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Surface Organometallic Chemistry of Tin: Reaction of $(n\text{-}C_4H_9)_3SnH$ with the Surface of a Silica–Alumina. A ^{13}C and ^{119}Sn Solid-State NMR Investigation

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Introduction

We recently undertook to develop the surface organometallic chemistry of Sn in reactions between various organotin complexes and the surfaces of partially dehydroxylated silica[1] and alumina.[2] We showed that $Sn(n\text{-}C_4H_9)_4$ and $(n\text{-}C_4H_9)_3SnH$ react at 150 and 25 °C, respectively, with the silanol groups of silica according to the following reactions:[1,2]

$$\equiv Si\text{–}OH + Sn(n\text{-}C_4H_9)_4 \rightarrow \equiv Si\text{–}O\text{–}Sn(n\text{-}C_4H_9)_3 + n\text{-}C_4H_{10}$$

$$\equiv Si\text{–}OH + (n\text{-}C_4H_9)_3SnH \rightarrow \equiv Si\text{–}O\text{–}Sn(n\text{-}C_4H_9)_3 + H_2$$

In the surface organotin fragments, Sn is tetracoordinated as deduced from the solid-state ^{119}Sn MAS NMR data.[1] Indeed, the strong chemical shift dependence of the Sn nucleus on coordination number[3] allows us to use this parameter to distinguish between various coordination modes of this atom in surface organometallic chemistry.

A similar reaction was observed with the tin hydride complex on alumina at room temperature:[2]

$$>Al\text{–}OH + (n\text{-}C_4H_9)_3SnH \rightarrow >Al\text{–}O\text{–}Sn(n\text{-}C_4H_9)_3 + H_2$$

However, in this complex, the ^{119}Sn MAS NMR data suggest that Sn is mostly pentacoordinate, due to interaction between the tributyltin fragment and surface OH or O atoms situated in close vicinity to the Sn atoms.[2] Apparently, the O atoms of silica and alumina behave quite differently toward Sn in the same organometallic fragment.

It was therefore of interest to study the reactivity of $(n\text{-}C_4H_9)_3SnH$ with a silica–alumina surface in order to determine whether it is possible to distinguish between surface organometallic fragments of Sn coordinated to ≡Si–O or to >Al–O surface oxygen atoms.

Experimental Section

Materials. The silica–alumina was composed of 87% silica and 13% alumina, with a surface area of 300 m^2/g. It was pretreated under dynamic vacuum (10^{-4} Torr) at 500 °C, $SiO_2\text{–}Al_2O_{3(500)}$, or 200 °C, $SiO_2\text{–}Al_2O_{3(200)}$ for 13 h.

$(n\text{-}C_4H_9)_3SnH$ (Strem) and $Sn(n\text{-}C_4H_9)_4$ (Merck) were used as received. $(n\text{-}C_4H_9)_3SnH$ was introduced to the samples by microsyringe via a septum. The evolved gases (H_2, C_4H_8, C_4H_{10}, etc.) were analyzed quantitatively and qualitatively by volumetric analysis (using a Texas Intruments gauge) and by GC.

MAS NMR Spectroscopy. MAS NMR spectra were recorded on a Bruker MSL-300 spectrometer operating at 75.47, 78.17, and 111.9 MHz for ^{13}C, ^{27}Al, and ^{119}Sn, respectively. The probe was a commercial double-tuned 7 mm double-bearing system from Bruker allowing spinning frequencies up to 4 kHz. The samples were introduced into a zirconia rotor under a dry nitrogen atmosphere in a glovebox and tightly closed. Boil-off from liquid nitrogen was used for both bearing and driving the rotors. Under these conditions, no decomposition of the samples was observed during the course of the experiments.

