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Communication

Reactivity of a C,N-chelated stannylene with chalcogens ☆

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ABSTRACT

The stannylene $\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2Sn$ (**1**) was reacted with oxygen, sulfur, selenium, tellurium, and carbon disulfide. The reactions with heavier chalcogens led to the rapid formation of 1:1 dinuclear adducts which were characterized by elemental analysis, ESI-MS measurements, ^1H NMR spectroscopy, and structurally characterized by X-ray diffraction (in the case of reaction products with S_8 (**3**) and Te (**5**)). The reaction of **1** with carbon disulfide and elemental sulfur yields the remarkable compound $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}Sn\}_2(\mu^2\text{-}S_2C{=}CS_2)$ (**3a**). The stability and reactivity of compounds **1**–**5** were rationalized at DFT/TZ2P level.

1. Introduction

The reactivity of higher congeners of carbenes e.g. silylenes, germylenes, stannylenes and plumbylenes has been studied very extensively in the last twenty years [1].

The stannylene $(L^{CN})_2Sn$ [2] (**1**) where L^{CN} is the chelating ligand (2-(*N*,*N*-dimethylaminomethyl)phenyl-) was reacted with the Negishi reagent [3] or molybdenum and tungsten complexes [4] to give carbene-like adducts or products of an oxidative addition. The reactivity of **1** with azobenzene produce di- or trinuclear species by C–H bond activation [5]. **1** also reacts with oxygen to give $[(L^{CN})_2SnO]_n$ (**2**) [6] which activate carbon dioxide to form $\{\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2Sn\}_2(\mu\text{-}O)(\mu\text{-}CO_3)$ (**2b** [7]). **2** is able to condensate also with silanols and ethylene glycol.

In this paper, we expand the reactivity studies of **1** to the higher chalcogens.

Organotin(IV) chalcogenides nowadays the object of an ever-increasing research interest mainly because of interesting structural features [1a] and promising reactivities. The diorganotin sulfides form different structures, depending on the nature of the organic substituents that range from cyclic trimers ($(Me_2SnS)_3$ and $(Ph_2SnS)_3$ [8]) to polymeric systems $(i\text{Pr}_2SnS)_n$ [9]. Dimeric structures with a planar Sn_2S_2 cyclic arrangement can be stabilized by bulky $(t\text{Bu}_2SnS)_2$ [10], $[(2,4,6\text{-}i\text{Pr}_3C_6H_2)_2SnS]_2$ [11] or various chelating ligands [12]. Two chelating rings (bicyclo-Sn-$(CH_2CH_2CH_2)_2NMe$) supporting an equilibrium between dimer and trimer [12a,d]. Dimers are stabilized by aliphatic [12b] $\text{-}CH_2CH_2CH_2NMe_2$ or aromatic O,C,O-chelating [12e] ligands. Unusual $RR'SnY_4$ rings (Y = S [13a,b], Se [13c,d]) were reported with bulky aryls were reported recently [13]. These tetrachalcogenostannolanes can disaggregate to give isolable products containing tin–sulfur and tin–selenium double bonds [14]. Recently, we have reported on the reactivity of O,C,O-chelated diorganotin dichlorides with sodium sulfide to give dimeric sulfides and their further reactivity with iodine [15]. By a stannylene oxidation with elemental or metallic chalcogen, mixed oxo-sulfides [16b], naphthyl-based ligand tin selenides and tellurides [16a] or similar compounds [16c] derived from Lappert's stannylene used for MOCVD deposition of corresponding chalcogenides were prepared. During the completion of this work, the preparation of cyclo-$[(L^{CN})_2SnS]_2$ (**3**) could be achieved by reaction of diorganotin dichloride with sodium sulfide [17].

