

Contribution

The development of new chemistry on multiple-bond compounds with heavier main group elements

Renji Okazaki, Professor,
Faculty of Science,
Japan Women's University

1. Introduction

The multiple-bond compounds including second period elements such as olefin, imine (Schiff base), ketone, acetylene, nitrile *etc.* are stable compounds and play a very important role in organic chemistry. Contrary to this, multiple-bond compounds containing elements from the third period onward (named as heavier main group elements), have long bond distances and their π bond energy generated through the overlapping of p-orbitals is low so that they are extremely unstable. Examples of π bond energy are shown in Table 1.¹

C=C	65	N=N	60	C=O	77
C=Si	38	P=N	44	C=S	52
Si=Si	25	P=P	34	Si=S	50

Table 1. π bond energy associated with double-bond including the multiple-bond of heavier main group elements. (kcal mol⁻¹) [MP4/EXT//3-21G(d)]

Due to such instability, up to the 1960, the so-called “double-bond rule”² has been described in textbooks as “the stable double-bond containing elements from third period onward is not in existence.”

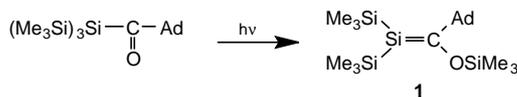
However, evidence confirming that these compounds exist in cryogenic matrix or gas phase as short-lived species, has accumulated from studies arising from the latter half of the 1960s to the 1970s. Stable compounds having P=C bonds³ as well as Si=C⁴, Si=Si⁵ and P=P⁶ have been synthesized and isolated for the first time in 1978 and 1981 respectively. Since then, chemistry with respect to multiple-bond compounds associated with heavier main group elements has developed rapidly and approaches the leading theme in main group element chemistry. In this paper, we describe recent developments in the field, focusing on the author's studies.

2. Double-bond compounds containing group 14 elements (silicon, germanium, tin, lead):

2.1 Heavier main group element analogues of an alkene:

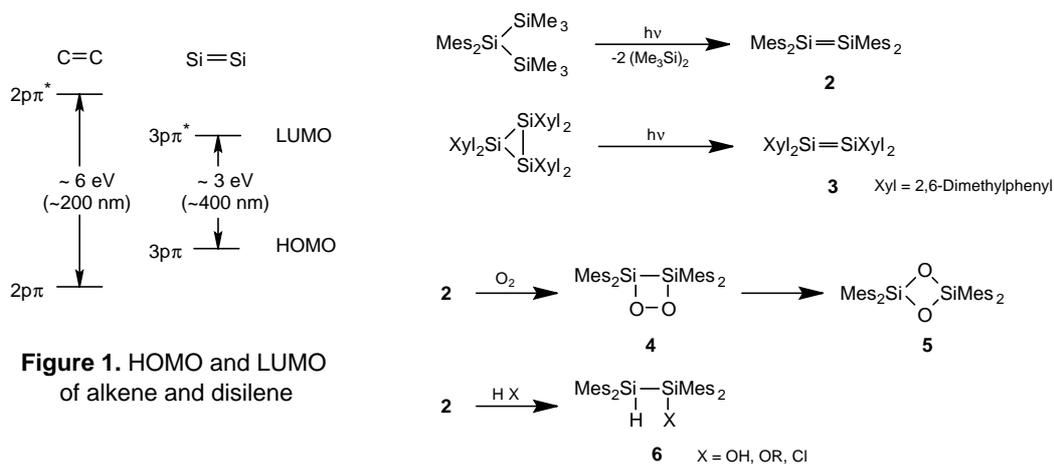
2.1.1 Disilene (Si-Si double-bond compounds) : ⁷

C-C double-bond compounds (alkene) represented by ethylene play an important role in organic chemistry. Normally an alkene is a stable compound in spite of its having moderate reactivity. Therefore, it was natural that we would try to synthesize such double-bond compounds containing silicon belonging to the same group of 14 located under carbon. However, such trials since end of the 19th century resulted in failure. The product obtained has proved to be its oligomer or polymer instead of the double-bond compound in question. Under the circumstances, based on such experiences, the aforementioned “double-bond rule” has come into existence. It has been confirmed that the introduction of sterically demanding substituents onto carbon and silicon containing the double-bond would be effective as a means of preventing polymerization. This method is either named as kinetic stabilization, in view of the fact that it stabilizes by lowering the reaction rate associated with unstable chemical species, or is named as steric protection since it protects the highly reactive double-bond by utilizing bulky substituents. By employing this technique, in 1981 silene **1** (Ad=1-adamantyl) having the first stable carbon-silicon double-bond and disilene **2** (Mes=mesityl) having a silicon-silicon double-bond were reported by Brook *et al.*⁴ and West *et al.*⁵ respectively. Shortly after the report by West, Masamune *et al.* synthesized disilene **3** using a different method.⁸ Afterward, several synthetic methods preparing silene⁹ and disilene⁷ were developed so that currently a considerable number of stable compounds of such types are known.

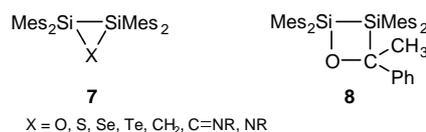


Silene **1**, disilene **2** and disilene **3** are stable under inert atmosphere but they show extremely high reactivity because disilene has high HOMO and lower LUMO, compared with olefin as indicated in Figure 1. This is the reason why disilene is yellow, as opposed to the colorless olefins.

