Synthesis and characterisation of stannanechalcogenones; X-ray structures of $[R^N(R^N)Sn(\mu\text{-}S)]_2$ and $[(R^N)_2Sn{=}E]$ $[R^N = CH(SiMe_3)C_9H_6N\text{-}8$; E = Se, Te]

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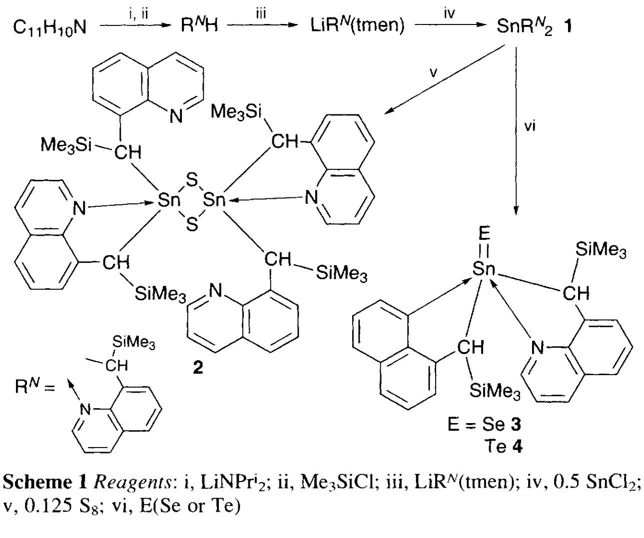
The tin(II) alkyl $(R^N)_2Sn$ 1 $[R^N = CH(SiMe_3)C_9H_6N\text{-}8]$ reacts with elemental chalcogens in thf to afford thermally stable dimeric dialkylstannane-thione $[R^N(R^N)Sn(\mu\text{-}S)]_2$ 2 and monomeric dialkylstannane-selone and -tellurone $[(R^N)_2Sn{=}E]$ (E = Se 3, Te 4) in good yields; ^{119}Sn NMR spectra of 3 and 4 display satellites with coupling constants $^1J_{^{119}Sn-^{77}Se}$ 2966.3 Hz and $^1J_{^{119}Sn-^{125}Te}$ 7808.3 Hz; the tin–chalcogen distances from single-crystal X-ray analysis are 2.47 (av.), 2.398 and 2.618 Å for 2, 3 and 4 respectively.

Compounds containing a double bond between Group 14 and 16 elements have attracted interest since some reactive species of these thioketone analogues were detected.[1] Nevertheless, thermally stable compounds with M=E bonds (M = Si, Ge, Sn; E = S, Se, Te) have been isolated.[2–11] These compounds were either base-stabilized,[2,4] or generated using a sterically hindered protecting group as in $R^1R^2Ge{=}E$ [R^1 = {2,4,6-tris[bis(trimethyl)silyl]methyl}phenyl; R^2 = 2,4,6-tris(isopropylmethyl)phenyl; E = S, Se].[3,5,8,11] For the heavier congeners, thermally stable dialkylstannane–tellurones $R_2Sn{=}Te$, in particular, are scarcely found. Dialkylstannanethiones such as $Bu^t_2Sn{=}S$ and $Ph_2Sn{=}S$ are known to exist as transient species which readily form dimers and trimers.[12] The stannanethione $R^1R^2Sn{=}S$ was found to dimerise readily at > 90 °C, and the structures of $[R^1R^2Sn(\mu\text{-}E)]_2$ (E = S, Se) have been reported.[8,11] We now report (*i*) the synthesis (Scheme 1) of a tin(II) alkyl $[(R^N)_2Sn]$ 1 $[R^N = CH(SiMe_3)C_9H_6N\text{-}8]$, a dimeric stannanethione $[R^N(R^N)Sn(\mu\text{-}S)]_2$ 2 and the monomeric stannane-selone and -tellurone $[(R^N)_2Sn{=}E]$ (E = Se 3, Te 4); (*ii*) ^{119}Sn NMR data for 1–4, ^{77}Se NMR data for 3 and ^{125}Te NMR data for 4;† and (*iii*) single-crystal X-ray analyses‡ of 2 (Fig. 1), 3 and 4 (Fig. 2). Compound 4 is the first example of a compound having a terminal Sn=Te bond to be unequivocally characterised from spectroscopic and crystallographic data.



