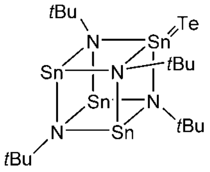
Cluster Compounds

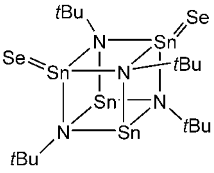
Complete Chalcogenation of Tin(II) Centers in an Imidotin Cluster**

Tristram Chivers* and Dana J. Eisler

The use of inorganic rings or clusters as precursors to industrially important materials such as inorganic polymers,[1] nanomaterials,[2] or semiconductors[3] represents an active area of contemporary inorganic chemistry. In the latter category the design of suitable precursors for the low band-gap semiconductors SnE (E = Se, Te), which have applications in thermoelectric devices and for optoelectronic materials, is of current interest.[4,5] Suitably chosen complexes containing terminal Sn=E bonds would appear to be candidates for this purpose.[6] In particular, imidotin chalcogenides of the type $[(\mathrm{ESn}\mu_3\text{-NR})_4]$ (E = Se, Te) may act as single-source precursors of these binary semiconductors by the energetically favorable elimination of the diazene RN=NR. However, investigations of the reactions of the neutral cluster $[(\mathrm{Sn}\mu_3\text{-N}t\mathrm{Bu})_4]$ with chalcogens have revealed that oxidation is limited to one tin(II) center for E = Te (**A**) or two tin(II) centers in the case of E = Se (**B**).[7] To address this synthetic challenge, we have adopted a strategy that was successful for the generation of the previously inaccessible P–Te ligands $[(\mathrm{TePPh_2})_2\mathrm{N}]^-$ and $[\mathrm{Te(N}t\mathrm{Bu)P(\mu\text{-}N}t\mathrm{Bu)_2P(N}t\mathrm{Bu)Te}]^{2-}$.[8] That approach involved the formation of anionic imidophosphorus(III) reagents by metalation with NaH or *n*BuLi, prior to reaction with tellurium.[8]

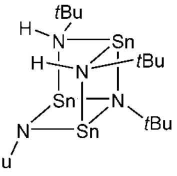


A

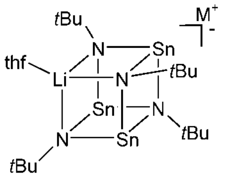


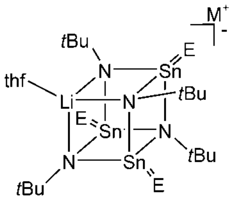
B

Application of this methodology to imidotin cages involves the use of the amido/imido *seco*-cube $[\mathrm{Sn_3(\mu_3\text{-}N}t\mathrm{Bu)(\mu_2\text{-}N}t\mathrm{Bu)(\mu_2\text{-}NH}t\mathrm{Bu)_2}]$ (**1**) reported by Veith et al.[9] We disclose here that the anionic cluster in $[\mathrm{Li(thf)_4}][(\mathrm{thf})\mathrm{LiSn_3(\mu_3\text{-}N}t\mathrm{Bu)_4}]$ (**2a**), which is readily generated by dilithiation of **1** with *n*BuLi, exhibits a dramatic increase in the reactivity of the tin(II) centers towards chalcogens compared to that of the neutral cluster $[(\mathrm{Sn}\mu_3\text{-N}t\mathrm{Bu})_4]$. Complete chalcogenation to give the trichalcogenides



1





2a M$^+$ = [Li(thf)$_4$]
2b M$^+$ = [(thf)Li([12]crown-4)]

3a E= Se, M$^+$ = [Li(thf)$_4$]
3b E= Se, M$^+$ = [(thf)Li([12]crown-4)]
4 E= Te, M$^+$ = [Li(thf)$_4$]

$[\mathrm{Li(thf)_4}][(\mathrm{thf})\mathrm{LiSn_3E_3(\mu_3\text{-}N}t\mathrm{Bu)_4}]$ (**3a**, E = Se; **4**, E = Te) occurs rapidly under mild conditions and in high yields. The characterization of these imidotin chalcogenides in the solid state by X-ray crystallography and in solution by multinuclear NMR spectroscopy (^{1}H, ^{7}Li, ^{119}Sn, ^{77}Se, and ^{125}Te) is reported.

