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Award Accounts

The Chemical Society of Japan Award for Creative Work for 2002

Synthesis of Aromatic Species Containing a Heavier Group 14 Element by Taking Advantage of Kinetic Stabilization

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In this Account, the syntheses, structures, and properties of novel aromatic species containing a heavier group 14 element were delineated with systematic comparison, focusing on their aromaticity. Several kinds of silaaromatic compounds, such as silabenzene, 1- and 2-silanaphthalenes, and 9-silaanthracene, which are a very interesting class of novel π-bonding systems containing a silicon atom, were successfully synthesized and isolated as stable compounds by taking advantage of the kinetic stabilization afforded by introduction of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). A similar synthetic approach can be applied to the cases of the first stable germaaromatics, such as germabenzene and 2-germanaphthalene. The molecular structures of the newly obtained metallaaromatic species were systematically investigated based on X-ray crystallographic analysis and spectroscopic studies together with theoretical calculations. During this study, a variety of new reactivities for these metallaaromatic species were revealed and some new insights and deeper knowledge were obtained about the aromaticity of metallaaromatic compounds of heavier group 14 elements.

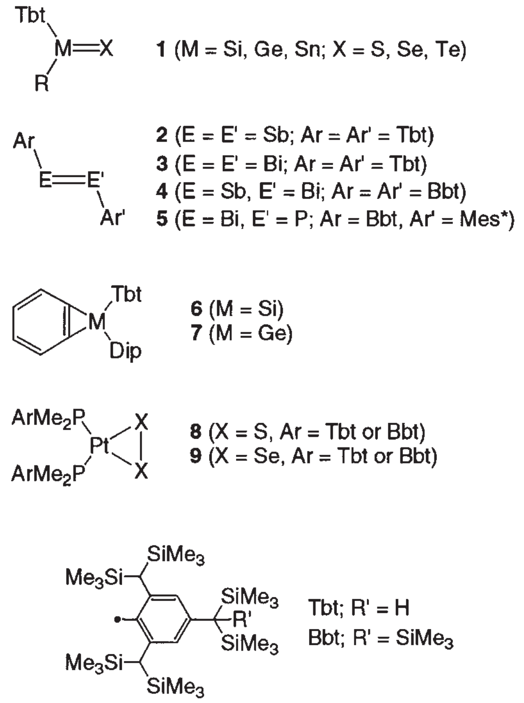
The periodic system of elements (the periodic table) defines elements with the same number of valence electrons as forming a family (element group) in which the individual elements and their compounds exhibit similar chemical and physical properties. Since chemistry has been developed on the basis of this periodic system, it is very important to promote our understandings of this system more in detail, i.e., to compare the similarities and differences between the elements and their compounds from various points of view. Meanwhile, low-coordinate species of main group elements of the second row such as carbenes, olefins, carbonyl compounds (e.g., ketones, aldehydes, esters, amides, etc.), aromatic compounds, and azo compounds have played very important, key roles in organic chemistry. Although extensive studies have been devoted to these species, not only from the viewpoints of physical organic chemistry but also from the standpoints of synthetic chemistry and material sciences, the heavier element analogues of such low-coordinate species of second row elements have only been postulated in many reactions as reactive intermediates. The chemistry of low-coordinate main group element compounds has been undeveloped, most probably due to their high reactivity and instability under ambient conditions.

At the beginning of the 20th century, all attempts at synthesizing the doubly bonded species of heavier main group elements have proved unsuccessful, leading to cyclic oligomers or polymers containing only single covalent bonds. These findings and theoretical treatments led to the view that "*elements having a principal quantum number greater than two should not be able to form pπ–pπ bonds with themselves or with other elements*", the so-called "*classical double bond rule*".[1] However, this rule was disproved by the spectroscopic detection of a compound having a multiple P–C bond in 1961.[2] Furthermore, the isolation of a stable phosphene (P=C) was reported in 1978,[3] and in 1981 stable diphosphene (P=P),[4] silene (Si=C),[5] and disilene (Si=Si)[6] were successively synthesized by taking advantage of "*steric protection*".

For the stabilization of highly reactive compounds, there are two conceivable methodologies: i.e., *thermodynamic stabilization* and *kinetic stabilization*. The former is defined as stabilization of the ground state by the mesomeric effect of neighboring heteroatoms, attachment of an electron-donating or -withdrawing substituents, or complexation with transition metals. The latter is stabilization resulting from raising the transition state by taking advantage of steric protection with bulky groups, which prevents oligomerization or reactions with other reagents such as oxygen and water. *Kinetic stabilization* is obviously superior to thermodynamic stabilization, since the latter perturbs the intrinsic nature of the species more largely than the former does.

On the other hand, in the course of our study on sterically congested molecules, we have developed an extremely bulky aromatic substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and 2,6-bis[bis(trimethylsilyl)-methyl]-4-tris(trimethylsilyl)methylphenyl (denoted as Bbt hereafter), which were found to be very effective steric protection groups for a variety of reactive species of heavier main

Published on the web March 12, 2004; DOI 10.1246/bcsj.77.429



1 (M = Si, Ge, Sn; X = S, Se, Te)

2 (E = E' = Sb; Ar = Ar' = Tbt)
3 (E = E' = Bi; Ar = Ar' = Tbt)
4 (E = Sb, E' = Bi; Ar = Ar' = Bbt)
5 (E = Bi, E' = P; Ar = Bbt, Ar' = Mes*)

6 (M = Si)
7 (M = Ge)

8 (X = S, Ar = Tbt or Bbt)
9 (X = Se, Ar = Tbt or Bbt)

Tbt; R' = H
Bbt; R' = SiMe$_3$

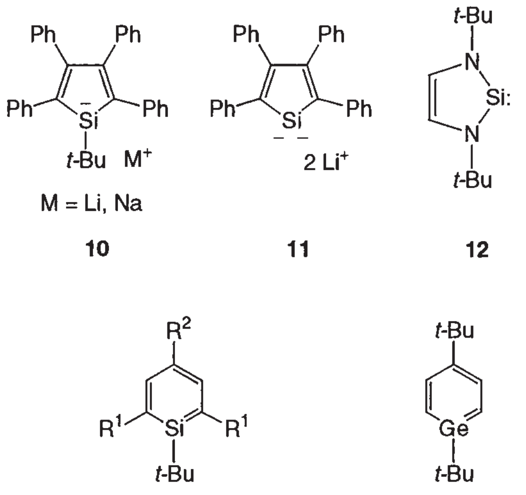
Chart 1.

group element compounds.[7] With such new, powerful protection groups in hand, we have synthesized a variety of unprecedented low-coordinate compounds of heavier main group elements as stable compounds. We have already succeeded in the isolation of various novel species such as a family of group 14 element–group 16 element double-bond compounds: i.e., *heavy ketones* [**1**; Tbt(Ar)M=X; M = Si, Ge, Sn, Pb; X = S, Se, Te],[7a,b,e] and a series of homo- and hetero-nuclear doubly bonded compounds between heavier group 15 elements [TbtM=MTbt, M = Sb (**2**), Bi (**3**); BbtSb=BiBbt (**4**); BbtBi=PMes* (**5**), Mes* = 2,4,6-tri-*t*-butylphenyl] (Chart 1).[7e,8]

In addition, we have also successfully synthesized novel species containing a small ring such as the metallacyclopropabenzenes [Tbt(Dip)MC$_6$H$_4$; M = Si (**6**), Ge (**7**); Dip = 2,6-diisopropylphenyl];[9] these are the first examples of stable heteracyclopropabenzenes, and the unprecedented platinum–dichalcogenido complexes, [PtX$_2$(ArMe$_2$P)$_2$] [X = S (**8**), Se (**9**); Ar = Tbt or Bbt].[10] Their successful isolation and characterization will provide us with a new research field and valuable information about the potential utility of heavier element compounds.

