Generation of an Organotellurium(II) Cation

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We expected that the chemical trapping products of lowcoordinated tellurenyl cation species can also be kinetically stabilized by the Tbt or Bbt group. Recently, we have reported the halogenation reactions of Bbt-substituted ditelluride, BbtTeTeBbt, leading to the formation of the $\mathrm{Te}^{\mathrm{II}}\mathrm{-}\mathrm{Te}^{\mathrm{IV}}$ mixed-valent tellurenyl fluoride, BbtTeTe(F)₂Bbt, and tellurenyl halides, BbtTeX (X = Cl, Br, I). During the dehalogen-

Introduction

A number of studies on sulfur(II) cations, RS⁺, have been reported, and they have raised interest in many research fields.^[1] Although analogous species of selenium(II) and tellurium(II) cations have also attracted much attention, only a few examples are known, because they are difficult to isolate as a result of their intrinsic high reactivity.^[2] Thus, only a few chalcogen(II) cationic species have been structurally characterized to date.^[3] The tellurium(II) cation, [2,6-(Me₂NCH₂)₂C₆H₃Te]⁺ PF₆⁻, was stabilized by intramolecular coordination of the N atom, though no structural details were disclosed.^[4] Recently, by applying the (N,C,N) "pincer" ligand, Silvestru and co-workers have succeeded in the first isolation of tellurium(II) cation species as stable crystals.^[5]

On the other hand, methyl or 4-fluorophenyl-substituted ditelluride was reported to be oxidized by nitrosonium salts, giving the corresponding transient tellurium(II) cation species.^[6] The generation of the tellurium(II) cationic species was confirmed only by the isolation of the corresponding phosphane adduct. In recent studies, there are two remarkable reports on the trapping reaction of tellurium(II) cation species, where synthesis of aryltellurium(II) cations stabilized by the coordination of NHC (Scheme 4)^[7] and the [1+2] adducts of tellurium(II) cations with alkynes^[8] were reported by the Beckmann and Seppelt groups, respectively. Meanwhile, we have succeeded in the first chemical trapping of a stibinidene (R-Sb:), which exhibits a structure that is isoelectronic to that of a tellurium(II) cation, by tak-

ation reactions of these tellurium halides, it is rational to postulate the formation of a tellurenyl cation species as an intermediate. In this paper, we report the successful trapping of tellurenyl cation species with butadienes or triphenylphosphane, and the regeneration of the tellurenyl cation species by thermal retro [1+4] cycloaddition of the diene adducts.

ing advantage of a bulky aryl substituent, Tbt, or Bbt group.^[9,10] Accordingly, we expected that the chemical trapping products of low-coordinated tellurium(II) cation species can be kinetically stabilized by the Tbt or Bbt group. Recently, we have reported the halogenation reactions of Bbt-substituted ditelluride, BbtTeTeBbt, leading to the formation of the mixed-valent ditelluride difluoride, BbtTe- $Te(F)_2Bbt$ (2) and tellurium(II) halides, BbtTeX (3, X = Br, 4, X = I.^[11] It is rational to postulate the formation of tellurium(II) cation species 1 as an intermediate during the dehalogenation reactions of 2-4. In this paper, we present the successful trapping of tellurium(II) cation species 1⁺ with butadienes or triphenylphosphane and the regeneration of 1^+ by thermal retro [1+4] cycloaddition of the diene adducts.

Results and Discussion

BbtTeTe(F)₂Bbt (2) was treated with 2 equiv. of TMSOTf or TMSNTf₂ in the presence of isoprene or 2,3-dimethyl-1,3-butadiene in hexane at -40 °C for 1 h. The color changed from dark-red to colorless, and then a colorless solid precipitated. The crude product was recrystallized from CH₂Cl₂/hexane. As a result, the corresponding diene adducts 5, 6, and 8 were obtained in yields of 70, 88, and 77%, respectively. On the other hand, the reaction of BbtTeI (4) with $AgBF_4$ in the presence of 2,3-dimethyl-1,3butadiene afforded diene adduct 7 (71%, Scheme 1). The debromination reaction of 3 with AgOTf in the presence of 2,3-dimethyl-1,3-butadiene (Scheme 2) also afforded cycloadduct 6 (66%), which is identical with the product obtained from 2. Thus, the formation of [1+4] adducts 5–8 is most likely to have proceeded through an intermediate tellurium(II) cation species generated by the dehalogenation reactions of 2 and 3.

