

## Communications to the Editor

### Hexakis(2,4,6-triisopropylphenyl)cyclotristannane ( $R_2Sn$ )<sub>3</sub> and Tetrakis(2,4,6-triisopropylphenyl)distannene ( $R_2Sn$ )<sub>2</sub>. Their Unprecedented Thermal Interconversion and the First Solution Spectral Characterization of a Distannene

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The synthesis of the titled cyclotristannane (**1**) which we outline below has led to the discovery of three remarkable phenomena: (1) Photolysis of **1** in methylcyclohexane at  $-78^\circ\text{C}$  provides the corresponding distannene (**2**) quantitatively (Scheme I), (2) compound **2** reverts to **1** and, in fact, **1** is in thermal equilibrium with **2** over a wide range of temperature, **2** being favored at higher temperatures (Scheme I), and (3) **2** has a dimeric<sup>1</sup> structure in solution, thus disclosing, for the first time, the solution spectra of a distannene derivative. Tetrakis[bis(trimethylsilyl)methyl]distannene (**3**), the only known example of a distannene (which exists as such in crystalline form), is reported to dissociate completely into the corresponding stannylene (**3a**) in solution.<sup>2</sup> It should be also pointed out that <sup>119</sup>Sn NMR spectroscopy has been used as a diagnostic tool for the determination of the degree of oligomerization, *n*, in cyclopolystannanes ( $R'_2Sn$ )<sub>*n*</sub>. By this new technique<sup>3</sup> the intensities of the satellite signals [due to the coupling with <sup>117</sup>Sn (*I*=1/2, natural abundance 7.67%)] relative to the main resonance provide the basis for the structural assignments of **1** and **2**.

**Synthesis of 1** (Scheme II). The synthesis of **1** is closely patterned after that previously reported for the synthesis of hexakis(2,6-diethylphenyl)cyclotristannane (Ar = 2,6-diethylphenyl in **1**).<sup>4a</sup> Thus, reaction of tin tetrabromide with (2,4,6-triisopropylphenyl)magnesium bromide followed by alkali treatment provides cyclotristannoxane **4**,<sup>5,6</sup> which is in turn converted to the dichloride **5**<sup>5</sup> with concentrated hydrochloric acid. After dropwise addition of a dark green solution of lithium naphthalenide in 1,2-dimethoxyethane (DME) to a solution of **5** in DME at  $-78^\circ\text{C}$ , the mixture is warmed to room temperature.

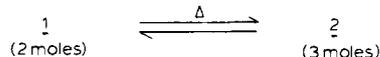
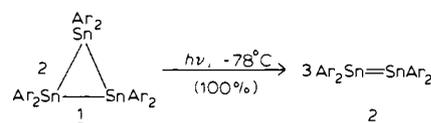
(1) With reference to the corresponding stannylene ( $Ar_2Sn$ ) monomer.  
(2) (a) Davidson, P. J.; Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2268. (b) Fjeldberg, T.; Haaland, A.; Lappert, M. F.; Schilling, B. E. R.; Seip, R.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1407.

(3) Sita, L. R.; Masamune, S. the technique to be published elsewhere.  
(4) For ( $R_2Sn$ )<sub>*n*</sub>, see: (a) Masamune, S.; Sita, L. R.; Williams, D. J. *J. Am. Chem. Soc.* **1983**, *105*, 630. (b) Neumann, W. P.; Fu, J. *J. Organomet. Chem.* **1984**, *273*, 295. (c) Fu, J.; Neumann, W. P. *Ibid* **1984**, *272*, C5. For the synthesis of ( $R_2M$ )<sub>*n*</sub> where M = Si (d-g), M = Ge (h,i), see: (d) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. (e) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333. (f) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781. (g) Schäfer, A.; Weidenbruch, M.; Peters, K.; Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302. (h) Masamune, S.; Hanzawa, Y.; Williams, D. J. *J. Am. Chem. Soc.* **1982**, *104*, 6136. (i) Snow, J. T.; Murakami, S.; Masamune, S.; Williams, D. S. *Tetrahedron Lett.* **1984**, *25*, 4191.

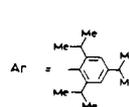
(5) Experimental details of Scheme II, including spectral data of all new compounds as well as copies of actual spectra of **1**, **2**, **7**, and **8**, are provided in the supplementary material.

(6) Compound **4** is yet another member of this rare class of compounds. For other examples, see ref 4a and: Puff, H.; Schuh, W.; Sievers, R.; Waid, W.; Zimmer, R. *J. Organomet. Chem.* **1984**, *260*, 271. The crystal structure of **4** will be recorded in: Sita, L. R. Ph.D. Dissertation, MIT, 1985.

