Reactions of a Highly Crowded Cyclic Stannylene with Iodoalkanes, Enones, and Dienes. Inhibition of Nucleophilic Substitution at Tin(IV) Centers

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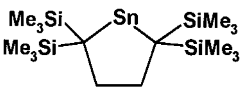
The cyclic stannylene $\overline{\mathrm{RSnR}}$ (**2**; RR = $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$) reacted with alkyl iodides R′I (R′ = Et, ${}^iPr$) to give the Sn^{IV} compounds $\overline{\mathrm{RSnR'IR}}$ (**6b**,**c**), which were converted by treatment with silver trifluoroacetate into $\overline{\mathrm{RSnR'(OCOCF_3)R}}$ (**7b**,**c**). Reactions of the stannylene **2** with appropriate enones or diones yielded the products $\overline{\mathrm{RRS}}\mathrm{n}\underline{\mathrm{OC(Et)=CHCH_2}}$ (**10**), $\overline{\mathrm{RRS}}\mathrm{n}\underline{\mathrm{OCPh=CPhO}}$ (**11**), $\overline{\mathrm{RRS}}\mathrm{n}\underline{\mathrm{OC_6H_2\text{-}3,5\text{-}{}^tBu_2O}}$ (**12**), and $\overline{\mathrm{RRS}}\mathrm{n}\underline{\mathrm{OC_{14}H_8O}}$ (**13**) ($OC_{14}H_8O$ = 9,10-phenanthrenediolato). The crystal structures of **6b**, **7b**,**c**, and **10**−**13** have been determined. Treatment of **2** with water, alcohols, or phenol led to ring opening. There is evidence from ESR spectroscopy that the oxidative additions of diones involve radical intermediates. The compound $\overline{\mathrm{RSnMeIR}}$ (**6a**) reacted with ICl to give the chloride $\overline{\mathrm{RSnMeClR}}$ (**15**), but, in contrast to the previously described crowded trialkyltin halides $(Me_3Si)_3CSnMe_2X$ (X = Cl, I), neither **6a** nor **15** reacted with nucleophilic reagents.

Introduction

Diorganostannanediyls (stannylenes), SnR_2, have commonly been obtained as reactive intermediates from the dissociation of distannenes R_2SnSnR_2, and their reactions, including cycloadditions, oxidative additions, and complex formation with transition-metal species, have been studied.[1−6] Few stannylenes have been characterized in the solid state as stable monomeric species. The previously reported examples are the cyclic silicon-substituted species **1**[7,8] and **2**,[9] the diarylstannylenes



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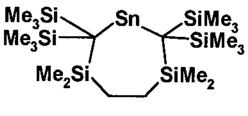

2

$[Sn(C_6H_2R'_3\text{-}2,4,6)_2]$

3a R′ = CF_3 , **3b** R′ = ${}^tBu$

3c R′ = ${}^iPr$

$[Sn\{CH(SiMe_3)_2\}_2]$

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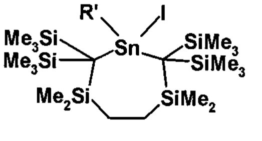

6a R′ = Me, **6b** R′ = Et, **6c** R′ = ${}^iPr$

$[Sn(C_6H_2R'_3\text{-}2,4,6)_2]$ (R′ = CF_3 (**3a**),[10] ${}^tBu$ (**3b**)[11]) and $[Sn(C_6H_2\{CH(SiMe_3)_2\}_3\text{-}2,4,6)(C_6H_2R'_3\text{-}2,4,6)]$ (R′ = ${}^iPr$, cyclo-C_6H_{11}, $CH(CH_2CH_3)_2$),[12−16] the stannylene $[Sn\{CH(SiMe_3)_2\}_2]$ (**4**)[17,18] (which is dimeric in the solid[19] but has been shown by electron diffraction to be monomeric in the gas phase[20]), and the germylstannylene

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for **6b**, **7b**,**c**, and **11**−**13**

	6b	**7b**	**7c**	**11**	**12**	**13**
X	I	O^{c,d}	O^d	O	O	O
Sn−X	2.7598(4)	2.109(3)	2.097(4)	2.005(3)	2.004(2), 2.026(2)	2.020(2)^a
Sn−C(R′)	2.219(4)	2.166(5)	2.202(6)			
Sn−CSi$_3$	2.268(4)^a	2.226(5)^a	2.257(6)^a	2.199(5)	2.202(3)^a	2.189(3)^a
C1,2−Si	1.926(4)^a	1.925(6)^a	1.927(6)^a	1.917^e	1.924(4)^g	1.927(3)^i
Si−Me	1.880(5)^a	1.892(7)^a	1.878(6)^a	1.854^f	1.875(4)^a	1.876(4)^a
Si−CH$_2$	1.876(5)^a	1.900(6)^a	1.874(7)^a	2.082(10)^f	1.886(4)^a	1.897(4)^a
CH$_2$−CH$_2$	1.564(6)^b	1.536(7)^c	1.546(8)	1.564(16)	1.557(5)	1.544(5)
X−Sn−CSi$_3$	104.42(10), 107.67(11)	96.45(17)^a	95.27(19)^a	103.63(17), 108.46(17)	103.77(10)^h	104.05(11)^j
X−Sn−C(R′)	101.14(12)	110.87(18)	109.6(2)			
O−Sn−O				83.51(8)	84.21(8)	84.35(8)
C1−Sn−C2	128.26(15)	128.99(19)	129.9(2)	136.5(3)	136.16(11)	136.93(11)
C1−Sn−C(R′)	107.41(16)	107.8(2)	118.4(2)			
C2−Sn−C(R′)	104.86(16)	113.0(2)	103.6(2)			
Sn−C−Si$_{exo}$	109.21(18)−117.8(2)	106.5(2)−112.9(2)	107.3(3)−115.3(3)	106.6(2), 108.1(2)	106.65(15)−110.88(15)	106.80(14)−110.04(15)
Sn−C−Si$_{endo}$	104.08(18)^a	111.4(2)^a	110.3(3)^a	108.6(3)	109.79(13), 108.10(14)	108.23(14), 110.36(13)
C1,2−Si−CH$_2$	111.0(2), 112.88(19)	111.1(2), 115.6(2)	114.4(3)^a	106.0(3)	108.66(16), 115.37(15)	108.09(15), 114.83(15)
Si$_{exo}$−C−Si$_{exo}$	106.1(2), 104.1(2)	107.8(3)^a	107.4(3)^a	110.1(3)	109.66(16), 108.95(14)	109.44(16), 111.27(16)
Si$_{exo}$−C−Si$_{endo}$	109.1(4)−112.6(2)	109.3(3)^a	108.6(3)^a	110.3(2), 113.0(3)	108.22(16)−113.09(17)	109.74(15)−112.03(16)
Me−Si−Me	99.5(2)−107.8(2)	101.5(3)−115.6(2)	101.3(3)−106.6(3)	104.4(5)−108.0(6)	102.74(18)−108.6(2)	102.86(19)−108.8(2)
C1,2−Si−Me	111.0(2)−117.8(2)	110.0(3)−115.4(3)	111.5(3)−117.1(3)	111.2(3)−123.5(4)	109.05(17)−117.53(14)	110.08(16)−116.09(16)
Si−C−C	116.5(3), 119.7(3)	118.1(4), 127.0(4)	120.8(5), 116.5(4)	120.9(7), 118.8(8)	118.4(3), 123.9(2)	117.6(3), 123.8(2)
Me−Si−CH$_2$	102.6(2)−106.9(2)	100.7(3)−111.6(3)	103.3(3)−106.4(3)	98.0(5), 103.9(5)	100.32(17)−109.94(19)	101.40(18)−110.02(18)