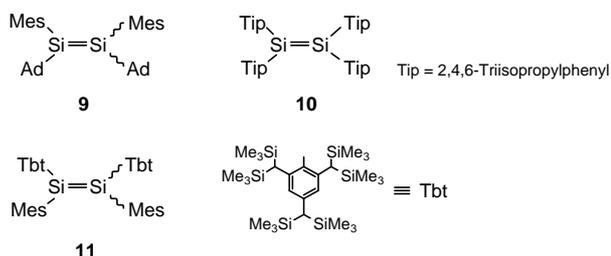
Disilene **2** reacts with oxygen and produces **5** by way of **4**.¹⁰ Further, it undergoes the addition reaction with water, alcohol, acids, *etc.* and readily produces **6**.¹¹



It is possible to synthesize many silicon compounds having new structures utilizing the high reactivity of disilene despite the fact that it is difficult to synthesize them through other methods. For example, by reacting with oxygen, sulfur, selenium, tellurium, diazomethane, isonitrile, azide *etc.* as well as reacting with ketones such as acetophenone, *etc.*, the undermentioned tricyclic compounds **7** including silicon¹² as well as the tetracyclic compounds **8** can be synthesized respectively.¹³



Disilenes **2** and **3** decompose immediately on contact with air. Their stability can be increased by adding bulkier substituents to the silicon. For example, the room temperature half-lives of compounds **9** and **10** is on the order of one day due to the presence of the bulky adamantyl and triisopropylphenyl substituents. We have been able to synthesize relatively stable compound **11** with half-life of about one month at room temperature, which makes it manageable in air. This compound has the bulky 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group (Tbt). The Tbt group has four bulky trimethylsilyl groups at the ortho positions. However, there is enough space at the 1 position, since the benzyl position is substituted with hydrogen, and this allows for sufficient reactivity to undergo the functional group transformation at that position. As has been shown, the Tbt group is extremely useful for stabilizing the high period multiple bonds which usually have high reactivity.



Disilene **11** is interesting in that it has the extremely bulky Tbt groups so that Si-Si double-bond is effectively protected in three dimensions. On the other hand, the silicon-silicon bond is lengthened in comparison with other disilenes so that it easily dissociates to silylene.¹⁶ X-ray crystal structure analysis of disilene **11** (*trans* form) is shown in Figure 2.¹⁶ The length of Si-Si bond is 2.228 Å which is the longest among disilenes with bulky aryl substituents.

In solution, **11** dissociates to silylene gradually at room temperature and rather rapidly at 70 °C. Therefore, *trans*-**11** isomerizes to *cis*-**11** and *cis*-**11** to *trans*-**11** respectively even at room temperature by way of the dissociation to silylene. It is known that the isomerization of olefins is generated not by the cleavage of the C-C bond, but by the rotation of the bond. Also, in case of the already known disilenes having relatively smaller sized substituents on silicon, isomerization is through the rotation of the Si-Si bond in the same way as in olefins. It is interesting to know that **11** is the first disilene which isomerizes based on the dissociation-association mechanism (Figure 3). Although silylene has been generated by means of thermolysis or photolysis at relatively high temperatures up to now, the discovery of the method for generating silylene under mild conditions has made it possible for many new organic silicon compounds to be synthesized, despite the fact that it had been difficult to synthesize them using the previous methods. Several examples are shown in Figure 4.^{16,18,19}

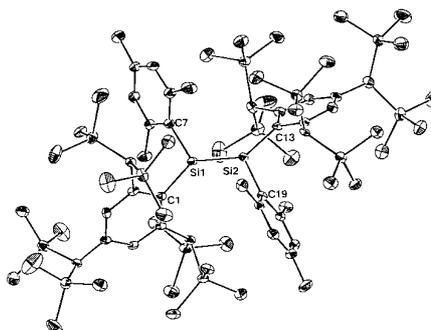


Figure 2. Molecular structure of disilene *trans*-**11**.

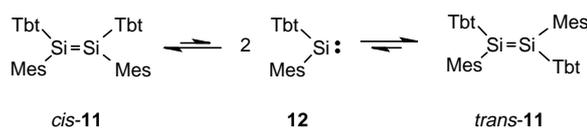


Figure 3. *cis-trans* Isomerization based on the dissociation-association mechanism of disilene **11**.

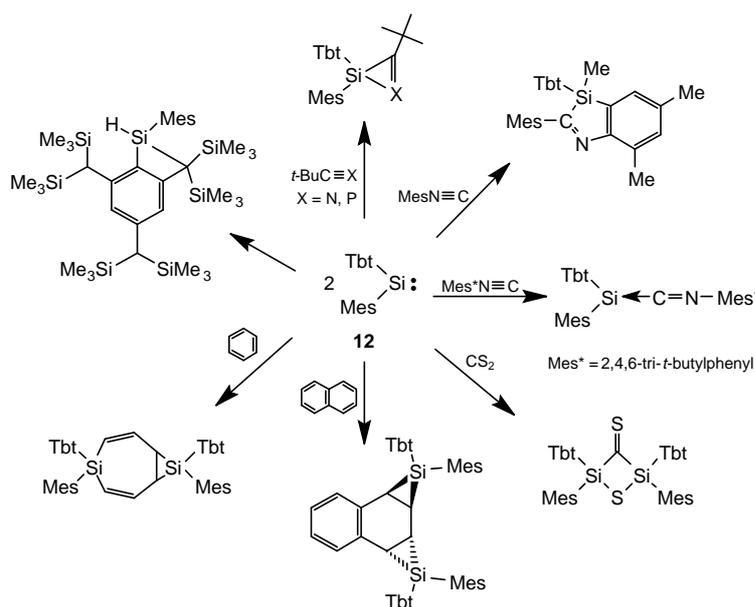
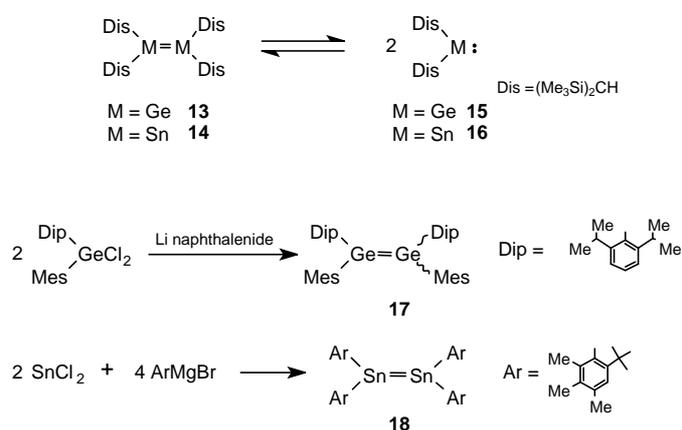


Figure 4. Reactions of silylene **12**.^{16,18,19}

2.1.2 The double-bond compounds of germanium, tin, and lead (digermene, distannene and diplumbene):²⁰

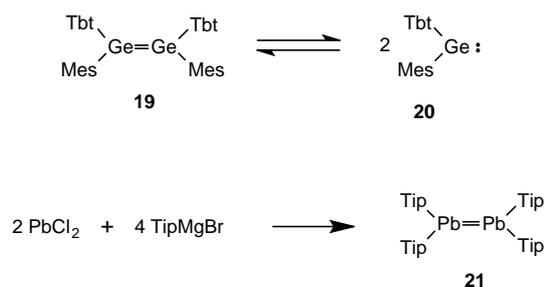
The double-bond compounds (named as digermene, distannene and diplumbene respectively) consisting of germanium, tin and lead belonging to the same group as silicon are still more unstable since the π bond energy with respect to Ge=Ge, Sn=Sn and Pb=Pb is lower in comparison to the π bond energy involved in Si=Si. On the other hand, germylene, stannylene and plumbylene of bivalent chemical species generated through dissociation of the double-bond in question are more stable. Thus, it is important to have moderate sized substituents for stable double-bond compounds.