The reaction of **1** with two equivalents of *n*-butyllithium in THF produces the anionic heterobimetallic cubane **2a** as a solvent-separated ion pair in 40% yield; complex **2b** was prepared from **2a** and [12]crown-4. Wright and co-workers have reported the formation of the related complex $[\mathrm{Li(thf)_4}][\mathrm{Sn_3Li(thf)(\mu_3\text{-}N}t\mathrm{Bu)(\mu_3\text{-}NC_{10}H_7)_3}]$ by the reaction of $[(\mathrm{Sn}\mu_3\text{-N}t\mathrm{Bu})_4]$ with three equivalents of $\mathrm{C_{10}H_7NHLi}$.[10] The ^{1}H NMR spectrum of complex **2a** exhibits two resonances in a 3:1 ratio for the *t*Bu protons, and a single resonance is observed in the ^{119}Sn NMR spectrum; both of these observations are consistent with local C_3 symmetry for the anion in **2a**. The ^{7}Li NMR spectrum of **2a** shows two well-separated resonances, indicating that the $[\mathrm{Sn_3Li(\mu_3\text{-}N}t\mathrm{Bu)_4}]$ cluster remains intact, even in THF solution.

The reaction of **2a** with slightly more than three equivalents of selenium in THF readily produces the tristannaselone **3a** in essentially quantitative yields within several minutes at room temperature. Complex **3b** was obtained in a similar manner from **2b** and selenium. The tristannatellone **4** can also be synthesized from **2a** and a slight excess of tellurium at room temperature in about 1 h. However, the reaction proceeds more rapidly with gentle heating (20 min, 40 °C) to give **4** in 73% yield. The mild reaction conditions necessary to produce the fully chalcogenated complexes **3a**, **3b**, and **4** are in striking contrast to those used to prepare the partially chalcogenated complexes **A** and **B**, which require boiling toluene and long reaction times (24–48 h).[7] Clearly, the negative charge in the anion of **2a** results in a dramatic enhancement of the susceptibility of the Sn$^{\mathrm{II}}$ centers towards oxidation. The complexes **3a**, **3b**, and **4** were characterized by multinuclear NMR spectroscopy, elemental analyses and, in the case of **3b** and **4**, by X-ray crystallography.

X-ray structural determinations of **3b**[11] and **4**[12] revealed the presence of three terminal Sn=E bonds in each complex (**3b**, E = Se; **4**, E = Te) (Figure 1 and 2, respectively). For **3b**

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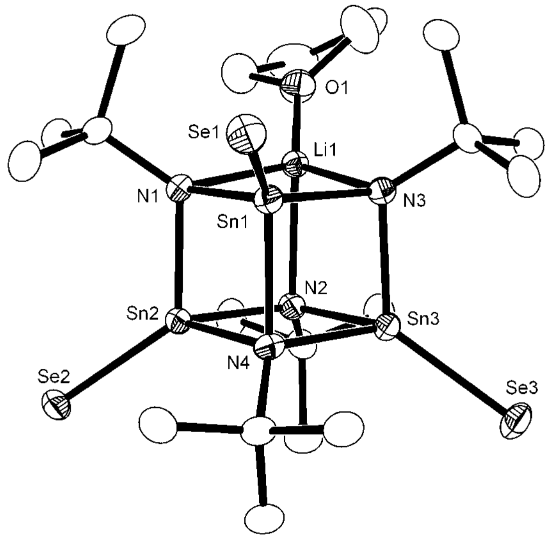

Figure 1. X-ray crystal structure of the anion in **3b**; selected bond lengths [Å]: Sn1-Se1 2.397(1), Sn2-Se2 2.391(1), Sn3-Se3 2.386(1). Thermal ellipsoids are shown at the 30% probability level.