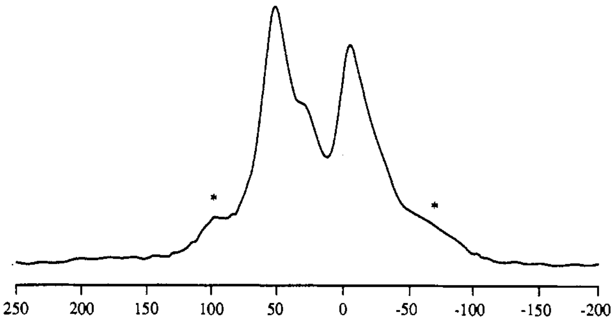

Figure 1. ^{27}Al MAS NMR spectrum of silica–alumina$_{(25)}$.

For ^{13}C NMR, the following typical cross-polarization sequence was used: 90° rotation of the ^1H magnetization (impulsion length 6.2 μs), followed by contact between C and H during T_c = 5 ms, and finally recording of the spectrum under high-power decoupling. The delay between each scan was fixed at 5 s, to allow for the complete relaxation of ^1H nuclei. Chemical shifts are reported with respect to TMS, using adamantane as an external reference (δ = 37.7 ppm for the highest chemical shift). In some cases, adamantane was directly added to the sample in the rotor in order to provide an internal reference. No chemical shift variation was noted by comparison to use of an external reference.

^{27}Al MAS NMR spectrum of the fully hydrated silica–alumina was recorded by using a single impulse sequence. The delay between scans was 1 s, and the number of scans was typically 500. For quantitative results, a short flip angle (2 μs, corresponding to less than 10°) was used, leading to the same response of Al atoms with different e^2qQ parameters. The chemical shifts are reported relative to 1 M $Al(H_2O)_6(NO_3)_3$ used as an external reference.

^{119}Sn NMR spectra were recorded by using a single impulse and high-power decoupling. The delay between scans was 2.5 s, resulting in complete relaxation of the ^{119}Sn nuclei. Chemical shifts are reported relative to $SnMe_4$ used as an external reference using the IUPAC convention for chemical shifts (a higher chemical shift value corresponding to a higher frequency).

The chemical shifts uncertainties can be estimated to 0.3, 0.5, and 1 ppm for ^{13}C, ^{27}Al, and ^{119}Sn respectively.

Infrared Spectroscopy. Infrared spectra were recorded on a Fourier Transform Nicolet 10-MX spectrometer using a special cell equipped with CaF_2 windows for *in situ* experiments.

Results

The silica-alumina starting material was first characterized by ^{27}Al MAS NMR, in order to observe and assign the various Al coordination numbers. Figure 1 shows two main peaks at −2 and 51 ppm and a shoulder at 31 ppm. In agreement with previous studies carried out on similar silica–aluminas, the peaks at −2 and 51 ppm are ascribed to tetra- and hexacoordinate Al, respectively.[4–9] The shoulder at 31 ppm has already been assigned to pentacoordinate Al.[10–12]

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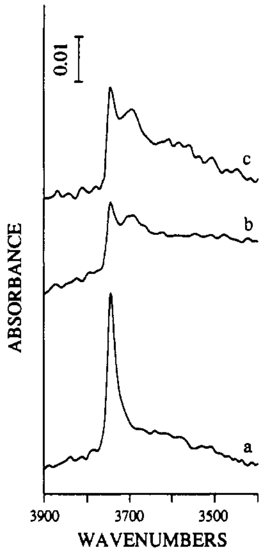

Figure 2. Infrared spectra, in the spectral 3400–3900-cm^{-1} region, of (a) silica–alumina$_{(500)}$, (b) the sample in part a just after introduction of Bu$_3$SnH at 25 °C, and (c) the sample in part b after 12 h at 25 °C (5.9% Sn).

