

Note

A novel tin (II) dithioether complex

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Abstract

Organotin and related tin containing compounds are a recurring motif in organometallic chemistry. Here we report a new complex resulting from the reaction of tin (II) chloride with a dithioether diallyl ether ligand created as a side product from other research in our lab. This new complex is reasonably stable and can be synthesized on the bench top with no extraordinary measures required to exclude air or moisture. Its crystal structure reveals a five coordinate pseudo-square pyramidal geometry around tin, with the ligand binding the metal through its thioether sulfurs and the chlorides bridging.

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1. Introduction

Organotin compounds are a mainstay of modern organic synthesis, with such procedures as reductions with tributyltin hydride [1], the addition of carbon–tin bonds to alkynes and dienes [2], the Stille reaction [3], and hydrostannation [4] all well known and widely practiced. Of particular interest to the authors' research are the reactions of tin with allyl and sulfur species. The chemistry of tin with allyl groups is interesting and well studied. Lithium tributyl tin or tin (II) fluoride, when combined with diethyl aluminum chloride, will react with allyl phosphates to replace the phosphate with a tin species [5]. Tin (II) fluorides will also insert into the carbon–iodide bond of a trimethylsilyl substituted allyl iodide [6]. In the presence of a palladium catalyst, similar insertions will occur for tin (II) chloride and allyl acetates [7] or allyl alcohols [8]. Tributyltin hydride, meanwhile, has been reported to cleave sulfur–carbon bonds in dithianes, resulting in addition of the thiols to the tin [9]. Therefore, it is likely that a compound with both allyl and sulfide (thioether) functionality would form inter-

esting products with tin and, if soluble, might provide an opportunity to generate some new ¹¹⁹Sn data. Such a ligand, a dithioether diallyl ether (Fig. 1), has been produced as a byproduct of the authors' research [10]. In this paper, we would like to report the unique structure generated by its reaction with tin (II) chloride in diethyl ether (Fig. 1).

2. Results and discussion

The X-ray structure of our tin dithioether diallyl (Fig. 2) reveals that the tin (II) atoms are in a five coordinate pseudo-square pyramidal geometry gained via chloride bridging, not counting the secondary interaction suggested by the O–Sn distance of 2.887(4) Å. The bond length for the terminal chloride (2.467(2) Å) is comparable to that found in tin (IV) chloride thioether complexes, while the length of the bridging Cl–Sn bond is, of course, slightly longer (2.759(2) Å). Although halide bridging is a motif not seen in similar tin (IV) thioethers, it has been found in other tin (II) [11] and tin (IV) [12] compounds. The square pyramidal geometry also appears to be new to tin-thioether chemistry, but not to tin chemistry in general [13]. Both sulfurs form bonds in the equatorial plane, along

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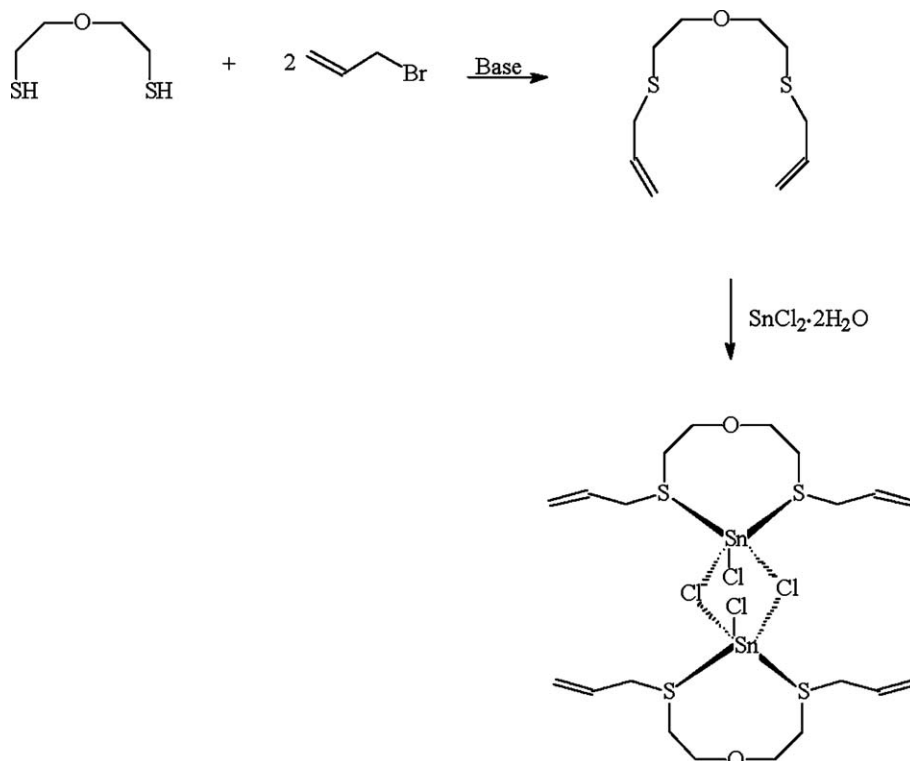