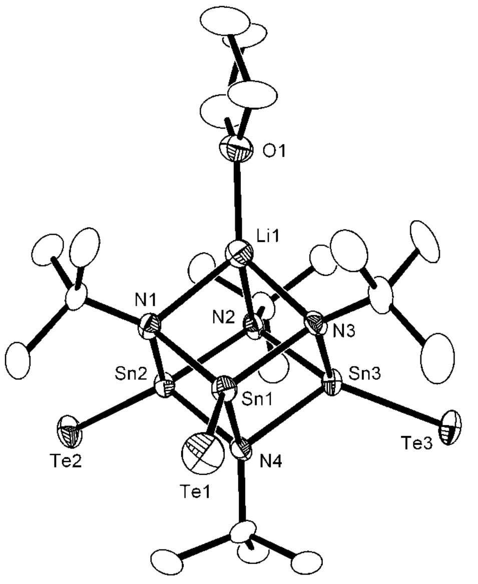

Figure 2. X-ray crystal structure of the anion in **4**; selected bond lengths [Å]: Sn1-Te1 2.613(1), Sn2-Te2 2.605(1), Sn3-Te3 2.610(1). Thermal ellipsoids are shown at the 30% probability level.

the Sn=Se bond lengths are nearly equal, with a mean value of 2.391(1) Å, slightly longer than the average Sn=Se bond length of 2.367(1) Å in the structurally related neutral complex **B**.[7] The average Sn=Te bond length of 2.609(1) Å in **4** is significantly longer than the corresponding bond in **A** (2.589(1) Å),[7] and slightly shorter than the distance of 2.618(1) Å observed in the five-coordinate complex [{CH(SiMe$_3$)C$_9$H$_6$N-8}$_2$SnTe].[13] The environments of the four-coordinate Sn^{IV} centers are highly distorted from tetrahedral in both structures, with bond angles in the range 83.6(2)–129.2(1)° in **3b** and 83.4(3)–129.0(2)° in **4**. The tin–nitrogen distances in **3b** and **4** show similar trends. The unique nitrogen center, which caps all three tin atoms, exhibits significantly longer Sn–N distances (**3b**, 2.174(4)–2.184(4) Å; **4**, 2.15(1)–2.18(1) Å) in comparison to the nitrogen centers that bridge two tin atoms and the lithium atom (**3b**, 2.082(4)–2.105(4) Å; **4**, 2.07(1)–2.12(1) Å).

The solution NMR data for the complexes **3a**, **3b**, and **4** are consistent with the presence of a single species with local C_3 symmetry in each case. For example, the ^{1}H NMR spectra show two resonances in a 3:1 ratio for the N*t*Bu protons, as expected. In the ^{7}Li NMR spectra of the complexes **3a**, **3b**, and **4**, the resonance in the region $\delta = 1.7$–1.8 ppm is shifted significantly from that observed for the parent clusters **2a** or **2b** ($\delta = 2.6$ ppm), and is therefore attributed to the lithium cation that is part of the cubane cluster. For the complexes **3a** and **3b**, nearly identical NMR data were obtained, and so the data obtained for **3a** will serve as an example. The ^{119}Sn NMR spectrum of **3a** shows a single sharp resonance at $\delta = -133$ ppm, with well-resolved ^{77}Se satellites. The magnitude of $^1J_{\mathrm{Sn,Se}}$ (3180 Hz) is comparable to the values in the range 2950–3450 Hz found for five-coordinate complexes.[13,14] A single resonance is also observed in the ^{77}Se NMR spectrum, with well-resolved ^{117}Sn/^{119}Sn satellites. The room-temperature ^{119}Sn NMR spectrum of **4** exhibits a single resonance at $\delta = -450$ ppm, which is considerably broader than that observed for **3a** and no ^{125}Te satellites are observed, presumably as a result of chalcogen exchange. Consistently, at 213 K, this resonance becomes sharper, and ^{125}Te satellites can be detected. The value of the $^1J_{\mathrm{Te,Sn}}$ coupling (8400 Hz) is consistent with an Sn=Te terminal bond.[13] A single resonance at $\delta = -314$ ppm was observed in the ^{125}Te NMR spectrum of **4**, however poor solubility at low temperature prohibited the observation of well-resolved tin satellites.

