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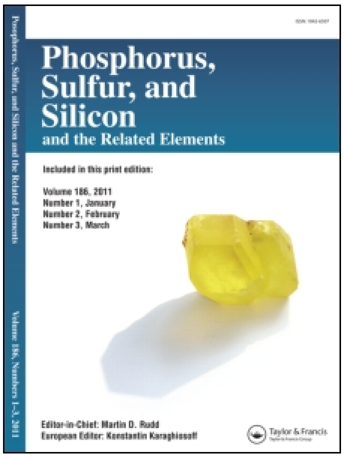

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New Aspects in the Chemistry of "Heavy Ketones": Stable Metallaneselones and Metallanetellones

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NEW ASPECTS IN THE CHEMISTRY OF "HEAVY KETONES": STABLE METALLANESELONES AND METALLANETELLONES

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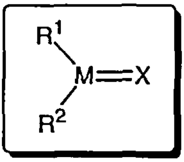
Stable metallaneselones and metallanetellones [Tbt(R)M=X; M = Si, Ge, Sn, X = Se and Te], , *i.e.*, a new family of double-bond compounds between heavier group 14 elements and chalcogen atoms (*"heavy ketones"*), are synthesized by taking advantage of kinetic stabilization using an extremely bulky and efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt). The molecular structures and chemical properties of these new double-bond species are also described.

Keywords: double-bond compounds; kinetic stabilization; group 14 elements; chalcogen atoms; cyclic polychalcogenide; dechalcogenation; X-ray structural analysis

INTRODUCTION

For the past decades, it was considered that double-bond compounds of heavier main-group elements would not be stable because of their weak pπ–pπ bonding (so called *"double-bond rule"*). Since the isolation of the first stable double-bond compounds containing heavier group 14 or 15 elements such as Si=C[1], Si=Si[2], and P=P[3], however, remarkable progress has been made in the chemistry of unsaturated compounds of heavier typical elements, especially in the field of group 14 elements[4]. In the chemistry of low-coordinate compounds of group 14 elements (Si, Ge, Sn, and Pb), the double bond compounds between such elements and chalcogen atoms [$R^1R^2M=X$ (1); M = Si, Ge, Sn, and Pb; X = O, S, Se, and Te; we coin *"heavy ketones"* for them] are among the most fascinating and challenging target molecules because of their interesting bonding character and potential synthetic utility.



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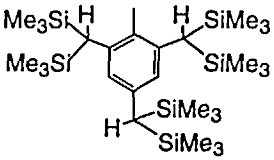
Heavy Ketones

M: Si, Ge, Sn, Pb
X: O, S, Se, Te



Tbt group

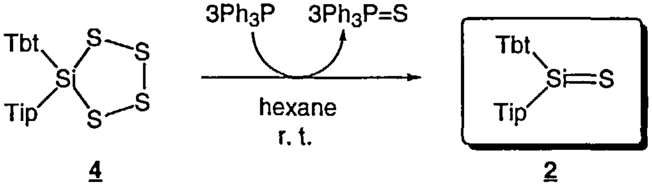
Although there have recently been reported several examples of thermodynamically stabilized silanethione[5], silaneselone[5], and germathiourea[6], they are considerably perturbed by the intramolecular coordination of a nitrogen lone pair in the neighborhood of the double bond. On the other hand, no example of successful isolation using kinetic stabilization had been described for *"heavy ketones"* until we have recently succeeded in the synthesis and X-ray structural determination of some "heavy thiones" such as silanethione (2) [Tbt(Tip)Si=S; Tip = 2,4,6-triisopropylphenyl][7] and germanethione (3) [Tbt(Tip)Ge=S][8] by taking advantage of an extremely bulky and efficient steric protection group developed by us, *i. e.*, 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl (denoted as Tbt hereafter) [9]. The difficulty in isolation is obviously because bulky substituents for steric protection can be introduced only on the group 14 elements and hence their oligomerization cannot be efficiently suppressed.

This article describes a brief account of the syntheses, structures, and reactivities of their heavier congeners, *i.e.* metallaneselones and metallanetellones [Tbt(R)M=X; M = Si, Ge, and Sn; X = Se, Te].

