η^2-disulfides (S1–S2Cl, S3–S4) and an oxo ligand (O1). This orientation is populated 87% of the time. In orientation b the disulfide S1X–S7 serves as a bridge the same way S8–S7 does in orientation a. In orientation b the ligand sites S2Cl and Cl1S are populated by a chloride and a sulfur atom, respectively. The dimer contains pseudo-seven-coordinate Mo(VI) ions. The ligands define a distorted-pentagonal-bipyramidal arrangement similar to the one observed in $[Mo_4O_4S_{18}]^{2-}$. Intramolecular bond distances and angles in IV (Tables VI and VII) are very similar to those in III. The Mo–Cl_{eq} bond length at 2.388 (3) Å is slightly shorter than the one observed in the *cis-mer* pentagonal-bipyramidal complex $Mo(O)Cl_2(Et_2NCS_2)_2$.[38] In this complex the Mo–Cl distance associated with the equatorial chloride lies at 2.417 (1) Å. In the same complex, the Mo–Cl_{ax} bond across the axial oxo ligand at 2.504 (1) Å is nearly 0.1 Å longer than the Mo–Cl_{eq} bond. This is due to the strong trans effect of the oxo group.

X-ray crystallography does not distinguish between a chloride (Cl^-) ligand and a hydrosulfido (SH^-) ligand. For this reason two formulations were considered: (a) $[Mo_2O_2S_8Cl]^-$ and (b) $[Mo_2O_2S_8SH]^-$. Formulation b would be analogous to the thiotungstate $[(\mu\text{-}\eta^2,\eta^1\text{-}S_2)W_2(S)_2(\eta^2\text{-}S_2)_3SH]^-$, $[W_2S_{11}H]^-$[39] anion. Elemental analysis for chloride indicated that formulation a is the chemically correct one. Single-crystal structure determination of the iodo analogue, $[Mo_2O_2S_8I]^-$,[40] obtained from the reaction of $(Et_4N)_2[Mo_2O_2S_{9.14}]$ with NiI_2, shows that a halide substitution for a sulfide is indeed taking place. In the structure of the $[Mo_2O_2S_8I]_2^-$ anion ($R = 0.04$) no disorder is encountered and, as in IV, the Mo coordination sphere geometry and the Mo—S and Mo═O bond lengths in this complex are similar to those in III. The Mo–I length is 2.766 (2) Å.

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Note Added in Proof. Recently the synthesis and structural characterization of the $Ta_2S_{11}^{4-}$ and $Nb_4Se_{22}^{6-}$ anions were reported (Schreiner, S.; Aleandri, L. E.; Kang, D.; Ibers, J. A. *Inorg. Chem.* **1989**, *28*, 392). These complexes are closely related structurally to the $[Mo_2O_2S_9]^{2-}$ and $[Mo_4O_4S_{18}]^{2-}$ anions reported herein.

Supplementary Material Available: Table S1, listing thermal parameters and hydrogen atom positions for I, and Tables S2–S4, listing thermal parameters, hydrogen atom positions, and detailed bond distances and angles for II–IV (24 pages); Tables S5–S8, listing observed and calculated structure factors for I–IV (48 pages). Ordering information is given on any current masthead page.

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Selective and Sequential Reduction of Polyhalosilanes with Alkyltin Hydrides

John J. D'Errico[†] and Kenneth G. Sharp*

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The reactions between alkyltin hydrides and a variety of polyhalo- and mixed halosilanes have been investigated. For $SiCl_4$ and $SiCl_3H$, the reductions proceed in a stepwise manner to yield the monoreduced species as the major products. The reduction of $SiBr_4$ occurs much faster to yield a mixture of $SiBr_3H$ and SiH_4, or, in the vapor phase, $SiBr_3H$ as the sole product. SiF_3X (X = Br, Cl) is converted into SiF_3H, with no further reduction of SiF_3H observed upon addition of a second equivalent of alkyltin hydride. SiF_2HX compounds (X = Br, Cl) are obtained from SiF_2X_2 and are converted into SiF_2H_2 with excess Me_3SnH. Redistribution becomes competitive with reduction in reactions between Me_3SnH and $SiFBr_3$, leading to mixtures of SiH_4, SiF_2H_2, and SiF_3H. The major products in the reaction between $SiCl_2Br_2$ and Me_3SnH are $SiCl_3H$ and SiH_4 (no $SiCl_2H_2$ was observed). Several probable intermediates were independently synthesized and allowed to react with Me_3SnH. Together with deuterium labeling experiments, these reactions shed light on the mechanisms involved in these systems. In particular, the reactions appear not to proceed via free radicals.

