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A Kinetically Stabilized Stannanetellone, a Tin−Tellurium Double-Bonded Compound

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Summary: A kinetically stabilized stannanetellone was synthesized by the telluration of an extremely hindered stannylene with (n-Bu)$_3$P═Te. The structure of the stannanetellone was determined by X-ray crystallographic analysis.

Compounds containing a double bond between heavier group 14 and 16 elements,[1−4] i.e., heavier congeners of a ketone (called "*heavy ketones*"), are fascinating synthetic targets. We have already reported the syntheses and isolations of the kinetically stabilized heavy ketones Tbt(Ar)Si═X and Tbt(R)Ge═X (Ar = Dip, Tip; R = Tip, Dis; X = S, Se, Te) by taking advantage of an efficient steric protection substituent, the Tbt group.[1a−c,h,i] In Chart 1 these abbreviations are defined. Although we have reported the attempted synthesis of a lead−sulfur double-bonded compound protected by the Tbt group, Tbt$_2$Pb═S, it was found that the plumbanethione could be generated and trapped at low temperature but underwent ready isomerization to the corresponding plumbylene (Tbt(TbtS)Pb:) via the migration of the Tbt group at ambient temperature.[5] Therefore, it should be of great interest whether the compounds having an Sn═X (X = S, Se, Te) bond have real existence in a ketone form (R$_2$Sn═X) or a stannylene form (R(RX)Sn:). To date, some examples of thermodynamically stabilized Sn═X systems such as **1**−**3**[3] have been reported (Chart 2), but they are highly perturbed by the electron donation from the neighboring nitrogen atoms, as evidenced by their high-field chemical shifts in their ^{119}Sn NMR spectra. On the other hand, we recently reported the synthesis and isolation of the kinetically stabilized stannanechalcogenones Tbt(Ditp)Sn═S[4c] and Tbt(Ditp)Sn═Se[4b,c] (Chart 1), examples of the intrinsic nature of tin−chalcogen double-bond compounds. To extend this chemistry, we became interested in the synthesis of an as yet unknown, kinetically stabilized tin−tellurium double-bonded compound (stannanetellone). The elucidation of properties of a stannanetellone is important for the systematic understanding of the heavy ketones.

Chart 1

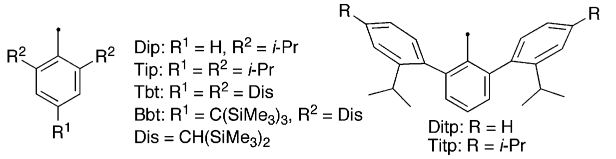
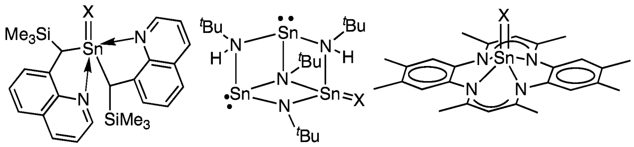


Chart 2



1a: X = S
1b: X = Se
1c: X = Te

2a: X = S
2b: X = Se
2c: X = Te

3a: X = S
3b: X = Se

We present here the synthesis and isolation of a stable stannanetellone by taking advantage of the kinetic stabilization afforded by the combination of 2,6-bis[bis(trimethylsilyl)-methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) and 2,2″,4,4″-tetraisopropyl-*m*-terphenyl-2′-yl (Titp) substituents on the tin atom, together with a crystallographic structural analysis.

Stannylene **5**, a possible precursor for the synthesis of a stable stannanetellone, was readily obtained by the reduction of the corresponding dibromostannane **4** with KC$_8$ in benzene at room temperature (Scheme 1).[6] Stannylene **5** was isolated as air- and moisture-sensitive deep purple crystals in 52% yield. The ^{119}Sn NMR spectrum of **5** in C$_6$D$_6$ showed only one signal at 1657 ppm relative to tetramethylstannane (δ 0), which is a characteristic chemical shift of a divalent organotin compound.[7] The molecular structure of **5** was determined by X-ray crystallographic analysis (Figure S1, Supporting Information).

