

New Progress in the Chemistry of Stable Metallaaromatic Compounds of Heavier Group 14 Elements

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ABSTRACT

By taking advantage of kinetic stabilization afforded by introduction of an efficient steric protection group, several kinds of sila-aromatic compounds, such as silabenzene, 1- and 2-silanaphthalenes, and 9-silaanthracene, were successfully synthesized and isolated as stable compounds. The first stable germaaromatics, such as germabenzene and 2-germanaphthalene, were also synthesized by the use of a similar synthetic approach. Most of their molecular structures were definitively determined by X-ray crystallographic analysis. The novel molecular structures and unique reactivities of these metallaaromatic species are discussed on the basis of the experimental results together with those obtained by theoretical calculations, focusing on their aromaticity.

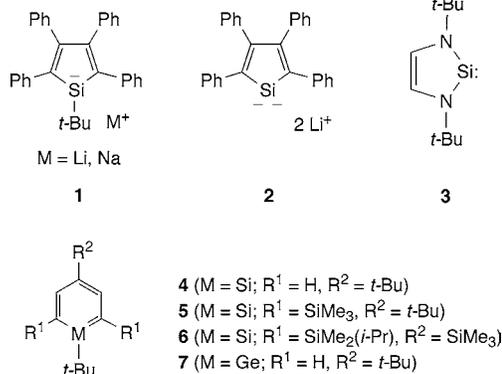
Introduction

Silaaromatic compounds,¹ i.e., Si-containing $[4n+2]$ π ring systems, have attracted much attention in recent decades, since they represent the heavier congeners of carbocyclic aromatic compounds,² which play very important roles in organic chemistry. Although the aromatic character of silole anions and dianions such as **1** and **2**,³ as well as that of cyclic diaminosilylene **3** (Chart 1),⁴ was recently revealed from both experimental and theoretical standpoints, simple neutral sila-aromatic compounds are known to be highly reactive. Such silabenzenoids have only been characterized in low-temperature matrices or postulated as transient intermediates in some trapping reactions.^{5,6}

While nonconjugated, Si-containing doubly bonded compounds have already been synthesized as stable molecules by taking advantage of kinetic stabilization,⁷ no silabenzene stable at ambient temperature has ever been reported until our successful results. It was reported that

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Chart 1



1,4-di-*tert*-butyl-1-silabenzene **4** readily dimerized at 0 °C to give the corresponding $[2 + 2]$ dimer.⁸ The more crowded 1,4-di-*tert*-butyl-2,6-bis(trimethylsilyl)-1-silabenzene **5** was reportedly stable below –100 °C and observed by low-temperature NMR measurements,⁹ though only in a special solvent (THF/ether/petroleum ether, 4:1:1), suggesting the coordination with the solvent (most likely THF) as judged by the ²⁹Si NMR chemical shift ($\delta_{\text{Si}} = 26.8$). 1-*tert*-Butyl-2,6-bis(dimethylisopropylsilyl)-4-trimethylsilyl-1-silabenzene **6** was also generated under argon flow, but it was found to be stable only at –180 °C.¹⁰

2-Methyl-2-silanaphthalene has been postulated as an intermediate in the N_2 -flow pyrolysis of the corresponding allylsilane precursor at 650 °C,⁶ 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.⁵ The situation for the chemistry of germaaromatics is almost the same as that of silaaromatics.^{11–14} Thus, syntheses of several examples of stable ionic species^{11,13} and the dimerization and intermolecular trapping of 1,4-di-*tert*-butylgermabenzene **7**¹⁴ have been reported, while stable neutral germaaromatics have been elusive until quite recently.

Meanwhile, many theoretical calculations have been reported for sila- and disilabenzenes,^{1c,d} and the results indicate that silabenzenes have a π -electron-delocalized structure and considerable aromaticity.¹⁵ This implies that silaarenes might exist as stable molecules if their high reactivity could be suppressed by some protection. In view of the successful kinetic stabilization of stable doubly bonded organosilicon compounds,^{1a,7,16} stable sila-aromatic compounds are expected to be synthesizable using an appropriate bulky substituent. In this connection, we have already developed an extremely bulky and effective steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt),¹⁷ and applied it to the synthesis and isolation of a variety of novel reactive species of heavier main group elements. For example, a stable silanethione¹⁸ and its heavier element analogues **8** (Chart 2)^{19,20} were successfully synthesized utilizing a Tbt group in combination with another considerably bulky substituent. The first stable

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Chart 2

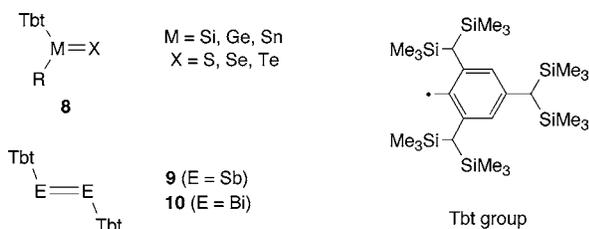
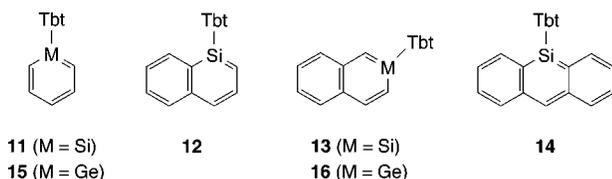


