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Synthesis and Characterization of Three-coordinated Tin(II)

Chalcogenide Compounds from Chlorostannylene Supported by

 β -diketiminato Ligand

Mingdong Zhong,^{†, a} Yi Ding,^{†, a} Da Jin,^a Xiaoli Ma,^{*, a} Yashuai Liu,^a Ben Yan,^a Ying Yang,^b Jiong Peng,^a and Zhi Yang^{*, a, c}

^a School of Chemistry and Chemical Engineering, Beijing Institute of Technology, 100081 Beijing (P. R. China)

^b School of Chemistry and Chemical Engineering, Central South University, 410083 Changsha (P. R. China)

^c State Key Laboratory of Elemento-organic Chemistry, Nankai University, 300071 Tianjin (P. R. China)

[†] These authors contributed equally to this work.

fax: (+86) 10-68914503; e-mail: maxiaoli@bit.edu.cn; zhiyang@bit.edu.cn.

ABSTRACT

The stable chlorostannylene(II) LSnCl **1** reacted with bases or salts (KOH, *t*-BuOK, Ph₃CSLi or Li₂S), respectively, which led to the formation of a variety three-coordinated tin(II) chalcogens (O or S) (compounds **2**-**5**). Compounds **2** and **5** are bridged bimetallic organotins(II) supported by a bidentate β -diketiminato ligand. Furthermore, the catalytic activity of compounds **2**-**5** for hydroboration with benzaldehyde and acetophenone was investigated, respectively. In the X-ray analyses of all stannylene chalcogenide compounds, the pyramidalization on the tin center are useful to enhanced *p*-character of lone pair. All compounds were characterized by ¹H NMR and ¹³C NMR spectroscopy, single crystal X-ray structural analysis and elemental analysis.

Keywords:

Three-coordinated Tin(II) Chalcogenide bridging Chlorostannylene(II) β -diketiminato ligands Bimetallic organotins

1. Introduction

Owe to the special physical properties and difference from those carbons [1, 2], tin(II) compounds (stannylenes) are well-known and have been investigated as heavier group 14 analogues of carbenes. But they easily dimerize without steric protection, so bulky substituents are necessary to stabilize these species. An alternative strategy for stabilization is the utilization coordination ability by the introduction of anionic chelating ligands such as β -diketiminato, amidinate, aminotroponiminate, dipyrromethene or diimidosulfinate [3-9]. Among the reported stannylenes, we are most interested in the stable N-heterocyclic stannylenes because of their potential to replace N-heterocyclic carbene ligands in metal complexes. Low-coordinated stannylenes have two covalent bonds with high *p*-orbital for complexation and adopt a variety of geometries from a typically two-coordinated bent structure to a four-coordinated pseudo-trigonal bipyramidal structure in which the octet rule is violated [10]. While three-coordinated six-membered stannylenes is unusual, especially, supported by β -diketiminato ligand. Chloride is the reactive ligand and is easily replaced by other small, reactived ligands, such as alkoxide, amide, azide, triflate, and hydride [11]. So after LSnCl-type compounds have been isolated [9], chlorostannylenes are the preferable precursors for the synthesis of organotin derivatives.

Increasing interest in the chemistry of organotin chalcogenides arises from their intriguing chemical and providing possible technological applications in the fields of photocatalysis, semiconductors, fast-ion conductivity, separation, and ion exchange [12]. Recently, Roman Jambor and co-workers used intramolecularly coordinating *built-in* N,C,N-coordinating pincer-type ligands for the synthesis and stabilization of the reactive distannyne [($\{2,6-(Me_2NCH_2)_2C_6H_3\}Sn$)₂]. The reaction of distannyne with the chalcogenide elements as the oxidizing agent reported so many interesting organotin chalcogenides compounds, the classical structrues of monoorganotin chalcogenides (**A**, **E**, **G** and **H**), triseleneoxo/tritelluro stannonic acid anhydride (**B** and **D**) and organotin(II)-tin(II)-oxo cluster (**F**) were showed in the Scheme **1** [13].

We also reported on amido ligand supported tin(II) sulfide and selenide clusters in 2015 [14]. So the low-coordinated stannylenes compounds are fascinating to us.

