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Reactions of a Highly Crowded Triorganotin Iodide with Silver Salts. Migration of a Methyl Group from Silicon to Tin within a Cation

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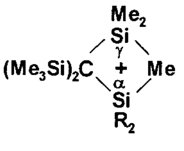
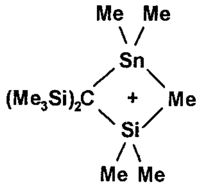
Reaction of the highly crowded organotin iodide $CH_2Me_2Si(Me_3Si)_2CSnMeIC(SiMe_3)_2SiMe_2CH_2$ with $AgBF_4$ gives the fluoride $CH_2Me_2Si(Me_3Si)_2CSnMeFC(SiMe_3)_2SiMe_2CH_2$. Reaction with $AgOSO_2C_6H_4Me$ followed by workup in moist air gives the hydroxide $CH_2Me_2Si(Me_3Si)_2CSnMe(OH)C(SiMe_3)_2SiMe_2CH_2$, **2f**. With $AgOSO_2CF_3$ the product is the organosilicon trifluoromethanesulfonate $CH_2Me_2Si(Me_3Si)_2CSnMe_2C(SiMe_3)(SiMe_2OSO_2CF_3)SiMe_2CH_2$, **5**, formed apparently by an unprecedented 1,3-migration of a methyl group from silicon to tin within a cation. Compound **5** and $Ph_3SiOSO_2CF_3$ are the first silicon trifluoromethanesulfonates to be characterized by X-ray structure determinations. In both the Si−O bonds are long, ca. 1.75 Å, consistent with the ready nucleophilic displacement of $[OSO_2CF_3]^-$ from silicon centers. The crystal structures of the fluoride $CH_2Me_2Si(Me_3Si)_2CSn(CH_2Ph)FC(SiMe_3)_2SiMe_2CH_2$ and the hydroxide **2f** have also been determined.

Introduction

Reactions of organosilicon iodides $(Me_3Si)_3CSiR_2I$ with silver salts AgX are known to give rearranged products $(Me_3Si)_2C(SiR_2Me)(SiMe_2X)$, sometimes virtually exclusively, e.g., when R = Ph, and sometimes along with the unrearranged isomer $(Me_3Si)_3CSiR_2X$, e.g., when R = Et.[1,2] The rearrangement is attributed to the formation of a methyl-bridged cation **I**, which can be attacked by the anion X^- either at the α-Si atom to give unrearranged product or at the γ-Si atom to give the rearranged product. The extent of rearrangement is often, but not always, determined by the relative degree of steric hindrance to attack at the α- and γ-silicon atoms, but it can also be influenced by the nature of X and the solvent.[3]

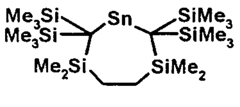


I

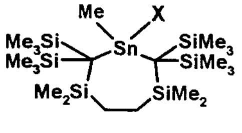


II

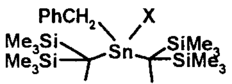
Analogous migration of a methyl group from tin to silicon was observed when the silicon iodide $(Me_3Si)_2C(SnMe_3)(SiMe_2I)$ was treated with silver salts AgX (X = $OCOCH_3$, $OCOCF_3$, or OSO_2CF_3) in CH_2Cl_2, the products being wholly the rearranged $(Me_3Si)_3CSnMe_2X$.[4] The rearrangement is consistent with formation of the bridged cation **II** by anchimeric assistance to the leaving of the iodide ion. Subsequent attack of X^- occurs at the larger, and thus less hindered, metal center, i.e., at tin. In the course of our studies on the triorganotin iodide **2a**, containing the bidentate "trisiamyl" ligand $C(SiMe_3)_2SiMe_2CH_2CH_2Me_2Si(Me_3Si)_2C$, we have observed an example of migration of a methyl group in the opposite direction, from silicon to tin. Compound **2a** is obtained by oxidative addition of MeI to the cyclic stannylene **1**.[5]



1



2a, X = I; **2b**, X = BF_4; **2c**, X = F; **2d**, X = $OCOCF_3$; **2e**, X = $OSO_2C_6H_4Me$; **2f**, X = OH; **2g**, X = OSO_2CF_3



3a, X = F; 3b, X = Br

$(2,4,6\text{-}Me_3C_6H_2)_3SnOH$
4

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10.1021/om011079z CCC: \$22.00
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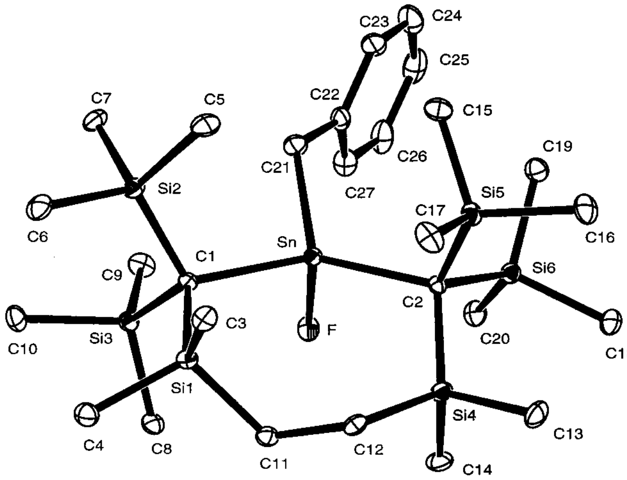


Figure 1. Molecular structure of **3a**.

