Organometallics **1999,** *18,* 4700−4705

Formation of Novel Tetrasulfido Tin Complexes and Their Ability To Catalyze the Cyclotrimerization of Aryl Isocyanates

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Received May 27, 1999

Unusual cyclic tin tetrasulfido complexes $\{(CyNC(R)NCy)[N(SiMe_3)_2]\}SnS_4$ (Cy = cyclohexyl; R = Me (**3**), ^{t}Bu (**4**)) were prepared by the reaction of elemental sulfur with newly reported divalent tin starting materials $[CyNC(R)NCy]Sn[N(SiMe_3)_2]$ (R = Me (**1**), ^{t}Bu (**2**)). Compounds **3** and **4** were further converted to dimeric bridging sulfido complexes, $\{(CyNC(R)NCy)[N(SiMe_3)_2]Sn(\mu\text{-}S)\}_2$ (R = Me (**5**), ^{t}Bu (**6**)), which can also be derived from the oxidative addition of sulfur atom sources (e.g., propylene sulfide) to **1** and **2**, respectively. Single-crystal X-ray diffraction studies of **2**, **4**, and **6** are presented. Compounds **3** and **4** are outstanding catalysts for the cyclotrimerization of aryl isocyanates to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates) at room temperature. The results of a single-crystal X-ray analysis of triphenylisocyanurate (**7**) are also reported.

Our efforts to elucidate the factors that lead to unusual structural features and consequently to remarkable reactivity for the p-block metals have focused on employing amidinate anions as potentially tunable supporting ligands in complexes of these elements. For example, bulky trialkyl amidinates provide the environment for the preparation of novel terminal chalcogenido complexes of group 14 metals {e.g., $S{=}Sn(C_6H_{11}NC(^tBu)NC_6H_{11})_2$, $Se{=}Ge[C_6H_{11}NC(Me)NC_6H_{11}][N(SiMe_3)_2]$}.[1,2] The observation of terminal chalcogenido species for Ge compounds having a combination of amido and amidinato ligands prompted our investigation of the Sn(II) analogues. We now describe the synthesis of new cyclic tin tetrasulfido complexes derived from the oxidation of (alkylamidinato)(amido)Sn(II) species with elemental sulfur. These novel compounds function as outstanding catalysts for the rapid and selective catalytic cyclotrimerization of aryl isocyanates to yield isocyanurates.

Results and Discussion

Compounds **1** and **2** were obtained from the sequential reaction of $SnCl_2$ with 1 equiv of the appropriate lithium amidinate followed by addition of 1 equiv of lithium bis(trimethylsilyl)amide. Both complexes have been characterized by spectroscopic means, microanalysis, and subsequent reactivity. In particular, the ^{1}H and ^{13}C NMR spectra of these species are consistent with our formulation and remeniscent of the Ge analogues $[CyNC(R)NCy]GeN(SiMe_3)_2$ (R = Me, ^{t}Bu).[2]

In the case of **2**, X-ray structural analysis (Table 1) revealed that the Sn coordination geometry is as depicted in Scheme 1 and consisted of the nitrogen centers of one bidentate amidinate and the bis(trimethylsilyl)amido nitrogen. Figure 1 provides the molecular geometry and atom numbering schemes for **2** and shows that the metal center resides in a distorted tetrahedral environment with one vertex occupied by a stereochemically active lone pair of electrons. The result is an overall pyramidal ligand array around the M(II) center. The planarity of the amidinate ligand is confirmed by the fact that the sum of the internal angles for the four-membered Sn−amidinate ring is 358.2(4)°. The corresponding C13−N1 and C13−N2 bond lengths (average 1.34 Å) are consistent with delocalization of the π bond in the N−C−N unit of the ligand. This complex exhibits two slightly different M−N(amidinate) bond distances with values that are in line with those observed for reported complexes of these ligands.[1,3] The Sn−N(amido) distance (2.134(4) Å) is only slightly longer than in $Sn[N(SiMe_3)_2]_2$ (2.09(1) Å).[4] The structural features of these complexes are similar to the Ge analogues which generated terminal chalcogenido complexes upon reaction with elemental chalcogens.[2]

Sulfido Complexes. Reactions of **1** and **2** with elemental sulfur proceeded efficiently, as shown in Scheme 1, to yield complexes with chelating bidentate S_4^{2-} ligands. A rich variety of transition metal complexes with this type of ligand is known, and these species possess unique structures and reactivities.[5,6] In contrast, main group analogues are relatively rare.[7−10]

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[1] Zhou,Y.; Richeson, D. S. *J. Am. Chem. Soc.* **1996**, *118*, 10850.

[2] Foley, S.; Bensimon, C.; Richeson, D. *J. Am. Chem. Soc.* **1997**, *119*, 10359.

[3] Zhou, Y.; Richeson, D. S. *Inorg. Chem.* **1997**, *36*, 501, and references therein.

[4] Fjeldberg, T.; Hope, H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639. Lappert, M. F.; Power, P. P.; Slade, M. J.; Hedberg, L.; Hedberg, K.; Schomaker, V. *J. Chem. Soc., Chem. Commun.* **1979**, 369.

[5] For reviews of polysulfido complexes see: (a) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. (b) Draganjac, M.; Rauchfuss, T. B. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 742.

[6] For reviews of polychalcogenido complexes see: (a) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195. (b) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223. (c) Dubois, M. R. *Chem. Rev.* **1989**, *89*, 1.

