

**Figure 2.**  $^{23}\text{Na}$  ion line width plotted as a function of temperature for native DNA (O), denatured DNA (□), and an ethidium-DNA complex at an  $\tau$  value of 0.072 (Δ).

to treating these results, the solid line in Figure 1 has been plotted by assuming that there is a quadratic dependence of the bound-sodium relaxation rate on the nucleic acid charge density and that the  $^{23}\text{Na}^+$  relaxation rate can be separated into a term due to the free solution relaxation of  $^{23}\text{Na}^+$  and another term due to relaxation of sodium ions associated with the DNA double helix.<sup>13,14,17</sup> Similar effects have been seen in this  $\alpha$  range in pH titrations of anionic synthetic polymers.<sup>13,14,18</sup> Although the

(15)  $^{23}\text{Na}$  NMR measurements were performed on a Bruker WM-250 spectrometer equipped with a broad-band (10 mm) tunable probe at 66.13 MHz. Typically, a sweep width of 5000 Hz, 8K data points, a  $90^\circ$  pulse and 400-600 transients were used. All measurements were made under nondecoupling conditions. Line width values are bandwidths at half-peak intensity determined digitally. Temperature control and measurements were made by utilizing a Bruker VT1000 unit and were maintained to within  $\pm 0.5^\circ\text{C}$ . DNA sample preparation was as specified previously.<sup>16</sup> For titration experiments, microliter aliquots of a known concentration (determined by using  $\epsilon_{480} 5750 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>9</sup> of a stock solution of ethidium bromide were added to a DNA sample in an NMR tube directly and measurements taken. DNA samples were prepared at 0.01 M DNA phosphate in a PIPES buffer adjusted to pH 7 with NaOH and containing 0.0125 M NaCl,  $10^{-3}$  M PIPES,  $10^{-4}$  M EDTA, and 20%  $\text{D}_2\text{O}$ .

(16) Wilson, W. D.; Keel, R. A.; Mariam, Y. H. *J. Am. Chem. Soc.* **1981**, *103*, 6267.

(17) For the analysis of the results of Figure 1, we have used the theory developed by Leyte and co-workers for  $^{23}\text{Na}^+$  relaxation in the presence of a polyanion and simple salt.<sup>13,14</sup> The fractions of bound- and free-sodium ions at varying ethidium concentrations were calculated by using the following results for ethidium-DNA interactions:<sup>9</sup> neighbor exclusion binding with an equilibrium constant of  $10^6$  under these conditions and 0.8  $\text{Na}^+$  ion released per bound ethidium. The average charge density of an ethidium binding site on the DNA double helix was calculated by assuming four changes per two base pairs (6.8 Å) or 1.7 Å between charges. This gives the literature value of 4.2 for the charge density parameter ( $\xi$ ) for DNA.<sup>1</sup> On addition of ethidium to these two base pairs, the distance is increased to 10.2 Å and the charge is reduced by one unit so that the average spacing becomes 3.4 Å between charges and  $\xi$  is reduced to 2.1. Other average charge densities and  $\xi$  values were calculated by assuming a linear change between these two values as the fractional saturation of ethidium sites is increased from 0% to 100%. For comparisons with pH titrations this corresponds to a change in  $\alpha$  from 1.0 (free DNA) to 0.5 for DNA saturated with ethidium. A linear correspondence between  $\alpha$  and fractional saturation with ethidium is assumed. Constants in the equation for relaxation rate<sup>13,14</sup> were grouped together, and this single constant was used as a variable parameter to obtain the best-fit line to the data points in Figure 1. A free solution line width of 7 Hz for  $^{23}\text{Na}^+$  was determined experimentally. The  $\tau$  values in the figure were calculated for each fractional saturation value for ethidium. Several experiments have indicated that with synthetic polymers the  $^{23}\text{Na}$  relaxation behavior becomes more complex below  $\alpha$  values of approximately 0.3,<sup>13,14,18</sup> perhaps due to conformational changes in the highly neutralized polymers. We have not been able to go below an  $\alpha$  of 0.5 with ethidium, but the fact that the line width at this low  $\alpha$  value approaches the value for free sodium ions suggests that such complicating effects may not be as significant with conformationally more rigid polymers like DNA.

theoretical line in Figure 1 is a reasonable fit to the points, the actual line width decrease is obviously steeper than predicted. This agrees with the finding that larger amounts of  $\text{Na}^+$  are released by intercalators binding to DNA than would be expected from their charges.<sup>7-9</sup> Errors in the theory such as the assumed constancy of the  $\text{Na}^+$ -DNA average separation distance, constancy of the quadrupole coupling constant, and the cylindrical smeared charge model for point charges in the DNA-ethidium complex could also contribute to the systematic difference between the experimental results and the theoretical prediction in Figure 1.