1. Silaaromatic Compounds and Related Species

Silaaromatic compounds,[11] i.e., Si-containing $[4n+2]\pi$ ring systems, have attracted much attention in recent decades, since they represent the heavier congeners of the carbocyclic aromatic compounds[12] which are a key class of substances in organic chemistry. Although the aromatic character of silole anions and dianions such as **10** and **11**,[13] as well as that of cyclic diaminosilylene **12**,[14] was recently revealed from both experimental and theoretical standpoints, simple silaaromatic compounds such as silabenzenes and disilabenzenes are known to be highly reactive and have only been characterized in low-temperature matrices or in the gas phase on the basis of photoelectron, UV/vis, and IR spectra (Chart 2).[15] Some trapping reactions supporting the formation of silabenzenes and disilabenzenes were also reported.[16]



M = Li, Na

10 **11** **12**

13 (R^1 = H, R^2 = *t*-Bu)
14 (R^1 = SiMe$_3$, R^2 = *t*-Bu)
15 (R^1 = SiMe$_2$(*i*-Pr), R^2 = SiMe$_3$)

16

Chart 2.

Meanwhile, non-conjugated doubly bonded compounds containing a silicon atom have already been synthesized as stable molecules by taking advantage of kinetic stabilization, namely, by introducing bulky substituents around the reactive double bonds.[17] Although applications of this method to stabilize silabenzenes have also been reported, no silabenzene stable at ambient temperature had ever been reported until our successful results (Chart 2). It was reported that 1,4-di-*t*-butyl-1-silabenzene **13** readily dimerized at 0 °C to give the corresponding [2 + 2] dimer.[18] The more crowded 1,4-di-*t*-butyl-2,6-bis(trimethylsilyl)-1-silabenzene **14** was reportedly stable below −100 °C and could be observed by low-temperature NMR measurements.[19] However, it was stable at low temperature only in a special solvent (THF/ether/petroleum ether, 4:1:1) and clearly coordinated with the solvent (most likely THF) as judged by the relatively high field ^{29}Si NMR chemical shift ($\delta_{Si} = 26.8$). Although a more hindered silabenzene, 1-*t*-butyl-2,6-bis(dimethylisopropylsilyl)-4-trimethylsilyl-1-silabenzene **15**, was generated under argon flow, it was found to be stable only at −180 °C.[20] As for other silaaromatics having a more extended conjugated system, such as silanaphthalenes and silaanthracenes, a few examples have been known, but they are restricted to those of transient intermediates and/or matrix-isolated examples. 2-Methyl-2-silanaphthalene was postulated as an intermediate in the N$_2$-flow pyrolysis of the corresponding allylsilane precursor at 650 °C,[16a] while there are some reports of the chemical trapping of intermediary silaanthracenes and the observation of unstable silaanthracenes by UV/vis spectroscopy in matrices at low temperature.[15g–i] The situation for the chemistry of germaaromatics is almost the same as that of silaaromatics.[21–24] Thus, syntheses of several examples of stable ionic species[21,23] and also the dimerization and intermolecular trapping of 1,4-di-*t*-butylgermabenzene **16**[24] have been reported (Chart 2). However, stable neutral germaaromatics have been elusive until quite recently.

Many theoretical calculations have been reported for sila- and disilabenzenes,[11c,e] and they indicate that silabenzenes have a delocalized structure and considerable aromaticity (e.g., ~80% of benzene from energetic criteria[25]). This implies that silaarenes might exist as stable molecules if their high reactivity could be suppressed by some protection. In view of the increasing number of stable doubly-bonded organosilicon compounds which were successfully synthesized by taking advantage of the method of kinetic stabilization,[11a,17,26] stable silaaromatic compounds are expected to be synthesizable using appropriately bulky substituents.

As mentioned in the previous section, we have already developed an extremely bulky and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter),[27] and many novel reactive species have been prepared as stable compounds by taking advantage of this Tbt group. Since it has been fully demonstrated that Tbt group is very effective to stabilize the highly reactive, low-coordinated species of heavier main group elements such as *heavy ketones* (**1**),[7,28] we next applied Tbt group to the kinetic stabilization of an unexplored class of low-coordinated species of heavier group 14 elements such as sila- and germaaromatic compounds, which can be regarded as more sophisticated doubly bonded systems containing a heavier group 14 element.

2. Synthesis and Isolation

Up to now, we have succeeded in the synthesis and isolation of several kinds of silaaromatic compounds bearing a Tbt group on the sp^2-silicon atom, such as silabenzene **17**,[29] 1- and 2-silanaphthalenes (**18**[30] and **19**[31]), and 9-silaanthracene **20**,[32] (Chart 3) as stable compounds. Furthermore, the first stable germabenzene **21**[33] and 2-germanaphthalene **22**[34] (Chart 3) were also synthesized by the use of a similar synthetic approach. In this article, the recent progress in the chemistry of metallaaromatic compounds of heavier group 14 elements (*denoted as heavy aromatics in this account*) is outlined, with a systematic comparison between the parent aromatic hydrocarbons and their heavier congeners.

In view of the isolation of such a highly reactive species in a pure form, it is necessary to develop suitable synthetic methods (e.g., high yields and mild reaction conditions) for sila- and germaaromatics. As the final step of the syntheses, we chose simple dehydrohalogenation reactions of the corresponding cyclic halometallane precursors having a Tbt group on the central group 14 elements using an appropriate base. As a typical example, the synthetic route for boromosilane **23**, the precursor of 2-silanaphthalene **19**, is shown in Scheme 1.[31]

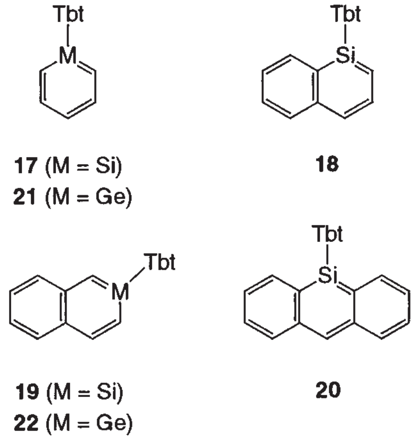
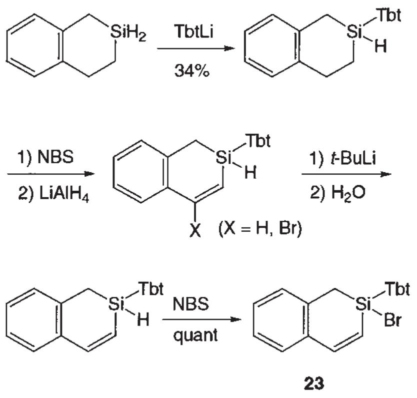
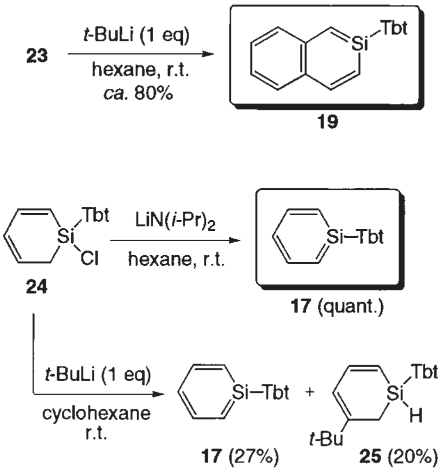


Chart 3.

