Inorg. Chem. **1994**, *33*, 1099–1102 **1099**

Surface Organometallic Chemistry of Tin: Formation of the Grafted Organometallic Complex $(>Si-O)_2Sn(n-C_4H_9)_2$ by Reaction of $H_2Sn(n-C_4H_9)_2$ with the Surface of a Partially Dehydroxylated Silica

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Received June 10, 1993[⊗]

Reaction of $H_2Sn(n-C_4H_9)_2$ with the surface of Aerosil silica dehydroxylated at 200 or 500 °C was followed by surface microanalysis, quantitative analysis of the evolved gases, ^{13}C CP-MAS NMR, and infrared spectroscopy. At room temperature after a short period of interaction, the starting complex is simply physisorbed on the silica surface. Two types of weak interactions occur between surface silanols and both the CH groups of the butyl ligands and the tin hydride(s). For longer periods of interaction and/or higher temperature, a well-defined surface species $(>Si-O)_2SnBu_2$ (**2**) is formed on both types of silica. The infrared and ^{13}C CP-MAS data are consistent with a hydrogen-bonding interaction between surface butyl ligands and surface silanols. Possible formation of $(>Si-O)Sn(H)Bu_2$ as an intermediate in the formation of **2** is discussed.

Introduction

There are few examples of (relatively) well-defined surface organometallic fragments grafted onto the surfaces of inorganic oxides.[1] However, the synthesis of well-defined surface organometallic fragments is an important goal in the field of SOMC as well as for catalytic purposes and molecular separations in zeolites.[2] We have previously shown that a relatively well-defined species, $>Si-O-SnBu_3$ (**1**) can be obtained on the surfaces of $SiO_{2(200)}$ or $SiO_{2(500)}$ by several routes:[3]

$$>Si-OH + SnBu_4 \xrightarrow{150\ °C} >Si-O-SnBu_3 + n\text{-}C_4H_{10} \qquad (1)$$

$$>Si-OH + HSnBu_3 \xrightarrow{25\ °C} >Si-O-SnBu_3 + H_2 \qquad (2)$$

1 has been fully characterized by ^{13}C CP-MAS and ^{119}Sn MAS NMR, analytical measurements, and IR spectroscopy. In this contribution, we wish to report the synthesis of another well defined species, $(>Si-O)_2SnBu_2$ (**2**), which is obtained by reaction of Bu_2SnH_2 with a silica surface partially dehydroxylated at 200 or 500 °C.

Experimental Section

Materials. Aerosil silica from Degussa with a surface area of 200 $m^2\ g^{-1}$ was dehydrated and dehydroxylated for 14 h under dynamic vacuum (10^{-4} Torr), either at 200 °C ($SiO_{2(200)}$) or at 500 °C ($SiO_{2(500)}$).

Bu_2SnH_2 was synthesized by the reaction of $LiAlH_4$ with Bu_2SnCl_2 according to a previously described procedure.[4] The complex was purified by distillation under reduced pressure (75 °C, 12 Torr). Its IR spectrum contains ν(C–H) bands at 2958, 2918, 2872, and 2854 cm^{-1}, δ(C–H) bands at 1464, 1457, 1420, 1377, 1358, and 1341 cm^{-1}, and a ν(Sn–H) band at 1835 cm^{-1}. In the ^1H NMR spectrum the hydride resonance is situated at 4.42 ppm ($\delta(Bu_2SnH_2)$)($CDCl_3$). The ^{13}C NMR ($CDCl_3$) resonances of the *n*-butyl carbons are situated at 7.3 (C_α), 13.8 (C_δ), 27.2 (C_γ), and 30.8 (C_β) ppm, in agreement with literature data.[5–7] Microanalysis was consistent with the formula Bu_2SnH_2.

Procedure for Grafting Bu_2SnH_2. After treatment of the silica surface at the desired temperature, liquid Bu_2SnH_2 was introduced (via a syringe through a septum) into a glass reaction vessel maintained under vacuum (10^{-4} Torr). This procedure was used for IR studies on compressed disks of silica, as well as for analytical or solid-state NMR experiments.