Introduction

Historically, the reduction of polyhalosilanes using conventional hydridic reducing agents has led to completely hydrogenated species.[1] When $LiAlH_4$ is used, it is not possible to obtain partially reduced species, even when a deficiency of the reducing agent is present. Other hydrides such as NaH and CaH_2 have been used with some success.[2,3] However, elevated temperatures (300 °C) or a catalyst such as Al_2Cl_6 is required. The latter can promote extensive redistribution reactions.

Partial substitution of hydrogen for chlorine in polychlorosilanes such as $MeSiCl_3$ can be effected via H/Cl redistribution with trialkylsilanes in the presence of catalytic quantities of Al_2Cl_6.[4] A superior catalyst—tetraalkylammonium chloride—allows H/Cl exchange between di- and triorganosilanes without skeletal participation.[5]

Organotin hydrides have long been known as effective reducing agents in organic chemistry, and their reactivity patterns have been well documented.[6] Our interest in the work described in this report lay in evaluating alkyltin hydrides as reducing agents for a variety of halosilanes.[7] A particular area of interest was the selective reduction of one halogen species to the exclusion of another in molecules such as SiF_2Br_2 and $SiCl_2Br_2$. To our knowledge, such preferential reduction of halogen has not been previously demonstrated in a polyhalosilane.

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[7] Although the term "reduction" should be reserved for formal changes in oxidation state, we will adhere to the usage of the term common in halosilane chemistry to describe the conversion of Si–X (X = Br, Cl) into Si–H in exchange reactions.

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Table I. Room-Temperature Reactions between Halosilanes and Me_3SnH[a]

halosilane	time, h	product mixture
$SiCl_4$	36	$SiCl_4$ (50%), $SiCl_3H$ (25–30%), $SiCl_2H_2$ (15%), SiH_4 (10%)
$SiCl_3H$	12	$SiCl_3H$ (44%), $SiCl_2H_2$ (41%), SiH_4 (15%)
$SiBr_4$	0.25	$SiBr_4$ (60%),[b] $SiBr_3H$ (20%),[b] SiH_4 (20%)
SiF_3Br[c]	6–8	SiF_3H (95%), SiF_2H_2 (trace), SiH_4 (trace)
SiF_3Cl	60	SiF_3H (95%), SiF_2H_2 (trace), SiH_4 (trace)
$SiFBr_3$[d]	0.5	SiH_4 (60%), SiF_3H (20%), SiF_2H_2 (20%)
$SiCl_2Br_2$[e]	2	$SiCl_3H$ (35–40%), SiH_4 (40%), $SiCl_2HBr$ (10%)[b]
$SiCl_3Br$	3	$SiCl_3H$ (85%), SiH_4 (5%), $SiCl_4$ (5%)

[a] Unless otherwise noted, equimolar amounts of halosilanes and Me_3SnH were used. [b] Estimated from IR spectra. [c] The same results were obtained with Et_3SnH or Me_2SnH_2. [d] Three equivalents of Me_3SnH was used. [e] Two equivalents of Me_3SnH was used.

Experimental Section

Spectral Measurements. NMR tubes (5 mm o.d., wall thickness 0.77 mm) were flamed out and degassed prior to loading. Toluene-d_8 was the solvent used in each case. High-resolution ^1H and ^{19}F NMR spectra were obtained on a Varian XL200 instrument operating at 200 and 188 MHz, respectively. Infrared spectra were obtained on a Nicolet 5SXB Fourier transform spectrometer with a resolution of 2 cm^{-1}. Mass spectral data were obtained on a Hewlett-Packard 5970A mass spectrometer.

