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Accounts

The Chemistry of Germanium-Containing Heavy Ketones[1]

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The recent applications of an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt in this article), to the kinetic stabilization of a series of doubly bonded compounds between germanium and heavier chalcogen atoms (we coin the expression "germanium-containing heavy ketones" for this family of heavier congeners of germanone) are described. Combination of a Tbt group with some other bulky aromatic or alkyl substituent enabled us to synthesize the novel germanium-containing double-bond species [Tbt(R)Ge=X; R = 2,4,6-triisopropylphenyl (Tip) or bis(trimethylsilyl)methyl (Dis)] such as germanethiones (X = S), germaneselones (X = Se), and germanetellones (X = Te) as stable crystalline compounds, while the germanone [Tbt(Tip)Ge=O], the most reactive species among the germanium-containing heavy ketones, was found to be very difficult to isolate and was evidenced only by the trapping reactions. The X-ray crystallographic analysis of the isolated germanium-containing heavy ketones revealed a completely trigonal planar geometry around their germachalcogenocarbonyl units and their ideally doubly bonded character, which was also confirmed by their spectroscopic data.

1 Double-Bond Species of Heavier Main-Group Elements

It was commonly accepted for many years that compounds having double bonds between heavier main-group elements would not be as stable as the second-row element compounds. Such a view is sometimes referred to as the "classical double-bond rule".[2] Due to many unsuccessful attempts to synthesize such species and to the assumptions of theoreticians, this field was not developed until the 1970s.

In the 1960s, transient molecules with double bonds between the heavier group 14 and 15 elements were detected spectroscopically or implicated from trapping experiments. The breakthrough in this field was the isolation in 1978 of the first stable compound with P=C[3] and in 1981 of some stable compounds with P=P,[4] Si=C,[5] and Si=Si[6] double bonds. Researchers understood from these successful syntheses that oligomerization would be thwarted if sufficiently large ligands were utilized.

In the case of germanium, since the isolation of digermenes (germanium–germanium double-bond compounds) by Lappert[7] and Masamune,[8] many studies have been performed on stable compounds of the germanium double-bond species. When we started the study on germanium–chalcogen double-bond species, several kinds of germanium-containing unsaturated species such as Ge=C, Ge=Ge, Ge=N, Ge=P, and Ge=S double-bond compounds have already been isolated by kinetic stabilization or thermodynamic stabilization.[9]

1.1 Germanium–Chalcogen Double-Bond Species.[9,10]

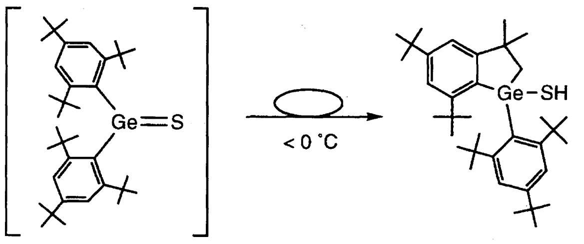
The chemistry of germanone and germanethione has been essentially that of elusive reaction intermediates. Early studies described thermal generation of RR′Ge=X species by various β-eliminations of linear germoxanes or germathianes, cycloreversions of small-ring germacycles, and oxygenation or sulfurization reactions of germylenes.[11] A survey of the more recent results shows that only two compounds with an intramolecular base stabilized Ge–S double bond have appeared in the literature, but no germanone has been isolated. On the other hand, very little has been known about the chemistry of germaneselones and germanetellones except for terminal chalcogenido complexes thermodynamically stabilized with a special nitrogen-containing ligand (vide infra).

(1) Transient Germanium–Chalcogen Double-Bond Species. There are many reports on the transient germanethiones and germanones; the main preparative methods of these are reactions of transient germylenes with chalcogen sources or cycloreversion of small-ring compounds containing germanium and the corresponding chalcogen atom.[9]

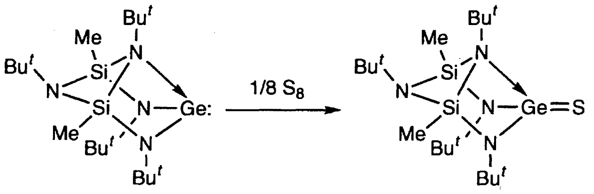
Two of those reports are concerned with attempts of the synthesis of kinetically stabilized germanethiones, using relatively bulky 2,4,6-tri-*t*-butylphenyl[12] and mesityl groups.[13] However, their isolation was unsuccessful because they underwent intramolecular cyclization (Scheme 1) or dimerization. Similarly, the intermediacy of dimesitylgermaneselone was proposed in the thermolysis of selenadigermirane, which underwent dimerization to give diselenadigermetane.[13] This is the only example of a transient germaneselone.

(2) Stable Germanium–Chalcogen Double-Bond Species. There have been only two examples of Ge–S double-bond compounds and one each for Ge–Se and Ge–Te double-bond compounds, but all of them are stabilized by the intramolecular coordination of a nitrogen ligand to the germanium center.

In 1989, Veith and his co-workers reported the synthesis of a base-stabilized Ge–S double-bond species **1** (Scheme 2). The X-ray structural analysis[14] shows that the sum of the bond angles around Ge atom was 355°, which indicates the geometry for the Ge atom can be described as distorted tetrahedral, or better still as trigonal planar with an additional bond (N→Ge). The Ge–S bond distance of 2.063(3) Å was about 0.2 Å shorter than the value for a Ge–S single bond. The ^{1}H NMR showed three signals assigned to non-equivalent *t*-butyl, which also indicate this coordination of the nitrogen atom.



Scheme 1.



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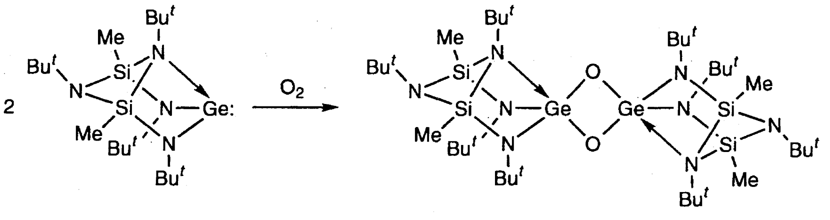
Scheme 2.

The synthesis of a germanone bearing the same substituent was also studied by Veith et al. (Scheme 3),[14a] but the trial was unsuccessful, since it resulted in the formation of **2**, a dimer of the corresponding germanium-oxygen double-bond species. This is most likely due to the high polarity of the Ge=O bond[15] in spite of the thermodynamical stabilization.

Meanwhile, Parkin and his co-workers have also reported the synthesis of a series of terminal chalcogenido complexes of germanium **3**, **4**, and **5** (Scheme 4).[16] X-Ray structural analyses of **3**, **4**, and **5** revealed that they have unique germachalcogenourea structures stabilized by the intramolecular coordination of nitrogen atoms. The central Ge–X (X = S, Se, Te) bond of **3**, **4**, and **5** should be represented by a resonance structure, Ge$^+$–X$^-$ ↔ Ge=X, because their bond lengths are somewhat elongated compared to the sums of theoretically predicted double-bond covalent radii.

1.2 Synthetic Strategies for Stable Germanium-Containing Heavy Ketones. With these situations in mind, we started some investigations on the systematic synthesis of stable germanium–chalcogen double-bond species (germanium-containing heavy ketones) to elucidate their intrinsic bond character.

For the stabilization of such highly reactive compounds, there are generally two conceivable methodologies, i.e., thermodynamic and kinetic stabilization. The former is defined as stabilization of the ground state by the mesomeric effect of neighboring heteroatoms, attachment of an electron-do-



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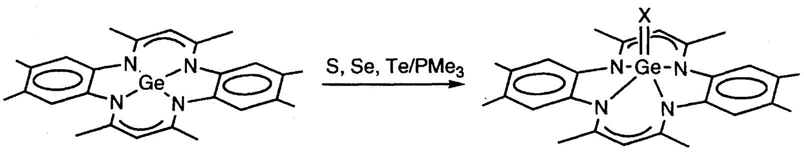
Scheme 3.



3: X = S
4: X = Se
5: X = Te

Scheme 4.

nating or -withdrawing substituents, or complexation with transition metals. The latter is stabilization resulting from raising the transition state of the reactions the reactive species may undergo (e.g., oligomerization or reactions with other reagents such as oxygen and water) by taking advantage of steric protection with bulky groups.

Although thermodynamic stabilization is very useful, it considerably perturbs the electronic structure of the ground state, changes the properties of the species, and hence is not suitable to study the intrinsic character of the highly reactive species. For instance, compounds **3**, **4**, and **5** are thermodynamically stabilized by the intramolecular interaction of the lone pair of nitrogen atoms with the Ge=X double bond, their germanium–chalcogen bonds being elongated as compared with the values theoretically predicted.

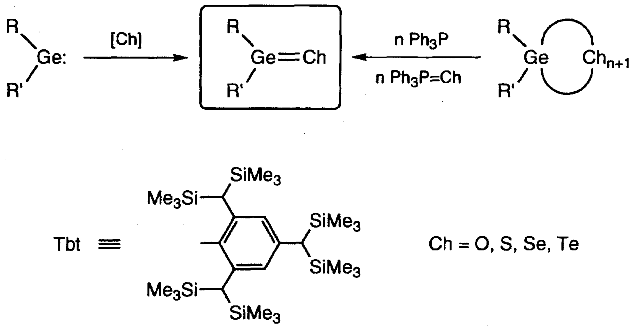
Kinetic stabilization is obviously superior to thermodynamic stabilization since the former causes less perturbation to the intrinsic nature of the species. The drawback of this method is that there is some possibility of changing the reactivity owing to the steric hindrance. Considering that the most serious problem for the isolation of the highly reactive species is self-polymerization in many cases, one must choose the steric protection groups which are large enough to prevent the intermolecular reaction with itself but small enough to be able to examine the reactivities.

The stabilization of germanium-containing heavy ketones seems to require rather large steric protection groups because these groups can be introduced only on the germanium atom, in contrast to other doubly bonded germanium species so far isolated, such as digermenes ($\mathrm{R_2Ge{=}GeR_2}$)[9,17] or germaphosphenes ($\mathrm{R_2Ge{=}PR}$).[18] Although 2,4,6-tri-*t*-butylphenyl group is known to be a very useful kinetic protection group for highly reactive species such as thioaldehyde[19] or selenoaldehyde,[20] it proved to be useless for germanethione as mentioned above (Scheme 1).[12]

We have chosen 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group (denoted as Tbt) as a steric protection group for the synthesis of germanium-containing heavy ketones because it is expected to be large enough to prevent the self oligomerization but to have a space around the germanium atom wide enough to react with small molecules in contrast to 2,4,6-tri-*t*-butylphenyl group. Moreover, it has been recently found that the Tbt group is a useful steric protection group for the kinetic stabilization of a variety of highly reactive chemical species containing heavier main group elements.[21]

A variety of preparation methods are known for transient germanium–chalcogen double-bond species; some of them seemed to be also useful for the synthesis of kinetically stabilized systems. Indeed, the reaction of a germylene with an appropriate chalcogen source was found to be one of the most versatile and general methods for the synthesis of stable germanium-containing heavy ketones (Scheme 5).