Scheme 1 *Reagents*: i, $LiNPr^i_2$; ii, Me_3SiCl; iii, $LiR^N(tmen)$; iv, 0.5 $SnCl_2$; v, 0.125 S_8; vi, E(Se or Te)

$[Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2]$ 1 was prepared by the reaction of $SnCl_2$ with 2 mol equiv. of the alkylating agent $LiR^N(tmen)$, (tmen = trimethyleneethylenediamine) which was prepared by lithiation of 8-(trimethylsilyl)methylquinoline HR^N with $LiNPr^i_2$ in conjunction with tmen. The red-orange crystalline compound 1 obtained has been shown by X-ray analysis tobe a monomeric tin(II) alkyl, SnR^N_2. The geometry at the tin centre (sum of bond angles 317.2°) is consistent with the presence of a stereochemically active lone-pair, as in the cases of $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$ and $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}Cl]$.[13] Subsequent reaction of 1 with stoichiometric amounts of elemental chalcogens in thf afforded the corresponding thermally stable dialkylstannane–thione, –selone and –tellurone in good yields. These thermally stable chalcogenones have been isolated as thf or toluene solvates, being characterised by their C,H,N elemental analyses, FAB mass spectra, ^1H, ^{119}Sn and ^{77}Se (for 3) and ^{125}Te (for 4) NMR spectra. Compound 2 was found to be a sulfido bridged dimer as determined by X-ray structural analysis (Fig. 1). Compounds 3 and 4 were crystallized in solvated forms and their X-ray structures determined. Other methods for synthesising compounds with a metal–chalcogen double bond involved either dechalcogenation of 1,2,3,4,5-tetrachalcogenastannolanes or germolanes, or the reaction of a dialkyl metal complex with styrene episulfide.[11] The five-coordinate functionalised silane $R'(Ph)SiH_2$ (R' = 8-dimethylamino-1-naphthyl) reacts with sulfur or selenium to produce the corresponding silanethione $R'(Ph)Si{=}S$ and silaneselone $R'(Ph)Si{=}Se$.[2] Previous work on the direct reaction of metal amides $[M\{N(SiMe_3)_2\}_2]$ (M = Ge, Sn) with chalcogens yielded the appropriate metal(IV) oxidation product [M{N(Si-

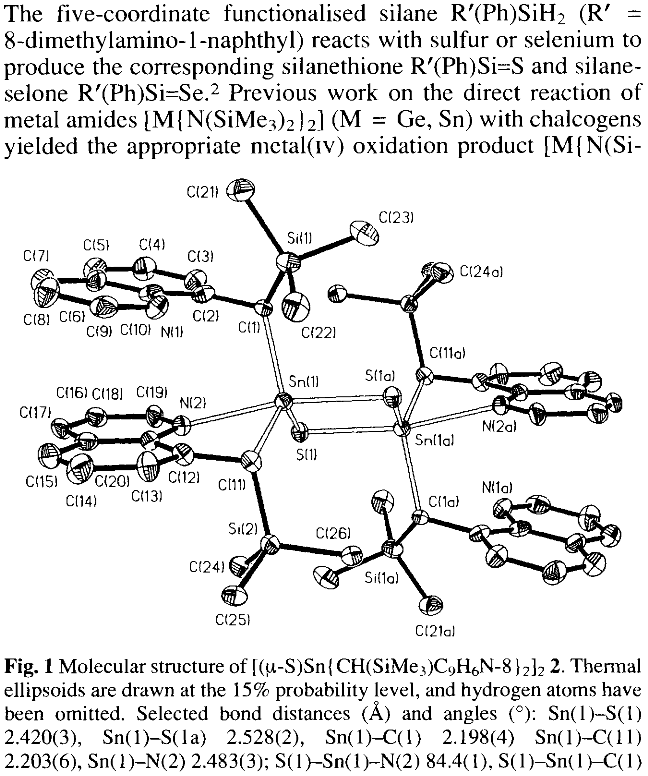


Fig. 1 Molecular structure of $[(\mu\text{-}S)Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2]_2$ **2**. Thermal ellipsoids are drawn at the 15% probability level, and hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Sn(1)–S(1) 2.420(3), Sn(1)–S(1a) 2.528(2), Sn(1)–C(1) 2.198(4) Sn(1)–C(11) 2.203(6), Sn(1)–N(2) 2.483(3); S(1)–Sn(1)–N(2) 84.4(1), S(1)–Sn(1)–C(1) 112.2(2), N(2)–Sn(1)–C(1) 91.9(1), S(1)–Sn(1)–C(11) 124.8(1), N(2)–Sn(1)–C(11) 73.0(1), C(1)–Sn(1)–C(11) 118.2(2), S(1)–Sn(1)–S(1a) 89.2(1), N(2)–Sn(1)–S(1a) 168.6(1), C(1)–Sn(1)–S(1a) 99.2(1), C(11)–Sn(1)–S(1a) 103.4(1).