[a] Average value with esd of individual measurements in parentheses. No value differs significantly from the average. [b] $CH_2-CH_3 = 1.488(7)$ Å, $Sn-C-CH_3 = 121.0(3)°$. [c] $CH_2-CH_3 = 1.529(8)$ Å, $Sn-C-CH_3 = 122.1(4)°$. $Sn-O-C = 133.8(3)°$. [d] Values for one of the independent molecules. Bond lengths show no significant differences between the two molecules, but torsion angles show significant differences in the conformations of the eight-membered rings. [e] Average value. Individual values $Si-C1 = 1.891(5)$ Å, $Si-C2 = 1.930(5)$ Å, $Si-C3 = 1.930(5)$ Å. [f] Values unreliable because of disorder. [g] Values from 1.910(3) to 1.950(3) Å. [h] O2−Sn−C1; $O2-Sn-C2 = 104.20(9)°$, $O1-Sn-C1 = 108.31(10)°$, $O1-Sn-C2 = 107.51(9)°$. [i] Values from 1.910(3) to 1.951(3) Å. [j] O1−Sn−C1; $O2-Sn-C2 = 104.34(11)°$, $O1-Sn-C2 = 107.52(10)°$, $O2-Sn-C1 = 107.25(10)°$.

$Sn(C_6H_3Mes_2\text{-}2,6)Ge^tBu_3$.[21] Crowding at the Sn^{II} center is clearly crucial both in making it possible to isolate a particular stannylene in the first place and in influencing its reactivity.[13] In some cases the crowding results in rearrangement; e.g., the compound **3b** isomerizes to $Sn(C_6H_2{}^tBu_3\text{-}2,4,6)(CH_2C(CH_3)_2C_6H_3tBu_2\text{-}3,5)$, which can be trapped by reaction with 3,5-di-*tert*-butyl-1,2-benzoquinone.[22]

In this paper we report some reactions of the cyclic stannylene $\overline{\mathrm{RSnR}}$ (**2**; RR = $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$) with alkyl iodides, dienes, and enones and X-ray structure determinations of several of the products. We show that the crowding at the Sn^{IV} centers in $\overline{\mathrm{RSnMeIR}}$ (**6a**) and $\overline{\mathrm{RSnMeClR}}$ (**15**) inhibits nucleophilic substitution.

Results and Discussion

A new one-pot synthesis of the hexasilane $(Me_3Si)_2CHSiMe_2CH_2CH_2SiMe_2CH(SiMe_3)_2$ (**5**), the precursor of the stannylene **2**, was shown to be more convenient than the two-step process described previously (see the Experimental Section).[23]

Reactions with Alkyl Halides. We showed previously that treatment of **2** with iodomethane gave the compound **6a**.[9] As the crystals diffracted only weakly and the X-ray data could not be refined to below $R = 11\%$, we will not discuss the structure further. To study crowding at the tin center in more detail, we made the ethyl analogue **6b**, which gave good diffraction data. The structure is shown in Figure 1, and selected bond lengths and angles are given in Table 1. The Sn−I (2.7598(4) Å) and Sn−C (2.219(4) and 2.268(4) Å) distances are significantly longer than those in other tetrahedrally coordinated organotin iodides (Sn−I = 2.668(1)−2.729(1) Å and Sn−C = 2.115(7)−2.187(4) Å[24−29]), reflecting the crowding at the tin center by the

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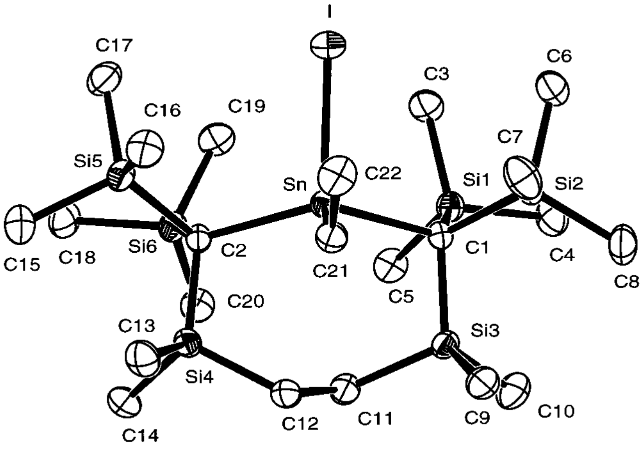


Figure 1. Molecular structure of **6b**.

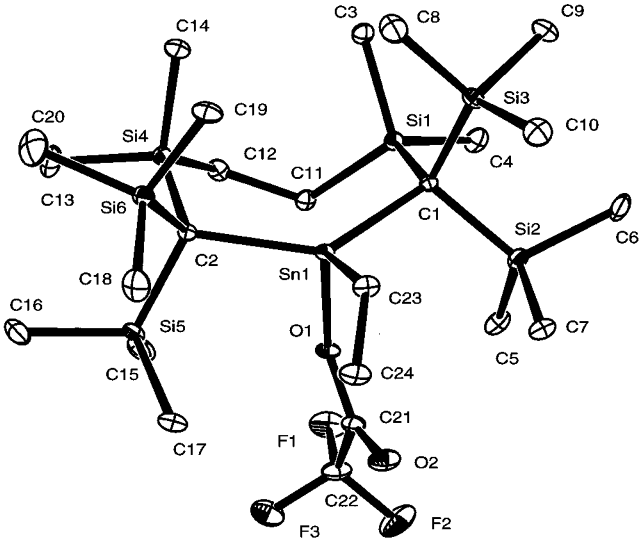
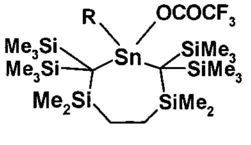


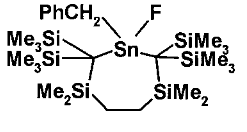
Figure 2. Molecular structure of **7b**.

SiMe$_3$ substituents in the chelate ring. A similar effect has been observed in triaryltin iodides, the Sn−I (2.752(2) Å) and possibly the Sn−C bonds (2.160(6) Å) in Sn(C$_6$H$_2$Me$_3$-2,4,6)$_3$I[30] being longer than the corresponding bonds in SnPh$_3$I (2.7060(8) and mean 2.124(7) Å, respectively[31]).

