Multiple Bonds between Sn and S: Synthesis and Structural Characterization of (CyNC(tBu)NCy)2Sn=S and [(CyNC(Me)NCy)2Sn(μ-S)]2

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Abstract: Two new sulfido complexes of tin have been prepared by the reaction of styrene sulfide with novel tin(II) amidinate complexes. These compounds exhibit two very different bonding modes for the sulfido ligand; in one case, S=Sn(CyNC(tBu)NCy)2 (**3**), a terminal Sn=S moiety was found while in the other case, [(CyNC(Me)NCy)2Sn-(μ-S)]2 (**4**), a bridging sulfido dimer is observed. The starting complexes were prepared by the reaction of 2 equiv of the appropriate lithium amidinate with SnCl2 to yield the new species Sn(CyNC(R)NCy)2 [Cy = cyclohexyl; R = Me (**1**); R = tBu (**2**)]. This account represents the first report of (CyNC(tBu)NCy)− and the coordination chemistry of this bulky ligand. Spectroscopic and elemental analyses confirmed the formulas of all of these new species. Compounds **2**, **3,** and **4** were further characterized by X-ray crystallography. Compound **2** possesses a coordination geometry based on a trigonal bipyramid with one equatorial vertex occupied by the stereochemically active lone pair of electrons. Crystal data for **2**: monoclinic, $P2_1/c$, $a = 18.944(5)$ Å, $b = 10.604(2)$ Å, $c = 19.423(2)$ Å, $\beta = 95.99(1)°$, $Z = 4$, $R = 0.046$, $R_w = 0.049$. Crystal data for **3**: orthorhombic, $Cmcm$, $a = 12.3788(23)$ Å, $b = 14.1977(15)$ Å, $c = 20.670(3)$ Å, $Z = 4$, $R = 0.057$, $R_w = 0.070$. Crystal data for **4**: monoclinic, $P2/n$, $a = 13.0395(2)$ Å, $b = 13.0263(2)$ Å, $c = 23.8856(2)$ Å, $\beta = 95.719(3)°$, $R = 0.055$, R_w 0.044.

Introduction

Among the properties that are ascribed uniquely to the first-row elements of the periodic table is the ability to form multiple bonds. As one moves to the heavier congeners of these elements, the appearance of multiply bonded species declines. Recently, the challenge presented in preparing complexes with multiple bonds between group 14 metals and the chalcogens has occupied much attention. For example, isolation and structural characterization of species possessing Ge=S and Ge=Se moieties have been achieved through the kinetic stabilization provided by steric congestion/protection of this function (e.g. Tbt(Tip)Ge=S).[1,2] Alternatively, thermodynamic stability has been attained through the coordination of a base to the group 14 center and was employed to stabilize [η3-{(μ-tBuN)2(SiMeNtBu)2}]GeS.[3] The examples of stable terminal chalcogenides of Sn in solution include [tetra(aryl)porphyrin]-Sn=E (E = S, Se)[4] and Tbt(Tip)Sn=E (E = S, Se).[5] Neither of these species has been structurally characterized, and in fact, the latter exhibits a dimeric chalcogenido-bridge structure, [Tbt-(Tip)Sn(μ-E)]2, in the solid state. A versatile supporting ligand, octamethyldibenzotetraaza[14]annulene (Me8taa2−), was recently utilized for the preparation of precursors to tin and germanium terminal chalcogenido complexes.[6] The complexes [η4-Me8-

taa]Sn=E (E = S, Se) represent the only structurally characterized terminal chalcogenido complexes of tin.[6b,7]

Tin amidinates display a rich coordination chemistry with the metal in both the divalent and tetravalent oxidation states, however, these results have been, by and large, limited to use of the N-silylated benzamidinate.[8−10] Through modification of the organic substituents on the nitrogen atoms and at the bridge position, these ligands present an ideal system to explore the effects of steric bulk and electronic features on the coordinated metal center. For example, formamidinate ligands are known to favor unusual structural features in both transition metal and main group metal chemistry.[11,12] Our investigation of the coordination chemistry of amidinate anions has relied on their generation by the addition of alkyl anion equivalents to carbodiimides. For example, we have synthesized and crystallographically characterized complexes of the (CyNC(R)NCy)−