The facile chalcogen exchange between clusters can be used advantageously for the synthesis of partially chalcogenated derivatives. Thus, stoichiometric addition of **2a** to solutions of **3a** or **4** results in the rapid and clean formation of the corresponding mono- and dichalcogenated clusters. This approach produces analytically pure products more readily than the direct reaction of **2a** with elemental chalcogens. Details of the synthesis and characterization of the partially chalcogenated complexes will be reported in a full account of this work.

In summary, we have developed a new, high-yield, synthetic route to completely chalcogenated imidotin clusters, which proceeds rapidly under mild conditions. The Sn^{II} centers of the anionic cubane in the solvent-separated ion pairs **2a** or **2b** show remarkable reactivity towards chalcogenation. Furthermore, the dilithio complexes **3** and **4** obtained by this route are potential synthons for the generation of a variety of heterobimetallic imidotin chalcogenides, which may serve as a source of ternary semiconductors by the thermal elimination of the diazene *t*BuN=N*t*Bu.[15]

Experimental Section

All reactions and the manipulations of products were performed under an argon atmosphere by using standard Schlenk techniques or an inert atmosphere glove box. NMR spectra were obtained on [D$_8$]THF solutions at 298 K (unless otherwise noted) using a Bruker AMX 300 spectrometer. ^{77}Se, ^{119}Sn, and ^{125}Te NMR spectra were referenced to the external standards $(SePh)_2$, $SnMe_4$, and $(TePh)_2$, respectively. The reagent **1** was prepared by modification of the literature procedure.[9]

2a: A solution of **1** (9.00 g, 14.0 mmol) in THF (100 mL) was cooled to −78 °C to form a yellow slurry, and a cold (−78 °C) THF solution (60 mL) of *n*-butyllithium (1.6 M in hexane, 17.5 mL, 28.0 mmol) was added dropwise by using a cannula over 40 min. The resulting clear orange solution was stirred for 30 min at −78 °C, then allowed to warm slowly to room temperature, and stirred for an additional 45 min. The solvent was removed under vacuum and the yellow-orange residue was washed with hexanes (4 × 50 mL). The remaining solid was dissolved in diethyl ether (200 mL) and the solution was concentrated to about 100 mL, resulting in the precipitation of fine yellow crystals of **2a** (5.50 g, 39 %). Elemental analysis calcd (%) for **2a** (with loss of one THF) $C_{32}H_{68}N_4Li_2O_4Sn_3$: C 40.76, H 7.27, N 6.79; found: C 40.32, H 7.40, N 6.49; ^{1}H NMR: $\delta = 1.32$ (s, 27 H; N*t*Bu), 1.35 (s, 9 H; N*t*Bu), 1.78 (m, 20 H; THF), 3.63 ppm (m, 20 H; THF); ^{7}Li NMR: $\delta = -0.62$ (s; $[Li(thf)_4]^+$), 2.63 ppm (s; $[(thf)LiSn_3(NtBu)_4]^-$); ^{119}Sn NMR: $\delta = 538$ ppm (s).