Reaction of the iodide **6b** with AgOCOCF$_3$ gave the trifluoroacetate **7b**, with the structure shown in Figure 2. The bond lengths and angles (Table 1) are identical within experimental uncertainty with corresponding parameters for the previously reported compound **7a**.[9] In both compounds the tin−alkyl bonds are significantly shorter than the Sn−C bonds within the chelate ring; the latter are probably elongated by repulsion between the SiMe$_3$ substituents at the 2,7-positions in the ring and the exocyclic groups attached to tin. The Sn−C bonds in **7b** are shorter than those in the iodide **6b**, reflecting the fact that the tin center is less encumbered with oxygen in place of iodine in the coordination sphere, but are the same within the experimental uncertainty as those in the fluoride **8**,[32] which has a smaller halogen attached to tin. The Sn−O bonds in **7b** (2.109(3) Å) are slightly longer than those in the open-chain trifluoroacetate (CF$_3$COO)$_2$SnMeRRSnMe(OOCCF$_3$)$_2$ (2.031(7)−2.046(6) Å)[9] and similar to those in the five-coordinate compounds **9** (2.05(4)−2.149(4) Å).[33]



7a R = Me, **7b** R = Et, **7c** R = ^{i}Pr



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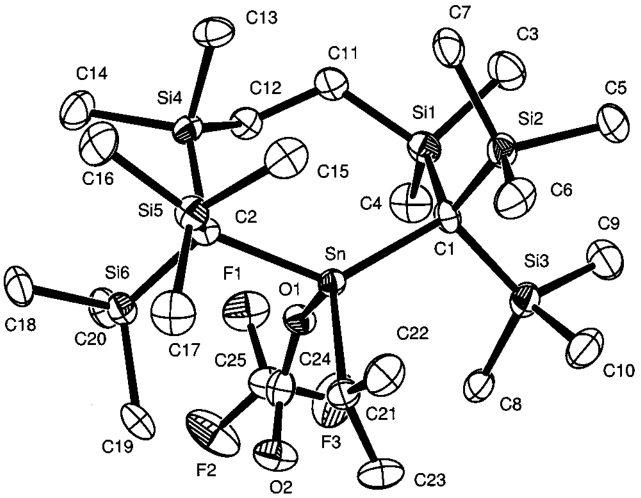
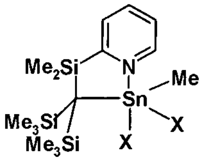


Figure 3. Molecular structure of **7c**.



9a X = OCOCF$_3$,
9b X = OSO$_2$C$_6$H$_4$Me-4

To increase the crowding at the tin center we attempted to make the isopropyl derivative **6c**. This proved to be much less stable than **6b**, and we were unable to isolate a pure sample. We did, however, show that **6c** had been formed by converting it in reasonably good yield, without isolation, into the trifluoroacetate **7c**. This was stable and was satisfactorily characterized by elemental analysis, NMR spectroscopy and an X-ray structure determination. The structure is shown in Figure 3, and selected bond lengths and angles are given in Table 1. In general, there is no significant difference between the values of the bond lengths and angles for **7b** and the corresponding values for **7c**. The Sn−C(R) bonds are 2.166(5) and 2.202(6) Å in **7b**,**c**, respectively, and the Sn−CSi$_3$ bonds are 2.226(5) and 2.257(6) Å. The differences of five standard deviations between the values for the two compounds are probably real and reflect the increased congestion at the tin atom on replacement of Et by ^{i}Pr.

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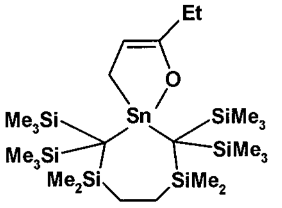
Reactions of **6a** with silver salts, and an interesting rearrangement involving migration of methyl from silicon to tin following reaction with $AgOSO_2CF_3$, are discussed elsewhere.[32]

Reaction of 2 with Protic Species. The stannylene **4** reacts cleanly with water and methanol to give the crystalline products $\{(Me_3Si)_2CH\}_2SnHOR$ (R = H, Me), which were characterized by X-ray structure determinations.[34] We expected, therefore, that the compound **2** would behave in a similar way. Compound **2** reacted rapidly with water, but we failed to identify the white solid product, which was insoluble in common organic solvents and thus was probably polymeric. The reactions of **2** with alcohols or phenol gave complex mixtures of soluble products, the NMR spectra of which suggested that the ring had opened.

Reactions with Dienes and Enones. Several previously reported stannylenes SnR''_2, e.g. **3b**,[22] **3c**,[35] **4**,[18,36] $Sn(C_6H_2R'\text{-}2,4,6)(C_6H_2\{CH(SiMe_3)_2\}_3\text{-}2,4,6)$ ($R' = {}^iPr$, Cy, $CH(CH_2CH_3)_2$),[13,15] and $Sn(C_6H_3Mes_2\text{-}2,6)Ge^tBu_3$.[21] were shown to react with dienes to give the 1,1-diorganostannacyclo-3,4-pentene oxidative addition products, e.g. $R''_2\overline{SnCH_2CH{=}CHCH_2}$, from butadiene. However, the more crowded stannylene **2** failed to react with 1,4-diphenyl-, 2,3-diphenyl-, and 2,3-dimethyl-1,3-butadiene under conditions similar to those used previously (it also did not react with phenylacetylene). Like the stannylene **4**,[37] it reacted cleanly with 1-penten-3-one (ethyl vinyl ketone) and gave the bicyclic compound **10**. The structure (Figure 4) was clearly established by NMR, mass spectrometry, and an X-ray study, but disorder associated with the orientation of the $\overline{SnC{=}CCO}$ metallacycle led to uncertainties in the bond lengths and angles, precluding detailed discussion.



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Reactions with Diones. Previously reported stannylenes, reacted with various diones to give compounds containing five-membered $\overline{SnOC{=}CO}$ rings.[13,22,35,38] These were characterized by spectroscopic studies, but no X-ray structure determinations were reported. Compound **2** reacted with diphenylethane-1,2-dione (benzil), 3,5-di-*tert*-butyl-1,2-benzoquinone, and 9,10-phenanthrenedione to give the products **11**−**13**, respectively. They were isolated in good yield and characterized by analysis, spectroscopic studies, and X-ray structure determinations. The molecular structures are illustrated in Figures 5−7, and bond lengths and angles, given in Table 1, are discussed in the next section.

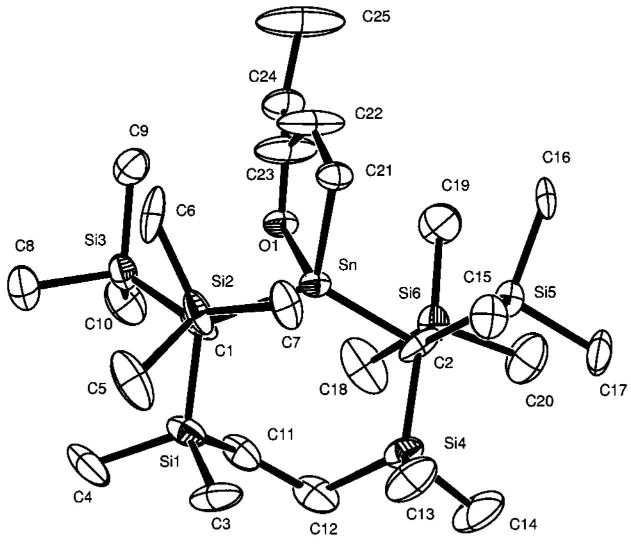

Figure 4. Molecular structure of **10**.

