

Heteroatom chemistry in Asia: Past, present, and future*

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Abstract: The contribution of Asian chemists to the International Conference on Heteroatom Chemistry (ICHAC) meetings, several topics in low- and high-coordination main group element chemistry mainly in Japan, and our contributions to heteroatom chemistry are described. Other important compounds from other countries will also be presented.

Keywords: heavier main group element chemistry; heteroatom chemistry; organic chemistry; organometallic chemistry; reaction mechanisms.

INTRODUCTION

Heteroatom chemistry has supported organic chemistry by providing synthetic methodologies for C–C bond formation. The Wittig reaction and hydroboration are representative examples that were developed by Wittig and Brown, respectively, who received the Nobel Prize in chemistry in 1987. Since then, many reactions utilizing characteristics of heteroatoms have been developed. Heteroatom chemistry has gradually shifted to organic element chemistry treating mainly chemical properties such as bonding modes, structural features, etc. based on the characteristics of the heteroatom or main group element. Here, I wish to overview such heteroatom chemistry through reports on symposiums and research funds related to heteroatom chemistry in Japan, the Asian contribution to conferences from the 1st to 9th International Conferences on Heteroatom Chemistry (ICHAC) in oral and poster presentations, chemistry of compounds bearing low- and high-coordination main group elements, the contribution of our group to heteroatom chemistry, and future heteroatom chemistry.

SYMPOSIUMS AND RESEARCH FUNDS RELATED TO HETEROATOM CHEMISTRY IN JAPAN

Symposiums

In 1967, Oae, who was chair of the 1st ICHAC, a father of sulfur chemistry, started the 1st Symposium on Organic Sulfur Chemistry (1st to 6th), together with Hori and Kaji. Mukaiyama and Inamoto started the 1st Symposium on Organophosphorus Compounds in 1972. In 1973, these symposiums were combined and continued as the Symposium on Organic Sulfur and Phosphorus Compounds (1st to 16th). In 1987, the 1st ICHAC was held mainly by leaders of this sulfur and phosphorus symposium in Kobe. In 1990, three years after the successful end of the 1st ICHAC, the name of the Symposium on Organic Sulfur and Phosphorus Compounds was changed to the Symposium on Heteroatom Chemistry (17th to

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32nd). In 2006, its name was changed again to the Symposium on Organic Main Group Element Chemistry (33rd to present). In the last year, the 48th symposium was held in Kanazawa.

In 1974, the Symposium on Organometallic Chemistry (21st to present) started as a symposium related to heteroatom chemistry. This symposium originally came from the Symposium on Organosilicon Chemistry, which Watase started as a chair of the Organosilicon Chemistry Division of the Kinki Chemistry Society in 1954, and which was later joined by Kumada, Sakurai, and Ando. In the last year, the 58th symposium was held in Nagoya. Recently, the number of chemists who attend both symposiums has been increasing.

Research funds supporting heteroatom chemistry

Heteroatom chemistry has been financially supported by research funds, namely, Grants-in-Aid for Scientific Research on Priority Areas by Akiba (1989–1992), Tamao (1997–2000), Tatsumi (2002–2005), and Miyaura (2006–2009) and a Grant-in-Aid for Scientific Research on Innovative Areas by Akasaka (2008–2012). These are big projects, which more than 100 researchers have joined for research based on a common theme, and many heteroatom chemists have benefitted from these funds.

ASIAN CONTRIBUTION TO ICHAC IN ORAL AND POSTER PRESENTATIONS

Here, Asia includes Turkey, Israel, Jordan, Iran, Iraq, Saudi Arabia, Oman, Pakistan, India, Bangladesh, Thailand, Malaysia, Mongolia, China, Taiwan, Hong Kong, Korea, Japan, Australia, and New Zealand, which are Asian countries that have contributed to oral and/or poster presentations more than once.

Oral presentations include plenary lectures, invited or session lectures, and general oral presentations. Figure 1 shows the contribution from Asia, America, Europe, and Africa to oral presentations, and their contribution to poster presentations is shown in Fig. 2. Numbers in Figs. 1 and 2 show the Japanese contribution in Asia. For oral presentations, except for the 5th and 6th conferences, which were held in Canada and Poland, respectively, the Asian contribution was comparable to or higher compared with others. The contribution from Japan to oral presentations was always the highest in Asia, except for the 7th conference, where that from China was the highest.

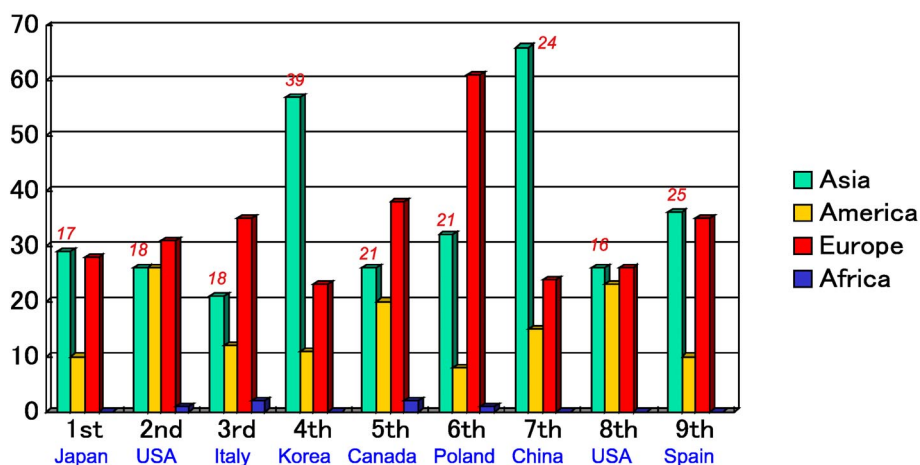


Fig. 1 Contribution of Asia, America, Europe, and Africa to oral presentations including plenary lectures and invited or session lectures.

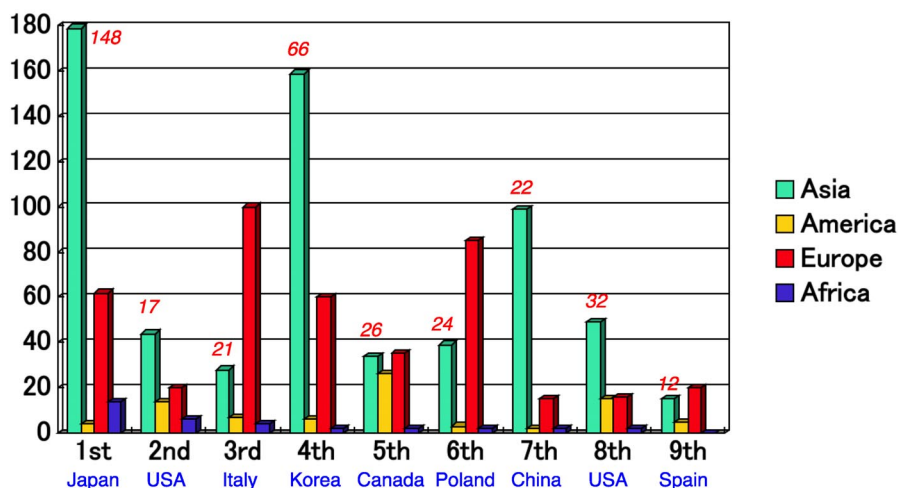


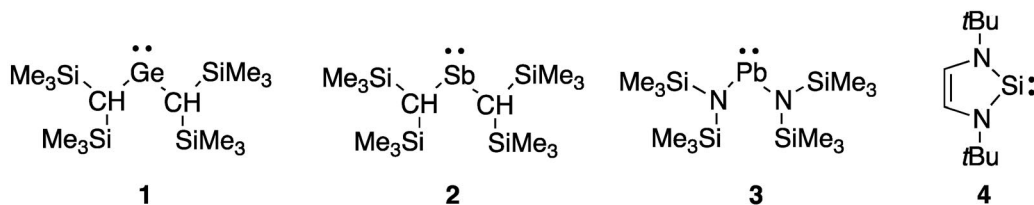
Fig. 2 Contribution of Asia, America, Europe, and Africa to poster presentations.