Chart 3



distibene **9**²¹ and dibismuthene **10**,²² long-sought, unprecedented doubly bonded systems, were also synthesized by introducing Tbt groups on each terminal group 15 element. Since it has been fully demonstrated that the Tbt group is very effective in stabilizing the highly reactive, low-coordinated species of heavier main group elements, we next applied it to the kinetic stabilization of an unexplored class of low-coordinated species of heavier group 14 elements, such as sila- and germaaromatic compounds.

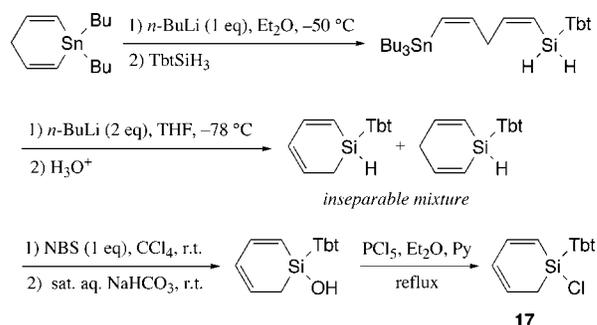
Until now, several kinds of silaaromatic compounds bearing a Tbt group on the sp² silicon atom, such as silabenzene **1**,²³ 1- and 2-silanaphthalenes (**12**²⁴ and **13**²⁵), and 9-silanthracene **14** (Chart 3),²⁶ were successfully synthesized and isolated as stable compounds. Furthermore, the first stable germabenzene **15**²⁷ and 2-germanaphthalene **16**²⁸ were also synthesized using a similar synthetic approach. In this Account, the recent progress in the chemistry of metallaaromatic compounds of heavier group 14 elements is outlined with the systematic comparison between the parent aromatic hydrocarbons and their heavier congeners.

Synthesis and Isolation

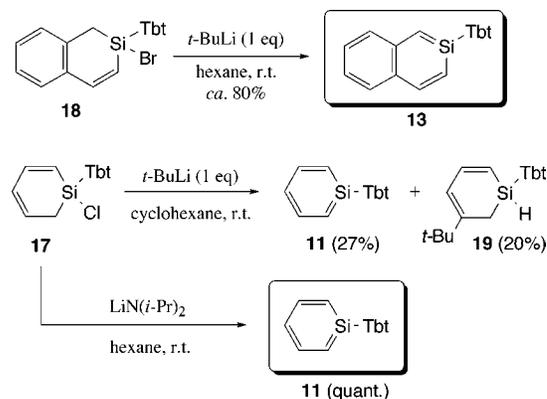
For the isolation of such a highly reactive species in a pure form, it is necessary to develop suitable synthetic methods (e.g., high yields and mild reaction conditions). As the final step, we chose simple dehydrohalogenation reactions of the corresponding cyclic halometallane precursors using an appropriate base. The synthetic route for chlorosilane **17**, the precursor of silabenzene **11**, is shown as a representative case in Scheme 1.²³

Another important factor for the effective synthesis is the choice of a base. For example, 2-silanaphthalene **13** was successfully synthesized by the treatment of bromosilane **18** with *t*-BuLi in hexane,²⁵ while similar treatment of chlorosilane **17** resulted in the formation of the undesired *tert*-butylated product **19**, together with the expected silabenzene **11** (Scheme 2).^{23b} The formation of **19** might be interpreted in terms of the initial electron transfer from *t*-BuLi to **17**, followed by the recombination of the resulting radical intermediates. This problem was