Furthermore, we have developed a new and efficient synthetic method for stable germanethiones and germaneselones, i.e. germanium-sulfur and germanium–selenium double-bond compounds, via dechalcogenation reactions of the corresponding overcrowded germanium-containing cyclic polychalcogenides with a phosphine reagent (Scheme 5). Although this method is much superior to that via germylenes in view of the easy separation and isolation of the heavy ketones by simple filtration of the phosphine chalcogenides formed, it cannot be applicable to the synthesis of germanones and germanetellones due to the lack of stable precursors, i.e. cyclic polyoxides and polytellurides.



Scheme 5.

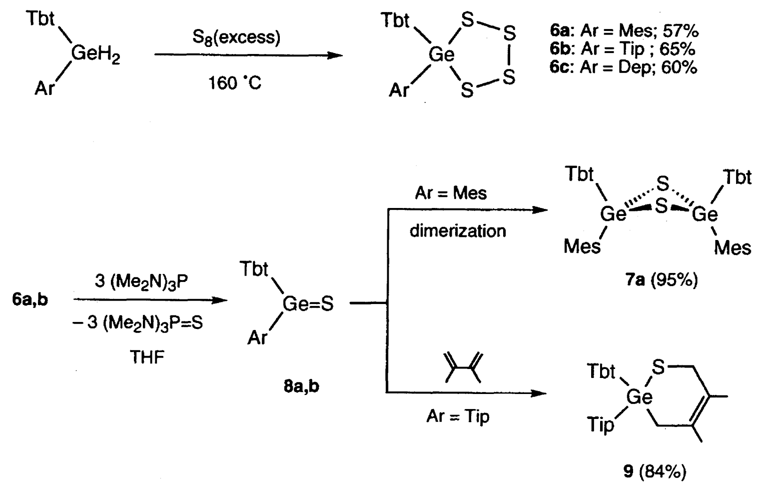
By taking advantage of these two synthetic strategies we have succeeded in the synthesis and isolation of a series of stable germanium-containing heavy ketones bearing a Tbt group.

2. Stable Diaryl-Substituted Germanethione and Germaneselone

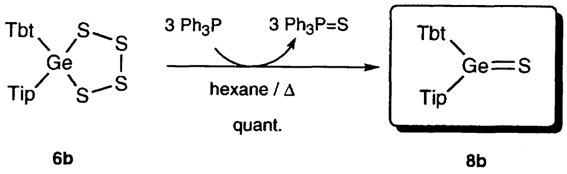
2.1. Synthesis of a Stable Diarylgermanethione. (1) Syntheses of Overcrowded Tetrathiagermolanes. Previously, we have described the synthesis of novel cyclic polysulfides 1,2,3,4,5-tetrathiagermolanes $\mathrm{Tbt(Mes)GeS_4}$ (**6a**; Mes = mesityl), $\mathrm{Tbt(Tip)GeS_4}$ **6b**, $\mathrm{Tbt(Dep)GeS_4}$ (**6c**; Dep = 2,6-diethylphenyl) bearing two bulky aryl groups.[22,23] In expectation of synthesizing germanethiones, these cyclic polysulfides were desulfurized with 3 molar amounts of hexamethylphosphorous triamide. But the desulfurization of tetrathiolane **6a** resulted in the formation of 1,3,2,4-dithiadigermetane **7a**, a dimer of germanethione Tbt(Mes)Ge=S **8a**, suggesting the combination of Tbt and Mes groups is not sufficient to stabilize the reactive Ge=S double bond of **8a** (Scheme 6).[24] By contrast, desulfurization of **6b** bearing a bulkier Tip group gave germanethione Tbt(Tip)Ge=S **8b**, no dimer corresponding to **7a** being formed. The generation of germanethione **8b** was confirmed by a trapping reaction with 2,3-dimethyl-1,3-butadiene (Scheme 8).[25] The high yield of the [2+4] cycloaddition product **9** prompted us to examine the isolation of germanethione **8b**.

(2) Isolation of a Stable Diarylgermanethione.[25] Since germanethione Tbt(Tip)Ge=S **8b** was considered to be highly reactive toward water and oxygen, tetrathiagermolane **6b** was desulfurized with 3 molar amounts of triphenylphosphine in hexane under argon atmosphere in a glovebox. Germanethione **8b** was obtained as orange-yellow crystals quantitatively after filtration of the triphenylphosphine sulfide formed (Scheme 7). It should be noted that **8b** is the first kinetically stabilized isolable germanethione.[25]

Germanethione **8b** is very sensitive toward moisture but



Scheme 6.

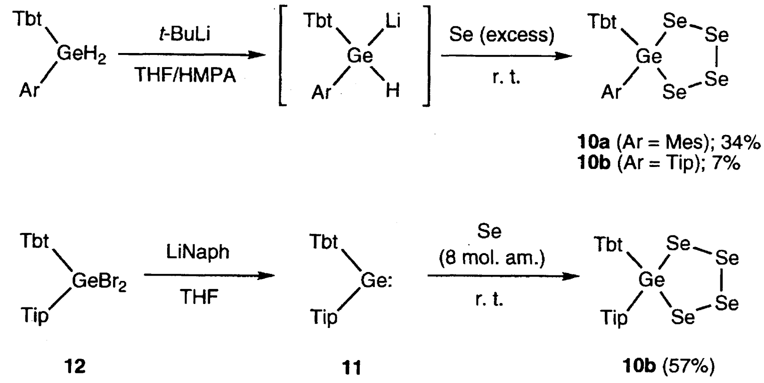


Scheme 7.

thermally quite stable; **8b** melted at 163—165 °C without decomposition, and no change was observed even after heating of its hexane solution at 160 °C for 3 d in a sealed tube. A hexane solution of **8b** was orange-yellow, showing an absorption maximum at 450 nm which is attributed to n–π^* transition of the Ge=S double bond. On the other hand, no change in color was observed throughout the desulfurization of less hindered tetrathiagermolane **6a** leading to **7a**, most probably due to the extremely fast dimerization of **8a**. Similar desulfurization of tetrathiagermolane **6c** bearing a Dep group, medium in size between Mes and Tip, also gave a dimer of the corresponding germanethione Tbt(Dep)Ge=S **8c**. At the beginning of the reaction, however, the electronic spectrum of the hexane solution showed the appearance of a transient absorption at 450 nm attributable to intermediary germanethione **8c**. These results can be reasonably interpreted in terms of the bulkiness of protection groups on the germanium atom, indicating that the combination of Tbt and Tip groups is necessary to isolate a germanethione.

2.2. Synthesis of a Stable Diarylgermaneselone. The successful isolation and characterization of the first stable germanethione **8b** by taking advantage of the kinetic stabilization using Tbt group prompted us to extend this chemistry to its selenium analogue, i.e., germaneselone. Although Parkin and his co-workers have recently isolated germaselenourea **4** stabilized by intramolecular coordination of nitrogen atoms onto Ge atom,[16] there had been no report on the synthesis and isolation of genuine germaneselones until our project started. Since overcrowded cyclic polyselenides $RR'Ge(Se)_n$ were thought to be good precursors of kinetically stabilized germaneselones as in the case of germanethione **8b**, the synthesis of cyclic polyselenides bearing bulky aryl groups on the germanium was first examined.

(1) Synthesis of Cyclic Polyselenides Containing Germanium. In contrast to the extensive studies on transition metal polyselenido complexes,[26] there has been no report on germanium-containing cyclic polyselenides such as $RR'Ge(Se)_n$ until we reported the first synthesis of stable tetraselenagermolane **10a** via the reaction of germanide anion with elemental selenium (Scheme 8).[22,27] In contrast to the case of **10a**, the more sterically congested germyl anion bearing Tbt and Tip groups reacted with elemental selenium to afford polyselenide **10b** only in 7% yield, probably owing to the relatively high stability of the germylanion and the insolubility of elemental selenium (Scheme 8).[27] For the efficient



Scheme 8.

synthesis of **10b**, therefore, it was necessary to develop a more reactive and useful germanium reagent.

On the other hand, we have already described the generation of the first stable diarylgermylene Tbt(Tip)Ge: **11** by the reaction of GeI_2 with TbtLi and TipLi though in a very low yield.[28] We further found that **11** can be prepared more effectively by the reductive debromination of the corresponding dibromogermane **12** with lithium naphthalenide. The overcrowded diarylgermylene **11** thus generated was allowed to react with an excess amount of elemental selenium to give tetraselenagermolane **10b** in 57% yield (Scheme 8).

(2) Synthesis of a Stable Diarylgermaneselones.[29] Deselenation of **10a** with triphenylphosphine in hexane at 90 °C in a sealed tube gave 1,3,2,4-diselenadigermetane **13**, a dimer of the corresponding germaneselone Tbt(Mes)Ge=Se, even in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene, showing the high reactivity of a germaneselone and the insufficient steric protection by the combination of Tbt and Mes groups (Scheme 9).[30] X-Ray crystallographic analysis of **13** revealed the *cis*-conformation of its diselenadigermetane ring, which releases the steric hindrance effectively as also observed in 1,3,2,4-dithiadigermetane **7a**.[24]

By contrast, deselenation of **10b** with 3 molar amounts of triphenylphosphine in refluxing hexane under argon resulted in the quantitative isolation of the first stable germaneselone **14** as red crystals (Scheme 9).[29] Dimerization of **14** was not observed even in refluxing hexane, in spite of the bond distance of Ge=Se being longer than that of Ge=S. Germaneselone **14** was extremely sensitive to moisture but thermally quite stable under inert atmosphere (**14**; mp 191—194 °C). One can see that the combination of Tbt and Tip groups is effective enough to stabilize the reactive germaselenocarbonyl unit of **14**, as in the case of germanethione **8b**.

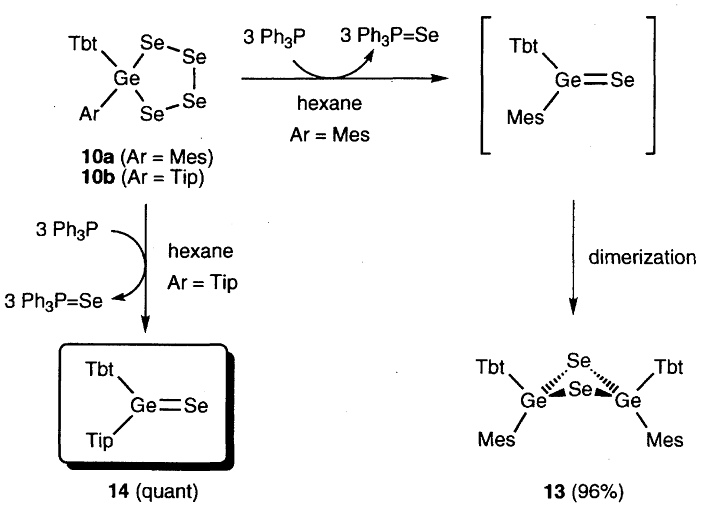
3. Stable Diaryl-Substituted Germanetellone

In contrast to the extensive studies on thiocarbonyl and selenocarbonyl compounds,[31] the chemistry of tellurocarbonyl compounds has been much less studied owing to their instabilities.[31b,32] The chemistry of a germanetellone, the germanium analogue of a tellone, has also been very little explored. Theoretical calculations for $H_2Ge{=}Te$ at B3LYP/TZ(d,p) level have predicted that it has even smaller σ (59.1 kcal mol^{-1}) and π (30.3 kcal mol^{-1}) bond energies than those of the corresponding germanethione and germaneselone, but exists at an energy minimum, suggesting the possibility of its isolation.[33]

Parkin et al. have already reported the synthesis and crystallographic structure of germatellurourea **5**, which is stabilized by intramolecular coordination of nitrogen atoms onto Ge atoms.[16] This is the only report on the chemistry of germanium–tellurium double-bond species so far, and no stable example of germanetellone has been described yet. A study of germanetellone is significant not only to clarify its character by itself but also to elucidate the properties of germanium-containing heavy ketones systematically.