In this context, we focused our attention on β -diketiminato LH (L = HC(CMeNAr)₂, Ar = 2,6-Et₂C₆H₃) as the ligand to support three-coordinated stannylenes [15]. Four three-coordinated tin(II) chalcogenides were easily synthesized by simple reaction routes and isolated in high yields based on LSnCl **1**, which opened a new synthesis route for organotin chalcogenides. To our surprise, we have synthesized two novel chalcogenide (O and S) bridging bidentate ligand bimetallic tin(II).

2. Results and discussion

Compound LSnCl **1** was prepared from the reaction of LH with *n*-BuLi and SnCl₂ (Scheme **2**) in a molar ratio of 1:1. The reaction of **1** with excess KOH refluxed at 70°C resulted in the products of LSn(μ -O)SnL (2). Compounds **3** and **4** were prepared from **1** with *t*-BuOK and Ph₃CSLi in the same ratio, respectively. Then LSn(μ -S)SnL·C₇H₈ (5) was prepared from the reaction of **1** with Li₂S in a molar ratio of 2:1.

All these compounds (1-5) were characterized by NMR spectroscopic studies as well as by elemental analysis. Compound 1 was published in another journal by our group [16]. In the ¹H NMR spectrum of compound 2, the resonance for methyl protons of the ethyl groups were observed as two triplets (δ : 1.12-1.16 and 1.19-1.23 ppm), while the those of methine protons appeared as a quarter (δ : 2.61-2.63 ppm) and two multiplets (δ : 2.64-2.66 and 2.98-3.03 ppm), the splitting pattern was asymmetric probably due to steric congestion. The C-*Me* and γ -*H* protons appeared as two sharp singlets at δ : 1.75 and 5.25 ppm, as well as the benzene ring protons resonate as a multiplet (δ : 7.08-7.19 ppm). All of the protons were perfectly presented in a 12:8:1:1:6 intensity ratio successively. In compound 4, the resonance for the C-*Me* and γ -*H* protons were slightly upfield shifted (singlets, δ : 1.62 and 4.79 ppm) in comparison to those of compound 2. Further, the methyl and methine protons of the ethyl groups were divided into a triplet and two multiplets, and the protons were also

slightly upfield shifted (δ : 1.07-1.11, 2.39-2.44 and 2.49-2.55 ppm). In compound **5**, γ -*H* protons were slightly upfield shifted (singlets, δ : 4.93 ppm), whereas the rest of their protons were no significant chemical shifted in comparison to those of compound **4**.

Compounds 2, 3, and 4 were isolated from a concentrated *n*-hexane solution, while 5 got crystals from toluene. All crystals are highly soluble in common organic solvents such as toluene, dichloromethane, and tetrahydrofuran, respectively. Complex 2, 4, and 5 crystallized in the monoclinic space group C2/c, $P2_1/c$, and $P2_1/c$ in Table 1, respectively. Complex 3 crystallized in the triclinic space group P-1 in Table 1. The molecular structures of 2-5 are shown in Figure 1-4.

Each three-coordinated tin center in compounds 2, 3, 4, and 5 comprising two nitrogen atoms from the supporting β -diketiminato ligand, one chalcogenide atom (oxygen for 2 and 3, sulfur for 4 and 5). The sum of the bond angles around each tin atom is almost the same (273.2° 2, 268.63° 3 and 273.6° 4), it varies slightly for compound 5 (Sn(1): 269.08° and Sn(2): 267.33°). Therefore, all the tin(II) atoms have a distorted trigonal-pyramidal geometry.