In Figure 2  $^{23}\text{Na}^+$  line widths in native, denatured, and ethidium-DNA solutions are shown as a function of temperature. For native DNA there is a continuous decrease in line width up to the denaturation region of the double helix (the  $T_m$  is approximately  $63^\circ\text{C}$  under these conditions) at which point a break in the curve occurs with a more pronounced decrease in the line width. This is a direct illustration of the cooperative conformational change, the release of  $\text{Na}^+$  ions, and mobility changes that occur on DNA denaturation. When the heated sample was quickly cooled to yield denatured DNA at low temperature and then reheated, a smooth change in relaxation rate was observed with no breaks in the curve (Figure 2). The decrease in line width as temperature is increased also is important in illustrating that  $\text{Na}^+$  is in the fast-exchange region under these conditions<sup>2</sup> and agrees with other results obtained on heating native DNA.<sup>19</sup>

These experiments using intercalators and heating illustrate the utility of  $^{23}\text{Na}$  NMR in monitoring DNA conformational changes and binding interactions.

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**Registry No.** Sodium, 7440-23-5; ethidium bromide, 1239-45-8.

(18) Gustavsson, H.; Lindman, B.; Bull, T. *J. Am. Chem. Soc.* **1978**, *100*, 4655.

(19) Levij, M.; de Bleijser; Leyte, J. C. *Bull. Magn. Reson.* **1980**, *2*, 388.

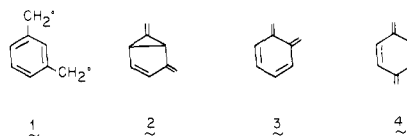
## Electron Spin Resonance Spectroscopy of the Triplet State of *m*-Xylylene

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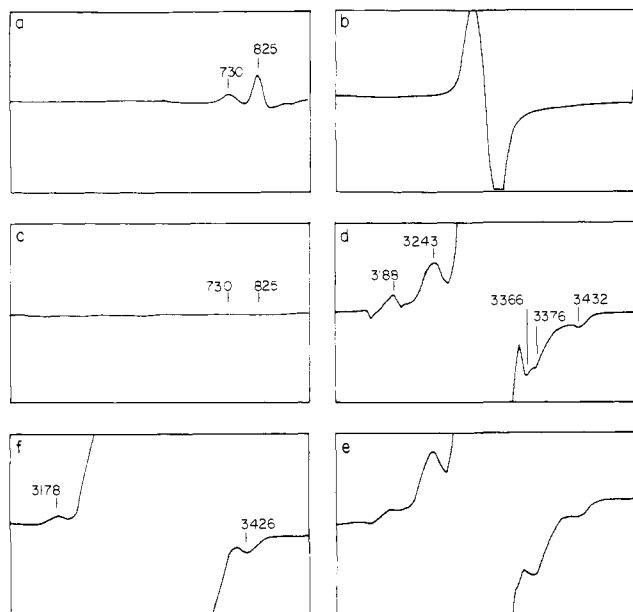
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*m*-Xylylene (1,3-benzoquinodimethane, **1**) has no Kekulé



structure that fully satisfies the valency of every carbon without recourse to the formation of a highly strained compound such as **2**.<sup>1</sup> It is fundamentally different in electronic structure than the ortho and para isomers **3** and **4**.<sup>2</sup>

(1) Studies of *m*-xylylene as a reactive intermediate in solution are quite limited. The first cyclophane synthesis was accomplished by treatment of dibromide **9** with sodium, through the possible intervention of **1**: Pellegrin, M. *Recl. Trav. Chim Pays-Bas* **1899**, *18*, 458. The most convincing modern study of a simple analogue of **1** concerns the tetramethyl derivative: Gajewski, J. J.; Chang, M.-J.; Stang, P.-J.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2096.



