Structural variations in aromatic 2π -electron three-membered rings of the main group elements

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Abstract. Structural variations of different 2π -aromatic three-membered ring systems of main group elements, especially group 14 and 13 elements as compared to the classical description of cyclopropenyl cation has been reviewed in this article. The structures of heavier analogues as well as group 13 analogues of cyclopropenyl cation showed an emergence of dramatic structural patterns which do not conform to the general norms of carbon chemistry. Isolobal analogies between the main group fragments have been efficiently used to explain the peculiarities observed in these three-membered ring systems.

Keywords. Three-membered ring; 2π -aromaticity; isolobal analogy; non-planarity.

1. Introduction

Thought processes in the structural chemistry of main group elements are influenced largely by the chemistry of the first row elements, especially that of carbon. This is especially true of aromaticity. Benzene is the ideal aromatic compound to which all other systems are compared. This remains true even for 2π -electron aromatics. Synthesis and structural characterization of the planar 2π -aromatic cyclopropenyl cation and its derivative was the beginning of this exploration.¹ The electronic structure description of cyclopropenyl cation in terms of the Walsh orbitals for the bonding in the in-plane three-membered ring skeleton,² the three $2c-2e$ bonds of the exocyclic bonds and the 2π -aromaticity³ have stood in good stead over the years. Isoelectronic replacement of a carbon of the ring by other group elements is expected to retain this description. Yet, experimental observations indicate dramatic variations that exist outside the norms of carbon chemistry. The basic unit of tetrahedral tetracoordination of carbon is not followed among many heavier elements of the same group. Over the years, we have studied a variety of saturated and unsaturated three-membered rings involving main group elements. Our attempt has been to start with two well-known organic structures, the cyclopropenyl cation (**1**) and the cyclopropane (**2**), and explore the dramatic variations that emerge when the carbon atoms are replaced by other elements of the same period such as boron and heavier elements of their groups (figure 1). We

concentrate here more on instances where there is substantial deviation from the description of cyclopropenyl cation.

It is difficult to imagine that Ge_3H_3^+ , and heavier analogues prefer a structure with bridging hydrogens, **3** (figure 2).⁴ Nor is it possible to guess that Pb_3H_6 , while retaining the three-membered ring structure, twists each PbH_2 group cyclically to obtain a C_{3h} structure **4** (figure 2), even though a bridged structure **5** (figure 2) is lower in energy.⁵ While these appear abnormal, there are several X-ray structures of the three-membered rings which belong to these categories. For example, $\text{Ga}_3\text{R}_3^{2-}$ (**6**, figure 2) which is isoelectronic to C_3H_3^+ has a C_{3h} geometry.⁶ Similarly, the plumbacyclopropane effectively has a three-membered ring skeleton with C_{3h} symmetry. We review here the structural patterns that emerge in these substitutional processes and explain these structural variations, largely selected from our results.

2. Structures of cyclopropenyl cation and its heavier analogues

We begin with a study to see how far the structure of C_3H_3^+ serves as a general model for the heavier analogues A_3H_3^+ ($\text{A} = \text{Si}, \text{Ge}, \text{Sn}$ and Pb). A detailed study on group 14 analogues of the cyclopropenyl cation indicated that C_3H_3^+ and Si_3H_3^+ prefer the classical D_{3h} structure (**7**, figure 3) as the most stable ones.^{4,7} However, Ge_3H_3^+ , Sn_3H_3^+ , and Pb_3H_3^+ adopt a H-bridged C_{3v} structure (**8**, figure 3) over classical D_{3h} structure. All H-bridged C_{3v} structures (**8**) are minima with the exception of C_3H_3^+ , for which it is not a stationary

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Figure 1. Structure of cyclopropenyl cation (**1**) and cyclopropane (**2**).