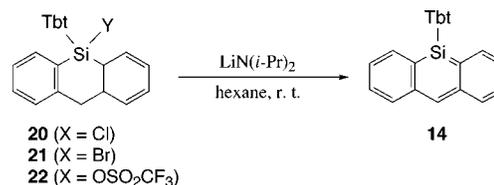
Scheme 1



Scheme 2

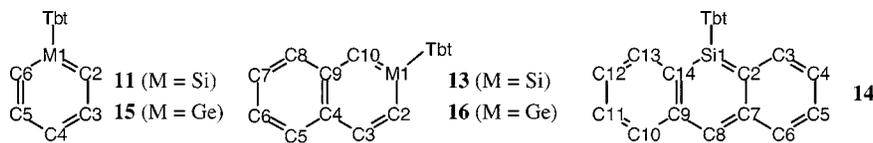


Scheme 3



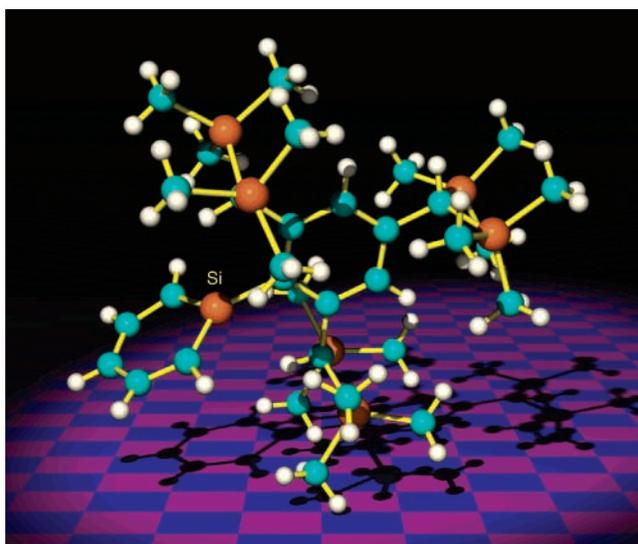
successfully solved by the use of lithium diisopropylamide (LDA) as a base to give **11** almost quantitatively. For the syntheses of 1-silanaphthalene **12**,²⁴ 9-silanthracene **14**,²⁶ germabenzene **15**,²⁷ and 2-germanaphthalene **16**,²⁸ LDA was found to be the best among the bases examined. In addition, in the case of 9-silanthracene **14**,²⁶ the leaving ability of the substituent on the silicon atom played a very crucial role. Although the use of halosilanes **20** and **21** as precursors resulted in very low yields of **14**, as judged by trapping experiments with MeOH,²⁹ the treatment of silyltriflate **22** with LDA in benzene gave the expected **14** quantitatively (Scheme 3).²⁶

Except for **12**,²⁴ which was found to undergo gradual dimerization in solution at room temperature (*vide infra*), **11** and **13**–**16** were isolated as stable crystalline compounds, indicating the high ability of the Tbt group as a steric protecting group. Recently, matrix isolation and intermolecular trapping reactions have been described for the 9-silanthracenes having a 2,4,6-triisopropylphenyl or 2,4,6-tri-*tert*-butylphenyl group, but these species are reportedly not isolable.³⁰ This fact implies the indispensability of an extremely bulky substituent such as Tbt for the isolation of kinetically stabilized metallaaromatic compounds.

Table 1. Selected Structural Parameters for Metallaaromatic Compounds **11** and **13–16**

	compound									
	11^a		15^b		13^c		16^d		14^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)
ΣM (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 Reference 23. ^b Reference 27. ^c Reference 25. ^d Reference 28. ^e Reference 26.

**FIGURE 1.** Molecular structure of Tbt-substituted silabenzene **11**.

Structures and Spectroscopic Properties

X-ray Crystallographic Analysis. The most important structural features of aromatic compounds are the planarity of their aromatic rings and the ring bond lengths, lying between those of typical double and single bonds, which result from the delocalization of π -electrons of their aromatic rings. From the viewpoints of systematic comparison, it is of great significance to perform an X-ray crystallographic analysis of the metallaaromatic compounds obtained here. Fortunately, most of them were isolated as stable crystalline compounds, reflecting the high crystallinity of the Tbt-substituted compounds, which 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 ball-and-stick drawing for silabenzene **11** is shown in Figure 1, which clearly indicates that the planar silabenzene ring is nicely protected by the bulky Tbt group.

All metallaaromatic ring systems examined here have an almost planar aromatic ring, and the geometry around the central silicon or germanium atom is completely

trigonal planar, suggesting the delocalization of π -electrons in these ring systems. Almost equal distances were observed for the group 14 metal–carbon bonds in both sila- and germabenzenes **11** and **15**, while a small extent of bond alternation was recognized for 2-sila- and 2-germanaphthalenes **13** and **16**, as in the case of parent naphthalene. Taking into account the fact that the C–C bond lengths in these metallaaromatic rings are comparable with those reported for parent benzene and naphthalene,² it should be concluded that 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 theoretical calculations at the B3LYP/6-31G(d) level for some model compounds, suggesting little steric and electronic influence of the Tbt group.

In addition, it was revealed that all of the compounds have a large dihedral angle [from 69° (for **14**) to 89° (for **16**)] 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 that 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. To elucidate the conjugative stabilizing effect of the aryl group, we have performed theoretical calculations for the relative stability of 1-phenylsilabenzene **23** and 1-mesitylsilabenzene **24** with varying dihedral angles between the aryl substituent plane and the silabenzene ring plane (Figure 2).³¹

Figure 2 indicates that the conformation with the phenyl group perpendicularly oriented is the most unstable one for **23**, but the difference from the most stable coplanar conformer is only about 2 kcal/mol, regardless of the level of theory used for the calculations. In the case of **24**, such a coplanar conformation is the most unfavor-

