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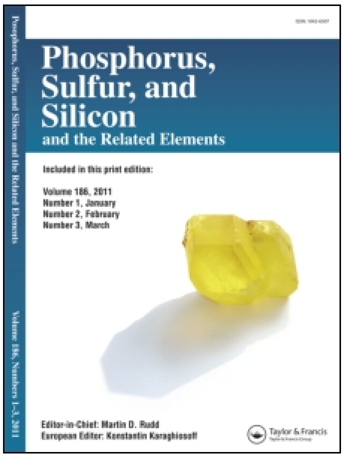

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Renji Okazaki; Masaichi Saito; Norihiro Tokitoh

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STABLE STANNANESELONE AND DISELENASTANNIRANE: NOVEL ORGANOTIN COMPOUNDS DERIVED FROM AN EXTREMELY HINDERED TETRASELENASTANNOLANE

RENJI OKAZAKI, MASAICHI SAITO† and
NORIHIRO TOKITOH
Department of Chemistry, Graduate School of Science, The
University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan.

The first kinetically stabilized stannaneselone, Tbt(Ditp)Sn=Se (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl; Ditp = 2,2"-diisopropyl-*m*-terphenyl-2'-yl), with a tin–selenium double bond and a stable diselenastannirane, Tbt(Ditp)$SnSe_2$ were synthesized by deselenation of the corresponding tetraselenastannolane, Tbt(Ditp)$SnSe_4$ with 3 equiv. and 2 equiv. triphenylphosphine, respectively. The X-ray structural analysis of the stannaneselone revealed that it has a trigonal planar structure with the Sn–Se bond length of 2.375(3) Å, which is approximately 9% shorter than that of the corresponding single bond and the shortest among Sn–Se bond lengths so far reported. The molecular structure of diselenastannirane determined by X-ray analysis shows that it has an unusually long Se–Se bond (2.524 Å), about 0.2 Å longer than a typical Se–Se single bond.

Keywords: stannanethione; stannaneselone; diselenastannirane; steric protection; dechalcogenation; tetrachalcogenastannolanes

INTRODUCTION

In recent decades, significant progress has been made in the chemistry of heavier main group elements with unusual coordination states and strained molecular structures, especially in the field of group 14 elements.[1] Although one can see a number of reports on the synthesis and isolation of stable doubly bonded organosilicon compounds and their germanium analogs,[2] the chemistry of such species containing tin has been still less explored.

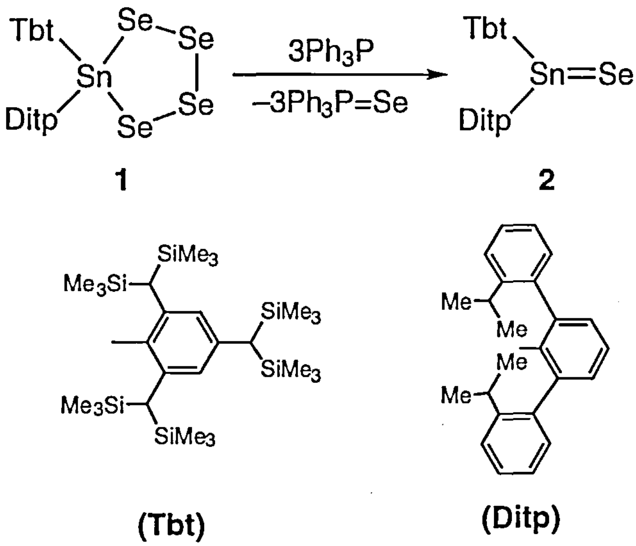
We previously reported that tetrachalcogenametallolanes Tbt(Ar)MX_4 (M = Si, Ge; X = S, Se) bearing an extremely bulky substituent, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt), are good precursors of heavier element analogues of ketones, Tbt(Ar)M=X,[3] which we refer to as "heavy ketones". We have also found that various types of metallacycles can be synthesized using these heavy ketones.[3]

We report here that the deselenation of a tetraselenastannolane by a phosphine reagent affords a stannaneselone without intramolecular coordination or a diselenastannirane, depending on the equivalence of the phosphine reagent used. Each of them represents the first isolation of such a species.