SYNTHESIS OF STABLE METALLANESELONES

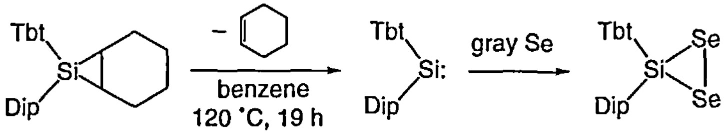
1. Stable Silaneselone

Although we have already succeeded in the synthesis and isolation of the first kinetically stabilized silanethione **2** by the treatment of Tbt and Tip substituted tetrathiasilolane **4** [10] with three equivalents of triphenylphosphine in hexane at room temperature. Silanethione **2** is isolated as yellow crystals [λ_{max} (hexane) = 396 nm (ε 50), δ_{Si}(benzene-d_6) = 166.67] and quite stable in the absence of water and oxygen[7].



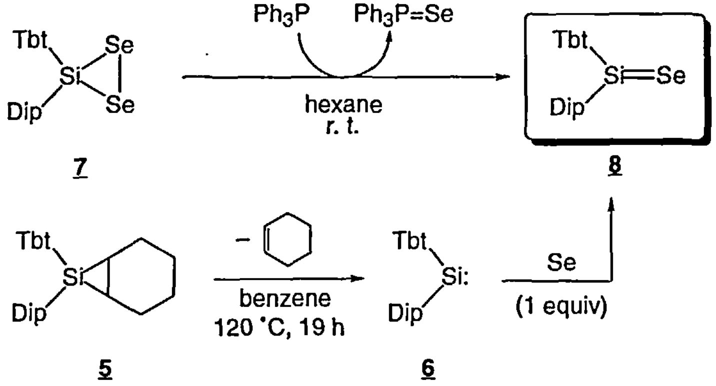
Silanethione **2** readily undergoes reactions with methanol, phenyl isothiocyanate, mesitonitrile oxide, and 2,3-dimethyl-1,3-butadiene to give the corresponding adducts, indicating a high reactivity of the silathiocarbonyl unit[7]. The structure of **2** was established by X-ray crystallographic analysis. The bond distance of Si=S is 1.948 Å, which is about 9% shorter than typical Si–S single bond lengths, indicating a double bond nature of the silicon-sulfur bond of **2**. Another important structural feature of **2** is its trigonal planar geometry with the sum of the bond angles around Si being 359.9°.

The successful isolation of silanethione **2** prompted us to examine the kinetic stabilization of its heavier congener, silaneselone, using Tbt group. Since tetraselenasilolane, Tbt(Tip)SiSe$_4$, was not obtained by a synthetic method similar to that for its sulfur analogue **4**, we had to develop another precursor for the kinetically stabilized silaneselone. In the course of our study on the synthesis of sterically congested organosilicon compounds we have found that the Tbt and Dip (2,6-diisopropylphenyl) substituted silanorcarane derivative **5** is a good precursor of the corresponding silylene **6**[11].



5 6 7

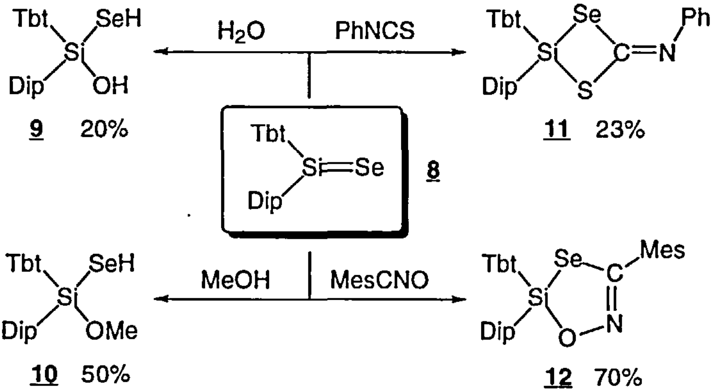
The thermolysis of silacyclopropane **5** in the presence of an excess amount of elemental selenium in benzene (120 °C, 19 h) resulted in an almost exclusive formation of a new cyclic diselenide **7** as air- and moisture-sensitive red solid. Diselenasilirane **7** is the first example of a stable diselenirane and it showed characteristic signals in its ^{29}Si-NMR (δ_{Si} = -174) and ^{77}Se-NMR (δ_{Se} = -44).