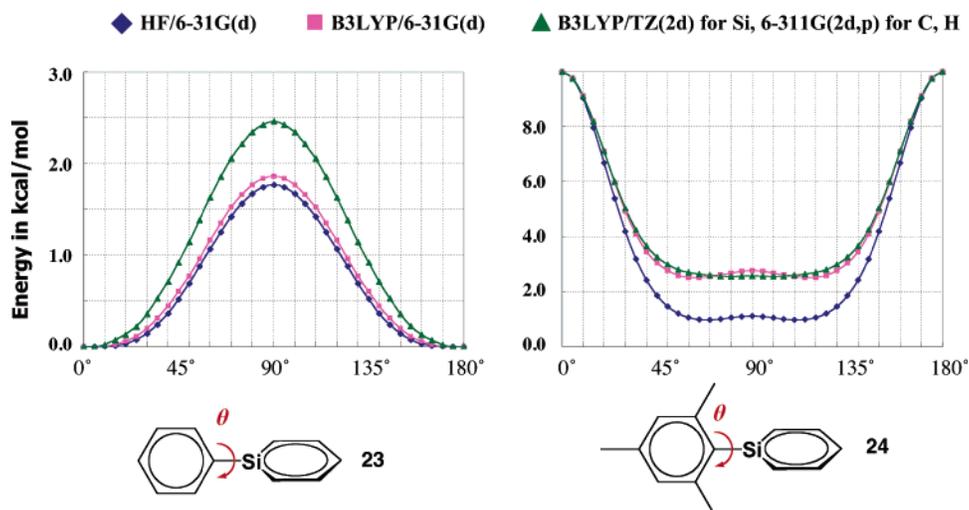


FIGURE 2. Potential energy surface for Ph- and Mes-substituted silabenzenes, **23** and **24**.

able situation, as expected due to steric repulsion, while it was found that the energy level was almost invariant between the dihedral angles of 50 and 90°. In the cases of both **23** and **24**, the lengths of the Si=C bond between the two aromatic rings varied within the range of 1.7752–1.7755 Å, suggesting that the conjugative effect does not have a significant influence on the nature of the sila-aromatic ring system.

NMR Spectra. As for the sila-aromatic compounds, ^{29}Si NMR spectroscopy provides us with useful information about the electronic and structural environments of their central silicon atom. All sila-aromatics **11–14** showed characteristically low-field signals in the ^{29}Si NMR spectra [93.6 (**11**²³), 91.7 (**12**²⁴), 87.3 (**13**²⁵), and 87.2 (**14**²⁶) ppm in C_6D_6], suggesting the sp^2 character of their ring silicon atoms. These chemical shifts are at lower field than those for the previously reported marginally stable silabenzene (**5**; $\delta_{\text{Si}} = 26.8$),⁹ and almost no spectral change was observed even on measurement in the presence of ethereal solvent such as in $\text{THF}:\text{C}_6\text{D}_6 = 6:1$ (the largest $\Delta\delta$ was 0.4 ppm for **14**). These results strongly indicate not only sp^2 character for their ring silicon atoms but also the effective steric protection afforded by the bulky Tbt group, which completely blocks their silicon atoms from coordination with the ethereal solvent. In other words, Märkl's silabenzene **5** might be stabilized with the bulky substituents (*t*-Bu and Me_3Si groups) together with the coordination of Lewis-basic, ethereal solvent such as ether and/or THF.⁹

^1H and ^{13}C NMR spectral data of **11–14**, fully assigned by 2D NMR techniques, also supported their molecular structures. The nice agreement of the observed chemical shifts with those obtained by theoretical calculations of several model compounds indicated that little perturbation occurred with the aromatic Tbt group on the silicon atom. A similar conclusion was made for germaaromatic compounds **15** and **16** by the study on their ^1H and ^{13}C NMR spectra.

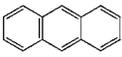
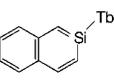
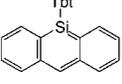
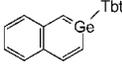
Of particular note among the ^1H NMR spectral data is that the chemical shifts for the ring protons of **11–16** are all shifted to lower field by ca. 0.5–1.0 ppm compared

with those of precursors. This distinct low-field shift of the ring protons should be noted as one type of experimental evidence for the ring current effect of these metallaaromatic systems.

UV–Vis and Raman Spectra. To examine the similarities and differences between metallaaromatic compounds and the parent aromatic hydrocarbons, the UV–vis and Raman spectra of **11–16** were measured.^{23–26} In the electronic spectra, all sila-aromatic compounds showed remarkable red-shifts for their ^1B , $^1\text{L}_a$, and $^1\text{L}_b$ 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 **11–16**, together with those for the carbon analogues. Interestingly, the absorption maxima of germabenzene **15**²⁷ and 2-germanaphthalene **16**²⁸ showed almost no shift compared with their silicon analogues **11**²³ and **13**,²⁵ despite being clearly red-shifted in comparison with those of the parent aromatic hydrocarbons. These results indicate that the HOMO–LUMO energy gap of the cyclic $[4n + 2]$ π electron systems containing a heavier group 14 element is much smaller than that of the corresponding hydrocarbons while the differences between the silicon and germanium analogues are very small. Although the sila-aromatic species examined here have an extremely bulky Tbt group on the central silicon atom, their electronic spectra closely resembled those reported for the transient sila-aromatics measured in low-temperature matrices, indicating the very little perturbation by the steric protection afforded by Tbt group.