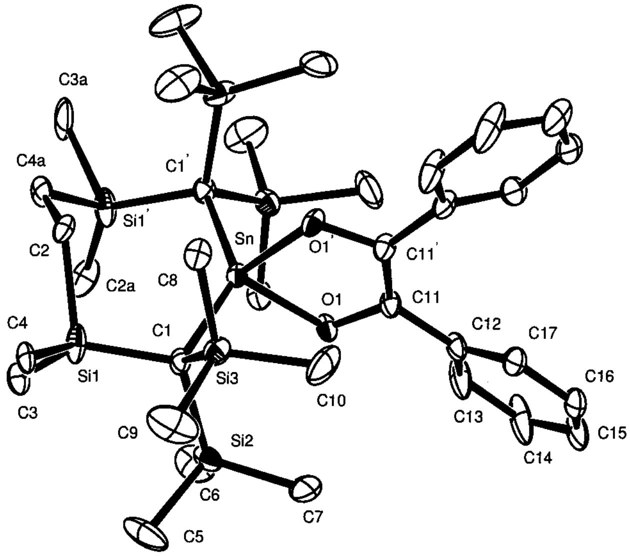

Figure 5. Molecular structure of **11**.

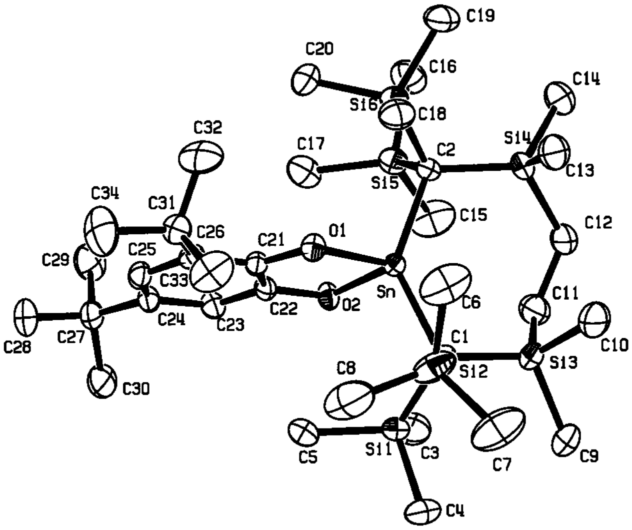

Figure 6. Molecular structure of **12**.

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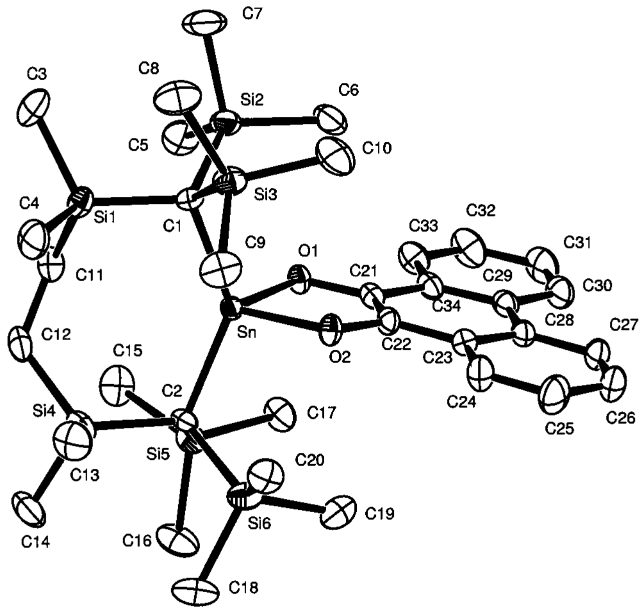
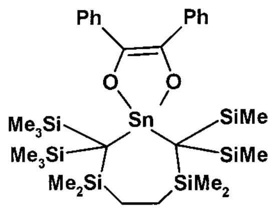


Figure 7. Molecular structure of **13**.

When solutions of **2** and 9,10-phenanthrenedione in carefully degassed toluene were mixed at −78 °C and the sample tube was immediately inserted into the cavity of an ESR spectrometer, two broad signals with fine structure were observed. These were reproducible and persisted for some hours at −90 °C but faded overnight or on warming. Under higher resolution one signal shows well-resolved proton hyperfine structure consistent with that of the known spectrum of the 9,10-phenanthrenedione radical anion.[39,41] Similarly, the spectrum of the 1,2-acenaphthylenedione radical anion[40,41] was observed when solutions of **2** and acenaphthylenedione were mixed under the same conditions. We consider that these results provide prima facie evidence that the oxidative additions proceed via radical intermediates.

Molecular Structures. There are no statistically significant variations in intraligand Si−C and C−C bond lengths in all the compounds investigated. The Si−Me bonds are consistently shorter than the inner C1−Si bonds, in keeping with the general trend observed for tin compounds containing the $C(SiMe_3)_3$ ligand.[42] There is wide variation in the angles in the 1,5,3-disilastannaepan (SnCSiCCSiC) ring, which can adopt a range of conformations that vary from molecule to molecule. This conformational variation is shown in crystallographic disorder: in **7b**, for example, alternative conformations of the chelating ligand are distributed over the sites of one of the independent molecules in the asymmetric unit, in **7c** molecules with different ligand conformations occupy different sites, and in **11** only the CH_2CH_2 linkage is disordered so that the molecule as a whole lies on a crystallographic 2-fold axis.

There has been much discussion concerning the steric and electronic factors that determine the coordination geometry in Sn^{IV} compounds.[43,44] Besides readily identified covalent bonds, there are usually weaker inter- or intramolecular "secondary interactions", so that the angles between the four strongest bonds are greatly distorted from the tetrahedral value. The structural data obtained in the present study make it possible to discuss the tin coordination geometry where secondary interactions have been excluded by the general crowding at the metal. We consider first the bond lengths in compounds **11**−**13**, in which the coordination of the tin atom is very similar. The Sn−O bonds (2.005(3)−2.026(2) Å) are significantly shorter than those in the trifluoroacetates **7b**,**c**, reflecting the fact that replacement of methyl by oxygen reduces crowding at the tin center, but they are not as short as those (1.955(3) Å) in the polystannasiloxane $[OSiPh_2OSn^tBu_2OSiPh_2]_n$ (**14**).[45] The principal Sn−O bonds in most other compounds containing the SnC_2O_2 core are longer (2.041(8)−2.116(5) Å), but there are usually secondary interactions also.[44,46−49] The Sn−C bonds in **11**−**13** are also shorter than the endocyclic bonds in **7b**,**c** but a little longer than most Sn−C bonds in acyclic compounds. In general, the lengths of Sn−C bonds are not very sensitive to the presence or absence of secondary interactions, and values are nearly always in the range 2.10−2.12 Å. The O−Sn−O angles (ca. 84°) are much smaller than the tetrahedral value, and the C−Sn−C angles (136−137°) are much wider, as is found in acyclic compounds in which tin forms two bonds to carbon and two to oxygen, e.g. $SnMe\{C(SiMe_3)_3\}(OCOCF_3)_2$[9] (O−Sn−O = 92.2(3)°; C−Sn−C = 130.0(4)°), $[SnMe\{C(SiMe_3)_3\}(ONO_2)]_2O$[50]



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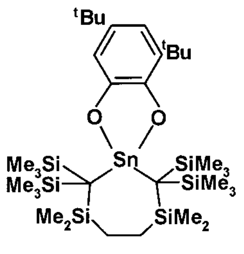

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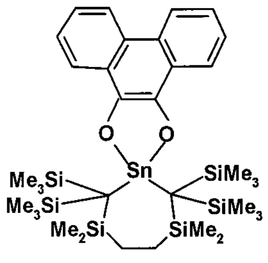

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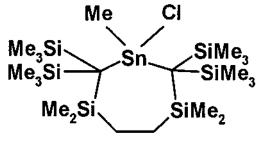
(93.1(4)°; 123.3(5)°), and **14** (102.17(13)°; 125.3(2)°). The angles reflect significant steric effects as well as the established tendency of the bonds to the more electronegative groups attached to tetrahedral centers to have greater p character.[51,52] Values of O−Sn−O range from 73 to 86° and values of C−Sn−C from 131 to 147° in compounds in which there are significant secondary interactions. [44,46−49]

Reactions of the Iodide 6a with Nucleophiles. Neither the iodide **6a** nor the chloride $\overline{RSnMeClR}$ (**15**) (obtained from the reaction between **6a** and ICl) reacted with NaN_3 or KNCS in a variety of organic solvents.