2. Results and discussion

The stannylene $(L^{CN})_2Sn$ (**1**) reacts (Fig. 1) under reflux conditions and strictly inert atmosphere with elemental sulfur (**3**), selenium (**4**) and tellurium (**5**) in benzene essentially quantitatively. The identity of the isolated compounds was ascertained by elemental analysis, ESI/MS spectrometry and ^1H NMR spectroscopy. The measurement of ^{119}Sn spectra revealed to be quite complicated because of the low solubility of compounds **3**–**5** in toluene and THF and instability in chlorinated solvents and upon air

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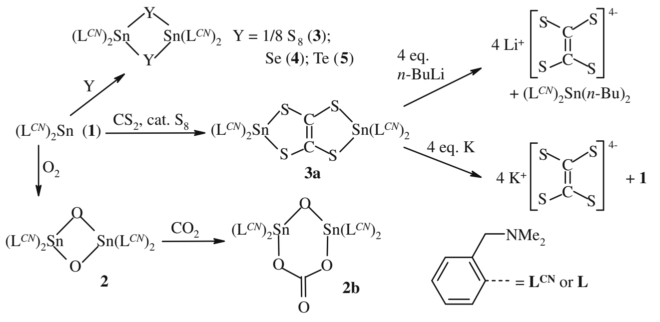

Fig. 1. Reactivity of **1**.

exposure. In chloroform, $(L^{CN})_2SnCl_2$ was observed as a product of the decomposition of **3–5**, even when the solvent was stored over stabilizing silver foils, which agrees with our previous findings on the reactivity of chelated organotin sulfides towards iodine [15]. On the other hand, the broadening of the signals in ^1H NMR spectra is an indication of dynamic exchange of substituents on the tin centre.

The X-ray diffraction techniques were used for structural studies of **3** (redetermined more precisely than in Ref. [17]) and **5**. The structures of **3**–**5** are centrosymmetric dimers consisting of two diorganotin moieties bridged by two chalcogen atoms in a nearly symmetrical manner within a Sn_2Y_2 (Y = S or Te) planar arrangement. The bond distances and bond angles of Sn–Y and Y–Sn–Y (see Fig. 2, Fig. S1 and S2 captions, Supporting Information) are comparable to previously published data [12b,e,15] and the tellurium-tin [16c] distances are significantly elongated in comparison to tin-sulfur ones. The tin atom coordination geometries can be described in two different ways (i) as distorted octahedral with C,C-transoid geometry (as described in Ref. [17]; for more information on **3** and **3**$\cdot CDCl_3$ and a comparative picture of **3** and **5,** see Supporting Information) or (ii) a bi-capped distorted tetrahedral geometry with rather long Sn–N distances in both **3** and **5** (for **5**: Sn(1)–N(1) 2.984(2), Sn(1)–N(2) 2.958(2)).

As it was shown previously [6] $[(L^{CN})_2SnO]_n$ can exist in different forms: there is equilibrium between monomer ($n = 1$) and dimer ($n = 2$) in solution. The trimer ($n = 3$) and tetramer ($n = 4$) were isolated in the solid state from different solvents. Consequently, there was particular interest in comparing the relative stability of the heavier congeners $[(L^{CN})_2SnX]_n$ (X = S, Se, Te; $n = 1–4$) of **2** using theoretical calculations (for details see Supporting Information). It was found that the dissociation energies of the dimers decrease significantly with increasing atomic number: O > S > Se > Te, from 25.6 kcal/mol for X=O down to 6.5 kcal/mol for X=Te (Table 1). Thus $(L^{CN})_2Sn{=}X$ species including Sn=X double bonds are feasible synthetic targets especially in case of selenium or tellurium. We suppose that monomeric species may be isolated if more steric bulky introduced in the aryl groups or as complexes with Lewis acids $(L^{CN})_2Sn{=}X \rightarrow LA$.