CP-MAS NMR. Spectra were recorded on a Bruker MSL-300 spectrometer operating at 75.47 MHz for ^{13}C and equipped with a classical double bearing probe allowing a rotation frequency of 3–4 kHz. Spectra were recorded using cross-polarization (90° for ^1H = 6.2 μs; contact time, 5 ms). The delay between each scan was fixed at 5 seconds, to allow complete relaxation of ^1H nuclei. Chemical shifts are given relative to TMS (external reference) and were confirmed with an internal reference (adamantane, position of the highest peak at 37.7 ppm).

Infrared Spectroscopy. IR spectra were recorded on a Fourier Transform Nicolet 10-MX. The spectra were recorded *in situ* in a cell with CaF_2 windows, according to a previously described procedure.[8]

Analytical Data. The gases evolved during the surface reaction were analyzed qualitatively and quantitatively by GC. Detection and titration of evolved hydrogen were carried out with a catharometer detector after separation on 5-Å molecular sieves. Hydrocarbons were analyzed by FID after separation on a capillary column, 50 m × 0.32 mm.

Results

Reaction of Bu_2SnH_2 with $SiO_{2(200)}$. When Bu_2SnH_2 was brought into contact with the surface of $silica_{(200)}$ in the absence

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[⊗] Abstract published in *Advance ACS Abstracts*, January 15, 1994.

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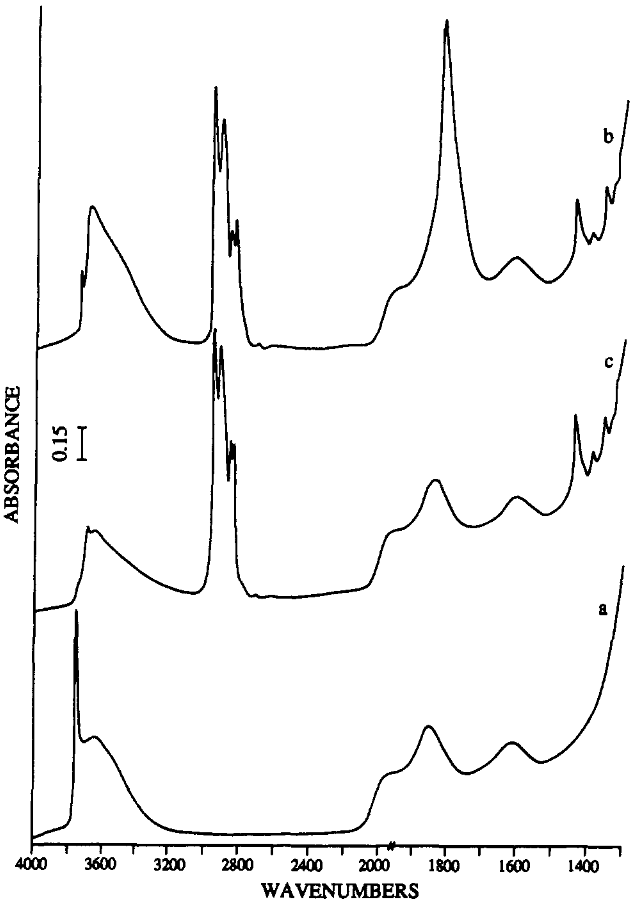


Figure 1. IR spectra of (a) silica$_{(200)}$, (b) silica$_{(200)}$ after reaction with Bu_2SnH_2 at room temperature, and (c) silica$_{(200)}$ after reaction for 24 h at 25 °C and then 8 h at 100 °C.

of solvent, the intensity of the ν(OH) band at 3747 cm^{-1} corresponding to terminal silanols decreased instantaneously (Figure 1a,b). Two new bands were observed at lower frequency, a sharp band at 3697 cm^{-1} and a broad band at 3600 cm^{-1}. Simultaneously bands characteristic of the butyl groups were observed: ν(C–H) at 2962, 2924, 2876, and 2855 cm^{-1}; δ(C–H) at 1466 and 1379 cm^{-1}. Interestingly, two bands at 1837 (s) and 1799 (sh) cm^{-1} are attributed to ν(C–H) whereas Bu_2SnH_2 exhibits only one band in solution at 1835 (s) cm^{-1}.