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These observations are significant, since for the organotin halides $(Me_3Si)_3CSnMe_2X$ nucleophilic attack by Br^-, I^-, SCN^-, or $OCOCH_3{}^-$ proceeds readily.[53] As far as we are aware, there have been no previous reports of the inhibition of nucleophilic attack in triorganotin halides. The tin centers in compounds in **6a** and **15** and related species are probably the most crowded to be studied to date.[32]

The compound **6a** reacted rapidly with $LiAlH_4$ and more slowly with $NaBH_4$, but we were unable to isolate the hydride $\overline{RSnMeHR}$. The product in each case was the hexasilane **5**, indicating that the metallacycle was broken during the reaction. We previously observed cleavage of a Sn−C bond by $LiAlH_4$ when $(PhMe_2Si)_3CSnMe_2Cl$ was treated with $LiAlH_4$ to give an 87% yield of $(PhMe_2Si)_3CH$.[50] When **6a** was treated at room temperature with the much milder reducing agent Et_3SiH, no reaction was observed.

Experimental Section

Air and moisture were excluded as far as possible from all reactions by use of flame-dried glassware and standard Schlenk procedures with Ar as blanket gas. NMR spectra of samples in C_6D_6 were recorded at 500.1 (^1H), 125.8 (^{13}C), 150.8 (^{19}F), 99.4 (^{29}Si), and 186.4 MHz (^{119}Sn); chemical shifts are with respect to $SiMe_4$, $CFCl_3$, or $SnMe_4$, and coupling constants involving tin are given for ^{119}Sn only. The intensities of quaternary ^{13}C and ^{29}Si signals were enhanced by polarization transfer. EI mass spectra were obtained at 70 eV; *m*/*z* values are given for species containing ^{28}Si and ^{120}Sn, and the fragment $(Me_3Si)_2CSiMe_2CH_2$ is denoted by R.

$(Me_3Si)_2CHSiMe_2CH_2CH_2SiMe_2CH(SiMe_3)_2$ (5). A solution of $(Me_3Si)_2CHBr$ (14.7 g, 0.061 mol) in Et_2O (100 mL) was added dropwise to a suspension of lithium powder (1.29 g) in a solution of 1,2-bis(chlorodimethylsilyl)ethane (5.9 g, 0.027 mol) in boiling Et_2O (200 mL). The mixture was heated under reflux for 24 h and then filtered, and the filtrate was extracted with hexanes. The extract was dried with $MgSO_4$, the solvent was removed under reduced pressure, and the residue was distilled at 140−150 °C/0.001 mmHg to give an oil, which was crystallized from ethanol at −30 °C. The white solid (11.5 g, 92%), mp 43.5−44.5 °C, had NMR spectra that were identical with those obtained for a sample made by a two-step process.[23]

$\overline{CH_2Me_2Si(Me_3Si)_2CSnEtIC(SiMe_3)_2SiMe_2CH_2}$ (6b). Neat EtI (1.00 g, 6.41 mmol) was added to a solution of **2**[9] (0.30 g, 0.52 mmol) in hexane (20 mL). The solution, which became colorless after 30 min, was stirred for a further 3 h. The solvent was then removed under vacuum, and the residue was dissolved in CH_2Cl_2. The solution was kept at −30 °C to give **6b** as colorless needles (0.32 g, 84%), mp 141−144 °C dec. Anal. Calcd for $C_{22}H_{57}ISi_6Sn$: C, 35.91; H, 7.81. Found: C, 35.84; H, 7.94. ^1H NMR: δ 0.32 and 0.39 (6H, s, $SiMe_2$), 0.42 and 0.53 (18H, s, $SiMe_3$), 0.72−0.97 (4H, m, CH_2Si), 1.4−1.6 (5H, m, Et) (the spectra of triethyltin halides are not first order[54]). ^{13}C NMR: δ 6.0 and 6.5 ($SiMe_2$), 8.3 ($^1J_{SiC}$ = 19.5 Hz) and 8.7 ($^1J_{SiC}$ = 17.2 Hz) ($SiMe_3$), 13.6 ($\mathit{C}H_3CH_2$), 14.2 ($^3J_{SiC}$ = 16.7 Hz, $CH_3\mathit{C}H_2$), 19.6 (CH_2Si), 22.9 (CSi_3Sn). ^{29}Si NMR: δ 0.26 and 0.30 ($SiMe_3$), 1.96 ($SiMe_2$). ^{119}Sn NMR: δ 21.3. MS: *m*/*z* 721 (5, M − Me), 707 (40, M − Et), 619 (10, M − Et − $SiMe_4$), 491 (15, $RSnICH_2$), 463 (30, RSnI − CH_2), 393 (70, $RSnEtCH_2$), 201 (100, $Me_3SiC(SiMe_2)_2$), 73 (85).

$\overline{CH_2Me_2Si(Me_3Si)_2CSnEt(O_2CCF_3)(SiMe_3)_2SiMe_2CH_2}$ (7b). The iodide **6b** (0.30 g, 0.41 mmol) was dissolved in hexane (20 mL), and $AgOCOCF_3$ (0.50 g, 2.26 mmol) was added. The mixture was stirred overnight at room temperature and then filtered through Celite, and the solvent was removed from the filtrate. The residue was dissolved in heptane (2 mL) and the solution kept at 5 °C to give colorless needles of **7b** (0.22 g, 74%), mp 177−180 °C. Anal. Calcd for $C_{24}H_{57}F_3O_2Si_6Sn$: C, 39.93; H, 7.96. Found: C, 39.91; H, 7.98. ^1H NMR: δ 0.28 and 0.37 (18H, s, $SiMe_3$), 0.30 and 0.40 (6H, s, $SiMe_2$), 0.88−1.20 (4H, m, CH_2), 1.62 (3H, t, $^3J_{HH}$ = 7.8 Hz, $^3J_{SnH}$ = 117 Hz, $C\mathit{H}_3CH_2$), 1.89 ($^3J_{HH}$ = 7.8, $^2J_{SnH}$ = 43 Hz, 2H, q, $CH_3C\mathit{H}_2$). ^{13}C NMR: δ 5.5 and 5.7 ($SiMe_2$), 7.0 ($^1J_{SiC}$ = 19 Hz) and 8.1 ($^1J_{SiC}$ = 29 Hz) ($SiMe_3$), 11.7 ($\mathit{C}H_3CH_2$), 14.3 (CH_2Si), 25.6 ($^3J_{CSi}$ = 35 Hz, $^1J_{SnC}$ = 296 Hz, $CH_3\mathit{C}H_2$), 25.6 ($J_{CSi,CSn}$ = 27, 34 Hz, CSi_3Sn), 116.2 ($^1J_{CF}$ = 290 Hz, q, CF_3), 158.7 ($^2J_{CF}$ = 39 Hz, q, CO). The signals for CH_2 and CSi_3, superimposed at 298 K, were separated at 323 K. ^{19}F NMR: δ −72.9. ^{29}Si NMR: δ −3.1 and 0.38 ($SiMe_3$), 2.66 ($SiMe_2$). ^{119}Sn NMR: δ 141.1 (qt, $^3J_{SnH}$ = 117 Hz, $^2J_{SnH}$ = 43 Hz). MS: *m*/*z* 707 (1, M − Me), 693 (4, M − Et), 609 (1, M − $OCOCF_3$), 393 (15, $RSnEtCH_2$), 365 (10, RSnEt − CH_2), 201 (100), 73 (95).