point on the Potential energy surface (PES). Upon optimization, it leads to another H-bridged planar structure with D_{3h} symmetry (**10**, figure 3), which is a third-order saddle point. The NBO analysis of the H-bridged non-planar C_{3v} structures of $A_3H_3^+$ (**8**) shows that the A–H bond atomic orbitals for A = Ge, Sn and Pb, have nearly pure p -character and high percentage of s -character of the lone pair orbitals. Greater stability of the bridged C_{3v} structure over classical D_{3h} structure for heavier species is due to their reluctance of using the valence s orbital in bonding. Increase in A–A bond length reduces the strength of π bonding. Higher preferences of the bridged structures as compared to the classical structure for heavier analogues of $C_3H_3^+$ can also be analysed in terms of the preference of protonation of A_3^{2-} anion (**11**, scheme 1), which has two different protonation sites. Structures **7** and **8** can be formed by either protonating at the lone pairs (which leads to the A–H bond formation in **7**) or at the A–A bond giving rise to A–H–A bridges in **8** or **9/10** as shown in scheme 1. As we go down the group, the heavier elements tend to prefer divalent arrangements owing to their propensity to hold lone pairs on themselves. This behaviour is reflected in the % of s orbital contribution in the A_3^{2-} lone pairs, which increases in the order $47 > 72 > 80 > 82 > 88$ as we go from C to Pb. Hence, protonation at the A–A bond will

be easier than that of the lone pairs for heavier elements which eventually leads to the bridged structure. Thus, heavier elements have periodic variations of their own.

3. Group 13 analogues of cyclopropenyl cation

The group 13 analogues of cyclopropenyl cation where only one carbon atom is replaced are neutral. The boron analogue of cyclopropenyl cation, borirene, C_2BH_3 (**12**, figure 4) is estimated to be stable and its derivative has been synthesized (**13**, figure 4).⁸ Synthesis of borirene by the reaction of pulsed beam of boron atoms with unsaturated hydrocarbons such as ethylene has been reported.⁹ The resonance stabilization energy of borirene is only about 70% of that of $C_3H_3^+$.¹⁰ The gas phase synthesis of neutral and ionic AlC_2H_4 provided another dimension to the three-membered ring chemistry.¹¹

Schleyer and coworkers calculated the relative energies of the isomers of isoelectronic diboriranyl anion, $CB_2H_3^-$ (**14**, figure 4) and showed that the three-membered ring structure with C_{2v} symmetry is the most stable one.¹² Though the parent diboriranyl anion has not yet been identified conclusively, its derivative with bulky substituents has been successfully isolated and characterized by NMR (**15**, figure 4).¹³

Replacement of the CH groups by isolobal BH^- groups in the $C_3H_3^+$ gives $B_3H_3^{2-}$. Computational studies show that the minimum energy structure of $B_3H_3^{2-}$ has a D_{3h} geometry (**16**, scheme 2) similar to that of $C_3H_3^+$ ion.¹⁴ Sequential protonation of $B_3H_3^{2-}$ generates structures $B_3H_4^-$, B_3H_5 and $B_3H_6^+$ (scheme 2).^{14a,d,e,15} All these species are aromatic in nature with 2π electrons. The most stable isomer of $B_3H_4^-$ has planar structure (**17**) with one bridging hydrogen atom. Second protonation on $B_3H_3^{2-}$ generates B_3H_5 (**18**), which has a planar 2π -aromatic structure with two bridging hydrogen atoms. It is expected that the introduction of the third proton will give rise to a structure where all the three

Figure 2. Structure of cationic $Ge_3H_3^+$ (**3**), the skewed and H-bridged structure of Pb_3H_6 (**4** and **5**) and dianionic $Ga_3R_3^{2-}$ (**6**).