3.1. Synthesis by the Telluration of an Overcrowded Germylene Generated by the Reduction of a Diaryldibromogermane.[34,35] In view of the successful isolation of stable germanethione **8b** and germaneselone **14** (see Section 2.2), an overcrowded cyclic polytelluride was expected to be a useful precursor for a germanetellone, if one was available. Since diarylgermylene **11** would be an appropriate germanium source for the preparation of cyclic polytelluride as in the case of the reaction with selenium, an excess amount of elemental tellurium was added to the germylene **11** generated in situ from dibromogermane **12** and lithium naphthalenide. However, no isolable cyclic polytelluride was obtained probably owing to the instability of polytellurides.

Next, diarylgermylene **11** was allowed to react with equimolar amount of elemental tellurium in THF to synthesize a germanetellone directly. The color of the solution gradually changed over 10 h from blue (λ_{max} = 581 nm) due to **11** to green (λ_{max} = 623 nm), which is indicative of the generation of a germanetellone **15**, because of the red shift in the absorption maximum compared to germaneselone **14** (λ_{max} = 510 nm in THF).[29] The addition of mesitonitrile oxide as a trapping reagent to this green solution resulted in the formation of oxatellurazagermole **16**, the [3+2] cyclo-



Scheme 9.

adduct of germanetellone Tbt(Tip)Ge=Te **15**, in 37% yield (Scheme 10).[34,35]

This is the first generation and direct observation of a kinetically stabilized germanetellone. The conversion of **12** to germanetellone **15** was, however, considered to be insufficient, judging from the low yield of **16**, which was most likely due to the insolubility of elemental tellurium. When tributylphosphine telluride[36] was added as a soluble tellurium source, germanetellone **15** was formed immediately as confirmed by its electronic spectrum. Trapping of **15** with mesitonitrile oxide, however, gave the corresponding [3+2] cycloadduct **16** in a lower yield (27%) owing to the instability of **15** in the presence of tributylphosphine. This was indicated by the precipitation of tellurium as black powder immediately after the addition of mesitonitrile oxide.

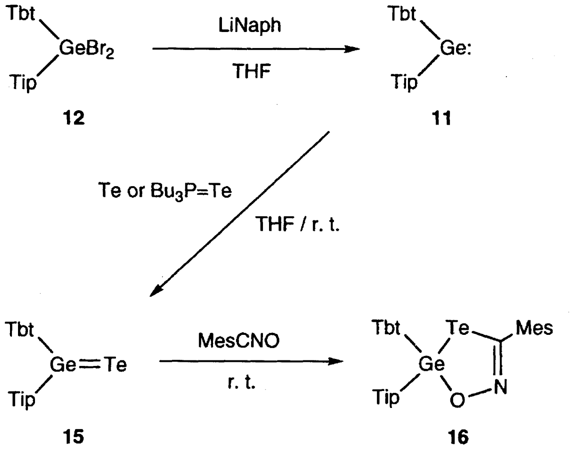
These results suggest the generation of germanetellone **15** which is stable in solution at room temperature, but an alternative synthetic method for **15** was considered to be necessary for its isolation, because the final solution of **15** obtained by the above-mentioned reaction should contain inevitable by-products such as naphthalene, tributylphosphine, and lithium bromide.

3.2. Synthesis by the Telluration of an Overcrowded Germylene Generated by the Thermal Retrocycloaddition of a Germirene. (1) Generation of a Germylene by the Thermolysis of a Germirene. It has been reported that germylenes and other divalent species of group 14 elements (silylenes and stannylenes) can be generated from strained small ring compounds.[37] Among them the most fascinating groups of compounds are silicon, germanium and tin analogues of cyclopropenes, and there have been a number of reports on the generation of silylenes by thermolysis or photolysis of silirenes (silacyclopropenes).[38] By contrast, no cycloreversion of a germirene into a germylene is known so far, although several stable germirenes have been reported.[39,40]

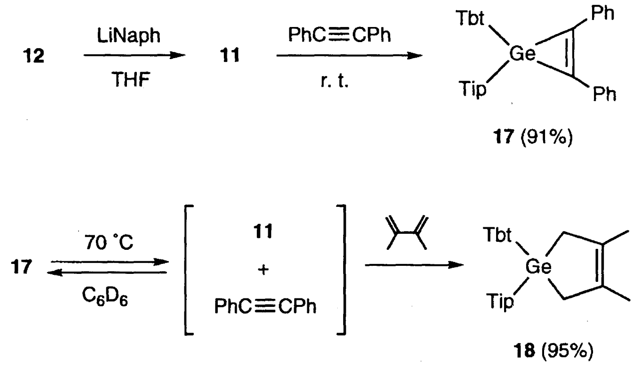
On the other hand, recent theoretical studies on the thermodynamics of the reactions: $MH_2 + HC{\equiv}CH \rightarrow c\text{-}[H_2MC_2H_2]$ ($M = C$, Si, Ge, Sn)[41] showed that the formation of cyclopropene from CH_2 and acetylene is the most highly exothermic reaction and the reaction exothermicity steadily decreases as one proceeds from $M = C$ to Sn. This trend is due to both the decrease in stability of metallacyclopropenes and the increase in that of divalent species MH_2,[42] and experimentally supported by the properties of the first stannacyclopropene derivative, 8,8-bis[bis(trimethylsilyl)methyl]-2,2,6,6-tetramethyl-4-thia-8-stannabicyclo[5.1.0]oct-1(7)ene, which was observed to be in thermal equilibrium in solution with its parent stannylene and acetylene fragments, with the latter being favored at temperatures above −16 °C.[43] These results suggest the possibility of the thermal generation of germylenes from the corresponding germirenes.

At first, the synthesis of a germirene suitable as a precursor of an overcrowded diarylgermylene was examined. Germylene **11** generated from dibromogermane **12** and lithium naphthalenide was allowed to react with diphenylacetylene to afford germirene **17** in good yield as white crystals (Scheme 11).[44] This germirene is kinetically stable owing to the bulky groups, in contrast to the previously reported germirenes[39] which are known to be hydrolyzed rapidly in air. Since the thermal lability of germirene **17** was indicated by decomposition at 118—120 °C in the solid state, a benzene-d_6 solution of germirene **17** and 2,3-dimethyl-1,3-butadiene in an NMR tube was heated while the solution was being monitored by ^{1}H NMR. Only a slight change was observed at 50 °C, but heating up to 70 °C for 9 h gave germacyclopentene **18** (95%) and diphenylacetylene (100%) with complete consumption of the starting material (Scheme 11). This cheletropic reaction is reversible; in the absence of the trapping reagent, the colorless solution at room temperature turns pale blue at 50 °C showing the regeneration of germylene **11**, and becomes colorless again on cooling. These results indicate that germirene **17** is a useful precursor for diarylgermylene Tbt(Tip)Ge: **11** under neutral conditions without forming any reactive byproducts.[44]

(2) Synthesis and Isolation of a Stable Germanetellone.[34,35] For the synthesis of germanetellone **15**, germirene **17** and equimolar amount of elemental tellurium were allowed to react in benzene-d_6 at 80 °C, and the reaction was monitored by ^{1}H NMR. Heating for 9 d led to the appearance of new signals along with those of diphenylacetylene at the expense of those assigned to **17**, and the solution turned green. The sealed tube was opened in a glovebox filled with



Scheme 10.



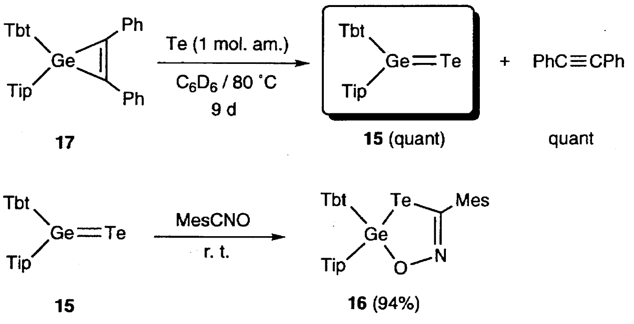
Scheme 11.

argon and mesitonitrile oxide was added to the solution to afford [3+2] cycloadduct **16** in 94% yield (Scheme 12).[34,35] These results clearly showed the almost quantitative generation of germanetellone **15**. Removal of the solvent from the green solution without the addition of mesitonitrile oxide gave germanetellone **15** quantitatively as green crystals (Scheme 12).[34,35] This is the first isolation of a kinetically stabilized germanetellone. Germanetellone **15** was sensitive toward moisture, especially in solution, but thermally quite stable; **15** melted at 205—210 °C without decomposition.

4. Crystal Structures of Diaryl-Substituted Germanium-Containing Heavy Ketones

The molecular structures of diaryl-substituted germanium-containing heavy ketones, Tbt(Tip)Ge=X [**8b** (X = S),[25] **14** (X = Se),[29] and **15** (X = Te)[34,35]], were all determined by X-ray crystallographic analysis to show that they are completely isomorphous and their germachalcogenocarbonyl units are effectively protected by the two bulky aryl groups (Figs. 1a—1c).

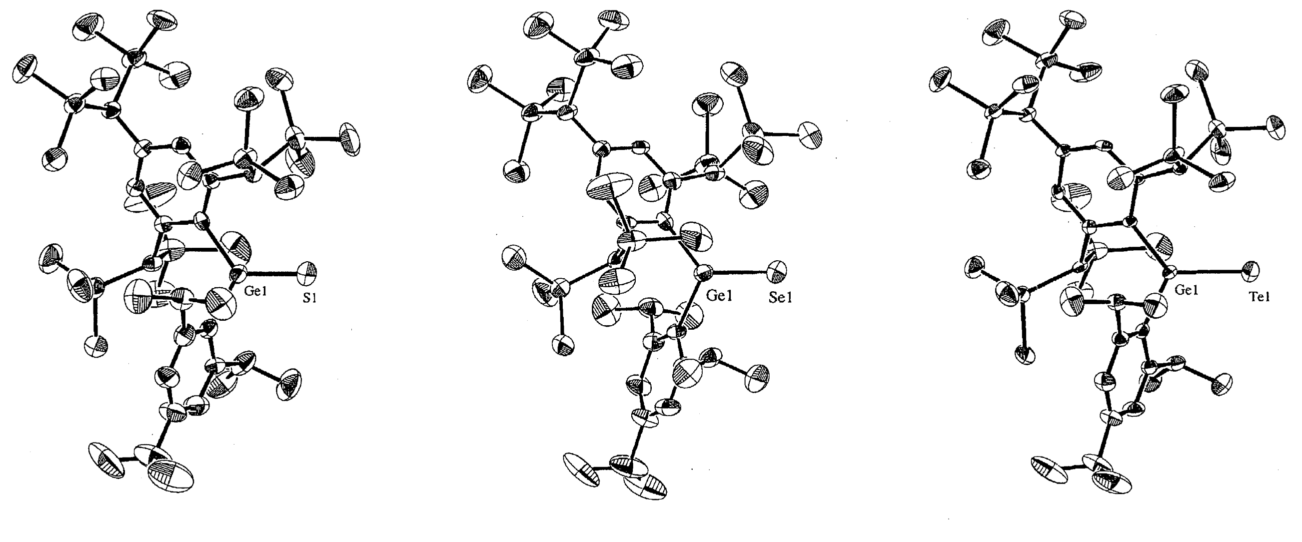
Their packing diagrams indicate that no intermolecular interaction exists even in the solid state; the shortest intermolecular distances between the germanium and chalcogen atoms are 5.91 Å for **8b**, 5.69 Å for **14**, and 5.49 Å for **15**, which are much longer than the sums of van der Waals radii of germanium and the corresponding chalcogen atoms (3.90 Å for Ge···S, 4.00 Å for Ge···Se, and 4.14 Å for Ge···Te). The intramolecular germanium–chalcogen distances in **8b** and **14** are 2.049(3) and 2.180(2) Å, respectively, both being 9% shorter than the typical Ge–S and Ge–Se single bond lengths.[45] It is also notable that even the Ge–Te bond length in **15** [2.398(1) Å] is 8% shorter than that reported for typical Ge–Te single bonds.[45] The geometries around the germanium atoms of **8b**, **14**, and **15** are also revealed to be completely trigonal planar, the sums of angles being 359.6° for **8b**, 359.3° for **14**, and 359.5° for **15**. All the structural features of **8b**, **14**, and **15** here obtained are in good agreement with those obtained for the parent molecules, $H_2Ge{=}X$ (X = S, Se, Te) by theoretical calculations (vide infra).[22]



Scheme 12.