$\overline{CH_2Me_2Si(Me_3Si)_2CSn(^iPr)(O_2CCF_3)C(SiMe_3)_2SiMe_2CH_2}$ (7c). When neat ^iPrI (1.00 g, 5.88 mmol) was added to a solution of the stannylene **2** (0.40 g, 0.69 mmol) in hexane (20 mL), the mixture slowly became colorless as it was stirred for 3 h. The solvent and unchanged ^iPrI were then removed under vacuum, and the residue was dissolved in CH_2Cl_2 (20 mL). Dry $AgOCOCF_3$ (0.50 g, 2.26 mmol) was added to the solution, and the mixture was stirred overnight and then filtered through Celite. The solvent was removed from the filtrate under vacuum to give a white solid. This was dissolved in heptane (2 mL), and the solution was kept at 5 °C to give colorless needles of **7c** (0.32 g, 63%), mp 128−132 °C. Anal. Calcd for $C_{25}H_{59}F_3O_2Si_6Sn$: C, 40.80; H, 8.08. Found: C, 40.93; H, 8.18. ^1H NMR: δ 0.29 and 0.39 (18H, s, $SiMe_3$), 0.33 and 0.41 (6H, s, $SiMe_2$), 0.91−1.35 (4H, m, CH_2Si), 1.65 (6H, d, $^3J_{HH}$ = 7.4 Hz, $^3J_{SnH}$ = 118 Hz, $(C\mathit{H}_3)_2CH$), 2.65 (1H, sep, $^3J_{HH}$ = 7.4 Hz, $^2J_{SnH}$ = 50 Hz, $(CH_3)_2C\mathit{H}$). ^{13}C NMR: δ 6.1 and 6.2 ($SiMe_2$), 7.3 and 8.4 ($SiMe_3$), 14.3 (CH_2Si), 23.4 ($\mathit{C}H_3)_2CH$), 28.4 (J = 14 and 26 Hz, CSi_3Sn), 37.4 ($^1J_{CSn}$ = 327 Hz, $(CH_3)_2\mathit{C}H$), 116.4 ($^1J_{CF}$ = 291 Hz, q, CF_3), 158.2 ($^2J_{CF}$ = 38 Hz, q, CO). ^{19}F NMR: δ −72.5. ^{29}Si NMR: δ −3.1 ($^2J_{SiSn}$ = 47 Hz), 0.1 ($^2J_{SiSn}$ = 37 Hz, $SiMe_3$), 2.3 ($^2J_{SiSn}$ = 47 Hz, $SiMe_2$). ^{119}Sn NMR: δ 127 (dsep, $^2J_{SnH}$ = 48 Hz, $^3J_{SnH}$ = 117 Hz). MS: *m*/*z* 721 (5, M − Me), 693 (25, M − ^iPr), 623 (5, M − $OCOCF_3$), 597 (5), 477

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(5), 449 (20), 407 (20), 336 (40), 299 (60), 217 (100, $(Me_3Si)_2CHSiMe_2$), 201 (90).

Reaction of the Stannylene 2 with Protic Species. (a) With Water. Air-free water (0.5 mL) was added to a purple solution of **2** (0.30 g, 0.52 mmol) in THF (20 mL) at room temperature. The color was immediately discharged, with formation of a white solid that was insoluble in THF, Et_2O, benzene, hexane, CH_2Cl_2, and $CHCl_3$. No NMR spectra could be obtained. The reaction was repeated at −78 °C, but with the same result.

(b) With Methanol. MeOH (0.5 mL) was added to a solution of **2** (0.25 g, 0.43 mmol) in THF (10 mL) at 0 °C. After a few minutes the mixture became colorless; it was then filtered, and the solvent was removed to leave a white solid. This was soluble in THF, Et_2O, and hexane, but attempts to obtain crystals from these solvents were not successful. The ^1H NMR spectrum of a sample of the solid in C_6D_6 showed that the complex mixture of products included the hexasilane **5**, identified by its signal at δ −0.67.

(c) With Phenol. When PhOH (0.10 g, 1.06 mmol) was added to a solution of **2** (0.60 g, 1.04 mmol) in THF (20 mL), the purple color was discharged. The mixture was stirred for 10 h, and the solvent was then removed. The ^1H NMR spectrum of the residue again showed that **5** was present in the complex mixture.

Reactions of 2 with Dienes. When a solution of 1,4-diphenyl-1,3-butadiene (0.11 g, 0.52 mmol) and **2** (0.30 g, 0.52 mmol) in hexane (20 mL) was stirred for 3 days, the ^1H NMR spectrum showed that no reaction had occurred. Likewise, there was no reaction after 3 days at room temperature and then 24 h under reflux when 2,3-dimethyl-1,3-butadiene was used, or after 2 days at room temperature with 2,3-diphenyl-1,3-butadiene in either hexane or benzene.

$(Me_3Si)_2CSiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CSnOCEt{=}CHCH_2$ (10). A solution of ethyl vinyl ketone (0.044 g, 0.52 mmol) in toluene (10 mL) was added dropwise to a solution of **2** (0.30 g, 0.52 mmol) in toluene (10 mL). After 5 min the purple solution became colorless. The mixture was stirred for 1 h, and then the solvent was removed under reduced pressure and the white residue was crystallized from hexane to give **10** as colorless plates (0.27 g, 78%), mp 156−158 °C. Anal. Calcd for $C_{25}H_{60}OSi_6Sn$: C, 45.2; H, 9.1. Found: C, 45.1; H, 9.1. ^1H NMR: δ 0.33 and 0.34 (6H, s, $SiMe_2$), 0.31 and 0.43 (18H, s, $SiMe_3$), 0.92−1.10 (4H, m, CH_2Si), 1.12 (3H, t, $^2J_{HH}$ = 7.5 Hz, CH_2CH_3), 2.07 (2H, dt, $CHCH_2$), 2.22 (2H, q, CH_3CH_2), 4.94 (1H, dd, $CHCH_2$). ^{13}C NMR: δ 6.6 ($^1J_{SiC}$ = 10.4 Hz, $SiMe_2$), 7.1 ($^1J_{CSi}$ = 15.4 Hz, $SiMe_3$), 7.6 ($^1J_{SiC}$ = 22.7 Hz, $SiMe_3$), 7.8 ($^1J_{SiC}$ = 27.1 Hz, $SiMe_2$), 11.3 (CH_3), 17.2 (CH_2Si), 24.2 ($^1J_{SiC}$ = 36 Hz, CSi_3Sn), 27.0 ($^1J_{SnC}$ = 287 Hz, CH_2Sn), 29.2 ($^3J_{SnC}$ = 18 Hz, CH_2CH_3), 93.7 (CH); 166.1 (CO). ^{29}Si NMR: δ −0.79 ($^2J_{SnSi}$ = 21.6 Hz) and 1.01 ($^2J_{SnSi}$ = 42.5 Hz, $SiMe_3$), 0.51 ($^2J_{SnSi}$ = 41.6 Hz, $SiMe_2$). ^{119}Sn NMR: δ 136.1 (dt, $^2J_{SnH}$ = 31.3 Hz, $^3J_{SnH}$ = 162.2 Hz). MS: *m/z* 649 (5, M − Me), 580 (40, SnR_2), 351 (60, RSnH), 336 (RSn − CH_2), 217 (80 $(Me_3Si)_2CHSiMe_2$).