[7] A tris(pyrazolylborate)InS_4 complex is reported in: Reger, D. L.; Coan, P. S. *Inorg. Chem.* **1995**, *34*, 6226.

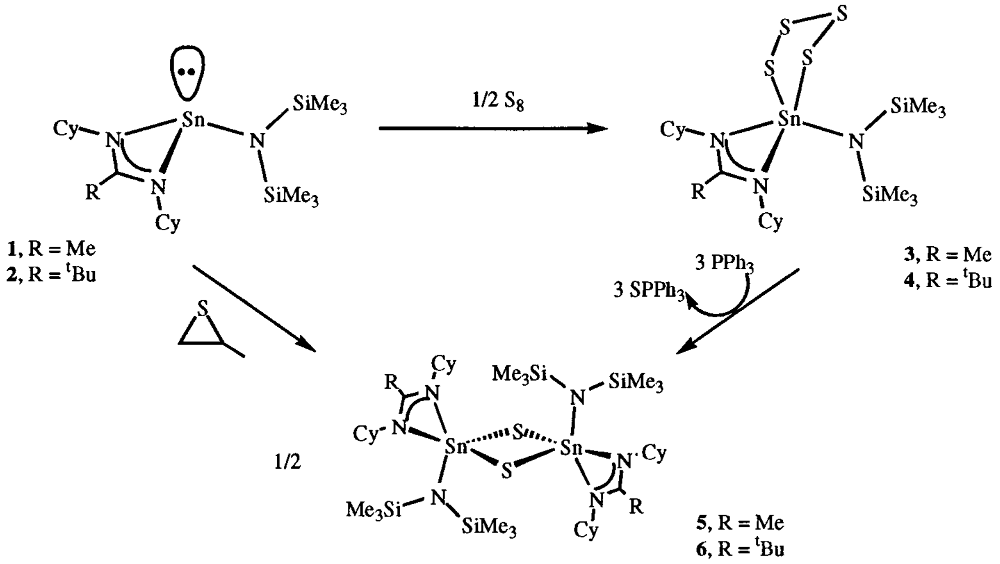
10.1021/om990405w CCC: $18.00
Publication on Web 10/22/1999

Table 1. Crystallographic Data for 2, 4, 6, and 7

	2	**4**	6	**7**
empirical formula	$C_{23}H_{49}N_3Si_2Sn$	$C_{23}H_{49}N_3S_4Si_2Sn$	$C_{46}H_{98}N_6S_2Si_4Sn_2$	$C_{27}H_{21}N_3O_3$
fw	542.52	670.76	1149.16	435.47
temp (K)	203(2)	203(2)	203(2)	203(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
unit cell dimen (Å, deg)	$a = 11.266(3)$ $b = 12.173(3)$ $c = 12.877(4)$ $\alpha = 67.321(4)$ $\beta = 66.285(4)$ $\gamma = 70.237(4)$	$a = 10.5767(7)$ $b = 10.7715(7)$ $c = 15.255(1)$ $\gamma = 84.472(1)$ $\beta = 85.874(1)$ $\gamma = 68.747(1)$	$a = 10.842(1)$ $b = 12.040(1)$ $c = 13.492(1)$ $\alpha = 71.051(2)$ $\beta = 69.605(2)$ $\gamma = 63.381(2)$	$a = 13.882(2)$ $b = 13.666(2)$ $c = 12.630(2)$ $\alpha = 90$ $\beta = 96.512(3)$ $\gamma = 90$
volume (Å^3)	1456.4(7)	1610.9(2)	1445.6(3)	2380.7(7)
Z	2	2	1	4
density (calc) (Mg/m^3)	1.237	1.383	1.320	1.215
abs coeff (mm^{-1})	0.973	1.144	1.054	0.081
$F(000)$	572	700	604	912
goodness-of-fit on F^2 [a]	1.109	1.003	1.016	1.031
final R indices [$I > 2\sigma(I)$][b]	R1 = 0.0444, wR2 = 0.1236	R1 = 0.0359, wR2 = 0.0743	R1 = 0.0345, wR2 = 0.0601	R1 = 0.0685, wR2 = 0.1774
R indices (all data)	R1 = 0.0491, wR2 = 0.1254	R1 = 0.0457, wR2 = 0.0815	R1 = 0.0528, wR2 = 0.0612	R1 = 0.1305, wR2 = 0.1955

[a] GooF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$: n = number of reflections, p = total number of parameters. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Scheme 1



Outstanding exceptions in this area are a series of group 14 complexes employing bulky aryl substitutents, e.g., Tbt(Mes)MS_4 (M = Si, Ge, Sn; X = S, Se; Mes = mesityl; Tbt = 2,4,6-[$(SiMe_3)_2CH]_3C_6H_2$) and Tbt(Tip)MS_4 (M = Si, Ge, Sn, Pb; Tip = 2,4,6-[$(CH_3)_2CH]_3C_6H_2$).[8] The stability of these species has been attributed to the efficient steric protection offered by the Tbt ligand. These compounds serve as precursors to both stable and transient terminal sulfido complexes via chalcogen atom abstraction routes.[11] It should be noted that the bis(amido) complexes, M(II)[$N(SiMe_3)_2]_2$ (M = Ge, Sn), undergo rapid reaction with chalcogens (Ch = S, Se, Te) to yield the bridged dimers (μ-Ch)$_2$\{M[$N(SiMe_3)_2]_2$\}$_2$.[12]

The structural details of **4** are displayed in Figure 2 as provided by a single-crystal X-ray diffraction study (Table 1). This complex exhibits the Sn(IV) center in a

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(8) (a) Saito, M.; Tokitoh, N.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, *119*, 11124. (b) Tokitoh, N.; Kano, N.; Shibata, K.; Okazaki, R. *Organometallics* **1995**, *14*, 3121. (c) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Organometallics* **1995**, *14*, 1008. (d) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351. (e) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Tetrahedron Lett.* **1992**, *33*, 2531. (f) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6151. (g) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *112*, 7047.