The strongest Raman lines observed for **11–16** and the corresponding aromatic hydrocarbons are also summarized in Table 2.^{23–28} The experimentally observed Raman shifts for the metallaaromatic species and the parent hydrocarbons are reasonably reproduced by theoretical calculations.³² Although the vibrational frequencies for metallaaromatics were observed at somewhat smaller wavenumbers than those for the carbon analogues, the similarity among their in-plane vibrational modes is clearly confirmed by calculations (Figure 3). In Figure 3

Table 2. Spectroscopic Comparison between Metallaaromatics 11–16 and the Corresponding Aromatic Hydrocarbons

	Benzene Series	Naphthalene Series	Anthracene Series
			
λ_{\max} (nm) ^a	256	312	375
ν_{obsd} (cm ⁻¹) ^b	1600	1382	1401
ν_{calcd} (cm ⁻¹) ^c	1590	1360	1387
		 	
	11	12 13	14
λ_{\max} (nm) ^a	331	378	387
ν_{obsd} (cm ⁻¹) ^b	1530	1340	1368
ν_{calcd} (cm ⁻¹) ^c	1527	1330	1338
			Not isolated yet.
	15	16	
λ_{\max} (nm) ^a	326	386	
ν_{obsd} (cm ⁻¹) ^b	1600	1363	
ν_{calcd} (cm ⁻¹) ^c	1590	1356	

^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.

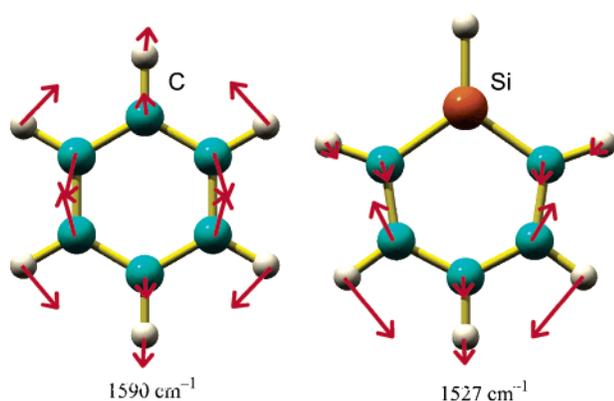


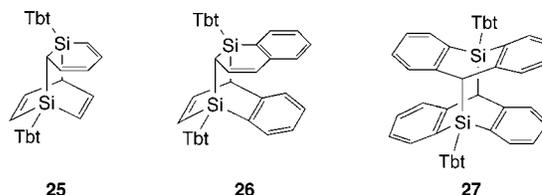
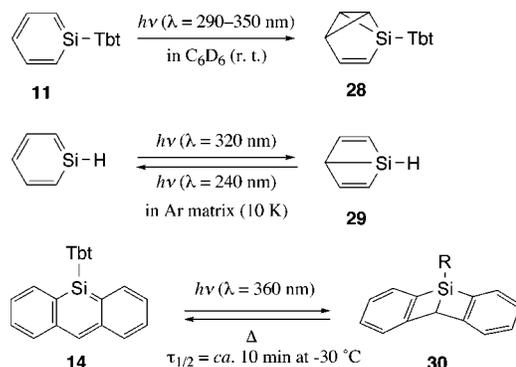
FIGURE 3. Schematic drawings of the vibrational modes for the strongest in-plane vibrations of benzene and silabenzene.

are shown the schematic drawings for the vibrational modes of silabenzene **11** and benzene as representatives.

Consequently, it is experimentally shown again that the replacement of one of the ring carbons in the aromatic hydrocarbons with a heavier group 14 element has no large influence on the spectroscopic properties of the resulting $[4n + 2]$ π -conjugated metallacycles compared with the parent carbon analogues.

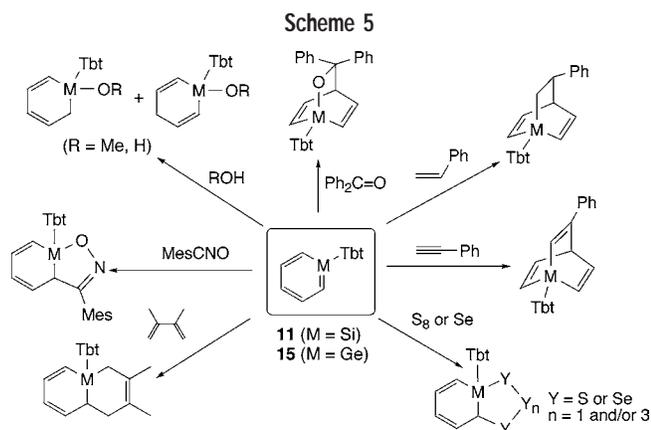
Reactivity and Aromaticity

Thermal and Photochemical Stability. Although all silaaromatic species **11–14** were isolated as stable crystal-

