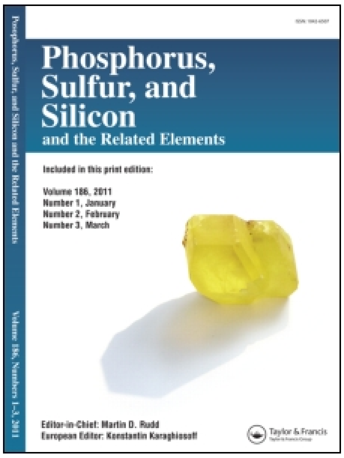

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Synthesis and Characterization of the First Stable Stannanetelone

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The first example of a stable stannanetellone was synthesized and isolated by taking advantage of kinetic stabilization afforded by the combination of steric protecting groups, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt) and 2,2″,4,4″-tetraisopropyl-m-terphenyl-2′-yl groups. The structural parameters and spectroscopic data of the isolated stannanetellone were systematically compared with those previously reported for the lighter congeners, i. e., the stannanethione and stannaneselone. Attempted synthesis of a stannanetellone by the reaction of dilithiostannane with tellurium dichloride is also described.

Keywords dilithiostannane; kinetic stabilization; stannanetellone; stannanethione; stannanesellone; steric protection

INTRODUCTION

Since ketones play very important roles in organic chemistry, much interest has been focused on the chemistry of double-bond compounds between heavier group 14 and group 16 elements, i.e., "*heavy ketones*."[1,2] We have already succeeded in the synthesis and isolation of various *heavy ketones* as stable compounds by taking advantage of the method of kinetic stabilization.[1a–d,3] Although there has been no report on the synthesis of a stable tin–tellurium doubly bonded compound, except for a few thermodynamically stabilized systems, we have recently succeeded in the synthesis and isolation of a stannanetellone kinetically

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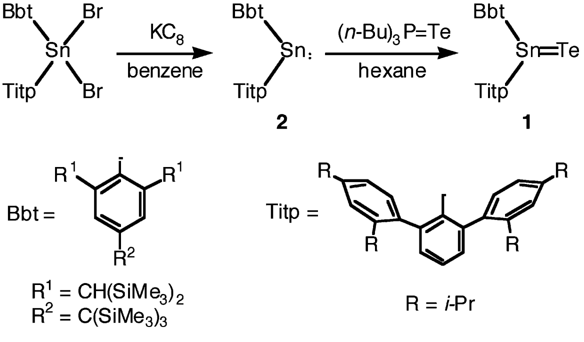
stabilized by the combination of 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl] phenyl (Bbt) and 2,2″,4,4″ tetraisopropyl-*m*-terphenyl-2′-yl (Titp) groups.[4] Here, we describe the results of several synthetic approaches toward a stable stannanetellone together with the structural and spectroscopic characterization of the isolated stannanetellone.

RESULTS AND DISCUSSIONS

Synthesis of Stable Stannanetellone and Stannanethione

Stannanetellone **1** was synthesized by the reaction of the corresponding overcrowded stannylene **2**, which was prepared by the reduction of Bbt(Titp)$SnBr_2$ using KC_8 in benzene, with $(n\text{–}Bu)_3P\text{=}Te$ in hexane at −40°C. Stannanetellone **1** was isolated by recrystallization from hexane as light green, moisture-sensitive crystals in 73% yield (Scheme 1). In contrast to the ready photochemical decomposition of kinetically stabilized Telluroketones,[5] **1** was found to be stable toward light. In the electronic spectrum in hexane, **1** showed two absorption maxima at 436 ($\varepsilon = 1400$) and 646 nm ($\varepsilon = 80$), which could be assigned to the π-π^* and n-π^* electron transitions for the Sn = Te chromophore, respectively.



SCHEME 1

In the ^{119}Sn NMR spectrum, **1** showed only one broad signal at 282 ppm, which can be assignable to the low-field chemical shift of a tin-containing double-bond compound. The ^{125}Te NMR chemical shift for **1** was observed as a singlet signal at 1007 ppm, which was similar to those of germanetellones (1143 and 1009 ppm in C_6D_6).[1a–d]

The molecular structure of **1** was determined by the X-ray crystallographic analysis. The space-filling model drawing of **1** (Figure 1) shows that the Sn=Te bond was effectively protected by the *o*-$CH(SiMe_3)_2$ unit of Bbt group and the isopropyl units of Titp group. The Sn1–Te1 bond