	7 (D_{3h})	8 (C_{3v})	9 (D_{3h})	10 (D_{3h})
C	0.0 (0)	-	-	194.8 (3)
Si	0.0 (0)	23.7 (0)	55.6 (3)	53.5 (3)
Ge	0.0 (0)	-17.4 (0)	5.5 (3)	-
Sn	0.0 (1)	-32.4 (0)	-15.7 (3)	-
Pb	0.0 (3)	-63.3 (0)	-48.1 (3)	-

Figure 3. Schematic representation of cyclic isomers of $A_3H_3^+$ ($A = C - Pb$) cation. Relative energies in kcal/mol, number of imaginary frequencies in parentheses.

Scheme 1. Formation of classical (7) and non-classical bridged structures (8, 9 or 10) through protonation of A_3^{2-} anion (11).

Figure 4. Borirene (12), derivative of borirene (Mes = Mesityl group) (13), Diboriranyl anion (14), and its derivative (15) ($R = Si(CH_3)_3$, $R_1 = C(CH_3)_3$).

bridging and three terminal hydrogen atoms remain in the plane of the B_3 ring. However, it is found that the planar D_{3h} structure (20, figure 5) is a transition state and the non-planar C_{3v} aromatic structure (19, figure 5) is the most stable isomer. This is regarded as the first three-membered nonplanar 2π -aromatic system, which is known in gas phase and its derivative was recently synthesized.¹⁶

What is the reason for the non-planarity of the bridging and terminal hydrogens in the most stable structure of $B_3H_6^+$? Detailed electronic structures of B_3H_5 and $B_3H_6^+$ provide an explanation. The Molecular Orbitals (MOs) of B_3H_5 can be constructed from B_3H_3 and H_2 fragment MOs. The three in-plane Walsh orbitals (a'_1 and e') and the π -MO (a'_2) of the B_3H_3 ring are shown in figure 6.

Scheme 2. Sequential protonation of $\text{B}_3\text{H}_3^{2-}$ to B_3H_6^+ .

Interactions of degenerate e' orbitals of the B_3H_3 ring with the bonding and antibonding MOs of H_2 lead to stabilization of the respective MOs. Similarly, the MOs of planar B_3H_6^+ can be constructed from B_3H_3 and H_3^+ fragment MOs.¹⁷ The degenerate MOs of the H_3^+ find a profitable interaction with the degenerate e' orbitals of B_3H_3 . On the other hand, the a'_1 orbitals of planar B_3H_3 and H_3^+ fragments do not interact strongly because they are directed away from each other. The a'_1 orbital of H_3^+ cannot interact with the π -MO of the borocyclic ring because it is in the nodal plane of the π -MO and hence overlap is zero. A correlation diagram between the planar and the non-planar B_3H_6^+ shows a dramatic stabilization of the π -MO in going from planar (D_{3h}) to non-planar (C_{3v}) structure (figure 7).¹⁷ In the non-planar structure, the totally symmetric MO (a'_1) of H_3^+ will find the right symmetry to interact with the π -MO of B_3H_3 ring and hence, stabilizes it.

Steric repulsion between the terminal hydrogen and the bridging hydrogen in the planar structures may also contribute to their instability over the non-planar

structure. Distance between the terminal hydrogen (H_t) and the bridging hydrogen (H_b) increases from 1.88 Å, which is an unusually short H—H non-bonded distance¹⁸ to 2.08 Å as we go from planar to non-planar B_3H_6^+ , and hence steric repulsion is minimized. In this context, it is important to note that substituents have a large influence on the structure and stability of the three-membered borocyclic rings. *Ab initio* calculations showed that the lithiated derivatives of B_3H_6^+ prefer a planar structure.¹⁷