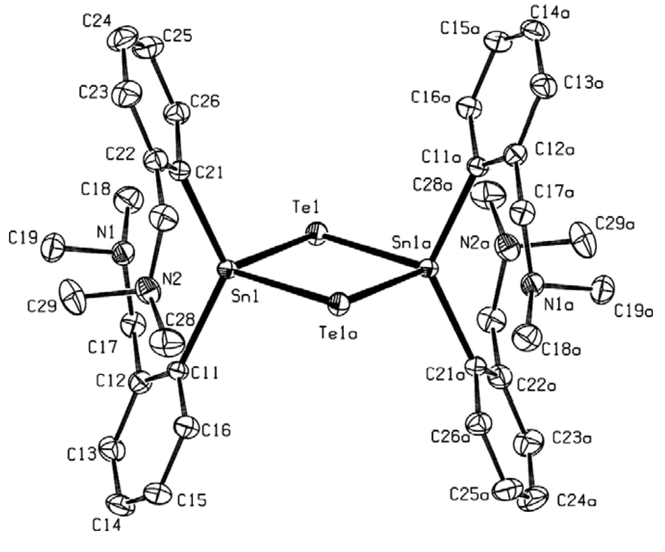

Fig. 2. Molecular structure of **5**, an ORTEP presentation, hydrogen atoms are omitted for clarity 50% probability level, selected interatomic distances (Å) and angles (°): Sn(1)–Te(1) 2.7712(2), Sn(1)–N(1) 2.984(2), Sn(1)–N(2) 2.958(2), C(21)–Sn(1)–C(11) 129.46(8), C(21)–Sn(1)–Te(1) 106.31(6), C(11)–Sn(1)–Te(1) 108.17(6), Te(1)–Sn(1)–Te(1a) 94.346(6), Sn(1)–Te(1)–Sn(1a) 85.653(6), N(1)–Sn(1)–N(2) 107.27(5).

No tri- or tetramers of $(L^{CN})_2SnX$ (X = S, Se, Te) were obtained experimentally. Indeed, while for oxygen derivatives calculated relative ΔG^0 of trimer and tetramer are -0.5 and 2.3 kcal/mol, respectively, for the heavier congeners ΔG^0 are positive (4.4–4.9 kcal/mol for trimers and 5.7–6.6 kcal/mol for tetramers – see Supporting Information).

Upon exposure to air, $\{\{2\text{-}[(CH_3)_2NCH_2]C_6H_4\}_2Sn\}_2(\mu\text{-}O)(\mu\text{-}CO_3)$ (**2b** [7]) was found to be the main product of the decomposition of **3–5**.

The reaction of **1** with S_8 in CS_2 was performed in order to prepare sulfur-containing analogs of the bridged carbonato specie **2b** but the reaction of **1** proceeds more rapidly with the CS_2 than with elemental sulfur to yield solely $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}Sn\}_2(\mu^2\text{-}S_2C{=}CS_2)$ (**3a**). Similar structure was proposed as an intermediate of reaction of a stannylene towards CS_2 and unsaturated hydrocarbons in mid-ninetieth [18]. The reactivity and structures was also studied by theoretical approach [19]. When polymerized, they reveal interesting applications mainly in non-linear optics [20]. Also the coordination compounds of this moiety are quite important [21]. The presence of sulfur in the reaction is not necessary but it seems to promote in someway the reaction. The activation of two CS_2 molecules leads to the formation of a new carbon–carbon double bond and, indirectly to the formation of two fused five-membered stanna-dithia rings. The dinuclear compound **3a** reacts with four equivalents of *n*-BuLi or potassium mirror to give $(C_2S_4)^{4-}$ ions, $(L^{CN})_2Sn(n\text{-}Bu)_2$ [22] in the case of butyllithium and stannylene **1** in the case of potassium reaction (Fig. 1 – see Section 3). The presence of $(C_2S_4)^{4-}$ ions, first obtained by heating of Na/Hg and CS_2 [23], was evaluated by reaction with MeI to give known species [24].

The structure of **3a** is described as a centrosymmetric dimer with two organotin fragments connected by $(S_2C{=}CS_2)^{2-}$ moiety, where the C–C distance (1.342(9) Å) reveals double bond character similarly as in previously described compounds of rhodium and tin wearing related ligands [25]. Organotin parts reveal close geometry to above-mentioned and reported structures. The double bond character of $S_2C{\cdots}CS_2$ is also supported by ^{13}C NMR shift value found for this function to be 117.7 ppm.

The reaction of oxide **2** with excess of CS_2 in diethylether solution led to the immediate formation of oxo-carbonate **2b** and rather insoluble sulfide **3**. This result was evaluated by the help of ^1H and ^{119}Sn NMR spectroscopy (see Fig. 3).

