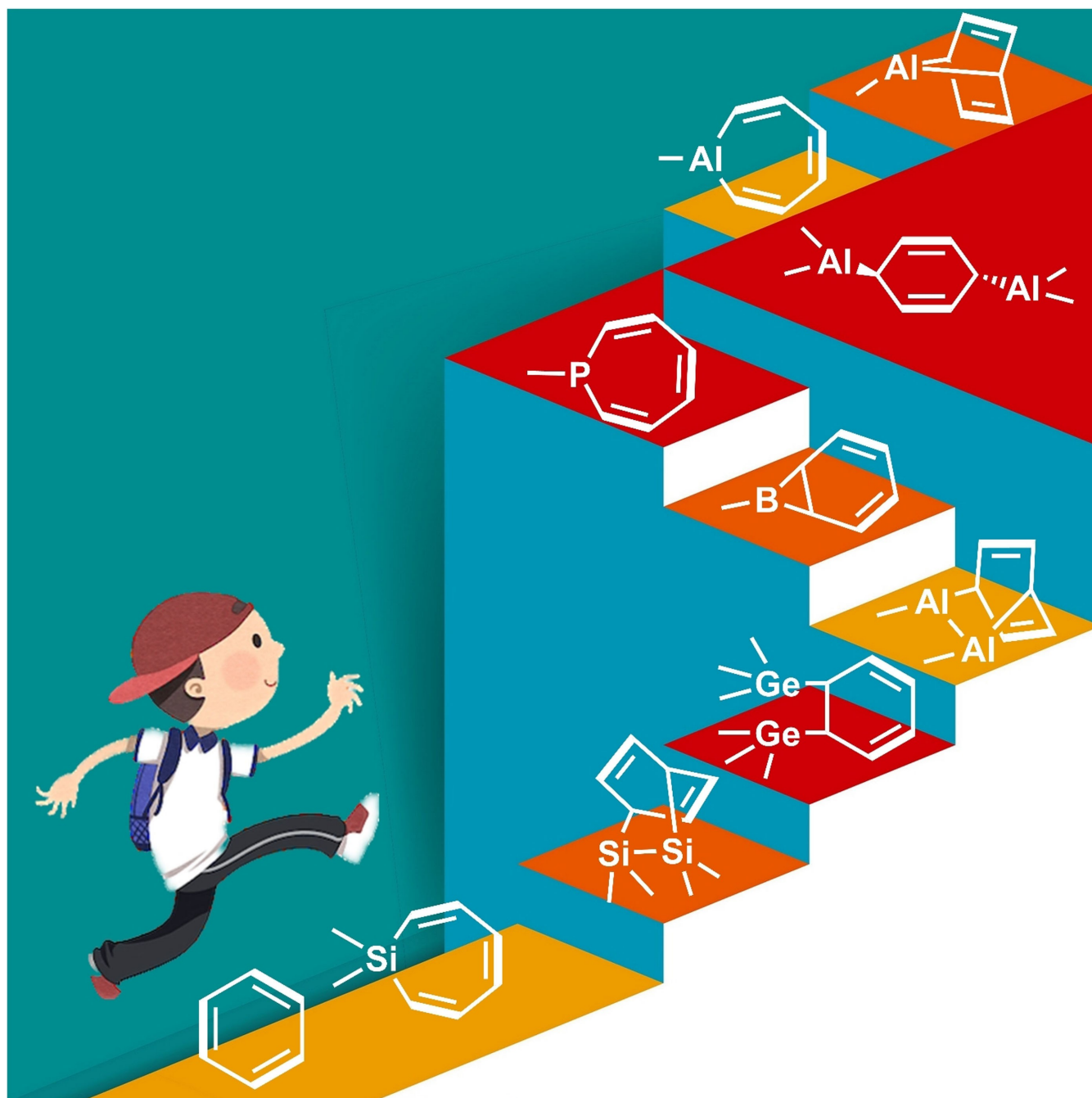


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Dearomatization of C₆ Aromatic Hydrocarbons by Main Group Complexes

Huaiyuan Zhu,^[a] Shiori Fujimori,^[a] Arseni Kostenko,^[a] and Shigeyoshi Inoue^{*[a]}

The dearomatization reaction is a powerful method for transformation of simple aromatic compounds to unique chemical architectures rapidly in synthetic chemistry. Over the past decades, the chemistry in this field has evolved significantly and various important organic compounds such as crucial bioactive molecules have been synthesized through dearomatization. In general, photochemical conditions or assistance by transition metals are required for dearomatization of rigid arenes. Recently, main-group elements, especially naturally abundant elements in the Earth's crust, have attracted attention as they

have low toxicity and are cost-effective compared to the late transition metals. In recent decades, a variety of low-valent main-group molecules, which enable the activation of stable aromatic compounds under mild conditions, have been developed. This minireview highlights the developments in the chemistry of dearomatization of C_6 aromatic hydrocarbons by main-group compounds leading to the formation of seven-membered EC_6 (E = main-group elements) ring or cycloaddition products.

1. Introduction

Aromatic compounds, i.e., $[4n+2]\pi$ electron ring systems, are fundamental chemical motifs that are widely encountered in nature and extensively utilized as essential building blocks and functional moieties in pharmaceuticals, perfumes, dyes, electronic materials, etc. Dearomatization is one of the efficient

routes for arene transformation and a key step in organic synthesis for important bioactive molecules, such as antiviral and pain management medications.^[1]

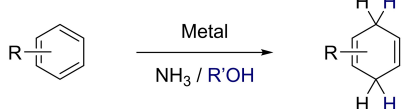
Among the notable classical approaches in arene dearomatization is the Birch reduction, a process that converts arenes into cyclohexadienes using a combination of liquid ammonia and an alcohol with an alkali metal (Scheme 1a).^[2] Likewise, the Büchner ring expansion reaction, in which seven-membered C_7 ring products are formed by the reaction of benzene and carbene species, followed by rearrangement of the corresponding norcaradiene.^[3] In the last several decades, the chemistry of dearomatization has grown significantly and has been subject to many recent reviews. In many cases, the dearomatization of arenes undergoes by (i) two-electronic processes such as dissolving metal reductions^[4] and organometallic additions^[5] or (ii) one-electronic processes such as enzymatic,^[6] oxidative,^[7] photochemical^[8] reactions and radical-radical anion coupling.^[9]

Main-group elements belonging to the s- and p-blocks in the periodic table contain some of the most naturally abundant elements in the Earth's crust. Such main-group compounds are manufactured as commercially valuable chemicals (e.g. aluminum alloy and trichlorosilane). Over the past decade, main-group element chemistry has evolved significantly, being brought into the spotlight due to the environmentally friendly and cost-effective nature of many s- and p-block elements when compared with transition metals, which are often employed in catalysis. Various low-valent main-group compounds, in which the HOMO and the LUMO exhibit a dual donor/acceptor character mimicking the reactivity of transition metal complexes in activation of small molecules and catalytic reactions, have attracted special attention.^[10]

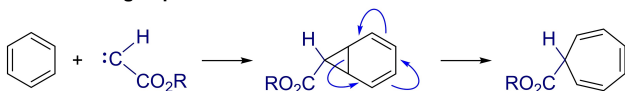
The fascinating nature of low-valent main-group compounds also enables them to activate benzene and its derivatives. The groups of Aldridge and Goicoechea achieved the first oxidative addition of a benzene C–H bond by a single main-group center, anionic Al(I) complex.^[11] Additional reported reactivities include formal deprotonation of benzene C–H by boron^[12] or aluminum anion,^[13] C–H activation of benzene by two boron atoms of diazadiborane in concerted manner,^[14] and the aromatic C–H activation of benzene derivatives such as toluene and C_6F_5H by main-group compounds.^[15] In addition to activation of arenes, some low-valent main-group compounds are able to dearomatize C_6 aromatic hydrocarbons. We have classified the dearomatization of C_6 aromatic hydrocarbons by main-group compounds into two categories: (i) cycloaddition

(a) Classic Named Reactions for Dearomatization

Birch Reduction

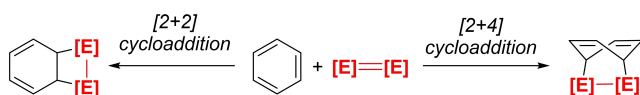


Büchner Ring-expansion

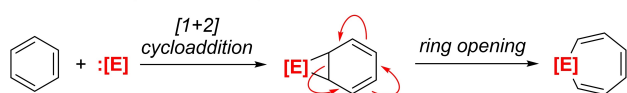


(b) Dearomatization by Low-valent Main-group Compounds

Cycloaddition Reactions



Büchner Ring-expansion-type Reactions



$[E] = ER_x$
 E = main-group elements

Scheme 1. (a) Classic named reactions for dearomatization and (b) Dearomatization by low-valent main-group compounds.

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Part of a Special Collection on the p-block elements.

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reactions and (ii) Büchner-ring-expansion-type reactions (Scheme 1b). Main-group compounds in low oxidation states such as Si(II) and Al(I) possess high-energy (pseudo) lone pairs and available empty orbitals. A synergic interaction between the frontier orbitals of these main-group molecules with the π^* -orbitals of arenes and their π -system induces cycloaddition reactions. Some highly reactive cycloaddition products undergo further ring-expansion reactions. The focus of this review is the dearomatization of C_6 aromatic hydrocarbons by main-group compounds, which leads to the formation of seven-membered EC_6 (E = main-group element) ring or cycloaddition products.