$(Me_3Si)_2CSiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CSnOCPh{=}CPhO$ (11). A solution of benzil (0.072 g, 0. 343 mmol) in hexane (20 mL) was added dropwise to a solution of **2** (0.200 g, 0.345 mmol) in hexane (20 mL). The color of the solution changed from purple to brown and finally orange. The volume was reduced to 3 mL, and the solution was kept at −30 °C to give **11** as orange-red plates (0.25 g, 92%), mp 163 °C. Anal. Calcd for $C_{34}H_{62}O_2Si_6Sn$: C, 51.7; H, 7.9. Found: C, 51.7; H, 8.1. ^1H NMR: δ 0.30 (12H, s, $SiMe_2$), 0.43 (36H, s, $SiMe_3$), 0.93 (4H, s, CH_2), 6.99 (2H, t, *p*-H), 7.12 (4H, dd, *m*-H), 7.75 (4H, d, *o*-H). ^{13}C NMR: δ 6.5 ($SiMe_2$), 7.0 ($SiMe_3$), 17.5 (CH_2Si), 34.4 ($^1J_{SiC}$ = 27 Hz, $^1J_{SiC}$ = 51 Hz, CSi_3Sn), 126.4, 128.8, 139.1, 140.3 (Ph). ^{29}Si NMR: δ 0.6 ($SiMe_2$), 1.8 ($^2J_{SiSn}$ = 51.7 Hz, $SiMe_3$). ^{119}Sn NMR: δ 36.6. MS: *m/z* 790 (20, M), 775 (2, M − Me), 580 (40, SnR_2), 336 (40, RSn − CH_2), 217 (100), 201 (95), 105 (80, PhCO), 73 (87).

$(Me_3Si)_2CSiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CSnOC_6H_2\text{-}tBu_2O$ (12). A solution of 3,5-di-*tert*-butyl-1,2-benzoquinone (0.095 g, 0.43 mmol) in hexane (25 mL) was added dropwise to a solution of **2** (0.25 g, 0.43 mmol) in hexane (15 mL). The color changed from purple to brown and then yellow. The mixture was stirred for 1 h, the solvent was removed under vacuum, and the residue was recrystallized from pentane at −30 °C to give **12** as yellow plates (0.30 g, 0.87%), mp 202 °C. Anal. Calcd for $C_{34}H_{72}O_2Si_6Sn$: C, 51.04; H, 9.07. Found: C, 51.17; H, 9.15. ^1H NMR: δ 0.26 and 0.35 (6H, s, $SiMe_2$), 0.33 and 0.37 (18H, s, $SiMe_3$), 0.95 (4H, s, CH_2), 1.38 and 1.71 (9H, s, ^tBu), 6.99 (1H, d, $^4J_{HH}$ = 2.4 Hz, CH), 7.01 (1H, d, $^4J_{HH}$ = 2.4 Hz, CH). ^{13}C NMR: δ 5.9 ($^3J_{CSn}$ = 13 Hz), and 7.09 ($SiMe_2$), 7.12 ($^3J_{CSn}$ = 21.6 Hz, $^1J_{SiC}$ = 52.8 Hz) and 7.13 ($^3J_{CSn}$ = 20.2 Hz, $^1J_{SiC}$ = 52 Hz) ($SiMe_3$), 17.2 (CH_2Si), 31.9 and 32.0 (^tBu), 34.4 and 35.5 (CC_4), 34.7($^1J_{SiC}$ = 53.8, 28.0 Hz, CSi_3Sn); 113.7, 134.9, 140.6, 148.3, 152.5 (ring). ^{29}Si NMR: δ 0.3 and 0.7 ($SiMe_3$), 2.5 ($SiMe_2$). ^{119}Sn NMR: δ 37.5. MS: *m/z* 800 (10, M), 581 (6, SnR_2H), 556 (5), 541 (13), 217 (100).

$(Me_3Si)_2CSiMe_2CH_2CH_2Me_2Si(Me_3Si)_2CSnOC_{14}H_8O$ (13). A solution of 9,10-phenanthrenedione (0.107 g, 0.52 mmol) in Et_2O (20 mL) was added to a solution of **2** (0.3 g, 0.52 mmol) in hexane (20 mL). The color changed to yellow. The solvent was removed under vacuum, the residue was dissolved in hexane (3 mL), and the solution was kept at 5 °C to give **13** as orange plates (0.31 g, 76%), mp 245−249 °C. Anal. Calcd for $C_{34}H_{60}O_2Si_6Sn$: C, 51.8, H, 7.7. Found: C, 51.8; H, 7.8. ^1H NMR: δ 0.29 (36H, s, $SiMe_3$), 0.31 (12H, s, $SiMe_2$), 0.98 (4H, s, CH_2), 7.38 (ddd), 7.60 (ddd), 8.53 (ddd), 8.58 (ddd) (CH). ^{13}C NMR: δ 6.4 ($SiMe_2$), 6.9 ($SiMe_3$), 17.6 (CH_2Si), 35.3 ($^1J_{CSi}$ = 42.5, 27.3 Hz, CSi_3Sn), 122.1, 123.2, 123.5, 126.4, 126.6, 129.2, 141.9 (CH). ^{29}Si NMR: δ 0.71 ($SiMe_2$), 1.92 ($^1J_{SiC}$ = 52.5 Hz, $SiMe_3$). ^{119}Sn NMR: δ 58.4. MS: *m/z* 788 (75, M), 773 (5, M − Me), 529 (50), 379 (20), 328 (45), 201 (100), 180 (25), 73 (60).