We have investigated the reactivity of CS_2 towards stannylene **1** and sulfide **3** by theoretical methods. It was found that insertion of CS_2 into **3** yielding sulfur analog of carbonate **2b** is an energetically unfavorable process (Scheme 2, see Supporting Information). On the other hand, stannylene **1** binds one molecule of CS_2 to give adduct $(L^{CN})_2Sn{\cdot}CS_2$ which lies higher in energy than initial reactants. It is interesting to stress that no minimum on the potential energy surface corresponding to adduct of stannylene **1** with CO_2 was found. We suppose that $(L^{CN})_2Sn{\cdot}CS_2$ is the intermediate in the formation of **3a**. Dimerization of $(L^{CN})_2Sn{\cdot}CS_2$ to give **3a** is strongly exothermic.

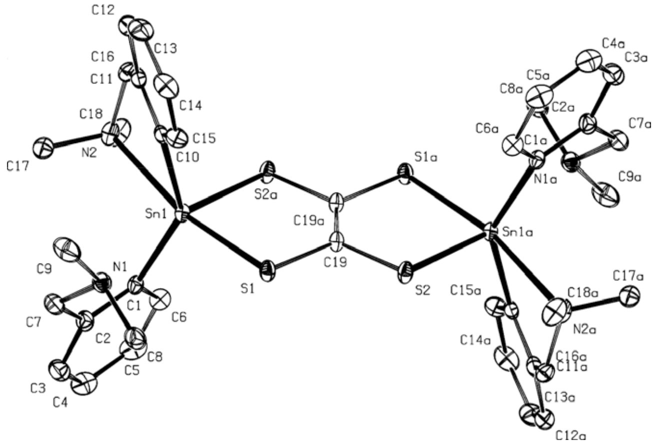

Fig. 3. Molecular structure of **3a**·2 THF, an ORTEP presentation, hydrogen atoms and THF molecules are omitted for clarity, 50% probability level, selected interatomic distances (Å) and angles (°): Sn(1)–S(2) 2.4622(15), Sn(1)–S(1) 2.4703(15), Sn(1)–N(2) 2.598(5), S(1)–C(19) 1.770(6), S(2)–C(19) 1.768(6), S(2)–Sn(1) 2.4622(15), C(19)–C(19a) 1.342(9), S(2)–Sn(1)–S(1) 87.20(5), S(2)–Sn(1)–N(2) 83.89(11), S(1)–Sn(1)–N(2) 168.35(12).

3. Experimental

3.1. General methods

3.1.1. NMR spectroscopy

The NMR spectra were recorded as solutions in toluene-d8 or benzene-d6 on a Bruker Avance 500 spectrometer (equipped with Z-gradient 5 mm probe) at 300 K ^1H (500.13 MHz) and $^{119}Sn\{^1H\}$ (186.50 MHz). The solutions were obtained by dissolving of 40 mg of each compound in 0.5 ml of deuterated solvents. $^{13}C\{^1H\}$ NMR spectra were measured at 90.35 MHz in five millimetre wide-zone tuneable sampler. The values of ^1H chemical shifts were calibrated to internal standard – tetramethylsilane ($\delta(^1H) = 0.00$ ppm) or to residual signals of benzene ($\delta(^1H) = 7.16$ ppm), toluene ($\delta(^1H) = 2.09$ ppm). The values of ^{13}C chemical shifts were calibrated to signals of benzene ($\delta(^{13}C) = 128.3$ ppm), and ^{119}Sn chemical shifts to external Me_4Sn (0.0 ppm). The solutions were obtained by dissolving of 20 mg of each compound in 0.5 ml of deuterated solvents. The problems with measurement of ^{119}Sn NMR spectra of **3**, **3a**, **4** and **5** are probably caused by dynamic behavior and low solubility of compounds in common solvents.

3.1.2. X-ray crystallography

Data for crystals were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), and graphite monochromator. The structures were solved by direct methods (SIR92 [26]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL97 [27]). Heavy atoms were refined anisotropically. Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of treatment of crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety. Absorption corrections were carried on, using Gaussian integration from crystal shape for **3**, **3**.$CHCl_3$, **3a**, and **5** [28]. CCDC Deposition numbers: 684122–684125.