These properties clearly show that each of the germanium-containing heavy ketones **8b**, **14**, and **15** has a genuine double-bond character, whereas the Ge–S bond length of the base-stabilized Veith's germathiourea **1** [2.063(3) Å][14] and the germanium-chalcogen distances in the Parkin's terminal germanium–chalcogenido complexes **3** [Ge–S; 2.100(2) Å], **4** [2.247(1) Å], and **5** [2.466(1) Å][16] are all much longer than the corresponding germanium–chalcogen bond lengths in **8b**, **14**, and **15**; these thermodynamically stabilized germachalcogenoureas are electronically perturbed by coordination of intramolecular nitrogen atoms.

The π-planes of the two aryl groups (Tbt and Tip) of **8b**, **14**, and **15** are arranged almost perpendicular to each other (the dihedral angle between them are 89° in all cases), and neither of them are coplanar with the germachalcogenocarbonyl π plane due to their steric bulkiness, the dihedral angles between these two aromatic π-planes and the Ge=X π-plane being 39° (Tbt) and 70° (Tip) for **8b**, 38° (Tbt) and 72° (Tip) for **14**, and 39° (Tbt) and 71° (Tip) for **15**.



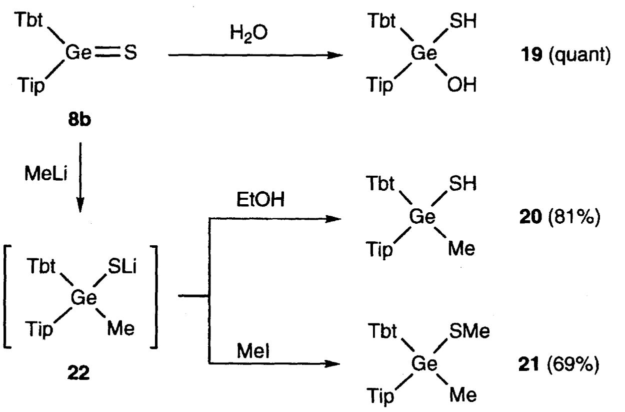
(a) (b) (c)

Fig. 1. ORTEP drawings of the diaryl-substituted germanium-containing heavy ketones (30% probability thermal ellipsoid plot). (a) Tbt(Tip)Ge=S (**8b**), (b) Tbt(Tip)Ge=Se (**14**), and (c) Tbt(Tip)Ge=Te (**15**).

5. Reactions of Diaryl-Substituted Germanium-Containing Heavy Ketones

(1) Reactions of Diarylgermanethione 8b. Germanethione **8b** was allowed to react with water to give hydroxy(mercapto)germane **19** (Scheme 13). Exposure of **8b** to air also afforded **19** quantitatively, suggesting the high reactivity of the Ge=S bond to water. Addition of methyllithium to **8b**, followed by quenching with ethanol and methyl iodide, resulted in the formation of **20** and **21**, respectively, indicating the polarization of the Ge=S bond like $Ge^{\delta+}{=}S^{\delta-}$ and the initial formation of germanethiolate ion **22** (Scheme 13).

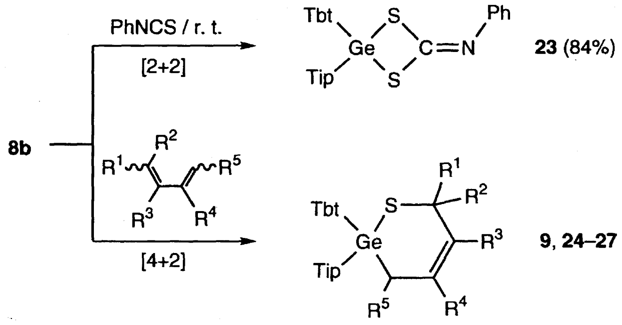
These results are in contrast to those observed in the reactions of thiocarbonyl compounds with alkyllithiums, in which thiophilic reactions also take place together with normal carbophilic addition reactions.[46]



Scheme 13.

The double-bond character of the Ge=S unit in **8b** manifested itself in the cycloaddition reactions with various 2π and 4π systems (Scheme 14). For example, phenyl isothiocyanate reacted smoothly with **8b** at room temperature to afford [2+2] cycloadduct **23** in 84%.[24] This is the first example of imino-substituted 1,3,2-dithiagermetane.[47] 1,3-Dienes also reacted with germanethione **8b** to give [4+2] cycloadducts **9** and **24**—**27** in moderate to good yields, except in the case of 1,4-disubstituted dienes (Table 1).

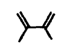
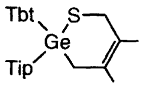
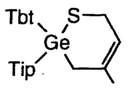
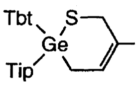
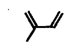
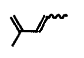
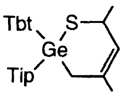
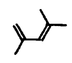
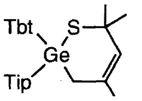
There has been no report on any Diels–Alder reaction of germanethiones. Ando and his co-workers reported that dimesitylgermanethione underwent dimerization to give 1,3,2,4-dithiadigermetane with no formation of [4+2] adduct even when the germanethione was generated in the presence of 2,3-dimethyl-1,3-butadiene.[13] The very fast dimerization



Scheme 14.

Table 1. [4+2] Cycloaddition Reactions of Germanethione **8b** with 1,3-Dienes[a)]

$$\mathbf{8b}\ \xrightarrow[\text{solvent}/\Delta]{\text{1,3-diene}}\ [4+2]\text{cycloadduct}$$

Entry	Diene (mol. am.)	Temp/°C	Product (yield)
1	 (10)	90	 **9** (84%)
2	(10)	90	 **24** (70%) +  **25** (8%)
3	 (10)	150	(36%) + (36%)
4	(15)	90	(76%) + (8%)
5	 (20)	50	 **26** (89%)
6	 (20)	90	 **27** (50%)
7	 (5)	r. t.—150	No reaction
8	 (10)	r. t.—150	No reaction

a) Reactions were carried out in hexane except for Entry 4 where the solvent was THF.

was also observed in the case of Tbt(Mes)Ge=S **8a** even in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (vide supra).[24] It was not until thermally stable germanethione **8b** was synthesized that the dienophilic character of a germanethione was demonstrated.[25]

Regiochemistry of the Diels–Alder reactions was examined using unsymmetrically substituted 1, 3-dienes (Entries 2—6). Reaction with isoprene at 90 °C gave two regioisomers **24** and **25** in the ratio of 9 : 1. Similar selectivity and reaction rate were observed also in THF (Entry 4). The observed regioselectivity is consistent with the frontier molecular orbital interpretation based on the PM3 calculation.[48] Regiochemistry observed here and its interpretation are similar to those already reported for the cycloaddition of thioaldehydes.[49]

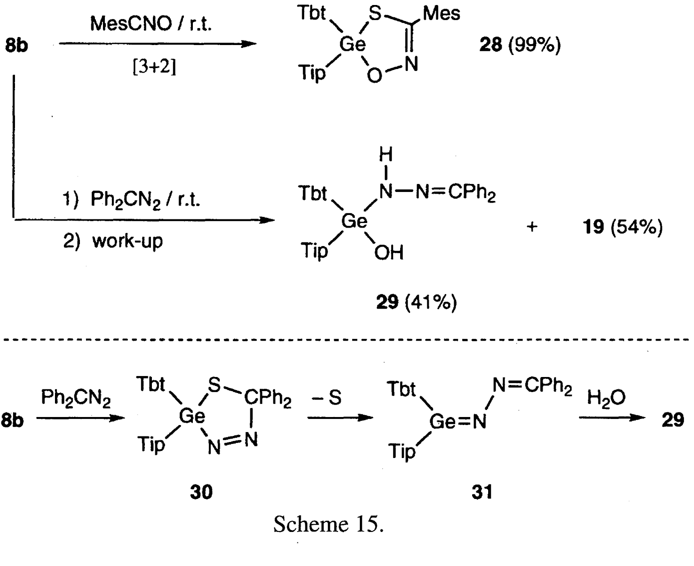
It is noteworthy that exclusive formation of single cycloadducts **26** and **27** were observed in the reactions with 2-methyl-1,3-pentadiene and 2,4-dimethyl-1,3-pentadiene, respectively (Entries 5 and 6). These high regioselectivities are explicable in terms of steric effect as well as the favorable orbital overlap. This interpretation is supported by the fact that the reaction with 2,4-hexadiene did not give a corresponding adduct (Entry 8). In Entry 3, the regioselectivity was lost when the reaction was carried out at 150 °C. Furthermore, heating of **24** in hexane at 150 °C afforded **24** and **25** in the ratio of 1 : 1. These results clearly show that retro Diels–Alder reaction proceeded at 150 °C. Examination of the CPK model indicates no difference between **24** and **25** in the steric interaction of the methyl group in the diene moiety with the two aryl groups on the Ge atom. When compound **25** was heated at 150 °C, the color of the solution changed from colorless to orange-yellow suggesting the regeneration of germanethione **8b**; in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene, regenerated **8b** was effectively trapped to give the corresponding cycloadduct **9** in high yield. These results also clearly show the occurrence of the retro Diels–Alder reaction.

Reactions of germanethione **8b** with 1,3-dipolar reagents were also examined. In the reaction of **8b** with mesitonitrile oxide, oxathiazagermole **28** was obtained in 99% yield (Scheme 15). Reaction of **8b** with diphenyldiazomethane afforded compound **29** along with hydroxy(mercapto)germane **19**, which is most likely derived from unreacted **8b**. A plausible mechanism for the formation of **29** is shown in Scheme 15. Germanethione **8b** undergoes [3+2] addition to give an intermediary cycloadduct **30** at the initial step, but it may lose a sulfur atom leading to **31** which is eventually isolated as **29** by reaction with water during the workup procedure because of its high reactivity. Although dimerization of $Mes_2Ge=N-N=CR_2$ (CR_2 = fluorenylidene) has already been reported,[50] dimerization did not proceed in the case of **31** because of effective steric protection.