RESULTS AND DISCUSSION

Tetraselenastannolane Tbt(Ditp)$SnSe_4$ (**1**; Ditp = 2,2"-diisopropyl-*m*-terphenyl-2'-yl) was easily obtained in 38% yield (Scheme 1) by the reactions of the corresponding stannylene Tbt(Ditp)Sn: with excess of elemental selenium. Our previous observation that Tbt(Tip)Sn=Se (Tip = 2,4,6-triisopropylphenyl) readily dimerized at ambient temperature and its ^{119}Sn NMR was unable to be measured led us to use a much bulkier Ditp group[4] instead of Tip group after some trials with other substituents.

When Tbt(Ditp)$SnSe_4$ (**1**) was allowed to react with 3 equiv. triphenylphosphine in refluxing hexane for 2 h under argon, the solution turned deep red and a ^{119}Sn NMR signal was observed at 440 ppm, indicating the formation of stannaneselone **2**. Filtration of triphenylphosphine selenide insoluble in hexane, followed by removal of hexane resulted in the isolation of the stable stannaneselone **2** as red crystals in 84% yield. Compound **2** represents the first kinetically stabilized stannaneselone although those thermodynamically stabilized by intramolecular coordination have been reported.[5]



Scheme 1

The molecular structure of stannaneselone **2** was determined by X-ray crystallographic analysis. The ORTEP drawing (Figure 1) shows that the stannaselenocarbonyl unit is effectively protected by one disyl group in Tbt and two isopropyl groups in Ditp which are directed toward the Sn=Se bond in order to avoid the steric repulsion with the Tbt group. The Sn–Se distance (2.375(3) Å) is approximately 9% shorter than a Sn–Se single bond length (2.55-2.60 Å) and slightly shorter than that of the Parkin's terminal selenido complex (2.39 Å).[5] The geometry around the tin atom is trigonal planar, the sum of the angles being 359.9 °, indicative of structural similarity to a ketone.

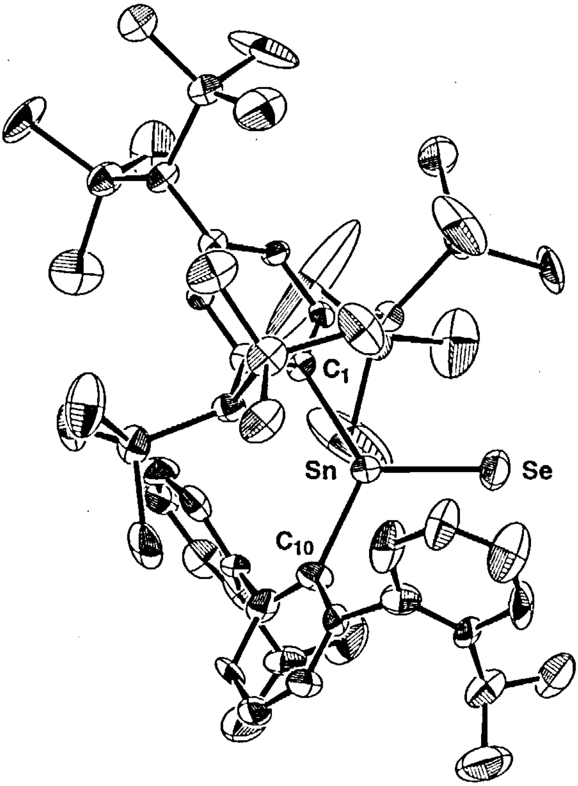
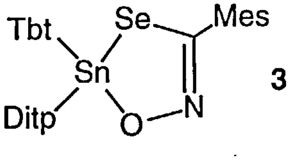


FIGURE 1. ORTEP drawing of Tbt(Ditp)Sn=Se (**2**).