The telluration of **5** using (n-Bu)$_3$P═Te as a tellurium source[1c,8] was achieved at −40 °C. Stannanetellone **6** was isolated as light green crystals by recrystallization from hexane in 73% yield (Scheme 1). Stannanetellone **6** was very sensitive toward moisture but surprisingly stable toward light, in sharp

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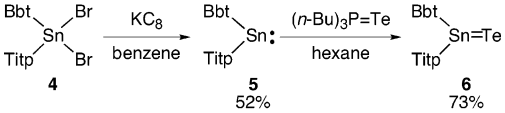
10.1021/om0604627 CCC: $33.50

Scheme 1



contrast to the carbon analogues, telluroketones, which are known to be extremely labile even under fluorescent light.[9] The UV−vis spectrum of **6** in hexane showed two absorption maxima at 436 (ϵ = 1400) and 646 nm (ϵ = 80), which were assigned to the $\pi-\pi^*$ and n$-\pi^*$ electron transitions for the Sn=Te chromophore, respectively.[10] The λ_{max} value of 646 nm for the n$-\pi^*$ transition is larger than those for any of the other corresponding heavy ketones, Tbt(Ar)M=X (M = Si, Ge; X = S, Se, Te) and Tbt(Ar)Sn=X (X = S, Se), and this result is consistent with the tendency that the n$-\pi^*$ absorptions of heavy ketones are systematically red-shifted with increasing atomic number of the group 14 and 16 elements.[1]

The NMR spectra of stannanetellone **6** displayed the characteristic features expected of a tin−tellurium double-bond compound. That is, the ^{119}Sn NMR spectrum showed only one broad signal at 282 ppm,[11] which could be assigned to the sp^2 tin atom of the stannanetellone **6**. In contrast to the case for **1c** and **2c** (−350 and −397 ppm),[3d,h] the low-field chemical shift of **6** was characteristic of a double-bonded compound containing a tin atom.[12] The ^{125}Te NMR spectrum of **6** showed a singlet signal at 1007 ppm, similar to those of germanetellones reported earlier (1143 and 1009 ppm in C_6D_6).[2]

The structural parameters of stannanetellone **6** were definitively determined by X-ray crystallographic analysis at −170 °C (Figure 1).[13] One can see that the Sn=Te bond of **6** is effectively protected by the *o*-CH(SiMe$_3$)$_2$ units of the Bbt group and an *o*-isopropyl group of the Titp group. The Sn1−Te1 bond distance (2.5705(6) Å) is shorter by about 6.5% than the average for Sn−Te single bonds[14] and is in good agreement with the calculated Sn=Te bond length of Ph$_2$Sn=Te (2.589 Å). The length of the Sn=Te bond of **6** was slightly shorter than those of **1c** and **2c** (2.618(1) and 2.603(1) Å, respectively).[3d,h] The tin atom of **6** was found to have a completely trigonal planar geometry (the sum of the angles being 359.68°), indicating the structural similarity to the carbonyl carbon atoms of ketones.

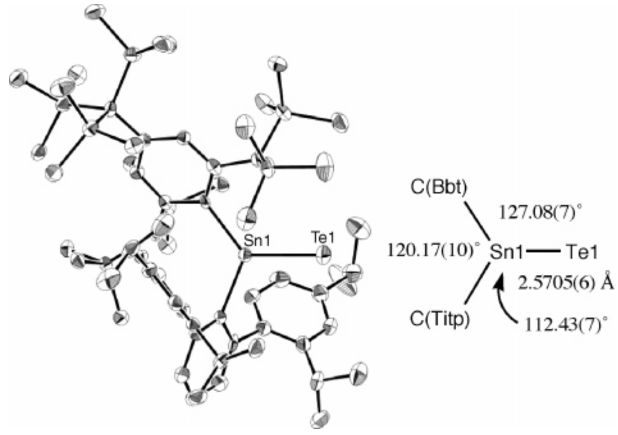
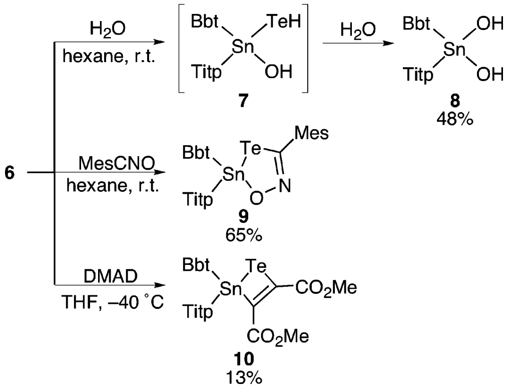


Figure 1. ORTEP drawing of Bbt(Titp)Sn=Te (**6**) with thermal ellipsoid plots (50% probability). Hydrogen atoms and a hexane molecule are omitted for clarity.