(9) The compound $[N(Et)_4]_2\{[Sn(S_4)_3]_{0.4}[Sn(S_4)_2(S_6)]_{0.6}\}$, which consists of $[Sn(S_4)_3]^{2-}$ and $[Sn(S_4)_2(S_6)]^{2-}$ anions, has been reported. Muller, A.; Schimanski, J.; Romer, M.; Bogge, H.; Baumann, F.-W.; Eltzner, W.; Krickemeyer, E.; Billerbeck, U. *Chimia* **1985**, *39*, 25.

(10) Steudel et al. have prepared $(C_6H_5)_2M(S_4)$ (M = Ge, Si), which are reported to be stable only below −20 °C. Albertsen, J.; Steudel, R. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1992**, *65*, 165. Steudel, R. In *Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; p 233.

(11) (a) Kano, N.; Tokitoh, N.; Okazaki, R. *Chem. Lett.* **1997**, 277. (b) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578. (c) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316. (d) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (e) Tokitoh, N.; Matsumoto, T.; Ichida, H.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6877.

(12) Hitchcock, P. B.; Jang, E.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1995**, 3179. Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F.; Leung, W.-P. Rai, A. K.; Taylor, R. E. *Polyhedron* **1991**, *10*, 1203.

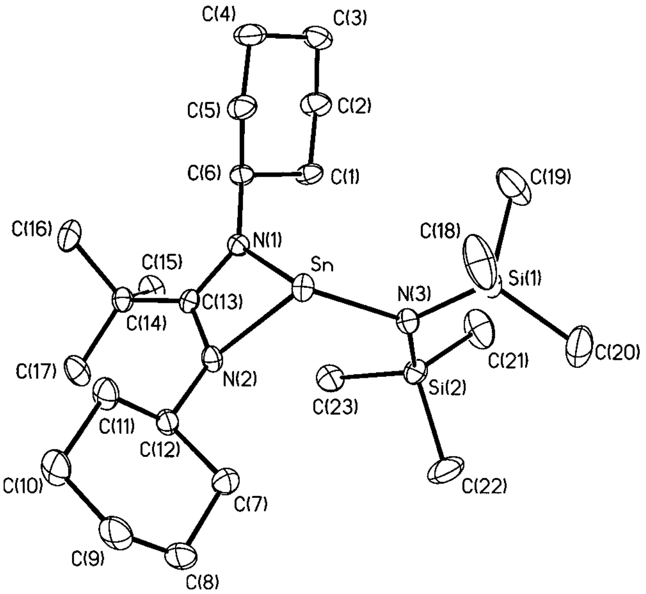

Figure 1. Molecular structure and atom-numbering scheme for (CyNC(^{t}Bu)NCy)Sn[N(SiMe$_3$)$_2$] (**2**) (Cy = cyclohexyl). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg.): Sn−N(3) 2.134(4), Sn−N(1) 2.192(4), Sn−N(2) 2.216(4), Si(1)−N(3)1.728(4), Si(2)−N(3) 1.732(4), N(1)−C(13) 1.330(5), N(1)−C(6) 1.465(5), N(2)−C(13) 1.354(6), N(2)−C(12) 1.443(5), N(3)−Sn−N(1) 101.3(1), N(3)−Sn−N(2) 105.3(1), N(1)−Sn−N(2) 59.4(1), C(13)−N(1)−C(6) 131.8(4), C(13)−N(1)−Sn 95.7(3), C(6)−N(1)−Sn 131.5(3), C(13)−N(2)−C(12) 130.4(4), C(13)−N(2)−Sn 93.9(2), C(12)−N(2)−Sn 124.3(3), Si(1)−N(3)−Si(2) 120.7(2), Si(1)−N(3)−Sn 110.4(2), Si(2)−N(3)−Sn 128.8(2), N(1)−C(13)−N(2) 109.2(4), N(1)−C(13)−C(14) 123.1(4), N(2)−C(13)−C(14) 127.7(4).