Although digermene **13**^{21,22} and distannene **14**^{21,22} were previously synthesized by Lappert *et al.* in the 1970s prior to the synthesis of disilene **2**, it was impossible to study the properties of Ge=Ge and Sn=Sn since they existed in the form of germylene **15** and stannylene **16** respectively in solution despite the fact that they existed in solid phase as double-bond compounds. After the synthesis of disilenes **2** and **3**, a study to synthesize digermene and distannene without causing dissociation was carried out. As a result, the compounds **17**²³ and **18**²⁴ were synthesized.



Although digermene **17** does not dissociate to germylene, digermene **19** having larger substituents easily dissociates to germylene **20** and there is an equilibrium between both entities.²⁵

In 1999, diplumbene **21** with a double-bond between lead atoms occupying the lowest place in the periodic table was also synthesized.²⁶ Therefore, stable double-bond compounds between the same elements belonging to group 14 have been completed in the period of 18 years after the synthesis of disilene **2** by West *et al.*



The compounds of R₂M=MR₂ (M=Si, Ge, Sn, Pb) such as **2**, **17-19**, **21** have interesting structural characteristics which are different from olefins. These compounds have a so-called “*trans*-bent-type structure”.^{7,20} As shown in Figure 5, two substituents on one M and two substituents on the other M are bent in *trans* form with θ , the bent angle from the plane growing larger as the atomic number increases. Although details are not described in the paper, it has been revealed that the bent angle is determined by the difference of energy between singlet and triplet states of R₂M: and it is more apt to take such a bent structure in proportion to the extent of the stability of the singlet state.

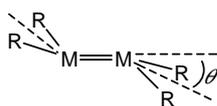
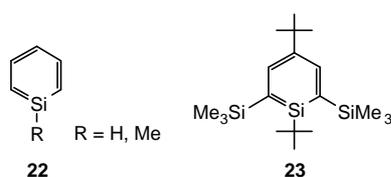


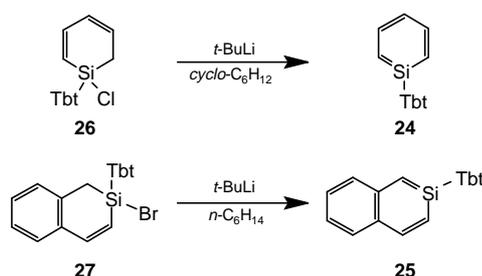
Figure 5. The *trans*-bent-type structure of R₂M=MR₂ (M=Si, Ge, Sn, Pb).

2.2 Aromatic compounds containing silicon²⁷

With alkenes, the primary organic compounds having unsaturated bonds are aromatic compounds including benzene, naphthalene *etc.* Therefore, the question of whether compounds where carbon in benzene and naphthalene is substituted by silicon exhibits aromatic properties is of great interest. Over the period of the 1970s to the 1980s a large number of studies have been carried out. It has been identified that in cryogenic matrices (argon matrix of 10 K, for example) or in the gas phase, silabenzene **22** (R=H, Me) having simple substituents such as hydrogen, methyl group *etc.* on silicon exists even in a short life and the UV, IR spectra *etc.* have been determined.²⁸ In the meantime, **23** reported by Märkl *et al.* in 1988 has been a sole compound with moderate stability, despite the fact that many trials have been made to isolate silabenzenes as a stable compound²⁹. Although **23** is sterically protected by a *t*-butyl group on silicon and two trimethylsilyl groups at the *ortho*-position, it is stable only in solution under -100 °C. Furthermore, endocyclic silicon secures stability by the coordination of THF among solvents as will be described later.



We have succeeded in isolating silabenzene **24**³⁰ and silanaphthalene **25**³¹ as stable crystals at room temperature respectively by applying the outstanding protection ability of the Tbt group to the synthesis of aromatic compounds containing silicon. The synthetic precursors of **24** and **25** are halosilanes **26** and **27** respectively. The products are obtained by dehydrohalogenation of the precursors using *t*-butyllithium.



Both **24** and **25** are colorless crystals which are so extremely stable under inert atmosphere that they do not change at all either in crystalline state or in solution.²⁹ According to ²⁹Si NMR, chemical shifts of endocyclic silicon are 87.3 and 92.5 respectively which exist in the low magnetic field region characteristic of sp² silicon. This is totally different from the chemical shift of 26.8 for compound **23** by Märkl *et al.* Under such circumstances, it is considered that **23** clearly is coordinated by THF as a solvent so that it is stabilized to a great extent accordingly. The coupling constant of endocyclic silicon is shown in the Figure 6. The coupling constant between two neighboring atoms correlates with the bond order involved in the linkage. According to the Figure 6, the coupling constant of silabenzene **24** is intermediate between the two coupling constants of silanaphthalene **25**, which is exactly consistent with the relationship of the bond order in benzene and naphthalene. Additionally, the coupling constant of a typical Si-C single bond is approx. 50 Hz. Therefore, the Si-C bonds of **24** and **25** clearly assume a double-bond character. As a result, delocalization of π electrons clearly exists in **24** and **25** and they assume aromatic characteristics.

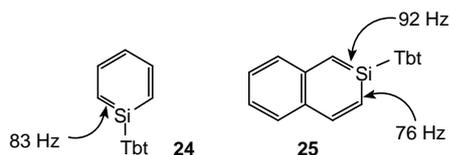


Figure 6. ¹J_{SiC} value of silabenzene **24** and silanaphthalene **25**.