Scheme 2



Stannanetellone **6** was found to undergo some addition reactions with small molecules (Scheme 2). Hydrolysis of **6** gave dihydroxystannane **8**, most probably via intermediate **7**. Mesitonitrile oxide reacted as a 1,3-dipole reagent with **6** to give the expected [2 + 3] cycloadduct **9**. The reaction of **6** with dimethyl acetylenedicarboxylate (DMAD) resulted in the formation of the corresponding [2 + 2] cycloadduct **10**. The reaction mode of **6** was found to be similar to those of other heavy ketones.[1,4]

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Supporting Information Available: Text, tables, and figures giving experimental details, theoretical calculations, and ^{1}H NMR spectra for **5**, **6**, **9**, and **10** and CIF files giving X-ray structural data for **5**, **6**, **8**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) For recent examples of the use of (*n*-Bu)$_3$P=Te as a tellurium source, see: (a) Sasamori, T.; Mieda, E.; Takeda, N.; Tokitoh, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 3717. (b) Zhang, T.; Piers, W. E.; Parvez, M. *Can. J. Chem.* **2002**, *80*, 1524. (c) Knight, L. K.; Piers, W. E.; McDonald, R. *Chem. Eur. J.* **2000**, *6*, 4322.

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(10) Assignments of the observed two absorption maxima for **6** are reasonably supported by the TDDFT(B3LYP) calculations for Ph$_2$Sn=Te (406 ($\pi-\pi^*$) and 612 nm (n$-\pi^*$)). (Figure S4, Supporting Information).

(11) Although the coupling constant between ^{119}Sn and ^{125}Te is thought to be diagnostic of the degree of the multiple-bond character, it was not observed by ^{119}Sn and ^{125}Te NMR spectroscopy.

(12) Sn=Sn: (a) Goldberg, D. E.; Harris, D. H.; Lappert, M. F.; Thomas, K. M. *J. Chem. Soc., Chem. Commun.* **1976**, 261. (b) Wiberg, N.; Lerner, H.-W.; Vasisht, S.-K.; Wagner, S.; Karaghiosoff, K.; Nöth, H.; Poikwar, W. *Eur. J. Inorg. Chem.* **1999**, 1211. Sn=C: (c) Meyer, H.; Baum, G.; Massa, W.; Berger, S.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 546. (d) Anselme, G.; Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *Organometallics* **1992**, *11*, 2748. (e) Mizuhata, Y.; Takeda, N.; Sasamori, T.; Tokitoh, N. *Chem. Commun.* **2005**, 5876. Sn=Si: (f) Sekiguchi, A.; Izumi, R.; Lee, V. Y.; Ichinohe, M. *J. Am. Chem. Soc.* **2002**, *124*, 14822. Sn=Ge: (g) Chaubon, M. A.; Escudié, J.; Ranaivonjatovo, H.; Satge, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2621. (h) Sekiguchi, A.; Izumi, R.; Lee, V. Y.; Ichinohe, M. *Organometallics* **2003**, *22*, 1483. (i) Schäfer, A.; Saak, W.; Weidenbruch, M. *Organometallics* **2003**, *22*, 215. Sn=P: (j) Couret, C.; Escudié, J.; Satgé, J.; Raharinirina, A.; Andrriamizaka, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 8280. (k) Ranaivonjatovo, H.; Escudié, J.; Couret, C.; Satgé, J. *J. Chem. Soc., Chem. Commun.* **1992**, 1047. Sn=N: (l) Ossig, G.; Meller, A.; Freitag, S.; Herbst-Irmer, R. *J. Chem. Soc., Chem. Commun.* **1993**, 497.

(13) Crystallographic data for **6**: $C_{66}H_{118}Si_7SnTe$, M_r = 1354.52, monoclinic, space group $P2_1/c$, a = 13.871(4) Å, b = 22.050(6) Å, c = 23.776(6) Å, β = 90.492(3)°, V = 7272(3) Å^3, Z = 4, D_c = 1.237 g cm^{-3}, μ = 0.895 cm^{-1}, R1 = 0.0362, wR2(all data) = 0.1142. GOF = 1.244, largest diff peak and hole 1.718 and −0.996 e Å^{-3} (around the Te atom).

(14) The average of Sn−Te single bonds in X−Sn−Te−X systems (26 examples) is 2.751 Å (Cambridge Structural Database).