Materials and General Procedures. The alkyltin hydrides used in this study—Me_3SnH, Me_3SnD, Me_2SnH_2, and Et_3SnH—were prepared from the $LiAlH_4$ ($LiAlD_4$) reduction of the corresponding alkyltin halides.[8] All manipulations were conducted in the absence of air and moisture with use of a recirculating-atmosphere drybox (N_2 atmosphere), Schlenk techniques (Ar atmosphere), or a grease-free glass high-vacuum line (background pressure $<10^{-4}$ Torr). The reactions were performed in a fixed U-trap on a high-vacuum line in the absence of solvent; liquid was often present in the bottom of the trap. Typically, 2-5 mmol of each reactant was used. The progress of the reactions was monitored by observing changes in the Si–H (2400–2000 cm^{-1}) and Sn–H (1900–1750 cm^{-1}) stretching regions of the IR spectra. The Sn byproducts of these reactions were shown to be R_3SnX and R_2SnX_2 (X = Cl, Br) by their ^1H NMR and IR spectra.[6] The results of several room-temperature reactions between halosilanes and Me_3SnH are collected in Table I. The relative amounts of $SiCl_xH_{4-x}$ (x = 0, 2, 3) quoted in Table I were obtained by using IR calibration curves.[9] The SiF_xH_{4-x} (x = 2–4) mixtures (see Table I) resulting from several reactions could not be purified on a volatility basis; the amount of each component was estimated from IR spectra. *Caution*! Mixtures containing SiH_4 and/or $SiCl_2H_2$ should be handled with care as they are liable to form explosive mixtures with air.

Calibration Curves for $SiCl_3H$, $SiCl_2H_2$, and SiH_4. The area and peak height of the Q branch of the Si–H stretch of $SiCl_2H_2$ and SiH_4 were monitored vs pressure. For $SiCl_3H$, the Si–H bend at 806 cm^{-1} was monitored, due to interference from the R branch of the Si–H stretch of $SiCl_2H_2$. Several test mixtures of these three compounds were analyzed by using these calibration curves; these indicated an accuracy of 5% for $SiCl_3H$ and $SiCl_2H_2$ and 1% for SiH_4.

The following sections describe experiments performed under conditions different from those cited in Table I.

Reactions of Me_3SnH with $SiBr_4$. (a) $SiBr_4$, Me_3SnH, and $CF_2{=}CF_2$ (1:1:2) were warmed to room temperature for 30 min. An IR spectrum indicated a product distribution which was the same as that described in the absence of tetrafluoroethylene (see Table I).

(b) Equimolar quantities of $SiBr_4$ and Me_3SnH were mixed together in the gas phase for 12 h at room temperature. An IR spectrum of the mixture indicated the sole product to be $SiBr_3H$.[10]

Preparation of Bromofluoro- and Chlorofluorosilanes. SiF_xBr_{4-x} and SiF_xCl_{4-x} (x = 1–4)[11-14] were obtained from the thermal redistribution of SiF_4 and $SiBr_4$ or $SiCl_4$ (300–350 °C, 24 h). For SiF_3Cl, an Si–F stretch was observed at 1010 cm^{-1} that was not reported in the cited reference.[12]

Reactions of Alkyltin Hydrides with SiF_2Br_2. An equimolar mixture of Me_3SnH and SiF_2Br_2 was warmed to room temperature for 12 h. The products were passed through a trap cooled to −131 °C (pentane, to remove Me_3SnBr) into a trap cooled to −196 °C. The material held at −196 °C was analyzed by IR and ^1H and ^{19}F NMR spectroscopy; these data were consistent with the new compound SiF_2HBr (90% isolated yield, 95% pure). IR (cm^{-1}): 2283 (m), 979 (s), 969 (s), 888 (vs), 832 (s), 826 (s), 469 (m). ^1H NMR: 4.99 ppm (t), J_{H-F} = 80.5 Hz, J_{H-Si} = 378.8 Hz. ^{19}F NMR: −81.7 ppm (d, relative to external $CFCl_3$), J_{F-H} = 80.4 Hz, J_{F-Si} = 320.0 Hz. Features due to SiF_3H and SiH_4 were also observed in the IR and NMR spectra of SiF_2HBr.