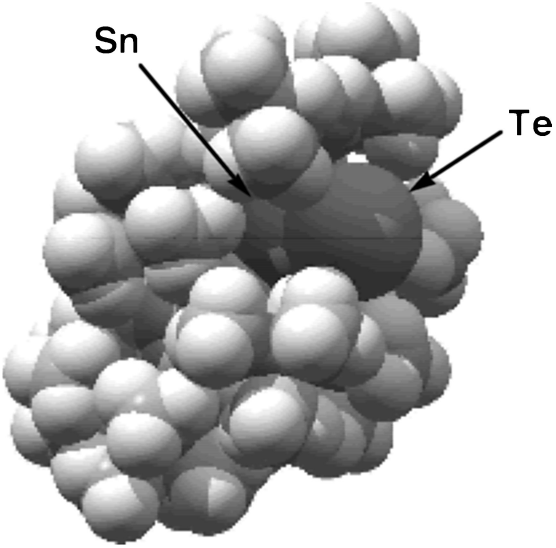


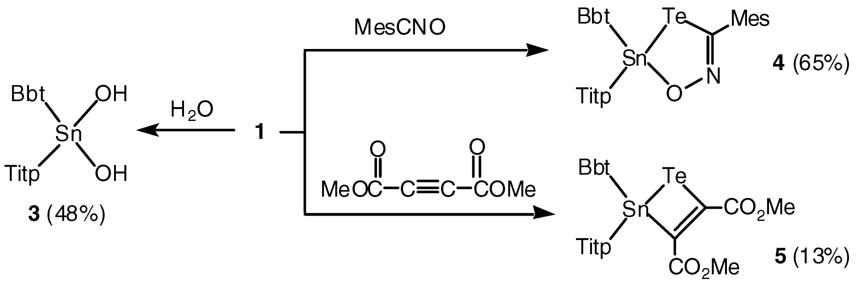
FIGURE 1 Modecular structure of **1**.

distance experimentally obtained for **1** [2.5705(6) Å] is shorter by about 6.5 % than the average of Sn—Te single bonds,[6] and in good agreement with the calculated Sn=Te bond length of $Ph_2Sn{=}Te$ (2.589 Å). It should be noted that the sum of the angles around the central tin atom was found to be 359.68°, indicating the completely planar geometry similar to that of the carbonyl carbon atoms of ketones.

Stannanetellone **1** was found to undergo the addition reaction with small molecules such as water to give dihydroxystannane **3**. Mesitonitrileoxide, a 1,3-dipolar reagent, also reacted with the tin-tellurium double bond of **1** to give [2+3] cycloadduct **4**. The reaction of **1** with dimethyl acetylenedicarboxylate resulted in the formation of the corresponding [2+2] cycloadduct **5** (Scheme 2). The reaction mode of stannanetellone **1** was found to be almost similar to those of the previously reported *heavy ketones*.[1a–d,3]

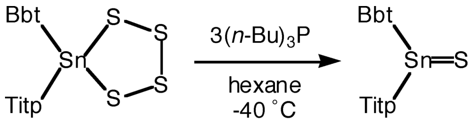
Thus, the direct telluration of the overcrowded stannylene **2** bearing Bbt and Titp groups gave the first stable stannanetellone **1**, which was found to have a completely trigonal planar geometry around the tin atom with a remarkably short Sn–Te bond. It should be noted that stannanetellone **1**, which does not undergo any dimerization and/or isomerization at ambient temperature, is the heaviest analogue of stable "*heavy ketones*."

As for the tin-chalcogen double-bond systems, we have already succeeded in the synthesis of stable stannanethione and



SCHEME 2

stannaneselone, Tbt(Ditp)Sn=Ch [Ch=S (**6**); Ch=Se (**7**); Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Ditp = 2,2″-diisopropyl-*m*-terphenyl-2′-yl].[3] However, the crystallographic structural analysis of stannanethione **6** has not been achieved yet due to its low crystallinity. With the successful results for the case of stannanetellone **1**, we applied the combination of Bbt and Titp groups to the kinetic stabilization of stannanethione. In order to synthesize Bbt(Titp)Sn=S (**9**) we used the corresponding bulky tetrathiastannolane **8** as a precursor as in the case of **6**. Similarly to the synthesis of **6**,[3] treatment of **8** with 3 equiv of tributylphosphine in hexane at −40°C, followed by removal of tributyphosphine sulfide gave orange crystals of **9** (Scheme 3). Although stannanethione **9** was highly moisture-sensitive, it survives in a benzene solution as a stable compound without any decomposition even on heating at 60°C for 3 h in a sealed tube. Furthermore, we have succeeded in the X-ray structural analysis of stannanethione **9** as expected. The Sn1–S1 bond distance [2.221(3) Å] is shorter by about 9% than those of typical tin–sulfur single bonds and in good agreement with the calculated Sn=S bond length of $Ph_2Sn=S$ (2.254 Å). The calculated natural atomic Mulliken charges on the sp^2 tin and sulfur atoms in the model system, $Ph_2Sn=S$, are +0.741 and −0.430, respectively (at B3LYP/6-31+G(d) [TZ(2d) for Sn] level), indicating that stannanethiones should have a considerable extent of a polarized $Sn^{\delta+}=S^{\delta-}$ double-bond character.