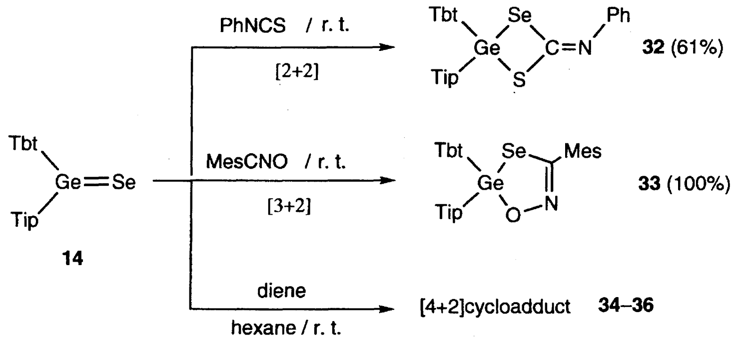
(2) Reactions of Diarylgermaneselone 14.[29] The double-bond character of the Ge=Se bond of **14** appeared also in its cycloaddition reactions (Scheme 16). Germaneselone **14** was allowed to react with phenyl isothiocyanate at room temperature to give imino-substituted thiaselenagermetane **32**, [2+2] adduct of **14**, in 61% yield. Reaction with mesitonitrile oxide afforded the corresponding [3+2] adduct **33** (100%). Diels–Alder reactions with dienes were also examined for **14** (Scheme 16 and Table 2). In Entry 1, **14** was allowed to react with 10 molar amounts of 2,3-dimethyl-1,3-butadiene to afford [4+2] cycloadduct **34** in low yield. Although this [4+2] cycloaddition reaction proceeded at room temperature very slowly, the use of a large excess of the diene (40 molar amounts) increased the yield up to 84% (Entry 2).

In the reaction with isoprene, the germaneselone gave two regioisomers **35** and **36** in 51 and 35% yields, respectively (Entry 3). Here, the more favorable regioisomer was the same as in the case of germanethione **8b**, and this regiochemistry was similar to that in the reported Diels–Alder reactions of selenoaldehydes.[51] It is noteworthy that the selectivity was lower than that observed for germanethione **8b**. The low selectivity is probably explicable in terms of the smaller activation energies in Diels–Alder and retro Diels–Alder reactions of germaneselone **14** than those of germanethione **8b**.

Heating of a hexane solution of **34** at 50 °C caused a change

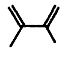
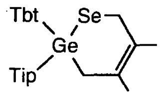
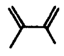
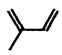
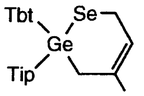
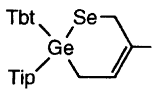


Scheme 15.

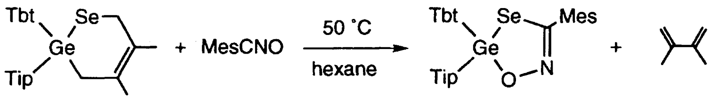


Scheme 16.

Table 2. [4+2] Cycloaddition Reactions of Germaneselone **14** with Dienes

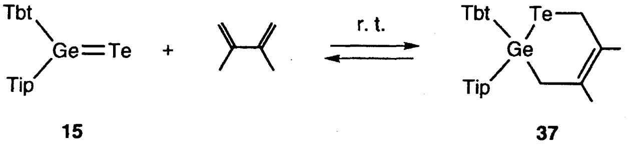
Entry	Diene (mol. am.)	Time/h	Temp	Products (yield)
1	 (10)	10	90 °C	 **34** (22%)
2	 (40)	2	90 °C	**34** (84%)
3	 (40)	10	r. t.	 +  **35** (51%) **36** (35%)

in color from colorless to red, indicating the occurrence of a retro Diels–Alder reaction into germaneselone **14** and 2,3-dimethyl-1,3-butadiene. The regeneration of germaneselone **14** was confirmed by a trapping reaction with mesitonitrile oxide to afford **33** in 90% yield (Scheme 17).



Scheme 17.

(3) Reactions of Diarylgermanetellone 15.[34,35] Although it was somewhat difficult to investigate the reactivity of the germanetellone **15** due to the relatively high instability of the reaction products as compared to the cases of germanethione **8b** and germaneselone **14**, the double-bond character of the Ge=Te bond of **15** was revealed in its cycloaddition reactions. The reaction of **15** with mesitonitrile oxide, already mentioned in Schemes 10 and 12, gave the corresponding [3+2] cycloadduct **16**, which was found to be exceptionally stable among the reaction products of **15**, in high yield. Germanetellone **15** underwent Diels–Alder reaction with a large excess of 2,3-dimethyl-1,3-butadiene, giving the [4+2] cycloadduct **37** in 70% yield, but the green color of **15** still remained after the addition of 50 molar amounts of the diene (Scheme 18). This is in sharp contrast to the reaction of germaneselone **14** where almost all of **14** was consumed in the presence of 40 molar amounts of dienes within 10 h at room temperature.



Scheme 18.

The cycloadduct **37** gradually underwent retro Diels–Alder reaction even at 20 °C in solution, as suggested by the change in color of the solution. The green color ($\lambda_{max} = 640$ nm) was observed in hexane immediately after heating to 30 °C (Scheme 18). These results show that **15** has a lower activation energy for both Diels–Alder and retro Diels–Alder reactions than those for germanethione **8b** and germaneselone **14**, owing to the lower germatellurocarbonyl LUMO.

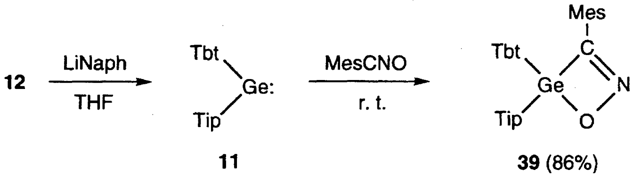
6. Kinetically Stabilized Diarylgermanone

Although germanium–oxygen double-bond species, i.e. germanones, have been postulated as reactive intermediates in many reactions, neither thermodynamically nor kinetically stabilized germanone has been isolated so far. As mentioned in the previous section, an approach to a thermodynamically stabilized germanone was unsuccessful and resulted in the formation of dioxadigermetane **2**, a dimer of the corresponding germanium–oxygen double-bond species, though germathiourea **1** bearing the same substituent was isolated as a monomer (vide supra).[26a] This lability is most likely due to the high polarity of the Ge=O bond, which has been predicted by ab initio calculations for dimethylgermanone.[15,52]

6.1. Generation and Reactions of a Kinetically Stabilized Diarylgermanone. The most straightforward approach to a germanone would be the reaction of germylene Tbt(Tip)Ge: **11** with an oxygen source such as that used for the formation of **2**.[14a] The oxidation of **11** must be performed under absolutely anhydrous conditions because of the expected extremely high reactivity of a germanone toward water. We first treated germylene **11** with dimethyl sulfoxide or nitrosobenzene, which was used as an oxygen source for germanones in the literature.[53] These reactions were unsuccessful, however, affording many unidentified products, and hence other reagents were attempted.

(1) Reaction of Germylene 11 with Mesitonitrile Oxide. Mesitonitrile oxide was chosen as an oxidizing reagent because it was expected to act not only as an oxygen source but also as a good trapping reagent for germanone Tbt(Tip)-Ge=O **38** thus formed. As already mentioned in the previous sections, mesitonitrile oxide is a good 1,3-dipolar reagent to trap Tbt(Tip)Ge=X [X = S (**8b**), Se (**14**), and Te (**15**)].

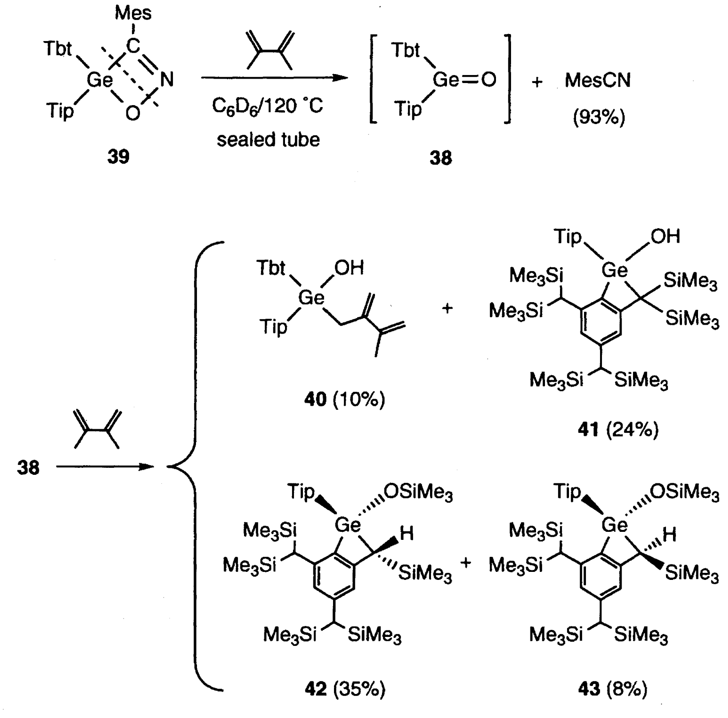
When germylene **11** generated from dibromogermane **12** and lithium naphthalenide was allowed to react with 2 molar amounts of mesitonitrile oxide, oxazagermete **39**, [3+1] adduct of germylene **11**, was obtained unexpectedly (Scheme 19).[54] This represents the first synthesis of an oxazagermete; the structure of **39** was determined by X-ray crystallographic analysis.[54] There have been several reports on oxazetes (carbon analogues of oxazagermete); they were observed as a reactive intermediate in the thermal and photochemical reactions of α,β-unsaturated nitro compounds,[55] and some oxazetes having bulky substituents were isolated, although no X-ray structural analysis was reported.[56]



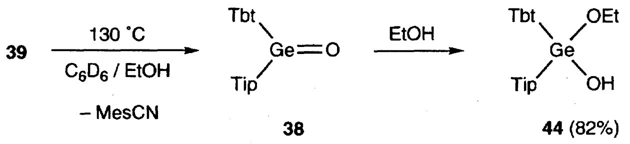
Scheme 19.

(2) Generation of Diarylgermanone 38 by Thermolysis of Oxazagermete.[54] Since oxazetes are known to undergo thermal cycloreversion into the corresponding ketone and nitrile,[55c,56,57] oxazagermete **39** was also expected to dissociate into germanone **38** and mesitonitrile. When a benzene-d_6 solution of oxazagermete **39** and 2,3-dimethyl-1,3-butadiene as a trapping reagent was heated in a sealed tube (120 °C, 12 h), hydroxygermane **40** (an ene reaction product of germanone **38** with the butadiene) and three kinds of benzogermacyclobutene derivatives **41**—**43** were obtained together with an almost quantitative formation of mesitonitrile, indicating the generation of germanone **38** (Scheme 20). The relative configurations of diastereomers **42** and **43** were determined by X-ray structural analysis of **43**.[58] du Mont et al. have already reported a similar intramolecular cyclization reaction of bis(2,4,6-tri-*t*-butylphenyl)germanethione (Scheme 1).[12]

Generation of germanone **38** was also confirmed by the thermal reaction of **39** in the presence of ethanol, which gave ethoxy(hydroxy)germane **44**, an ethanol adduct of **38**, in 82% (Scheme 21).[54] The intermolecular reaction with ethanol was faster than the intramolecular silyl and hydrogen migrations mentioned above. It was also confirmed by ^{1}H NMR in the thermolysis (120 °C in benzene-d_6) of oxazagermete **39** in



Scheme 20.