Chart 4**Scheme 4**

line compounds, they showed some difference in their stability in solution (Chart 4). Silabenzene **11** has high thermal stability in solution, and no dimerization was observed on heating **11** in hexane at 100 °C for a long time.²³ However, on standing for 4 months, the hexane solution of **11** in C₆D₆ resulted in the formation (ca. 50%) of the corresponding $[4 + 2]$ dimer **25**, the structure of which was confirmed by X-ray crystallographic analysis.³³ Since the dimer readily undergoes thermal retrocycloaddition on heating in C₆D₆ at 80 °C, this dimerization reaction might be an endothermic reaction, in contrast to the case with **11**. On the other hand, 2-silanaphthalene **13** does not undergo any dimerization, even on heating or standing.²⁵ 9-Silaanthracene **14** was found to be stable at room temperature either in solution or in the solid state,²⁶ but it underwent thermal dimerization at higher temperatures (110 °C in C₆D₆ for 15 days or 180 °C in the solid state within 1 h) to give the $[4 + 4]$ cycloaddition product **27** quantitatively.³⁴ The $[4 + 4]$ dimer of **14** is thermally very stable, and it was found that no thermal dissociation of **27** to the initial 9-silaanthracene **14** 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 at a high level of theory should be necessary to disclose the origin of such differences.

Photochemical isomerization was also examined for the kinetically stabilized silaaromatics (Scheme 4). When silabenzene **11** was irradiated with light of $\lambda = 290\text{--}350$ nm in C₆D₆, a novel photochemical valence isomerization



took place to give the corresponding silabenzvalene **28** as the sole product.^{23b} This result is in sharp contrast to the photochemical valence isomerization of the matrix-isolated parent silabenzene into the Dewar-type silabenzene **29**,^{5c} the formation of which was evidenced only by IR spectroscopic data, indicative of the sp^3 -SiH moiety.^{5e} 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,^{23b} it is very difficult to assign the photoisomerized product of the parent silabenzene as the Dewar-type silabenzene absolutely. On the other hand, the irradiation of 9-silaanthracene **14** in C_6D_6 with light of 300–500 nm resulted in almost quantitative formation of 9,10-Dewar-9-silaanthracene **30**.³⁴ The molecular structure of **30** was supported by the 1H , ^{13}C , and ^{29}Si NMR data and chemically confirmed by the ready thermal interconversion to the initial 9-silaanthracene **14**. 9,10-Dewar-9-silaanthracene **30** was found to be marginally stable at low temperature, and its half-life time in hexane at $-30^\circ C$ is estimated to be about 10 min.

Addition Reactions. All the metallaaromatic species kinetically stabilized by the Tbt group showed high reactivity toward reagents such as water, methanol, styrene, phenylacetylene, mesitronitrile oxide, benzophenone, and 2,3-dimethylbuta-1,3-diene. Some of them were allowed to react with elemental chalcogens, such as sulfur and selenium, to give several kinds of unique cyclic chalcogenides as the cycloadducts.^{24,25,28,35} In Scheme 5 are summarized the reactions of metallabenzenes **11** and **15** as representatives.

Interestingly, metallabenzenes **11** and **15** and 1-silaphthalene **12** were found to undergo 1,2- and/or 1,4-addition reactions, depending on the character of the reactants, while 2-metallaphthalenes **13** and **16** afforded only 1,2-addition reaction products. The remarkable reactivity of the metallaaromatic species **11–16** toward addition reactions implies that their aromatic stabilization energies are insufficient to suppress the inherent high reactivity of the $M=C$ bonds ($M = Si, Ge$).

Transition Metal Complexation as an η^6 -Arene Ligand. Unfortunately, due to the instability of the substrates under the reaction conditions used, clear experimental

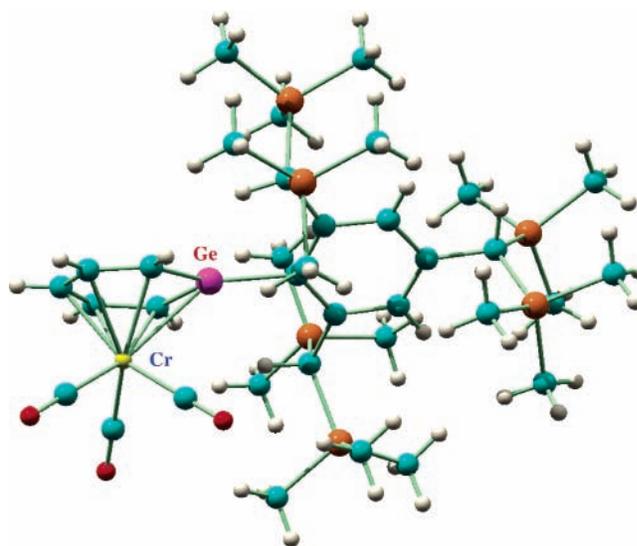
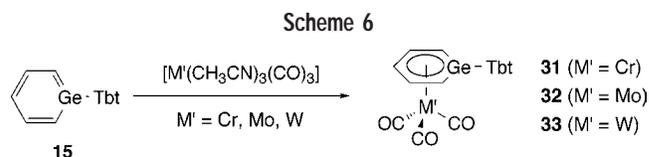