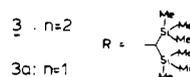
Scheme I



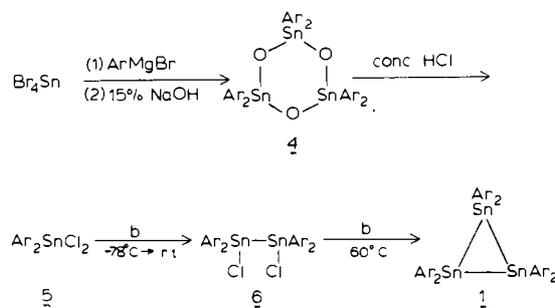
For **1** and **2**:



( $R_2Sn$ )<sub>*n*</sub>



Scheme II<sup>a</sup>



<sup>a</sup> Ar = 2,4,6-triisopropylphenyl. <sup>b</sup> Lithium naphthalenide/DME.

If the reaction is worked up at this point, the dichlorodistannane **6** is the only isolable product.<sup>5</sup> Further heating at  $60^\circ\text{C}$  followed by the usual workup and recrystallization provides orange-red crystals (**1**).<sup>7</sup> Compound **1** exhibits physical properties fully consistent with the cyclotrimeric<sup>1</sup> structure ( $C_{30}H_{46}Sn_3$ ): mass spectrum (field desorption) parent  $M^+$  cluster  $m/z$  1569–1583 and  $m/z$  1044–1058 (dimer);<sup>5</sup> UV (methylcyclohexane)  $\lambda_{\text{max}}$  300 nm ( $\log \epsilon$  4.74) tailing off into the visible region,  $\lambda$  450 nm ( $\log \epsilon$  3.24);<sup>8</sup> <sup>1</sup>H NMR shows the steric congestion of the ortho isopropyl groups.<sup>5</sup> A <sup>119</sup>Sn NMR (100.74 MHz, <sup>1</sup>H decoupled, methylcyclohexane-*d*<sub>14</sub>)<sup>9</sup>  $\delta$  (ppm from  $Me_4Sn$ , negative for high field) shows a single resonance at  $-378.9$  with two and only two tin-tin coupling satellites [ $^1J(^{119}Sn-^{117}Sn) = 3017$  Hz]. The fact that each satellite peak is 7.4% as intense as that of the parent peak shows that **1** has a cyclotrimeric structure<sup>10</sup> and excludes the possibility of it being dimeric<sup>1</sup> or cyclotetrameric.<sup>1,11</sup> The above

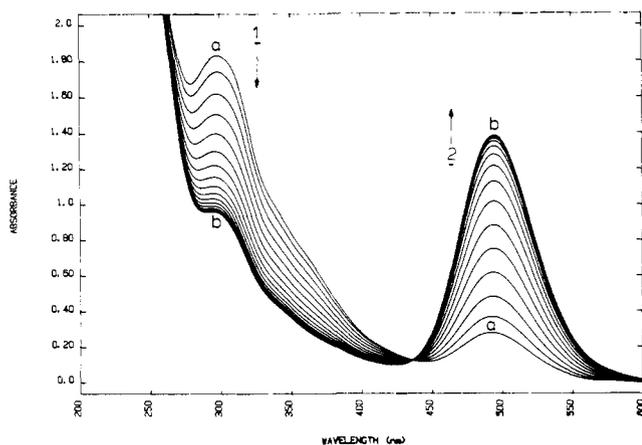
(7) Compound **1** can be alternatively prepared by the reduction of **6** with lithium naphthalenide (2 equiv) in a manner analogous to the formation of hexa-*tert*-butylcyclotrisilane. See ref 4g.

(8) The UV spectrum of **1** is very similar to that of hexakis(2,6-diethylphenyl)cyclotristannane.<sup>4a</sup> See the supplementary material.

(9) Harris, R. K.; Mann, B. E., Eds. "NMR and the Periodic Table"; Academic Press: New York, 1978; Chapter 10.

(10) Since all Sn nuclei in cyclopolystannanes (and **2**) are equivalent, this comparison of the satellite relative intensities is justified and holds true for all cases studied. Cf.  $\delta$   $-416.5$ ,  $^1J(^{119}Sn-^{117}Sn) = 2285$  Hz; 8.2% of parent peak for hexakis(2,6-diethylphenyl)cyclotristannane (Ar = 2,6-diethylphenyl in **1**) which has been X-ray analyzed.

