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Reactions of Incompletely-Condensed Silsesquioxanes with Pentamethylantimony: A New Synthesis of Metallasilsesquioxanes with Important Implications for the Chemistry of Silica Surfaces

Frank J. Feher,* Theodore A. Budzichowski,† Kamyar Rahimian, and Joseph W. Ziller

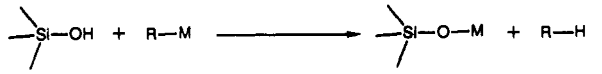
Contribution from the Department of Chemistry, University of California, Irvine, California 92717. *Received November 4, 1991*

Abstract: The reactions of the incompletely condensed polyhedral oligosilsesquioxanes $(c\text{-}C_6H_{11})_7Si_7O_9(OH)_3$ (**1a**), $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)(OH)_2$ (**2a**), $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)_2(OH)$ (**3a**), $(c\text{-}C_6H_{11})_8Si_8O_{10}(OH)_2$ (**4a**), and $(c\text{-}C_6H_{11})_7Si_7O_{10}(OH)$ (**5a**) with excess Me_5Sb result in the formation of the corresponding stibonium-substituted silsesquioxanes $(c\text{-}C_6H_{11})_7Si_7O_9(OSbMe_4)_3$ (**1b**), $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)(OSbMe_4)_2$ (**2b**), $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)_2(OSbMe_4)$ (**3b**), $(c\text{-}C_6H_{11})_8Si_8O_{10}(OSbMe_4)_2$ (**4b**), and $(c\text{-}C_6H_{11})_7Si_7O_{10}(OSbMe_4)$ (**5b**) in high yields. These stibonium siloxides show enhanced reactivity toward main-group and transition-metal halide complexes and provide an alternative route for the preparation of metallasilsesquioxanes. The reaction of **1a** with 1 equiv of Me_5Sb is much faster than the reactions of Me_5Sb with silanols containing fewer than three mutually hydrogen-bonded siloxy groups. This suggests that multiply hydrogen-bonded surface sites are more reactive toward nucleophilic organometallic reagents than either isolated surface silanols or isolated pairs of geminally or vicinally hydrogen-bonded siloxy groups.

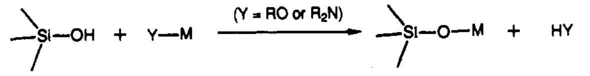
Introduction

We recently described the synthesis and characterization of a number of incompletely-condensed silsesquioxanes (i.e., **1a**–**5a**, Chart I) that offer excellent potential as models for hydroxylated silica surface sites.[1] These compounds also exhibit a rich coordination chemistry and are ideally suited as ligands in homogeneous models for silica-supported transition-metal complexes.[2]

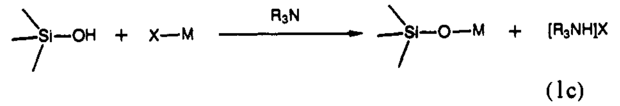
Until now our syntheses[2,3] of heteroatom- and transition-metal-containing silsesquioxanes have relied on three fairly general methodologies that are frequently utilized to synthesize simple alkoxide and siloxide complexes: (1) the reaction of silanols such as **1a**–**5a** with metal alkyl complexes (reaction 1a), (2) the metathesis of **1a**–**5a** for less acidic alkoxide or amide ligands (reaction 1b), and (3) the base-assisted (e.g., Et_3N) reactions of **1a**–**5a** with active metal halide complexes (reaction 1c).



(1a)



(1b)



(1c)

These three reactions can be used to synthesize a wide range of interesting metallasilsesquioxanes, but each has its limitations. For example, the protonolysis of metal alkyl complexes (reaction 1a) only works well with the reactive alkyl complexes of electropositive metals (e.g., Ti, Zr, V, Al). Similarly, amine-assisted reactions of **1a**–**5a** with metal chlorides (reaction 1c) require reactive metal halide complexes. In addition, this methodology is only useful in cases where the starting materials and products do not react with the amine or its hydrochloride salt and when cyclodehydration of the incompletely-condensed silsesquioxane (e.g., **1a** and **2a**) is not a significant side reaction.[2d]

Noticeably absent from our synthetic arsenal has been the reaction of anionic equivalents of **1a**–**5a** with metal halide complexes. Although this method is by far the most common method for synthesizing metal complexes of alkoxides and siloxides[4]—particularly those complexes derived from relatively nonreactive late-transition-metal halide complexes[5]—the susceptibility of silsesquioxane frameworks toward cleavage and/or polymerization by moderately nucleophilic reagents[6] has until now prevented its utilization.

In this paper we describe an interesting variation on this strategy, which exploits the tendency of 5-coordinate tetraalkyl stibonium siloxides to donate siloxide anions. Tetramethylstibonium silsesquioxanes (**1b**–**5b**), which can be easily prepared from the reactions of Me_5Sb with the parent silanols (**1a**–**5a**), are excellent latent sources of siloxide anions.[7,8] These soft anion

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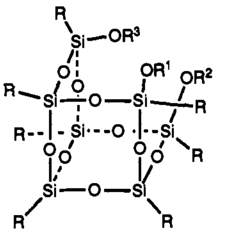
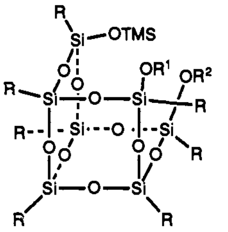
Chart I



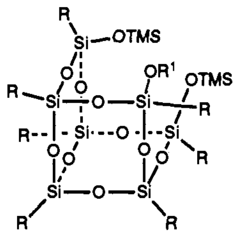
(R = c-C_6H_{11})

1a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = R^3 = SbMe_4$
c $R^1 = R^2 = H$; $R^3 = SbMe_4$
d $R^1 = H$; $R^2 = R^3 = SbMe_4$



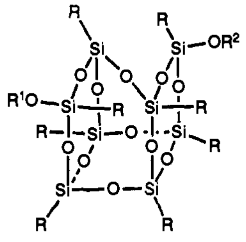
(R = c-C_6H_{11})

2a $R^1 = R^2 = H$
b $R^1 = R^2 = SbMe_4$
c $R^1 = H$; $R^2 = SbMe_4$



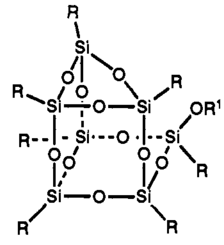
(R = c-C_6H_{11})

3a $R^1 = H$
b $R^1 = SbMe_4$



(R = c-C_6H_{11})

4a $R^1 = R^2 = H$
b $R^1 = R^2 = SbMe_4$



(R = c-C_6H_{11})

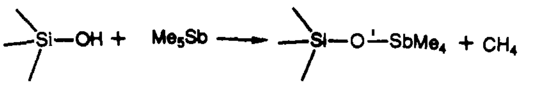
5a $R^1 = H$
b $R^1 = SbMe_4$

sources do not promote skeletal rearrangements in silsesquioxane frameworks[3b,c] and can be used to effect a number of interesting synthetic transformations, including the synthesis of metallasilsesquioxanes.

A number of observations concerning the reactivity of Me_5Sb toward incompletely-condensed silsesquioxanes also have important implications for the chemistry of hydroxylated silica surfaces. These will be discussed in detail.