7 8 5 6

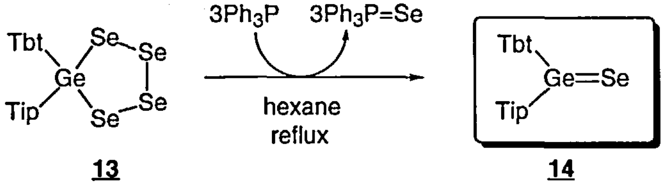
Diselenasilirane **7** was deselenated by an equimolar amount of triphenylphosphine in hexane at room temperature to afford the expected silaneselone **8** as an orange solid, which is found to be identical with the product of the reaction of the silylene **6** with an equimolar amount of elemental selenium by comparison of their ^{29}Si-NMR (δ_{Si} = 174) and ^{77}Se-NMR (δ_{Se} = 635). The characteristic low-field ^{29}Si-NMR chemical shift of **8** as in the case of silanethione **2** together with its $^{1}J_{Si-Se}$ value (298 Hz) strongly indicate the double-bond character of silaneselone **8**. In the electronic spectra, silaneselone **8** showed an absorption maxima at 456 nm (ε 200) in THF, which is 60 nm longer than that of silanethione **2** (*vide supra*)[7].

Silaneselone **8** thus obtained was found to be stable at room temperature reflecting the steric congestion due to the two bulky protecting groups (Tbt and Dip), but it still retains the high reactivity towards some small molecules such as water, methanol, phenyl isothiocyanate, and mesitonitrile oxide to afford the corresponding adducts **9–12** as shown in the following scheme.



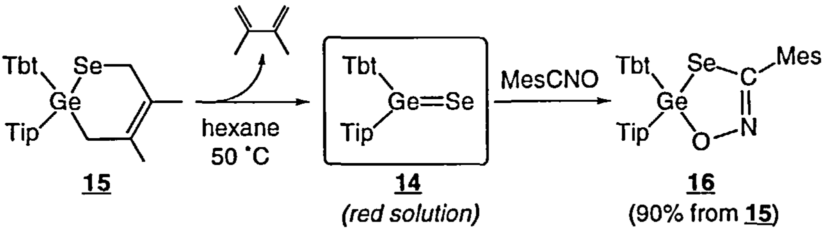
2. Stable Germaneselone

In contrast to the case of silicon-containing cyclic polyselenides, Tbt- and Tip-substituted 1,2,3,4,5-tetraselenagermolane **13** is readily prepared by the reductive debromination of the corresponding dibromogermane Tbt(Tip)GeBr$_2$ with lithium naphthalenide followed by the treatment with elemental selenium[12]. Deselenation of **13** with three equivalent molar amount of triphenylphosphine in refluxing hexane afforded the kinetically stabilized germaneselone **14** almost quantitatively[13].



Germaneselone **14** was isolated as stable red crystals [mp. 191–194 °C; λ_{max} (hexane) = 519 nm (ε 140)][13] and it showed a characteristic Raman line at 382 cm^{-1} (ND: YAG laser), which is reasonably smaller than that (521 cm^{-1}) of its sulfur analogue, *i.e.* germanethione Tbt(Tip)Ge=S (**3**)[8]. The molecular structure of **14** was successfully determined by X-ray crystallographic analysis[13], which revealed that **14** has a completely trigonal planar geometry around the central germanium atom as in the case of the germanethione **3** and the expectedly shortened Ge–Se distance [2.180(2) Å] as compared to the normal Ge–Se single bond lengths (*ca.* 9% shortening).

Despite the presence of bulky steric protection groups on the germanium atom, **14** readily undergoes cycloaddition reactions with a variety of reagents such as phenyl isothiocyanate, mesitonitrile oxide, and 2,3-dimethyl-1,3-butadiene in high yields under much milder conditions (room temperature in hexane)[13] than those for silanethione **2**[7] and germanethione **3**[8].