**Figure 1.** ESR spectroscopy of bis(carbene) **7** and *m*-xylylene (**1**); see text for details. Spectra a and c are centered at 500 gauss and are 1000 gauss wide. Spectra b and d-f are centered at 3310 gauss and are 400 gauss wide. The peak positions shown are in gauss.

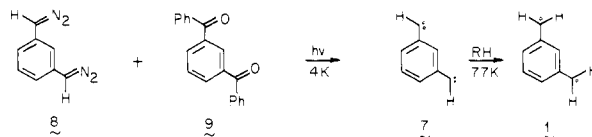
*m*-Xylylene is closely related to other non-Kekulé structures such as trimethylenemethane (**5**) and tetramethyleneethane (**6**).



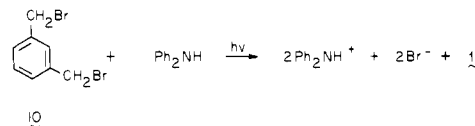
A simple HMO calculation of **1**, **5**, or **6** reveals that in each compound, two  $\pi$  electrons must be distributed into a pair of degenerate nonbonding molecular orbitals.<sup>3</sup> One therefore expects that **1**, **5**, and **6** should have triplet ground states.<sup>4</sup> The HMO prediction is in full agreement with simple PMO analyses of the non-Kekulé hydrocarbons.<sup>5</sup> *o*- and *p*-xylylene, in contrast, are predicted to have a non-zero HOMO-LUMO splitting and singlet ground states.<sup>3</sup> The thermodynamic instability of **1** relative to **3** and **4** has been demonstrated by Pollack et al.<sup>6</sup> The heat of formation of biradical **1** is at least 23 kcal/mol more positive than biradicaloids **3** and **4**. The nature of the ground-state multiplicities of **3**-**6** have been determined experimentally. *o*- and *p*-xylylene are undoubtedly singlets.<sup>7</sup> The ground (or at least very low lying) triplet states of trimethylenemethane and tetramethyleneethane have been detected by ESR.<sup>8</sup> Migiridicyan and Baudet have reported the excitation spectrum of **1** in a 77 K hydrocarbon matrix, obtained by exhaustive UV photolysis of *m*-xylylene.<sup>9</sup> These

authors conclude that the electronic spectrum is most consistent with a triplet biradical. We herein report the detection of the triplet state of *m*-xylylene by ESR, in accord with simple theoretical expectations.

In 1963 Trozzolo et al. reported the ESR spectrum of the quintet state 1,3-dehydrobenzoquinodimethane (**7**), obtained by photolysis of bis(diazo) compound **8** at 4 K in a host matrix of ketone **9**.<sup>10</sup>



We reasoned that the generation of **7** in a more reactive matrix might give **1** via double hydrogen atom transfer.<sup>11</sup> Photolysis of **8** ( $\lambda > 320$  nm) in ethanol-*d*<sub>6</sub> at 22 K for 25 min gave rise to the stable, known spectrum of **7** (Figure 1a), no biradical, and a small amount of free radical (Figure 1b). As the temperature was raised to 77 K the quintet spectrum disappeared (Figure 1c) and was replaced by the spectrum of a biradical (Figure 1d;  $|D/hc| = 0.011$  cm<sup>-1</sup>,  $|E/hc| \leq 0.001$  cm<sup>-1</sup>). Cooling the sample back to 24 K did not regenerate the quintet spectrum. The biradical spectrum was still present upon cooling (Figure 1e). It is possible to observe an isotope effect on the sequence. Photolysis of **8** in ethanol at 20 K gives both the quintet and the biradical spectra. The quintet decay can not be frozen out at 20 K in ethanol as it can be in ethanol-*d*<sub>6</sub>. This demonstrates that the carrier of the biradical spectrum is associated with the dark reaction of the quintet with the matrix.<sup>12</sup> This spectrum is not assigned to a radical pair as the same spectrum is observed in toluene, methanol, diethyl ether, and 2-methyltetrahydrofuran (2-MTHF).<sup>13</sup> Biradical spectra were not observed upon photolysis of the para isomer of bis(diazo) compound **8**. Significantly, the biradical spectrum is not observed at 77 K in perfluorinated alkane matrices, although the quintet is indefinitely stable under these conditions. The biradical spectrum is assigned to *m*-xylylene as the same splitting pattern can be obtained from a different precursor. Photolysis of a 2-MTHF or ethanol matrix containing a 1:10 mixture of dibromide **10** and diphenylamine (DPA) gives the



spectrum shown in Figure 1f. Photolysis of **10** or DPA separately in 2-MTHF leads to a free-radical signal but not the biradical splitting pattern.