Results and Discussion

Reactions of Incompletely-Condensed Silsesquioxanes with Me_5Sb. The reaction of alcohols and silanols with pentamethylantimony was discovered by Schmidbaur more than 20 years ago.[7] This reaction is normally selective for exactly one methyl group of the antimony reagent and produces alkoxide and siloxide complexes with excellent donor capabilities.[3b,c,7,8]



(2)

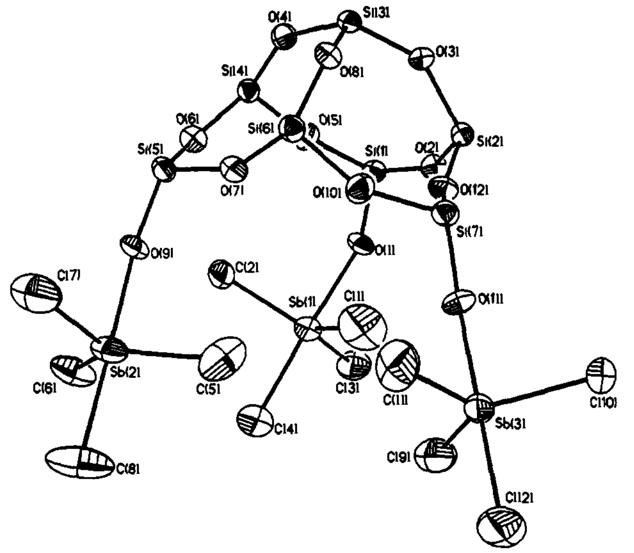


Figure 1. ORTEP plot of **1b** with thermal ellipsoids plotted at the 50% probability level. The cyclohexyl carbon atoms and the *n*-hexane molecule of solvation have been omitted for clarity. Selected internuclear distances (Å) and intrabond angles (deg) are as follows: Sb(1)–O(1), 2.118 (4); Sb(2)–O(2), 2.126 (4); Sb(3)–O(11), 2.109 (4); av $Sb–C_{eq}$, 2.097 (7); av $Sb–C_{ax}$, 2.175 (9); av Si–O(Sb), 1.581 (5); av Si–O(Si), 1.625 (4); av Si–C, 1.865 (6); Sb(1)–O(1)–Si(1), 140.7 (2); Sb(2)–O(9)–Si(5), 143.7 (2); Sb(3)–O(11)–Si(7), 150.4 (2); av $O–Sb–C_{ax}$, 101.5 (4); av $O–Sb–C_{eq}$, 85.9 (2); av $C_{ax}–Sb–C_{eq}$, 101.3 (4); Si–O–Si, 139.7–167.7.

The reactions of **1a**–**5a** with excess Me_5Sb (C_6H_6, 50–60 °C, 2–4 h) produce quantitative (NMR) yields of the corresponding stibonium-substituted derivatives **1b**–**5b**. Complete reaction of all silanol groups—free from side reactions—was readily demonstrated by evaporating the volatiles and analyzing the crude product by NMR spectroscopy. In the case of **1b**, for example, both the ^{29}Si NMR spectrum and the methine (SiCH) region of the ^{13}C NMR spectrum exhibited three resonances with relative integrated intensities of 3:3:1; ^1H NMR spectroscopy established the presence of three equivalent Me_4Sb groups, while the presence of 5-coordinate antimony centers was clearly indicated by the ^{13}C chemical shift of the Me_4Sb groups, which appeared downfield of 10 ppm (in C_6D_6).[3b,c] Similar spectroscopic data were observed for **2b**–**5b**.

The NMR spectral data for **1b**–**5b** allow for straightforward structural assignments, but there is one interesting feature worth noting. One cyclohexyl methine ^{13}C resonance, which has a relative intensity proportional to the number of $SbMe_4$ groups present in the molecule, occurs at relatively low field (approx δ 27 in C_6D_6) within the region where cyclohexyl methylene groups are normally observed (CH_2; δ 31–27 ppm) and must be located on the basis of a ^{13}C DEPT90 NMR spectrum. In contrast, all previously reported diamagnetic derivatives of **1a**–**5a** provide ^{13}C NMR spectra with well-separated regions of cyclohexyl methylene (CH_2; δ 31–27 ppm) and methine (Si-CH; δ 26–22) resonances. While it is not obvious how Me_4Sb substitution induces deshielding of the ipso-carbon on adjacent cyclohexyl groups, this effect provides a useful spectroscopic handle for identifying the presence of covalently bonded Me_4Sb groups.

The spectroscopic data and solubility properties (vide infra) of **1b**–**5b** are suggestive of strong covalent bonding between oxygen and antimony in these systems, but the steric requirements of such arrangements—particularly in **1b**—appear to be quite demanding. In order to test for the possible formation of free ions or tight ion pairs, a single-crystal X-ray diffraction study was performed on **1b**; an ORTEP plot of **1b** is shown in Figure 1.

The *n*-hexane solvate of **1b** crystallizes as discrete molecules in the space group $P2_1/n$ with no close intermolecular contacts. The three covalently bonded $SbMe_4$ groups adopt trigonal-bipyramidal geometries with O occupying the expected axial positions.[9] The average nonbonded interatomic Si–Si distance between ad-

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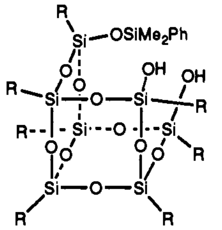
jacent ($SiOSbMe_4$) groups is 5.4 Å, which is substantially larger than the analogous distances observed in the hydrogen-bonded solid-state dimers of **1a** (4.9 Å)[1a] and **6** (4.2 Å),[1b] but all Si–O bond distances and interbond angles fall within the ranges observed previously for derivatives of heptameric "T_7" silsesquioxanes.[1-3] The Si_7O_9 framework obviously has no difficulty accommodating the steric demands of three large Me_4Sb groups.



6 $R = c\text{-}C_6H_{11}$

The reactions of **1a**–**5a** with excess Me_5Sb are conceptually simple; the product in each case results from the reaction of Me_5Sb with every siloxy group in the molecule. In light of our previous work on the trimethylsilylation of **1a**–**4a**,[1b] which uncovered a number of interesting reactivity trends with important implications for the preparation of modified silicas, we were interested in investigating the reactions of **1a** and **2a** with substoichiometric amounts of Me_5Sb.

The reaction of trisilanol **1a** with 0.1–0.2 equiv of Me_5Sb (0.01 M, $CDCl_3$, 30 °C) occurs rapidly upon mixing ($t_{1/2} \sim 3$ min) to afford a product mixture that exhibits a surprisingly simple ^{13}C NMR spectrum. The methine region of this spectrum consists of three resonances with relative integrated intensities of 3:3:1, rather than two sets of resonances for unreacted **1a** and the expected monostibnated product (i.e., **1c**). The addition of more Me_5Sb (up to a total of 1 equiv of Sb per **1a**) rapidly produced more methane and changed the chemical shifts observed in the ^{13}C NMR spectrum, but the 3:3:1 multiplicity for methine resonances remained uneffected. Subsequent additions of Me_5Sb beyond a total of 1 equiv per **1a** had no immediate effect at room temperature, and resonances attributable to unreacted Me_5Sb were observable in both the ^1H and ^{13}C NMR spectra of the reaction mixture. Further reactions between Me_5Sb and the remaining silanol groups present in the system were, however, observable when the reaction mixtures were heated above 40–50 °C (vide infra).