2. Cycloaddition Reactions

The high-lying nature of HOMO at the element center of the low-valent main group compounds, enable them to activate inert arenes leading to the corresponding cycloaddition products. The first example of a cycloaddition reaction of aromatic compounds with main-group compounds was reported by Peddle and co-worker in 1972.^[16] A transient disilene ($Me_2Si=SiMe_2$), formed by the reduction of the corresponding dichlorodisilane, reacted with anthracene, naphthalene or biphenyl to form [2+4] cycloaddition products. In addition, the aromatic ligand exchange from **1b–c** to **1a** is achievable (Scheme 2a). In photolysis of **1b** with a low pressure mercury lamp under argon, unpredicted 1,2-silyl migration, followed by a cycloaddition occurred via diradical coupling to give disilatricyclo[3.3.0.0]octane **2**, which can be converted back to **1b** upon heating to 200 °C.^[17] Similarly, the germanium analogue,

digermbicyclo[2.2.2]octadiene **1d**, was prepared by Neumann and co-workers by the reduction of dimethyldichlorogermane and lithium anthracene (Scheme 2a).^[18]

In 2019, Driess and co-workers isolated disilabicyclo[2.2.2]octadiene **5** by the reaction of bis(silylene)-stabilized silylone **3** with one equivalent of N_2O forming a transient disilene **4**, followed by the intramolecular [2+4] cycloaddition with the ligand-based phenyl ring (Scheme 2b).^[19] With the same bis(silylene) ligand system, they also disclosed the reactivity of bis(silylene) **6** towards isocyanide, leading to the bis(silylene)-coordinated isocyanide **7**. The subsequent [1+4] cycloaddition of a silylene with the xylene group gave a (silyl)(imido)silene derivative **8** (Scheme 2c), which can react further with small molecules such as carbon monoxide and isocyanide.^[20] The thermal equilibrium of **7** and **8** was revealed by DFT calculations. In the reaction of a dibromodisilene **10**, which is generated by the reduction of tribromoaminosilane **9** by lithium naphthalenide, with naphthalene, a [2+2] cycloaddition occurred to afford the cycloaddition product **11** (Scheme 2d).^[21]

A few examples of [2+4] cycloadditions of arenes with transient disilyne $[R-Si\equiv Si-R]$ have been reported as well. In 1986, the West group demonstrated the first [2+4] cycloaddition of anthracene with the transient dimethyldisilyne **13** (generated by thermal decomposition of **12**). Thus formed the transient disilene **14**, further reacts with another anthracene to give the bis-anthracene adduct **15** (Scheme 2e).^[22] Very recently, Cui and co-workers reported the isolation of the N-heterocyclic-boryl-stabilized disilyne **16** that can react with toluene at room temperature to form **18** (Scheme 2f).^[23] A plausible mechanism involves the formation of the transient **17** via the [2+4]



Huaiyuan Zhu was born in 1994 in Zhejiang, China. He received his M.Sc degree in chemistry in 2019 from Hangzhou Normal University under the supervision of Prof. Zhifang Li on the reactivity investigation of dialkylgermylene toward acyl chloride and the synthesis of novel low-valent boron species. In 2020, he joined the group of Prof. Shigeyoshi Inoue at Technical University of Munich as a Ph.D student. His current research interests focus on the synthesis and reactivity of acyclic iminosilylene.



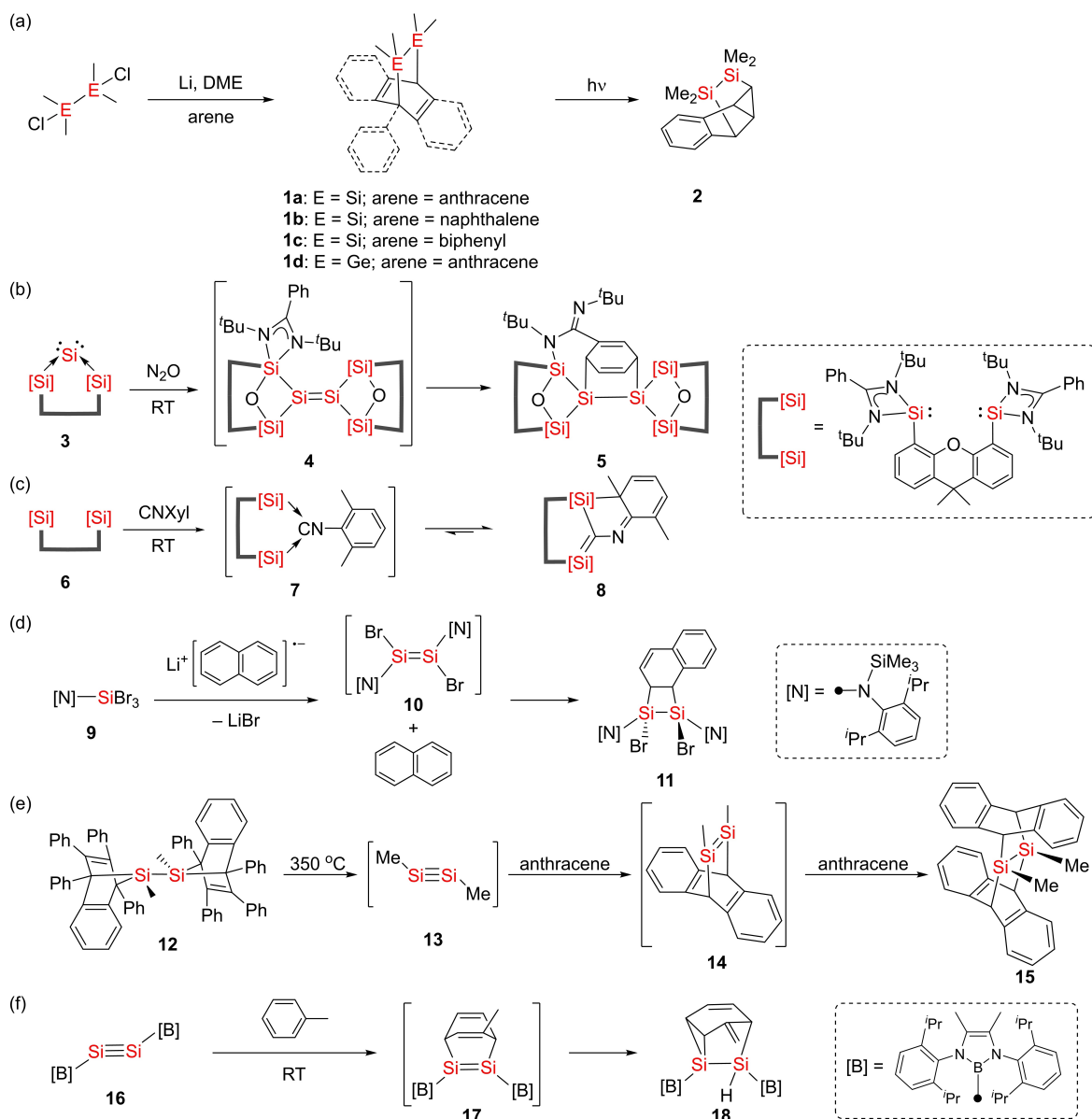
Shiori Fujimori obtained her M.Sc. and Ph.D. degree in chemistry in 2019 at Kyoto University under the supervision of Prof. Norihiro Tokitoh on the synthesis of novel aromatic compounds containing heavier group 14 elements. In October 2019, she was awarded a Eurotech-Marie Curie Fellowship and joined the group of Prof. Inoue at the TU München. She continued her stay at Technical University of Munich as an Alexander von Humboldt Fellow where she pursued her interest in low-valent silicon chemistry.



Arseni Kostenko obtained his bachelor degree in Molecular Biochemistry in Technion Israel Institute of Technology, proceeding to Master Degree and PhD in field of silicon chemistry under the Supervision of Prof. Yitzhak Apeloig. In 2016 he received the Alexander von Humboldt fellowship and joined the group of Prof. Matthias Driess in Technical University of Berlin. Since 2021 Dr. Kostenko has been working in the group Prof. Shigeyoshi Inoue at Technical University of Munich studying computationally structure and reactivity of low valent main group element based compounds.



Shigeyoshi Inoue obtained his Ph.D. from the University of Tsukuba in 2008 supervised by Prof. Akira Sekiguchi. Following postdoctoral study at the TU Berlin with Prof. Matthias Driess, he established an independent research group within the framework of the Sofja Kovalevskaja program in 2010. Since 2015 he has been on the faculty at the Technical University of Munich (TUM). His research interests include the synthesis and reactivity of main group compounds with unusual structures and unique electronic properties, with the goal of finding novel applications in synthesis, catalysis and materials science.