Addition of a second equivalent of Me_3SnH resulted in the disappearance of SiF_2HBr and the formation of SiF_2H_2 (90% yield). The amounts of SiF_3H and SiH_4 increased slightly (to ca. 5% each). No further reduction of SiF_2H_2 was observed upon addition of excess Me_3SnH. The same results were observed with Et_3SnH and Me_2SnH_2.

Reaction of Me_3SnH with SiF_2Cl_2. Equimolar quantities of Me_3SnH and SiF_2Cl_2 were warmed to room temperature; the new compound SiF_2HCl appeared after 1 h, and its concentration increased over the course of 3.5 days. The mixture was passed through a trap cooled to −131 °C (to remove Me_3SnBr) into a trap cooled to −196 °C. The following spectral data refer to SiF_2HCl held at −196 °C. IR (cm^{-1}): 2293 (m), 985 (s), 975 (s), 900 (s), 839 (m), 832 (sh), 582 (m). ^1H NMR: 4.41 ppm (t). ^{19}F NMR: −123.0 ppm (d), J_{H-F} = 84.2 Hz. Small quantities of SiF_3H, SiH_4, and $SiFCl_2H$[15] (ca. 5% each) were observed during the synthesis of SiF_2HCl. A second equivalent of Me_3SnH was added, and the reaction was monitored for an additional 2.5 days. During this time, SiF_2HCl was converted to SiF_2H_2. The concentrations of SiF_3H (10%) and SiH_4 (10%) also increased.

Reaction of SiF_3Br with Vitride. SiF_3Br (0.2 mmol) was condensed into a Vitride solution (70% $NaAlH_2(OCH_2CH_2OCH_3)_2$ in toluene, 0.5 mmol) and warmed to room temperature for 10 min. An IR spectrum of the volatile compounds indicated the presence of SiH_4 (99%) and a trace of SiF_3H.

Reactions of Me_3SnH with $SiCl_2HBr$.[16] The following data pertain to $SiCl_2HBr$. IR (cm^{-1}): 2252 (w), 796 (s), 596 (m), 552 (m), 422 (w). MS (m/e(relative intensity)): 178 (100), 144 (25), 100 (43), 81 (20), 80 (9), 63 (43), 35 (25). ^1H NMR 5.79 ppm, J_{H-Si} = 366.3 Hz.

(a) Equimolar quantities of $SiCl_2HBr$ and Me_3SnH were condensed into a cold finger attached to an IR cell. After 10 min at room temperature, peaks due to $SiCl_3H$, $SiClHBr_2$ (vide infra), and a trace of SiH_4 appeared. The concentrations of these compounds increased during 40 min, at which time a weak absorption was observed at 2233 cm^{-1}. This frequency is midway between those of $SiCl_2H_2$ (2236 cm^{-1}) and $SiBr_2H_2$ (2229 cm^{-1}) and is assigned to $SiClBrH_2$.[17] After 2 h, the mixture contained $SiCl_3H$ (45–50%), SiH_4 (31%), and a small amount of $SiClHBr_2$ (<5%); the remainder consisted of unreacted $SiCl_2HBr$.