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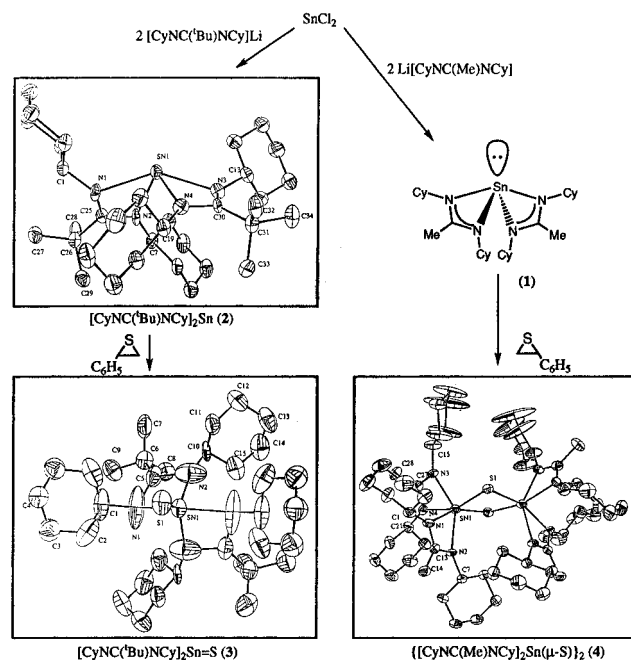(12) (a) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1996**, *35*, 1423. (b) Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1996**, *35*, 2448.

Figure 1. Reaction sequence for the synthesis of complexes **1−4**. Molecular structure and atom numbering schemes for [CyNC('Bu)-NCy]₂Sn (**2**), [CyNC('Bu)NCy]₂Sn=S (**3**), and {[CyNC(Me)NCy]₂Sn-(μ-S)}₂ (**4**) (Cy = cyclohexyl). Hydrogen atoms and solvent molecules have been omitted for clarity.

(Cy = cyclohexyl; R = Me, 'Bu) and (Me₃SiNC('Bu)NSiMe₃)⁻ anions which were generated by the addition of appropriate alkyllithium reagent to CyN=C=NCy, dicyclohexylcarbodiimide and Me₃SiN=C=NSiMe₃, bis(trimethylsilyl)carbodiimide, respectively.[12]

We report the synthesis of a unique family of tin−sulfido complexes in which a change to a remote portion of the ligand dramatically affects the stability of the terminal Sn=S bond. The new bulky amidinate ligand, (CyNC('Bu)NCy)⁻, provided the supporting environment for a structurally characterized terminal Sn=S complex which is unique in the absence of macrocyclic supporting ligation. By simply changing the 'Bu group of the amidinate ligand to Me, a bridging mode for the sulfido group was obtained. These results provide a unique example for the structural characterization of these two bonding modes of the chalcogenido ligand within one family of compounds.[13]

Results and Discussion

The *in situ* preparation of (CyNC(R)NCy)Li (R = Me, 'Bu) followed by addition of SnCl₂ generated the Sn(II) complexes **1** and **2** in greater than 70% isolated yields (Figure 1). Both of these compounds have been thoroughly characterized by spectroscopic means, microanalysis and subsequent reactivity. Compound **2** was further characterized through a single-crystal X-ray diffraction study.[14] As can be seen in Figure 1, **2** possesses a geometry derived from a distorted trigonal bipyramid in which one equatorial vertex is occupied by a stereochemically active lone pair of electrons and N1 and N3 are in pseudoaxial positions.[15] The amidinate rings are approximately planar with the average axial Sn-N bonds (2.38 Å) and slightly longer than the average equatorial Sn−N bonds (2.19 Å). The average of these four bonds (2.287 Å) is slightly longer than that of the structurally characterized Sn(IV) benzamidinate complex (2.143 Å).[8d]

(13) A similar example of both bridging and terminal bonding modes for S atoms can be found in refs 1(a) and 1(d) where the replacement of a ligand on the metal center results in the isolation of monomeric Tbt(Tip)-Ge=S or dimeric [Tbt(Mes)Ge(μ-S)]₂.