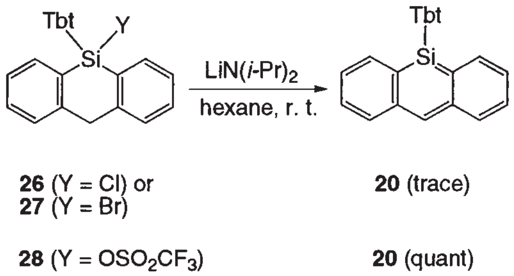


Scheme 1.



Scheme 2.

Another important factor for the effective synthesis is the choice of a base. For example, 2-silanaphthalene **19** was successfully synthesized by the treatment of bromosilane **23** with *t*-BuLi in hexane,[31] while similar treatment of chlorosilane **24** resulted in the formation of undesired *t*-butylated product **25** together with the expected silabenzene **17** (Scheme 2).[29b] The formation of **25** might be interpreted in terms of the initial electron transfer from *t*-BuLi to **24**, followed by the recombination of the resulting radical intermediates. This problem was successfully solved by the use of lithium diisopropylamide (LDA) as a base to give **17** in an almost quantitative yield. In other cases, such as 1-silanaphthalene **18**,[30] 9-silaanathracene **20**,[32] germabenzene **21**,[33] and 2-germanaphthalene **22**,[34] LDA was found to be the best among the bases examined. In addition, in the case of the synthesis of 9-silaanthracene **20**,[32] the leaving ability of the substituent on the silicon atom played a very crucial role. The use of halosilanes **26** and **27** as precursors resulted in very low yields of 9-silaanthracene **20**, as judged by the trapping experiments with MeOH;[35] the treatment of silyl triflate **28** with LDA in benzene gave the expected **20** in an almost quantitative yield[32] (Scheme 3).



Scheme 3.

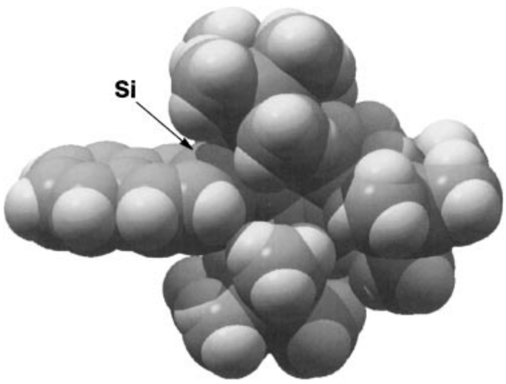
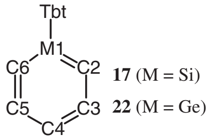
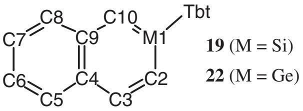
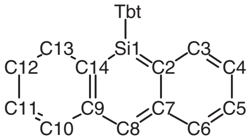


Fig. 1. Space-filling model drawing of 2-Tbt-2-silanaphthalene (**19**).

Table 1. Selected Structural Parameters for Metallaaromatic Compounds **17** and **19**–**22**

Compound	 **17** (M = Si) **22** (M = Ge)		 **19** (M = Si) **22** (M = Ge)		
	17a)	**21**b)	**19**c)	**22**d)	**20**e)
Bond lengths/Å	Si1–C2 1.765(4)	Ge1–C2 1.829(2)	Si1–C2 1.800(3)	Ge1–C2 1.859(5)	Si1–C2 1.787(3)
	Si1–C6 1.770(4)	Ge1–C6 1.827(2)	Si1–C10 1.728(3)	Ge1–C10 1.803(5)	Si1–C14 1.784(3)
	C2–C3 1.391(6)	C2–C3 1.389(3)	C2–C3 1.359(3)	C2–C3 1.368(7)	C2–C7 1.442(4)
	C3–C4 1.399(6)	C3–C4 1.389(3)	C3–C4 1.438(3)	C3–C4 1.429(8)	C7–C8 1.398(4)
	C4–C5 1.381(6)	C4–C5 1.385(3)	C4–C9 1.431(3)	C4–C9 1.430(7)	C8–C9 1.399(4)
	C5–C6 1.394(7)	C5–C6 1.396(3)	C9–C10 1.433(3)	C9–C10 1.450(8)	C9–C14 1.446(4)
$\Sigma\angle$M/deg	359.8	360.0	360.0	360.0	360.0
$\Sigma\angle$MC$_5$ ring/deg	720.0	720.0	720.0	720.0	720.0
Tbt/MC$_5$ /deg	84.6	73.8	83.9	88.8	69.0

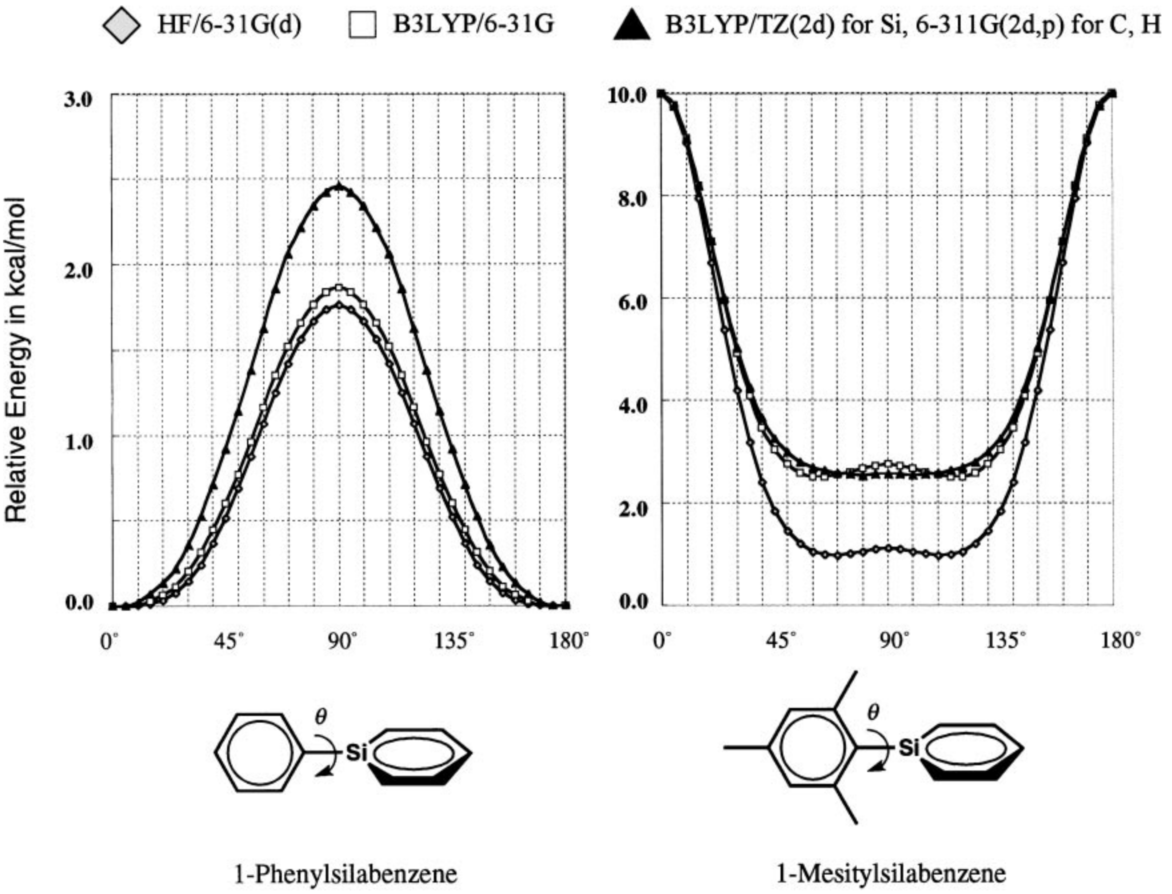
a) Ref. 29. b) Ref. 33. c) Ref. 31. d) Ref. 34. e) Ref. 32.