2b: A solution of [12]crown-4 (0.40 mL, 2.42 mmol) in THF (25 mL) was added to a solution of **2a** (2.50 g, 2.46 mmol) in THF (50 mL) by using a cannula, and the mixture was stirred for 30 min at 25 °C. The solvent was removed under vacuum and the residue was washed with cold diethyl ether (50 mL) to give **2b** as a pale yellow solid (1.88 g, 78 %). Elemental analysis calcd (%) for **2b** (with loss of 0.5 THF) $C_{30}H_{64}N_4Li_2O_{5.5}Sn_3$: C 38.38, H 6.87, N 5.97; found: C 38.14, H 6.77, N 6.60; ^{1}H NMR: $\delta = 1.34$ (s, 27 H; N*t*Bu), 1.37 (s, 9 H; N*t*Bu), 1.78 (m, 8 H; THF), 3.63 (m, 8 H; THF), 3.84 ppm (s, 16 H; [12]crown-4); ^{7}Li NMR: $\delta = -0.47$ (s; $[(thf)Li([12]crown\text{-}4)]^+$), 2.61 ppm (s; $[(thf)LiSn_3(NtBu)_4]^-$); ^{119}Sn NMR: $\delta = 534$ ppm (s).

3a: A mixture of **2a** (0.600 g, 0.59 mmol) and gray selenium powder (0.160 g, 2.03 mmol) in THF (20 mL) was stirred for 5 min at 25 °C. The resulting deep yellow solution was filtered though a 0.45µm pore size filter disk, concentrated to about 5 mL, and **3a** was precipitated as a yellow solid (0.720 g, 97 %) by the addition of diethyl ether. Elemental analysis calcd (%) for $C_{36}H_{76}N_4Li_2O_5Se_3Sn_3$: C 34.54, H 6.12, N 4.48; found: C 33.74, H 5.86, N 4.58; ^{1}H NMR: $\delta =$ 1.47 (s, 27 H; N*t*Bu), 1.57 (s, 9 H; N*t*Bu), 1.77 (m, 20 H; THF), 3.61 ppm (m, 20 H; THF); ^{7}Li NMR: $\delta = -0.60$ (s; $[Li(thf)_4]^{+)}$, 1.75 ppm (s; $[(thf)LiSn_3(NtBu)_4]^{-)}$; ^{77}Se NMR: $\delta = -174$ ppm (s, $^1J_{^{119}Sn,^{77}Se} = 3185$ Hz, $^1J_{^{117}Sn,^{77}Se} = 3065$ Hz); ^{119}Sn NMR: $\delta = -133$ ppm (s, $^2J_{^{119}Sn,^{117}Sn} = 305$ Hz, $^1J_{^{119}Sn,^{77}Se} = 3180$ Hz).

3b: This complex was prepared similarly from **2b** (0.200 g, 0.21 mmol) and gray selenium powder (0.053 g, 0.67 mmol) and obtained as a yellow solid (0.228 g, 91 %). Elemental analysis calcd (%) for $C_{32}H_{68}N_4Li_2O_6Se_3Sn_3$: C 31.72, H 5.66, N 4.62; found: C 31.84, H 5.87, N 4.47; ^{1}H NMR: $\delta = 1.50$ (s, 27 H; N*t*Bu), 1.60 (s, 9 H; N*t*Bu), 1.78 (m, 8 H; THF), 3.63 (m, 8 H; THF), 3.85 ppm (s, 16 H; [12]crown-4); ^{7}Li NMR: $\delta = -0.44$ (s; $[(thf)Li([12]crown\text{-}4)]^{+)}$, 1.72 ppm (s; $[(thf)LiSn_3(NtBu)_4]^{-)}$; ^{77}Se NMR: $\delta = -172$ ppm (s, $^1J_{^{119}Sn,^{77}Se} =$ 3174 Hz, $^1J_{^{117}Sn,^{77}Se} = 3030$ Hz); ^{119}Sn NMR: $\delta = -133$ ppm (s, $^2J_{^{119}Sn,^{117}Sn} = 312$ Hz, $^1J_{^{119}Sn,^{77}Se} = 3200$ Hz). X-ray quality crystals of **3b** were obtained by slow diffusion of *n*-hexane into a THF solution.