Isolobal analogy has been a powerful tool to build bridges between organic and inorganic chemistry. Apart from these, the analogy has been instrumental in predicting new molecules with various unique bonding patterns. For example, the Dewar–Chatt–Duncanson (DCD) model explains the bonding in metal–olefin π complexes through σ donation and π back donation between ligand and metal. According to this model, the back donation happens from filled metal d-orbital to the π^* orbital of the ligand. However, isolobal replacement of B–H group in B_3H_5 by appropriate metal fragment makes an interesting case. Replacement of one of the B–H fragments in B_3H_5 by 14 electron isolobal transition metal fragments such as $\text{Cr}(\text{CO})_4$, $\text{Fe}(\text{CO})_3$ or $\text{Co}(\text{Cp})$ leads to the structures **21–23** (figure 8) in which the B–B distances decrease (1.64 Å, 1.60 Å and 1.60 Å for complex **21**, **22** and **23**, respectively) as compared to the same (1.75 Å) in isolated planar B_2H_4 molecule (**24**).¹⁹ The bonding in **21** can be described by the interaction between the planar B_2H_4 fragment and the $\text{Cr}(\text{CO})_4$ fragment. The isolated planar B_2H_4 fragment has a vacant π MO (LUMO). The interaction diagram (figure 9) for complex **21** shows that the B_2H_4 acts as a four electron donor where the 2 B–H σ bonds ($1b_1$ and $1a_1$) donate their electron pairs to the vacant d-orbitals ($1b_1$ and $2a_1$) of the $\text{Cr}(\text{CO})_4$ fragment. Contrastingly, in this case, the back donation occurs from metal d-orbital ($1b_2$) to the vacant π MO (not π^* MO) of B_2H_4 , resulting

Figure 5. Structures **19** and **20**, relative energies (kcal/mol) at the B3LYP/6-311++G** level of theory and the number of imaginary frequencies (in parentheses) for B_3H_6^+ .

Figure 6. MOs of B_3H_3 and H_3^+ fragments.

in decrease in the B–B bond length. Thus, we witness a unique case of bonding in this complex in which reversal of popular DCD model is observed. Following the successful synthesis of a B–B triple bonded molecule,²⁰ this has been used to form a π complex with platinum, which is a novel π system where the B–B π bond is strengthened due to back π donation from metal fragment,²¹ supporting such reversal of DCD model.

The three-membered rings with 2π electrons take another dimension by the development of silaboranes, molecules composed of silicon, boron and hydrogen. Boron and silicon which are diagonally related in the periodic table are expected to exhibit much more interesting chemistry when they form mixed hydrides. The electronegativity of B and Si (2.0 and 1.8, respectively) are quite comparable. A novel entry to the compounds of silaboranes emerged with the analogy between the trivalent boron and divalent silicon.²² The isolobal analogy between the trivalent boron and divalent silicon is shown in scheme 3.²²

The two fragments, BH_3 and SiH_2 are termed as isolobal, where one of the B–H bond pair orbital in BH_3 is equated to the lone pair orbital in SiH_2 , leaving the perpendicular p orbital in BH_3 and SiH_2 vacant. Based on this isolobal analogy, the structure

of SiB_2H_4 (**25**, figure 10a)²³ can be justified from B_3H_5 (**18**) by equating a B–H bond to silicon with

Figure 7. Correlation diagram showing a dramatic stabilization of the π -MO in going from planar (D_{3h}) to nonplanar (C_{3v}) structure.

Figure 8. Structures of (a) $\text{Cr(CO)}_4\text{B}_2\text{H}_4$ (**21**), $\text{Fe(CO)}_3\text{B}_2\text{H}_4$ (**22**), $\text{Co(Cp)B}_2\text{H}_4$ (**23**) and (b) isolated B_2H_4 (**24**).

Figure 9. Interaction diagram showing the interaction between B_2H_4 and Cr(CO)_4 fragments in $\text{Cr(CO)}_4\text{B}_2\text{H}_4$ complex.