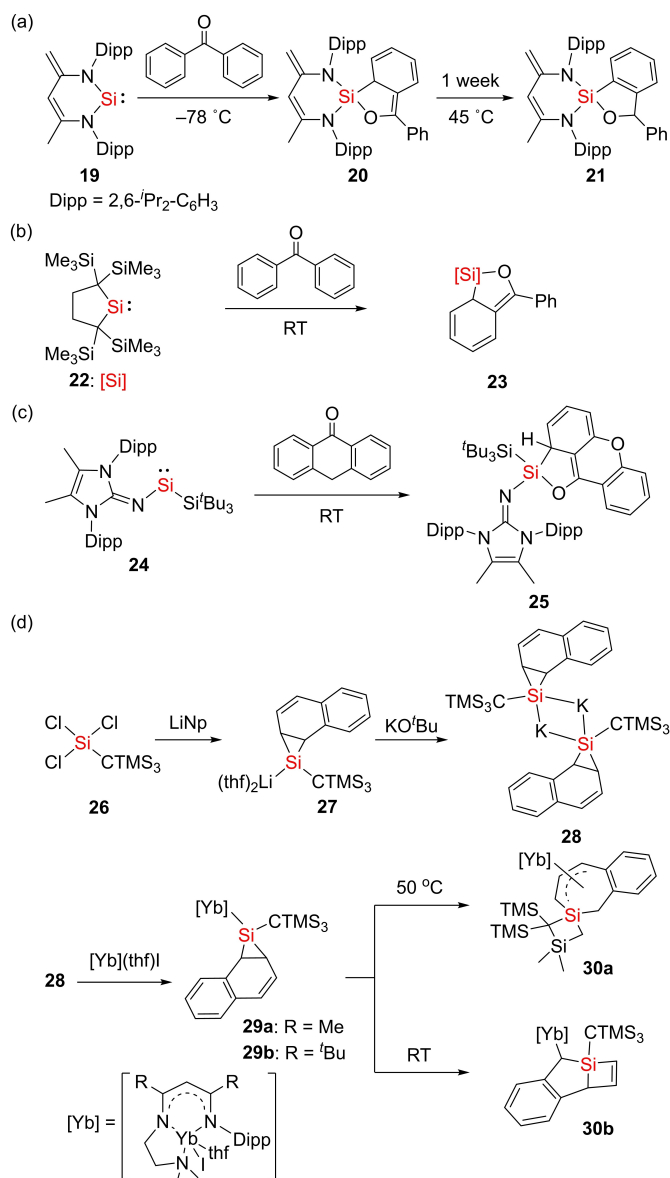


Scheme 2. Cycloaddition of arenes by low-valent silicon or germanium compounds.

cycloaddition of toluene by disilyne **16**, followed by the intramolecular activation of the benzylic C–H bond by the Si=Si double bond in **17** to give the final product **18**.

Some silylenes (:SiR_2) are also known to activate aromatic compounds. The six-membered NHSi (N-heterocyclic silylene) **19** dearomatized benzophenone at -78°C to give compound **20**, which can be considered as the first example of dearomative [1+4] cycloaddition by an isolable main-group element center (Scheme 3a).^[24] Upon heating **20** to 45°C in hexane for one week, the rearomatized oxasilacycle **21** was obtained via 1,3-hydrogen migration. Similarly, the cyclic dialkylsilylene **22** can undergo dearomative [1+4] cycloaddition of benzophenone as well as various functionalized benzophenones to form the corresponding [1+4] cycloaddition products (Scheme 3b).^[25] In the reaction of acyclic imino(silyl)silylene **24** with xanthone at ambient temperature, similar [1+4] cyclo-

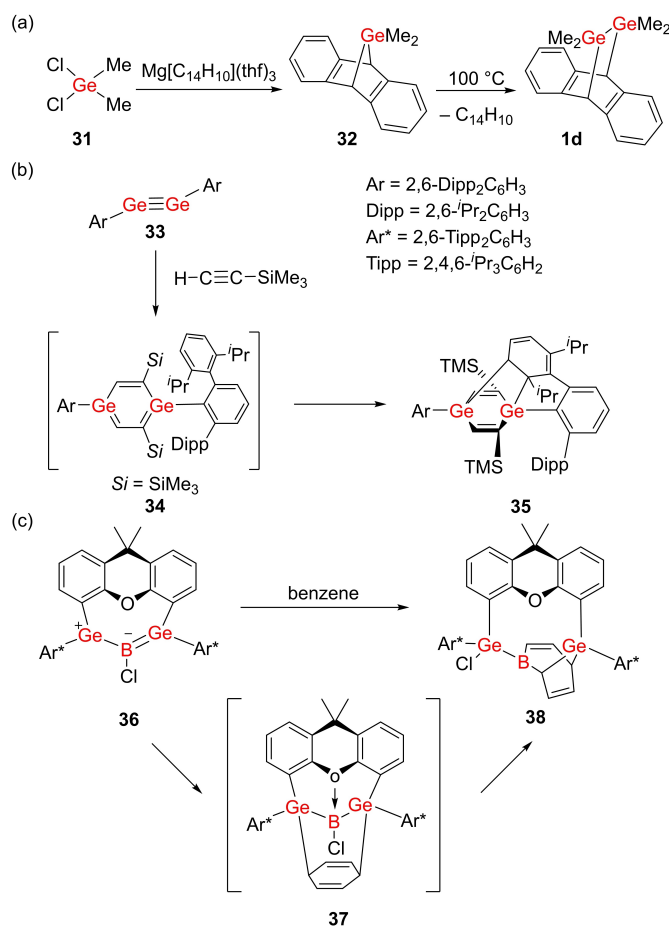
addition product **25** was obtained (Scheme 3c).^[26] Compound **25** is stable even when heated to 100°C and rearomatized reaction was not observed. In addition, the first example of insertion of metal-substituted silylene fragment into an aromatic ring of naphthalene and further ring opening and rearrangement were investigated by Lee,^[27] Chen, Peng and co-workers (Scheme 3d).^[28] Treatment of a trichlorosilane $\text{Cl}_3\text{SiC}(\text{SiMe}_3)_3$ (**26**) with 3.8 equivalents of lithium naphthalenide at -35°C afforded a [1+2] cycloaddition product **27**, which was first generated by bromodilithiosilane and naphthalene at 110°C by the Lee group in 2008.^[27] Treatment of **27** with an equivalent of KO^tBu at room temperature provided the silacyclopropanyl potassium **28** via transmetalation. Furthermore, the reaction of **28** with the divalent ytterbium iodide furnished divalent ytterbium silacyclopropanyl complexes **29a–b**. When **29a** was heated to 50°C , C–H activation and ring



Scheme 3. Cycloaddition of arenes by silylenes.

expansion occurred to yield **30a**. On the other hand, **29b** undergoes C–C cleavage and follow-up 4 π electrocyclicization at room temperature to afford **30b**. Cummins and co-workers reported that a “masked germylene” **32**, obtained by the reaction of Me₂GeCl₂ with Mg(C₁₄H₁₀), converted to **1d** at 100 °C via the insertion of transient dimethylgermylene into Ge–C bond of **32** (Scheme 4a).^[29] Dearomatization by a 1,4-digerma-benzene is also known. In 2004, Power and co-workers reported reactivity of the digermine **33** towards alkynes (Scheme 4b).^[30] In the reaction of **33** with HC≡CSiMe₃, the 1,4-digerma-benzene **34** was generated in situ allowing for an intramolecular [4 + 2] cycloaddition reaction with a Dipp moiety of the aryl group to give the bicyclic complex **35**.

Very recently, the Wesemann group reported the synthesis of boradigermaallyl **36** and its boron-germanium cooperative dearomatization of benzene to form the seven-membered

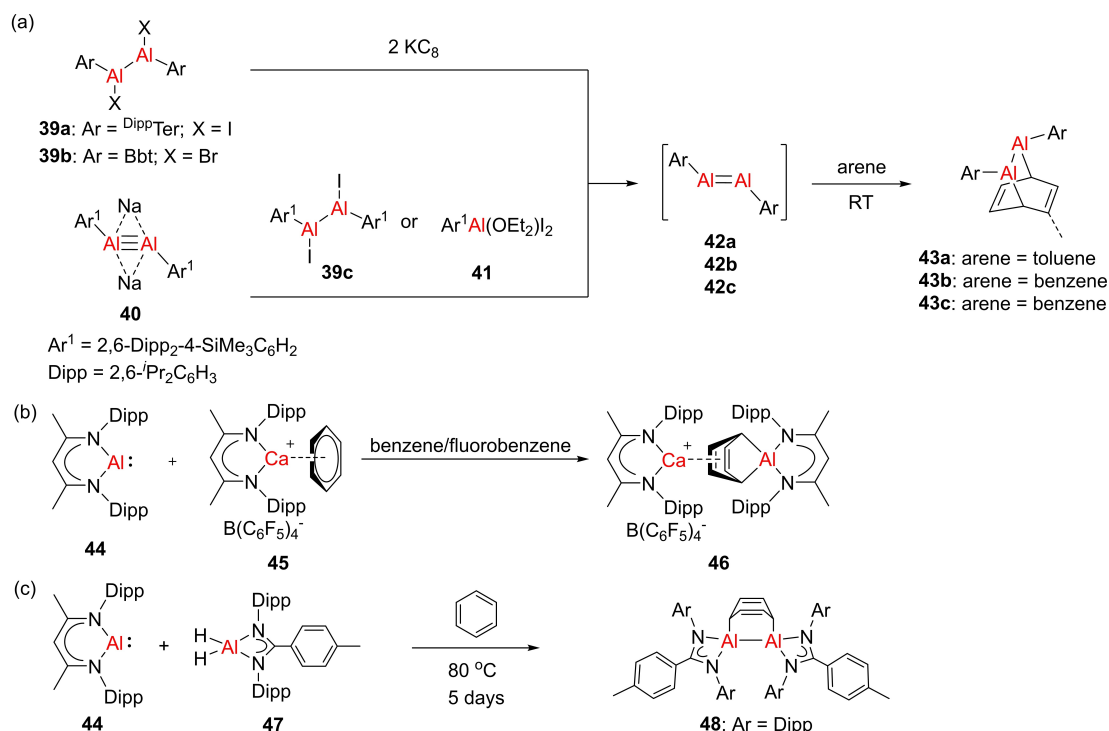


Scheme 4. Cycloaddition of arenes by germanium compounds.