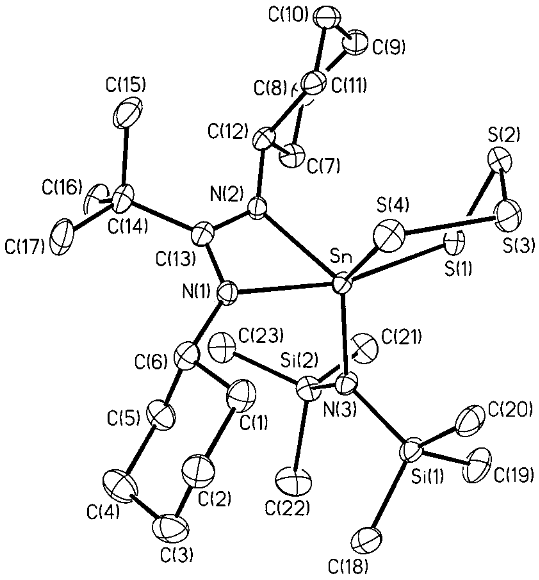

Figure 2. Molecular structure and atom-numbering scheme for {(CyNC(^{t}Bu)NCy)[N(SiMe$_3$)$_2$]}SnS$_4$ (**4**) (Cy = cyclohexyl). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Sn−N(3) 2.065(2), Sn−N(2) 2.136(2), Sn−N(1) 2.217(3), Sn−S(4) 2.4637(9), Sn−S(1) 2.5230(10), Sn−C(13) 2.644(3), S(1)−S(2) 2.0610(14), S(2)−S(3) 2.0450(16), S(3)−S(4) 2.0622(16), N(3)−Sn−N(2) 119.05(10), N(3)−Sn−N(1) 98.57(10), N(2)−Sn−N(1) 60.53(9), N(3)−Sn−S(4) 131.89(8), N(2)−Sn−S(4) 105.03(7), N(1)−Sn−S(4) 86.34(7), N(3)−Sn−S(1) 91.94(8), N(2)−Sn−S(1) 105.94(7), N(1)−Sn−S(1) 165.80(7), S(4)−Sn−S(1) 93.77(3), S(2)−S(1)−Sn 101.15(5), S(3)−S(2)−S(1) 102.00(6), S(2)−S(3)−S(4) 102.96(6), S(3)−S(4)−Sn 103.16(5).

distorted five-coordinate geometry consisting of a bidentate amidinate, the bis(trimethylsilyl)amido ligand, and the S1 and S4 centers of a chelating tetrasulfido ligand. The five-membered SnS$_4$ ring is in a distorted half-chair conformation with S2 and S3 deviating on either side of the S1−Sn−S4 plane by 0.707 and 0.500 Å, respectively. The S1−Sn−S4 angle of 93.77(3)° is similar to structurally characterized SnS$_4$ rings.[8d,9] The S−S bond distances exhibit distinct alternation (S1−S2 2.0610(14), S2−S3 2.0450(16), S3−S4 2.0622(16) Å) with the average being slightly shorter than the 2.050 Å average S−S bond observed for orthorhombic sulfur.[13]

As anticipated, reaction of **3** or **4** with PPh$_3$ lead to abstraction of ring sulfur atoms, with the ultimate products being complexes **5** and **6**. Spectroscopic and microanalytical data for **5** and **6** allowed confirmation of their constitutions, and single-crystal X-ray diffraction studies revealed that these compounds are dimers of presumed transient terminal sulfido intermediate complexes. An ORTEP diagram for **6** is shown in Figure 3. From this figure it is clear that **6** is a dimeric species with bridging sulfido ligands resulting in a planar four-membered [Sn(μ-S)]$_2$ unit. The coordination sphere of the Sn atom is completed by amido and bidentate amidinato ligands which are arranged in a trans orientation relative to the [Sn(μ-S)]$_2$ core. Compounds **5** and **6** could also be prepared in a rapid and complete reaction of **1** and **2** with sulfur atom sources (e.g., styrene sulfide, propylene sulfide) following the redox pathway outlined in Scheme 1. These same species could not be obtained in a clean manner by direct reaction of the Sn(II) starting material (**1** or **2**) with elemental sulfur. Tin sulfides can exhibit a range of aggregation, the degree of which is known to depend on the steric bulk of the supporting ligands bonded to tin and the availability of intramolecular bases for coordination to the metal center.[12,14−17]

The fact that the reported Sn compounds favor singly bonded, bridging sulfur centers while the Ge analogues were found to be terminal is consistent with the steric observations made in our previous investigations.[1] Furthermore, the fact that, unlike their Ge analogues, **1** and **2** did not react with elemental Se is consistent with the relative stabilities of Sn(II) and Ge(II) toward oxidation.

Catalytic Cyclotrimerization of Isocyanates. In an attempt to trap the presumed terminal sulfido intermediate in the reaction of **3** or **4** with PPh$_3$ using aryl isocyanates, we discovered that the tetrasulfido

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[13] Complete structural details for S$_8$ measured at T = 203 K are provided in the Supporting Information. Crystal system: orthorhombic. Space group: *Fddd*. Cell parameters: a = 10.402(2) Å, b = 12.771(2) Å, c = 24.400(4) Å.

[14] Puff, H.; Bertram, G.; Ebeling, B.; Franken, M.; Gattermayer, R.; Hundt, R.; Schuh, W.; Zimmer, R. *J. Organomet. Chem.* **1989**, *379*, 235, and references therein.

[15] Jung, O.-S.; Hwa, J.; Sohn, Y. S. *Polyhedron* **1989**, *8*, 2557.

[16] Jurkschat, K.; Van Dreumel, S.; Dyson, G.; Dakternieks, D.; Bastow, T. J.; Smith, M. E.; Drager, M. *Polyhedron* **1992**, *11*, 2747, and references therein.

[17] Leung, W.-P.; Kwok, W.-H.; Law, L. T. C.; Zhou, Z.-Y.; Mak, T. C. W. *Chem. Commun.* **1996**, 505.