The X-ray crystal structure analysis of **25** is shown in Figure 7. The ringed part of silanaphthalene is situated on the plane, and endocyclic silicon and the three atoms bonded to it are situated on the same plane. Further, the endocyclic silicon with high reactivity is completely protected by the Tbt group as is clear from the space-filling model (b).

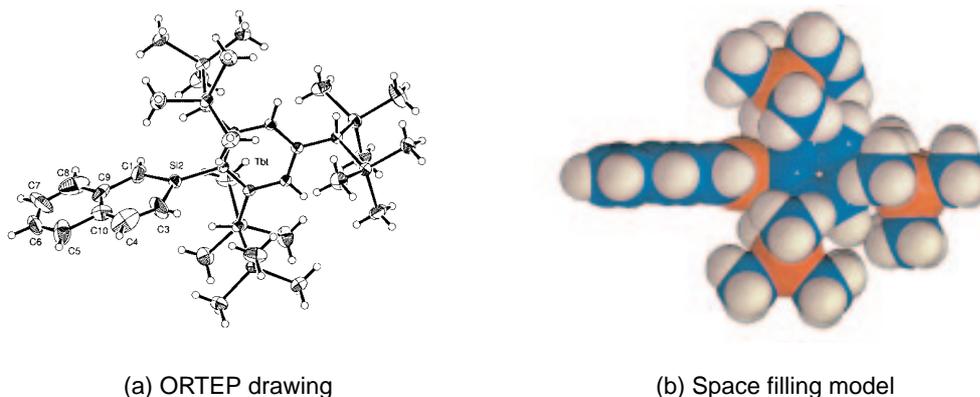


Figure 7. Molecular structure of silanaphthalene.

The electronic spectra of **24** and **25** were fundamentally similar to each other despite the fact that they shifted to longer wavelengths than the corresponding benzene and naphthalene. This also supports the case that **24** and **25** have aromatic character. Meanwhile, theoretical quantum calculations of the aromatic character have become more reliable. Schleyer *et al.* propose that NICS (Nucleus-Independent Chemical Shift) is a good index with respect to aromatic character.³² As a result of NICS computation carried out concerning silabenzene as well as 1-sila-, 2-sila- and 9-silanaphthalene, it was determined that their aromatic characters were nearly the same despite the fact that they were slightly lower than benzene and naphthalene, and further, there were almost no differences between the three isomers of silanaphthalene with respect to aromatic character.³¹ The results of the computation are consistent with the experimental results obtained from NMR, UV, X-ray crystal structure analysis *etc.* The reactivity of **24** and **25** is very high despite the fact that they have extremely bulky substituents on silicon and their presumed aromatic character. Several examples of their reactions are shown in Figure 8. We conclude that this is based on the high reactivity associated with the Si=C double-bond exceeding the stability from the aromatic character involved in silabenzene and silanaphthalene.

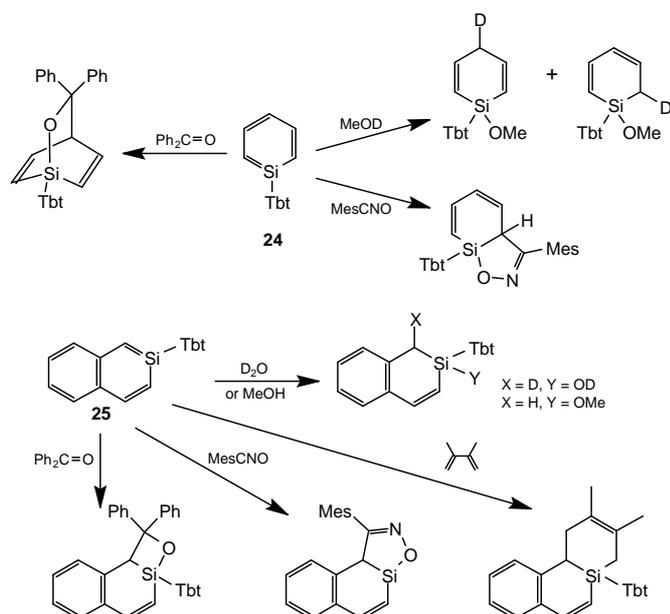
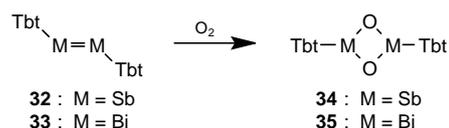


Figure 8. Reactions related to silabenzene **24** and silanaphthalene **25**.

32 and **33** are relatively stable compounds in the crystalline state so we may handle them in air for short periods. However, they gradually react with oxygen in air to produce the four-membered ring compounds, **34** and **35**. It is of great interest that the reaction proceeds by maintaining crystal phase and produces single crystals of **34** and **35**.^{35,36} By tracing the reaction with **32** using rapid X-ray diffraction equipment, it is found that the reaction suddenly starts after approximately a 20 hour induction period. It is assumed that oxygen enters into **32** from the surface of the crystals and the reaction between oxygen and **32** proceeds at a stretch like falling dominos after oxygen reaches a critical concentration in the crystal. It is extremely interesting that there are no examples of such reagents from outside reacting while maintaining a single crystal phase.



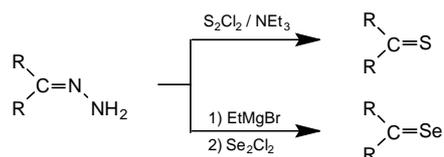
4. Double-bond compounds containing group 16 elements (sulfur, selenium and tellurium)

It is no exaggeration to say that the most important double-bonded compounds produced by second period elements in organic chemistry, particularly in organic synthetic chemistry, are carbonyl compounds as represented by aldehydes, ketones *etc.* It is extremely interesting to study the effect of replacing oxygen in the carbonyl group with the high periodic elements in question.