Fig. 1. The synthesis of the diallyl dithioether ligand and its reaction with tin (II) chloride.

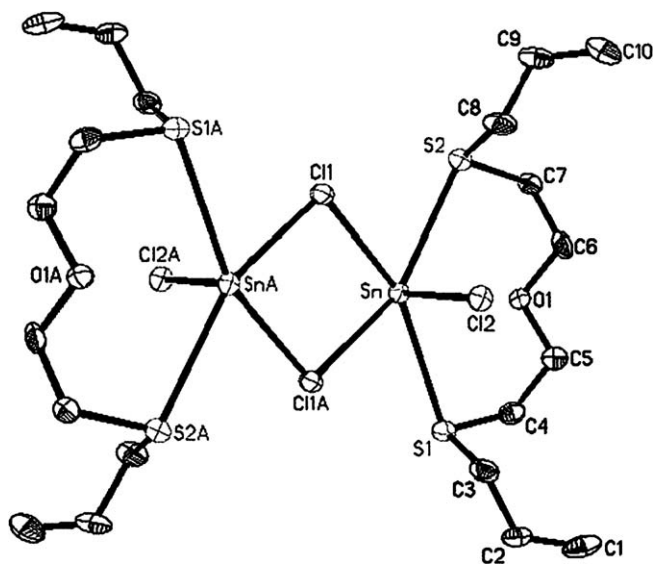


Fig. 2. The tin dithioether diallyl dimer.

with the bridging chlorides. The terminal chloride is axial, with the apparently open axial coordination site occupied by a stereochemically active lone pair. The sum of the equatorial angles is $359.3(2)^\circ$, making them almost perfectly planar. The tin–sulfur bonds are longer than those in tin (IV) thioethers (approximately 3.031(1) versus 2.6–2.7 Å [14–16]). This lengthening of the dative bond can be attributed to the greater electron density on a +2 center as opposed to +4 center. The tin oxygen distance of

2.887(4) Å is well within the sum of van der Waals radii (3.69 Å [17]), suggesting that there is, while perhaps not a true bond, a real interaction between these atoms. Including this interaction in the coordination sphere would put the tin in the rare pentagonal mono-pyramidal geometry [18].

The fact that this compound was recovered at all is quite interesting. Much of the previous work with tin (IV) halides has been performed under rigorous air-sensitive conditions due to the instability of these halides to atmospheric water. However, this comparable tin (II) complex was formed on the bench top, without any special effort being made to exclude water. Therefore, this complex appears to be somewhat more robust than its predecessors. However, if heated under vacuum or left open to the atmosphere for prolonged periods, it will decompose into a thick, yellow gel.