Results and Discussion

Reaction of the Iodide 2a with AgBF$_4$. We considered that it might be possible to obtain compounds containing three-coordinate tin cations by replacement of the iodide in **2a** by less nucleophilic anions. We first treated **2a** with AgBF$_4$. There was no reaction in hexane. In THF the initial product was probably the fluoride-bridged tetrafluoroborate **2b**, but after workup the only crystalline product was the fluoride **2c**. The compounds $(Me_3Si)_3CSnR'_2BF_4$ (R' = Me or Ph) were previously[6] found to lose BF$_3$ readily, especially in the presence of donor solvents such as methanol. We could not obtain crystals of **2c** suitable for an X-ray structure determination, but the high solubility in organic solvents and the spectroscopic data [in particular the value, 2396 Hz, of $^1J_{SnF}$ (lit. values 2256−2463 Hz[6,7])] are characteristic of triorganotin fluorides that contain bulky organic groups and in consequence crystallize in lattices consisting of discrete molecules with no significant secondary Sn···F contacts.[6,8]

The benzyl compound **3a** was made similarly in good yield by treatment of the stannylene **1** with benzyl bromide and then AgBF$_4$. The bromide intermediate **3b** was not isolated. Spectroscopic data were very similar to those of **2c**, and the structure, determined by an X-ray study, is shown in Figure 1. The data in Table 1 indicate that the Sn−F bond length [1.956(2) Å] is the same, within experimental uncertainty, as those [1.957(4)−1.965(8) Å] in the previously characterized four-coordinate organotin fluorides.[6,8]

Reaction of the Iodide 2a with AgOCOCF$_3$ and AgOSO$_2$C$_6$H$_4$Me. When the organotin iodide was treated with silver trifluoroacetate, it gave, in 76% yield after recrystallization, the product of direct replacement of I^- by $CF_3CO_2^-$, i.e., compound **2d**, the identity of which was indicated by NMR spectroscopy and confirmed by a crystal structure determination.[5]

The reaction of **2a** with silver *p*-toluenesulfonate (tosylate) gave the tin tosylate **2e**. We did not isolate this in a pure state, but its formation is confirmed by the fact that on workup in moist air we obtained the crystalline tin hydroxide **2f**. This was characterized by elemental analysis, a sharp ν(OH) absorption at 3667 cm^{-1}, and NMR spectroscopy. Its structure was determined by an X-ray study. The solid was found to consist of discrete molecules (Figure 2) with no intermolecular O···O distances less than 4 Å. Only one other compound R$_3$SnOH containing four-coordinate tin has previously been structurally characterized, namely, trimesityltin hydroxide **4**,[8] which adopts a structure consisting of discrete molecules, like that of **2f**. Other organotin hydroxides form hydrogen-bonded dimers[9,10] or polymers containing five-coordinate tin.[11] Bond lengths and angles in **2f** are given in Table 1. The Sn−O bond length [2.000(3) Å] is the same as that in **4**, confirming this as the "normal" distance from four-coordinate tin to oxygen. The distance is slightly shorter than that [2.102(3) Å] in **2d**, perhaps a reflection of the weak nucleophilicity of trifluoracetate, but the other corresponding bond lengths and angles are not significantly different in the two compounds.

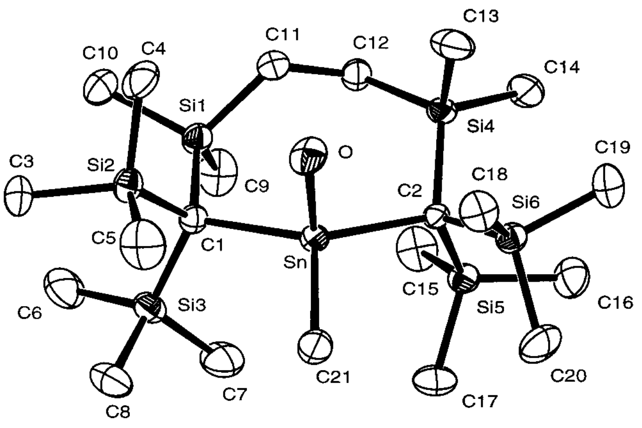
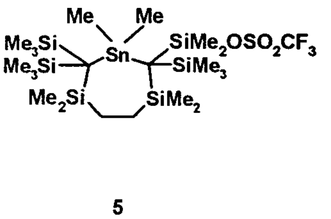


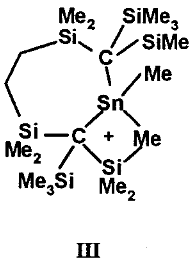
Figure 2. Molecular structure of **2f**.