We have previously observed[3] that hydrogen bonding between the CH_3 groups of an alkane or an organometallic compound and surface silanol groups results in the shift of the ν(OH) band of the terminal silanol groups from 3747 to 3697 cm^{-1}. This shift in infrared frequency was also observed with the species $\gg$Si–O–SnBu$_3$. In the present case, the band situated at 3697 cm^{-1} is rather narrow. Consequently we assume that we are again dealing with hydrogen bonding between some of the alkyl groups of adsorbed Bu_2SnH_2 and the remaining silanols, i.e., $\gg$C–H$\cdots$OH.

The shoulder at 1799 cm^{-1}, superimposed on the tail of the strong band at 1837 cm^{-1}, likely corresponds to a shifted tin hydride vibration. If the tin hydride interacts with surface silanols, a specific band should be observed in the ν(OH) region of the silica. A shoulder at 3600 cm^{-1}, which could arise from such an interaction, is indeed present. The bands at 3600 and 1799 cm^{-1} are also formed by interaction of Bu_3SnH with silica$_{(200)}$ at room temperature, but not during the room temperature physisorption of $SnBu_4$ on silica$_{(200)}$.[3] The bands at 3600 and 1799 cm^{-1} exhibit a parallel decrease in intensity with time. We therefore conclude that these bands are the results of an interaction between the tin hydride and the silanols.

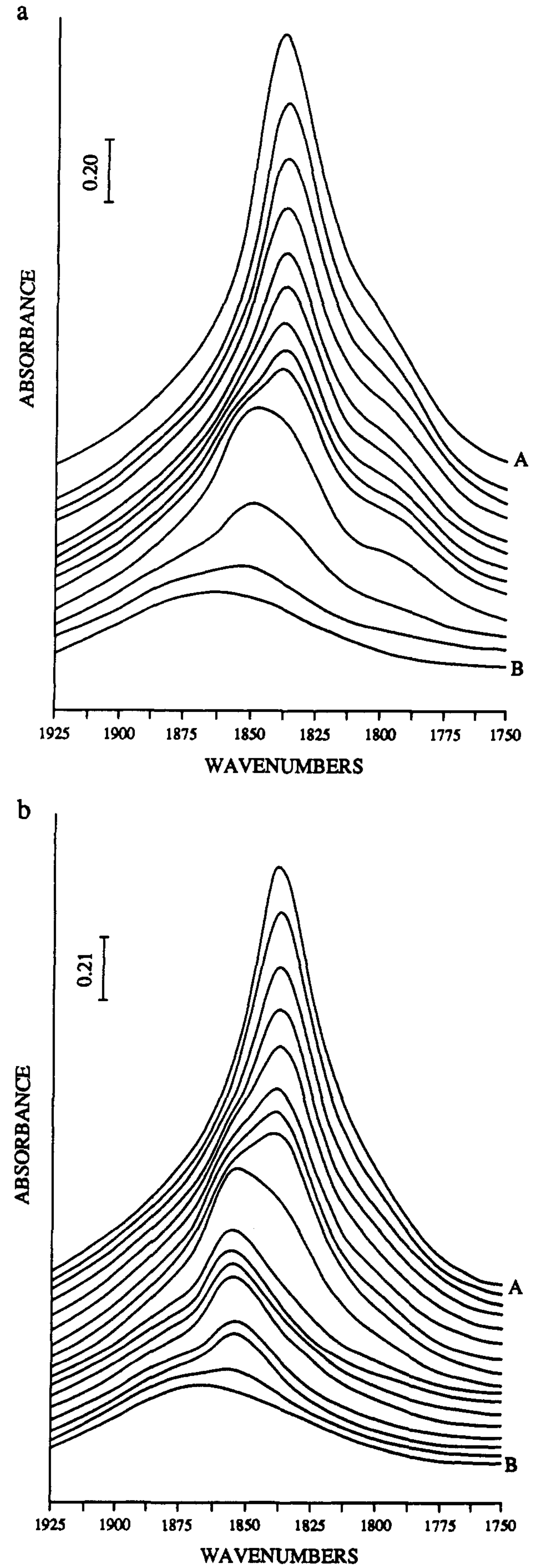


Figure 2. Evolution of the IR spectra in the ν(Sn–H) region as a function of time. Reaction of Bu_2SnH_2 with (a) silica$_{(200)}$ and (b) silica$_{(500)}$.