Treatment of these two new species with styrene sulfide followed the redox pathway outlined in Figure 1. In both cases the reaction was rapid and complete (>90% yield). While spectroscopic and microanalytical data for both products provided formulas, a firm indication that **3** and **4** were not isostructural was first indicated by the observation of a dramatic difference in the ¹¹⁹Sn NMR chemical shifts for **3** and **4**; complex **3** exhibited a ¹¹⁹Sn resonance at −236.2 ppm relative to SnMe₄, while for complex **4**, a signal at −484.4 ppm was observed. For comparison, the Sn(II) starting materials, **1** and **2**, exhibited ¹¹⁹Sn NMR signals at −272.0 and −223.0 ppm, respectively. As a result, we undertook an investigation of the structures of **3** and **4** by single-crystal X-ray diffraction.

Complex **3** crystallized in the orthorhombic space group *Cmcm* with Z = 4.[16] From Figure 1 it is clear that the most outstanding structural feature in this molecule is the terminal Sn=S bond. The bond length, Sn1−S1, of 2.280(5) Å correlates favorably with the only comparable report in the literature of 2.274(3) Å.[6b] The Sn=S bond in **3** is shorter than the terminal sulfur linkages found for a series of polythioanions which span a range of 2.325−2.381 Å.[7] The distorted trigonal bipyramidal Sn coordination geometry in this complex is similar to that of the Sn(II) starting material (**2**) with the Sn−S vector residing in the equatorial site previously occupied by the lone electron pair and N1 and N1a in the pseudoaxial sites. Not surprisingly, the Sn−N bonds for **3** are shorter than in the starting material **2**. There are no striking differences between these complexes for the structural parameters within the ligands.

In surprising contrast to **3**, the structural analysis of **4** (see Figure 1) revealed a dimeric [(C₁₄H₂₅N₂)₂SnS]₂ complex with a C₂ axis perpendicular to the nearly square (Sn−μ-S)₂ ring.[17] The Sn atoms have pseudooctahedral coordination geometries and the two Sn-S distances (2.434(2) Å, 2.476(2) Å) are, as expected, significantly longer than in **3**.

Through changes to the substituent on the central carbon of the NCN unit in two amidinate ligands, we have been able to

(14) Selected bond distances (Å) and bond angles (deg) for **2**: Sn1−N1, 2.363(5); Sn1−N2, 2.203(5); Sn1−N3, 2.394(5); Sn1−N4, 2.186(5); N1−C1, 1.478(8); N1−C25, 1.327(8); N2−C7, 1.460(8); N2−C25, 1.329-(8); N3−C13, 1.444(8); N3−C30, 1.341(8); N4−C19, 1.448(8); N4−C30, 1.368(8); N1−Sn1−N2, 57.1(2); N1−C25−N2, 110.9(5); N1−Sn1−N3, 144.3(3); N1−C25−C26, 126.0(6); N1−Sn1−N4, 98.3(2); N2−C25−C26, 122.9(6); N2−Sn1−N3, 96.1(2); N4−C19−C20, 110.3(5); N2−Sn1−N4, 95.0(2); N4−C19−C24, 110.6(5); N3−Sn1−N4, 57.7(2); N3−C30−N4, 110.0(5); N3−C30−C31, 128.7(6); N1−N1−C1, 124.9(4); N4−C30−C31, 121.3(6); Sn1−N1−C25, 92.0(4); C1−N1−C25, 127.0(5); Sn1−N2−C7, 133.7(4); Sn1−N2−C25, 99.3(4); C7−N2−C25, 127.0(5); Sn1−N3−C13, 130.0(4); Sn1−N3−C30, 91.1(4); C13−N3−C30, 128.5(5); Sn1−N4−C19, 130.9(4); Sn1−N4−C30, 99.7(4); C19−N4−C30, 129.5(5); N2−C7−C12, 110.3(5).