The ready formation of the hydroxide **2f** from the tosylate **2e** is puzzling, since we have shown that reactions of the iodide **2a** with nucleophiles are in general slow.[12] Indeed, the tin centers in four-coordinate compounds bearing the trisiamyl ligand are probably the most crowded ever studied. It is however possible that there is less hindrance to displacement of the smaller oxygen of tosylate than of the larger iodine.

Reaction of the Iodide 2a with AgOSO$_2$CF$_3$. In an attempt to make the tin trifluoromethanesulfonate (triflate) **2g**, we treated the iodide **2a** with AgOSO$_2$CF$_3$. The product obtained in 68% yield after recrystallization was the silicon triflate **5**, as indicated by NMR spectroscopy (including a two-dimensional $^1H-^{29}Si$ shift correlation) and confirmed by a crystal structure determination (Figure 3 and Table 1).



5



III

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Table 1. Selected Bond Lengths (Å) and Angles (deg)

For **2f**			
Sn−Me	2.149(5)	C2−Si4	1.915(4)
Sn−C1	2.221(4)	C2−Si5	1.907(4)
Sn−C2	2.229(4)	C2−Si6	1.931(4)
Sn−O	2.000(3)	Si−Me	1.889(5)[a]
C1−Si1	1.907(4)	Si−CH_2	1.872(5)[a]
C1−Si2	1.946(4)	CH_2−CH_2	1.549(7)
C1−Si3	1.888(4)		
C1−Sn−C2	133.38(14)	Me−Sn−O	106.6(2)
Me−Sn−C	108.5(2)[a]	C1−Sn−O	95.77(14)
Me−Si−Me	102.7(3)−107.2(3)	C2−Sn−O	99.84(14)
C1,2−Si−Me	109.9(2)−115.9(2)	Si−C−Si	104.80(18)−114.07(19)
C1,2−Si−CH_2	111.7(2), 115.4(2)	Me−Si−CH_2	101.7(2)−108.5(3)
Sn−C−Si(exo)	104.80(18)−114.07(19)	Si−C−C	117.7(4), 121.1(4)
Sn−C−Si(endo)	107.78(18), 109.71(19)		
For **3a**[b]			
Sn−F	1.956(2)	C1−Si	1.924(5)[a]
Sn−C(21)	2.178(5)	Si−Me	1.875(5)[a]
Sn−C1	2.227(5)	Si−CH_2	1.871(5)[a]
Sn−C2	2.216(5)	CH_2−CH_2	1.551(7)
C1−Sn−C2	133.17(18)	F−Sn−C(21)	102.37(17)
C1−Sn−C(21)	101.9(2)	F−Sn−C(ring)	98.28(14), 96.20(14)
C2−Sn−C(21)	117.9(2)	Si−C−Si(exo)	108.0(2), 109.1(3)
Me−Si−Me	102.7(3)−107.5(3)	Si−C−Si(endo)	108.4(2)−111.1(2)
C1,2−Si−Me	111.3(2)−115.7(2)	C1,2−Si−CH_2	111.5(2), 115.8(2)
Sn−C−Si(exo)	105.7(2)−111.8(2)	Si−C−C	118.0(3), 119.7(4)
Sn−C−Si(endo)	109.9(2), 112.2(2)	Me−Si−CH_2	102.7(3)−107.8(2)
For **5**			
Sn−C21	2.162(6)	C1−Si1	1.861(5)
Sn−C22	2.149(5)	C1−Si2	1.958(5)
Sn−C1	2.286(5)	C1−Si3	1.915(6)
Sn−C2	2.251(5)	C2−Si4	1.906(6)
Si−O	1.760(4)	C2−Si5	1.917(6)
S−O1	1.521(4)	C2−Si6	1.907(5)
S−O2	1.418(5)	Si−Me	1.878(6)[a]
S−O3	1.424(5)	Si−CH_2	1.893(6)[a]
S−C	1.834(7)	CH_2−CH_2	1.536(8)
Me−Sn−Me	106.3(2)	Si−C−Si	106.3(3)−111.9(3)
C1−Sn−C2	127.45(19)	O1−S−O2	111.7(2)
Me−Sn−C	103.5(2)−108.6(2)	O1−S−O3	110.3(3)
Sn−C−Si	106.4(2)−114.4(2)	O2−S−O3	120.9(3)
Me−Si−Me	101.7(3)−107.7(3)	Si−O−S	132.2(2)
C1,2−Si−Me	112.6(3)−119.5(3)	Me−Si−CH_2	102.9(3)−107.3(3)
C1,2−Si−CH_2	115.1(2), 112.0(3)	Si−C−C	118.7(4), 121.4(4)
For **7**			
Si−O1	1.743(2)	S−O3	1.414(2)
S−O1	1.531(2)	S−C19	1.819(3)
S−O2	1.420(2)	Si−C	1.850(2)[a]
C−Si−C	113.72(11)[a]	Si−O1−S	120.05(11)
O−Si−C1	106.14(9)	O1−S−O2	111.55(10)
O−Si−C7	101.06(9)	O1−S−O3	111.06(10)
O−Si−C13	107.14(9)	O2−S−O3	120.73(12)