boracycle **38**. The reaction proceeds by the insertion of boron into the C–C bond of the cyclohexadiene **37**, which is initially generated by [4 + 3] cycloaddition of **36** with benzene (Scheme 4c). In the same report, the authors also presented the [4 + 3] cycloaddition of **36** with anthracene.^[31]

In 2003, the first example of a [2 + 4] cycloaddition of arenes by a low-valent aluminum compound was reported by Power and co-workers (Scheme 5a).^[32] The reduction of 1,2-diiododialane Ar₂Al₂I₂ **39a** [Ar = 2,6-DippC₆H₃, Dipp = 2,6-*i*-Pr₂C₆H₃] with KC₈ led to the generation of the corresponding dialumene **42a** in situ, which can react with toluene to furnish the [2 + 4] cycloaddition product **43a**.

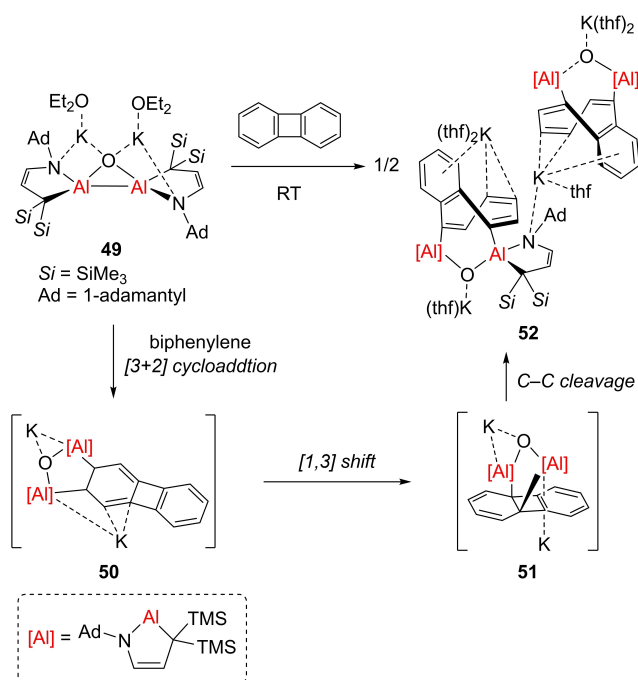
Similarly, in 2013, Tokitoh and co-workers reported the isolation of the dialumene-benzene adduct **43b** obtained by the reduction of the 1,2-dibromodialane Bbt₂Al₂Br₂ **39b** (Bbt = 2,6-[CH(SiMe₃)₂]₂C₆H₃) with 2 equivalents of KC₈ in benzene (Scheme 5a).^[33] Compound **43b** can act as a masked dialumene that was revealed by the exchange reactions of **43b** with C₆D₆, naphthalene, anthracene and bis(trimethylsilyl)acetylene at room temperature forming the corresponding trapping products, dialumene-C₆D₆, -naphthalene or -anthracene adduct or 1,2-dialuminacyclobutene, respectively. The Power group also prepared a similar dialumene-benzene adduct **43c** by the reaction of dianionic dialuminyne **40** with **39c** or **41** in benzene,



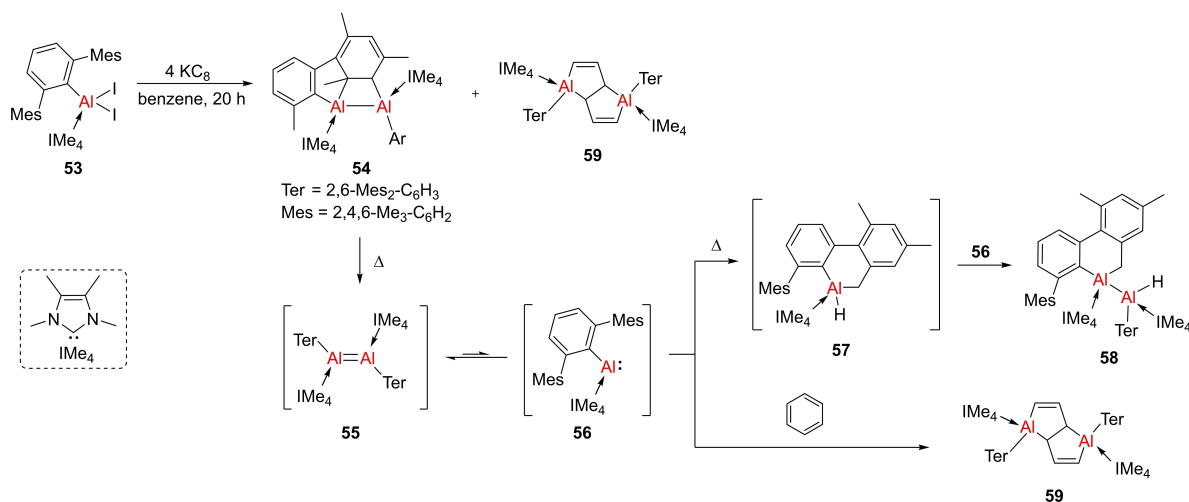
Scheme 5. Cycloaddition of arenes by low-valent aluminum compounds.

whereas **43c** was not obtained in the reduction of the corresponding 1,2-diiododialane **39c** (Scheme 5a).^[34] In 2018, the Harder group reported facile benzene reduction by Ca²⁺/Al^I Lewis Acid/Base Combination (Scheme 5b). Treatment of alumylene stabilized by a β -diketiminate ligand **44** with [(BDI)Ca⁺·C₆H₆][B(C₆F₅)₄⁻] **45** in benzene/fluorobenzene (4:1) at room temperature resulted in the formation of a [1 + 4] cycloaddition product **46**, in which aluminanorborene strongly coordinates to the Ca²⁺ metal ion.^[35] However, alumylene **44** easily reacts with polycyclic aromatic hydrocarbons, such as naphthalene, anthracene and biphenylene, forming [1 + 4] cycloaddition adducts.^[36] In addition, Bakewell and co-workers reported the isolation of the dialumene-benzene adduct **48** by a [2 + 4] cycloaddition of the corresponding dialumene, formed in the reaction of dihydroalane **47** with alumylene **44**, which acts as a reducing agent at 80 °C in benzene (Scheme 5c).^[37] Biphenylene is also activated by the aluminum analog of oxirane **49** bearing a highly strained Al–Al σ -bond at room temperature to form 5,10-di-Al-substituted benzocyclooctatetraene scaffold **52** (Scheme 6).^[38] The computational studies revealed that **49** underwent the dearomatic [2 + 2] cycloaddition with the Al–Al bond cleavage to generate the intermediate **50**. The subsequent two steps [1,3] sigmatropic aluminum shift led to generation of the five-membered ring **51**, which underwent C–C bond cleavage to give the final product **52**.

In 2022, the Braunschweig group reported the facile deconstruction of aromatic compounds by a transient base-stabilized arylaluminum.^[39] Treatment of diiodoarylalane **53** with excess KC₈ in benzene at room temperature for 20 h

Scheme 6. Dearomatization of biphenylene by dianionic dialane **49**.

afforded a mixture of the [2 + 2] cycloaddition product **55** and the dialumacycle **59** in a ratio of 4:1 (Scheme 7).^[39] In the same reaction in hexane, **53** was fully converted into **54** after 20 days at ambient temperature. When a benzene solution of the isolated [2 + 2] cycloaddition product **54** was heated to 100 °C, compound **58** was obtained together with **59** as a minor