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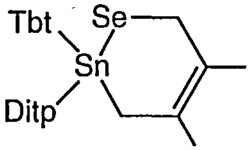

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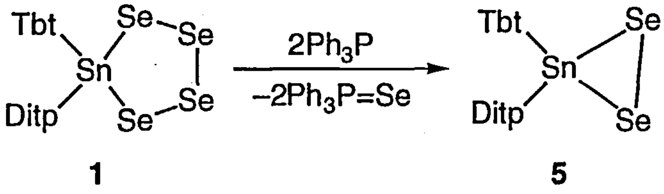
Stannaneselone **2** thus obtained reacted with mesitonitrile oxide and 2,3-dimethyl-1,3-butadiene to afford the corresponding cycloadducts **3** and **4** in 90 and 60%, respectively like silicon and germanium analogues.[3] It should be noted that the introduction of the Ditp group of high steric demand enables the isolation of **2**, yet it does not retard the reactivity of **2** with a small reagent.

Interestingly, treatment of **1** with 2 equiv. of triphenylphosphine in hexane at room temperature, followed by removal of triphenylphosphine selenide gave orange-red crystals of diselenastannirane **5** in 56% (Scheme 2). In ^{119}Sn NMR a broad signal was observed at –406 ppm assignable to **5**. This high-field signal is characteristic of tin-containing three-membered compounds (e. g., Sn–Sn–Se, –393 ppm[6]). The ^{77}Se NMR also showed a characteristic high-field signal at –193 ppm as have been similarly observed for a Sn–Sn–Se (–378 ppm) ring systems.[6]



Scheme 2

These spectral data were consistent with the diselenastannirane structure, but the molecular structure of **5** was finally established by X-ray crystallographic analysis (Figure 2). The diselenastannirane ring system of **5** forms an equilateral triangle. It is noted that the Se–Se bond is very long (2.524(4) Å), about 0.2 Å longer than the typical Se–Se single bond although the Sn–Se bond lengths

(2.528(2), 2.532(3) Å) are slightly shorter than a typical Sn–Se bond length (2.58 Å).

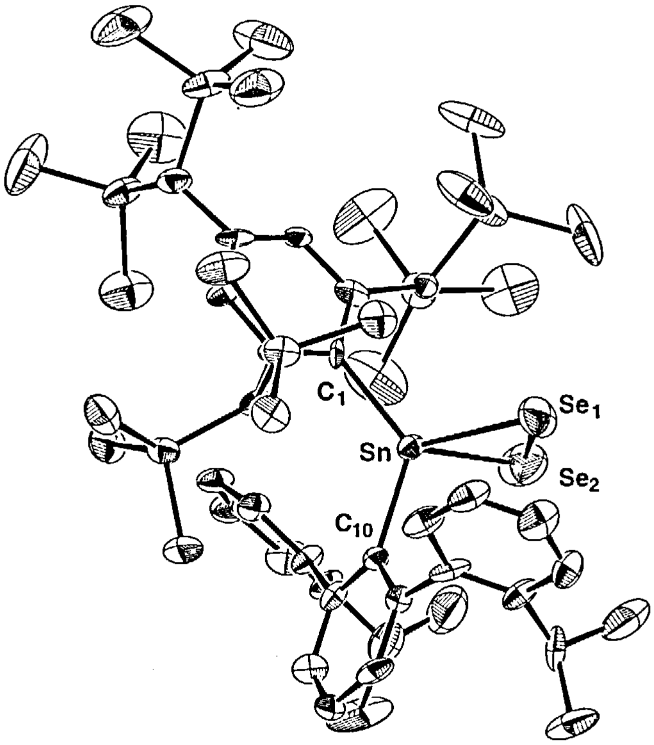


FIGURE 2. ORTEP drawing of Diselenastannirane (**5**).

Compound **5** is noteworthy not only as the first example of a diselenastannirane, but also as the first three-membered heterocycle containing two selenium atoms.

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† Present address: Department of Chemistry, Faculty of Science, Saitama University, Japan.

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