Scheme 3. Schematic representation of isolobal analogy between BH_3 and SiH_2 .

a lone pair. It has been found that 2π -aromatic structures with divalent silicon are lower in energy than the conventional H-bridged structure (**26**, figure 10a) envisaged for SiB_2H_4 . In fact, the structure **26** is a transition state, unlike the carborane (**28**, figure 10b), where it is reported to be a minimum.^{15a} Tracing the direction of the imaginary frequency of **26** leads to a low symmetry structure **27**, in which all the hydrogens

Figure 10. (a) Isomers of SiB_2H_4 and most stable structure of (b) CB_2H_4 and (c) Si_2BH_3 . Relative energies (kcal/mol) at MP4/6-31G* level of theory, number of imaginary frequencies in parentheses.

Figure 11. Most stable isomers of $\text{Al}_3\text{H}_3^{2-}$ (30) and $\text{Ga}_3\text{H}_3^{2-}$ (31).

Scheme 4. Interaction of the σ lone pairs with the p orbitals of Ga-H fragments.

lie outside the BBSi plane. The structure 27 is 17.5 kcal/mol higher in energy than the most stable isomer (25) of SiB_2H_4 at MP4/6-31G* level of theory. The chemistry of three-membered silaborane has been extended by studying the isomers of Si_2BH_3 ,²⁴ the neutral analogue of Si_3H_3^+ . A cyclic 2π electron delocalized structure (29, figure 10c) with a planar tetra-coordinated boron and a $3c-2e$ Si-H-Si bond is reported as the global minimum.²⁴

It is evident that there is a significant difference in the silicon chemistry as compared to the carbon analogue. It has been found to be true for the elements of group 13 also. Study of the homocyclic three-membered

hydrides of group 13 elements (B, Al, Ga) showed that the three-membered ring structures composed of Al and Ga exhibit different structural properties in comparison to boron.²⁵ For example, the most stable structures of $\text{Al}_3\text{H}_3^{2-}$ (30, figure 11) and $\text{Ga}_3\text{H}_3^{2-}$ (31, figure 11) are the hydrogen-bridged structures with planar tetra-coordinated heavy atoms; whereas for $\text{B}_3\text{H}_3^{2-}$, a structure with three terminal hydrogens is the global minimum. These isomers (30 and 31) are 1.8 and

Figure 12. Classical D_{3h} structures of $\text{Al}_3\text{H}_3^{2-}$ (32), $\text{Ga}_3\text{H}_3^{2-}$ (33) and the C_{3h} structure of $\text{Ga}_3\text{H}_3^{2-}$ (6).

Figure 13. Most stable structures of $B_3H_n^m$, $B_2AlH_n^m$, $BAl_2H_n^m$ and $Al_3H_n^m$ ($n = 3 - 6$, $m = -2$ to $+1$) calculated at B3LYP/6-311++G** level of theory.

6.8 kcal/mol more stable than the classical D_{3h} structures (32 and 33, figure 12) for Al and Ga, respectively. Although the structure similar to the global minima of $Al_3H_3^{2-}$ and $Ga_3H_3^{2-}$ for $B_3H_3^{2-}$ is a minimum, it is 58 kcal/mol higher in energy than the most stable one at B3LYP/6-311+G* level of theory, which highlights the dramatic difference between B and its heavier analogues. It is interesting to note that an isomer similar to 30 and 31 is the global minimum for the isoelectronic Si_2BH_3 (29).²⁴ Though the classical D_{3h} structure 32 for Al is also minimum, a similar

structure 33 for Ga is a transition structure for the inter-conversion of C_{3h} structures (6); the energy difference between 33 and 6 is negligible. A similar distortion from D_{3h} to C_{3h} is also seen in Pb_3H_6 .²⁶ The experimentally determined X-ray structures ($Na_2[Ga_3R_3]$ and $K_2[Ga_3R_3]$, where $R = 2,6-Mes_2C_6H_3$) have C_{3h} symmetry.⁶ The bonding picture of 6 can be constructed from Ga–H fragments in their singlet ground states with a σ lone pair and two p orbitals in orthogonal planes. The σ lone pair in Ga has high percentage of s character and does not prefer to

Figure 14. Protonation route of $B_2AlH_n^m$ ($n = 3 - 6$, $m = -2$ to $+1$) isomers. Relative energies are calculated at B3LYP/6-311++G** level of theory.

