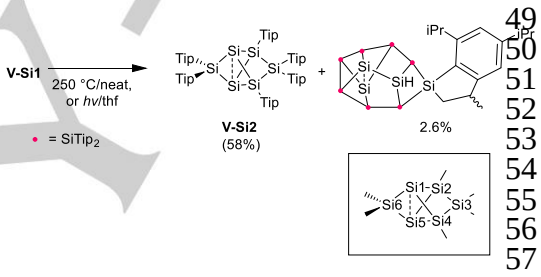
The solid-state structure of **V-Si1** exhibits a tricyclic chair-like structure with a central rhomboid Si_4 ring. The six silicon atoms are in three different oxidation states, +**II** ($SiTip_2$), +**I** (SiTip), and 0 (Si).

The bond length of Si1−Si3 is only slightly longer than Si1−Si3', both being at the shorter end of typical Si−Si single bonds. Theoretical analysis reveals that the six mobile electrons are delocalized over the central four-membered ring leading the π-, σ- and non-bonding interaction, which can be described by the resonance forms **A** and **B** (Scheme 36).



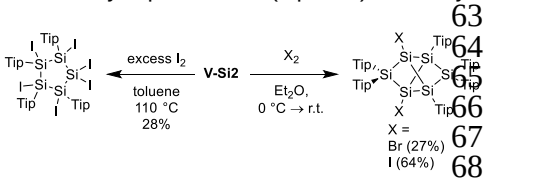
Scheme 36. Resonance forms for **V-Si1**.

Compound **V-Si1** undergoes thermal or photochemical valence isomerization to give **V-Si2** in 58% yield (Scheme 37). [83] The solid-state structure of **V-Si2** represents the global minimum of the Si_6H_6 potential energy surface. The distance of 2.7076(8) Å between the unsubstituted bridgehead silicon atoms Si1−Si5 is significantly longer than the other Si−Si single bond lengths (2.3536(6) - 2.3819(5) Å). Theoretical calculation revealed that there is no interstitial bond between Si1−Si5, while it is presented in the carbon analogue of propellane.[84]



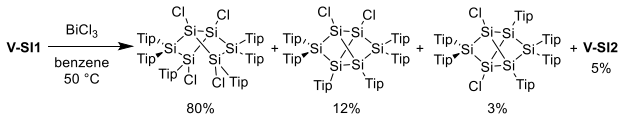
Scheme 37. Synthesis of **V-Si2** by the isomerization of **V-Si1**.

Treatment of **V-Si2** with bromine (Br_2) or iodine (I_2) at room temperature afforded the 1,5-dihalogenated derivatives (Scheme 38). While the reaction of **V-Si2** with excess iodine at 110°C gave hexaiodocyclopentasilane ($Tip_3Si_5I_6$) in 28 % yield.[57]



Scheme 38. Reactions of **V-Si2**.

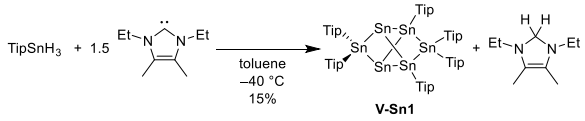
While the reactions of **V-Si1** with elemental chlorine (Cl_2) and Br_2 gave a complex mixture, the halogenation of **V-Si1** with $BiCl_3$ afforded a mixture of multiple products (Scheme 39).



Scheme 39. Reaction of **V-Si1** with $BiCl_3$.

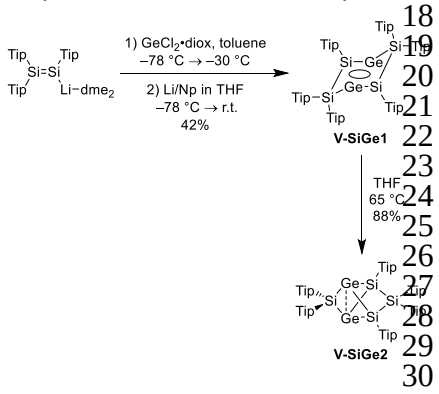
Recently, functionalization of the Si2, Si4 and Si6 atoms in **V-Si2** has been developed.[85]

In 2014, the Wesemann group isolated the isostructural tin analogue $Sn_6(Tip)_6$. The reaction of $TipSnH_3$ with a carbene proceeded at –40 °C, and after workup crystals of **V-Sn1** were gained in 15% yield (Scheme 40).[86]



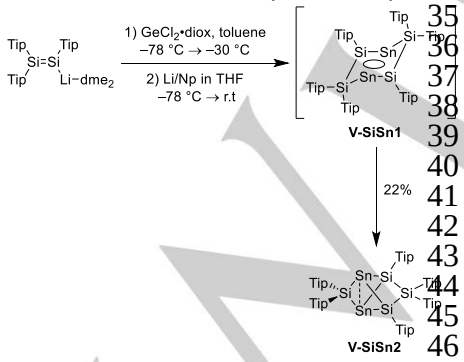
Scheme 40. Preparation of **V-Sn1**.