On the one hand, for poster presentations, the contribution from America is quite low and the contribution from Asia is much more than that from Europe, except for the 3rd and 6th conferences (Italy and Poland, respectively). Contribution from Japan to poster presentations was also the highest in Asia in all conferences, except for the 2nd, 4th, and 6th conferences, where the highest contribution was from India, Korea, and China, respectively. It can be concluded that contribution from Asia is high in most ICHAC conferences or reasonable for some cases considering the places outside Asia. Contribution from Japan in Asia can be concluded similarly.

CHEMISTRY OF COMPOUNDS BEARING LOW-COORDINATED MAIN GROUP ELEMENTS

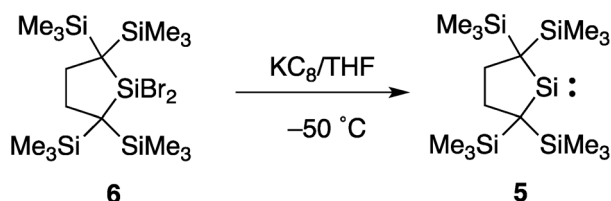
Divalent species containing heavier group 14 elements

As earlier investigations, Lappert et al. reported heavier group 14 element analogues of carbenes, germylene **1** [1], stannylene **2** [2], and plumbylene **3** [3], as shown in Scheme 1. These are stabilized by steric protection and π -donation from the heteroatom to a vacant orbital of the central atom. West and Denk reported *N*-heterocyclic (NHC) silylene **4** [4] as a silicon analogue of Arduengo's NHC carbene [5].



Scheme 1 Germylene **1**, stannylene **2**, plumbylene **3**, and NHC silylene **4**.

Kira et al. succeeded in synthesizing the first stable dialkylsilylene **5** by reduction of the corresponding dibromide **6** with potassium graphite (Scheme 2) [6]. The X-ray analysis showed this as a

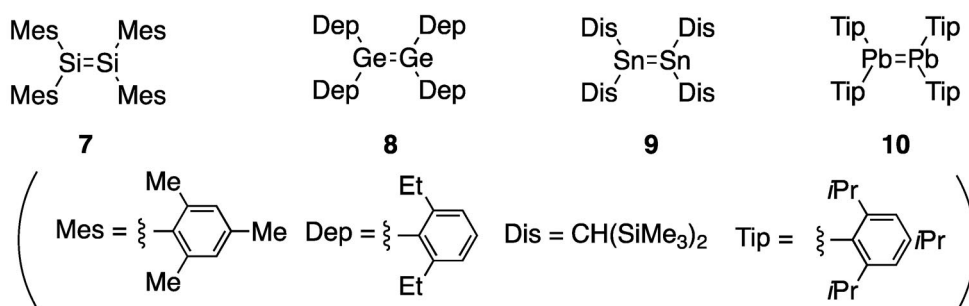


Scheme 2 Synthetic route to dialkylsilylene **5**.

Japanese war helmet (Kabuto)-shaped molecule that nicely prohibits its dimerization. The ^{29}Si -NMR chemical shift was 507.4 ppm, which is a characteristic for low-valent silicon species.

Compounds with a double bond between heavier main group elements

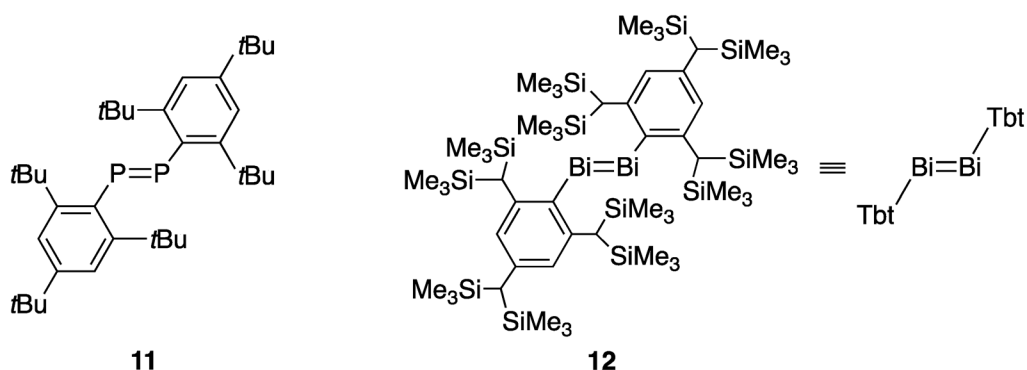
As double bond compounds between heavier group 14 elements, disilene **7** [7] and its heavier element analogues, digermene **8** [8], distannene **9** [9], and diplumbene **10** [10], were synthesized (Scheme 3). Tetramesityldisilene (**7**) was synthesized by West et al. as the first Si–Si doubly bonded compound. It is interesting to point out that bulkier substituents must be introduced on going from the third to the sixth row.



Scheme 3 Disilene **7**, digermene **8**, distannene **9**, and diplumbene **10**.

The year 1981 was a memorable year, when the double bond rule that compounds with a double bond between heavier elements below the third row do not exist, was violated by successful syntheses of stable disilene **7** [7] by West et al. in the United States and diphosphene **11** [11], by Yoshifuji and Inamoto et al. in Japan (Schemes 3 and 4).

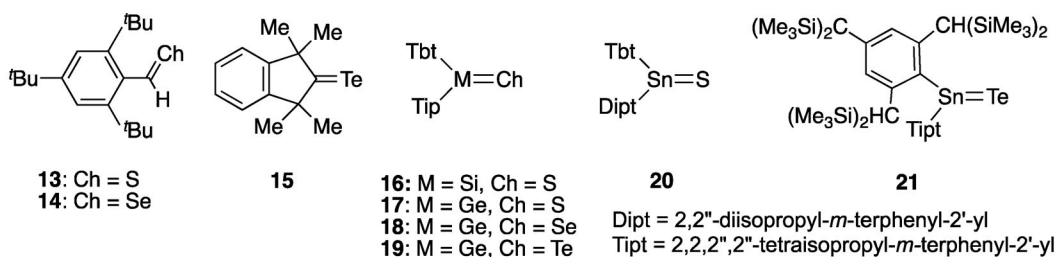
The disilene was stabilized by introduction of mesityl group as a steric protection group, the much bulkier 2,4,6-tri-*tert*-butylphenyl group was needed for the diphosphene, because four steric protecting groups can be introduced to the disilene, while only two groups are available for the diphosphene. The heaviest element analogues of these series, namely, diplumbene **10** [10] and dibismuthene **12** [12], were successfully synthesized by Weidenbruch et al. and Tokitoh and Okazaki et al., respectively, although much bulkier groups than mesityl and 2,4,6-tri-*tert*-butylphenyl groups were necessary as shown in Schemes 3 and 4. Structural features of these series are as follows: the compounds in the heavier group 14 series have *trans*-bent structures, while the heavier group 15 series have planar structures, however, the carbon-pnictogen-pnictogen angles are much smaller than 120° , which are considered as different phenomena originating from the difficulty of hybridization between s- and p-orbitals in heavier elements in sharp contrast with each second-row element.



Scheme 4 Diphosphene **11** and dibismuthene **12**.