form the traditional sp^2 hybrid orbitals which are commonly observed in carbon and boron. Thus, the bonding of this structure (**6**) can be explained as a donor–acceptor complex of three singlet Ga–H units as shown in scheme 4, in which the lone pair of one Ga–H unit is donated to the vacant p orbital of the

adjacent Ga–H unit. The Ga–Ga distance in **6** is about 0.07 Å longer than those in the experimental structures, $Na_2[Ga_3R_3]$ and $K_2[Ga_3R_3]$.

Greater structural diversity has been observed when we go from the homocyclic three-membered ring systems to heterocyclic systems containing B and Al. The

most stable structures of $B_3H_n^m$, $B_2AlH_n^m$, $BAI_2H_n^m$ and $Al_3H_n^m$ ($n = 3-6$, $m = -2$ to $+1$) are shown in figure 13. A dramatic structural alteration is observed as boron atoms in $B_3H_n^m$ are systematically substituted by aluminum atoms.²⁷ The most stable structure of $B_3H_3^{2-}$ has a classical D_{3h} geometry. Similar structures for $B_2AlH_3^{2-}$, $BAI_2H_3^{2-}$ and $Al_3H_3^{2-}$ are higher energy minima on the PES of the respective species. A significant alteration in the most stable structure (**34**) occurs upon substitution of one of the boron atoms of $B_3H_3^{2-}$ by an aluminum atom. The most stable structure of $B_2AlH_3^{2-}$ has a bridging hydrogen atom at the Al–B bond and a lone pair on the aluminum atom. Such structural alteration has emerged to accommodate the lone pair on the aluminum atom which results in planar tetracoordinated boron. Further substitution of the second boron atom by an aluminum atom results in $BAI_2H_3^{2-}$ (**38**). The most stable structure rearranges itself to attain a lone pair on both the aluminum atoms by efficiently keeping the bridging hydrogen at the weaker Al–Al bond. A similar structure is most stable for $Al_3H_3^{2-}$ (**30**), but it is a first-order saddle point for $B_2AlH_3^{2-}$.

Unlike $B_3H_3^{2-}$ which has only one site (B–B bond) available for protonation, the most stable structure of $B_2AlH_3^{2-}$ (**34**) has three different protonation sites (figure 14). These are the lone pairs on aluminum atom, the Al–B bond and the B–B bond. The protonation at the Al–B bond leads to the most stable structure of $B_2AlH_4^-$ (**35**), which has two bridging hydrogens at the Al–B bonds and a lone pair on aluminum atom. Similar structure has been observed as first-order and second-order saddle points for the homocyclic boron and aluminum analogs, respectively. Protonation on the aluminum lone pair leads to the structure **51**, which is 14.9 kcal higher in energy than the global minimum structure; whereas protonation at the B–B bond converges to the global minimum structure (**35**).

Structure **35** can undergo protonation either at the B–B bond or at the lone pair on aluminum.

Scheme 5. Interaction of Al lone pair with the vacant π -MO of B_2H_4 fragment in **46**.

Protonation at the B–B bond gives rise to the most stable structure of B_2AlH_5 (**36**). It has three out-of-plane bridging hydrogen atoms and a lone pair on aluminum. It should be noted that the first and the second protonations on the most stable structure of $B_2AlH_3^{2-}$ retain the lone pair on aluminum atom (figure 14). The di- and triprotonated structures, B_2AlH_5 (**36**) and $B_2AlH_6^+$ (**37**) are similar to the most stable structure of $B_3H_6^+$ (**19**). Planar alternatives of these structures are second-order saddle points on the PES. The explanation given for the higher stability of non-planar structures over the planar one for the tri-bridged structure of $B_3H_6^+$ holds good for structures **36** and **37** also. Protonation at the aluminum lone pair of structure **35** generates an interesting di-bridged structure (**56**, figure 14), where the bridging and terminal hydrogen atoms are not in the plane of the three-membered ring. Similar structure does not exist for B_3H_5 . Electronic structure of the di-bridged B_2AlH_5 (**56**) will be discussed in detail later.