Additional support of the assignment is provided by the  $|D/hc|$  parameter. As expected, the  $|D/hc|$  value is smaller than that of Berson's quinomethide **11**<sup>14</sup> but larger than that of Schlenk's hydrocarbon **12**.<sup>15</sup>

(2) (a) Coulson, C. A.; Craig, D. P.; Maccoll, A.; Follman, A. *Discuss. Faraday Soc.* **1947**, *2*, 36. (b) Namiot, A. J.; Dyatkina, M. E.; Syrkin, Y. K. *Dokl. Akad. Nauk SSSR* **1945**, *48*, 267. (c) Pullman, A.; Berthier, G.; Pullman, B. *Bull. Soc. Chim Fr.* **1948**, *15*, 450. (d) Gleichen, G. J.; Newkirk, D. D.; Arnold, J. C. *J. Am. Chem. Soc.* **1978**, *95*, 2526. (e) Baudet, J. *J. Chim. Phys., Phys.-Chim. Biol.* **1971**, *68*, 191. (f) Kolshorn, H.; Meier, K. *Z. Naturforsch. A* **1977**, *32A*, 780.

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(6) Pollack, S. K.; Raine, B. C.; Hehre, W.-J. *J. Am. Chem. Soc.* **1981**, *103*, 6308.

(7) (a) Williams, D. J.; Pearson, J. M.; Levy, M. *J. Am. Chem. Soc.* **1970**, *92*, 1436. (b) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.

(8) (a) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. (b) Dowd, P. *J. Am. Chem. Soc.* **1960**, *92*, 1066. (c) Roth, V. W. R.; Erker, G. *Angew. Chem.* **1973**, *85*, 510.

(9) (a) Migiridicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400. (b) For an unsuccessful attempt to observe *m*-xylylene see: Tseng, K. L.; Michl, J. *Ibid.* **1977**, *99*, 4842.

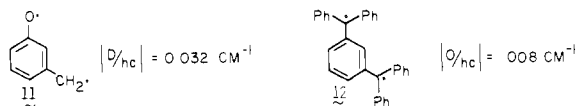
(10) Trozzolo, A. M.; Murray, R. W.; Smolinsky, G.; Yager, W. A.; Wasserman, E. *J. Am. Chem. Soc.* **1963**, *85*, 2526.

(11) (a) Senthilnathan, V. P.; Platz, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7637. (b) Senthilnathan, V. P.; Platz, M. S. *Ibid.* **1981**, *103*, 5503. (c) Wright, B. B.; Senthilnathan, V. P.; Platz, M. S.; McCurdy, C. W., Jr. *Tetrahedron Lett.* **1982**, *23*, 833.

(12) Thurnauer and Closs have observed a 250-gauss biradical splitting upon photolysis of diphenyldiazomethane in toluene (Thurnauer, M. Ph.D. Thesis, University of Chicago, 1974). This spectrum cannot be due to hydrogen atom transfer as it is also observed in hexafluorobenzene and perfluorinated alkane matrices. Furthermore, this spectrum is formed immediately upon photolysis of the diphenyldiazomethane in all matrices at 4 K. The carrier of this spectrum is not presently known, but it is not due to thermal reaction of diphenylcarbene with matrices.

(13) If the biradical spectrum was due to a radical pair due to monohydrogen atom abstraction, a constant 240-gauss splitting should not be observed. This follows from the different geometry and spin distribution that must occur upon changing the matrix derived radical component of the pair.

(14) Rule, M.; Matlin, A. R.; Dougherty, D. A.; Hilinsky, E.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098.