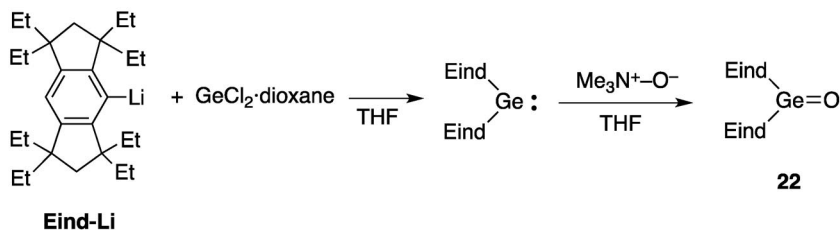
Heavy aldehydes and ketones

Thiobenzaldehyde **13** [13] and selenobenzaldehyde **14** [14] were reported relatively early by Okazaki et al. by taking advantage of kinetic stabilization by the 2,4,6-tri-*tert*-butylphenyl group. Telluroketone **15**, which is stable in solution, was also obtained by the same group [15]. For other heavy ketones, silanethione **16** [16], germanethione **17** [17], germaneselone **18** [18], germanetellone **19** [19], and even stannaneselone **20** [20] were synthesized by Tokitoh and Okazaki et al. using combinations of Tbt and Tip groups or Tbt and Dipt groups or Bbt and Tipt as steric protecting groups. Recently, Tokitoh et al. reported stannanetellone **21** [21] stabilized by Bbt and Tipt groups (Scheme 5).



Scheme 5 Heavy aldehydes **13** and **14** and ketones **15**–**21**.

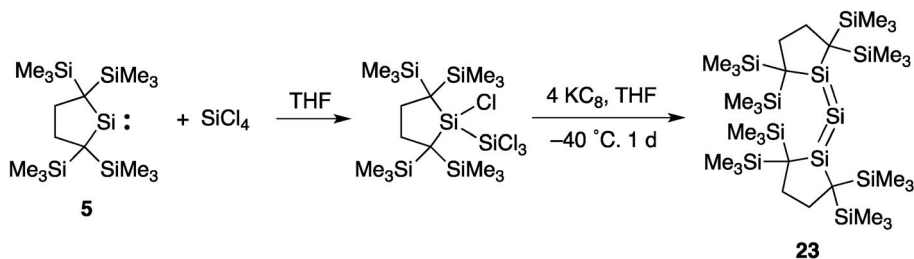
Very recently, Tamao and Matsuo et al. succeeded in synthesizing the first stable germanone **22** by taking advantage of effective steric protection of the Eind group originally developed by their group (Scheme 6) [22]. This has a trigonal planar structure around the germanium atom.



Scheme 6 Synthetic route to germanone **22**.

Heterocumulenes containing heavier main group elements

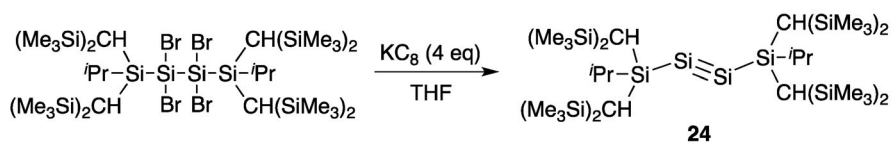
As phosphorus-containing examples, a 1,3-diphosphaallene [23] and a 1-phosphaallene [24] bearing 2,4,6-tri-*tert*-butylphenyl group(s) as a steric protecting group were synthesized. These molecules are not linear, but slightly bent, which is a different feature from the ketene or carbodiimide. Kira et al. succeeded in synthesizing the trisila analogue, trisilaallene **23** [25], which has a bent structure with disorder (Scheme 7).



Scheme 7 Synthetic route to trisilaallene **23**.

Heavier analogues of acetylene

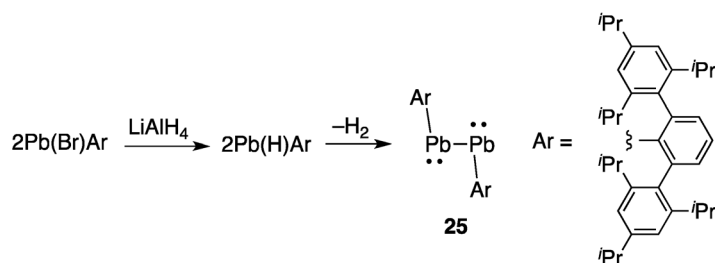
Heavier analogues of acetylene have been synthesized. In 2004, Sekiguchi et al. and Wiberg et al. independently reported the first Si–Si triple bond compounds [26,27]. Sekiguchi's compound **24** was synthesized as an emerald green crystal by reduction of the corresponding tetrabromodisilane with potassium graphite (Scheme 8) [26]. The X-ray analysis showed that it has a *trans*-bent structure, which is completely different from acetylene. The bond length is shorter than a double bond length, indicating a real Si–Si triple bond.



Scheme 8 Synthetic route to disilyne **24**.

Very recently, an aryl-substituted digermylene was synthesized by Tokitoh et al. and shown to have a Ge–Ge triple bond [28]. For this type of compound, the situation changes completely on going farther down in the periodic table. Power et al. succeeded in synthesizing a lead analogue **25** of acetylene (Scheme 9) and showed that the Pb–Pb bond is not a triple bond at all, but a single bond and concluded that this compound should be recognized as a bis-plumbylene [29].

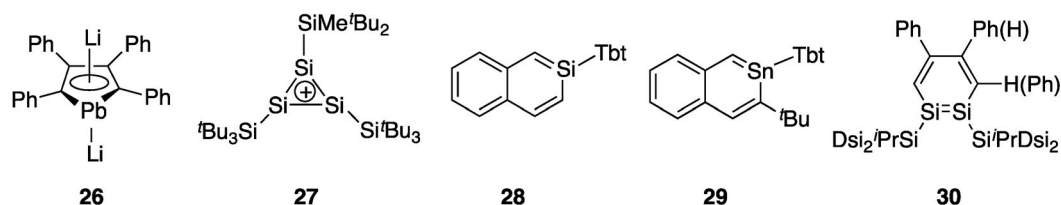
Recently, Robinson et al. reported naked main group diatomics such as diborene [30], disilene [31], and a P₂ complex [32] stabilized by NHC as new types of unsaturated compounds.



Scheme 9 Synthetic route to lead analogue **25** of acetylene.

Aromatic species containing heavier group 14 elements

Among them, heavy metallocyclopentadienides were the first to be synthesized. Silanole dianions [33] were synthesized as the first example, and then germanium analogues were also synthesized [34]. Disilagerma and trisila versions were also reported by Sekiguchi et al. [35,36]. Very recently, Saito et al. succeeded in synthesizing heavier analogues, stannole dianion [37], and plumbole dianion **26** (Scheme 10) and concluded that even plumbole dianion **26** has aromaticity from the fact that there is no bond alternation between the endocyclic C–C bonds and that it has a negative nucleus-independent chemical shift (NICS) value [38].



Scheme 10 Plumbole dianion **26**, trisilacyclopropenium **27**, 2-silanaphthalene **28**, 2-stannanaphthalene **29**, and 1,2-disilabenzene **30**.

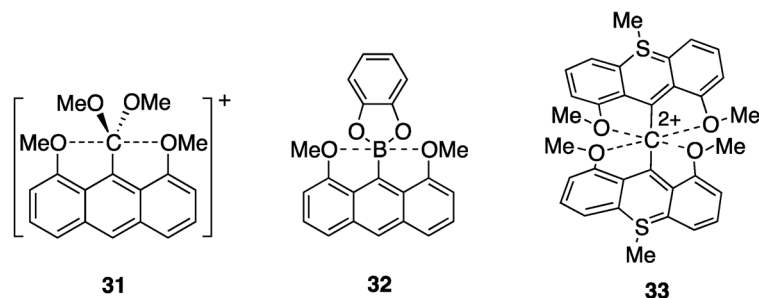
Aromatic cation species were also synthesized. Sekiguchi et al. succeeded in obtaining the trisilacyclopropenium cation **27** (Scheme 10), which is a trisila analogue of the aromatic cyclopropenium cation, as a salt with tetrakis(4-*tert*-butyl-2,3,5,6-tetrafluorophenyl)borate [39]. The X-ray analysis showed that this is a completely free silycenium cation without interaction with a counter anion.