In compound **2**, the Sn–N and Sn–O bond lengths are 2.214 Å, 2.229Å, and 1.9923 Å, respectively, and almost similar distances shown in compound **3** (Sn–N: 2.1916, 2.1922 Å, and Sn–O: 2.0233 Å). The lengths of the Sn–N and Sn–O bonds in compound **3** are almost similar present in [HC(CMeNAr)₂]SnO'Bu (Ar=2,6-^{*i*}Pr₂C₆H₄) (2.2015, 2.2100, and 2.0179 Å) [17]. The average Sn–O bridging bond distance in **2** (1.9923 Å) is shorter than the average Sn–O ligand bond distance in **3** (2.0233 Å) and similar Sn–O bridging bond length in {[C₆H₃-2,6-(Me₂NCH₂)₂]Sn}₂O (1.9931Å) [13g]. The N–Sn–N bond angles in compounds **2** and **3** (83.71° and 84.3°) are larger than [HC(CMeNAr)₂]SnO'Bu (Ar = 2,6-^{*i*}Pr₂C₆H₄) (83.02°) [17]. The bridging oxygen in the Sn–O–Sn moiety in compound **2** shows a bent geometry with the Sn–O–Sn bond angle of 137.23°, which is larger than the Sn–O–C bond angle of 124.48° in compound **3** and similar Sn-O-Sn bond angle of 139.88° present in {[C₆H₃-2,6-(Me₂NCH₂)₂]Sn}₂O [13g]. While the bond distances of Sn-O in **2** (1.9923 Å) is shorter than **3** (2.0233 Å), but the Sn-N bond lengths in **2** (2.214, 2.229 Å) is

larger than **3** (2.1916, 2.1922 Å). It can be ascribed to the steric effect of oxygen-bridged bimetallic organotin.

In compound **4**, the Sn–N and Sn–S bond lengths are 2.204, 2.234 Å, and 2.5353 Å, respectively, and almost similar distances shown in compound **5** (Sn–N and Sn–S bond: 2.205, 2.227Å, and 2.468 Å). The lengths of the Sn–S bonds in compounds **4** and **5** are slightly longer than the Sn–S bonds (2.451 and 2.4207 Å) presented in $\{[PhS(N^{t}Bu)_{2}]SnCl(\mu-S)\}_{2}$ [18] and shorter than bis(metallylene) sulfide compounds Sn–S bonds in $\{[C_{6}H_{3}-2,6-(Me_{2}NCH_{2})_{2}]Sn\}_{2}S$ (2.4758 and 2.4889 Å) [13b].

In compound 5, the bridging sulfur in the Sn–S–Sn moiety shows a bent geometry with an Sn–S–Sn bond angle of 108.00°, which is also larger than the Sn–S–C bond angle of 104.5° in compound 4 and Sn–S–Sn bond angle of 104.27° in $\{[C_6H_3-2,6-(Me_2NCH_2)_2]Sn\}_2S$ [13b], but smaller than triseleneoxo/tritelluro stannonic acid anhydride in $\{[C_6H_3-2,6-(Me_2NCH_2)_2]SnTe\}_2S$ (112.18°) [13e].

The molecular geometries for **2** and **5** were provided in Figures 2 and 5, respectively, the two complexes have similar structural features. However, the bond angle of Sn(1)-O(1)-Sn(1.1) (137.23°) in **2** is larger than the corresponding angle in **5** (Sn(1)-S(1)-Sn(2) 108.00°), and the bond length of Sn-O (1.9923 Å) in **2** is slightly shorter than the corresponding Sn-S bond length in **5** (2.468 Å), as expected. While the bond angle of Sn(1)-O(1)-C(26) (124.48°) in **3** is larger than the corresponding angle in **4** (Sn(1)-S(1)-C(26) 104.50°), and the bond length of Sn-O (2.0233 Å) in **3** is slightly shorter than the corresponding Sn-S bond length in **4** (2.5353 Å). This indicates that ionic interactions of the bridged atom with the central metal tin(II) atom in the ligand decrease from O to S due to the difference of the bridged atomic radii.

1 equiv. HBPin was reacted with 1 equiv. of benzaldehyde or acetophenone by the additions of 3% equiv. compound **2**, **3**, **4**, or **5** in CDCl₃ as the catalysts within 2 or 6 hours at room temperature, respectively. The results of the catalytic hydroborations are summarized in Table 2. The experimental results revealed that compounds **2-5** are active catalysts for hydroboration of benzaldehyde or acetophenone and show up to 73% or 50% yield which was concluded from ¹H NMR spectroscopic analysis, respectively.

The yields of hydroboration were calculated by the characteristic peaks of the remaining reactants and products from ¹H NMR spectroscopic. In comparison, the hydroboration of benzaldehyde or acetophenone showed lower reactivity in the absence of any catalyst. It is clear from the results presented in Table 2 that the catalysis **3** and **4** in hydroboration of benzaldehyde or acetophenone is obviously more efficient than **2** and **5**, because compound **2** and **5** larger steric hindrance. Obviously, the yields of different catalytic hydroboration reactions of the benzaldehyde or acetophenone are almost same. Thus, we presume that compound **2**, **3**, **4**, or **5** has the similar reactivity in the hydroboration of benzaldehyde or acetophenone.

