

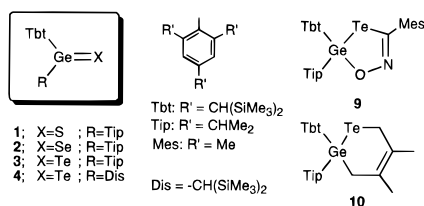
First Stable Germanetellones: Syntheses and Crystal Structures of the Heaviest Germanium–Chalcogen Double-Bond Compound

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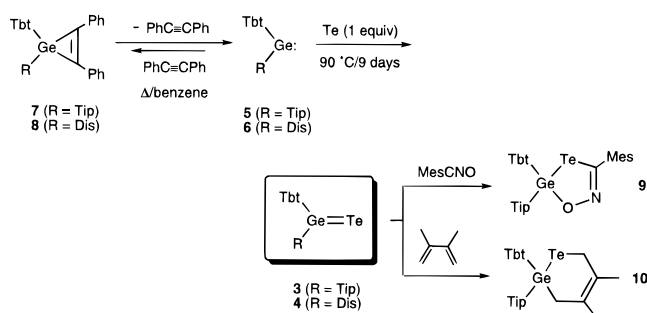
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In view of the central importance of the carbonyl group in organic chemistry, interest in the chemistry of its heavier chalcogen analogues has remarkably increased in recent years.¹ Although thio- and selenocarbonyl compounds have been actively investigated and reliable synthetic methods for stable species have been developed,¹ very little is known for tellurocarbonyl compounds except for electronically stabilized² or transient short-lived species,³ and no stable telluroketone had been described until we recently reported the synthesis of 1,1,3,3-tetramethylindantellone,⁴ the first telluroketone stable in solution.



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 et al. on the isolation and characterization of the terminal tellurido complex of germanium supported by ligation of the macrocyclic octamethylbenzotetraza[14]-annulene dianion.⁵ Meanwhile, we recently succeeded in the synthesis of stable germanethione⁶ and germaneselone⁷ having carbon substituents on germanium, *i.e.*, Tbt(Tip)Ge=X (**1**, X = S; **2**, X = Se; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Tip = 2,4,6-triisopropylphenyl) and their X-ray structural analyses, which revealed a considerable shortening of their

Scheme 1



germanium–chalcogen bond lengths indicative of the unambiguous double-bond character and complete trigonal planar geometry around the germanium atom as in the case of ketones. Here, we present the syntheses and crystal structures of the first stable germanetellones **3** and **4** which are worthy of note not only as the heaviest congeners of this family of germanium–chalcogen double-bond compounds but also as the first examples of the crystallographic analysis of a tellurium analogue of a ketone.

For the synthesis of germanetellones **3** and **4**, we took advantage of the direct telluration of germirenes Tbt(R)Ge: (**5**, R = Tip; **6**, R = Dis) with elemental tellurium since we recently found that **5** and **6** were cleanly and efficiently generated by the thermal cycloreversion of germirenes **7** and **8** (Scheme 1).⁸ Thus, germirene **7** and 1 equiv of elemental tellurium were allowed to react in benzene-*d*₆ at 90 °C in a sealed tube for 9 days, after which time the solution turned green and the ¹H NMR indicated the complete consumption of **7** and the appearance of new signals in addition to those of diphenylacetylene. The sealed tube was opened in a glovebox filled with argon, and mesitronitrile oxide was added to the solution to afford a [3+2]-cycloadduct, **9**, in 94% yield, clearly indicating the generation of germanetellone **3** in high yield.^{9,10} The germanetellone **3** thus prepared was also allowed to react with 2,3-dimethyl-1,3-butadiene to give the corresponding [4+2]-cycloadduct **10** in 70% yield.¹⁰ Removal of the solvent from the green solution without the addition of mesitronitrile oxide gave germanetellone **3** as a stable, green crystalline compound together with the colorless crystals of diphenylacetylene in almost quantitative yields as judged by ¹H NMR, from which pure crystals of **3**¹¹ were sorted out, taking advantage of its characteristic green color (Scheme 1). This is the first isolation of a kinetically stabilized

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(9) The germanethione **1** and germaneselone **2** also reacted with mesitronitrile oxide to give the corresponding [3+2]-cycloadducts in excellent yields.^{6,7}

(10) Experimental procedures and the physical properties of the reaction products for the cycloaddition reactions of **3** with mesitronitrile oxide and 2,3-dimethyl-1,3-butadiene are described in the Supporting Information.