4: A mixture of **2a** (0.600 g, 0.59 mmol) and tellurium powder (0.260 g, 2.04 mmol) in THF (30 mL) was stirred for 20 min at 40 °C. The resulting deep orange solution was filtered though a 0.45 µm pore size filter disk, concentrated to about 5 mL, and diethyl ether (1 mL) was added to give **4** as red crystals (0.600 g, 73 %). Elemental analysis calcd (%) for $C_{36}H_{76}N_4Li_2O_5Sn_3Te_3$: C 30.93, H 5.48, N 4.01; found: C 30.79, H 5.61, N 4.07; ^{1}H NMR: $\delta = 1.52$ (s, 27 H; N*t*Bu), 1.62 (s, 9 H; N*t*Bu), 1.78 (m, 20 H; THF), 3.62 ppm (m, 20 H; THF); ^{7}Li NMR: $\delta =$ −0.70 (s; $[Li(thf)_4)]^+$), 1.82 ppm (s; $[(thf)LiSn_3\{NtBu\}_4]$); ^{119}Sn NMR (213 K): $\delta = -439$ ppm (s, $^1J_{^{125}Te,^{119}Sn} = 8400$ Hz); ^{125}Te NMR: $\delta =$ −313 ppm. X-ray quality crystals of **4** were obtained by slow diffusion of *n*-hexane into a THF solution.

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[11] Crystal data for **3b**: 2 $(C_{32}H_{68}N_4Li_2O_6Se_3Sn_3)\cdot 0.5(C_4H_8O)$, $M_r =$ 2459.52, monoclinic, space group $P2_1/c$, $a = 26.332(5)$, $b =$ 10.920(2), $c = 36.260(7)$ Å, $\beta = 107.51(3)°$, $V = 9943(3)$ Å^3, $Z =$ 4, $\rho_{calcd} = 1.643$ g cm^{-3}, $\mu = 3.731$ mm^{-1}, $T = 173(2)$ K. A yellow platelike crystal (0.20 × 0.12 × 0.05 mm^3) was coated with Paratone 8277 oil and mounted on a glass fiber. Data were collected on a Nonius Kappa CCD diffractometer by using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by Patterson techniques and refined by least-squares calculations (SHELXL-97). Of the 84 930 reflections collected, 22 185 were unique ($R_{int} = 0.071$) and used to refine 891 parameters. Complex **3b** crystallizes with two independent but chemically equivalent molecules in the asymmetric unit. The disorder in the [12]crown-4 unit and the coordinated and lattice-bound THF molecules was treated by using appropriate models. Refinement was carried out on F^2 against all independent reflections and converged at $R_1 = 0.050$ (for 15 995 reflections with $I > 2\sigma(I)$) and $wR_2 = 0.133$ (for all data).

[12] Crystal data for **4**: 6 $(C_{36}H_{76}N_4Li_2O_5Sn_3Te_3)\cdot 0.5(C_6H_{14})$, $M_r =$ 8429.63, triclinic, space group $P\bar{1}$, $a = 23.401(5)$, $b = 26.126(5)$, $c = 26.459(5)$ Å, $\alpha = 84.97(3)$, $\beta = 84.26(3)$, $\chi = 83.01(3)°$, $V =$ 15 929(6) Å^3, $Z = 2$, $\rho_{calcd} = 1.758$ g cm^{-3}, $\mu = 3.053$ mm^{-1}, $T =$ 173(2) K. Crystal size : 0.16 × 0.06 × 0.06 mm^3. Data collection, structure solution and refinement followed the procedures outlined above for **3b**. Of the 182 994 reflections collected, 55 941 were unique ($R_{int} = 0.071$) and used to refine 2556 parameters. Complex **4** crystallizes with six independent, but chemically equivalent molecules in the asymmetric unit. Disorder in the cubane and THF molecules was treated by using appropriate models. Refinement converged at $R_1 = 0.071$ (for 35 294 reflections with $I > 2\sigma(I)$) and $wR_2 = 0.177$ (for all data). CCDC-241572 (**3b**) and CCDC-241573 (**4**) contain the supple-

mentary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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