3. Experimental

3.1. General procedures

All manipulations were carried out under a purified nitrogen atmosphere using Schlenk techniques or inside an Etelux MB 200G glovebox. All solvents were refluxed over the appropriate drying agent and distilled prior to use. Commercially available chemicals were purchased from *J*&*K* chemical or VAS and used as received. LH and LSnCl were prepared as described in the literature [15, 16]. Elemental analyses were performed by the Analytical Instrumentation Center of the Beijing Institute of Technology. NMR spectra were recorded on Bruker AM 400 spectrometers. Melting points were measured in sealed glass tubes and were not corrected.

3.2. Synthesis of complexes

Synthesis of $LSn(\mu-O)SnL(2)$

To chlorostannylene LSnCl **1** (0.516 g, 1.0 mmol) in toluene (15 mL) was added drop by drop to a solution of KOH (0.224 g, 4 mmol) excess in toluene (15 mL) under ambient temperature. This mixture was heated at 70 °C for 6 h, cooled, and filtered. Then the solvent was removed in vacuum. The solid was extracted with *n*-hexane (10 mL), and the extract was stored at -18 °C in a freezer for 3 days, and X-ray-quality colorless crystals of **2** were obtained. An additional crop of **2** was obtained from the mother liquor. Total yield: 0.62 g (63%). Mp: 185-187 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ 1.12-1.16 (*t*, 6 H, CH₂*Me*), 1.19-1.23 (*t*, 6 H, CH₂*Me*), 1.75 (*s*,

6 H, *Me*), 2.61-2.63 (*q*, 4 H, C*H*₂Me), 2.64-2.66 (*sept*, 2 H, C*H*₂Me), 2.98-3.03 (*sept*, 2 H, C*H*₂Me), 5.25 (*s*, 1 H, γ -C*H*), 7.06-7.19 (*m*, 6 H, 2,6-Et₂C₆*H*₃) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): δ 13.39, 13.52, 14.17, 22.62, 23.18, 23.61, 23.91 [2,6-(CH₃CH₂)₂C₆H₃, 2,6-(CH₃CH₂)₂C₆H₃, CH₃CN, (CH₃)*C*=N], 99.21 (γ -CH), 124.83, 124.95, 125.61, 125.92, 136.71, 136.85, 139.39, 141.64 (*ipso-*, *o-*, *p-*, *m-*C), 164.52 (NCMe) ppm. Anal. Calcd for C₅₀H₆₆N₄OSn₂ (976.45): C, 61.50; H, 6.81, N, 5.74. Found: C, 61.58; H, 6.89, N, 5.54.

Synthesis of $LSn(\mu-O)$ -^{*t*}Bu (3)

To *t*-BuOK (0.123 g, 1.1 mmol) in toluene (15 mL) was added drop by drop to a solution of chlorostannylene LSnCl **1** (0.516 g, 1.0 mmol) in toluene (15 mL) under ambient temperature to stirring for 24 h and filtered. Then the solvent was removed in vacuum. The solid was extracted with *n*-hexane (10 mL), and the extract was stored at -18 °C in a freezer for 7 days, and X-ray-quality colorless crystals of **3** were obtained. An additional crop of **3** was obtained from the mother liquor. Yield 0.37 g (67%). Mp: 151-155 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ 1.07-1.11 (*d*, 12 H, CH₂*Me*), 1.20, 1.40 (*s*, 9 H, C(C*H*₃)₃), 1.61 (*s*, 6 H, *Me*), 2.28-2.41 (*sept*, 4 H, C*H*₂Me), 2.44-2.55 (*sept*, 4 H, C*H*₂Me), 4.78 (*s*, 1 H, γ -C*H*), 6.99-7.18 (*m*, 6 H, 2,6-Et₂C₆*H*₃) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): δ 12.59, 13.39, 19.54, 21.67, 23.61, 26.58, 28.68, 30.91 [2,6-(CH₃CH₂)₂C₆H₃, 2,6-(CH₃CH₂)₂C₆H₃, CH₃CN, (CH₃)*C*=N], 92.35 (γ -CH), 123.63, 124.83, 136.85, 141.34 (*ipso-*, *o-*, *p-*, *m*-C), 159.92 (NCMe) ppm. Anal. Calcd for C₂₉H₄₂N₂OSn (553.34): 62.94; H, 7.65, N, 5.06. Found: C, 62.98; H, 7.52, N, 5.15.