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Scheme 1. Synthesis of diene adducts 5-8.



Scheme 2.

On the other hand, the reaction of 2 with TMSOTf or TMSNTf₂ in the presence of triphenylphosphane gave the corresponding phosphane adducts 9 and 11 as yellow solids in yields of 67% and 54%, respectively. The reaction of BbtTeBr (3) with AgBF₄ in the presence of triphenylphosphane afforded phosphane adduct 10 (67%, Scheme 3). Since the blank experiments of the treatment of tellurium(II) halides 2 and 3 with dienes and phosphanes in the absence of TMSOTf or Ag⁺ salt resulted in no reactions, the formation of phosphane adducts 9, 10, and 11 from 2 mentioned above strongly suggest the generation of 1⁺ species.



Scheme 3. Synthesis of phosphane adducts 9-11.

The molecular structures of **5–11** were unambiguously determined by X-ray crystallographic analysis.^[12] The molecular structures of **6** and **9** are shown in Figures 1 and 2. All cycloadducts exhibit pseudo-trigonal-bipyramidal geometry as hypervalent species.^[13] The phosphane adducts **9–11** exhibit T-shaped structures, slightly distorted for steric reasons [as can be seen in compound **9**; C–Te–P 103.25(8)°, Te–P–O 76.91(5)°]. The P–Te–O angle in **9** is almost linear [174.95(9)°]. These remarkable structural parameters are

similar to those of PPh₃Te(Ph)I.^[14] There are weak interactions between Te⁺ and counterion. It was found that the interactions increase in the order TfO⁻ > BF₄⁻ > NTf₂⁻ on the basis of the observed Te⁺···counterion distances (Table 1), and there seems to be almost negligible interaction between NTf⁻ and Te⁺ in **11**. The Te⁺···anion distances of carbene adducts **12** and **13** (Scheme 4) are 3.270(4) (Te···Cl) and 3.651(6) Å (Te···I), which are shorter than the sums of the van der Waals radii, 3.81 and 4.04 Å, respectively. In contrast, the Te···O distance in **11** is 3.605(3) Å, which is longer than the sum of the van der Waals radii (3.60 Å). However, the phosphane adduct PhTe(PPh₃)I contains a rather covalent Te–I bond [3.0930(9) Å].



Figure 1. Molecular structure of 6 with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.



Figure 2. Molecular structure of 9 with thermal ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity.

The ¹²⁵Te NMR chemical shifts of telluronium compounds **5–11** in CDCl₃ are shown in Table 1. The signals for the diene adducts, excluding compound **5**, appeared at around 600 ppm, while those of the phosphane adducts were observed at around 465 ppm.^[15] No reason can be offered for the observed signal of compound **5** at 713 ppm. These results indicate that the central Te^{IV} moieties of diene adducts **6–8** would be slightly affected by the counteranion depending on the distance, and the electronic effects of the

Table 1. Some structural parameters and ¹²⁵Te NMR chemical shifts for compounds 5-11.

	5	6	7	8	9	10	11
Te–anion distance [Å] Sum of the van der Waals radii ^[16] [Å] ¹²⁵ Te NMR chemical shifts [ppm]	2.916(9) Te–O: 3.60 713	2.894(5) Te-O: 3.60 613	2.955(8) Te-F: 3.24 607	2.988(5) Te-O: 3.60 593	3.072(2) Te-O: 3.60 464	3.189(3) Te-F: 3.24 463	3.605(3) Te–O: 3.60 465



Scheme 4. Reported carbene adducts of aryltellurium(II) cations 12 and 13.

counteranion toward those of phosphane adducts 9-11 would be negligible.