$CH_2Me_2Si(Me_3Si)_2CSnMeClC(SiMe_3)_2SiMe_2CH_2$ (15). A solution of ICl (0.07 g, 0.43 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **6a** (0.30 g, 0.42 mmol) in CH_2Cl_2 (10 mL). The mass spectrum of a sample taken from the mixture after 20 h showed the M − Me peak from **6a**, but this was absent when a sample was taken after a further 24 h. The solvent was removed, the residue was dissolved in Et_2O, and the solution was shaken with aqueous $Na_2S_2O_3$ to remove iodine and then dried over $MgSO_4$. The solvent was removed under vacuum to leave a white solid, which was recrystallized from CCl_4 at −30 °C to give colorless plates of **15** (0.23 g, 88%), mp 252−255 °C dec. Anal. Calcd for $C_{21}H_{55}ClSi_6Sn$: C, 40.01; H, 8.79. Found: C, 40.13; H, 8.51. ^1H NMR: δ 0.37 and 0.54 (18H, s, $SiMe_3$), 0.39 and 0.56 (6H, s, $SiMe_2$), 0.94−1.35 (4H, m, CH_2), 1.03 ($^2J_{HSn}$ = 45.3 Hz, 3H, s, SnMe). ^{13}C NMR: δ 5.4 and 5.7 ($SiMe_2$), 7.7 ($^1J_{SiC}$ = 23.0 Hz), 8.4 ($^1J_{SiC}$ = 18.2 Hz, $SiMe_3$), 12.7 (SnMe), 14.1 (CH_2), 22.7 ($^1J_{SiC}$ = 29.2 Hz, $^1J_{SnC}$ = 83.2 Hz, CSi_3Sn). ^{29}Si NMR: δ −2.2 ($^2J_{SiSn}$ = 14.9 Hz), 0.5 ($^2J_{SiSn}$ = 45.7 Hz, $SiMe_3$), 2.8 ($^2J_{SiSn}$ = 45.8 Hz, $SiMe_2$). ^{119}Sn NMR: δ 104.8 (q, $^2J_{HSn}$ = 43 Hz). MS: *m/z* 615 (3, M − Me), 399 (20, RRSnCl − $(Me_3Si)_2C{=}SiMe_2$), 379 (40, RRSnMe − $(Me_3Si)_2C{=}SiMe_2$), 217 (80), 201 (100), 73 (80).

Reactions of 6a with Nucleophiles. (a) With $LiAlH_4$. Compound **6a** (0.4 g, 0.55 mmol) was treated with $LiAlH_4$ (0.20 g, 5.26 mmol) in THF (20 mL), and the colorless mixture was stirred for 1 h and then added to a cold solution of NH_4Cl. Extraction with hexanes was followed by drying of the extract over Na_2SO_4 and removal of the solvent under vacuum. The NMR and mass spectra of the residue were identical with those of the hexasilane **5**.

Table 2. Summary of Crystallographic Data for 6b·CH_2Cl_2, 7b,c, and 10−13

	6b·CH_2Cl_2	**7b**	**7c**	**10**	**11**	**12**	**13**
formula	$C_{22}H_{57}ISi_6$-$Sn\cdot 0.5CH_2Cl_2$	$C_{24}H_{57}F_3O_2$-Si_6Sn	$C_{25}H_{59}F_3O_2$-Si_6Sn	$C_{25}H_{60}O$-Si_6Sn	$C_{34}H_{62}O_2$-Si_6Sn	$C_{34}H_{72}O_2$-Si_6Sn	$C_{34}H_{60}O_2$-Si_6Sn
fw	778.27	721.93	735.95	663.96	790.07	800.15	788.05
T/K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	tetragonal	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group (No.)	$P4_2/n$ (86)	$Pna2_1$ (33)	$P2/n$ (14)	$Pnam$ (62)	$C2/c$ (15)	$P2_12_12_1$ (19)	$P2_1/n$ (14)
a/Å	27.4200(10)	34.0509(9)	9.5492(2)	12.4200(4)	14.4034(5)	11.2943(2)	17.4461(5)
b/Å	27.4200(9)	9.3173(1)	44.979(2)	13.7856(5)	18.5094(11)	16.6702(3)	11.7903(4)
c/Å	9.2590(3)	22.2269(6)	17.0348(8)	20.4785(5)	15.9964(7)	23.2637(4)	20.6079(6)
α/deg	90	90	90	90	90	90	90
β/deg	90	90	92.488(3)	90	104.854(3)	90	110.406(2)
γ/deg	90	90	90	90	90	90	90
U/Å^3	6961.4(4)	7051.8(3)	7309.8(5)	3506.3(2)	4122.1(3)	4380.1(1)	3972.9(2)
Z	8	8	8	4	4	4	4
μ/mm^{-1}	1.92	0.96	0.93	0.95	0.82	0.77	0.85
R1, wR2 ($I > 2\sigma(I)$)	0.058, 0.145	0.041, 0.088	0.060, 0.115	0.056, 0.128	0.054, 0.135	0.033, 0.069	0.042, 0.093
all data	0.090, 0.163	0.052, 0.093	0.118, 0.134	0.059, 0.130	0.069, 0.147	0.039, 0.072	0.064, 0.103
no. of measd/ indep rflns/R(int)	43 058/10 082/ 0.121	29 430/11 504/ 0.052	36 277/12 237/ 0.117	15 311/3161/ 0.081	10 703/3586/ 0.071	23 404/10 357/ 0.043	26 196/9453/ 0.051
no. of rflns with $I > 2\sigma(I)$	7063	10065	7441	2976	2946	9479	7212

(b) With $NaBH_4$. When **6a** (0.40 g, 0.55 mmol) in THF (20 mL) was treated with $NaBH_4$ (0.20 g, 5.26 mmol), it was converted after 5 days wholly into compound **5**, as shown by NMR and mass spectra.

(c) With Et_3SiH. Compound **6a** was recovered unchanged when it was treated with Et_3SiH for 5 days under the conditions used with $NaBH_4$.

(d) With NaN_3. Compound **6a** was recovered unchanged (i) when a sample (0.20 g, 0.28 mmol) was treated for 2 days with NaN_3 (0.50 g, 7.69 mmol) in a stirred mixture of Et_2O (10 mL) and MeCN (10 mL) and (ii) when a sample (0.20 g, 0.28 mmol) in Et_2O (20 mL) was stirred for 3 days with NaN_3 (0.50 g, 7.69 mmol) in H_2O (20 mL).

(e) With KSCN. Compound **6a** was again recovered unchanged when a sample (0.20 g, 0.28 mmol) in ^{n}PrOH (100 mL) containing KSCN (0.20 g, 2.06 mmol) was stirred overnight.

Crystallography. Data were collected on a Kappa CCD diffractometer, and the structures were solved by direct methods. Further details are given in Table 2. Refinement was by full-matrix least squares (SHELXL-97) with non-H atoms isotropic and H atoms in the riding mode. The crystals of **6b** contained 0.5 mol CH_2Cl_2, from which it was recrystallized. The Si4, Si5, and Si6 atoms of one of the two independent molecules of **7b** are disordered 0.76:0.24 over two sets of sites sharing a common connected C atom site. This corresponds to the presence of two alternative conformations of the chelating ring. For **7c** the two independent molecules differ in the ring conformation. The molecules of **10** were disordered across the crystallographic mirror plane with Sn, O, C21, C22, and C23 lying on the plane. Chemically equivalent bonds were constrained by use of SADI and U_{ij} values by DELU. An attempted refinement of an ordered structure in $Pna2_1$ resulted in a high wR2 = 0.252 and peaks in the difference map clearly indicating disorder. The molecules of **11** lie on crystallographic 2-fold axes with the carbon atoms bound to Si1 disordered over two sets of positions, corresponding to disorder of the CH_2CH_2 linkage over two conformations. In **12** there is only slight disorder with very low (0.08) occupancy of alternative positions for Si4, Si5, and Si6. In Figures 1−7 the thermal ellipsoids are for 50% probability.

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Supporting Information Available: Tables showing details of crystal structure determinations, atom coordinates, equivalent isotropic displacement factors, bond lengths and angles, and hydrogen coordinates for compounds **6b**, **7b**,**c**, and **9**−**12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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