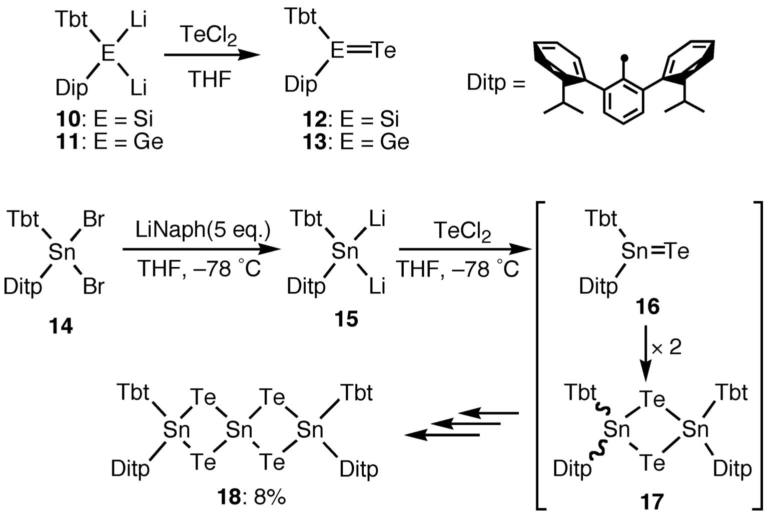


8 **9** (56%)

SCHEME 3

Attempted Synthesis of Stannanetellone by the Reaction of Dilithiostannane with $TeCl_2$

On the other hand, it is well known that dilithiosilanes and dilithiogermanes are useful for the preparation of double-bond compounds of heavier group 14 elements.[7] We have already reported the synthesis of silanetellone **12** and germanetellone **13** by the reactions of overcrowded dilithiometallanes **10** and **11** with tellurium(II) dichloride, respectively (Scheme 4).[7g] Taking into account of these results, the dilithiostannane should be a good precursor for the synthesis of a tin-tellurium double-bond compound. We reported that tin-chalcogen double-bond compounds having Tbt and 2,4,6-triisopropylphenyl (Tip) groups on the tin atom easily underwent self-dimerization giving 1,3,2,4-dichalcogenadistannetanes at room temperature.[8]In order to stabilize a stannanethione and stannanesellone effectively, it was thought to be necessary to use a combination of extremely bulky ligands such as 2,2″-diisopropylphenyl-*m*-terphenyl-2′-yl (Ditp) and Tbt group.[3] Therefore, we tried the synthesis of stannanetellone having Tbt and Ditp groups. However, the treatment of Tbt(Ditp)$SnLi_2$ (**15**)[9] with tellurium(II) dichloride in THF at −78°C did not afford the expected stannanetellone **16** but resulted in the formation of a unique cyclic compound **18** (8%) along with TbtTeTeTbt (11%), DitpH (70%) and TbtH (73%). Orange crystals of **18** are stable under air at least for a several weeks. The ^{119}Sn NMR signals of the cyclic compound,



SCHEME 4

spirobi(ditelluradistannetane) **18**, were observed at −149, −384, and −387 ppm in C_6D_6. The ^{125}Te NMR chemical shifts of **18** were observed at 762.9, 765.0, 766.0, 771.3 ppm in C_6D_6. The molecular structure of **18** was finally determined by the X-ray crystallographic analysis. Both two ditelluradistannetane rings were found to be nearly planar (the sums of interior bond angles are 359.99° and 359.91°, 00respectively). The three tin atoms were situated in a linear alignment (the angle of Sn2–Sn1–Sn3: 179.9°). All the Sn–Te bond lengths of **18** [2.7445(13)–2.7661(13) Å] are in the range of Sn—Te distances reported for 1,3,2,4-ditelluradistannetanes, $[(Dis)_2SnTe]_2$ [Dis = $CH(SiMe_3)_2$] [2.756(1) and 2.771(1) Å][10a] and $[(t\text{-}Bu)_2SnTe]_2$ [2.754(1) and 2.758(1) Å].[10b]