Over time, the intensities of the ν(C–H) and δ(C–H) bands remained constant, whereas the band at 1835 cm^{-1} due to the ν(Sn–H) mode of physisorbed Bu_2SnH_2 decreased in intensity (Figure 2a). An intermediate band at 1854 cm^{-1} was observed. Finally, after 100 h at room temperature or after heating at 100

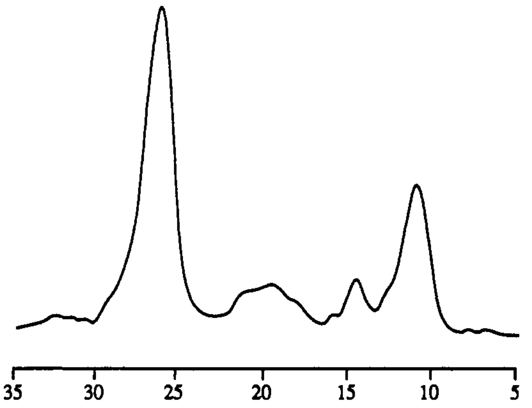


Figure 3. ^{13}C CP-MAS NMR spectra after reaction of Bu_2SnH_2 with silica$_{(200)}$ for 48 h at 100 °C.

°C for 8 h, no bands were present in the ν(Sn–H) region (Figure 1c). Simultaneously, the band at 3600 cm^{-1} disappeared.

During the reaction between Bu_2SnH_2 and silica$_{(200)}$, H_2 is evolved. At 100 °C, the reaction was complete in 8 h. The amount of evolved hydrogen was then equal to 2 ± 0.05 mol per mole of grafted tin. No hydrocarbon was evolved at this temperature. When the same experiment was carried out with a large quantity of silica$_{(200)}$ (e.g., 1 g instead of 0.02 g), the surface reaction was slower and a temperature of 150 °C was necessary to obtain 2 mol of H_2 evolved per mole of grafted tin. However, the reaction is also slightly less selective since some butane was evolved (0.2 mol per mole of grafted tin). The elemental analysis of the corresponding sample showed the presence of 2 molar equiv of C_4 per mole of grafted tin (3.8% Sn; 3.1% C; C_4/Sn = 2.0).

The ^{13}C CP-MAS NMR spectrum of a sample obtained by the reaction of Bu_2SnH_2 with silica$_{(200)}$ at 100 °C for 8 h contains four signals at 11.3, 14.7, 20.0, and 26.5 ppm (Figure 3). By comparison with the spectrum of the model compound $Bu_2Sn(OMe)_2$, the peaks at 20.0 and 26.5 ppm are attributed to the α-carbon and ($\beta + \gamma$)-carbons of the *n*-butyl chain, respectively. The signal at ca. 20 ppm is very broad (line width ca. 200 Hz) compared to the other peaks (line width ca. 100 Hz). This is probably due to the variety of grafting sites on silica, to be discussed later.

Reaction of Bu_2SnH_2 with silica$_{(500)}$. Similar observations were made with silica$_{(500)}$. Adsorption of Bu_2SnH_2 on silica$_{(500)}$ at room temperature resulted in a decrease in the intensity of the ν(O–H) band at 3747 cm^{-1} due to linear silanols, and the appearance of bands at 3698 and 3600 cm^{-1} (Figure 4a,b). The ν(C–H) and δ(C–H) bands corresponding to the butyl groups were observed at the same frequencies as on silica$_{(200)}$. The ν(Sn–H) bands at 1837 and 1799 cm^{-1} were also observed. The same explanation is proposed: Bu_2SnH_2 forms hydrogen bonds with silanol groups via aliphatic C–H groups as well as via a tin hydride ligand.