(b) Equimolar amounts of $SiCl_2HBr$ and Me_3SnD were condensed into a trap and warmed to room temperature for 3 h. An IR spectrum indicated that the major products of the reaction were $SiCl_3H$ and SiH_xD_{4-x}. There was no evidence for the formation of $SiCl_3D$.[18]

Reaction of Me_3SnH with $SiClHBr_2$. The following data pertain to $SiClHBr_2$. IR (cm^{-1}): 2245 (w), 783 (s), 573 (m), 481 (m), 389 (w). MS (m/e (relative intensity)): 221 (100), 186 (19), 142 (51), 107 (25), 80 (20), 81 (52), 63 (52), 35 (20). ^1H NMR 5.58 ppm, J_{H-Si} = 360.5 Hz. Equimolar quantities of $SiClHBr_2$ (a trace of $SiCl_2HBr$ was also present) and Me_3SnH were condensed into a cold finger attached to an IR cell. After 5 min at room temperature, the amount of $SiCl_2HBr$ increased and peaks due to $SiBr_3H$ appeared. After 10 min, the concentrations of $SiCl_2HBr$ and $SiBr_3H$ increased and peaks due to $SiCl_3H$ and SiH_4 appeared. The concentrations of these four compounds increased over the next 30 min, at which point $SiClH_3$[9] and $SiClBrH_2$ (2233 cm^{-1}) appeared. There was no evidence for the formation of $SiCl_2H_2$ or $SiBr_2H_2$.

Reactions of Alkyltin Hydrides with Organosilanes. No reaction was observed when equimolar quantities of various organosilanes (Me_3SiCl,

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Me_2SiCl_2, $MeSiCl_3$, $MeSiCl_2H$, Me_3SiOMe, and $PhSiCl_3$) and alkyltin hydrides were heated to 60–75 °C for several hours.

Results and Discussion

Reactions of Alkyltin Hydrides with Chloro- and Bromosilanes. The primary products in the reactions of the alkyltin hydrides with $SiCl_4$ and $SiCl_3H$ ((1) and (2)) are the monoreduced species

$$\mathrm{Me_3SnH + SiCl_4 \rightarrow \underset{25\text{–}30\%}{SiCl_3H} + \underset{15\%}{SiCl_2H_2} + \underset{10\%}{SiH_4} + Me_3SnCl} \qquad (1)$$

$$\underset{\substack{n = 2,\ \mathrm{R = Me} \\ n = 3,\ \mathrm{R = Me,\ Et}}}{\mathrm{R}_n\mathrm{SnH}_{4-n}} + \mathrm{SiCl_3H} \rightarrow \underset{41\%}{\mathrm{SiCl_2H_2}} + \underset{15\%}{\mathrm{SiH_4}} + \mathrm{R}_n\mathrm{SnCl}_{4-n} \qquad (2)$$

$SiCl_3H$ and $SiCl_2H_2$, respectively. In each case, unreacted starting material (50% of the $SiCl_4$ in (1), 44% of the $SiCl_3H$ in (2)) remains in the mixture. These results stand in contrast to those obtained with conventional reducing agents such as $LiAlH_4$, with which it is not possible to obtain partially reduced species.[1]

The formation of SiH_4 in (1) and (2) could result from redistribution reactions and/or successive reductions. If a redistribution process were responsible for the observed products, then one would expect to see $SiCl_4$ in eq 2. Since this molecule was not observed, the reduction appears to be kinetically controlled. That is, the rate of reduction decreases in the order $SiClH_3 > SiCl_2H_2 > SiCl_3H$. This sequence may be related to steric effects. Although increasing chloro substitution results in a more electropositive silicon atom, it may also sterically hinder attack of the tin hydride. Similar results were reported by Burg,[19] who investigated the stability of trialkylamine adducts of chlorosilanes. Very weak adducts were observed with $SiCl_4$, with stronger complexes formed with $SiCl_3H$ and $SiCl_2H_2$. These results were rationalized in terms of steric crowding.

The results shown in (1) and (2) were obtained when the reactions were performed in the condensed phase. No reaction was observed when $SiCl_4$ or $SiCl_3H$ was allowed to react with Me_3SnH in the vapor phase, even after the mixtures were warmed to 80 °C for 12 h.