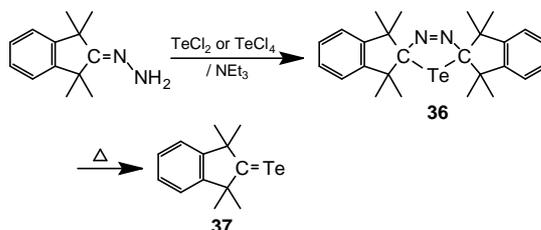
4.1 Telluroketone

Although thioketone ($\text{R}_2\text{C}=\text{S}$) where sulfur replaces oxygen has been long known, selenoketone ($\text{R}_2\text{C}=\text{Se}$) was first synthesized in the middle of the 1970s by Barton *et al.*³⁷ Barton, *et al.* were unable to synthesize telluroketone ($\text{R}_2\text{C}=\text{Te}$).

We have developed a reaction with hydrazone and disulfur dichloride³⁸ or diselenium dichloride³⁹ as a new synthetic method for thioketone and selenoketone.



We obtained the heterocyclic telluradiazoline **36** containing new tellurium by applying the said reaction to tellurium dichloride or tellurium tetrachloride,^{40a} from which we were able to synthesize the first stable telluroketone **37** through this thermolysis.^{40b}



4.2 The heavier element analogues of ketones (heavy ketones)

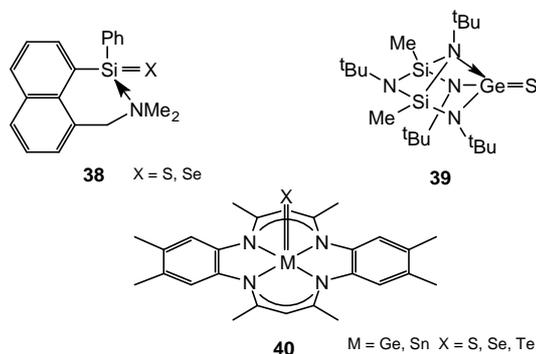
If the ketone carbon is replaced by higher periodic elements from group 14, such as silicon, germanium, tin, or lead, the resulting compound is a heavy element analogue of a ketone which we refer to as a heavy ketone. Furthermore, if the oxygen is replaced by other elements of group 16, such as sulfur, selenium, or tellurium, the resulting compound is also referred to as a heavy ketone.

As indicated in Table 2, the energies of the σ and π bonds of a carbon-oxygen double bond are approximately equal. On the other hand, in all of the heavy ketones, the σ bond is much stronger than the π bond. Thus, while a ketone readily undergoes addition and elimination reactions, heavy ketones favor addition reaction where a π bond is replaced by two more energetically stable σ bonds. For these energetic reasons, it is difficult to synthesize heavy ketone compounds. We have been able to synthesize heavy ketone compounds where bulky substituents reduce the reactivity of the π bond.

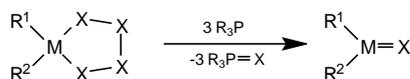
H ₂ M=X		X			
		O	S	Se	Te
H ₂ C=X	σ	93.6	73.0	65.1	57.5
	π	95.3	54.6	43.2	32.0
	$\sigma + \pi$	188.9	127.6	108.3	89.5
H ₂ Si=X	σ	119.7	81.6	73.7	63.2
	π	58.5	47.0	40.7	32.9
	$\sigma + \pi$	178.2	128.6	114.4	96.1
H ₂ Ge=X	σ	101.5	74.1	67.8	59.1
	π	45.9	41.1	36.3	30.3
	$\sigma + \pi$	147.4	115.2	104.1	89.4
H ₂ Sn=X	σ	94.8	69.3	64.3	56.4
	π	32.8	33.5	30.6	26.3
	$\sigma + \pi$	127.6	102.8	94.9	82.7
H ₂ Pb=X	σ	80.9	60.9	57.0	50.3
	π	29.0	30.0	27.8	24.4
	$\sigma + \pi$	109.9	90.9	84.8	74.7

Table 2. σ and π bond energies of H₂M=X (M=C, Si, Ge, Sn, Pb; X=O, S, Se, Te) (kcal mol⁻¹) [B3LYP/TZ(d,p)]

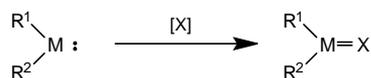
Many synthetic trials have been performed to synthesize doubly bonded compounds related to the heavy ketones. Several examples are shown in compounds 38 - 40. Some are not truly double-bond compounds, since to some extent the double bond character is stabilized by the coordination of heteroatoms.



On this occasion too, we were able to synthesize many of the stable heavy ketones by using the high steric protection ability of the Tbt group. The two synthetic methods utilized are shown in Figure 10. In general, method (1) is more common, but when the synthesis of 1,2,3,4-tetrachalcogenametallorenes as the starting material is so not easy method (2) would be useful.



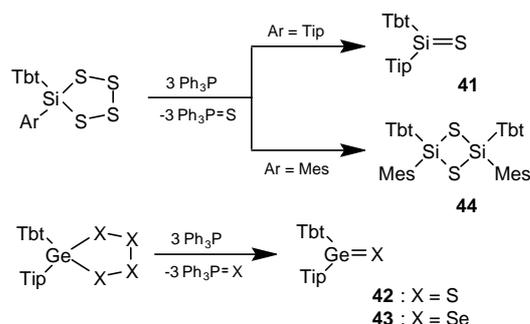
- (1) The dechalcogenation reaction of 1,2,3,4-tetrachalcogenametallorenes using phosphorus reagents.



- (2) Chalcogenation of divalent chemical species.

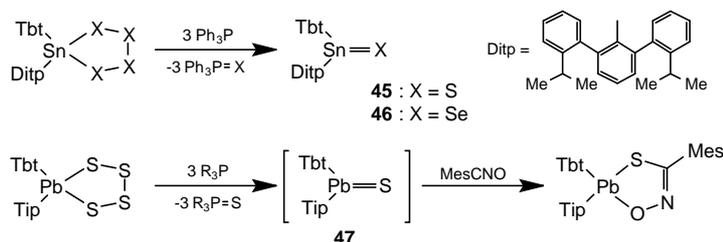
Figure 10. Synthetic approaches to heavy ketones.

It is possible to isolate silanethione **41**,⁴² germanethione **42**,^{46,47} and germaneselone **43**,^{47,48} as stable compounds respectively when Tbt and Tip groups coexist on the group 14 elements.