Synthesis of $LSn(\mu-S)CPh_3$ (4)

To chlorostannylene LSnCl **1** (0.516 g, 1.0 mmol) in toluene (15 mL) was added drop by drop to a solution of Ph₃CSLi(0.311 g, 1.1 mmol) in toluene (15 mL) under ambient temperature to stirring for 24 h and filtered. Then the solvent was removed in vacuum. The solid was extracted with *n*-hexane (10 mL), and the extract was stored at -18 °C in a freezer for 7 days, and X-ray-quality colorless crystals of **4** were obtained. An additional crop of **4** was obtained from the mother liquor. Yield 0.44 g (58%). Mp: 147-148 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ 1.07-1.11 (*t*, 12 H, CH₂*Me*),

1.62 (*s*, 6 H, *Me*), 2.39-2.44 (*sept*, 4 H, CH₂Me), 2.49-2.55 (*sept*, 4 H, CH₂Me), 4.79 (*s*, 1 H, γ -CH), 6.98-7.00 (*m*, 6 H, 2,6-Et₂C₆H₃), 7.15-7.20 (*m*, 15 H, CC₆H₅) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): δ 13.40, 19.53, 20.42, 23.61, 28.67 [2,6-(CH₃CH₂)₂C₆H₃, 2,6-(CH₃CH₂)₂C₆H₃, CH₃CN, (CH₃)C=N, SCPh₃], 92.36 (γ -CH), 123.62, 123.64, 124.25, 124.83, 126.00, 126.03, 126.57, 126.88, 126.90, 127.18, 127.25, 127.98, 128.77, 129.03, 129.09, 129.89, 136.79, 136.82, 141.31 (*ipso-*, *o-*, *p-*, *m*-C), 159.90 (NCMe) ppm. Anal. Calcd for C₄₄H₄₈N₂SSn (755.59): C, 69.94; H, 6.40, N, 3.71. Found: C, 70.22; H, 6.27, N, 3.83.

Synthesis of $LSn(\mu-S)SnL \cdot C_7H_8(5)$

To chlorostannylene LSnCl **1** (0.516 g, 1.0 mmol) in toluene (15 mL) was added drop by drop to a solution of Li₂S (0.023 g, 0.55 mmol) in toluene (10 mL) under ambient temperature. The mixture was stirred overnight at room temperature and filtered. The solution was concentrated to 8 ml and stored at -18 °C in a freezer for 2 days, and X-ray-quality yellow block crystals of 5 were obtained. An additional crop of **5** was obtained from the mother liquor. Total yield 0.78 g (72%). Mp: 176-178 °C. ¹H NMR (400 MHz, CDCl₃, 298 K, TMS): δ 1.07-1.16 (*t*, 12 H, CH₂*Me*), 1.64 (*s*, 6 H, *Me*), 2.45-2.49 (*sept*, 8 H, CH₂Me), 2.51 [*s*, 3 H, LSn(μ -S)SnL·C₆H₅CH₃], 4.93 (*s*, 1 H, γ -CH), 7.07 (*m*, 6 H, 2,6-Et₂C₆H₃) ppm. ¹³C NMR (100 MHz, CDCl₃, 298 K, TMS): δ 14.94, 20.58, 24.65, 24.96, 39.39, 39.60, 39.81, 40.02, 40.23, 40.43, 40.48, 40.64 [2,6-(CH₃CH₂)₂C₆H₃, LSn(μ -S)SnL·C₆H₅CH₃, 2,6-(CH₃CH₂)₂C₆H₃, CH₃CN, (CH₃)*C*=N], 94.31 (γ -CH), 125.30, 126.54, 137.70, 142.15 (*ipso-*, *o-*, *p-*, *m*-C), 161.14 (*NCMe*) ppm. Anal. Calcd for C₅₀H₆₆N₄SSn₂·C₇H₈ (1084.64): C, 60.50; H, 6.70; N, 5,64. Found: C, 60.89; H, 6.77; N, 5.33.