$Me_3)_2\}_2(\mu\text{-}E)]_n$ (E = S, Se, Te).[14] Note that the heavier chalcogen congeners are less stable, as shown by the behaviour of an Sn–Te compound which is thermally and particularly photochemically unstable, as it gradually decomposes to tin amide and tellurium metal.[14] The present method provides a direct synthetic route from tin(II) dialkyl *via* oxidative addition to stannanechalcogenones. The thermal stability of **2**–**4** is attributable to the steric demand of the trimethylsilyl-substituted α-carbon in ligand R^N and *N*-coordination *via* quinolyl coordination.

Compounds **2**–**4** are less lipophilic than **1**. The change in colour of these compounds, from pale yellow (**2**), through yellow-orange (**3**) to red (**4**), is indicative of charge transfer from E to a vacant metal-centred d-orbital (n → π* transition). The ^{119}Sn NMR spectra of **2**–**4** display singlet signals with satellites due to coupling of ^{119}Sn to ^{77}Se (I = 1/2, 7.6%) and ^{119}Sn to ^{125}Te (I = 1/2, 7.1%) for **3** and **4**, respectively. The large coupling constants, $^1J_{^{119}Sn-^{77}Se}$ (2966.3 Hz) and $^1J_{^{119}Sn-^{125}Te}$ (7808.3 Hz) are consistent with directly bonded Sn=Se and Sn=Te moieties. In contrast, the corresponding coupling constants for $[Sn\{N(SiMe_3)_2\}_2(\mu\text{-}E)]_n$ (E = Se, Te) are 1128 and 2700 Hz, respectively.[14] The ^{119}Sn NMR chemical shifts of **1**–**4** lie in the range δ 141 to −351, which are very different from the value of δ 2208 for stannanethione $R^1R^2Sn{=}S$, but comparable to those of tin(II) alkyls containing the pyridine-functionalised alkyl ligand $[Sn\{C(SiMe_3)_2C_5H_4N\text{-}2\}_2]$.[13] This is probably due to the shielding effect of the Sn atom as a consequence of coordination from the quinolyl group.

X-Ray crystallographic analysis established the dimeric structure of **2** (Fig. 1) and the monomeric molecular structures of **3** and **4** (Fig. 2) in their 1 : 1 thf and toluene solvates, respectively. The Sn–S distance (av.) of 2.47 Å in **2** is slightly longer than that [2.44 Å (av.)] in $[R^1R^2Sn(\mu\text{-}S)]_2$. As a consequence of steric congestion around Sn, one of the N-functionalised alkyl ligands bonded to the metal centre behaves as a monodentate C-centred ligand, whilst in **3** and **4**, each alkyl ligand R^N is bonded to the metal in a chelate fashion and the five-coordinate Sn is bonded directly to the axial ligand Se and Te at 2.398 and 2.618 Å, respectively. The Sn–Se distance in **3** is significantly shorter than that in the selenium bridged dimers $[R^1R^2Sn(\mu\text{-}Se)]_2$ [2.57 Å (av.)] and $[(mes)R^2Sn(\mu\text{-}Se)]_2$ (2.562 Å; mes = mesityl).[11] The 7% reduction in bond length is consistent with enhanced contribution of π-bonding between Sn and Se. The Sn–Te bond distance of 2.618 Å in **4** is smaller than the sum of the covalent radii of Sn (1.40 Å) and Te (1.37 Å). Sn displays square-pyramidal coordination, the sum of the bond angles involving the basal ligand atoms being 333.7 and 332° for **3** and **4**, respectively. The decrease in the Sn–C_α and Sn–N distances in **3** and **4** when compared with the corresponding distances in **1** is a consequence of the change in oxidation state from Sn^{II} to Sn^{IV}.