The condensed-phase Me_3SnH reduction of $SiBr_4$ (1:1 molar ratio) to $SiBr_3H$ (20%) and SiH_4 (20%) occurs at a much faster rate than that observed for the chlorosilanes. (As with the chlorosilanes, unreacted $SiBr_4$ (60%) remained in the mixture.) This observation is consistent with the Si–Br bond strength being ca. 15 kcal/mol weaker than the Si–Cl bond.[20]

When $SiBr_4$ and Me_3SnH are mixed together in the vapor phase, the only reduced species observed is $SiBr_3H$. A possible explanation for the difference in reactivity when this reaction is performed in the condensed and vapor phases is that the tin hydride promotes H/Br redistribution much more effectively in the condensed phase. The initial product $SiBr_3H$ would then be converted into $SiBr_4$ and $SiBr_2H_2$; the latter molecule is then available for additional redistribution reactions or could be directly reduced to SiH_4 by Me_3SnH.

Reactions of Alkyltin Hydrides with Halofluorosilanes. In a manner similar to that observed for mixed halofluorodisilanes,[21] alkyltin hydrides selectively reduced SiF_3X (X = Br, Cl) to SiF_3H (eq 3). As with the tetrahalosilanes, the reduction of the silicon–bromine bond was appreciably faster than that of the silicon–chlorine bond. There was no evidence of further reduction or redistribution of SiF_3H on exposure to excess Me_3SnH. This type of selective reduction has been observed in the reaction of tributyltin hydride with alkyl halides[22] but had not been previously observed with halosilanes.

$$\underset{\substack{n = 2,\ \mathrm{R = Me} \\ n = 3,\ \mathrm{R = Me,\ Et}}}{\mathrm{R}_n\mathrm{SnH}_{4-n}} + \underset{\mathrm{X = Br,\ Cl}}{\mathrm{SiF_3X}} \rightarrow \underset{>95\%}{\mathrm{SiF_3H}} + \underset{\text{trace}}{\mathrm{SiF_2H_2}} + \underset{\text{trace}}{\mathrm{SiH_4}} + \mathrm{R}_n\mathrm{SnX}_{4-n} \qquad (3)$$

Reducing agents such as $LiAlH_4$[1] and alkylaluminum hydrides[23] are known to easily reduce fluorosilanes. Indeed, when the reaction in eq 3 was attempted with Vitride ($NaAlH_2(OCH_2CH_2OCH_3)_2$), a 99% yield of SiH_4 was obtained. Similar results were observed with bromofluorodisilanes.[21]

The selective, stepwise reductive properties of alkyltin hydrides were further demonstrated in their reactions with SiF_2Br_2, in which a 90% yield of SiF_2HBr was isolated. This appears to be the first synthesis of SiF_2HBr; it has been cited in two theoretical papers,[13,24] in which the frequencies of the fundamental vibrations of all the halogen derivatives of silane and germane were calculated. The calculated and experimental frequencies of SiF_2HBr differ by an average of 2.5%, which is within the accuracy of 3% claimed by the authors.[13]

SiF_2HBr is cleanly converted into SiF_2H_2 upon addition of a second equivalent of alkyltin hydride. Difluorosilane does not undergo further reduction or redistribution reactions in the presence of excess tin hydride. However, small quantities of SiF_3H and SiH_4 were observed during the synthesis of SiF_2HBr and its subsequent conversion of SiF_2H_2. These results suggest that SiF_2HBr can undergo F/Br redistribution (eq 4) to some extent. $SiFBr_2H$ may then react with Me_3SnH to ultimately form SiH_4, SiF_2H_2, and SiF_3H (vide infra).

$$\mathrm{2SiF_2HBr \rightarrow SiF_3H + SiFBr_2H} \qquad (4)$$

The reaction between SiF_2Cl_2 and Me_3SnH resulted in the formation of SiF_2HCl (80%). In this case, the reaction occurred much more slowly. As a probable consequence, the chloro derivatives underwent F/Cl redistribution (4) to a greater extent, leading to higher concentrations of SiF_3H and SiH_4. Evidence for this redistribution was obtained by the observation of small amounts of $SiFCl_2H$.[15]