3.3. General procedure for the hydroboration of terminal alkynes by **2***,* **3***,* **4***, and* **5***.*

1 mmol benzaldehyde, HBPin (1 mmol) and CDCl_3 (3 mL) were loaded in a dried *J*-Young Tube under nitrogen atmosphere, respectively. The mixture was placed in a sealed environment and stirred at room temperature and the progress was investigated by ¹H NMR spectroscopy.

The catalyst was added to a solution of benzaldehyde with HBPin (0.155 mL, 1 mmol) in CDCl_3 (3 ml) under nitrogen atmosphere. The mixture was placed in a

sealed environment and stirred at room temperature for 2 h. The catalyst include compound **2**, **3**, **4**, and **5**. The products were determined by ¹H NMR spectroscopy.

Hydroboration of acetophenone catalyzed by compounds **2**, **3**, **4**, and **5** utilized similar method mentioned above except reacted 6 hours.

4. Conclusion

The preparation and fully characterization of two types of chalcogenide organotin have been investigated. While with the 2,6-Et₂C₆H₃ group on the nitrogen atoms all compounds were formed in a η^2 -chelating six-membered SnN₂C₃ ring. For the substitution reaction of chlorostannylene **1** with *t*-BuOK and Ph₃CSLi afforded the corresponding three-coordinated tin compounds **3** and **4** with the Sn-E (E = O, S) bond. In sharp contrast, chlorostannylene **1** reacted with KOH and Li₂S generated to bridged-complexes. Compounds **2** and **5** possessed a chalcogenide (O and S) bridging bidentate ligand organometallic tin. In the X-ray analyses of all stannylene chalcogenide compounds, the pyramidalization on the tin center would be useful to enhanced *p*-character of lone pair on the tin center. These compounds are of particular interest as they present not only the first example of stannylene supported by β -diketiminato ligand but also the new bimetallic of the β -diketiminato ligand toward tin(II) chalcogenide compounds. Further investigation of applications of those tin(II) chalcogenide compounds are now under way.

Appendix A. Supplementary material

CCDC 1825808 (for LSn(μ -O)SnL **2**), 1825806 (for LSn(μ -O)-^{*t*}Bu **3**), 1825807 (for LSn(μ -S)CPh₃ **4**), and 1825805 (for LSn(μ -S)SnL·C₇H₈ **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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Scheme 1. The classical structrues of intramolecularly coordinating pincer-type ligand.



Scheme 2. Preparation of compounds 2, 3, 4, and 5.

Compound	2	3	4	5
Empirical formula	$C_{50}H_{66}N_4OSn_2$	$C_{29}H_{42}N_2OSn$	$C_{44}H_{48}N_2SSn$	$C_{50}H_{66}N_4SSn_2 \cdot C_7H_8$
Formula weight	976.45	553.34	755.59	1084.64
Temperature (K)	153.15	153.15	153.15	153.15
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	C12/c1	<i>P</i> -1	$P2_{1}/c$	<i>P</i> 12 ₁ /c1
<i>a</i> (Å)	26.109(5)	9.0844(15)	13.9329(17)	20.573(4)
<i>b</i> (Å)	8.6988(16)	10.7118(18)	24.043(3)	23.562(5)
<i>c</i> (Å)	23.310(5)	15.150(3)	33.443(4)	22.481(5)
α (deg)	90	103.219(2)	90	90
β (deg)	118.612(2)	97.020(2)	94.102(1)	103.16(3)
γ (deg)	90	95.425	90	90
$V(\text{\AA}^3)$	4647.6(16)	1413.0(4)	11174(2)	10611(4)
Ζ	4	2	12	8
$\rho_{\rm c} ({\rm g/cm}^3)$	1.395	1.301	1.347	1.358
μ/mm^{-1}	1.004	0.926	0.775	1.020
Crystal size(mm)	0.28×0.28×0.18	0.45×0.43×0.18	0.29×0.24×0.16	0.35×0.34×0.31
Θ range (deg)	4.83 to 63.00	3.94 to 63.02	4.88 to 59.80	2.04 to 50
Reflections collected	27183	21109	32027	59860
Independent reflections	0.0289	0.0286	0.0547	0.0522
Data/restraints/paramet	7641/92/295	9259/0/308	32027/0/1315	18645/1772/1244
F(000)	2008	576	4704	4480
$R1^{\rm a}, wR2^{\rm b}(I > 2\sigma(I))$	0.0462, 0.0859	0.0376, 0.0825	0.0599, 0.1543	0.1017, 0.1897
$R1^{a}$, $wR2^{b}$ (all data)	0.0512, 0.0888	0.0421, 0.0857	0.0741, 0.1646	0.1158, 0.1994