The most stable mono-protonated structure of $BAI_2H_3^-$ (**39**) is similar to the most stable structures of B_2AlH_5 (**36**), $B_2AlH_6^+$ (**37**) and $B_3H_6^+$ (**19**) as all of these structures have three out-of-plane bridging hydrogens. It has lone pairs on both Al atoms, similar to the most stable structure of $BAI_2H_3^{2-}$ (**38**). The di- and

Figure 15. Di-protonated structures of B_2AlH_5 (**56** and **63**), BAl_2H_5 (**40** and **64**) and Al_3H_5 (**43** and **65**) showing the structures with non-planar hydrogen atoms are stabler than the planar structures. Relative energies (kcal/mol) at the B3LYP/6-311++G** level of theory and the number of imaginary frequencies (in parenthesis) are given.

Figure 16. Correlation diagram showing stabilization of the π -MO in going from planar to non-planar structure.

triprotonated structures (**40** and **41**) of $\text{BAI}_2\text{H}_3^{2-}$ do not have lone pairs on aluminum atoms. The mono- and diprotonated structures of $\text{Al}_3\text{H}_3^{2-}$ (**42** and **43**) are similar to the most stable structures of B_3H_4^- (**17**) and B_3H_5 (**18**), respectively, but the bridging and the terminal hydrogens are not in the plane of the three-membered ring. The most stable structure of Al_3H_6^+ has a rather unusual structure (**44**). It has a planar tetracoordinated aluminum atom having a lone pair and two hexacoordinated aluminum atoms.

The protonation study reveals another interesting observation when we compare the di-protonated structure of $\text{B}_3\text{H}_3^{2-}$, i.e. B_3H_5 with those of mixed systems such as B_2AlH_5 and BAI_2H_5 as well as with

Al_3H_5 .^{27b} As pointed out earlier, the most stable structure of B_3H_5 is a planar di-bridged structure (**18**). Similar structures for B_2AlH_5 , BAI_2H_5 and Al_3H_5 are not minima (figure 15). The planar di-bridged structure for B_2AlH_5 (**63**) and BAI_2H_5 (**64**) are first-order saddle points whereas the same for Al_3H_5 (**65**) is a second-order saddle point (figure 15). All these structures lead to non-planar structures (**56**, **40** and **43** in figure 15) upon optimization along the direction of the imaginary frequency. It should be noted that similar non-planar structure does not exist for B_3H_5 . The bonding description given earlier to explain the structure of planar B_3H_5 is not adequate to explain the non-planarity of the structures observed for B_2AlH_5 , BAI_2H_5 and Al_3H_5 . Higher stability of the non-planar structures over planar ones for B_2AlH_5 , BAI_2H_5 and Al_3H_5 is due to the propensity of aluminum to retain the lone pair. Bonding in B_2AlH_5 can be described by the interaction between a planar B_2H_4 unit with a Al-H unit. Here, a π -type $3c-2e$ bond is formed by a donor-acceptor kind of interaction, where the lone pair of Al-H fragment donates its lone pair to the vacant π -MO of the planar B_2H_4 unit as shown in scheme 5. Unlike non-planar B_3H_6^+ , where the π -MO is stabilized through the interaction with the out-of-plane bridging hydrogens,^{15a} for B_2AlH_5 , stabilization of π -MO arises due to interaction with the lone pair of the Al-H unit. A MO correlation diagram (figure 16) between the planar and nonplanar isomers showing the stabilization of the π -MO supports this bonding scheme. Similar bonding description applies to the non-planar structures of BAI_2H_5 and Al_3H_5 .