The spectrum generated by photolysis of bis(diazo) compound **8** obeys the simple form of the Curie law between 30 and 77 K at 0.01 mW.<sup>16,17</sup> The triplet is the ground state or within a few calories per mole of the ground state as predicted by theory.<sup>2,3,5</sup>

Finally, we have attempted to reproduce the experimental conditions of Migiridicyan and Baudet.<sup>9</sup> Photolysis of a 0.01 M solution of mesitylene in 3-methylpentane with 2537-Å light generated an ESR spectrum similar to that obtained from reaction of **7** at 77 K. The former spectrum is consistent with methyl-substituted **1**. Attempts to observe **1** by analogous irradiation of *m*-xylene were unsuccessful.

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**Registry No.** **1**, 32714-83-3; **7**, 25768-05-2; **8**, 18456-73-0; **10**, 626-15-3.

(15) Kothe, G.; Denkel, K. H.; Sümmerrmann, W. *Angew Chem., Int. Ed. Engl.* **1970**, *9*, 906.

(16) Breslow, R.; Chang, H.-W.; Hill, R.; Wasserman, E. *J. Am. Chem. Soc.* **1967**, *89*, 1112.

(17) At higher microwave power the ESR signal of **1** is saturated, which leads to apparent violations of the Curie law.

## Cyclotristannoxane (R<sub>2</sub>SnO)<sub>3</sub> and Cyclotristannane (R<sub>2</sub>Sn)<sub>3</sub> Systems. Synthesis and Crystal Structures

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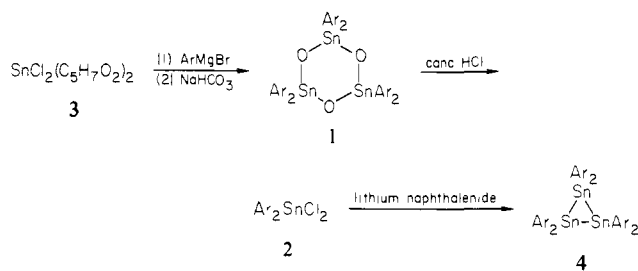
We describe herein the synthesis and crystal structures of two compounds, hexakis(2,6-diethylphenyl)cyclotristannoxane (**1**) and hexakis(2,6-diethylphenyl)cyclotristannane (**2**). The latter cyclotristannane system obviously constitutes the smallest cyclic framework made exclusively of tin atoms<sup>1</sup>, while compound **1** is a rare crystalline diorgano tin oxide that possesses a discrete molecular structure with tetracoordinate tin atoms.<sup>2</sup> The alkaline hydrolysis of diorgano tin dihalides, the most common method of preparing the corresponding tin oxide, always in the past led to the formation of insoluble polymeric compounds exhibiting wide melting ranges as well as Mössbauer spectra indicative of pentacoordinate tin.<sup>3</sup> Crystallographic analyses of both **1** and **2**

(1) Four-membered and larger ring systems have long been known. For reviews, see: (a) Gilman, H.; Atwell, W. H.; Cortledge, F. K. *Adv. Organomet. Chem.* **1964**, *4*, 1. (b) Armitage, D. A. "Inorganic Rings and Cages"; Edward Arnold: London, **1972**; Chapter 4. Also see references quoted in: (c) Neumann, W. P. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1978**, *3*, 51. (d) Ishikawa, M.; Kumada, M. *Ibid.* **1979**, *4*, 7. (e) Neumann, W. P. *Nachr. Chem. Tech. Lab.* **1982**, *30*, 191.

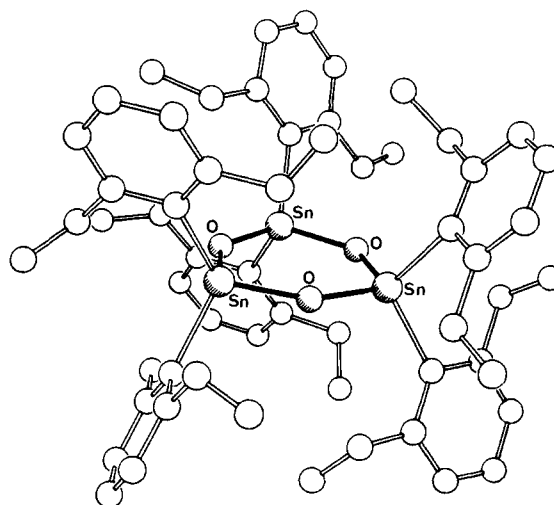
(2) Di-*tert*-butyltin oxide postulated to exist as the trimer (*t*-Bu<sub>2</sub>SnO)<sub>3</sub> in solution is the only other diorgano tin oxide with tetracoordinate tin atoms [(a) Chu, C. K.; Murray, J. D. *J. Chem. Soc. A* **1971**, 360]. For the crystal structure of this compound, see: (b) Puff, H.; Sievers, R.; Zimmer, R.; Schuh, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 591.

