into the NMR tube, which was cooled to −196 °C and then sealed. The product $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ was identified by its ^1H NMR, ^{13}C NMR, IR, and mass spectra.[40]

Preparation of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C}\{OB(Ph)Cl\}B(Cl)]$. $PhBCl_2$ (100 mg (0.630 mmol) in 1 mL of hexane) was pipetted into a 30-mL reaction vessel containing $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (77.8 mg, 0.0900 mmol) in the drybox. The reaction mixture was degassed at −78 °C, and CH_2Cl_2 (8 mL) was added. The mixture was stirred for 1 h, resulting in a color change from bright yellow to colorless. After removal of the volatile components, the residue was washed with hexanes to give white $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C}\{OB(Ph)Cl\}B(Cl)]$ in 92% yield (84.7 mg, 0.083 mmol). NMR data are listed in Table II. IR spectrum (ν_{CO}; CH_2Cl_2): 2010 (m), 2034 (vs, br), 2075 (s), 2097 (s), 2118 cm^{-1} (w). Mass spectrum (EI): calc for $^{12}C_{16}{}^1H_8{}^{11}B_2{}^{37}Cl_2{}^{16}O_{10}{}^{192}Os_3$, $m/e = 1032$; obs, $m/e = 1032$.

Reaction of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C}\{OB(Ph)Cl\}B(Cl)]$ with BCl_3. Excess BCl_3 (0.235 mmol) was condensed into a reaction flask containing a CD_2Cl_2 solution (0.5 mL) of $(\mu\text{-H})_3Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-C}\{OB(Ph)Cl\}B(Cl)]$ (79.6 mg, 0.778 mmol). The reaction vessel was equipped with an NMR tube side arm. The reaction mixture was stirred for 1 h, and then it was decanted into the NMR tube, which was cooled to −196 °C and then sealed. ^{11}B NMR spectrum: 57.4 (br s, $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CBCl}_2)$), 54.8 ($PhBCl_2$), 26.6 ppm ($B_3Cl_3O_3$).

Preparation of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-BCH}_2)$. Diborane (0.858 mmole) was condensed at −196 °C into a 25-mL reaction flask containing a THF solution (7 mL) of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCO})$ (93.3 mg, 0.108 mmol). The reaction mixture was warmed to room temperature and stirred for 30 min, with formation of a white precipitate. Volatiles were pumped away, and the residue was extracted with toluene, leaving behind solid B_2O_3. Volatiles were pumped away from the extract to yield a light yellow solid. Recrystallization from diethyl ether produced $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-BCH}_2)$ in 80% yield (73.5 mg, 0.086 mmol) based on the cluster starting material. NMR data are listed in Table I. IR spectrum (ν_{CO}; C_6H_{12}): 1985 (m), 1993 (w), 2015 (s), 2034 (s), 2054 (s), 2076 (s), 2107 cm^{-1} (m).

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Preparation and Characterization of Tris(trimethylsilyl)silyl Derivatives of Tin. X-ray Crystal Structure of $Cl_2Sn[Si(Si(CH_3)_3)_3]_2$

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Six new [tris(trimethylsilyl)silyl]tin(IV) compounds, $R_{4-x}Sn[Si(SiMe_3)_3]_x$ (R = Me, $x = 1, 2$; R = *n*-Bu, $x = 1, 2$; R = Cl, $x = 1, 2$) have been prepared and characterized, including ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra, which were consistent with the expected structures. An X-ray structure determination of $Cl_2Sn[Si(SiMe_3)_3]_2$ revealed a pronounced distortion of the tetrahedral geometry around tin induced by the large steric requirements of the $Si(SiMe_3)_3$ groups. Crystals of $C_{18}H_{54}Cl_2Si_8Sn$ were monoclinic, $C2/c$, with $a = 16.050\ (4)$ Å, $b = 10.014\ (2)$ Å, $c = 47.289\ (10)$ a, $\beta = 90.17°$, $V = 7600$ Å^3, and $Z = 8$. The compound was more stable toward atmospheric moisture than comparable organotin dichlorides. Attempts to make the germanium analogue of the dichlorostannane via reaction of $GeCl_4$ with 2 equiv of $(THF)_3LiSi(Si(CH_3)_3)_3$ gave the dimer $[Cl_2GeSi(SiMe_3)_3]_2$ instead.