Slow consecutive surface reactions result in a decrease of intensity of the ν(Sn–H) band at 1837 cm^{-1}, followed by the appearance of a new ν(Sn–H) band at 1854 cm^{-1} which finally disappears after 24 h (Figures 2b and 4c) at 100 °C. Note that the reaction is finished only after 24 h, instead of after 8 h on silica$_{(200)}$. The reason for this difference in kinetic behavior may be the different concentrations and/or mobilities of adjacent silanols on the two silicas.

An analysis of the gas phase at the end of the experiment revealed the evolution of 1.9 mol of H_2 per mole of grafted tin. Microanalysis of the product confirmed the presence of 2 mol of C_4 per mole of grafted tin (2.7% Sn; 2.0% C; C_4/Sn = 1.8). The ^{13}C CP-MAS NMR spectrum of the sample after reaction is almost identical to that obtained on silica$_{(200)}$ (Table 1).

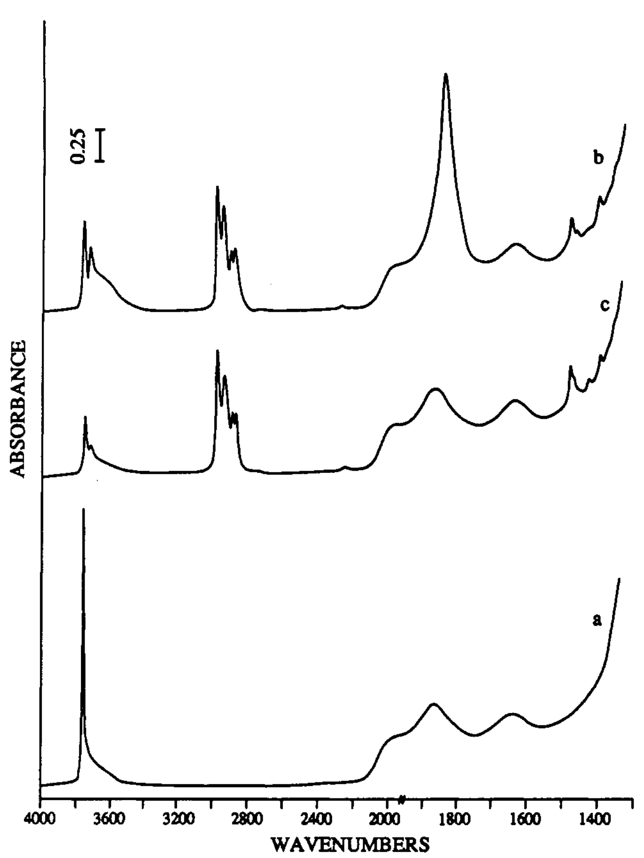


Figure 4. IR spectra of (a) silica$_{(500)}$, (b) silica$_{(500)}$ after reaction with Bu_2SnH_2 at room temperature, and (c) silica$_{(500)}$ after reaction for 24 h at 25 °C and then 24 h at 100 °C.

Discussion

Bu_2SnH_2 interacts with the surface of silica at room temperature via hydrogen bonding between the C–H and Sn–H groups of the starting material and the surface silanols. This hydrogen bonding is characterized by a low-frequency shift of the ν(O–H) bands of the silanols (to 3697 and 3600 cm^{-1}) as well as a low-frequency shift of the tin hydride band.

On both silica$_{(200)}$ and silica$_{(500)}$, the hydride ligands react progressively with surface protons with evolution of 2 mol of H_2 per mole of grafted tin. As the Sn loading is always lower than the quantity of available silanols (% Sn = 3.8 on silica$_{(200)}$ and 2.7 on silica$_{(500)}$), we propose that Bu_2SnH_2 reacts with the surface according to eq 3.

$$2{>}\text{Si–OH} + \text{Bu}_2\text{SnH}_2 \rightarrow \underset{\mathbf{2}}{({>}\text{SiO})_2\text{SnBu}_2} + \text{H}_2 \qquad (3)$$

Another possible explanation (reaction of the hydride with a surface Si–O–Si bridge) can be discarded due to the low dehydroxylation temperature of silica. Strained, reactive sites are formed only at high temperature (higher than 600 °C). Unstrained sites exist at lower temperature, but formation of H_2 instead of Si–H argues against reaction with a Si–O–Si bridge.