A comparative study among the most stable structures of B_3H_6^+ , B_2AlH_5 and BAI_2H_4^- and tri-hydrogen bridged structure of $\text{Al}_3\text{H}_3^{2-}$ brings out an interesting structural relationship (figure 17). Replacing one of

Figure 17. (a) Most stable structures of B_3H_6^+ , B_2AlH_5 and BAI_2H_4^- and tri-hydrogen bridged structure of $\text{Al}_3\text{H}_3^{2-}$ showing (b) isolobal analogy between trivalent boron and divalent aluminum anion.

Figure 18. π -MO originates from π^* MOs of each CO group in $\text{C}_3\text{O}_3^{2-}$ species.

the BH groups in B_3H_6^+ (**19**) by Al^- having lone pair results in the most stable structure of BAl_2H_5 (**36**). Similarly, systematic substitutions of the other two BH groups by Al^- units lead to the most stable structure of BAl_2H_4^- (**39**) and a trihydrogen-bridged structure of $\text{Al}_3\text{H}_3^{2-}$ (**66**), respectively. The structure **66** is 7.9 kcal/mol higher in energy than the most stable structure (**30**) at B3LYP/6-311+G* level of theory.²⁵ This structural relationship indicates that there exists an isolobal

analogy between trivalent boron and divalent aluminum anion (figure 17b).

4. 2π -Aromaticity arising from π^* fragment molecular orbitals

The traditional 2π -aromaticity of three-membered rings discussed so far originates from the overlap of pure p orbitals perpendicular to the plane of the molecule. Aromaticity is also possible from the overlap of fragment molecular orbitals which are antibonding in the fragments. For example, CO has a pair of vacant π^* orbitals. In the triangular D_{3h} arrangement of $(\text{CO})_3$, bonding combination of the three π^* MOs perpendicular to C_3 plane is strongly C–C bonding and very weakly C–O antibonding. Occupancy of this MO (figure 18) gives $\text{C}_3\text{O}_3^{2-}$ which is a stable dianion and is synthesized.²⁸ A similar delocalization involving pseudo π^* orbitals of PF_3 is anticipated in the triangular $(\text{PF}_3)_3$ so that its dianion is calculated to be aromatic (see figure 19).²⁹

Figure 19. Qualitative fragment molecular orbital (FMO) diagram of $(\text{PF}_3)_3^{2-}$ showing formation of π -MO from pseudo π^* -MO of PF_3 fragments.

5. Summary

A comparative study between cyclopropenyl cation and its heavier analogues shows an emergence of fascinating structural diversity as we move down the group. It is observed that the structural pattern emerges for the heavier elements, especially beyond second group does not conform to the general norms of the carbon chemistry. For example, H-bridged structures are preferred over classical structure for heavier elements such as Ge, Sn and Pb. Preference for H-bridged structures is accounted by their tendency to retain a lone pair on them. The group 13 analogues of $C_3H_3^+$ are also discussed. Non-planarity of the bridging and terminal hydrogens for the most stable structure of $B_3H_6^+$ is due to the stabilization of the π -MO through interaction with the non-planar bridging hydrogens and minimization of steric repulsion between the terminal and the bridging hydrogen atoms. Isolobal replacement of one B–H group in B_3H_5 with 14-electron metal fragment gives rise to a unique bonding pattern, showing reversal of the famous DCD model. Isolobal analogy between tricoordinated boron and divalent silicon is very useful in explaining the structures of SiB_2H_4 . A dramatic structural diversity is observed in going from $B_3H_3^{2-}$ to $B_2AlH_3^{2-}$, $BAI_2H_3^{2-}$ and $Al_3H_3^{2-}$. This structural diversity is due to the preference of lower coordination on aluminum, higher coordination on boron and the higher multi-centre bonding capability of boron. A unique case of $(PF_3)_3^{2-}$ is observed where 2π -aromaticity originates from the overlap of pseudo π^* fragment molecular orbitals of three PF_3 groups.

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