(3) This behavior is in sharp contrast with that of the analogous oxides of silicon and germanium, which readily form cyclotrisiloxanes and cyclotrigermoxane, respectively. See ref 1b and the following: Metlesics, W.; Zeiss, H. *J. Am. Chem. Soc.* **1960**, *82*, 3324.

### Scheme I<sup>a</sup>



<sup>a</sup> Ar = 2,6-diethylphenyl.



**Figure 1.** Crystal structure of **1**: Sn-O bond lengths 1.929 (6)–1.961 (6) Å; Sn-O-Sn bond angles 135.6 (3), 135.9 (3), and 137.1 (3)°; Sn-Ar bond lengths 2.138 (6)–2.169 (9) Å.

confirm the structural assignments of these compounds based on spectral data and further reveal several unique and intriguing structural features.

**Synthesis of 1 and 2.** The synthesis of **2** follows the approach previously adopted for that of the silicon analogue<sup>4</sup> as shown in Scheme I. Thus adding (2,6-diethylphenyl)magnesium bromide (47 mmol) in 1:5 benzene/ether (60 mL) to a solution of bis-(2,4-pentanedionato)tin dichloride **3**<sup>5</sup> (23.5 mmol) in benzene (50 mL)<sup>6</sup> and then heating the reaction mixture at reflux for 2 h provide a crude product that, upon treatment with saturated aqueous sodium bicarbonate, gives rise to colorless crystals, mp >300 °C (33% yield, recrystallized from benzene). Spectral data of this compound are as follows: mass spectrum (field desorption), M<sup>+</sup>, cluster *m/z* (1196–1211), in agreement with that calculated for the trimeric molecular formula (C<sub>20</sub>H<sub>26</sub>OSn)<sub>3</sub>;<sup>7</sup> <sup>119</sup>Sn NMR (CCl<sub>4</sub>) δ (ppm from Me<sub>4</sub>Sn) –125.02;<sup>8</sup> IR (CHCl<sub>3</sub>) ν<sub>SnOSn</sub> 710 cm<sup>-1</sup>; UV (cyclohexane) λ<sub>max</sub> (log ε) 270 nm (3.64), 278 nm (3.61); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 0.85 (t, 6 H), 2.84 (q, 4 H), 6.95 (d, 2 H), 7.19 (t, 1 H). Treatment of **1** with concentrated hydrochloric acid effects its quantitative conversion to **4**, mp 67.5–68.5 °C. After dropwise addition of **4** (900 mg, 2 mmol) in dimethoxyethane (DME, 10 mL) to a dark green solution of lithium naphthalenide at –78 °C [prepared from naphthalene (500 mg, 3.9 mmol) in DME (15 mL) and lithium wire (27 mg, 3.9 mmol)], the mixture is stirred at the same temperature for 15 min and at room temperature for 2 h, resulting in a bright yellow

(4) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150. Also see: Masamune, S.; Hanzawa, Y.; Williams, D. *J. Am. Chem. Soc.* **1982**, *104*, 6136.

(5) Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1924**, 125, 372.

(6) Following the procedure developed by: Chandrasekaran, R. K.; Venkataraman, S.; Koola, J. D. *J. Organomet. Chem.* **1981**, *215*, C43.

(7) Detailed information is supplied in the supplementary material.

(8) The δ value of the <sup>119</sup>Sn signal of (Me<sub>2</sub>SnS)<sub>3</sub> is –128; Davies, A. G.; Harrison, P. G.; Kennedy, J. D.; Mitchell, T. N.; Puddephatt, R. J.; McFarlane, W. *J. Chem. Soc. C* **1969**, 1136.