Except for 1-silanaphthalene **18**,[30] which was found to undergo gradual dimerization in solution at room temperature (vide infra), all the sila- and germaaromatic compounds **17** and **19**–**22** were isolated as stable crystalline compounds, indicating the high ability of Tbt group as a steric protecting group. Recently, Nishiyama et al. reported the matrix isolation and intermolecular trapping reactions of less hindered 9-silaanthracenes having a 2,4,6-triisopropylphenyl or 2,4,6-tri-*t*-butylphenyl group on the silicon atom, but these species are reportedly not isolable.[36] This fact implies the indispensability of an extremely bulky substituent such as Tbt for the isolation of kinetically stabilized metallaaromatic compounds.

Structures and Spectroscopic Properties

X-ray Crystallographic Analysis. The most important structural features of aromatic compounds are the planarity for their aromatic rings and the ring-bond lengths lying between those of the typical double and single bonds, which result from the delocalization of π-electrons of their aromatic rings. From the viewpoints of a systematic comparison between the aromatic hydrocarbons and their heavier congeners, it is of great significance to perform the crystallographic analysis of the metallaaromatic compounds obtained here. Fortunately, most of them were isolated as stable crystalline compounds and we could prepare single crystals suitable for X-ray structural analysis. The high crystallinity of the Tbt-substituted compounds is an unexpected benefit for us. The structural parameters of the analyzed metallaaromatics are summarized in Table 1 together with their atom-numbering schemes. As a representative, the space-filling model drawing for 2-silanaphthalene **19** is shown in Fig. 1, which clearly indicates that the planar silanaphthalene ring is nicely protected by the bulky Tbt group.

All metallaaromatic ring systems examined here have an almost completely planar aromatic ring. The geometry around the central silicon or germanium atom is also completely trigonal planar, suggesting the delocalization of π-electrons in these ring systems. As for the bond lengths of the aromatic ring, almost equal distances were observed for the group 14 metal–carbon bonds in both sila- and germabenzenes **17** and **21**, while a small extent of bond alternation was recognized for 2-sila- and



1-Phenylsilabenzene

1-Mesitylsilabenzene

Fig. 2. Potential energy surface for Ph- and Mes-substituted silabenzenes.

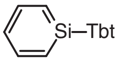
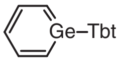
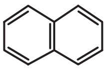
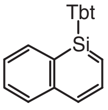
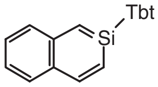
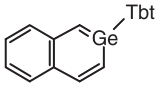
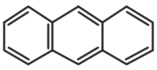
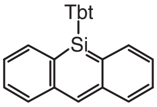
2-germanaphthalenes **19** and **22** as in the case of parent naphthalene. When we take into account the fact that the C–C bond lengths in these metallaaromatic rings are comparable with those reported for parent benzene and naphthalene,[12] one should conclude that the replacement of one carbon with a heavier group 14 element such as a silicon or germanium atom does not disturb the delocalization of π-electrons in the monometallaaromatic ring systems. Furthermore, the crystallographically revealed structural features of these new metallaaromatic species are in good agreement with those obtained by the theoretical calculations with B3LYP/6-31G(d) level for some model compounds, suggesting that the introduction of a Tbt group on the central metal atom causes little steric or electronic influence.

In addition, crystallographic analysis of these metallaaromatic systems revealed that all of them have a large dihedral angle [from 69° (for **20**) through 89° (for **22**)] between the Tbt group and the plane of the metallaaromatic ring in the solid state (Table 1). Since the theoretically optimized molecular structures of the Tbt-substituted sila- and germabenzenes showed the benzene plane of the Tbt group is almost perpendicular to that of each metallaaromatic ring, the experimentally observed geometry might result from the least hindered conformation for the extremely bulky Tbt group and the packing energy. In order to elucidate the stabilizing effect of conjugation of the aryl protecting group with the central metallaromatic ring system, we have performed the theoretical calculations for the relative stability of 1-phenylsilabenzene and 1-mesitylsilabenzene while varying the dihedral angle between the phenyl plane and the silabenzene ring plane (Fig. 2).[37]

The results shown in Fig. 2 indicate that the conformation with the phenyl group perpendicularly oriented is the most unstable, but the difference from the most stable coplanar conformer is only about 2 kcal/mol, regardless of the level of the theories used for the calculations. In the case of the Mes-substituted system, such a coplanar conformation is the most unfavorable situation, as expected, due to the steric repulsion caused by the two ortho methyl groups, while it was found that the energy level was almost invariable between the dihedral angles of 50 and 90°. In cases of both 1-phenylsilabenzene and 1-mesitylsilabenzene, the lengths of the Si=C bond between the two aromatic rings varied within the range of 1.7752 to 1.7755 Å, suggesting that the conjugative effect does not exert a significant influence on the nature of the silaaromatic ring system.

NMR Spectra. As for the silaaromatic compounds, ^{29}Si NMR spectroscopy provides us with useful information about the electronic and structural environments of their central silicon atom. All four newly obtained silaaromatics **17**–**20** showed characteristically low-field signals in their ^{29}Si NMR spectra [93.6 (**17**[29]), 91.7 (**18**[30]), 87.3 (**19**[31]), and 87.2 (**20**[32]) ppm in C_6D_6] suggesting the sp^2 character of their ring silicon atoms. These chemical shifts are much more low-fielded than the shift for the previously reported marginally stable silabenzene (**14**; $\delta_{\mathrm{Si}} = 26.8$).[19] Almost no spectral change was observed even on measurement in the presence of ethereal solvent such as that in THF:C_6D_6 = 6:1 (the largest $\Delta\delta$: 0.4 ppm for

Table 2. Spectroscopic Comparison between Metallaaromatics **17**–**22** and the Corresponding Aromatic Hydrocarbons

Benzene series		 **17**		 **21**
λ_{max} a)/nm	256	331		326
ν_{obsd} b)/cm^{-1}	1600	1530		1600
ν_{calcd} c)/cm^{-1}	1590	1527		1590
Naphthalene series		 **18**	 **19**	 **22**
λ_{max} a)/nm	312	378	387	386
ν_{obsd} b)/cm^{-1}	1382	1340	1368	1363
ν_{calcd} c)/cm^{-1}	1360	1330	1349	1356
Anthracene series		 **20**		Not isolated yet.
λ_{max} a)/nm	375	503		
ν_{obsd} b)/cm^{-1}	1401	1359		
ν_{calcd} c)/cm^{-1}	1387	1338		

a) Observed absorption maxima at the longest wavelength. b) Observed wavenumbers of the strongest Raman shift. c) Calculated wavenumbers of the strongest vibrational frequencies for H-substituted models.