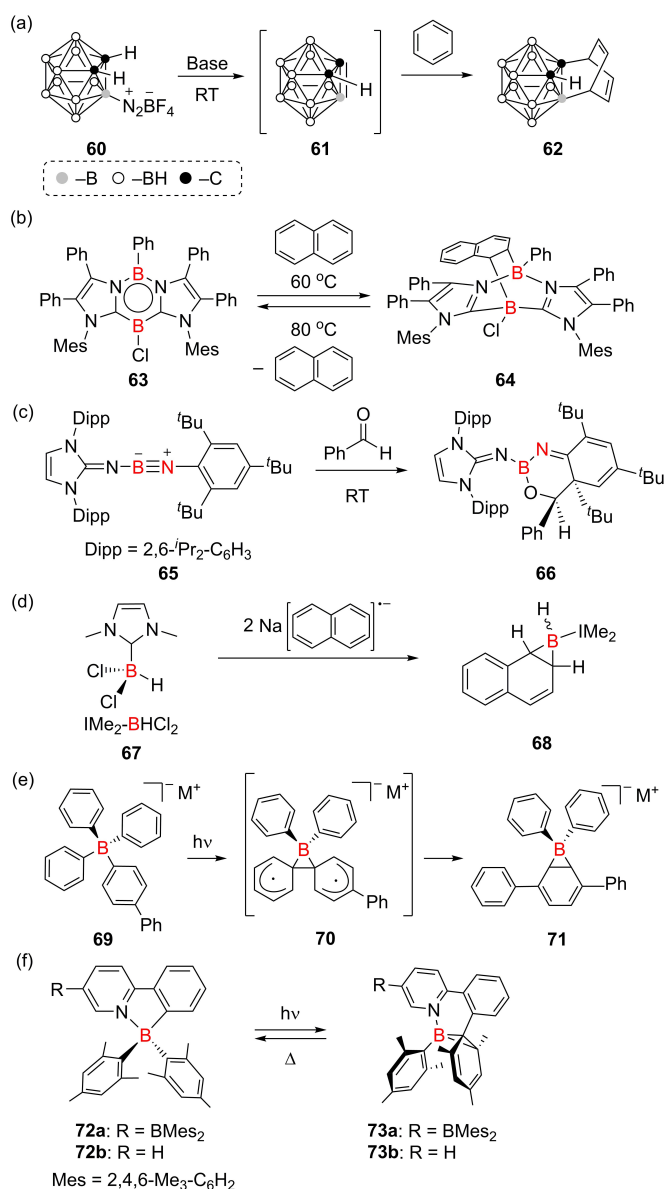
Scheme 7. Cycloaddition of arenes by low-valent aluminum compounds.

product. DFT calculations support a reaction mechanism involving the generation of an equilibrium mixture of dialumene **55** and the transient arylyluminum **56**. Subsequent intramolecular C–H activation in aluminene **56** forming the hydridoalane intermediate **57**, followed by a formal insertion of another molecule of **56** into the Al–H bond in **57**, provides the final product **58**. In contrast, formation of the pentalene product **59** involves the reaction of the transient aluminene **56** with benzene.

Besides aluminum compounds, other group 13 compounds are known to show a dearomatization of C_6 aromatic hydrocarbons via [2+4] cycloaddition. In 2014, Xie and co-workers reported the first transient 1,3-dehydro-*o*-carborane **61** with a carbon boron multiple bond character that was generated in the reaction of 3-diazonium-*o*-carborane tetrafluoroborate **60** with a base such as LDA, LiHMDS and $NaNH_2$ (Scheme 8a). **61** underwent [4+2] cycloaddition with benzene to give the corresponding benzene adduct **62**.^[40] The Kinjo group reported the isolation of a diazadiborinine **63** in 2019.^[14] Treatment of **63** with excess amount of naphthalene furnished a [4+2] cycloaddition compound **64** at 60 °C (Scheme 8b). Additionally, **64** underwent a cycloreversion at 80 °C to regenerate **63** and naphthalene. Besides naphthalene, biphenylene, anthracene and tetracene were dearomatized by **63** to give the corresponding addition products, which also proceeded retro[4+2] cycloaddition reactions at 80 or 140 °C forming the corresponding arene along with **63**. In the reaction of aryliminoborane **65** with benzaldehyde, reported by Kong and co-workers, the [2+4] cycloaddition occurred at room temperature to afford a fused bicycle **66** (Scheme 8c).^[41] They also disclosed the intramolecular [2+3] cycloaddition of BNN-1,3-dipoles with aryl substituent.^[42] Additionally, naphthalene was dearomatized by a boron compound in the reaction of the NHC-stabilized dichloroborane **67** with 2 equivalents of sodium naphthalenide to generate cycloaddition products, a mixture of diastereoisomers **68** in the 1:1 ratio (Scheme 8d).^[43] However, in 2020, the Braunschweig group reported the trapping of a borirane

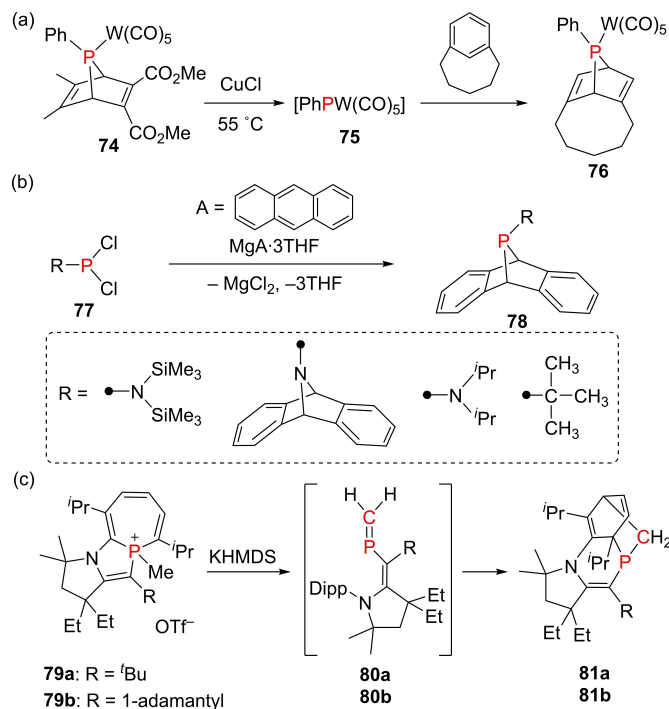
intermediate in the reduction of arylborane to diborene, which was considered as the intermolecular [1+2] cycloaddition of transient borylene with arylborane precursor.^[44] Dearomatization through photoreactivity of tetraarylborates has been also reported. In 1988, Schuster and co-workers isolated a borirane anion **71** by irradiation of tetraphenylborate **69** at 254 nm (Scheme 8e).^[45] A plausible reaction mechanism involves di- π -borate rearrangement, where excitation at 254 nm led to an excited-state C–C coupled biradical **70**.^[46] The Wang group reported the first example of organoborons that show reversible photo-thermal color switching via intramolecular C–C bond formation/breaking (Scheme 8f).^[47] Organoborons **72 a-b** underwent photoreactions upon exposure to UV light (365 nm) to form the corresponding dearomatized products **73 a-b**, that were fully converted back to **72 a-b** after heating (ca. 60 °C) in C_6D_6 in the dark. The choice of substituents on the B center makes a great impact on the switching properties of the boron compounds.^[48] For instance, photoisomerization of naphthalene supported tetraorganoboron compounds resulted in the formation of borepins.^[49] In addition, less bulky aryl groups (e.g. phenyl)^[50] or those bearing a strong electron-donating ligand (e.g. NMe_2)^[51] give photochemically stable boron compounds due to the strong B– C_{Ar} bonds and the introduction of electronic transitions which disfavor isomerization. Similar dearomative photoisomerization of organoboron compounds via intramolecular C–C bond formation was also reported by Yamaguchi and Milstein group.^[52]

Some phosphorus compounds have also been shown to activate aromatic compounds. In 1998, the Bickelhaupt and Lammertsma group reported the first dearomative [1+4] cycloaddition of the terminal phosphinidene complex **75**, which was generated from treatment of the phosphanorbornadiene derivative **74** with 10% of CuCl as a catalyst in toluene at 55 °C, with [5]metacyclophane (Scheme 9a).^[53] The Cummins group achieved the facile synthesis of an unprotected phosphanorbornadiene derivative **78** by treatment of phosphorus dichlorides **77** with magnesium anthracene complex (Scheme 9b).^[54] As



Scheme 8. Dearomatization of arenes by Boron Compounds.

predicted, compounds **78** can be converted to the corresponding transient phosphinidene upon heating to 80 °C with concerted loss of an anthracene and the phosphinidenes were trapped by 1,3-cyclohexadiene. A reversible intramolecular [2 + 4] cycloaddition of phosphalkenes **80 a-b** to arenes was reported by Stephan and co-workers in 2019 (Scheme 9c).^[55] The seven-membered ring phosphepinium cations **79 a-b** were deprotonated by KHMDS affording transient phosphalkenes **80 a-b** which underwent an intramolecular [2 + 4] cycloaddition with the aromatic ring on Dipp group to form the 2-phosphabicyclo[2.2.2]octadiene **81 a-b**. The equilibrium between **80 b** bearing a less bulky substituent and the cycloaddition product **81 b** was revealed at room temperature.



Scheme 9. Dearomatization of Arenes by Phosphine Compounds.