The complex is sparingly soluble in deuterio-chloroform, permitting NMR studies to be performed. The ^1H and ^{13}C NMR of the complex and the decomposition product are identical to that of the free ligand, emphasizing either the weakness of the donor–acceptor bonding in this system or some disassociation in solution. The ^{119}Sn NMR of the complex showed a single, sharp peak at -125.8 ppm. There has been a wide range of ^{119}Sn chemical shifts reported for Sn(II). For example, Lappert has reported shifts from 766 to -193 ppm for two coordinate tin (II) [19]. By comparison, the presumably five coordinate species $\text{SnCl}_2 \cdot (\text{THF})_x$ appears at -238 ppm [20]. Five coordinate organotin (IV) species with bridging chlorides have been

reported at -221 ppm [12], while other five coordinate tin (IV) species were found to range from $+25$ to -329 ppm [21] or from -27.0 to -248.6 ppm [22]. A series of six coordinate tin (IV) tetrachloride dithioethers were found to have shifts from -578 to -560 ppm [15]. Therefore, -125.8 ppm does not appear unreasonable for a chloride containing Sn(II) dithioether. It is very possible, however, that some disassociation occurs and the solution is monomeric rather than a dimer in solution. The ^{119}Sn NMR of the yellow gel resulting from complex decomposition showed four sharp peaks at 900.0 , 843.7 , 702.5 , and -859.4 ppm. This clearly shows that there are a variety of Sn environments present after decomposition. It is worth noting that all but the peak at -843.7 ppm are outside the range expected for Sn(II) and probably represent 4 and 5 coordinate Sn(IV) species.

3. Conclusion

The existence of this compound stands as an example of one of the fortuitous coincidences that often occur in research. Our group did not set out intending to create diallyl dithioether ligands; rather, they were the undesired product of a failed synthetic procedure. However, that undesired product has led to a new and interesting compound. Clearly there is room for further research on the reactions of Sn(II) species with thioethers.

4. Experimental

All reagents were purchased from Aldrich or Acros chemical companies and were reagent grade or better unless otherwise noted. NMR measurements were taken on a Varian Gemini 200 MHz NMR Spectrometer. Mass spectral data was gathered using a JEOL JMS-700T magnetic sector instrument.

Diallyl dithioether ligand: Sodium metal (1.4 g, 61 mmol) was dissolved in absolute ethanol. To this solution was added 2-mercaptoethyl ether (4.0 mL, 31 mmol), followed by 30 min of stirring. Then allyl bromide (5.3 mL, 61 mmol) was added and a white suspension immediately formed. This was refluxed for 3 h, then the ethanol was removed under vacuum, the residue acidified with dilute hydrochloric acid, and extracted with methylene chloride. The methylene chloride was permitted to evaporate, leaving behind the desired product. Yield: 5.78 g (87%) ^1H NMR (CDCl_3 , 200 MHz, δ ppm): 5.79 (m, 2H), 5.15 (d, 2H), 5.05 (s, 2H), 3.61 (t, 4H), 3.15 (d, 4H), 2.64 (t, 4H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 29.9, 35.0,

70.4, 117.1, 134.3; GC-MS: one peak at RT = 14.30 min, $m/z = 177$ ($\text{M}^+ - 1\text{-allyl}$).

Ligand-SnCl₂ complex: tin (II) chloride dihydrate (1.0 g, 4.6 mmol) was dissolved in diethyl ether. To this was added 2O2S3diene (0.97 g, 4.4 mmol) and the solution was refluxed for 24 h. During the course of the reflux, a white precipitate, identified as the complex by NMR, formed. The suspension was filtered and the filtrate placed in a freezer at -30 °C, where non-merohedrally twinned crystals eventually formed. Yield: 1.03 g (28.7%) ^1H NMR: 2.65 (tr, 2H), 3.15 (d, 2H), 3.60 (tr, 2H), 5.11 (m, 2H), 5.75 (m, 1H); ^{13}C NMR (CDCl_3 , 200 MHz, δ ppm): 29.9, 35.0, 70.4, 117.1, 134.3; ^{119}Sn NMR (CDCl_3 , 200 MHz, δ ppm): -125.8

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