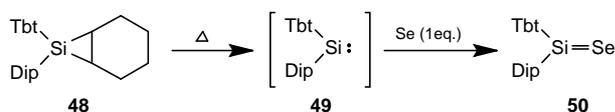


However, when Tip is replaced with a smaller Mes group, the isolated compound is **44**, a dimer, although we are able to confirm that Tbt(Mes)Si=S is produced as an intermediate through the trapped reaction. So it is important to have the steric protection of bulky substituents in order to isolate heavy ketones.⁴² The method based on the combination of Tbt and Tip substituents is not sufficient to synthesize heavy ketones containing tin. This is due to the reason that the reactivity is elevated as the energy involved in the double-bond containing tin goes down while the steric protecting effect does not function efficiently as the double-bond around Sn becomes longer. However, we are also able to isolate stannanethione **45**⁴⁹ and stannaneselone **46**⁵⁰ in a stable state by means of changing Tip to the Ditp group which is a larger substituent.

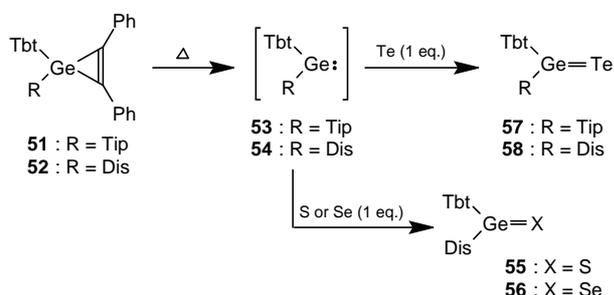
It is possible to confirm plumbanethione **47** in desulfurization at low temperature by using the trapping reaction but isolation has not been possible.⁵¹



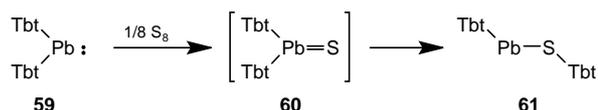
We were unable to synthesize the corresponding tetraselenasilorane ($\text{R}_1\text{R}_2\text{SiSe}_4$) so we could not synthesize silaneselone ($\text{R}_1\text{R}_2\text{Si}=\text{Se}$) by deselenation. However, we were able to synthesize silaneselone **50** through the selenation reaction by using silacyclopropane **48** as a precursor of silylene **49**.⁵²



In reference to germanium, germacyclopropenes **51**, **52** function as good precursors of germynes **53**, **54**.⁵³ We are able to obtain germanethione **55** and germaneselone **56** by heating **52** in the presence of sulfur and selenium.⁴⁷ This reaction is particularly effective for the synthesis of Ge-Te double-bond compounds and we were able to synthesize germanetellones **57**, **58**.⁵⁴



When we react the isolated plumbylene **59** with one equivalent of sulfur, we obtain plumbylene **61**, a divalent chemical species. We were unable to obtain plumbanethione **60**.⁵⁵



Therefore, the 2-coordinated type **61** is more stable than 3-coordinated type **60** in the case of lead. This is consistent with the results of quantum chemical computations that show HPb(SH) is more stable than H₂Pb=S by approx. 39 kcal/mol.^{41a} Heavy ketones related to lead have different properties from the light analogues.

All of the synthesized heavy ketones are observed to be colored crystals (**41**: yellow; **42**, **55**, yellowish orange-colored; **43**, **45**, **46**, **50**, **56**: red; **57**, **58**: green). The structures of silanethione **41**, germanethione **42**, germanesilone **43**, **56**, stannanesilone **46** and germanetellone **57**, **58** were determined by X-ray crystal structure analysis. The molecular structure of silanethione **41** is shown in Figure 11.⁴²

The structural characteristics worthy of attention are that the total bond angle around silicon is 360° with trigonal planar coordination and the Si-S bond distance is 1.948 Å, which is shorter than the ordinary Si-S single bond by approx. 9 % so that obviously it has the double-bond character. All of these data were identical structural characteristics to ketone. It has been experimentally shown that heavy ketones are structurally equivalent to ketone. Other heavy ketones determined by X-ray crystal structure analysis assume the same structural characteristics.

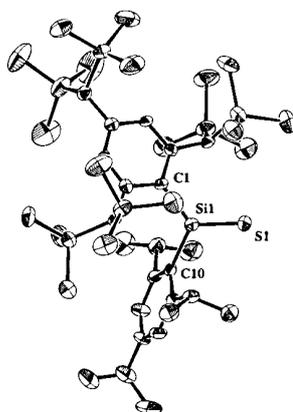
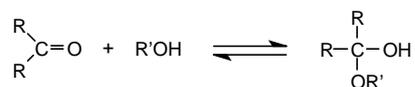


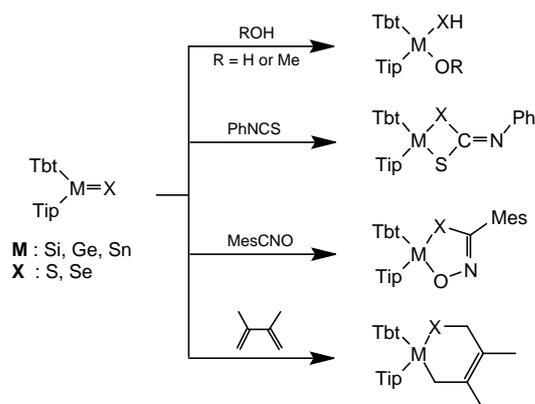
Figure 11. The molecular structure of silanethione **41**.

The important reactivity characteristic related to the carbonyl group is reversibility in the reaction of a carbon-oxygen double-bond as shown in the reaction with water and alcohol. The reaction in question proceeds based on the mechanism of addition-elimination by way of a tetracoordinated intermediate.



The approximate equalization of σ bond energy and π bond energy associated with C=O bond as seen in Table 2 has made the aforementioned possible. However, in case of heavy ketones, the addition reaction is remarkably exothermic and irreversible for a reason that π bond energy is lower than σ bond energy to a great extent. Actually, all of the synthesized heavy ketones promptly react with water, alcohol *etc.* and give rise to the tetracoordinated addition product. In addition, as opposed to the case with ketone,

they easily make the cycloadditional reaction with unsaturated chemical species such as phenyl isothiocyanate, mesitonitrile oxide, 2,3-dimethylbutadiene *etc.*⁴²⁻⁵⁰ We are able to synthesize new heterocyclic compounds by using these reactions despite the fact that it is difficult to synthesize them by using one of the other methods.