3.1.3. ESI Mass spectrometry

In the mass spectrometry, the positive-ion electrospray ionization ESI mass spectra were measured on an Esquire3000 ion trap analyzer (Bruker Daltonics, Bremen, Germany) in the range m/z 100–2000, and negative-ion ESI mass spectra were measured on the Platform quadrupole analyzer (Micromass, UK) in the range m/z 15-600. The ion trap was tuned to give an optimum response for m/z 500. The samples were dissolved in acetonitrile and analyzed by direct infusion at a flow rate of 1–3 μL/min.

3.2. Calculation procedure

All calculations were done at the DFT level of theory. Geometry optimizations were carried out using the PBE generalized gradient functional [29,30]. The triple zeta valence basis set including polarization functions TZ2P {3,1,1/3,1,1/1,1} for Sn, C, N, O, S, Se, Te atoms and {3,1,1/1} for H atom was used. Innermost electrons for Sn, C, N, O, S, Se, Te atoms were treated using the ECP-SBKJC relativistic effective core potentials [31]. Total energies E, zero point vibration energies ZPE, $E^0 = E + ZPE$, H^0, G^0 were calculated for all stationary points. Vibration frequencies were used to characterize stationary points as minima. All calculations were performed using the PRIRODA program [32]. The same approach and program were previously used in studies of various types of germanium and tin compounds [33].

3.3. Synthetic procedures

$(L^{CN})_2Sn$ (**1**)[2] was prepared according to published procedures. All solvents and starting compounds were obtained from commercial sources (Sigma–Aldrich), S, metallic Se, and Te used as powders of 99.98% purity, CS_2 anhydrous 99% and used without further purification. Toluene, THF, diethylether, benzene, n-hexane, n-pentane were dried over and distilled from sodium, degassed and stored over potassium mirror under argon. Standard Schlenk techniques were used for all manipulations under an argon atmosphere.

3.3.1. $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu^2\text{-}S)_2$. (**3**)

Stannylene **1** (1 g, 3.96 mmol) was dissolved in benzene or toluene (50 mL) and an excess of S_8 (250 mg) was added in one portion. The heterogenous reaction mixture was heated to reflux for 5 h. Yellowish solid was obtained by filtration and evaporation of reaction mixture in typically ~60% yield. ^1H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.36 (broad, 4H, H(6)); 7.25 (m, 8H, H(4, 5)); 7.04 (m, 4H, H(3)); 3.46 (broad, 8H, NCH_2); 1.88 (broad, 24H, $N(CH_3)_2$). Elemental analysis (%): Anal. Calc. for $C_{36}H_{50}N_4O_3Sn_2$ (824.20): C, 52.46; H, 6.11; N, 6.80. Found: C, 52.3; H, 6.1; N, 6.7%. MW = 840; Positive-ion MS: m/z 841 $[M+H]^+$; m/z 706 $[M+H-LH]^+$; m/z 421 $[L_2Sn{=}S+H]^+$, 100%. MS/MS of m/z 841: m/z 706 $[M+H-LH]^+$; m/z 421 $[L_2Sn{=}S+H]^+$; m/z 254 $[LSn]^+$. M.p.: 283–285 °C.

3.3.2. $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu^2\text{-}S_2C{=}CS_2)$ (**3a**)

Addition of an excess of CS_2 (10 mL) to stannylene **1** (1 g, 3.96 mmol) and a trace amount of S_8 (3 mg) in benzene (50 mL) at room temperature led to immediate formation of yellowish precipitate. This was washed with toluene and crystallized from THF yielding typically 82–94% of **3a**. ^1H NMR (500.13 MHz, THF, 300 K, ppm): 8.19 (broad, 4H, H(6)); 7.18 (m, 8H, H(4, 5)); 6.97 (broad, 4H, H(3)); 3.72 (s, 2H, NCH_2); 2.45 (s, 24H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (THF-d8, 300 K, ppm): 146.5, 143.9, 143.8, 143.3, 138.1, 137.7, 129.8, 117.7 ($S_2C{=}CS_2$), 66.3 and 66.1 for CH_2N, 46.6 and 46.4 for $N(CH_3)_2$. Elemental analysis (%): Anal. Calc. for $C_{38}H_{48}N_4S_4Sn_2$ (806.19): C, 49.26; H, 5.22; N, 6.04. Found: C, 49.2; H, 5.1; N, 6.1%. M.p.: 253–257 °C.