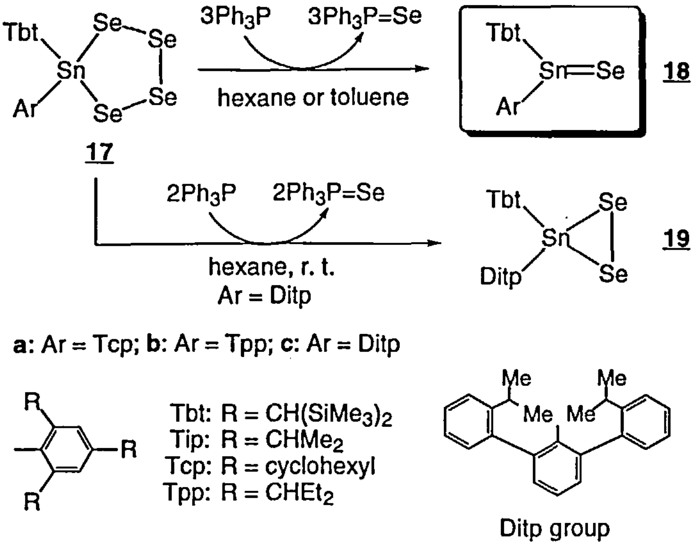


Interestingly, isolated [2+4]cycloadduct **15** was found to undergo a ready retro-[2+4]cycloaddition reaction on heating (50 °C in hexane) to regenerate the germaneselone **14**, which was effectively trapped by mesitonitrile oxide giving the corresponding [2+3]cycloadduct **16** in 90% yield. This fact shows that the germaselenacyclohexane derivative **15** can be used as a stable precursor for germaneselone **14**.

3. Stable Stannaneselone

As for low-coordinated tin compounds, some stable double-bond species with group 14 (Sn=Sn[14], Sn=C[15], and Sn=C=N[16]) and group 15 elements (Sn=N[17] and Sn=P[18]) have been synthesized, but tin–chalcogen double-bond compounds so far reported are restricted to those thermodynamically stabilized by intramolecular coordination[19], which are highly perturbed by electron donation from neighboring nitrogen atoms to an electron-deficient tin center as evidenced by their high-field chemical shifts in ^{119}Sn NMR. Although we also described the synthetic approach to tin–chalcogen double-bond compounds, Tbt(Tip)Sn=X (X = S, Se), by dechalcogenation of 1,2,3,4,5-tetrachalcogenastannolanes[20] and chalcogenation of the corresponding stannylene[21], they were found to be stable only in solution and dimerize in the solid state.

Quite recently, however, we have found that the deselenation of a tetraselenastannolane by a phosphine reagent affords a stannaneselone without intramolecular coordination or a diselenastannirane, depending on the equivalence of the phosphine reagent used. Tetraselenastannolanes Tbt(Ar)SnSe$_4$ (**17**) [**17a**, Ar = 2,4,6-tricyclohexylphenyl (Tcp); **17b**, Ar = 2,4,6-tris(1-ethylpropyl)phenyl (Tpp); **17c**, Ar = 2,2"-diisopropyl-*m*-terphenyl-2'-yl (Ditp)], precursors for the synthesis of tin–selenium double-bond compounds, were easily obtained by the reactions of Tbt(Ar)Sn: with an excess amount of elemental selenium. Our previous observation that Tbt(Tip)Sn=Se readily dimerized at ambient temperature so that its ^{119}Sn NMR was unable to be measured[21] led us to use a bulkier Tcp or Tpp group instead of Tip group.



Treatment of Tbt(Tcp)$SnSe_4$ **17a** with 3 equiv. triphenylphosphine in toluene gave a deep red solution, whose ^{119}Sn signal showed a signal at 556 ppm assignable to stannaneselone **18a**. This low-field chemical shift is characteristic of low-coordinated tin, *e.g.*, $R_2Sn{=}SnR_2$ (725[14a], 427.5[14b] ppm), $R_2Sn{=}CR'_2$ (835[15a], 288[15b] ppm), $R_2Sn{=}PR'$ (658.3[18a], 499.5[18b] ppm), indicating that stannaneselone **18a** displays an intrinsic nature of tin–selenium double-bond compounds, in sharp contrast to the Parkin's terminal selenido complex whose ^{119}Sn NMR appears at a much higher field (–444 ppm)[19a]. Similarly, the reaction of Tbt(Tpp)$SnSe_4$ **17b** with 3 equiv. triphenylphosphine also gave stannaneselone **18b** (δ_{Sn}: 547 ppm). Although stannaneselones **18a** and **18b** were stable in solution for a short time at room temperature, the deep red color of the solution gradually disappeared over a few hours.