Table 1. Crystal data and structure refinement for 2-5.

 $R1^{a}, wR2^{c}(\text{all data}) = 0.0512, 0.0888 = 0.0421, 0.0858$ $R = \Sigma ||F_{0}| - |F_{c}|| / \Sigma |F_{0}|. \ ^{b}wR2 = [\Sigma w(F_{0}^{2} - F_{c}^{2})^{2} / \Sigma (F_{0}^{2})]^{1/2}.$



Figure 1. Molecular structure of 2 in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)-O(1) 1.9923(11), Sn(1)-N(1) 2.214(2), Sn(1)-N(2) 2.229(2); O(1)-Sn(1)-N(1) 97.30(6), O(1)-Sn(1)-N(2) 92.20(10), N(1)-Sn(1)-N(2) 83.71(8), Sn(1)-O(1)-Sn(1-2) 137.23(14).

>CC



Figure 2. Molecular structure of **3** in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)-O(1) 2.0233(14), Sn(1)-N(1) 2.1916(16), Sn(1)-N(2) 2.1922(17), O(1)-C(2)6 1.424(2); O(1)-Sn(1)-N(1) 91.33(6), O(1)-Sn(1)-N(2) 93.00(6), N(1)-Sn(1)-N(2) 84.30(6), C(26)-O(1)-Sn(1) 124.48(14).



Figure 3. Molecular structure of **4** in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)-N(1) 2.234(3), Sn(1)-N(2) 2.204(3), Sn(1)-S(1) 2.5353(9), S(1)-(26) 1.890(3); N(1)-Sn(1)-N(2) 83.51(11), N(1)-Sn(1)-S(1) 92.06(7), N(2)-Sn(1)-S(1) 98.04(8), C(26)-S(1)-Sn(1) 104.50(11).



Figure 4. Molecular structure of 5 in crystals. Thermal ellipsoids are drawn at 50% level. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)-S(1) = 2.467(2), Sn(1)-N(1) = 2.227(6), Sn(1)-N(2) = 2.205(7), Sn(2)-S(1) = 2.468(2), Sn(2)-N(3) = 2.207(7), Sn(2)-N(3) = 2.220(7); N(1)-Sn(1)-S(1) = 88.15(18), N(2)-Sn(1)-S(1) = 96.43(19), N(1)-Sn(1)-N(2) = 84.5(2), N(3)-Sn(2)-S(1) = 96.43(19), N(4)-Sn(2)-S(1) = 88.03(19), Sn(1)-S(1)-Sn(2) = 108.00(9).



Table 2. Hydroboration of benzaldehyde and acetophenone catalyzed by 2-5.^a

[a] All reactions carried out in CDCl₃ at room temperature using 1 equiv of HBPin. [b] Conversion was determined by NMR spectroscopy on the basis of the consumption of the aldehyde/ketone, and the identity of the product was confirmed by PhCH₂OBPin or Ph(CH₃)CHOBPin resonances.

Rock

Graphical Abstract

We synthesized two chalcogenide bridging bidentate β -diketiminato ligand bimetallic organotins and two three-coordinated chalcogenide Tin(II) compounds by the stable chlorostannylene(II).



Highlights

- characterized two bridged bimetallic fully 1. Synthesized and organotins(II) and two bridged chalcogens (O or S) organotins(II) organometallic compounds.
- 2. The catalytic activity of tin(II) chalcogens (O or S) compounds 2-5 for hydroboration with benzaldehyde and acetophenone was investigated.

phene