After the attempted synthesis of a silabenzene by Märkel et al. [40], Tokitoh and Okazaki et al. opened the chemistry of neutral aromatic compounds containing heavier group 14 elements. As the first example, 2-silanaphthalene **28** (Scheme 10) was synthesized by taking advantage of kinetic stabilization by the Tbt group [41]. Its aromaticity was confirmed by a planar structure without bond alternation, a negative NICS value similar to that of naphthalene, etc. This chemistry has been continued by Tokitoh et al. and now tin analogue **29** (Scheme 9) has been successfully synthesized [42]. In 2007, Sekiguchi et al. reported the synthesis and characterization of 1,2-disilabenzene **30** (Scheme 10) by (2 + 2 + 2)-cycloaddition of disilyne **24** with 2 molar equiv of phenylacetylene [43]. Very recently, Tokitoh et al. reported 1,2-disilabenzene containing aromatic Bbt groups at the 1,2-positions [44].

CHEMISTRY OF COMPOUNDS BEARING HIGH-COORDINATION MAIN GROUP ELEMENTS

Second-row element compounds

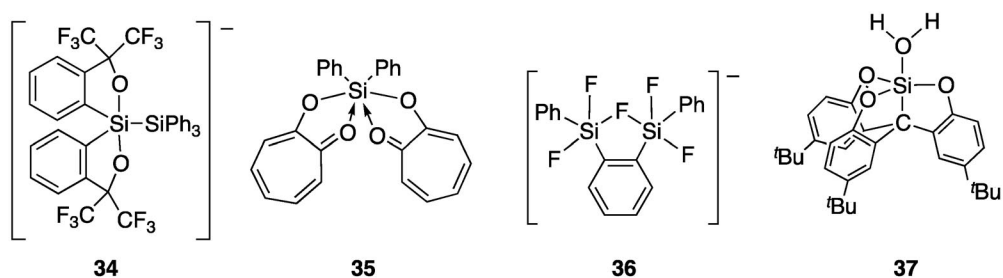
First, high-coordination carbon and boron compounds, which were expected to be difficult to synthesize, are described. The pentacoordinated carbon species **31** [45], pentacoordinated boron compound **32** [46], and hexacoordinated carbon species **33** [47] were synthesized and characterized by Yamamoto and Akiba et al. (Scheme 11). Their structures were determined by X-ray analysis, and bond paths were observed between the central atom and oxygen atoms by Atoms in Molecule calculations.



Scheme 11 Highly coordinated carbon and boron species **31–33**.

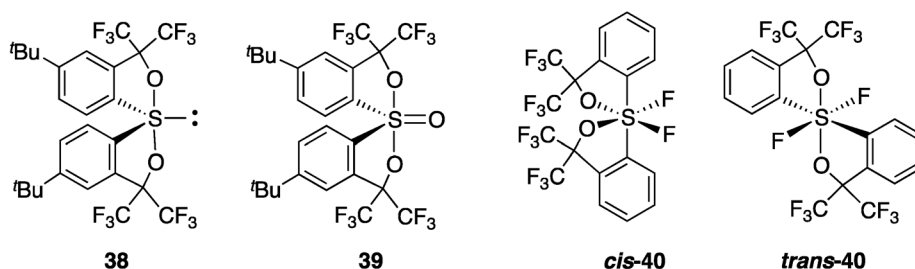
Heavier main group element compounds

Among many high-coordination silicon compounds reported previously, four species **34–37** by Japanese contributors are shown in Scheme 12 [48–51]. Sakurai and Kira et al. reported the first silylsilicate **34** with tetracoordinated silicon and anionic pentacoordinated silicon [48] and neutral hexacoordinated compound **35** [49]. Tamao et al. reported the first pentacoordinated fluorine-bridged compound **36** [50]. 5-Carbasilatrane **37** is one of our contributions to high-coordination silicon chemistry, which is a water-coordinated neutral silane. Interestingly, a dimeric structure in the solid state can be recognized as a frozen intermediate of the hydrolysis in a triaryloxysilane [51].



Scheme 12 Highly coordinated silicon species **34–37**.

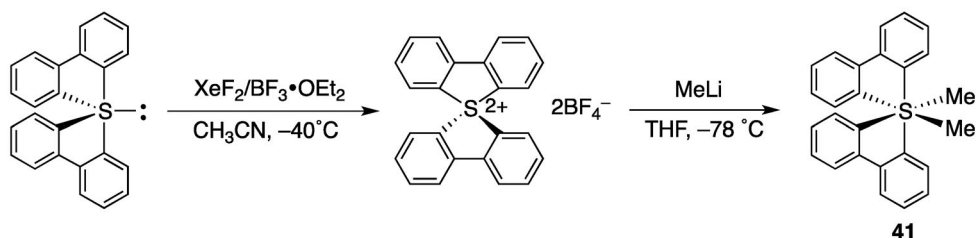
As high-coordination group 16 element compounds, a variety of compounds have been reported by Martin et al. [52–54], Kapovits et al. [55], and Furukawa and Fujihara et al. [56]. For early examples by Martin et al., sulfurane **38** [52], sulfurane oxide **39** [53], and difluorosulfuranes *cis*-**40** and *trans*-**40** [54] are shown in Scheme 13. These bidentate ligands developed by Martin are called Martin ligands and are very useful ligands to stabilize the highly coordinated state. Their X-ray analysis



Scheme 13 Sulfurane **38**, sulfurane oxide **39**, and difluoropersulfuranes *cis*-**40** and *trans*-**40**.

showed that they have a pseudotrigonal bipyramidal, trigonal bipyramidal, and octahedral structures, respectively.

Very recently, Sato, Furukawa, and Nabeshima et al. succeeded in synthesizing all carbon persulfurane **41** [57] by taking advantage of the high reactivity of the sulfurane dication, which was originally synthesized from the corresponding sulfurane (Scheme 14). The structure of **41** was determined by X-ray analysis to be octahedral.



Scheme 14 Synthetic route to all carbon persulfurane **41**.

As its heaviest analogues, hexaaryltellurium compounds, Ph_6Te and $(4\text{-CF}_3\text{C}_6\text{H}_4)_6\text{Te}$ with octahedral structures had already been synthesized by Akiba et al. using quite pure synthetic intermediates [58].

CONTRIBUTION FROM OUR GROUP TO HETEROATOM CHEMISTRY

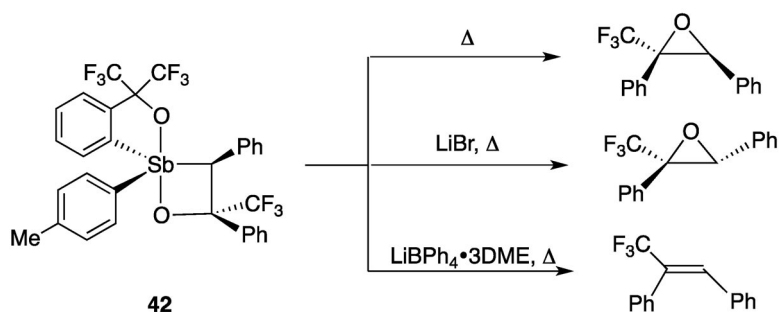
Among our contributions to main group element chemistry, three topics, namely, chemistry of four-membered ring compounds containing high-coordination main group elements, photocontrol of the coordination number of a main group element utilizing photoisomerization of an azobenzene unit, and the “Asura” bond compound are described.