The unsuccessful attempts at the isolation of a stable stannaneselone by using the combination of Tbt-Tcp and Tbt-Tpp groups prompted us to develop a ligand even bulkier than Tcp and Tpp. We have introduced a new efficient steric protection group having a *m*-terphenyl skeleton, Ditp (2,2"-diisopropyl-*m*-terphenyl-2'-yl)[22]. When Tbt(Ditp)$SnSe_4$ **17c** was allowed to react with 3 equiv. triphenylphosphine in refluxing hexane for 2 h, the solution turned deep red and a ^{119}Sn NMR signal was observed at 440 ppm, indicating the formation of stannaneselone **18c**. Filtration of triphenylphosphine selenide insoluble in hexane, followed by removal of hexane resulted in the isolation of the stable stannaneselone **18c** as red crystals in 84% yield[23].

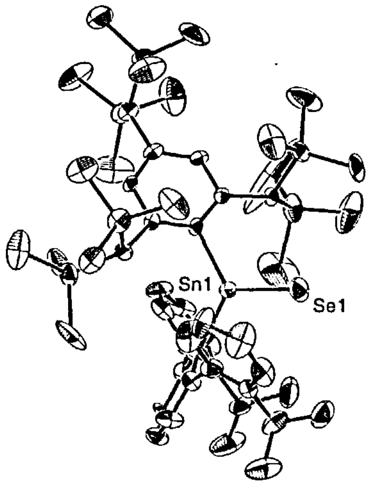


Figure 1. Molecular Structure of **18c**.

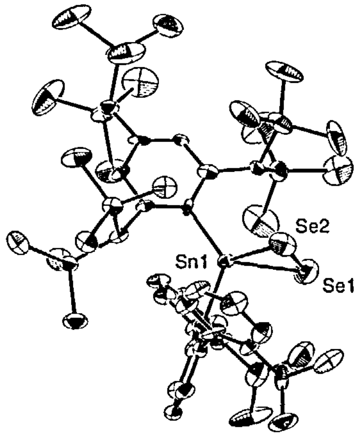


Figure 2. Molecular Structure of **19**.

The structure of **18c** was determined by X-ray crystallographic analysis[23]. The ORTEP drawing (Figure 1) shows that the stannaselenocarbonyl unit is effectively protected by one bis(trimethylsilyl)-methyl group in Tbt and two isopropyl groups in Ditp which are directed toward the Sn=Se bond in order to avoid the steric repulsion with the Tbt group. The Sn–Se distance [2.375(3) Å] is approximately 9% shorter than a Sn–Se single bond length (2.55–2.60 Å)[24] and slightly shorter than that of the Parkin's terminal selenido complex (2.39 Å)[19a]. The geometry around the tin atom is trigonal planar, the sum of the angles being 359.9 °, indicative of its structural similarity to a ketone.

Interestingly, treatment of **18c** with 2 equiv. of triphenylphosphine in hexane at room temperature, followed by removal of triphenylphosphine selenide gave orange-red crystals of diselenastannirane **19** (56%). The molecular structure of **19** was finally established by X-ray crystallographic analysis (Figure 2). The diselenastannirane ring system of **19** forms an equilateral triangle. It is noted that the Se–Se bond is very long [2.524(4) Å], about 0.2 Å longer than the typical Se–Se single bond[25] although the Sn–Se bond lengths [2.528(2), 2.532(3) Å] are almost equal to typical Sn–Se bond lengths (2.58 Å)[24].

The successful deselenation mentioned above indicates that the dechalcogenation of a tetrachalcogenametallolane with appropriate ligands may constitute a useful synthetic method for compounds with unique structure.