The surface hydroxyl groups of silica–alumina$_{(500)}$ were observed by infrared spectroscopy (Figure 2a). In agreement with other studies,[13–19] only one band is observed at 3747 cm^{-1}, corresponding to the stretching vibration ν(O–H). This band corresponds to isolated silanol groups. No other well-defined peak, which could be ascribed to >AlOH groups, is detected. This can be explained easily. Indeed, basic >AlOH groups near acidic ≡SiOH groups would lead to condensation as >Al–O–Si≡ with formation of water.

Interaction of (n-C$_4$H$_9$)$_3$SnH with silica-alumina$_{(500)}$ at 25 °C yields a product whose IR spectrum contains ν(C–H) vibrations at 2958, 2924, 2872, and 2855 cm^{-1} and δ(CH$_2$) and δ(CH$_3$) vibrations at 1465, 1453, 1418, 1381, 1361, and 1342 cm^{-1}. These bands are characteristic of butyl groups.[20] A band at 1809 cm^{-1} is typical of the ν(Sn–H) vibration of (n-C$_4$H$_9$)$_3$SnH.[21–25] The silanol band at 3747 cm^{-1} of the silica–alumina decreases in intensity instantaneously and is replaced by a new broad band situated around 3700 cm^{-1} (Figure 2b). This shift in frequency of the silanol groups was observed during the interaction of (n-C$_4$H$_9$)$_3$SnH or Sn(n-C$_4$H$_9$)$_4$ with silica$_{(500)}$.[1] It has been unambiguously assigned,[1] by the conjunction of IR and ^{13}C CP-MAS solid-state NMR, to the formation of hydrogen bonds between the terminal C–H bonds of the butyl ligands and O–H groups of the silica surface. In the case of silica–alumina, a similar interpretation seems reasonable.

At 25 °C, the ν(Sn–H) vibration decreases in intensity with time, whereas the ν(C–H) and δ(CH$_2$), δ(CH$_3$) vibrations remain unchanged (Figure 3). The reaction is complete after 12 h. At the same time, 1.0 ± 0.1 mol of H$_2$ is evolved per mole of grafted Sn. No hydrocarbons were detected in the gas phase, indicating that the alkyl ligands remain intact at this temperature and do not react with any surface functional group to produce alkane or alkene. Even after completion of the reaction, the broad band at 3700 cm^{-1} is still present (Figure 2c), demonstrating that the butyl ligands continue to hydrogen bond to surface silanols.

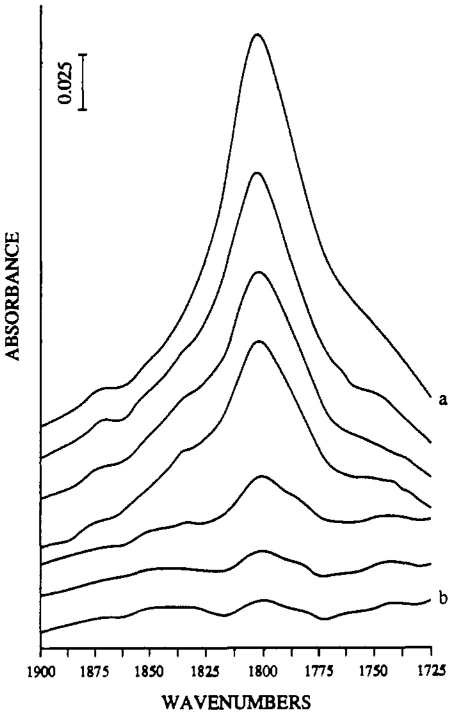

Figure 3. Evolution with time of the infrared spectrum in the ν(Sn–H) bands region during the reaction at 25 °C of Bu$_3$SnH with the surface of a silica–alumina$_{(500)}$, from (a) $t = 0$ to (b) $t = 12$ h.