The above results encouraged us to explore the alkyltin hydrides' interactions with $SiFBr_3$, anticipating a convenient synthesis of $SiFH_3$. Several routes to $SiFH_3$ exist, but they involve handling dangerous and/or difficult to synthesize starting materials.[25-28] The reaction between $SiFBr_3$ and 3 equiv of Me_3SnH resulted in the formation of SiH_4 (60%), SiF_2H_2 (20%), and SiF_3H (20%). Thus, $SiFBr_3$ appears to be undergoing reduction to $SiFH_3$, at which point F/H redistribution reactions become important.[29] Redistribution of intermediate bromofluorosilanes cannot be ruled out, however, as small amounts of SiF_2HBr were observed during the reaction. The reduction of $SiFH_3$ to SiH_4 is also a possibility.

Reactions of Alkyltin Hydrides with Mixed Bromochlorosilanes. An unanticipated series of reactions was observed when $SiCl_2Br_2$ was allowed to react with Me_3SnH (eq 5). Rather than the expected $SiCl_2H_2$, a mixture of $SiCl_3H$, SiH_4, and a small amount of $SiCl_2HBr$ was obtained.

$$\mathrm{SiCl_2Br_2 + 2Me_3SnH \rightarrow \underset{35\text{–}40\%}{SiCl_3H} + \underset{40\%}{SiH_4} + \underset{10\%}{SiCl_2HBr} + 2Me_3SnBr} \qquad (5)$$

In a separate experiment, $SiCl_2HBr$ was combined with Me_3SnH in a 1:1 molar ratio. The products of this reaction consisted of $SiCl_3H$ (45–50%), SiH_4 (31%), and a small amount of $SiClHBr_2$ (<5%); the remainder consisted of unreacted $SiCl_2HBr$. These results suggest that $SiCl_2HBr$ rapidly undergoes Cl/Br redistribution (eq 6).[30] The fact that $SiCl_2HBr$ undergoes

$$\mathrm{2SiCl_2HBr \rightarrow SiCl_3H + SiClHBr_2} \qquad (6)$$

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redistribution prior to reduction was demonstrated during its reaction with Me_3SnD. If reduction occurred first, with $SiCl_3H$ formed from H/Cl redistribution of $SiCl_2H_2$, then $SiCl_3D$ should have been present in the product mixture via redistribution of $SiCl_2HD$. However, only $SiCl_3H$ was observed.

From these results, it appears that $SiClHBr_2$ may be the source of SiH_4 in (5). To test this hypothesis, $SiClHBr_2$ was independently synthesized and allowed to react with Me_3SnH. As with the other bromochlorosilanes in this study, Cl/Br redistribution (eq 7) is the preferred pathway during the initial stages

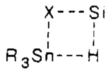
$$2SiClHBr_2 \rightarrow SiCl_2HBr + SiBr_3H \qquad (7)$$

of the reaction. The $SiCl_2HBr$ from (7) is then available for additional Br/Cl redistributions; indeed, $SiCl_3H$ is observed early in the reaction (see (6)). The reaction mixture also contained $SiClBrH_2$, $SiClH_3$, and SiH_4, all of which could result from the stepwise reduction of $SiClHBr_2$. Alternatively, SiH_4 could be formed from the reduction of $SiBr_3H$ (eq 7).

The final bromochlorosilane to be examined in this study was $SiCl_3Br$. The primary product in the reaction with Me_3SnH was $SiCl_3H$ (85%), although small amounts of $SiCl_4$ (5%) and SiH_4 (5%) were also observed. The redistribution of $SiCl_3Br$ would lead to the formation of $SiCl_4$ and $SiCl_2Br_2$. The latter compound would ultimately be associated with the formation of SiH_4 (see (5)).