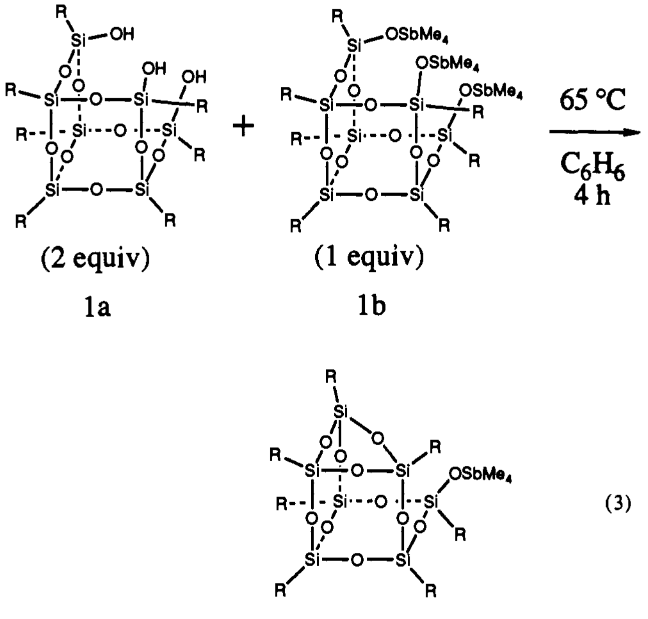
The similarities between the NMR spectra obtained for all reactions of **1a** with less than 1 equiv of Me_5Sb strongly suggested that the observed spectra were time-averaged due to rapid exchange of Me_4Sb groups with silanol protons remaining in the system. Unfortunately, numerous attempts to "freeze out" the suspected exchange process were unsuccessful. If such an exchange process equilibrates *H*-OSi and *Me₄Sb*-OSi groups between all siloxy groups in the system, the barrier to this process must be lower than (10 kcal/mol)[10] because the ^{13}C NMR spectrum is unchanged by cooling from 25 to –40 °C.

The apparent fluxional behavior of **1c** suggested that identical mixtures could be formed by conproportionation reactions of **1a** and **1b**. This was indeed the case. Within seconds of mixing at 25 °C in C_6D_6 or $CDCl_3$, the conproportionation of **1a** (2 equiv) and **1b** (1 equiv) produces a mixture that is spectroscopically (^{13}C, ^1H NMR) indistinguishable from one prepared by the reaction of **1a** with 1 equiv of Me_5Sb. We suspect that the major species present in solution is indeed **1c**, but it has not been possible to isolate any partially stibnated silanol products from the reaction because these products appear to be unstable with respect to cyclocondensation (vide infra).

Analogously, the conproportionation of **1a** and **1b** in a 1:2 ratio produces the same product mixture obtained from the reaction of **1a** with 2 equiv of Me_5Sb. In this case, however, the mixture appears to contain several (≥3) rapidly equilibrating silsesquioxanes with comparable free energies of formation. At room temperature, the methine region of the ^{13}C NMR spectrum is indicative of C_{3v} molecular symmetry, consistent with rapid exchange between *Me₄Sb*-OSi and *H*-OSi groups. Upon cooling to –40 °C, this spectrum broadens and partially decoalesces to a pattern that is far too complex for a single C_s-symmetric molecule (e.g., **1d**). All attempts to separate this mixture were unsuccessful.

In contrast to the rapid reaction of **1a** with a single equivalent of Me_5Sb, the reaction of a second equivalent of Me_5Sb is much slower and normally requires a prolonged reaction time and/or heating (2–4 h, 50–60 °C). Comparably slow reactions were also observed for the reactions of **2a**, **3a**, and **4a** with Me_5Sb. It was not possible to obtain individual rate constants for the reactions of our polyhydroxylic silanols with Me_5Sb because intermolecular Me_4Sb transfers between incompletely-condensed silsesquioxanes are much more facile than the reactions of **1c**, **2a**,**b**, **3a**, or **4a** with Me_5Sb. Nevertheless, it is abundantly clear that the reaction of **1a** with a single equivalent of Me_5Sb is much faster than the reactions of Me_5Sb with silsesquioxanes possessing fewer than three potentially hydrogen-bonded siloxy groups. The similarity of this trend in reactivity to that observed in our previous study[1b] on the silylation reactions of **1a**–**4a** is striking. The implications of this result on the chemistry of silica surfaces will be discussed later.

Me₄Sb-Mediated Cyclodehydration of Incompletely-Condensed Silsesquioxanes: A Competing Side Reaction. While studying the conproportionation reaction between 2 equiv of **1a** and 1 equiv of **1b** (2 eq), it was noted that a new compound with static C_s-molecular symmetry was obtained in virtually quantitative yield if the mixture was heated at 60 °C for 4 h. This compound was identified as cyclodehydrated product **5b** on the basis of NMR spectral data, mass spectrometry, combustion analysis, and independent synthesis from the reaction of **5a** with Me_5Sb (reaction 3). A similar cyclodehydration reaction affords **7** in 80% yield when a 1:1 mixture of **2a** and **2b** is heated in C_6H_6 (reaction 4). Both cyclodehydration reactions appear to be significantly slower than the reactions of Me_5Sb with siloxy groups, but they can



(2 equiv) **1a**

(1 equiv) **1b**

5b (3)

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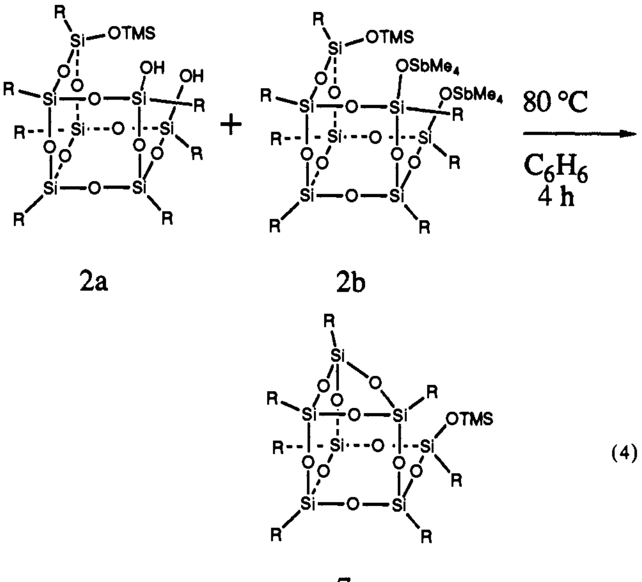
(10) (a) At a coalescence temperature of –40 °C the rate of exchange between two ^{13}C resonances (1:1) differing by 0.5 ppm (62.5 Hz) would correspond to a $\Delta G^{\ddagger}$ of 11 kcal/mol.[10b] Since Me_4Sb substitution deshields adjacent methine carbons by much more than 0.5 ppm, the lack of detectable broadening for the time-averaged methine resonances indicates that $\Delta G^{\ddagger}$ for the exchange process must be much lower than 11 kcal/mol. (b) Calculated by using eq 6.3c in: Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982; p 79.



2a 2b

7

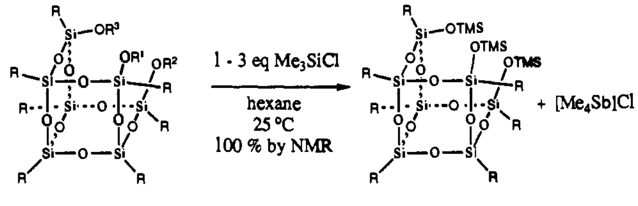
present problems during the synthesis of **1b** and **2b** if substoichiometric amounts of Me_5Sb are used in the reaction.

The mechanism for the formation of **5b** and **7** was not immediately obvious because both **1a** and **2a** are indefinitely stable in solution—and both are stable to extended heating at temperatures as high as 150 °C—but our previous observation[1a] that Et_3N catalyzed the cyclodehydration of **1a** to **5a** suggested that both reactions were base-catalyzed. Since the most logical base in these reactions was Me_4SbOH—which could be formed either via the cyclocondensation of **1c** or **2c** or from the reaction of Me_5Sb with traces of water—the reactions of **1a** and **2a** with Me_4SbOH were examined. In both cases, it was found that small amounts of Me_4SbOH ($\sim$3 mol %) could cleanly and efficiently catalyze cyclodehydration of the incompletely-condensed silsesquioxane frameworks (C_6H_6, 80 °C). On a preparative scale, both reactions are most efficient when performed in a Dean-Stark apparatus to azeotropically remove water as it is formed.