The further reactivity of **3a** was investigated. **3a** (1 mmol in THF) reacts with four equivalents of n-BuLi (1.6 M in hexanes) to give $(C_2S_4)^{4-}$ ion and $(L^{CN})_2Sn(n\text{-}Bu)_2$ [22] (identified by ^1H and ^{119}Sn NMR spectroscopy) at room temperature immediately. $(C_2S_4)^{4-}$ ion was identified using the same procedure as known

$(MeO)_4(C_2S_4)$ when derivatized with MeI [24]. In the case of reaction of **3a** (1 mmol in THF) with K (four molar equivalents), potassium was vacuo sublimed to the walls of Schlenck tube and **3a** added. The stannylene **1** (identified by ^1H and ^{119}Sn NMR spectroscopy) and $K_4C_2S_4$ complex (identified similarly as described above) were the only products.

*3.3.3. $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu^2\text{-}Se)_2$. (**4**)*

$\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu^2\text{-}Se)_2$ (**4**) was prepared similarly to **3**. Yellow solid was obtained by filtration and evaporation of reaction mixture in typically ~70% yield. ^1H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.30 (broad, 4H, H(6)); 7.22 (m, 8H, H(4, 5)); 6.99 (d, 4H, H(3), $^3J(^1H, ^1H) = 7.0$ Hz); 3.56 (broad, 8H, NCH_2); 1.93 (broad, 24H, $N(CH_3)_2$). Elemental analysis (%): Anal. Calc. for $C_{36}H_{48}N_4O_2Sn_2$ (806.19): C, 53.64; H, 6.00; N, 6.95. Found: C, 53.7; H, 6.1; N, 7.1%. MW = 936; Positive-ion MS: *m*/*z* 937 $[M+H]^+$; *m*/*z* 802 $[M+H-LH]^+$; *m*/*z* 469 $[L_2Sn{=}Se+H]^+$, 100%. MS/MS of *m*/*z* 937: *m*/*z* 802 $[M+H-LH]^+$; *m*/*z* 602 $[M+H-SnSe-LH]^+$; *m*/*z* 469 $[L_2Sn{=}Se+H]^+$. M. p.: 262–264 °C.

*3.3.4. $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu^2\text{-}Te)_2$. (**5**)*

$\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu^2\text{-}Te)_2$ (**5**) was prepared similarly to **3**. Greenish solid was obtained by filtration and evaporation of reaction mixture in typically ~75% yield. ^1H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.31 (broad, 4H, H(6), $^3J(^1H, ^{119}Sn) = 87$ Hz); 7.05 (m, 8H, H(4, 5)); 6.84 (d, 4H, H(3), $^3J(^1H, ^1H) = 7.1$ Hz); 3.52 (broad, 8H, NCH_2); 1.91 (broad, 24H, $N(CH_3)_2$). Elemental analysis (%): Anal. Calc. for $C_{36}H_{48}N_4O_2Sn_2$ (806.19): C, 53.64; H, 6.00; N, 6.95. Found: C, 53.7; H, 6.0; N, 7.0%. MW = 1036; Positive-ion MS: *m*/*z* 1037 $[M+H]^+$; *m*/*z* 902 $[M+H-LH]^+$; *m*/*z* 519 $[L_2Sn{=}Te+H]^+$, 100%. MS/MS of *m*/*z* 1037: *m*/*z* 902 $[M+H-LH]^+$; *m*/*z* 652 $[M+H-SnTe-LH]^+$; *m*/*z* 519 $[L_2Sn{=}Te+H]^+$; *m*/*z* 384 $[LSn{=}Te]^+$. M.p.: 279–281 °C.

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Appendix A. Supplementary data

CCDC 684122–684125 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.05.001.

References

[1] (a) A.G. Davies, Organotin Chemistry, VCH, Weinheim, FRG, 1997 and 2004.;
(b) M. Driess, H. Grützmacher, Angew. Chem., Int. Ed. Engl. 35 (1996) 828;
(c) M. Weidenbruch, Eur. J. Inorg. Chem. (1999) 373;
(d) M. Weidenbruch, J. Organomet. Chem. 39 (2002) 646;
(e) P. Jutzi, N. Burford, Chem. Rev. 99 (1999) 969.