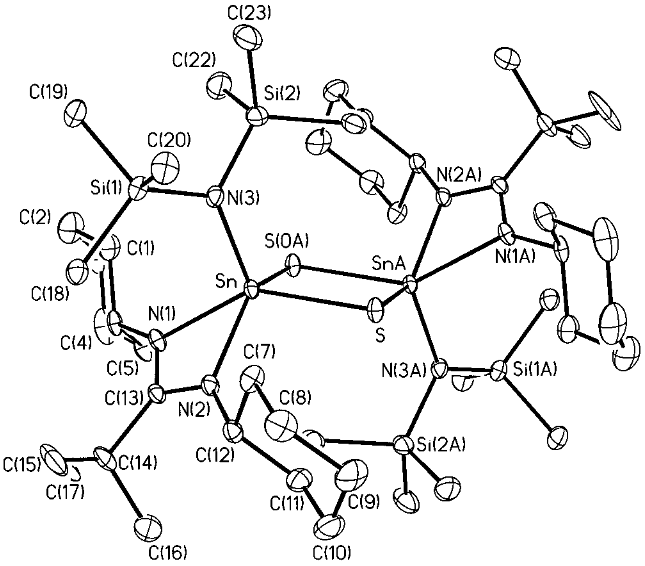
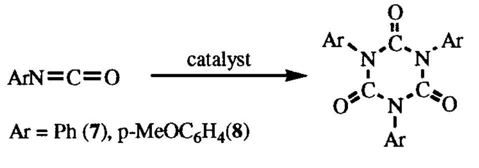


Figure 3. Molecular structure and atom-numbering scheme for $\{(CyNC(^tBu)NCy)[N(SiMe_3)_2]Sn(\mu\text{-}S)\}_2$ (**6**). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Sn−N(3) 2.068(2), Sn−N(2) 2.169(3), Sn−N(1) 2.218(3), Sn−S(0A) 2.4373(8), Sn−S 2.4685(8), S−Sn(A) 2.4373(8) N(3)−Sn−N(2) 111.48(10), N(3)−Sn-N(1) 104.48(10), N(2)−Sn−N(1) 59.35(9), N(3)−Sn−S(0A) 111.08(7), N(2)−Sn−S(0A) 134.01(7), N(1)−Sn−S(0A) 93.66(7), N(3)−Sn−S 108.18(7), N(2)−Sn−S 94.34(7), N(1)−Sn−S 144.04(7), S(0A)−Sn−S 88.40(3), Sn(A)−S−Sn 91.60(3).

complexes **3** and **4** are outstanding catalysts for the cyclotrimerization of aryl isocyanates to yield triaryl isocyanurates (eq 1). Triaryl isocyanurates are useful



(1)

activators for anionic polymerization of ϵ-caprolactams to nylon-6 and are known to substantially enhance the stability of polyurethane networks and coating materials with respect to thermal resistance, flame retardation, chemical resistance, and film-forming characteristics.[18−26] Various isocyanate trimerization catalysts have been described, with a majority of the conventional catalysts being anions or neutral Lewis bases.[17−21] Typical catalysts are organic acid salts and tertiary amines.[20] However, some metal-based systems have been described, and a Lewis acid pathway could be envisioned for these systems.[22−25] Conventional catalysts for isocyanurate formation suffer from low activity, necessitating severe conditions, poor selectivity resulting in byproducts, and difficulty in separating the catalysts from the product. Our catalyst system appears to address these difficulties.

Table 2. Data for the Cyclotrimerization of Aryl Isocyanates To Yield Triarylisocyanurates[a]

catalyst	substrate	time (min)	isolated yield (%)
3	C_6H_5NCO	12	95
3	p-$MeOC_6H_4NCO$	14	95
4	C_6H_5NCO	60	68
4	p-$MeOC_6H_4NCO$	90	77
$P(MeNCH_2CH_2)_3N$[b]	C_6H_5NCO	2	94
$P(MeNCH_2CH_2)_3N$[b]	p-$MeOC_6H_4NCO$	5	94
CsF[c]	C_6H_5NCO	20	80.2
NEt_3	C_6H_5NCO	20	0
AcOK	C_6H_5NCO	20	0

[a] All reactions carried out in neat isocyanate at room temperature. [b] Data from ref 16. [c] Data from ref 17.

The catalytic activity of species **3** and **4** is superior to or comparable to literature species (Table 2). The tetrasulfido complex **3** catalyzes the trimerization of phenyl isocyanate quantitatively and purely within minutes of addition of complex to neat isocyanate. For example, with 2 mol % catalyst a 95% isolated yield of pure triphenyl isocyanurate is obtained within 12 min at room temperature. In fact, the purity offered by our system permitted the isolation of single crystals of isocyanurate when the reaction was carried out in benzene, thus allowing for a structural determination of **7** (Table 1). Figure 4 provides the ORTEP diagram of **7**.

A comparison with both conventional and recently reported catalysts is provided by Table 2. In particular it is notable that under similar experimental conditions, triethylamine and potassium acetate, commonly employed catalysts, are inactive toward triphenyl isocyanurate production. Only the phosphine superbase, $P(MeNCH_2CH_2)_3N$,[17] gives a comparable performance to the tin tetrasulfido species.

The tetrasulfido catalysts can be recycled without apparent loss of activity. When an active catalyst system was probed by ^1H NMR, only the starting SnS_4 complex (**3** or **4**) was observed, no byproducts were evident, and no degradation of the starting material was noticed.