Introduction

Several reports have described the preparation of metal compounds bearing the tris(trimethylsilyl)methyl and tris(trimethylsilyl)silyl substituents. Derivatives of the former involving Hg,[1] Au,[1] Ge,[1,2] and Sn[1-4] have been described along with examples involving a number of d-block metal compounds[5-10] and one tin compound[11] incorporating the latter. Our interest in these substituents derives from their exceptionally large steric demands, which, in some cases, appear to convey improved thermal stability to their compounds, compared to analogous trimethylsilyl-bearing structures.[7,12] Except in the case of the linear MR_2 compounds (M = Zn, Cd, Hg; R = $Si(SiMe_3)_3$), where steric interactions between substituents should be minimal, and $[(Me_3Si)Si]_2Sn(\mu\text{-Cl})Li(THF)_3$, where the Si–Sn–Si bond angle is unusually large at 114.2°, there are no other structurally characterized examples of tris(trimethylsilyl)silyl derivatives that contain more than one such group. It is not clear whether this is due to destabilizing intramolecular steric interactions when more than one large substituent is present or to other factors. Since the utility of bulky substituents in the stabilization of unusual structural and bonding features is well-known, we elected to attempt the synthesis of selected tris(trimethylsilyl)silyl–tin compounds in order to better understand the effect of the bulky group on the behavior and thermal stability of such compounds. We wish to report here the preparation and characterization of new tin(IV) derivatives, $R_{4-x}Sn[Si(SiMe_3)_3]_x$ (R = Me, $x = 1, 2$; R = *n*-Bu, $x = 1, 2$; R = Cl, $x = 1, 2$), and X-ray structure determination on Cl_2Sn-

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$[Si(Si(CH_3)_3)_3]_2$ and some aspects of the chemical behavior of these compounds.

Experimental Section

All manipulations were carried out by using Schlenk techniques under an atmosphere of argon unless otherwise stated. Hygroscopic solids were handled in a Vacuum Atmospheres glovebox under dry nitrogen. Diethyl ether and tetrahydrofuran were distilled from $LiAlH_4$ under nitrogen. Pentane and hexane were distilled from sodium under argon. Elemental analyses were performed by Atlantic Microlaboratories and Galbraith Laboratories. ^1H and ^{13}C NMR spectra were recorded on an IBM/Brucker AF-80 spectrometer. ^{29}Si (56.6 MHz) and ^{119}Sn (111.8 MHz) ^1H-decoupled NMR spectra were obtained by using a General Electric NT-300 wide-bore spectrometer. IR spectra were obtained on a Perkin Elmer Model 1330 infrared spectrophotometer with samples either pressed between AgBr windows or mulled with Nujol. The lithium silyl $(THF)_3LiSi(Si(CH_3)_3)_3$ was prepared according to a published procedure.[13]

$(CH_3)_2Sn[Si(Si(CH_3)_3)_3]_2$ (I). To 30 mL of a diethyl ether solution of $(THF)_3LiSi(Si(CH_3)_3)_3$ (956.2 mg, 2.03 mmol), held at −78 °C, was added dropwise 25 mL of a diethyl ether solution of $(CH_3)_2SnCl_2$ (223 mg, 1.015 mmol) while vigorous stirring was maintained. The reaction mixture was stirred for 6 h at −78 °C and then was allowed to warm to ambient temperature. Stirring was continued overnight, after which volatiles were removed in vacuo, leaving a white residue, which was stirred with pentane (2 × 20 mL) over a 4-h period. The solution was filtered under argon, and the filtrate, upon concentration and cooling to −50 °C, gave a white crystalline product, which was dried under vacuum (500 mg, 70%); mp 110 °C. Anal. Calcd for $C_{20}H_{60}Si_8Sn$: C, 37.3; H, 9.39 Found: C, 36.7; H, 9.36. IR (cm^{-1}): 2620 w, 1305 w, 1255 sh, 1245 s, 1040 w, 825 vs, 720 w, 680 s, 620 s, 495 w, 470 w, 415 w, 340 m.

$(CH_3)_3SnSi(Si(CH_3)_3)_3$ (II). The foregoing procedure was repeated with $(CH_3)_3SnCl$ (728.4 mg, 3.65 mmol) and $(THF)_3LiSi(Si(CH_3)_3)_3$ (1721.9 mg, 3.65 mmol) in diethyl ether. The reaction mixture was stirred at ambient temperature overnight and then worked up as for compound I to give a white crystalline product (600 mg, 40%), mp 255–260 °C. Anal. Calcd for $C_{12}H_{36}Si_4Sn$: C, 35.0; H, 8.82. Found: C, 34.5; H, 8.70. IR (cm^{-1}): 2635 w, 2340 w, 1935 w, 1870 w, 1695 w, 1035 w, 1235 s, 1180 w, 1040 m, 975 w, 830 vs, br, 680 s, 615 s, 555 w, 510 s, 500 s, 460 s, 400 w, 375 w, 355 w.