The origin of the Me_4SbO group in **5b** was originally puzzling because water produced via cyclodehydration of **1a** would normally be expected to rapidly hydrolyze any available Sb–O–Si linkages.[7a] Much to our surprise, however, the condensation of SiOH and Me_4SbOH groups is quite rapid and appears to favor the heterosiloxane when performed in an anhydrous solvent: the reaction of **5a** with 1 equiv of Me_4SbOH (0.04 M in C_6D_6, 25 °C) affords **5b** in >95% NMR yield within 1–2 h of mixing. It therefore seems likely that the **5b** isolated from the reaction of **1a** with Me_5Sb (1 equiv) is probably formed from the reaction of **5a** and Me_4SbOH, which is driven to completion during evaporation of the solvent and volatiles (which also removes water).

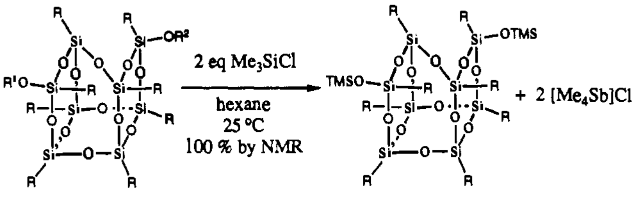
The exact mechanism by which this cyclodehydration reaction occurs is not known, but the presence of discrete hydroxide ions in benzene seems unlikely. In light of (i) the known chemistry[7,8,11] of tetramethylstibonium siloxides, alkoxides, and hydroxides; (ii) the ability of Me_4Sb-stabilized silsesquioxanes to dissociate Me_4Sb ions;[3b] and (iii) the ability of electron-withdrawing[6a] silsesquioxane frameworks to stabilize anionic charges,[3b] we favor the mechanism depicted in Scheme I. We have not yet explored the generality of this cyclodehydration reaction with other polysilanols, but the Me_4SbOH-catalyzed cyclodehydration of **1a** is currently the best method available for the synthesis of **5a**.

Tetramethylstibonium Silsesquioxides as Anionic Equivalents of Incompletely-Condensed Silsesquioxanes. The delicate balance between the ability of Me_4Sb^+ ions to coordinate siloxide anions and the pronounced tendency of the resulting 5-coordinate tetramethylstibonium "pseudosalts" to be heterolytically cleaved at the Sb center (i.e., $Me_4SbOSiR_3 \rightarrow [Me_4Sb]^+ + [OSiR_3]^-$) provide a convenient method for tempering the reactivity of these otherwise powerful nucleophiles.[8a,d,e] In the cases of **1b**–**5b**, the heterosiloxane bonds are stable enough to prevent the destructive polymerization of silsesquioxane frameworks, yet labile enough to react with a variety of electrophiles in nonpolar media. For example, the reactions of **1b**–**3b** or **4b** with Me_3SiCl occur immediately upon mixing in hexane to afford quantitative (NMR) yields of **8** and **9**, respectively.



1b $R^1 = R^2 = R^3 = SbMe_4$
2b $R^1 = TMS$; $R^2 = R^3 = SbMe_4$
3b $R^1 = R^2 = TMS$; $R^3 = SbMe_4$

8



4b $R^1 = R^2 = SbMe_4$

9

Antimony-stabilized silsesquioxides can also be used to prepare a variety of transition-metal and heteroatom-containing polyhedral oligosilsesquioxanes. As illustrated in Scheme II, the reactions of **1b** with $CpTiCl_3$, $MeGeCl_3$, $MeSnCl_3$, PCl_3, and $SbCl_3$ all occur rapidly upon mixing to afford high yields of the corresponding metallasilsesquioxanes. In most cases, the yields are quantitative by NMR spectroscopy and a crude product of very high purity is obtained simply by removing the volatiles in vacuo, extracting the residue with benzene or hexane, and evaporating the solvent.

In principle, Me_4Sb-stabilized silsesquioxane anions could be used to prepare metallasilsesquioxanes from any potentially labile metal halide complex. There are, however, a number of side reactions that will inherently limit the scope of their utility. First, high-valent transition-metal halide complexes containing very electrophilic metal centers tend to form "ate" complexes, either by trapping $[Me_4Sb]X$ as it forms or by displacement of $[Me_4Sb]^+$ from the heterosiloxane without concomitant dissociation of halide from the transition metal. This problem is frequently encountered during the synthesis of electrophilic metal alkoxides from metal halides and an alkali-metal alkoxide, but it is exasperated by the much lower lattice energy of $[Me_4Sb]X$ relative to that of alkali-metal halides. For example, the reactions of **2b** with $TiBr_4$ and MoO_2Cl_2 both afford large amounts of tetramethylstibonium salts containing the known and very stable $[TiBr_6]^{-2}$ and $[MoO_2Cl_4]^{-2}$ ions.[12] Formation of these ate complexes would be synthetically tolerable if extra $TiBr_4$ and MoO_2Cl_2 could be added to scavenge the $[Me_4Sb]X$ produced during the reactions, but this strategy does not appear to work; regardless of the stoichiometry, only complex mixtures of inseparable silsesquioxane products are formed.

A second side reaction is the formal cyclodehydration of **1a** and **2a** via intramolecular attack at silicon rather than the metal center (reaction 5). As might be expected, this reaction is a serious problem with certain classes of high-valent reagents that can produce excellent leaving groups on silicon atoms, such as MO_2Cl_2 (M = Cr, Mo), $ReOCl_4$, and $POCl_3$. Given that many of these

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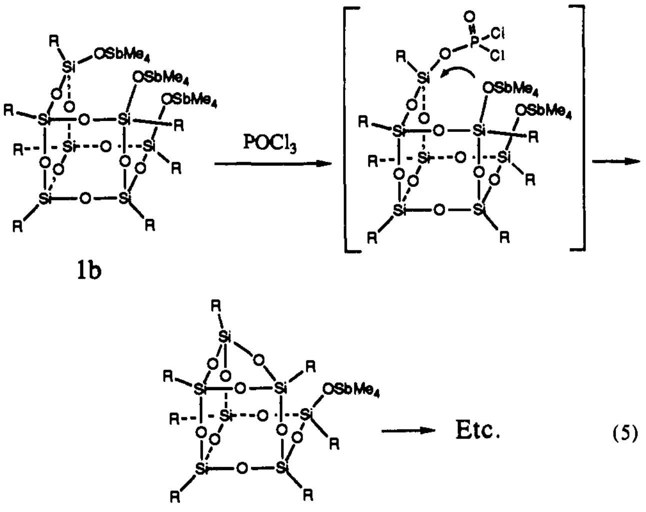


(5)

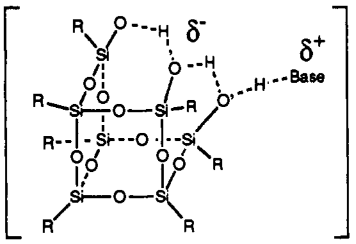
same reagents are also prone to form ate complexes, the cyclodehydration side reaction (as well as ate formation) can probably be avoided by using less electrophilic reagents.