[2] K. Angermund, K. Jonas, C. Kruger, J.L. Latten, Y.-H. Tsay, J. Organomet. Chem. 17 (1988) 353.

[3] J. Bareš, P. Richard, P. Meunier, N. Pirio, Z. Padělková, Z. Černošek, I. Císařová, A. Růžička, Organometallics, Article ASAP, doi:10.1021/om801120a.

[4] Z. Padělková, I. Císařová, K. Fejfarová, J. Holubová, A. Růžička, J. Holeček, Collect. Czech. Chem. Commun. 72 (2007) 629.

[5] Z. Padělková, M.S. Nechaev, A. Lyčka, J. Holubová, T.A. Zevaco, A. Růžička, Eur. J. Inorg. Chem., Early View, doi:10.1002/ejic.200900181.

[6] Z. Padělková, M.S. Nechaev, Z. Černošek, J. Brus, A. Růžička, Organometallics 27 (2008) 5303.

[7] Z. Padělková, H. Vaňkátová, I. Císařová, M.S. Nechaev, T.A. Zevaco, O. Walter, A. Růžička, Organometallics 28 (2009) 2629.

[8] (a) H.J. Jacobsen, B. Krebs, J. Organomet. Chem. 136 (1977) 333;
(b) B.M. Schmidt, M. Dräger, J. Organomet. Chem. 63 (1990) 399.

[9] H. Puff, A. Bongartz, R. Sievers, R. Zimmer, Angew. Chem., Int. Ed. 17 (1978) 939.

[10] H. Puff, G. Bertram, B. Ebeling, M. Franken, R. Gattermayer, R. Hundt, W. Schuh, R. Zimmer, J. Organomet. Chem. 379 (1989) 235.

[11] P. Brown, M.F. Mahon, K.C. Molloy, J. Chem. Soc., Chem. Commun. (1989) 1621.

[12] (a) B.M. Schmidt, M. Dräger, K. Jurkschat, J. Organomet. Chem. 43 (1991) 410;
(b) K. Jurkschat, S. van Dreumel, G. Dyson, D. Dakternieks, T.J. Bastow, M.E. Smith, M. Dräger, Polyhedron 11 (1992) 2747;
(c) O.S. Jung, J.H. Jeong, Y.S. Sohn, Polyhedron 8 (1989) 2557;
(d) D. Schollmeyer, J. Kalbitz, H. Hartung, A. Tzschach, K. Jurkschat, Bull. Soc. Chim. Belg. 97 (1988) 1075;
(e) M. Mehring, Ch. Löw, M. Schürmann, F. Uhlig, K. Jurkschat, B. Mahieu, Organometallics 19 (2000) 4613.

[13] (a) Y. Matsuhashi, N. Tokitoh, R. Okazaki, Organometallics 12 (1993) 2573;
(b) N. Tokitoh, H. Suzuki, T. Matsumoto, Y. Matsuhashi, R. Okazaki, M. Goto, J. Am. Chem. Soc. 113 (1991) 7047;
(c) N. Tokitoh, Y. Matsuhashi, R. Okazaki, Tetrahedron Lett. 32 (1991) 6151;
(d) Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto, S. Nagase, Organometallics 12 (1993) 1351;
(e) For a review see: N. Takeda, N. Tokitoh, R. Okazaki; in: F. Devillanova (Ed.), Handbook of Chalcogen Chemistry, New Perspectives in Sulfur, Selenium and Tellurium, The Royal Society of Chemistry, Cambridge, UK, 2007, p. 107 (Chapter 3).

[14] (a) M. Saito, N. Tokitoh, R. Okazaki, J. Am. Chem. Soc. 126 (2004) 15572;
(b) N. Tokitoh, M. Saito, R. Okazaki, J. Am. Chem. Soc. 115 (1993) 2065;
(c) M. Saito, N. Tokitoh, R. Okazaki, Organometallics 15 (1996) 4531.

[15] L. Dostál, R. Jambor, A. Růžička, R. Jirásko, J. Taraba, J. Holeček, J. Organomet. Chem. 692 (2007) 3750.