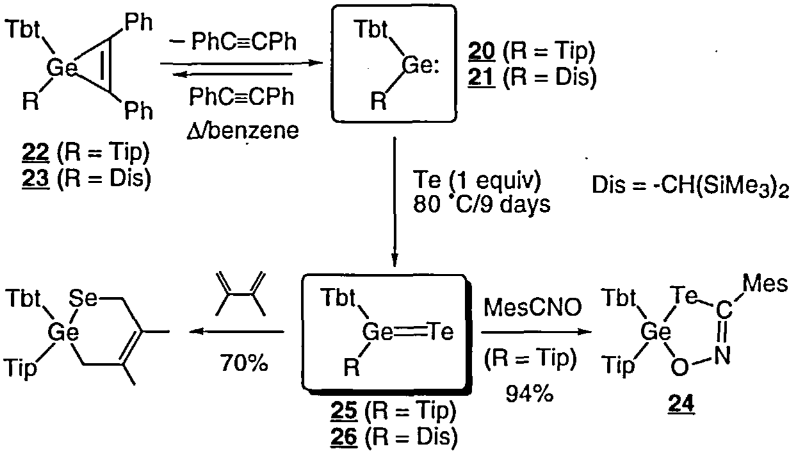
SYNTHESIS OF STABLE METALLANETELLONES

Stable Germanetellones

Although thio- and selenocarbonyl compounds have been actively investigated and reliable synthetic methods for stable species have been developed, very little is known for tellurocarbonyl compounds except for electronically stabilized or transient short-lived species, and no stable telluroketone had been described until the synthesis of the first stable telluroketone, 1,1,3,3,-tetramethylindanetellone, was recently reported[26]. The chemistry of a germanetellone, a germanium analogue of a tellone, has also been very little explored, and as for the germanium-tellurium double-bond species there has been only one report by Parkin on the isolation and characterization of the terminal tellurido complex of germanium supported by ligation of the macrocyclic octamethyldibenzotetraza[14]annulene dianion[14].

Meanwhile, we have succeeded in the synthesis of stable germanethione and germaneselone, *i.e.*, Tbt(Tip)Ge=X (**3**: X=S[8]; **14**: X=Se[13]) by taking advantage of the Tbt group as a steric protection group, and their X-ray structural analyses revealed a considerable shortening of their germanium-chalcogen bond lengths which indicates the unambiguous double-bond character and complete trigonal planar geometry around the germanium atom as in the case of ketones (*vide supra*). These successful results prompted us to apply the Tbt group to the kinetic stabilization of germanetellones, *i.e.* the heaviest congeners of this family of germanium-chalcogen double-bond compounds.

For the synthesis of germanetellones, we took advantage of the direct telluration of germylenes Tbt(R)Ge: [**20**: R = Tip; **21**: R = bis(trimethylsilyl)methyl (Dis)] with elemental tellurium since we recently found that **20** and **21** were cleanly and efficiently generated by the thermal cycloreversion of germirenes **22** and **23**[27]. Thus, germirene **22** and 1 equiv of elemental tellurium were allowed to react in benzene-d_6 at 80 °C in a sealed tube for 9 days, after which time the solution turned green and the ^{1}H-NMR indicated the complete consumption of **22** and the appearance of new signals in addition to those of diphenylacetylene. The sealed tube was opened in a glovebox filled with argon and mesitonitrile oxide was added to the solution to afford a [3+2]-cycloadduct **24** in 94% yield, clearly indicating the generation of germanetellone **25** in high yield. Removal of the solvent from the green solution without the addition of mesitonitrile oxide gave germanetellone **25** as a stable, green crystalline compound together with the colorless crystals of diphenylacetylene, from which pure crystals of **25** were sorted out taking advantage of its characteristic green color. This is the first isolation of a kinetically stabilized diarylgermanetellone[29]. Under similar reaction conditions, germirene **23** bearing a Dis group also reacted with elemental tellurium to afford the expected alkylaryl substituted germanetellone **26** as stable blue-green crystals in a quantitative yield[28].



Germanetellones **25** and **26** were very sensitive toward moisture especially in solution but thermally quite stable; **25** and **26** melted at 205–210 and 200–203 °C, respectively, without decomposition and no dimerization was observed in solution up to 90 °C [^{1}H NMR (C_6D_6, sealed tube)]. Interestingly, **25** and **26** are quite stable toward light either in solution or in the solid state in sharp contrast to the stable telluroketone, 1,1,3,3-tetra-methylindanetellone, which is extremely light sensitive even toward the fluorescent light[26]. Both **25** and **26** showed characteristic absorption maxima attributed to n-π^* transitions of the Ge=Te unit [636 (for **25**) and 599 (for **26**) nm in benzene] with the diaryl substituted **25** being red shifted (37 nm) compared with the alkylaryl substituted **26**. These absorption maxima were red shifted relative to those observed for germanethione **3**[8] and germaneselone **14**[13] [444 nm (for **3**) and 513 nm (for **14**) in benzene].

The ^{125}Te NMR of **25** and **26** in C_6D_6 showed singlet signals in the region as low as 1143 and 1009 ppm, respectively, indicating the

sp^2 character of the germatellurocarbonyl group. The observation of a lower field ^{125}Te-NMR signal for the diaryl substituted **25** than that for the alkylaryl substituted **26** agrees with the trend observed in their electronic spectra with **25** being more red shifted as expected from the known correlation between the shielding constant σ and ΔE[29].