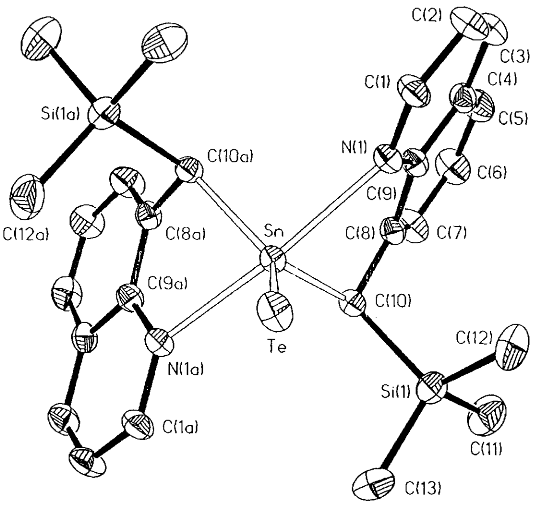


Fig. 2 Molecular structure of $[Te{=}Sn\{CH(SiMe_3)C_9H_6N\text{-}8\}_2]$ **4**. Thermal ellipsoids are drawn at the 35% probability level, and hydrogen atoms have been omitted. Selected bond distances (Å) and angles (°): Sn–Te 2.618(1), Sn–C(10) 2.174(5), Sn–C(10a) 2.174(5), Sn–N(1) 2.382(4), Sn–N(1a) 2.382(4)]; Te–Sn–N(1) 101.5(1), Te–Sn–C(10) 127.3(1), N(1)–Sn–C(10) 75.2(1), Te–Sn–N(1a) 101.5(1), N(1)–Sn–N(1a) 157.1(2), C(10)–Sn–N(1a) 90.8(1), C(10)–Sn–C(10a) 105.5(3), N(1a)–Sn–C(10a) 75.2(1). Compound **3** has a similar molecular structure with a two-fold symmetry axis passing through the Sn=Se double bond. Selected bond distances (Å) and angles (°): Sn–Se 2.398(1), Sn–C(10) 2.190(6), Sn–C(23) 2.183(6), Sn–N(1) 2.361(4), Sn–N(2) 2.390(4); Se–Sn–N(1) 99.5(1), Se–Sn(1)–C(10) 127.3(2) N(1)–Sn–C(10) 75.9(2), Se–Sn–N(2) 102.5(1), N(1)–Sn–N(2) 158.0(2), C(10)–Sn–N(2) 91.0(2), Se–Sn–C(23) 125.4(2), N(1)–Sn–C(23) 91.7(2), C(10)–Sn–C(23) 107.3(2) N(2)–Sn–C(23) 75.1(2).

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Footnotes

† *Selected spectral data*: at 298 K; ^{119}Sn, 186.5 MHz, $SnMe_4$ (ext.), ^{77}Se, 95.41 MHz Me_2Se_2 (ext.); ^{125}Te, 157.92 MHz, $Te(S_2CEt)_2$ (ext.)]. **1**: $^{119}Sn\{^1H\}$ NMR (C_6D_6) δ 141.73(s). **2**: $^{119}Sn\{^1H\}$ NMR (C_6D_6 δ −43.25 (br s). **3**: $^{119}Sn\{^1H\}$ NMR (thf–C_6D_6) δ −111.55 [s, $^1J_{^{119}Sn-^{77}Se}$ 2950.5 Hz]; $^{77}Se\{^1H\}$ (thf–C_6D_6) δ −734.8 [s, $^1J_{^{77}Se-^{119}Sn}$ 2966.3 Hz]. **4**: $^{119}Sn\{^1H\}$ NMR (thf–C_6D_6) δ −350.34 [s, $^1J_{^{119}Sn-^{125}Te}$ 7808.3 Hz]; $^{125}Te\{^1H\}$ (thf–C_6D_6) δ −2030.63 [s, $^1J_{^{119}Sn-^{125}Te}$ 7808.3 Hz].

‡ *X-Ray analysis*: single crystals were sealed in 0.3 mm Lindemann glass capillaries under argon. X-Ray data were collected using Mo-Kα radiation (λ = 0.71073 Å). $C_{26}H_{32}N_2Si_2Sn$ **1**, M = 574.4, triclinic, $P\bar{1}$ (no. 2), a = 10.553(1), b = 16.095(3), c = 16.192(3) Å, α = 79.257(9), β = 86.09(1), γ = 87.01(2)°, R = 0.036 for 7575 observed data $[|F_o| \geqslant 3\sigma(|F_o|]$; $[C_{26}H_{32}N_2SSi_2Sn]_2\cdot C_4H_8O$ **2**, M = 1231.04, monoclinic, $C2/c$ (no. 15), a = 29.659(3), b = 10.444(1), c = 21.673(2) Å, β = 106.0043(1)°, R = 0.059 for 3271 observed data $[F_o \geqslant 6\sigma(F_o)]$; $C_{26}H_{32}N_2SeSi_2Sn\cdot C_4H_8O$ **3**, M = 698.5, monoclinic, $P2_1/c$ (no. 14), a = 14.456(3), b = 10.700(2), c = 21.915(4) Å, β = 109.26(3)°, R = 0.046 for 3813 observed data $[I \geqslant 4\sigma(I)]$; $C_{26}H_{32}N_2Si_2SnTe\cdot C_7H_8$ **4**, M = 745, orthorhombic, $Pnna$ (no. 52), a = 14.5840(10), b = 14.6490(10), c = 15.7260(10) Å, R = 0.029 for 1944 observed $[|F_o| \geqslant 4\sigma|F_o|]$. Structure solution and refinement were carried out on a PC 486 using SHELXTL-PC. Atomic coordinates, bond lengths and angles, the thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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