Implications for Silica Surface Chemistry. Although the primary focus of this work was to develop a new method for the preparation of metallasilsesquioxanes, the results from this study have a number of important implications for the chemistry of silica surfaces. First, the high selectivity of Me$_5$Sb toward monoprotonolysis provides a number of exciting possibilities for the preparation of modified silicas. Unlike more conventional metal alkyl reagents (e.g., AlR$_3$, RMgX, RLi, etc.), which can possess more than one active metal–carbon bond and are reactive enough to cleave surface siloxane bonds,[13] Me$_5$Sb should only react with surface silanol groups to produce chemisorbed Me$_4$Sb groups. This, in principle, provides a strict accounting of sterically accessible silanol groups without modifying the network structure of the surface. One possible analytical application for this reaction would be an assay to determine the number of sterically accessible siloxy groups, which could be conveniently calculated from the number of chemisorbed Me$_4$Sb groups (determined by IR spectroscopy), the amount of methane produced, or the total amount of antimony or carbon present on a sample of known surface area.

Perhaps of more immediate interest, however, are the opportunities available for the preparation of new surface-modified silicas and silica-supported catalysts by the reactions of Me$_5$Sb-modified silicas with reactive main-group or transition-metal halides. Aside from the innumerable opportunities for new materials, the facility with which **1b–5b** react with electrophiles presents the possibility that higher surface coverages could be obtained with current surface-modifying agents (e.g., chlorosilanes) by first treating dry silica surfaces with Me$_5$Sb to activate the siloxy groups toward electrophilic reagents.

A more significant and far less speculative implication of our work stems from the unexpectedly high reactivity of Me$_5$Sb toward **1a**. Although it was not possible to measure rate constants, it is clear that the reaction of Me$_5$Sb with one silanol group on **1a** occurs much faster than the reaction of a second silanol group or the reactions of Me$_5$Sb with structurally similar silanols possessing fewer than three potentially hydrogen-bonded siloxy groups. Extrapolation of this work to silica surfaces implies that silica surface sites possessing at least three mutually hydrogen-bonded siloxy groups should be much more reactive toward Me$_5$Sb than isolated surface silanols, as well as sites containing isolated pairs of geminally or vicinally hydrogen-bonded siloxy groups. If these multiply hydrogen-bonded sites represent a significant proportion of sites with hydrogen-bonded siloxy groups, it should be possible to selectively functionalize these sites using Me$_5$Sb. Other basic metal alkyl reagents (e.g., R$_3$Al, RMgX, R$_2$Zn, RLi, etc.) would be expected to exhibit similar reactivity patterns, but any selectivity should be greatly attenuated due to the much greater reactivity of these strongly nucleophilic organometallic reagents.

It is interesting to compare selectivities for the reactions of **1a–4a** and Me$_5$Sb with the trimethylsilylation reactions that we described earlier,[1b] where it was demonstrated that the monosilylation of **1a** (Me$_3$SiCl, 5% Et$_3$N/THF, 25 °C) occurred at least 3 orders of magnitude faster than the silylation reactions of **2a–4a**. Our explanation for the enhanced reactivity of **1a** toward Me$_3$SiCl/Et$_3$N invoked hydrogen bonding between the three siloxy groups in **1a** to stabilize a contact ion pair (i.e., **14**) that was uniquely capable of rapidly reacting with Me$_3$SiCl via a mechanism that was not available to the silanols containing less than three mutually hydrogen-bonded siloxy groups.



14

The reaction of **1a** with Me$_5$Sb is obviously different in many respects, but because the only plausible mechanisms for the reactions of silanols with Me$_5$Sb involve protonolysis of Sb–C bonds, it seems highly probable that the origin of the rate enhancement is the same—namely, that hydrogen bonding in **1a** dramatically decreases its pK_a (i.e., increases its acidity) relative to silanols with less extensive hydrogen bonding (e.g., **1c**,**d**, **2a–4a**). Trisilanol **1a** reacts much faster with Me$_5$Sb than **1c** and **1d** because it is much more acidic. These effects are expected on the basis of numerous studies on the pK_a's of polyhydroxylic compounds;[14] they should also be expected on silica surfaces.

Concluding Remarks

The reactions of incompletely-condensed silsesquioxanes with excess pentamethylantimony afford high yields of the corresponding tetramethylstibonium silsesquioxides. These hydrocarbon-soluble Me$_4$SbO-substituted silsesquioxanes are stable with respect to autocatalytic framework cleavage reactions, but nucleophilic enough to react rapidly with a variety of transition-metal and main-group halide complexes; they appear to be versatile anionic equivalents of incompletely-condensed silsesquioxanes.

The high specificity of Me$_5$Sb toward monoprotonolysis and the pronounced tendency of Me$_4$Sb–OSi linkages to heterolytically dissociate also provides a number of interesting possibilities for the preparation of surface-modified silicas. On the basis of our work it is reasonable to expect that pretreatment of silica surfaces with Me$_5$Sb will enhance the reactivity of the siloxy groups toward electrophilic reagents. This in turn should produce higher surface coverages without compromising the integrity of the SiO surface structure. Perhaps more exciting is the possibility that multiply hydrogen-bonded sites can be selectively functionalized in the presence of isolated surface silanols and hydrogen-bonded pairs