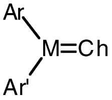
Although the formation mechanism of cyclic compound **18** is not clear at present, the formation of the final product (**18**) is most likely interpreted in terms of a mechanism similar to the case of the formation of a spirobi(dithiadisiletane) in the reaction of a silylene with S_8 via the corresponding silanethione and silanethione dimer.[11] Thus, **18** might be formed via the dimerization of the initially generated stannanetellone **16** and the subsequent reactions of the resulted stannanetellone dimer (**17**). Although it was found to be difficult to synthesize a stable stannanetellone by this synthetic method, it was suggested that more effective combination of the steric protection groups is necessary to synthesize and isolate a stable stannanetellone.

Comparison of Structural Parameters among Heavy Ketones

With stable stannanethione **9** and stannanetellone **1** in hands, we can make a systematic comparison among the diaryl-substituted *heavy ketones*, such as the structural parameters, spectroscopic properties, chemical reactivities, etc. For example, the experimentally obtained structural parameters [d(M=Ch) Å, % bond-shortening parameters, and $\Sigma\angle M$ /deg] are summarized in Table 1 together with those theoretically optimized.

In all cases, the bond distances between the group 14 elements and chalcogen atoms determined by X-ray structural analysis are in good agreement with those obtained by theoretical calculations. Although they show similar percentage bond-shortening values around 9%, stannanetellone **1** has clearly smaller percentage bond-shortening parameter (7%) as compared with the other *heavy ketones*. Even having such differences, all *heavy ketones* have $\Sigma\angle M$ /deg values nearly 360° indicating the similarity among the ketones and other *heavy ketones*.

TABLE I Structural Parameters of Diaryl-substituted *Heavy Ketones*.

	Ar	Tbt	Tbt	Tbt	Tbt	Bbt	Tbt	Bbt
	Ar′	Tip	Tip	Tip	Tip	Tilp	Dilp	Tilp
	M	Si	Ge	Ge	Ge	Sn	Sn	Sn
	Ch	S	S	Se	Te	S	Se	Te
	d(M-ch)/A	1.984(4)	2.049(3)	2.180(2)	2.398(1)	2.221(3)	2.375(3)	2.5705(6)
Observed	% bond shortening	9	9	9	9	8.9	9	7
	Σ∠M/deg	359.9	359.4	359.3	359.5	359.4	359.9	359.7
	d(M-Ch)/Å	1.945	2.042	2.174	2.373	2222	2.346	2.543
Calcd[1]	% bond shortening	9.4	9.5	92	8.6	8.9	8.5	8.1

1) Calcd at B3LYP/6-31+G(d) [TZ(2d) for Sn] level.
2) Tip = 2,4,6 -triisopropylpheny 1.

CONCLUSIONS

By taking advantage of a new combination of steric protecting groups, Bbt and Titp, we have succeeded in the synthesis and isolation of the first stable stannanetellone, Bbt(Titp)Sn=Te (**1**), as light green crystals. All the spectroscopic data and structural parameters of **1** indicated that stannanetellone **1** has a double bond between its tin and tellurium atoms and the trigonal planar geometry around the tin center, as well as the central carbon atom of ketones.

In addition to the successful isolation of stannanetellone **1**, the combination of Bbt and Titp groups was found to be useful to isolate stannanethione **9** as stable crystals suitable for the X-ray crystallographic analysis.[12] At this stage, the crystallographic analysis was completed for all the tin-containing *heavy ketone* series. It should be noted that the definite bond-shortening as compared with the corresponding single bonds and the completely planar geometry for the central tin atom were observed even in the heaviest combination of tin-tellurium double-bond, as well as the other lighter congeners (RR'M=Ch; M=Si, Ge; Ch=S, Se, Te). This is in sharp contrast to the case of lead-containing *heavy ketones* (RR'Pb=Ch; Ch=S, Se, Te), which were reported to be very difficult to isolate and predicted to undergo migration of the substituent giving the corresponding plumbylene isomer.

The chemistry of *heavy ketones* is now entering a new stage, in which the double-bond properties of these new species will be utilized as the key to the development of new functions and materials.

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