FIGURE 4. Molecular structure of $[Cr(\eta^6\text{-germabenzene})(CO)_3]$ **31**.



evidence has not yet been obtained for the electrophilic substitution reactions of metallaaromatic species **11–16**, though it may be of great interest among the reactivities of such novel aromatic systems. Recently, however, it was found that the complexation of germabenzene **15** with some tricarbonyl complexes of group 6 metals resulted in the formation of the corresponding η^6 -germabenzene–transition metal complexes **31–33** as stable crystalline compounds (Scheme 6).³⁶

Thus, the ligand-exchange reaction of $[Cr(CH_3CN)_3(CO)_3]$ ^{37a} with **15** afforded the first η^6 -germabenzene complex of Cr, $[(\eta^6\text{-}C_5H_5GeTbt)Cr(CO)_3]$ (**31**), as yellow crystals in 58% isolated yield. Using similar conditions,³⁷ the corresponding Mo and W complexes, **32** and **33**, were synthesized as yellow crystals in 67 and 65% yields, respectively. The η^6 -coordination mode of the germabenzene complexes **31–33** were definitely confirmed by X-ray crystallographic analysis. In Figure 4 is shown the molecular structure of complex **31** as a representative.³⁶

Complexes **31–33** 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 **31–33** in C_6D_6 at $120^\circ C$ in a sealed tube for a few days. Complexes **31–33** were found to be somewhat more stable than the free germabenzene **15** toward air and moisture, reflecting the thermodynamic stabilization afforded by the coordination to the tricarbonylmetal center of group 6 metals. However, they are still moisture-sensitive and undergo ready addition of water exclusively to their 1,2-positions, to give the corresponding 1,2-adduct quantitatively in all cases. The high regioselectivity observed for the water addition to **31–33** is in sharp contrast to the competitive 1,2- and 1,4-addition of water to free germabenzene **15**.²⁷ The successful complexation of germ-

Table 3. Observed ^1H and ^{13}C NMR Chemical Shifts (ppm) for η^6 -Germabenzene Complexes **31–**33** and Free Germabenzene **15**^a**

	31 (M = Cr)	32 (M = Mo)	33 (M = W)	15
H2	3.95	4.05	4.04	7.85
H3	4.98	5.17	4.86	8.06
H4	4.73	4.73	4.75	6.72
C2	100.91	103.11	98.51	132.23
C3	85.87	83.77	80.02	140.96
C4	83.00	81.64	79.64	114.56
$^{13}\text{C}=\text{O}$	235.05	222.19	211.88	–

^a Measured in benzene-*d*₆.

abenzene **15** with tricarbonyl transition metals of group 6 is of great importance from the viewpoint of the experimental evidence for the typical reactivity of aromatic compounds.

In the ^1H and ^{13}C NMR spectra of **31**–**33**, a 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, a behavior which is very similar to that of transition metal complexes of aromatic hydrocarbons. In addition, the ^{13}C NMR chemical shifts for the carbonyl carbons of **31**–**33** (δ = 235.05, 222.19, and 211.88 ppm) are quite similar to those for $(\eta^6\text{-mesitylene})\text{M}'(\text{CO})_3$ [235.1 ppm ($\text{M}' = \text{Cr}$), 223.7 ($\text{M}' = \text{Mo}$), and 212.6 ($\text{M}' = \text{W}$) ppm], respectively.³⁸ In the UV–vis spectra, **31**–**33** all showed slightly red-shifted absorption maxima compared with those of **15**²⁷ and also those of the corresponding η^6 -benzene tricarbonylmetal complexes, $[(\eta^6\text{-C}_6\text{H}_6)\text{M}'(\text{CO})_3]$; $\text{M}' = \text{Cr}, \text{Mo}, \text{W}$].³⁹

Of particular note among the spectral data of **31**–**33** are the stretching frequencies (ν_{CO}) of **31** (1867, 1887, and 1954 cm^{-1}), **32** (1865, 1883, and 1952 cm^{-1}), and **33** (1865, 1883, and 1952 cm^{-1}), which were observed at lower wavenumbers than those of $(\eta^6\text{-C}_6\text{H}_6)\text{M}'(\text{CO})_3$ [1915 and 1982 cm^{-1} ($\text{M}' = \text{Cr}$),^{40a} 1913 and 1983 cm^{-1} ($\text{M} = \text{Mo}$),^{40b} and 1916 and 1990 cm^{-1} ($\text{M}' = \text{W}$)^{40c}]. These results suggest that the benzene ligands in $(\eta^6\text{-C}_6\text{H}_6)\text{M}'(\text{CO})_3$ ($\text{M}' = \text{Cr}, \text{Mo},$ and W) are more electron-donating than the germabenzene ligand in **31**–**33**. All stretching frequencies observed for complexes **31**–**33** were in good agreement with those obtained for the unsubstituted model complexes by theoretical calculations.³⁶