(11) **3**: green crystals, mp 205–210 °C; ¹H NMR (C₆D₆, 500 MHz, 300 K) δ 0.15 (s, 18H), 0.20 (s, 18H), 0.24 (s, 18H), 1.18 (d, J = 6.9 Hz, 6H), 1.32 (d, J = 6.9 Hz, 6H), 1.40 (d, J = 6.9 Hz, 6H), 1.49 (s, 1H), 2.72 (sept, J = 6.9 Hz, 1H), 3.57 (br s, 1H), 3.67 (sept, J = 6.9 Hz, 2H), 3.88 (br s, 1H), 6.49 (s, 1H), 6.65 (s, 1H), 7.03 (s, 2H); ¹³C NMR (C₆D₆, 125 MHz, 300 K) δ 1.16 (q), 1.57 (q), 1.63 (q), 22.22 (q), 24.09 (q), 26.97 (q), 28.24 (d), 28.50 (d), 32.03 (d), 34.67 (d × 2), 34.81 (d), 123.28 (d × 2), 125.30 (d), 130.49 (d), 146.79 (s), 147.04 (s), 148.95 (s), 149.44 (s), 150.27 (s × 2), 151.64 (s), 155.42 (s); ¹²⁵Te NMR (C₆D₆, 85.1 MHz, 300 K) δ 1143; UV–vis (hexane) λ_{max} 640 (ε 180); high-resolution FAB-MS, obsd m/z 955.3307 ([M + H]⁺), calcd for C₄₂H₈₃⁷²GeSi₆¹²⁸Te 955.3375. **4**: blue-green crystals, mp 200–203 °C; ¹H NMR (C₆D₆, 500 MHz, 300 K) δ 0.15 (s, 18H), 0.30 (br s, 18H), 0.31 (br s, 18H), 0.48 (s, 18H), 1.48 (s, 1H), 2.93 (s, 1H), 2.98 (br s, 1H), 3.30 (br s, 1H), 6.48 (br s, 1H), 6.63 (br s, 1H); ¹³C NMR (C₆D₆, 125 MHz, 300 K) δ 1.02 (q), 1.99 (q), 2.22 (q), 4.24 (q), 29.18 (d), 30.46 (d), 31.64 (d), 50.49 (d), 124.37 (d), 129.82 (d), 146.47 (s), 147.08 (s), 148.35 (s × 2); ¹²⁵Te NMR (C₆D₆, 85.1 MHz, 300 K) δ 1009; UV–vis (hexane) λ_{max} 604 (ε 119); high-resolution FAB-MS, obsd m/z 912.2589 (M⁺), calcd for C₃₄H₇₈⁷⁴GeSi₈¹³⁰Te 912.2541 (or C₃₄H₇₈⁷⁴GeSi₈¹²⁸Te 912.2514).

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diarylgermanetellone. Under similar reaction conditions, germirene **8** bearing a bis(trimethylsilyl)methyl (Dis) group also reacted with elemental tellurium to afford the expected alkylaryl-substituted germanetellone **4**¹¹ as stable blue-green crystals in a quantitative yield (Scheme 1).

Germanetellones **3** and **4** were very sensitive toward moisture especially in solution but thermally very stable; **3** and **4** melted at 205–210 and 200–203 °C, respectively, without decomposition, and no dimerization was observed in solution up to 90 °C [¹H NMR (C₆D₆, sealed tube)]. Interestingly, **3** and **4** are quite stable toward light either in solution or in the solid state in sharp contrast to the stable telluroketone 1,1,3,3-tetramethylindantellone, which is extremely light sensitive even toward the fluorescent light.⁴ Both **3** and **4** showed characteristic absorption maxima attributed to *n*– π^* transitions of the Ge=Te unit [636 (for **3**) and 599 (for **4**) nm in benzene], with the diaryl-substituted **3** being red shifted (37 nm) compared with the alkylaryl-substituted **4**. These absorption maxima were red shifted relative to those observed for germanethione **1**⁶ and germaneselone **2**⁷ [444 (for **1**) and 513 (for **2**) nm in benzene]. The ¹²⁵Te NMR of **3** and **4** in C₆D₆ showed singlet signals in the region at 1143 and 1009 ppm, respectively, although it is at much higher field than that of 1,1,3,3-tetramethylindantellone (2858 ppm in CDCl₃).⁴