(15) For a similar Sn(II) structure with the diiminophosphinate ligand [Ph₂P(NSiMe₃)₂⁻], see: Kilimann, U.; Noltemeyer, M.; Edelmann, F. T. *J. Organomet. Chem.* **1993**, *443*, 35.

(16) Selected bond distances (Å) and bond angles (deg) for **3**: Sn1−N1, 2.19(1); Sn1−N2, 2.09(1); N1−C1, 1.47(2); N1−C5, 1.69(2); N2−C5, 1.70(2); S1−Sn1−N1, 107.9(3); S1−Sn1−N2, 130.0(3); N1−Sn1−N1a, 144.2(4); N1−Sn1−N2, 78.6(2); N2−Sn1−N2b, 100.0(5); N2−C10−C11, 108.1(13); Sn1−N1−C1, 136.1(8); C5−N2−C10c, 113.0(11); Sn1−N1−C5, 85.5(7); N1−C5−C6, 129.0(13); C1−N1−C5, 115.1(7); C5−C6−C8, 105.9(14); Sn1−N2−C5, 88.5(8); Sn1−N2−C10, 157.5(7); N1−C5−N2, 106.4(11); N2−C5−C6, 122.7(14); C5−C6−C7, 115.3(15).

(17) Selected bond distances (Å) and bond angles (deg) for **4**: Sn1−N1, 2.226(5); N1−C1, 1.456(7); Sn1−N2, 2.264(4); N1−C13, 1.315(7); Sn1−N3, 2.215(4); N2−C7, 1.475(7); Sn1−N4, 2.226(4); N2−C13, 1.345-(8); S1−Sn1a, 2.4757(16); N3−C15, 1.466(8); N4−C21, 1.466(7); N3−C27, 1.322(8); N4−C27, 1.305(7); S1−Sn1−S1a, 88.95(5); N2−Sn1−N3, 143.1(2); S1−Sn1−N1, 157.1(1); N2−Sn1−N4, 93.17(2); S1−Sn1−N2, 98.6(1); N3−Sn1−N4, 59.1(2); S1−Sn1−N3, 107.9(1); Sn1−S1−Sn1a, 89.24(5); S1−Sn1−N4, 97.1(1); C1−N1−C13, 123.9(5); S1a−Sn1−N1, 93.6(1); Sn1−N2−C13, 92.7(3); S1a−Sn1−N2, 108.4(1); C7−N2−C13, 121.3(4); S1a−Sn1−N3, 97.6(1); Sn1−N3−C27, 94.0(3); S1a−Sn1−N4, 156.6(1); C15−N3−C27, 124.2(5); N1−Sn1−N2, 59.1(2); Sn1−N4−C27, 94.0(4); N1−Sn1−N3, 94.3(2); C21−N4−C27, 124.1(5).

prepare both terminal sulfido and μ-sulfido complexes of Sn. X-ray crystallographic studies and spectroscopic parameters confirm the features of these complexes. We suggest that the fact that an alteration to a remote substituent of the amidinate ligand leads to a profound change in the structure of the product is due to the steric congestion of the ᵗBu-substituted amidinate. Formation of a monomeric species is favored by relaxation of the ligand strain and interligand repulsions that would be present in a dimeric framework. Our continuing investigations are oriented at dissecting the steric and electronic features that influence the formation and reactivity of these tin−sulfido compounds and their germanium analogues.

Experimental Section

General Procedure. All reactions were carried out either in a nitrogen-filled drybox or under nitrogen using standard Schlenk-line techniques. Diethyl ether, hexane, and THF were distilled under nitrogen from potassium. Deuterated benzene was dried by vacuum transfer from potassium. MeLi (1.4 M in diethyl ether), ᵗBuLi (1.7 M in hexane), $SnCl_2$, and dicyclohexylcarbodiimide were purchased from Aldrich and used without further purification.