(11) Unlike the cyclotristannanes in which only  $^1J(^{119}Sn-^{117}Sn)$  is possible, cyclopolystannanes, where  $n \geq 4$ , can exhibit longer range couplings. Thus octakis(trimethylsilylmethyl)cyclotetrastannane (Belsky, V. K.; Zemlyansky, N. N.; Kolosova, N. D.; Borisova, I. V. *J. Organomet. Chem.* **1981**, *215*, 41) shows a single resonance at  $-76.8$  with  $^1J(^{119}Sn-^{117}Sn) = 624$  Hz and  $^2J(^{119}Sn-^{117}Sn) = 3850$  Hz (Sita, L. R., unpublished results).



**Figure 1.** Thermal conversion of **1** to **2** as followed by UV spectroscopy (methylcyclohexane, spectra taken every 5 s) at 90 °C. Curve a represents mixture of **1** and **2** after near thermal equilibration of UV cell; curve b represents equilibrium mixture of **1** and **2** at 90 °C.

mass spectral data alone, even with the FD technique, are not adequate for the molecular weight assignments of compounds of this type.

**Photochemical Conversion of 1 into 2.** Quantitative conversion to **2** can be achieved through photolysis of solutions of **1** (methylcyclohexane) at -78 °C using a Hanovia high-pressure lamp (pyrex filter). A  $^1\text{H}$  NMR spectrum (250 MHz, methylcyclohexane- $d_{14}$ , -68 °C) taken immediately after photolysis shows new signals at  $\delta$  0.93 (d, relative intensity 6), 1.16 (d, 12), 2.74 (sept, 1), 3.22 (m, 2), and 6.91 (s, 2) and are assigned to **2** as the sole product with no trace of **1**.<sup>12</sup> Prolonged photolysis of **2** at -78 °C leads to no photodecomposition; however, upon warming to 0 °C **2** is converted back cleanly to **1**. Unambiguous proof that **2** in solution exists solely as a dimeric<sup>1</sup> form is demonstrated by the  $^{119}\text{Sn}$  NMR [100.74 MHz, -68 °C,  $^1\text{H}$  decoupled, methylcyclohexane- $d_{14}$ ],  $\delta$  (ppm from  $\text{Me}_4\text{Sn}$ )] A single resonance at +427.3 is accompanied by two tin-tin coupling satellites [ $^1J$  ( $^{119}\text{Sn}$ - $^{117}\text{Sn}$ ) = 2930 Hz] of relative peak intensities, 3.8% of parent peak, which are expected only for a structure possessing two directly bonded tin atoms.<sup>13</sup> Solutions of **2** around -70 °C are intensely red, showing an absorption maximum  $\lambda_{\text{max}}$  494 nm ( $\log \epsilon$  4.59),<sup>5</sup> and are extremely air- and moisture-sensitive.

**Thermal Equilibrium between 1 and 2.** At 0 °C or lower temperatures to -78 °C, cyclotristannane **1** is thermodynamically stable in an inert solvent and **2** is converted to **1** only slowly, thus permitting one to record the spectra of **2** (see above). However, at room temperature or above, rapid equilibration between **1** and **2**, with **2** being favored at higher temperatures, occurs. This process can be followed by  $^1\text{H}$  NMR and/or UV spectroscopy. For instance, Figure 1 shows the rate of formation of **2** (after thermal equilibration of the UV cell) at 90 °C as followed by UV spectroscopy: approximate equilibrium ratio of  $[\mathbf{2}]/[\mathbf{1}] = 2.09$  at 90 °C and approximate time required for 95% completion of the equilibration,  $\tau = 165$  s, starting with an initial concentration of **1** (solution prepared at 0 °C) =  $2.18 \times 10^{-3}$  M (at 50 °C equilibrium ratio 1.30,  $\tau$  300 s at 70 °C; 0.49, 1300 s). This equilibration phenomenon was totally unexpected and is perhaps unprecedented. Its simplest explanation may be offered by invoking the intermediacy of the corresponding stannylene **2a** ( $\text{R} = 2,4,6\text{-triisopropylphenyl}$  in **3a**) which is generated relatively slowly from either **1** or **2** but rapidly adds to **2** or dimerized, as formulated by  $2(\mathbf{1}) \rightleftharpoons [2(\mathbf{2}) + 2(\mathbf{2a})] \rightleftharpoons 3(\mathbf{2})$ .<sup>14</sup> This sequence

(12) Using an internal standard, this photoconversion is shown to produce 3 mol of **2** from 2 mol of **1**.

(13)  $^1J$  ( $^{119}\text{Sn}$ - $^{117}\text{Sn}$ ) for  $\text{Me}_2\text{Sn-SnMe}_2$  is 4211 Hz with similar satellite intensities observed for **2**: Mitchell, T. N. *J. Organomet. Chem.* **1974**, *70*, C1. (Also: Sita, L. R., unpublished results.)