$(n\text{-}Bu)_2Sn[Si(Si(CH_3)_3)_3]_2$ (III). A diethyl ether solution (30 mL) of $(THF)_3LiSi(Si(CH_3)_3)_3$ (2933.3 mg, 6.22 mmol) was added to a solution of $(n\text{-}Bu)_2SnCl_2$ (946.0 mg, 3.11 mmol) in diethyl ether cooled to −78 °C. The reaction mixture was stirred vigorously for 10 h at −78 °C followed by 50 h of stirring at ambient temperature and workup as described for compound I, yielding a white crystalline, solid product (1382.6 mg, 61%). After the product was recrystallized from diethyl ether its melting point was 75 °C. Anal. Calcd for $C_{26}H_{72}Si_8Sn$: C, 42.9; H, 9.96. Found: C, 42.7; H, 10.1. IR (cm^{-1}); 2065 w, 1920 m, 1860 m, 1700 w, 1330 w, 1295 w, 1230 s, 1165 w, 1135 m, 1060 w, 1030 m, 1000 w, 950 s, 830 vs, br, 670 s, 645 m, 610 s, 585 w, 485 w, 465 w, 430 s, 400 m.

$(n\text{-}Bu)_3SnSi(Si(CH_3)_3)_3$ (IV). A diethyl ether solution (30 mL) of $(THF)_3LiSi(Si(CH_3)_3)_3$ (1668.4 mg, 3.54 mmol) was added dropwise to a vigorously stirred ethereal solution (35 mL) of $n\text{-}Bu_3SnCl$ (1152.9 mg, 3.54 mmol) held at −78 °C. The reaction mixure was stirred for 9 h at −78 °C and then for 12 h at ambient temperature, after which volatiles were removed in vacuo, leaving a white powder and a viscous liquid, which were stirred with 40 mL of pentane for 1 h and filtered under argon. Removal of the pentane afforded the viscous, colorless liquid product, which was held under dynamic vacuum for 2 days until a constant weight was obtained (1875.4 mg, 100%): bp 235 °C dec. IR (neat, cm^{-1}): 2920 s, br, 2600 w, 1455 m, 1400 sh, 1375 w, 1235 s, 1180 w, 1040 s, br, 975 w, 810 s, 740 w, 680 nm, 660 w, 615 m, 520 w, 450 w, 375 w.

$Cl_2Sn[Si(Si(CH_3)_3)_3]_2$ (V). To a stirred hexane solution (30 mL) of $SnCl_4$ (1231 mg, 4.725 mmol) at −78 °C was added dropwise $(THF)_3LiSi(Si(CH_3)_3)_3)$ (4451.4 mg, 9.45 mmol) in hexane (50 mL). The reaction mixture was stirred for 10 h at −78 °C and then for 8 h at ambient temperature, after which hexane was removed in vacuo. The residue was stirred with 60 mL of benzene, and the solid residue was removed by filtration under argon. Benzene was removed from the filtrate in vacuo, and the residue was extracted with 50 mL of diethyl ether. When the diethyl ether solution was cooled at −50 °C, a white solid product was obtained (1000 mg, 40%). Single crystals were grown from a solution of the product in pentane refrigerated for 2 days; mp 145 °C dec. Anal. Calcd for $C_{18}H_{54}Si_8SnCl_2$: C, 31.6; H, 7.90. Found: C, 30.8; H, 7.65. IR (cm^{-1}): 2610 w, 1925 w, 1860 w, 1305 m, 1230 s, 1075 w, 1055 sh, 830 vs, br, 675 s, 605 s, 440 s, 390 w, 365 w, 300 w.

Table I. Crystallographic Data for $Cl_2Sn[Si(Si(CH_3)_3)_3]_2$ (V)

$C_{18}H_{54}Cl_2Si_8Sn$	$C2/c$ (monoclinic)
fw = 685.03	T = 22 °C
a = 16.050 (4) Å	λ = 0.71073 Å
b = 10.014 (2) Å	ρ_{calcd} = 1.20 g cm^{-3}
c = 47.289 (10) Å	μ = 10.7 cm^{-1}
β = 90.17 (2) Å	$R(\sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$ = 0.065
V = 7600 Å	$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$ = 0.053
Z = 8	