Chemistry of four-membered ring compounds containing high-coordination main group elements

Since the first report on “Novel synthetic route to isolable pentacoordinate 1,2-oxaphosphetanes and mechanism of their thermolysis, the second step of the Wittig reaction” [59], we have investigated several types of four-membered ring compounds containing high-coordination main group elements (B, Si, Ge, Sn, P, Sb, S, Se, Te, and I). Most of them are synthesized by taking advantage of the stabilizing effect of the Martin ligand on highly coordinated states. These results have been summarized as review and account articles [60–64]. These compounds showed three main reactivities, depending on the group

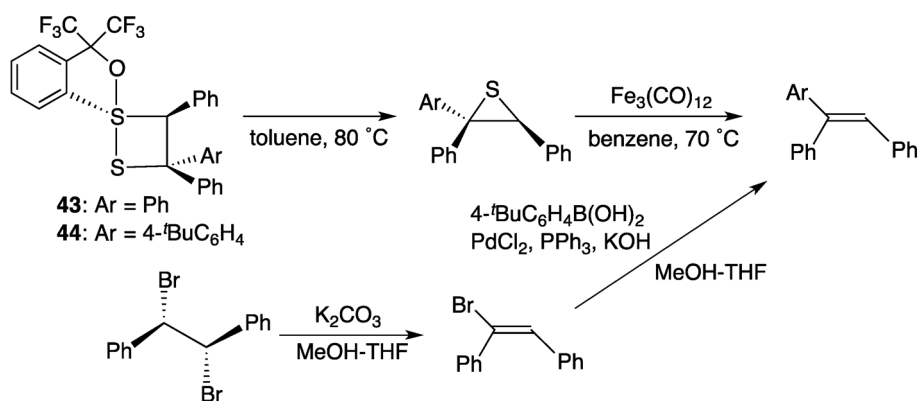
of the central atoms. The first one is the reactivity as intermediates of the Wittig-type reaction, that is, their thermolyses give the corresponding alkenes in the cases of the compounds containing B, Si, Ge, Sn, and P. The second reactivity is the three-membered ring formation, which is strongly related to the Corey–Chaykovsky reaction, in the cases of some S- or Se-containing compounds. The third type is the reactivity as intermediates in the homo-Brook rearrangement; that is, giving the corresponding alcohols after hydrolysis in the cases of the compounds containing silicon with a proton source and less steric hindrance at the 3-position. Interestingly, X-ray analysis showed that they have distorted trigonal bipyramidal structures or pseudotrigonal bipyramidal structures. The iodine analogue was shown to have a T-shaped structure [65]. Here, two relatively recent examples, namely, a pentacoordinated 1,2-oxastibetane and a tetracoordinated dithietane, are shown.

As a heavier group 15 element analogue of pentacoordinated 1,2-oxaphosphetane, we synthesized pentacoordinated 1,2-oxastibetane **42** (Scheme 15) and showed it has a crystal structure similar to that of 1,2-oxaphosphetane by X-ray crystallographic analysis [66]. However, the reactivity was completely different from that of the phosphorus analogue, despite the same group 15 element as phosphorus (Scheme 15). That is, its thermolysis gave the corresponding epoxide with retention of configuration. This selectively gave two different products, the corresponding epoxide with inversion of configuration and an alkene with retention of configuration by changing the reaction conditions, in the presence of LiBr or LiBPh₄·3DME, so that we called this compound a “chameleon compound” (Scheme 15). Further investigations showed that during thermolysis in the presence of LiBPh₄·3DME, the corresponding hexacoordinated 1,2-oxastibetanide formed by migration of the phenyl anion from tetraphenylborate to the antimony of **42** is a reactive intermediate, which gave the corresponding alkene. The difference in the reactivity between phosphorus and antimony compounds would stem from the difference in the bond energy between P=O and Sb=O bonds.



Scheme 15 Pentacoordinated 1,2-oxastibetane **42** and its thermolyses under different conditions.

Very recently, we succeeded in synthesizing tetracoordinated dithietane **43**, sulfur analogues of tetracoordinated 1,2-oxathietanes. The structure was determined by the X-ray crystallographic analysis to be a pseudotrigonal bipyramid with oxygen and sulfur at the equatorial positions [67]. This compound showed a reactivity similar to that of the usual disulfides. Furthermore, thermolysis gave the corresponding thiirane, whose relative stereochemistry at the 3- and 4-positions was shown to be maintained by using 4-phenyl-4-(4-*tert*-butylphenyl) derivative **44** [68] (Scheme 16). This is the third example of these compounds, which undergo ligand coupling to give the corresponding three-membered ring compound with retention of configuration.

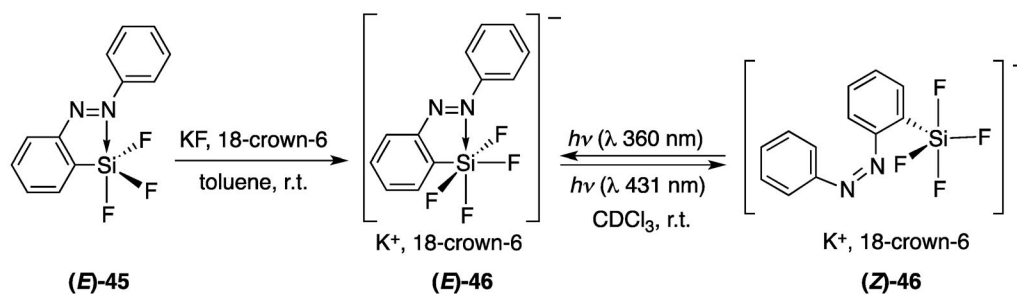


Scheme 16 Tetracoordinated 1,2-dithietanes **43** and **44** and thirane formation from **44** with retention of configuration.

Photocontrol of the coordination number of main group elements utilizing azobenzenes

To photocontrol of the coordination number of main group elements, we thought to introduce a main group element to the 2-position of azobenzene, which is well known as a chromophore and has an azo group available for coordination. If so, the coordination number can be controlled by photoirradiation, because the coordination of the nitrogen is broken or rebuilt by photoisomerization. If one can control the coordination number, one can also control the reactivity by irradiation. Initially, silicon compounds are described. We synthesized 2-trifluorosilylazobenzene (**45**), which was shown to have a penta-coordinated silicon both in solution and in the solid state by variable-temperature NMR and X-ray crystallographic analysis [69].

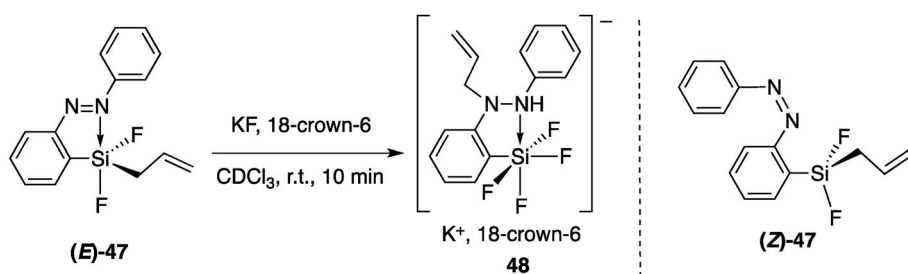
Hexacoordinated tetrafluorosilicate (*E*)-**46** was obtained by treatment of **45** with KF in the presence of 18-crown-6 at room temperature. Interconversion between (*E*)-**46** with coordination number 6 and (*Z*)-**46** with coordination number 5 was achieved under irradiation at 360 and 431 nm (Scheme 17) [69]. We could isolate both isomers and obtain single crystals suitable for X-ray crystal analysis. X-ray crystallographic analysis showed that (*E*)-**46** has an octahedral structure consisting of four fluorine, one nitrogen, and one carbon atoms, where the nitrogen and carbon atoms are *cis* to each other, while (*Z*)-**46** has a trigonal bipyramidal structure consisting of four fluorine and one carbon atoms, where two fluorine atoms occupy the apical positions, because the nitrogen of the azo group can no longer coordinate to the silicon in (*Z*)-**46** [69].



Scheme 17 2-Trifluorosilylazobenzene (*E*)-**45**, formation of tetrafluorosilicate (*E*)-**46**, and interconversion between (*E*)-**46** and (*Z*)-**46** (coordination number change between 6 and 5).