A ^{13}C CP-MAS NMR spectrum of the sample after complete reaction exhibits four peaks at 11.3, 13.1, 26.6, and 15.0 ppm (Figure 4b), already observed[1] in the case of silica-supported species ≡Si–O–Sn(n-C$_4$H$_9$)$_3$ (Figure 4a, Table 1). By analogy with the previous study, we assign the most intense peak at 26.6 ppm to the β- and γ-carbons of the butyl ligands and the peak at 15.0 ppm to the α-carbon. The peaks at 11.3 and 13.1 ppm are due to the terminal carbon of the butyl ligand with (C$_{\delta'}$) or without (C$_\delta$) hydrogen bonding to silanol groups. This NMR interpretation is in agreement with the IR results (presence of a broad silanol band at ca. 3700 cm^{-1}).

The ^{119}Sn MAS NMR spectrum of the same sample has two peaks at −83 and 102 ppm (Figure 5b, Table 1). The peak at −83 ppm is due to a very small fraction of unreacted (n-C$_4$H$_9$)$_3$SnH. The peak at 102 ppm was previously observed for ≡Si–O–Sn(n-C$_4$H$_9$)$_3$ (Figure 5a)[1] and is in the range of chemical shifts observed for molecular analogues such as Bu$_3$Sn(OSiPh$_3$). It is ascribed to the same surface organometallic complex, in which tin is tetracoordinate.[3]

Microanalysis of this sample gave 8.41% by weight of C for 6.67% by weight of Sn, or a molar ratio of 3.1 C$_4$ per Sn. Analytical, NMR and IR data therefore agree with the following overall stoichiometric reaction between HSn(n-C$_4$H$_9$)$_3$ and the silanol groups of silica-alumina$_{(500)}$:

$$\equiv\text{Si–OH} + \text{HSn}(n\text{-C}_4\text{H}_9)_3 \rightarrow \equiv\text{Si–O–Sn}(n\text{-C}_4\text{H}_9)_3 + \text{H}_2$$

Surprisingly, almost identical results were obtained on a silica-alumina$_{(200)}$. The reaction is complete in about 12 h, as shown by the disappearance of ν(Sn–H) while the ν(C–H) and δ(CH$_2$), δ(CH$_3$) vibrations remain constant. Simultaneously, 1.0 mol of H$_2$ per mole of grafted Sn is evolved, without any detectable

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Table 1. ^{13}C and ^{119}Sn NMR Chemical Shifts (δ, ppm) of Surface Complexes Obtained by the Reaction of $(n\text{-}C_4H_9)_3SnH$ with the Surface of Silica–Aluminum and Comparative Data for Similar Surface Complexes (a) and for Relevant Molecular Analogues in Solution (b)

	species	% Sn by wt[f]	^{13}C					^{119}Sn	CN[a]	ref
			C_α	C_β	C_γ	C_δ	$C_{\delta'}$			
			(a) Surface Complexes							
$SiO_2–Al_2O_{3(500)}$	b	6.7	15.0	26.6	26.6	13.1	11.3	102	*b*	*c*
$SiO_2–Al_2O_{3(200)}$	b	7.1	15.0	26.5	26.5	12.8	11.3	101	*b*	*c*
$SiO_{2(500)}$	$\equiv SiOSnBu_3$	4.8	15.2	26.7	26.7	13.0	11.3	105	4	1
$\alpha\text{-}Al_2O_{3(500)}$	$>AlOSnBu_3$	6.8	15–19	26.9	26.9	13.1	11.3	–227/–171	5	2
			(b) Solution Species							
	Bu_3SnH[d]		8.3	30.2	27.2	13.7		–83	4	23
	Bu_3SnOMe[d]		14.1	28.4	27.4	13.7		83	4	23, 24
	$Bu_3SnOSiPh_3$[d]		16.5	27.8	27.1	13.7		94	4	1
	$Bu_2Sn(O\text{-}iPr)_2$[d]		19.2	27.5	27.0	13.6		–34	4	23, 24
	Bu_3SnCl[d]		17.3	27.6	26.5	13.3		133	4	25
	Bu_3SnCl[e]		21.3	27.7	26.5	13.2		–35	5	25

[a] Coordination number. [b] Species obtained by reaction of $(n\text{-}C_4H_9)_3SnH$ with the surface of silica–alumina. [c] This work. [d] In $CDCl_3$ solution (noncoordinating solvent). [e] In hexamethylphosphortriamide solution. [f] Weight of tin in the sample.