The molecular structures of both **25** and **26** were revealed by X-ray crystallographic analysis and the ORTEP drawing of **25** is shown in Figure 3. In each case the germatellurocarbonyl unit is effectively protected by the bulky substituents and no intermolecular interaction exists even in the solid state; the shortest intermolecular distances between Ge and Te atoms for **25** and **26** were found to be 5.49 and 7.98 Å, respectively, which are considerably longer than the sum of the van der Waals radii of Ge and Te atoms (4.16 Å). The germatellurocarbonyl units of **25** and **26** have completely trigonal planar geometry, the sum of bond angles around the germanium atom being 359.5 ° (for **25**) and 360.0 ° (for **26**). The Ge–Te bond distances of **25** and **26** [2.398(1) and 2.384(2) Å] are *ca.* 8% shorter than those reported for typical Ge–Te single bonds (2.59–2.60 Å)[30] and in good agreement with the calculated bond length of $H_2Ge{=}Te$ (2.36 Å)[31], showing an unambiguous double-bond character between germanium and tellurium. These values for **25** and **26** are significantly shorter than that reported for Parkin's compound [2.446(1) Å][19a], clearly indicating the "genuine" double-bond nature of **25** and **26**. In germanetellone **25**, there seems no significant conjugation between the two aryl groups and the Ge=Te bond in the solid state judging from their dihedral angles between the aryl planes and the π-plane of the germatellurocarbonyl unit, *i. e.*, 39° for the Tbt group and 71 ° for the Tip group, the values of which are almost similar to those of germanethione **3**[8] and germaneselone **14**[13]. In the case of **26**, an even larger value (57 °) was observed for the dihedral angle between the π planes of the Tbt and Ge=Te groups.

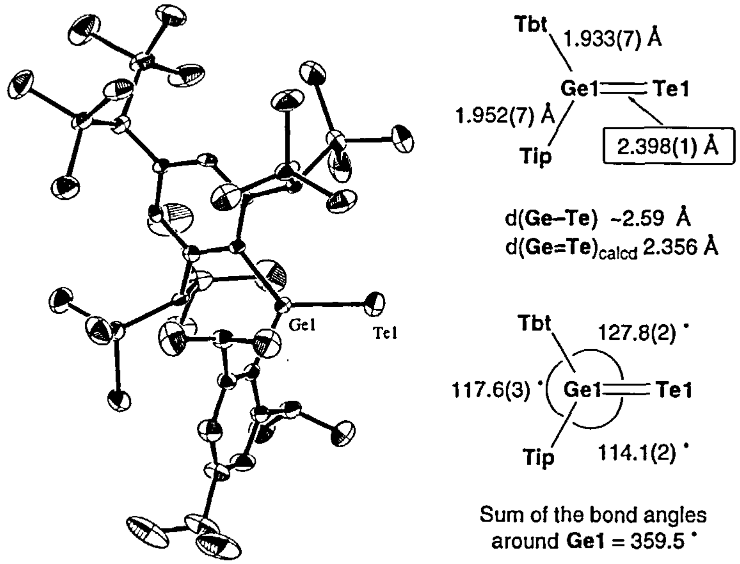


Figure 3. Molecular Structure of Tbt(Tip)Ge=Te (**25**).

CONCLUSION

The development of a new and effective steric protection group (Tbt) led us to the first isolation of a number of stable metallaneselones and metallanetellones Tbt(R)M=X (M = Si, Ge, Te; X = Se, Te). Molecular structures of these stable heavy ketones have been crystallographically analyzed; the heavy ketones have a completely trigonal planar geometry around the central metals and a genuine double-bond nature for the M=X bonds.

In spite of the presence of two highly crowded substituents on the group 14 elements, these heavy ketones 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 heterocycles. 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 suggests that many other congeners will also be 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 these unknown heavy ketones is currently in progress.

Acknowledgments

The co-workers who participated in this work are cited in the references. The author express his sincerest gratitude to Prof. Renji Okazaki (The University of Tokyo) for his collaboration and encouragement. The author is grateful to the Ministry of Education, Science, Sports and Culture, Japan, the Sumitomo Foundation, and the Yamada Science Foundation for the financial support. The gift of chemicals from ASAI Germanium Research Institute, Shin-etsu Chemical Co., Ltd., and Tosoh Akzo Co., Ltd. is also acknowledged.

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