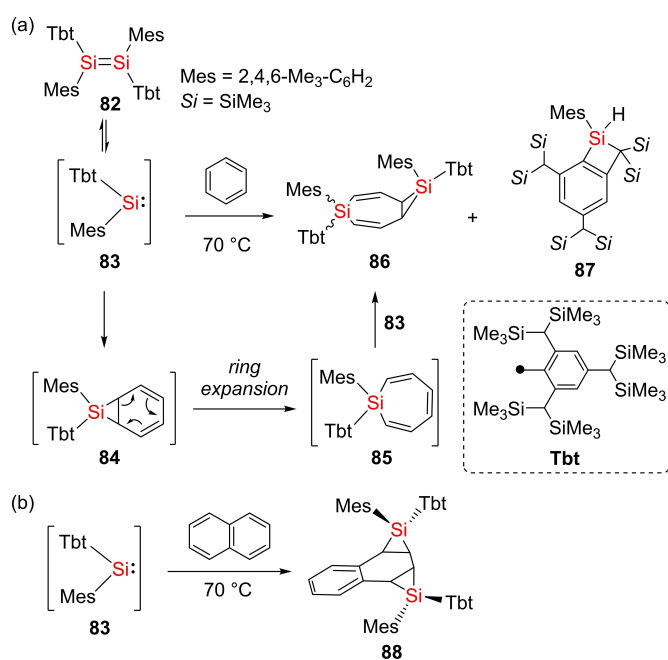
3. Büchner Ring Expansion Type

Some main-group compounds are known to undergo cycloaddition reactions, followed by the Büchner ring expansion to form the seven-membered ring products in the reaction with aromatic compounds. In synthetic chemistry, Büchner ring expansion, in which carbenes undergo [1 + 2] cycloaddition with an aromatic C–C bond in benzene derivatives, followed by the ring expansion and afford the corresponding cycloheptatrienes, has played an important role as a method for construction of seven-membered rings. In 1885, the first example of such ring expansion reactivity was discovered by Büchner and co-workers.^[3] In 2017, the triplet ground state carbene chemistry was complemented by the discovery of reversible Büchner ring expansion featuring excited singlet diamidocarbenes.^[56] In contrast to carbenes, which can exist in the singlet or triplet ground state (depending on substituents), most main-group carbenoids possess a singlet state. Among these carbenoids, only a few achieved dearomatization of C₆ aromatic hydrocarbons with Büchner ring expansion mechanism.

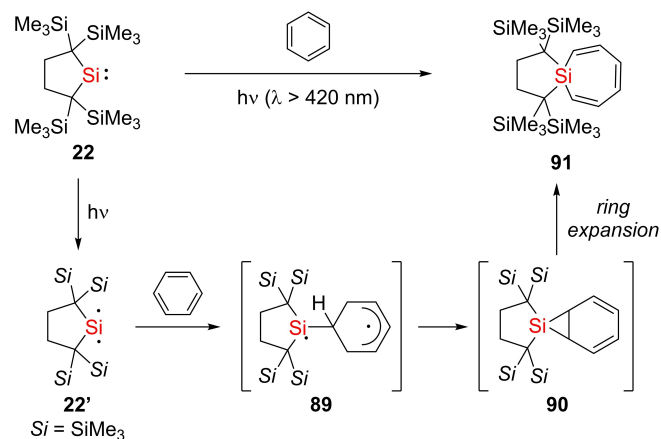
In main-group chemistry, the Büchner-ring-expansion-type-dearomatization reactivity of C₆ aromatic hydrocarbons has been observed by using low-valent main-group molecules. Some silylenes (R₂Si:), i.e., the silicon analogues of carbenes (R₂C:), are known to undergo the ring expansion to form the seven-membered ring products. In 1994, Okazaki and co-workers reported the first [1 + 2] cycloaddition of a transient silylene **83** (which is in equilibrium with the corresponding disilene **82**) with benzene, leading to a generation of a bicyclic silane **86** together with intramolecular cycloaddition product **87**

(Scheme 10a).^[57] A plausible mechanism involves the [1+2] cycloaddition of the silylene **83** with benzene to generate a cycloaddition intermediate **84**, which underwent ring expansion to form a seven-membered ring compound **85**. Subsequent [1+2] cycloaddition of the highly reactive silylene **83** with **85** afforded the final product **86**. In the reaction of the silylene **83**/disilene **82** equilibrium mixture with naphthalene, the [1+2] cycloaddition product **88** was obtained while the ring expansion product was not observed (Scheme 10b).

A similar ring expansion reaction of benzene with low-valent silicon compound was reported by Kira and co-workers in 2002. When a benzene solution of an isolable silylene **22** was irradiated ($\lambda=420$ nm) at ambient temperature, the corresponding silepin **91** formed (Scheme 11).^[58] The computational studies implied that irradiation of silylene **22** in benzene gave the singlet excited state of silylene **22'** that reacts with benzene

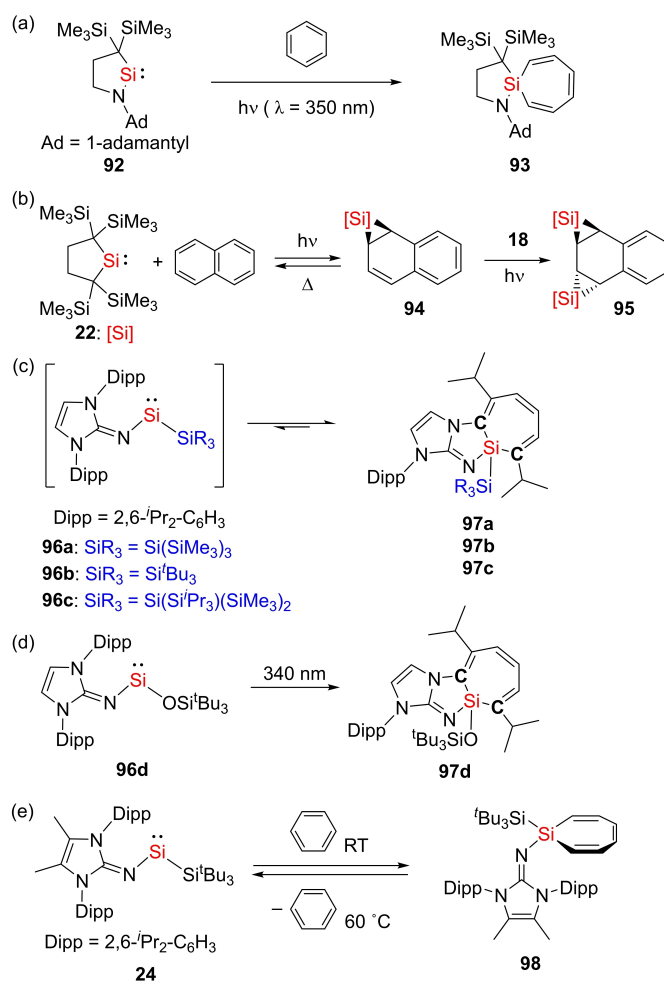


Scheme 10. Dearomatization of benzene and naphthalene by silylene **83**.



Scheme 11. Dearomatization of benzene by silylene **22**.

to form the 1,3-biradical intermediate **89**. Subsequent cyclization to an intermediate **90**, followed by ring expansion provides the final silepin **91**.^[59] A similar ring expansion reaction, in which a cyclic alkyl amino silylene **92** activated benzene upon irradiation at $\lambda=350$ nm to form a silepin **93**, was reported by the Iwamoto group (Scheme 12a).^[60] In addition, irradiation of a mixture of silylene **22** with naphthalene in hexane at room temperature afforded a mixture of mono- (**94**) and bis- (**95**) adducts in the 1:1 ratio (Scheme 12b). When the mono-adduct **94** was heated to 60 °C in the dark, thermal dissociation regenerated the naphthalene and **22**, whereas the bis-adduct **95** was produced by the photochemical reaction of **22** with **94**. Our group reported the isolation of imino(silyl)silepins **97a-c** that are in equilibrium with their monomeric silylenes **96a-c** (Scheme 12c).^[61] Silepins **97a-c** were formed through the intramolecular insertion reaction of the in situ generated silylenes **96a-c** into the C=C bond of the aromatic ligand framework. On the other hand, the imino(siloxy)silylene **96d** can be isolable at ambient temperature, whereas irradiation ($\lambda=340$ nm) of **96d** in THF or benzene gave the corresponding silepin **97d** (Scheme 12d).^[62] Very recently, we reported the synthesis and isolation of the imino(silyl)silylene **24** bearing a N-heterocyclic imine ligand with a methylated backbone, which

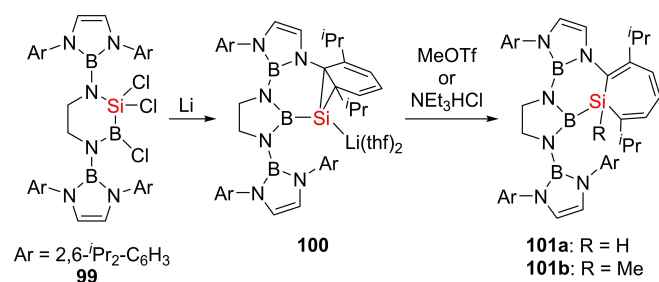


Scheme 12. Dearomatization of arenes by silylenes.