Sn[C_6H_{11}NC(Me)NC$_6$H$_{11}$]$_2$ (1). A Schlenk flask was charged with dicyclohexylcarbodiimide (1.36 g, 6.60 mmol), diethyl ether (20 mL), and a stir bar. To this solution was added MeLi (4.8 mL, 1.4 M, 6.60 mmol), and the mixture was stirred for an additional 30 min. In a separate Schlenk flask, $SnCl_2$ was dissolved in 20 mL of THF (0.62 g, 3.30 mmol). The two Schlenk flasks were cooled to −78 °C in a dry ice/acetone bath, and the $SnCl_2$ solution was combined with the amidinate solution *via* cannula. The reaction mixture was stirred overnight, and the reaction temperature was allowed to warm to room temperature slowly. The solvent was removed under oil pump vacuum, and the residue was extracted with 40 mL of hexane. The solution was concentrated to ca. 15 mL, and the mixture was put in the freezer for 3 days. The resulting white crystals of **1** were collected by filtration and dried (1.44 g, 78%, 2.57 mmol). Mp (sealed): 147−149 °C. IR (Nujol, cm^{-1}): 1516 (s). ^{1}H NMR (C_6D_6, ppm): 3.25 (br, C_6H_{11}, 4H), 1.95−1.15 (m, C_6H_{11}, 40H), 1.63 (s, Me, 6H). ^{13}C NMR (C_6D_6, ppm): 165.5 (s, NCN), 56.5, 36.3, 26.4, 26.2 (4s, C_6H_{11}), 12.6 (s, Me). ^{119}Sn NMR (C_6D_6, ppm): −272.0. Anal. Calcd for $C_{28}H_{50}N_4$Sn: C, 59.90; H, 8.98; N, 9.98. Found: C, 59.69; H, 9.20; N, 9.93.

Sn[C_6H_{11}NC(CMe$_3$)NC$_6$H$_{11}$]$_2$ (2). A Schlenk flask was charged with dicyclohexylcarbodiimide (1.36 g, 6.60 mmol), diethyl ether (35 mL) and a stir bar. To this solution was slowly added ᵗBuLi (3.9 mL, 1.7 M in hexane, 6.60 mmol) and the mixture was stirred for an additional 30 min. $SnCl_2$ (0.63 g, 3.30 mmol) was added and the reaction mixture was stirred overnight. The solvent was removed under oil pump vacuum, and the residue was extracted with 40 mL of hexane. The hexane was removed under vacuum, and the pale yellow powder was dissolved in 10 mL of ether. After the mixture was cooled to −30 °C for 3 days, the resulting colorless crystals of **2** were collected by filtration and dried (1.55 g, 72%, 2.40 mmol). Mp (sealed): 103−105 °C. IR (thin film, cm^{-1}): 2927 (vs), 2846 (s), 1594 (w), 1488 (m), 1446 (s), 1425 (s),1356 (s), 1342 (s). ^{1}H NMR (C_6D_6, ppm): 4.07 (br, C_6H_{11}, 4H), 2.05−1.15 (m, C_6H_{11}, CMe$_3$, 76H). ^{119}Sn NMR (C_6D_6, ppm): −223.0. Anal. Calcd for $C_{34}H_{62}N_4$Sn: C, 63.26; H, 9.68; N, 8.68. Found: C 63.47; H, 9.86; N, 8.45.

[[C_6H_{11}NC(Me)NC$_6$H$_{11}$]$_2$SnS]$_2$ (3). Complex **1** (0.80 g, 1.43 mmol) was dissolved in 15 mL of hexane followed by the addition of excess styrene sulfide. The reaction mixture was stirred at room temperature overnight. The resulting white solid was collected by filtration and dried under oil pump vacuum (0.79 g, 93%, 1.33 mmol). Crystals were obtained by cooling a concentrated THF solution of **3** to −30 °C. Mp

(sealed): 239−241 °C. IR (Nujol, cm^{-1}): 1514 (s). ^{1}H NMR (C_6D_6, ppm): 3.37 (br, C_6H_{11}, 8H), 2.22−1.22 (m, C_6H_{11}, 80H), 1.72 (s, Me, 12H). ^{119}Sn NMR (THF, ppm): −484.4. Anal. Calcd for $C_{56}H_{100}N_8S_2Sn_2$: C, 56.67; H, 8.49; N, 9.44. Found: C, 56.42; H, 8.69; N, 9.16.