Heteronuclear isomers $E_2Si_4(Tip)_6$ (E = Ge, Sn) were also reported by the group of Berger and Scheschkewitz.[87] The reaction of a lithium disilenide with $GeCl_2$·dioxane and subsequent reduction with one equivalent of Li/Np resulted in the formation of the digermatetrasila-analogue **V-SiGe1** (Scheme 41). In contrast to **V-Si1**, **V-SiGe1** slowly rearranges to the propellane type global minimum isomer **V-SiGe2** in solution even at room temperature, and conversion completes after 12 hours at 65 °C.



Scheme 41. Synthesis of **V-SiGe1** and rearrangement to **V-SiGe2**.

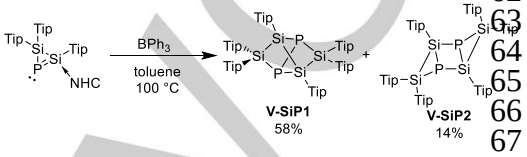
In the case of E = Sn, the propellane-type species **V-SiSn2** was directly obtained, suggesting that **V-SiSn1** may be generated as the transient intermediate (Scheme 42).



Scheme 42. Synthesis of **V-SiSn2** thorough **V-SiSn1**.

6.3. Group 14/15

In 2019, Scheschkewitz and co-workers reported the synthesis of two Si_4P_2 isomers.[88] Dimerization of the Si_2P three-membered ring precursor by heating in the presence of Lewis acid BPh_3, gave a mixture of **V-SiP1** (58%) and **V-SiP2** (14%) (Scheme 43). **V-SiP1** and **V-SiP2** correspond to the global minimum isomer (**V-Si2**) and a chair-like conformation (**V-Si1**) of hexasilabenzene, respectively. **V-SiP1** possesses a typical single P-P bond (2.243(1) Å), while the Si-P (2.281(1) – 2.300(1) Å) and Si-Si bonds (2.354(1) –2.462(1) Å) are slightly longer than the corresponding typical single bonds. **V-SiP2** features a centrosymmetric diamond-shaped Si_2P_2 moiety with two short Si-P (2.2372(4) Å) and two long Si-P bonds (2.3210(4) Å).



Scheme 43 Formation of Si_4P_2 isomers **V-SiP1** and **V-SiP2**.

7. Conclusion

Synthetically, oligomerization of the proper precursor via reductive dehalogenation has been widely employed for the construction of inorganic benzene valence isomers thus far. Of importance is the control of the oligomerization process which is achieved by optimizing the reaction condition as well as tuning the steric and electronic properties of the substituents.

Currently, for the benzene analogues (Table 3, Type-**I**), the isolated examples are limited to the heteroatomic systems ($E_3E'_3$ or $E_2E'_4$), and the homoatomic inorganic system (E_6), similar to benzene, has never been described. By contrast, all of the reported inorganic prismanes (Table 6, Type-**II**) are based on the homoatomic and heavier group 14-element system. The reported inorganic Dewar-type benzenes (Table 7, Type-**III**) are limited to the B_3N_3 skeleton involving B−N single and double bonds. So far, only a silicon analogue of benzvalene (Table 8, Type-**IV**) has been isolated. It is explicit that construction of inorganic benzene valence isomers is still synthetically challenging, and the study of the reactivity of most derivatives has still remained unexplored.

Electronically, since totally 18 electrons are required in principle as the skeletal electrons of the benzene valence isomers, incorporation of group 13 elements into the skeletal framework has to be accompanied by the addition of electrons, by combining with group 15 elements or two-electron donors (Lewis bases or by reduction). The former induces the polarization of the skeletal bonds whereas the latter leads to electron-rich molecules. Because of its larger atomic radii (longer bond distance), as well as, the flexibility of the oxidation state compared with carbon, the uses of heavier elements in the skeletal core allows access to the diverse geometric motives (Table 10, Type-**V**), that cannot be accessible with the carbon (C_6) system. Collectively, the electronic feature (for instance its aromatic nature) of inorganic derivatives may differ significantly from that of the carbon-based counterparts, which indicates their potential applications in the various fields such as material science. We predict the future of inorganic benzene valence isomers is bright and fascinating.

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Table 3. The selected structural parameters and chemical shifts of inorganic benzenes **I**.