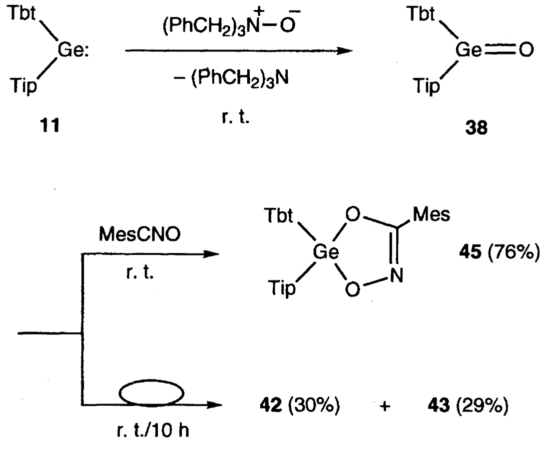
Scheme 21.

the presence of 0.3 molar amounts of ethanol. In the initial stage, the ethanol adduct **44** was observed exclusively, and, after consumption of ethanol, the rearrangement reaction to **41**, **42**, and **43** occurred.

These results indicate that the intramolecular rearrangement of germanone **38** is unavoidable at such high temperatures as are necessary for the thermolysis of **39**.

(3) Reaction of Germylene 11 with Tribenzylamine Oxide.[58] Tribenzylamine oxide, which was also considered to be suitable as a dry oxygen source, was added at room temperature to the blue solution of germylene **11** generated from dibromogermane **12** and lithium naphthalenide. The color of the solution turned colorless immediately. Mesitonitrile oxide was added to this solution to give dioxazagermole **45** (76%), [3+2] adduct of germanone **38**, clearly showing that germanone **38** was formed also by this reaction and was stable in solution at ambient temperature (Scheme 22). This represents the first experimental demonstration of a germanone which is stable in solution.[58]

When the solution of **38** thus formed was stirred for 10 h in the absence of mesitonitrile oxide, compounds **42** and **43** were obtained in the ratio 1 : 1, indicating the occurrence of the rearrangement of a trimethylsilyl group also under this condition. This is in contrast to the fact that the corresponding germanethione **8b** synthesized from the germylene **11** and 1/8 molar amount of S_8 under the same conditions gave no rearranged product. The ratio of **42** to **43** (1 : 1) was different from that in the thermal reaction of oxazagermete **39** shown in Scheme 20. The plausible mechanism is shown in Scheme 23. Since the solution contains tribenzylamine and a small amount of hydroxide generated from lithium naphthalenide and unremovable moisture, they might coordinate to the germanium atom to enhance the anionic character of the oxygen atom of the Ge=O group. The oxygen anion then undergoes a nucleophilic attack on the trimethylsilyl group of Tbt group to give a relatively stable benzyl anion, which slowly cyclizes to afford compounds **42** and **43** in the ratio of 1 : 1. When compounds **42** and **43** were allowed to stand overnight in the presence of either tribenzylamine or lithium hydroxide in THF at room temperature, the starting materials were quantitatively recovered, indicating the absence of an equilibrium between the two diastereomers.



Scheme 22.

7. Alkyl, aryl-Disubstituted Germanium-Containing Heavy Ketones

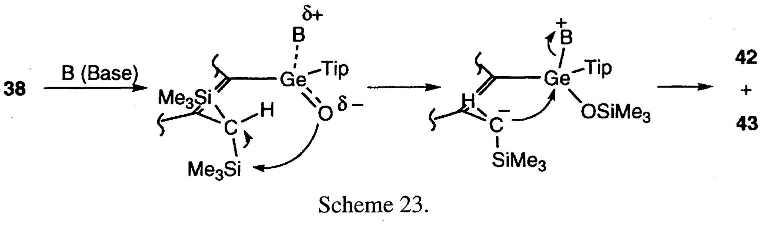
In the previous sections, syntheses, structures, and reactivities of kinetically stabilized germanium-chalcogen double-bond species Tbt(Tip)Ge=X (X = O, S, Se, Te) having two aryl groups on the germanium atom were described. As observed in thiocarbonyl compounds,[31a] there is a possibility that the aryl groups stabilize the germacarbonyl unit by conjugative interaction, although such effects appear negligible in our germanium-containing heavy ketones in view of the steric hindrance between the two aryl groups as well as the observed bond lengths of the Ge=X bonds.

In order to investigate more closely the effects of the aryl groups, we examined the synthesis of a new family of germanium–chalcogen double-bond species Tbt(Dis)Ge=X [X = S, Se, Te; Dis = $CH(SiMe_3)_2$] bearing a bulky alkyl group, bis(trimethylsilyl)methyl (denoted as Dis), instead of Tip. The effectiveness of Dis group as a steric protection group has been reported for many highly reactive species.[59] In this section is described the synthesis of alkyl substituted Tbt(Dis)-Ge=X focusing on the ability of steric protection and the effect on chemical reactivities of Dis group.

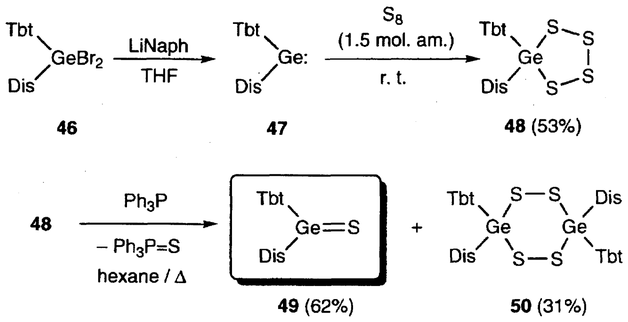
7.1. Synthesis of Alkyl, aryl-Disubstituted Germanethione by Desulfurization Method.

A new type of 1,2,3,4,5-tetrathiagermolane **48** bearing Tbt and Dis groups on the germanium atom was prepared as stable yellow crystals by a route similar to that for Tbt(Tip)GeS_4 **6b**, i.e., the reductive debromination of dibromogermane **46** with lithium naphthalenide leading to the formation of germylene **47** followed by the reaction of the resulting germylene **47** with elemental sulfur (Scheme 24).[60]

Desulfurization of tetrathiagermolane **48** was carried out



Scheme 23.



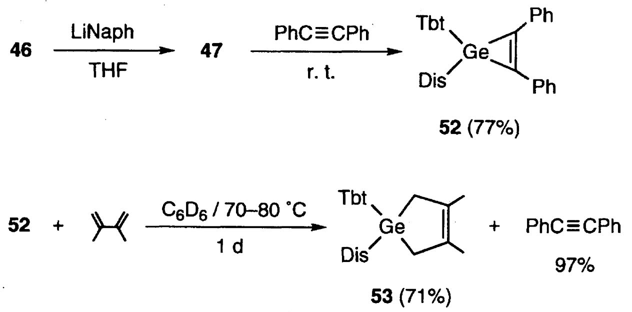
Scheme 24.

using 3 molar amounts of triphenylphosphine in hexane in a manner similar to that for germanethione **8b** to afford germanethione **49** as yellow crystals. However, the yield was only 62% owing to the formation of unexpected tetrathiadigermacyclohexane **50** as insoluble white solids (Scheme 24). The corresponding tetrathiadigermacyclohexane was not obtained in the desulfurization of Tbt(Tip)GeS_4 **6b**.

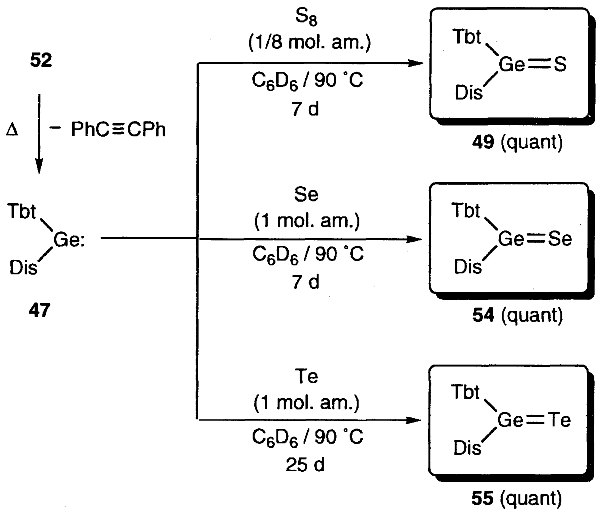
Since we have succeeded in the synthesis of 1,2,3,4,5-tetraselenagermolane Tbt(Dis)$GeSe_4$ **51**, the selenium analogue of **48**, the deselenation of **51** will also be a new synthetic route for germaneselone Tbt(Dis)Ge=Se.[60]

7.2. Synthesis of Alkyl, aryl-Disubstituted Germanium-Containing Heavy Ketones by Chalcogenation of a Germylene. In the hope of isolating the alkyl,aryl-disubstituted germanium-containing heavy ketones systematically we next examined the chalcogenation of alkyl,aryl-disubstituted germylene **47** generated by the cycloreversion of germirene **52**. Germirene **52** was readily prepared from germylene **47** and diphenylacetylene as in the case of diaryl-substituted system **17**,[44] and was heated at 80 °C in the presence of 2,3-dimethyl-1,3-butadiene to give the corresponding [4+1] adduct **53** (71%) together with diphenylacetylene (97%), indicating that germirene **52** is also a useful precursor of germylene Tbt(Dis)Ge: **47** (Scheme 25).

Thermal reaction of germirene **52** was performed in the presence of 1/8 molar amount of S_8 to give germanethione Tbt(Dis)Ge=S (**49**) quantitatively, which was isolated as yellow crystals in a glovebox under pure argon (Scheme 26). Similarly, germaneselone Tbt(Dis)Ge=Se (**54**) and germanetellone Tbt(Dis)Ge=Te (**55**) were also synthesized quantitatively and isolated as orange-red and blue-green crystals, respectively (Scheme 26).[35b] Although the reactions of germylene **50** with elemental sulfur and selenium are completed after a week, that with tellurium was very slow and needed more than three weeks to finish most likely due to the extremely low solubility of tellurium powder.



Scheme 25.



Scheme 26.

7.3. Crystal Structures of Germaneselone 54 and Germanetellone 55. Although we have not obtained single crystals of germanethione **49** suitable for crystallographic analysis yet, molecular structures of germaneselone **54** and germanetellone **55**[45a] were successfully determined by X-ray crystallographic analysis. The ORTEP drawings of **54** and **55** are shown in Figs. 2a and 2b, respectively. The sums of the bond angles around the germanium atom are 360.0° in both cases, indicating a completely trigonal planar geometry of the germaselenocarbonyl and germatellurocarbonyl units as observed in the diaryl-substituted systems, Tbt(Tip)Ge=X (X = S, Se, Te). The Ge=X bond distances of **54** [2.173(3) Å (Ge=Se)] and **55** [2.384(2) Å (Ge=Te)] are similar to or a little shorter than those of germaneselone **14** [2.180(2) Å][29] and germanetellone **15** [2.398(1) Å],[35b] which are somewhat shorter than those of typical single bonds.[40]

The ORTEP drawings of **54** and **55** show that the Dis group effectively protects the germanium–chalcogen double bond as expected, especially owing to the conformation of the Dis group in which trimethylsilyl groups on the Dis group are directed toward the germachalcogenocarbonyl unit on account of the steric repulsion between Dis and Tbt. Similar effects were reported in an isolated monomeric germylene Tsi(Dis)Ge: (Tsi = $C(SiMe_3)_3$),[61] the germanium atom of which is well protected because α-hydrogen on Dis is directed toward Tsi, owing to the steric repulsion, in contrast to the case of germylene Dis_2Ge: which is reported to be in equilibrium with digermene ($Dis_2Ge=GeDis_2$) in solution.[7c,7d]

Some differences about the character of the steric protection groups, Tip and Dis, appear. In Fig. 3 are shown the schematic views of steric protections in Tbt(Tip)Ge=Se (**14**) and Tbt(Dis)Ge=Se (**54**).