20). These results strongly indicated not only the sp^2 character for their ring silicon atoms but also the effective steric protection afforded by the bulky Tbt group, which completely prevents their silicon atoms from coordination of the ethereal solvent. In other words, the Märkl's silabenzene **14** might be stabilized due to the bulky substituents (*t*-Bu and Me_3Si groups) together with the coordination of the Lewis-basic, ethereal solvent such as ether and/or THF they used.[19]

^{1}H and ^{13}C NMR spectral data of these silaaromatics, fully assigned by 2D NMR technique, also supported their assigned molecular structures. The nice agreement of the observed chemical shifts with those obtained by the theoretical calculations of several model compounds indicated that there was little perturbation with the aromatic Tbt group on the silicon atoms. A similar conclusion was drawn for germaaromatic compounds **21** and **22** by the study of their ^{1}H and ^{13}C NMR spectra.

Of particular note among the ^{1}H NMR spectral data is the fact that the chemical shifts for the ring protons of these metallaaromatic compounds are all shifted to lower field by ca. 0.5 to 1.0 ppm compared with those of precursors. This distinct low-field shift of the ring protons should be noted as one example of the experimental evidence for the ring current effect of these metallaaromatic systems.

UV–Vis and Raman Spectra. In order to examine the similarities and differences between the newly obtained metallaaromatic compounds **17**–**22** and the parent aromatic hydrocarbons, their UV–vis and Ramam spectra were measured.[29–34] In the electronic spectra, all silaaromatic compounds showed remarkable red-shifts for their ^{1}B, ^{1}L$_a$, and ^{1}L$_b$ bands as compared with those reported for the corresponding parent aromatic hydrocarbons. In Table 2 are summarized the experimentally observed absorption maxima at the longest wavelength for the metallaaromatic compounds **17**–**22** together with those for their carbon analogues. Interestingly, in the electronic spectra, the absorption maxima of germabenzene **21**[33] and 2-germanaphthalene **22**[34] showed almost no shift compared with their silicon analogues **17**[29] and **19**,[31] though they were clearly red-shifted in comparison with those of the parent aromatic hydrocarbons. These results indicate that the HOMO–LUMO energy gap of the cyclic $[4n+2]\pi$ electron systems containing a heavier group 14 element is much larger than that of the corresponding hydrocarbons, but almost identical to each other as for the silicon and germanium analogues. Although the silaaromatic species examined here have an extremely bulky Tbt group on the central silicon atom, their electronic spectra closely resembled those reported for the transient silaaromatics measured in the low-temperature matrices, indicating very little perturbation thanks to the steric protection afforded by Tbt group.

Raman spectra were measured to study the vibrational frequencies of the metallaaromatic species of heavier group 14 elements. The strongest three Raman lines observed for each species, i.e., **17**–**22** and the corresponding aromatic hydrocarbons, are also summarized in Table 2.[29–34] The experimentally ob-

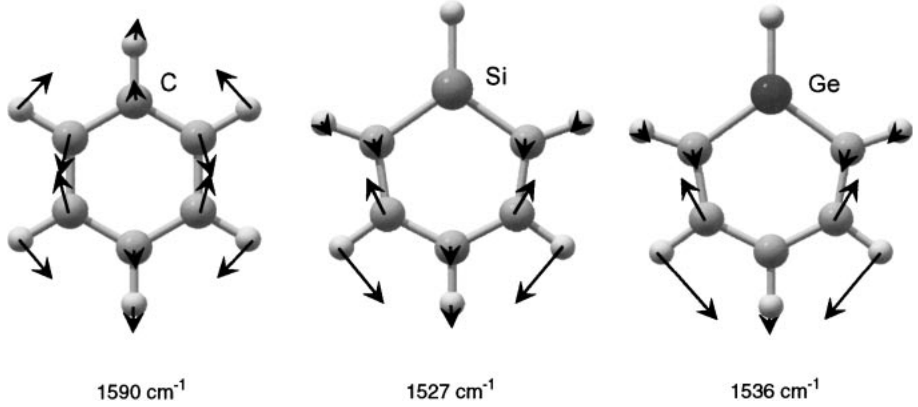


Fig. 3. Schematic drawings of the vibrational modes for the strongest in-plane vibrations of benzene, silabenzene, and germabenzene.

served Raman shifts for the metallaaromatic species and the parent hydrocarbons are reasonably reproduced by theoretical calculations,[38] suggesting the skeletal similarity in these aromatic ring systems, although those for metallaaromatics were observed at somewhat shorter wave numbers than those of carbon analogues. In addition, the similarity among their vibrational modes is also confirmed by calculations. Figure 3 shows the schematic drawings for the vibrational modes of silabenzene **17** and benzene as representatives.

Consequently, we have experimental evidence that the replacement of one of the ring carbons in the aromatic hydrocarbons with a heavier group 14 element makes no big difference in the spectroscopic properties of the resulting $[4n + 2]\pi$ conjugated metallacycles of group 14 elements as compared with the parent carbon analogues.

Reactivity and Aromaticity

Thermal and Photochemical Stability. Although all silaaromatic species here synthesized, i.e., silabenzene **17**, 1- and 2-silanaphthalenes **18** and **19**, and 9-silaanthracene **20**, were isolated as stable crystalline compounds, they showed some differences in their stability in solution (Chart 4).

Silabenzene **17** has high thermal stability in solution and no dimerization was observed on heating in hexane at 100 °C for a long time.[29] However, standing the hexane solution of **17** in C_6D_6 for 4 months resulted in the formation (ca. 50%) of the corresponding [4 + 2] dimer **29**, the structure of which was confirmed by X-ray crystallographic analysis.[39] Since the dimer readily undergoes thermal retrocycloaddition on heating in C_6D_6 at 80 °C, this dimerization reaction might be an endothermic reaction. 1-Silanaphthalene **18** also undergoes thermal dimerization in C_6D_6 to give the corresponding [4 + 2] cycloadduct **30** (at r. t. for 1 month and at 100 °C for 12 h) in an almost quantitative yield.[30] However, the dimer of 1-silanaphthalene **30** is quite stable even on heating in C_6D_6 at 120 °C, suggesting that the dimerization process of **18** is an exothermic reaction, in contrast to the case of silabenzene **17**. On the other hand, 2-silanaphthalene **19** does not undergo any dimerization on heating in solution up to 120 °C for a long time.[31] 9-Silaanthracene **20** was found to be stable at room temperature either in solution or in the solid state,[32] but it underwent thermal dimerization at higher temperatures (110 °C in C_6D_6 for 15 days or 180 °C in the solid state within 1 h) to give the [4 + 4] cycloaddition product **31** quantitatively.[40] The [4 + 4] dimerization of **20** might be an exothermic reaction, and hence no thermal dissociation of **31** to the initial 9-silaanthracene **20** was observed even on heating at 300 °C. It is very interesting that the thermal stability of the Tbt-substituted silaaromatics varies depending on the fused ring skeletons and/or the position of the silicon atom. Full calculations on the real molecule systems with high level of theory are necessary to disclose the origin for such a subtle difference.