Mechanistic Considerations. Organotin hydrides typically react with organic halides and unsaturated bonds via a free-radical mechanism. These reactions require either heating or initiation by a free-radical source.[22] However, in the case of the polyhalosilanes and mixed halosilanes, the reactions proceeded at room temperature and in the absence of free-radical initiators. In addition, the reaction of Me_3SnH with $SiBr_4$ was performed in the presence of $CF_2{=}CF_2$. Under free-radical conditions, products attributable to addition of the tin hydride to the olefin should be apparent.[31] However, neither the rate of reaction nor the product distribution was affected. Additional evidence for a non-free-radical path comes from reactions involving halofluorodisilanes,[21] in which there was no evidence for the formation of monosilanes.

A mechanism that is consistent with these observations involves a four-centered transition state (I) in which there is a pairwise exchange between the silicon and tin atoms. It seems unlikely that polar transition states[32] play an important role in these reductions, as many of these reactions occur in the gas phase.[21]



I

Alkyltin hydrides proved ineffective as reducing agents toward a variety of alkyl- and aryl-substituted halosilanes. A U.S. patent[33] described the reduction of various chlorosilanes (e.g. $MeSiCl_3$, Me_3SiCl) using alkyltin hydrides in the presence of a group III catalyst such as Al_2Me_6.

Conclusion

Organotin hydrides have demonstrated selective, stepwise reducing properties toward a variety of polyhalosilanes. For $SiCl_4$ and $SiCl_3H$, the major products of the reductions were $SiCl_3H$ and $SiCl_2H_2$, respectively. The course of the reaction of $SiBr_4$ with Me_3SnH depends on the phase of the reactants: vapor-phase reaction leads exclusively to $SiBr_3H$, while liquid-phase reaction also generates silane.

The alkyltin hydrides proved to be selective reducing agents for the Si–X (X = Br, Cl) bond in halofluorosilanes. Thus, SiF_3X was converted to SiF_3H with no evidence for further reduction of the Si–F bonds. For SiF_2Br_2, the new compound SiF_2HBr was isolated in 90% yield. Addition of a second equivalent of tin hydride resulted in the conversion of SiF_2HBr to SiF_2H_2. Similar results were observed with SiF_2Cl_2. For $SiFBr_3$, redistribution reactions are competitive with reduction, resulting in a mixture of SiF_3H, SiF_2H_2, and SiH_4.

$SiCl_2Br_2$ reacts with 2 equiv of Me_3SnH to form $SiCl_3H$, SiH_4, and a small amount of $SiCl_2HBr$. No $SiCl_2H_2$ was observed in the mixture. For $SiCl_2HBr$, deuterium labeling experiments demonstrated that Cl/Br redistribution precedes reduction. $SiCl_3Br$ is primarily reduced to $SiCl_3H$, although redistribution takes place to a small extent to form $SiCl_4$ and $SiCl_2Br_2$.

The reactions between alkyltin hydrides and halosilanes proceed at room temperature and in the absence of free-radical initiators. Indeed, the reaction between $SiBr_4$ and Me_3SnH was unaffected by the presence of $CF_2{=}CF_2$, a free-radical scavenger. This leads us to suggest a four-centered transition state for the H–X (X = Cl, Br) exchange between tin and silicon.

Registry No. Me_3SnH, 1631-73-8; $SiCl_4$, 10026-04-7; $SiCl_3H$, 10025-78-2; $SiBr_4$, 7789-66-4; SiF_3Br, 14049-39-9; SiF_3Cl, 14049-36-6; $SiFBr_3$, 18356-67-7; $SiCl_2Br_2$, 13465-75-3; $SiCl_3Br$, 13465-74-2; Et_3SnH, 997-50-2; Me_2SnH_2, 2067-76-7; Me_3SiCl, 75-77-4; Me_2SiCl_2, 75-78-5; $MeSiCl_3$, 75-79-6; $MeSiCl_2H$, 75-54-7; Me_3SiOMe, 1825-61-2; $PhSiCl_3$, 98-13-5; $NaAlH_2(OCH_2CH_2OCH_3)_2$, 22722-98-1.

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(30) In the absence of catalysts, prolonged heating (e.g. 40 h, 90 °C) is required for the Cl/Br redistribution of $SiCl_2HBr$. See ref 16.

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