[16] (a) W.-P. Leung, W.-H. Kwok, L.T.C. Law, Z.-Y. Zhou, T.C.W. Mak, Chem. Commun. (1996) 505;
(b) P. Brown, M.F. Mahon, K.C. Molloy, J. Chem. Soc., Chem. Commun. (1989) 1621;
(c) J.J. Schneider, J. Hagen, O. Heinemann, J. Bruckmann, C. Krüger, Thin Solid Films 304 (1997) 144.

[17] R.A. Varga, K. Jurkschat, C. Silvestru, Eur. J. Inorg. Chem. 5 (2008) 708.

[18] M. Saito, N. Tokitoh, R. Okazaki, Organometallics 14 (1995) 3620.

[19] G. Frenking, J. Am. Chem. Soc. 113 (1991) 2476.

[20] (a) For example: M.R. Bryce, Aldrichim. Acta 18 (1985) 73;
(b) M. Fujiwara, S. Takamizawa, W. Mori, K. Yamaguchi, Mol. Cryst. Liq. Cryst. 1 (1996) 279.

[21] (a) For the first complexes see for example: M.F. Lappert, D.B. Shaw, G.M. McLaughlin, J. Chem. Soc., Dalton Trans. (1979) 427;
(b) B. Cetinkaya, P.B. Hitchcock, M.F. Lappert, P.L. Pye, D.B. Shaw, J. Chem. Soc. Dalton Trans. (1979) 434.

[22] (a) A. Růžička, V. Pejchal, J. Holeček, A. Lyčka, K. Jacob, Collect. Czech. Chem. Commun. 63 (1998) 977;
(b) M. Biesemans, J.C. Martins, R. Willem, A. Lyčka, A. Růžička, J. Holeček, Magn. Reson. Chem. 40 (2002) 65.

[23] (a) M. Herrmann, J. Prakt. Chem. 79 (1860) 448;
(b) M. Guignet, Bull. Soc. Chim. Fr. 3 (1861) 111.

[24] (a) R.R. Schumaker, E.M. Engler, J. Am. Chem. Soc. 99 (1977) 5521;
(b) U. Schöllkopf, E. Wiskott, Angew. Chem., Int. Ed. Engl. 2 (1963) 485;
(c) D.M. Lemal, E.H. Banitt, Tetrahedron Lett. (1964) 245.

[25] (a) C. Bianchini, C. Mealli, A. Meli, M. Sabat, P. Zanello, J. Am. Chem. Soc. 109 (1987) 185;
(b) J. Bordinhao, N.M. Comerlato, G.B. Ferreira, R.A. Howie, C.X.A. da Silva, J.L. Wardell, J. Organomet. Chem. 691 (2006) 1598.

[26] A. Altomare, G. Cascarone, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 1045.

[27] G.M. Sheldrick, SHELXL-97, A Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[28] P. Coppens, in: F.R. Ahmed, S.R. Hall, C.P. Huber (Eds.), Crystallographic Computing, Munksgaard, Copenhagen, 1970, pp. 255–270.

[29] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[30] (a) M. Ernzerhof, G.E. Scuseria, J. Chem. Phys. 110 (1999) 5029;
(b) C. Adamo, V. Barone, J. Chem. Phys. 110 (1999) 6158.

[31] (a) W.J. Stevens, H. Basch, M. Krauss, J. Chem. Phys. 81 (1984) 6026;
(b) W.J. Stevens, M. Krauss, H. Basch, P.G. Jasien, Can. J. Chem. (1992) 612;
(c) T.R. Cundari, W.J. Stevens, J. Chem. Phys. 98 (1993) 5555.

[32] (a) D.N. Laikov, Chem. Phys. Lett. 281 (1997) 151;
(b) D.N. Laikov, Yu.A. Ustynyuk, Russ. Chem. Bull. 54 (2005) 820.

[33] (a) See for example: V.N. Khrustalev, I.A. Portnyagin, M.S. Nechaev, S.S. Bukalov, L.A. Leites, Dalton Trans. (2007) 3489;
(b) V.N. Khrustalev, O.V. Chernov, R.R. Aysin, I.A. Portnyagin, M.S. Nechaev, S.S. Bukalov, Dalton Trans. (2008) 1140.