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Generation and detection of tellurane [10–Te–4(C4)] and selenurane [10–Se–4(C4)] having alkyl and aryl ligands

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Abstract—Formation of 2,2'-biphenylylenedimethylselenurane and -tellurane was observed by the ¹H, ¹³C, ⁷⁷Se, and ¹²⁵Te NMR studies at low temperature, in the reactions of dibenzoselenophene *Se*-oxide and 2,2'-biphenylylenedibromotellurane with methyllithium. These hypervalent compounds were unstable and decomposed at room temperature to give the corresponding dibenzochalcogenophenes quantitatively. © 2005 Elsevier Ltd. All rights reserved.

Hypervalent compounds of main group elements have attracted attention as a key compound for generation of new functional molecules.¹ Though σ -tetracoordinated chalcogen species (chalcogenuranes) [10–M–4, M = S, Se, Te]² are in general less stable than usual chalcogen species, which obey the octet rule, chalcogenuranes can be stabilized by the strongly electronegative atoms (oxygen, nitrogen, fluorine, etc.) and electron-withdrawing ligands on the apical positions. Five-membered ring also contributes the stabilization due to fixation of the hypervalent structure (TBP configuration). Several chalcogenuranes bearing only carbon ligands have been reported, but most of the corresponding isolable compounds have been stabilized by one or two five-membered ring connecting apical and equatorial positions.³

We have systematically studied the syntheses and characterization of organo-chalcogenuranes [10–M–4(C4), M = S, Se, Te], and have succeeded in detection and isolation of the new chalcogenuranes having only carbon ligands.⁴ However the ligands employed in the preparation of these chalcogenuranes (IV) have been restricted to aryl groups. Gedridge et al. prepared tetramethyland tetravinyl-telluranes as a hypervalent organotellurium (IV) compound.⁵ Hellwinkel et al. and Hori et al.

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tried to prepare telluranes and sulfuranes bearing biphenylylene and alkyl ligands, but they could not succeed even in the detection of such telluranes and sulfuranes.^{6,11} Although hexacoordinated hypervalent chalcogen (VI) species, pertelluranes having alkyl and/or aryl ligands recently have been reported by Morrison et al. and Akiba et al.,⁷ the direct detection and isolation of sulfurane and selenurane [10-M-4(C4), M = S, Se] having at least one alkyl ligand have never been reported. We, therefore, tried to synthesize and characterize the hypervalent chalcogen compounds (IV) having alkyl and aryl ligands. Here we report the first generation of 2,2'-biphenylylenedialkylchalcogenuranes and their reactivities.

In general, telluranes (IV) are more stable than the corresponding selenurane (IV) and sulfurane (IV). Thus, we tried first to prepare 2,2'-biphenylylenedimethyltellurane (**2a**) [10–Te–4(C4)]. When 2.2 equimolar amounts of MeLi (1.02 M, diethylether solution) were added to a suspension of 2,2'-biphenylylenedibromotellurane (**1**) in anhydrous tetrahydrofuran- d_8 (THF- d_8) in an NMR tube (ϕ 5 mm) under an argon atmosphere at -78 °C, the mixture turned to a yellow homogeneous solution. Structure of the product **2a** was identified by the ¹H, ¹³C, ¹²⁵Te NMR experiments at low temperature⁸ (Scheme 1).

The ¹H and ¹³C NMR spectra of the product 2a in the aromatic region revealed that the two benzene rings on the biphenylylene group are equivalent. In the ¹H

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Scheme 1. Preparation of chalcogenuranes having alkyl and aryl ligands.

NMR two doublet and two triplet peaks assigned to the aromatic rings were observed. A set of six peaks in ¹³C NMR clearly indicates that there is one kind of benzene rings.⁹ Interestingly, the ¹H signal of the methyl protons on **2a** appeared at 1.67 ppm together with satellite peaks due to ${}^{1}\text{H}{-}^{125}\text{Te}$ spin-spin coupling (${}^{2}J_{\text{H-Te}} =$ 36.0 Hz) as shown in Figure 1. The integral ratio of these satellite peaks and the total peaks is nearly equal to the natural abundance of 125 Te atoms. Furthermore, the proton non-decoupled ¹²⁵Te signal of 2a in THF- d_8 appeared at 154 ppm as a septet due to a spin-spin coupling between the tellurium and the hydrogen nuclei of the two methyl groups (${}^{2}J_{\text{Te-H}} = 36.0 \text{ Hz}$). The ${}^{2}J_{\text{Te-H}}$ value is nearly the same with that of Me_4Te (34.0 Hz). These results suggest that the two methyl ligands combine directly with the central tellurium atom and the pseudorotation of 2a took place rapidly on the NMR time scale at low temperature.¹⁰

Next, we tried to prepare the 2,2'-biphenylylenedimethylselenurane (**2b**) [10–Se–4(C4)]. A suspension of dibenzo-



Figure 1. Proton non-decoupling ¹²⁵Te NMR (126 MHz, THF- d_8 , -78 °C) (left) and ¹H NMR (400 MHz, THF- d_8 , -78 °C) (right) of **2a**.

selenophene Se-oxide (4) reacted with 2.2 equimolar amounts of MeLi (1.02 M, diethylether solution) in the presence of trimethylsilyl triflate (Me₃SiOTf) in anhydrous tetrahydrofuran- d_8 in an NMR tube (ϕ 5 mm) under an argon atmosphere at -90 °C. The mixture turned to a pale yellow homogeneous solution. This product **2b** was characterized by the ¹H, ¹³C, ⁷⁷Se NMR experiments at -90 °C.⁸