(14) Although not spectroscopically detected, **2a** can indeed be trapped from solution mixtures of **1** and **2** with reagents such as 2,3-dimethyl-1,3-butadiene and tri-*n*-butyltin hydride at room temperature.

of reactions constitutes one possible route through which **1** is formed from **6** in this particular instance.<sup>4c,g</sup>

A few comments on the spectral properties of **1** and **2** are in order. The remarkable low-field  $^{119}\text{Sn}$  NMR chemical shift resulting from strongly deshielded tin atoms in **2** can be compared to the low-field  $^{29}\text{Si}$  NMR chemical shifts observed for  $\text{Si}=\text{C}^{15}$  and  $\text{Si}=\text{Si}^{16}$  double bonds. The electronic spectrum of **2** is also characterized by the intense absorption in the visible region in a similar manner to those of tetrakis(2,6-diethylphenyl)disilene (**7**) [ $\lambda_{\text{max}}$  272 nm ( $\log \epsilon$  3.84), 340 (3.44), 422 (3.80)]<sup>4c,e</sup> and tetrakis(2,6-diethylphenyl)digermene (**8**) [ $\lambda_{\text{max}}$  263 nm ( $\log \epsilon$  4.11), 412 (3.92)].<sup>4c,e</sup> All of these dimetallenes, **2**, **7**, and **8**, retain structural integrity in solution, and these facts suggest the possibility that they might all have similar structural features. Since **7** and **8**<sup>4c,i</sup> have twist-double-bond structures with no or little ( $\chi_{\text{Ge}} = 15^\circ$ ) pyramidalization, respectively,<sup>17</sup> the crystallographic analysis of **2** (which we intend to pursue) may not reveal as pronounced a trans-bent structure<sup>18</sup> as that of **3** ( $\chi_{\text{Sn}} = 41^\circ$ ).<sup>2</sup> Even for this reason alone, the crystal structure of **2** attracts great interest.

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**Supplementary Material Available:** Full experimental details of Scheme II, including spectral data of new compounds and copies of spectra of **1**, **2**, **7**, and **8** (8 pages). Ordering information is given on any current masthead page.

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(16) West, R. *Pure Appl. Chem.* **1984**, *56*, 163.

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(18) Recent theoretical investigations all agree that distannene ( $\text{H}_2\text{Sn}=\text{SnH}_2$ ) should have a trans-bent structure. (a) Fjeldberg, T.; Haaland, A.; Schilling, B. E. R.; Volden, H. V.; Lappert, M. F.; Thorne, A. J. *J. Organomet. Chem.* **1984**, *276*, C1. (b) Pauling, L. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 3871. (c) Dewar, M. J. S.; Grady, G. L.; Kuhn, D. R.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6773. (d) Gleghorn, J. T.; Hammond, N. D. *A. Chem. Phys. Lett.* **1984**, *105A*, 621.

## NMR Spectra of $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_2\text{SiMe}_3\text{Li}(\text{pmdeta})$ and $(\text{C}_5(\text{CH}_3)_5)\text{IrH}_3\text{Li}(\text{pmdeta})$ : The First Direct Observation of Resolved $^7\text{Li}$ - $^1\text{H}$ Coupling

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Observation of scalar spin-spin coupling between  $^7\text{Li}$  and  $^{13}\text{C}$  in the nuclear magnetic resonance spectra of these nuclei has been critical in determining degrees of oligomerization for organolithium species in solution.<sup>1</sup> Recently, coupling between  $^7\text{Li}$  and  $^{31}\text{P}$  nuclei was reported for a series of phosphidolithium dimers  $[\text{LiPR}_2]_2$ ,

(1) (a) Lindman, B.; Forsen, S. In "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 166. (b) Wardell, J. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Section 2.4.2.3 and references therein. (c) McKeever, L. D.; Waake, R.; Doran, M. A.; Baker, E. B. *J. Am. Chem. Soc.* **1968**, *90*, 3244; (d) *Ibid.* **1969**, *91*, 1057. (e) McKeever, L. D.; Waake, R. *J. Chem. Soc., Chem. Commun.* **1969**, 750. (f) Fraenkel, G.; Fraenkel, A. M.; Geckle, M. J.; Schloss, F. *J. Am. Chem. Soc.* **1979**, *101*, 4745. (g) Fraenkel, G.; Henrichs, M.; Hewitt, J. M.; Su, B. M.; Geckle, M. J. *Ibid.* **1980**, *102*, 3345. (h) Seebach, D.; Hassig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308.