$(THF)Cl_3SnSi(Si(CH_3)_3)_3$ (VI). A hexane solution (80 mL) of $(THF)_3LiSi(Si(CH_3)_3)_3$ (2372 mg, 5.03 mmol) was added dropwise to a solution of $SnCl_4$ (1312 mg, 5.03 mmol) in hexane (50 mL) kept at −78 °C. The reaction mixture was stirred for 9 h at −78 °C and then for 40 h at ambient temperature. Workup as described for compound V gave a white solid product (1188 mg, 50%), mp 165 °C dec. Anal. Calcd for $C_{13}H_{35}OSi_4SnCl_3$: C, 28.7; H, 6.50. Found: C, 28.4; H, 7.30. IR (cm^{-1}) 2400 sh, 1680 w, 1330 sh, 1255 s, 1055 s, br, 710 w, 640 m, 625 m, 555 sh.

$(THF)Sn[Si(Si(CH_3)_3)_3]_2$ (VII). An ether solution (70 mL) of $(THF)_3LiSi(Si(CH_3)_3)_3$ (1933 mg, 4.1 mmol) was added to a cooled (−78 °C) ether suspension (50 mL) of $SnCl_2$ (389 mg, 2.05 mmol). The reaction mixture was stirred vigorously for 8 h at −78 °C and then at ambient temperature for 60 h. Workup as described for compound I gave a white solid product (620 mg, 44%), mp 140 °C. Anal. Calcd for $C_{22}H_{62}OSi_8Sn$: C, 38.5; H, 9.11. Found: C, 37.8; H, 9.36.

X-ray Structure Determination of V. Candidate specimens from the analytical sample of V were examined microscopically. A large, clear colorless multifaceted block having approximate dimensions 0.35 × 0.42 × 0.45 mm was mounted in a random orientation on a Nicolet R3m/V automated diffractometer. Since the compound was expected to be hygroscopic, the sample was coated with a thin layer of epoxy. The structure determination was carried out at ambient temperature. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table I. The Laue system was determined to be $2/m$, and from the systematic absences noted, the space group was shown to be either Cc or $C2/c$. The space group $C2/c$ was chosen on the basis of analysis of the unitary structure factors, which showed centric statistics. Intensities were measured by using the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed a 20% decay over the 5 days of the experiment. Upon visual examination, portions of the sample surface were seen to have turned milky white, most likely due to some slight attack by water vapor despite the epoxy barrier. In reduction of the data, Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the small absorption coefficient and uniform sample shape. The extraordinarily long c axis caused a certain amount of interference between neighboring peaks at low angles, most noticeably for low values of k. Therefore the data had to be carefully scrutinized for signs of peak overlap and any affected reflections discarded due to mismeasurement. Approximately 2% of the data had to be eliminated on this basis.

The structure was solved by the SHELXTL Patterson interpretation program, which revealed the position of the Sn atom in the asymmetric unit. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single nonvariable isotropic temperature factor. After all shift/esd ratios were less than 0.1, convergence was reached at the residual factors listed in Table I. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.7 e/Å^3, located near Cl(1). All calculations were made by using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Results and Discussion

Reaction of trialkyltin chlorides with $(THF)_3LiSi(SiMe_3)_3$ in diethyl ether produced new organotin silyls according to eq 1,

$$R_3SnCl + (THF)_3LiSi(SiMe_3)_3 \xrightarrow[-78\ °C\ \text{to room temp}]{} R_3SnSi(SiMe_3)_3 + LiCl \quad (1)$$

where R = Me or n-Bu. The reaction goes to completion with

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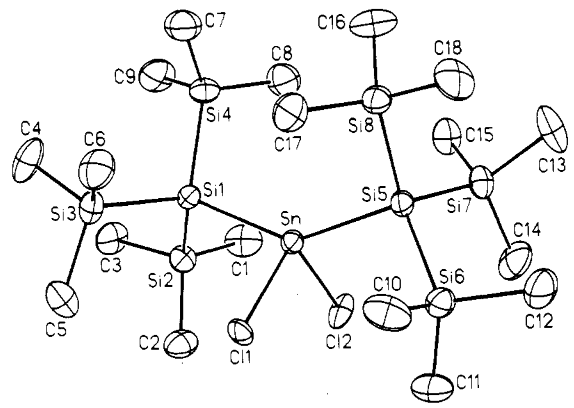

Figure 1. Molecular structure of V showing the atom-labeling scheme. The thermal ellipsoids are 30% equiprobability envelopes, with hydrogens omitted for clarity.