Thermolysis of 5 in $[D_6]$ benzene in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (120 °C for 1 h in a sealed tube) afforded the corresponding diene-exchanged product 6 quantitatively. Moreover, 6 was heated in the presence of 10 equiv. of triphenylphosphane in $[D_6]$ benzene to give phosphane adduct 9 quantitatively. These results can be most likely interpreted in terms of the intermediacy of the tellurium(II) cations $(1^{+} [TfO]^{-})$ in the thermal retrocycloaddition of the diene adduct 6 (Scheme 5). Thermolysis of **6** in the absence of a trapping reagent under the same conditions resulted in the formation of a red solution containing a sole product, compound X. Although compound X would be the expected species 1⁺[OTf]⁻, it has not been identified yet because it was difficult to perform detailed spectroscopic analysis of the product due to its extreme instability even in an inert atmosphere, giving BbtTe-TeBbt.



Scheme 5. Thermolysis of diene adduct 5.

Further investigation on the synthesis and isolation of tellurium(II) cations with a new bulky ligand is currently in progress.

Experimental Section

Compounds 5, 6, and 8: To a hexane solution (10 mL for 5, 5 mL for 6, 8) of BbtTeTe(F)₂Bbt (2) (100 mg, 64.8 µmol for 5, 50.0 mg, 32.4 µmol for 6, 8) in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene (0.5 mL) was added trimethylsilyl trifluoro-methansulfonate (23.4 mL, 12.3 µmol for 5 11.7 µL, 64.8 µmol for 6) or *N*-trimethylsilyl bis(trifluoromethanesufonyl)imide (14.9 µL, 64.8 µmol for 8), and the reaction mixture was stirred for 1 h at -78 °C. The mixture was then warmed up to room temperature. The colorless precipitates were washed with hexane and dried in vacuo. Analytically pure samples were obtained by crystallization from CH₂Cl₂/hexane. Yields: 70% (87.7 mg, 90.5 µmol) for 5, 88% (56.0 mg, 57.0 µmol) for 6, and 77% (55.7 mg, 50.0 µmol) for 8.

Compound 7: To a benzene (10 mL) solution of BbtTeI (100 mg, 11.4 μ mol) in the presence of an excess amount of 2,3-dimethyl-1,3-buadiene (0.5 mL) was added AgBF₄ (22.1 mg, 11.4 μ mol) in

benzene (5 mL), and the mixture was stirred for 1 h at 0 °C. The mixture was then warmed up to room temperature. The resulting white precipitate was filtered and recrystallized from toluene at -40 C to afford a colorless solid. Yield: 71% (74.5 mg, 80.9 µmol).

Compounds 9 and 11: To a hexane (10 mL) solution of BbtTeTe-(F₂)Bbt (2) (50 mg, 32.4 µmol) in the presence of triphenylphosphane (15.0 mg, 48.6 µmol, 1.5 equiv.) was added trimethylsilyl trifluoromethansulfonate (11.7 µL, 64.8 µmol for 9) or *N*-trimethylsilyl bis(trifluoromethanesufonyl)imide (14.9 µL, 64.8 µmol for 11), and the mixture was stirred for 1 h at -78 °C. The mixture was then warmed up to room temperature. Filtration of the reaction mixture followed by purification with gel permeation liquid chromatography afforded the phosphane adducts. Analytically pure samples were obtained by crystallization from CH₂Cl₂/hexane for 9, toluene for 11. Yields: 67% (50.5 mg, 43.4 µmol) for 9 and 54% (45.5 mg, 0.0351 mmol) for 11.

Compound 10: To a benzene (10 mL) solution of BbtTeBr (50 mg, 60.0 μ mol) in the presence of PPh₃ (23.6 mg, 90.0 μ mol) was added AgBF₄ (11.7 mg, 60.0 μ mol) in benzene (5 mL), and the mixture was stirred for 1 h at 0 °C. The mixture was then warmed up to room temperature. Filtration of the reaction mixture followed by purification with gel permeation liquid chromatography afforded the crude product. An analytically pure sample of **10** was obtained by crystallization from CH₂Cl₂/hexane. Yield: 67% (44.2 mg, 40.1 μ mol).

Supporting Information (see footnote on the first page of this article): General procedures, analytical data, and X-ray diffraction studies for compounds **5**–11.

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