Theoretical Calculations

Nucleus-Independent Chemical Shifts (NICSSs). As can be seen in the previous sections, the structural and spectroscopic features of kinetically stabilized metallaaromatic species **11**–**16** 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. We have performed further theoretical calculations of NICS(1)s (nucleus-independent chemical shifts),⁴¹ the values of which indicate their aromaticity. Consequently, it was found that mono-metallaaromatic species have quite large absolute values, as is the case with the parent aromatic hydrocarbon systems (Figure 5). Although the isolated metallaaro-

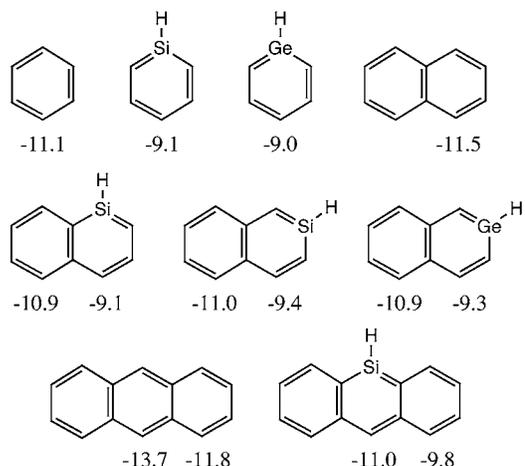
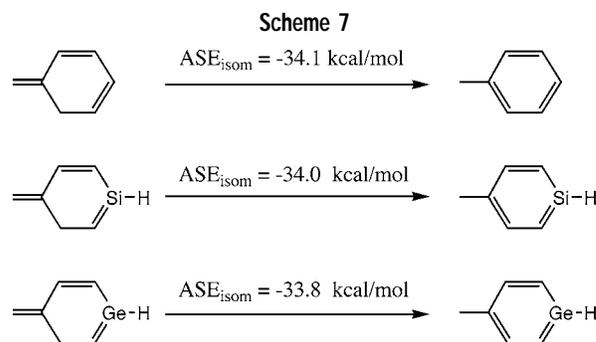


FIGURE 5. NICS(1) values (ppm) for heavy aromatic systems calculated at the B3LYP/6-311G(d) (6-311G(3d)) on Si and Ge//B3LYP/6-31G(d) level.



omatics **11**–**16** showed high reactivity toward a variety of addition reactions across their metal–carbon double bonds, it should be noted that calculated NICS values of all parent metallaaromatic species indicate their considerably high aromaticity.

Aromatic Stabilization Energies (ASEs). This apparent contradiction can be most likely interpreted in terms of the highly exothermic addition reactions of $\text{M}=\text{C}$ double bonds, which might not be suppressed by the aromatic stabilization energies (ASEs) for the metallaaromatic species containing a heavier group 14 element. For example, the ASEs of benzene, silabenzene, and germabenzene were estimated by quantitative energetic evaluation using the DFT-computed isodesmic isomerization energies of nonaromatic polyenes into the methyl-substituted aromatic isomers at the B3LYP/6-311+G(d,p)//Opt level (Scheme 7).⁴²

Since this method is based on the introduction of a methyl group, which has little effect on arene aromaticity and the isomerization reactions involving highly similar structures, the evaluations deduced here are self-consistent.⁴² As a result, the ASEs of silabenzene and germabenzene systems (34.0 and 33.8 kcal/mol) are found to be similar to that of the parent benzene system (34.1 kcal/mol). On the other hand, theoretical calculations (B3LYP/6-311+G(d,p)) revealed that the $\text{Si}=\text{C}$ or $\text{Ge}=\text{C}$ double bonds are inherently more reactive than the $\text{C}=\text{C}$ double bond, and the addition of water to $\text{H}_2\text{M}=\text{CH}_2$ [$\Delta H = -64.3$ ($\text{M} = \text{Si}$) and -48.0 ($\text{M} = \text{Ge}$) kcal/mol] is found to be

considerably more exothermic than that of ethylene ($\Delta H = -7.1$ kcal/mol).

Conclusion and Outlook

We have succeeded in the synthesis and isolation of the first examples of stable neutral metallaaromatic compounds of heavier group 14 elements (*heavy aromatics*) by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt). With stable examples of *heavy aromatics* in hand, we could demonstrate experimentally their planarity and other structural features indicating the delocalization of π -electrons in their metallaaromatic rings. These experimental results were in good agreement with those obtained by theoretical calculations. The *heavy aromatics* synthesized here were allowed to react with various reagents showing 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 were synthesized by the ligand-exchange reactions of Tbt-substituted germabenzene with $M'(\text{CH}_3\text{CN})_3(\text{CO})_3$ ($M' = \text{Cr}, \text{Mo}, \text{and W}$), showing the aromatic character of a germabenzene from the standpoint of its chemical reactivity. In addition, the aromaticity of *heavy aromatics* was evaluated by theoretical calculations, and the large negative NICS(1) values and ASE values strongly support the ring current effects and aromatic stabilization of *heavy aromatics*.

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

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