the abstraction of chloride under mild conditions (ambient temperature) attesting to the higher reactivity of the [tris(trimethylsilyl)silyl]lithium reagent towards trialkyltin chlorides as compared to [tris(trimethylsilyl)methyl]lithium ($LiC(SiMe_3)_3$) where similar reactions occurred only under reflux conditions.[2,4] Also, the thermal stability of these silyl–silyl derivatives appears to be less than that of comparable silyl–methyl derivatives. For example, $Me_3SnSi(SiMe_3)_3$ melts with decomposition at 255–260 °C while the analogous $Me_3SnC(SiMe_3)_3$ does not decompose until 356 °C.[2]

Treatment of dialkyltin chlorides with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ in ether under similar conditions afforded $R_2Sn[Si(SiMe_3)_3]_2$ according to eq 2, where R = Me or *n*-Bu.

$$R_2SnCl_2 + 2(THF)_3LiSi(SiMe_3)_3 \xrightarrow[-78\ ^\circ C\ \text{to room temp}]{} R_2Sn[Si(SiMe_3)_3]_2 + 2LiCl \quad (2)$$

Analytically pure products were obtained in good yields by crystallization from pentane at -50 °C. To our knowledge, analogous $R_2Sn[C(SiMe_3)_3]_2$ species have not yet been reported in the literature. Dialkyltin derivatives with tris(trimethylsilyl)silyl substituents are thermally less stable than comparable trialkyl derivatives and melt at rather low temperatures. Even though the molecules are expected to be kinetically stabilized by the two bulky tris(trimethylsilyl)silyl groups, their thermal stability is less, perhaps owing to intramolecular steric interactions between these groups evident in the molecular structure of $Cl_2SnSi(SiMe_3)_3]_2$ (vide infra).

Tin tetrachloride reacts with one equivalent of $(THF)_3LiSi(SiMe_3)_3$ in hexane at ambient temperature to produce the trichloro derivative of [tris(trimethylsilyl)silyl]stannane, which was isolated as a monotetrahydrofuran solvate as indicated by elemental analyses and ^1H NMR (δ 1.36, mult; δ 3.71, mult). Preparation of the analogous [tris(trimethylsilyl)methyl]stannane derivative[1] required refluxing of a benzene–THF solution of $SnCl_4$ and $LiC(SiMe_3)_3$, again indicative of a somewhat lesser reactivity of the lithium tris(trimethylsilyl)methyl reagent as compared to the lithium silyl. On the other hand, where comparisons could be made, $Sn-C(SiMe_3)_3$ derivatives showed greater thermal stability than comparable $Sn-Si(SiMe_3)_3$ derivatives.

Reaction of $SnCl_4$ with 2 equiv of $(THF)_3LiSi(SiMe_3)_3$ either in hexane or in ether afforded moderate yields of the air-stable $Cl_2Sn[Si(SiMe_3)_3]_2$ (V) according to eq 3.

$$SnCl_4 + 2(THF)_3LiSi(SiMe_3)_3 \xrightarrow[-78\ ^\circ C\ \text{to room temp}]{\text{hexane}} Cl_2Sn[Si(SiMe_3)_3]_2 + 2LiCl \quad (3)$$

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic[a] Displacement Parameters ($Å^2 \times 10^3$)

	x	*y*	*z*	*U*(eq)
Sn	2734 (1)	6044 (1)	1226 (1)	40 (1)
Cl(1)	1278 (1)	6412 (3)	1347 (1)	52 (1)
Cl(2)	3052 (2)	8222 (2)	1027 (1)	67 (1)
Si(1)	3399 (2)	6046 (3)	1729 (1)	42 (1)
Si(2)	3762 (2)	8288 (3)	1817 (1)	58 (1)
Si(3)	2418 (2)	5279 (4)	2063 (1)	60 (1)
Si(4)	4592 (2)	4678 (3)	1739 (1)	58 (1)
Si(5)	2668 (2)	4684 (3)	759 (1)	43 (1)
Si(6)	1372 (2)	5229 (3)	550 (1)	57 (1)
Si(7)	3769 (2)	5347 (3)	461 (1)	60 (1)
Si(8)	2736 (2)	2406 (3)	876 (1)	50 (1)
C(1)	4632 (7)	8774 (11)	1593 (3)	90 (6)
C(2)	2845 (7)	9411 (10)	1763 (3)	80 (5)
C(3)	4126 (8)	8431 (12)	2197 (2)	95 (6)
C(4)	3024 (8)	5025 (13)	2401 (2)	103 (6)
C(5)	1560 (7)	6543 (12)	2129 (3)	96 (6)
C(6)	1908 (8)	3656 (11)	1954 (3)	88 (6)
C(7)	4293 (8)	2834 (11)	1790 (3)	94 (6)
C(8)	5199 (7)	4897 (13)	1417 (3)	94 (6)
C(9)	5303 (8)	5210 (13)	2029 (3)	98 (6)
C(10)	483 (7)	4310 (11)	721 (3)	88 (6)
C(11)	1157 (8)	7070 (10)	554 (3)	86 (6)
C(12)	1408 (8)	4672 (12)	172 (2)	88 (6)
C(13)	3884 (7)	4000 (13)	187 (2)	95 (6)
C(14)	3535 (8)	6982 (12)	283 (3)	101 (7)
C(15)	4781 (7)	5468 (12)	644 (2)	78 (5)
C(16)	3818 (7)	1906 (11)	946 (3)	100 (7)
C(17)	2034 (8)	2064 (11)	1175 (2)	88 (6)
C(18)	2345 (8)	1399 (10)	572 (3)	91 (6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å)