[a] Mean value; esd's are for individual measurements, none of which differs significantly from the mean. [b] Values for one of the independent molecules. Bond lengths show no significant differences between the two molecules; there are small differences in bond angles.

Immediately after the addition of $AgOSO_2CF_3$ to the solution of **2a** in CD_2Cl_2 the only peak in the ^{19}F NMR spectrum, at δ −80.2, can be assigned to the silver salt itself. After several hours at room temperature another peak appears at δ −79.3; this then decays and is replaced by the signal at δ −77.4 due to **5**. We tenta-

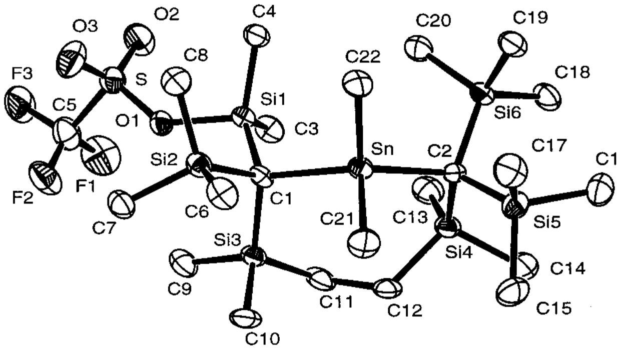

Figure 3. Molecular structure of **5**.

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tively assume that the initial product is the tin triflate **2g**, which then ionizes, with anchimeric assistance by a methyl group on silicon, to give the bridged cation **III** and triflate anion. Comparison of **II** and **III** shows that the tin atom in **III** is much the more crowded. Hence, whereas any ionization of triflate from the previously characterized $(Me_3Si)_3CSnMe_2OSO_2CF_3$ to give **II** leads to reattachment at tin so that no rearrangement is observed, similar ionization of triflate from **2g** leads, sometimes at least, to irreversible attachment to the silicon atom of the bridge, reattachment at the larger tin atom being hindered by the crowding there. This crowding is evident from the fact that the tin atom bears two tris(triorganosilyl)methyl substituents, whereas the silicon atom bears only one bulky bis(triorganosilyl)-(trisorganostannyl)methyl group. No rearrangement has so far been observed for the trifluoroacetate **2d**, suggesting that, if there is any ionization of this compound, the equilibrium concentration of the ionic species is much lower than that of the triflate. The formation of **5** may also be favored by the formation of the strong Si−O bond, but within the limits of accuracy of the available data,[13,14] the sum of the energies for a Si−O and a Sn−Me bond (ca. 500 + 270 kJ mol^{-1}) is similar to that for a Si−Me and a Sn−O bond (ca. 370 + 400 kJ mol^{-1}).

In an attempt to obtain the unrearranged triflate **2g**, we treated the hydroxide **2f** with 1 equiv of CF_3SO_2Cl in CD_2Cl_2 in an NMR tube. No reaction was detected during several days, presumably because the hydroxide is well protected by the bulky ligand. When an excess of CF_3SO_2Cl was added, the **2f** was completely consumed to produce a complex mixture of products, none of which could be identified as **5**. Further work is therefore necessary before we can be sure that the intermediate **2g** is indeed involved in the formation of **5**.

The bond lengths and angles within the $\overline{\text{SnCSiCCSiC}}$ ring in **5** are similar to those in **2f**, **3a**, and related crowded Sn^{IV} compounds,[5,12] but those involving the tin and silicon centers require some comment. The only bonds to tin are from carbon so that, in the absence of marked steric or electronic effects, the C−Sn−C angles are expected to be about 109°. The exocyclic Me−Sn−Me angle [106.3(2)°] is slightly less than the tetrahedral value, but significantly wider than the exocyclic O−Sn−O angles (83−84°) in compounds containing the same ring system.[12] The wider exocyclic angle in **5** reflects the larger size of methyl than of oxygen as well as the greater s character in Sn−C than in Sn−O bonds. The endocyclic C−Sn−C angle [127.45(19)°] is markedly wider than 109°, indicating that crowding within the seven-membered bidentate ligand holds the carbon atoms apart. A similar effect is found in the stannylene **1**, where there is a lone pair in place of the two exocyclic methyl groups of **5**; the C−Sn−C angle (118°)[5] is wider than those (96−104°) in acyclic stannylenes[15−18] and the less crowded cyclic stannylene **6** [C−Sn−C 86.7(2)°].[19] The mean Sn−C(ring) bond length in **5** [2.269(5) Å] is slightly longer than that [2.227(5) Å] in the unrearranged compound **2d**, but there is no significant difference in the average exocyclic Sn−Me bond lengths [2.155(6) Å in **5** and 2.160(4) Å in **2d**].