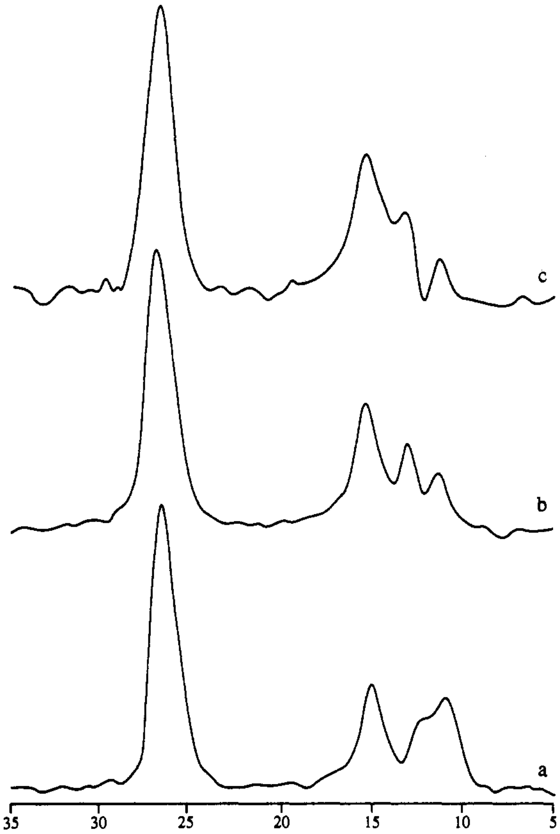


Figure 4. ^{13}C CP-MAS NMR spectra of the solids obtained after reaction of Bu_3SnH at 25 °C with (a), for comparison, silica$_{(500)}$, (b) silica–alumina$_{(500)}$, and (c) silica–alumina$_{(200)}$.

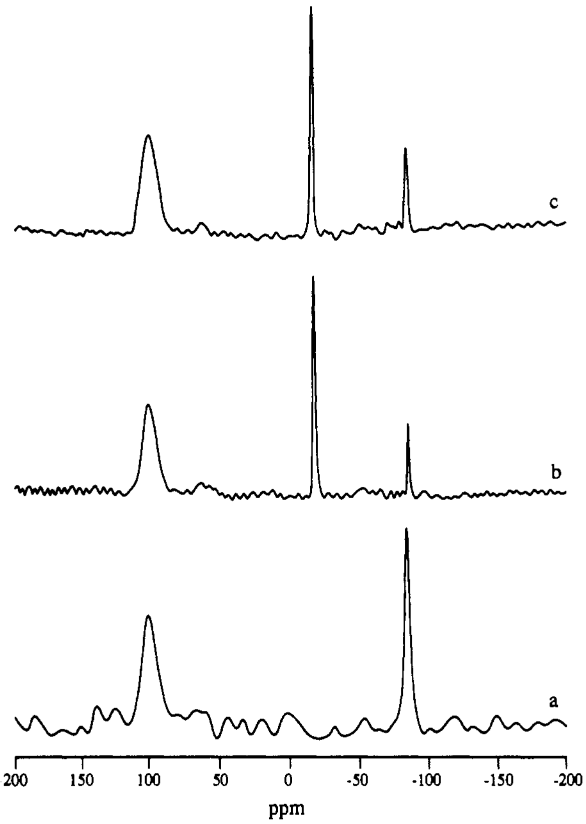
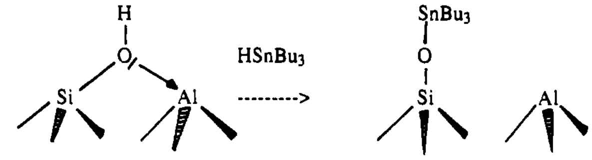


Figure 5. ^{119}Sn MAS NMR spectra of the solids obtained after reaction of Bu_3SnH at 25 °C with (a), for comparison, silica$_{(500)}$, (b) silica–alumina$_{(500)}$, and (c) silica–alumina$_{(200)}$ (peak at –13 ppm: $SnBu_4$, internal reference).