Sn–Cl(1)	2.435 (2)	Sn–Cl(2)	2.431 (3)
Sn–Si(1)	2.604 (3)	Sn–Si(5)	2.597 (3)
Si(1)–Si(2)	2.356 (4)	Si(1)–Si(3)	2.362 (4)
Si(1)–Si(4)	2.356 (4)	Si(5)–Si(6)	2.365 (4)
Si(5)–Si(7)	2.358 (4)	Si(5)–Si(8)	2.350 (4)

Table IV. Selected Bond Angles (deg)

Cl(1)–Sn–Cl(2)	99.1 (1)	Cl(1)–Sn–Si(1)	100.2 (1)
Cl(2)–Sn–Si(1)	105.5 (1)	Cl(1)–Sn–Si(5)	104.0 (1)
Cl(2)–Sn–Si(5)	98.6 (1)	Si(1)–Sn–Si(5)	142.5 (1)
Sn–Si(1)–Si(2)	105.2 (1)	Sn–Si(1)–Si(3)	109.8 (1)
Si(2)–Si(1)–Si(3)	111.0 (2)	Sn–Si(1)–Si(4)	110.4 (1)
Si(2)–Si(1)–Si(4)	110.5 (2)	Si(3)–Si(1)–Si(4)	109.9 (2)
Si(1)–Si(2)–C(1)	110.0 (4)	Si(1)–Si(2)–C(2)	110.8 (4)
Si(1)–Si(2)–C(3)	108.3 (4)	Si(1)–Si(3)–C(4)	105.5 (4)
Si(1)–Si(3)–C(5)	112.3 (4)	Si(1)–Si(3)–C(6)	112.8 (4)
Si(1)–Si(4)–C(7)	111.0 (4)	Si(1)–Si(4)–C(8)	110.4 (4)
Si(1)–Si(4)–C(9)	110.2 (4)	Sn–Si(5)–Si(6)	105.6 (1)
Sn–Si(5)–Si(7)	109.4 (1)	Si(6)–Si(5)–Si(7)	110.2 (2)
Sn–Si(5)–Si(8)	107.8 (1)	Si(6)–Si(5)–Si(8)	111.3 (2)
Si(7)–Si(5)–Si(8)	112.4 (2)	Si(5)–Si(6)–C(10)	112.0 (4)
Si(5)–Si(6)–C(11)	112.5 (4)	Si(5)–Si(6)–C(12)	107.5 (4)
Si(5)–Si(7)–C(13)	106.6 (4)	Si(5)–Si(7)–C(14)	111.4 (4)
Si(5)–Si(7)–C(15)	113.5 (4)	Si(5)–Si(8)–C(16)	110.5 (4)
Si(5)–Si(8)–C(17)	109.5 (4)	Si(5)–Si(8)–C(18)	109.1 (4)

Description of the Structure of V. Clear, colorless crystals of V were grown from pentane at about 0 °C. Crystal and data collection parameters are summarized in Table I. Geometric parameters are listed in Tables II–IV. As shown in Figure 1, V exhibits only approximately tetrahedral coordination geometry around the tin. The most significant distortion present is that in the Si(1)–Sn–Si(5) bond angle, which, at 142.5 (1)°, is strikingly greater than the expected tetrahedral angle and appears to reflect a major steric conflict between the two tris(trimethylsilyl)silyl groups. In accord with this are a small Cl–Sn–Cl angle, 99.1 (1)°, the considerable difference between the angles Cl(1)–Sn–Si(1), 100.2 (1)°, and Cl(1)–Sn–Si(5), 104.0 (1)°, and the fact that the angle Sn–Si(1)–Si(4), 110.4 (1)°, where the $Si(4)Me_3$ group is opposite the neighboring $Si(SiMe_3)_3$ group, exceeds the tetrahedral angle, while Sn–Si(5)–Si(6), 105.6 (1)°, where $Si(6)Me_3$ is opposite the two chlorines, is much smaller than the tetrahedral angle. It is worth mentioning that the geometry of the $Si(SiMe_3)_3$ groups is not appreciably distorted. For example, the average Si–Si–Si angle is 110.9° with a spread of 2.3°, which may be compared to $Zn[Si(SiMe_3)_3]_2$, in which the linear Si–Zn–Si skeleton should minimize steric strain between the silyl groups, where the average