The ¹H and ¹³C NMR spectra of the compound **2b** in the aromatic region supported equivalence of the two benzene rings in the biphenylylene group. These signal patterns were similar to those of **2a**. The methyl protons on **2b** appeared as a main peak at 1.74 ppm together with the satellite peaks due to spin–spin coupling between the hydrogen and the selenium nuclei $({}^{2}J_{H-Se} = 17.5 \text{ Hz})$ in ¹H NMR (Fig. 2). Intensity of the satellite peaks depended on the natural abundance of the ⁷⁷Se nucleus. The proton non-decoupled ⁷⁷Se signal of **2b** appeared at 210 ppm as a septet due to ⁷⁷Se–¹H spin–spin coupling (${}^{2}J_{Se-H} = 17.5 \text{ Hz}$). Consequently, the two methyl ligands are considered to be located directly on the central selenium atom and pseudorotation in **2b** occurred faster compared to the NMR time

 $J_{Se-H} = 17.5 \text{ Hz}$ $J_{H-Se} = 17.5 \text{ Hz}$ 1.80 1.70ppm ppm

Figure 2. Proton non-decoupling ⁷⁷Se NMR (76 MHz, THF- d_8 , -90 °C) (left) and ¹H NMR (400 MHz, THF- d_8 , -90 °C) (right) of **2b**.

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scale even at low temperature.¹⁰ Thus we could succeeded in the direct detection of 2,2'-biphenylylenedimethylselenurane **2b** by low temperature NMR experiments. As far as we know, this is the first detection of selenurane [10-Se-4(C4)] containing alkyl ligands.

Trost et al. and Hori et al. have reported the generation and reactivities of 2,2'-biphenylylene diaryl sulfuranes [10–S–4(C4)].¹¹ They prospected that these sulfuranes should have a configuration similar to that of products **2a,b.** Immediate ligand coupling reactions of 2,2'-biphenylylene diaryl sulfuranes usually proceed at room temperature to afford the corresponding *o*-terphenyl aryl sulfide derivatives quantitatively. On the other hand, both products **2a,b** decomposed to give only dibenzotellurophene **3** or dibenzoselenophene **5** quantitatively, which are probably produced by the ligand coupling reaction without a ring-opening of dibenzochalcogenophene moiety. The other corresponding ligand coupling product of **2a,b**, ethane, could not be detected by NMR experiments at room temperature.^{11e}

Furthermore, we tried to prepare the 2,2'-biphenylylenedimethylsulfurane (2c, X=S) [10-S-4(C4)] using dibenzothiophene S-oxide 6 according to a method similar to that for the corresponding selenurane 2b. However, the corresponding sulfurane 2c could not be detected by NMR experiments even at -90 °C, and only dibenzothiophene 7 as a final product was observed by NMR experiments at room temperature.^{11d,e}

In conclusion, we reported that the formation of 2,2'biphenylylenedimethyltellurane **2a** and -selenurane **2b** having alkyl and aryl ligands was detected in the reactions of the corresponding precursors **1** and **4** with methyllithium by various NMR spectroscopies at low temperature. In each chalcogenurane (IV), pseudorotation between two ligands on the central atom should take place rapidly on the NMR time scale even under low temperature and chalcogenuranes **2** decomposed at room temperature to give the corresponding dibenzochalcogenophenes quantitatively. Further studies are in progress to detect and isolate novel chalcogenanes having other carbon ligands.

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Supplementary data

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- ¹H NMR 8. 2,2'-Biphenylylenedimethyltellurane (2a); (400 MHz, THF- d_8 , -78 °C) δ 1.67 (s, with satellite peaks: $J_{H-Te} = 36.0 \text{ Hz}, 6H$, 7.29 (t, J = 8.0 Hz, 2H, 4-ArH), 7.37 (t, J = 8.0 Hz, 2H, 5-ArH), 7.62 (d, J = 8.0 Hz, 2H, 3-ArH),8.10 (d, J = 8.0 Hz, 2H, 6-ArH). ¹³C NMR (100 MHz, THF- d_8 , -78 °C) δ 20.7, 122.9, 128.6, 129.4, 132.0, 139.4, 144.6. ¹²⁵Te NMR (126.3 MHz, THF- d_8 , -78 °C) δ 154 (sept, $J_{\text{Te-H}} = 36.0 \text{ Hz}$, relative to Me₂Te). 2,2'-Biphenylylenedimethylselenurane (2b); ¹H NMR (400 MHz, THF d_8 , -90 °C) δ 1.74 (s, with satellite peaks: $J_{\text{H-Se}} = 17.5 \text{ Hz}$, 6H), 7.38 (t, J = 8.0 Hz, 2H, 4-ArH), 7.45 (t, J = 8.0 Hz, 2H, 3-ArH), 7.96 (d, J = 8.0 Hz, 2H, 3-ArH), 8.23 (d, J = 8.0 Hz, 2H, 6-ArH). ¹³C NMR (100 MHz, THF- d_8 , -90 °C) δ 23.7, 123.8, 125.6, 126.9, 127.7, 139.3, 140.3. ⁷⁷Se NMR (76 MHz, THF- d_8 , -90 °C) δ 210 (sept, $J_{Se-H} =$ 17.5 Hz, relative to Me₂Se). The ¹H and ¹³C NMR chemical shifts of both products 2a, b were assigned by the cross peaks observed in the two dimensional NMR spectra.
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