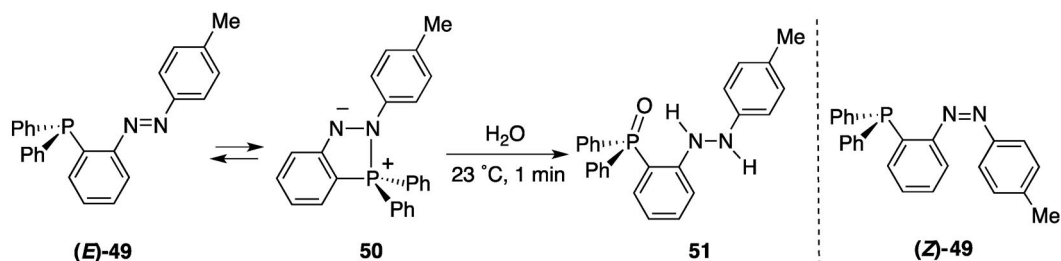
If the coordination number were changed, the reactivity also should be changed. Therefore, we next attempted to photocontrol the reactivity by irradiation. We synthesized allylsilane (*E*)-**47** [70] and tried the Hosomi–Sakurai reaction using this pentacoordinated allylsilane and benzaldehyde. However, no reaction took place, because the coordination is not strong enough to promote the reaction. To increase the coordination number of the silicon, we added KF to a solution of (*E*)-**47** in the presence of 18-crown-6, resulting in allyl-migration from silicon to nitrogen atoms to give the corresponding *N*-allylhydrazinosilicate **48** at room temperature within 10 min (Scheme 18).

Interestingly, under the same conditions, (*Z*)-**47** formed by irradiation of (*E*)-**47** did not undergo the allyl-migration at all, but the reaction occurred again when (*E*)-**47** was formed by irradiation [70]. Further investigations showed that this migration occurred intramolecularly via a six-membered transition state (γ -attack of the allyl group) [71]. Thus, we could demonstrate photocontrol of go or stop of the allyl migration reaction.



Scheme 18 Allyl migration of allylsilane (*E*)-**47** giving *N*-allylhydrazinosilicate **48**, and (*Z*)-**47**.

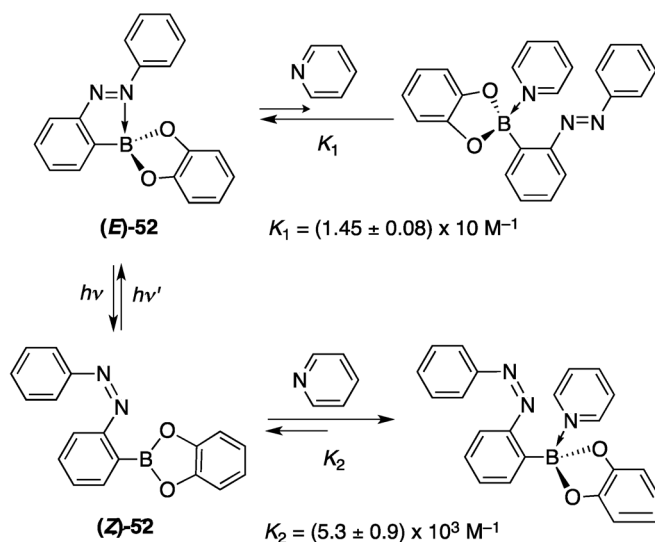
Next, we attempted to introduce a diphenylphosphino group to the 2-position of azobenzene instead of the silyl group. Thus obtained (*E*)-**49** was found to be in equilibrium with the inner phosphonium salt **50**, which formed by nucleophilic attack of the phosphorus lone pair on the nitrogen of the azo group of (*E*)-**49** [72]. The inner phosphonium salt **50** can be recognized as an intramolecular intermediate of the Mitsunobu reagent, which readily hydrolyzes to give the corresponding hydrazinophosphine oxide **51** (23 °C, 1 min). The hydrolysis reaction did not occur in (*Z*)-**49** formed by photoisomerization of (*E*)-**49** under the same reaction conditions (Scheme 19). Thus, we could control the hydrolysis reactivity by irradiation.



Scheme 19 Equilibration between phosphinoazobenzene (*E*)-**49** and inner phosphonium salt **50**, its hydrolysis giving hydrazinophosphine oxide **51**, and (*Z*)-**49**.

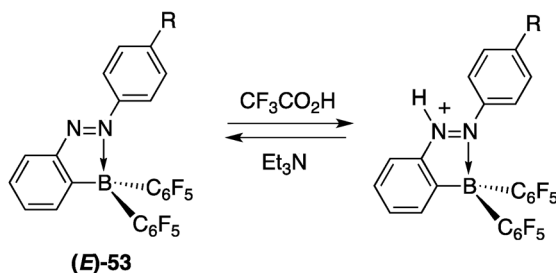
If a boron group could be introduced to the 2-position of azobenzene, one nitrogen of the azo group could coordinate to the boron center in the *E*-isomer, but not in the *Z*-isomer. Therefore, catecholborane (*E*)-**52** does not show Lewis acidity toward Lewis bases unless competing with the intra-

molecular coordination of the nitrogen, while the boron center of (**Z**)-**52** is free of nitrogen-coordination, which can act as a Lewis acid. Consequently, we can control the Lewis acidity by photoisomerization. We estimated the complex formation constant of (**Z**)-**52** with pyridine to be 350 times larger than that of (**E**)-**52** using the degree of up-field shift of the ^{11}B NMR signal from each chemical shift of free (**E**)-**52** and (**Z**)-**52** (Scheme 20) [73].



Scheme 20 Complex formation constants of catecholboranes (**E**)-**52** and (**Z**)-**52** with pyridine.

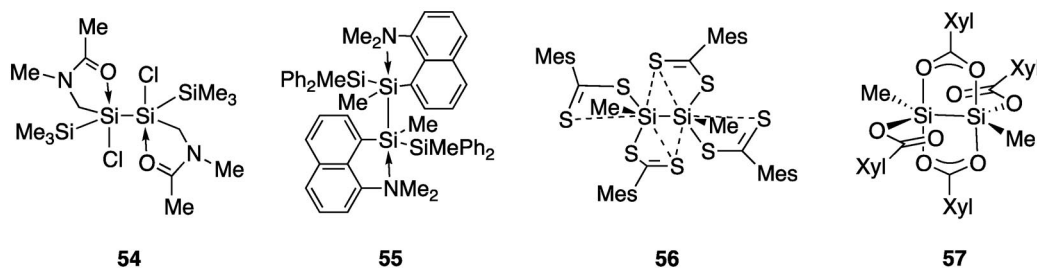
During the investigation, we succeeded in synthesizing fluorescent azobenzenes (**E**)-**53** ($\text{R} = \text{H}$) by the introduction of bis(pentafluorophenyl) groups to the boron (Scheme 21) [74]. They showed green-colored fluorescence instead of photoisomerization. Upon adding a methoxy group at the 4'-position, the fluorescence quantum yield was increased from 0.23 to 0.76, which was the largest value among fluorescent azobenzenes at that time [74]. However, a 4'-*tert*-butyldimethylsiloxy derivative showed higher value (0.90) than the 4'-methoxy derivative in hexane [75], but now the latter shows the highest value of 0.98 in CH_2Cl_2 [76]. One of the fluorescent azobenzenes could be used as a pH responsible material (Scheme 21) [77] and also another as a vital stain [75]. Water-solubility is very important to act as a vital stain, so that we improved the solubility and can now synthesize water-soluble fluorescent azobenzenes [76].



Scheme 21 Fluorescence quenching and recovery of fluorescent azobenzene (**E**)-**53** by acid and base.