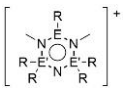
		E	E'	R	R'	E–E' (Å)	Ring conformation	E NMR (ppm)	E' NMR (ppm)	λ_{max} (nm)	ref
	I-BN1	B	N	H	H	1.4355(21)	planar	28.5	-	203	13, 47
	I-BP2	B	P	Mes	Cy	1.833(6)–1.851(6)	planar	52.6	51.9	-	17, 18
	I-BP3	B	P	Mes	Ph	1.839(3)–1.845(2)	planar	52.5	42.5	-	18
	I-BP4	B	P	Mes	Mes	-	planar	49.6	40.4	-	18
	**I-BP5**	B	P	Mes	tBu	-	planar	53.9	60.5	-	18
	I-BP6	B	P	Ph	Mes	-	planar	50.2	14.5	-	18
	I-AlN1	Al	N	Me	Dip	1.782(4)	planar	168	-	-	20
	I-AlP1	Al	P	Mes*	Ph	2.323(3)–2.336(3)	non-planar boat	-	−144.2	-	21
	I-AlAs1	Al	As	Mes*	Ph	2.418(3)–2.435(3)	non-planar boat	-	-	-	21
	I-GaP1	Ga	P	triph	Cy	2.283(4)–2.338(5)	non-planar	-	−61	-	22
	I-BO1	B	O	H	-	1.3758(21)	planar	-	-	-	27
	I-BS1	B	S	SH	-	1.795–1.824	planar	56.56	-	-	32
	**I-BS3**	B	S	Br	-	1.741(28)–1.879(30)	planar	54.45	-	-	32
	I-BSe1	B	Se	Ph	-	1.93 (ave.)	planar	-	-	-	34
	I-GeN1	N	Ge	Dip	-	1.859 (2) (ave.)	planar	-	-	-	36
	I-PN1	P	N	Cl	-	1.581(5)	Nearly-planar	19.3	-	200	41, 48
	**I-SiP1**	Si	P		-	2.1512(12)–2.1608(13)	planar	70.6	−241.9	332	35
	I-SiAs1	Si	As		-	2.157(3)–2.367(3)	planar	70.4	-	-	35
	**I-BN3**	B	N	Cl/PMe_3	Mes	B–N: 1.432(5), 1.464(5) B–B: 1.622(6)	planar	38.6/20.8	-	607	15
	**I-BNP1**	B	P	Cl	Cl	B–N: 1.429(10) N–P: 1.624(6)	planar	31.7	35.0	-	23

Table 4. The selected NICS values of inorganic benzenes **I**.

		E	E'	R	R'	NICS(0)	NICS(1)	level
	**I-CC1**	C	C	H	H	–8.2	–10.4	a
	I-BN1	B	N	H	H	–1.9	–2.7	b
	I-BP'	B	P	H	H	–8.3	–6.9	b
	I-AlN'	Al	N	H	H	–2.1	–0.6	b
	I-AlP'	Al	P	H	H	–4.8	–3.2	b
	I-AlAs'	Al	As	H	H	–5.5	–3.9	b
	I-GaP'	Ga	P	H	H	–5.2	–3.8	b
	**I-BO1**	B	O	H	-	–0.3	–1.9	b
	I-BS'	B	S	H	-	–1.3	–3.1	b
	I-BSe'	B	Se	H	-	–0.9	–2.7	b
	I-PN1	P	N	H	-	–1.2	0	a
	**I-PN'**	P	N	Cl		–4.9	–3.1	a
	I-SiP1	Si	P		-	–4.7	–2.8	c
	I-SiAs1	Si	As		-	–5.3	–3.4	c
	**I-BN3**	B	N	Cl/PMe3	Mes	–3.93	–4.59	d

[a] Calculated at the PBE0/ 6-311++G** level of theory. Ref [51b].

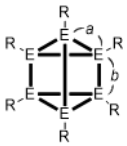
[b] Calculated at the B3LYP/6-31+G level of theory. Ref [51a].

[c] Calculated at the BP86/TZVPP level of theory. Ref [35].

[d] Calculated at the B3LYP/6-311G level of theory. Ref [15].

Table 6. The selected structural parameters of inorganic prismanes **II** (ED = electron diffraction, XRD = X-ray diffraction).