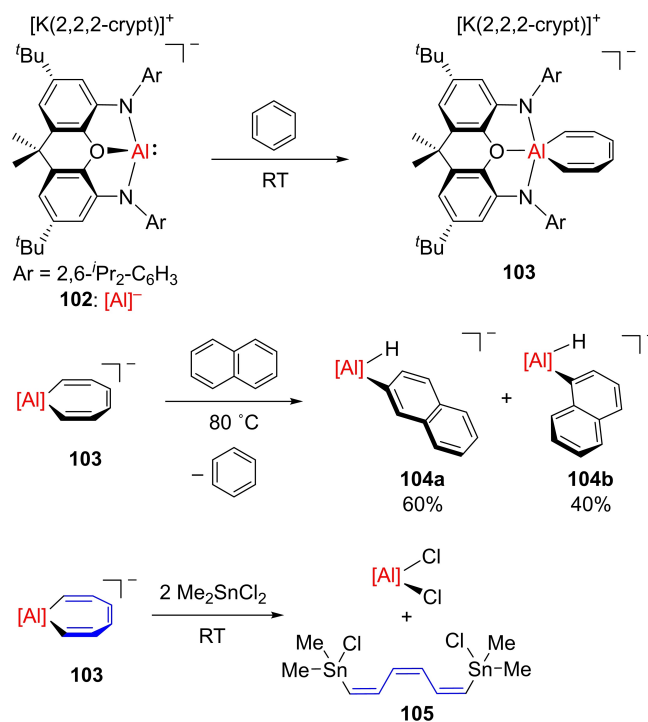
prevents the intramolecular silylene insertion into the C=C bond of the aryl substituent (Scheme 12e).^[63] Instead, the silylene **24** slowly reacts with benzene at room temperature to form the silepin **98** via the insertion into the C=C bond in benzene. Silepin **98** could be isolated by heating a benzene solution of **24** at 40 °C for 1 week in 40% yield. Furthermore, silylene **24** was regenerated upon heating a C₆D₆ solution of **98** to 60 °C. Benzene derivatives, 1,4-difluorobenzene and 1,4-bis(trifluoromethyl)benzene, also converted to the corresponding silepins in the reaction with **24**. Computational studies revealed the ambiphilic nature of **24** inducing the facile addition of the silylene to an aromatic C=C bond where the important initial step involves both interactions between the lone pair on the Si center with the π*-orbitals of an arene and the Si vacant *p*-orbital with the arene π-system.

The Cui group also reported the ring-expansion products **101 a–b** via the salt metathesis of the corresponding silanorcaradiene **100**, obtained by the reduction of **99** with lithium (Scheme 13).^[64]

Besides silicon species, several examples of the Büchner ring-expansion-type dearomatization by low-valent aluminum compounds have been reported. In 2018, Aldridge, Goicoechea and co-workers achieved the isolation of the dimeric potassium aluminyl compound, that acts as an aluminum nucleophile and undergoes the formal oxidative addition of the C–H bond in benzene.^[11] Additionally, the monomeric aluminyl compound **102** was synthesized by the addition of 2.2.2-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) to a THF solution of the dimeric potassium aluminyl compound.^[65] Aluminyl compound **102**, with an energetically high-lying aluminum-centered lone pair, inserts into the C–C bond of benzene at room temperature to form the ring expansion product, the aluminepin **103** (Scheme 14). DFT calculations revealed that the initial step in this reaction is [1+2] cycloaddition forming a bicyclic intermediate followed by ring expansion to form **103**. The process for the C–C bond cleavage in benzene by **102** is a thermally reversible reaction and a mixture of **104 a** and **104 b** was obtained by treatment of **103** with naphthalene in benzene at 80 °C. Furthermore, selectivity of Al–C bond activation with **103** allows for the formation of a functionalized acyclic product from benzene. Thus, a tin-containing acyclic triene **105** was obtained by the reaction of the aluminepin **103** with Me₂SnCl₂ in benzene at room temperature. In contrast, dialkylaluminyl anion only reacts with



Scheme 13. Dearomatization by silicon compound.

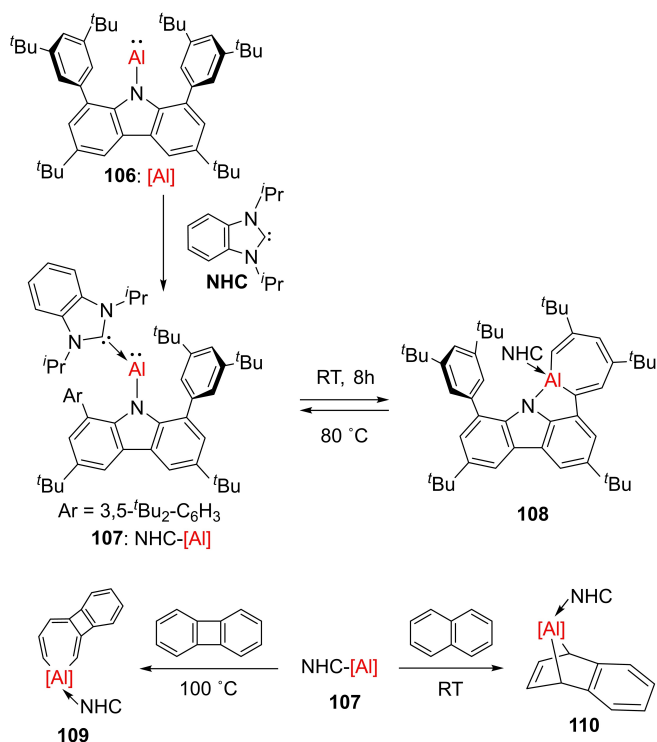
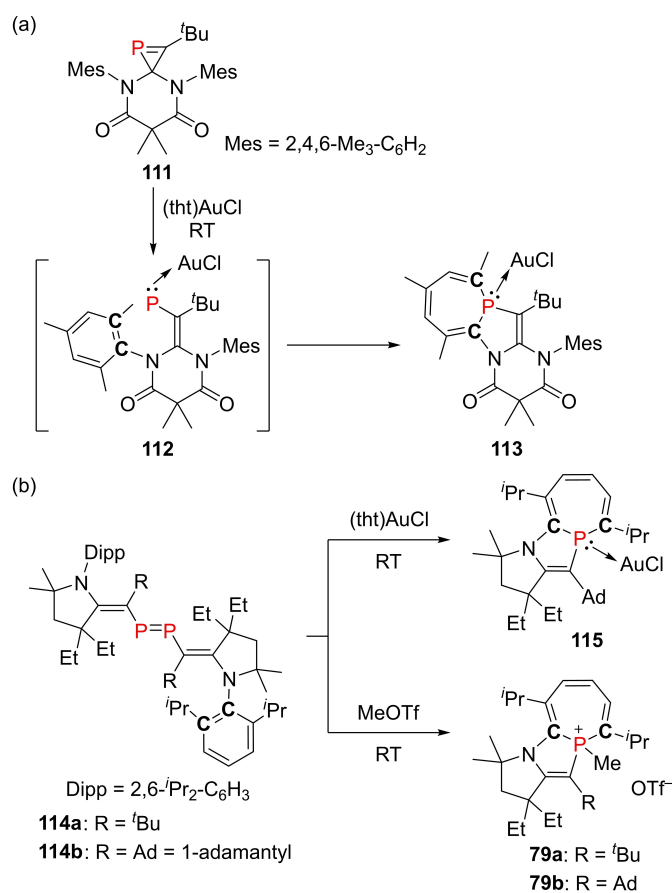


Scheme 14. Dearomatization of benzene by aluminyl compound **102**.

naphthalene and anthracene, giving to [1+4] cycloaddition adduct.^[66]

In 2021, the Liu group reported the isolation of carbazolyalumylene **106** that was obtained by the reduction of the corresponding carbazolyl aluminum diiodide.^[67] The coordination of **106** with an NHC decreases the HOMO-LUMO gap that led to enhancing the reactivity of the NHC-stabilized alumylene **107** (Scheme 15). While **107** is stable at room temperature in the solid state for few days, it slowly converted into the ring expansion product **108** within 8 h via intramolecular insertion.^[68] Transformation of **107** to **108** was found to be reversible at elevated temperature. The NHC-stabilized alumylene **107** also dearomatized biphenylene to give the intermolecular ring expansion product **109**, whereas the reaction with naphthalene led to formation of [1+4] cycloaddition product **110**.

Stephen and co-workers reported the first example of a phosphorus analog of the Büchner ring expansion reaction.^[69] In the reaction of the phosphirene **111**, which is shown to react as a vinyl-phosphinidene **112** generated via phosphirene-phosphinidene rearrangement, with (thf)AuCl, intramolecular phosphinidene-insertion into the C–C bond of the mesityl group occurred to form a seven-membered ring product **113** (Scheme 16a). Similarly, treatment of the diphosphene **114 b** with (thf)AuCl resulted in the formation of **115** via phosphinidene insertion into an aromatic C–C bond of the Dipp group (Scheme 16b).^[69b] Diphosphenes **114 a–b** also react with MeOTf to provide the corresponding ring expansion products **79 a–b**.