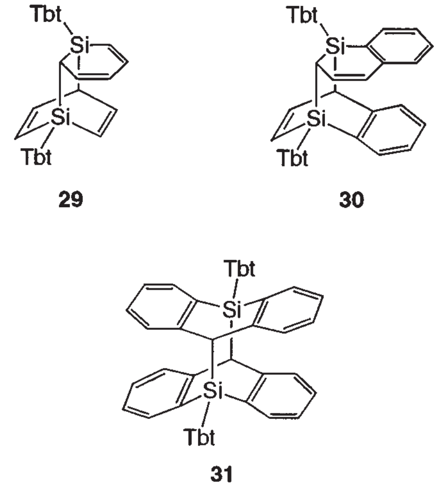
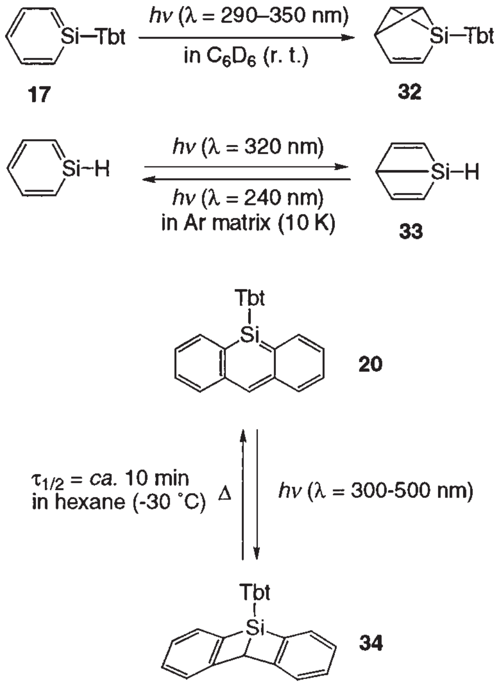


Chart 4.

Photochemical isomerization was also examined for the kinetically stabilized silaaromatics (Scheme 4). When silabenzene **17** was irradiated with the light from 290 through 350 nm in C_6D_6, a novel photochemical valence isomerization took place to give the corresponding silabenzvalene **32** as a sole product.[29b] This result is in sharp contrast to the photochemical valence isomerization of matrix-isolated parent silabenzene into the Dewar-type silabenzene **33**,[15e] the formation of which was only evidenced by the IR spectroscopic data indicative of sp^3-SiH moiety.[15e] Since DFT calculations (B3LYP/6-31G(d) level) on the relative stability of several valence isomers of silabenzene showed that the energy difference between the Dewar-type silabenzene and silabenzvalene is very small,[29b] it is very difficult to assign the photo-isomerized product of the parent silabenzene as the Dewar-type silabenzene absolutely. On the other hand, the irradiation of the C_6D_6 solution of 9-silaanthracene **20** with the light of 300–500 nm resulted in the almost quantitative formation of the corresponding Dewar-type silaanthracene **34**.[40] The molecular structure of **34** was supported by the ^{1}H, ^{13}C, and ^{29}Si NMR data and chemically confirmed by the ready thermal interconversion to the initial 9-silaanthracene **20**. 9,10-Dewar-9-silaanthracene **34** was found to be marginally stable at low temperature and the half-life time in hexane at −30 °C is estimated as about 10 min.

Addition Reactions. All the metallaaromatic species kinetically stabilized by Tbt group showed considerably high reactivity toward the reagents such as water, methanol, styrene, phenylacetylene, mesitonitrile oxide, benzophenone, and 2,3-dimethylbuta-1,3-diene. Some of them were allowed to react with elemental chalcogen such as sulfur and selenium to give several kinds of unique cyclic chalcogenides as the cycloadducts.[30,31b,34,41] In Scheme 5 are summarized the reactions of metallabenzenes **17** and **21** as the representative cases.

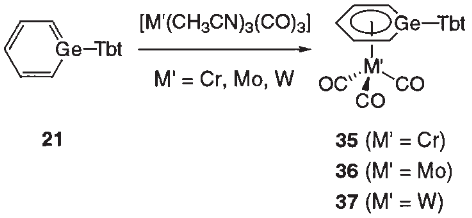


Scheme 4.

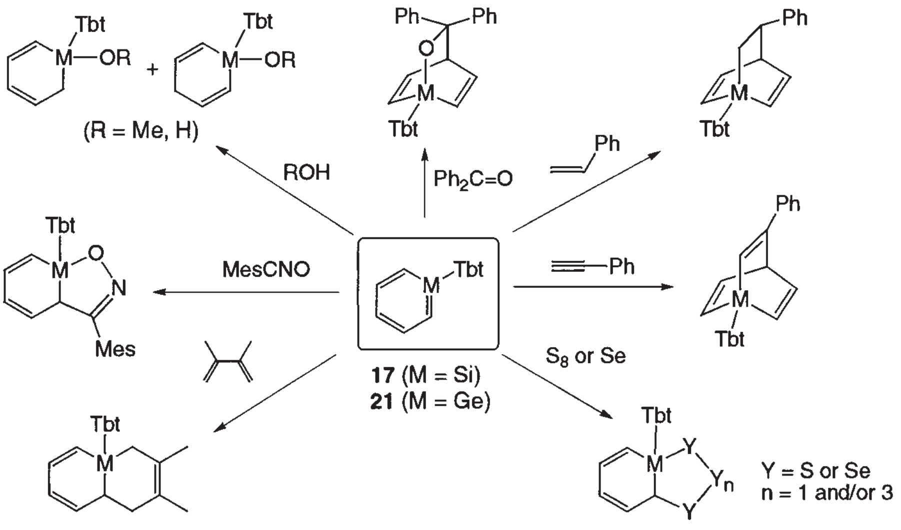
Interestingly, metallabenzenes (**17** and **21**) and 1-silanphthalene **18** were found to undergo 1,2- and/or 1,4-addition reactions depending on the character of the reactants, while 2-metallaaromatic systems **19** and **22** afforded only 1,2-addition reaction products. The remarkable reactivity of the metallaaromatic species **17**–**22** towards addition reactions implies that their aromatic stabilization energies are insufficient to suppress the inherently high reactivity of the M=C bonds (M = Si, Ge).

Transition Metal Complexation as an η^6-Arene Ligand. Unfortunately, clear experimental evidence has not been obtained yet for the electrophilic substitution reactions of metallaaromatic species **17**–**22**, which may be the greatest point of interest among the reactivities of such novel aromatic systems, due to the instability of the substrates under the reaction conditions used. Recently, however, it was found that the complexation of germabenzene **21** with some tricarbonyl complexes of group 6 metals resulted in the formation of the corresponding η^6-germabenzene–transition metal complexes **35**–**37** as stable crystalline compounds[42] (Scheme 6).

Thus, the ligand exchange reaction of $[\mathrm{Cr(CH_3CN)_3(CO)_3}]$[43a] with **21** afforded the first η^6-germabenzene complex of Cr, $[(\eta^6\text{-}\mathrm{C_5H_5GeTbt})\mathrm{Cr(CO)_3}]$ (**35**), as yellow crystals in 58% isolated yield. Using similar conditions,[43] the corresponding Mo and W complexes, **36** and **37**, were synthesized as yellow crystals in 67 and 65% yields, respectively. The η^6-coordi-



Scheme 6.



Scheme 5.