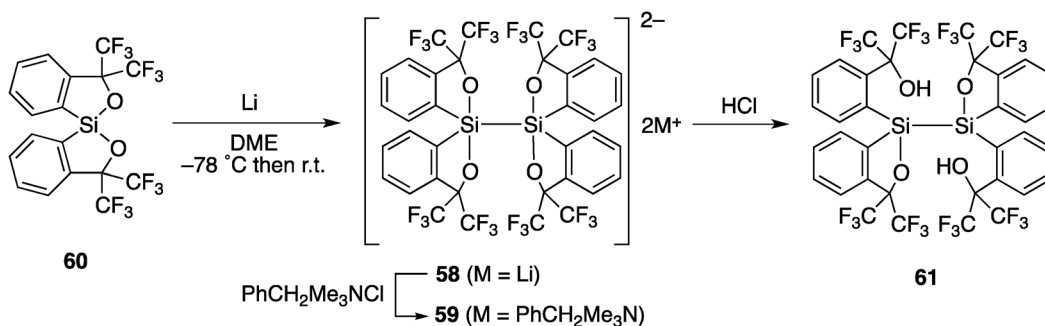
“Asura-BOND” COMPOUND

Besides the above-mentioned silylsilicate **34**, several types of highly coordinated silicon compounds with a Si–Si bond have been reported so far (Scheme 22). Tetrasilanes **54** and **55** with two neutral penta-coordinated silicon atoms by carbonyl oxygen and nitrogen lone pairs were also reported by Tanaka et al. [78] and Tamao et al. [79], respectively. We also synthesized the neutral compounds **56** and **57** with two heptacoordinated and pentacoordinated silicon atoms by sulfur- and oxygen-coordination, respectively [80,81]. However, there was no report on dianionic disilicate at that time, because it seemed very difficult to overcome the electrostatic and steric repulsions.



Scheme 22 Compounds **54**–**57** with a Si–Si bond containing highly coordinated silicon atoms.

We have overcome this difficulty and succeeded in synthesizing dianionic silicon species **58** and **59** with a bond containing two pentacoordinated silicon atoms [82]. The reaction of spirosilane **60** with lithium metal in 1,2-dimethoxyethane (DME) gave the desired dilithium salt **58** as a colorless solid (Scheme 23). This is the first dianionic disilicate. Surprisingly, this was stable in both air and water despite the presence of the two negative charges. In the ^{29}Si NMR, a signal was observed at δ –58.9 ppm, which is a reasonable value for pentacoordinated silicon compounds.



Scheme 23 Synthesis of disilicates **58** and **59** and their reactions with HCl giving **61**.

X-ray analysis of bis(benzyltrimethylammonium) disilicate **59** (Scheme 23) was carried out successfully to show that this compound has a direct bond (2.364 Å) between pentacoordinated silicon atoms, which is close to the average Si–Si single bond length of 2.34 Å of usual disilanes, despite the anticipated electronic repulsion and steric repulsion. %TBPe and %TBP_a, which are used as an indicator of how close the structure is to trigonal bipyramidal, were calculated to be 100 and 99 %, indicating that the silicon atoms have an almost ideal trigonal bipyramidal structure.

Electronic repulsion is considered to decrease by the distribution of negative charge to the periphery, namely, oxygen and carbon atoms at the positions adjacent to the silicon atoms, giving a positive

charge to the silicon atoms, which was supported by theoretical calculations of the atomic charges, while steric repulsion is reduced by rotation around the Si–Si bond, as shown by the very large O–Si–Si–O torsion angle (66.64°).

Protonation by HCl occurred on both oxygen atoms to give disilane **61**, showing that the oxygen atoms bonded to the silicon atom are basic (Scheme 23). Its UV–vis absorption band was observed at 258 nm, which is red-shifted compared with that (241 nm) of the usual reference disilane Ph₃SiSiPh₃. Cyclic voltammetry showed a low oxidation potential ($E_{pa} = -0.22$ and 0.83 V) compared with Ph₃SiSiPh₃ ($E_{pa} = 0.95$ V). Thus, this compound has the three above-mentioned characteristic properties. The Asura statue is well known to have three faces, six hands, and two legs. As eight bonds extend from the Si–Si body of the disilicate and the above three properties can be recognized as six hands + two legs + three faces, we named this compound an “Asura bond” compound from the structural similarity.

FUTURE HETEROATOM CHEMISTRY

Related fields to heteroatom chemistry now are π -electron chemistry, organic synthesis, materials science, molecular recognition, transition-metal chemistry, and polymer science. Interdisciplinary research between heteroatom chemistry and the above-mentioned related fields is now ongoing, although which field is more heavily weighted depends on each researcher. In heteroatom chemistry, element chemistry concerning both low- and high-coordination element compounds has been developed independently and affected by other related chemistry. In the future, combined chemistry between low- and high-coordination compounds will be important from the viewpoint not only of fundamental chemistry, but also of materials science. Although this may be one direction of future heteroatom chemistry, I think future heteroatom chemistry should be opened in different dimensions and further developed by young chemists. Therefore, I wish to get the following message out to the young chemists, “HOW TO DO OR NOT TO DO HETEROATOM CHEMISTRY. THAT IS THE QUESTION”.

Because of page limitations, I did not describe materials science. Finally, I thank all heteroatom chemists not only in Japan, but also throughout the world.

REFERENCES

1. P. J. Davidson, D. H. Harris, M. F. Lappert. *J. Chem. Soc., Dalton Trans.* 2268 (1976).
2. J. D. Cotton, P. J. Davidson, M. F. Lappert, J. D. Donaldson, J. Silvet. *J. Chem. Soc., Dalton Trans.* 2286 (1976).
3. T. Fjeeldberg, H. Hope, M. F. Lappert, P. P. Power, A. J. Thorne. *J. Chem. Soc., Chem. Commun.* 639 (1983).
4. M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner, N. Metzler. *J. Am. Chem. Soc.* **116**, 2691 (1994).
5. A. J. Arduengo III, R. L. Harlow, M. Kline. *J. Am. Chem. Soc.* **113**, 361 (1991).
6. M. Kira, S. Ishida, T. Iwamoto, C. Kabuto. *J. Am. Chem. Soc.* **121**, 9722 (1999).
7. R. West, M. J. Fink, J. Michl. *Science* **214**, 1343 (1981).
8. J. T. Snow, S. Murakami, S. Masamune, D. J. Williams. *Tetrahedron Lett.* **25**, 4191 (1984).
9. P. J. Davidson, M. F. Lappert. *J. Chem. Soc., Chem. Commun.* 317a (1973).
10. M. Strümann, W. Saak, H. Marsmann, M. Weidenbruch. *Angew. Chem., Int. Ed.* **38**, 187 (1999).
11. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi. *J. Am. Chem. Soc.* **103**, 4587 (1981).
12. N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase. *Science* **277**, 78 (1997).
13. R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, N. Inamoto. *J. Chem. Soc., Chem. Commun.* 1187 (1982).
14. R. Okazaki, N. Kumon, N. Inamoto. *J. Am. Chem. Soc.* **111**, 5949 (1989).
15. M. Minoura, T. Kawashima, R. Okazaki. *J. Am. Chem. Soc.* **113**, 7019 (1993).