The superior catalytic nature of **3** and **4** is reflected in their ability to readily trimerize aryl isocyanates with electron-donating substituents. In the case of *p*-methoxyphenyl isocyanate, a substrate which is noted for its reduced reactivity and difficulty in generating the corresponding isocyanurate, complex **3** displayed no decrease in reactivity and produced $[p\text{-}MeO(C_6H_4)NCO]_3$ in 95% isolated yield within 14 min at room temperature.[18,20]

The mechanism for this catalytic transformation is a current point of investigation. The possibility of a Lewis acid-based pathway may be supported by our preliminary observation that other Sn amidinate and amido complexes are effective albeit inferior isocyanurate trimerization catalysts. A Lewis base pathway may receive some support from the observation by Okazaki

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(18) Tang, J.; Mohan, T.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 4931, and references therein. Tang, J.; Verkade, J. G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 896, and references therein.

(19) Nambu, Y.; Endo, T. *J. Org. Chem.* **1993**, *58*, 1932, and references therein.

(20) (a) Mizura, J.; Yokozawa, T.; Endo, T. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1545. (b) Endo, T.; Suike, J. JP 1989 01226878 A2 (Cl. C07D251/34); *Chem. Abstr.* **1990**, *112*, 77236v.

(21) Tanimoto, F.; Kitano, H. JP 72 22,558 (Cl. C07D) 1972; *Chem. Abstr.* **1972**, *77*, 88546f. Kitano, H.; Tanimoto, F.; Miura, J. JP 73 26,-022 (Cl. C07D) 1973; *Chem. Abstr.* **1973**, *79*, 115642j.

(22) Spirkova, M.; Kubin, M.; Spacek, P.; Krakovsky, I.; Dusek, K. *J. Appl. Polym. Sci.* **1994**, *53*, 1435. Spirkova, M.; Kubin, M.; Spacek, P.; Krakovsky, I.; Dusek, K. *J. Appl. Polym. Sci.* **1994**, *52*, 895.

(23) Srinivas, B.; Chang, C.-C.; Chen, C.-H.; Chiang, M. Y.; Chen, I.-T.; Wang, Y.; Lee, G.-H. *J. Chem. Soc., Dalton Trans.* **1997**, 957.

(24) Villa, J. F.; Powell, H. B. *Synth. React. Inorg. Metal-Org. Chem.* **1976**, *6*, 59.

(25) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 6858.

(26) Noltes, J. G.; Boersma, J. *J. Organomet. Chem.* **1967**, *7*, P 6.

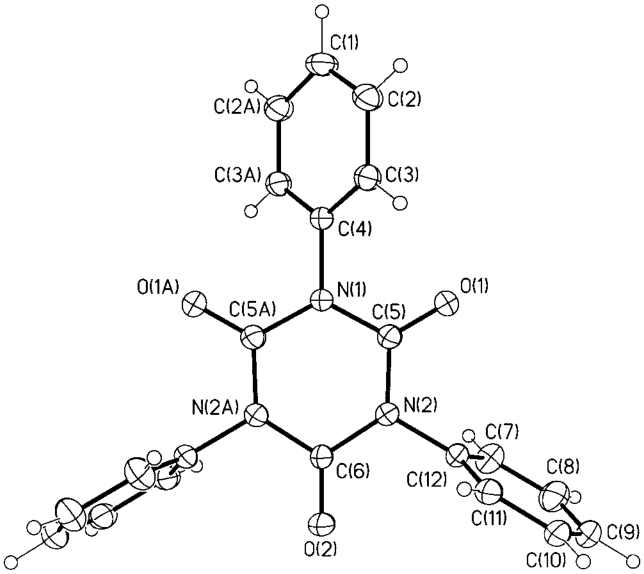

Figure 4. Molecular structure and atom-numbering scheme for $(PhNCO)_3$ (**7**). Selected bond distances (Å) and angles (deg): O(1)−C(5) 1.211(3), O(2)−C(6) 1.203(4), N(1)−C(5) 1.395(3), N(1)−C(4) 1.458(4), N(2)−C(5) 1.387(3), N(2)−C(6) 1.391(3), N(2)−C(12) 1.455(3), C(5)−N(1)−C(5)a 123.6(3), C(5)−N(1)−C(4) 118.22(13), C(5)−N(2)−C(6) 124.7(2), C(5)−N(2)−C(12) 118.15(19), C(6)−N(2)−C(12) 117.18(19), C(3)−C(4)−N(1) 119.30(15), O(1)−C(5)−N(2) 121.9(2), O(1)−C(5)−N(1) 122.3(2), N(2)−C(5)−N(1) 115.8(2), O(2)−C(6)−N(2) 122.46(14), N(2)A−C(6)−N(2) 115.1(3).

et al. of the nucleophilic behavior for the β-S in the Ar_2SnS_4 and Ar_2GeS_4 complexes that they reported.[8c,27]

Conclusion

In summary, these results add significantly to the limited number of structurally characterized main group cyclopolychalcogenido complexes and will help to delineate the steric and electronic features that stabilize and influence the reactivity of such species. The reactivity of **1** and **2** contrasts with the reported Ge(II/IV) analogues yielding cyclic tetrasulfido species (**3** and **4**) and μ-sulfido complexes (**5** and **6**) rather than terminal species. The cyclo-SnS_4 complexes are interesting and very effective catalysts for isocyanate trimerization. We are currently attempting to clarify the details regarding the catalyst lifetime and activity as well as illustrate the selectivity of this system. Furthermore, we hope to extend these efforts to include identification of the features that favor isocyanate dimer, trimer, and polymer formation.