Table V. NMR Data

compd	δ				
	^{1}H[a]	^{13}C[a]	^{29}Si[a]		^{119}Sn[b]
			Si(*Si*Me$_3$)$_3$	*Si*(SiMe$_3$)$_3$	
Cl$_2$Sn[Si(SiMe$_3$)$_3$]$_2$	0.42	3.45	−5.5	−55	648.1
(THF)Cl$_3$SnSi(SiMe$_3$)$_3$	0.39 (s), 1.36 (mult), 3.71 (mult)	3.41	−8.1	−45	647.9
Me$_2$Sn[Si(SiMe$_3$)$_3$]$_2$	0.33 (s), 0.56 (s)	3.97, 2.98 (s)	−5.6	−132.9	−175.1
Me$_3$SnSi(SiMe$_3$)$_3$	0.27 (s), 0.30 (s)	3.05, −7.79	−6.1	−136.6	−69.4
Bu$_2$Sn[Si(SiMe$_3$)$_3$]$_2$	0.38 (s), 1.7 (q), 1.4 (q), 1.3 (q), 1.0 (t)	4.28, 31.8, 28.7, 13.7, 3.1	−5.7	−121.0	−72.2
Bu$_3$SnSi(SiMe$_3$)$_3$	0.23 (s), 1.5 (q), 1.3 (q), 1.0 (q), 0.9 (t)	3.63, 30.6, 27.5, 13.8, 2.65	−6.2	−136.7	−63.6
(THF)Sn[Si(SiMe$_3$)$_3$]$_2$	0.26 (s), 1.29 (mult), 3.1 (mult)	3.69			−1182.8

[a] Reference tetramethylsilane. [b] Reference tetramethylstannane.

Si–Si–Si angle was only a little greater at 112.2 (3)°.[7] The Sn–Si bond length, 2.604 (3) Å, is slightly longer than the sum of the covalent radii of Sn(IV), 1.40 Å,[12] and Si, 1.18 Å,[12] but somewhat shorter than the average Sn–Si bond length in [(Me$_3$Si)$_3$Si]$_2$Sn(μ-Cl)Li(THF)$_3$ (2.673 (12) Å[11]), which, however, contains three-coordinate,divalent tin in contrast to the tetracoordinate tin(IV).

NMR Data. The NMR parameters for the new compounds are listed in Table V. In all cases, spectra were consistent with the composition and expected structures of the new compounds. The ^{1}H and ^{13}C chemical shifts of the SiMe$_3$ groups in R$_3$SnSi(SiMe$_3$)$_3$ and R$_2$Sn[Si(SiMe$_3$)$_3$]$_2$ differ only minimally from those reported for d-block metal–Si(SiMe$_3$)$_3$ derivatives such as Zn[Si(SiMe$_3$)$_3$]$_2$[7] and Cp*Cl$_2$MSi(SiMe$_3$)$_3$ (M = Zr, Hf).[8] Neither does replacement of the alkyl groups on tin in the silylstannanes with chlorines induce significant shifts in these resonances. More diagnostic of the presence of Si(SiMe$_3$)$_3$ groups are the ^{29}Si NMR parameters, all of which (Table V) fall in the ranges δ −45 to −150 and δ −2.8 to −7.2 expected for *Si*(SiMe$_3$)$_3$ and Si(*Si*Me$_3$)$_3$, respectively.[7-10] In accord with previous observations[7] that the ^{29}Si chemical shift of *Si*(SiMe$_3$)$_3$ varies markedly with electronic and structural differences, we noted a nearly 80 ppm difference in δ(^{29}Si) between Me$_2$Sn[Si(SiMe$_3$)$_3$]$_2$ and Cl$_2$Sn[Si(SiMe$_3$)$_3$]$_2$. Such a sizable difference between parameters for silicons that are bonded to the same type and number of atoms appears to support the contention that the paramagnetic shielding term dominates the observed ^{29}Si shift such that moderate substituent electronegativity differences lead to large chemical shift dissimilarities.[7,14] It is also notable that δ(^{119}Sn) values for these silylstannanes follow a pattern which resembles that of the *Si*(SiMe$_3$)$_3$ δ(^{29}Si) shifts but with even greater shift differences; the ^{119}Sn values for the dimethyl- and dichlorostannanes differ by 823 ppm (Table V), again attributable to the influence of the paramagnetic shielding term in tin chemical shifts.[15]