5. Conclusion

A large number of multiple bond compounds containing high period elements of groups 14, 15 and 16 have been synthesized on the basis of kinetic stabilization by using bulky substituents. Further, several multiple bond compounds containing elements in group 13 have been also synthesized although we have not referred to them in this paper. The multiple bond compounds related to high period elements have established a new field in organic chemistry and inorganic chemistry with unique compounds having interesting structures and reactivity. However, a large number of compounds awaiting synthesis are still left in this field. For example, there are triple bond compounds between elements in group 14, $R-M\equiv M-R$, heavy ketones containing oxygen, $R_2M=O$ ($M=Si, Ge, Sn$ and Pb), and aromatic compounds containing Ge, Sn and Pb *etc.*

The results described in this paper have been obtained through the efforts of many students (whose names are listed in References) under the leadership of Dr. Nobuhiro Tokitoh, currently Professor of Kyoto University. I would like to thank them. In addition, the author would also like to acknowledge Dr. Mao Minoura (Faculty of Science, Kitasato University) for his kind cooperation during preparation of the manuscript.

References

- 1) M. W. Schmidt, P. N. Truong, M. S. Gordon, *J. Am. Chem. Soc.*, **109**, 5217 (1987); P. v. R. Schleyer, D. Kost, *J. Am. Chem. Soc.*, **110**, 2105 (1988).
- 2) K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).
- 3) T. C. Klebach, R. Lourens, F. Bickelhaupt, *J. Am. Chem. Soc.*, **100**, 4886 (1978).
- 4) A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, **1981**, 191.
- 5) R. West, M. J. Fink, J. Michl, *Science*, **214**, 1343 (1981).
- 6) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Am. Chem. Soc.*, **103**, 4587 (1981).
- 7) Review: R. Okazaki, R. West, *Adv. Organomet. Chem.*, **39**, 233 (1996).
- 8) S. Masamune, Y. Hanzawa, S. Murakami, T. Bally, J. F. Blount, *J. Am. Chem. Soc.*, **104**, 1150 (1982).
- 9) Review: A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.*, **39**, 71 (1996).
- 10) A. J. Millevolte, D. R. Powell, S. G. Johnson, R. West, *Organometallics*, **11**, 1091 (1992); K. L. McKillop, G. R. Gillette, D. R. Powell, R. West, *J. Am. Chem. Soc.*, **114**, 5203 (1992); H. Sohn, R. P. Tan, D. R. Powell, R. West, *Organometallics*, **13**, 1390 (1994).