In view of the intramolecular structural parameters, the dimerization of **14** might be mainly prevented by the intermolecular repulsion between the extremely bulky aryl

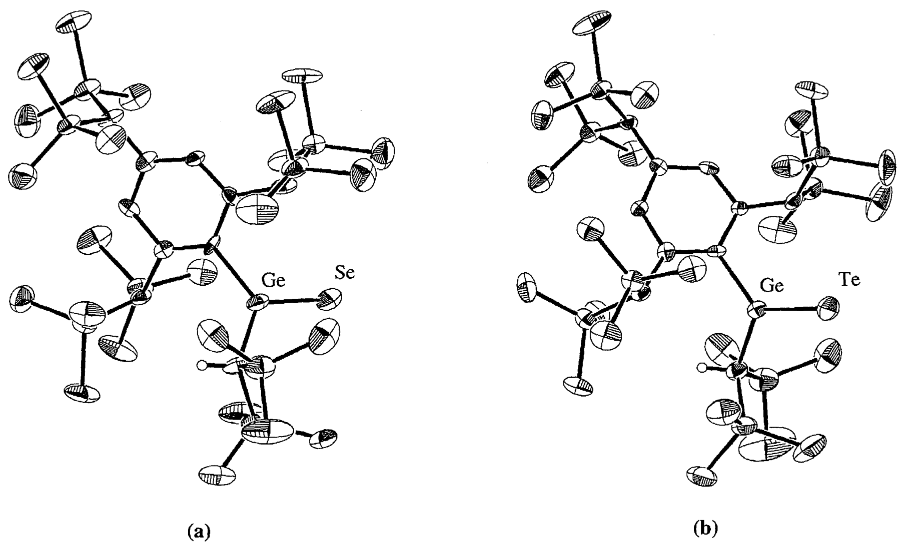


Fig. 2. ORTEP drawings of the alkyl,aryl-disubstituted germanium-containing heavy ketones (30% probability thermal ellipsoid plot). (a) Tbt(Dis)Ge=Se (**54**) and (b) Tbt(Dis)Ge=Te (**55**).

groups, which peripherally interferes with an approach of another germaneselone molecule. On the other hand, the germaselenocarbonyl unit of **54** seems to be rather protected by the more effective steric hindrance due to Dis group itself, which directly protects against the intermolecular attack of the selenium atom onto the germanium atom. Intramolecular distances between the selenium atom and Tip or Dis group show that Dis group in **54** is situated more closely to the germanium–selenium double bond compared to Tip group in **14**, while the distance between Se atom and Tbt group in **54** are similar to that of **14**. This structural feature may be common to germanetellone **55** and germanethione **49**, thus affecting their chemical reactivities.

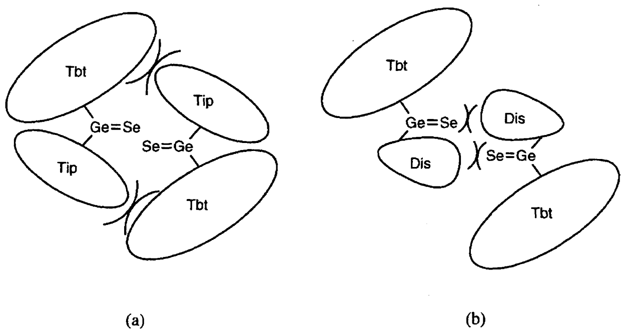
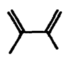
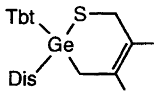
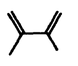
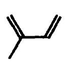
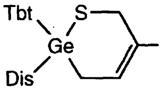
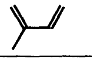
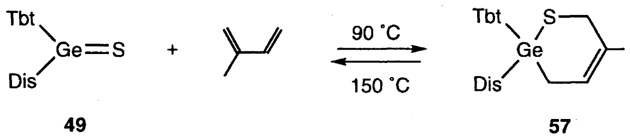


Fig. 3. The steric hindrance in the dimerization of germaneselones. (a) Tbt(Tip)Ge=Se (**14**) and (b) Tbt(Dis)Ge=Se (**54**).

7.4. Diels-Alder Reactions of Germanethione 49. In order to elucidate the influence of the difference of steric protection group on the reactivity of the germanium-containing heavy ketones, the Diels–Alder reactions of germanethione **49** with some dienes were examined. The results are summarized in Table 3. Since the reaction rate of **49** (33% cycloadduct formation with 2,3-dimethyl-1,3-butadiene at 90 °C for 20 h; Entry 1 in Table 3) was slower than that of Tbt(Tip)Ge=S (**8b**) (84% at 90 °C for 10 h^{25}; Entry 1 in Table 1), an excess amount of a diene was added in other entries. In the reaction with isoprene only one isomer **57** was obtained as a cycloaddition product of **49** (Entry 3) and the regiochemistry was opposite to that of germanethione **8b**.

Table 3. [4+2] Cycloaddition Reactions of Germanethione **49** with Dienes

Entry	Diene (mol. am.)	Time/h	Temp/°C	Products (yield)		
1	 (10)	20	90		**56**	(33%)
2	 (50)	70	90		**56**	(50%)
3	 (50)	10	90		**57**	(62%)
4	 (50)	10	150		**57**	(67%)



Scheme 27.

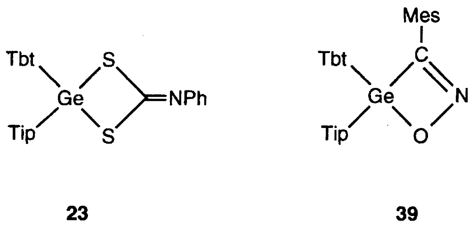
These results indicated the large steric congestion around the germanium atom of **49**, which was also suggested by the molecular structures of similarly substituted germaneselone **54** and germanetellone **55** (Fig. 3), and the regioselectivity in Entry 3 seems to be controlled only by the steric hindrance.

Furthermore, retro Diels–Alder reaction from **57** to **49** was observed as in the case of diaryl-substituted system. The isoprene adduct **57** in hexane was heated to 150 °C in a sealed tube to afford a yellow solution, suggesting the regeneration of germanethione **49** (Scheme 27). Since the yellow color due to **49** disappeared at 90 °C and this color change was reversible, the selectivity observed in the reaction with isoprene at 150 °C shows that **57** is a product of thermodynamic control.

8. Comparison of the Properties of Germanium-Containing Heavy Ketones

We have summarized all the structural and physical properties of the germanium–chalcogen double bond species Tbt(R)Ge=X (R = Tip, Dis; X = S, Se, Te) isolated in the present study. The influence of differences in the chalcogen atoms X (X = S, Se, Te) and the substituents R (R = Tip or Dis) on the properties of germanium-containing heavy ketones will be mainly discussed, including the results obtained by a theoretical study.

8.1. Physical Properties of Germanethione, Germaneselone, and Germanetellone. (1) Structural Properties. The characteristic structural parameters of Tbt(Tip)Ge=X and Tbt(Dis)Ge=X are summarized in Table 4. The observed bond lengths between germanium and the substituents (Tbt, Tip, Dis) resemble each other and are a little shorter than the Ge(sp^3)–C bond lengths of other compounds such as **23**[47] and **39**[54] which were subjected to X-ray structural analyses (Scheme 28). The Ge=X bonds are naturally elongated on going from S to Te. The extent of bond reduction on going from Ge(sp^3)–X to Ge(sp^2)=X are slightly smaller in the germanetellones compared to the germanethiones and germaneselones.



Scheme 28.

Table 5. Calculated Single and Double Bond Lengths (Å) at the B3LYP/TZ(d,p) Level

	X			
	O	S	Se	Te
H_3C–XH	1.421	1.835	1.979	2.165
H_2C=X	1.200	1.617	1.758	1.949
Δ[a)]	15.5	11.9	11.1	10.0
H_3Ge–XH	1.788	2.256	2.393	2.596
H_2Ge=X	1.634	2.042	2.174	2.373
Δ[a)]	8.6	9.5	9.2	8.6

a) Value of % reduction in a bond length defined as [(single bond length − double bond length)/single bond length] × 100.

The bond lengths between germanium and chalcogen atoms were calculated for both single and double bonds at B3LYP/TZ(d,p) level,[33] and the results are listed in Table 5 together with those for carbon–chalcogen bonds. The experimentally observed values for Tbt(Tip)Ge=X and Tbt(Dis)Ge=X shown in Table 4 are in fairly good agreement with the calculated ones, considering that the observed distance of ketones (1.21 Å)[62] is slightly longer than the calculated one

Table 6. The Electronic Spectra of Tbt(R)Ge=X (n–π*) (nm)[a)]

X	S	Se	Te
Tbt(Tip)Ge=X	444 (450)	513 (519)	636 (640)
Tbt(Dis)Ge=X	427 (432)	486 (492)	599 (604)

a) In benzene (in hexane).

Table 4. The Structural Parameters of Tbt(R)Ge=X

R	Tip			Dis	
X	S	Se	Te	Se	Te
Compound	**8b**	**14**	**15**	**54**	**55**
Ge–X (Å)	2.049(3)	2.180(2)	2.398(1)	2.173(3)	2.384(2)
% Bond reduction[a)]	9%	9%	8%	9%	8%
Ge–Tbt (Å)	1.953(9)	1.932(9)	1.933(7)	1.99(1)	1.981(9)
Ge–R (Å)	1.91(1)	1.945(9)	1.952(7)	1.92(2)	1.92(1)
Tbt–Ge–R (deg)	118.4(4)	119.1(4)	117.6(3)	119.7(6)	118.0(4)
Tbt–Ge–X (deg)	124.8(3)	126.4(3)	127.8(2)	122.5(4)	123.3(3)
R–Ge–X (deg)	116.2(3)	113.8(3)	114.1(2)	117.8(4)	118.7(3)
$\sum\angle$Ge (deg)	359.4	359.3	359.5	360.0	360.0

a) The bond shortening (%) compared to the corresponding single bond lengths.

(1.20 Å). Moreover, the calculated value for the % bond reduction, Δ, shows the same tendency as the observed one; the shortening for a germanetellone is smaller than a germanethione and a germaneselone. This can be accounted for by the small overlapping of π orbitals between germanium and tellurium.