16. H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki. *J. Am. Chem. Soc.* **116**, 11578 (1994).
17. N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki. *J. Am. Chem. Soc.* **113**, 8855 (1993).
18. T. Matsumoto, N. Tokitoh, R. Okazaki. *Angew. Chem., Int. Ed. Engl.* **33**, 2316 (1994).
19. N. Tokitoh, T. Matsumoto, R. Okazaki. *J. Am. Chem. Soc.* **119**, 2337 (1997).
20. M. Saito, N. Tokitoh, R. Okazaki. *J. Am. Chem. Soc.* **119**, 11124 (1997).
21. T. Tajima, N. Takeda, T. Sasamori, N. Tokitoh. *Organometallics* **25**, 3552 (2006).
22. L. Li, T. Fukawa, T. Matsuo, D. Hashizume, H. Fueno, K. Tanaka, K. Tamao. *Nat. Chem.* **4**, 361 (2012).
23. H. H. Karsch, H.-U. Reisacher, G. Müller. *Angew. Chem., Int. Ed. Engl.* **23**, 618 (1984).
24. R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkaus, F. Knoch. *Angew. Chem., Int. Ed. Engl.* **23**, 619 (1984).
25. S. Ishida, T. Iawamoto, C. Kabuto, M. Kira. *Nature* **421**, 725 (2003).
26. A. Sekiguchi, R. Kinjo, M. Ichinohe. *Science* **306**, 1755 (2004).
27. N. Wiberg, S. K. Vasisht, G. Fischer, P. Mayer. *Z. Anorg. Allg. Chem.* **630**, 1823 (2004).
28. Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh. *J. Am. Chem. Soc.* **128**, 1023 (2006).
29. L. Pu, B. Twamley, P. P. Power. *J. Am. Chem. Soc.* **122**, 3524 (2000).
30. Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson. *J. Am. Chem. Soc.* **129**, 12412 (2007).
31. Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson. *Science* **321**, 1069 (2008).
32. Y. Wang, Y. Xie, P. Wei, C. S. Wannere, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson. *J. Am. Chem. Soc.* **130**, 14970 (2008).
33. J.-H. Hong, P. Boudjouk, S. Castellino. *Organometallics* **13**, 3387 (1994).
34. R. West, H. Sohn, D. R. Powell, T. Müller, Y. Apeloig. *Angew. Chem., Int. Ed. Engl.* **35**, 1002 (1996).
35. V. Ya. Lee, R. Kato, M. Ichinohe, A. Sekiguchi. *J. Am. Chem. Soc.* **127**, 13142 (2005).
36. H. Yasuda, V. Ya Lee, A. Sekiguchi. *J. Am. Chem. Soc.* **131**, 6352 (2009).
37. M. Saito, R. Haga, M. Yoshioka. *Chem. Commun.* 1003 (2002).
38. M. Saito, M. Sakaguchi, T. Tajima, K. Ishimura, S. Nagase, M. Hada. *Science* **328**, 339 (2010).
39. M. Ichinohe, M. Igarashi, K. Sanuki, A. Sekiguchi. *J. Am. Chem. Soc.* **127**, 9978 (2005).
40. G. Märkl, W. Schlosser. *Angew. Chem., Int. Ed. Engl.* **27**, 963 (1988).
41. N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P. v. R. Schleyer, H. Jiao. *J. Am. Chem. Soc.* **119**, 6951 (1997).
42. Y. Mizuhata, T. Sasamori, N. Takeda, N. Tokitoh. *J. Am. Chem. Soc.* **128**, 1050 (2006).
43. R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto, S. Nagase. *J. Am. Chem. Soc.* **129**, 7766 (2007).
44. J. S. Han, T. Sasamori, Y. Mizuhata, N. Tokitoh. *Dalton Trans.* **39**, 9238 (2010).
45. K.-y. Akiba, M. Yamashita, Y. Yamamoto, S. Nagase. *J. Am. Chem. Soc.* **121**, 10644 (1999).
46. M. Yamashita, Y. Yamamoto, K.-y. Akiba, S. Nagase. *Angew. Chem., Int. Ed.* **39**, 4055 (2000).
47. T. Yamaguchi, Y. Yamamoto, D. Kinoshita, K.-y. Akiba, Y. Zhang, C. A. Reed, D. Hashizume, F. Iwasaki. *J. Am. Chem. Soc.* **130**, 6894 (2008).
48. M. Kira, K. Sato, C. Kabuto, H. Sakurai. *J. Am. Chem. Soc.* **111**, 3747 (1989).
49. M. Kira, L. C. Zhang, C. Kabuto, H. Sakurai. *Chem. Lett.* 659 (1995).
50. K. Tamao, T. Hayashi, Y. Ito, M. Shiro. *J. Am. Chem. Soc.* **112**, 2422 (1990).
51. J. Kobayashi, K. Kawasguchi, T. Kawashima. *J. Am. Chem. Soc.* **126**, 16318 (2004).
52. J. C. Martin, R. J. Arhart. *J. Am. Chem. Soc.* **94**, 4997 (1972).
53. J. C. Martin, E. F. Perozzi. *J. Am. Chem. Soc.* **96**, 3155 (1974).
54. R. S. Michalak, J. C. Martin. *J. Am. Chem. Soc.* **104**, 1683 (1982).
55. For example, see: I. Kapovits, A. Kálmán. *J. Chem. Soc., Chem. Commun.* 649 (1971).

56. For example, see: H. Fujihara, H. Mima, M. Ikegami, N. Furukawa. *J. Am. Chem. Soc.* **113**, 6337 (1991).
57. S. Sato, K. Matsunaga, E. Horn, N. Furukawa, T. Nabeshima. *J. Am. Chem. Soc.* **128**, 6778 (2006).
58. M. Minoura, T. Sagami, K.-y. Akiba, C. Modrakowski, A. Sudau, K. Seppelt, S. Wallenhausser. *Angew. Chem., Int. Ed.* **35**, 2660 (1996).
59. T. Kawashima, K. Kato, R. Okazaki. *J. Am. Chem. Soc.* **114**, 4008 (1992).
60. T. Kawashima, R. Okazaki. *Synlett* 600 (1996).
61. T. Kawashima. In *Chemistry of Hypervalent Compounds*, K.-y. Akiba (Ed.), pp. 171–210, Wiley-VCH, New York (1999).
62. T. Kawashima, R. Okazaki. In *Advances in Strained and Interesting Organic Molecules*, B. Halton (Ed.), pp. 1–41, JAI Press, Stamford (1999).
63. T. Kawashima. *Bull. Chem. Soc. Jpn.* **74**, 471 (2003).
64. T. Kawashima. *Coord. Chem. Rev.* **244**, 137 (2003).
65. T. Kawashima, K. Hoshiba, N. Kano. *J. Am. Chem. Soc.* **123**, 1507 (2001).
66. Y. Uchiyama, N. Kano, T. Kawashima. *J. Am. Chem. Soc.* **125**, 13346 (2003).
67. N. Kano, Y. Itoh, Y. Watanabe, S. Kusaka, T. Kawashima. *Angew. Chem., Int. Ed.* **47**, 9430 (2008).
68. S. Kusaka, N. Kano, T. Kawashima. *Heteroatom Chem.* **21**, 412 (2010).
69. N. Kano, F. Komatsu, T. Kawashima. *J. Am. Chem. Soc.* **123**, 10778 (2001).
70. N. Kano, M. Yamamura, T. Kawashima. *J. Am. Chem. Soc.* **126**, 6250 (2004).
71. M. Yamamura, N. Kano, T. Kawashima. *J. Organomet. Chem.* **692**, 313 (2007).
72. M. Yamamura, N. Kano, T. Kawashima. *J. Am. Chem. Soc.* **127**, 11954 (2005).
73. N. Kano, J. Yoshino, T. Kawashima. *Org. Lett.* **7**, 3909 (2005).
74. J. Yoshino, N. Kano, T. Kawashima. *Chem. Commun.* 559 (2007).
75. J. Yoshino, A. Furuta, T. Kambe, H. Itoi, N. Kano, T. Kawashima, Y. Ito, M. Asashima. *Chem.—Eur. J.* **16**, 5026 (2010).
76. H. Itoi, T. Kambe, N. Kano, T. Kawashima. *Inorg. Chim. Acta* **381**, 117 (2012).
77. J. Yoshino, N. Kano, T. Kawashima. *Chem. Lett.* **37**, 960 (2008).
78. I. El-Sayed, Y. Hatanaka, C. Muguruma, S. Shimada, M. Tanaka, N. Koga, M. Mikami. *J. Am. Chem. Soc.* **121**, 5095 (1999).
79. K. Tamao, M. Asahara, T. Saeki, A. Toshimitsu. *Angew. Chem., Int. Ed.* **38**, 335 (1999).
80. N. Kano, N. Nakagawa, T. Kawashima. *Angew. Chem., Int. Ed.* **40**, 3450 (2001).
81. N. Kano, N. Nakagawa, Y. Shinozaki, T. Kawashima, Y. Sato, Y. Naruse, S. Inagaki. *Organometallics* **24**, 2823 (2005).
82. N. Kano, H. Miyake, K. Sasaki, T. Kawashima, N. Mizorogi, S. Nagase. *Nat. Chem.* **2**, 112 (2010).