Considering the various ν(Sn–H) bands observed during the reaction, it seems plausible that reaction 3 occurs according to a stepwise mechanisms. With time, the intense band at 1837 cm^{-1} corresponding to Bu_2SnH_2 decreases while a new band at 1854 cm^{-1} appears and then disappears. The first reaction on the surface may be

$${>}\text{Si–OH} + \text{Bu}_2\text{SnH}_2 \rightarrow \underset{\mathbf{3}}{{>}\text{Si–O–Sn(H)Bu}_2} + \text{H}_2 \qquad (4)$$

However evidence in favor of **3** is speculative at the present time. Due to the high reactivity of **3**, it is difficult to confirm such a hypothesis.

Table 1. ^{13}C CP-MAS NMR Data Obtained for the Product of the Reaction of H_2SnBu_2 with Silica$_{(200)}$ and Silica$_{(500)}$ and Comparison with Model Compounds

surface	molecular precursor	expected surface organometallic species	δ (ppm) C_α	C_β	C_γ	C_δ	C_δ'	ref
$SiO_{2(200)}$	Bu_2SnH_2	$\geqslant SiOSn(H)Bu_2$	14.7	26.5	26.5	13.0[c]	11.3	b
$SiO_{2(200)}$	Bu_2SnH_2	$(\geqslant SiO)_2SnBu_2$	20.0	26.5	26.5	13.0[c]	11.3	b
$SiO_{2(500)}$	Bu_2SnH_2	$\geqslant SiOSn(H)Bu_2$	14.9	26.8	26.8	12.9[c]	11.3	b
$SiO_{2(500)}$	Bu_2SnH_2	$(\geqslant SiO)_2SnBu_2$	20.2	26.8	26.8	12.9[c]	11.3	b
a	Bu_2SnH_2		7.3	30.8	27.2	13.8		b
a	Bu_3SnH		8.3	30.2	27.3	13.7		9
a	$SnBu_4$		9.1	29.6	27.6	13.7		9
$SiO_{2(200)}$	Bu_3SnH	$\geqslant SiOSnBu_3$	15.2	26.7	26.7	12.9	11.3	3
$SiO_{2(500)}$	Bu_3SnH	$\geqslant SiOSnBu_3$	15.2	26.7	26.7	13.0	11.3	3
a	$Bu_3SnOSiPh_3$		16.5	27.8	27.1	13.7		3
a	$Bu_3Sn(OMe)$		14.1	28.4	27.4	13.7		9
a	$Bu_2Sn(OMe)_2$		19.5	27.8	27.2	13.8		9

[a] In solution ($CDCl_3$). [b] This work.

Evidence for reaction 3 and species **2** is much more conclusive, based on the analytical data, $C_4/Sn = 2 \pm 0.1$ for silica$_{(200)}$ and silica$_{(500)}$, the 1 mol of H_2 evolved per mole of grafted tin, and no evidence for a significant amount of evolved hydrocarbon. Also the intensities of the ν(C–H) and δ(C–H) bands were constant throughout the reaction up to 200 °C, confirming the fact that the butyl ligands remain coordinated to tin. Finally, evidence for the proposed structure **2** was obtained from a detailed analysis of the ^{13}C CP-MAS NMR spectrum. The resonances of the α-, β-, and γ-C are similar to those of the model compound $(n\text{-}C_4H_9)_2Sn(OCH_3)_2$ (Table 1). The δ-C resonance was not found at ca. 13.8 ppm, but a shoulder (reproducible from one experiment to another) was observed at 13.0 ppm. There are two other resonances at 11.3 and 14.7 ppm (vide supra) which deserve some comment. The resonance at 11.3 ppm is probably due to a C–H bond hydrogen bonded to a surface silanol or a surface oxygen. A similar band was previously observed for $(\geqslant Si\text{–}O)Sn(n\text{-}C_4H_9)_3$,[3] but is not observed for model compounds such as $Bu_2Sn\text{–}O\text{–}SiR_3$, $Bu_3Sn(OMe)$, and $Bu_2Sn(OMe)_2$ (Table 1). This resonance is therefore attributed to the δ-C of the butyl chain of the grafted complex.