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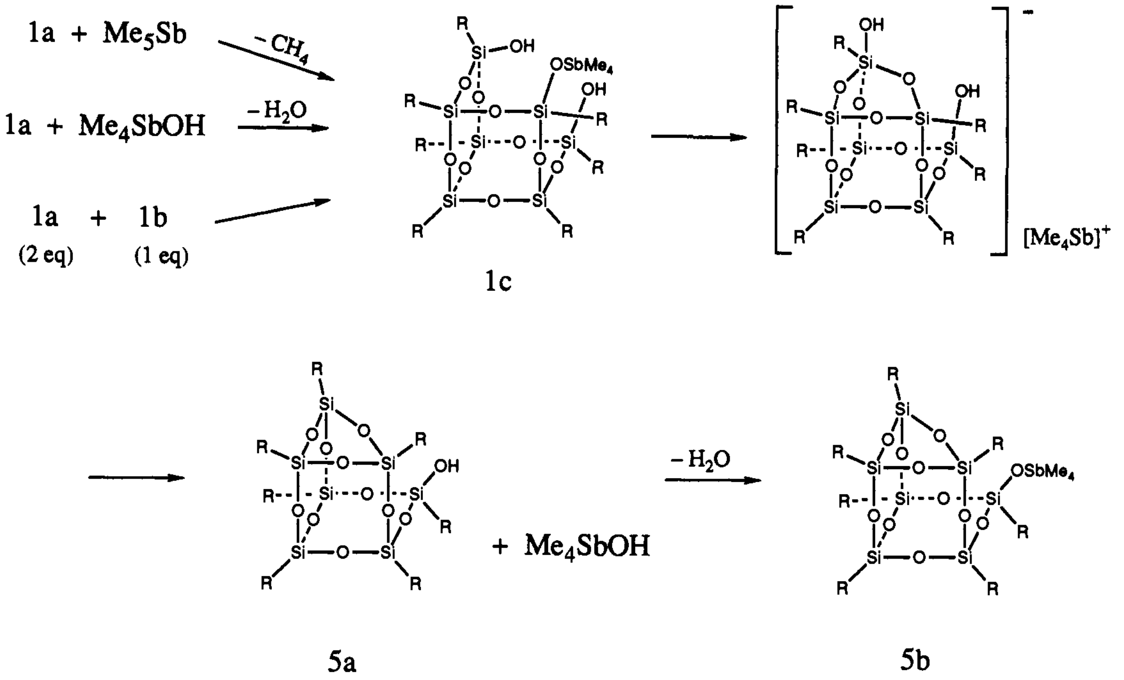
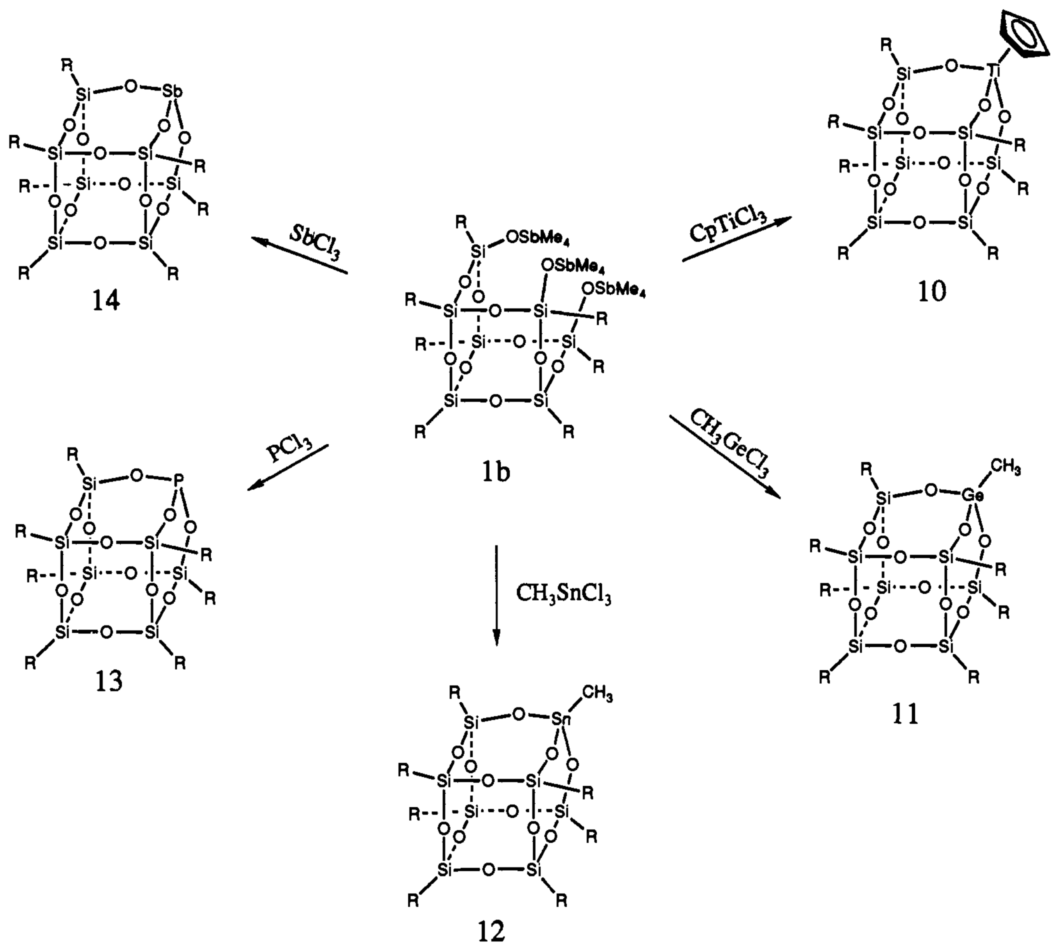
Scheme I



Scheme II



of silanols. We will report our efforts to explore these and other possible uses for Me_5Sb-modified silicas in due course.

Experimental Section

General experimental protocol for the synthesis and purification of **1a**–**6a** appear elsewhere.[1a,b] Pentamethylantimony[11c] and tetramethylantimony hydroxide[11a] were prepared according to literature procedures. Except where noted all operations were performed under a nitrogen atmosphere either on a high vacuum line with modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-lab.

Benzene and hexanes were distilled from dark purple solutions of potassium benzophenone ketyl containing tetraglyme. Diethyl ether was distilled from sodium benzophenone ketyl. Tetrahydrofuran and C_6D_6 were distilled from potassium benzophenone ketyl. All spectra were recorded on a General Electric GN-500 (^{1}H, 500.1 MHz; ^{13}C, 125.03 MHz; ^{29}Si, 99.36 MHz) NMR spectrometer. The CH_2 and CH resonances in the ^{13}C spectra were assigned by using standard DEPT pulse sequences.

General Procedure of the Syntheses of 1b–4b. In a typical reaction, pentamethylantimony (200% based on the number of silanols present) was added with stirring to a solution of the silanol (1.00 g) in benzene (25 mL). In the case of **1a**, an initial vigorous evolution of methane occurs; this was allowed to subside before continuing. The reaction mixture was heated for 2–4 h at 50–60 °C (oil bath), then the solvent and volatiles were removed in vacuo—first at 25 °C (1 Torr, 1 h), then at 60 °C (0.01 Torr, 8 h). Spectroscopic analysis (^{1}H, ^{13}C NMR) at this point generally indicated that the yields were quantitative and that product purities were greater than 98%. Samples of **1b–4b** obtained in this fashion were suitable for most purposes. Procedures for the preparation of analytically pure samples and characterization data are listed below.

1b. The crude product was dissolved in hot hexanes (~30 mL) and filtered. Reduction of the filtrate to ~15 mL in vacuo and cooling to −34 °C for 2 days afforded **1b** as a white microcrystalline solid, which was collected by filtration, washed with cold hexanes, and dried in vacuo at 60 °C overnight. Yield: 1.18 g, 76%. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.3–0.8 (br m's, 77 H), 1.093 (s, 36 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.87, 28.73, 28.71, 28.39, 27.96, 27.61, 27.58, 27.39 (6:6:6:6:5:3:2:1 for CH_2), 27.81, 26.44, 24.16 (3:3:1 for CH), 11.83 ($Sb(CH_3)_4$). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 28.27, 28.20, 27.91, 27.66, 27.35, 27.16, 27.05, 26.75 (CH_2), 26.95, 25.63, 23.36 (3:3:1 for CH), 11.89 ($Sb(CH_3)_4$). $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_6D_6, 25 °C): δ −67.94, −70.58, −71.87 (1:3:3). MS (70 eV, 200 °C; relative intensity): *m/e* 1053 ($M^+ - (SbMe_4)_2O$, *c*-C_6H_{11}; 38%), 870 ($M^+ - (SbMe_4)_2O$, $SbMe_4$, *c*-C_6H_{11}; 100%). Anal. Calcd for $C_{54}H_{113}O_{12}Sb_3Si_7$ (found): C, 42.77 (42.72); H, 7.51 (7.50). Mp: 184–187 °C.

2b. The crude product was dissolved in hexanes (~10 mL) and filtered. Cooling of the filtrate to −34 °C for 1 week afforded **2b** as a white solid, which was rapidly collected by vacuum filtration, washed with cold (−34 °C) hexanes, and dried in vacuo at 60 °C overnight. Yield: 1.02 g, 76%. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.30–0.85 (br m's, 77 H), 1.10 (s, 24 H), 0.33 (s, 9 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.79, 28.71, 28.68, 28.66, 28.50, 28.27, 28.18, 28.16, 27.93, 27.87, 27.61, 27.55, 27.51, 27.46, 27.31 (for CH_2), 27.58, 26.46, 26.32, 26.09, 24.00 (2:1:1:2:1 for CH), 11.69 ($Sb(CH_3)_4$), 2.52 ($Si(CH_3)_3$). $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_6D_6, 25 °C): δ −67.85, −67.57, −70.01, −70.69, −71.84 (1:1:2:1:1 for $RSiO_{3/2}$), 7.47 ($Si(CH_3)_3$). MS (70 eV, 200 °C; relative intensity): *m/e* 1011 ($M^+ - SbMe_4)_2O$, CH_3; 4%), 943.344 ($M^+ - SbMe_4OSbMe_4$, *c*-C_6H_{11}; 100%), 861 ($M^+ - SbMe_4OSbMe_4$, *c*-C_6H_{11}, *c*-C_6H_{10}). Anal. Calcd for $C_{53}H_{110}O_{13}Sb_2Si_8$ (found): C, 45.22 (45.55); H, 7.88 (8.08). Mp: 205–220 °C (dec).