	E	R	*a* (Å)	*b* (Å)		ref
	C	H	1.507	1.549	calcd.[a]	60
		H	1.500	1.585	ED	61
		Me	1.540	1.551	ED	62
	Si	H	2.359	2.375	calcd. [a, (b)]	60
II-Si1			2.374–2.387	2.365–2.389	XRD	56
II-Si2			2.3656(14)–2.3906(14)	2.3667(14)–2.3789(13)	XRD	57
II-Si3			2.352(8)–2.371(8)	2.356(9)–2.362(9)	XRD	58
	Ge	H	2.502	2.507	calcd. [b]	60
II-Ge1			2.578(6)–2.584(6)	2.516(6)–2.526(6)	XRD	63
II-Ge2			2.497(1)–2.507(1)	2.465(1)–2.475(1)	XRD	56
	Sn	H			calcd. [b]	60
II-Sn1			2.907(1)–2.941(1)	2.903(1)–2.907(2)	XRD	64
II-Sn2			2.839(7)–2.866(10)	2.811(10)–2.827(10)	XRD	66
II-Sn3			3.1549(9)–3.2873(12)	2.9693(12)–3.1203(10)	XRD	67



[a] Calculated at the RMP2/6-31G(d) level of theory.

[b] Calculated at the CEP-31G(d) level of theory.

Table 7. The selected structural parameters and chemical shifts of inorganic Dewar benzene isomers **III**.

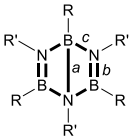
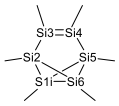
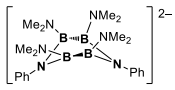
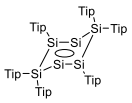
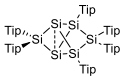
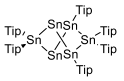
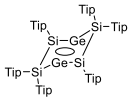
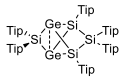
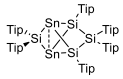
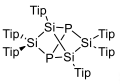
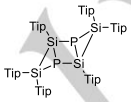
		R	R'	*a* (Å)	*b* (Å)	*c* (Å)	^{11}B NMR (ppm)	ref
	III-BN1	iPr	tBu	1.752(5)	1.364(6)–1.384(6)	1.548(5)–1.564(5)	31.1 (14N: –244)	69
	**III-BN3**	tBu	iPr	-	-	-	29.9 35.9, 13.1 (–50 °C)	72
	III-BN4	Ph	tBu	1.741(4)	1.370(4)–1.376(4)	1.539(4)–1.556(4)	30.0	73
	III-BN6	C_8H_{15}	Me	-	-	-	30.8	75
	/III-BN6'	Me	C_8H_{15}				22.6, 33.4 (–60 °C)	

Table 8. The selected structural parameters of **IV-Si1**.



Si3−Si4	2.212(2) Å
ΣSi3, ΣSi4	349.5°, 352.2°
trans-bend angle	42.5°, 36.5°
twist angle	16.2°

Table 10. The selected structural parameter and chemical shift of other inorganic benzene isomers **V**.

	structure	Bond length (Å)	NMR (ppm)	ref
V–BN1		B–B: 1.673(9)–1.700(9) B–N: 1.466(7)–1.535(8)	^{11}B: 12.9	80
V–Si1		(square) Si–Si: 2.3034(5), 2.3275(5) (triangle) Si–Si: 2.3375(5)–2.3581(5)	^{29}Si: 124.6, –84.8, –89.3	81
V–Si2		Si–Si: 2.3536(6)–2.3819(5) Si···Si: 2.7076(8)	^{29}Si: 174.6, 14.8, 7.5, –274.2	83
V–Sn1		Sn–Sn: 2.7992(4)–2.8890(4) Sn···Sn: 3.3704(4), Sn(2)–Sn(5) 3.5729(4)	–	86
V–SiGe1		(square) Si–Ge: 2.3601(9), 2.3878(9) (triangle) Si–Si: 2.3402(12), Si–Ge: 2.4297(10)	^{29}Si: 185.8, –88.6	87
V–SiGe2		Si–Si: 2.3722(5) Si–Ge: 2.4161(4)–2.4566(4) Ge···Ge: 2.7820(2)	^{29}Si: 236.0, 29.8, 14.5	87
V–SiSn2		Si–Si: 2.3856(10) Si–Sn: 2.6017(8)–2.6565(8) Sn···Sn: 3.1099(3)	^{29}Si: 284.4, 52.7, 23.8 ^{119}Sn: –1260.19	87
V–SiP1		Si–Si: 2.354(1)–2.462(1) P–Si: 2.281(1)–2.300(1) P–P: 2.243(1)	^{29}Si: 32.1, –1.4 ^{31}P: –120.6, –134.4	88
V–SiP2		(square) Si–P: 2.2372(4), 2.3210(4) (triangle) Si–Si: 2.3210(4), Si–P: 2.3002(4)	^{29}Si: –83.6, –91.4 ^{31}P: –182.9	88