Other Derivatives. Our attempts to prepare the Ge and Si analogues of V have, so far, proved unsuccessful. Analytical results for the germanium product (H, 6.68; C, 27.8; Cl, 18.1) were consistent with the empirical formula GeCl$_2$Si(SiMe$_3$)$_3$ (Calcd: H, 6.96; C, 27.6; Cl, 18.1) indicative of the presence of one Si(SiMe$_3$)$_3$ per germanium instead of two. Our formulation of the product as a, presumably Ge–Ge-bonded, dimer was confirmed by its field desorption mass spectrum,[16] which exhibited a molecular ion and appropriate fragments for [GeCl$_2$Si(SiMe$_3$)$_3$]$_2$. As noted in the discussion of the crystal structure of Cl$_2$Sn[Si(SiMe$_3$)$_3$]$_2$, the unusually large Si–Sn–Si angle suggests marked steric strain between the two bulky substituents. A similar molecule with Ge as the central atom should experience even greater steric strain, perhaps resulting in the destabilizatiuon of a Ge–Si bond, leading to homolytic bond cleavage followed by formation of the Ge–Ge-bonded dimer. Preliminary attempts to replace SnCl$_4$ with SiCl$_4$ in eq 3, in order to further study the effect of central atom size on the stability of bis(tris(trimethylsilyl)silyl derivatives of group 14 elements also failed to produce the Si analogue of V.

The extreme steric demands of the tris(trimethylsilyl)silyl group suggested to us that it might be suitable for stabilizing a monomeric, two-coordinate stannylene compound. In diethyl ether, SnCl$_2$ reacts with (THF)$_3$LiSi(SiMe$_3$)$_3$ according to eq 4.

$$\mathrm{SnCl_2 + 2(THF)_3LiSi(SiMe_3)_3 \xrightarrow[-78\ ^{\circ}C\ \text{to room temp}]{} (THF)Sn[Si(SiMe_3)_3]_2 + 2LiCl} \quad (4)$$

Crystallization from pentane afforded analytically pure (THF)Sn[Si(SiMe$_3$)$_3$]$_2$. The presence of Sn(II) in the product was confirmed by its ^{119}Sn NMR spectrum (δ −1182.8).[17] We were unable to obtain crystals suitable for a structure determination, but after preparing the compound, we became aware of an earlier report[11] that the reaction of SnCl$_2$ with (THF)$_3$LiSi(SiMe$_3$)$_3$ in hexane gave [(Me$_3$Si)Si]$_2$Sn(μ-Cl)Li(THF)$_3$, which exhibited a rather unexpected structural feature involving coordination of tin to LiCl(THF) moiety via a chloride bridge. It is thus probable that the THF molecule in our product is also coordinated to the tin atom. Unfortunately, the spectrocopic data included in the previous report do not allow a comparison with those of our product.

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Supplementary Material Available: Tables SI–SV, listing data collection and processing parameters, hydrogen atomic coordinates, intramolecular bond distances, intramolecular bond angles, and anisotropic displacement parameters (4 pages); a listing of structure factors for V (21 pages). Ordering information is given on any current masthead page.

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(14) Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; p 326. This work reviews the effect of the local paramagnetic shielding term on δ(^{29}Si).

(15) Harris, R. K.; Kennedy, J. D.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; p 345. These authors point out that increases in substituent electronegativity generally lead to decreases in ^{119}Sn shielding with magnitudes too large to be attributable to electron density variations, therrefore implicating the local paramagnetic shielding term.

(16) Details of the mass spectrum of the Ge dimer will be included in a manuscript describing Si(SiMe$_3$)$_3$ derivatives of Ge(IV) based on work currently underway in this laboratory.

(17) The markedly higher field ^{119}Sn NMR shift of this compound compared to the Sn(IV) species is consistent with the presence of divalent tin for which a range of about −200 to −2500 ppm is reported: Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981; p 169. However, since there is overlap in the chemical shift ranges of Sn(II) and certain types of Sn(IV) structures, the chemical shift is not definitive proof of the oxidation state.