Scheme 1



hydrocarbon products. The ^{13}C CP-MAS NMR spectrum (Figure 4c, Table 1) and the ^{119}Sn MAS NMR spectrum (Figure 5c, Table 1) are very similar to those obtained on silica–alumina$_{(500)}$ although a supplementary shoulder is detectable at ca. 14 ppm. Finally, microanalysis (7.07% Sn, 8.77% C) gives a molar ratio C_4/Sn equal to 3.0, in agreement with reaction 1.

Discussion

$(n\text{-}C_4H_9)_3SnH$ reacts with the surface of silica–alumina in a manner very similar to that observed for silica and alumina. The surface complex which is obtained on silica–alumina has the same formula as on silica, that is, $\equiv SiO–Sn(n\text{-}C_4H_9)_3$. The most striking result is that no ^{119}Sn NMR signal is observed in the –200 ppm region which would correspond to the surface complex $>AlO–Sn(n\text{-}C_4H_9)_3$.[2] It is known that $(n\text{-}C_4H_9)_3SnH$ reacts with the surface of alumina at this temperature.[2] The apparent absence of reaction of the tin hydride complex with the surface >Al–OH groups of silica–alumina is probably due to the different acidities of the ≡SiOH and >AlOH groups. It is also possible that the product is not detected by ^{119}Sn NMR on our sample of silica–alumina which contains only 13% alumina. However, our previous results obtained on alumina itself indicate that this is unlikely, due to the high sensitivity of the ^{119}Sn nucleus in solid-state NMR. Another possibility is that, on silica–alumina, the hydroxyl groups coordinated to aluminum atoms are eliminated first during the dehydroxylation process.[17] This hypothesis is supported by the fact that >Al–OH groups at the surface of a silica–alumina are not detected by infrared spectroscopy. However, on silica–alumina$_{(200)}$, one would expect there to be some remaining >Al–OH groups.

A reasonable explanation is that the hydroxyl groups coordinated to the aluminum atoms are also coordinated to the silicon atom in a bridging manner in order to compensate for the difference in charge between silicon and aluminum (Scheme 1).

Such bridging hydroxyl groups would not be readily detected by infrared spectroscopy. After reaction with the tin hydride complex, the surface structure and spectroscopic data of the grafted organotin complex would likely be the same regardless of whether the tin is coordinated to a site similar to those on silica or to a site with an adjacent Lewis acidic aluminum atom.

Additions and Corrections

1993, Volume 32

Vicente Rives,* Francisco M. Labajos, Maria A. Ulibarri, and Pilar Malet: A New Hydrotalcite-like Compound Containing V^{3+} Ions in the Layers.

Page 5000. The indexing of X-ray diffraction peaks given in Figure 1 is incorrect. The corrected figure is presented below.

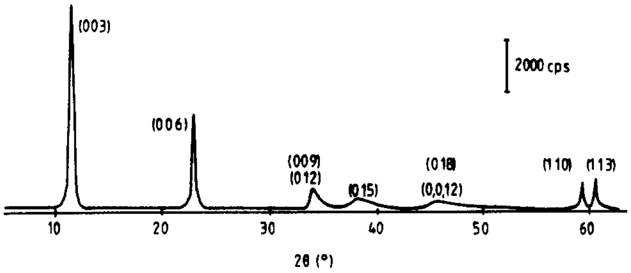


Figure 1. X-ray diffraction diagram of Mg,V–CO_3 double hydroxide.