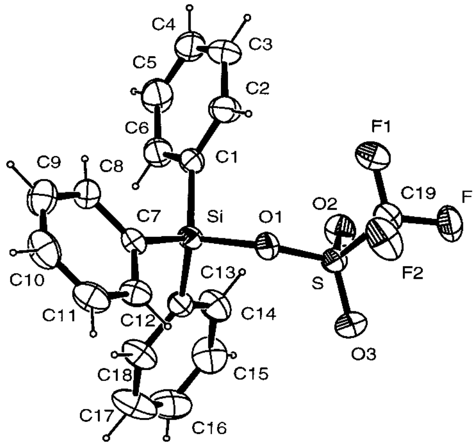
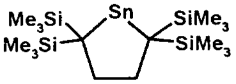


Figure 4. Molecular structure of **7**.



6

$Ph_3SiOSO_2CF_3$

7

$(Me_3Si)_3CSiPhHSO_2C_6H_4Me$

8

Silicon Triflates. The length of the Si−O bond in **5**, 1.760(4) Å, is significantly greater than those, 1.64−1.66 Å,[20] normally observed for Si−O bonds. As no structural data for silicon triflates were available in the literature for comparison, we determined the crystal structure of $Ph_3SiOSO_2CF_3$, **7**. This compound has been made in sulfolane, and cryoscopic measurements have shown that it is not dissociated.[21] The molecular structure is shown in Figure 4, and bond lengths and angles are given in Table 1. The Si−O bond is slightly shorter [1.743(2) Å] than that in **5**, but similar to those in the cyanate $(Me_3Si)_2(PhMe_2Si)CSiMe_2OCN$ [1.756(10) Å][22] and the perchlorate $Ph_3SiOClO_3$ [mean 1.744(4) Å].[23] Distances of 1.74−1.76 Å correspond to Pauling covalent bond orders of 0.68−0.62, implying that there is a significant ionic component in the bonding.[24] Silylium cation character in compounds R_3SiY is also reflected in the mean value of the C−Si−C angles. For **5** the average C−Si1−C angle (115.4°) is slightly higher than

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the C−Si−C angles in **7** (113.7°) and $Ph_3SiOClO_3$ (113.6°) and at the lower end of the range (115−117°) found in a series of *closo*-$CB_{11}H_6Br_6$ derivatives, which have bond orders of about 0.4.[25] The wide C−Si−C angles in **5** are associated with short Si(1)−C bond distances; the Si(1)−C(1) distance [1.861(5) Å] is significantly smaller than the other Si−C(1,2) distances [mean 1.920(6) Å], and the Si(1)−Me distances [1.866(6) and 1.854(5) Å] are only just within three standard deviations (determined from experimental values for individual measurements) of the mean Si−Me distance for the molecule as a whole. These distances reflect the delocalization of the partial positive charge on the atom Si(1).

This is also shown by the marked shifts to high frequency of the resonance corresponding to ^{29}Si atoms adjacent to triflate; ^{29}Si shifts are at δ −2.6 to +2.7 in **2d**, −0.9 to 2.4 and 39.4 in **5**, 80−100 in carborane derivatives, and 225 for the unsolvated trimesitylsilyl cation.[26] The shift in **7** (δ 3.6) is similar to that (3.0) in $Ph_3SiOClO_3$.[23,25] A similar comparison may be made of tin chemical shifts: namely, δ 16.9 in **5**, 232 in the triflate $(Me_3Si)_3CSnMe_2OSO_2CF_3$[27] (cf. 148.5 in **2d**, 461.2 in crystalline $[Bu_3Sn]^+[CB_{11}Me_{12}]^-$,[28] and 806 in the trimesitylstannyl cation).[26]

The compounds $(Me_3Si)_3CSiMe_2Y$ with Y = $OClO_3$, OSO_2CF_3, or OCN are comparable in reactivity toward MeOH and much more reactive than, for example, $(Me_3Si)_3CSiMe_2I$. It is reasonable to associate the high reactivity with the lengths of the Si−O bonds and with the relatively weak coordination (and high leaving ability) of the three oxygen-centered ligands. In keeping with this, the Si−O bond in the *p*-toluenesulfonate (tosylate) $(Me_3Si)_3CSiPhHOSO_2C_6H_4Me$-*p*, **8**,[2a] which is much less reactive than **7** toward MeOH, is somewhat shorter [1.716(8) Å] than that in **7**. The long Si−O bond in **7** is associated with short S−O and S═O bonds [1.531(2) and mean 1.417(2) Å, respectively]. The corresponding bond distances in **5** are 1.521(4) and 1.421(5) Å, respectively, and in **8** 1.587(7) Å [1.549(7) Å in a second molecule] and 1.430(8) Å.[29] It is noteworthy that in both **5** and **7** there is no significant difference between the O−S−O(2) and O−S−O(3) angles, in contrast to the data for **8** and some organic tosylates.