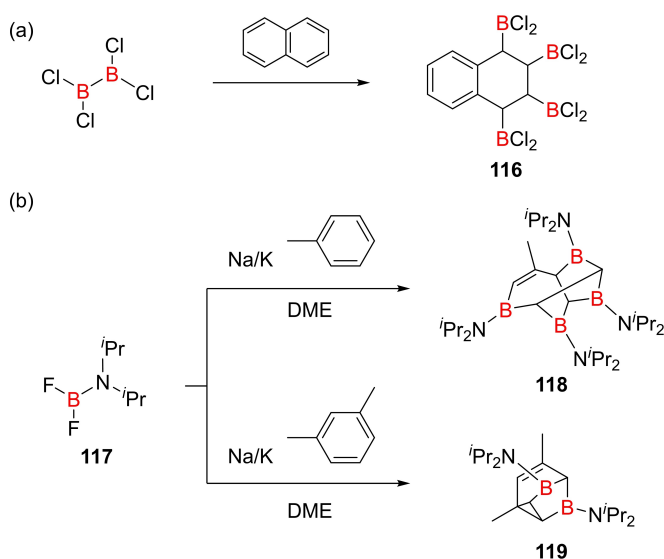
Scheme 15. Dearomatization of arenes by NHC-stabilized alumylene **107**.

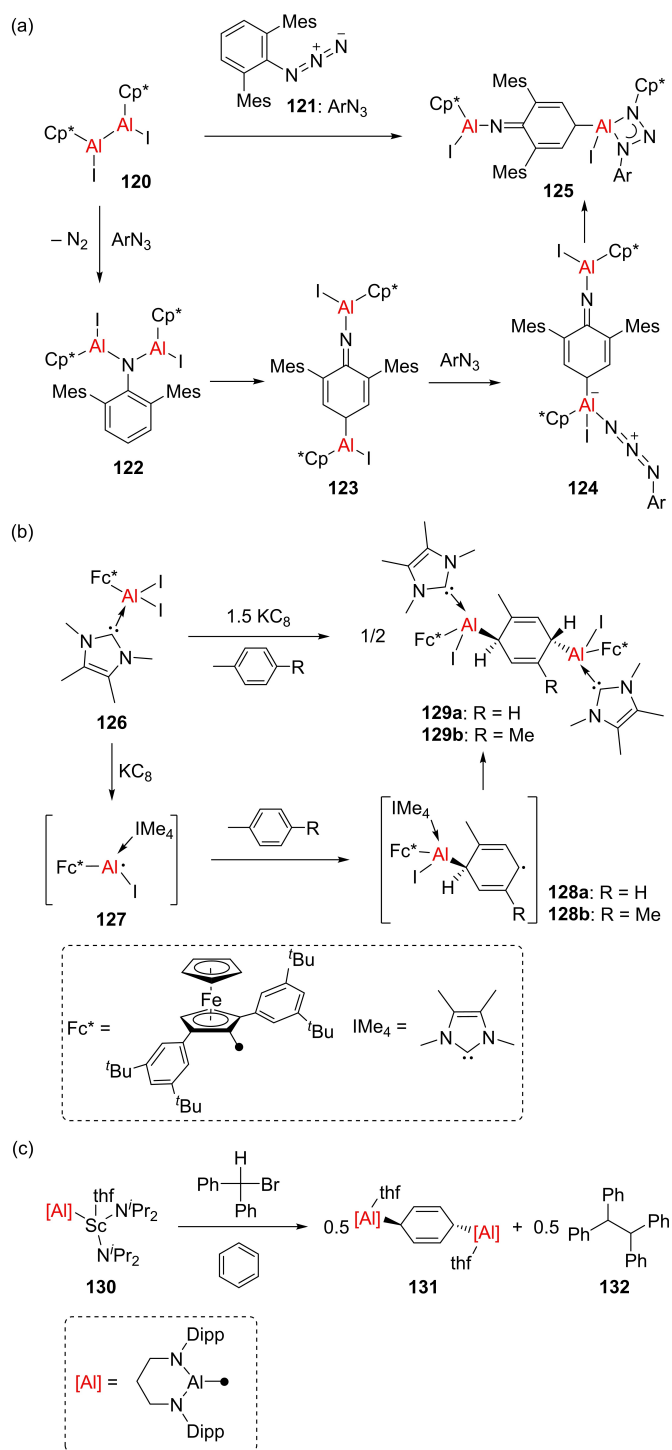
Scheme 16. Intramolecular transient phosphinidenes insertion into aromatic C–C bond.

4. Other Types of Dearomatization Reactions

In addition to dearomatization of aromatic C₆ hydrocarbon rings through the cycloaddition or further ring expansion reaction, several other types of dearomatization pathways such as the coupling of heteroatoms to a carbon of C₆ aromatic hydrocarbon ring are known. The addition of arenes can be tracked back to 1961, Fox and Wartik reported the addition reaction of diboron tetrachloride B₂Cl₄ with naphthalene at room temperature, led to the formation of a dearomatized benzene derivative **116** (Scheme 17a).^[70] However, there was no direct evidence to support this structure since **116** is a viscous liquid and decomposes at 145 °C. In 1989, the Meller group achieved the dearomatized boracycles **118** and **119** by the reduction of aminodifluoroborane **117** in dimethoxyethane (DME) in the presence of toluene or *m*-xylene, respectively (Scheme 17b).^[71] It is plausible that the toluene ring was split into C₂ and C₄ units or the *m*-xylene ring was opened by the transient amino-borylene and rearranged to form the final products **118** or **119**.

Another type of dearomatization by an aluminum compound was reported by the Arnold group in 2008 (Scheme 18a).^[72] When the diiododialane **120** was treated with 2 equivalents of aryl azide **121**, oxidative cleavage of the Al–Al bond provided compound **125**. A plausible mechanism involves oxidation of the Al–Al bond in **120** by aryl azide **121**, which provided a dimeric iminoalane intermediate **122**, followed by migration of one aluminum fragment to the *para*-position on the central aryl ring to form an intermediate **123** bearing an electron deficient *para*-aluminum atom, that was trapped by another molecule of **121**. Subsequent migration of Cp* in **124** to the adjacent N atom and triazene ring formation gave the final product **125**. Braunschweig and co-workers reported the cross-coupling of an Al center to aromatic solvents via radical mechanism (Scheme 18b).^[73] Reduction of the ferrocenyl-based NHC-stabilized aluminum(III) diiodide **126** in toluene or *p*-xylene with 1.5 equivalents of K₂C₈ afforded **129a–b**, whereas the same

Scheme 17. C₆ Aromatic hydrocarbons Activation by boron compounds.



Scheme 18. C₆ aromatic hydrocarbons Activation by aluminum compounds.

reduction in hexane led to the formation of a dialane [(NHC)Fc*-(I)Al-(I)Fc*(NHC)] (NHC = :C[N(Me)C(Me)]₂; Fc* = 2,5-bis(3,5-di-*tert*-butylphenyl)-1-ferrocenyl). The postulated mechanism involves the formation of an aluminum radical **127**. Subsequent coupling with an aromatic ring (toluene or *p*-xylene) leads to the generation of a radical **128a–b**, followed by the reaction with another molecule of **127**, which provides the final product **129a–b**. Similar benzene activation was reported by the

Andrada group upon the reduction of iodoalane in benzene very recently.^[74]

Additionally, Yamashita and co-workers reported a benzene activation by an Al–Sc complex (Scheme 18c).^[75] Treatment of the Al–Sc complex **130** with benzene in the presence of alkyl bromide (Ph₂CHBr) resulted in the formation of a 1,4-dialumylated cyclohexadiene **131** together with a concomitant formation of the alkyl-alkyl coupled product **132**. Computational studies revealed the formation of **131** may proceed via an ionic two-step process, involving the activation of alkyl bromide and benzene, enabled by cooperation of Al and Sc centers.

5. Summary and Outlook

In synthetic chemistry, the dearomatization reaction is an efficient method of transforming simple arenes into highly functionalized structures. One of the significant discoveries is Büchner ring expansion reaction; seven-membered C₇ ring products are formed by the reaction of arenes and carbene species, followed by rearrangement of the corresponding norcaradiene. In most cases, the dearomatization of arenes involves either (i) two-electron processes (e.g., dissolving metal reductions and organometallic additions) or (ii) one-electron processes (e.g., enzymatic, oxidative, photochemical reactions and radical-radical anion coupling). Recent progress in main-group chemistry indicates the potential of main-group molecules containing naturally abundant elements in the Earth's crust for this purpose. Low-valent main-group compounds bearing a high energy HOMO and an energetically accessible LUMO enable the activation of stable aromatic compounds under mild conditions. In this minireview, we have summarized examples of dearomatization of C₆ aromatic hydrocarbons by main-group compounds. The disruption of the aromaticity of arenes is grouped into two categories: (i) [2 + 2], [2 + 4], [1 + 2] and other cycloaddition reactions and (ii) Büchner ring expansion type reactions. In addition, some examples of the reversibility of the insertion process, a key step in catalytic processes, have been discovered. It was revealed that imino(silyl)silylenes show equilibrium intra/intermolecular insertion reactions into the C=C bond of the aromatic ligand framework. Additionally, the NHC-stabilized alumylene undergoes reversible intermolecular ring expansion. We believe that the reversibility of activation of aromatic hydrocarbons by low-valent main-group compounds may lead to the utilization of naturally abundant elements in catalytic transformations, such as benzene substitution.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: aromatic C₆ hydrocarbon · Büchner ring expansion reaction · cycloaddition · dearomatization · low-valent main-group elements

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