The molecular structures of both **3** and **4** were revealed by X-ray crystallographic analysis,¹² and the ORTEP drawing of **4** is shown in Figure 1. 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 **3** and **4** 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 **3** and **4** have completely trigonal planar geometry, the sum of bond angles around the germanium atom being 359.5° (for **3**) and 360.0° (for **4**). The Ge–Te bond distances of **3** and **4** [2.398(1) and 2.384(2) Å] are ca. 8% shorter than those reported for typical germanium–tellurium single bonds (2.59–2.60 Å)¹³ and in good agreement with the calculated bond length of H₂Ge=Te (2.36 Å),¹⁴ showing an unambiguous double-bond character between germanium and tellurium.¹⁵ These values for **3** and **4** are still shorter than that reported for Parkin's compound [2.446(1) Å],⁵ clearly indicating the double-bond nature of **3** and **4**. In germanetellone **3**, there seems to be no

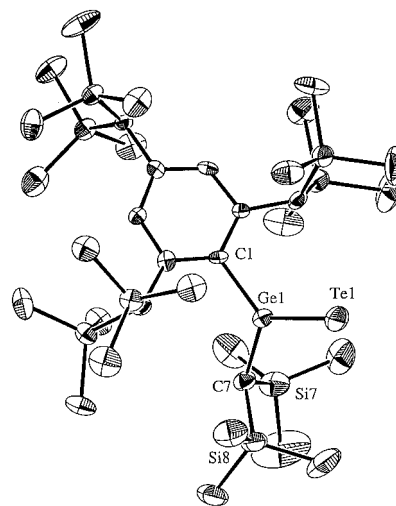


Figure 1. ORTEP drawing of germanetellone Tbt(Dis)Ge=Te (**4**) with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg): Ge(1)–Te(1) 2.384(2), Ge(1)–C(1) 1.981(9), Ge(1)–C(7) 1.924(11); Te(1)–Ge(1)–C(1) 123.3(3), Te(1)–Ge(1)–C(7) 118.7(3), C(1)–Ge(1)–C(7) 118.0(4).

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 **1**⁶ and germaneselone **2**.⁷ In the case of **4**, an even larger value (57°) was observed for the dihedral angle between the planes of the Tbt and Ge=Te groups.

In conclusion, we have synthesized both diaryl- and alkylarylgermanetellones **3** and **4** and determined their crystallographic structures. In view of the fact that no isolable compound has been reported even for a telluroketone, it should be noted that **3** and **4** bearing carbon substituents on the Ge atom can be isolated as thermally and photochemically stable crystalline compounds which have a Ge–Te double bond as revealed by X-ray crystallography.

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Supporting Information Available: Experimental procedures for the synthesis and reaction of germanetellone **3** with physical properties of the starting materials and reaction products **7–9**, and crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **3** and **4** (71 pages). See any current masthead page for ordering and Internet access instructions.

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(12) Crystallographic data for **3**: C₄₂H₈₂GeSi₆Te, MW = 955.81, triclinic, space group *P*1, *a* = 13.541(7) Å, *b* = 20.613(8) Å, *c* = 9.778(5) Å, α = 97.14(4)°, β = 90.81(5)°, γ = 97.98(4)°, *V* = 2683(2) Å³, *Z* = 2, *D*_c = 1.183 g cm⁻³, μ = 12.62 cm⁻¹, *R* (*R*_w) = 0.057 (0.042). Crystallographic data for **4**: C₃₄H₇₈GeSi₈Te, MW = 911.86, triclinic, space group *P*1, *a* = 12.841(8) Å, *b* = 22.118(8) Å, *c* = 9.534(6) Å, α = 91.73(4)°, β = 109.49(5)°, γ = 87.82(4)°, *V* = 2557(2) Å³, *Z* = 2, *D*_c = 1.184 g cm⁻³, μ = 13.65 cm⁻¹, *R* (*R*_w) = 0.046 (0.057). Full details for the crystallographic analysis of **3** and **4** are described in the Supporting Information.

(13) A search of the Cambridge Crystallographic Database indicates the following metrical data for Ge–Te single bonds (given in the order of the mean value, range, and number of observations of the distribution): 2.59 Å, 2.59–2.60 Å, and 8. For example, see: Weidenbruch, M.; Ritschl, A.; Peters, K.; Schnering, H. G. *J. Organomet. Chem.* **1992**, *437*, C25.

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