3b. The crude product was dissolved in hexanes (~7.5 mL) and filtered. Cooling the filtrate to −34 °C for 1 week afford a white solid, which was rapidly collected by vacuum filtration and dried in vacuo (60 °C, 0.01 Torr, 8 h). The recrystallized product is highly soluble in hexane and must be collected quickly to prevent its dissolution upon warming. Yield: 0.62 g, 53%. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.3–0.8 (br m's, 89 H), 0.335 (s, 18 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.70, 28.65, 28.44, 28.32, 28.20, 28.06, 28.04, 27.96, 27.91, 27.78, 27.58, 27.47, 27.41, 27.35, 27.23 (for CH_2), 27.31, 26.25, 25.96, 25.75, 23.84 (1:2:2:1:1 for CH), 11.56 ($Sb(CH_3)_4$), 2.44 ($Si(CH_3)_3$). $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_6D_6, 25 °C): δ −67.73, −68.64, −69.26, −70.18, −71.81 (1:2:1:2:1 for $R\mathit{Si}O_{3/2}$), 8.30 ($\mathit{Si}(CH_3)_3$). MS (70 eV, 200 °C; relative intensity): *m/e* 1283 ($M^+ - CH_3$; 5%), 1085 ($M^+ - SbMe_4OMe$; 65%), 1017 ($M^+ - SbMe_4$, *c*-C_6H_{11}; 70%), 943 ($M^+ - SbMe_4OTMS$, *c*-C_6H_{11}; 100%). Anal. Calcd for $C_{52}H_{107}O_{12}SbSi_9$ (found): C, 48.08 (47.94); H, 8.30 (7.91). Mp: 258–263 °C (dec).

4b. The crude product was recrystallized by allowing acetonitrile to slowly diffuse into a benzene solution **4b**. The large well-formed rods that formed over several days were collected by vacuum filtration, washed with C_6H_6/MeCN, and dried in vacuo at 70 °C overnight. Yield: 1.19 g, 90%. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.3–0.9 (br m's, 88 H), d 0.979 (s, 24 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.71, 28.62, 28.54, 28.46, 28.23, 28.11, 28.03, 28.00, 27.86, 27.83, 27.61, 27.52, 27.40 (for CH_2), 26.57, 25.10, 24.66, 24.61 (1:1:1:1 for CH), 11.17 ($SbMe_4$). $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_6D_6, 25 °C): δ −67.15, −68.26, −69.87, −70.19 (1:1:1:1). MS (70 eV, 200 °C; relative intensity): *m/e* 1015 ($M^+ - 2SbMe_4$, C_6H_{11}; 100%), 931 ($M^+ - 2SbMe_4$, $2C_6H_{11}$; 20%), 849 ($M^+ - 2SbMe_4$, $3C_6H_{11}$; 10%). Anal. Calcd for $C_{56}H_{112}O_{13}Sb_2Si_8$ (found): C, 46.02 (45.58); H, 7.72 (8.02). Mp: 260–265 °C (dec).

Synthesis of 5b. Solid **1a** (642 mg, 0.659 mmol) and **1b** (500 mg, 0.330 mmol) were dissolved in 20 mL of THF and heated with stirring at 65 °C. After 2 h the solvent was removed in vacuo to afford a quantitative yield (1.14 g) of **5b** as a white amorphous foam. Due to its extremely high solubility in common organic solvents, we have been unable to recrystallize **5b**. The spectroscopically and analytically pure samples prepared by the above procedure were, however, identical with samples prepared by the reaction of **5a** with Me_5Sb. Yield: 1.08 g, 96%. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 2.3–0.9 (br m's, 77 H), 1.046 (s, 12 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.76, 28.54, 27.96, 27.93, 27.86, 27.80, 27.71, 27.57, 27.54, 27.48, 27.30, 27.20, 27.08, 26.96, 26.86 (for CH_2), 26.80, 24.57, 24.03, 24.00, 23.23 (1:2:1:2:1 for CH), 11.05 ($Sb(CH_3)_4$). $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_6D_6, 25 °C): δ −55.88, −58.79, −66.16, −68.98, −70.6 (br) (1:2:1:2:1). MS (70 eV, 200 °C; relative intensity): *m/e* 1121 ($M^+ - 2CH_4$; 10%), 1053 ($M^+ - CH_4$, *c*-C_6H_{11}; 25%), 871 ($M^+ - SbMe_4OH$, *c*-C_6H_{11}; 100%). Anal. Calcd for $C_{46}H_{89}O_{11}SbSi_7$ (found): C, 48.62 (49.03); H, 7.89 (8.17). Mp: 180–185 °C.

Reactions of 1b–4b with TMSCl. In a general reaction, chlorotrimethylsilane (1.05 equiv per Sb) was added with stirring to a solution of **1b–4b** (50 mg) in hexane (2.5 mL). Precipitation of $[Me_4Sb]Cl$ was noted immediately upon mixing. After 30 min of stirring at 25 °C, the solution was filtered and the solvent was removed in vacuo to afford a quantitative yield of $(c\text{-}C_6H_{11})_7Si_7O_9(OTMS)_3$ (**8**) or $(c\text{-}C_6H_{11})_8Si_8O_{10}(OTMS)_2$ (**9**), which were identical in all respects with samples prepared by the silylation of **1a** and **4a**.[1a,b]

Synthesis of 10. $CpTiCl_3$ (51 mg, 0.231 mmol) was added with stirring to a solution of **1b** (350 mg, 0.231 mmol) in benzene (20 mL). Precipitation of $[Me_4Sb]Cl$ was noted immediately upon mixing. After stirring for 30 min at 25 °C, the solution was filtered and the solvent was removed in vacuo to afford a white amorphous foam. Extraction with hexanes (~5 mL) and filtering removed the final traces of $[Me_4Sb]Cl$ (< 5 mg); cooling to −34 °C for 1 week afforded a white microcrystalline solid, which was collected by vacuum filtration and dried in vacuo (70 °C, 0.01 Torr) overnight. Yield: 172 mg, 69%. ^{1}H NMR (500.1 MHz, C_6D_6, 25 °C): δ 6.284 (s, 5 H), 2.1–0.9 (br m's, 77 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, $CDCl_3$, 25 °C): δ 116.53 (C_5H_5), 28.03, 28.00, 27.83, 27.78, 27.51, 27.40, 27.32, 27.29 (CH_2), 24.24, 23.92, 23.86 (3:3:1 for CH). $^{29}Si\{^1H\}$ NMR (99.35 MHz, C_6D_6, 25 °C): δ −66.20, −68.71, −69.50 (3:1:3). MS (70 eV, 200 °C; relative intensity): *m/e* 1082 (M^+; 1.5%), 1015 ($M^+ - C_5H_5$; 3.1%), 999 (M^+ − *c*-C_6H_{11}; 100%). Anal. Calcd for $C_{47}H_{82}O_{12}Si_7Ti$ (found): C, 52.09 (52.13); H, 7.63 (7.55). Mp: 350–400 °C (dec without melting).