Experimental Section

Air and moisture were excluded as far as possible by the use of flame-dried glassware and Ar as blanket gas. The stannylene **1** and the iodide **2a** were made as described previously.[5]

$CH_2Me_2Si(Me_3Si)_2CSnFMeC(SiMe_3)_2SiMe_2CH_2$, 2c. Powdered $AgBF_4$ (0.25 g, 1.28 mmol) was added in a single portion to a solution of **2a** (0.41 g, 0.57 mmol) in hexane (25 mL), and the suspension was stirred for 15 h at room temperature. The ^1H NMR spectrum of a small sample showed that no reaction had occurred. THF (5 mL) was added, and the suspension was stirred for 4 h. The volatile material was removed under vacuum to leave a slightly sticky solid, which was extracted with hexane (20 mL). The extract was filtered, the volume of the filtrate was reduced to 5 mL, and colorless needles of **2c**, mp 241−244 °C (0.26 g, 74%), separated at −30 °C. Anal. Calcd for $C_{21}H_{55}FSi_6Sn$: C, 41.1; H, 9.0. Found: C, 41.3; H, 9.2. ^1H NMR (C_6D_6): δ 0.26 and 0.43 (18H, s, $SiMe_3$), 0.28 and 0.32 (6H, s, $SiMe_2$), 0.85 (3H, d, $^3J_{HF}$ = 3.0 Hz, $^2J_{SnH}$ = 48.5 Hz, SnMe), 0.91−1.15 (4H, m, CH_2). ^{13}C NMR: δ 4.7 (s, $SiMe_2$), 5.1 (d, $^4J_{FC}$ = 5.0 Hz, $SiMe_2$), 6.69 and 6.70 ($SiMe_3$), 12.0 (d, $^2J_{CF}$ = 9.4 Hz, SnMe), 14.2 (CH_2), 21.8 (d, $^2J_{CF}$ = 11.7 Hz, CSi_3-Sn). ^{19}F NMR: δ −161.1 ($^1J_{SnF}$ = 2396 Hz). ^{29}Si NMR: δ −3.0 (d, $^3J_{SiF}$ = 6.1 Hz, $SiMe_3$), 0.4 (d, $^3J_{SiF}$ = 4.5 Hz, $SiMe_3$), 2.6 (d, $^3J_{SiF}$ = 1.2 Hz, $SiMe_2$). ^{119}Sn NMR: δ 108.9 ($^1J_{SnF}$ = 2404, $^2J_{SnH}$ = 46 Hz). MS: *m*/*z* 599 (30, M − Me), 379 (90, M − $(Me_3Si)_2CSiMe_2F$), 351 (60, M − $(Me_3Si)_2CSiMe_2F$ − C_2H_4), 263 (30, $SnMeC(SiMe_2)_2$), 201 (100, $Me_3SiC(SiMe_2)_2$), 73 (97, $SiMe_3$).

$CH_2Me_2Si(Me_3Si)_2CSnF(CH_2C_6H_5)C(SiMe_3)_2SiMe_2CH_2$, 3a. Benzyl bromide (0.089 g, 0.52 mmol) was added to a solution of **1** (0.30 g, 0.52 mmol) in hexane (30 mL). After 5 min the solution became colorless and the solvent was removed under reduced pressure to leave a sticky solid. This was immediately dissolved in CH_2Cl_2 (30 mL), and $AgBF_4$ (0.3 g, 1.5 mmol) was added to the mixture, which was stirred for 18 h at room temperature, then filtered. The solvent was removed from the filtrate under vacuum to give a white residue. This was dissolved in the minimum amount of hexane (about 2 mL), and the solution was left at room temperature to give **3a** as colorless plates (0.21 g, 75%), mp 180−183 °C. Anal. Calcd for $C_{27}H_{59}FSi_6Sn$: C, 47.0; H, 8.6. Found: C, 46.8; H, 8.8. ^1H NMR: δ 0.28 and 0.40 (18H, s, $SiMe_3$), 0.35 and 0.39 (6H, s, $SiMe_2$), 0.90−0.98 (ddd) and 1.12−1.20 (2H, ddd, CH_2), 3.07 (2H, d, $^3J_{HF}$ = 3.9 Hz, $^2J_{SnH}$ = 56 Hz, CH_2Ph), 6.99 (^1H, tt, *p*-H), 7.13 (2H, dd, *m*-H), 7.44 (2H, d, *o*-H). ^{13}C NMR: δ 5.4 and 6.3 ($^4J_{CF}$ = 9.6 Hz, $SiMe_2$), 6.9 ($^4J_{CF}$ = 4.6 Hz), 7.1 ($SiMe_3$), 15.3 (CH_2Si), 25.9 ($^2J_{CF}$ = 6.4 Hz, $^1J_{SnC}$ = 51 Hz, CSi_3-Sn), 38.5 ($^2J_{CF}$ = 6.1 Hz, d, CH_2Ph), 125.8 (*p*-C), 128.6 (*m*-C), 130.7 (*o*-C), 138.8 (*i*-C). ^{19}F NMR: δ −165.7 ($^1J_{SnF}$ = 2559 Hz). ^{29}Si NMR: δ −2.5 ($^3J_{SiF}$ = 5.2 Hz), 0.6 (d, $^3J_{SiF}$ = 4.8 Hz, $SiMe_3$), 1.8 (s, $SiMe_2$). ^{119}Sn NMR: δ 60.7 (d, $^1J_{SnF}$ = 2561 Hz). MS: *m*/*z* 675 (3, M − Me), 599 (44, M − Bz), 379 (25), 263 (20), 201 (90), 91 (50, Bz), 73 (100, $SiMe_3$).