- 11) D. N. Roark, G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972); D. J. DeYoung, M. J. Fink, J. Michl, R. West, *Main Group Met. Chem.*, **1**, 19 (1987).
- 12) H. Piana, U. Schubert, *J. Organomet. Chem.*, **348**, C19 (1988); G. R. Gillette, R. West, *J. Organomet. Chem.*, **394**, 45 (1990); H. B. Yokelson, A. J. Millevolte, G. R. Gillette, R. West, *J. Am. Chem. Soc.*, **109**, 6865 (1987); R. West, D. J. DeYoung, K. J. Haller, *J. Am. Chem. Soc.*, **107**, 4942 (1985); R. P. Tan, G. R. Gillette, D. R. Powell, R. West, *Organometallics*, **10**, 546 (1991); H. B. Yokelson, A. J. Millevolte, K. J. Haller, R. West, *J. Chem. Soc., Chem. Commun.*, **1987**, 1605.
- 13) M. J. Fink, D. J. DeYoung, R. West, J. Michl, *J. Am. Chem. Soc.*, **105**, 1070 (1983); P. Boudjouk, B.-H. Han, K. R. Anderson, *J. Am. Chem. Soc.*, **104**, 4992 (1982); P. Boudjouk, *Nachr. Chem., Tech. Lab.*, **31**, 798 (1983); A. D. Fanta, D. J. DeYoung, J. Belzner, R. West, *Organometallics*, **10**, 3466 (1991).
- 14) B. D. Shepherd, D. R. Powell, R. West, *Organometallics*, **8**, 2664 (1989).
- 15) R. S. Archibald, Y. van den Winkel, D. R. Powell, R. West, *J. Organomet. Chem.*, **446**, 67 (1993); H. Watanabe, K. Takeuchi, N. Fukawa, M. Kato, M. Goto, Y. Nagai, *Chem. Lett.*, **1987**, 1341.
- 16) N. Tokitoh, H. Suzuki, R. Okazaki, K. Ogawa, *J. Am. Chem. Soc.*, **115**, 10428 (1993); H. Suzuki, N. Tokitoh, R. Okazaki, J. Harada, K. Ogawa, S. Tomoda, M. Goto, *Organometallics*, **14**, 1016 (1995); H. Suzuki, N. Tokitoh, R. Okazaki, *Bull. Chem. Soc. Jpn.*, **68**, 2471 (1995).
- 17) a) R. Okazaki, M. Unno, N. Inamoto, *Chem. Lett.*, **1987**, 2293. b) R. Okazaki, N. Tokitoh, T. Matsumoto, in "Synthetic Methods of Organometallic and Inorganic Chemistry," ed by W. A. Herrmann, Thieme, New York (1996) Vol. 2, p. 260.
- 18) H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.*, **116**, 11572 (1994).
- 19) N. Tokitoh, H. Suzuki, R. Okazaki, *J. Chem. Soc., Chem. Commun.*, **1996**, 125; N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.*, **119**, 1456 (1997).
- 20) Review: K. Baines, W. G. Stibbs, *Adv. Organomet. Chem.*, **39**, 275 (1996).
- 21) P. J. Davidson, D. H. Harris, M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1976**, 2268.
- 22) D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, **1986**, 2387.
- 23) S. A. Batcheller, T. Tsumuraya, O. Tempkin, W. M. Davis, S. Masamune, *J. Am. Chem. Soc.*, **112**, 9394 (1990).
- 24) M. Weidenbruch, H. Killian, K. Peters, H. G. v. Schnering, *Chem. Ber.*, **128**, 983 (1995).
- 25) K. Kishikawa, N. Tokitoh, R. Okazaki, *Chem. Lett.*, **1998**, 239.
- 26) M. Stürmann, W. Saak, H. Marsmann, M. Weidenbruch, *Angew. Chem., Int. Ed.*, **38**, 187 (1999).
- 27) Y. Apeloig, M. Karni, in "The Chemistry of Organic Silicon Compounds," ed by Z. Rappoport, Y. Apeloig, Wiley, New York (1998) Vol. 2, Chapter 1.
- 28) T. J. Barton, D. Banasink, *J. Am. Chem. Soc.*, **99**, 5199 (1977); H. Bock, R. A. Bowling, B. Solouki, T. J. Barton, G. T. Burns, *J. Am. Chem. Soc.*, **102**, 429 (1980); T. J. Barton, G. T. Burns, *J. Am. Chem. Soc.*, **100**, 5246 (1978); G. Maier, G. Mihm, H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, **19**, 52 (1980).
- 29) G. Märkl, W. Schlosser, *Angew. Chem., Int. Ed. Engl.*, **27**, 963 (1988).
- 30) K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, *Angew. Chem., Int. Ed.*, **39**, 634 (2000).
- 31) N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P. v. R. Schleyer, H. Jiao, *J. Am. Chem. Soc.*, **119**, 6951 (1997); K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, P. v. R. Schleyer, H. Jiao, *J. Am. Chem. Soc.*, **122**, 5648 (2000).
- 32) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.*, **118**, 6317 (1996).
- 33) M. Yoshifuji, in "Multiple Bonds and Low Coordination in Phosphorus Chemistry," ed by M. Regitz, O. J. Scherer, Thieme, New York (1990), Chapter 9.
- 34) A. Cowley, J. G. Lasck, N. C. Norman, M. Pakulski, *J. Am. Chem. Soc.*, **105**, 5506 (1983).
- 35) N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.*, **120**, 433 (1998).
- 36) N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, *Science*, **277**, 78 (1997).
- 37) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, F. S. Guziec, Jr., *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2079.
- 38) R. Okazaki, K. Inoue, N. Inamoto, *Bull. Chem. Soc. Jpn.*, **54**, 3541 (1981).
- 39) A. Ishii, R. Okazaki, N. Inamoto, *Bull. Chem. Soc. Jpn.*, **61**, 861 (1988).
- 40) a) M. Minoura, T. Kawashima, N. Tokitoh, R. Okazaki, *Tetrahedron*, **53**, 8137 (1997). b) M. Minoura, T. Kawashima, R. Okazaki, *J. Am. Chem. Soc.*, **115**, 7019 (1993); M. Minoura, T. Kawashima, R. Okazaki, *Tetrahedron Lett.*, **38**, 2501 (1997).
- 41) Reviews: a) N. Kano, N. Tokitoh, R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi (J. Synth. Org. Chem. Japan)*, **56**, 919 (1998). b) N. Tokitoh, T. Matsumoto, R. Okazaki, *Bull. Chem. Soc. Jpn.*, **72**, 1665 (1999). c) N. Tokitoh, R. Okazaki, in "The Chemistry of Organic Silicon Compounds," ed by Z. Rappoport, Y. Apeloig, Wiley, New York (1998) Vol. 2, Chapter 17.
- 42) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, *J. Am. Chem. Soc.*, **120**, 11096 (1998).
- 43) R. Arya, J. Boyer, F. Carré, R. Corriu, G. Lanneau, J. Lapasset, M. Perrot, C. Priou, *Angew. Chem., Int. Ed. Engl.*, **28**, 1016 (1989).
- 44) a) M. Veith, S. Becker, V. Huch, *Angew. Chem., Int. Ed. Engl.*, **28**, 1237 (1989). b) M. Veith, A. Detemple, V. Huch, *Chem. Ber.*, **124**, 1135 (1991). c) M. Veith, A. Detemple, *Phosphorus, Sulfur, Silicon*, **65**, 17 (1992).

- 45) a) M. C. Kuchta, G. Parkin, *J. Chem. Soc., Chem. Commun.*, **1994**, 1351. b) M. C. Kuchta, G. Parkin, *J. Am. Chem. Soc.*, **116**, 8372 (1994). c) W.-P. Leung, W.-H. Kwok, L. T. C. Law, Z.-Y. Zhou, T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, **1996**, 505.
- 46) N. Tokitoh, T. Matsumoto, K. Manmaru, R. Okazaki, *J. Am. Chem. Soc.*, **115**, 8855 (1993).
- 47) T. Matsumoto, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.*, **121**, 8811 (1999).
- 48) T. Matsumoto, N. Tokitoh, R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **33**, 2316 (1994).
- 49) M. Saito, Ph.D. Thesis, The University of Tokyo, 1996.
- 50) M. Saito, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.*, **119**, 11124 (1997).
- 51) N. Kano, N. Tokitoh, R. Okazaki, *Chem. Lett.*, **1997**, 277; N. Kano, N. Tokitoh, R. Okazaki, *Organometallics*, **16**, 4237 (1997).
- 52) T. Sadahiro, N. Tokitoh, R. Okazaki, unpublished results.
- 53) N. Tokitoh, K. Kishikawa, T. Matsumoto, R. Okazaki, *Chem. Lett.*, **1995**, 827.
- 54) N. Tokitoh, T. Matsumoto, R. Okazaki, *J. Am. Chem. Soc.*, **119**, 2337 (1997).
- 55) N. Kano, Ph.D. Thesis, The University of Tokyo, 1998.

Introduction of the author :

Renji Okazaki

Professor, Faculty of Science, Japan Women's University

Born in Tokyo in 1937 and graduated from Department of Chemistry, Faculty of Science, The University of Tokyo in 1961. Completed the Doctor's Course at the Graduate School, The University of Tokyo in 1966. The present post was gained since 1998 by way of holding research associate, associate professor and professor in succession at Faculty of Science, The University of Tokyo. Received The Divisional Award (Organic Chemistry) of The Chemical Society of Japan in 1988, Alexander von Humboldt Award in 1998, The Chemical Society of Japan Award in 1999. The present vice-president of The Chemical Society of Japan and Editor-in-Chief of Bulletin of The Chemical Society of Japan.

Specialized in organoheteroatom chemistry, organometallic chemistry, particularly a study for stabilizing the unstable chemical species utilizing new steric protection groups.