Syntheses of 11–14. The reactions of **1b** with $MeGeCl_3$, $MeSnCl_3$, PCl_3, and $SbCl_3$ were performed by using the procedure described above for the preparation of **10**. The result products $[c\text{-}C_6H_{11})_7Si_7O_{12}(GeMe)]$ (**11**),[1a] $[(c\text{-}C_6H_{11})_7Si_7O_{12}(SnMe)]$ (**12**),[1a] $[(c\text{-}C_6H_{11})_7Si_7O_{12}P]$ (**13**),[2d] and $[c\text{-}C_6H_{11})_7Si_7O_{12}Sb]$ (**14**),[2d] were obtained in yields of 88%, 85%, 92%, and 92%, respectively, after hexane extraction and evaporation of the volatiles. The crude products were of high purity (>95% by NMR) and were identical in all respects with authentic samples prepared from the Et_3N-catalyzed reactions of **1a** with $MeGeCl_3$, $MeSnCl_3$, PCl_3, and $SbCl_3$.[1a,2d]

Me_4SbOH-Catalyzed Cyclodehydration of 1a. A solution of **1a** (495 mg, 0.508 mmol) and Me_4SbOH (3 mg, 0.015 mmol) in benzene (60 mL) was refluxed for 15 h under nitrogen in a Dean-Stark apparatus filled with 4-Å molecular sieves. A ^{13}C NMR spectrum of the crude product obtained by evaporating the solvent in vacuo (25 °C, 0.1 Torr) was identical in all respects with that of a sample of **5a** prepared by the dehydration of **1a** with highly activated molecular sieves.[1a]

Me_4SbOH-Catalyzed Cyclodehydration of 2a. A solution of **2a** (134 mg, 0.128 mmol) and Me_4SbOH (1 mg, 0.005 mmol) in benzene (35 mL) was refluxed for 15 h under nitrogen in a Dean-Stark apparatus filled with 4-Å molecular sieves. A ^{13}C NMR spectrum of the crude product obtained by evaporating the solvent in vacuo (25 °C, 0.1 Torr) was identical in all respects with that of a sample of **7** prepared by the silylation of **5a** with $TMSCl/Et_3N$.[1a]

Reaction of 5a with Me_4SbOH. A solution of **5a** (24 mg, 0.025 mmol) and Me_4SbOH (5 mg, 0.025 mmol) in C_6D_6 (0.6 mL) was stirred for 2.5 h at 25 °C. Analysis of the reaction mixture by integrating resonances in the methine region of the ^{13}C NMR spectrum indicated the presence of **5a** and **5b** in a ratio of 5:95.

Collection of X-ray Diffraction Data for $(c\text{-}C_6H_{11})_7Si_7O_9(OSbMe_4)_3$ (1b). Crystals of **1b** suitable for X-ray diffraction were grown by allowing hexane to diffuse into a saturated benzene solution of **1b**. Crystal data for **1b** $[C_{54}H_{113}O_{12}Si_7Sb_3\cdot{}^1/_2(C_6H_{14})$ (fw 1555.4)] are as follows: monoclinic $P2_1/n$, a = 15.085 (3) Å, b = 21.046 (3) Å, c = 23.892 (3) Å, β = 106.108 (13)°; V = 7288 (2) Å^3; D_{calc} = 1.418 g/cm^3 (Z = 4). A total of 9020 unique reflections with $4.0 \le 2\theta \le 45.0°$ were collected on a Syntex $P2_1$ diffractometer at −90 °C with use of graphite monochromated Mo Kα radiation. The structure was solved by direct methods (SHELXTL-PLUS). Full-matrix least-squares refinement of positional and thermal parameters (Anisotropic for Si, O, C, Sb) led to convergence with $R_F = 4.7\%$, $R_{wF} = 5.3\%$, and GOF = 1.67 for 713 variables refined against those 8438 data with $|F_o| > 2.0\sigma|F_o|$. All other details regarding the crystal structure appear in the supplementary material.

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Supplementary Material Available: X-ray crystal data for **1b**, including experimental procedures, tables of crystal data, atomic coordinates, thermal parameters, bond lengths, bond angles, and ORTEP figures (14 pages); tables of calculated and observed structure factors for **1b** (33 pages). Ordering information is given on any current masthead page.

Conformations, Spectroscopy, and Photochemistry of Methyl Phenanthrene-9-carboxylate, Phenanthrene-9-carboxamides, and Their Lewis Acid Complexes[1]

Frederick D. Lewis,* Steven V. Barancyk, and Eric L. Burch

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113. *Received September 25, 1991. Revised Manuscript Received December 31, 1991*

Abstract: The spectroscopic properties and photochemical behavior of methyl phenanthrene-9-carboxylate and of a primary, secondary, and tertiary phenanthrene-9-carboxamides have been investigated in the absence and presence of strong Lewis acids. The ground-state conformations of the free and complexed molecules have been investigated by means of NMR and Gaussian 88 calculations. The dihedral angle between the phenanthrene and the carbonyl group is found to be dependent upon the bulk of the 9-substituent and upon Lewis acid complexation. Complexation also changes the secondary amide conformation from syn to anti. Both the phenanthrenes and their complexes are strongly fluorescent. Equilibrium constants for complex formation have been determined by means of fluorescence titrations. Rate constants for both radiative and nonradiative singlet-state decay increase upon complexation. The nonradiative rate constants for several boron halide complexes display a heavy-atom effect, which is larger for tertiary vs primary amides. Complexation results in an increase in both ester and amide singlet-state reactivity with simple alkenes.

Introduction

We have previously reported that Lewis acid complexation can result in marked changes in the conformation, spectroscopic properties, and photochemical behavior of cinnamic esters[2] and amides[3] and of their heterocyclic analogues, coumarin[4] and 2-quinolone.[1b] In the case of several cinnamic acids and amides, highly selective $E \rightarrow Z$ photoisomerization is observed in the presence of Lewis acids, as a consequence of selective ground-state complexation of the E isomer and Lewis acid-induced changes in the absorption spectra and photoisomerization quantum yields.[2a,3] Lewis acid-enhanced photodimerization and stereospecific cross-cycloaddition is observed for cinnamic esters,[2b] coumarin,[4] and 2-quinolones.[1b] These changes are attributed to increases in electrophilicity and singlet-state lifetimes for the complexed vs noncomplexed organic molecules. In the case of coumarin and quinolone, complexation on oxygen results in a change in the configuration of the lowest singlet state from n,π^* to π,π^*, resulting in a marked increase in singlet lifetime.[1b]

We report here the results of our investigation of the structure and photochemical behavior of methyl phenanthrene-9-carboxylate (PE), several related amides (1°PA, 2°PA, and 3°PA), and their Lewis acid complexes. Lewis acid complexation is found to have a pronounced effect on ground-state conformation, photophysical behavior, and photochemical reactivity. Of special significance is the decrease in singlet lifetime for boron halide complexes, which is attributed to a heavy-atom effect on the nonradiative-decay rate constant.

Results and Discussion

Ground-State Structures. ^{1}H NMR data for PE, the three amides, and their Lewis acid complexes are summarized in Table I along with literature data for phenanthrene and 9-acetylphenanthrene. The large downfield shift for H(8) and H(10) in the 9-carbonylphenanthrenes has been noted previously and attributed to a preferred s-trans conformation for the carbonyl and the C(9)-C(10) bond,[5] similar to that for the 1-carbonylnaphthalenes.[6] The downfield shifts for both H(8) and H(10) are significantly smaller for the amides vs the ester and decrease with increasing N-alkylation. The magnetic anisotropy diagrams of Jackman and Sternhell[7] for the carbonyl group indicate that an increase in the dihedral angle between the phenanthrene ring and the carbonyl group from 0° to 90° should result in an upfield shift of ca. 1.1 for H(8). Thus the observed changes are indicative of an increase in the dihedral angle from ca. 5° in the case of PE to ca. 90° for 3°PA, with intermediate values for 1°PA and 2°PA. The assignment of the upfield methyl signal to the syn methyl group in 3°PA is consistent with both previous assignments for

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