The chemical shifts of the β-, γ-, and δ-C of the grafted complexes $(\geqslant Si\text{–}O)SnBu_3$ and $(\geqslant Si\text{–}O)_2SnBu_2$ are very similar. Only the α-C resonances differ.

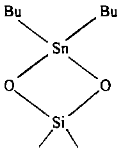
The chemical shift variation for α-C is similar to that observed for the model complexes $Bu_{4-n}Sn(OMe)_n$ ($n = 0, 1, 2$). The increase in line width for $(\geqslant Si\text{–}O)_2SnBu_2$ compared to $(\geqslant Si\text{–}O)SnBu_3$ is probably due to lack of rotation about the O–Sn bond in the former complex, resulting in less averaging of the α-C environment.

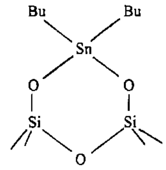
The peak at 14.7 ppm may correspond to the species $(\geqslant Si\text{–}O)Sn(H)Bu_2$. Although we have been unable to find a model compound corresponding to a monoalkoxy monohydridodialkyltin(IV), we believe that such an interpretation is plausible. In compounds of the family SnH_xBu_{4-x} ($x = 0, 1, 2$), the α-C resonance shifts only slightly upon substitution of a butyl ligand by a hydride, but a change in the number of Si–O–Sn bonds causes a large shift (Table 1).

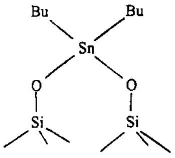
Attempts to prepare $(\geqslant Si\text{–}O)Sn(H)Bu_2$ by reaction of silica with an excess of Bu_2SnH_2 failed. The behavior was the same as that observed at low Sn loading. A simple explanation was obtained by molecular modeling. Due to its bulkiness, the amount of Bu_2SnH_2 which can be adsorbed on the silica surface is always lower than the quantity of silanols. However, the ν(Sn–H) band varies in shape as a function of the pretreatment temperature of the silica (which is responsible for the different apparent intensity ratios of the ν(Sn–H) and δ(C–H) bands), showing that the reaction mechanism is at least partly dependent on the silanol density.

Conclusion

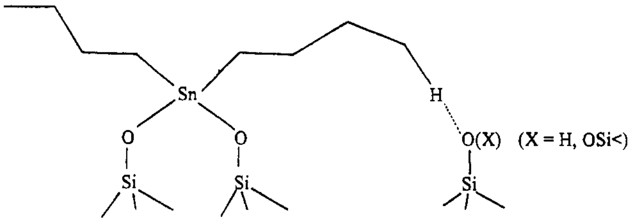
Reaction of H_2SnBu_2 with silica dehydroxylated either at 200 or 500 °C leads to the formation of the well-defined surface complex $(\geqslant Si\text{–}O)_2SnBu_2$ (**2**), which has been fully characterized by surface microanalysis, quantitative analysis of the evolved gases, ^{13}C CP-MAS NMR, and infrared spectroscopy. The possible surface structures of **2** depend on the nature of the silanols present on silica. Since similar results are obtained on silica$_{(200)}$ and silica$_{(500)}$, we may assume that the dibutyl tin fragment is grafted to two adjacent oxygen atoms on the silica. The following configurations are reasonable:







From the ^{13}C NMR data, we infer that surface organometallic fragments also interact with other silanols or oxygen atoms as shown:



In subsequent papers of this series, we will report the thermal decomposition of **1** and **2** on the silica surface and the surface mobility of the butyl groups as a function of temperature. The implications of these results in molecular separation (by grafting such complexes at the pore openings on the external surface of zeolites) will also be considered.