$CH_2Me_2Si(Me_3Si)_2CSn(OH)MeC(SiMe_3)_2SiMe_2CH_2$, 2e. A solution of **2a** (0.39 g, 0.54 mmol) in CH_2Cl_2 (25 mL) was added to a stirred slurry of $AgO_3SC_6H_4Me$ (0.77 g, 2.76 mmol) in CH_2Cl_2 (30 mL). The suspension was stirred in the absence of light for 14 h, then filtered, and solvent was removed from the filtrate. Attempts to crystallize the residue at low temperature were unsuccessful, so a solution in hexane was allowed to evaporate slowly in the open air to produce **2e** as colorless crystals suitable for an X-ray diffraction study (ca. 0.15 g, 45%). Anal. Calcd for $C_{21}H_{56}OSi_6Sn$: C, 41.3; H, 9.17. Found: C, 41.3; H, 9.25. ^1H NMR: δ 0.10 and 0.30 (6H, s, $SiMe_2$), 0.29, 0.33 (18H, s, $SiMe_3$), 0.74 (3H, s, $^2J_{SnH}$ = 48 Hz, SnMe), 0.90−1.53 (4H, m, CH_2). ^{13}C NMR: δ −0.8 ($SiMe_2$), 2.7, 3.0 ($SiMe_3$), 9.7 (CH_2), 14.8 (CSi_3). ^{29}Si NMR: δ −2.6 and −0.5 ($SiMe_3$), 2.5 ($SiMe_2$). ^{119}Sn NMR: δ 68.4. IR (Nujol mull): 3667 cm^{-1} (ν(OH)). MS: *m*/*z* 597 (50, M − Me), 453 (10, M − Me − Me_3SiCH═$SiMe_2$), 425 (30, M − Me − $Me_3SiCHSiMe_2CH_2CH_2$), 381 (30, M − Me − $(Me_3Si)_2C$═$SiMe_2$), 309 (10), 275 (40), 217 (90, $(Me_3Si)_2CHSiMe_2$), 147 (20), 129 (60), 73 (100).

$CH_2Me_2Si(Me_3Si)_2CSnMe_2C(SiMe_2OSO_2CF_3)(SiMe_3)SiMe_2CH_2$, 5. Silver triflate (0.50 g, 1.95 mmol) was added to a solution of the iodide **2a** (0.30 g, 0.41 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred for 5 h at room temperature, then filtered, and the solvent was removed under vacuum. The residue was dissolved in hexane and the solution kept at −30

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Table 2. Summary of Crystallographic Data for 2f, 3a, 5, and 7

	2f	**3a**	**5**	**7**
chemical formula	$C_{21}H_{56}OSi_6Sn$	$C_{27}H_{59}FSi_6Sn$	$C_{22}H_{55}F_3O_3SSi_6Sn$	$C_{19}H_{15}F_3O_3SSi$
fw	611.89	689.97	743.95	408.46
T/K	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	$C2/c$	$P\bar{1}$ No. 2	$P2_1/n$	$P2_1/c$
a/Å	36.930(2)	9.3336(3)	13.0809(10)	10.3023(4)
b/Å	9.1769(3)	19.3177(9)	16.3780(7)	9.0227(6)
c/Å	22.9057(13)	20.2094(9)	17.1546(13)	20.3428(12)
α/deg		91.816(2)		
β/deg	124.694(2)	94.810(3)	107.052(3)	91.934(4)
γ/deg		94.102(2)		
U/Å^3	6382.7(6)	3619.1(3)	3513.6(4)	1889.9(2)
Z	8	4	4	4
μ/mm^{-1}	1.27	0.93	1.03	0.28
R1 wR2, $I > 2\sigma(I)$	0.046, 0.102	0.050, 0.096	0.053, 0.121	0.042, 0.093
all data	0.060, 0.108	0.085, 0.109	0.081, 0.133	0.062, 0.102
no. of measured/indep rflns /R(int)	15114/5584/0.076	25413/12716/0.066	20193/6151/0.090	9355/3313/0.055
no. of rflns with $I > 2\sigma(I)$	4666	9023	4508	2508