[C_6H_{11}NC(CMe$_3$)NC$_6$H$_{11}$]$_2$SnS (4). Complex **2** (1.00 g, 1.55 mmol) was dissolved in 15 mL of hexane followed by the addition of excess styrene sulfide. The reaction mixture was stirred at room temperature overnight. The resulting white solid was collected by filtration and dried under oil pump vacuum (0.95 g, 90%, 1.40 mmol). Crystals were obtained by cooling a concentrated THF/ether (1:1 vol.) solution of complex **4** to −30 °C. Mp (sealed) 222−224 °C. Spectroscopic data: IR (Nujol, cm^{-1}): 1488 (m), 1456 (s), 1432 (s). ^{1}H NMR (C_6D_6, ppm): 3.90 (br, C_6H_{11}, 4H), 1.84−1.05 (m, C_6H_{11}, 40H), 1.18 (s, CMe$_3$, 18H). ^{119}Sn NMR (C_6D_6, ppm): −236.2. Anal. Calcd for $C_{34}H_{62}N_4$-SSn: C, 60.26; H, 9.22; N, 8.27. Found: C, 60.42; H, 9.39; N, 8.28.

X-ray Crystallography. Intensity data were collected on a Rigaku diffractometer at −153 °C using the $\omega-2\theta$ scan technique to a maximum 2θ value of 50° for crystals mounted on glass fibers. Cell constants and orientation matrices were obtained from the least-squares refinement of 25 carefully centered high-angle reflections. Redundant reflections were removed from the data set. The intensities of three representative reflections were measured after every 150 reflections to monitor the crystal and instrument stability. Data were corrected for Lorentz and polarization effects and absorption (ψ scan). The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were located in the difference Fourier maps and refined isotropically in the case of favorable observation/parameter ratio. The final cycle of full-matrix least-squares refinement was based on the number of observed reflections with [$I > 2.5\sigma(I)$]. Anomalous dispersion effects were included in the F_{calc}. All calculations were performed using the NRCVAX package. Full details of the data collection, refinement, and final atomic coordinates are reported in the Supporting Information.

Summary of Crystal Data. Complex 2: space group $P2_1/c$ (monoclinic); $a = 18.944(5)$ Å, $b = 10.604(2)$ Å, $c = 19.423(2)$ Å, $\beta = 95.99(1)$; $Z = 4$; empirical formula $C_{34}H_{62}N_4$Sn + (C_4H_{10}O); $F(000) = 1543.65$; number of unique reflections = 3997; $R = 0.046$, $R_w = 0.049$.

Complex 3: space group $Cmcm$ (orthorhombic); $a = 12.3788(23)$ Å, $b = 14.1977(15)$ Å, $c = 20.670(3)$ Å; $Z = 4$; empirical formula $C_{34}H_{62}N_4$SnS; $F(000) = 1468.51$; number of unique reflections = 1029; $R_F = 0.057$, $R_w = 0.070$. The Sn and S atoms were found on special positions. The positions of some of the ligand atoms, which were found to be disordered over two locations, were modeled by splitting the occupancy over the two sites.

Complex 4: space group $P2/n$ (monoclinic); $a = 13.0395(2)$ Å, $b = 13.0263(2)$ Å, $c = 23.8856(2)$ Å, $\beta = 95.719(3)°$; $Z = 2$; empirical formula $C_{56}H_{100}N_8Sn_2S_2$, this structure also contained 1 molecule of benzene and 4 molecules of THF in the crystal lattice; $F(000) = 1637.47$; number of unique reflections = 6936; $R_F = 0.055$, $R_w = 0.044$.

Supporting Information Available: A listing providing a description of the structural solutions, tables of atomic positions, thermal parameters, crystallographic data, bond distances and angles, and ORTEP drawings for compounds **2**−**4** (40 pages). See any current masthead page for ordering and Internet access instructions.