Experimental Details

General Procedure. All manipulations were carried out either in a Vacuum Atmospheres drybox or under nitrogen using standard Schlenk-line techniques. Diethyl ether, hexane, toluene, benzene, and deuterated benzene were distilled under nitrogen from Na/K alloy. MeLi (1.4 M in diethyl ether), ^{t}BuLi (1.7 M in pentane), $SnCl_2$, dicyclohexylcarbodiimide, $LiN(SiMe_3)_2$, phenyl isocyanate, *p*-methoxyphenyl isocyanate, and propylene sulfide were purchased from Aldrich and used without further purification. S_8 was recrystallized from toluene. NMR spectra were run on a GEMINI 200 MHz spectrometer with deuterated benzene as a solvent and internal standard. All elemental analyses were run on a Perkin-Elmer PE CHN 4000 elemental analysis system.

$[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2]$ (1). To a solution of dicyclohexylcarbodiimide (0.653 g, 3.16 mmol) in diethyl ether (60 mL) was added MeLi (2.26 mL, 1.4 M, 3.16 mmol). After 30 min, 1 equiv of $SnCl_2$ (0.600 g, 3.15 mmol) was added to this mixture, which was stirred for 1.5 h. Lithium bis(trimethylsilylamide) (0.530 g, 3.16 mmol) was then added to the reaction mixture. The solution was stirred for another 12 h and filtered to remove the white LiCl precipitate. The solvent was removed under vacuum, at which point a yellow oil was observed as the sole product (1.49 g, 94% yield). ^{1}H NMR (C_6D_6, ppm): 3.09 (br, C_6H_{11}, 2H); 1.97−1.02 (m, C_6H_{11}, 20H); 1.35 (s, Me, 3H); 0.47 (s, $SiMe_3$, 18H). ^{119}Sn NMR (C_6D_6, ppm vs $SnMe_4$): 17.6.

$[C_6H_{11}NC(^tBu)NC_6H_{11}]Sn[N(SiMe_3)_2]$ (2). To a solution of dicyclohexylcarbodiimide (0.816 g, 3.97 mmol) in diethyl ether (60 mL) was added ^{t}BuLi (2.33 mL, 1.7 M, 3.96 mmol). After 15 min, 1 equiv of $SnCl_2$ (0.750 g, 3.96 mmol) was added to this mixture, which was stirred for 2 h. Lithium bis(trimethylsilylamide) (0.663 g, 3.96 mmol) was then added to the reaction mixture. The solution was stirred for another 14 h, filtered to remove the white LiCl precipitate, and evaporated to dryness. White crystals were obtained from diethyl ether at −34 °C (2.010 g, 94% yield). Mp: 82−84 °C. ^{1}H NMR (C_6D_6, ppm): 3.87 (br, C_6H_{11}, 2H); 2.16−0.92 (m, C_6H_{11}, 20H); 1.16 (s, ^{t}Bu, 9H); 0.48 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6, ppm): 173.5 (s, N*C*^{t}BuN); 55.6, 41.0, 35.7, 25.9 (4s, C_6H_{11}); 41.8 (s, *C*$(CH_3)_3$); 29.5 (s, C(*C*$H_3)_3$); 5.3 (s, $SiMe_3$). ^{119}Sn NMR (C_6D_6, ppm vs $SnMe_4$): 10.3. Anal. Calcd for $C_{23}H_{49}N_3Si_2Sn$: C 50.92; H 9.10; N 7.75. Found: C 50.73; H 8.88; N 7.41.

$[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2]S_4$ (3). To a solution of **1** (0.230 g, 0.460 mmol) in diethyl ether (5 mL) was added 0.5 equiv of S_8 (0.060 g, 0.234 mmol). The solution was allowed to react for 3 h. A small amount of insoluble white precipitate formed, which was filtered off. Yellow crystals were obtained from diethyl ether at −34 °C (0.19 g, 66% yield). Mp: 133 °C (dec). ^{1}H NMR (C_6D_6, ppm): 3.30 (br, C_6H_{11}, 2H); 1.87−0.96 (m, C_6H_{11}, 20H); 1.23 (s, Me, 3H); 0.40 (s, $SiMe_3$, 18H). ^{13}C NMR (C_6D_6, ppm): 168.3 (s, N*C*MeN); 56.2, 35.4, 25.7, 12.3 (4s, C_6H_{11}); 26.0 (s, C*C*H_3); 5.3 (s, $SiMe_3$). ^{119}Sn NMR (C_6D_6, ppm vs $SnMe_4$): 156.5. Anal. Calcd for $C_{20}H_{43}N_3Si_2S_4Sn$: C 38.21; H 6.89; N 6.68. Found: C 37.12; H 6.63; N 6.09.