°C to give colorless needles of **5** (0.21 g, 68%), mp 181−183 °C. Anal. Calcd for $C_{22}H_{55}F_3O_3Si_6SSn$: C, 35.5; H, 7.45. Found: C, 35.6; H, 7.56. ^{1}H NMR (CD_2Cl_2, for numbering see Figure 1): δ 0.29 and 0.30 (3H, s, Si^4Me_2), 0.31, (18H, $Si^{5,6}$-Me_3), 0.34 and 0.35 (3H, s, Si^3Me_2), 0.35 (9H, s, Si^2Me_3), 0.66 (3H, s, $^2J_{119SnC} = 46.8$ Hz, SnMe), 0.7 (3H, s, $^2J_{119SnH} = 48.2$ Hz, SnMe), 0.77, 0.82 (3H, s, Si^1Me_2), 0.85−1.00 (4H, m, CH_2). ^{13}C NMR (CD_2Cl_2): δ 4.88, 4.96, 6.10, and 7.30 ($Si^{3,4}Me_2$), 7.40 (Si^1Me_2), 7.82 and 7.85 ($Si^{5,6}Me_3$), 8.19, 8.47, (SnMe), 11.9, 12.6 (CSi_3Sn), 13.9, 14.1 (CH_2), 118.6 (q, $^1J_{CF} = 317.8$ Hz, CF_3). ^{19}F NMR (CD_2Cl_2): δ −79.3. ^{29}Si NMR (CD_2Cl_2): δ −0.89 and −0.75 ($Si^{5,6}Me_3$), −0.2 (Si^2Me_3), 1.7 (Si^4Me_2), 2.4 (Si^3Me_3), 39.4 (Si^1Me_2). ^{119}Sn NMR (CD_2Cl_2): δ 16.9 (qq). MS: m/z 744 (1%, M), 729 (6, M − Me), 513 (10, M − $C(SiMe_3)_3$), 379 (M − $C(SiMe_3)_2(SiMe_2OTf)$), 335 (40, $(Me_2Si)_2CSiMe_2OTf$), 201(100, $Me_3SiC(SiMe_2)_2$), 73 (80) (Tf = SO_2CF_3).

$Ph_3SiOSO_2CF_3$, 7. An excess of $AgOSO_2CF_3$ (1.57 g, 6.10 mmol) was added to a solution of Ph_3SiCl (0.90 g, 3.05 mmol) in CH_2Cl_2 (40 mL) with exclusion of light. The solution was stirred for 2 days, then the solvent was removed under vacuum, and the residue was extracted with hexane (20 mL). The extract was filtered, and the filtrate reduced to 10 mL and kept at −30 °C to give colorless crystals of **7** (0.92 g, 74%). Anal. Calcd for $C_{19}H_{15}F_3O_3SSi$: C, 55.9; H, 3.7. Found: C, 55.8; H, 3.6. ^{1}H NMR ($CDCl_3$): δ 7.54 (2H, dd, *m*-H), 7.61 (1H, d, *p*-H), 7.71 (2H, d, *o*-H). ^{13}C NMR (CD_2Cl_2): δ 118.75 (q, $^1J_{CF}$ = 317.9 Hz CF_3), 128.8 (*m*-C), 132.4 (*p*-C), 135.9 (*o*-C). ^{19}F NMR: δ −79.2. ^{29}Si NMR: δ 3.6. MS: m/z 408 (10, M), 259 (5, $SiPh_3$), 201 (30, $SiPh_2F$) 78 (100).

Crystallography. Data were collected on a Kappa CCD diffractometer by use of Mo Kα radiation, and structure refinement was by the SHELXL-97 program.[30] Further details are given in Table 2. An absorption correction was applied for **5** but not for **7**. The atoms Si4B, Si5B, and Si6B of one of the independent molecules of **3a** are disordered 0.87:0.13 over two sets of sites sharing a common connected C atom site. This corresponds to alternative conformations of the chelating ring. Molecules of **2f** are disordered 0.89:0.11 over an approximate mirror plane through C1, C2, and O. There are common C1, C2, O, and C(Si) sites and resolved low-occupancy sites for Sn, Si, C11, C12, and C21.

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Supporting Information Available: Tables showing details of crystal structure determinations, atom coordinates, equivalent isotropic displacement factors, bond lengths, bond angles, and hydrogen coordinates for compounds **2f**, **3a**, **5**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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