(2) UV-vis Spectra. The electronic spectra of the germanium-containing heavy ketones showed characteristic absorption maxima attributable to their n–π* transitions as shown in Table 6, in which one can see a change in the observed absorption maxima (n–π*) owing to the difference in group 16 elements, i.e., a red-shift on going from germanethione to germanetellone, depending on the energy level of chalcogens. On the other hand, we have already reported the electronic spectra for related group 14-group 16 element double-bond compounds such as thione TbtCHS (**58**),[63] silanethione Tbt(Tip)Si=S (**59**),[33,64] and stannanethione Tbt(Tip)Sn=S (**60**).[65] The observed values for these heavy ketones are summarized in Table 7 together with calculated absorption maxima (n–π*) and the energy gap of HOMO (n) and LUMO (π*) for $H_2M=S$.[33,66]

It is interesting that the observed λ_{max} also depends on the element of group 14. The absorption maximum is much blue-shifted on going from thione **58** to silanethione **59**, whereas those for **59**, germanethione **8b**, and stannanethione **60** are red-shifted with increasing the atomic number of the group 14 elements. This trend is also found in the calculated values for $H_2M=S$ (M = C, Si, Ge, Sn). Since calculated $\Delta\varepsilon_{n\pi^*}$ values increase continuously from $H_2Sn=S$ to $H_2C=S$, a long wavelength absorption for $H_2C=S$ (and hence for **58**) most likely results from a large repulsion integral ($J_{n\pi^*}$) for the carbon-sulfur double bond as in the case of $H_2C=O$ vs. $H_2Si=O$.[67]

(3) Vibrational Frequencies. Strong Raman shifts characteristic of the germanium–chalcogen double bonds were observed for germanethiones **8b** and **49** and germaneselones **14** and **53**, while we have not measured the Raman spectra of germanetellones yet. The observed vibrational frequencies are listed in Table 8 along with the calculated ones. Germanethione **8b** showed a characteristic strong Raman shift at 521 cm^{-1}, attributed to the stretching of the germathiocarbonyl unit. Nefedov and his co-workers have already reported the IR spectrum for dimethylgermanethione in argon matrix at 17—18 K and assigned an absorption at 518 cm^{-1} to the stretching of Ge=S bond.[34,68] The high frequency of the Ge=S stretch suggests a considerable double-bond character in this polar bond; stretching vibrations of Ge–S single bond normally appear near 410 cm^{-1}.[69]

Table 7. Electronic Spectra of Double-Bond Compounds between Group 14 Elements and Sulfur

Observed[a)]		Calcd[b)]		
	λ_{max}/nm		λ_{max}/nm	$\Delta\varepsilon_{n\pi^*}$/eV[c)]
Tbt(H)C=S (**58**)	587	$H_2C=S$	460	10.81
Tbt(Tip)Si=S (**59**)	396	$H_2Si=S$	352	10.27
Tbt(Tip)Ge=S (**8b**)	450	$H_2Ge=S$	367	9.87
Tbt(Tip)Sn=S (**60**)	473	$H_2Sn=S$	381	9.22

a) In hexane. b) CIS/TZ(d,p)//B3LYP/TZ(d,p).
c) $\varepsilon_{LUMO}-\varepsilon_{HOMO}$.

Table 8. Vibrational Frequencies of Ge=X Stretching (cm^{-1})

X	S	Se
Tbt(Tip)Ge=X	521	381
Tbt(Dis)Ge=X	512	386
$H_2Ge=X$ (calcd)[a)]	594	412

a) HF/DZ+*d*.

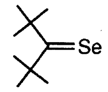
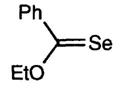
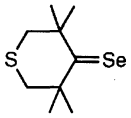
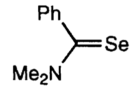
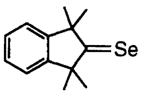
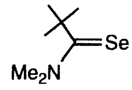
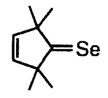
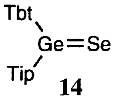
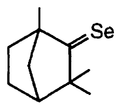
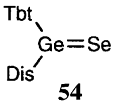
One must keep in mind that the values obtained by SCF calculation are known to be always higher than the observed value as exemplified by $H_2C=O$ [2123 cm^{-1} (SCF calculation)[70] vs. 1746 cm^{-1} (observed)].[71] In view of this tendency, the values obtained for germanethiones and germaneselones agree well with the calculated ones. In other words, the vibrational frequencies observed here are strong evidence for their genuine double-bond character.

(4) NMR Spectra. The double-bond character of germaneselones and germanetellones are shown in the ^{77}Se and ^{125}Te NMR, respectively. The ^{77}Se NMR spectra of germaneselones **14** and **54** show singlet signals at 941 and 872 ppm, respectively, at much lower field than those for compounds containing a Ge–Se single bond. It is reported that the ^{77}Se chemical shift of $(H_3Ge)_2Se$ is −612 ppm [relative to $(H_3C)_2Se$],[72] while those of most of dialkyl selenoketones are in the range between 1600 and 2200 ppm.[73] In the ^{125}Te NMR spectra of germanetellones **15** and **55**, singlet signals were observed at 1143 and 1009 ppm, respectively. The noticeable down-field chemical shifts in the ^{77}Se and ^{125}Te NMR spectra of germaneselones and germanetellones here observed are indicative of the large anisotropy effect of the germanium–chalcogen double bonds.

It has been reported that ^{77}Se chemical shifts of selenocarbonyl compounds correlate with the energies of their n–π* transition (λ_{max}): $\delta(^{77}Se) = 5.891\lambda_{max} - 2020$ with a correlation coefficient $r = 0.996$ ($r^2 = 0.991$).[74] The observed ^{77}Se chemical shifts and λ_{max} (n–π*) for the selenocarbonyl compounds are summarized in Table 9 together with those for the germaneselones **14** and **54**.

The correlation of $\delta(^{77}Se)$ vs. λ_{max} (n–π*) was examined for all the selenocarbonyl compounds in Table 9 and germaneselones **14** and **54**. Interestingly, the plot is also linear (correlation coefficient $r^2 = 0.991$) (Fig. 4). For large atoms, the paramagnetic screening term, σ_p, dominates the chemical shift terms. Equation 1 relates σ_p to ΔE^{-1} (an average electron excitation energy), $\langle r^{-3}\rangle$ (the mean inverse cube radius for 2p orbitals), and Q_{AA} and Q_{AB} (the elements of the charge density and bond order matrix in the molecular orbitals of the unperturbed molecule).[75] If this approximate equation is applicable to selenium, the experimental $\delta(^{77}Se)$ vs. λ_{max} (n–π*) correlation observed here implies that σ_p follows ΔE^{-1} with $\langle r^{-3}\rangle Q_{AA}$ and Q_{AB} either being constant or

Table 9. $\delta(^{77}Se)$ and λ_{max} of Selenoketones, Selenoamides, a Selenoester, and Germaneselones

Compounds	$\delta(^{77}Se)$[a]	λ_{max}/nm[b]	Compounds	$\delta(^{77}Se)$[a]	λ_{max}/nm[b]
	2131	710		915	512
	2135	689		733	455
	1844	628,658[d]		640	453
	1803	623,656[d]	 **14**	941	519[c]
	1613	616	 **54**	872	492[c]

a) $\delta(^{77}Se)$ in ppm downfield from Me_2Se. b) In cyclohexane. c) In hexane. d) The longer wavelength absorption is used to fit the linear relationship.

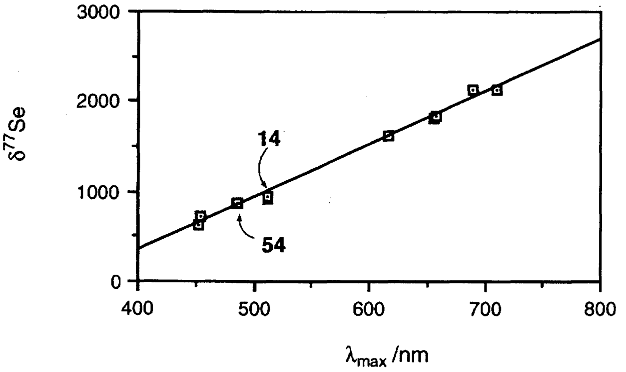


Fig. 4. Plot of $\delta(^{77}Se)$ in ppm from Me_2Se as reference vs. λ_{max}. $\delta(^{77}Se) = 5.903\lambda_{max} - 2031$ ($r^2 = 0.991$).

varying proportionately with ΔE^{-1} also in germaneselones. The term ΔE^{-1} appears to be well correlated with the energies of the n–π* transitions.

$$\sigma_p = -\frac{K}{\Delta E} < r^{-3} > (Q_{AA} + \sum_{B} Q_{AB}) \quad (1)$$

8.2. Comparison between Tbt(Tip)Ge=X and Tbt(Dis)Ge=X. The most important factor responsible for the difference between Tbt(Tip)Ge=X and Tbt(Dis)Ge=X would be the degree of conjugation of the germacarbonyl unit with substituents. This effect is expected to appear most clearly in the electronic spectra. Inspection of the observed values summarized in Table 6 reveals that the n–π* absorption maxima observed in the series of Tbt(Dis)Ge=X (X = S, Se, Te) are blue-shifted compared with those of the corresponding Tbt(Tip)Ge=X. This trend agrees with the results obtained by the ^{77}Se and ^{125}Te NMR where Tbt(Tip)Ge=X resonate at lower fields than Tbt(Tip)Ge=X, since the shielding constant σ is correlated to ΔE as shown in Eq. 1.

9. Concluding Remarks

The development of a new and effective steric protection group (Tbt) led us to the first isolation of stable germanium-containing heavy ketones, Tbt(R)Ge=X (X = S, Se, Te). Crystallographic structural analysis of these stable heavy ketones have revealed that they have a completely trigonal planar geometry around the central germanium atom and a genuine double-bond nature for their germanium–chalcogen bonds. In contrast to the heavier congeners, kinetically stabilized diarylgermanone, Tbt(Tip)Ge=O, was found to be still too reactive to be isolated. We have obtained some evidence, however, for the monomeric germanone stable in solution.

In spite of the presence of two highly crowded substituents on the group 14 elements, the germanium-containing heavy ketones here obtained undergo [2+2], [2+3], and [2+4] cycloaddition reactions with phenyl isothiocyanate, mesitonitrile oxide, and 2,3-dimethyl-1,3-butadiene, respectively, affording a variety of novel types of cyclic organogermanium compounds. Thus, these heavy ketones are interesting not only from theoretical and structural viewpoints but also from a synthetic viewpoint. The successful isolation of these heavy ketones here described strongly suggests that multiply bonded compounds of higher row elements are capable of existence as stable species if they are set up with an appropriate combination of steric protection groups. A further study on the synthesis and isolation of such unknown multiply bonded species of heavier main group element is currently in progress.

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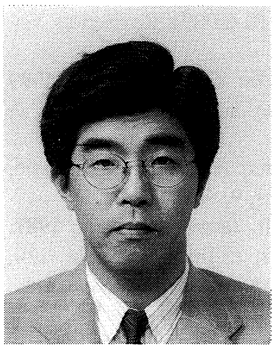

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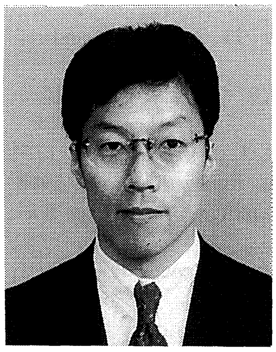

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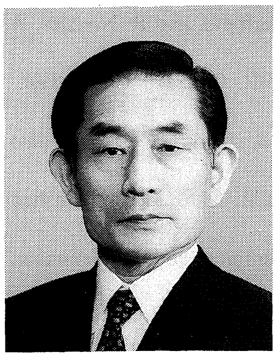

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