$[C_6H_{11}NC(^tBu)NC_6H_{11}]Sn[N(SiMe_3)_2]S_4$ (4). To a solution of **2** (0.450 g, 0.829 mmol) in diethyl ether (20 mL) was added 0.5 equiv of S_8 (0.106 g, 0.415 mmol). The solution was allowed to react for 18 h. A small amount of insoluble white precipitate formed, which was filtered off. Yellow crystals were obtained from diethyl ether at −34 °C (0.38 g, 68% yield). Mp: 79−81 °C. ^{1}H NMR (C_6D_6, ppm): 3.72 (br, C_6H_{11}, 2H); 2.15−0.83 (m, C_6H_{11}, 20H); 1.08 (s, ^{t}Bu, 9H); 0.43 (s, $SiMe_3$, 18H). ^{119}Sn NMR (C_6D_6, ppm vs $SnMe_4$): 154.8. Anal. Calcd for $C_{23}H_{49}N_3Si_2S_4Sn$: C 41.18; H 7.36; N 6.26. Found: C 40.31; H 7.06; N 5.53.

$\{[C_6H_{11}NC(Me)NC_6H_{11}]Sn[N(SiMe_3)_2]S\}_2$ (5). To a solution of **1** (0.300 g, 0.600 mmol) in toluene (5 mL) was added excess propylene sulfide (0.180 g). The homogeneous solution was allowed to react for 5 days, after which sparingly soluble white crystals were obtained at room temperature (0.285 g, 89% yield). Mp: 172−173 °C. ^{1}H NMR ($CDCl_3$, ppm): 3.30 (br, C_6H_{11}, 2H); 1.97−1.05 (m, C_6H_{11}, 20H); 1.52 (s, Me, 3H); 0.43 (s, $SiMe_3$, 18H). Anal. Calcd for $C_{20}H_{43}N_3Si_2SnS$: C 45.11; H 8.14; N 7.89. Found: C 45.46; H 7.95; N 7.60.

$\{[C_6H_{11}NC(^tBu)NC_6H_{11}]Sn[N(SiMe_3)_2]S\}_2$ (6). To a solution of **2** (0.288 g, 0.531 mmol) in diethyl ether (4 mL) was added excess styrene sulfide (0.144 g). The homogeneous solution was allowed to react for 2 days, after which sparingly soluble white crystals were obtained at room temperature (0.276 g, 90% yield). Mp: 168−170 °C. ^{1}H NMR ($CDCl_3$, ppm): 3.65 (br, C_6H_{11}, 2H); 2.10−0.90 (m, C_6H_{11}, 20H); 1.39 (s, Me,

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(27) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R. *Organometallics* **1994**, *13*, 4387.

3H); 0.38 (s, $SiMe_3$, 18H). Anal. Calcd for $C_{23}H_{49}N_3Si_2SnS$: C 48.08; H 8.60; N 7.31. Found: C 47.71; H 8.79; N 7.61.

Reaction of 3 with PPh_3 To Form 5. To a solution of **3** (0.150 g, 0.239 mmol) in ether (5 mL) was added 3 equiv of triphenylphosphine (0.188 g, 0.718 mmol). Complex **5** slowly crystallized out of solution over 12 h. Crystals were isolated and washed with toluene (3 × 5 mL) and dried in vacuo (0.132 g, 98% yield).

Reaction of 4 with PPh_3 To Form 6. To a solution of **4** (0.150 g, 0.224 mmol) in ether (5 mL) was added 3 equiv of triphenylphosphine (0.176 g, 0.672 mmol). Complex **6** slowly crystallized out of solution over 12 h. Crystals were isolated and washed with toluene (3 × 5 mL) and dried in vacuo (0.117 g, 91% yield).

$(PhNCO)_3$ from 3. To complex **3** (0.200 g, 0.318 mmol) was added phenyl isocyanate (50 equiv, 1.890 g, 15.9 mmol). A crystalline white solid precipitated out of the yellow solution. After 12 min, the white solid was crushed into a powder and washed with 7 mL of benzene for 5 repetitions, filtered, and dried in vacuo to give 1.80 g (95.2% yield) of $(PhNCO)_3$. ^1H NMR ($CDCl_3$, ppm): 7.41−7.56 (m, C_6H_5). Anal. Calcd for $C_{21}H_{15}N_3O_3$: C 70.59; H 4.20; N 11.76. Found: C 70.80; H 4.50; N 11.50. Mp: 281.6−282.1 °C (lit. mp 281.0−281.5 °C). X-ray structural analysis confirmed the identity of this compound. Catalyst **3** was isolated by extraction with benzene, and the reaction with phenyl isocyanate was repeated with a 93% yield of $(PhNCO)_3$.

(p-$MeOC_6H_4NCO)_3$ from 3. To complex **3** (0.025 g, 0.040 mmol) was added *p*-methoxyphenyl isocyanate (50 equiv, 0.296 g, 2.00 mmol). A crystalline white solid precipitated out of the yellow solution. After 14 min, the white solid was crushed into a powder and washed with 5 mL of benzene for 5 repetitions, filtered, and dried in vacuo to give 0.281 g (95% yield) of (p-$OMePhNCO)_3$. ^1H NMR ($CDCl_3$, ppm): 3.70 (s, 9H, OCH_3), 6.85 (d, 6H, C_6H_4; $^3J_{HH} = 9.2$ Hz), 7.16 (d, 6H, C_6H_4; $^3J_{HH} = 9.2$ Hz). Mp: 258−259 °C (lit. mp 261 °C).

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

Supporting Information Available: Tables of X-ray diffraction data including atomic positions, thermal parameters, crystallographic data, bond distances and angles, and ORTEP drawings for compounds **2**, **4**, **6**, **7**, and S_8. This material can be obtained free of charge via the Internet at http://pubs.acs.org.

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