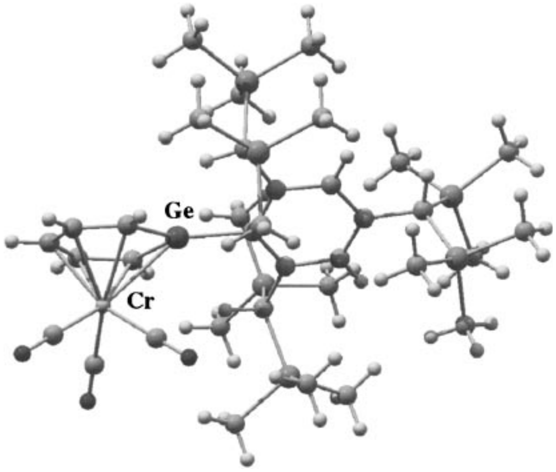


Fig. 4. Molecular structure of [Cr(η^6-germabenzene)(CO)$_3$] **35**.

nation modes of the germabenzene complexes **35**–**37** were definitely confirmed by the X-ray crystallographic analysis. In Fig. 4 is shown the molecular structure of complex **35** as the representative.[42]

Germabenzene complexes **35**–**37** are thermally quite stable either in the solid state or in solution under argon atmosphere, and no detectable change was observed in the thermolysis of **35**–**37** in C_6D_6 at 120 °C in a sealed tube for a few days. Complexes **35**–**37** were found to be somewhat more stable than the free germabenzene **21** toward air and moisture, reflecting the thermodynamic stabilization afforded by the coordination to the tricarbonyl metal center of group 6 metals. However, they are still moisture-sensitive and undergo addition of water exclusively to their 1,2-positions within a few minutes, on exposure to the open air, to give the corresponding 1,2-adduct in a quantitative yield in all cases. The high regioselectivity observed for the water addition to metal-complexed germabenzenes **35**–**37** is in a sharp contrast to the competitive 1,2- and 1,4-addition of water to free germabenzene **21**.[33] Anyhow, the successful complexation of germabenzene **21** with tricarbonyl transition metals of group 6 here described is of great importance from the viewpoint of the experimental evidence for the typical reactivity of aromatic compounds.

With stable and pure samples in hand, the electronic properties of newly obtained η^6-germabenzene complexes **35**–**37** were analyzed spectroscopically. In their ^{1}H and ^{13}C NMR spectra considerable upfield-shift of signals on complexation was observed for the protons and carbons (Table 3) due to the reduction of π-electron density in the germabenzene ring, which is very similar behavior to that of transition metal complexes of aromatic hydrocarbons. In addition, the ^{13}C NMR chemical shifts for the carbonyl carbons of **35**–**37** (δ = 235.05, 222.19, and 211.88 ppm) are quite similar to those for [(η^6-mesitylene)M′(CO)$_3$] [235.1 (M′ = Cr), 223.7 (M′ = Mo), and 212.6 (M′ = W) ppm], respectively.[44] In the UV–vis spectra, all the complexes **35**–**37** showed slightly red-shifted absorption maxima compared with those of free germabenzene **21**[33] and also compared with those of the corresponding η^6-benzene tricarbonyl metal complexes, [(η^6-C_6H_6)M′(CO)$_3$] (M′ = Cr, Mo, W).[45]

Of particular note among the spectral data of complexes **35**–**37** is the stretching frequencies (ν_{CO}) of **35** (1867, 1887, and 1954 cm^{-1}), **36** (1865, 1883, and 1952 cm^{-1}), and **37** (1865, 1883, and 1952 cm^{-1}), which were observed at lower wave numbers compared to those of the corresponding benzene complexes, [(η^6-C_6H_6)M′(CO)$_3$] [1915 and 1982 cm^{-1} (M′ = Cr),[46a] 1913 and 1983 cm^{-1} (M = Mo),[46b] and 1916 and 1990 cm^{-1} (M′ = W)[46c]]. These results suggest that the benzene ligands in [(η^6-C_6H_6)M′(CO)$_3$] (M′ = Cr, Mo, and W) are more electron-donating than the garmabenzene ligand in complexes **35**–**37**. All stretching frequencies observed for complexes **35**–**37** are in good agreement with those obtained for the unsubstituted model complexes by theoretical calculations.[42]

The structural and spectroscopic similarities between the η^6-germabenzene complexes **35**–**37** and the corresponding η^6-benzene complexes coordinated with group 6 transition metals are of great importance as one of the experimental proofs for the aromatic character of metallaaromatic species of heavier group 14 elements.

Theoretical Calculations

Nucleus Independent Chemical Shifts (NICSs). As can be seen in the previous sections, the structural and spectroscopic features of kinetically stabilized metallaaromatic species **17**–**22** are in good agreement with those obtained for the less hindered model compounds by theoretical calculations, strongly suggesting that the bulky aromatic substituent (Tbt) does not perturb the intrinsic characters for the metallaaromatic species. As for their aromaticity, we have performed further theoretical calculations of NICS(1)s (Nucleus Independent Chemical Shifts)[47] and found that mono-metallaaromatic species have considerably large absolute values, though being slightly smaller than those of the parent aromatic hydrocarbon systems (Fig. 5).

In spite of the high aromaticity suggested by the NICS calculations mentioned above, it should be noted again that the isolated metallaaromatics **17**–**22** showed high reactivity toward a variety of addition reactions across the metal–carbon double bonds.

Aromatic Stablization Energies (ASEs). This apparent

Table 3. Observed ^{1}H and ^{13}C NMR Chemical Shifts (ppm) for η^6-Germabenzene Complexes **35**–**37** and Free Germabenzene **21**[a)]

Compounds	H2	H3	H4	C2	C3	C4	^{13}C=O
35 (M = Cr)	3.95	4.98	4.73	100.91	85.87	83.00	235.05
36 (M = Mo)	4.05	5.17	4.73	103.11	83.77	81.64	222.19
37 (M = W)	4.04	4.86	4.75	98.51	80.02	79.64	211.88
21	7.85	8.06	6.72	132.23	140.96	114.56	—

a) Measured in benzene-d_6.

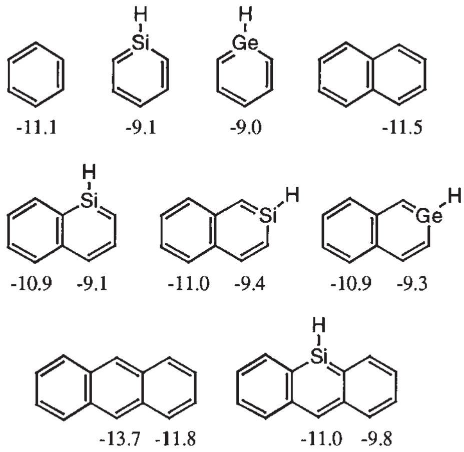
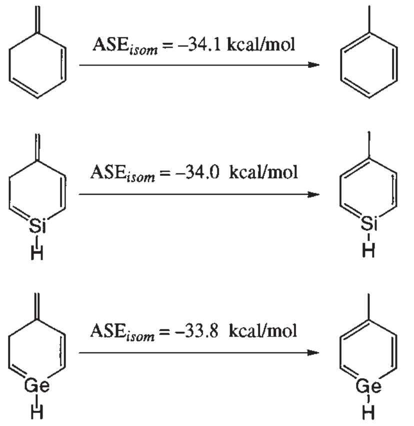


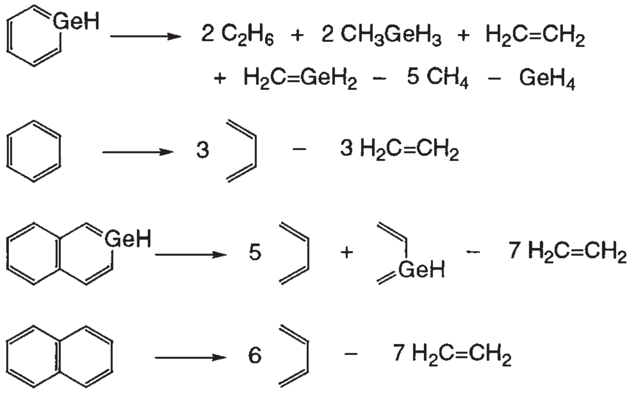
Fig. 5. NICS(1) values (ppm) for heavy aromatic systems calculated at the B3LYP/6-311G(d) (6-311G(3d) on Si and Ge)//B3LYP/6-31G(d) level.



Scheme 7.

contradiction can be most likely interpreted as meaning that the aromatic stabilization energies (ASEs) for the metallaaromatic species containing a heavier group 14 element are insufficient to suppress the extremely high reactivity toward addition reactions. For example, the ASEs of benzene, silabenzene, and germabenzene were estimated by the quantitative energetic evaluation using the DFT-computed isodesmic isomerization energies of nonaromatic polyenes into the methyl-substituted aromatic isomers (Scheme 7).[48]

Since this method is based on the introduction of a methyl group having little effect on arene aromaticity and on the isomerization reactions involving highly similar structures, the evaluations deduced here are self-consistent.[48] As a result, the ASEs of silabenzene and germanaphthalene systems (34.0 and 33.8 kcal/mol) are found to be almost identical to that of the parent benzene system (34.1 kcal/mol). On the other hand, theoretical calculations (B3LYP/6-311G+G(d,p)) revealed that the Si=C or Ge=C double bonds are inherently more reactive than the C=C double bond, and the addition reactions of water to $H_2M=CH_2$ [$\Delta H = -64.3$ (M = Si) and -48.0 (M = Ge) kcal/mol] are found to be much more exothermic than that of ethylene ($\Delta H = -7.1$ kcal/mol).



Scheme 8. Increment scheme for the evaluation of $\chi_{M'}$ values for some germaaromatics and related hydrocarbons.

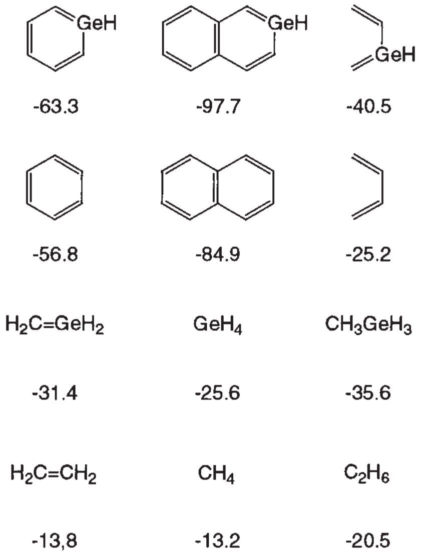


Fig. 6. Calculated χ_M values (ppm cgs) for some germaaromatics and related hydrocarbons at the CSGT-HF/6-31G(d) level.

Diamagnetic Susceptibility Exaltation (Λ). Diamagnetic susceptibility exaltation (Λ) is known to be another measure of aromaticity.[49] The Λ value is defined as the difference between the diamagnetic susceptibility of the system under investigation (χ_M) and the diamagnetic susceptibility for a hypothetical reference system without cyclic electron delocalization ($\chi_{M'}$): $\Lambda = \chi_M - \chi_{M'}$.

We have performed the evaluation of the $\chi_{M'}$ for unsubstituted germabenzene and 2-germanaphthalane and the corresponding aromatic hydrocarbons by employing Scheme 8[50] and also the calculations of their χ_M values at the CSGT-HF/6-31G(d) level (Fig. 6). As shown in Fig. 7, germabenzene and 2-germanaphthalene showed large negative Λ values (-19.5 and -27.9 ppm, respectively), which are comparable to those for benzene (-22.7 ppm) and naphthalene (-30.4 ppm). Thus, the magnetic criterion also indicated that germaaromatic species have the same ring current effects as the corresponding hydrocarbon aromatic compounds have.

Conclusion and Outlook

We have succeeded in the synthesis and isolation of the first examples of stable neutral metallaaromatic compounds of

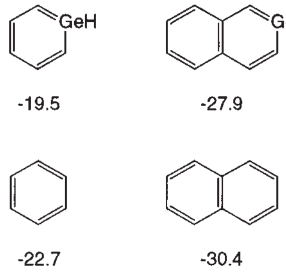


Fig. 7. Calculated Λ values (ppm cgs) for some germaaromatics and related hydrocarbons at the CSGT-HF/6-31G(d) level.

heavier group 14 elements by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (Tbt). The molecular structures of kinetically stabilized metallaaromatics obtained here were discussed on the basis of their NMR, UV/vis, and Raman spectra, and X-ray crystallographic analysis. The deshielding observed in the ^{1}H NMR spectra of these systems strongly indicated the existence of the same ring current effect as observed for aromatic hydrocarbon species. UV/vis and Raman spectra of the metallaaromatic species showed patterns that closely resembled those of the corresponding hydrocarbon analogues, indicating the similarity in their molecular frameworks, though the intrinsic bathochromic shifts (UV/vis) and low wavenumber shifts (Raman) were clearly observed for the heavy aromatics. X-ray crystallographic analyses experimentally demonstrated the planarity and other structural features that indicate the delocalization of π-electrons in the metallaaromatic rings. These experimental results were in good agreement with those obtained by theoretical calculations.

The *heavy aromatics* here synthesized were allowed to react with various reagents that show the high reactivity as metal–carbon double bonds and/or their vinylogues. Although they are kinetically stabilized with the bulky Tbt group, some of them were found to undergo thermal dimerization reactions. Tbt-substituted silabenzene underwent photochemical valence isomerization into the corresponding silabenzvalene, while the irradiation of 9-Tbt-9-silaanthracene resulted in the formation of novel 9,10-Dewar-9-silaanthracene. Furthermore, the first stable η^6-germabenzene complexes **35–37** were synthesized by the ligand exchange reactions of Tbt-substituted germabenzene **21** with [M′(CH$_3$CN)$_3$(CO)$_3$] (M′ = Cr, Mo, and W). These results are the first examples that show the aromatic character of a germabenzene from the standpoint of its chemical reactivity. The aromaticity of metallaaromatic species of heavier group 14 elements was also evaluated by theoretical calculations [NICSs, ASEs, and diamagnetic susceptibility exaltation (Λ)]. Large negative NICS and Λ values, and theoretical energetic evaluations strongly support the ring current effects and aromatic stabilization of the *heavy aromatics* here synthesized.

In contrast to the successful isolation and characterization of the kinetically stabilized sila- and germaaromatic compounds here described, their heavier congeners such as stannabenzene or plumbabenzene are still elusive and neither their isolation nor spectroscopic detection has been achieved. In addition, the synthesis of aromatic systems containing multiple heavier group 14 elements such as dimetallabenzenes still remains as the next target. The concept of kinetic stabilization should certainly be of great use for the synthesis of these unprecedented *heavy aromatic species*.

The author is grateful to the graduate students and collaborators, whose names are cited in the references, for their invaluable contributions. This work was partially supported by Grants-in-Aid for the COE Research on Elements Science [No. 12CE2005], the Scientific Research on Priority Areas [No. 1407213], and the 21 COE Kyoto University Alliance for Chemistry (Novel Organic Materials Creation & Transformation Project), from the Ministry of Education, Culture, Sports, Science and Technology. Computation time was provided at the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University.

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